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Template-Assisted Stereoselective Photocyclodimerization of 2-Anthracenecarboxylic Acid by Bispyridinio-Appended γ-Cyclodextrin

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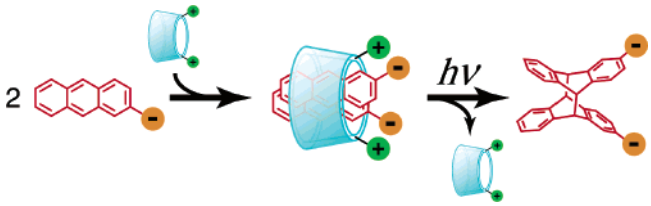

Four kinds of bispyridinio-appended γ-cyclodextrin (γ-CD) were prepared to make a molecular flask for controlling the stereoselectivity of photocyclodimerization of 2-anthracenecarboxylate. When the photocyclodimerization of 2-anthracenecarboxylate was carried out in the presence of A,E-bispyridinio-appended γ-CD, the relative yield of one of the configurational isomers, the head-to-head/anti-isomer, was increased 1.8-fold compared to the corresponding yield in the presence of unmodified γ-CD or in the absence of any γ-CD. The optical yields of the photocyclodimerization reaction products also increased more than 10-fold by the addition of bispyridinio-appended γ-CD compared with unmodified γ-CD.

1. Introduction

Chiral photochemistry, or photochirogenesis, has currently been attracting great interest because photochemical induction of molecular chirality possesses several advantages over thermal or enzymatic asymmetric reaction.[1−3] For example, photochemical reactions often provide a direct and efficient route to one-step syntheses of thermally inaccessible or difficult-to-attain compounds. Photochemical reactions are driven by the absorption of high-energy photons and proceed through an excited state, which renders them inherently free from temperature restrictions. They are, therefore, advantageous for investigating the effect of the entropy factor upon stereoselectivity over a wide range of temperature or pressure without undergoing any essential changes in reaction mechanism or intermediates formed.

It was recently reported that the stereochemistry of some photoproducts are inverted at a critical temperature (To), above which the optical yield increased with increasing temperature.[4] Pressure, solvent, concentration, and substituent flexibility can be also used as tools for controlling the stereochemistry and stereoselectivity of photoproducts. However, lifetimes of the electronically excited state are very short. Observation of transient species is difficult and detail structures of reaction intermediates are not clear in most cases. Some bimolecular photoreactions are known in which various configurational isomers arise, but their selectivity is not high.

Supramolecular systems with chiral and well-defined 3D structures can be reasonably expected to manipulate the stereochemistry of photochemical reactions. Cyclodextrin, with its well-defined 3D structure, is a promising material for photochirogenesis. Cyclodextrins (CDs) are cyclic oligosaccharides, mostly consisting of six, seven, and eight D-glucose residues joined by α-1,4-linkages for α-, β-, and γ-CD, respectively. γ-CD has a large central cavity that can accommodate two molecular species.[5−7] Because of this unique property, γ-CD can be used as a

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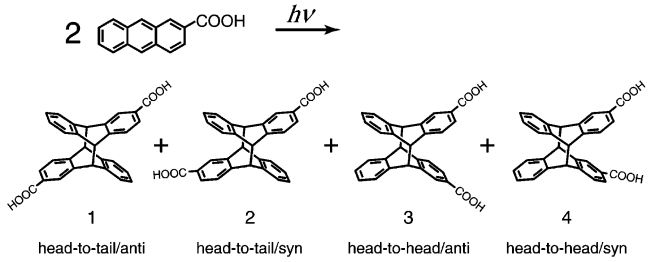
SCHEME 1. Photocyclodimerization of 2-Anthracencarboxylates



molecular flask or vessel, in which interactions or reactions between two guest molecules are facilitated.[8,9] Regio- and stereoselective reaction between two substrates can be mediated in the γ-CD cavity.

