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Photoreversible Circular Dichroism Change of 1,2-Bis(1-benzothiophen-3-yl)perfluorocyclopentene Modified Cyclodextrin

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Abstract: γ-Cyclodextrin having photochromic 1,2-bis(1-benzothiophen-3-yl)perfluorocyclopentene was synthesized. The circular dichroism and the optical rotation of the modified cyclodextrin reversibly changed in aqueous solution by alternate irradiation with UV/visible light. © 1999 Elsevier Science Ltd. All rights reserved.

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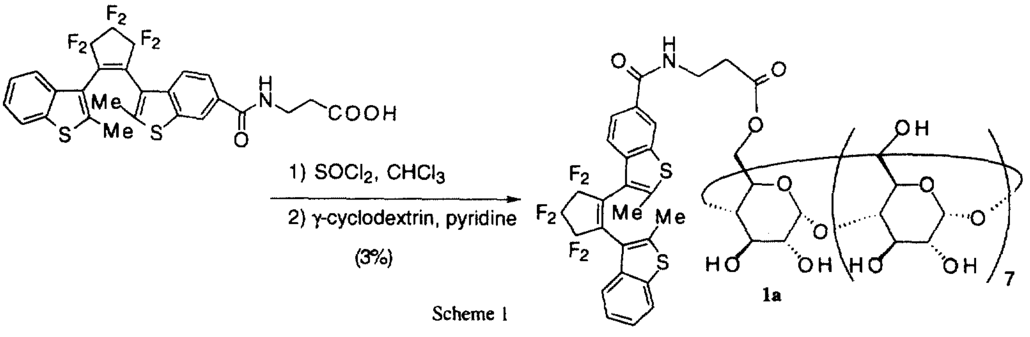
Diarylethenes with heterocyclic aryl rings undergo thermally irreversible and fatigue resistant photochromic reactions.[1] Recently we have reported that the addition of β- or γ-cyclodextrins to an aqueous solution of 1,2-bis(1-benzothiophen-3-yl)perfluorocyclopentene-disulfonate results in the formation of inclusion complexes and the photocyclization quantum yields increase due to the conformational restriction in the cavity.[2] The induced circular dichroism (ICD) of the complex reversibly changed by photoirradiation.[3]

Various types of dye modified cyclodextrins have been studied for sensory systems.[4] In this study a photochromic diarylethene modified cyclodextrin was synthesized in an attempt to form a stable inclusion complex, which shows an efficient reversible ICD change.



Scheme 1

The preparation of 1,2-bis(1-benzothiophen-3-yl)perfluorocyclopentene modified γ-cyclodextrin is shown in Scheme 1.

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Compound **1a** (open form) was obtained by treatment of acyl chloride of the diarylethene with γ-cyclodextrin in dry pyridine and was purified with a reversed phase HPLC.[5]

Figure 1 shows the absorption spectral change of **1** (open form + closed form) in aqueous solution by irradiation with 313 nm light. Upon irradiation with 313 nm light, the initial colorless solution turned red and new absorption bands appeared at 356 and 520 nm. The spectrum returned to the initial one by irradiation with visible light (>460 nm) (shown as dotted line). Similar photoinduced spectral change was also observed in methanol solution.

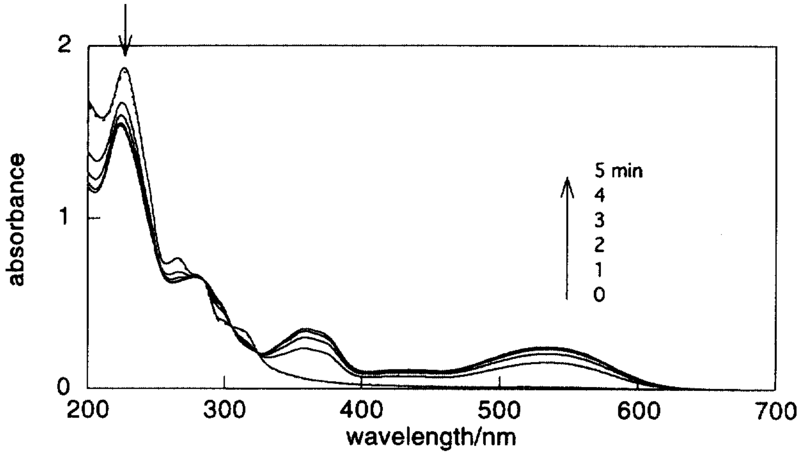

Fig. 1. Absorption spectral change of 1 in aqueous solution by irradiation with 313 nm light ([1] $=5.6\times10^{-5}$ mol dm^{-3}).

