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Supramolecular complexation and photocyclodimerization of methyl 3-methoxy-2-naphthoate with modified γ-cyclodextrins*

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Abstract: A series of modified γ-cyclodextrins (CDs) were prepared as chiral host for catalyzing the enantiodifferentiating photocyclodimerization of methyl 3-methoxy-2-naphthoate (NA). The complexation behavior of NA with modified γ-CDs was studied by UV–vis, fluorescence, and circular dichroism spectroscopies. All of the modified γ-CDs formed stable 1:2 host–guest complex with NA, and binding affinities for two-step complexation critically depended on the structure of modified γ-CDs. The enantioselectivity of NA photocyclodimerization was also significantly affected by the modification of γ-CD. The secondary rim-modification considerably reduced the enantioselectivity, for which the interrupted hydrogen-bonding network, leading to a flexible CD skeleton, is most probably responsible.

Keywords: methyl 3-methoxy-2-naphthoate; modified γ-cyclodextrins; photocyclodimerization; supramolecular photochirogenesis.

INTRODUCTION

Photochirogenesis, or photochemical asymmetric synthesis, is an attractive alternative to the thermochemical (catalytic and enzymatic) counterpart, but is still a challenging topic for chemists due to the inherently short-lived, weak excited-state interactions and also the lack of knowledge and methodologies for its critical manipulation [1–5]. However, recent studies revealed that the supramolecular approach enables us to more critically control the photochirogenic process and significantly improve the stereochemical outcomes through noncovalent chiral interactions in both ground and excited states [2–5]. We thus applied the supramolecular approach to the enantiodifferentiating photocyclodimerization of methyl 3-methoxy-2-naphthoate (NA) [6–8]. As shown in Scheme 1, the photocyclodimerization of NA is a two-step (two-photon) process, composed of the first intermolecular

