Photochromism of Dithienylethenes Included in Cyclodextrins

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The effect of inclusion of diarylethenes in cyclodextrin cavities on cyclization quantum yields and on circular dichroism (CD) spectral changes by photoirradiation was studied. The addition of β- and γ-cyclodextrins to an aqueous solution of the open-ring form of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophene-6-sulfonate) (**1a**) increased the ratio of the antiparallel conformation. The enrichment of antiparallel conformation caused an increase in the photocyclization quantum yield of **1a**. The CD spectral intensity of the mixtures of **1a** or 2,2′,4,4′-tetramethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(thiophen-5-yl-(phenyl-4-sulfonate)) (**2a**) and cyclodextrins in aqueous solution increased with the increasing concentration of cyclodextrins. The induced CD spectrum of **1** in β-cyclodextrin reversibly changed from negative to positive by UV irradiation. The spectral change was attributed to the change in the direction of transition moment of **1** in the cavity.

Photochromic compounds are classified into two categories, thermally reversible and irreversible compounds.[1] Azobenzenes and spirobenzopyrans belong to the former and furylfulgides and dithienylethenes to the latter. The thermally irreversible photochromic compounds are potentially applicable to various types of optoelectronic devices, such as optical memory media[2] and photooptical switching devices.[3] Among the thermally irreversible compounds, diarylethenes having heterocyclic aryl groups are promising candidates for the practical applications because of their fatigue-resistant characteristic.[4] The photochromic reaction of diarylethenes is based on the reversible hexatriene−cyclohexadiene-type photocyclization as shown in Figure 1. The open-ring form of the diarylethene has two conformations, parallel and antiparallel. The photocyclization can proceed only from the antiparallel conformation, while the parallel conformation is photochemically inactive.[4] The existence of the parallel conformation limits the quantum yield for ring-closure reaction.[5] One of the approaches to increase the cyclization quantum yield is to increase the ratio of the antiparallel conformation. Inclusion of the diarylethene into a microcavity, such as cyclodextrins, favors the antiparallel conformation.[6]

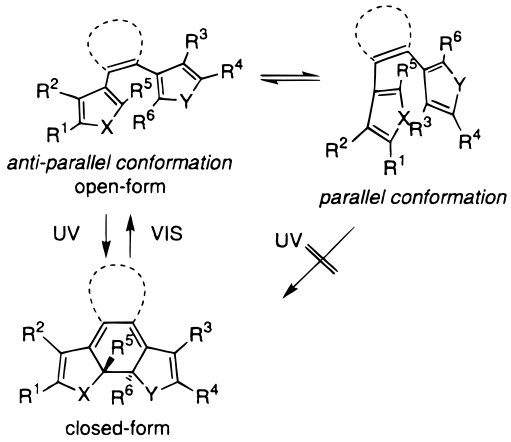

Figure 1. Reaction scheme of diarylethene with five-membered heterocyclic aryl groups.

Circular dichroism (CD) spectral changes accompanying photochromic reactions have been reported[7] for dissymmetrical alkenes,[8] bilirubin-IIIα,[9] liquid crystals,[10] [4*n*]annulenes,[11] fulgides,[12] spiropyranes,[13] and dithie-

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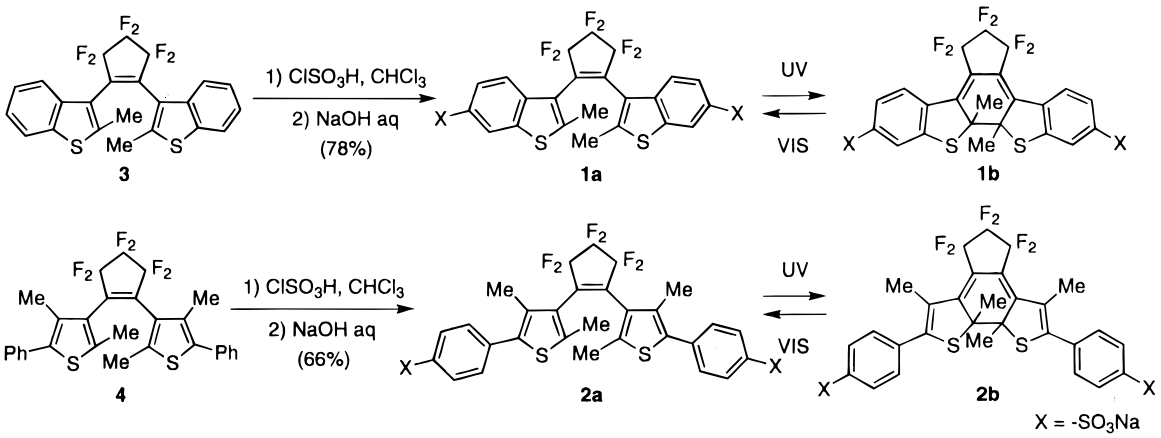
Scheme 1



nylethenes.[14] Such chiral property changes are useful for optical display[10] as well as photooptical switching. When molecules are included in cyclodextrin cavities, the asymmetric environment causes the induced CD spectra.[15,16] If the guest molecules undergo photochromism, the CD spectra are expected to be changed by photoirradiation.[17]

In this paper, we examined the effect of inclusion of thermally irreversible diarylethenes in cyclodextrin cavities on cyclization quantum yields and on CD spectral changes by photoirradiation.

