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Morphology Observation and J-Aggregation Characteristics of Merocyanine Dye with Arachidic Acid LB Films

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In order to confirm the application possibility to the molecular electronic device, the morphological property of arachidic acid (AA) was investigated. We have determined morphology by BAM and AFM. π-A curves investigated surface pressure of this LB film from liquid to solid state ranged between 40 to 45 mN/m. BAM images investigated the different states of AA LB film. When the surface pressure reaches at 40 mN/m, the monolayer was deposited onto the hydrophilic glass substrates by Y-type deposition. We investigated morphological property of arachidic acid by AFM. As a result, we obtained the frequency characteristic and morphology of LB films from controlling the deposited layers. In this paper, I review this subject mainly based on our recent results in merocyanine dye. LB films of merocyanine dye, mixed with arachidic acid, exhibit J-aggregate formation and have been serving as typical systems in revealing the physical and structural aspects of nano-sized molecular aggregates constructed as muiltilayers.

Keywords: AFM; J-aggregate; LB film; merocyanine dye

1. INTRODUCTION

Langmuir-Blodgett (LB) technique attracts much attention as a tool for arranging various kinds of molecules into the form of monolayer

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assemblies. The Langmuir-Blodgett (LB) technique represents one of the few methods by which organic films of controlled thickness, uniform surface, and highly ordered structure may be deposited onto a substrate. Langmuir-Blodgett films are made by pulling a substrate through a monolayer of amphiphilie molecules at the air-water interface [1,2].

In this paper, I review this subject mainly based on our recent results typical systems in revealing the physical and structural aspects of nanosized molecular aggregates constructed as monolayers [3]. The J-aggregates of the functional dye molecules are characterized by the sharp red shift band and a strong photoluminescence with a small stokes shift. With respect to J-aggregates, because they essentially result from the specific interactions between transition dipole moments of molecules, there would be various kinds of molecules forming J-aggregates. In this respect, it would be desirable to characterize the aggregates by employing more than two complimentary techniques to obtain detailed information. For such example, I note here the case of LB films of a merocyanine, lightly substituted merocyanie dye [6Me-Ds] diluted with arachidic acid. Without trigger, the macrocycle plane is tilted with respect to the normal direction of the substrate while it becomes almost vertical to the substrate when added with trigger. This drastic change of molecular orientation has been directly visualized as a clear change of the Cu^{2+} ion, the analysis of which has yielded a detailed angular distribution function of the z-axis (the normal direction of the macrocycle plane). The obtained distribution function, in turn, has been found to precisely reproduce the dichroic behaviors of in-plane J-band and out-of-plane resulted from the interactions between two degenerate transition dipole moments of each molecular. Thus, the drastic orientation change of molecules due to triggers has been established, providing a new method of controlling the orientation of molecules due to microscopic molecular interaction [4].

And we observed morphology by tapping mode. Tapping mode AFM cantilever with attached tip is oscillated at its resonant frequency and scanned across the sample surface. Constant oscillation amplitude (and thus a constant tip-sample interaction) are maintained during scanning. Typical amplitudes are $20 \sim 100$ nm. The amplitude of the oscillations changes when the tip scans over bumps or depressions on a surface.

We have been focusing our attention on the control of the J-aggregate formation of surface-active merocyanie dye molecular. These dye molecular, shown Figure 1 surface-active merocyanine dye, abbreviated as, 6-methyl [6Me-Ds]. [6Me-Ds] mixed with arachidic acid ($CH_3(CH_2)_{18}COOH$, AA) in a molar ratio of [6Me-Ds]/(C_{20}) = 1:2 is stable Y-type multilayer in chloroform solution [5].

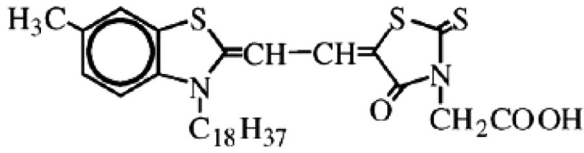

FIGURE 1 Chemical structure of merocyanine dye.

