

Self-Assembled Spiral Nanoarchitecture and Supramolecular Chirality in Langmuir–Blodgett Films of an Achiral Amphiphilic Barbituric Acid

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Nature uses chirality as one of the key structural factors to perform a series of complicated functions.^{1,2} Generally, chirality of a system involves intrinsically chiral molecules and chiral assemblies.³ A chiral molecule has an asymmetric carbon atom or conformational asymmetry. Chiral assemblies are often achieved by noncovalent interactions between chiral molecules or between chiral building blocks.⁴ In more specific cases, chiral assemblies could be constructed by achiral molecules.⁵ The latter is important because it relates to the origin of chirality and the symmetry breaking of a system. An air/water interface provided a two-dimensionally confined environment, and chiral supramolecular assemblies could be obtained from achiral molecules through interfacial molecular interactions.^{6,7} In this communication, we report a new type of chiral supramolecular assembly from an achiral molecule. The used achiral molecule is a derivative of barbituric acid, (5-(4-(*N*-methyl-*N*-hexadecylamino-benzylidene)-2,4,6-(1*H*, 3*H*)-pyrimidinetrione, BA). Barbituric acid derivatives have been widely investigated concerning their complementary H-bonding with melamine and other related compounds.⁸ However, fewer have been reported on the H-bonding between barbituric acid derivatives themselves. We have found that the amphiphilic BA can form a chiral Langmuir–Blodgett (LB) film through the air/water interface. More interestingly, spiral nano-architectures were observed in the LB film. To the best of our knowledge, this may be the first report on the formation of spiral nano-architecture by an achiral molecule at the interface.

Figure 1 (left) shows the surface pressure–area (π -*A*) isotherms of BA monolayers. The isotherms showed distinct inflection points and plateau regions, which changed with the subphase temperatures.⁹ The monolayer could be transferred onto solid substrates at different surface pressures by the horizontal lifting method. Spectra c and d in Figure 1 (right) show the UV–vis spectrum of a 30-layer LB film in comparison with that of BA in chloroform solution. An absorption band was observed at 485 nm in both the LB film and chloroform solution. The band can be assigned to the intramolecular charge-transfer band. An additional strong absorption band was observed at 450 nm for the film. This band was only observed in the LB film and showed a large blue shift in comparison with the band at 485 nm; it can be assigned to the H-aggregate of the BA molecules in the LB film.⁸

It was interesting to note that the LB films showed a Cotton effect (CE) when they were subjected to the circular dichroism (CD) measurements.^{10,11} Spectra a and b in Figure 1 (right) show the CD spectra of LB film transferred at 30 mN/m from the water surface in different batches at 20 °C. CD signal was observed at 485 nm and 410 nm with a crossover at 440 nm. It can be regarded as composed of two components. One is from the H-aggregate which showed a split CE. This indicated that strong exciton coupling

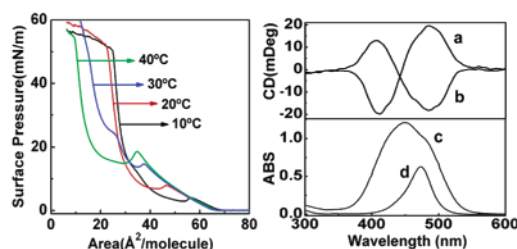


Figure 1. (Left) Surface pressure–area (π -*A*) isotherms of BA monolayers on water surface at different temperatures. (Right) UV–vis and CD spectra of BA films. (a) and (b): CD spectra of BA films fabricated in different batches. (c) UV–vis spectra of LB film deposited on the quartz plate at 30 mN/m and BA in chloroform solution (d).

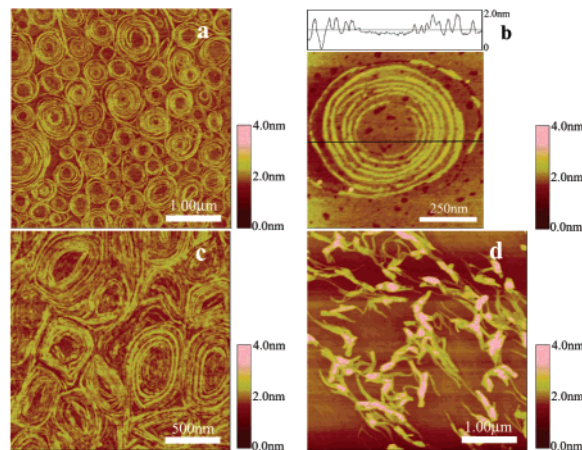


Figure 2. AFM images of one-layer LB films deposited at various surface pressures at 20 °C (a) and (b) 7 mN/m (c) 20 mN/m (d) 30 mN/m after inflection point.

