

[Communication]

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一含肉桂酸的单链Bola型两亲分子在有机溶剂中的光致二聚和聚集行为

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摘要 制备了一种含肉桂酸基团的 Bola 型两亲分子 HDC(4-(10-羟基癸氧基)-10-羟基癸基肉桂酸酯). 第一次观察到该分子在有机溶剂中经紫外光照发生光致二聚. 分离出来的二聚 HDC 在 20% 的乙醇/水混合溶剂中能形成球形的囊泡. 同时发现溶剂的介电常数大小与光致二聚过程密切相关, 介电常数的大小不仅关系到反应发生与否, 而且直接影响到反应的速率.

关键词: Bola 型两亲分子, 肉桂酸衍生物, 光致二聚, 聚集

中图分类号: O647

Photodimerization and Aggregation in Organic Solution of a Single Chain Bolaamphiphilic Cinnamic Acid Derivative

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Abstract Single chain bolaamphiphile containing cinnamyl moiety [4-(ω -hydroxydecanyloxy) (ω -hydroxydecanyl) cinnamate, abr. HDC] was designed and synthesized. The photodimerization of the HDC molecules induced by UV light was the first time realized in organic solutions. The dimerized HDC was separated and formed spherical vesicles in 20% ethanol/water mixed solvents. The solvents' dielectric constants were found to play an important role in the photodimerization process. Both the occurrence of the photodimerization reaction and the rate of the reaction were affected by the dielectric constant value of the solvents.

Keywords: Bolaamphiphile, Cinnamic acid derivative, Photodimerization, Aggregation

Bolaamphiphiles are the molecules with two hydrophilic head groups connected by one or two long hydrophobic chains. For their superior membrane formation ability^[1-2] and abundant aggregation behaviors^[3-8], bolaamphiphiles have attracted great interests over the past two decades. It has been found that the aggregate morphologies formed by these bolaamphiphiles are dependent on their head group properties^[9-15]. In addition, the structure of the hydrophobic chains connecting the two head groups also plays an important role on the aggregate formation of the bolaamphiphiles^[4, 15-16]. However, compared with the numer-

ous studies on effects of head group structures, the reports on the hydrophobic chain effects are relatively rare.

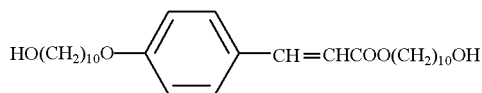
On the other hand, cinnamic acid and its derivatives have been the subject of classical topochemistry for their four-center-type 2+2 photocyclodimerization in crystalline state and other organized assemblies^[17-20]. Usually, photoreaction can not take place for single chain cinnamic acid derivatives in homogeneous solution. Tanaka *et al.*^[21] investigated the photoreaction of OCA (4-octadecanoxycinnamic acid) in chloroform and only the *cis*-isomer was obtained. The fact that dimerization of single chain

Received: September 22, 2005; Revised: October 25, 2005. *Correspondent, E-mail: jbhuan@pku.edu.cn; Tel: 010-62753557.

国家自然科学基金 (20233010, 20373003, 20425310), 教育部博士点资助项目

cinnamic acid derivatives does not occur in organic solutions has greatly restricted the application of these compounds in organic systems since many important chemical reactions were carried out in organic medium.

Considering the important significance of both bolaform amphiphiles and cinnamic derivatives in the research of membrane mimetic chemistry, we synthesized a new kind of bolaamphiphiles containing cinnamyl group (HDC, Scheme 1) and studied its photodimerization in organic solution and its aggregation behavior in ethanol/water suspensions. It is the first report that the single-chained HDC amphiphilic molecules dimerized in some organic solutions. The dielectric constants of the organic solvents are closely related with the photodimerization reaction. In addition, different from monomers, the dimerized HDC molecules can self-assemble into globular vesicles, which clearly displayed the influence of hydrophobic chain on the aggregation behavior.