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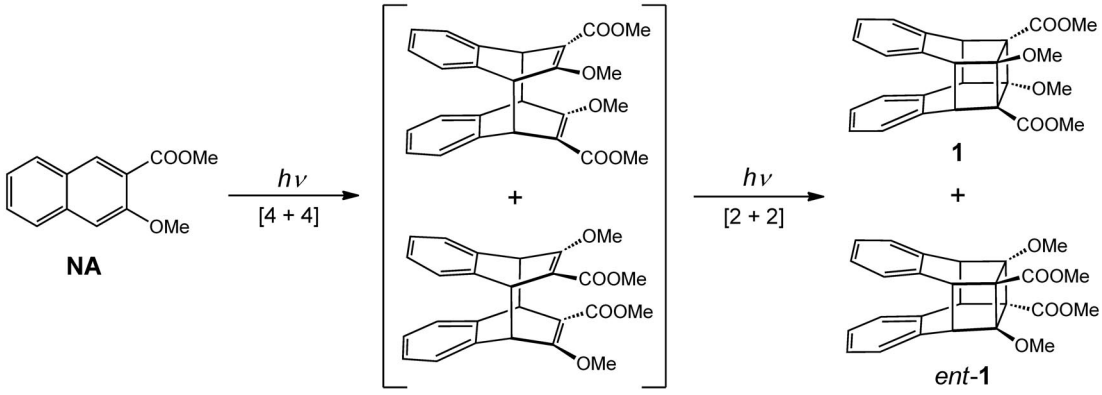
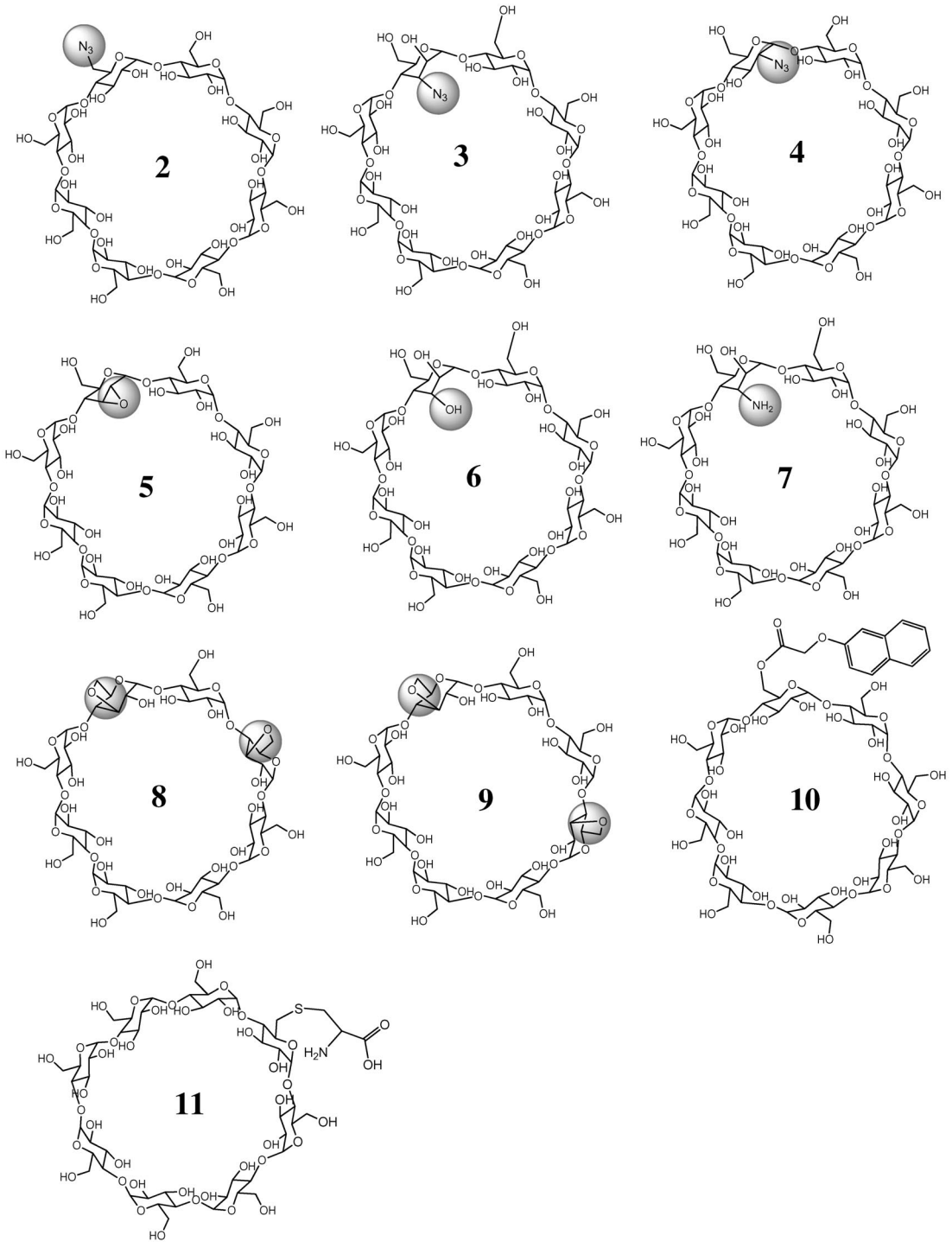


Scheme 1 Stepwise [4 + 4] and [2 + 2] photocyclodimerization of NA to enantiomeric cubane-like compound **1**.

[4 + 4] photocyclodimerization in anti-head-to-head fashion and the subsequent intramolecular [2 + 2] photocyclodimerization of the [4 + 4] cyclodimer to give chiral cubane-like cyclodimer **1** upon absorption of a second photon. Although NA is photochemically almost inert in aqueous solution, the photocyclodimerization is significantly facilitated upon 1:2 host–guest complexation with native γ-cyclodextrin (CD) in aqueous solution. The enhanced local concentration and favorable face-to-face conformation of two NA molecules encapsulated in a CD cavity are jointly responsible for the dramatically enhanced photoreactivity. Thus, cyclodimer **1** was obtained as a sole photoproduct in up to 48 % enantiomeric excess (ee) upon irradiation of NA with native γ-CD in aqueous solution at 0.5 °C, indicating that γ-CD is an excellent chiral host for this photochirogenic system.

