

Orientation of *n*-Octadecane in Langmuir-Blodgett films of Merocyanine dye - Arachidic acid - *n*-Octadecane Ternary System

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We have studied the structures of the blue-shifted H- and the red-shifted J-bands formed in the mixed Langmuir-Blodgett (LB) films of the merocyanine dye (MS)-arachidic acid (C₂₀)-*n*-octadecane (AL₁₈) with the molar mixing ratio [MS]:[C₂₀]:[AL₁₈]=1:2:*x* (0 ≤ *x* ≤ 5.0). The orientation of AL₁₈ which induces blue-shifted bands in LB films of the MS-C₂₀-AL₁₈ ternary systems has been investigated employing the deuterated *n*-octadecane (AL₁₈-*d*) by means of the polarizing infrared absorption spectroscopy. The results indicate that the long axis of the AL₁₈-*d* molecule with the all-trans conformation is almost perpendicular to the film surface in all the MS-C₂₀-AL₁₈ ternary systems.

Keywords: merocyanine dye, H-aggregate, blue-shifted band, ternary system, deuterated *n*-octadecane, polarizing infrared absorption spectroscopy

1. INTRODUCTION

A great deal of attention has been paid toward potential applications of organized molecular films to various molecular devices such as organic solar cells, optical memory media or nonlinear optical devices.^{1,2)} Among them, one of the most attracting subjects is to control the aggregation states of functional molecules such as dyes in organized two-dimensional assembly systems.¹⁻³⁾

As the technique to fabricate the organized ultrathin system, the Langmuir-Blodgett (LB) technique is one of the most promising methods, because it enables us to prepare organic thin films with functional parts in regular arrangements.¹⁾ As for the film-forming materials, our attention is focused on the merocyanine dye (MS) shown in Fig. 1, since it has been so far reported that the sunlight efficiencies of up to about 1% are obtained in the vacuum-evaporated films containing the merocyanine dye⁴⁾, suggesting the importance of the MS aggregation state in the system.

As is well known, the MS-arachidic acid (C₂₀) binary LB films exhibit a sharp absorption band at 590 nm⁵⁻¹⁰⁾, which is red-shifted from that of the MS monomer peak at around 540 nm⁹⁾, when they are prepared under the conventional subphase condition containing Cd²⁺, as shown in Fig. 2. The red-shifted band is called J-band and the optical characteristics are ascribed to a specific alignment of MS, that is, J-aggregate.⁵⁻¹²⁾

On the other hand, we have found that a blue-shifted band at 505 nm or 520 nm is induced when *n*-alkane (AL_{*n*}) species such as *n*-octadecane (AL₁₈) are added to the MS-C₂₀ binary system, indicating that the MS aggregation state can be easily tuned by the amount of AL₁₈.¹³⁻¹⁷⁾ The 505-nm band is assigned to an H-band

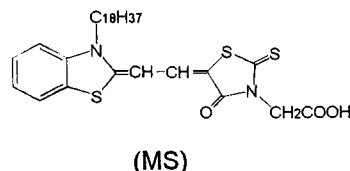


Figure 1 The chemical structure of the merocyanine dye (MS).

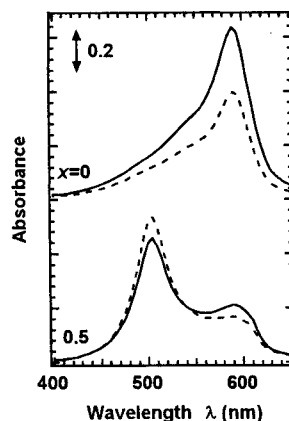


Figure 2 The absorption spectra of the mixed LB films of the merocyanine dye (MS)-arachidic acid (C₂₀) binary and the MS-C₂₀-*n*-octadecane (AL₁₈) ternary systems. The molar mixing ratio [MS]:[C₂₀]:[AL₁₈]=1:2:*x*, where *x*=0 and *x*=0.5. The solid and the dashed lines refer to the absorption spectra A_{||} and A_⊥, respectively.

