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# Formation of Blue-Shifted Band in Merocyanine LB Films

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**Abstract** A blue-shifted band has been formed in the merocyanine dye - arachidic acid mixed LB films by adding octadecane molecule of various molar mixing ratios. The polarizing UV-visible absorption spectrum measurements revealed that the formation of molecular aggregates is sensitive to the mixing ratio of octadecane as a third component. The surface pressure - area isotherms indicated that a certain amount of octadecane molecule does not exist in the empty space of merocyanine dye even if mixing ratio of octadecane is small.

**Keywords** Merocyanine dye, H-band, Ternary system, UV-visible absorption spectrum, surface pressure - area isotherms

## INTRODUCTION

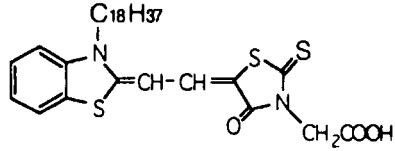
We have found that a blue-shifted band around 505 nm is induced when an n-alkane species is added to the mixed LB films of merocyanine dye (MS) - arachidic acid ($C_{20}$) binary system. In previous papers, we have shown that the blue-shifted band is characterized as an H-band,[1,2] while the 590-nm red-shifted band observed for the same binary system is referred to as a J-band.[3-12] We have reported that the blue-shifted band originates from the H-aggregate according to the theory of flow orientation combined with the extended dipole model.[1,2]

We have investigated the relation between the formation of blue-shifted

band and the molar mixing ratio of n-alkane species. In this paper, we report the formation of blue-shifted band which depends on the molar mixing ratio of octadecane as the candidate and discuss the structure of mixed LB films of ternary system.

## EXPERIMENTAL

The surface-active merocyanine dye (MS) shown in Fig. 1, arachidic acid ($C_{20}$) and octadecane ($AL_n$ ; $CH_3(CH_2)_{n-2}CH_3$, n=18) were used as the film-forming materials. MS, $C_{20}$ and $AL_{18}$ were purchased from Japanese Research Institute for Photosensitising Dyes, Co., Fluka Chemie AG and Kanto Chemical Co., Inc., respectively. They were used without further purification. The molar mixing ratios of binary and ternary systems were [MS]:[$C_{20}$]:[$AL_{18}$]=1:2:x (x=0, 1, 2, 3, 4).




(MS)

FIGURE 1 Chemical structure of merocyanine dye (MS).

The spreading solutions and the aqueous subphase were prepared as reported previously.[1,2] The subphase was kept at about 17 ℃. Surface pressure-area isotherms of the mixed monolayers were measured at a compression rate of 0.0375 Å²/molecule · sec using a KSV 5000 trough. The monolayer was transferred onto a solid substrate by the vertical dipping method at a surface pressure of about 25 mN/m. The dipping velocity was about 25 mm/min for both upward and downward strokes. A glass substrate precoated with five monolayers of cadmium arachidate ($CdC_{20}$) was used.

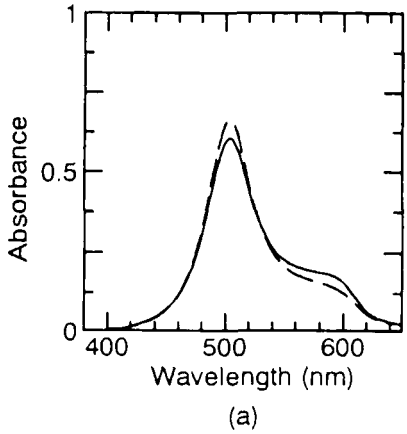
Twenty monolayers of the mixed system were deposited onto both sides of $CdC_{20}$-coated substrate. The UV-visible absorption spectra $A_{\parallel}$ and $A_{\perp}$ were measured using a normal incident of linearly polarized light with the electric vector either parallel or perpendicular to the dipping direction,

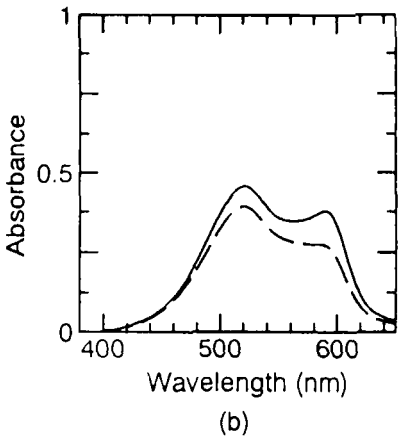
respectively, immediately after the sample preparation.

## RESULTS AND DISCUSSION

### UV-visible absorption spectra

Figure 2(a) shows the absorption spectra of ternary system of x=1 ([MS]:[$C_{20}$]:[$AL_{18}$]=1:2:1); solid and dashed lines refer to the absorption spectra $A_{\parallel}$ and $A_{\perp}$, respectively. The absorption maximum located around 505 nm is markedly blue-shifted from that of monomer band (540 nm). This H-band is 0.15 eV blue-shifted from the monomer peak. The fully developed H-band coexists with a J-band component located around 590 nm.



