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Fatigue resistance of photochromic diarylethene in the presence of cyclodextrins with different pore sizes

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Abstract

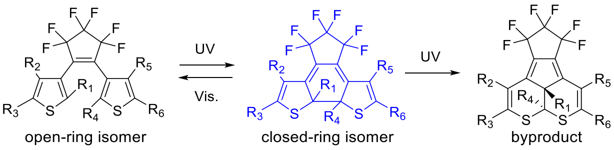
Among the various types of photochromic compounds, diarylethenes have good fatigue resistance, but further improvement is required. In this study, we investigated the photochromic reaction behavior and its fatigue resistance by included in cyclodextrin (CD), which is a cyclic host molecule with three different pore sizes. A water-soluble diarylethene (**DE1**) synthesized in this work exhibited reversible photochromism in water. The continuous irradiation with UV light resulted in the formation of its byproduct. The addition of αCD showed no improvement of fatigue resistance. However, the addition of βCD and γCD suppressed a side reaction to result in the improvement of fatigue resistance. Especially, the addition of γCD gave a large improvement. To clarify the relationship between fatigue resistance of **DE1** and the pore size of CD, the host-guest interaction between **DE1** and CD was investigated using NOESY spectrum. The results indicate that the depth of **DE1** included in CD shows a large effect on suppression of the side reaction of **DE1**.

Keywords: diarylethene, fatigue resistance, cyclodextrin

1. Introduction

Photochromic molecules can switch various physical properties in response to light, and are attracting attention in a wide range of research fields such as photochemistry, physical chemistry, material chemistry, crystal chemistry, and biochemistry.[1] Among various photochromic compounds such as azobenzene, spiropyran, hexaarylbiimidazole, naphthopyrane, furyl fulgide, and diarylethene, diarylethene has good fatigue resistance, high sensitivity, rapid responsiveness, and high reactivity in the solid state. Due to their properties, it is one of the promising compounds for applications such as single molecule optical memory, optical sensor, radiation sensor, and photoactuator.[2–4] However, further improvement of fatigue resistance is required for practical use.

The photochromic reaction of diarylethene is based on the electrocyclic reactions between the open-ring isomer and the closed-ring isomer upon alternating ultraviolet (UV) and visible light irradiation (Scheme 1). However, when the repeating cycles between the open-ring isomer and the closed-ring isomer increase, byproducts are gradually produced to result in poor switching performance. One of the byproducts is well-known to be produced by irradiation of the closed-ring isomer with UV light, as shown in Scheme 1.[5–8] The absorption maximum wavelength of the byproduct, which is photostable, is slightly shorter than that of the closed-ring isomer in the visible light region. Other byproducts are also reported in the literature as minor byproducts.[6,9]

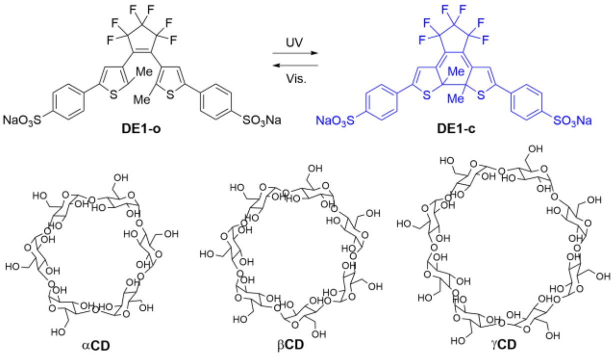


Scheme 1. Photochromic reaction and side reaction of diarylethene.

Although diarylethenes having high fatigue resistance were reported to undergo photochromic cycles more than 10^4 times,[2,5,10,11] it is strongly desired to further improve fatigue resistance. Several approaches have been reported to improve fatigue resistance of diarylethene, including introduction of attractive groups.[12–14] However, changing the chemical structure not only improves fatigue resistance, but also changes optical properties such as photochromic reactivities and absorption wavelength. To use well-designed diarylethenes having a specific photochromic performance in a practical application without further molecular structural changes, it is necessary to improve fatigue resistance by adding additives. Herein, we have focused on host-guest chemistry, which allows molecules to be assembled using non-covalent bonds between molecules. Clarifying what kind of interaction between the molecules affects fatigue resistance of diarylethene opens up future possibilities for improving fatigue resistance of all diarylethenes by additives. In recent years, research on photochemistry applying supramolecular chemistry and host-guest chemistry has attracted attention, and several examples of achieving skillful functionality by incorporating diarylethene and other photochromic compounds into host-guest systems have been reported.[15,16] The examples of realizing a non-covalent multicolor luminescent material with supramolecular nanofibers composed of diarylethene and cucurbituril and carbon dots,[17] and controlling the thermal ring-opening reaction by inclusion of a cationic diarylethene in a crown ether,[18] and constructing a host supramolecular system that controls the inclusion ability in response to light composed of diarylethene and palladium ions has been reported.[19]

