Supramolecular enantiodifferentiating photoisomerization of (*Z*,*Z*)-1,3-cyclooctadiene included and sensitized by naphthalene-modified cyclodextrins†

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Received (in Durham, UK) 23rd October 2006, Accepted 9th January 2007
First published as an Advance Article on the web 5th February 2007
DOI: 10.1039/b615353d

Three naphthalene-modified cyclodextrins (CDs) **3–5** were synthesized as supramolecular chiral photosensitizing hosts for enantiodifferentiating photoisomerization of (*Z*,*Z*)-1,3-cyclooctadiene (**1ZZ**) to its *E*,*Z*-isomer (**1EZ**). In aqueous methanolic solutions, β-CD-based sensitizer **4** binds **1ZZ** in its chiral cavity much more strongly than α- and γ-CD homologues **3** and **5**. Accelerated, often static, fluorescence quenching of these naphthalene-modified CDs was observed upon inclusion of **1ZZ**. The photoisomerization of **1ZZ** mediated by **3–5** yielded enantiomeric **1EZ** in modest yields. The enantiomeric excesses (*ee*'s) obtained with α- and β-CD-based sensitizers **3** and **4**, both of which have relatively small cavities, are less sensitive to temperature, demonstrating the low-entropy nature of the α- and β-CD complexes. In contrast, increasing reaction temperature significantly diminished the product's *ee* and even caused a switching of enantioselectivity upon photoisomerization sensitized by γ-CD-based **5**, revealing that the entropy factor plays a crucial role in the wide cavity of γ-CD.

Introduction

Chirality control of photoreactions is a crucial yet challenging topic of current synthetic organic chemistry.[1] Among the photochirogenic strategies proposed for the photochemical chirality induction in solution, asymmetric photosensitization has been demonstrated to be the most efficient in view of the chiral source efficiency, allowing us to perform the enantio- and diastereodifferentiating photoreactions in the presence of a catalytic amount of chiral sensitizer.[2] In a typical chiral photosensitization, chirality transfer occurs in the exciplex intermediate formed upon interaction of a photoexcited sensitizer with a prochiral substrate. However, the interaction in the electronically excited state is relatively weak, short-lived and susceptible to the environmental variants such as temperature and solvent properties. Consequently, highly enantioselective photosensitization is so far limited in number and was realized by optimizing the chiral sensitizer structure as well as the environmental variants.[3]

Supramolecular photochirogenesis, which utilizes the chiral supramolecular interactions in both ground and excited states, has recently emerged as an intriguing extension of conventional chiral photochemistry.[1d] In supramolecular photochirogenic reactions, the chirality induction relies more on the ground-state complexation of chiral supramolecular host with photosubstrate. Chiral hosts, such as cyclodextrins (CDs),[4] chirally modified zeolite supercages,[5] chiral Kemp's triacid derivatives[6] and biomolecules,[7] have been successfully employed to induce or enhance the enantioselectivity of the product's photochemical reactions.

Sensitizer-modified chiral hosts open a new channel to supramolecular chiral photosensitization, which combines the advantages of asymmetric photosensitization (high chiral-source efficiency) and supramolecular photochirogenesis (intimate interactions). Supramolecular asymmetric photosensitization was first examined with the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene to its (*E*)-isomer using arenecarboxylate-appended CDs as sensitizing hosts.[4b,c] Indeed, these CD-based sensitizers gave much higher *E*/*Z* ratios at the photostationary state than those obtained with the corresponding non-supramolecular chiral sensitizers. Furthermore, up to 24% enantiomeric excess (*ee*) of (*E*)-cyclooctene was obtained upon supramolecular photosensitization with arenecarboxylate-appended CDs, which is significantly higher than those obtained upon photosensitization with conventional chiral sensitizers or upon direct photolysis of a solid state inclusion complex of β-CD with (*Z*)-cyclooctene.[8] Recently, the same photoreaction was investigated with other supramolecular sensitizers such as chiral nanopores,[9] chiral sensitizer-modified zeolite supercages.[10]

