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Cucurbit[8]uril-mediated photodimerization of alkyl 2-naphthoate in aqueous solution

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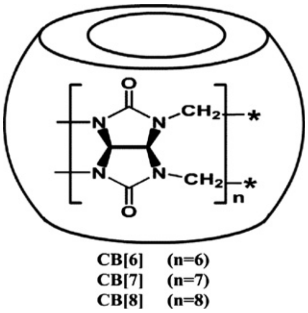
Abstract

The photodimerization of methyl 2-naphthoate (**1**), ethyl 2-naphthoate (**2**) and butyl 2-naphthoate (**3**) in cucurbituril (CB) aqueous solution was investigated. The product distribution and fluorescence spectral changes suggest that CB[8] can encapsulate two molecules of alkyl 2-naphthoate (**1** or **2**) and thereby facilitate a *cubane-like* photodimer formation. Subtle changes in either cavity size of CB[*n*] or alkyl substitutes can significantly modulate the interaction of CB[*n*] with 2-naphthoate derivatives affording remarkable alterations in their photochemical reactivity.

Keywords: Photodimerization; Cubane-like photodimer of alkyl 2-naphthoate; Cucurbit[*n*]uril; Host–guest interactions

The isolation of a first photodimer in the naphthalene series appeared in 1963,[1] albeit the photodimerization of anthracene has been known for over a century.[2–5] Unlike anthracene, naphthalene itself does not undergo photodimerization, but irradiation of alkyl 2-naphthoate results in a *cubane-like anti*-head-to-head photodimer. The rigid *cubane-like* photodimers, bonding that occurs between the substituted rings and the substitutes are in a head-to-tail orientation,[6–15] are of importance in organic synthesis and are solar energy storage.[9–15] However, the quantum yield for the photodimerization of naphthalene derivatives is much lower than that of the corresponding anthracene derivatives[1,2,6–8] when the reaction is carried out in organic solutions.

Cucurbituril (CB), a family of pumpkin like macrocyclic host with five, six, seven, eight or ten methylene-bridged glycoluril units, respectively,[16–18] features a hydrophobic cavity and polar carbonyl groups surrounding the portals (Scheme 1). The varying cavity and portal size of CB[*n*] are known to show remarkable affinity and selectivity towards guest molecules in aqueous solution.[16–18] Notably, CB[8] is able to bring two aromatic molecules together within the cavity. Kim[19,20] and Ramamurthy[21–23] recently found that CB[8] mediates the photodimerization of diaminostilbene, cinnamic acid, *trans*-1,2-bis(*n*-pyridyl)-ethylenes and stilbazoles either in solid state or in aqueous solution.



Scheme 1. The structure of cucurbit[*n*]uril.

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Table 1
Conversion and yield for the photodimerization of **1**–**3** in the absence and presence of CB[*n*] at room temperature, respectively

Substrate	Solvent	Irradiation time (h)	Conversion[a] (%)	Yield (%)
1	C_6H_{12}	8.0	15.0	>95
1	H_2O	8.0	0	—
1@CB[8]	H_2O	0.30	25.1	~100
1@CB[8]	H_2O	0.75	45.0	~100
1@CB[8]	H_2O	2.0	61.0	~100
2	H_2O	2.0	6.2	~100
2@CB[8]	H_2O	2.0	45.1	~100
2@CB[7]	H_2O	2.0	6.7	~100
3	H_2O	2.0	4.0	~100
3@CB[8]	H_2O	2.0	5.0	~100
3@CB[7]	H_2O	2.0	5.0	~100

[a] Conversion was calculated by integrating the 1H (8.61–8.62 ppm) of 2-naphthoate and 8H (6.94–7.26 ppm) of the photodimer.

Inspired by these studies, we investigated the photodimerization of alkyl 2-naphthoate in CB[*n*] aqueous solution. It was expected that CB[*n*] can bring two reactants of alkyl 2-naphthoate into close proximity with desired orientations, thereby facilitating the photodimerization to take place in high yield. At the same time, the product distribution may provide valuable information on the interaction between CB[*n*] and the introduced alkyl 2-naphthoate. In the present work, we report that the solubility of the water-insoluble neutral alkyl 2-naphthoate is enhanced upon addition of CB[8] in aqueous solution. Subtle change in either cavity size of CB[*n*] or alkyl substitutes can significantly modulate the interaction of CB[*n*] with 2-naphthoate derivatives, therefore resulting in remarkable alterations in their photochemical reactivity.

