

# Unprecedented parallel packing of unsymmetrical bolaamphiphiles driven by $\pi$ - $\pi$ stacking of cinnamoyl groups†

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The self-assembly and molecular packing mode of a novel, unsymmetrical bolaamphiphile, sodium 4-(6-hydroxyhexyloxy) cinnamate (SHHC) was studied. Tube-like structures were obtained in SHHC aqueous solution at pH 9.2. Upon UV irradiation, the SHHC molecules in the system were found to undergo four-center-type photocyclodimerization and photoisomerization. The combination of IR, XRD and Zeta potential results suggested the formation of a tail-to-tail type bilayer membrane structure: the SHHC molecules stretched upright with the cinnamate headgroups toward the outside in each layer, whereas the tail OH groups of two layers remained inside and formed interlayer hydrogen bonds. This parallel packing mode of SHHC molecules in the membrane was also confirmed by the pH-induced self-assembly transition. With increasing pH from 9.2 to 12.0, the low-curvature tubes transformed into spherical vesicles, which was in line with the increased outer leaflet head group area as increasing pH. Our results demonstrated that upon careful molecular design, the orientation of unsymmetrical bolaamphiphiles can be controlled;  $\pi$ - $\pi$  interactions between cinnamoyl groups were found to be strong enough to drive the formation of well-oriented molecular assemblies.

## Introduction

Over the past years, self-organized structures of bolaamphiphiles have attracted increasing attention owing to their rich morphologies.<sup>1-4</sup> So far, a full spectrum of molecular assemblies has been observed in the systems of bolaamphiphiles, including micelles,<sup>5,6</sup> vesicles,<sup>7,8</sup> lamellae,<sup>9</sup> ribbons,<sup>10</sup> fibers<sup>11-13</sup> and tubes.<sup>14-19</sup> Among this work, the relationship between the morphology of the self-assembled structures and the chemical structure of unsymmetrical bolaamphiphiles is of special interest. Different from those symmetrical analogues with two identical head groups attached to each end of a hydrophobic chain, the unsymmetrical bolaamphiphiles have two different head groups, which are usually of different sizes and properties.<sup>20</sup> Such molecular structures are supposed to readily form unsymmetrical monolayer lipid membranes (MLM) with different inner and outer leaflets. A few successful examples have been achieved in this aspect.<sup>7,12,15,21,22</sup> However, most unsymmetrical bolaamphiphiles are found to form symmetrical MLM due to the favorable antiparallel packing of the molecules.<sup>9,10,23-25</sup> So far, the delicate manipulation of the molecular packing motif is still a challenge that restricts the development of the study on the unsymmetrical bolaamphiphiles. In order to have a better understanding on the molecular structure that determines the packing mode of the molecules in the membrane formed from unsymmetrical

bolaamphiphiles, we are interested to regulate the molecular packing mode *via* proper molecular design.

Inspired by the commonly seen antiparallel packing of unsymmetrical bolaamphiphiles, we realized that a strong interaction between the homohead-groups must be introduced to obtain a parallel packing of the unsymmetrical bolaamphiphiles. Moreover, in order to facilitate the examination of the symmetry of the membrane formed by the designed molecules, the incorporation of an easy-to-check functional group in proximity to one head of the unsymmetrical bolaamphiphiles is necessary. Taking these two considerations together, we designed a simple unsymmetrical bolaamphiphile that contains a cinnamate group. Cinnamate groups, which are photo responsive as well as pH sensitive, are able to undergo four-center-type 2 + 2 photocyclodimerizations when two such groups are in the range of 3.6–4.1 Å.<sup>26-28</sup> This reaction is commonly observed with cinnamate acid derivatives in a crystalline state where the cinnamoyl groups are parallel to each other and in close proximity. This is also applicable when amphiphiles containing cinnamoyl groups self-assemble into ordered molecular assemblies, such as vesicles and LB films,<sup>29-32</sup> since parallel packing of the molecules in these structures is the only choice. In our design, sodium cinnamate is used as one of the polar heads of the unsymmetrical bolaamphiphile, where the  $\pi$ - $\pi$  stacking between the cinnamoyl groups is expected to drive the parallel packing of the molecules. The other small polar head we choose for the molecule is OH, to use its weak polarity. These two head groups are connected *via* an alkyl chain consisting of 6 carbons, to weaken the hydrophobic interaction contributed by the alkyl chains so as to highlight the strength of the  $\pi$ - $\pi$  stacking interaction between those cinnamoyl groups.