Two 2-anthracenecarboxylates undergo photocyclodimerization to produce four kinds of configurational isomers (Scheme 1).[10,11] The relative yield of each configurational isomer is dependent on the degree of steric hindrance and electrostatic repulsion between the two carboxylate units or dipole−dipole interaction of the two 2-anthracenecarboxylate molecules. γ-Cyclodextrin is able to accommodate two molecules of 2-anthracenecarboxylates or 2-anthracenesulfonates and can be used as a molecular flask for the photocyclodimerization reaction.[9−15] When the photocyclodimerization of 2-anthracenecarboxylate is carried out in the presence of γ-CD, the reaction is accelerated but the relative yield of the configurational isomers scarcely changes. The hydrophobic interaction in the CD cavity alone is insufficient for the regulation of the relative yield. Addition of another interaction such as an ion interaction is needed to regulate the relative yield. If γ-CD were modified with two cation-charged moieties at the two glucose units, its binding affinity for 2-anthracenecarboxylates would increase because of electrostatic interactions. Furthermore, the main product of the photocyclodimerization of 2-anthracenecarboxylate would be the head-to-head isomers in the presence of cation-charged γ-CD, although the main product is the head-to-tail isomers even in the presence of γ-CD.

We recently reported that modification of γ-CD with two pyridinio moieties at A and D glucose units is effective in increasing the intensity of the excimer fluorescence of 2-naphthylacetate.[16] This increase is derived from the formation of the 1:2 complex of 2-naphthylacetate in the cation-charged γ-CD 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. Therefore, we expected that a bispyridinio-modified γ-cyclodextrin (**Py2-γ-CD**), in which the two glucose units are derivatized with two pyridinium cations, might regulate the selectivities for the configuration and stereochemistry of the photocyclodimerization of 2-anthracenecarboxylate. We anticipated further that the modified position at the primary face of γ-CD would cause a difference in the ratio of head-to-head/anti to head-to-head/syn isomer. The optical yield of the head-to-head/anti-isomer would also depend on the position modified. In this paper, we report a remarkable template effect of bispyridinio-modified γ-CD for the photocyclodimerization of 2-anthracenecarboxylate.

2. Experimental Section

2.1 Materials. Synthesis of Py2(AE)-γ-CD. 6A,6E-Bistosyl-γ-CD[17] (100 mg) was heated in pyridine (20 mL) at 80 °C for 12 h to obtain 6A,6E-bispyridinio-γ-CD (**Py2(AE)-γ-CD**). The reaction mixture was concentrated under reduced pressure. The crude product was dissolved in water followed by column chromatography on QAE Sephadex A-25 to change counteranions of **Py2(AE)-γ-CD** from TsO^- to Cl^-. The lyophilization of the fraction containing the desired product gave a white powder (67.2 mg, yield 72.4%).

MALDI-TOFMS: *m/z*: calcd for $C_{58}H_{88}O_{38}N_2$: 1420.5; found: 1420.8 $[M]^+$.

Synthesis of Py2(AB)-γ-CD. Py2(AB)-γ-CD was synthesized from 6A,6B-bistosyl-γ-CD by the same method as for **Py2(AE)-γ-CD** (63.0 mg, yield 67.8%).

MALDI-TOFMS: *m/z*: calcd for $C_{58}H_{88}O_{38}N_2$: 1420.5; found: 1420.4 $[M]^+$.

Synthesis of Py2(AC)-γ-CD. Py2(AC)-γ-CD was synthesized from 6A,6C-bistosyl-γ-CD by the same method as for **Py2(AE)-γ-CD** (77.0 mg, yield 83.0%).

MALDI-TOFMS: *m/z*: calcd for $C_{58}H_{88}O_{38}N_2$: 1420.5; found: 1420.1 $[M]^+$.

Synthesis of Py2(AD)-γ-CD. Py2(AD)-γ-CD was synthesized from 6A,6D-bistosyl-γ-CD by the same method as for **Py2(AE)-γ-CD** (73.8 mg, yield 79.9%).

MALDI-TOFMS: *m/z*: calcd for $C_{58}H_{88}O_{38}N_2$: 1420.5; found: 1420.4 $[M]^+$.

Synthesis of Py-γ-CD. Py-γ-CD was synthesized from 6-monotosyl-γ-CD by the same method as for **Py2(AE)-γ-CD** (80.0 mg, yield 81.7%).

MALDI-TOFMS: *m/z*: calcd for $C_{53}H_{84}O_{39}N_1$: 1358.5; found: 1358.4 $[M]^+$.