Scheme 1 Structure of HDC

1 Experimental section

1.1 Synthesis of HDC

HDC was synthesized according to the following procedure: Firstly, 1-bromo-10-hydroxydecane was prepared from the corresponding diol and hydrobromic acid^[22] (Beijing Chemical Co., A.R.). Then a mixture of 4-hydroxyl cinnamic acid (Sigma Co., 1.64 g, 0.01 mol), 1-bromo-10-hydroxydecane (2.40 g, 0.01 mol) and 7 cm³ potassium hydroxide (1.12 g, 0.02 mol) aqueous solution in 100 cm³ of acetone was refluxed for 72 h. The reaction mixture was acidized with 3 mol·dm⁻³ HCl and then poured into a large amount of distilled water. White solid was obtained after the solution being cooled. The solid was further purified by recrystallization three times from acetone. m.p.: 83~85 °C. ¹H NMR (200 MHz, CDCl₃, TMS): δ: 7.6 (1H, d, Ph—CH=CH—), 7.4(2H, d, Ph—CH=CH), 6.9(2H, d, Ph—O), 6.3 (1H, d, Ph—CH=CH), 4.2 (2H, t, —CH₂COO), 4.0 (2H, t, CH₂—O—Ph), 3.6 (4H, t, CH₂—OH), 2.1 (2H, t, OH), 1.3~1.7(32H, m, CH₂). Anal: Calcd for C₂₉H₄₈O₅: C, 73.11; H, 10.08; O, 16.81. Found: C, 72.93; H, 10.08.

1.2 Methods

The cast films were prepared by spreading a few drops of samples on CaF₂ for FT-IR and slowly drying in atmosphere at room temperature. FT-IR spectra were recorded on a Nicolet Magna-IR 750 Fourier transform spectrometer operating at 4 cm⁻¹ resolution. The photodimerization process of HDC in chloroform and other organic solvents was carried out by irradiation

using 254 nm UV light in quartz cell. The distance between the irradiation source and the sample was kept at 5 cm. Absorbance changes accompanying photodimerization of HDC were tracked with a Shimadzu UV-250.

The suspensions of HDC before UV irradiation were obtained by directly sonicating 0.9 mg·dm⁻³ HDC in 20% ethanol/water (V/V). The dimerized HDC suspensions were prepared by evaporating the solvent from the UV irradiated CHCl₃ solution of HDC, then re-dispersing the solids into the 20% ethanol/water mixed solvents.

Replica for TEM observation was prepared by Freeze-fracture method with a JEE-4X vacuum evaporator. The vacuum is less than 1.33 × 10⁻³ Pa, specimen temperature: -100 °C~-110 °C. TEM observation was conducted on a JEM-100 CX(II) electron microscope.

2 Results and Discussion

In previous literatures, usually single-chain cinnamic acid derivatives were thought not to undergo photodimerization in organic solvents^[21]. However, we found that bolaamphiphile HDC can be photodimerized in CHCl₃, as revealed both by FT-IR(Fig.1) and UV (Fig.2) measurements.

The CHCl₃ solution of HDC is clear and homogeneous. After irradiation, the characteristic IR absorption bands of the monomer at 977 cm⁻¹(CH-deformation mode of *trans*-alkenes) and 1639 cm⁻¹ (C=C stretching mode) disappeared. In addition, the absorption at 1707 cm⁻¹(CO-conjugated stretching mode) was replaced by a band at 1743 cm⁻¹. The new formed band corresponds to the isolated C=O stretching mode of the ester group. In agreement, the UV absorbance at the maximum of the monomeric HDC (310 nm) decreased with irradiation time. We further examined the ¹H NMR spectrum of the dimerized HDC and it was shown in Fig.3. It can be seen from Fig.3 that after 16 h UV irradiation, the characteristic C=C—H at 7.6 and 6.4 disappeared, which also indicated the occurrence of photodimeriza-