The good enantioselectivity obtained with native γ-CD promoted us to expand the range of chiral host to modified γ-CDs and examine the effects of structural modification on both complexation and photocyclodimerization behavior of NA as well as the correlation of their affinity to NA with the ee of photoproduct **1**. In our previous studies, we demonstrated that the supramolecular photochirogenesis is a critical function of the host structure and even an apparently small alteration in host structure can cause dramatic changes in guest affinity and product selectivity [9–14]. In this study, we chose a series of modified γ-CDs **2–11**, shown in Scheme 2 to elucidate the effect of modification on the supramolecular complexation and photochirogenesis. A similar strategy was successful in the photocyclodimerization of anthracenecarboxylic acid [14–21].



Scheme 2 Modified γ-CDs used for mediating photocyclodimerization of NA. The modified part(s) are highlighted with shaded circle.

EXPERIMENTAL

γ-CD and NA were purchased from Tokyo Chemistry Industry Co., and used without further purification. Modified γ-CDs **2–11** were synthesized according to the procedures reported previously [20–22]. UV–vis spectra were recorded on a JASCO V-560 spectrometer, and circular dichroism spectra on a JASCO J-820YH spectropolarimeter. Fluorescence spectra were measured with a JASCO FP-6500 spectrofluorimeter.

An aqueous solution containing NA (0.9 mM) and modified γ-CD (0.15 mM) was sealed in a Pyrex tube under an argon atmosphere and then irradiated at 0.5 °C or at room temperature (only for host **5**) for 3 h at $\lambda > 280$ nm with a 500 W high-pressure mercury lamp. The irradiated solution was extracted with dichloromethane and the extract was subjected to high-performance liquid chromatography (HPLC) analysis on a Daicel OJ-H column with an *n*-hexane/2-propanol eluent [7,8].

RESULTS AND DISCUSSIONS

Guest NA has no specific functional group to actively interact with host CDs, and therefore the van der Waals, hydrophobic, and dipole–dipole interactions are expected to play dominant roles upon complexation with γ-CD hosts. This is significantly different from the anthracenecarboxylate case, where the use of electrostatic interaction through cationic modification is the key principle in designing modified γ-CDs [16,18,21]. In the present supramolecular photochirogenesis system, more crucial is to optimize the size and shape of CD cavity for better chiral stacking of NAs in the cavity. Hence, we prepared a series of modified γ-CDs **2–11**, which possess a substituent of varying size at 2-, 3- or 6-position (**2–4**, **6**, **7**, **10**, **11**), an altrose unit (**3**, **6**, **7**), and/or dehydrated ether unit(s) (**5**, **8**, **9**). Most of the prepared hosts, excepting **2**, **10**, and **11**, are modified at the secondary rim, which is known to be more effective in affecting the size/shape/flexibility of CD cavity due to the disrupted hydrogen-bonding network and the inverted configuration. For **2**, **10**, and **11**, modified at the primary rim, no such dramatic change is induced upon modification and therefore the original skeleton will not be greatly changed.

Native γ-CD forms a 1:2 host–guest complex with NA as proven by the Job plot showing the largest intensity change at a mole fraction of 0.33 [7]. This seems reasonable, since the large γ-CD cavity is capable of accommodating two aromatic guest molecules of suitable size. In the present study, UV–vis, fluorescence, and circular dichroism spectroscopic investigations were carried out to confirm the 1:2 complexation and also to elucidate the effects of modification on the complexation behavior of γ-CDs with NA.

