

상호혼합에 의한 메로시아닌 색소 단분자막의 2차원 거동 및 J-회합체 형성

論 文

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Two-Dimensional Behavior and J-Aggregate Formation of Merocyanine Dye Monolayers in Mutual Mixing

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Abstract - J-aggregates in the mutual mixing LB films of $[6\text{Me-DS}]_{1-x}[\text{DO}]_x$, $[\text{DS}]_{1-x}[\text{DO}]_x$ and $[\text{DSe}]_{1-x}[\text{DO}]_x$ have been studied by optical absorption, fluorescence and surface pressure-area isotherms. In $[6\text{Me-DS}]_{1-x}[\text{DO}]_x$ films, sharp J-band absorption and fluorescence of $[6\text{Me-DS}]$ are linearly shifted to the longer wavelength for the replacement of $[6\text{Me-DS}]$ by $[\text{DO}]$. According to the x , a smooth shift of the limited area has been cleared. In the $[\text{DS}]-[\text{DO}]$ system, the J-band is enhanced at 1:1 composition and strong fluorescence is also observed. Also, the presence of phase separation was suggested in the $[\text{DSe}]-[\text{DO}]$ system, because the absorption spectra were decomposed into $[\text{DSe}]$ and $[\text{DO}]$ spectra. On the other hand, in the pressure-area isothermal study, reduction in the molecular occupying area of monolayers has been clarified. This could be ascribed to the enhancement of molecular ordering in J-aggregates. These facts are also believed to reflect the most closely packed arrangement of chromophores in the merocyanine dye monolayers. Thus, it was confirmed that the interaction between mixed dye molecules and the $\text{CdCl}_2+\text{KHCO}_3$ subphases affected the J-aggregates of the LB films. Also, it is thought that the J-aggregates are formed non-dimensionally in LB films, such as solution synthesized $[\text{DX}:\text{DO}]$ assemblies on mixing.

Key Words : J-aggregates, Optical Absorption and Fluorescence Spectra, Merocyanine Dyes

1. Introduction

Dye aggregation, characterized by the close packing of chromophores and strong coupling, is of practical and theoretical interest because of particular photophysical behavior and distinct spectral features [1]. This study on the aggregation of merocyanine dyes aims to investigate the optical-physical behavior and the anisotropy of molecules. Especially, H. Kuhn provides a theoretical understanding of dye aggregation for LB films through the shift of optical absorption peaks [2,3]. In the study on this optical behavior, the most interesting result is that of the J-aggregates of cyanine dyes, interaction through structural analysis and functional behavior of dye aggregates [4].

The anisotropy of merocyanine LB films mixed with arachidic acid (C_{20}) has already been reported [5,6]. The J-aggregates of dye molecules have been confirmed in these systems. In the case of LB films for each dye molecule and for mixed molecules, new properties such as the shift of optical absorption peak have been observed

[7]. For example, a strong fluorescence peak was observed in the mixed LB film of $[\text{DS}]_{0.5}[\text{DO}]_{0.5}$ system [8,9].

In this paper we report on the aggregate formation in mixed monolayers with arachidate and in several long-chain merocyanine dyes with different unsymmetrical structures and modified hydrophilic groups, measured by surface pressure-area isotherms and the optical absorption and fluorescence spectra of the built-up films. Furthermore, the effects of subphases in forming J-aggregates of dye molecules have been investigated through surface pressure-area isotherms, and the shifts of absorption peaks by the change of mutual mixing have also been measured. The fluorescence properties of LB films obtained by mutual mixing dye molecules in various methods will be reported, using fluorescence spectra.

2. Experimental

The LB films were prepared by the standard vertical dipping method on glass plates for optical absorption and fluorescence measurements. The substrates were coated with five monolayers of cadmium arachidate to give a hydrophobic surface. The most pronounced J-like band was observed for the ratio $\text{DX}:\text{C}_{20}=1:2$ at a pressure 30mN/m . Three mixed solutions of DX ($X=\text{O}, \text{S}, \text{and Se}$)

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and 6Me-DS with C₂₀ in CHCl₃ were used as originals and they were further mixed with appropriate ratios to give a binary mixture system, and multilayers consisted of up to 20 monolayers deposited on glass substrates from a subphase (pH, 6.1~6.2) containing 4×10⁻⁴ M CdCl₂ and 2×10⁻⁵ M KHCO₃ at 20~21°C.