Therefore, the aim of this paper is to investigate the molecular packing and self-assembling behaviors of the delicately designed

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unsymmetrical bolaamphiphile, sodium 4-(6-hydroxyhexyloxy) cinnamate (SHHC). We are curious to find out whether the  $\pi$ - $\pi$  stacking of cinnamate groups is strong enough to drive a parallel packing of the SHHC molecules in their self-assemblies. TEM, XRD, UV, IR and pH variation experiments were used to examine the system. It was pleasing to note that parallel packing of SHHC molecules indeed took place. Our results demonstrate that through proper molecular design, control of the packing mode of unsymmetrical bolaamphiphiles can be easily achieved, which paves the way for fabricating unsymmetrical molecular assemblies on a large scale.

## Experimental section

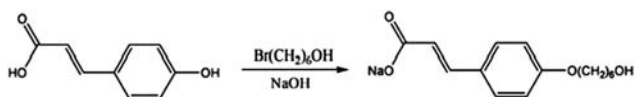
### Materials

**Synthesis of SHHC.** 1-bromo-6-hydroxyhexane was prepared from the corresponding diol and hydrobromic acid<sup>33</sup> (Beijing Chemical Co. A.R.). A mixture of 1-bromo-6-hydroxyhexane (2.18 g, 0.012 mole) and 4-hydroxycinnamic acid (1.64 g, 0.01 mole) in 40 cm<sup>3</sup> ethanol was added into 10 cm<sup>3</sup> of 2 mol L<sup>-1</sup> NaOH aqueous solution. This mixture was allowed to react for 24 h under magnetic stirring at 60 °C. Then the reaction mixture was cooled and filtered to collect solid, brownish products. The crude product was purified by re-crystallization from ethanol-water (volume ratio 4/1) 5 times to obtain a white solid (1.04 g). Final yield: 36%. <sup>1</sup>H NMR (D<sub>2</sub>O, 200MHz):  $\delta$  (ppm): 7.45 (d, 1 H), 7.2 (d, 2 H), 6.9 (d, 2 H), 6.3 (d, 1 H), 4.0 (t, 2 H), 3.5 (t, 2 H), 1.6–1.7 (m, 2 H), 1.3–1.5 (m, 6 H). Elemental analysis, calculated: C: 62.93%, H: 6.64%; found: C: 62.75%, H: 6.37%.

### Methods

**Preparation of samples.** The solutions were obtained by dissolving the solid SHHC powder in 0.01 mol L<sup>-1</sup> borax buffer solution (pH 9.2) and ultrapure water (Milli-Q, 18.2 M $\Omega$  cm). Upon addition of NaOH aqueous solution, the pH of SHHC in ultrapure water was adjusted to 12.0 using a SevenMulti type pH meter with InLab Semi-Micro electrodes (Mettler Toledo, Switzerland). These samples were vortex mixed and allowed to equilibrate for at least one week at 25 °C. All analytical measurements were performed at 25 °C.

**Dynamic light scattering measurements.** Light scattering measurements were performed with a Brookhaven light scattering apparatus, equipped with a 400 mW argon ion laser operating at a wavelength of 532 nm. A refractive index matching bath of filtered *cis*-decalin surrounded the cylindrical scattering cell, and the temperature was controlled at 25  $\pm$  0.5 °C using a Haake C35 thermostat.



**Scheme 1** The synthetic pathway to the asymmetrical bolaamphiphile SHHC.

**Transmission electron microscopy (TEM).** One drop of the sample dispersion was placed onto a formvar-coated copper grid and the excess liquid was sucked away by filter paper. Then one drop of staining agent (2% uranyl acetate aqueous solution) was dropped onto the sample grid by the same process as above. Negatively stained TEM micrographs were obtained with a JEOL-100 CX II transmission electron microscopy.

**UV-vis measurements.** The SHHC solutions containing cinnamoyl moieties in quartz test tubes were irradiated using a high-pressure Hg lamp system of 500 W. After different irradiation times, the resulting diluted solutions (0.1 mmol dm<sup>-3</sup>) were analyzed at 25 °C by an UV-vis spectrometer equipped with a thermostatic bath.