Cyclodextrin (CD) is known as a cyclic host molecule that can include a hydrophobic molecule as a guest molecule in a cavity, and there are three types of CDs such as α, β, and γ-cyclodextrins with different cavity sizes.[20] Since these have different numbers of repeating units of glucose, the pore diameters are different, and the pore diameters increase in the order of αCD, βCD, and γCD. There are also several studies on the inclusion effect of CD on the photochromic reactivity of diarylethene.[21–23] For example, a diarylethene derivative having a benzothiophene skeleton as an aryl group showed a higher quantum yield in the photocyclization reaction when it was included in the CD because the diarylethene was incorporated in a photoreactive antiparallel conformation.[21] However, there is no report on the improvement of fatigue resistance of diarylethene by included in CD. Recently, it has been reported that fatigue resistance of diarylethene is improved by included in cucurbituril, which is a cyclic host molecule.[24] However, the improvement of fatigue resistance of diarylethene is small, and it has not been considered how the host molecule affected the general side reaction of diarylethene at the molecular level by comparing host molecules with different pore sizes.

In this study, diarylethene having sodium sulfonate groups at the *p*-position of the lateral phenyl ring (**DE1**) was newly synthesized, and fatigue resistance of **DE1** including αCD, βCD, or γCD in water was compared (Scheme 2). We also investigated the host-guest interaction between **DE1** and CD to clarify how the pore size of cyclodextrin affects the side reaction of diarylethene. This would be new information for improving fatigue resistance of diarylethene.



Scheme 2. Photochromic reaction of **DE1** and three types of cyclodextrins.

2. Experimental

General Information

All solvents were distilled before use. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Biospin Avance 300 nanobay. Nuclear Overhauser effect spectroscopy (NOESY) was conducted with a Bruker Biospin Avance III HD 600. The chemical shift of HOD in D$_2$O (4.70 ppm) was used as reference. High resolution mass spectrum (HR-MS) was acquired by a Bruker FT-ICR/solariX mass spectrometer. Fatigue resistance was measured by continuous irradiation with UV light at 313 nm (70 mW cm^{-2}) to detect absorbance the closed-ring isomer in the stirring solution of water using a SHIMADZU UV-2600 absorption spectrometer. A mercury-xenon lamp (MORITEX MUV-202U) was used as the light source, and monochromatic light at 313 nm was obtained by passing the light through a 313 nm bandpass filter. The association constant K_a by a supramolecular titration was determined using a software of supramolecular.org.[25]

Materials

Three types of CDs (αCD, βCD, and γCD) purchased from Wako Pure Chemical Industries, Ltd. were used as they were. Diarylethene **DE1-o** was synthesized as follows: 1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene[26] (830 mg, 1.6 mmol) was dissolved in chloroform (5.0 mL) under argon atmosphere. Chlorosulfonic acid (610 mg, 5.2 mmol) was slowly added dropwise to the solution at room temperature. After the reaction for 2.5 h, adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by NaOH aqueous solution, extracted with water, washed with saturated NaCl aqueous solution, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (acetone/methanol = 3:1) and recrystallization from methanol to give 420 mg of **DE1-o** in 39% yield as a white powder. **DE1-o**: ^{1}H NMR (300 MHz, D$_2$O) δ = 1.86 (s, 6H, CH$_3$), 7.52 (s, 2H, Thienyl H), 7.64 (d, J = 8.7 Hz, 4H, Aromatic H) 7.69 (d, J = 8.7 Hz, 4H, Aromatic H). ^{13}C NMR (75 MHz, methanol-d$_4$) δ = 14.6, 124.4, 126.3, 127.1, 127.9, 136.2, 142.9, 143.7, 145.8. HR-MS (MALDI, negative) m/z = 700.9631 ([M − Na]$^-$). Calcd. for $C_{27}H_{16}F_6NaO_6S_4^-$ = 700.9637.

