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Photochemical Conversion from Flexible Host to Rigid Host of a Doubly Capped γ-Cyclodextrin

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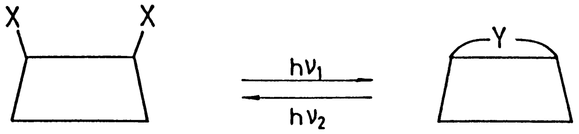
γ-Cyclodextrin bearing two anthracene moieties (**1**) exhibited an exciton coupling band of R-helicity as well as excimer emission. Photoirradiation caused dimerization of the appended moieties, converting **1** from flexible host to rigid host.

γ-Cyclodextrin (γ-CD), which consists of eight glucose units, has a central cavity of ca. 8.5 Å diameter.[1)] Two guest molecules can be included into its relatively large cavity.[2)] This property allows γ-CD to be used as a molecular flask in which two species can meet, as shown by facilitated formation of excimers[3)] and charge-transfer complexes[4)] as well as enhanced photodimerization.[5)] Another interesting aspect of γ-CD is the unique binding behavior of its derivatives; two aromatic moieties covalently linked with γ-CD enable γ-CD to include one guest molecule by changing their positions[2b)] while an aromatic moiety acts as a spacer which narrows the large cavity.[6)] In these γ-CD derivatives, flexibility of the appended moieties is prerequisite for nice fitting between host and guest. We wish to report here the first example of the conversion from flexible host to rigid host of **1** (Eq. 1)



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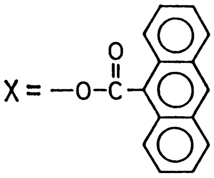

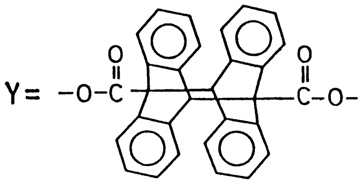

where two anthracene moieties undergo intramolecular photodimerization. Since the cavity is made too shallow or fully occupied by anthracene photodimer, photochemical switching of guest binding from good host (living host) to poor host (dead host) may be expected.

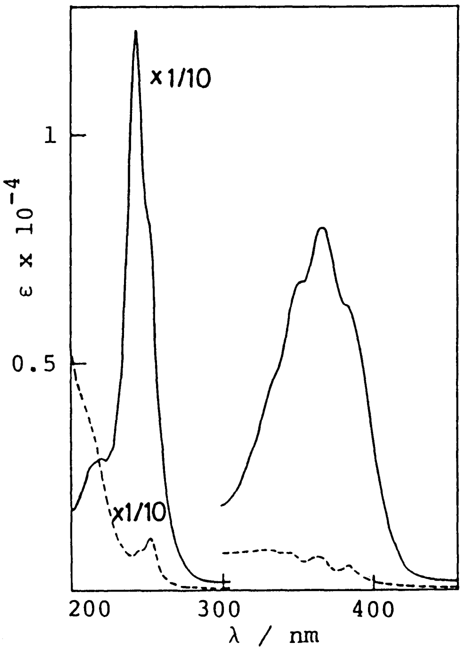

Fig. 1. Absorption spectra of **1** before (——) and after (- - -) photoirradiation in an aqueous 10% ethylene glycol solution.

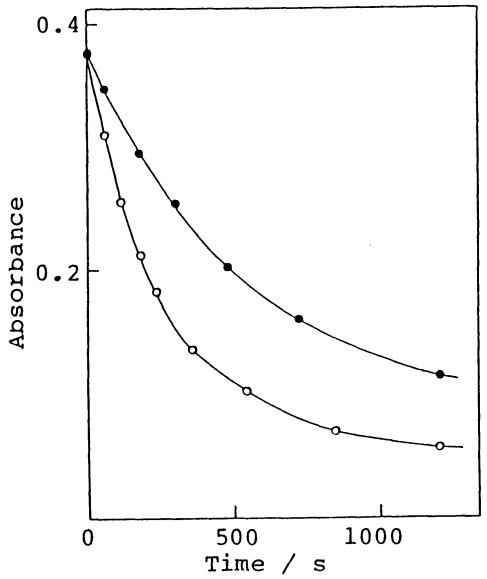

Fig. 2. Photoinduced changes in absorption at 367 nm of **1** (5.0×10^{-5} mol dm^{-3}), alone (○) and in the presence of l-borneol (●, 2.0×10^{-3} mol dm^{-3}).