2.2 Methods. A solution of 2-anthracenecarboxylic acid (0.1 mM, 1.0 mL) in sodium carbonate buffer (pH 9.1, 20 mM, 5% ethylene glycol) in a quartz cell was deaerated with nitrogen for 10 min. The solution was photoirradiated with a 200 W Hg−Xe lamp ($\lambda > 370$ nm) equipped with an optical glass filter (Toshiba UV-35) during continuous nitrogen bubbling. At regular intervals, small aliquots of the solution were taken, suitably diluted, and assayed by HPLC. HPLC analyses were performed with tandem columns (Nakarai COSMOSIL 5C18-AR2 and Daisel Chiralcel OJ-RH) and a linear gradient elution of acetonitrile/water with 0.1% trifluoroacetic acid (from 45% to 75% in volume) was applied. Relative yield and enantiomeric excesses (%ee) were determined by the peak area on the HPLC chromatogram detected by the absorbance at 220 nm. The sign of the ee is defined as positive, if the yield of the first enantiomer on the chromatogram is higher than the second one.[10]

The rates used in the calculation of rate constants were averages of at least three determinations that agreed to within 3%. The relative yields and %ee of the product isomers were also averages of at least three determinations that agreed to within 5%.

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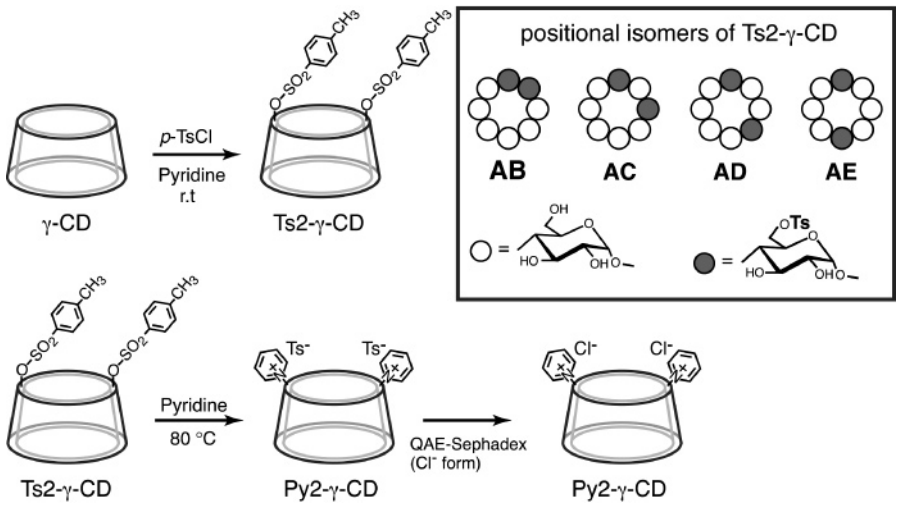
SCHEME 2. Syntheses of Bis-pyridinio-modified γ-Cyclodextrins



3. Results and Discussion

Syntheses of Pyridinio-Appended γ-Cyclodextrins. Two pyridinium groups were introduced to γ-cyclodextrin (γ-CD) at the primary hydroxyl side to regulate the orientation of 2-anthracenecarboxylate in the γ-CD cavity (Scheme 2). When two different glucose units of γ-CD are modified with the same two functional groups, there are four kinds of positional isomers. The bistosyl γ-CDs were prepared by the reported method.[17] The bistosyl γ-CDs were heated in pyridine at 80 °C for 12 h to obtain bispyridinio-γ-CDs (**Py2-γ-CDs**).[16,18,19] Counteranions of **Py2-γ-CD** were changed from TsO^- to Cl^- by ion exchange chromatography. The monopyridinio-modified γ-CD (**Py-γ-CD**) was also prepared by a similar method.

