Critical stereocontrol by inter-amino distance of supramolecular photocyclodimerization of 2-anthracenecarboxylate mediated by 6-(ω-aminoalkylamino)-γ-cyclodextrins

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A series of 6-(ω-aminoalkylamino)-6-deoxy-γ-cyclodextrins (CDs) **5–8** with varying inter-amino distances were synthesized to control the stereoselectivity of [4 + 4] photocyclodimerization of 2-anthracenecarboxylate (AC). Complexation behavior of these CD hosts with AC was studied in aqueous solutions by UV-vis and circular dichroism spectral titration. Supramolecular photocyclodimerization of AC mediated by the CDs was performed in water as well as in water–methanol mixture to reveal that aminopropylamino-CD **6** leads to the formation of *head-to-head* photodimers **3** and **4** in highest yields, while aminobutylamino-CD **7** affords chiral *syn-head-to-tail* and *anti-head-to-head* photodimers **2** and **3** in highest enantioselectivities. These results indicate that the inter-amino distance critically control the product's stereo- and enantioselectivities through the electrostatic interactions of two anionic AC guests with the dicationic sidechain attached to the γ-CD rim and can be used as a convenient, yet effective, tool for manipulating the stereochemical outcomes of supramolecular photochirogenesis.

Introduction

As an alternative to the conventional thermal and enzymatic counterparts, chiral photochemistry provides a unique route to chiral compounds,[1] which are indispensable in various fields of science and technology, including chemistry, pharmacology, medicine, and agrochemistry.[2,3] However, achieving a high level of stereochemical control in photochirogenesis performed in solution is still a great challenge. One of the promising strategies is to achieve the chiral information transfer to a guest substrate accommodated in the chiral environment of supramolecular host. In this methodology, non-covalent interactions, such as van der Waals, hydrogen bonding, electrostatic, π–π and hydrophobic interactions, manipulate the inter- and intramolecular chirality transfer processes in the ground and excited states. Zeolites modified with chiral inductors,[4–6] hydrogen-bonding templates,[7–10] chiral crystal lattices,[11] cyclodextrins[12–25] and some proteins[26–28] have been explored as chiral supramolecular environment for asymmetric photochemical reactions. These hosts share one feature or function that guest substrate(s) are preoriented in the chiral environment of the host's binding site prior to photoirradiation to guarantee efficient chirality transfer.

Of the above hosts, cyclodextrin (CD) is particularly attractive and versatile as a chiral molecular flask for photochirogenesis, possessing an inherently chiral cavity that binds a variety of organic molecules in aqueous solutions and also being UV-transparent and chemically modifiable. These advantages enable us to apply CD hosts to various types of asymmetric photoreactions, such as photoisomerization, photocyclization, photocycloaddition and photodimerization.[17,29] In our recent studies, we have established the enantiodifferentiating [4 + 4] photocyclodimerization of 2-anthracenecarboxylate (AC) as a model photochirogenic system for investigating how the photochemical chirality transfer occurs and is influenced by a variety of internal and external factors.[12,16–23]

Photoirradiation of AC in solution leads to the formation of four [4 + 4] stereoisomers, *i.e.*, *anti-* and *syn-head-to-tail* (HT) dimers (**1** and **2**) and *anti-* and *syn-head-to-head* (HH) dimers (**3** and **4**) (Scheme 1), of which **2** and **3** are chiral. We have shown that the photocyclodimerization of AC performed in the presence of native γ-CD as a chiral host gives **2** as a major product in 32% enantiomeric excess (ee) and **3** as a minor product in ee of $<5\%$, while the use of aminoethylamino-CD **5** appreciably enhances the formation of HH dimers as well as the ee of **3** to 15% through the electrostatic interaction, and interestingly *N*,*N*-dialkylated CDs **9** and **10** afford **3** in much higher ee's of $>40\%$.[25,30] Despite the dramatic effect of *N*-alkylation on the product's ee, no systematic study has been done on the effects of the distance of two amino groups introduced to the sidechain of γ-CD. In this study, a series of 6-(ω-aminoalkylamino)-6-deoxy-γ-cyclodextrins **5–8** with varying inter-amino distance (defined by the number of methylenes between the two amino groups; n = 2, 3, 4 and 6) were synthesized by reacting 6-*O*-tosyl-γ-CD with an excess amount of 1,*n*-diaminoalkanes to elucidate how the inter-amino distance affects the complexation and photocyclodimerization behavior of AC.