3. Results and Discussion

Characterization of DE1

The photochromic reaction behavior of **DE1** in water was examined. The maximum absorption wavelength of **DE1-o** in water is 308 nm, and upon irradiation with UV light at 313 nm a visible absorption band of **DE1-c** appeared at 596 nm. In addition, the colored **DE1-c** returned to the original **DE1-o** by irradiation with visible light (> 470 nm). Figure 1a shows the changes in the absorption spectra of **DE1** in water, and Table 1 summarizes the photochromic properties of **DE1**. The photocyclization quantum yield of **DE1-o** in water upon irradiation with UV light at 313 nm showed a very high value of $\Phi_{o\to c}$ = 0.73. Since the sodium sulfonate groups of **DE1-o** are dissociated into 2Na$^+$ and the dianions of **DE1-o**, **DE1-o** prefers the antiparallel formation by the repulsion of the dianions in water to result in the high cyclization quantum yield.[27] The photocycloreversion quantum yield of **DE-c** was determined to be 0.0040.

Photochromic Properties and Fatigue Resistance in the Presence of CD

Photochromic behavior of **DE1** in the presence of 100 equivalents of αCD, βCD, and γCD in water was examined. Figure 1b-d show the absorption spectral changes of these samples. In the experiment, the absorbance at the irradiation wavelength of 313 nm was adjusted to 0.97 in four samples. No significant difference was observed in the absorption spectral changes by addition of any CDs. Next, the photocyclization quantum yield of **DE1-o** associated with the addition of CD was examined as shown in Figure S1. All the samples showed the same quantum yields, and it was found that photocyclization quantum yield of **DE1-o** did not change with the addition of any CDs. This result differs from the fact that reported previously for the disulfonate of 1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene.[21] **DE1-o** has a high proportion of the antiparallel conformations even in the absence of CD. Therefore, the proportion of the antiparallel conformation was not affected by the inclusion of **DE1-o** in CD.

Next, fatigue resistance of **DE1** with the addition of CD was examined. Upon irradiation to the **DE1-o** aqueous solution with UV light at 313 nm, the absorption band at 596 nm derived

Table 1. Photochromic characteristics of **DE1** and **DE1** with 100 equivalents of CD added in H_2O.

CD	**DE1-o**		**DE1-c**		Quantum yields		Conversion^c/%
	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ε/M^{-1} cm^{-1}	$\Phi_{o\to c}{}^a$	$\Phi_{c\to o}{}^b$	
none	308	39400	596	15500	0.73	0.0040	96
αCD	308	39400	596	15500^d	0.76	–^{e}	96
βCD	308	36300	596	15500^d	0.74	–^{e}	91
γCD	308	37200	596	15500^d	0.73	–^{e}	92

[a] Irradiation with 313 nm light. [b] Irradiation with 575 nm light. [c] The cyclization conversion ratio upon irradiation with 313 nm light. [d] Assuming no change by CD addition. [e] Not determined.

from **DE1-c** gradually increased according to the photoisomerization reaction from **DE1-o** to **DE1-c**. The irradiation for 6 seconds reached a maximum absorbance at 596 nm at the photostationary state (PSS) (Figure 2a). With further UV irradiation, the absorption band at 596 nm gradually decreased (Figure 2b). The result indicates that absorbance at 596 nm was reduced by a side reaction from **DE1-c**. A slight blue shift in the visible absorption band was observed in Figure 2d, suggesting that it is due to the formation of a byproduct.[6,7] This experiment was also carried out in the presence of 100 equivalents of αCD, βCD, and γCD to compare fatigue resistance. The absorbance at 596 nm, which is derived from **DE1-c**, was also plotted against the UV irradiation time (Figure 2a,b). Although no significant difference for photocyclization reactivity from **DE1-o** to **DE1-c** was observed with the addition of CD (Figure 2a), a difference for the byproduct formation was observed by further continuous irradiation with UV light. The absorbance at 596 nm in the **DE1** aqueous solution without CD and with αCD decreased considerably due to the side reaction associated with UV irradiation and became less than half of the original after UV irradiation for 2000 seconds (Figure 2d). On the other hand, in the **DE1-o** aqueous solution with βCD and γCD, the decays of the absorbance at 596 nm due to the side reaction was gradual. It was found that the addition of βCD and γCD suppressed the side reactions and improved fatigue resistance. Moreover, the **DE1** aqueous solution with γCD, which has the largest pore size, has considerably improved fatigue resistance as compared with the **DE1** aqueous solution with βCD, and the decrease in absorbance is suppressed to about 35% even after 2000 seconds. From this result, it was clarified that fatigue resistance of **DE1** was deeply related to the pore size of the added CD.

