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Wavelength-controlled supramolecular photocyclodimerization of anthracenecarboxylate mediated by γ -cyclodextrins†

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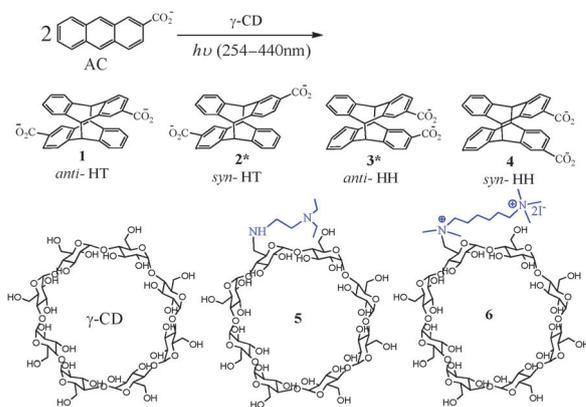
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Stereochemical outcomes were critically tuned by excitation wavelength in the supramolecular photocyclodimerization of 2-anthracenecarboxylic acid mediated by native and diamino-modified γ -cyclodextrins.

Photochiogenesis provides us with a direct access to chiral compounds alternative to thermal counterparts.¹ Nevertheless, controlling stereochemistry in photochiogenesis still remains a great challenge and hence a variety of methodologies have hitherto been proposed for manipulating the stereochemical outcomes by optimizing the electronic and structural properties of the substrate, chirogen and sensitizer, as well as the external factors such as temperature, solvent and pressure.² In the foregoing photochiogenic studies,^{1,2} the fundamental, and practically the only, strategy is to kinetically or thermodynamically discriminate a pair of diastereomeric transition states or intermediates by making a difference in free energy (ΔG). In this study to explore a new controlling factor beyond ΔG , we employed the excitation wavelength as a new tool unique to photochemistry for controlling the stereochemical outcomes of a supramolecular photochiogenic reaction.

Upon photoirradiation, 2-anthracenecarboxylate (AC) affords two each of *head-to-tail* (HT) and *head-to-head* (HH) cyclodimers **1–4**, of which *syn*-HT **2** and *anti*-HH **3** are chiral (Scheme 1). Various chiral supramolecular hosts, including γ -cyclodextrins (CDs), proteins, chiral templates, chiral liquid crystals and gels, have been employed to mediate this chiral photoreaction.^{3,4}

It is well accepted that the Kasha's rule⁵ is obeyed and the photophysical and photochemical processes are independent of excitation wavelength in most organic compounds.⁶ Nevertheless, the following findings prompted us to explore such a possibility particularly in the photocyclodimerization of AC mediated by γ -CD: (i) γ -CD includes two ACs to form stereoisomeric 1:2 complexes precursor to cyclodimers **1–4**



Scheme 1 Photocyclodimerization of AC mediated by γ -CDs.

(Fig. 1a); (ii) the 1:2 complexation accelerates the photocyclodimerization; (iii) the stereoselectivity of the photoreaction is determined primarily by the population of the precursor complexes. If these precursor complexes differ in the absorption spectrum, one can selectively excite specific species by choosing proper irradiation wavelength, which relieves us from the fetters of the ground-state thermodynamics. This idea emerged from a rather common observation that complexing AC with γ -CD led to apparent spectral changes (Fig. 1b); thus, the band broadening observed implies the coexistence of multiple AC pairs having different spectra. Similarly, the circular dichroism spectral titration of AC with γ -CD showed obvious band-broadening and a drift of the isodichroic point for the exciton-coupled ¹B_u band (Fig. S5 in the ESI†), suggesting the coexistence of multiple AC–CD species.