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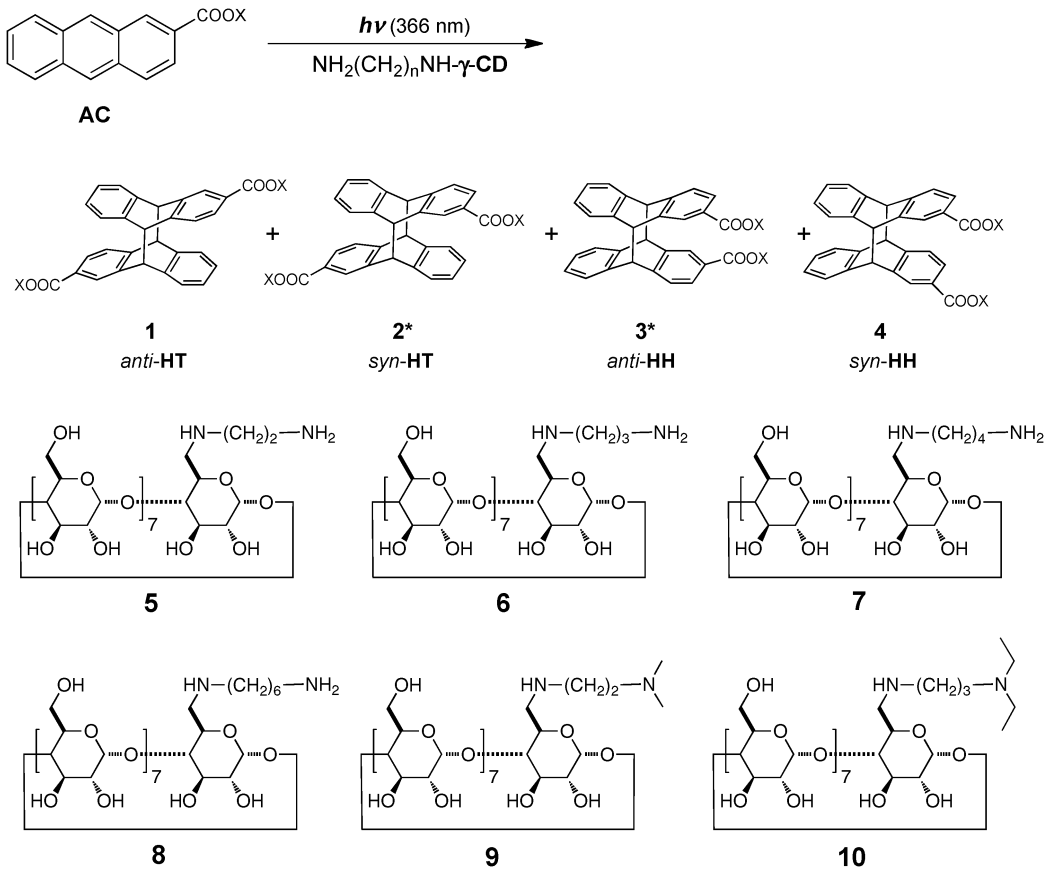

Scheme 1 Photocyclodimerization of 2-anthracenecarboxylate (AC) mediated by ω-aminoalkylamino-γ-cyclodextrins **5–10**.

Results and discussion

Binding studies

The complexation behavior of AC with modified γ-CDs was studied in aqueous buffer solutions by UV-vis and circular dichroism spectrometry. It is well established that two AC molecules are included stepwise in a γ-CD cavity to form a ternary complex. As exemplified in Fig. 1a, the addition of host **7** to an aqueous buffer solution of AC led to a decrease of the AC absorption at 387 and 364 nm with an accompanying bathochromic shift, which is ascribed to the π–π stacking of two ACs co-included in a single CD cavity. The circular dichroism spectra of AC in the presence of hosts **5–7** revealed a strong exciton couplet at the main band (centered at *ca.* 260 nm), clearly indicating the co-inclusion of two ACs in a single CD cavity (Fig. 1b).

