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Photo- and Halochromic Multicolor Switching System Consisting of Diarylethene and Malachite Green Moieties

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Abstract

A diarylethene with an attached malachite green moiety was synthesized. The diarylethene moiety undergoes reversible cyclization and cycloreversion reactions by alternate irradiation with UV (313 nm) and visible (435 nm) light, while the malachite green moiety reversibly changes between neutral, monocationic, and dicationic states up to the proton concentration. The photochromic and halochromic reactions could be controlled, and this provided a multi-reversible system with six states. The cyclization and cycloreversion quantum yields of the diarylethene moiety were dependent on the states of the malachite green moiety.

Introduction

Photochromism is defined as a reversible transformation of a chemical species between two forms having different absorption spectra induced in one or both directions by photoirradiation.[1] Photochromic compounds have been applied for many photoresponsive systems and switches, and thus a wide variety of photochromic compounds have been synthesized.[1-5] When more than one input for example pH changes (proton),[6-8] redox,[9] another photon,[10] or heat[11,12] is used, the number of available states increases, leading to systems capable of performing complex functions.

System which respond to a given combination of multiple stimuli open new ways to complex switches (logic gates) at the molecular scale.[13-15] In the photochromic families, diarylethenes have been effectively applied in many fields such as memory and switches due to their thermal stability of both isomers and their fatigue resistant property.[3,5] And, many photochromic system with multiple states have been developed. Some of the purposes are the increment of the capacity of the recording memory, full color display, and logic gates.[16-20] Additionally, by incorporating pyridine or acid moieties in a photochromic diarylethene system, the protonation and de-protonation processes are introduced to the photochromic ability, and they affected the absorption spectra and quantum yields.[21-33] Such systems are also the examples of multi-state photochromic systems or gated-photochromic systems.[29-33] Up to now combination of two photochromic system in one molecule have been also reported. Samat *et al.* have developed pioneering biphotochromic compounds containing spiropyran linked to chromene, but this dyad presented some drawbacks due to the loss of photochromic properties in the presence of oxygen and thermally unstable states.[34] And Pozzo *et al.* have followed the synthesis of the biphotochromic system: dithienylethene – indolinooxazolidine hybrid with four different color states.[35] Here, we synthesized a diarylethene derivative with a malachite green moiety as a pendant group having three states: neutral, monocationic, and dicationic states. Furthermore, by considering these states under both open- and closed-ring isomeric states, we studied the photochromism and halochromism of these six states to clarify the effect of combining two dyes as shown in Figure 1.

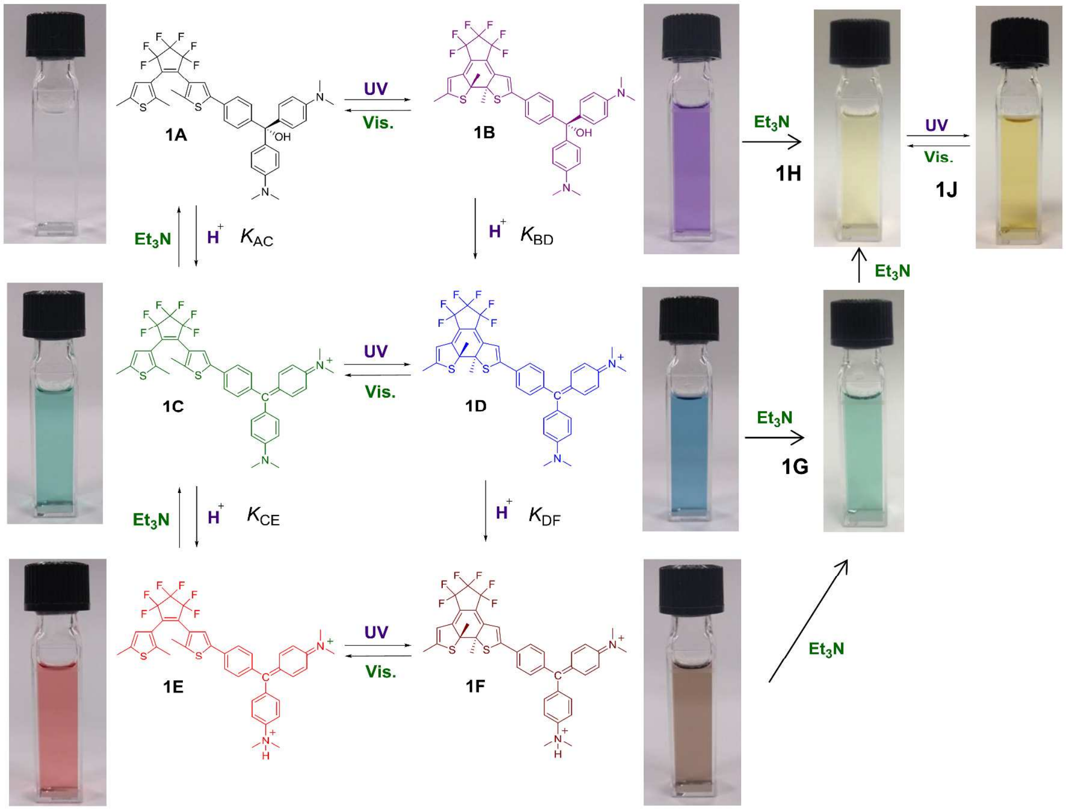
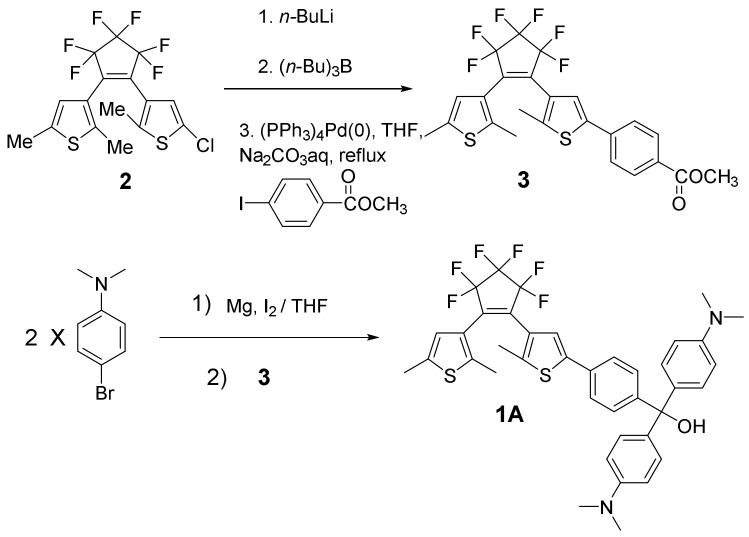


Figure 1. Multicolor switching system consisting of diarylethene and malachite green moieties.

Results and Discussion

Synthesis and photochromic property of 1A

A diarylethene having a malachite green moiety was prepared according to Scheme 1. An asymmetric diarylethene **2** was prepared according to the conventional method.[36] *p*-Substituted phenyl iodide was reacted with **2** in a Suzuki-Miyaura coupling reaction to form **3**, which was reacted with 2 mole of a Grignard reagent to obtain **1A** (Scheme 1). The structure was ascertained by not only ^{1}H NMR spectra and elemental analysis but also X-ray crystal analysis (Supporting Information Fig. S1).