Binding Affinities of Pyridinio-Appended γ-Cyclodextrins. The stoichiometry of the complex of **Py2-γ-CD** with 2-anthracenecarboxylate (**2-AC**) was confirmed. A Job plot of the change in the absorption intensity at 396 nm gave a peak at 0.67 meaning that the ratio [**Py2-γ-CD**]:[**2-AC**] = 1:2, when [**Py2-γ-CD**] + [**2-AC**] = 0.1 mM (Figure 1). This result indicates that the major species at this concentration is a 1:2 host/guest complex. The stoichiometry of the complex of unmodified γ-CD with 2-anthracenecarboxylate has been reported in detail.[10] The association constant for unmodified γ-CD and 2-anthracenecarboxylate making a 1:1 complex and that making a 1:2 complex is 161 M^{-1} and 38 500 M^{-1} at 25 °C, respectively. This implied that the stoichiometry of the major portion of the complex of **Py2-γ-CD** under the reaction conditions is the 1:2 host/guest species, if inclusion behavior of **Py2-γ-CD** is similar to that of unmodified γ-CD.

The binding constant of **Py2-γ-CD** for 2-anthracenecarboxylate was estimated from the dependence of the absorption intensity of 2-anthracenecarboxylate at 386 nm on the concentration of **Py2-γ-CD** using nonlinear square fitting to the 1:2-host/guest-type equation (Table 1).[20] The binding constant of **Py2(AE)-γ-CD** for 2-anthracenecarboxylate is 9.37 × 10^7 M^{-2}, which is 12-fold greater than that of unmodified γ-CD. The binding constants of the other bispyridinio-modified γ-CDs (AB, AC, and AD isomer) are only ca. twice that of unmodified γ-CD, and the binding constant of mono-pyridinio-modified γ-CD (**Py-γ-CD**) for 2-anthracenecarboxylate is 1.7-fold greater than that of unmodified γ-CD. This result suggests that both the carboxylate anions of the two 2-anthracenecarboxylate molecules interact with the two pyridinium cations of **Py2(AE)-γ-CD** and that these two ion interactions cooperatively stabilize the 1:2 inclusion complex in **Py2(AE)-γ-CD**. Two pyridinium cations of **Py2-γ-CD** in the AB, AC, and AD isomers increase the

TABLE 1. Binding Constants of Unmodified γ-CD and Pyridinio-appended γ-CDs for 2-Anthracenecarboxylate

	K_b [a]/10^7 M^{-2}
γ-CD	0.80 ± 0.023
Py-γ-CD	1.37 ± 0.08
Py2(AB)-γ-CD	1.79 ± 0.13
Py2(AC)-γ-CD	1.62 ± 0.06
Py2(AD)-γ-CD	1.74 ± 0.03
Py2(AE)-γ-CD	9.37 ± 0.48

[a] $K_b = \dfrac{[\mathbf{CD}\cdot\mathbf{2\text{-}AC_2}]}{[\mathbf{CD}][\mathbf{2\text{-}AC}]^2}$

[**2-AC**] = 0.1 mM, [**CD**] = 0 ∼ 1.2 mM in sodium carbonate buffer (pH 9.1, 5% ethylene glycol) at 25 °C.

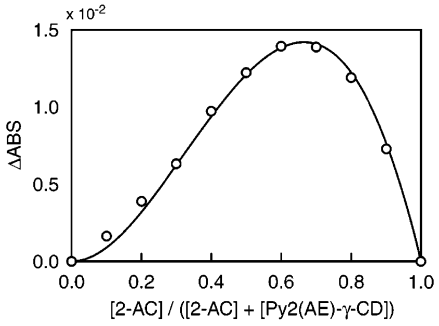


FIGURE 1. Job plot of the change in absorption spectrum for the complex of **Py2(AE)-γ-CD** with 2-anthracenecarboxylate ([**Py2(AE)-γ-CD**] + [**2-AC**] = 1 × 10^{-4} M) in sodium carbonate buffer (pH 9.1, 5% ethylene glycol) at 25 °C.

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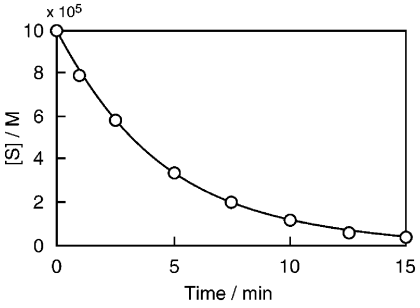

FIGURE 2. Time course of concentration of 2-anthracenecarboxylate in the photodimerization reaction in the presence of **Py2(AE)-γ-CD**; [**2-AC**] = 1×10^{-4} M, [**Py2(AE)-γ-CD**] = 3×10^{-3} M, in sodium carbonate buffer (pH 9.1, 5% ethylene glycol) at 25 °C under N_2; irradiated with 200 W Hg−Xe lamp ($\lambda >$ 370 nm).