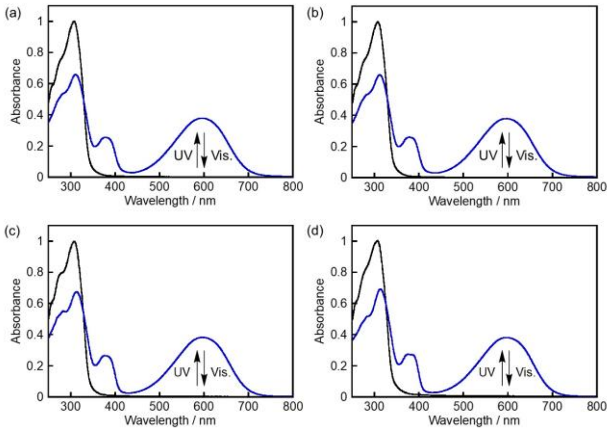


Fig 1. Absorption spectral changes of **DE1** (a) without CD, [**DE1-o**] = 25.4 μM, (b) with αCD, [**DE1-o**] = 25.4 μM, [αCD] = 2.54 mM, (c) with βCD, [**DE1-o**] = 27.6 μM, [βCD] = 2.76 mM, (d) with γCD, [**DE1-o**] = 27.0 μM, [γCD] = 2.70 mM, in H_2O upon alternating irradiation with 313 nm light and visible light.

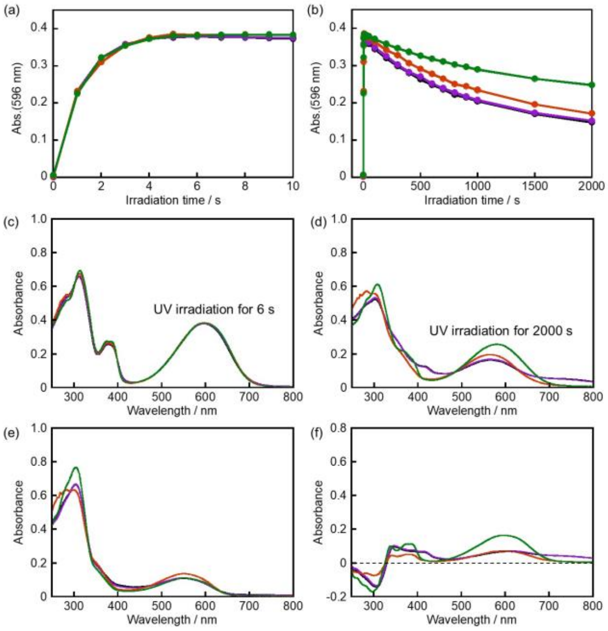


Fig. 2 (a, b) Absorbance changes of **DE1-c** without any CD (black) and with αCD (purple), βCD (red), and γCD (green) upon irradiation at 313 nm in water and absorption spectra after irradiating UV light at 313 nm for (c) 6 and (d) 2000 seconds. (e) Absorption spectra of the samples irradiated with UV light for 2000 seconds to be followed by sufficient irradiation with visible light. (f) Difference spectra between (d) and (e). All samples were carried out under the concentration conditions shown in Figure 1.

Spectroscopic Analysis of Byproducts

The continuous UV irradiation to diarylethenes for a long time results in the formation of some byproducts. The well-known major byproduct has absorption at a wavelength several nm shorter than the absorption band of the closed-ring isomer in the visible region. The samples irradiated with UV light for 2000