Scheme 1. Synthetic procedure of **1A**

Photo- and Halochromism of the system

The photochromism and halochromism of **1A** is summarized in Figure 1. **1A** in the acetonitrile solution is colorless. Upon UV irradiation (313 nm), a cyclization reaction of the diarylethene moiety proceeded and the color changed to red-purple (**1B**). Malachite green is also well known as a photochromic compound, but it is necessary to irradiate it with deep UV light ($\lambda \sim 280$ nm).[36] Therefore, the photoisomerization of malachite green moiety cannot be achieved by using 313 nm UV irradiation. The absorption spectral changes of **1A** in the acetonitrile solution are shown in Fig. 2. **1A** shows the absorption maxima at 267 nm (ε: 5.25×10^4 $M^{-1}cm^{-1}$). Upon UV irradiation, the band decreased with an increase in the absorption band of **1B** at 555 nm (ε: 1.40×10^4 $M^{-1}cm^{-1}$) and reached a photostationary state (**1A: 1B**=11:89). Upon visible light irradiation ($\lambda > 480$ nm) to the solution, the color disappeared and the spectrum reverted to that of **1A**. These spectral changes were monitored by ^{1}H NMR spectroscopy and assigned to the cyclization and cycloreversion reactions of the diarylethene moiety of **1A**. The results are shown in Figure 3. The signals of methyl protons and aromatic protons on the thiophene rings of the open-ring state of the diarylethene moiety were observed at 1.66 and 2.19 ppm (methyl protons), and at 6.57 and 7.11 ppm (aromatic protons). Upon UV irradiation, the signals attributed to the methyl and aromatic protons on the thiophene rings of the closed-ring state of the diarylethene moiety appeared at 1.87, 1.89, and 2.01 ppm (methyl protons), and at 5.92 and 6.53 ppm (aromatic protons). These signals disappeared upon visible light irradiation. The ^{1}H NMR spectral changes corresponding to previous system have been reported during the photoisomerization of diarylethenes.[37] Similar ^{1}H NMR spectral changes were observed during photoisomerization under acidic conditions (S. I. Figs S2. and S3.). The quantum yields of the cyclization and cycloreversion reactions were measured to be 0.30 (313 nm) and 0.044 (492 nm), respectively.

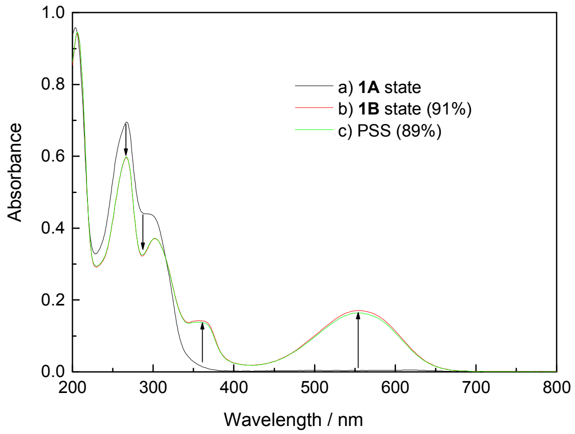


Figure 2. Absorption spectral changes of **1A** in acetonitrile (1.32 × 10^{-5} M). a) **1A** state, b) **1B** state (**1A**: pure **1B** = 9:91), c) Photostationary state under 313 nm light irradiation (**1A**: pure **1B** = 11: 89)

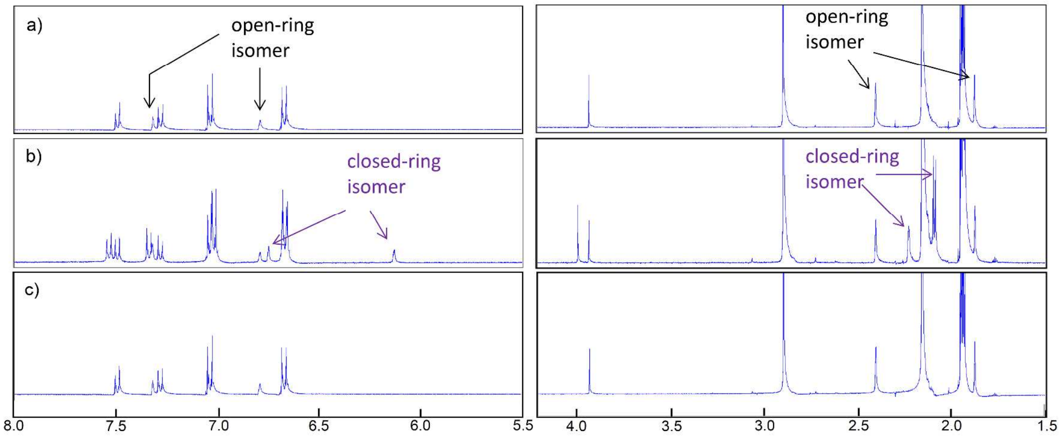


Figure 3. ^{1}H NMR Spectral changes of **1A** in acetonitrile-d_3, a) before UV irradiation; b) after UV irradiation; c) upon visible light (λ > 480 nm) irradiation

It is well known that the malachite green undergoes halochromism depending on proton concentration.[38] In our experimental condition (acetonitrile solution), malachite green is colorless without addition of an acid source. The proton concentration was controlled by addition of trifluoromethanesulfonic acid (TFMSA) in the acetonitrile solutions. TFMSA is a strong acid that is often used for pH control in organic solvents.[8,27] The solution showed a brilliant green color by adding a small amount of TFMSA ($-\log[H^+] = 6.0 \sim 3.5$), and then the color changed to red by further addition of TFMSA ($-\log[H^+] < 2.0$). Therefore it was expected that the malachite green moiety of **1A** as well as **1B** (PSS state of **1A:1B**=11:89) would show halochromism depending on the proton concentration accompanied with the changes in the photochromic reactivity of the diarylethene moiety. The conversions among neutral, monocationic and dicationic states of **1A** and **1B** by controlling the added amount of TFMSA are summarized in Figure 4.