The stepwise association constants for the 1 : 1 (K_1) and 1 : 2 complex (K_2) formation were determined by the nonlinear least-squares analysis of the UV-vis or circular dichroism spectral titration data (Fig. 1a and c) and the results are listed in Table 1.

Although we determined the association constants under rather limited conditions, the K_1 and K_2 values obtained for

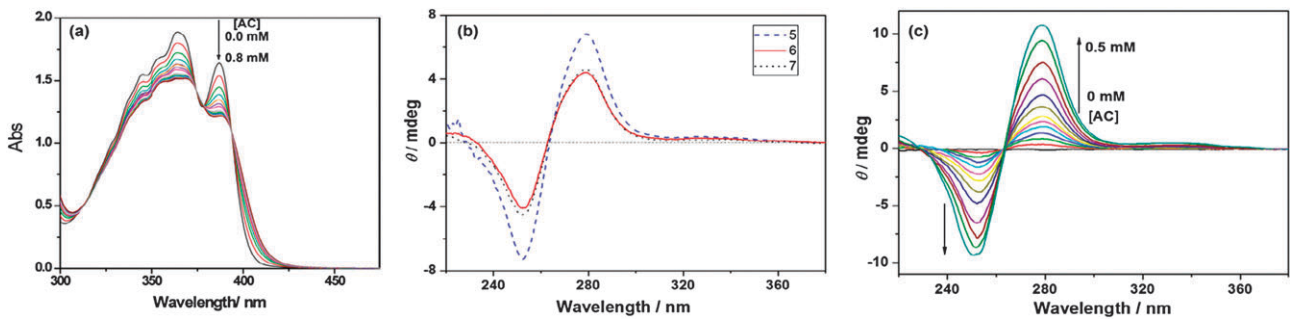

Fig. 1 (a) UV-vis spectral changes upon addition of 0, 0.04, 0.08, 0.12, 0.16, 0.2, 0.24, 0.28, 0.32, 0.36, 0.40, 0.44, 0.48, 0.52, 0.56, 0.60, 0.64, 0.68, 0.72, 0.76 and 0.80 mM **7** to a borate buffer solution of AC (0.2 mM) at 0 °C. (b) Circular dichroism spectra of AC (0.5 mM) in the presence of 1 mM **5** (dashed line), **6** (solid line) and **7** (dotted line) in borate buffer solutions at 25 °C. (c) Circular dichroism spectral changes upon addition of 0, 0.02, 0.05, 0.07, 0.09, 0.11, 0.13, 0.17, 0.20, 0.30, 0.40, 0.47 and 0.50 mM AC to a borate buffer solution of **6** (0.015 mM) at 25 °C measured in a 0.1 cm-path length cell.

Table 1 Association constants for the stepwise 1 : 1 and 1 : 2 complexation of AC with native and modified γ-CDs in borate buffer solution

		Association constant			
Host	Temperature/°C	K_1/M^{-1}	K_2/M^{-1}	$K_1K_2/10^6\ M^{-2}$	K_2/K_1
γ-CD[a]	25	161	38 500	6.2	239
	5	206	201 000	41.4	976
5 (n = 2)[b]	25	185	36 900	6.8	199
	0	321	183 000	58.7	570
6 (n = 3)[c]	25	116	69 700	8.1	601
7 (n = 4)[d]	0	892	26 900	24.0	30
8 (n = 6)[d]	0	337	49 500	16.7	147

[a] Ref. 7. [b] Ref. 8. [c] Determined by circular dichroism spectral titration. [d] Determined by UV-vis spectral titration.

5–8 reveal a couple of interesting features of the AC complexation by the CD hosts with a diamino sidechain. In general, the K_2 value is roughly one-to-two orders of magnitude large than the K_1 value, revealing the high preference of these hosts for ternary complexation. It is also of note that, despite the apparently large variations in both K_1 and K_2 caused by introducing the diamino sidechain and changing the inter-amino distance in **5–8**, the overall association constant K_1K_2 stays in a relatively narrow range of 6–8 × 10^6 M^{-2} at 25 °C and 17–59 × 10^6 M^{-2} at 0–5 °C, indicating the existence of some compensation between K_1 and K_2. In contrast, the preference for 1 : 2 complexation is significantly affected by the sidechain substitution to give the K_2/K_1 ratios ranging from 200–600 at 25 °C and more widely from 30–980 at 0–5 °C. This seems reasonable, since the introduction of a diamino sidechain of different inter-amino distance should critically affect the orientation and conformation of the two AC molecules accommodated in the CD cavity.

