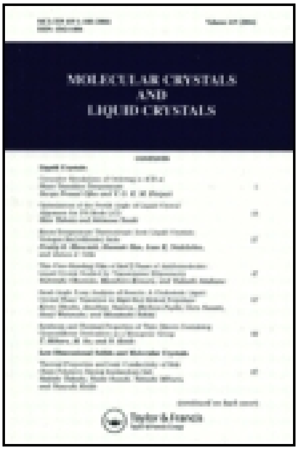

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THE MUTUAL MIXING EFFECT IN THE LB FILMS OF MEROCYANINE DYES

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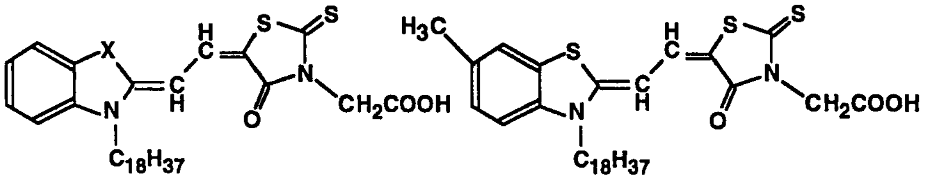
Abstract The mutual mixing effect in the LB films of four kinds of merocyanine dyes have been investigated by optical absorption and fluorescence measurements. In single component films, DSe, DS and 6-methyl DS (6Me-DS) can form J-like aggregates but not for DO. In [6Me-DS]-[DO] system, a sharp J-band peak linearly shifts to the longer wavelength for the replacement of 6Me-DS by DO. In [DS]-[DO] system, [DS]:[DO]=1:1 film shows a both sharp J-band absorption and fluorescence peak. The behavior are understood by the formation of the 'solid solution' for [6Me-DS]-[DO] and the 'intermolecular compound' for [DS]-[DO]. Furthermore, the spectrum of [DO]-[DSe] system shows the presence of the 'phase separation'. These results would relate to an interesting problem, what we may call a '2-dimensional phase diagram' in J-aggregates.

INTRODUCTION

The formation of J-aggregates is one of the important subjects for molecular arrangement of dye (1). The characteristic red-shifted bands in the optical absorption spectra, suggesting the presence of the J-aggregate, have been observed in merocyanine-dye LB films (2, 3). Figure 1 shows molecular structure of surface-active merocyanine dyes for LB films (a): X=O (DO); X=S (DS); X=Se (DSe) and (b): 6-methyl DS (6Me-DS). ESR spectroscopy of DS films has revealed a well-defined in-plane molecular orientation that is consistent with the flow-orientation of J-aggregates (4). As has been reported previously, DX mixed with arachidic acid (C_{20}) with a molar ratio DX:C_{20} = 1:2 are stable for Y-type multilayer (2-5) and hereafter solutions of these 1:2 mixture in $CHCl_3$ and its LB films are simply abbreviated as [DX]. Optical properties of these surface-active merocyanine dye LB films can be classified into three-types, that is, the [6Me-DS] films show sharp J-band absorption and strong fluorescence, the [DS] and [DSe] show broad J-like absorption and almost no fluorescence and the [DO] films do not show J-band. In such case, it would be an interesting subject to study the mutual mixing effects because the functional properties of LB films are considered to be strongly dependent on the molecular species and their microscopic structures (3-6).

Here we report the formation of J aggregates in a mixed merocyanine-dye LB films containing a non J-aggregate forming dye, DO, in a single component case.



(a) DX: (X = O, S or Se) **(b) 6Me-DS**

FIGURE 1 Molecular structure of surface-active merocyanine dyes for LB films (a): X=O (DO); X=S (DS); X=Se (DSe) and (b): 6-methyl DS (6Me-DS)

EXPERIMENTAL

The LB films were prepared by the standard vertical dipping method on sheets of mylar (polyethylene terephthalate) for ESR and on glass plates for optical absorption and fluorescence measurements. The substrate was coated with five monolayers of cadmium arachidate to give a hydrophobic surface. The most pronounced J-like band was observed for the ratio DX:C_{20}=1:2 at a pressure of 25 mNm^{-1}. Three mixed solutions of DX (X=O, S and Se) and 6Me-DS with C_{20} in $CHCl_3$ were used as original and they were further mixed with appropriate ratios to give binary mixture system. Multilayers used consisted of up to 100 monolayers deposited on mylar and glass substrates from a subphase (pH, 6.1-6.2) containing 4×10^{-4} M $CdCl_2$ and 2×10^{-2} M $KHCO_3$ at 20-21 °C. Optical absorption spectra were measured using a double-beam spectrometer (MPS-2000, Shimadzu Co.) with polarizers. For the luminescence measurements, the sample multilayer was excited by the 540nm light from 100W Xe lamp through an interference filter. The emitted luminescence was detected using a lateral-scattering geometry.

RESULTS AND DISCUSSION

As described previously, [DSe], [DS] and [6Me-DS] show a characteristic red-shifted band around 590-600nm. On the other hand, [DO] shows no discernible aggregation and can be characterized as a single-peaked monomer band centered around 500nm. Optical absorption spectra of $[6Me\text{-}DS]_{1-x}[DO]_x$ mixed LB films are shown in Fig. 2 (a). The J-like band around 605nm which is observed in [6Me-DS] is maintained up to the [DO] concentration as high as around x=0.7. The continuous shift as varying x has been ascribed to the homogeneous mixing effect of two kinds of aggregates with different absorption peaks, as reported in the case of cyanine dyes by Penner and Möbius in ref (6). In the present study, however, DO doesn't show the J-band peak itself. The