Among the asymmetric photosensitizations of cycloalkene homologues examined, the geometrical isomerization of (*Z*,*Z*)-1,3-cyclooctadiene (**1ZZ**) to give planar chiral (*E*,*Z*)-1,3-cyclooctadiene (**1EZ**) (Scheme 1) appears to be the most difficult in which to achieve high enantioselectivity. Enantioselective synthesis of **1EZ** was not studied until recently.[11] A chiral mellitate yielded **1EZ** in the highest *ee* of 17.6% in pentane at −40 °C, while other chiral sensitizers based on the naphthalene or anthracene chromophore offered only very low or negligible *ee*'s. The enantioselectivity of the

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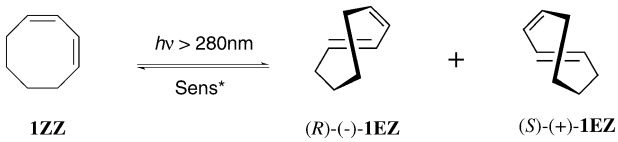
† Dedicated to Professor George W. Gokel on the occasion of his 60th birthday.



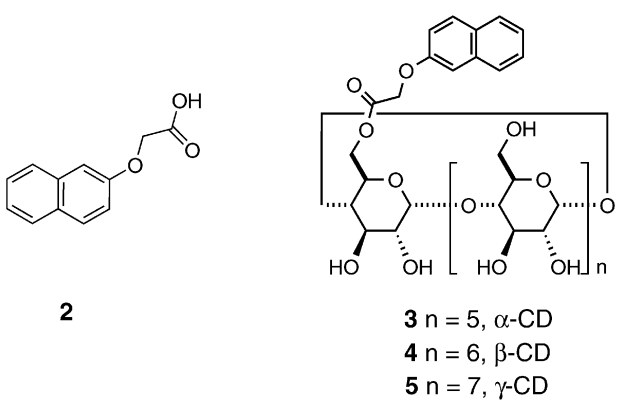
Scheme 1 Enantiodifferentiating photoisomerization of **1ZZ** mediated by chiral sensitizers.

photosensitization of **1ZZ** was demonstrated to be highly sensitive to the solvent polarity, and the use of polar solvents, such as acetonitrile, resulted in a dramatic decrease of the product's *ee*. In this context, it is interesting to examine the effect of chiral supramolecular photosensitizers on the asymmetric photoisomerization of **1ZZ**. In this work, we wish to report the first enantiodifferentiating photoisomerization of **1ZZ** included and sensitized by CD-based supramolecular sensitizing hosts.

Results and discussion

CDs are cyclic oligosaccharides comprising 6, 7 or 8 α-(1,4)-linked glucoside (α-, β- and γ-CD, respectively). These naturally occurring cone-shaped molecules, being readily available and inherently chiral, have been widely studied as supramolecular hosts for complexation with organic molecules.[12] The reactivity and selectivity may be significantly modified through embedding a reactant into the CD cavity.[13] In aqueous solution, the sensitizer moiety attached to the CD rim is included in its own cavity, and therefore the energy transfer to the substrate located outside the cavity is inhibited. Efficient photosensitization can occur only upon formation of a host–guest complex, in which the substrate occupies the chiral CD cavity and the sensitizer moiety is excluded from the cavity to perch on the CD rim.[4b,c]

We chose naphthalene as the sensitizer moiety and synthesized sensitizing CD hosts **3–5** (Scheme 2) by the reaction of sodium 2-naphthyloxyacetate with the corresponding 6-*O*-tosyl-CDs.[14] The binding behavior of **1ZZ** with the supramolecular sensitizers was studied by means of circular dichroism spectrometry. As exemplified in Fig. 1, **4** exhibits a strong positive Cotton effect at the ^1B_b transition of the naphthalene moiety, suggesting a self-included conformation (Scheme 3), as determined by the sector rule proposed by Kajtar *et al.*[15] The



Scheme 2 Naphthalene-substituted CD sensitizers.