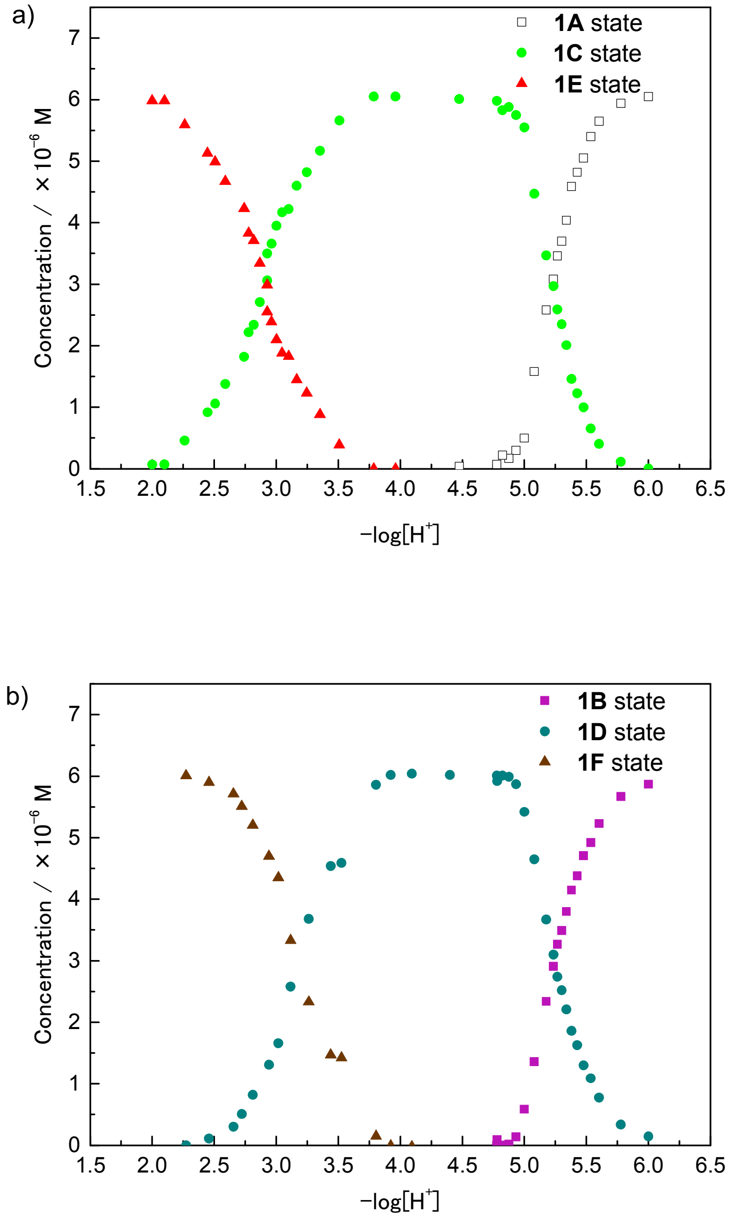


Figure 4. Concentrations of neutral, monocationic and dicationic states of malachite green moiety depending on proton concentration: a) open-ring isomeric and b) closed-ring isomeric states of diarylethene moiety.

The equivalent point between neutral and monocationic states and that between monocationic and dicationic states of **1A** and **1B** are summarized in Scheme 2. The apparent K_{AC} is expressed as

$$K_{\mathrm{AC}} = \frac{[\mathbf{1C}]}{[\mathbf{1A}][\mathrm{H}^+]}.$$

Similarly, we obtain

$$K_{\mathrm{BD}} = \frac{[\mathbf{1D}]}{[\mathbf{1B}][\mathrm{H}^+]}$$

$$K_{\mathrm{CE}} = \frac{[\mathbf{1E}]}{[\mathbf{1C}][\mathrm{H}^+]}$$

$$K_{\mathrm{DF}} = \frac{[\mathbf{1F}]}{[\mathbf{1D}][\mathrm{H}^+]}$$

$$\mathbf{1A} + \mathrm{H}^+ \overset{K_{\mathrm{AC}}}{\rightleftharpoons} \mathbf{1C} \qquad K_{\mathrm{AC}} = 1.8 \times 10^5$$

$$\mathbf{1B} + \mathrm{H}^+ \overset{K_{\mathrm{BD}}}{\rightleftharpoons} \mathbf{1D} \qquad K_{\mathrm{BD}} = 1.5 \times 10^5$$

$$\mathbf{1C} + \mathrm{H}^+ \overset{K_{\mathrm{CE}}}{\rightleftharpoons} \mathbf{1E} \qquad K_{\mathrm{CE}} = 8.3 \times 10^2$$

$$\mathbf{1D} + \mathrm{H}^+ \overset{K_{\mathrm{DF}}}{\rightleftharpoons} \mathbf{1F} \qquad K_{\mathrm{DF}} = 1.4 \times 10^3$$

Scheme 2

Here, the **1D** and **1F** states are formed from **1B** state by addition of TFMSA, **1D** and **1F** states should be expressed exactly as (**1C**:**1D**=11:89) and (**1E**:**1F**=11:89), respectively. The colored states **1B**, **1D**, and **1F** are thermally stable at room temperature and no absorption spectral changes were observed for several days in the dark. Comparing the

K values of the open- and closed-ring states of the diarylethene moiety, these values are almost the same in both states. And large values for K_{AC} and K_{BD} indicate that the slight addition of acid induces the monocationic states.

In the acidic conditions ($[H^+] = 1.67 \times 10^{-5}$ M), **1C** shows absorbance at 626 nm (ε: 9.6×10^4 $M^{-1}cm^{-1}$), which is green in color and attributed to the mono cationic state of the malachite green moiety. Upon UV irradiation (313 nm) of the solution, the color slightly changed to bluish green, and the spectral absorbance was changed to that indicated by the green line (λ_{max}: 633 nm, ε: 9.8×10^4 $M^{-1}cm^{-1}$) in Figure 5. Upon visible light ($\lambda > 430$ nm) irradiation of the solution, the color and the spectra recovered to those of the **1C** state. Compared to Fig. 2, the wavelengths of the spectral-change region are blue-shifted, and the usual ^{1}H NMR spectral changes due to the cyclization and cycloreversion reactions were observed accompanied with the color changes (S.I. Fig. S2). The quantum yields of the cyclization and cycloreversion reactions were found to be 0.012 (313 nm) and 1.45×10^{-3} (435 nm), respectively. The large decrease in the cyclization quantum yield is expected to be due to the energy transfer from diarylethene moiety to colored cationic form of malachite green moiety.[39] Dehydroxylation on the central carbon of the malachite green moiety changes the structure into conjugated structure and the absorption band consequently red-shifted longer than those of both diarylethene isomeric states. In the much higher proton concentration condition ([H^+] = 1.00×10^{-2} M), the dicationic state was formed in the malachite green moiety. The color changed to red as shown in Figure 1. The red color is also familiar to the closed-ring isomer of diarylethenes,[40] but, the diarylethene moiety remains as the open-ring form, i.e., **1E** (S.I. Fig. S3). Upon UV irradiation (313 nm), the color changed to brown accompanied with the cyclization reaction of the diarylethene moiety. The formation of **1E** is also ascertained by ^{1}H NMR (S.I. Fig. S3). Furthermore, the solution reverted to the **1E** state upon visible light irradiation ($\lambda > 480$ nm). The quantum yields of cyclization and cycloreversion reactions were also obtained, and these values are summarized in Table 1. Both quantum yields were similar to those of the monocationic state.