The compound **1** was prepared by the reaction of azobenzene-4,4'-disulfonyl γ-CD with sodium 9-anthracenecarboxylate in dimethyl sulfoxide according to the same procedure reported for the synthesis of bis(2-naphthylacetyl) γ-CD.[2b)] The purified product was identified by complete spectral and analytical data.[7)] The glucose units modified are assumed to be A,D and/or A,E from the examination of molecular models on the azobenzene-capped γ-CD.[2b)] The solubility of **1** in pure water is poor, so all experiments were carried out in an aqueous solution containing 10% (by volume) ethylene glycol. Figure 1 shows absorption spectra of **1** before and after photoirradiation. Upon photoirradiation with the light of wavelengths longer than 300 nm, a remarkable decrease in the absorption bands in the range of 300-400 nm was observed. This spectral change was the same as that reported by Tamaki[5a)] for photodimerization of 2-anthracenesulfonate in the presence of γ-CD. The subsequent irradiation with the light around 255 nm slightly recovers the anthracene-like

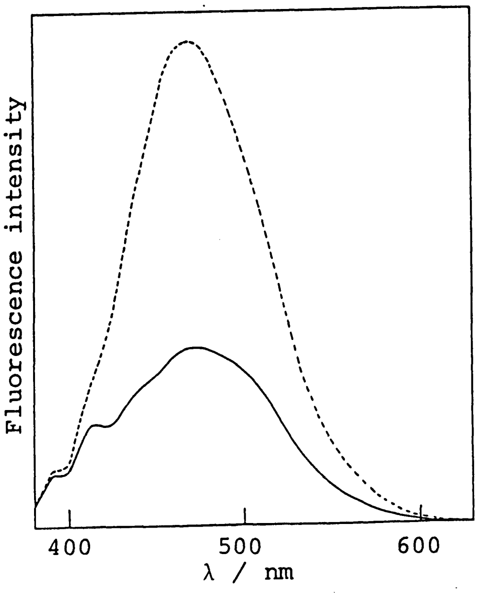

Fig. 3. Fluorescence spectra of **1** (4.3×10^{-5} mol dm^{-3}), alone (——) and in the presence of l-borneol (- - - , 1.1×10^{-3} mol dm^{-3}) in aqueous 10% ethylene glycol solutions.