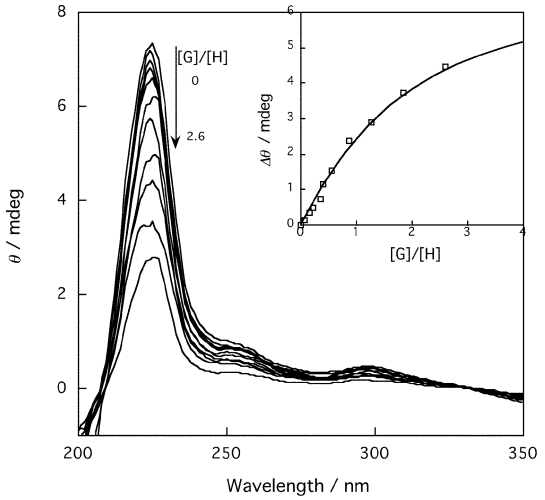
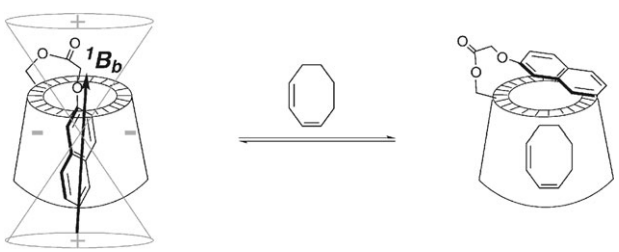


Fig. 1 Circular dichroism spectral changes upon addition of 0, 3, 7, 11, 17, 20, 27, 43, 63, 92 and 130 μM **1ZZ** to an aqueous solution of **4** (50 μM) at 25 °C. Inset: Curve-fitting analysis assuming 1 : 1 complexation stoichiometry.

circular dichroism intensity was gradually decreased upon increasing the concentration of **1ZZ**, indicating that the naphthalene moiety was excluded from the CD cavity upon inclusion of **1ZZ**. A nonlinear least squares regression analysis based on the circular dichroism intensity changes was performed to estimate the binding affinity of sensitizing host and **1ZZ** (Fig. 1 inset).

As can be seen from Table 1, the association constant obtained with β-CD-based sensitizer **4** in 20% aqueous methanol solution is 10–27 times larger than those obtained with α-CD-based **3** and γ-CD-based **5** in the same solution. This result indicates that only the β-CD cavity can nicely fit to the size of **1ZZ** while that of α- or γ-CD is too small or large to satisfy the size-matching requirement. As expected, increasing methanol contents in aqueous solution gave rise to a significant decrease of binding ability of **4**, for which the reduced solvent polarity is responsible. It is noted that the log K_s values of **4** plotted against the methanol contents give a nice linear relationship, indicating that the addition of methanol leads to a continuous change of the solvent polarity or hydrophobicity rather than any specific solvation to the complex.

As shown in Fig. 2, a gradual decrease of the fluorescence intensity was detected when **1ZZ** was added to the aerated aqueous methanol solution of **4** at room temperature. It is important to note that there are two possible causes for this guest-induced fluorescence quenching. The first is the energy transfer from singlet-excited naphthalene to complexed **1ZZ**



Scheme 3 Guest-induced conformational change of host **4**.