The NL-501-MWH (NLE Co.) moving wall type trough was used to obtain LB films and π-A isotherm was also measured by the LB trough. Optical absorption spectra were revealed using a double-beam spectrometer (MPS-2000, Shimadzu CO.) with polarizers. For luminescence measurements, sample multilayers were excited by 540 nm light from a 100W Xe lamp through an interference filter. The emitted luminescence was detected using a lateral-scattering geometry. The experimental instruments and conditions are summarized in Table 1:

Table 1. Instruments and deposition conditions.

trough	NL-501-MWH(NLE Co.) moving wall type
optical absorption	MPS-2000 (Shimadzu Co.)
fluorescence	lateral scattering geometry λ _{ex} = 540nm (100W Xe lamp)
materials	merocyanine [DX:(X=O,S or Se)],[6Me-DS]
samples	Y-type multilayer
substrate	glass plate (for optical absorption)
solute	DX 1×10 ⁻² mol/l } [DX] C ₂₀ 2×10 ⁻³ mol/l
solvent	CHCl ₃
deposition	vertical dipping method (dipping speed = 100 mm/min)
surface pressure	25 mN/m
buffer	CdCl ₂ 4×10 ⁻⁴ mol/l
	KHCO ₃ 2×10 ⁻⁵ mol/l
	pH 6.2
	temperature 20 ± 1 °C

3. Results and Discussion

In the case of L films for interaction with Cd²⁺ ions, it is known that the interaction with the amphiphilic function of spreading molecules is strong and that the aggregation status of L films is closely packed. Thus the dye LB films immersed in arachidic acid have been deposited using subphases with CdCl₂. But the LB films complexed with CdCl₂ show a collapse and dissociation status by physical and chemical treatment. It is known that the aggregation status of the LB films is changed by Cl⁻ ions. For example, in the case of merocyanine LB films included in arachidic acid complexed with CdCl₂, the J-aggregates of dye molecules are formed and have a blue color. The J-aggregates are dissociated and the dye becomes non-dimensional gas injection, etc. The same LB films have a red color with the same solution status.

The merocyanine dyes such as DX (X=O, S or Se) and

6Me-DS shown in Fig. 1 have been used to deposit LB films. Also Fig. 1 shows the absorption spectra of each dye molecule used in this study. The characteristics of LB films have been separated into three types; for example, [6Me-DS] LB films represent sharp J-band absorption around 610 nm and strong fluorescence. There is no fluorescence in [DS] and [DSe] LB films but a confirmed J-like band. [DO] LB films don't show a J-band [10]. The absorption peak in Fig. 1 showed that it is different from the solution of oriented chromophores induced by dipole-dipole interaction.

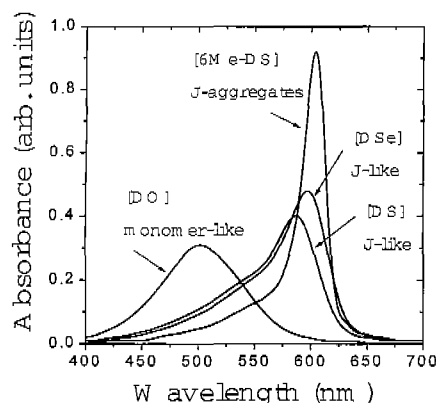
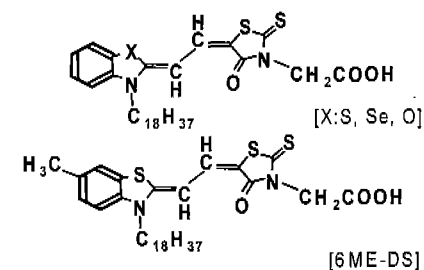


Fig. 1. Chemical structure and optical absorption spectra of the LB films of merocyanine dyes in this work.