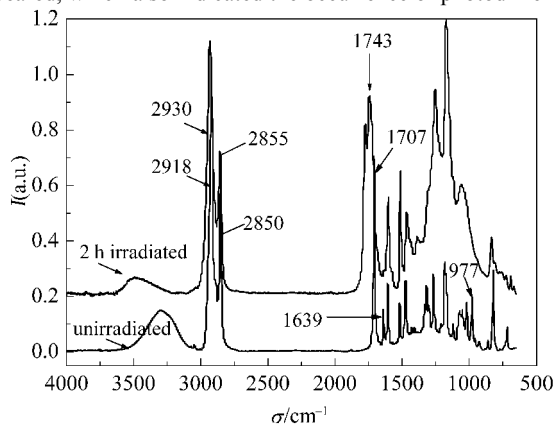


Fig.1 FT-IR Spectral changes induced by UV-irradiation for HDC in chloroform

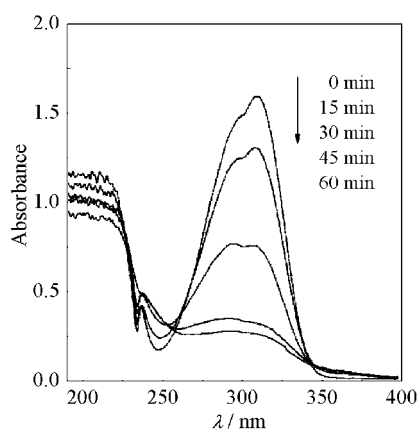


Fig.2 UV Spectral changes induced by UV irradiation for HDC in chloroform

tion of HDC in CHCl_3 . This result indicated that H-aggregates of HDC were formed in CHCl_3 , which is totally different from the previous researches that single chain cinnamic acid derivatives can not dimerize in CHCl_3 solutions.

In addition, the aggregation capability is also obviously changed after photo-induced process. HDC is insoluble in water while suspension can be formed for HDC in 5% ~ 30% (V/V) ethanol/water mixed solvents. Before UV irradiation, no aggregates were found by TEM in the 20% ethanol/water dispersions of HDC. However, after the solvent being evaporated from the

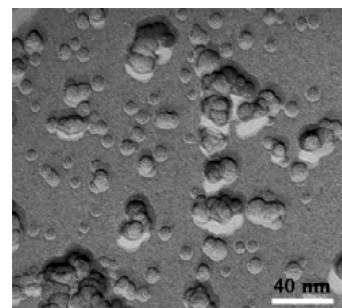


Fig.4 TEM image of the dimerized HDC in 20% ethanol/water (V/V) suspension

irradiated HDC/ CHCl_3 solution, the solute was redispersed into 20% ethanol/water mixed solvents and vesicles with radius of 5~15 nm were clearly seen (Fig.4), demonstrating that the photodimerized molecules have stronger vesicle-forming ability. This may be attributed to the formation of double chain structure of the photodimerized HDC molecules, since the double chain structure of amphiphiles is in favor of the formation of different sorts of aggregates^[7, 15]. As mentioned in the previous text, the former references have reported that single chain cinnamic acid derivatives cannot photodimerize in organic solvents while double chain or polymer cinnamic acid derivatives (with cinnamic acid groups in each chain) will dimerize upon UV irradiation, owing to the high local concentration of the reactive moieties within these molecules^[23-24].

It is well known that the orderly packing of the reactive center is the key factor for the occurrence of photodimerization of cinnamic acid derivatives^[23-24]. From Fig.1, we can find that the symmetric and asymmetric vibration appeared at 2850 and 2918 cm^{-1} respectively, indicating the ordered zigzag stacking of methylene group of HDC molecules^[25-27]. Thus the orderly packing of hydrocarbon skeleton of HDC makes the photo-reactive centers close to each other, and leads to the occurrence of photodimerization of HDC in chloroform. It is notable that after irradiation the CH_2 asymmetric and symmetric vibronic peaks moved to 2930 and 2855 cm^{-1} respectively, which is corresponding to the disordered state of the hydrocarbon chains^[25-27]. The wave-number variation may be accredited to the following factors: 1) the ring tension of the newly formed four-center ring is so strong that the ring will be deformed; 2) the hydrocarbon chains from different molecules will adopt preferential conformation around the four-center ring. The above factors will make the former orderly packing of HDC molecules (before UV irradiation) impossible (See scheme 2).