Table 1 Association constants for 1 : 1 complexation of sensitizing hosts **3–5** with guest substrate **1ZZ**[a]

Host	Solvent	K_s/M^{-1}
3	20% MeOH	310
4	H_2O	15 600
4	20% MeOH	8300
4	50% MeOH	1550
4	75% MeOH	220
5	20% MeOH	810

[a] Calculated from the data obtained by the circular dichroism spectral titration study performed at 25 °C.

to provide the electronically excited **1ZZ**. The rotational relaxation of the excited **1ZZ** and the subsequent decay will produce the desired photoproduct **1EZ**. The second possibility is the microenvironmental change around the naphthalene moiety from the hydrophobic CD cavity to the polar solvent, which is the most common cause for altering the photophysical properties of CD-linked chromophores.[16] To elucidate the influence of the conformational change of the naphthalene moiety on the fluorescent properties, a control experiment was carried out by adding 1-aminoadamantane to the aqueous solution of **4**. Upon complexation with 1-aminoadamantane, which is known to bind strongly with β-CD (log K = 5.04 with native β-CD),[12a] the naphthalene moiety will be excluded from the CD cavity to the bulk solution. However, the fluorescence spectrum of **4** was not substantially affected by the addition of 1-aminoadamantane at comparable concentrations (0–2 mM). This result suggests that the naphthalene fluorescence is actually insensitive to the environmental change, and hence the fluorescence quenching is attributable solely to the energy transfer to **1ZZ**. No exciplex fluorescence was observed for any of the sensitizers, which seems reasonable since the highly polar aqueous methanol solvent is unfavorable for exciplex formation.

The fluorescence quenching occurred also with sensitizers **2**, **3** and **5**. The Stern–Volmer plots gave excellent straight lines for all naphthalene derivatives examined (Fig. 3). The quenching rate constant (k_q) for each sensitizer was derived from the Stern–Volmer constants ($k_q\tau$) obtained as the slope of the plots and the fluorescence lifetime (τ) measured independently by the time-correlated single photon counting technique. As listed in Table 2, CD sensitizers **3–5** show much greater k_q values than that of **2** by factors of 1.5–6.1. The k_q values for **3–5** (5.0–20.9 × 10^9 M^{-1} s^{-1}) obviously exceed the association rate constants (in the order of 10^7–10^8 M^{-1} s^{-1})[17] for a guest penetrating into the CD cavity and even the diffusion rate constant in water (7.4 × 10^9 M^{-1} s^{-1}),[18] clearly indicating that this is a static quenching process between the excited naphthalene moiety and the included substrate within the CD cavity. It is however noted that not all of the complexed **1ZZ** necessarily lead to non-fluorescent ground-state complexes, as suggested from the fact that the Stern–Volmer constants are much smaller than the corresponding association constants. The fluorescence quenching is accelerated in the order of **4** > **5** > **3**, which shows a fair correlation with their binding affinity with **1ZZ**.

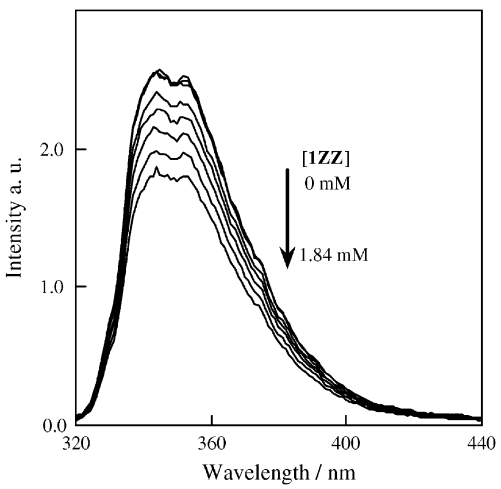


Fig. 2 Fluorescence spectra (excited at 300 nm) of 0.1 mM **4** in the presence of **1ZZ** of varying concentrations in 20% aqueous methanol solution at 25 °C.