Fig. 2 shows the absorption spectra of the mixed merocyanine LB films. In the optical absorption spectra observed in the mixed LB films of merocyanine dyes, the [DO] peak doesn't exist in the case of the mixed [DS]_{0.5}[DO]_{0.5} and [6Me-DS]_{0.5}[DO]_{0.5}, but exist in the mixed [6Me-DS]_{0.5}[DO]_{0.5}. Especially, the absorption peak of the mixed LB films was different from the calculated one, and the absorbance peak of [DO] and [DSe] has been shifted linearly except in [DSe]_{0.1}[DO]_{0.9} LB films. This means that the structure of the [DSe]_{1-x}[DO]_x system in LB films is considerably mixed.

The experimental results were different from those calculated for each dye molecule. The mixed LB films have structural characteristics which can confirm the reason for the absorption peak shift, but the LB films don't exhibit such structural characteristics. The formation of J-aggregates by the four types of mixing of

merocyanine dyes has been investigated through the absorption peaks.

Previous papers have investigated the shifts of absorption peaks by the changes in mixing effects [9]. The absorption spectra of [6Me-DS] show J-band peaks, [DS] and [DSe] J-like bands, and [DO] monomer bands. And the merocyanine dye mixed LB films, depending on [DO] concentration, have been investigated. In the $[DS]_{1-x}[DO]_x$ system, the shifts of an irregular absorption peak are observed. Especially, in the $[DS]_{0.5}[DO]_{0.5}$ system, the [DS] aggregates have been referred to not as J-bands but as J-like bands. It is understood that these results were under the influence of new structures by the mixing effect. In the $[6Me-DS]_{1-x}[DO]_x$ system, a sharp J-band peak is linearly shifted to the longer wavelength for the replacement of 6Me-DS by DO. However, the shifts of absorption peaks in the $[DSe]_{1-x}[DO]_x$ system were similar to those of the $[6Me-DS]_{1-x}[DO]_x$ system. The shifts of absorption peaks for [DSe] dye molecules decreased with the increase of [DO] concentration, different from the case of $[DSe]_{1-x}[DO]_x$ and $[6Me-DS]_{1-x}[DO]_x$ systems which showed main absorption peaks by [DO] dye molecules.

On the other hand, $[DS]_{0.5}[DO]_{0.5}$ LB films show strong fluorescence. In the experimental results which compare the fluorescence difference between the films by pure dye solution and the mixed films, a single emission peak can't be observed in the pure films except [6Me-DS].

Fluorescence characteristics of [6Me-DS] were thought to affect those of the $[6Me-DS]_{1-x}[DO]_x$ system. The fluorescence intensity in the $[6Me-DS]_{1-x}[DO]_x$ system was irregular but the fluorescence peaks were shifted with [DO] concentration. The fluorescence peaks of monomers showed that [DO], which doesn't exist in other mixing ratios of the $[6Me-DS]_{1-x}[DO]_x$ system, dose exists. We also investigated other concentrations for the $[DS]_{1-x}[DO]_x$ system; however, strong fluorescence from the J-aggregates of $[DS]_{0.5}[DO]_{0.5}$ LB films was not detected in pure [DS] LB films. This is the reason why [DS]'s aggregates have been called not as J-aggregates but as J-like aggregates. This would be related to the single emission peak with Stokes' shift characteristics of J-aggregates.

It is thought that these experimental results can be understood from the absorption spectra. The absorption bands by optical absorption spectra have a direct connection with fluorescence characteristics. For example, as shown in Fig. 2(a), the absorption peak of $[DS]_{0.5}[DO]_{0.5}$ didn't exist in [DS] LB films. It is thought that the $[DS]_{0.5}[DO]_{0.5}$ mixed LB films have J-band absorption peaks due to the mixing. As shown in Fig. 2(c), the absorption peak didn't exist because of the coexistence of J-like bands and monomer bands. This is due to the formation of LB films with a new absorption band.