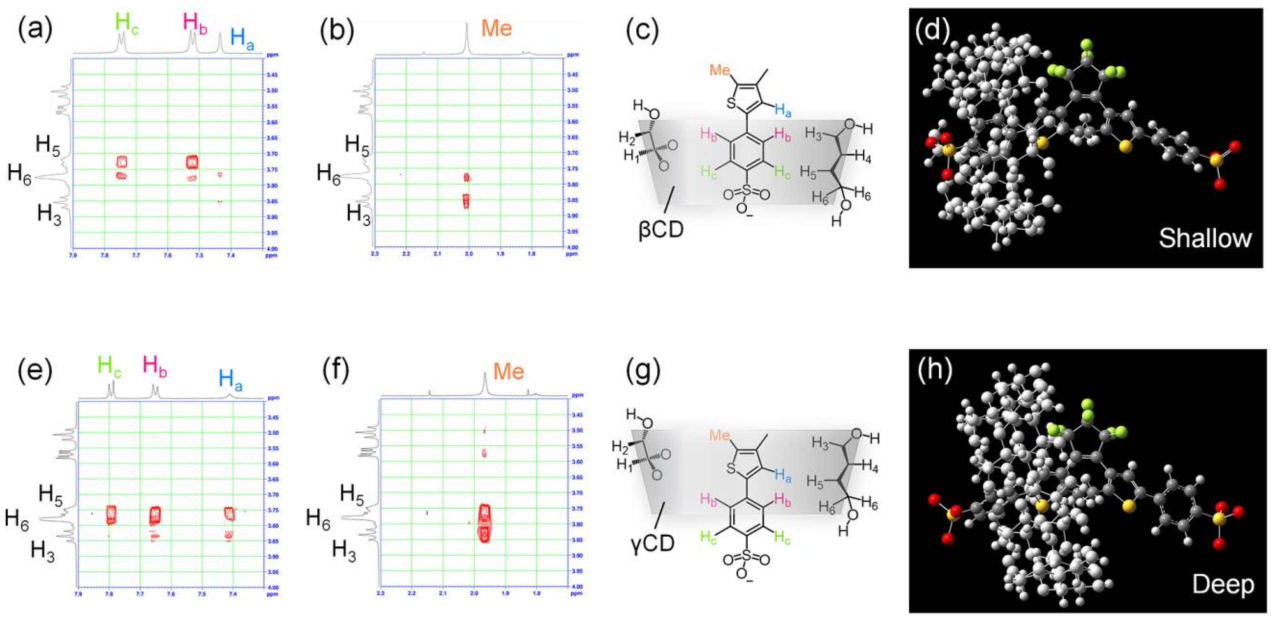


Fig. 3 NOESY spectra of (a,b) **DE1-o**@βCD and (e,f) **DE1-o**@γCD in water and schematic of (c,d) **DE1-o**@βCD and (g,h) **DE1-o**@γCD.

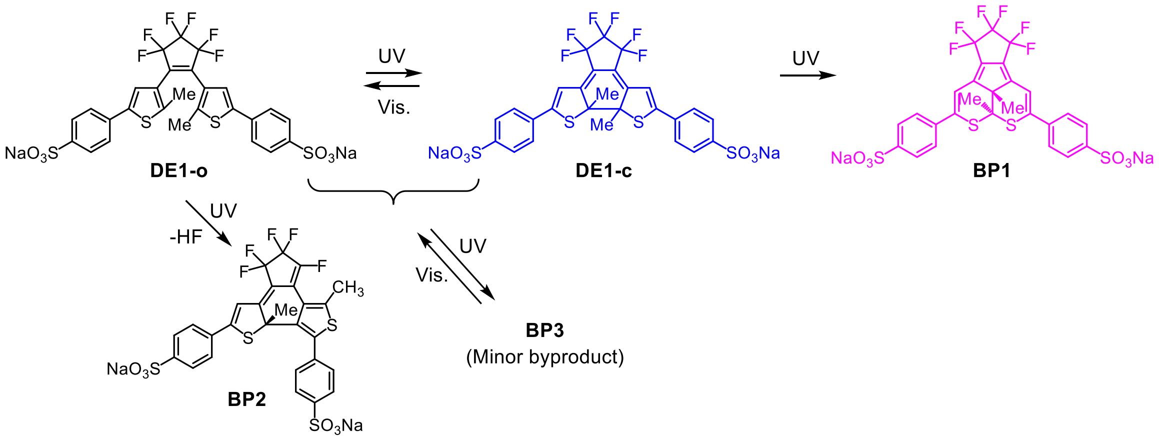
seconds shown in Figure 2d were irradiated with visible light (> 470 nm) to return from **DE1-c** to **DE1-o**. After the visible light irradiation, the absorption band in the visible region around 550 nm remained in all samples as shown in Figure 2e. This is ascribed to byproduct **BP1** (Scheme 3). The formation reaction of **BP1** occurred upon irradiation to **DE1-c** with UV light to the same extent without and with the addition of any CDs.

To clarify the components bleached by the visible light irradiation, the spectra in Figure 2e were subtracted from the spectra in Figure 2d. The results are shown in Figure 2f. The main component of the spectra is assigned to **DE1-c**, which returns to **DE1-o** by irradiation with visible light. The additional small band in the region of 700-800 nm was also observed for the samples without CD and with αCD (Scheme S2).