**Infrared (IR) spectra.** The SHHC solutions in test tubes were put into the vacuum drying equipment for 48 h. Then microscopic Fourier transform IR spectra were collected with a Nicolet iN10 MX spectrometer (Thermo Scientific, America) operating in the range of 4000 to 650 cm<sup>-1</sup>.

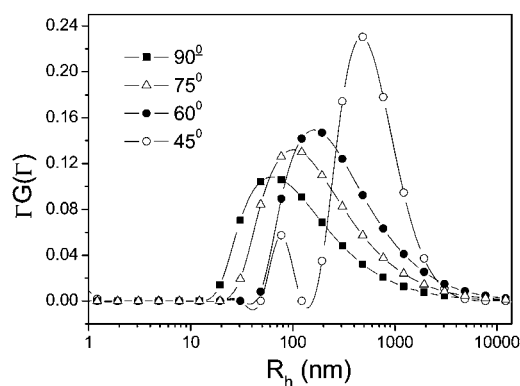
**X-ray diffraction (XRD).** Self-supported cast films for the XRD studies were prepared by dispersing the sample solutions in pre-cleaned glass slides. Then the slides loaded with sample solutions were dried over silica gel overnight to obtain a film of the self-assembled structures. Reflection XRD studies were carried out for the film with a model XKS-2000 X-ray diffractometer (Scintaginc). The X-ray beam was generated with a Cu anode, and the wavelength of the  $K_{\alpha 1}$  beam was 1.5406 Å. The X-ray beam was directed toward the film edge, and the scanning was done up to a  $2\theta$  value of 10°.

**Zeta potential measurement.** Zeta potentials were measured using a temperature-controlled ZetaPALS Zeta Potential Analyzer (Brookhaven Instruments Corporation).

## Results and discussion

### TEM observation

10 mM SHHC is insoluble in water at room temperature. Upon heating, the majority of the solids can be solubilized, but some



**Fig. 1** The hydrodynamic radii distribution of the self-assembled structures in 0.01 mol L<sup>-1</sup> SHHC solution measured at pH 9.2, 25 °C, in the presence of 10 mM NaCl.

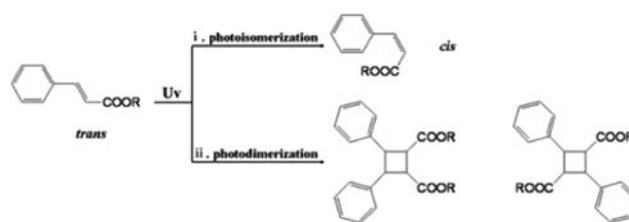
insoluble solids are still seen on the bottom of the test tube. However, at pH above 9, all the solids disappear and the system becomes a bluish, homogeneous phase at room temperature. Dynamic light scattering experiments indicated the presence of polydispersed large particles. As demonstrated in Fig. 1, the average hydrodynamic radius increases from 64 nm to 485 nm as the scattering angle changed from 90 to 45°, suggesting tube or rod like structures were formed.

The TEM micrographs revealed (Fig. 2a) formation of a large amount of tubular structures in this 10 mM SHHC solution. Their hollow nature can be clearly visualized in Fig. 2b. In fact, some separate vesicles were observed along with these tubes (See Fig. S1 in the ESI†). In addition, the wall thickness of the tubes, which can be obtained from Fig. 2b, is 3.7 nm. This value is about two times the stretched length of the SHHC molecule, which indicates that the walls of the tubes are formed by a bilayer of SHHC molecules. This will be discussed later, in combination with XRD results. Such tubular structures can be well repeated and observed easily in a full view of the microscope (See Fig. S1–2 in the ESI†). The tubes run several micrometres in length and 50–100 nm in diameter. Most tubes are closed at both ends, but in some cases open ends are observed as well. It seems that the curvature of the tubes is not homogenous. It was found that in some places the tubes are squeezed into vesicular structures. The heterogeneous curvature endows the tubes with good flexibility. These observations suggest that the unsymmetrical bolaamphiphilic SHHC is able to self-assemble into membrane structures in aqueous solution.

### Photosensitive self-assembly of SHHC

Next, we were interested in examining the molecular packing mode, namely, parallel or antiparallel orientation of the SHHC molecules in the membrane. To achieve this, the solution with tubular structures was exposed to UV irradiation. In principle, two photoreaction pathways are possible for the cinnamoyl units:<sup>34</sup> (i) *trans*–*cis* photoisomerization, and (ii) photocyclization (so-called photodimerization), as illustrated in Scheme 2.