Therefore, there is a single emission peak because of the existence of J-bands in the case of the absorption peaks for [6Me-DS] and $[6Me-DS]_{0.5}[DO]_{0.5}$. Then, it can be determined that the strong J-bands have a connection with the existence of fluorescence peaks.

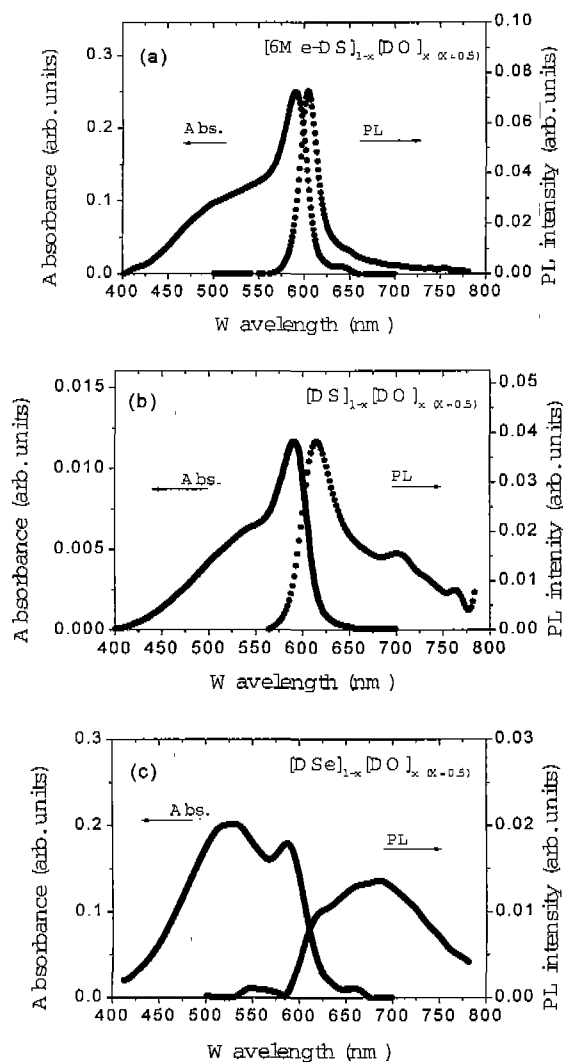


Fig. 2. Absorption and fluorescence spectra of the J-aggregates formed by the mixed LB films of merocyanine dyes. The intensities are normalized at the peak intensity.

In $[DS]_{0.5}[DO]_{0.5}$ and $[6Me-DS]_{0.5}[DO]_{0.5}$ LB films, Fig. 2 shows both sharp J-band absorption and fluorescence peaks. In particular, [6Me-DS] LB films show a single emission peak with a Stokes' shift observed. In experimental results, the $[6Me-DS]_{1-x}[DO]_x$ system is observed with shifts of peak positions by absorption and fluorescence spectra, but these characteristics in the case of a single emission peak can't be observed in mixed LB films except Fig. 2(b) of $[DS]_{0.5}[DO]_{0.5}$ LB films. And

these characteristics can't also be investigated in the $[DS]_{1-x}[DO]_x$ system.

In the $[6Me-DS]_{1-x}[DO]_x$ system, especially the fluorescence intensity in the $[6Me-DS]_{1-x}[DO]_x$ system was irregular but fluorescence peaks were shifted with $[DO]$ concentration. The fluorescence peaks of monomers showed that $[DO]$, which doesn't exist in other mixing ratios of $[6Me-DS]_{1-x}[DO]_x$, does exist.

On the other hand, the fluorescence characteristics as to the number of LB films were investigated to confirm the concentration dependence and existence of $[DO]$. The fluorescence intensity and monomer peaks of $[DO]$ increased with the number of LB films.