2. EXPERIMENTAL

Figure 1 is a chemical structure of arachidic acid (AA) and [6Me-Ds]. The AA with purity 99% was purchased with Kodak Co. and used as received. Separate chloroform solutions of each material were prepared with molar concentration of $\sim 1 \times 10^{-3}$ mol/l. The AA LB film was deposited on the glass substrate (1/4 the size of microscope slide glass). The substrate was sonicated once in ethanol and twice in ultra-pure water and was treated with ozone. The substrates were rinsed in ethanol and ultra-pure water and ozone again with treated hydrophilic before the LB film deposition. In order to certain whether substrate is hydrophilic property, we measured contact angle. The LB films were deposited by a vertical dipping method with a Langmuir trough equipped with a two compartment trough Type (NIMA, Type 610, UK). Then, the molecules were compressed by barrier at a speed of 20 mm/s until the surface pressure reached to 40 mN/m, at which the LB film was deposited. Since the substrate is hydrophilic, the deposition started at the first upward stroke of the substrate immersed in the subphase. Then the number of layers increased with each downward and upward strokes. Resulting LB films is a Y-type film. The dipping speed of the substrate was 15 mm/min. Sample was dried for a day. Then the morphologies were observed using AFM (DI, USA).

The LB films were fabricated by a standard vertical dipping method using containing $CdCl_2$ (3×10^{-4} M) and $KHCO_3$ (5×10^{-5} M) was $20 \sim 21^{\circ}$C. The pH of the subphase was controlled to be $6.1 \sim 6.2$. Y-type films of mixed dyes and AA were transferred either on glass and silicon wafer substrates [6].

3. RESULTS AND DISCUSSION

LB thin film of arachidic acid was produced by LB method. Limit area was about 27Å^2/mole in π-A isotherm of arachidic acid. In Figure 2, π-A curves shows that surface pressure of this LB film from liquid to solid state ranged between 40 to 45 mN/m. BAM images show the different states of LB films.

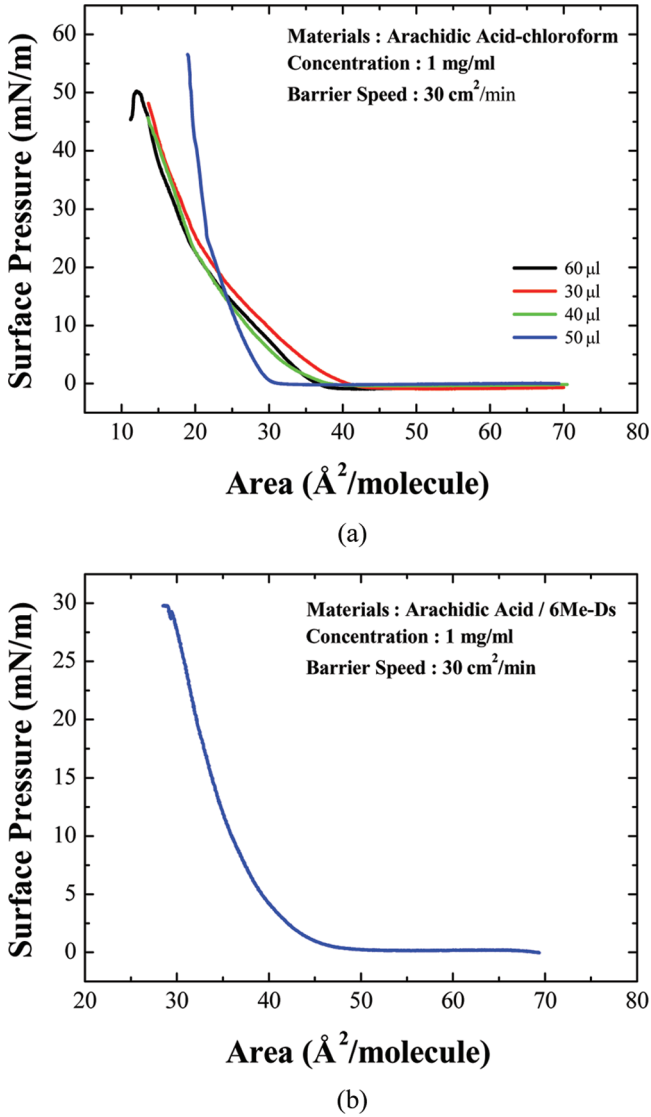

FIGURE 2 π-A isotherm of arachidic acid (a) merocyanine dye [6Me-Ds] (b).

This figure is various volume change. In this figure show various volume change, and volume change has nothing to do with surface pressure. Any volume has been steady state.