Here we considered the existence of three types of byproducts, **BP1**, **BP2**, and **BP3**. The expected molecular structures of **BP1**, **BP2**, and **BP3** are shown in Scheme 3. **BP1** is the main byproduct, which has the absorption band around 550 nm. **BP2** has no absorption in the visible region and is a structure similar to that previously reported as a byproduct of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene.[6] **BP3** is a minor byproduct with an absorption band around 750 nm as shown in Figure S2, whereas the structure is not identified. The detail mechanism for improving fatigue resistance is described in a later section.

Host-Guest Chemistry of DE1@CD

To clarify why fatigue resistance of **DE1** was improved by the addition of CD, and why γCD with a large pore size gave **DE1** much higher fatigue resistance than βCD, the host-guest chemistry for inclusion complex of **DE1** and CD was investigated. NOESY can detect the correlation between protons that are spatially close to each other, with strong peaks at closer locations. Therefore, the NOESY spectrum can ascertain the presence of inclusion from the correlation between the four types of protons (methyl proton, H_a, H_b, and H_c) in **DE1-o** and the protons (H_3, H_5, and H_6) inside the cavity of CD. The NOESY spectra were measured in a D_2O solution of **DE1-o** (0.5 mM) and αCD, βCD, or γCD (5.0 mM; 10 eq. relative to **DE1-o**). No correlation peak was observed in the **DE1-o**/αCD sample, suggesting that αCD has too small pore size to include **DE1-o** (Figures S3-S5). On the other hand, in the **DE1-o**/βCD sample,



Scheme 3. The expected molecular structures of byproducts from **DE1**.

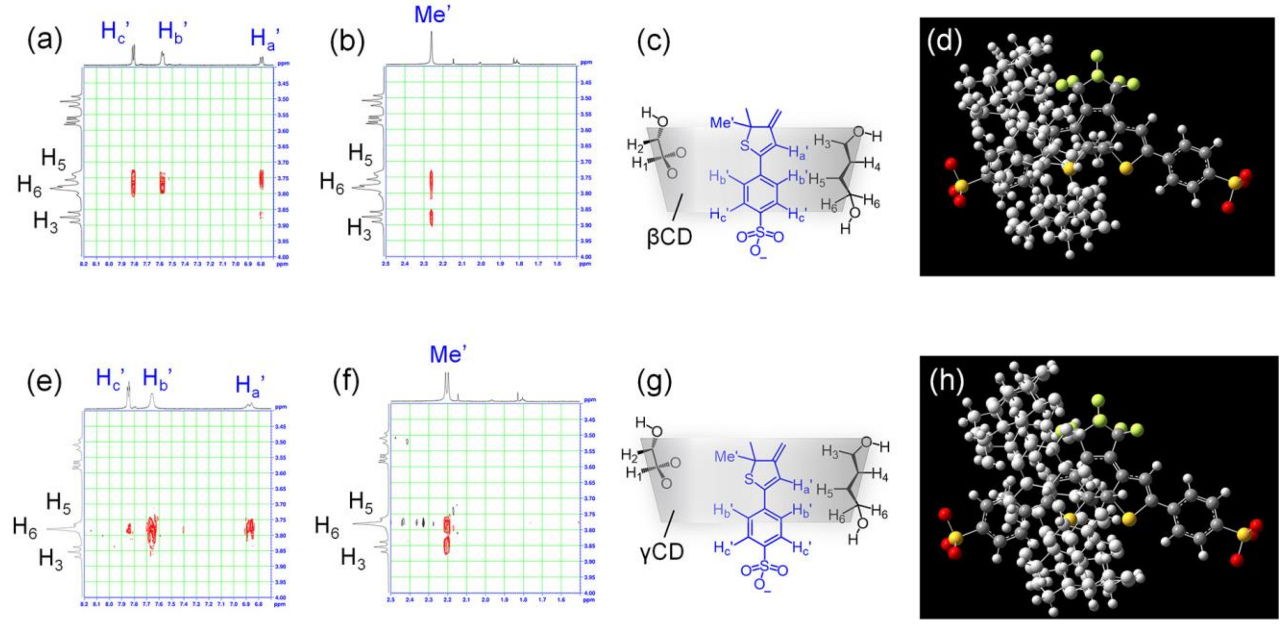


Fig. 4 NOESY spectra of (a,b) **DE1-c**@βCD and (e,f) **DE1-c**@γCD in water and schematic of (c,d) **DE1-c**@βCD and (g,h) **DE1-c**@γCD.