of the MS molecules based on the energy shift, the sharpness and the in-plane anisotropy of the band^{13,14,16,17)} in LB films of the MS-C₂₀-AL₁₈ ternary system with the molar mixing ratio

[MS]:[C₂₀]:[AL₁₈]=1:2:*x* in the range $0.5 \leq x \leq 1.5$, as exemplified in Fig. 2, while the 520-nm band is identified as the oligomeric band with the side-by-side alignments of the MS transition dipole moments for $1.5 < x$.¹⁶⁾ In order to reveal the mechanism of individual MS aggregates, it is indispensable to characterize their structures.

In previous papers, we have examined the aggregation state of MS using the extended dipole model.¹⁶⁾ The estimated minimum aggregation number and the slip angle between the long axis of the aggregate and the MS transition dipole moment are $N_{\min}=40$ and $\alpha=50^\circ$ for fully-developed H-aggregates for lower AL₁₈ contents, respectively. The aggregation number tends to decrease with increasing the AL₁₈ content. Furthermore, we have reported that the added AL₁₈ tends to fill the MS empty space which can accommodate two straight-hydrocarbon-chains^{14,15)}, and that the tendency is reflected in the layered structure along the stacking direction of the mixed LB films of the MS-C₂₀-AL₁₈ ternary system.¹⁵⁾

In this paper, we discuss the orientation of AL₁₈ added as the third component using the infrared transmission spectroscopy. In this respect, the deuterated *n*-octadecane (CD₃(CD₂)₁₆CD₃) is used to separate the infrared absorption bands of AL₁₈ from those of MS and C₂₀.

2. EXPERIMENTAL

MS, C₂₀ and *n*-octadecane-*d*₃₈ (CD₃(CD₂)₁₆CD₃, D 98 %, abbreviated as AL₁₈-*d*) were used as the film-forming materials. MS, C₂₀ and AL₁₈-*d* were purchased from Japanese Research Institute for Photosensitizing Dyes, Co., Fluka Chemie AG and Cambridge Isotope Laboratories, Inc., respectively, and were used without further purification. MS, C₂₀ and AL₁₈-*d* were dissolved in the freshly-distilled chloroform with the molar mixing ratios [MS]:[C₂₀]:[AL₁₈]=1:2:*x* ($0 \leq x \leq 5.0$). The concentration of MS was of the order of 10^{-4} M. The LB films were prepared by the standard vertical dipping method. The aqueous subphase and the deposition conditions were the same as given in the previous papers.¹³⁻¹⁷⁾ A CaF₂ substrate precoated with five monolayers of cadmium arachidate (CdC₂₀) was used. All the LB films were of Y-type with a transfer ratio around unity.

The infrared absorption spectrum measurements were carried out in the range from 4000 cm⁻¹ to 400 cm⁻¹ using a JASCO FT/IR-300 spectrometer. The spectrometer was purged with the nitrogen gas to minimize the amount of the water vapor present in the sample chamber. The absorption spectra were recorded at a 4-cm⁻¹ resolution by coadding 100 scans. The polarizing absorption spectra A_{\parallel} and A_{\perp} of the mixed LB films were measured using a linearly polarized light with the electric vector parallel and perpendicular to the dipping direction, respectively. The linearly polarized light was introduced with an incident angle α between the incident beam and the film normal, as shown in Fig. 3 (right-hand side). Fifty-layered mixed LB films deposited on both sides of the substrates were used as

the samples. The LB films of CdC₂₀ were fabricated as references for estimating the tilt angle θ of the long axis of AL₁₈-*d*. The measurements were carried out immediately after the sample preparation unless otherwise stated.