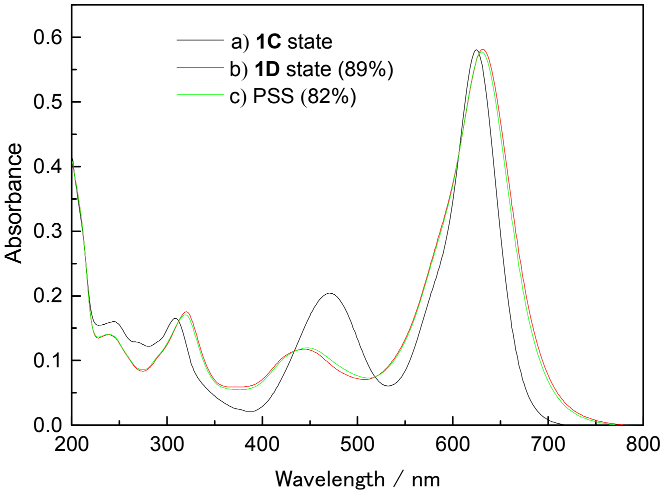


Figure 5. Absorption spectral changes between **1C** and **1D** states in acetonitrile (6.04 × 10^{-6} M). a) **1C** state, b) **1D** state (**1C**: pure **1D** = 11: 89), c) Photostationary state under 313 nm light irradiation (**1C**: pure **1D** = 18: 82)

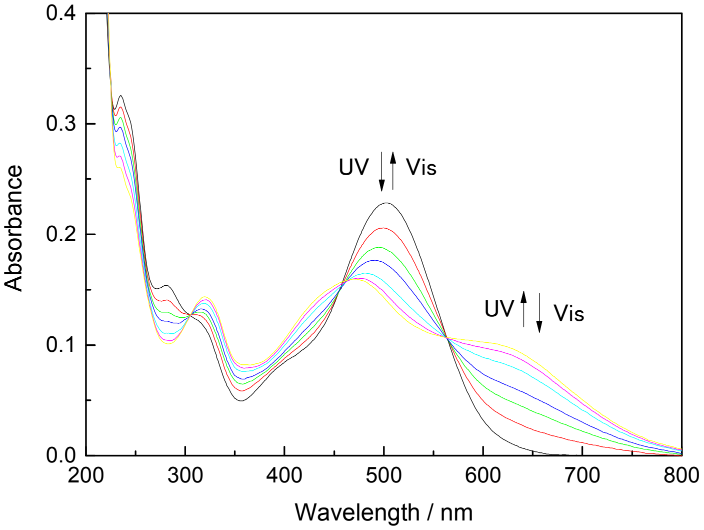


Figure 6. Absorption spectral changes between **1E** and **1F** states in acetonitrile (5.93 × 10^{-6} M). UV irradiation periods are 0, 10, 20, 30, 50, 70, 90 s, respectively.

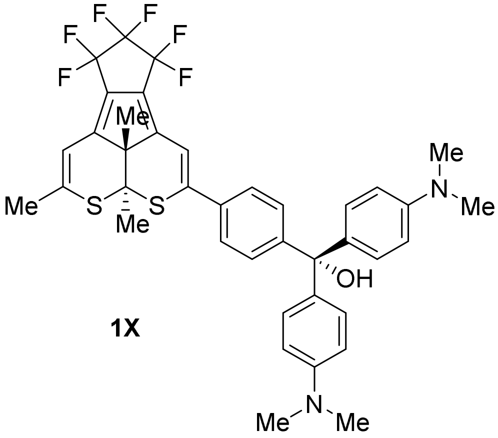
Table 1. Absorption coefficients of the six states and the quantum yields of cyclization and cycloreversion reactions of diarylethene moiety

	λ_{max}/nm	ε/M^{-1}cm^{-1}	Φ (λ^*/nm)
1A	267	52500	$\Phi_{A\rightarrow B} = 0.30$ (313)
1B	555	14000	$\Phi_{B\rightarrow A} = 0.044$ (492)
1C	625	96000	$\Phi_{C\rightarrow D} = 0.012$ (313)
1D	633	98000	$\Phi_{D\rightarrow C} = 1.45 \times 10^{-3}$ (435)
1E	502	38500	$\Phi_{E\rightarrow F} = 0.02$ (313)
1F	463	28000	$\Phi_{F\rightarrow E} = 1.5\times10^{-3}$ (313)

λ^***:** measured wavelengths of the monochromatic light

Photochromic reactions are always accompanied by rearrangement of chemical bonds. During the rearrangement, undesirable side reactions take place to some extent. Fatigue resistance for photochromic reactions between **1A** and **1B**, **1C** and **1D**, and **1E** and **1F** states were studied. This limits the number of cycles of photochromic reactions. For the fatigue resistance between **1A** and **1B**, measurement was carried out in acetonitrile solution (1.65×10^{-5} M) and UV (313 nm) light (15 s) and visible ($\lambda > 500$ nm) light (60 s) were alternatively irradiated to the solution and the absorption at 533 nm of λ_{max} of the closed-ring isomer of diarylethene moiety was monitored as shown in Fig S4. The fatigue resistance was defined as the number of photochromic cycles at which the absorbance of the closed-ring isomers decrease to 80% of the first cycle by

Irie,[5] therefore the fatigue resistance between **1A** and **1B** is 8 or 9 cycles (Fig. S4). During the repetition of photochromism, new band appeared at 528 nm, and the band was not disappeared upon visible light irradiation. This is attributable to the formation of the rearrangement product **1X**, whose bands are always appeared at shorter wavelengths compared to that of the appropriate closed-ring isomer, and they were often come across the photochromic reaction of diarylethene derivatives. [5, 41, 42]



1X

For fatigue resistance measurement of the photochromism between **1C** and **1D** state, alternate irradiation with 3 min of the UV light (313 nm) and 3 min of the visible light ($\lambda > 430$ nm for 3 min) was necessary, because of the low quantum yields. In this case, fatigue resistance was estimated by the decrease of the absorption band of **1C** at 471 nm (λ_{max}), and the intensity was decreased to 93%, 83%, 75%, and 69% after the repetition cycles. Therefore, the fatigue resistance between **1C** and **1D** is 2 or 3 cycles (Fig. S5).

For the fatigue resistance for photochromic reactions between **1E** and **1F,** the 313 nm light for 3 min and visible (λ > 640 nm) light for 20 min were irradiated alternatively, and the fatigue resistance was estimated by the decrease of the absorption band of **1E** at 502 nm (λ_{max}), and found out the intensity drop down below 80% of the initial value after 3 cycles (Fig. S6).

The thermal stability of the closed-ring state **1B** was examined. No spectral change of **1B** was observed after 24 h of heating at 70 °C in the dark as well as that of **1A**. The **1C** and **1D** states are thermally stable at 70 °C in the dark, however, **1E** and **1F** states are not thermally stable in the dark even at 70 °C, and spectral shift to monocationic states were observed (Fig. S7).