a correlation between the methyl protons in **DE1-o** and H_3 in βCD and a strong correlation between H_b and H_c in **DE1-o** and H_5 in βCD were confirmed (Figure 3a,b, Figure S6). This result indicates that βCD includes **DE1-o** to form the inclusion complex **DE1**-o@βCD. Subsequently, in the **DE1-o**/γCD sample, a strong correlation between the methyl protons in **DE1-o** and H_3, H_5, and H_6 in γCD and a strong correlation between H_b in **DE1-o** and H_6 in γCD were confirmed (Figure 3e,f, Figure S7). Therefore, γCD includes **DE1-o** to form the inclusion complex **DE1-o**@γCD. The changes in the chemical shifts of H_5 and H_6 in CD in the mixture of CD and **DE1-o** are shown in Figure S8. As expected, the chemical shifts for the **DE1-o**/αCD samples did not change. However, the chemical shifts for the **DE1-o**/βCD and **DE1-o**/γCD samples changed due to the difference in the ratio of **DE1-o** and CD, as shown in Figure S8. The job plots were applied to confirm the formation of a 1:1 inclusion complex, as shown in Figure S9. The maximum at 50% in the job plots indicates that both **DE1-o**/βCD and **DE1-o**/γCD form a 1:1 inclusion complex. By comparing these strong, weak, and silent correlations in NOESY spectra, we created an expected 1:1 inclusion complex model (Figure 3c,d,g,h). In **DE1-o**@βCD, relatively shallow inclusion is observed so that the phenyl ring of **DE1-o** is included in the central part of βCD (Figure 3c). In contrast, in **DE1-o**@γCD, the thiophene ring of **DE1-o** is in the central part of γCD (Figure 3g). From these results, it was found that there was a difference in the inclusion depth of **DE1-o** between **DE1-o**@βCD and **DE1-o**@γCD (Figure 3d,h). Next, the same sample was irradiated with 313 nm light and the NOESY spectra of **DE1-c** and each CD were measured (Figure 4, Figures S7,S10-S13). Similar to **DE1-o**, no correlation was found, and no inclusion was found in the **DE1-c**/αCD sample (Figures S10-S12). In contrast, compared with **DE1-o**@βCD, **DE1-c**@βCD showed a strong correlation between the methyl and H_a’ protons and the H_5 proton in CD (Figure 4a,b, Figure S12). It was stabilized at a slightly deeper inclusion position than **DE1-o**@βCD (Figure 4c,d). Compared with **DE1-o**@γCD, **DE1-c**@γCD has a smaller correlation between H_c’ and H_6, and a smaller correlation between the H_3 proton and the aromatic protons, H_a’ and H_b’, indicating that the CD is deeper inclusive (Figure 4e,f, Figure S14). Therefore, it was also stabilized at a slightly deeper inclusion position than **DE1-c**@γCD (Figure 4g,h). Thus, in the **DE1-c**@βCD and **DE1-o**@γCD samples, it was found that the inclusion depth was slightly deepened by the photochromic reaction from **DE1-o** to **DE1-c**. Even in **DE1-c**, γCD has deeper inclusion than βCD. This is due to the decrease in molecular volume from **DE1-o** to **DE1-c**. Diarylethenes undergo photochromism even in the crystalline phase without significant molecular volume changes.[3] This is one of the characteristics of photochromic diarylethenes. Therefore, the molecular structure change in diarylethene can easily proceed even in the pore of CD.

In addition, the shift of the methyl protons of **DE1-o** by UV irradiation and CD addition was measured by ^{1}H NMR in order to confirm the inclusion of **DE1-c** and CD (Figures S15-S17). As a result, the addition of αCD did not affect the chemical shift of **DE1**, but the addition of βCD and γCD shifted the chemical shift of the methyl protons of both **DE1-o** and **DE1-c** to the low magnetic field side. The results of the chemical shift in this experiment also support that both **DE1-o** and **DE1-c** are included in βCD and γCD.