*Cis*–*trans* isomerization occurs in all cases, whereas photodimerization only occurs in molecular assemblies where the two



Scheme 2 The photoreactions of the cinnamoyl moieties.

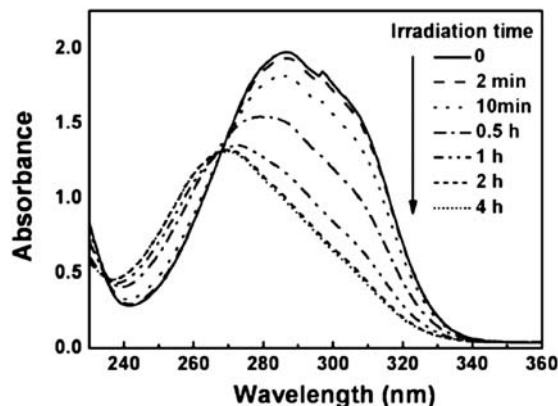


Fig. 3 UV absorption spectra with different irradiation times of 0.01 mol L<sup>-1</sup> SHHC solution at pH 9.2.

reactive C=C bonds are within a distance of 3.6–4.1 Å. The UV absorption spectra of the SHHC solution at various exposure times are shown in Fig. 3. Before UV irradiation, the SHHC solution exhibits an absorption maximum at 287 nm, which is ascribed to the absorption of cinnamoyl groups in the form of parallel packing.<sup>14</sup> The maximum absorption of noninteracting cinnamoyl groups in solution is usually observed above 310 nm; it is the occurrence of  $\pi$ – $\pi$  stacking in the parallel molecular array that leads to the blue shift of the absorbance band.<sup>15</sup> This UV result suggests that SHHC molecules indeed adopt parallel packing in the membrane. After irradiation, the intensity of the maximum at 287 nm decreases, meanwhile, the position of the maximum absorbance blue shifts to 270 nm. These changes can

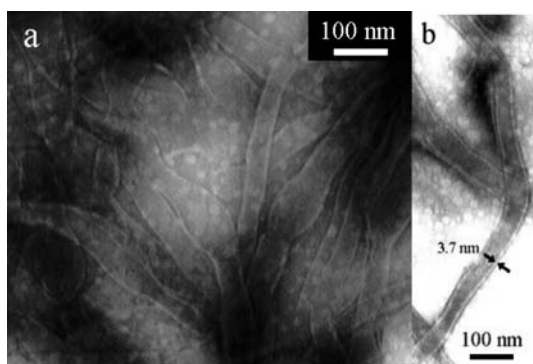


Fig. 2 TEM images of the aggregates formed in 0.01 mol L<sup>-1</sup> SHHC solution at pH 9.2 before UV irradiation. (a) Represents a general view, whereas (b) demonstrates the clearer tubular structure with a wall thickness of 3.7 nm.

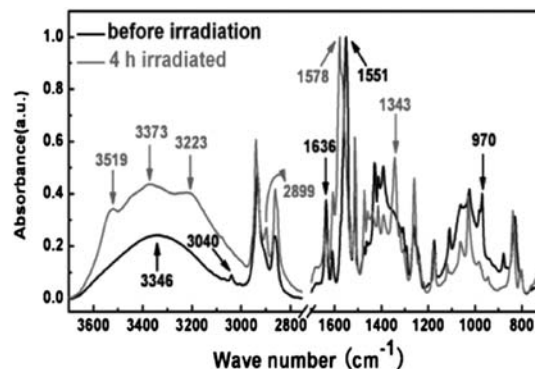


Fig. 4 IR spectra of 0.01 mol L<sup>-1</sup> SHHC solution before and after UV irradiation at pH 9.2.

be attributed to a loss of conjugation in cinnamoyl chromophores, which is due to the occurrence of photoreactions of the cinnamoyl groups in the tubular membrane of SHHC.<sup>16</sup> No noticeable changes were observed upon further prolongation of the irradiation time to more than 4 h, suggesting completion of the photo reaction in the system within 4 h.