TABLE 2. First-Order Rate Constants for Photocyclodimerization of 2-Anthracenecarboxylate in Various Conditions

additive	k/min^{-1}
none	0.259 ± 0.001
γ-CD	2.90 ± 0.02
Py-γ-CD	0.507 ± 0.003
Py2(AB)-γ-CD	0.185 ± 0.004
Py2(AC)-γ-CD	0.219 ± 0.003
Py2(AD)-γ-CD	0.188 ± 0.009
Py2(AE)-γ-CD	0.216 ± 0.005

binding affinities more than the single pyridinium cation in **Py-γ-CD**, but their cooperative effects are not large.

The product isomers of the photocyclodimerization reaction **1**, **2**, **3**, and **4** would be produced through the ground-state dimers **I**, **II**, **III**, and **IV**, respectively. The binding affinity results suggest that **Py2(AE)-γ-CD** would stabilize the head-to-head/anti-ground-state dimer (**III**), but **Py2(AD)-γ-CD** could not stabilize the head-to-head/anti-ground-state dimer (**III**). This result means that a slight difference in the position of the pyridinium cation greatly affects the binding affinity. From the point of view of molecular design, **Py2(AB)-γ-CD** or **Py2(AC)-γ-CD** would be expected to stabilize the head-to-head/syn-ground-state dimer (**IV**), but the binding affinity data show that the head-to-head/syn-ground-state dimer (**IV**) will be hardly stabilized by the **Py2(AB)-γ-CD** or **Py2(AC)-γ-CD**.

Photocyclodimerization Reaction of 2-Anthracenecarboxylate in the Presence of Pyridinio-Appended γ-Cyclodextrins. The photocyclodimerization reaction of 2-anthracenecarboxylate was carried out in the presence of **Py2-γ-CD**, **Py-γ-CD**, or unmodified γ-CD. As a control, the reaction was also performed in the absence of any γ-CD. The time course of the photocyclodimerization reaction of 2-anthracenecarboxylate in the presence of **Py2(AE)-γ-CD** is shown in Figure 2. This photocyclodimerization reaction is assumed to be first-order in 2-anthracenecarboxylate, as the plot of $\ln([S]/[S]_0)$ versus time is linear but the plot of $1/[S] - 1/[S]_0$ is curved.[21]

The first-order rate constants under all the conditions are shown in Table 2. The structure of the product isomer reflects the structure of the precursor ground-state dimer, because it is impossible either to exchange the orientation by the process of the dissociation and reassociation of the 2-anthracenecarboxylate or for 2-anthracenecarboxylate to react with the 1:1 inclusion complex within the lifetime of the excited singlet state (ca. 10 nanosecond).[16]

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TABLE 3. Relative Yields of the Product Isomers for Photocyclodimerization of 2-Anthracenecarboxylate in the Presence of an Additive

additive	isomer **1**	isomer **2**	isomer **3**	isomer **4**
none	37.1	34.2	17.2	11.6
γ-CD	26.9	37.8	17.5	17.8
Py-γ-CD	37.5	28.8	22.2	11.5
Py2(AB)-γ-CD	36.6	27.3	26.1	10.1
Py2(AC)-γ-CD	42.7	26.7	22.5	8.1
Py2(AD)-γ-CD	37.7	25.5	26.5	10.3
Py2(AE)-γ-CD	41.8	19.9	32.0	6.3