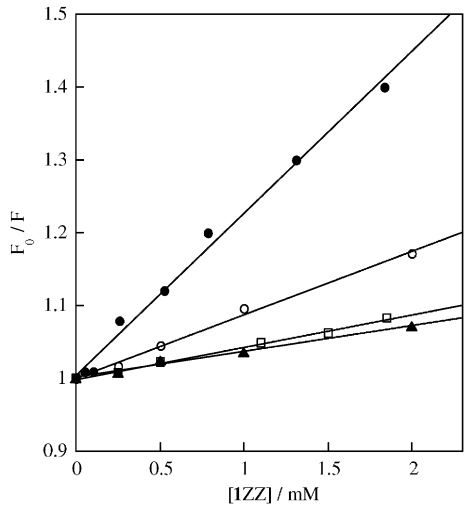


Fig. 3 Stern–Volmer plots obtained from fluorescence quenching of **2** (▲), **3** (□), **4** (●) and **5** (○) by **1ZZ** in 20% aqueous methanol solution.

The photosensitized geometrical isomerization of **1ZZ** was performed in the presence of a modified CD in aqueous methanolic solutions over a temperature range of −10 to 40 °C. After 3 h irradiation at > 280 nm with a high pressure mercury lamp, **1EZ** was produced as the sole product in good yield and modest enantioselectivity (Table 3). It turned out that the β-CD-based sensitizer **4** is most efficient for producing enantiomeric **1EZ** among the three supramolecular sensitizers.

Table 2 Fluorescence quenching of **2–5** by **1ZZ**[a]

Sensitizer	τ/ns	$k_q\tau/M^{-1}$	$k_q/10^9$ M^{-1} S^{-1}
2	10.7	36.2	3.4
3	9.1	45.1	5.0
4	10.6	222	20.9
5	9.3	88.2	9.5

[a] Measured in aerated 20% aqueous methanol solution at 25 °C.

Table 3 The yield and enantiomeric excess (*ee*) of **1ZE** obtained in enantiodifferentiating photoisomerization of **1ZZ** sensitized by **3–5**[a]

Sensitizer	Solvent	Temp. (°C)	Yield (%)	% *ee*	$\Delta\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
3	100% MeOH	0	24.5	0.0		
3	20% MeOH	0	19.6	1.7	−0.14	−0.25
		20	21.3	1.4		
		40	22.5	1.3		
4	100% MeOH	0	26.1	0.2		
4	40% MeOH	−10	26.2	3.8	−0.43	−1.00
		10	25.1	2.8		
		25	22.1	2.6		
		40	24.5	2.2		
4	20% MeOH	−5	22.3	4.6	−0.51	−1.1
		0	21.4	4.5		
		10	26.3	4.1		
		25	24.2	3.7		
		40	18.9	2.9		
4[b]	20% MeOH	0	19.6	4.4		
5	100% MeOH	0	25.3	0.1		
5	40% MeOH	0	28.8	2.7	−0.88	−2.8
		20	24.3	1.8		
		40	19.6	0.2		
5	20% MeOH	0	25.3	3.3	−1.8	−5.9
		10	21.7	2.1		
		25	24.3	0.4		
		40	25.9	−1.7		

[a] Irradiations were carried out with a high-pressure mercury lamp under argon atmosphere in Pyrex tubes for 3 h; >**1ZZ**] = 1 mM, [sensitizer] = 0.1 mM. [b] [**1ZZ**] = 0.1 mM, [sensitizer] = 0.1 mM.

In a typical photosensitization experiment in 20% aqueous methanol at 0 °C, **4** provides **1EZ** with an *ee* of 4.5% while **3** and **5** afford lower *ee*'s of 1.7 and 3.3%, respectively. This result may lead to a correlation between the size-matching and the chirality transfer efficiency in the supramolecular photochirogenesis. The cavity of α-CD is too small to fully include a **1ZZ** molecule, and **1ZZ** is most likely to be shallowly incorporated into the α-CD cavity from the larger opening at the secondary rim, which will certainly prohibit efficient chirality transfer from the α-CD cavity. While for γ-CD, the large cavity cannot strictly confine the orientation of ground state **1ZZ** or control the direction of rotational relaxation around the double bond of **1ZZ**. The reaction conversion and *ee* are not obviously influenced by changing the **[1ZZ]**/**[4]** ratio from 10 to 1 in 20% MeOH at 0 °C, demonstrating a catalytic role of the host in the sensitizing reaction.