Inclusion of water-insoluble alkyl 2-naphthoate within the cavity of CB[*n*] was achieved by sonication of alkyl 2-naphthoate with CB[*n*] in aqueous solution for 2 h at 50 °C. After filtration, the saturated solution was purged with nitrogen and then irradiated with light $\lambda > 280$ nm to protect photodimer from decomposition. The photochemical reaction was carried out in a Pyrex tube at room temperature. The product analysis was performed following extraction with chloroform. Compared with the host-free solution, the solubility and absorbance of **1** are enhanced upon addition of CB[8] in aqueous solution. Irradiation of **1** in the presence of CB[8] quickly decreased the absorbance at the typical bands for **1**. Generally, after 0.30 h, 0.75 h and 2 h of irradiation, the conversion of **1** approached to 25%, 45% and 61%, respectively, and the yield of the *cubane-like* photodimer was up to 100% based on the consumption of the starting material[24–26] (Table 1). By contrast, irradiation of **1**-saturated aqueous solution does not result in any photodimer formation. Compared with the conversion of **1** in cyclohexane solution, that is only 15% after 8 h irradiation,[14] it is evident that CB[8] templates the photodimerization of **1** with large rate acceleration in aqueous solution.

To examine whether the cavity size of CB and substituents on 2-naphthoate would affect the photodimerization, the photochemical dimerization of 2-naphthoate with different substituents in the presence of CB[8] or CB[7] was investigated. Obviously, the photodimer formation depends on the substituents very much (Table 1). For **1** with a small methyl group, the conversion was increased dramatically in the presence of CB[8]. In a similar way, CB[8] facilitated the photodimerization of **2** with ~8 times higher rate acceleration than that in water. Contrarily, **3** with large butyl group did not show rate acceleration at all. With respect to the correlations of the photodimerization efficiency shown in Table 1, the influence of the substituents on 2-naphthoate and cavity size of CB is indeed crucial. Irradiation of **2** or **3** in CB[7] aqueous solution afforded the *cubane-like* photodimers with an efficiency comparable to that in the absence of CB[7] host. All of the observations indicate that CB[8] can encapsulate two molecules of 2-naphthoate with small substituents and align them to favour the photodimerization. The cavity of CB[7] is too small to include a pair of 2-naphthoates within its cavity.

The interaction of CB with the alkyl 2-naphthoates **1**–**3** in aqueous solution was further confirmed by fluorescence analysis. Figure 1 shows the fluorescence spectra of **1**–**3** in the presence of CB[8]. All of the three compounds exhibit the fluorescent characteristics of 2-naphthoate monomer with maximum at 380 nm. Moreover, **1**@CB[8] and **2**@CB[8] show a long tail extending to lower energies. When the monomer band in the fluorescence spectra of **1**@CB[8], **2**@CB[8] and **3**@CB[8] was normalized to that of **1**, **2** and **3** in water, respectively, an excimer emission

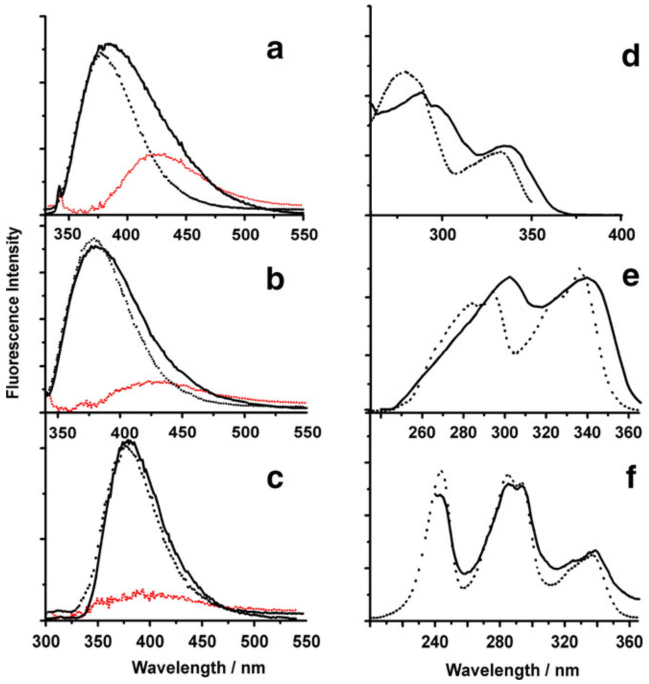
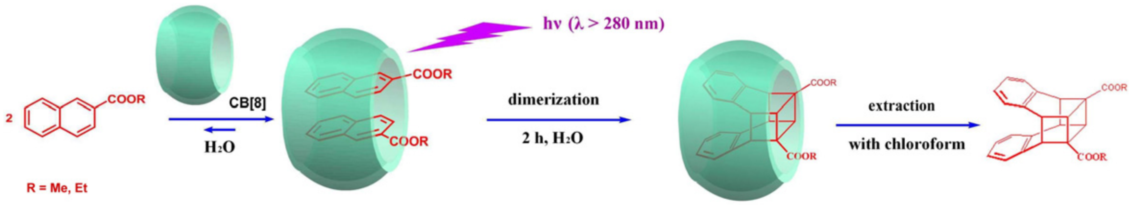


Fig. 1. The fluorescence spectra of **1**–**3** in the absence (······) and presence of CB[8] (—) in H_2O at room temperature for **1**: (a); **2**: (b); and **3**: (c), excited at 295 nm; the excitation spectra for monomer and excimer, monitored at 370 nm (······) and 440 nm (—), respectively, for **1**: (d); **2**: (e); and **3**: (f). The red line in fluorescence spectra (a, b and c) represents the excimer fluorescence of alkyl 2-naphthoate in the presence of CB[8].