The photodimerization was further confirmed by using IR spectroscopy. As seen in Fig. 4, striking changes of the vibration of carbonyl groups were observed. Before irradiation, the conjugated carbonyl groups in the form of sodium salt ( $-\text{COONa}$ ) have a strong stretching vibration band at  $1551\text{ cm}^{-1}$ .<sup>35</sup> Upon UV light irradiation, this band shifts from  $1551$  to  $1578\text{ cm}^{-1}$ , indicating the loss of conjugation of the carboxyl group. Moreover, the intensities of the vinylenic  $\text{C}=\text{C}$  stretching vibration band at  $1636\text{ cm}^{-1}$  is significantly lowered, and the  $=\text{C}-\text{H}$  stretching and deformation vibration bands at  $3040\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  disappear after 4 h irradiation.<sup>36-42</sup> These are powerful proofs for the loss of the vinylenic  $\text{C}=\text{C}$  bond due to photodimerization. Meanwhile, the appearance of the stretching and bending vibration of saturated  $\text{C}-\text{H}$  of the cyclobutane at  $2899$  and  $1343\text{ cm}^{-1}$ ,<sup>37</sup> respectively, after UV irradiation, unambiguously confirms the occurrence of the photodimerization in the tubular membranes formed by SHHC molecules.

It is noteworthy that a weak vinylenic  $\text{C}=\text{C}$  stretching vibration at  $1638\text{ cm}^{-1}$  still exists after 4 h irradiation. This suggests that the SHHC molecules are not completely dimerized. Photodimerization can hardly be 100% in all of the cinnamate derivative membranes because the single molecules left among dimerized ones have no chance to be dimerized any more. In our case, the amphiphilic nature of the SHHC molecules allows equilibrium between the separate SHHC molecules and those self-assembled ones. Therefore, both the separated SHHC molecules and those left in the membranes after photodimerization should be responsible for the uncompleted dimerization. Upon analysis of the integral area of the  $\text{C}=\text{C}$  vibration band using the  $\text{CH}_2$  symmetrical stretching vibration band at  $2863\text{ cm}^{-1}$  as a reference (which doesn't change upon UV irradiation), the degree of photodimerization is about 58%.<sup>36</sup> This dimerization yield is noticeably high compared with that of other cinnamate acid derivatives in similar dilute solutions. For instance, one of the highest photodimerization efficiencies reported by Bassani and co-workers<sup>43</sup> for cinnamates in dilute solution is about 45%. The high efficiency of the photodimerization indicates that the array of SHHC molecules in the membrane is highly ordered.

It should be pointed out that the photoreactions significantly affected the conformation of the SHHC molecules. This is evidenced by the variation of the stretching vibration band of the hydrogen bonds. Before UV irradiation, the hydrogen bonds exhibit a strong, broad band at  $3346\text{ cm}^{-1}$ , indicating the presence of hydrogen bonds with an average bond length and angle; after UV irradiation, this band splits into three groups,<sup>44,45</sup> suggesting formation of three categories of OH groups due to the rearrangement of the molecular orientation after photoreaction. This change of the molecular conformation disfavors the self-assembly of SHHC molecules, which results in the break of the tubular structures (see Fig. S3 in the ESI†).