Solvent has been demonstrated to play a crucial role in conventional asymmetric photosensitizations.[19] Recently, it was demonstrated that the product chirality is switched at an ambient temperature by changing the reaction medium from water to methanol in the photoisomerization of cyclooctene sensitized by a methoxybenzoyl-substituted β-CD.[4d] We investigated the solvent effect on the product chirality by performing the photoisomerization of **1ZZ** in aqueous solutions of different methanol contents. For both sensitizers **4** and **5**, the *ee* obtained in 40% aqueous methanol was much lower than that in 20% aqueous methanol. In pure methanol, the photoisomerization of **1ZZ** led to a negligible *ee*, irrespective of the host CD used. The reduced enantioselectivity at higher methanol contents is most probably due to the dominant contribution of the photosensitization occurring outside of the CD cavity, which is caused by the lower binding ability for both **1ZZ** and the naphthalene moiety. This result indicates that the CD-mediated photochirogenesis exhibits solvent-dependent behavior completely different from the conventional photosensitization, where the *ee* of **1EZ** is significantly decreased by increasing the solvent polarity.[11]

Lowering the reaction temperature only slightly enhanced the enantioselectivity in the photoisomerization mediated by **3** and **4**. This phenomenon is in sharp contrast to the highly temperature-dependent enantioselectivity demonstrated in non-supramolecular asymmetric photosensitizations.[20] However, it is in line with the previous observations that the entropy factor does not play an important role in the photoisomerization of cyclooctene included and sensitized by chromophore-modified β-CDs.[4c] On the other hand, the product *ee*'s in the photoisomerization sensitized by **5** in 20% aqueous methanol show an apparent decrease from 3.3% at 0 °C to 0.4% at 25 °C. When the temperature was further raised to 40 °C, a chirality switching occurred to give an opposite *ee* of −1.7%.

To quantitatively evaluate the entropy effect on the enantioselectivity of the photoreaction, the relative rate constants (k_R/k_S) were analyzed according to the differential Eyring equation (eqn 1). The temperature dependence profile of *ee* values obtained upon photosensitization with **3–5** is illustrated in Fig. 4. The natural logarithm of relative rate constant k_R/k_S, which is experimentally equivalent to the (100 + %*ee*)/(100 − %*ee*) ratio, was plotted against the reciprocal temperature to show a good linear relationship, suggesting that changing reaction temperature causes no alteration to the enantiodifferentiation mechanism. Interestingly, the differential entropy changes obtained in the photoisomerization sensitized by **5** (−2.8 and −5.9 J mol^{-1} K^{-1} in 40% and 20% aqueous methanol solution, respectively) are obviously higher than in that sensitized by **3** and **4** (ranging from −0.25 to −1.1 J mol^{-1}

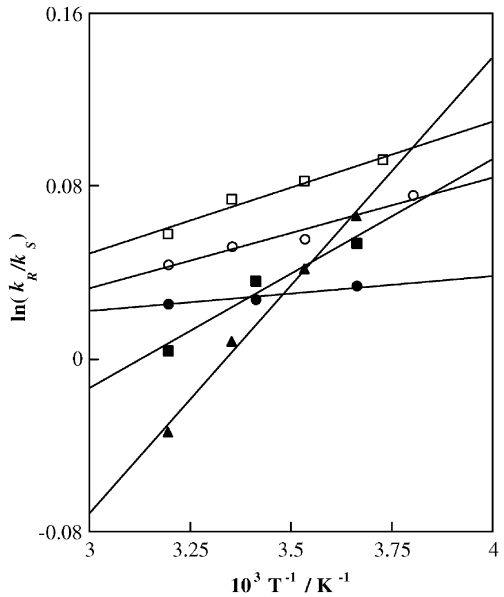


Fig. 4 Temperature dependence of the enantiomeric excess (*ee*) in the enantiodifferentiating photoisomerization of **1ZZ** sensitized by **3** in 20% aqueous MeOH (●), **4** in 20% aqueous MeOH (□), **4** in 40% aqueous MeOH (○), **5** in 20% aqueous MeOH (▲) and **5** in 40% aqueous MeOH (■).