HDC photodimerization reaction experiments were also performed in other organic solvents. It is notable that the UV absorbance of HDC in tetrahydrofuran, ethyl acetate and carbon tetrachloride also decreased with irradiation time (Fig.5). In contrast, UV spectra in acetone, isopropanol and *n*-butanol did not

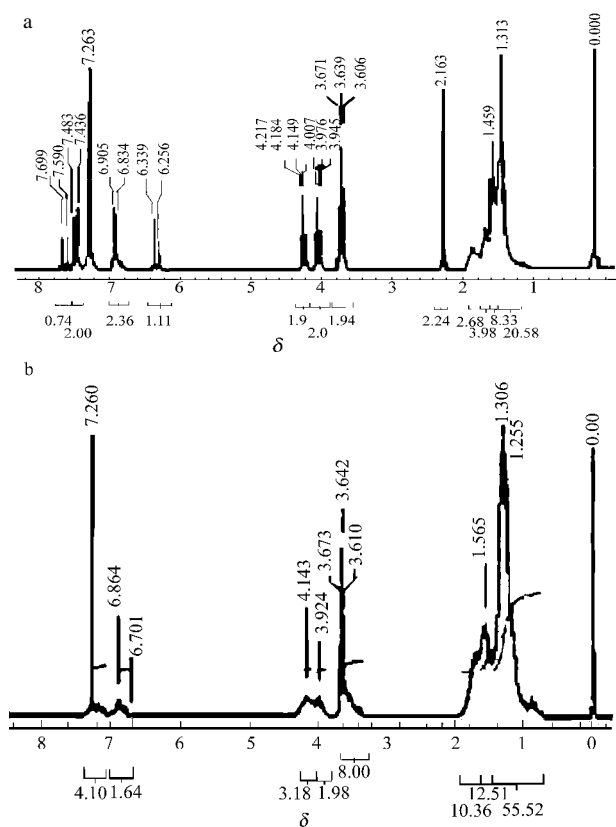
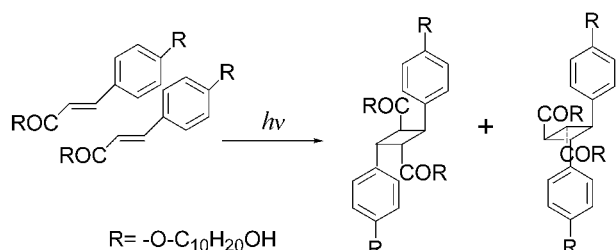


Fig.3 ^1H NMR spectra of HDC before (a) and after 16 h UV irradiation (b)



Scheme 2 Dimerization of HDC

change upon irradiation. The IR spectra also showed similar results. In Fig.6, it is clear that upon 2 h irradiation, the characteristic monomeric bands of HDC in tetrahydrofuran, ethyl acetate disappeared, but that in isopropanol kept unchanged. The experimental results about the photoreaction of HDC in organic solvents after UV irradiation were shown in Table 1.

It was worth to note that the photoreaction of HDC occurred in solvents with smaller values of dielectric constants; on the contrary, no dimerization was found in solvents with larger values of dielectric constants. This indicates that strong interaction existed between molecules and the solvents with higher dielectric constants, which leads to the HDC molecules separated and the photodimerization then forbidden. On the contrary, weaker interaction between molecules and solvents with lower dielectric constants made the close packing of two cinnamyl reactive centers possible, which causes the occurrence of dimerization in the organic solution.