The compound **1A** also showed the photochromism even in the crystalline state (Fig. S8), because the distance between the reactive carbon atoms is 3.566 Å which is shorter than 4 Å.[43] Upon UV irradiation to the crystals of **1A**, the color changed to purple indicating the formation of **1B**, then the color was erased by visible light irradiation. If we use this reaction in crystalline state, the fatigue resistance must be improved.[44]

Then the halochromism to low proton concentration was studied by addition of triethylamine (TEA). Initially, TEA addition was studied for the open-ring states, and

TEA (50 μL) addition to the **1E** state, the red color of **1E** changed to greenish-blue, then changed to transparent by further addition (+ 50 μL) of TEA. The spectral changes are shown in Figure 7a which also support the conversion from **1E**, to **1C**, followed by **1C** to **1A** by successive addition of TEA. This change is good agreement with that of malachite green in acetonitrile (Figure 7c). In contrast, TEA addition to **1F** showed different phenomena. Addition of 50 μL of TEA to **1F** state, the color changed to bluish green, then it changed to yellow by further addition of TEA. These states are depicted as **1G** and **1H**, respectively in Figure 1. The spectral changes are shown in Figure 7b. The absorption spectrum of **1G** is similar to **1C** instead of **1D**. The new absorption band appeared in the spectrum of **1H;** the spectrum of **1H** is different from any spectra of the closed-ring isomer of diarylethene **1B, 1D,** and **1F.**

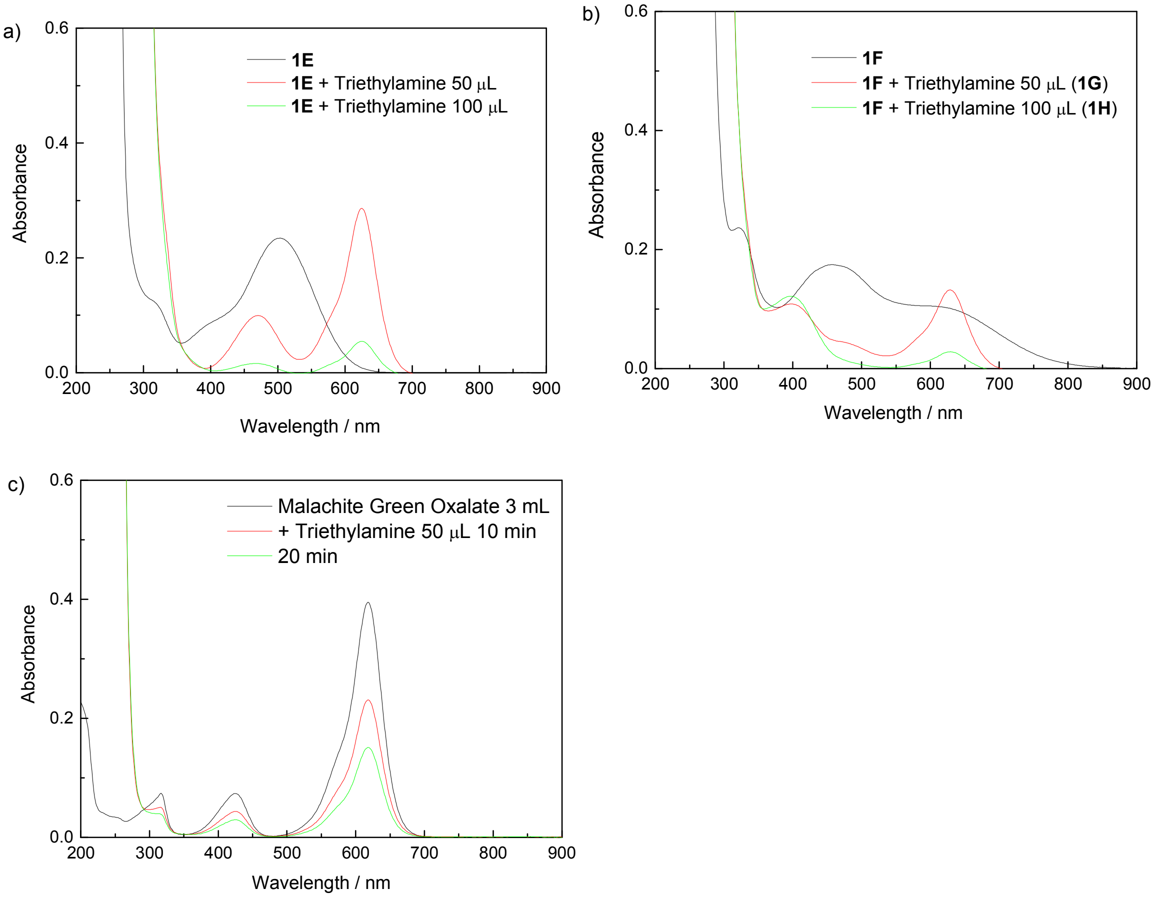


Figure 7. Absorption spectral changes of (a) **1E**, and (b) **1F** states by addition of triethylamine, and (c) absorption spectral changes of malachite green in acetonitrile by addiation of TEA.

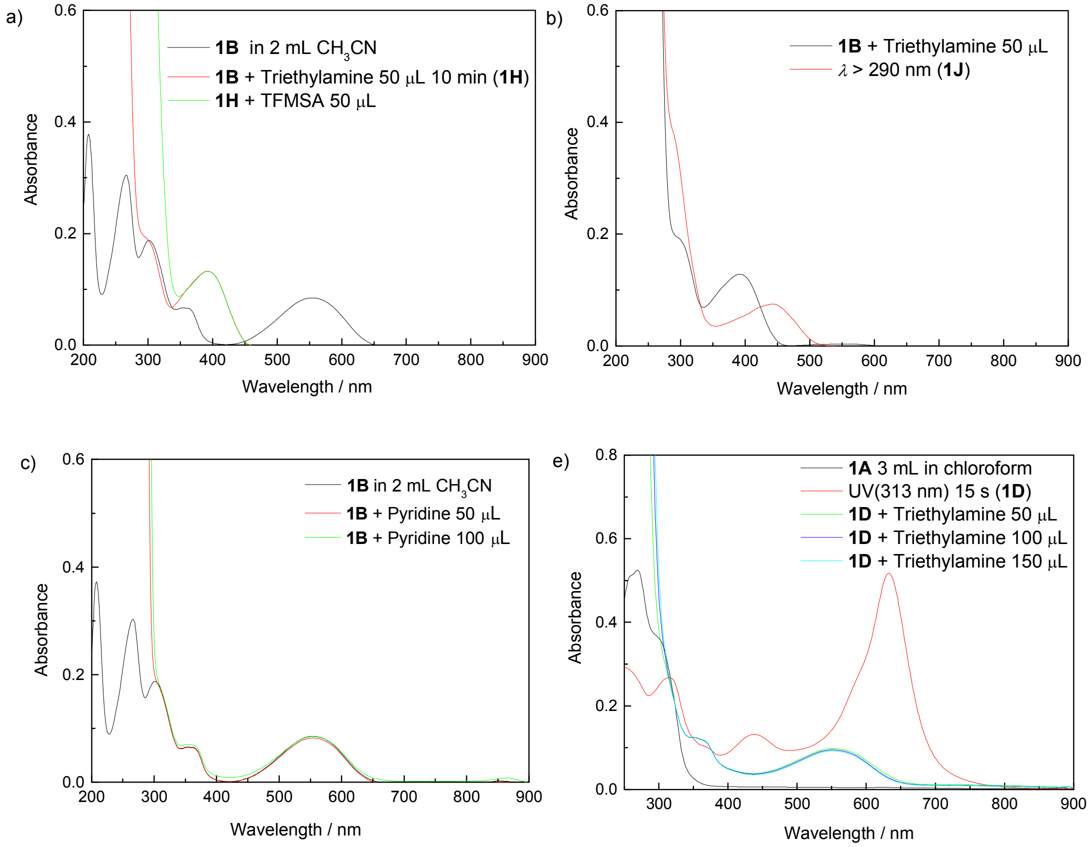


Figure 8. Absorption spectral changes of (a) acetonitrile solution of **1B** by addition of TEA followed by the addition of 1M TFMSA, (b) upon near UV light (λ > 290 nm) irradaition, (c) absorption spectral changes of acetonitrile solution of **1B** by addition of pyridine, (d) absorption spectral changes of chloroform solution of **1A** by UV (313 nm) irradaition followed by the addition of TEA.