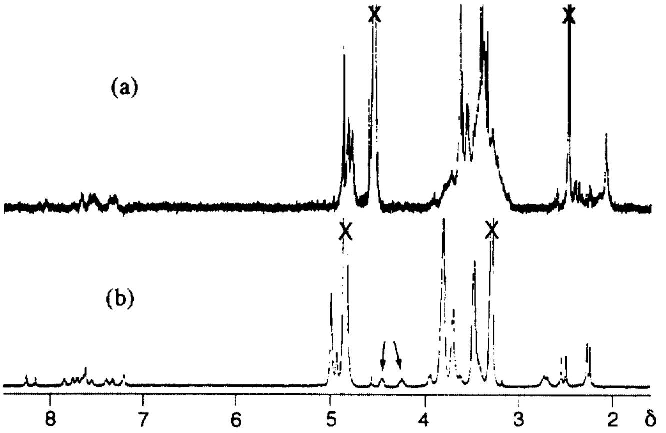

Fig. 2. ^{1}H NMR spectra (600 MHz) of **1a** in (a) D_2O/DMSO-d_6 (5:1) and (b) CD_3OD ([**1a**] $= 2.0\times10^{-3}$ mol dm^{-3}). Allows indicate methylene protons at 6-position.

The formation of a self-inclusion complex depends on the solvent. Figure 2 shows the ^{1}H NMR spectra of **1a** in (a) D_2O/DMSO-d_6 (5:1) and (b) CD_3OD. The methyl protons of the 1,2-bis(1-benzothiophen-3-yl)-perfluorocyclopentene moiety were observed as complex signals in aqueous solution, while in methanol solution these protons gave four singlets which are assigned to two kinds of methyl protons in two conformations.[6] Most of the signals of the cyclodextrin protons shifted to up-field in aqueous solution. These spectral changes in the two solvents indicate that **1a** is a self-inclusion complex in D_2O+DMSO-d_6 (1:5), but in CD_3OD the diarylethene moiety is out of the cyclodextrin cavity. Two 6-positional methylene protons of γ-cyclodextrin moiety, which were assigned by COSY, are shifted to lower magnetic field

(Fig. 2. (b) indicated by arrows). This result supports that diarylethene is introduced at a primary hydroxyl group (6-position) of γ-cyclodextrin. To confirm the structure of the self-inclusion complex of **1a** in an aqueous solution, the phase-sensitive NOESY spectrum (600 MHz, mixing time 600 ms) of **1a** was measured in D_2O+DMSO-d_6 (1:5) solution (Fig. 3). Although cyclodextrin protons were too complicated to be assigned, the NOEs were observed between methyl protons of **1a** and most of cyclodextrin protons. In addition, NOEs were observed between aromatic protons of the benzothiophene moieties and some of the cyclodextrin protons. On the other hand, any significant NOE was not found in NOESY spectrum of **1a** in CD_3OD solution. These results confirm the self-inclusion in D_2O/DMSO-d_6 solution. The up-field shift of the cyclodextrin protons is due to shielding effect by the ring current of the benzothiophene rings.

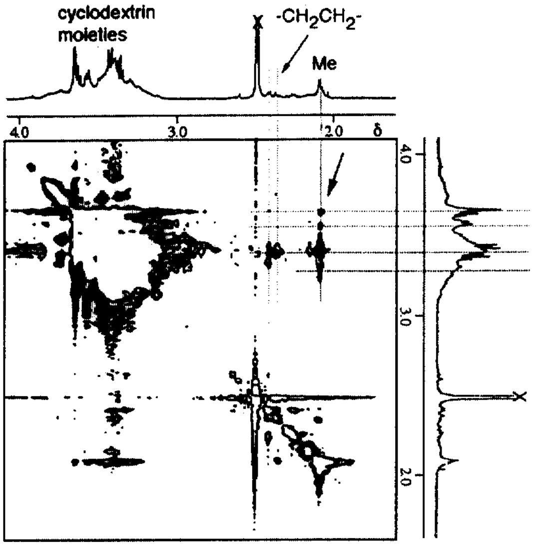

Fig. 3. NOESY spectrum of **1a** (in part) in D_2O+DMSO-d_6 (1:5) solution (600 MHz, 25 °C, mixing time 600 ms).