3. RESULTS AND DISCUSSION

In order to estimate the tilt angle θ of the long axis of the hydrocarbon chains against the film plane, a simple model^{18,19)} shown in Fig. 3 is introduced, where the all-trans conformation is assumed. The polar angles of vectors m and μ which represent the long axis of AL₁₈-*d* and the sum of the transition moments of the CD₂ or the CH₂ stretching vibration modes, respectively, are defined by θ and β (left-hand side). The incident beam of the linearly polarized light is along Z axis with

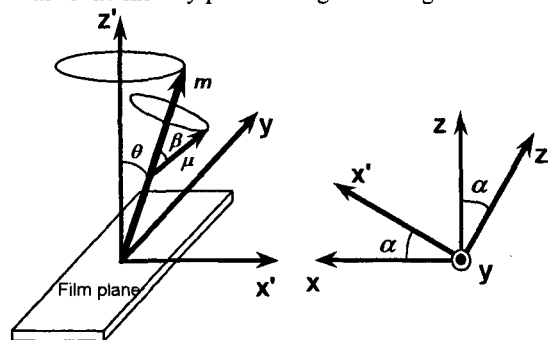


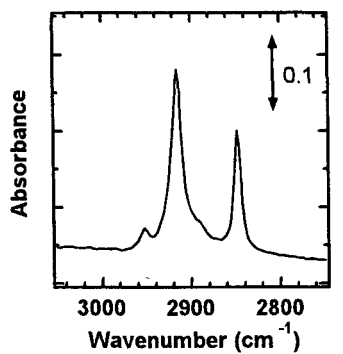
Figure 3 The model for estimating the tilt angle θ of the long axis of AL₁₈-*d*. The polar angles of vectors m and μ are defined by θ and β (left-hand side). The definition of the inclination angle α (right-hand side). α is the angle between the incident beam and the film normal. The incident beam of the linearly polarized light is along Z axis with its electric vector in X-Y plane.

its electric vector in X-Y plane, where $\alpha = \angle ZOZ' = \angle XOX'$ is the inclination angle (right-hand side). In the model, it is assumed that m and μ distribute uniformly with respect to Z' axis and m , respectively. In this case, the dichroic ratio $R (=A_{\parallel}/A_{\perp})$ can be expressed as

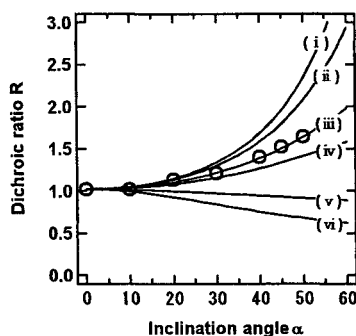
$$R = \frac{1 + \cos^2 \theta}{1 + \sin^2 \alpha + \cos^2 \theta (3 \cos^2 \alpha - 2)} \quad (1)$$

assuming $\beta = \pi/2$ allowing for the orthogonal relation between m and μ .

Let us first examine the tilt angle θ of the long axis of the hydrocarbon chains for the cadmium arachidate (CdC₂₀) LB films. Figure 4 (a) shows the polarizing infrared absorption spectra A_{\parallel} of the CdC₂₀ LB films, where the peaks at 2915 cm⁻¹ and 2848 cm⁻¹ are assigned to the antisymmetric and the symmetric CH₂ stretching bands of CdC₂₀, respectively. The peak positions are the same as those of the CdC₂₀ LB films in the earlier works¹⁸⁾, and no shift of both peaks is observed, indicating the all-trans conformation of CdC₂₀. It is noted that R-values of both peaks remain approximately unity for the case of the normal incident ($\alpha = 0^\circ$), which coincides with the assumption of the uniformly



(a)