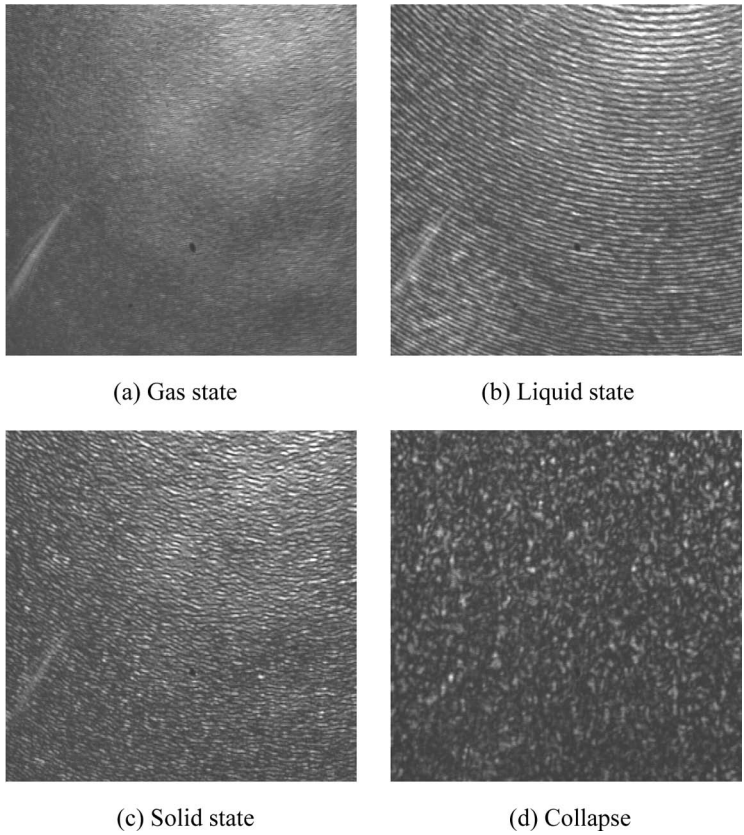

FIGURE 3 BAM images of arachidic acid.

Figure 3 is surface images of AA which was prepared and characterized by brewster angle microscope (BAM). BAM is a very attractive tool to study LB monolayer. Figure 3 shows the BAM images of the different states of the AA LB film. The state of molecules is scatter in gas state and herein molecules are condensation more than gas state in liquid state. In solid state (c), molecules are closely each other and molecules break in collapse state. As a result, it was found that produced a composite molecule at the air-water interface with a smooth and cohesive surface, and this optimal structure.

Figure 4 is an angle of bare glass and after hydrophilic treatment of glass by measured contact angle. If the degree is small, that surface energy is high. High surface energy means good wet ability and adhesion [8]. The observation that the contact angle of liquid drops on some substrates depends on their size was until now systematically

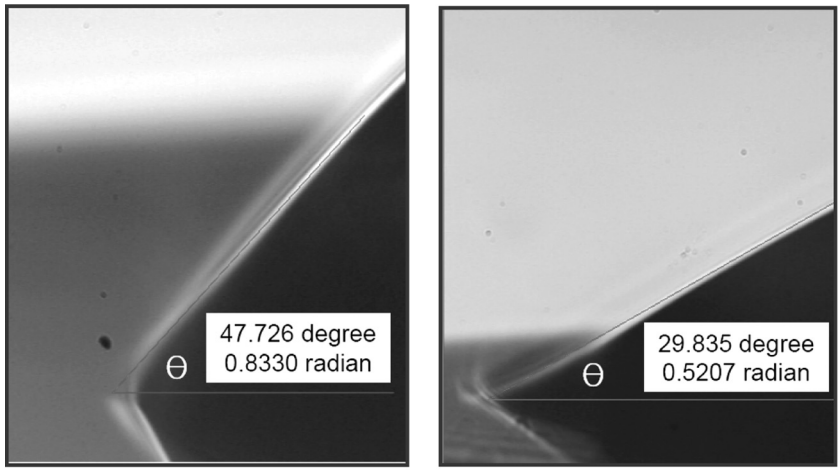

FIGURE 4 Contact angle of substrate before hydrophilic treatment (a) and after hydrophilic treatment (b).

interpreted using the three-phase line in equilibrium conditions of the sessile drop. Contact angle is decreased after hydrophilic treatment, because of good hydrophilic treatment. Contact angle measurement methods rely on surfaces being perfectly flat and smooth. However, in these studies contact angles were measured on compacted particles rather than on a perfectly flat surface.