Photocyclodimerization studies

Inclusion of two AC molecules in a CD cavity leads to the formation of six stereoisomeric, *i.e.* two enantiomeric and four diastereomeric, complexes which are precursors to achiral photocyclodimers **1** and **4** and enantiomeric **2** and **3**, respectively. The relative abundance of these precursor complexes cannot be determined directly by spectral examinations, but may be estimated from the distribution of the photocyclodimers obtained upon irradiation, since the quantum yield of photodimerization of AC in the presence of native γ-CD is high (0.4)[13] and the exchange equilibrium is too slow to alter the AC orientation in the CD cavity in the ns lifetime of excited AC.

Photodimerization of AC was carried out at wavelengths longer than 320 nm in the presence of hosts **5–8** in an aqueous buffer solution at ambient temperatures and also in a 1 : 1 mixture of aqueous buffer and methanol at lower temperatures. The relative yield and ee of each photodimer were determined by chiral HPLC analysis to give the results listed in Table 2.

Temperature effects

The relative yields of dimers **1–4** obtained upon irradiation in aqueous buffer solutions were insensitive to the host used or the inter-amino distance and also to the temperature, affording essentially the same distribution for hosts **5–8** over the temperature range of 0–35 °C. However, the ee of *syn*-HT dimer **2** was gradually increased by decreasing the temperature to reach the highest values of 36–38%, irrespective of the host used or the inter-amino distance, while the ee of *anti*-HH **3** was kept low (<5% ee) even at 0 °C for all the hosts examined.

In sharp contrast, the product distribution and the ee values became critical functions of the inter-amino distance and the temperature, when a 1 : 1 mixture of aqueous buffer and methanol (BM solvent) was used. In general, the yields of HH dimers **3** and **4** were increased at the expense of HT dimers **1** and in particular **2**. Thus, the HH-oriented complexes, which are precursors to **3** and **4**, are thought to be enthalpically stabilized at low temperatures in BM solution, where the electrostatic interactions between anionic AC and cationic sidechain become more effective than in water due to the lower dielectric constant.

The enantioselectivity of photocyclodimerization also suffered significant influence of the BM solvent to give much lower ee's for **2** but significantly enhanced ee's for **3**. As was the case in aqueous solution, the ee's of both **2** and **3** were highly temperature-dependent. In the case of host **7**, the chiral sense of **2** was inverted by lowering the temperature to give +8% ee at −10 °C but −11% ee at −50 °C. This indicates that the diastereomeric complexes, precursors to **2** and *ent*-**2**, have a relatively large difference in complexation entropy ($\Delta\Delta S^\circ$) that can overwhelm the enthalpic difference ($\Delta\Delta H^\circ$) at higher temperatures, since the relative stability ($\Delta\Delta G^\circ$) is a function of temperature: $\Delta\Delta G^\circ = \Delta\Delta H^\circ - T\Delta\Delta S^\circ$.

Effects of the inter-amino distance on product distribution

As can be seen from Table 2, the product distribution and the ee values obtained with modified CDs **5–8** in aqueous buffer do not appear to significantly differ from each other and even from those reported for native γ-CD.[8] This result clearly indicates that the electrostatic attraction between the dicationic sidechain and anionic AC is not strong enough to affect the orientation of ACs in the CD cavity at least in aqueous solution at ambient temperatures. Thus, the sterically and electrostatically hindered HH dimers **3** and **4** were inherently disfavored to give the small HH/HT ratios of 0.22–0.32 for the *anti* isomers (**3**/**1**) and 0.16–0.20 for the *syn* isomers (**4**/**2**) in aqueous solution at 0–35 °C, irrespective of the host employed. The *syn*/*anti* ratios, *i.e.* **2**/**1** and **4**/**3**, were also kept constant in narrow ranges of 1.02–1.12 and 0.65–0.81, respectively, although the **4**/**3** ratio obtained with **5** showed an appreciable increase at lower temperature. Although the ee of **2** gradually augmented with decreasing temperature to reach the highest values of 36–38% at 0 °C (and the ee of **3** never exceeded −5%), the inter-amino distance (n) did not greatly affect the ee of **2** at each temperature examined. The product distribution and the enantioselectivities obtained in this study are also very close to those obtained with native γ-CD. These results clearly reveal that the diamino sidechain is unable to manipulate the orientation of AC molecules in the CD cavity through the electrostatic interactions, most probably because the two amino groups on the side arm are fully hydrated and protrude into the bulk water.