Fig. 3 shows the Stokes' shifts about 8 nm shifts of peak positions of $[6Me-DS]$ LB films. However, in $[6Me-DS]_{0.2}[DO]_{0.8}$ LB films, the Stokes' shifts were observed over 50 nm of shifted peak positions. The reason that they can't be observed in another mixing ratio of $[6Me-DS]_{1-x}[DO]_x$ is due to the different mixing characteristics between dye molecules. In the case of mixing of $[6Me-DS]$ and $[DO]$, $[DO]$ molecules exist at non-dimension in LB films or obtained $[6Me-DS:DO]$ assemblies on mixing.

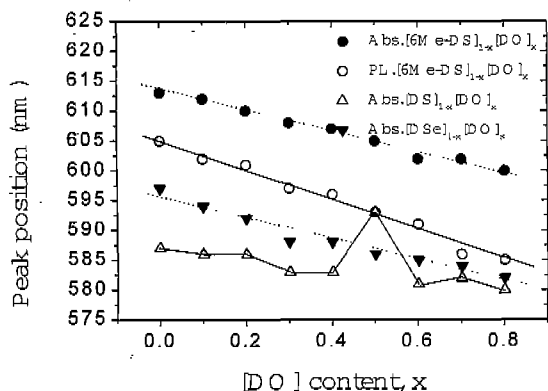


Fig. 3. The $[DO]$ concentration dependence of the J-band peak positions shifted by the $[6Me-DS]_{1-x}[DO]_x$ LB films of merocyanine dyes.

Fig. 4 shows the shifts of the limited area (A_c) and the collapse positions (P_c) of dye molecules as to the change of subphases at the air-water interface. The subphase of $CdCl_2+KHCO_3$ was used to investigate the correlation with J-aggregates. In Fig. 4, the subphase was $CdCl_2+KHCO_3$ and the experimental condition compared with J-aggregates of dye molecules. The limited area was compared with the decreased pure water when $CdCl_2+KHCO_3$ was used as a subphase. The same results have also been obtained in changing barrier speed and spreading volume of dye molecules.

Generally, in the case of $CdCl_2+KHCO_3$ as a subphase,

dye molecules are lying at the air-water interface in the gas phase but sinking under the air-water interface in the solid phase of high pressure. This means that a side chain of dye molecules exists under the air-water interface by the interaction with subphase Cd^{2+} ions.

The side chain of dye molecules exists on the air-water until the surface pressure is in the limited area, but that of dye molecules is under the air-water interface at the surface pressure over 70 mN/m. It is thought that the difference of the surface pressure-area ($\pi-A$) isotherms between pure water and $CdCl_2+KHCO_3$ is due to the change of molecular structure by interaction between subphases and the side chain of dye molecules. Thus, the interaction between subphases and dye molecules is related to the existence of J-aggregates in LB films.

Fig. 4 also shows the limited area and the collapse positions from surface pressure-area isotherms of $[DS]_{1-x}[DO]_x$, $[6Me-DS]_{1-x}[DO]_x$ and $[DSe]_{1-x}[DO]_x$. They affects the deposition status of LB films because these characteristics were determined by the structure of dye LB films and the occupied areas per molecule. The limited area and the collapse positions as the measurement of the optical absorption and fluorescence spectra, since LB films are on the substrates. Thus, the deposition status is determined by the status of the monolayer on the air-water interface.

By the analysis for the air-water interface of merocyanine dyes, in all cases, the limited area, obtained from the extrapolation of the linear part to zero pressure, suggests chromophore orientation with the long axis lying nearly flat on the surface and the short axis standing almost vertically. When the benzothiazol ring is carbon, the monolayer is found to be more condensed than the other cases. Furthermore, the number of methylene carbons is important between the rhodanine ring and compressibility with a higher collapsed pressure. These facts are thought to reflect the most closely packed arrangement of chromophores in the merocyanine dye monolayer [11].

On the other hand, the collapse positions of the mixed dye molecules show the change of surface pressure depending on the $[DO]$ concentration ratios. But the limited area obtained by the surface pressure-area isotherms didn't show a linear connection, such as absorption peaks. The limited area of $[DS]_{0.5}[DO]_{0.5}$ was different from that of other mixing ratios. It is considered that these characteristics are connected with J-bands and fluorescence peaks from the absorption spectra of $[DS]_{0.5}[DO]_{0.5}$ LB films. The monolayers of dye molecules on the air-water interface affect structural orientation.