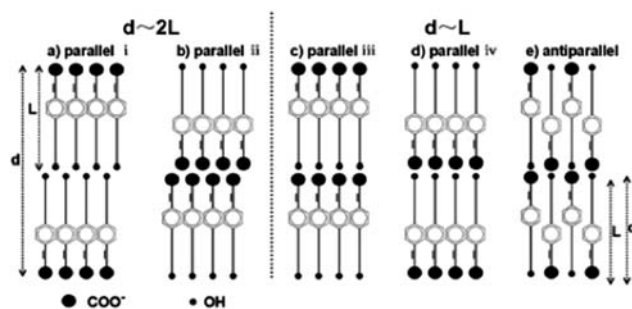
## Molecular packing in the membrane

The occurrence of photodimerization suggests that the cinnamoyl moieties of SHHC molecules are in a parallel mode. However, at this stage, we cannot tell exactly which molecular packing mode is present from those illustrated in Scheme 3. In order to find out the actual molecular arrangement in the membrane of the SHHC molecules, XRD experiments, which can obtain the membrane-stacking periodicity ( $d$ ), are required. It has been proved that the membrane structures can be well-preserved in casting films.<sup>16,18,46</sup> Therefore, the cast films of the SHHC solution was prepared and measured by XRD. Fig. 5 shows the XRD patterns of tubes dried on glass. The small-angle region shows the strong (001), (002), and (004) reflection peaks. The (003) reflection is very weak so that it is only discernible at high magnifications. These periodic diffraction peaks suggest the existence of well-defined lamellar structures.<sup>16,18,46</sup> According to the Bragg equation, the layer spacing is  $3.6\text{ nm}$ , which agrees very well with the TEM result given in Fig. 2b. Since the stretched molecular length of SHHC is  $1.8\text{ nm}$  (modelled by Chem 3D), this result indicates that double molecular layers are indeed formed in the membrane, in which the SHHC molecules take an upright, fully stretched conformation. In this regard, only two packing modes, namely Scheme 3a and b, are possible. Other modes in Scheme 3 give mono molecular layers.

Although both the packing modes in Scheme 3a and b are parallel packing, it is noteworthy that they are with different outmost groups. This allows us to differentiate these two packing modes by examining their surface electrical properties. Therefore, zeta potential measurements were carried out. The obtained zeta potential for the SHHC tubes at pH 9.2 is  $-50\text{ mV}$ , suggesting the outer leaflet of the tubes are composed of carboxyl groups. On the basis of the above experimental results, we can conclude that the SHHC molecules adopt mode Scheme 3a in the membrane, *i.e.*, parallel double molecular layers with the bulky cinnamoyl group towards the outside. Of course, we cannot exclude the possibility of a small fraction of SHHC molecules in the mode of 3b coexisting with 3a, but, in general, the bulky groups tend to be predominant in the outer leaflet.<sup>16</sup>

## PH responsive self-assembly of SHHC

The well-orientated molecular arrangement in the membrane allows for tailoring the self-assembled structures by pH



**Scheme 3** Possible molecular packing mode of SHHC molecules in the membrane. The large solid sphere (●) represents the carbonate group, whereas the small one (●) represents the hydroxyl group.

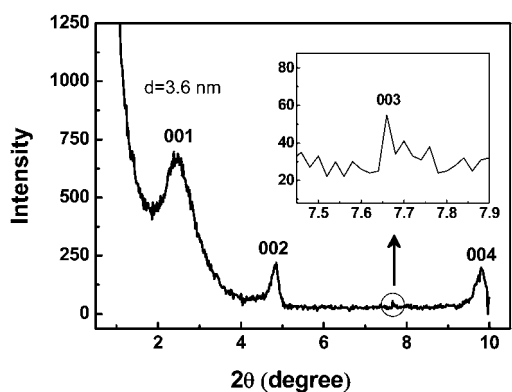


Fig. 5 XRD patterns of 0.01 mol L<sup>-1</sup> SHHC solution at pH = 9.2.

variations. As the pH of the system is increased to 12.0, predominant vesicular aggregates with diameters of 20–200 nm, together with some remaining tubes, were observed (Fig. 6a).

Meanwhile, dynamic light scattering results (Fig. 7) revealed the presence of smaller structures than those in the pH 9.2 systems. These structures are less angular dependent when compared with those in the pH 9.2 system, in line with the formation of predominant vesicles. The smaller angular dependence in this case may reflect the polydispersity of the vesicles and the remaining small fraction of tubular structures, as revealed in Fig. 6a.

The transition from tubes to vesicles with increasing pH is due to the increased repulsion between the cinnamate groups, which brought up the average head group area of the surfactants. Since the  $pK_b$  of SHHC is 5.4 (see Fig. S4 in the ESI†), the amount of cinnamate in the pH 12.0 system is about 1.20 times that in the pH 9.2 solution. That is, at pH 9.2, about 15% of the SHHC molecules are in the form of cinnamic acid, which is much more hydrophobic than those in the cinnamate form. Because the SHHC molecules in the acid form will be greatly enriched in the membranes, the fraction of SHHC in the cinnamate form in the membrane is less than 85%. Therefore, the fraction of SHHC in the cinnamate form in the pH 9.2 system is much smaller than that in the pH 12.0 system. This means that there will be considerable extra repulsion as the pH is increased from 9.2 to 12.0. According to Israelachvili,<sup>47</sup> the critical packing parameter ( $P$ ) is defined as  $P = v/la$ , where  $v$  is the volume of the hydrophobic tail of the surfactant molecule,  $a$  is the head group area at the aggregate/water interface, and  $l$  is the length of the hydrophobic chain. The curvature of the molecular assemblies

