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Remarkably Enhanced Excimer Formation of Naphthylacetate in Cation-Charged γ-Cyclodextrin

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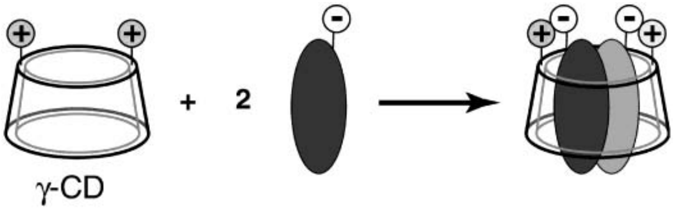
ABSTRACT



$6^A,6^D$-Bispyridinio-appended γ-cyclodextrin effectively enhanced the excimer fluorescence of 2-naphthylacetate. This increase derived from the increase of formation of the 1:2 complex between the cation-charged γ-cyclodextrin and 2-naphthylacetate by the electrostatic interaction between the host and the guest.

Cyclodextrins (CDs) are cyclic oligosaccharides, mostly consisting of six, seven, and eight glucose units joined by α-1,4-linkages for α-, β-, and γ-CD, respectively.[1−3] They have a remarkable property of accommodation of various organic molecules in their central cavity in aqueous solution, and have been used as molecular vessels for reactions, binding sites of enzyme models, solubilizers of water-insoluble substances, and molecular capsules for stabilizing unstable chemicals. γ-Cyclodextrin can accommodate two molecular species in its large cavity.[4,5] Because of this unique property, γ-cyclodextrin can be used as a molecular flask or vessel, in which interactions and reactions between two guest molecules are facilitated. Regio- and stereoselective reaction between two substrates would be achieved in the γ-CD cavity.[6,7] Two naphtharenes markedly make an excimer to show an excimer fluorescence in the presence of γ-CD, whereas the excimer scarcely forms in the presence of α- or β-CD.[4,5] Two 2-anthracenecarboxylic acids are photodimerized to produce four kinds of configurational isomers. Their relative yields of the configurational isomers are dependent on the degree of steric hindrance and electrostatic repulsion between two carboxylate units.[8] γ-Cyclodextrin can accommodate two 2-anthracenecarboxylic acids as guests and its cavity can be used as the molecular flask for photodimerization of 2-anthracenecarboxylic acids. When the photodimerization of 2-anthracenecarboxylic acids was carried out in the presence of γ-CD, the photodimerization reaction was accelerated and the relative yields of the configurational isomers were changed on the basis of stability of the inclusion complex.[8] Cation-charged CD is expected to make a larger amount of a 1:2 complex with anion-charged guests and to be a better molecular flask. In this paper we describe

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[†] Prof. Akihiko Ueno passed away on March 23, 2003.

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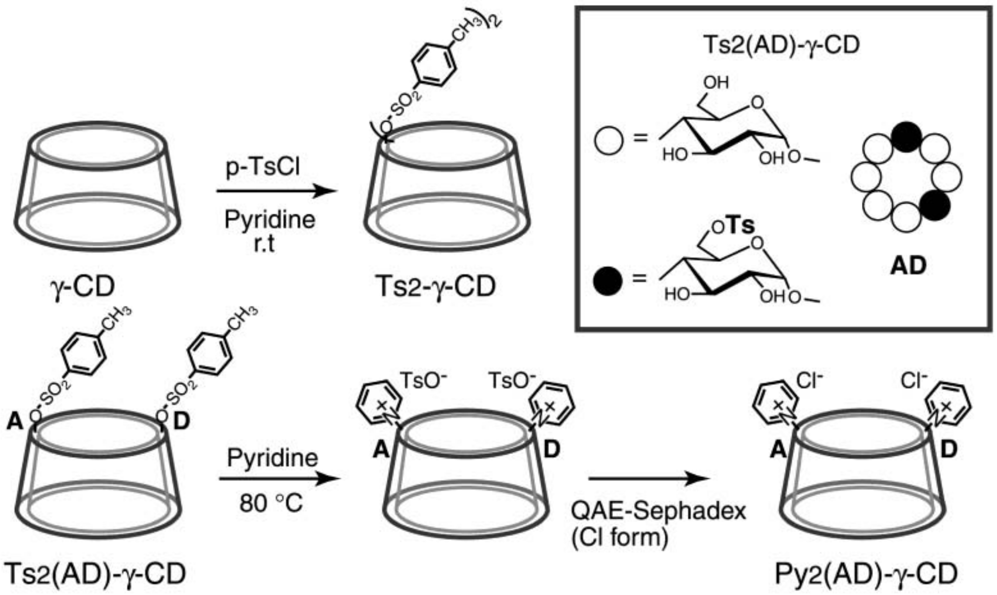
Scheme 1. Synthesis of 6A,6D-Bispyridinio-γ-CD (**Py2(AD)-γ-CD**)