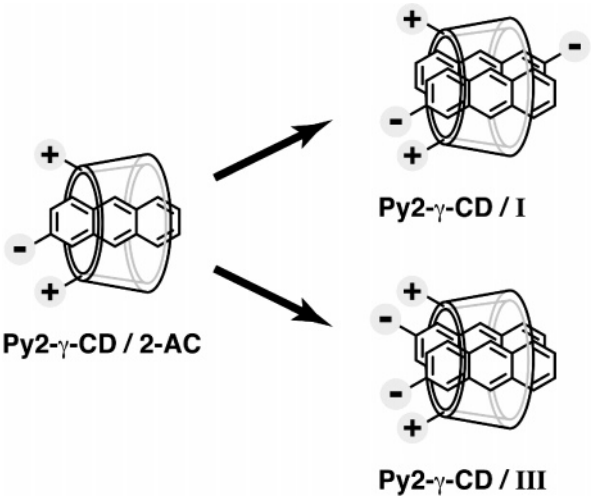
Each reaction rate in the presence of **Py2-γ-CDs** is smaller than that in the presence of unmodified γ-CD and that of 2-anthracenecarboxylate alone. The orientation of the 2-anthracenecarboxylate molecules in the **Py2-γ-CD** cavity will not be the same as that in the unmodified γ-CD cavity, and the orientation of precursor ground-state dimer in the **Py2-γ-CD** cavity would not be most suitable for the photocyclodimerization reaction. In the unmodified γ-CD, even though the orientation of the precursor ground-state dimer in the unmodified γ-CD cavity is not ideal for the transition state of the photocyclodimerization reaction, 2-anthracenecarboxylate can easily migrate to the most reactive position in the unmodified γ-CD cavity and the reaction is not suppressed in the inclusion complex. On the other hand, if the orientation of the precursor ground-state dimer in the **Py2-γ-CD** cavity is not suitable for the reaction, the rate of the reaction would be reduced, because the motion of 2-anthracenecarboxylate in the **Py2-γ-CD** cavity is suppressed by the ion interactions.

The relative yields for product isomers were determined by HPLC and are shown in Table 3. The relative yield of the isomer **3** increased 1.8-fold on the addition of **Py2(AE)-γ-CD**, whereas that of the isomer **2** fell by about a half. However, the effect of **Py-γ-CD** on changing the relative yields of the configurational isomers was small. These results suggest that the electrostatic interaction between the carboxylate anions of the substrates and the pyridinium cations at two positions of **Py2(AE)-γ-CD** could moderately regulate the configurational selectivity of the photocyclodimerization. The product isomer distribution primarily depends on the population of these orientational isomers in the ground state before photocyclodimerization. Our results indicate that the precursor ground-state dimer for the isomer **3** is stabilized by the two pyridinio cations of **Py2(AE)-γ-CD**.

The relative yield of the isomer **4** is lowest under all conditions and was not increased by **Py2(AB)-γ-CD** or **Py2(AC)-γ-CD,** although its enhancement was expected. This result is consistent with the result of the binding affinity of **Py2(AB)-γ-CD** and **Py2(AC)-γ-CD** for 2-anthracenecarboxylate.

The relative yield of the isomer **1** was almost the same under all conditions investigated. Even if the carboxylate anion of the first of the two 2-anthracenecarboxylate molecules involved in the 1:2 host/guest complex interacts with the pyridinium cation of the **Py2-γ-CD**, the second

SCHEME 3. Formation of Py2-γ-CD/I and Py2-γ-CD/III Complex from Py2-γ-CD/2-AC Complex



one is likely to be located in the head-to-tail position. Evidence for this comes from the observation that in aqueous solution the precursor ground-state dimer **I** is more stable. There is nothing to destabilize this precursor ground-state dimer in the **Py2-γ-CD** cavity (Scheme 3). The precursor ground-state dimer **I** is more stable than the precursor ground-state dimer **III** even in the presence of **Py2-γ-CD**, although the precursor ground-state dimer **III** is stabilized by the interaction of pyridinium cations of **Py2-γ-CD**. Therefore, the tendency of this head-to-tail accommodation is not changed in any of the cases investigated. In another mechanism, because the reactivity of the complex **Py2-γ-CD/I** is greater than that of the other complexes, the main product is the isomer **1**, even if the complex **Py2-γ-CD/I** is less than the complex **Py2-γ-CD/III**. The result of the affinity of **Py2-γ-CD** for 2-anthracenecarboxylate suggests that the latter mechanism is appropriate in the case of **Py2(AE)-γ-CD** and that the former mechanism is also possible for the other isomers of **Py2-γ-CD**.

The relative yield of the isomer **3** in the presence of **Py2(AE)-γ-CD** is larger than that in the presence of **Py2(AD)-γ-CD**, in which the position of pyridinium cation is different in only one glucose unit compared with the former. This result means that a slight difference in the position of the pyridinium cation greatly affects the stabilization of the precursor ground-state dimer. **Py2-(AE)-γ-CD** stabilizes the precursor ground-state dimer for the isomer **3** whereas **Py2(AD)-γ-CD** is unable to act similarly. This difference is revealed in the difference of binding constant for 2-anthracenecarboxylate (Table 1).