Photoirradiations of AC with γ -CD were carried out at various wavelengths ranging from 254 or 290 to 440 nm by using a xenon lamp fitted with a band-pass filter (fwhm = 10 nm). Indeed, both of the product distribution and ee were critical functions of irradiation wavelength, as shown in Table 1. Although the formation of HT dimers was dominant (83–92% in total) at all the wavelengths examined upon irradiation with native γ -CD, the yield of **1** varied widely from 31% (440 nm) to 55% (300 nm). Exactly the opposite behavior was observed for **2**, affording the lowest 33% yield at 330 nm and the highest 61% yield at 440 nm. The yields of HH dimers also significantly depended upon excitation wavelength,

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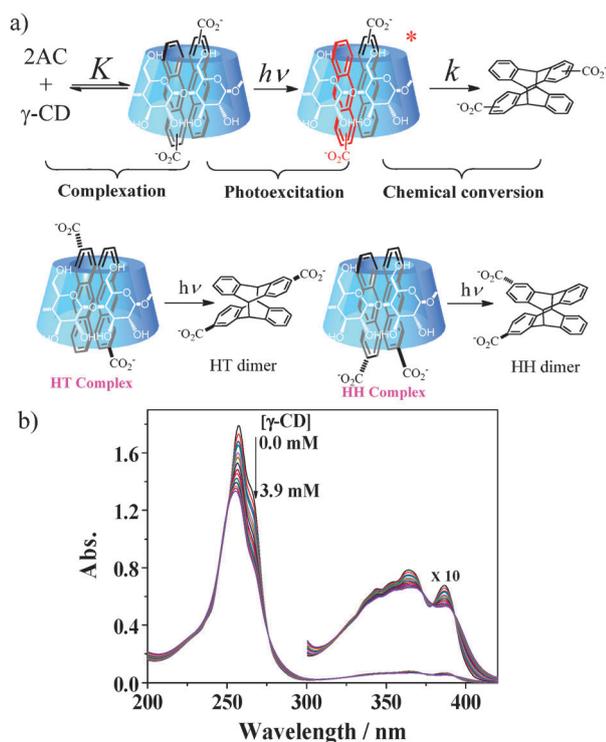


Fig. 1 (a) Stereodifferentiation mechanisms upon complexation and subsequent photocyclodimerization of AC with γ -CD. (b) UV-vis spectral changes of an aqueous buffer solution of 0.2 mM AC at pH 9 upon addition of γ -CD at 25 °C in a quartz cell (0.1 cm path length).

varying from 6% to 10% for **3** and from 2% to 7% for **4** in the same wavelength region.

The ee values of chiral **2** and **3** showed rather complicated wavelength-dependence. Thus, the highest ee of **2** (40–41%) was obtained upon irradiation at 254 nm and at 360–390 nm, while the lowest (24–25%) at 420–440 nm. In the case of **3**, even the chiral sense of product was switched by changing irradiation wavelength to afford the antipodes of –9% ee at 290 nm but of 12% ee at 440 nm. These results indicate that the spectral profile significantly differs for each of the six stereoisomeric 1 : 2 precursor complexes of AC with γ -CD as a consequence of different stacking geometries in *re/si*, *anti/syn* and HT/HH manner. Now, we can go beyond the diastereomeric selectivity predetermined by the complexation thermodynamics in the ground state by choosing the correct wavelength to enhance the ee.

As illustrated in Fig. 1a, the supramolecular photochirogenesis involves three steps, and the rate of dimer formation is a function of the concentration and extinction coefficient (ϵ) of the precursor complex (P) and its reactivity upon excitation. Hence, the enantiomer ratio (er) of **2** or **3** is expressed by eqn (1) as a product of the relative rate constant (k^+/k^-), excitation ratio (ϵ^+/ϵ^-) and relative concentration of precursor complexes ($[P^+]/[P^-]$):

$$\text{er} = (k^+/k^-)(\epsilon^+/\epsilon^-)([P^+]/[P^-]) \quad (1)$$

In eqn (1), the rate constants (k^+ and k^-) and the concentrations of P^+ and P^- remain constant as far as the temperature is kept constant, while the extinction coefficients (ϵ^+ and ϵ^-)

Table 1 Photocyclodimerization of AC irradiated at varying wavelengths in the presence of native and modified γ -CDs^a

