



## Original article

# Interfacial assembly and host–guest interaction of anthracene-conjugated L-glutamate dendron with cyclodextrin at the air/water interface



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## ABSTRACT

The interfacial assembly of photo-induced dimerization of atypical anthracene-containing amphiphilic dendron and host–guest interaction with  $\gamma$ -cyclodextrin has been investigated. It has been proved that even without long alkyl chain the amphiphilic dendron could still form stable Langmuir monolayer at the air/water interface. Through the host–guest interaction,  $\gamma$ -cyclodextrin can be used to encapsulate two headgroups of amphiphilic dendron in the antiparallel direction. However, the formed host–guest complex was sensitive to the surface pressure. Slight compression of surface pressure led amphiphilic dendron to reassemble into nanofibers through the strong  $\pi$ – $\pi$  stacking between headgroups. On the other hand, under *in situ* irradiation, the amphiphilic dendron was stabilized in the cavity of  $\gamma$ -cyclodextrin through headgroup dimerization and the host–guest complex further irregularly aggregated to nanoparticles. Meanwhile,  $\gamma$ -cyclodextrin, as a silencer, blocked the supramolecular chirality transfer. Our conclusion was demonstrated through UV/vis, FT-IR, CD spectrum and AFM images, respectively.

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## 1. Introduction

Since the concept of host–guest chemistry was firstly proposed by Donald J. Cram [1], the research based on the host–guest chemistry has rapidly developed and attracted great interest [2–7]. Cyclodextrin is a well-known class of host molecules and has advantages in its chiral cavity over crown and calyx[n]arene derivatives and therefore, cyclodextrin can be used to fabricate many chiral supramolecular systems [8]. Due to the specific shape of cyclodextrin hydrophobic cavities, cyclodextrin is capable of encapsulating small molecules. As reported, gamma-cyclodextrin ( $\gamma$ -CyD) with eight D-glucopyranose units, respectively, linked by  $\alpha$ -(1,4) linkages can form the host–guest complex with pyrene, anthracene, phenanthrene [9–11] or steroidal compounds [12]. The host–guest interaction between cyclodextrin and small molecules had wide range of applications, such as promoting organic reactions [13,14] and the stereoselectivity of photoreactions [15–18], constructing stimuli-responsive supramolecular assemblies [19], fabricating functional materials [20] and

mimicking the natural enzymatic systems [21]. On the other hand, the Langmuir–Blodgett (LB) technique is an important two-dimensional method to fabricate supramolecular ultra-thin films and showed some merits to regulate the self-assembly of amphiphiles at the air/water interface [22–25]. Some well-organized chiral supramolecular assemblies from achiral molecules containing cyclodextrins have been constructed through the host–guest interaction on the interface [26]. However, there are still few reports about the two-dimension interfacial self-assembly of atypical amphiphiles without long alkyl chains and *in situ* photoreactions in the hydrophobic cavity of cyclodextrins [27,28]. In this article, we designed a series of isomeric anthracene-containing L-glutamate dendrons, which differ in the substituted position on the anthracene ring. With the appropriate balance between the focal and peripheral groups, the amphiphilic dendron, *N*-(2-anthracenecarboxyl)-1,5-bis(L-glutamic acid diethylester)-L-glutamic diamide (2-AGE), could form the stable monolayer with  $\gamma$ -CyD through the host–guest interaction and photodimerization of 2-AGE dendron occurred *in situ* inside the cavities of  $\gamma$ -CyD. In contrast, due to the differences of substituted sites, the host–guest complex was not obtained between *N*-(9-anthracenecarboxyl)-1,5-bis(L-glutamic acid diethylester)-L-glutamic diamide (9-AGE) and  $\gamma$ -CyD.