Results and Discussion

1. Synthesis. Disulfonates **1a** and **2a** were synthesized by treatment of the corresponding diarylethenes[18,19] with chlorosulfonic acid and subsequent hydrolysis with 1% aqueous NaOH (Scheme 1).

Figure 2 shows the absorption spectral change of **1** (4.0×10^{-5} mol dm^{-3}) in an aqueous solution by irradiation with 313 nm light. The initial colorless solution turned red, and new absorption bands appeared at 358 and 529 nm. The red color is due to the closed ring form **1b**, of which the π-system is extended by the ring-closure reaction.[18] Upon visible (>480 nm) irradiation, the spectrum returned to the initial one. A solution of **2** in MeOH/water (1:4) also showed similar photochromism.

2. NMR Spectra of Diarylethenes in Cyclodextrins. Figure 3a shows the ^{1}H NMR spectrum of methyl groups of the open-ring form of **1a** in D_2O (3.0×10^{-3} mol dm^{-3}, 20 °C, 200 MHz). The methyl signals in parallel and antiparallel conformations are observed separately. This indicates that the conformational change takes place slowly relative to the NMR time scale (<56 Hz). The methyl protons at δ 2.27 (at higher magnetic field) and δ 2.55 (at lower magnetic field) are assigned to the antiparallel and the parallel conformations, respectively.[20] In this compound, the antiparallel conformation is favored and the ratio of antiparallel and parallel was 64:36. The absorption spectra of the two conformations are very similar to each other.[5] Therefore, this ratio means that only 64% of **1a** is photoreactive and the rest is photochemically inactive when they are photoexcited with 313 nm light. Upon addition of β-cyclodextrin to the solution, the ratio changed as shown in Figure 3b,c. When 10 equiv of β-cyclodextrin was added

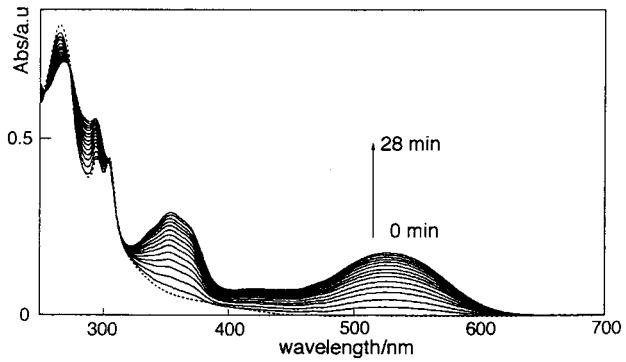


Figure 2. Absorption spectral change of **1** in aqueous solution ([**1**] = 4.0×10^{-5} mol dm^{-3}) upon irradiation with 313 nm light (0−28 min). Dotted line showed the spectrum after irradiation with >480 nm light (5 min).

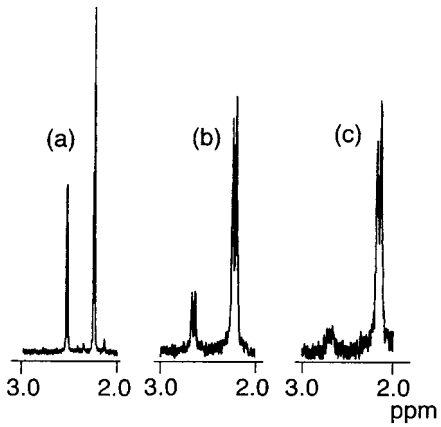


Figure 3. ^{1}H NMR spectrum (200 MHz, 20 °C) of methyl protons in D_2O ([**1a**] = 3.0×10^{-3} mol dm^{-3}): (a) **1a**, (b) **1a** + β-cyclodextrin (1:5), and (c) **1a** + β-cyclodextrin (1:10).

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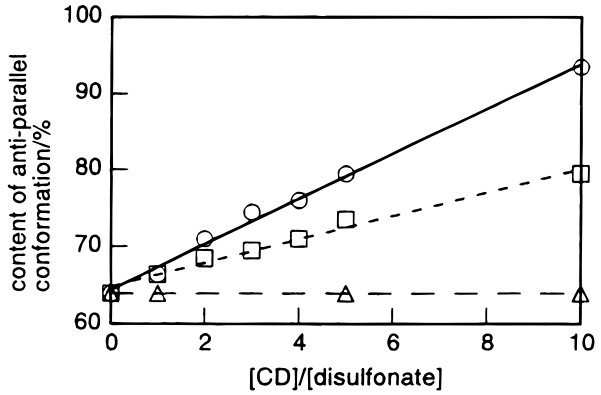

Figure 4. [CD]/[**1a**] vs content of antiparallel conformation determined by ^{1}H NMR spectroscopy ([**1a**] = 3.0×10^{-3} mol dm^{-3}), with α-cyclodextrin (triangle), with β-cyclodextrin (circle), and γ-cyclodextrin (square).

to the solution, the antiparallel conformer became dominant as shown in Figure 3c.

Figure 4 shows cyclodextrin concentration dependence of the ratio calculated from the NMR spectra. When 10 equiv of β-cyclodextrin is added, 94% of **1a** converts to the antiparallel conformation, while 80% converts to the antiparallel conformation when γ-cyclodextrin is added. The addition of α-cyclodextrin did not change the ratio of the conformations. The result indicates that the cavity of β-cyclodextrin is suitable for the antiparallel conformation of **1a**, whereas that of α-cyclodextrin is too small to include **1a**. The methyl protons of both conformations of **1a** were found to split upon addition of β-cyclodextrin. The split suggests that two methyl protons exist in different environments in the chiral cyclodextrin cavity.