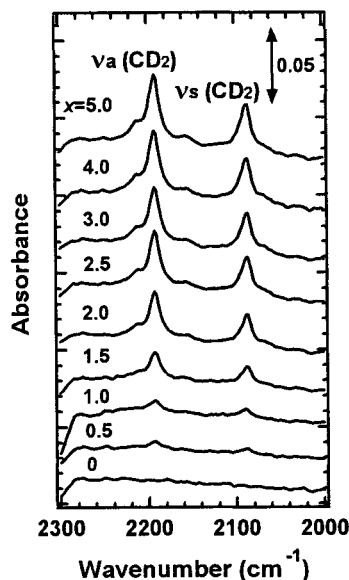


(b)

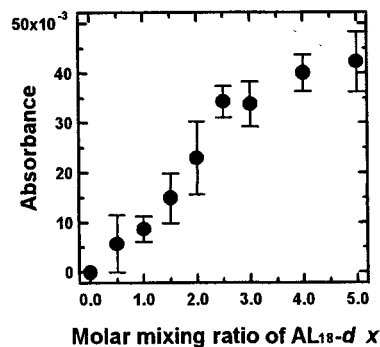
Figure 4 (a) The polarizing infrared absorption spectra A_{\parallel} of the cadmium arachidate (CdC_{20}) LB films. (b) The dichroic ratio R of the antisymmetric CH_2 stretching band for the CdC_{20} LB films plotted against the inclination angle α . The solid curves refer to the inclination-angle-dependence calculated using eq. (1); (i) $\theta=10^\circ$, (ii) $\theta=20^\circ$, (iii) $\theta=33^\circ$, (iv) $\theta=40^\circ$, (v) $\theta=60^\circ$ and (vi) $\theta=80^\circ$.

distributed azimuths of m and μ . Figure 4 (b) shows the dichroic ratio R of the antisymmetric CH_2 stretching band in the CdC_{20} LB films plotted against the inclination angle α . The solid curves refer to the inclination-angle-dependence calculated using eq. (1); (i) $\theta=10^\circ$, (ii) $\theta=20^\circ$, (iii) $\theta=33^\circ$, (iv) $\theta=40^\circ$, (v) $\theta=60^\circ$ and (vi) $\theta=80^\circ$. The best, least-squares fit is obtained for $\theta=33^\circ$. The similar tendency is also seen for the symmetric CH_2 stretching band of CdC_{20} . It has been so far known that the hydrocarbon chains in the pure fatty acid salt LB films, in general, can be approximated to be in the all-trans conformation with their long axis perpendicular to the film surface.²⁰⁻²²⁾ The result of the θ -value is currently postulated to be due to the estimation without the introduction of the refractive index and the multiple reflection of the thin films.

To be examined next is the orientation of AL_{18-d} added as the third component to the MS-C_{20} binary system using the same procedure. Figure 5 (a) shows the polarizing infrared absorption spectra A_{\parallel} of the mixed LB films of the MS-C_{20} binary and the $\text{MS-C}_{20}\text{-AL}_{18-d}$ ternary systems of



(a)



(b)

Figure 5 (a) The polarizing infrared absorption spectra A_{\parallel} of the mixed LB films of the MS-C_{20} binary and the $\text{MS-C}_{20}\text{-AL}_{18-d}$ ternary systems. The molar mixing ratio $[\text{MS}]:[\text{C}_{20}]:[\text{AL}_{18-d}]=1:2:x$ ($0 \leq x \leq 5.0$). (b) The peak heights of the infrared absorption spectra A_{\parallel} for the antisymmetric CD_2 stretching band of AL_{18-d} are plotted against the AL_{18-d} content x .