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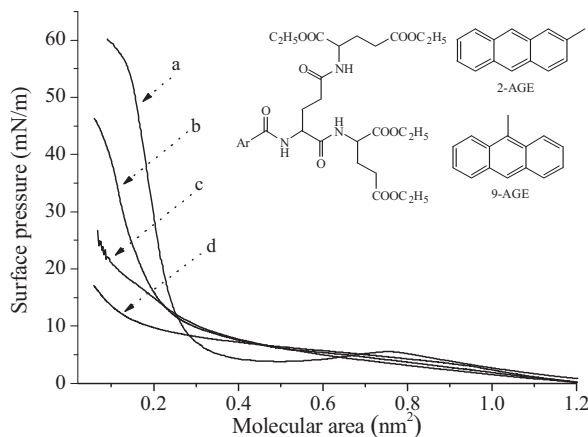
E-mail address: [liumh@iccas.ac.cn](mailto:liumh@iccas.ac.cn) (M.-H. Liu).

## 2. Experimental

The synthesis of 2-AGE and 9-AGE was reported by us previously [29].  $\gamma$ -CyD was purchased by Sigma–Aldrich. Deionized water used in our experiment was purified by Millipore Q system (18.2 M $\Omega$  cm). Chloroform used as spreading solvent is of analytical grade. The ultra-thin films of these dendritic compounds were fabricated by spreading 100  $\mu$ L chloroform solution (ca. 0.326 mmol/L) on pure water, or aqueous solution containing 1 mmol/L  $\gamma$ -CyD for 1 h. The surface pressure–area ( $\pi$ -A) isotherms were measured with a KSV film balance with a compression speed of 12 cm<sup>2</sup>/min at 20.0  $\pm$  0.2  $^{\circ}$ C. In order to observe the surface morphology, the LB films were deposited onto a newly cleaved mica surface at different surface pressures (0 mN/m, 5 mN/m and 15 mN/m) and the AFM images were measured with a Digital Instrument Nanoscope III Multimode system (Santa, Barbara, CA) with a silicon cantilever using the tapping mode. All the AFM images are shown in the height mode without any image processing, except flattening. The temperature was kept at 20  $^{\circ}$ C when these films were transferred. The LS films were produced by transferring the monolayer onto quartz and CaF<sub>2</sub> plates at a constant surface pressure of 5 mN/m through a horizontal lifting method. The UV/vis spectra were recorded with a JASCO UV-530 system. Circular dichroism (CD) spectra of the films were attained on a JASCO J-810 CD spectrometer. In the process of measurement, the films were placed perpendicular to the light path and rotated within the film plane to avoid polarization-dependent reflections and eliminate the possible angle dependence of the CD signals [30]. All the CD spectra are reproducible and no significant variations are observed for two identical samples. FTIR spectra were obtained on a Jasco FT/IR-660 plus spectrophotometer. The measurement was carried out over the scanning range from 1000 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Furthermore, *in situ* UV irradiation method used in our experiment was performed on the spreading films on  $\gamma$ -CyD surface by a 25 W UV lamp (365 nm) for 1 h, which was hung over the film at a distance of 15 cm.

## 3. Results and discussion

Fig. 1 shows the  $\pi$ -A isotherms of the dendritic compounds spread on a different subphase and with different methods. For 2-AGE spread on aqueous solution containing  $\gamma$ -CyD, the isotherm showed an onset surface pressure at 1.2 nm<sup>2</sup> per molecule. With the increasing of the surface pressure and although the L-glutamate dendron has no substituted alkyl chains, it can still form the stable Langmuir monolayer at the air/water interface. In comparison with



**Fig. 1.** Surface pressure–area ( $\pi$ -A) isotherms of the dendron compounds at 20  $^{\circ}$ C (a) 2-AGE, on pure water; (b) 2-AGE, on  $\gamma$ -CyD; (c) 9-AGE, on  $\gamma$ -CyD; (d) 2-AGE, on  $\gamma$ -CyD with *in situ* irradiation. The concentration of  $\gamma$ -CyD subphase is 1 mmol/L. The inset is the molecular structure of 2-AGE and 9-AGE.