In order to understand the character of the **1H** state, 50 μL of TEA was added to the **1B** state. The band attributed the closed-ring structure of the diarylethene moiety disappeared 10 min later after the addition of TEA and the same band found in the spectrum of **1H** at 392 nm was appeared accompanied with yellow coloration (Fig. 8a). During this process the cycloreversion reaction of the diarylethene moiety was observed. The thermal cycloreversion was also observed for the processes **1D** to **1G** as well as **1F** to **1G** by the addition of TEA. The process was monitored by ^{1}H NMR spectra. For example, we monitored the thermal cycloreversion of the closed-ring form of **1D** after addition of TEA. By addition of TEA, methyl signals of the closed-ring isomer at 2.227 ppm was disappeared and only a methyl signal at 2.406 ppm of the open-ring isomer was remained in CD_3CN. To the yellow solution of **1H**, 50 μL of TFMSA was added and no spectral change was observed (Fig. 8a). To the **1H** state, a light (λ > 290 nm) was irradiated, and a new band was appeared at 444 nm (**1J**) indicating the cyclization reaction (Fig. 8b). It partially reverted to **1H**, however, it was difficult to measure the quantum yield because of the by-product formation. These results support the TEA addition indicated the cycloreversion reaction of the closed-ring isomer of the diarylethene moiety. Such cycloreversion reaction was not observed by addition of pyridine (Figure 8c), nor addition of TEA in chloroform solution (Figure 8d, Figure S9).

In chloroform, **1A** converted to **1D** upon UV irradiation due to the trace amount of acid. By addition of TEA, the spectrum of **1B** was observed (Figure 8d). Such cycloreversion reaction by addition of TEA in acetonitrile was not observed in other diarylethene drivatives **4, 5**, and **6** (Figure S10).

The band at 630 nm in **1D** state is attributed to the merocyanine form of the malachite green moiety, therefore, we prepared the acetonitrile solution of malachite green, then added the TEA. Similar disappearance of the band was observed. We consider that by addition of TEA to the **1F** state in acetonitrile, conversion from merocyanine to triarylcarbinol was proceeded accompanied with the cycloreversion reaction of the diarylethene moiety. However, the more detailed study is necessary for the thermal cycloreversion reaction.

Conclusion

Here, we have described the six states of a photo- and halochromic system that consists of photochromic diarylethene and halochromic malachite green moieties. The condition of the malachite green moiety influenced the photochromic reactivity and the color of the dye. Quantum yield for cyclization and cycloreversion reactions between neutral states were 0.30 and 0.044, respectively. In contrast, these values are reduced to 0.012

and 1.45×10^{-3} for monocationic state, and 0.02 and 1.45×10^{-3} for dicationic state. And reversible halochromism was observed for open-ring isomer states **1A**, **1C** and **1E** with $K_{\mathrm{AC}} = 1.8 \times 10^{5}$ and $K_{\mathrm{CE}} = 8.3 \times 10^{2}$. For the closed-ring isomer states **1B**, **1D** and **1F**, $K_{\mathrm{BD}} = 1.5 \times 10^{5}$ and $K_{\mathrm{DF}} = 1.4 \times 10^{3}$ were obtained during addition of TFMSA, while cycloreversion reaction was observed by addition of TEA in acetonitrile. Such thermal cycloreversion reaction of the diarylethene moiety was newly observed. The phenomena were not observed in other diarylethene derivatives, indicating the influence of the conjugation with malachite green moiety. Further study is necessary to solve the interaction to induce TEA induced cycloreversion of diarylethene moiety. The multicolor system is interesting to form different remarkable colors, and thus the present data will contribute to the design of pH sensitive photoswitches especially for biological applications and their successful incorporation in various applications and in switchable molecular-based devices.

Experimental Section

General Information. All chemicals were purchased from commercial sources (TCI, Wako) and used as received without further purification unless stated otherwise. All solvents used were reagent grade and distilled before use. NMR spectra were recorded on a Bruker DPS400 (400 MHz) spectrometer at ambient temperature. Chemical shifts are denoted in δ units (ppm) relative to the solvent signals $CHCl_3$ (^1H NMR: $\delta = 7.26$ ppm) in $CDCl_3$ and CH_3CN (^1H NMR: $\delta = 1.94$ ppm) in CD_3CN. Mass spectra were measured on JEOL MS600 FAB-MS spectrometer using 3-nitrobenzyl alcohol as the matrix. UV light was irradiated with a hand lamp, SPECTROLINE Model EB-280C/J ($\lambda = 313$ nm). Visible light was irradiated with a 500 W Xe-arc lamp (USHIO SX-Ul501XQ). For the absorption spectral measurements, optical cells with 1 cm light path lengths were used for the absorption spectral measurement of the solutions. Quantum yields for the ring closing and ring opening of **1** were determined in hexane at room temperature. Light of appropriate wavelengths (313 nm for ring-closing and 517 nm for ring-opening reactions) was isolated by passing the output of the medium pressure mercury and Xe lamps through a monochromator (Jobin Yvon UV-10) with a long-pass filter (Toshiba Y-43, 430 nm) and then comparing it with those of 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene for the photochromism between **1A** and **1B** states, as standards.[45] Moreover, 1,2-bis(3-methylthiophen-2-yl)perfluorocyclopentene[46] and 1,2-bis[2-methyl-5-(5-trimethylsilylthiophen-2-yl)thiophene-3-yl]perfluorocyclopentene

(**6**)[47] were used as the standard for the photochromism between **1C** and **1D** and between **1E** and **1F**, respectively. The quantum yields of cyclization and cycloreversion reactions of **6** were 0.39 (λ; 313 nm) and 1.37×10^{-3} (λ; 492 nm), respectively. For the cyclization reaction, the initial slopes of the enhancement of photogenerated closed-ring isomers were compared to that of the standard, and for the cycloreversion reaction, the initial decrease of the closed-ring isomer upon visible light irradiation was compared with eq. 1, where the $A(t)$ and $A(0)$ are the time-dependent and initial absorptions and ε, ϕ, and I are the absorption coefficient, quantum yield, and light intensity, respectively.

$$\log A(t) = \log A(0) - \varepsilon\phi It \qquad (1)$$

X-ray crystallography was carried out using a CCD-based X-ray diffractometer (Bruker, SMART APEX) with MoK$_\alpha$ radiation (λ = 0.71073 Å). The temperature was controlled by a nitrogen-gas dispersion system (Japan Thermal Engineering, TC-190CP-CS-K). The data were collected as a series of ω-scan frames, each with a width of 0.3°/frame. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were determined by global refinement. The structure was solved by direct methods using SHELXS-97[48] and refined by full-matrix least-squares on F^2 using SHELXL-97.[49]

Synthesis: The synthetic procedure of compound **1A** is shown in Scheme 1, and the details are described below.

