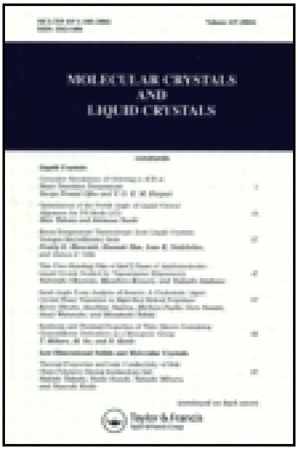

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Formation and Characterization of H-Like Band in Merocyanine Dye LB Films

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FORMATION AND CHARACTERIZATION OF H-LIKE BAND IN MEROCYANINE DYE LB FILMS

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Abstract The merocyanine-arachidic acid mixed LB films have been found to exhibit H-like band whose absorbance maximum is blue-shifted from that of monomer band. It is indicated that alkane molecules added to the mixed system induces the formation of H-like band.

INTRODUCTION

It is well known that merocyanine (MS)-arachidic acid (C20) mixed LB films, when they are prepared using the subphase containing Cd^{2+} under the conventional condition, are blue in color associated with a sharp absorbance peak around 590 nm. This absorption band shows the characteristics of J-band whose absorbance maximum is remarkably red-shifted from that of monomer band where it is considered that the J-band originates from the formation of dye aggregate.[1-8] Although the 590-nm band has been frequently reported, no attempts to form H-like band, of which absorbance maximum is markedly blue-shifted, have come to our knowledge.* In the present paper, we will report the formation and characterization of the H-like band.

EXPERIMENTAL

The Langmuir-Blodgett technique was employed for the sample preparation. The distilled water was purchased from Kanto Chemical Co., Inc., Japan. The subphase water,

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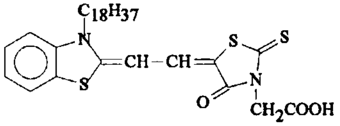
* H. Nakahara has reported on a blue-shifted band in the monolayers of an MS-methyl arachidate-hexadecan ternary system at air-water interface. This band was of transient nature and no discussion was given as to its origin.[5]

containing 4.5 × 10^{-4} M CdCl2 and 5.0 × 10^{-5} M NaHCO3 (pH 6.1-6.5), was kept at 17-20°C during monolayer deposition. Fig. 1 shows the chemical structures of merocyanine dye (MS), arachidic acid (C20) and hexadecane (HD). MS, C20 and HD were purchased from Japanese Research Institute for Photosensitizing Dyes, Co., Fluka Chemie AG, and Kanto Chemical Co., Inc., respectively. They were used without further purification.



MS

$CH_3-(CH_2)_{18}-COOH$

C20

$CH_3-(CH_2)_{14}-CH_3$

HD

FIGURE 1 Chemical structures of merocyanine dye (MS), arachidic acid (C20) and hexadecane (HD).

A glass substrate was precoated with five monolayers of cadmium arachidate (CdC20) to give a hydrophobic surface on both sides prior to the deposition of mixed monolayers. The chloroform of spectrograde, purchased either from Tokyo Kasei (solvent A) or from Dojin Kagaku (solvent B), was used as spreading solvent. The surface pressure was 25 mN/m. We prepared monolayers of a binary system with molar ratio [MS]:[C20]=1:2 and a ternary system with molar ratio [MS]:[C20]:[HD]=1:2:1. Twenty monolayers of MS were deposited at a velocity of 25 mm/min. onto both sides of the CdC20-coated substrate.

The absorption spectra $A_{\parallel}$ and $A_{\perp}$ were measured for each sample using a normal incident with the electric vector either parallel or perpendicular to the dipping direction, respectively, immediately after the sample preparation.

RESULTS AND DISCUSSION

Fig. 2 shows absorption spectra of MS-C20 binary system prepared using solvent A. The absorbance maximum is remarkably red-shifted from that of monomer band (540 nm). Main features of the spectra coincide well with those reported for the J-band in the earlier works. The J-band is located at 590 nm, by 0.2 eV red-shifted from the monomer peak (540 nm), and shows the in-plane anisotropy with the dichroic ratio $R > 1$, where R is defined as $R = A_{\parallel} / A_{\perp}$.

However, the blue-shifted band at about 510 nm is observed as shown in Fig. 3(a) or Fig. 3(b) when we use solvent B. We postulate that the blue-shifted band is an H-band since the spectral shape for the fully-developed case (Fig. 3(a)) is roughly mirror-symmetric with that of J-band (Fig. 2). The observed dichroic ratio, $R < 1$ for the blue-shifted band, is compatible with the above discussion. Fig. 3(b) shows the blue-shifted absorption shoulder around 510 nm and the red-shifted J -band around 590 nm.