the 2-AGE spreading on water which has been investigated previously [29], we found that an inflection point appearing at about surface pressure 8 mN/m on water was nonexistent when the subphase was changed to  $\gamma$ -CyD. These different isotherms indicated that there was an interaction between 2-AGE molecules and  $\gamma$ -CyD. However, after *in situ* irradiation of the process for 1 h, the isotherms showed a bad surface activity with the maximum surface pressure less than 20 mN/m. It was obviously know that *in situ* irradiation damaged the hydrophobic effect between the anthracene rings. With the increase of irradiation time, the hydrophobicity of the ultrathin films decreased. Another dendritic molecule 9-AGE also showed a slight surface activity at a very lower molecular area, indicating that 9-AGE did not form a stable monolayer on  $\gamma$ -CyD subphase.

To further disclose the differences in these systems, the ultrathin films of dendritic molecules were deposited on the mica surface by a vertical up-take with a speed of 2 mm/min and their morphology was detected. We have divided the isotherms into three pressure regions of film deposition. Region I is for the monolayer at a surface pressure of ca. 0 mN/m. Region II corresponds to the middle part of the isotherm where the surface pressure is between 3 mN/m and 5 mN/m. Region III represents the region above the second transition. Fig. 2A–C shows the AFM images of 9-AGE deposited from the  $\gamma$ -CyD subphase at different regions. The nanodots and nanosheets through the stacking of the nanodots were observed at Region I. With the increasing of surface pressure, the nanodots closely gathered to form the nanoparticles at Regions II and III, which suggested that there was no change on self-assembly of 9-AGE. When 2-AGE was spread on  $\gamma$ -CyD subphase, nanosheet structures with some nanodots were also formed at Region I. To our surprise, 2-AGE assembled into curly nanofiber structure for the film deposited at Region II. The nanofibers have an average height of about 1.7 nm as well as extending to several micrometers, which is similar to the morphology of 2-AGE deposited on pure water [27]. However, some nanodots were also observed at this state. When it compressed the monolayer further to 15 mN/m, the nanofibers stacked densely and the nanoparticles decreased. This result indicated that  $\gamma$ -CyD actually had influence on the self-assembly of 2-AGE at Region I, but the effect was dominated by surface pressure. Interestingly, all the nanofiber structures obtained at higher surface pressure had disappeared, and only remaining nanoparticles after *in situ* irradiation. The size of the nanoparticles is about 0.2–0.5  $\mu$ m and the average height is about 2 nm. With the increases of surface pressure, the nanoparticles arranged tightly and even overlapped.

In order to confirm the interaction between 2-AGE and  $\gamma$ -CyD, FT-IR spectra of LS films were measured (Fig. 3A). In the FTIR spectra of 2-AGE LS films obtained on  $\gamma$ -CyD subphase, strong vibration bands are observed at 3298, 1730, 1638, and 1539 cm<sup>-1</sup>, which were assigned to N–H stretching vibration, ester carbonyl stretching, and amide I and II, respectively. Compared with FTIR spectra of 2-AGE LS films fabricated under *in situ* irradiation and  $\gamma$ -CyD, a broad peak at 3356 cm<sup>-1</sup> was obviously observed due to the overlap of N–H and O–H stretching vibration, and further provided evidence that  $\gamma$ -CyD existed at the LS films. Moreover, the appearance of vibration band at 1474 cm<sup>-1</sup> evidently confirmed the formation of anthracene dimers, as was reported for hydrocarbon cages [31,32]. Additionally, the amide II band was broaden by the formation of dimers and amide I was shifted to higher wavenumbers, suggesting the weaken hydrogen bonds with *in situ* irradiation [33] in the LS films. In the UV/vis spectra of 2-AGE LS films (Fig. 3B), two absorption peaks of the anthracene group at 249 nm and 414 nm were observed, indicating that H-aggregates of the chromophore were in the film state [29]. Moreover, the CD spectrum with a positive Cotton effect in the

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