It is known that ICD is observed when chromophores are included in cyclodextrin cavities.[3,7] Figure 4 shows CD spectral change of **1** in aqueous solution (5.6x10^{-5} mol dm^{-3}) upon irradiation with 313 nm light. An aqueous solution of 100% open-ring form **1a** shows large negative ICD at 210 (Δε= -10.2), 230 (-5.5) and 266 (-5.2). In methanol solution, the ICD was not observed in the wavelength longer than 210 nm. This result also indicates that the diarylethene moiety is outside of the cavity in methanol. Upon irradiation with 313 nm light, these negative ICDs decreased and another negative ICDs increased at 356 and 520 nm which are assigned to the closed-ring form. The negative ICD at 356 and 520 nm indicates that the direction of these transition moments is nearly perpendicular to the cyclodextrin axis.[4],[8] The length of the long axis of bis(benzothiophenyl)cyclopentene is more than 10 Å,

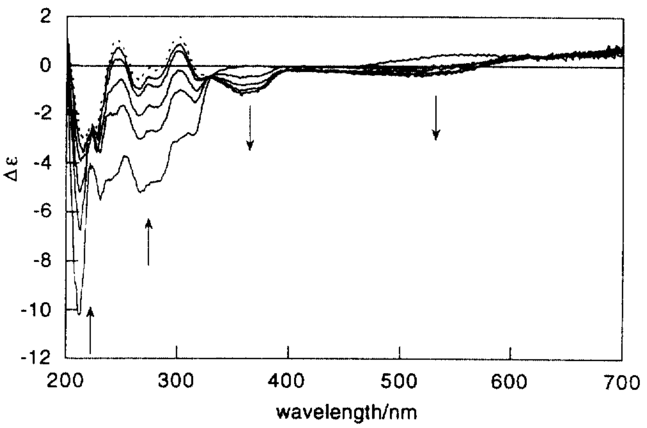

Fig. 4. CD spectral change of **1** in aqueous solution (5.6x10^{-5} mol dm^{-3}) upon irradiation with 313 nm light. Dotted line denotes photostationary state.

and the cavity size of γ-cyclodextrin is estimated as 8.5 Å.[8] The ICD spectral change suggests that the closed-ring form of the bis(1-benzothiophen-3-yl)perfluorocyclopentene moiety is included slightly slantwise as shown in Fig. 5.

Compound **1** changed reversibly its optical rotation by alternate irradiation with 313 nm and >460 nm light. Figure 6 shows the optical rotational change of **1** in aqueous solution at 630 nm. Small but significant change was observed in the optical rotation. At 630 nm there is no absorption band for **1**. Therefore, it is possible to follow the photochromic reaction by the optical rotation measurement without influencing on the reaction.[9]

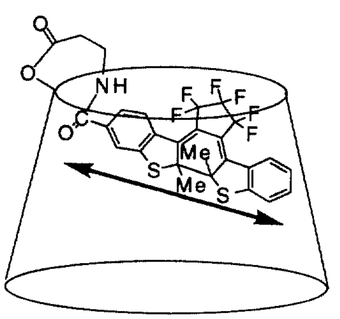

Fig. 5. Conceivable structure of the closed-ring form of **1**. Arrow denotes the direction of a transition moment.

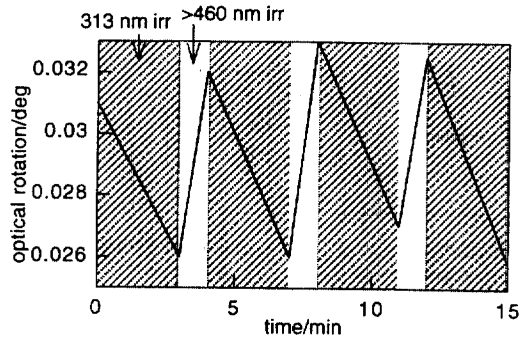

Fig. 6. Optical rotational change of **1** in aqueous solution at 630 nm by alternate irradiation with 313 nm light and >460 nm light (in water, c=0.023, 25 °C, cell length = 100 mm).

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