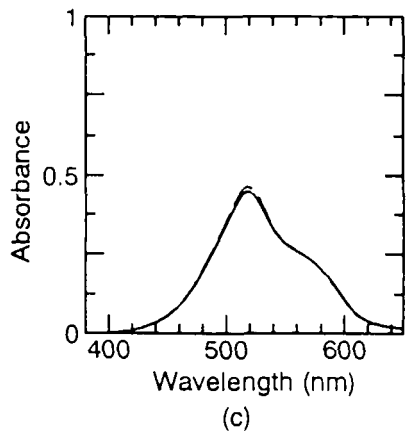




FIGURE 2 The absorption spectra of the ternary system of [MS]:[$C_{20}$]:[$AL_{18}$]=1:2:x. (a) x=1, (b) x=2 and (c) x=4. The absorbance $A_{\parallel}$ (—) and $A_{\perp}$ (···) per $2\times20$ monolayers are plotted against the wavelength $\lambda$.

Both H-band and J-band show the in-plane anisotropy with dichroic ratio $R<1$

and $R>1$, respectively, where R is defined as $R=A_{\parallel}/A_{\perp}$.

Figure 2(b) shows the absorption spectra of ternary system of x=2 ([MS]:[$C_{20}$]:[$AL_{18}$]=1:2:2). Both blue-shifted and red-shifted components coexist with their peak heights comparable to each other. The blue-shifted band, located at 520 nm in this case, is less blue-shifted (0.10 eV) and rather broader in shape than that for x=1. Both blue-shifted and red-shifted bands show $R>1$, suggesting that the component of red-shifted J-band overlaps with the blue-shifted band.

Figure 2(c) shows the absorption spectra of ternary system of x=4 ([MS]:[$C_{20}$]:[$AL_{18}$]=1:2:4). The values of R are nearly unity over the entire range. The blue-shifted band is located around 520 nm as is the case with x=2, while the red-shifted component decreases appreciably.

We can interpret these experimental results by the theory of flow orientation and the extended dipole model.[11,13] According to the theory of flow orientation, molecular aggregates, elongated in shape, tend to be arranged with their longer axes parallel to the dipping direction, in the case of vertical dipping method. The flow orientation effect depends on the rotatory friction coefficient of the aggregate, which is roughly proportional to the square of aggregate length. The dichroic ratio R tends to be unity as the size of aggregates decreases. Consequently, the monomer band of MS is isotropic (R=1) and located around 540 nm. The extended dipole model predicts that a red-shifted J-band with $R>1$ will appear if head-to-tail alignments of transition dipole moments are formed and that a blue-shifted H-band with $R<1$ will appear if side-by-side alignments of transition dipole moments are formed.

As discussed in the previous papers,[1,2] the 505-nm band and the 590-nm shoulder are identified as the H-band with $R<1$ and J-band with $R>1$, respectively. The behavior of R for x=2 is interpreted by the superposition of J-band with $R>1$ and the 520-nm band with $R\fallingdotseq 1$ which corresponds to the oligomeric character of aggregates. It is noted that the energy shift of 0.10 eV for the 520-nm band is plausible for the side-by-side dimers. For x=4, both $A_{\parallel}$ and $A_{\perp}$ spectra are identical with each other, showing that the 590-nm shoulder is also characterized with $R\fallingdotseq 1$. It is also noted that the isotropic

behavior is compatible with the tetramers of Mizutani et al.[14] and also the " hierarchical structure model " of Misawa and Kobayashi.[15] The estimation of the aggregation number is now underway.

Surface pressure -area isotherm measurement

The surface pressure - area isotherms composed of binary and ternary systems of x=0, 1, 2, 3 and 4 ([MS]:[$C_{20}$]:[$AL_{18}$]=1:2:x) were measured. From the isotherms for [MS]:[$C_{20}$]=1:2, we assume the values of occupied area of about 20 $Å^2$/molecule and 56 $Å^2$/molecule for $C_{20}$ and MS, respectively. Using the values, we can estimate the occupied area per molecule of $AL_{18}$ for each molar mixing ratio.

Figure 3 shows the occupied area per molecule of $AL_{18}$ at 25 (mN/m) plotted against the molar fraction f=x/(1+2+x). The average values of occupied area remain in the range of 4~7 $Å^2$/molecule, which are far smaller than the cross section (about 20 $Å^2$/molecule) of a hydrocarbon chain. This suggests that $AL_{18}$ molecules do not significantly contribute to the area of the monolayer at the air-water interface.

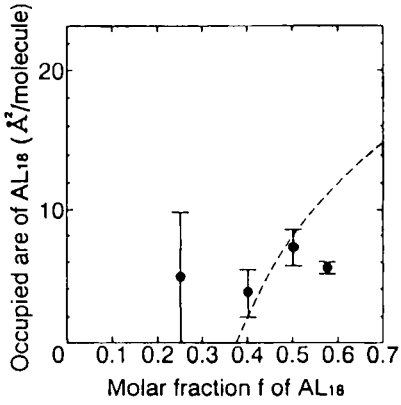



FIGURE 3 The occupied area per molecule of $AL_{18}$ at 25 mN/m is plotted against molar fraction f (f=x/(1+2+x)). The dashed line shows a theoretical curve which obtained from the present estimate.

According to Nakahara et al., each MS molecule in the binary system has an empty space which can accommodate two straight-chain hydrocarbons.[6] This suggests that $AL_{18}$ molecules in the present ternary system act as " fillers "[16-18] to trigger off the change in the aggregate structure.[19] If this is the case, the occupied area of $AL_{18}$ should be zero up to a certain value f=fc (fc=0.375 for the present estimate) and then increase monotonically tending to the limiting value (20 Å

$^2$/molecule). This picture, however, does not explain the present results, indicating a complicated equilibrium of $AL_{18}$ between inside and outside of empty space.

## ACKNOWLEDGMENT

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