Any appreciable NMR spectral change was not observed for **2a** in MeOH/water (1:4) (3.0×10^{-3} mol dm^{-3}, 20 °C, 200 MHz) even in the presence of 10 equiv of β-cyclodextrin. This is due to low concentration of the inclusion complex. CD spectral titration revealed that only 10% of **2a** is included in the cavity (see below).

The NOESY experiments are useful to determine the structure of the complex.[21] The packing structure of the inclusion complex was examined using a NOESY spectrum. Figure 5 shows the NOESY spectrum (600 MHz, mixing time 500 ms) of a mixture of **1a** (3.0×10^{-3} mol dm^{-3}) and β-cyclodextrin (3.0×10^{-2} mol dm^{-3}) in D_2O solution at 20 °C. A strong and a weak NOE signals were observed between protons at the 7- and 5-positions of a benzothiophene ring of **1a** and the methylene protons at the 6-position of β-cyclodextrin, respectively. When a guest **1a** is included in the cyclodextrin cavity from the secondary hydroxy group side, which is wider than the primary hydroxy group side,[22] the structure of a complex of **1a** and β-cyclodextrin is depicted as shown in Figure 6.

3. Quantum Yield Change by the Addition of Cyclodextrins. As described above, the diarylethene in the parallel conformation is not photoreactive. Therefore, the increase in the ratio of antiparallel to parallel conformations is expected to result in the increase in the cyclization quantum yield. Table 1 shows the cyclization quantum yields of **1a** by irradiation with 313 nm light.

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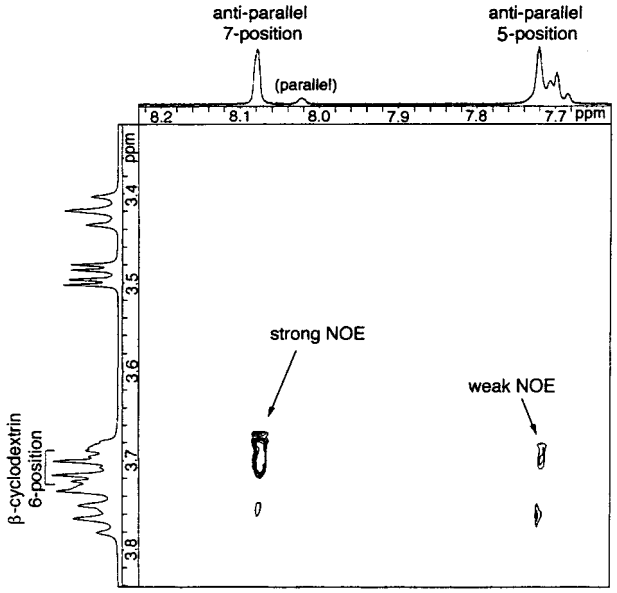

Figure 5. NOESY spectrum (in part, 600 MHz, 20 °C) of a mixture of **1a** (3.0×10^{-3} mol dm^{-3}) and β-cyclodextrin (3.0×10^{-2} mol dm^{-3}) in D_2O.

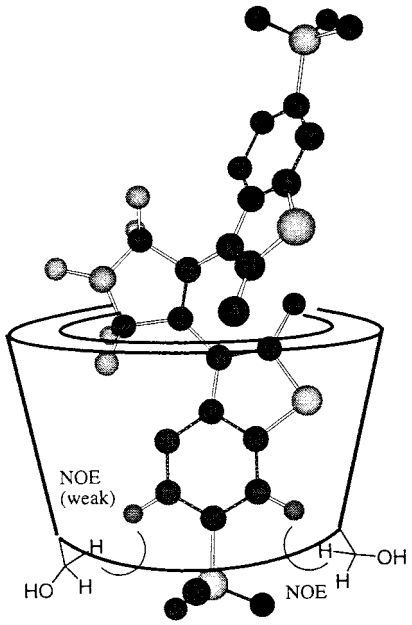

Figure 6. Conceivable structure of a complex of **1a** and β-cyclodextrin.

Table 1. Cyclization Quantum Yields of 1a Irradiated with 313 nm Light in the Presence of CD$_x$ in Aqueous Solution[a]

system	**1a**	**1a**[b]	**1a** + α-CD	**1a** + β-CD	**1a** + γ-CD
quantum yield	0.32	0.32	0.31	0.49	0.45

[a] [**1a**] = 4.0×10^{-5} mol dm^{-3}, [CD] = 8.0×10^{-3} mol dm^{-3}, 20 °C. [b] In MeOH.

The cyclization quantum yield of **1a** in the presence of 200 times excess β-cyclodextrin is about 1.5 times larger than that of **1a** in an aqueous solution. NMR measurement indicated that 97% of **1a** is in the antiparallel conformation in the presence of excess β-cyclodextrin. The increase in the quantum yield is due to the increase in the population of the antiparallel conformation.