UV–vis spectral study

Complexation of NA with **2–11** was qualitatively confirmed by the appreciable intensity change and peak shift observed in the UV–vis spectrum upon addition of modified γ-CD to NA. As exemplified in Fig. 1a, the addition of **4** to an aqueous solution of NA led to a gradual decrease of the absorbance of NA at 347 and 281 nm with accompanying slight bathochromic shift and band-broadening of the 281 nm peak. The Job plot at the total concentration of 0.3 mM gave a peak at the host fraction of 0.33, indicating the 1:2 stoichiometry. The red shift and band-broadening may be attributable to the stacking of NAs in the CD cavity. It is noteworthy, however, that the UV–vis spectral changes upon complexation are host-dependent, and much smaller changes were observed for hosts **8** (Fig. 1b) and **9**, indicating different binding affinity and cavity environment despite the common 1:2 stoichiometry.

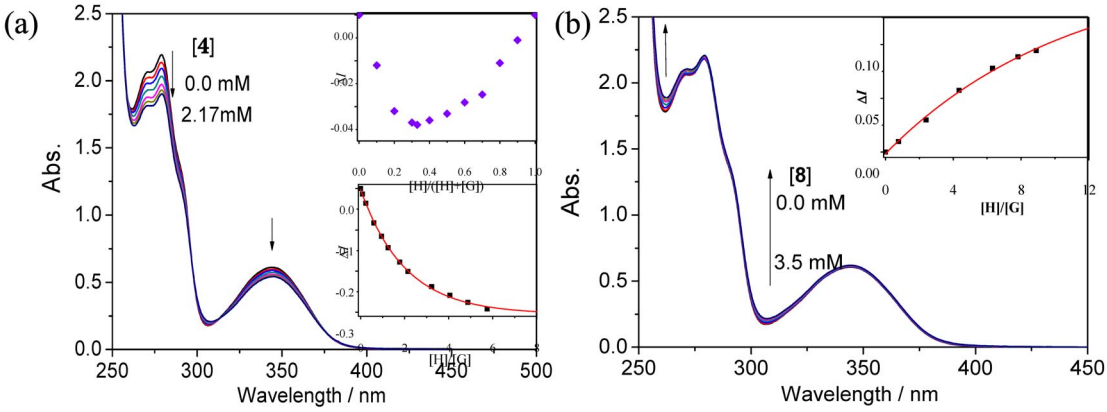


Fig. 1 UV–vis spectra of an aqueous solution of NA (0.4 mM) at 20 °C measured in a 1 mm cell upon addition of (a) **4** (0, 0.3, 0.6, 1.0, 1.5, 1.8, and 2.2 mM); Upper inset: A Job plot of the absorbance changes at 279 nm for complexation of NA with **4**; [NA] + [**4**] = 0.3 mM (fixed). Lower inset: Absorbance changes at 279 nm upon complexation of NA with **4** and a fitting curve assuming the stepwise 1:1 and 1:2 complexation. (b) **8** (0, 0.4, 1.0, 1.8, 2.6, 3.2, and 3.7 mM); Inset: Absorbance changes at 262 nm upon complexation and a fitting curve assuming the stepwise 1:1 and 1:2 complexation.

Circular dichroism spectral study

Circular dichroism spectra provided more direct evidence for the complexation of NA with modified γ-CD. Positive Cotton effect was induced to the ^1B_b band of NA (Fig. 2a) upon addition of **2**, overriding the original weak negative circular dichroism of **2**. According to the sector rule proposed by Kajtar et al. [23], the positive Cotton effect observed for the ^1B_b band of NA indicates longitudinal penetration of the naphthalene moiety into the γ-CD cavity. This seems reasonable as the length of NA (>8.7 Å) [24] is larger than the cavity diameter of γ-CD (7.5–8.3 Å) [25]. However, no clear exciton couplet was seen even at the highest concentration of NA (0.75 mM) employed. This is an unexpected result and needs some interpretation in view of the fact that a strong couplet is produced upon 1:2 complexation of anthracenecarboxylate with modified γ-CDs [21]. There are three cases that may lead to such a weak, monosignate circular dichroism signal for NA in γ-CD cavity: (1) only 1:1 complex is formed; (2) the