K^{-1}). This demonstrates that the asymmetric photoisomerization of **1ZZ** sensitized by γ-CD-based photosensitizer is more entropy-correlated than that sensitized by its α- and β-CD analogues, for which the larger and more flexible γ-CD cavity, which allows rotational and conformational freedoms of the complexed photosubstrate, would be responsible.

$$\ln(k_R/k_S) = \frac{-\Delta\Delta H^{\neq}_{R-S}}{RT} + \frac{\Delta\Delta S^{\neq}_{R-S}}{R} \qquad (1)$$

Conclusions

In this work, we prepared several naphthalene-substituted CD derivatives to investigate the supramolecular complexation and asymmetric photosensitization of **1ZZ**. The β-CD-based sensitizer **4** displayed much stronger complexation affinity with **1ZZ** than its α- and γ-CD analogues **3** and **5** due to the better size matching. The fluorescence quenching of **3–5** by **1ZZ** was significantly accelerated by the supramolecular complexation, and the quenching rate constant decreased in the order **4** > **5** > **3**, which correlates nicely with the order of binding ability of each host. The enantiodifferentiating photoisomerization of **1ZZ** sensitized by these supramolecular hosts produced **1ZE** with modest *ee*'s of up to 4.6%. Reducing the solvent polarity leads to a decrease of the enantioselectivity of the supramolecular photochirogenic reaction. The photoisomerization of **1ZZ** sensitized by α- and β-CD-based sensitizers **3** and **4** is only faintly entropy-controlled. In contrast, the entropy factor appears much more crucial in the photoreaction mediated by γ-CD sensitizer **5**.

Experimental

General

2-Naphthyloxyacetic acid and α-, β- and γ-cyclodextrins were purchased from Tokyo Chemical Industry and were vacuum-dried before use. ^{1}H and ^{13}C NMR spectra were obtained with a JEOL JNM-EX 400 spectrometer. FAB mass spectra were obtained with a JEOL JMS-DX303 mass spectrometer. UV-vis spectra were recorded by using a JASCO V560 spectrometer. Circular dichroism spectra were measured on a JASCO J-720WI spectropolarimeter. Fluorescence spectra and lifetime were measured on an Edinburgh FL920s spectrofluorimeter. Gas chromatographic analyses of the photoproducts were performed on a 30-m chiral capillary column (β-DEX 120 from SUPELCO) at 60 °C using a Shimadzu GC-17A instrument.

Syntheses of supramolecular sensitizers 3–5

A solution of 6-*O*-tosyl-cyclodextrin (1 mmol) and sodium 2-naphthyloxyacetate (0.672 g, 3 mmol) in 8 mL DMSO was stirred at 85 °C for 48 h. The reaction mixture was slowly poured into cold acetone to produce white precipitates, which were collected by filtration. After washing with acetone and drying under vacuum, the solid was dissolved in 10% aqueous methanol solution and applied on a reversed phase column (Lobar column Lichroprep RP 8, Merck). Gradient elution from 10% aqueous ethanol to 40% aqueous ethanol gave the corresponding 6-*O*-(2-naphthyloxyacetyl)-CDs in 5.2–7.1% yields.

