

Molecular Arrangement of a Bolaamphiphilic Anthracene Derivative in Langmuir-Blodgett Film

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Abstract: This paper reports the molecular assembly in the LB film of a novel bolaamphiphilic anthracene derivative (BISANS) in comparison with that of one-headed amphiphilic anthracene derivative (ANS). While ANS formed a stretched monolayer at the air/water interface, BISANS underwent aggregation to form crystal film on the water surface. Both of the H-aggregates and J-aggregates exist in the transferred LB films of bolaamphiphilic BISANS, only J-aggregates formed in the LB film of ANS.

Keywords: Bolaamphiphile, air/water interface, stretched monolayer.

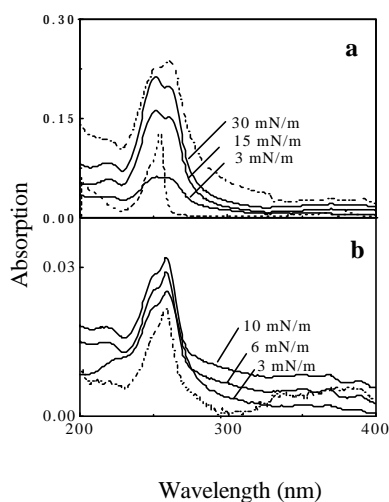
Langmuir monolayer at the air/water interface is the basis to understand the molecular arrangement and to fabricate the organized molecular films¹. Bolaamphiphiles describes the molecules in which two head functional groups are linked by one or two hydrophobic chains^{2,3}. In comparison with the one-headed amphiphile, abundant configurations of Langmuir monolayer are expected in bolaamphiphiles. Generally, three kinds of configurations of the Langmuir monolayers of bolaamphiphile at the air/water interface can be expected, *i.e.*, stretched, flat and U-shaped configurations. A variety of investigations on the bolaamphiphiles have reported these configurations^{4,5}. In a previous investigation, we have found that bolaamphiphiles with two head groups bound with a very short chain can be bent to form the U-shaped monolayer⁶. In this letter, we report the molecular assembly of a bolaamphiphile containing anthracene moiety in Langmuir-Blodgett films in comparison with that of the one-head long chain derivative based on surface pressure-area isotherms, SEM and UV-vis absorption spectra.

The structures of the bolaamphiphilic compounds used in this work are shown in **Figure 1**. The compounds were synthesized by the reaction of 1, 20-octadecanedicarboxylic acid with the corresponding 9-anthracenemethanol and were confirmed by ¹H-NMR⁷. The surface pressure-area (π -A) isotherms were recorded with a KSV minitrough with a compression speed of 5 mm·min⁻¹. The LB films were fabricated by a vertical method on KSV minitrough at a speed of 5 mm·min⁻¹. All the experiments were performed at room temperature.

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absorption band is observed at 261 nm in the ANS LB film (transferred under 3, 6, 10 mN/m), which shows a red shift comparing with that in methanol solution. This indicates that the chromophores of ANS take head to tail orientation or J-aggregates in LB film. In cast film, similar spectrum is observed. In the case of BISANS, the situation is different. It is worth noting that the 1B_b band is split into two bands at 251 and 261 nm in the BISANS LB film although only one absorption band was observed in solution. According to Kasha's theory, such kind of split can be related to the different aggregation in the molecular crystals. The blue-shifted band at 251 nm can be related to the face to face orientation or H-aggregates of the chromophores, while the red-shifted band at 261 nm to the head to tail orientation or J-aggregates of molecular chromophores of BISANS in LB film. It is interesting to note that the ratio of the peaks at 251 and 261 nm changed with surface pressure. Higher surface pressure favors the formation of H-aggregates. It should be noted that in the cast film of BISANS, similar split two bands are observed. But in this case, the intensity of the red-shifted band is higher than the blue-shifted band, which is more like the spectrum of the BISANS film transferred at lower surface pressure. This indicates that the molecules in cast film can also be ordered to some extent, but their arrangement is similar to that of the ordered film at very lower surface pressure.

Figure 4 Absorption spectra of the LB films and cast films of BISANS (a) and ANS (b) transferred at various surface pressures



In LB film (—) In solution (.....)
In case film (-----)

In addition, split is only found in the case of BISANS. This indicates that the bolaamphiphilic BISANS has great difference in the surface property compared with that of one-headed amphiphilic ANS. Such different arrangements are regarded to affect

their properties and photochemical reactions. Such work is underway in our laboratory.

Acknowledgments

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References and notes

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7. **ANS**: mp: 56.5-57.5°C, ¹H-NMR (300 MHz, CDCl₃), δ ppm: 0.89 (t, 3H, J = 5.82 Hz, -CH₃); 1.25~1.6 (m, 32H, -(CH₂)₁₆-); 2.35 (t, 2H, J = 7.41 Hz, -OCOCH₂-), 6.15 (s, 2H, -CH₂O-), 8.03 (d, 2H, J = 8.25 Hz), 8.33 (d, 2H, J=8.79 Hz), 8.53 (s, 1H). **BISANS**: mp: 62.0 - 63.0°C. ¹H-NMR (300 MHz, CDCl₃), δ ppm: 1.23 (m, 28H, -(CH₂)₁₄-), 1.62 (m, 4H, -(CH₂)₂-), 2.37 (t, 4H, J = 7.47 Hz, -OCOCH₂-), 6.17 (s, 4H, -CH₂O-), 7.31 ~ 7.23 (m, 8H), 8.06(d, 4H, J = 8.31 Hz), 8.32 (d, 4H, J = 8.79 Hz), 8.53 (s, 2H).

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