Table 2 Photocyclodimerization of AC in the presence and absence of native and modified γ-CDs **5–8**

				Relative yield[b] (%)				ee (%)		HH/HT		*syn*/*anti*	
Host	CD/AC	Solvent[a]	Temp./°C	**1**	**2**	**3**	**4**	**2**	**3**	**3**/**1** *anti*	**4**/**2** *syn*	**2**/**1** HT	**4**/**3** HH
γ-CD[c]	0	B	25	42	36	14	8	0	0	0.33	0.22	0.86	0.59
	5	B	25	43	45	7	5	32	−2	0.16	0.11	1.03	0.70
		BM	−50	49	33	11	7	33	−12	0.22 (≡1.0)[e]	0.12 (≡1.0)[e]	0.67 (≡1.0)[e]	0.63 (≡1.0)[e]
5 (n = 2)[d]	5	B	35	41	42	10	7	23	0	0.24	0.17	1.03	0.67
			25	41	43	9	7	27	−5	0.22	0.16	1.05	0.76
			15	40	44	9	7	30	−1	0.23	0.16	1.09	0.80
			0	40	44	9	7	36	0	0.23	0.16	1.12	0.81
		BM	−10	37	30	17	16	8	−4	0.46	0.53	0.80	0.96
			−30	33	24	18	25	12	−8	0.55	1.04	0.71	1.45
			−50	27	14	21	38	5	−15	0.78 (3.5)[e]	2.71 (22.6)[e]	0.52 (0.78)[e]	1.81 (2.9)[e]
6 (n = 3)[d]	5	B	0	40	42	10	8	34	−5	0.25	0.19	1.05	0.71
		BM	−50	30	16	26	28	2	−19	0.87 (4.0)[e]	1.75 (14.6)[e]	0.52 (0.78)[e]	1.11 (1.8)[e]
7 (n = 4)[d]	5	B	35	40	43	10	7	28	−4	0.25	0.16	1.13	0.76
			25	40	43	10	7	33	−3	0.25	0.16	1.11	0.73
			15	39	44	10	7	35	−3	0.26	0.16	1.07	0.72
			0	39	43	10	8	38	−2	0.26	0.19	1.08	0.73
		BM	−10	36	32	16	16	8	−19	0.44	0.50	0.90	0.99
			−30	33	23	20	24	−7	−24	0.61	1.04	0.69	1.22
			−50	36	18	22	24	−11	−32	0.61 (2.8)[e]	1.33 (11.1)[e]	0.50 (0.75)[e]	1.07 (1.7)[e]
8 (n = 6)[d]	5	B	35	38	43	12	7	29	−2	0.32	0.16	1.11	0.65
			25	39	42	11	8	31	−1	0.28	0.19	1.07	0.74
			15	40	42	11	7	36	−2	0.28	0.17	1.04	0.66
			0	40	41	11	8	38	−4	0.28	0.20	1.02	0.66
		BM	−10	37	34	17	12	8	−18	0.46	0.35	0.90	0.74
			−30	37	27	21	15	0	−23	0.57	0.56	0.71	0.71
			−50	41	19	25	15	0	−28	0.61 (2.8)[e]	0.79 (6.6)[e]	0.47 (0.70)[e]	0.57 (0.9)[e]

[a] Solvents B and BM stand for aqueous borate buffer (pH 7) and a 1 : 1 mixture of borate buffer and methanol (w/w), respectively. [b] Determined by chiral HPLC. [c] Ref. 7. [d] Inter-amino distance: n = number of methylenes between the two amino groups on the sidechain. [e] Enhancement relative to the value obtained with native γ-CD in BM at −50 °C.

We therefore reduced the solvent polarity by adding methanol to the borate buffer and the temperature down to −50 °C, where we can expect stronger electrostatic interactions and more critical manipulation of the stereochemical outcomes by changing the inter-amino distance of the sidechain. Indeed, the product distribution and the ee of **2** and **3** were critically controlled by the inter-amino distance (n) in a 1 : 1 mixture of aqueous buffer and methanol (BM solvent), as shown in Table 2.