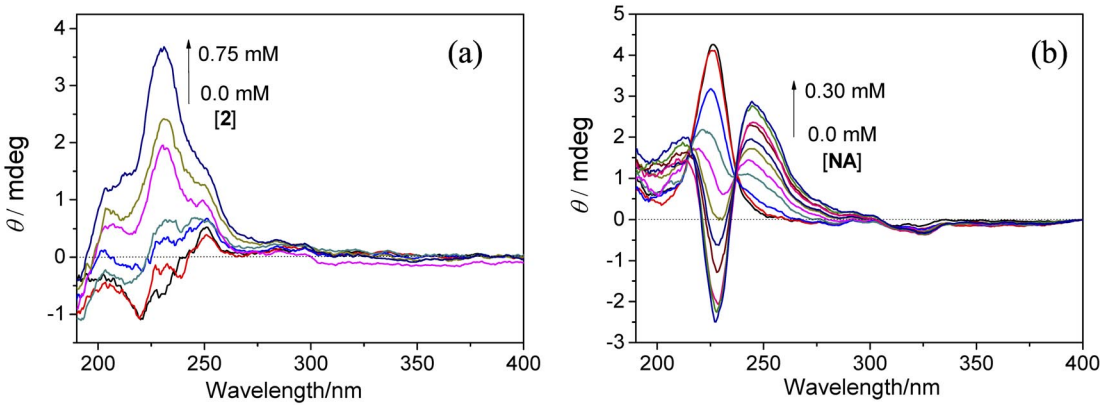


Fig. 2 Circular dichroism spectra of (a) an aqueous solution of NA (0.4 mM) upon addition of **2** (0, 0.025, 0.05, 0.125, 0.25, 0.5, and 0.75 mM) and (b) an aqueous solution of **10** (0.15 mM) upon addition of NA (0.009, 0.036, 0.08, 0.11, 0.15, 0.18, 0.22, 0.25, 0.27, and 0.30 mM) measured in a 1 mm cell.

diastereomeric pair of 1:2 complexes, precursor to the enantiomeric photocyclodimers, are "racemic" to each other to cancel the mirror-imaged couplets; and (3) the transition moments of two NAs in the cavity are oriented in an angle very close to parallel. The first one is unlikely, as judged from the high affinities in the order of 10^6 M^{-2} (see below), which are comparable to those for anthracenecarboxylate; indeed, simple calculations using the binding constants shown in Table 1 (below) indicate that 13–45 % of NA in the solution form 1:2 complex under the employed condition. The second possibility is not immediately ruled out but less probable, if we consider the formation of nonracemic **1** obtained upon photocyclodimerization via this precursor complex. The third mechanism is theoretically possible, as the magnitude of exciton couplet approaches to zero when the two coupling transitions become parallel [26,27]. In the present case, the transition moment of NA is likely to bisect the long molecular axis and the two transitions may be nearly parallel to each other in 1:2 NA–γ-CD complex.

Table 1 Stepwise 1:1 and 1:2 association constants (K_1 and K_2) of NA with native and modified γ-CDs **2–11**[a].

Hosts	K_1/M^{-1}	K_2/M^{-1}	$K_1K_2/10^6$ M^{-2}	Population[c]/%		
				Free NA	NA@γ-CD	NA_2@γ-CD
γ-CD[b]	280	24000	6.7	49.7	5.1	45.2
2	220	27000	5.9	51.6	4.3	44.1
3	210	12000	2.5	61.1	5.9	33.0
4	240	18000	4.3	54.8	5.4	39.8
5	320	21000	6.7	49.3	5.8	44.9
6	220	14000	3.1	58.8	5.7	35.5
7	190	15000	2.9	60.0	5.1	34.8
8	150	3000	0.45	79.3	7.3	13.4
9	180	2400	0.43	78.6	8.7	12.8
10	1680	5200	8.7	38.2	22.1	39.6
11	230	19000	4.4	54.8	5.2	40.1

[a]Determined by UV–vis spectral titrations at 20 °C and the subsequent nonlinear least squares fits of the titration data to the stepwise formation of 1:1 and 1:2 complexation model.
[b]Ref. [7].
[c]Calculated for a solution of $[NA]_{total}$ = 0.4 mM, $[\gamma\text{-CD}]_{total}$ = 0.75 mM.