The cyclization quantum yield of **1a** in the presence of 200 times excess γ-cyclodextrin is also increased due to

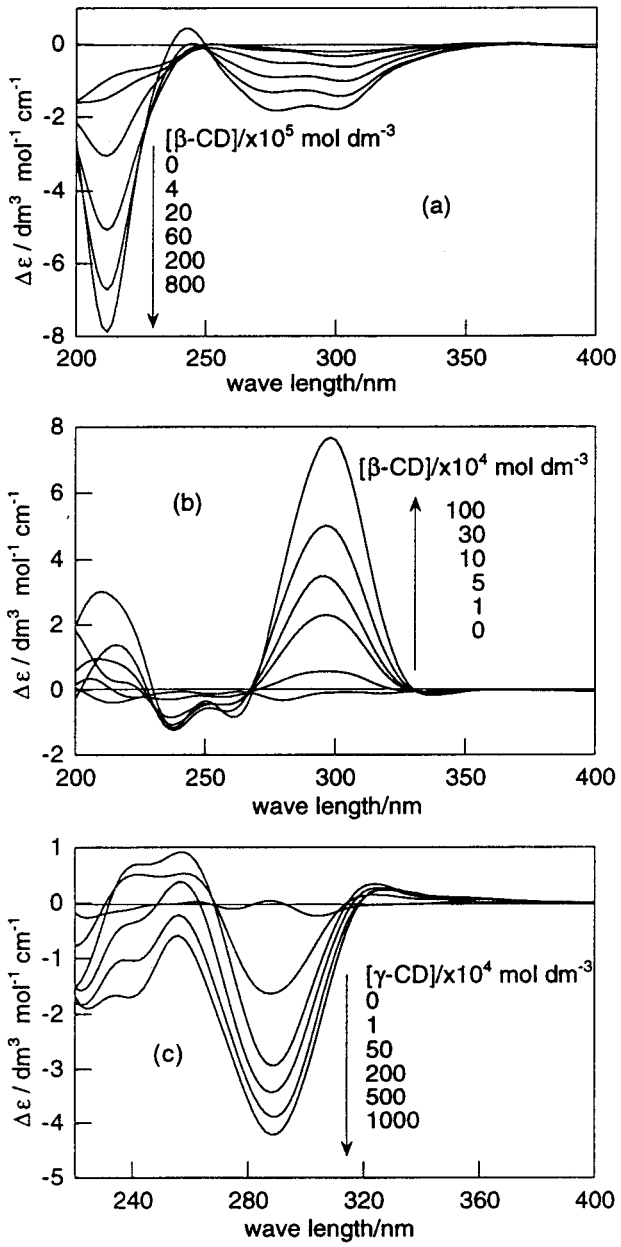

Figure 7. CD spectral change (20 °C) of (a) **1a** (4.0×10^{-5} mol dm^{-3}) in aqueous solution upon addition of β-cyclodextrin, (b) **2a** (1.0×10^{-4} mol dm^{-3}) in MeOH/water (1:4) solution upon addition of β-cyclodextrin, and (c) **2a** (1.0×10^{-4} mol dm^{-3}) in MeOH/water (1:4) solution upon addition of γ-cyclodextrin.

the enrichment of antiparallel conformation. On the other hand, no change was observed in either the ^{1}H NMR spectrum or the quantum yield for cyclization of **1a** in the presence of α-cyclodextrin. The enhancement of quantum yields in the presence of β- and γ-cyclodextrin is ascribed to the favorable antiparallel conformation of **1a** in the cyclodextrins' cavities.

4. CD Spectral Change by the Addition of Cyclodextrins. Figure 7a shows the CD spectral change of **1a** by the addition of β-cyclodextrin in an aqueous solution ([**1a**] = 4.0×10^{-5} mol dm^{-3}, [β-cyclodextrin] = $0-8.0 \times 10^{-3}$ mol dm^{-3}, 20 °C). The negative cotton effect appeared at 300, 276, and 212 nm, and the spectral intensity increased with the increasing concentration of β-cyclodextrin. The intensity increase indicates that β-cyclodextrin includes **1a** in the cavity, and the concentration of inclusion complex increases with an increase in cyclodextrin concentration. On the other hand, no remarkable CD spectral change was observed by the addition of γ-cyclodextrin, whose cavity is larger than for β-cyclodextrin, to an aqueous solution of **1a**. This indicates that the cavity of the γ-cyclodextrin is too large to fix the guest molecule **1a** in the cavity.

The addition of β-cyclodextrin to a solution of **2a** ([**2a**] = 1.0×10^{-4} mol dm^{-3}, [β-cyclodextrin] = $0-1.0 \times 10^{-2}$ mol dm^{-3}, 20 °C) in MeOH−water (1:4) increased the intensity of the CD spectrum, and the positive cotton effect was observed at 298 nm as shown in Figure 7b. The intensity of the spectrum is increased with an increase in the concentration of β-cyclodextrin. Figure 7c shows the CD spectral change by addition of γ-cyclodextrin to a solution of **2a** (1.0×10^{-4} mol dm^{-3}) in MeOH−water (1:4). The negative cotton effect was observed around 288 nm. The different behavior of the CD spectral change indicates that the structure of the complex is different between **2a** and β-cyclodextrin and **2a** and γ-cyclodextrin.

Hill plots of the complexation of **1a** with β-cyclodextrin in aqueous solution based on $\Delta\epsilon$ change at 212 nm gave stoichiometry and an association constant (K_{assoc}). From the slope, the stoichiometry of the complexation was determined to be 1:1 and from the intercept the association constant (K_{assoc}) was calculated to be 2190 mol^{-1} dm^3 at 20 °C. The stoichiometry and K_{assoc} of the complexation of **2a** with β-cyclodextrin in MeOH−water (1:4) were determined from the spectral change at 298 nm to be 1:1 and 260 mol^{-1} dm^3 at 20 °C, respectively. The stoichiometry and the association constant for the complexation of **2a** with γ-cyclodextrin could not be determined because of the complex CD spectral change by the addition of γ-cyclodextrin.