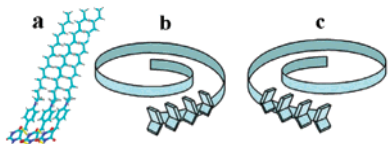
existed between the functional groups due to the H-aggregation. The other is corresponding to the intramolecular charge-transfer band of the BA film. It is further found that the sign of the CD signals could be completely opposite for the films fabricated in different batches, just as shown in Figure 1 (right), a and b. Such indetermination of chirality of the film is essentially the same as those reported on the chirality of the films obtained from achiral molecules, which could be due to a spontaneous symmetry breaking.^{5, 6, 7, 11}

AFM images of the one-layer LB films transferred onto freshly cleaved mica surface at different surface pressures were measured. For the film transferred at 5 mN/m, which was before the inflection point, a flat film without any obvious structures was obtained. When the film was compressed to the inflection point in the π -*A* isotherm, spiral nanofibers were observed (Figure 2, a, b). Interestingly, these spirals could wind in both a clockwise and an anticlockwise direction. When the deposition surface pressure was increased, the

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Scheme 1. (a) Hydrogen Bonding between BA Molecules and the Mechanism of the Formation of Spiral Superstructure (b) and (c) the Spirals of Two Enantiomeric Assembly



spirals became distorted and densely packed (Figure 2, c). If the monolayer was compressed to a higher surface pressure near collapse, fibers and some bright region could be seen. Careful investigation of these bright domains revealed that they could be regarded as distorted spirals due to the overcompression (Figure 2, d).

It has been reported that some chiral amphiphiles could form micrometer-scaled spirals at the air/water interface.⁹ The directions of the spirals depended on the chirality of the amphiphiles. On the basis of the above results of AFM and CD spectra, it can be suggested that BA could form chiral assemblies although the BA molecule itself was achiral. The formation of the supramolecular chirality of BA in the LB films could be explained in Scheme 1. When the spread BA molecules were compressed to the inflection points, the aromatic rings became closely packed. Due to the large aromatic rings and the H-bond interaction between the BA molecules, the neighboring aromatic rings would tilt from the same plane. If the subsequent BA molecule tilted in the same direction as the neighboring BA molecules, then the molecules could assemble into a chiral fiberlike nanostructure. Owing to the directionality nature of the H-bond,^{4b,8,12,13} the nanostructure will further curve in a certain direction to form spirals.

Hydrogen bonds could be formed between neighboring BA molecules as reported.^{8,12} We suggested that the carbonyls in 4- and 6-carbonyl of the pyrimidinetrione could form H-bonds with the hydrogen in the 1- and 3-N-H of the neighboring pyrimidinetrione (Scheme 1, a). In our LB films, the H-bond formation was confirmed by the FT-IR spectra of the film. In comparison with the vibration of carbonyl of BA in the KBr pellet, which was observed at 1724, 1692, and 1657 cm^{-1} , the vibration band shifted obviously in the film to 1747, 1733, 1718, 1699, 1683 cm^{-1} , indicating the H-bonding action between BA molecules.^{8d} The π - π stacking of the aromatic rings was verified by the UV-vis spectra, where they were arranged in a face-to-face way to form H-aggregate.^{4b,8d,13} These spectral data supported the above explanations of the supramolecular chirality of the LB films. Further supports were from the CD spectra and AFM image of the film deposited before the inflection points. In that region, both the alkyl chain and the headgroup of the BA molecule were relatively free; no overcrowded arrangement of the aromatic ring occurred. Therefore, we did not obtain any supramolecular chirality for the film deposited in that region.

It was noted that opposite CD signals could be obtained in different fabrication batches. For the film fabricated in one batch, the same CD signals were observed in the different positions of the same plate. This suggested that one predominant enantiomeric assembly was formed in the whole film. If one-handedness of the aggregate formed at very beginning, the subsequent assembly will follow that handedness due to a cooperative interaction.¹¹ However, the handedness of the starting aggregate was determined by chance.^{5,7,11} Subsequently, due to the directionality of the H-bond, these chiral assemblies will further rotate to form clockwise or anticlockwise spirals, as shown in Scheme 1, b and c. It was suggested that in every case, one enantiomeric assembly was

predominant and would determine the sign of CD signal, which was similar to the other symmetry-breaking systems.^{7,11}

It was further noted that the temperature of the subphase could affect the supramolecular chirality of the film. From the AFM images, the spirals disappeared with increasing the temperature of the subphase. Mixed spirals and nanofibers were observed for the film transferred at 30 °C, only fibers were obtained for the film transferred at 40 °C. The CD signal was weakened or even disappeared for the film fabricated at higher temperature. Because at higher temperatures, the molecules could be more active, the effect of the overcrowded arrangement of aromatic rings and the H-bonding became weaker.¹² Therefore, spirals as well as the chirality of the supramolecular assemblies were weakened or disappeared.

In conclusion, we found that an achiral amphiphilic BA derivative could show chirality and form spirals in the LB films. It was suggested that both the H-aggregation and the directional H-bond between the BA molecules were responsible for the supramolecular chirality as well as the spiral morphology of the LB film.

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Supporting Information Available: Experimental details; figures showing angle dependence of the CD amplitude, FTIR, CD, and AFM of the films fabricated at various conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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