1-{5-(4-methyl benzoate)-2-methylthien-3-yl}-2-(2,5-dimethylthien-3-yl)perfluoro-cyclopentene (3). In an argon atmosphere, 1.8 mL (2.88 mmol) of 1.6 M *n*-BuLi was added drop wise to the 10 mL of THF anhydrous solution containing 1.0 g (2.4 mmol) of 1-(5-chloro-2-methylthien-3-yl)-2-(2,5-dimethylthien-3-yl)perfluorocyclopentene (**2**)[35] at -78 °C and stirred for 1 h at this temperature. Then 0.84 mL (3.12 mmol) of $B(n\text{-}BuO)_3$ was added and stirred for 30 min at the same temperature, allowed to warm to ambient temperature, and finally stirred following 30 min at room temperature. To the mixture, 4.5 mL of 2M Na_2CO_3, 0.63 g (2.4 mmol) of methyl 4-iodobenzoate, and 0.1 g (0.086 mmol) of $(PPh_3)_4Pd(0)$ were added, and then the mixed solution was refluxed for 22 h. After the reaction was over, the mixture was allowed to cool to room temperature, followed by addition of 40 mL of water and 40 mL of ether. The water layer was separated and extracted with 30 mL of ether two times. The combined ether solution was mixed with the separated organic layer and dried over sodium sulfate anhydrous. After the sodium sulfate was removed, the solvent was evaporated in vacuo. The residue was purified with silica gel chromatography (hexane: ethyl acetate = 9: 1) followed by recrystallization from hexane to obtain 378.8 mg (0.73 mmol) of **5** as a brownish crystal in 30.5% yield.

3: mp. 141.2-142.0 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 1.94 (s, 3H), 2.42 (s, 3H), 3.93 (s, 3H), 6.73 (s, 1H), 7.36 (s, 1H), 7.59 (d, 2H, *J*=8.4 Hz), 8.04 ppm (d, 2H, *J*=8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.32, 14.53, 15.12, 52.18, 115.84, 123.97, 124.57, 125.20(2C), 129.13(2C), 130.34, 137.54, 137.91, 139.775, 139.800, 140.65, 142.60, 157.26, 177.97. IR (ν, KBr, cm^{-1}): 2917, 2354, 1722, 1602, 981, 1052, 1112, 1191, 1268, 1290, 1440, 1602, 1722, 2354, 2917. Mass 516 (M^+)(99), 517 (M^++1)(100)

DAE-MG (1A). In a dry argon atmosphere, 27.6 mg of iodine was added to a THF anhydrous containing 0.2674 g (12 mmol) of magnesium. To the mixture, a THF solution (12 mL) containing 2.0 g (10 mmol) of 4-bromo-*N,N'*-dimethylaniline was added drop wise and refluxed for 40 min. The solution turned to a grayish opaque color, indicating the formation of a Grignard reagent. The solution was allowed to cool down to ambient temperature. The solution was gradually added to a THF solution (5 mL) containing 202.2 mg (0.39 mmol) of **5** and refluxed for 1 h. After the reaction was over, small amount of water was added, and then the mixture was extracted after addition of 40 mL of 3 M HCL and 40 mL of chloroform. The water layer was separated and extracted with 30 mL of chloroform twice. The combined chloroform solution was mixed with a separated organic layer and dried over sodium sulfate anhydrous. After the sodium sulfate was separated, the solvent was evaporated in vacuo. The residue was purified with silica gel chromatography (chloroform: methanol = 9: 1) to obtain 104 mg (0.143 mmol) of **1A** in 36.5% yield.

1A: (mp. 153.4-154.3 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 1.96 (s, 3H), 2.42 (s, 3H), 3.39 (s, 12H), 3.46 (s, 1H), 6.73 (s, 1H), 6.99 (4H, *J*=9.2 Hz), 7.34 (d, 2H, *J*=8.4 Hz), 7.39 (d, 4H, *J*=9.2 Hz), 7.46 (s, 1H), 7.68 ppm (d, 2H, *J*=8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.27, 14.42, 15.10, 40.50 (4C), 81.33, 111.73 (4C), 122.32, 124.50, 124.62, 124.83, 125.93, 128.35 (2C), 128.75 (4C), 131.62 (2C), 135.15 (2C), 137.70, 139.77, 140.86, 141.91, 147.76, 149.56 (2C). IR (ν, KBr, cm^{-1}): 818, 895, 944, 983, 1050, 1106, 1133, 1191, 1272, 1340, 1444, 1479, 1517, 1567, 1612, 2360, 2801, 2917, 3451. (Fig. S11) Anal. Calcd for $C_{39}H_{36}F_6N_2OS_2$: C, 64.45; H, 4.99; N, 3.85. Found: C, 64.23; H, 5.12; N, 3.78. MS m/z 709 (M-17 (OH))

DAE-MG (1B). The acetonitrile solution of **1A** was irradiated UV light and reached to the photo-stationery state (**1A:1B =** 12:88). Then **1B** was obtained by recrystallization from acetonitrile. (mp. 270 °C (dec.)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.10 (s, 3H), 2.22 (s, 3H), 2.61 (s, 1H), 2.94 (s, 12H), 6.03 (s, 1H), 6.61 (s, 1H), 6.65 (d, 4H, *J* = 9.2 Hz), 7.10 (d, 4H, *J* =9.2 Hz), 7.39 (d, 2H, *J* = 8.8 Hz), 7.47 ppm (d, 2H, *J*=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.43, 24.81, 25.04, 32.99, 40.48 (4C), 41.27, 81.36, 111.74 (4C), 113.31, 114.16, 114.74, 115.83, 116.52, 126.15 (2C), 128.13 (2C), 128.74 (4C), 134.74 (2C), 140.65, 149.61 (2C), 150.69, 157.25. IR (ν, KBr, cm^{-1}) : 814, 908, 916, 1050, 1120, 1189, 1345, 1440, 1521, 1619, 2801, 2917, 3444, 3782. MS m/z 709 (M-17 (OH)). (Fig. S11)

^{1}H NMR measurement. The monitoring of photochromism was carried out in NMR tubes. Compound **1A** (3 mg) was dissolved in 0.75 mL of CD_3CN and the acidity was controlled by adding DCl (35 wt%, Aldlich).

X-ray crystal structure. Crystallographic data for the structural analysis of compound **1A** has been deposited at Cambridge Crystallographic Data Centre as No. CCDC 988706. The data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2, 1EZ, UK; fax: +44 1223 336033; E-mail:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Procedure of halochromism by addition of TEA

The solution of **1E** was prepared from acetonitrile solution of **1A** (5 mL of 7.26×10^{-6} M) and 300 μL of 1M TFMSA acetonitrile solution and stored 12 h to arrive at the equilibrium. After addition of 50 μL of TEA solution, the spectra were shifted to that of **1C** state. Further addition of TEA, the band of **1C** at 625 nm decreased and it reached to that of **1A**. The solution of **1F** state was prepared by addition of TFMSA as mentioned above to the **1B** solution prepared by UV (313 nm) irradiation (a photostationary state (**1A**:**1B**=12:88)). To the **1F** state, 1M TFMSA acetonitrile solution was added subsequently as same as that of **1E**. After addition of 50 μL TEA, the band was appeared around 630 nm and the solution was green (**1G**), which is similar to **1C** instead of **1D**. Further addition of TEA (total amount of 100 μL) induced the disappearance of the bands in 500-700 nm wavelengths region and the color of the **1H** was yellow as shown Figure 1. **1H** is different from **1A** state, because the new band was observed at 392 nm.