the excellent enhancement of excimer fluorescence of naphthylacetic acid by bispyridinio-modified γ-CD.

γ-Cyclodextrin was modified with two pyridinium units in the two particular glucose units. $6^A,6^D$-Bistosyl-γ-CD[9] was heated in pyridine at 80 °C for 12 h to obtain $6^A,6^D$-bispyridinio-γ-CD (**Py2(AD)-γ-CD**). Counteranions of **Py2(AD)-γ-CD** were changed to Cl^- by ion exchange chromatography. ^1H NMR data of the product were in fair agreement with the previously reported data.[10] The fluorescence intensity of 2-naphthylacetate around 450 nm was markedly enhanced in the presence of **Py2(AD)-γ-CD** in the pH 9.2 phosphate buffer, whereas the intensity was scarcely increased in the presence of γ-CD as shown in Figure 1. This fluorescence band around 450 nm can be assigned to the excimer emission.[4,5]Addition of bispyridinio-appended β-CD scarcely influenced the fluorescence spectrum and excitation spectrum of 2-naphthylacetate. These results suggest that the ability to accommodate two naphthylacetates of γ-CD is important for the excimer fluorescence, and **Py2(AD)-γ-CD** is quite effective for the excimer formation of 2-naphthylacetate.

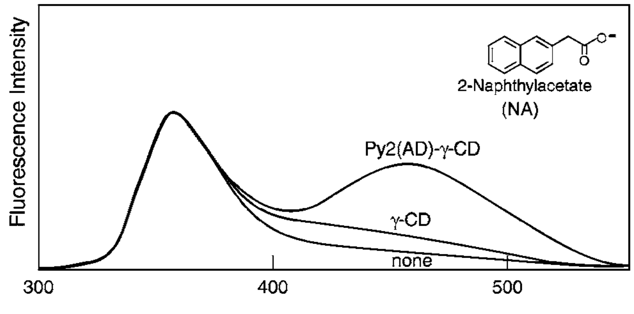


Figure 1. Fluorescence spectra of 2-naphthylacetate in the presence of γ-CD or **Py2(AD)-γ-CD** and in the absence of them in pH 9.2 carbonate buffer. Ex = 295 nm, [NA] = 1 mM, [**Py2(AD)-γ-CD**] = [γ-CD] = 1 mM.

When the excitation spectrum of 2-naphthylacetate was monitored at 450 nm, a new band appeared at longer wavelength as shown in Figure 2. This band around 350 nm would be ascribed to the ground-state dimer in the γ-CD cavity as reported by Yorozu and Itoh,[5,11] though the ground-state dimer cannot be confirmed by the absorption spectra. The intensities of the band around 350 nm in the excitation spectrum increased with an increased amount of **Py2(AD)-γ-CD**. The binding constant of **Py2(AD)-γ-CD** for the ground-state dimer was estimated to be 4.83×10^4 M^{-2} from the dependence of the intensity of the excitation spectrum at 350 nm on the concentration of **Py2(AD)-γ-CD** with use

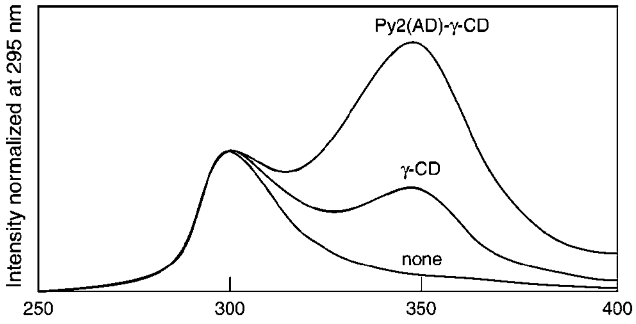


Figure 2. Excitation spectra of 2-naphthylacetate in the presence of γ-CD or **Py2(AD)-γ-CD** and in the absence of them in pH 9.2 carbonate buffer. Em = 450 nm, [NA] = 1 mM, [**Py2(AD)-γ-CD**] = [γ-CD] = 1 mM.