Induction of Enantiodifferentiation by Pyridinio-Appended γ-Cyclodextrins. There are enantiomers in the isomers **2** and **3**. The addition of **Py2-γ-CD** or **Py-γ-CD** induced enantiodifferentiating photocyclodimerization. **Py2(AE)-γ-CD** increased the enantiomeric excess (ee) 10-fold for the isomer **3**, compared with the reaction using unmodified γ-CD, and the sign of the ee in **Py2(AE)-γ-CD** is opposite to that in the unmodified γ-CD (Figure 3). The electrostatic interactions between the pyridinium cations and the carboxylate anions are highly effective in regulating the enantioselectivity, and this result suggests that both of the two electrostatic

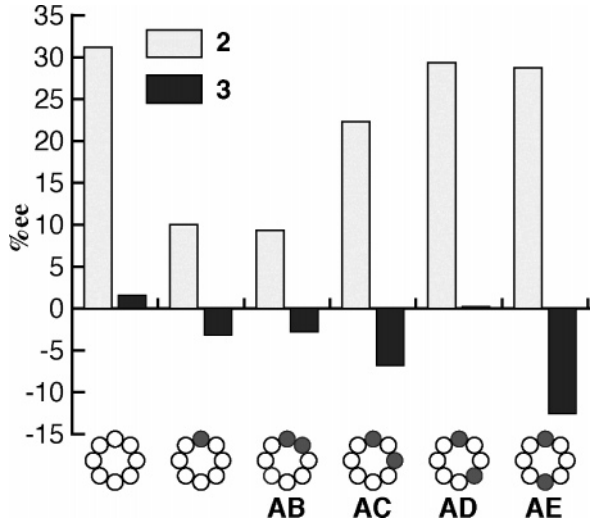


FIGURE 3. Effect of ion interaction on enantioselectivities for photocyclodimerization reaction of 2-anthracenecarboxylate; [**2-AC**] = 1×10^{-4} M, [**Py2-γ-CD**] = 7×10^{-4} M, in sodium carbonate buffer (pH 9.1, 5% ethylene glycol) under N_2 at 25 °C; irradiated with 200 W Hg−Xe lamp ($\lambda > 370$ nm) for 30 min. The sign of the ee is defined as positive if the yield of the first enantiomer on the chromatogram is higher than the second one.[10]

interactions are involved in the enantioselectivity. These electrostatic interactions between the pyridinium cations and the carboxylate anions in the cavity of **Py2(AE)-γ-CD** stabilize only one of the diastereomeric precursors of the isomer **3**, although interestingly, the stabilities of two diastereomeric precursors of the isomer **3** are almost the same in the unmodified γ-CD cavity.

The ee of the isomer **3** in the presence of **Py2(AD)-γ-CD** is almost zero, whereas **Py2(AE)-γ-CD** is quite effective in inducing an enantiomeric excess. This means that only a slight difference in the position of the pyridinium cation can greatly affect the stabilization of diastereomeric precursors.

Only one electrostatic interaction with the diastereomeric precursor of the isomer **2** in the cavity of **Py2(AE)-γ-CD** or **Py2(AD)-γ-CD** cannot perturb the relative stability of the diastereomeric precursors of the isomer **2**, and the ee of the isomer **2** in the presence of **Py2(AE)-γ-CD** or **Py2(AD)-γ-CD** is almost the same as that in the presence of unmodified γ-CD. This result suggests that the location of the 2-anthracenecarboxylate molecule interacting with pyridinium cation in the **Py2(AE)-γ-CD** or **Py2(AD)-γ-CD** cavity is similar to the location of one of the 2-anthracenecarboxylate molecules in the unmodified γ-CD cavity for making the isomer **2**. On the other hand, the location of the 2-anthracenecarboxylate molecule interacting with pyridinium cation in the **Py2(AC)-γ-CD** or **Py2(AB)-γ-CD** cavity must be different from the location of one of the 2-anthracenecarboxylate molecules in the unmodified γ-CD cavity. Although **Py2-γ-CD** can influence the orientation of only one of the 2-anthracenecarboxylate molecules, this causes the orientation of the other 2-anthracenecarboxylate molecules vis-à-vis the diastereomeric position for generating the isomer **2** to be modified. The ion interaction between the carboxylate anion of the substrate and the pyridinium cation of **Py2-γ-CD** decreases the difference in stability of the enantiomers of the isomer **2**. These results indicate that only