Here, we show that the angle value varies according to a power law with the drop volume and that the exponent can take very diverse values. The electrostatic repulsion would overcome the hydrophobic interaction between alkyl chains. As a result, chains uncoiled and were exposed at the outermost of the surfaces.

Figure 5 shows the optical absorption spectra of the mixed-dye films, [6Me-Ds]/(AA), for 1:2 mixing ratios. In the case pure dye system, the optical absorption spectra show distinct peaks at $555 \sim 560\,\text{nm}$ (a), and fabricated at $CdCl_2$ ($3 \times 10^{-4}\,\text{M}$) and $KHCO_3$ ($5 \times 10^{-5}\,\text{M}$) $20 \sim 21^{\circ}\text{C}$ the pH of the subphase was controlled to be $6.1 \sim 6.2$, optical absorption spectra show peak at $620 \sim 625\,\text{nm}$ (b). The sharp absorption spectra peaks wavelength shows the J-band due to the J-aggregation of the dye molecules. With increase of layers, the absorbance of the J-band increases almost linearly. Whatever the concentration of the dye is, the J-band peak wavelength and the band width almost stay the same [9].

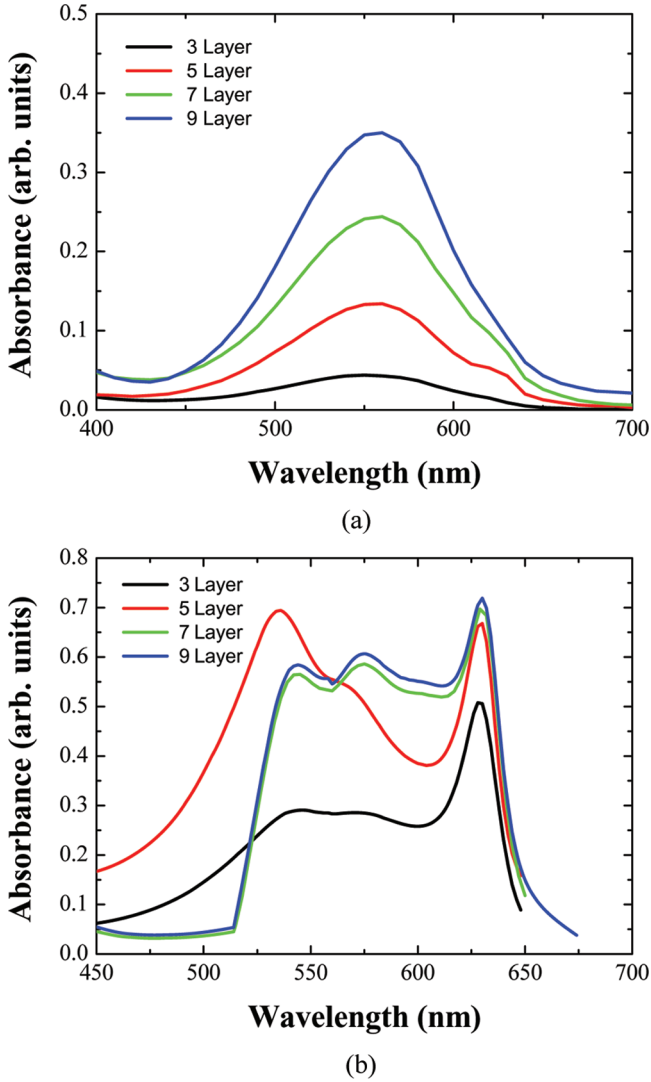

FIGURE 5 Optical absorption spectra of typical merocyanine dye. (a) absorption of merocyanine dye [6Me-DS] without Cd^{2+} (b) absorption of merocyanine dye [6Me-DS] with Cd^{2+}.