Finally, the association constant (K_a), which is an index showing the ease of inclusion in **DE1-o**@βCD and **DE1-o**@γCD, was examined by two methods. The first method utilizes the fact that the methyl protons of **DE1-o** in ^{1}H NMR are shifted by the addition of CD, and by preparing multiple samples with different concentrations of CD while keeping the constant concentration of **DE1-o**. The change in the chemical shift was simulated by fitting to calculate the association constant (Figures S18-S25). In the second method, the K_a value was calculated by the simulation of a supramolecular titration[25] for the change in the chemical shift of H_1 in CD (Figures S26-S33). Both results were in good agreement with the fitting curve in the simulation of the 1:1 inclusion complex, indicating that both **DE1-o**@βCD and **DE1-o**@γCD are formed in the 1:1 inclusion complex. From the average of these experimental values, the K_a values were determined as follows: $K_a = 1.7\times10^4\ M^{-1}$ for **DE1-o**@βCD and $K_a = 7.7\times10^3\ M^{-1}$ for **DE1-o**@γCD (Table S1). Contrary to expectations, the K_a value for γCD was smaller than that for βCD.

Calculating from the K_a values, it was found that the contribution of the inclusion complex is 98% for βCD and 95% for γCD under the conditions in Figures 1 and 2, indicating a quite high contribution of the inclusion complex for both samples. These results indicate that a difference in fatigue resistance in the presence of βCD and γCD is not due to the different K_a value.

Mechanism proposed for improving fatigue resistance

As results of the fatigue resistance experiments and spectroscopic analysis of byproducts, one of the byproducts, **BP1**, is the main component of byproducts, whereas **BP1** was produced to the same extent with and without the addition of any CDs. This indicates that the formation reaction of **BP1** proceeds even in a narrow inclusion space with a smaller free volume via a 1,2-ditropic transition.[11,28] Next, the formation reaction of **BP2**, which has no absorption in the visible region, is reported in the literature.[6] The unsymmetrical closed-ring isomer is expected to be produced by rotating the thienyl group (Scheme S1). The HF elimination can promote the formation of **BP2**. Therefore, it is considered that inclusion of **DE1-o** with βCD and γCD locks the rotation of thienyl group and suppresses the production of **BP2**. Furthermore, γCD can suppress the production of **BP2** more than βCD. Finally, the production of **BP3**, which is a more minor component, was suppressed by the addition of only βCD and γCD. Although the structure of **BP3** is unpredictable, the formation of **BP3** is also suppressed by a narrow inclusion space. We believe that CD can suppress the side reaction of diarylethene that progresses via large structural changes. This is a new mechanism for improving the fatigue resistance of diarylethene, and its inclusion in CD has shown the possibility of imparting fatigue resistance at the molecular level to diarylethene having an arbitrary structure.

4. Conclusion

A new diarylethene **DE1** showing good photochromic performance was synthesized. Comparing the fatigue resistance of **DE1** by adding αCD, βCD, and γCD, which are three types of cyclodextrins with different pore diameters, the fatigue resistance was improved by adding βCD and γCD. Furthermore, the addition of γCD significantly improved the fatigue resistance of **DE1**. By the spectroscopic analysis of byproducts, it was predicted that three types of byproducts, **BP1**, **BP2**, and **BP3**, were produced. As a result of investigating the host-guest interaction between **DE1** and each CD in order to clarify the cause of the improved fatigue resistance, no inclusions were found in αCD with a small pore size. On the other hand, relatively shallow inclusion complexes were confirmed in βCD in both **DE1-o** and **DE1-c**, and deep inclusion complexes were confirmed in γCD in both **DE1-o** and **DE1-c**. From these results, it is considered that the depth of inclusion of **DE1** is greatly dependent on fatigue resistance. The formation reaction of **BP2** requires a rotation of the thienyl group in the first stage, whereas this rotation can be locked by the deep inclusion of CD. Therefore, deep inclusion of CD suppresses the production of **BP2** and improves fatigue resistance. This is a new way to improve the fatigue resistance of diarylethene **DE1**.

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Notes

The authors declare no competing financial interests.

Supporting Information

Detailed results of photocyclization quantum yields, NMR spectroscopic data, and the determination of association constant are available in Supporting Information. This material is available on https://doi.org/10.1246/bcsj.********.

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Graphical Abstract

<Title>
Fatigue resistance of photochromic diarylethene in the presence of cyclodextrins with different pore sizes

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<Summary>

Inclusion in cyclodextrin (CD) improves fatigue resistance of diarylethene **DE1**. Moreover, the addition of γCD, which has a larger pore size and includes **DE1** deeper, has realized excellent fatigue resistance. Therefore, the suppression of the rotation of the thienyl group by CD suppresses the side reaction to result in the improvement of fatigue resistance.

<Diagram>