Host	Solvent (Temp)	λ /nm	Relative yield ^b /%				ee ^{b,c} /%		
			1	2	3	4	HT/HH	2	3
γ -CD	B ^d (0.5 °C)	254	33.3	52.7	7.4	6.6	6.1	39.9	3.6
		270	45.5	38.8	8.8	6.9	5.4	34.8	–5.4
		280	47.7	35.9	10.1	6.3	5.1	32.4	–8.3
		290	47.7	35.3	10.2	6.8	4.9	26.2	–8.8
		300	54.5	33.3	6.1	6.1	7.2	26.7	–4.4
		313	43.6	43.0	7.8	5.6	6.5	29.5	–5.7
		360	41.2	46.2	7.1	5.5	6.9	40.8	0.7
		380	41.2	47.0	7.0	4.8	7.5	40.1	3.5
		390	40.0	47.6	7.1	5.3	7.1	40.7	1.0
		420	39.7	49.7	7.2	3.4	8.4	24.7	4.7
		430	34.3	56.2	7.0	2.5	9.5	24.7	9.4
		440	30.7	60.9	6.6	1.8	10.9	24.1	11.9
5	B ^d (0.5 °C)	290	46.3	33.3	12.2	8.2	3.9	25.7	–10.8
		300	52.4	43.0	7.9	7.6	5.5	24.2	–10.5
		360	39.6	44.8	8.9	6.7	5.4	38.5	–2.6
		440	29.3	59.4	8.8	2.5	7.9	22.1	12.6
BM ^e (–70 °C)	290	32.3	8.4	27.4	31.9	0.7	–7.4	–54.6	
	300	37.1	9.9	22.0	31.0	0.9	–4.0	–55.8	
	360	30.6	16.0	26.9	26.5	0.9	7.3	–52.0	
	440	29.6	28.3	29.2	12.9	1.4	–1.4	–48.7	
6	B ^d (0.5 °C)	290	46.7	32.6	12.1	8.6	3.8	25.1	–20.8
		300	51.7	31.7	8.8	7.8	5.0	24.4	–20.1
		360	40.6	44.2	8.8	6.4	5.6	39.6	–13.3
		440	30.2	58.7	8.6	2.5	8.0	26.1	5.3

^a Deoxygenated aqueous solution containing 0.6 mM AC and 2 mM γ -CD derivative was irradiated for 2 h at a given wavelength using a xenon lamp fitted with an appropriate band-pass filter (fwhm = 10 nm). ^b Relative yield and ee were determined by chiral HPLC analysis. ^c The sign of ee is positive if the first eluted enantiomer is enriched, and *vice versa*; error in ee < 1%. ^d Solvent B: pH 9 aqueous buffer. ^e Solvent BM: a 2 : 5 (v/v) mixture of pH 5 phosphate buffer and methanol.

critically vary with excitation wavelength, enabling us to manipulate the er of the photoproduct.

Eqn (1) reveals the critical role of wavelength in the supramolecular photochirogenesis. To quantify the wavelength effect on ee, we may define a term “excitational excess (xx)” as the fractional difference in ϵ between two diastereomeric precursor complexes:

$$\text{xx} = (\epsilon^+ - \epsilon^-)/(\epsilon^+ + \epsilon^-) \quad (2)$$

By tentatively setting the same ϵ for two diastereomeric precursor complexes at the pseudo-isosbestic point of 380 nm (Fig. 1b), the xx values for **2** and **3** were calculated over the entire spectral range as shown in Fig. 2.