In contrast, a typical exciton couplet was induced upon addition of host **10** to an aqueous solution of NA. As illustrated in Fig. 2b, host **10**, possessing a naphthalene chromophore tethered to the primary rim of γ-CD, displays a positive Cotton effect in the absence of a guest, as a result of the self-inclusion of the naphthalene chromophore in its own cavity. Upon gradual addition of NA, the original positive Cotton effect peak was gradually replaced by a positive exciton couplet signal. Since the other modified γ-CDs exhibit no exciton coupling, this couplet observed upon complexation of NA with **10** is assigned to the coupling between the naphthalene chromophore in **10** and NA included in its cavity. The covalently attached naphthalene and included NA are deduced to be in a *P*-helical arrangement on the basis of the exciton chirality theory [26,27].

Fluorescence spectral study

Fluorescence titration experiments were performed at sub-μM and sub-mM concentrations in order to individually investigate the fluorescence spectral behavior of 1:1 and 1:2 complexes of NA with modified γ-CDs. As shown in Fig. 3a, a 0.4 μM aqueous solution of NA showed a broad emission at 429 nm, intensity of which was gradually increased upon addition of **2** to reach a plateau at host concentrations higher than 16 μM. In the presence of a 40- to 600-fold excess amount of host **2**, NA at 0.4 μM almost exclusively forms 1:1 complex to afford stronger fluorescence as a result of the environmental change

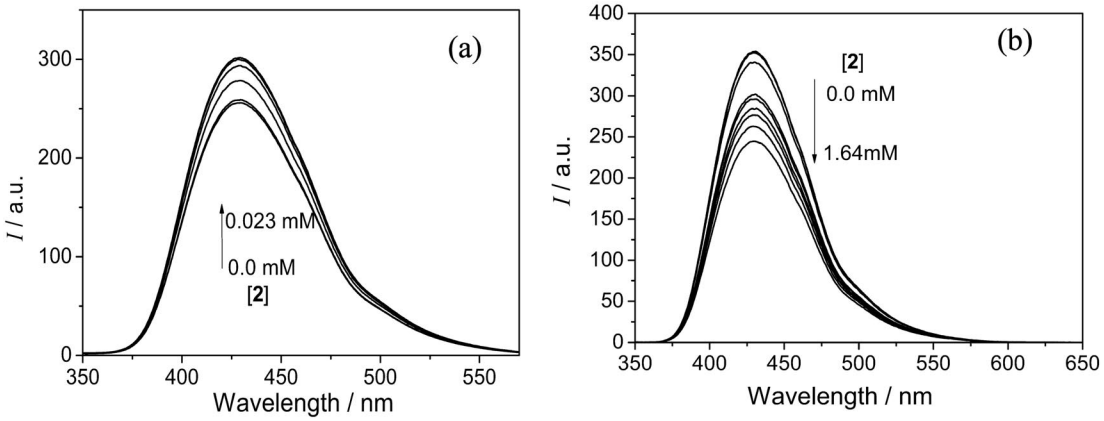


Fig. 3 Fluorescence spectra of (a) 0.4 μM NA upon addition of **2** (0, 0.66, 2.2, 9.9, 16, and 230 μM) and of 0.4 mM NA upon addition of **2** (0, 0.001, 0.01, 0.15, 0.2, 0.45, 0.81, 1.23, and 1.64 mM).

around NA from water to less polar CD cavity and the protection by CD walls from the collisional deactivation by solvent molecules. Similar fluorescence enhancement was observed for most of the other hosts, except for cysteine-modified γ-CD **11**. Addition of host **11** to the dilute NA solution led to fluorescence quenching, for which the electron transfer from the amino group in **11** to excited NA would be responsible.