Solution preparation of the fatigue resistance and thermal stability measurement

The acetonitrile solution of **1C** was prepared by mixing 2 mL of the acetonitrile solution (7.27×10^{-6} M) of **1A** and 5 μL of 3.0×10^{-3} M TFMSA acetonitrile solution. The acetonitrile solution of **1E** was prepared by mixing 5 mL of the acetonitrile solution (7.27×10^{-6} M) of **1A** and 300 μL of 1M TFMSA acetonitrile solution and 700 mL of acetonitrile.

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References

(1) H. Duerr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*; Elsevier, Amsterdam, 2003.

(2) G. H. Brown, *Photochromism*, Wiley-Interscience, New York, 1971.

(3) B. L. Feringa and W. B. Browne, *Molecular Switches*; Wiley-VCH, Weinheim, 2011.

(4) J. C. Crano, R. Guglielmetti, *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999; Vol. 1.

(5) M. Irie, *Chem. Rev*., **2000**, **100**, 1685−1716.

(6) F. Pina, M. J. Melo, M. Maestri, R. Ballardini and V. Balzani, *J. Am. Chem. Soc.*, 1997, **119**, 5556-5561.

(7) A. Roque, C. Lodeiro, F. Pina, M. Maestri, S. Dumas, P. Passaniti and V. Balzani, *J. Am. Chem. Soc.*, 2003, **125**, 987–994.

(8) Y. Yokoyama, T. Yamane and Y. Kurita, *J. Chem. Soc., Chem. Commun.,* 1991, 1722-1724.

(9) S. H. Kawai, S. L. Gilat, R. Posinet and J.-M. Lehn, *Chem. Eur. J.*, 1995, **1**, 285-293.

(10) M. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1993, **115**, 6442–6443.

(11) M. Irie, O. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894-9900.

(12) T. Yamaguchi, S. Hatano and J. Abe, *J. Phys. Chem. A,* 2014, **118**, 134−143.

(13) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515-1566.

(14) F. M. Raymo, *Adv. Mater*., 2002, **14**, 401-414.

(15) M. N. Stojanovic, T. E. Mitchell and D. Stefanovic, *J. Am. Chem. Soc*., 2002, **124**, 3555-3561.

(16) A. Perrier, F. Maurel and D. Jacquemin, *Acc. Chem. Res*., 2012, **45**, 1173-1182.

(17) K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura and M. Irie, *Chem. – Eur. J.*, 2005, **11**, 534-542.

(18) K. Higashiguchi, K. Matsuda and M. Irie, *Angew. Chem. Int. Ed.,* 2003, **42**, 3537-3540.

(19) K. Higashiguchi, K. Matsuda, N. Tanifuji and M. Irie, *J. Am. Chem. Soc.,* 2005, **127**, 8922-8923.

(20) M. Morimoto, S. Kobatake and M. Irie, *J. Am. Chem. Soc*., 2003, **125**, 11080-11087.

(21) K. Yumoto, M. Irie and K. Matsuda, *Org. Lett*., 2008, **10**, 2051-2054.

(22) Y. Odo, K. Matsuda and M. Irie, *Chem. Eur. J*., 2006, **12**, 4283 – 4288.

(23) K. Suzuki, T. Ubukata and Y. Yokoyama, *Chem. Commun*., 2012, **48**, 765–767.

(24) J. Massaad, J.-C. Micheau, C. Coudret, R. Sanchez, G. Guirado and S. Delbaere, *Chem. Eur. J.*, 2012, **18**, 6568–6575.

(25) K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi and M. Irie, *Tetrahedron*, 2001, **57**, 4559-4565.

(26) M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem*., 1995, **60**, 8305-8309.

(27) S. Kobatake and Y. Terakawa, *Chem. Commun.*, 2007, **17**, 1698-1700.

(28) H. Liu, X. Zhang, Z. Gao and Y. Chen, *J. Phys. Chem. A,* 2012, **116**, 9900-9903.

(29) S. H. Kawai, S. L. Gilat and J.-M. Lehn, *Eur. J. Org. Chem.,* 1999, 2359-2366.

(30) S. Pu, D. Jiang, W. Liu, G. Liu and S. Cui, *J. Mater. Chem.,* 2012, **22**, 3517-3526.

(31) S. Pu, Z. Tong, G. Liu and R. Wang, *J. Mater. Chem. C*, 2013, **1**, 4726-4739.

(32) G. Liu, S. Pu and R. Wang, *Org. Lett*., 2013, **15**, 980-983.

(33) S. Pu, C. Zheng, Q. Sun, G. Liu and C. Fan, *Chem. Commun*., 2013, **49**, 8036-8038.

(34) A. Samat, V. Loskin, K. Chamontin, D. Levi, G. Pepe and R. Guglielmetti, *Tetrahedron*, 2001, **57**, 7349‑7359.

(35) G. Sevez, J. Gan, S. Delbaere, G. Vermeersch, L. Sanguinet, E. Levillain and J.-L. Pozzo, *Photochem. Photobiol. Sci.*, 2010, **9**, 131-135.

(36) M. Irie and D. Kungwatchakun, *Macromolecules,* 1986, **19**, 2476-2480.

(37) M. Irie and M. Mohri, *J. Org. Chem.,* 1988, **53**, 803-808.

(38) H. Lund, A Theory of Halochromism, KOBENHAVN, **1931**.

(39) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759-760.

(40) S. Kobatake, T. Yamada, K. Uchida, N. Kato and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 2380–2386.

(41) M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem.Commun.* **1999**, 747-748

(42) A. Peters and N. R. Branda, *Adv. Mater. Opt. Electron.,* 2000*,* **10**, 245-249.

(43) S. Kobatake, K. Uchida, E. Tsuchida and M. Irie, *Chem. Commun.,* 2002, 2804-2805.

(44) S. Kobatake, M. Yamada, T. Yamada and M. Irie, *J. Am. Chem. Soc.* 1999, **121***,* 8450-8456.

(45) T. Sumi, Y. Takagi, A. Yagi, M. Morimoto and M. Irie, *Chem. Commun*., 2014, **50**, 3928-3930.

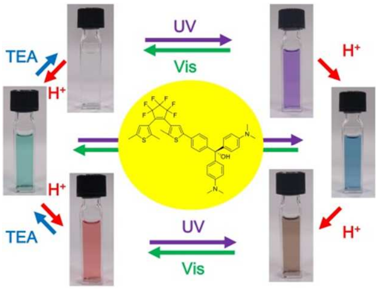
(46) T. Fukaminato, T. Kawai, S. Kobatake and M. Irie, *J. Phys. Chem. B*, 2003, **107**, 8372-8377.

(47) N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura and K. Uchida, *Langmuir*, 2013, **29**, 8164−8169.

(48) G. M. Sheldrick, *Acta Cryst*. **1990**, *A46*, 467.

(49) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen, Germany, **1997**.

Graphic Abstract



A diarylethene with a malachite green moiety was synthesized, and it showed multicolor states by photochromic and halochromic reactions.