It is also found that the dielectric constant values of the sol-

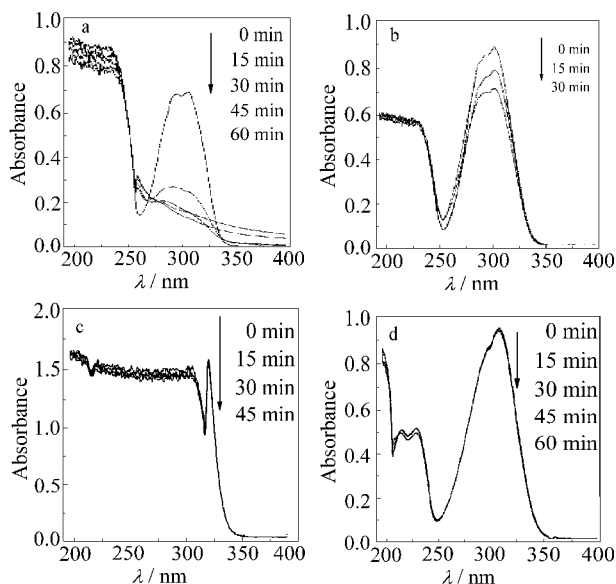


Fig.5 UV Spectra of HDC in different organic solvents under UV irradiation

The digital numbers beside the arrow represent the UV irradiation time. a) in carbon tetrachloride; b) in ethyl acetate; c) in acetone; d) in *n*-butanol. It was seen that the absorbance decreased apparently in a) and b) while they kept stable in c) and d).

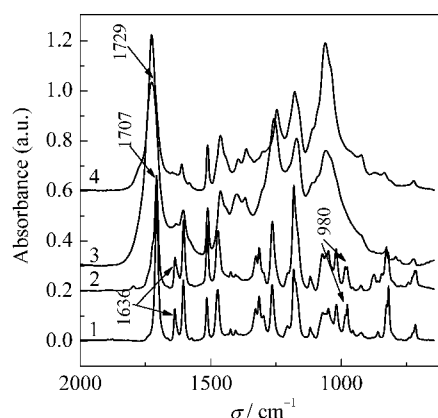


Fig.6 IR spectra of HDC in different organic solvents after UV irradiation

1) dichloromethane; 2) isopropanol; 3) ethyl acetate; 4) tetrahydrofuran

Table 1 The photoreaction of HDC in organic solvents with different dielectric constants

Solvent	Dielectric constants*	Reaction
Acetone	20.7	-
Isopropanol	18.3	-
<i>n</i> -Butanol	17.5	-
Dichloromethane	9.08	-
Tetrahydrofuran	7.58	+
Ethyl acetate	6.02	+
Chloroform	4.81	+
Carbon tetrachloride	2.24	+

-: no photoreaction occurred; +: photoreaction was observed

* from Lange's Handbook of Chemistry [28]

vents also influence the rate of the photo reaction in these systems. For example, the UV absorbance of HDC in CHCl₃ only decreased 22% after 15 min UV irradiation(Fig.2), while the absorbance in carbon tetrachloride (Fig.5 a) decreased 67% after the same irradiation time. Fig.7 illustrated the UV absorbance decreases of HDC in different organic solvents upon 15 min UV ir

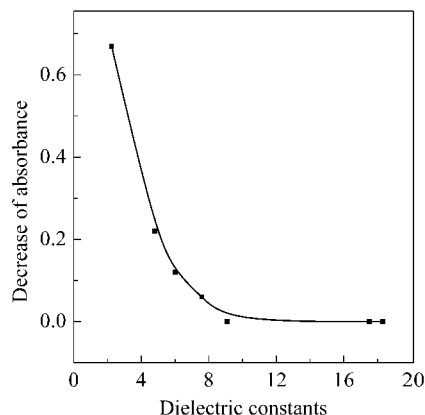


Fig.7 The relationship between the decrease of UV absorbance and the dipole moment of solvents

The concentration of HDC: $6.3 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$

radiation. It is clearly shown that the photoreaction in organic solvents will be faster with the decrease of the dielectric constants of the solvents when the dielectric constants of the solvents are smaller than 9.0. This result indicates that the interaction between solvent and solute molecules is a key factor to the photoreaction in the cinnamic acid derivative systems. It is valuable in expanding the photodimerizing reaction of cinnamic acid derivatives to the organic systems.

3 Conclusion

A new single chain photoreactive bolaamphiphile HDC containing cinnamic group was synthesized. UV and IR spectra revealed that the single chain HDC molecules dimerized in chloroform, carbon tetrachloride, ethyl acetate and tetrahydrofuran, while not in some other organic solvents, such as acetone, isopropanol *et al.* The photodimerization was closely related with dielectric constants of solvents. The dimerized HDC self-organized into globular vesicles in the 20% ethanol/water (V/V) suspensions. This may be attributed to that the double chain structure of the photodimerized product is in favor of molecular self-assembly.

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