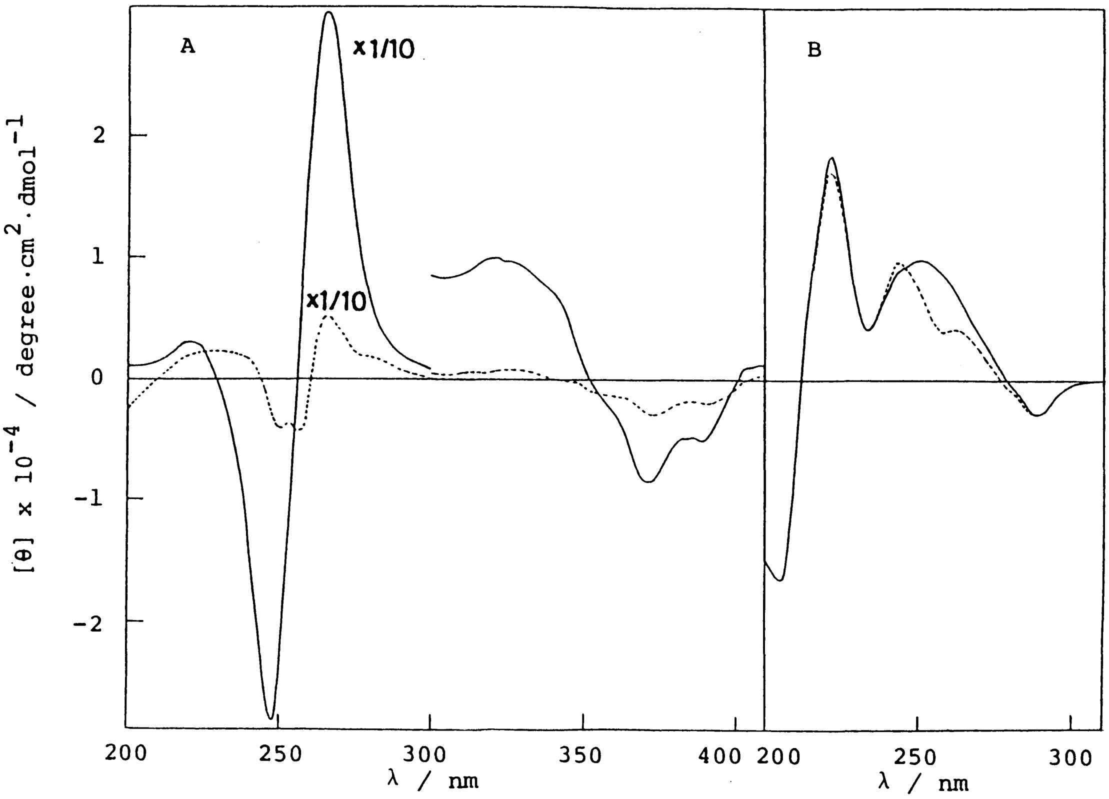

Fig. 4. Circular dichroism spectra of **1**, alone (——, 3.9×10^{-5} mol dm^{-3}) and in the presence of l-borneol (----, 2.0×10^{-3} mol dm^{-3}), in aqueous solutions before (A) and after (B) photoirradiation.

absorption bands again due to the cleavage of the dianthracene, increasing the molar absorption coefficient at 364 nm from 700 to 1400. Since both monomer and dimer absorb the incident light, the original anthracene absorption bands could not be attained. The switching between dimer and monomer is therefore partial in this system. It is noteworthy that l-borneol depresses the rate of photodimerization as shown in Fig. 2. This result suggests that the two anthracene moieties of **1** are positioned rather unfavorably for dimerization after guest accommodation.

Figure 3 shows fluorescence spectra of **1**, alone and in the presence of l-borneol as a guest. The host **1** exhibits a predominant excimer emission with the maximum around 474 nm, the intensity being remarkably enhanced by l-borneol. The wavelength of the excimer peak is slightly shifted to longer side in comparison with that of 1,2-di(1-anthryl)ethane (λ_f=460 nm),[8] but shorter than that of a 2:2 complex of 2-anthracenesulfonate and β-CD (λ_f=500 nm).[5] Since l-borneol retarded the photodimerization of the anthracene nuclei of **1** in spite of its enhancing effect on excimer emission, excimer formation itself may not be a prerequisite factor for the photodimerization.[5]

Figure 4 shows circular dichroism spectra of **1** before and after photoirradiation. The spectrum of **1** before photoirradiation exhibits negative bands in ^1L_a transition region (350 - 400 nm) and a couple of positive (266 nm) and negative (248 nm) bands in ^1B_b transition region of anthracene. The exciton coupling pattern in the ^1B_b transition region indicates that the mutual configuration of the two anthracene moieties in **1** is R-helix.[9)] The absolute intensities of all dichroism bands decrease with increasing l-borneol concentration. This behavior suggests that the guest molecule is included in the cavity of **1** by extruding two anthracene moieties from the cavity so as to make the moieties to act as hydrophobic caps.[2b)] The analysis of the circular dichroism variations induced by l-borneol gave 2900 mol^{-1} dm^3 as a binding constant. The circular dichroism pattern after photoirradiation is quite different, a new exciton coupling band appearing with peak and trough at 221 nm and 205 nm, respectively in addition to a trough at 288 nm and a peak at 251 nm. The intensities of the exciton coupling band and the trough at 288 nm are hardly affected by addition of l-borneol while the pattern of the circular dichroism peak around 251 nm is made distorted with a decrease of its intensity. Since the effect of guest addition was remarkable only within the wavelength region of the strong exciton coupling band of flexible form of **1** (230 - 270 nm), the circular dichroism behavior may be related with the fact that the photoirradiated sample contains a slight amount of flexible form of **1** (Fig. 1). The bands hardly affected by guest addition may therefore be attributable to the property of the rigid form of **1**. The results suggest that the rigid form of **1** is almost dead as host with its cavity fully occupied by the anthracene photodimer. The photoirradiation of **1** in the presence of l-borneol resulted in the same circular dichroism spectrum as that of **1** with the guest added after photoirradiation, so the dimerization is likely to proceed in the free form of **1** in an equilibrium mixture of free and complexed forms of **1**.

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7) Data for **1**: ^{1}H NMR (DMSO-d_6) δ=3.16-4.04 (m, 48H, CD protons other than C_1H and OH), 4.33-4.63 (m, 6H, O_6H), 4.80-5.07 (m, 8H, C_1H), 5.62-5.90 (m, 16H, O_2,O_3H), 7.44-7.63 (m, 8H, aromatic), 7.84-8.20 (m, 8H, aromatic), 8.55 (s, 2H, aromatic); Found: C, 51.64; H, 6.08. Calcd for $C_{78}H_{96}O_{42}\cdot 6H_2O$: C, 51.65; H, 6.00. IR (KBr, cm^{-1}) 1720 (ester).

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