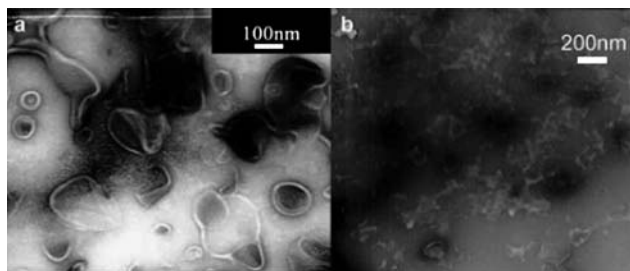


Fig. 6 TEM images of the aggregates formed in 0.01 mol L<sup>-1</sup> SHHC solution at pH 12.0 before (a) and after (b) 4 h UV irradiation.

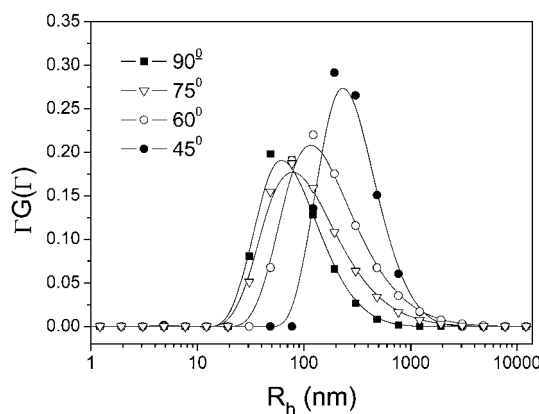


Fig. 7 The hydrodynamic radii distribution of the self-assembled structures in 0.01 mol L<sup>-1</sup> SHHC solution measured at pH 12.0, 25 °C.

increases when  $P$  decreases. This means that as the  $a$  value in our case increases with increasing pH,  $P$  is decreased, which favors formation of high-curvature self-assemblies. As we have discussed in previous work, vesicles have a smaller packing parameter than tubes.<sup>48</sup> That is why transition from tubes to vesicles occurs with increasing pH in the solution of SHHC.

As the pH rose to 12, the degree of photodimerization of SHHC was found to be 44%, lower than that at pH 9.2 (Fig. 8), which is in line with the parallel packing fashion of SHHC molecules. Because the repulsion between the head groups increases with increasing pH, it is more difficult for SHHC molecules to pack closely for the occurrence of dimerization. Again, the dimerization disfavors the presence of vesicles, but the lower efficiency of photodimerization allows some vesicles to remain even after 4 h photoreaction (Fig. 6b).

## Discussion

The driving force behind the parallel packing of SHHC molecules is  $\pi$ - $\pi$  stacking rather than hydrophobic interactions. The IR spectra suggest that the CH<sub>2</sub> groups are not densely packed, because the  $\nu_{as}$  and  $\nu_s$  appear at 2934 and 2863 cm<sup>-1</sup> (Table 1), respectively, before UV irradiation, which are in contrast with typical all-*trans* zig-zag conformations of methylene chains where the two vibrations occur at 2918 and 2847 cm<sup>-1</sup>.<sup>49–51</sup> Therefore,  $\pi$ - $\pi$  stacking is the dominant driving force for the formation of the membrane of SHHC. The strength of the  $\pi$ - $\pi$  stacking interaction between cinnamoyl groups hasn't been clearly elucidated in previous work, although it is well-known

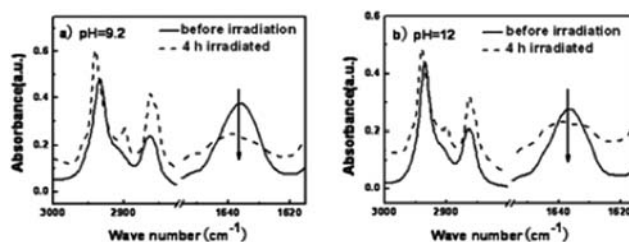
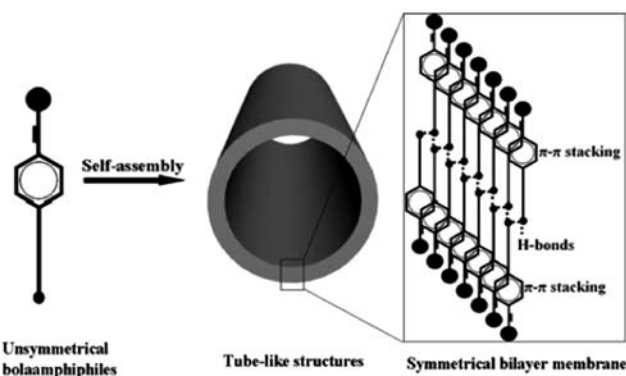


Fig. 8 IR spectra of 0.01 mol L<sup>-1</sup> SHHC solution before and after UV irradiation at different pH. (a) pH 9.2; (b) pH 12.0.