Scheme 2. Cucurbit[8]uril-mediated photodimerization of alkyl 2-naphthoate in aqueous solution.

was resolved with a maximum at 440 nm in **1**@CB[8] and **2**@CB[8]. No such emission band was observed in **3**@CB[8] (Fig. 1a–c). The excitation spectra for the monomer and excimer emissions, monitored at 370 and 440 nm, respectively, are generally similar but evidently red-shifted (Fig. 1d and e). These results suggest that the excimer originates from a pair of alkyl 2-naphthoate that exists prior to excitation, consistent with that observed in the photochemical dimerization. It should be also pointed out that the low intensity of the excimer emission relative to that of the monomer does not imply that the portion of paired alkyl 2-naphthoates is small, because the fluorescence quantum yield of excimer is much smaller than that of the monomer. On the other hand, the fluorescence spectra of **1**@CB[7], **2**@CB[7] and **3**@CB[7] together with **3**@CB[8] were not shifted at all, implying no excimer formation.

Such CB[8]-mediated photodimerization of alkyl 2-naphthoate may be illustrated in Scheme 2. The cavity of CB[8] accommodates two molecules of alkyl 2-naphthoate and aligns them in a geometry favourable for the photodimerization. Since the photodimerization of alkyl 2-naphthoate occurs between the substituted rings and the substitutes are in the head-to-tail orientation,[6–15] together with that it is impossible to exchange the orientation of 2-naphthoate within the lifetime of the singlet excited state, the structure of **1**@CB[8] and **2**@CB[8] reflects the orientation of the paired 2-naphthoates for the photodimerization in CB[8] aqueous solution. Either the small cavity of CB[7] or large butyl group of alkyl 2-naphthoate impede the inclusion of two molecules of alkyl 2-naphthoate in the cavity, no rate acceleration for the photodimerization, therefore, was observed.

In summary, we have demonstrated that CB[8] can mediate the photodimerization of alkyl 2-naphthoate in aqueous solution. Studies on the product distribution and fluorescence spectral changes reveal that CB[8] can encapsulate two molecules of 2-naphthoate and align them to favour the *cubane-like* photodimer formation. Subtle changes in either cavity size of CB[*n*] or alkyl substitutes can significantly modulate the interactions of CB[*n*] with 2-naphthoate derivatives to display remarkable changes in their photochemical reactivity.

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24. *Note*: The saturated solution of CB[*n*] and alkyl 2-naphthoate aqueous solution was irradiated with a 500 W high-pressure mercury lamp. A quartz jacket with water circulation was used to cool the lamp. A light filter was placed outside the quartz jacket to cut off light below 280 nm to protect photodimer from decomposition. After irradiation, the photodimer was extracted with chloroform and subjected to ^{1}H NMR analysis.

25. ^{1}H NMR ($CDCl_3$, ppm) data for **1**: 8.61 (s, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.53–7.61 (m, 2H), 3.99 (s, 3H); **2**: ^{1}H NMR: 8.62 (s, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.52–7.61 (m, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); **3**: 8.61 (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.52–7.61 (m, 2H), 4.40 (t, $J = 6.0$ Hz, 2H), 1.79–1.83 (m, 2H), 1.50–1.55 (m, 2H), 1.01 (t, $J = 7.9$ Hz, 3H).

26. ^{1}H NMR ($CDCl_3$, ppm) data for photodimer of **1**: 6.99–7.26 (m, 8H), 4.51 (d, $J = 12$ Hz, 2H), 4.39 (q, 2H), 3.82 (d, $J = 8$ Hz, 2H), 3.75 (s, 6H); photodimer of **2**: 6.94–7.01 (m, 8H), 4.51 (d, $J = 12$ Hz, 2H), 4.38 (q, 2H), 4.22 (q, $J = 7.0$ Hz, 4H), 3.80 (d, $J = 8.0$ Hz, 2H), 1.29 (t, $J = 7.0$ Hz, 6H); photodimer of **3**: 6.95–7.01 (m, 8H), 4.51 (d, $J = 8.0$ Hz, 2H), 4.36 (q, 2H), 4.16 (t, $J = 5.4$ Hz, 4H), 3.79 (d, $J = 8.0$ Hz, 2H), 1.62–1.69 (m, 4H), 1.37–1.47 (m, 4H), 0.96 (t, $J = 7.4$ Hz, 6H).