Thus, the decrease of the limited area of $[DS]_{0.5}[DO]_{0.5}$ represents the simultaneous formation of J-bands and high density films. It was confirmed that J-like bands of $[DS]$

were changed to the J-bands in $[DS]_{0.5}[DO]_{0.5}$ LB films. As a results, the shifts of the surface pressure-area isotherms occurred with the limited area of dye films, compared with the specific peaks obtained from the measurement of fluorescence peaks and the absorption peaks obtained from the mixed LB films. These changes of the surface pressure-area isotherms also have connections with hydration phenomena of the dye molecules and the change of molecular structure by the formation of interaction between dye molecules and subphases. It was assured that the interaction between the mixed dye molecules and the $CdCl_2+KHCO_3$ subphase affected the J-aggregates of LB films. Also, it is thought that the J-aggregates are formed non-dimensionally in LB films, such as solution synthesized $[DX:DO]$ assemblies on mixing.

$[6Me-DS]$ are linearly shifted to the longer wavelength for the replacement of $[6Me-DS]$ by $[DO]$. According to the x , a smooth shift of the limited area has been cleared. On the other hand, in the $[DS]-[DO]$ system, the J-band is enhanced at the 1:1 composition and strong fluorescence is also observed. And the presence of phase separation was suggested in the $[DSe]-[DO]$ system, because the absorption spectra were decomposed into $[DSe]$ and $[DO]$ spectra. From the pressure-area isothermal study, reduction in the molecular occupying area of $[DS]_{0.5}[DO]_{0.5}$ has been clarified. It could be ascribed to the enhancement of molecular ordering in J-aggregates. Thus, it is thought that the J-aggregates are formed non-dimensionally in LB films, such as solution synthesized $[DX:DO]$ assemblies on mixing.

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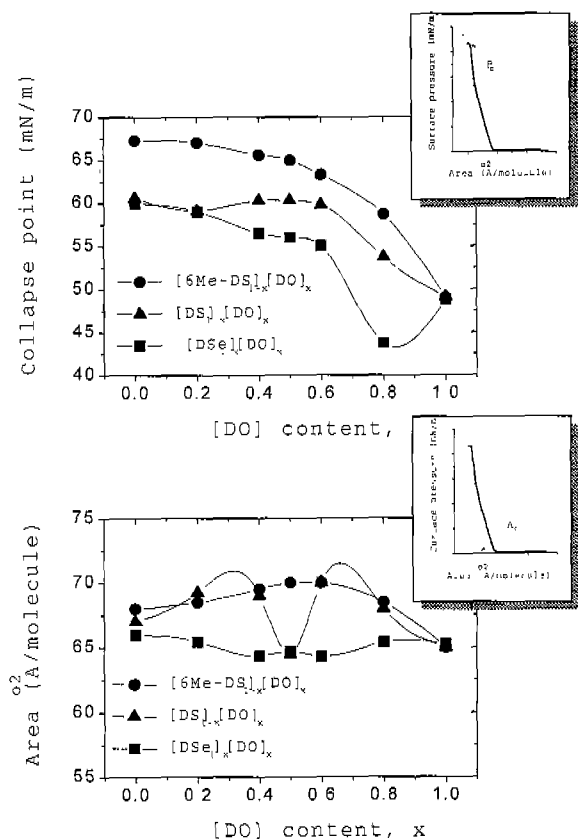


Fig. 4. Collapse positions and the limited area for the monolayers of the mixed merocyanine dyes measured by surface pressure-area ($\pi-A$) isotherms.

In conclusion, J-aggregates in the mutual mixing LB films of $[6Me-DS]_{1-x}[DO]_x$, $[DS]_{1-x}[DO]_x$ and $[DSe]_{1-x}[DO]_x$ have been studied by optical absorption, fluorescence and surface pressure-area isotherms. In $[6Me-DS]_{1-x}[DO]_x$ films, sharp J-band absorption and fluorescence of

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