6-*O*-(2-naphthyloxyacetyl)-α-CD (3). Yield: 7.1%, FAB-MS: 1179.4 $[M + Na]^+$. ^{1}H NMR (D_2O): δ 7.87 (d, 1H, J = 8.0 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.77 (d, 1H, J = 8.0 Hz), 7.47 (m, 1H), 7.38 (m, 1H), 7.21 (m, 2H), 4.93–4.82 (m, 6H), 4.55 (m, 1H), 4.33 (m, 2H), 3.92–3.37 (m, 30H), 3.21 (d, 1H, J = 9.2 Hz), 3.14 (d, 1H, J = 9.6 Hz), 3.07 (m, 1H). ^{13}C NMR (D_2O : DMSO-d_6 = 2.5 : 1, v/v): 169.34, 155.47, 134.19, 130.01, 129.11, 127.86, 127.14, 127.03, 124.53, 117.53, 107.34, 102.08, 82.51, 82.16, 82.07, 73.44, 72.40, 71.97, 69.28, 64.85, 64.47, 60.33.

6-*O*-(2-naphthyloxyacetyl)-β-CD (4). Yield: 5.2%, FAB-MS: 1341.5 $[M + Na]^+$. ^{1}H NMR (D_2O): δ 7.85–7.82 (m, 2H), 7.74 (d, 1H, J = 8.0 Hz), 7.43 (t, 1H, 1H, J = 7.6 Hz, J = 7.6 Hz), 7.35 (t, 1H, J = 7.6 Hz, J = 7.2 Hz), 7.17 (d, 1H, J = 8.0 Hz), 7.16 (s, 1H), 4.88–4.84 (m, 7H), 4.71 (m, 1H), 4.47 (m, 1H), 4.31–4.29 (m, 2H), 3.80–3.28 (m, 38H). ^{13}C NMR (D_2O : DMSO-d_6 = 2 : 1, v/v): δ 169.75, 155.97, 134.32, 130.12, 129.27, 127.97, 127.27, 127.18, 124.72, 118.63, 107.54, 102.65, 102.32, 102.13, 82.13, 81.72, 81.49, 73.48, 72.47, 69.63, 65.06, 64.61, 60.35.

6-*O*-(2-naphthyloxyacetyl)-γ-CD (5). Yield: 6.5%, FAB-MS: 1503.5 $[M + Na]^+$. ^{1}H NMR (D_2O : DMSO-d_6 = 3 : 2, v/v): δ 7.74 (d, 1H, J = 8.0 Hz), 7.66 (d, 1H, J = 8.8 Hz), 7.61 (d, 1H, J = 8.0 Hz), 7.49 (t, 1H, J = 7.2 Hz, J = 7.6 Hz), 7.40 (t, 1H, J = 7.2 Hz, J = 7.6 Hz), 7.12 (d, 1H, J = 8.8 Hz), 6.96 (s, 1H), 4.98–4.86 (m, 8H), 4.70 (d, 1H, J = 12.4 Hz), 4.00 (m, 1H), 3.86–3.22 (m, 46H). ^{13}C NMR (D_2O : DMSO-d_6 = 3 : 2, v/v): 170.05, 155.92, 134.32, 129.65, 129.20, 128.02, 127.55,

127.01, 125.10, 118.72, 107.21, 103.00, 102.46, 102.23, 101.95, 82.31, 81.56, 81.46, 81.24, 81.11, 73.91, 73.52, 73.45, 73.32, 73.20, 73.07, 72.92, 72.72, 72.56, 72.46, 72.37, 72.16, 71.10, 65.20, 60.41, 60.05.

Photolysis

All irradiations were carried out in a temperature-controlled water–ethylene glycol bath, using a 300 W high pressure mercury lamp fitted with a transparent Pyrex vacuum sleeve. Aqueous methanolic solutions containing **1ZZ** (1 mM) and a CD-sensitizer (0.1 mM) were irradiated in a Pyrex tube. The photolyzed solution was poured into a 10% aqueous KOH solution for decomplexation. The resultant mixture was extracted with pentane which was subjected to GC analysis.

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