The use of BM solvent dramatically enhanced the formation of HH dimers **3** and **4** in particular at low temperatures when **5–8** were used as hosts, which may be contrasted with the modest increases observed for native γ-CD under the comparable conditions (BM solvent at −50 °C). A closer look at the product distribution as a function of the inter-amino distance (n) disclosed interesting tendencies that cannot be revealed from the simple examination of the overall HH/HT ratio. Thus, the individual HH/HT ratios for *anti* and *syn* isomers, *i.e.* **3**/**1** and **4**/**2**, turned out to behave quite differently from each other as a function of n. As can be seen from the **3**/**1** and **4**/**2** ratios obtained with hosts **5–8** at −50 °C (Table 2), the HH/HT ratio of *anti* dimers (**3**/**1**) was kept in a narrow range of 0.61–0.87, whilst the HH/HT ratio of *syn* dimers (**4**/**2**) amounted to 2.71 for **5** (n = 2), and rapidly decreased to 1.75 for **6** (n = 3) and 1.33 for **7** (n = 4) and then to 0.79 for **8** (n = 6). Very similar trends were observed in the *syn*/*anti* ratios for HT and HH dimers, *i.e.* **2**/**1** and **4**/**3**, former of which stayed constant at 0.47–0.52, while the latter ratio gradually decreased from 1.81 at n = 2 to 1.11, 1.07, and then to 0.57 by increasing n from 2 to 6.

The overall effects of the diamino sidechain, BM solvent and low temperature on the photocyclodimerization may be better highlighted by comparing each of the HH/HT and *syn*/*anti* ratios obtained with hosts **5–8** in BM solvent at −50 °C with the corresponding value obtained with native γ-CD in aqueous buffer at 25 °C. As can be seen from the "degree of enhancement" values (relative to the corresponding value for native γ-CD in BM solvent at −50 °C) shown in the parentheses in Table 2, the introduction of diamino sidechain enhances the HH/HT ratio of *anti* dimer (**3**/**1**) by a factor of 2.8–4.0, which is however not sensitive to n. Interestingly, the degree of enhancement is much larger for the HH/HT ratio of *syn* dimer (**4**/**2**) and more critically depends on n, affording the largest value of 22.6 for **5** (n = 2) and gradually decreasing values of 14.6, 11.1 and 6.6 for **6** (n = 3), **7** (n = 4) and **8** (n = 6), respectively. This indicates that the HH/HT ratio is better controlled by the diamino sidechain in *syn*, rather than *anti*, dimers.

The *syn*/*anti* ratios showed more complicated behavior when a diamino sidechain of varying n was introduced. The

syn/*anti* ratio of HT dimer (**2**/**1**) was kept almost constant over the *n* used, while the *syn*/*anti* ratio of HH dimer (**4**/**3**) was enhanced by a factor of 1.7–2.9 at least for CDs with a shorter sidechain of up to $n = 4$, but then becomes smaller than that for native CD at $n = 6$.

These results demonstrate that the two amino groups introduced to the sidechain attract and hold anionic AC molecules to facilitate the formation of *syn*- and HH-oriented 1 : 2 complexes with γ-CD, and also that the inter-amino distance *n* can critically control the HH/HT and *syn*/*anti* ratios through the electrostatic interactions in less polar solvents. The influence from steric interaction between sidechain and ACs seems nonsignificant as the ROESY spectrum of D_2O solution containing **7** and AC shows no cross peak between protons of the 1,4-butyldiamine chain and AC. In the extreme case of $n = 2$, the product selectivity is switched from HT to HH and more modestly from *anti* to *syn*, eventually affording the sterically most hindered *syn*-HH dimer **4** as the major product (38% yield) among the four stereoisomers.