5. CD Spectral Change by Photoirradiation. It has been reported that the direction of the Cotton effect in induced CD spectrum of cyclodextrin inclusion complex is dependent on the direction of the transition moment of the chromophore in the cyclodextrin cavity.[16] It is reported that when the direction of the transition moment of the chromophore included in the cavity is polarized perpendicular to the axis of cyclodextrin, the complex shows negative ICD for the transition. If the direction of the transition moment is parallel to the axis, the ICD is positive. The cotton effect can give information concerning the direction of the transition moment or packing structure of the chromophore.

Figure 8a shows the CD spectral change of a mixture of **1** (4.0×10^{-5} mol dm^{-3}) and β-cyclodextrin (8.0×10^{-3} mol dm^{-3}) in aqueous solution by irradiation with 313 nm light. ^{1}H NMR and absorption spectral studies revealed that in the photostationary state the conversion of **1a** to the closed-ring form **1b** by irradiation with 313 nm light is 68%. Upon 313 nm irradiation, the troughs at 300, 276, and 212 nm disappear and the new peaks appear near 294 and 225 nm. These peaks increase with irradiation time. Irradiation with visible light (>480 nm) restores the original CD spectrum of the open-ring form as shown by the dotted line in Figure 8a. The CD spectral change suggests[16] that the transition moment of **1a** included in the β-cyclodextrin cavity at 212 nm is perpendicular to the cyclodextrin axis, whereas that of **1b** at 225 nm is parallel to the axis.

The CD spectral change of a mixture of **2** (1.0×10^{-4} mol dm^{-3}) and β-cyclodextrin (1.0×10^{-2} mol dm^{-3}) in MeOH/water (1:4) is shown in Figure 8b. Upon irradia-

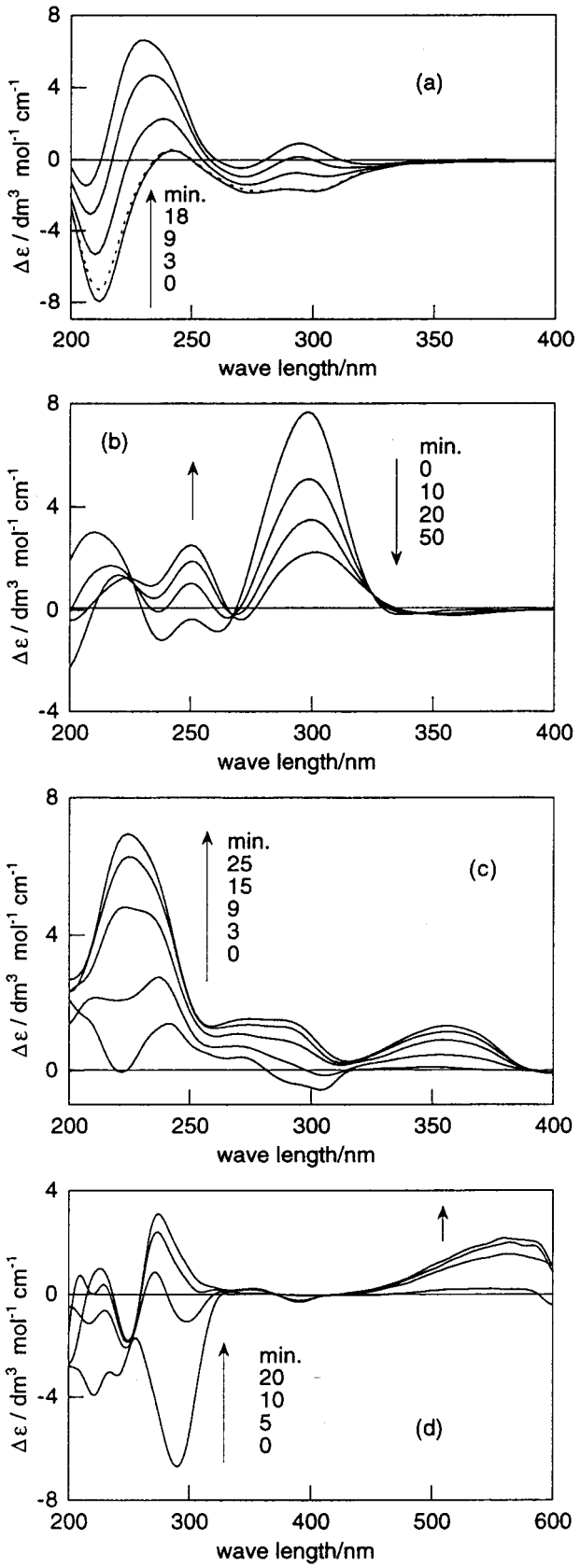

Figure 8. CD spectral change (20 °C) of mixtures of (a) **1** (4.0×10^{-5} mol dm^{-3}) and β-cyclodextrin (8.0×10^{-3} mol dm^{-3}) in aqueous solution, (b) **2** (1.0×10^{-4} mol dm^{-3}) and β-cyclodextrin (1.0×10^{-2} mol dm^{-3}) in MeOH/water (1:4) solution, (c) **1** (4.0×10^{-5} mol dm^{-3}) and γ-cyclodextrin (2.0×10^{-2} mol dm^{-3}) in aqueous solution, and (d) **2** (1.0×10^{-4} mol dm^{-3}) and γ-cyclodextrin (5.0×10^{-2} mol dm^{-3}) in MeOH/water (1:4) solution upon irradiation with 313 nm light. Dotted line in (a) showed the spectrum after irradiation with >480 nm light.