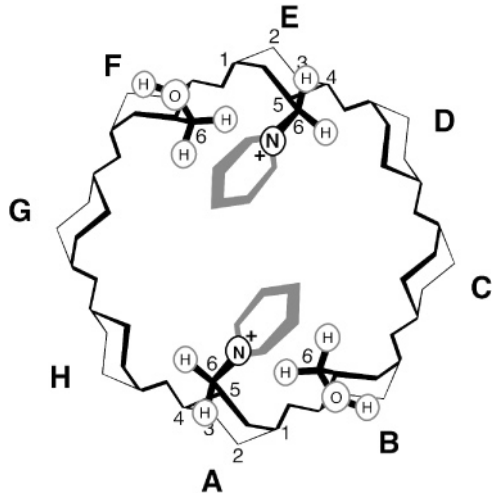


FIGURE 4. Estimated structures of **Py2(AE)-γ-CD**.

one ion interaction can improve the ee, if the interaction arranges one of the 2-anthracenecarboxylate molecules to a suitable position, to one in which one of the diastereomeric precursors of the isomer **2** is more favored than the other.

Estimated Structure of Pyridinio-Appended γ-Cyclodextrins. The detail structure of mono-pyridinio-appended β-CD (**Py-β-CD**) has already been studied by NMR techniques.[19,22] The C5−C6 bond of the glucopyranose unit can take a *gg* or *gt* conformer and only scarcely take a *tg* conformer.[23] Conformational analysis around the C5−C6 bond of the pyridinio-appended glucose unit (**G**−**A**) in **Py-β-CD** indicates that the main rotamer of the pyridinio-appended glucopyranose unit (**G**−**A**) is *gt* and that the pyridinium moiety mainly faces the adjacent glucose unit (**G**−**B**). Its ^{1}H resonances for H6 of **G**−**B** are abnormally shifted to upfield by 2.8 ppm by the anisotropic ring current effect of the pyridinium moiety, although the ^{1}H resonances for H6 of CD usually appear around 3.8 ppm. Though the ^{1}H resonances for H6 of the pyridinio-appended glucose units of **Py2-γ-CD** were not sufficiently separated from the ^{1}H resonances for H1 and the conformation around C5−C6 bond of the pyridinio-appended glucose unit could not be estimated by the analysis of the coupling constants of $J_{6a,5}$ and $J_{6b,5}$, the upfield shifted resonances were found around 2.7 and 2.9 ppm (Supporting Information). These upfield shifted resonances were assigned to H6 of unmodified glucose units by ^{1}H−^{13}C HSQC and ^{1}H−^{1}H COSY spectra. Because the spectral dispersions of ^{1}H resonances for **Py2-γ-CD** were not large, distortion of the CD ring is expected to be small. These resonances suggest that the main rotamers of the pyridinio-appended glucopyranose units are *gt* and that the pyridine moieties of **Py2-γ-CD** face the adjacent glucose units as shown in Figure 4. Two pyridinium moieties turn to the same direction. This conformation would contribute to improvement in the ee of the isomer **3**.

4. Conclusion

One of the positional isomers **Py2(AE)-γ-CD**, which has two pyridinium units at the **A** and **E** glucose units, is an effective molecular flask to regulate the configurational selectivity and the enantioselectivity of the photocyclodimerization of 2-anthracenecarboxylate. This regulation was due to electrostatic interactions between the pyridinium cations of the host molecule and the carboxylate anions of the guest molecules. Our results also show that a slight difference in the position of the pyridinium cation of **Py2-γ-CD** greatly affects the selectivity of relative yields and optical yields for the photocyclodimerization of 2-anthracenecarboxylate.

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Supporting Information Available: ^{1}H NMR spectra (500 MHz, D_2O) for pyridinio-modified CDs are provided. Assignments for characteristic resonances of pyridinio-modified CDs are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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