The AFM image of multi-layer LB films on the silicon wafer substrates are shown in Figure 6 is for the 7 layers and 9 layers dye mixed 1:2 ratio of [6Me-Ds]/AA. The images were recorded by

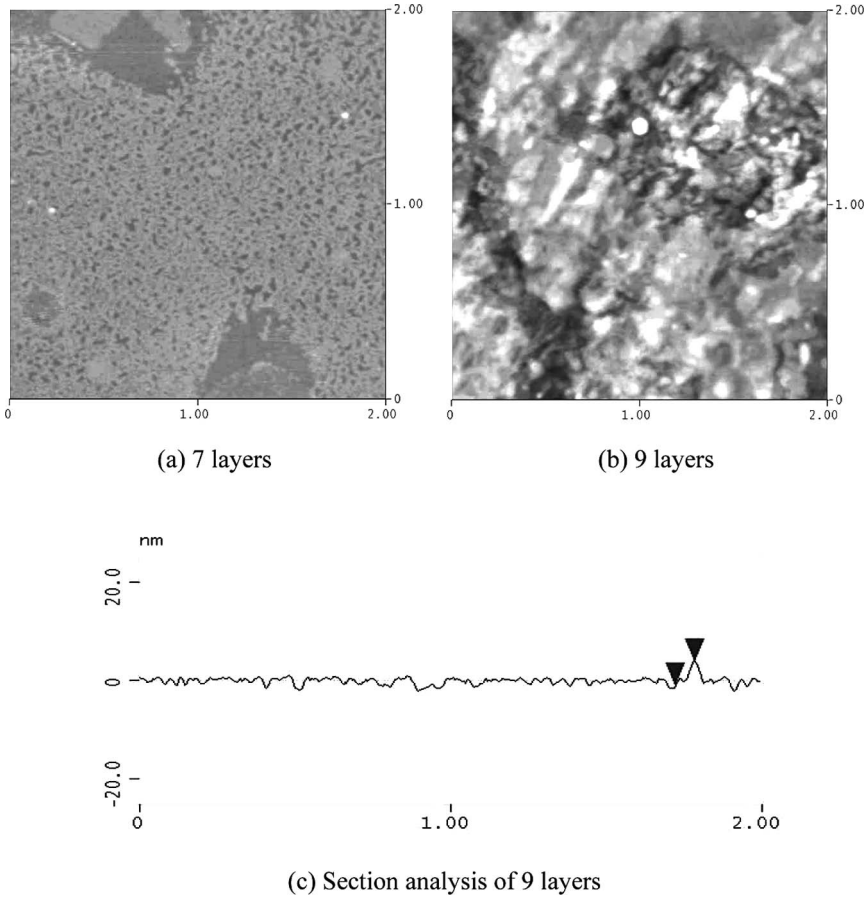

FIGURE 6 Morphologies of merocyanie dye [6Me-Ds] LB film with arachidic acid. (a) 7 layers (b) 9 layers (c) Section analysis of 9 layers.

Nanoscope IV with tapping-mode operation to obtain clear images with enhanced edges between molecular domains.

There, we found two distinct domains with different heights. The total areas of the lowland high-height domains have been determined by using graphic software. The fraction of the low-height domains agreed fairly well with those of the [6Me-DS] calculated by using the molar mixing ratio together with the molecular occupation area of the two components.

We repeated the scan several times at the same place to ensure that the film did not suffer from irreversible damage. The scan size is

$2 \times 2\,\mu m$ to $30 \times 30\,\mu m$. There, we found two distinct domains with different vertical distance [10].

We used the tapping-mode operation, the alkyl chain of AA and [6Me-Ds] may tilt from the normal to the substrate when the cantilever tip of the AFM scans. The banding of the alkyl chain of the [6Me-Ds] would be easier then that of the AA, because there is less interaction of the former due to looser packing of the chain.

4. CONCLUSION

In this paper, we have investigated the J-aggregation and its characterization in LB films of merocyanine dye mixed with arachidic acid by focusing firstly on the importance of the characterization of the structure and states J-aggregates, typical nano sized organic molecular aggregates of functional molecular. And we tried fabricated stable LB film mixed AA/[6Me-Ds]. The J-aggregates behave in the mutual mixing LB films of merocyanine dye have been investigated by optical absorbance. In mixed LB films of AA/[6Me-Ds], sharp J-band absorbance and fluorescence. Thus mixed LB films might be ascribed to the homogeneous mixing effect. It could be ascribed to enhancement of the molecular ordering in J-aggregates, and the multilayer of dye molecular on the air/water interface affect the structural.

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