Table 2. AM1-RPA Results for Open-Ring Form 3a (f > 0.1)

λ (nm)	TrX	TrY	TrZ	f
381	−0.296	0.001	−0.452	0.195
297	0.676	−0.001	0.276	0.356
280	0.463	0.001	−0.956	0.751
278	−0.600	−0.002	0.833	0.703
274	0.000	0.844	0.002	0.475
266	0.225	0.002	−0.874	0.543
254	−0.158	−0.002	0.700	0.343
244	0.000	1.054	0.002	0.741
241	−0.467	0.002	−1.039	0.865
238	−0.318	0.002	−0.797	0.491
220	−0.622	0.000	0.193	0.283

tion with 313 nm light, a peak at 298 nm decreases and a peak at 248 nm increases. Under the experimental conditions, the conversion of **2** is 91% in the photostationary state (313 nm).

Figure 8c shows the CD spectral change of a mixture of **1** (4.0×10^{-5} mol dm^{-3}) and γ-cyclodextrin (2.0×10^{-2} mol dm^{-3}) in aqueous solution by irradiation with 313 nm light. CPK molecular modeling study suggests that the increase in CD spectrum of a mixture of **1** and γ-cyclodextrin at 224 nm by 313 nm irradiation is ascribed to the rigid structure of **1b** in γ-cyclodextrin cavity, while in the case of **1a** and γ-cyclodextrin, there are various structures of complex and the CD spectral intensity is weak. A peak at 224 nm in **1b** and γ-cyclodextrin indicates that transition moment of **1b** at 224 nm is parallel to the cyclodextrin axis. In the case of **2** and γ-cyclodextrin (Figure 8d), a trough at 295 nm in CD spectrum of a mixture of **2a** and γ-cyclodextrin disappears and peaks around 280 and 570 nm appear.

The CD spectral change to positive in Figure 8a,c,d indicates that the transition moments of the closed-ring forms, which are rigid and rodlike structures, are parallel to the cyclodextrin axis.

The CD spectra changed by UV irradiation returned to the initial spectra upon irradiation with visible light (>480 nm).

The closed ring form of diarylethene **1b** and **2b** have C_2 symmetry.[14] Therefore, formation of one of the enantiomers in the CD cavity is anticipated. However, there was no remarkable difference between CD spectra of the two samples, which were formed in the presence of β-cyclodextrin and mixed with β-cyclodextrin later. This result indicates that CD spectra observed here are induced CD spectra and not the enrichment of an enantiomer of the closed-ring forms.

6. Calculation of Transition Moments. As described above, the photoreversible CD spectral changes are considered due to the transition moment changes of diarylethenes in the cyclodextrin cavity. To clarify the CD spectral changes by irradiation, the transition moments of the open- and closed-ring forms of a diarylethene were calculated. The transition moments of diarylethene **3** were calculated as a model for simplifying the calculation. Tables 2 and 3 show the list of electronic transitions of the open-ring form **3a** and the closed-ring form **3b**, whose f values are larger than 0.1. The calculations were carried out by the AM1-RPA method.[23,24] The coordinates of **3a** and **3b** for calculations are shown in Figure 9.

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Table 3. AM1-RPA Results for Closed-Ring Form 3b (f > 0.1)

λ (nm)	TrX	TrY	TrZ	f
528	−0.257	−0.404	0.119	0.162
430	0.333	−0.190	0.073	0.101
418	−0.428	0.245	−0.094	0.168
378	−0.277	−0.445	0.102	0.190
339	0.546	0.913	−0.110	0.763
302	−0.228	−0.387	0.031	0.135
284	−0.362	0.206	−0.078	0.120
265	−0.516	0.295	−0.114	0.244
254	0.616	1.085	0.014	1.037
245	−0.457	0.262	−0.101	0.192
226	−0.210	−0.366	0.004	0.119

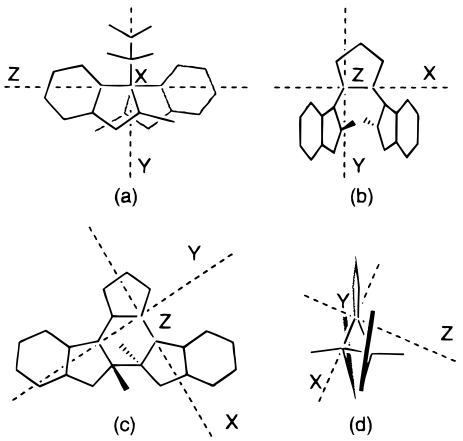

Figure 9. Coordinates of **3a** ((a) front view and (b) side view) and **3b** ((c) front view and (d) side view) for calculation.

The negative CD spectrum of the open-ring form at 212 nm corresponds to the calculated electric transitions around 240 nm with large f values such as 244 and 241 nm. The transition at 244 nm is parallel to the C_2 symmetry axis of **3a** as shown in Figure 10a,b. The NOESY spectrum of the complex of the open-ring form **1a** and β-cyclodextrin indicates that the C_2 symmetry axis of **1a** is perpendicular to the axis of β-cyclodextrin when **1a** is included in the cavity. Therefore, the CD spectrum at around 212 nm shows negative.