The blue-shifted band disappeared and the spectra in Fig. 2 were reproduced when solvent B was distilled. It is therefore strongly suggested that a component in solvent B acts as " lubricant" or " trigger molecule" to control the arrangement of dye molecule.[9,10] Such a component in a spectrograde chloroform should be chemically stable, colorless in the visible range and less volatile than chloroform. In this respect, alkanes may be appropriate candidate. Hexadecane and octadecane have been employed for forming J-bands of cyanine and merocyanine dyes in the LB films.[5,9] Recently Azumi et al. have shown that the orientation of a porphyrin molecule can be controlled by hexatriacontane.[10]

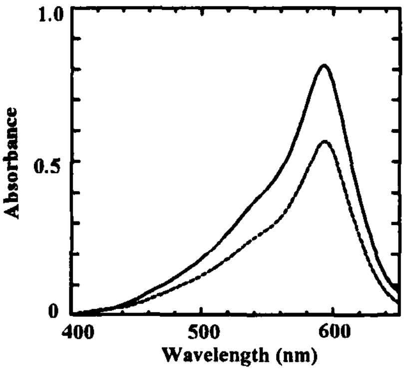


FIGURE 2 The absorption spectra of MS-C20 mixed LB films prepared using solvent A. The absorbances $A_{\parallel}$ (—) and $A_{\perp}$ (---) per 2 × 20 monolayers are plotted against the wavelength λ.

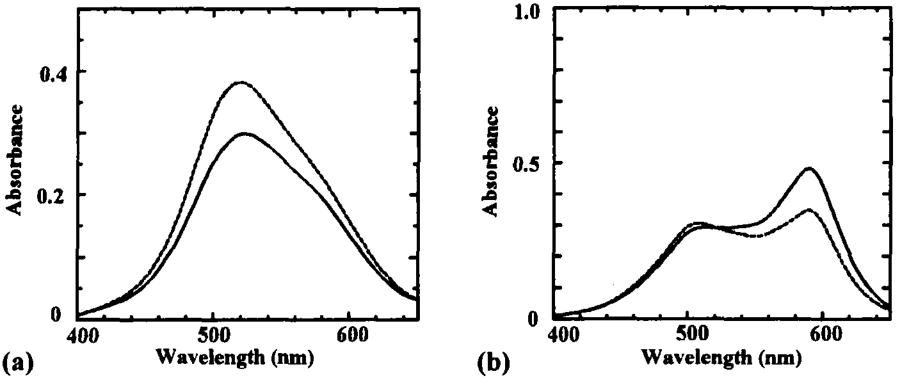


FIGURE 3 The absorption spectra of MS-C20 mixed LB films prepared using solvent B. The absorbances $A_{\parallel}$ (—) and $A_{\perp}$ (---) per 2×20 monolayers are plotted against the wavelength λ. (a) Fully-developed H-like band. (b) H-like and J-bands coexist.

A preliminary experiment was carried out employing hexadecane (HD) as trigger molecule to reproduce spectra shown in Fig. 3. Fig. 4 shows the typical absorption spectra of MS-C$_{20}$-HD mixed LB films prepared using distilled solvent B. The blue-shifted band is clearly seen, showing that HD acts as trigger molecule, while J-band remains.

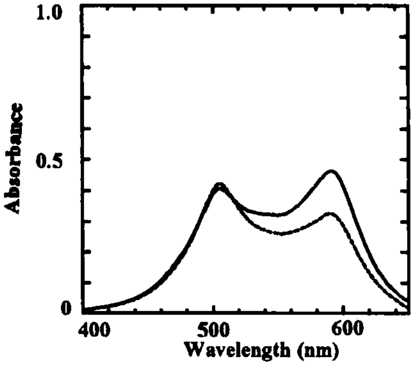


FIGURE 4 The absorption spectra of MS-C$_{20}$-HD mixed LB films prepared using distilled solvent B. The absorbance $A_{\parallel}$ (—) and $A_{\perp}$ (---) per 2×20 monolayers are plotted against the wavelength λ.

According to the theory of the flow orientation, molecular aggregates elongated in shape, tend to be arranged with their longer axes parallel to the dipping direction.[8] This indicates, together with the extended-dipole theory,[11] that J-band with $R > 1$ will appear if head-to-tail alignments of transition dipole moments are formed, and that H-band with $R < 1$ will appear if side-by-side alignments are formed. As is already mentioned, the anisotropic behavior in the present system is consistent with the above predictions. Further, the coexisted J- and H-like bands in Fig. 4 also hold these predictions at the corresponding wavelengths, respectively.

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