Effects of the inter-amino distance on enantioselectivity

The enantioselectivities of chiral dimers **2** and **3** are more difficult to control in general and often unpredictable. As readily recognized from the data shown in Table 2, the ee values obtained with the modified γ-CDs in aqueous buffer are essentially the same as those obtained with native γ-CD, indicating that the diamino sidechain does not influence the AC complexation at least in water. However, the use of aqueous buffer–methanol (BM) solvent led to dramatic changes in ee in particular at low temperatures. The ee of **2** was significantly decreased by introducing the diamino sidechain, as was the case with dimethylaminoethylamino-γ-CD which also gave **2** in ee less than 5%.[8] This does not mean that the diamino sidechain cannot affect the enantioface selectivity upon formation of a pair of diastereomeric 1 : 2 complexes precursor to enantiomeric dimer **2**, but rather indicates that the sidechain facilitates the 1 : 2 complexation in the epimeric manner to enhance the formation of antipodal (negatively signed) dimer **2**. In this regard, host **7** ($n = 4$) is most effective in *reducing* the ee of **2** or even *inverting* the chiral sense of photoproduct. Nevertheless, it is true that the enantioface of the first-included AC molecule is not effectively recognized by the second-penetrating AC molecule in the chiral CD cavity. This would be rationalized by assuming that the first AC molecule interacts almost equally with each of the two amino groups on the sidechain, leaving the corresponding diastereotopic open space for accommodating a second AC in HT fashion.

In sharp contrast, the enantioselectivity of *anti*-HH dimer **3** was greatly enhanced in general by using the less polar BM solvent to give moderate-to-good ee's of up to −32% at −50 °C. It is to note that the ee's obtained at −50 °C should be taken as the "minimum" values and could be higher, since we were unable to determine the association constants in BM solvent at lower temperatures due to some technical reasons (*e.g.*, fogging and deformation of the cryostat windows) and hence we are not fully sure if all of the added ACs are included in the CD cavity even at the low temperatures. However, it is also true that, without tight complexation of AC, such dramatic enhancement of the HH/HT and *syn*/*anti* ratios as well as the ee (from almost zero to 32%) cannot be achieved. Interestingly, the degree of enhancement was significantly larger for hosts **7** and **8** than for hosts **5** and **6**. The ee of **3** was a critical function of the inter-amino distance *n*, showing a sudden leap from −15% or −19% ee at $n = 2$–3 to −32% at $n = 4$ followed by a slight decrease to −28% at $n = 6$ (Table 2). It is interesting that the effect of the inter-amino distance maximizes at $n = 4$ for both of the chiral dimers **2** and **3**. Such similar ee profiles observed for **2** and **3** suggest that the 1 : 2 complexes precursor to *syn*-HT and *anti*-HH dimers share a common 1 : 1 complex.

Conclusion

In this study, we have examined the influence of the inter-amino distance on the supramolecular enantiodifferentiating [4 + 4] photocyclodimerization of AC mediated by ω-amino-alkylamino-γ-CDs **5–8** to reveal that the effect is almost negligible in water but becomes substantial in a less polar water–methanol mixture at low temperatures to afford distinctly different product distribution and enantiomeric excess. Thus, both of the HH/HT and *syn*/*anti* ratios and the ee values of **2** and **3** are critically manipulated by the diamino sidechain of varying inter-amino distance through the electrostatic interaction to overcome the steric hindrance and the electrostatic repulsion experienced by two AC molecules accommodated in a single γ-CD cavity. Although the highest enantioselectivities obtained in this study are not very impressive (−11% ee for **2** and −32% ee for **3**), the present strategy to control the stereochemical outcomes by adjusting the inter-amino distance may be combined with the *N*-alkylation technique for increasing the local hydrophobicity to eventually enhance the diastereoselectivity upon complexation and the enantioselectivity of photocyclodimerization product.

Experimental

General

γ-Cyclodextrin was purchased from Junsei, 2-anthracenecarboxylic acid from TCI and the other chemicals from Wako. All chemicals were used as received. 6-*O*-Tosyl-γ-cyclodextrin was prepared as described in a previous paper.[14]

^{1}H NMR spectra were recorded on a JEOL 400 MHz NMR spectrometer in D_2O at 20 °C. High-resolution mass spectra were recorded on an IonSpec QFT-ESI MS spectrometer. UV-vis spectra were measured in a quartz cell (10 mm) on a JASCO V-550 or V-560 spectrometer. CD spectra were recorded on a JASCO J-820 spectropolarimeter in a quartz cell (1 or 10 mm).