On the other hand, the positive CD spectrum of the closed-ring form at around 230 nm corresponds to the calculated transition at 254 nm, which is the only transition moment with a large f value as shown in Table 3. The transition moment is perpendicular to the C_2 symmetry axis as shown in Figure 10c,d. Therefore, the transition moment of **1b** is parallel to the axis of β-cyclodextrin, and the CD spectrum at 230 nm shows positive. Figure 11 shows the schematic representation of the transition moment change by photoirradiation. The CD spectral change from negative to positive is due to the transition moment change by the cyclization reaction of the diarylethene.

As described above, the ring-opening and the ring-closure reactions of diarylethenes are photoreversible. The reversible CD change of a mixture of **1** and β-cyclodextrin in aqueous solution by alternate irradiation with 313 nm (5 min) and >480 nm light (2 min) was demonstrated as shown in Figure 12.

Conclusions

The addition of β- and γ-cyclodextrins to **1** or **2** in aqueous solution increases the quantum yield of the ring-closure reaction by favorable inclusion of the photoreactive antiparallel conformations. The induced CD spectra were observed in the mixture of diarylethenes and cyclodextrins. The CD spectrum of a mixture of **1** and β-cyclodextrin changed from negative to positive by irradiation with 313 nm light. The CD spectral change is ascribed to the transition moment change of diarylethene in the cavity by photoirradiation. The calculation of the transition moments of **3** confirmed the photoreversible CD spectral change is due to the change in the direction of the transition moments of diarylethene by photoirradiation.

Experimental Section

General Remarks. ^{1}H NMR spectra were recorded at 200 MHz unless otherwise noted, and a 600 MHz instrument was used only for NOESY spectra. TSP was used as reference. Circular dichroism spectra were measured with a CD spectropolarimeter. A mercury lamp (1 kW) was used as a light source. Monochromic light was obtained by passing light through a monochromator.

Materials. 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (**3**)[18] and 1,2-bis(2,4-dimethyl-5-phenylthien-3-yl)hexafluorocyclopentene (**4**)[19] were synthesized according to the literature.

Sodium 2,2′-Dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophene-6-sulfonate) (1a). To a stirring solution of 1.5 g of **3** (3.2 mmol) in 6 mL of $CHCl_3$ was added 0.6 mL of chlorosulfonic acid dropwise at room temperature, and the reaction mixture was stirred for 1 h. The lower layer was withdrawn and was poured into 100 mL of NaOH aqueous solution. Saturated NaCl aqueous solution (100 mL) was poured into the mixture, and the formed white precipitate was collected by filtration. Recrystallization of the precipitate from methanol afforded 1.68 g of **1a** in 78% yield as white powder: mp >400 °C; ^{1}H NMR (D_2O, 20 °C) δ 2.27 (s, 3.84 H, ap), 2.55 (s, 2.16 H, p), 7.58−7.96 (m, 4H, ap and p), 8.14 (s, 0.72 H, p), 8.26 (s, 1.28 H, ap); although the spectrum shows parallel (p) and antiparallel (ap) conformation separately, these conformations exchange slowly relative to the NMR time scale;[19] MS m/z 673 (M^+). Anal. Calcd for $C_{23}H_{12}F_6O_6S_4Na_2 \cdot H_2O$: C, 40.00; H, 2.04. Found: C, 39.56; H, 2.27.

Sodium 2,2′,4,4′-Tetramethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(thiophen-5-yl(phenyl-4-sulfonate)) (2a). Compound **2a** was synthesized from **4** in 66% yield in a manner similar to that described for **1a**. **2a**: white powder; mp >400 °C; ^{1}H NMR (CD_3OD, 20 °C) δ 2.12 (s, 3 H, ap), 2.18 (s, 3 H, p), 2.36 (s, 3 H, p), 2.41 (s, 3 H, ap), 7.47 (d, 4 H, J = 9 Hz), 7.87 (d, 4 H, J = 9 Hz); although the spectrum shows parallel (p) and antiparallel (ap) conformations separately, these conformations exchange slowly relative to the NMR time scale; MS m/z = 753 $(M + 1)^+$. Anal. Calcd for $C_{29}H_{20}F_6O_6S_4Na_2 \cdot 2H_2O$: C, 44.20; H, 3.07. Found: C, 44.02; H, 3.25.

Quantum Yield Measurement. A water solution containing **1a** was divided into four cells, and then α, β, and γ-cyclodextrins were each added into the three cells. All four solutions have the same absorption (∼0.3) at 313 nm. Upon irradiation with 313 nm light, the absorption at 529 nm increased. By comparing the relative rates of the initial increases, we determined the relative quantum yields (the experimental error included in the relative quantum yields was less than 10%). The absolute quantum yields were determined by using furylfulgide (Aberchrome-540) as a reference.[25,26] We

(24) We thank the Computer Center of Tokyo Institute of Technology and the Institute for Molecular Science for their generous permission to use IBM SP2 computers, DEC AlphaServer8400, and Cray C916/12256 computers, respectively.