Interestingly, the fluorescence behavior turned out to be concentration-dependent due to the switching of the major complex species from 1:1 to 1:2 at high NA concentrations. Thus, in the experiment using a 0.4 mM NA solution, the fluorescence intensity of NA was diminished upon addition of host **2** (0–1.64 mM), as shown in Fig. 3b. This is likely to be caused by the facilitated photocyclodimerization of NAs in the 1:2 complex, as was the case with the photocyclodimerization of 2-anthracenecarboxylate in the presence of γ-CDs [15].

Binding affinity

The stepwise association constants (K_1 and K_2) for the 1:1 and 1:2 complexation of NA with modified γ-CDs were determined by analyzing the UV–vis titration data with the nonlinear square means method. As shown in Table 1, K_2 is consistently much larger than K_1 for all the γ-CD hosts examined, indicating the positive cooperation upon inclusion of a second NA. This behavior and the association constants are very similar to those observed for the anthracenecarboxylate complexation with γ-CD [15], and we suspect that NA and anthracenecarboxylate share the same complexation mechanism that the aromatic guest is insufficient in size to fill the γ-CD cavity to give a low K_1, but achieves close van der Waals contacts with CD walls and π–π stacking interactions upon 1:2 complexation with γ-CD to give a much larger K_2.

As can be seen from Table 1, the simple substitution at the primary or secondary rim of γ-CD did not greatly affect the overall binding affinity to NA, keeping the K_1 value in the order of 10^2 M^{-1} and K_2 in the order of 10^4 M^{-1}. Obvious deviations are found for dianhydro-γ-CDs **8** and **9** and naphthalene-appended γ-CD **10**, former two of which afford reduced K_2 in the order of 10^3 M^{-1} and the latter gave a significantly enhanced K_1 and much reduced K_2, while keeping the overall affinity in the order of 10^6 M^{-2}. The smaller K_2 for **8** and **9** seem reasonable, since the 3,6-anhydration destroys the original $^4C_1$ chair conformation of glucose as well as the hydrogen-bonding network at the second rim [28,29] to give a highly flexible distorted and shrunken cavity that is less suitable for inclusion of a second NA molecule. Hosts **3**, **6**, and **7**, possessing an altrose unit in $^1C_4$ chair conformation [30], also show an

appreciable decrease in K_2. However, the other conventional substituting modifications do not appear to affect the K_1 or K_2 value. In this connection, the much enhanced K_1 and reduced K_2 value for **10** may need further explanation. As demonstrated above in the circular dichroism spectral examination, the naphthyl substituent of **10** is included in its own cavity in the absence of guest, which facilitates the co-inclusion of the first NA guest to give a 6-fold larger K_1 than that for native γ-CD, but interferes further inclusion of NA to afford a 5-fold smaller K_2.

Photochemical reaction

Photoirradiation of an aqueous solution of NA (0.9 mM) was carried out at $\lambda > 280$ nm in the presence of modified γ-CD (0.15 mM) with a 500 W high-pressure mercury lamp. The irradiated sample solution was subjected to chiral HPLC analysis for ee of cyclodimer **1**. As shown in Table 2, modified γ-CDs **2–11** afforded **1** in moderate ee's, ranging from 6 to 39 %, which are more or less smaller than that (48 %) obtained for native γ-CD under comparable conditions.

Table 2 Enantiomeric excesses obtained in the photocyclodimerization of NA mediated by native and modified γ-CDs **2–11**[a].

host	γ-CD[b]	**2**	**3**	**4**	**5**[c]	**6**	**7**	**8**	**9**	**10**	**11**
% ee	48	33	20	9	20	27	29	17	6	29	39

[a]Aqueous solution of NA (0.9 mM) and γ-CD host (0.15 mM) was irradiated at $\lambda > 280$ nm and at 0.5°C, unless noted otherwise.
[b]Ref. [7].
[c]Irradiated at room temperature.