As can be seen from Fig. 2, the xx values obtained for the present system are modest, ranging from –18% to 1% for **2** and from –12% to 9% for **3**. Reasonably, the profile of xx is similar to that of ee, excepting the absolute value and sign. For **2**, the xx value is negative in general, indicating stronger absorption by the precursor complex to (–)**2** than that to (+)**2**. The positive ee's experimentally obtained for **2** indicate that the formation of (+)**2** is overwhelmingly favored upon complexation and photoconversion, but is disfavored upon excitation. For **3**, the complexation and photoconversion show only poor diastereoselectivities and the selectivity upon excitation dominates the product's ee. As a result, the ee reaches the most negative

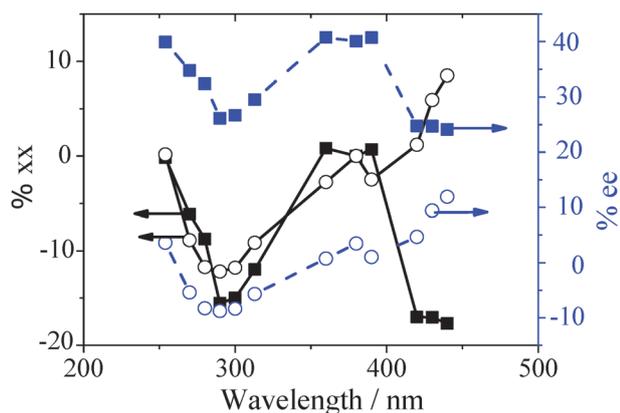


Fig. 2 Plots of ee (■) and xx (●) of **2** and of ee (○) and xx (○) of **3** as a function of wavelength upon irradiation of AC with native γ -CD.

(290 nm) and positive (440 nm) values exactly at the wavelengths where the xx value gives the extrema.

We further examined the photocyclodimerization of AC mediated by modified γ -CDs **5** and **6**, in which a dicationic side chain was introduced to improve the HH yield through electrostatic interactions. Indeed, the use of diamino- γ -CDs **5** and **6** only appreciably increased the total HH yield from 17% for native γ -CD to 20–21% and also the ee of **3** from –9% for native γ -CD to –11% and –21%, respectively, at least upon irradiation at 290 nm in aqueous buffer at 0.5 °C (Table 1).

Intriguingly, the wavelength effect turned out to be highly solvent- and temperature-dependent. Thus, the yield and ee obtained upon irradiation of AC with **5** revealed more dramatic wavelength dependencies in a less polar buffer–methanol mixture at –70 °C. As shown in Table 1, the major product was switched from 80–89% HT to 42–59% HH by changing the solvent from aqueous buffer at 0.5 °C to a buffer–methanol mixture at –70 °C, as a consequence of the enhanced electrostatic attraction between anionic ACs and the dicationic sidearm of **5**. In aqueous buffer at 0.5 °C, where little electrostatic attraction is operative, the yield and ee showed almost the same wavelength-dependence profiles as those observed for native γ -CD. However, very contrasting wavelength-dependence behavior was observed for the ee of **2**, varying from 22% to 38% at 0.5 °C but from –7% to 7% at –70 °C, and also for the ee of **3**, varying from –11% to 13% at 0.5 °C but from 49% to 56% at –70 °C, indicating that the distribution of precursor complexes was completely altered by the use of a less-polar buffer–methanol mixture at –70 °C. By optimizing the wavelength, solvent and temperature, the HH dimers were obtained in 59% combined yield and **3** in 55% ee upon irradiation at 290 nm in the BM solvent at –70 °C. The xx values were modest, ranging from 0.8% to –18% for **2** and from 4% to 14% for **3** (Table S1, ESI†).

In this study, we have demonstrated for the first time that the excitation wavelength can be used as a unique, convenient, yet powerful tool for manipulating the relative yield and ee of chiral photoproducts obtained in supramolecular photocyclodimerization, circumventing the inherent limitations of ground-state thermodynamics. In principle, the wavelength control is not limited to the present chiral photocyclodimerization but applicable generally to a wide variety of uni- and bimolecular photoreactions, if the supramolecular complexation generates orientational, conformational or diastereomeric isomers that differ in the absorption spectrum. The wavelength effect in supramolecular photochemistry may open a new channel to the chemo- and stereocontrol of photoreactions and in particular to the ultimate control of photochirogenic processes.

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