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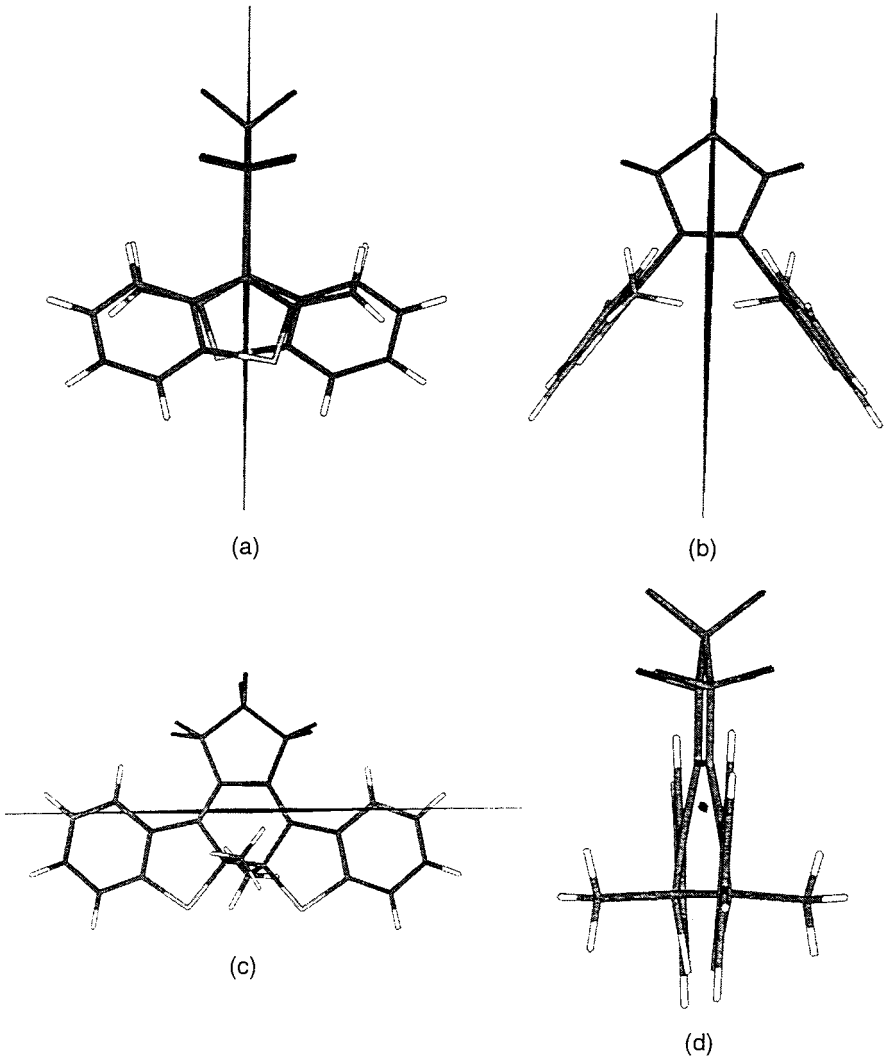

Figure 10. Calculated transition moment of the open-ring form of **3a** at 244 nm ((a) front view and (b) side view) and the closed-ring form of **3b** at 254 nm ((c) front view and (d) side view) calculated with AM1-RPA.

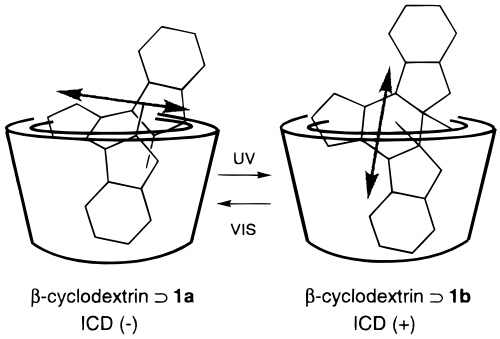

Figure 11. Schematic representation of the transition moment change of a **1** and β-cyclodextrin complex by photoirradiation.

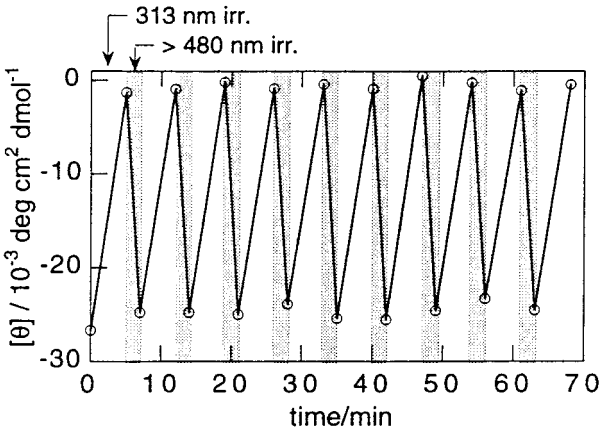

Figure 12. CD spectral change at 216 nm by alternate irradiation of a mixture of **1** (4.0×10^{-5} mol dm^{-3}) and β-cyclodextrin (8.0×10^{-3} mol dm^{-3}) in aqueous solution with 313 nm (5 min) and >480 nm light (2 min).

compared the rates of increases at 494 nm (Aberchrome-540) and at 529 nm (**1a**) by irradiation with 313 nm. By the use of ϵ values of both compounds (8200 and 9600 $M^{-1}cm^{-1}$, respectively) the absolute quantum yields were determined.

Calculations. The structures were optimized by the AM1 method[27] of the MOPAC program package.[28] The low-lying singlet electronic excitations were calculated in the random-phase approximation (RPA),[23a] using the AM1-RPA program.[23b] The RPA calculations included the lowest 1000 single-excitation configurations of the AM1 MOs. The RPA is particularly well suited to calculating electronic transition moments and oscillator strengths.[23a] The AM1-RPA method well reproduces the experimental transition energies and oscillator strengths of dyes and pigments.[23b] All the calculations were carried out

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using a Cray C90 computer at the computer center of Tokyo Institute of Technology.

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