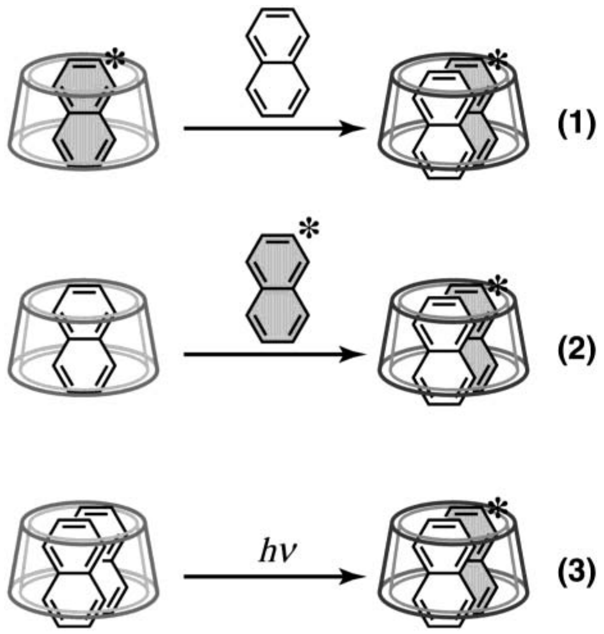


Figure 3. Possible mechanisms for the excimer formation. (1) The excited-state monomer in the γ-CD and the ground-state monomer in solution are reacted to form the excimer. (2) The ground-state monomer in the γ-CD and the excited-state monomer in solution are reacted to form the excimer. (3) One of two naphthylacetates in the γ-CD is excited to form the excimer.

of the curve-fitting to the 1:2-type Benesi−Hildebrand equation.[12]

There are three possible mechanisms for the formation of the excimer as shown in Figure 3. Because the enhancement of the monomer fluorescence of 2-naphthylacetate was not observed by the addition of **Py2(AD)-γ-CD**, the first mechanism is denied. The second mechanism is not likely to occur within the lifetime of the excited state of 2-naphthylacetate, since the concentration of the excited state of 2-naphthylacetate is too low in aqueous solution. Only the third mechanism is consistent with the observation of the new band in the excitation spectrum of 2-naphthylacetate in the presence of **Py2(AD)-γ-CD**. This mechanism is already proposed for the enhancement of the excimer fluorescence by the addition of γ-CD.[4,5] It is not obvious whether the structures of the fluorescent state of the ground-state dimer and the excimer are identical or different from each other.[5] Even if the excimer is not identical with the fluorescent of the ground-state dimer, two naphthylacetate molecules can be situated in various positions in the γ-CD cavity, and some kinds of 1:2 complexes can show the excimer emission. The increase of the excimer fluorescence intensity around 450 nm was consistent with the increase of the intensity of the band around 350 nm in the excitation spectrum. This relationship indicates that the emission of the excimer fluorescence derived mostly from the 1:2 complex of **Py2(AD)-γ-CD** and 2-naphthylacetate, although it is difficult to make clear whether the structure of this 1:2 complex and the ground-state dimer is identical or not.

The addition of 1 M NaCl decreased the intensity of the excimer fluorescence of 2-naphthylacetate. This result supports the charge interaction between **Py2(AD)-γ-CD** and 2-naphthylacetate.

In conclusion, modification of γ-CD with two pyridinio moieties at A and D glucose units is effective for the increase of the intensity of the excimer fluorescence of 2-naphthylacetate. This increase derived from the formation of the 1:2 complex of 2-naphthylacetate in the cation-charged γ-cyclodextrin cavity. This result also indicates that the charged interaction between the host and the guest can contribute to the formation of the 1:2 complex in the γ-CD cavity.

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