Binding studies

The association constants were determined by fitting the observed changes observed upon UV-vis and CD spectral titration of an AC solution with modified CD to a theoretical model, assuming the stepwise 1 : 2 complexation model, as

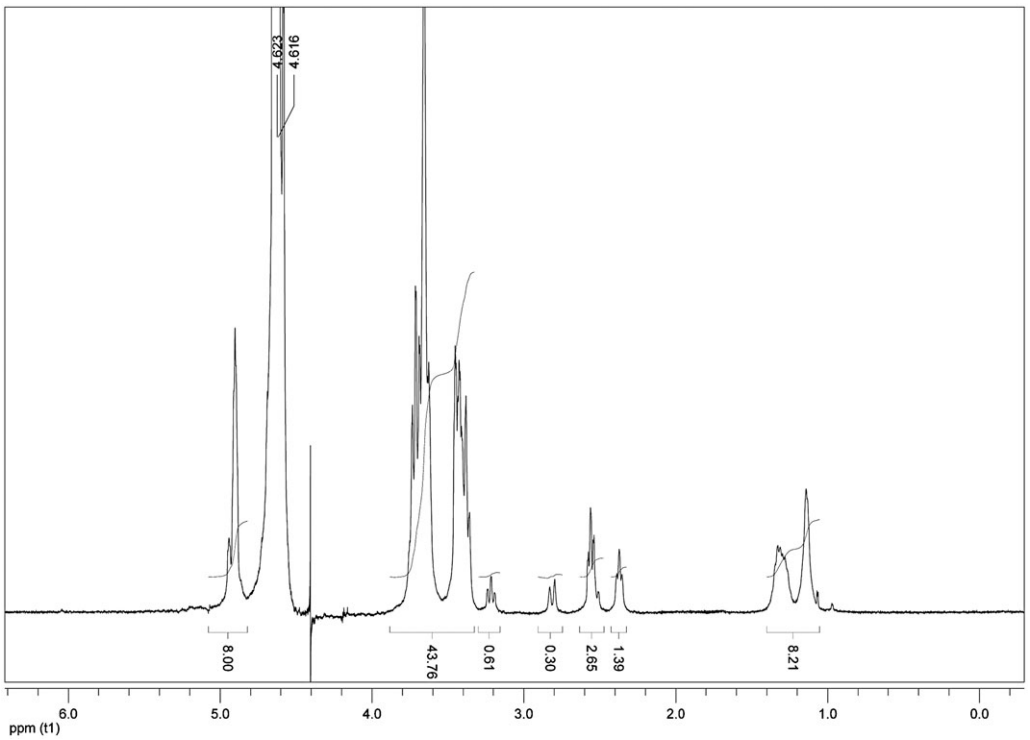

Fig. 2 400 MHz ^{1}H NMR spectrum of host **8** in D_2O.

described in our previous paper.[14] The titrations were conducted in a Unisoku cryostat installed in the spectrometer.

Photolysis

Photoirradiation was carried out at a given temperature in a Unisoku cryostat. Sample solution was charged in a quartz cell (10 mm), degassed with Ar bubbling, and then irradiated at 366 nm using an ultra high-pressure mercury lamp fitted with a glass filter (Toshiba UV-35). HPLC analysis was performed under the same conditions described in our previous studies.[14]

Syntheses of 6, 7 and 8

Hosts **6** and **7** were prepared by the reported procedures.[15] Host **8** was prepared by a similar method. In a round-bottom flask, 6-*p*-tosyl-γ-CD (300 mg) was dissolved in 1,6-diaminohexane (5 mL) under Ar atmosphere. The mixture was heated to 80 °C for 12 h, and the resulting solution was added dropwise to acetone (100 mL) with stirring to give a precipitate. The white precipitate was collected by centrifuging, dissolved in water and then freeze-dried to obtain the final product as a white powder.

8: HR-MS (ESI): *m*/*z* found: 1395.5515 [M + H], calcd: 1395.5507. ^{1}H NMR (400 MHz, D_2O): δ 4.96 (m, 8H), 3.76–3.37 (m, 44H), 3.23 (t, 1H, J = 6.4), 2.81 (d, 1H, J = 12.8), 2.56–2.54 (m, 4H), 2.37 (t, 2H, J = 7.2), 1.33–1.13 (m, 8H) (Fig. 2).

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