**Table 1** Characteristic infrared bands of the photosensitive SHHC molecules before and after UV irradiation

Frequency/cm <sup>-1</sup>		Assignment and description
Before	After	
3040	disappearance	=CH- stretching vibration
2934	2940	CH <sub>2</sub> asymmetric stretching vibration
2863	2863	CH <sub>2</sub> symmetric stretching vibration
None	2899	saturated C-H of the cyclobutane stretching vibration
1636	1638	vinylene C=C stretching vibration
1609	1607	C=C stretching vibration in benzene ring
None	1578	nonconjugated C=O in -COONa stretching vibration
1551	disappearance	conjugated C=O in -COONa stretching vibration
1515	1513	C=O stretching vibration in benzene ring
1475	1473	CH <sub>2</sub> bending vibration
None	1343	saturated C-H of the cyclobutane bending vibration
1262	1259	C-O-C asymmetric stretching vibration
1024	1029	C-O-C symmetric stretching vibration
970	disappearance	<i>trans</i> -vinylene C-H out-of-plane deformation

that these compounds undergo photodimerization in crystalline states and in ordered molecular assemblies. Previous reports all attribute the occurrence of photodimerization to the parallel packing of the cinnamoyl groups in the ordered molecular assemblies. In those works, the cinnamate acid derivatives are usually ordinary amphiphiles with long alkyl chains ( $n > 10$ ), where the strong hydrophobic interaction between the alkyl chains automatically drives the formation of molecular assemblies. Therefore, they can only adopt parallel packing of the cinnamoyl groups in the self-assembled structures. In those cases, no information about the 'self-assembly' of the cinnamoyl groups is noticed, and the occurrence of the photodimerization is considered as a regional confinement effect.<sup>31,52,53</sup> However, the SHHC molecule was designed in such a way that two orientations of the molecules in a membrane are possible; the alkyl chain between the bulky cinnamate group and the small hydroxyl group is short so that it does not generate appreciable



**Scheme 4** An illustration of the self-assembly and molecular packing mode of SHHC molecules in the membrane.

hydrophobic interactions. Therefore, our results demonstrate that the interaction between the cinnamoyl groups is so strong that it even overcomes the electrostatic repulsion between the COO<sup>-</sup> groups and drives the formation of well-oriented molecular assembly (Scheme 4). So, the occurrence of the photodimerization of cinnamoyl groups in any cinnamate acid derivatives is not only a regional confinement effect, but rather a kind of self-attraction behavior. To our knowledge, this is the first time a strong interaction between cinnamoyl groups has been found.

As a result of parallel packing of the SHHC molecules, the OH groups of the molecules are allowed to locate on the other side of the mono-molecular membrane. However, intramembrane hydrogen bonding is not favored due to the loose packing of the alkyl chain. As a result, intermembrane hydrogen bonding occurs. Therefore, a double layer membrane is formed (Scheme 4). Such hydrogen bonding is greatly affected by the photodimerization because of the change of the bond angle. This inspires us to investigate whether, if groups other than OH are used as the smaller head of a bolaamphiphile (when use sodium cinnamate as the bulky head), asymmetrical membranes with parallel molecular arrangements can be easily fabricated. Work on this aspect is ongoing in our lab.

## Conclusion

We have realized the unprecedented parallel packing of a simple symmetrical bolaamphiphile that contains a cinnamoyl group through delicate molecular design. The  $\pi$ - $\pi$  stacking interaction between cinnamoyl groups were found to be very strong and drove the parallel packing of the SHHC molecules. The  $\pi$ - $\pi$  stacking interaction is so strong that it can even overcome unfavorable electrostatic repulsion between the COO<sup>-</sup> groups. Our results demonstrate that by introduction of strong interactions in the vicinity of one head of bolaamphiphiles, unsymmetrical membranes can be readily fabricated.

## Acknowledgements

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