In this supramolecular photochirogenic system, the chiral anti-head-to-head arrangement is induced to a pair of NAs upon enantioface-differentiating stacking complexation in γ-CD cavity, and the diastereomeric excess (de) attained upon complexation is directly conveyed to the product's ee through the subsequent photocyclodimerization, or somewhat biased if the photocyclization of diastereomeric precursor complexes occurs at different efficiencies. In the present case, the energetically more favored, thus nicely stacked, diastereomeric complex is likely to photocyclodimerize more efficiently (at a faster rate) than the epimeric counterpart, achieving a synergetic enhancement of the original de in the subsequent photoreaction. Hence, the size/shape matching of host and guest as well as the host flexibility should play major roles in determining both the complexation de and product's ee. Indeed, the ee value was a critical function of the chemical structure of γ-CD host. In general, conformationally flexible secondary rim-modified CDs **3–9** gave smaller ee's (9–29 %) than primary rim-modified **2**, **10**, and **11** (29–39 % ee). In particular, the lowest 6–17 % ee's were obtained with highly flexible dianhydro-CDs **8** and **9**. We may deduce therefore that the increased skeletal flexibility, which often leads to a loss of the persistent cavity size and shape as well as the binding specificity, is primarily responsible for the lower ee's obtained with modified γ-CDs.

An obvious advantage of this supramolecular photochirogenic system is the photochemical inertness of NA in bulk solution, which totally eliminates the possible "contamination" by the racemic product arising from the photoreaction outside the cavity. This means that the binding affinity, normally a major factor in supramolecular photochirogenesis, is indispensable for the photocyclodimerization but is not related to the product's ee, as proven by the fact that host **8**, possessing an affinity comparable to **9**, gives a much higher ee of 20 %, while host **4**, possessing a much higher affinity than **8**, affords only a low 9 % ee.

Hosts **3**, **6**, and **7** share a common skeleton, in which one of the glucose units is replaced by altrose, but differ in the substituent at the 3-position of the altrose. However, host **3** with 3-azido

substituent afforded noticeably lower ee (20 %) than **6** (27 %) and **7** (29 %), suggesting that a minor structural alteration can lead to a large difference in enantioselectivity. This is not limited to the conformationally flexible mono-altrosized CDs. The same conclusion may be drawn for conformationally more robust all-glucose CDs, as the 6-azido substitution caused a significant decrease of ee from 48 % for native γ-CD to 33 % for **2**.

CONCLUSION

In this study to elucidate the supramolecular complexation and photochirogenesis behavior of NA with a series of rim- and skeleton-modified γ-CDs, we revealed: (1) all of these modified γ-CDs form stable 1:2 host–guest complexes with NA; (2) the binding affinity is less sensitive to simple rim substitution, preserving the original affinity of native γ-CD; (3) the naphthyl substituent introduced to the primary rim of CD, being originally included in its own cavity, facilitates the inclusion of first NA but discourages the second NA inclusion; (4) the skeleton modification, leading to flexible conformation and distorted cavity, lowers in particular the binding of second NA.

Despite the various modifications applied to γ-CD, the original intention to enhance the enantioselectivity of NA photocyclodimerization was not successful, but we have learned a couple of crucial lessons from the present study: (1) the flexible skeleton and distorted cavity are not particularly useful but rather disadvantageous in enhancing the diastereoselectivity upon 1:2 complexation; (2) the rational design of host suitable for the enantiodifferentiating photocyclodimerization of NA is more challenging than that for anthracenecarboxylate, due to the lack of noncovalently controllable functional group in the guest. However, a unique feature of NA as guest substrate is its photochemical inertness in the absence of host, which enables us to quantitatively determine the thermodynamic and activation parameters inherent to the supramolecular photochirogenic process and to more directly evaluate the effects of rim and skeletal modifications applied to γ-CD host. Our future task is to develop methodologies for manipulating the supramolecular photochirogenesis of guest substrate lacking a handle for noncovalent control through more precise and extensive examinations.

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