$[\text{MS}]:[\text{C}_{20}]:[\text{AL}_{18-d}]=1:2:x$ ($0 \leq x \leq 5.0$). The peaks at 2192 cm^{-1} and 2088 cm^{-1} are assigned to the antisymmetric and the symmetric CD_2 stretching bands of AL_{18-d} , respectively. The peak positions are identical with those of the LB films of the barium stearate deuterated²³⁾, and no shift of both peaks is observed. These results indicate the presence of AL_{18-d} with the all-trans conformation. Figure 5 (b) refers to the peak heights of the absorption spectra A_{\parallel} for the antisymmetric CD_2 stretching band of AL_{18-d} , each of which is plotted against the AL_{18-d} content x . A_{\parallel} is roughly proportional to x up to $x=2.5$, and varies linearly with a gentler slope for $x > 2.5$. The similar tendency is also obtained for the symmetric CD_2 stretching band of AL_{18-d} . It is also noted that R -values of both peaks are approximately unity for the case of $\alpha=0^\circ$ in all the

MS-C₂₀-AL₁₈-*d* ternary systems.

Figures 6 (a) and (b) show the values of the *x*-dependent θ for the antisymmetric and the symmetric CD₂ stretching bands of AL₁₈-*d*, respectively. For $1.0 < x$, the estimated θ -values from both bands remain at around 30° in the MS-C₂₀-AL₁₈-*d* ternary systems. For $x \leq 1.0$, however, the θ -values for both bands differ from one another, with those for the antisymmetric stretching systematically deviating upward. We currently postulate that the deviation is due to the insufficient signal to noise ratios, leading to uncertainty in determining the baseline.

The θ -values (ca. 30°) in Figs. 6 (a) and (b) and the R-behavior of AL₁₈-*d* are consistent with those for CdC₂₀ in Fig. 4 (b). Therefore, it is indicated that the long axis of the hydrocarbon chains for the AL₁₈-*d* molecules is almost perpendicular to the film surface in all the MS-C₂₀-AL₁₈ ternary systems, and that a picture that the long axis of AL₁₈-*d* is almost parallel to the film surface or the random orientation of AL₁₈-*d* is discarded as being implausible. In all the binary and the ternary systems, the evaluation of the orientation of the long axis of the hydrocarbon chains of MS and C₂₀ is now in progress.

In this paper, the orientation of the long axis of the hydrocarbon chains of AL₁₈-*d* has been examined. Furthermore, the orientation of the added AL₁₈-*d*, and that of hydrocarbons of MS and C₂₀ as well, should be accurately estimated using the models^{24,25} in which the reflection and the refractive index due to the thin films

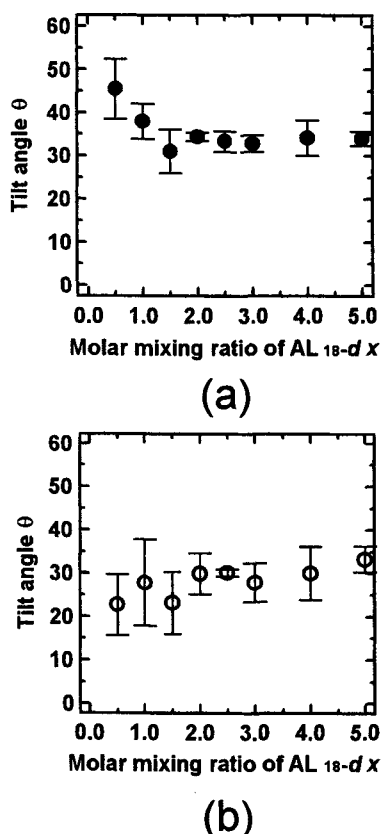


Figure 6 The tilt angles θ estimated from (a) the antisymmetric and (b) the symmetric CD₂ stretching bands of AL₁₈-*d* are plotted against the molar mixing ratio of AL₁₈-*d* *x*.

can be taken into account to provide the quantitative information about the molecular orientation.

4. ACKNOWLEDGEMENTS

The present authors would like to thank Prof. S. Kobinata and Dr. K. Ikegami for their valuable discussions and useful comments. The present authors would like to express their gratitude to Mr. M. Minai for his technical assistance of the sample holder for the infrared absorption spectroscopy measurements.

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(Received December 21, 2001; Accepted February 28, 2002)