6Me-DS molecules would form a 'solid solution' with DO in wide x regions and the most part of DO molecules associate to form J-like aggregates. Similar but clearly different behavior has been observed in another mixed systems, such as $[DS]_{1-x}[DO]_x$. As shown in Fig. 2 (b), optical absorption spectra of $[DS]_{1-x}[DO]_x$ mixed LB films show that the broad J-like band around 590nm which is observed in [DS] is maintained up to the [DO] concentration as high as x=0.7. The band width of J-band absorption for x=0.5 is rather smaller than that of x=0 ([DS]). Figure 3 shows the [DO] concentration dependence of the J-band peak position for $[6Me\text{-}DS]_{1-x}[DO]_x$ and $[DS]_{1-x}[DO]_x$. In the $[6Me\text{-}DS]_{1-x}[DO]_x$ system, the absorbance peak almost linearly shifts to a shorter wavelength with increasing x. On the other hand, in $[DS]_{1-x}[DO]_x$ system, the peak shift is not monotonic as shown in the figure. In order to further investigate the J-like aggregates of the $[DS]_{0.5}[DO]_{0.5}$ films, fluorescence measurements were carried out and a strong

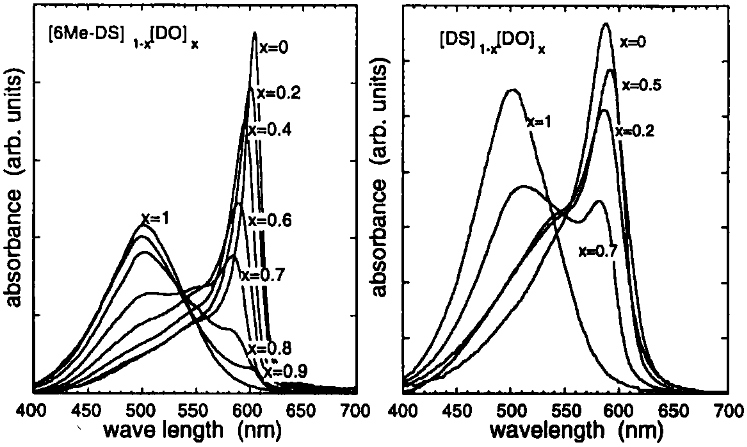


Figure 2 Optical absorption spectra of (a):$[6Me\text{-}DS]_{1-x}[DO]_x$ and (b):$[DS]_{1-x}[DO]_x$ mixed LB films.

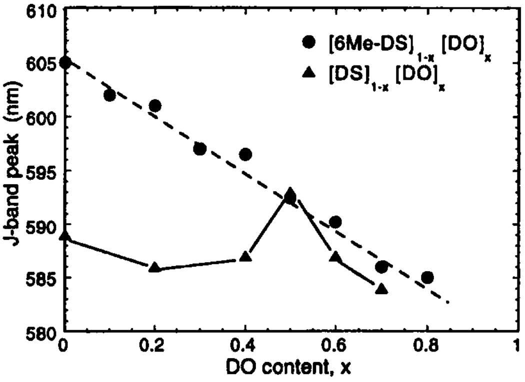


Fig.3 The [DO] concentration dependence of the J-band peak position for $[6Me\text{-}DS]_{1-x}[DO]_x$ and $[DS]_{1-x}[DO]_x$ mixed LB films.

fluorescence has been observed in $[DS]_{0.5}[DO]_{0.5}$ suggesting the well defined aggregates. We also investigated other concentration for $[DS]_{1-x}[DO]_x$ films, however, strong fluorescence from the J-aggregates of $[DS]_{0.5}[DO]_{0.5}$ system was not detected. Thus, we supposed that the observed red-shifted J-band for $[DS]_{0.5}[DO]_{0.5}$ is essentially different from [DS]'s absorption peak. The best known example of such case is so-called 'intermolecular compound'.

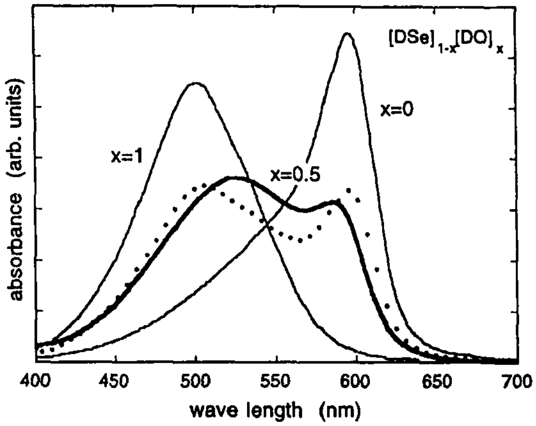


Fig.4 Optical absorption spectra of [DSe]0.5[DO]0.5 mixed LB films (thick solid curves), together with that of [DSe] and [DO] spectra (thin curves) for comparison. The dotted lines are calculated curves which obtained from [DSe]+[DO] spectra.

Finally, we comment on the [DSe]-[DO] system. Figure 4 shows optical absorption spectra of $[DSe]_{1-x}[DO]_x$ mixed LB films, the dotted line is calculated curve which is simply obtained from [DSe] spectra + [DO] spectra. As shown in this figure, the spectra of $[DSe]_{0.5}[DO]_{0.5}$ film were almost decomposed to [DSe] and [DO] spectra, suggesting phase separation. These results suggest that the ability of compound to form J aggregates is highly sensitive to mixing conditions. Small changes in environment can lead to the formation of different geometries with different spectroscopic properties. These 'solid solution', 'intermolecular compound' and 'phase separation' would relate to an interesting problem, what we may call a '2-dimensional phase diagram' in J-aggregates.

References

1. H. Kuhn, D. Möbius and H. Bücher, Techniques of Chemistry, (Wiley, New York, 1973) Vol. 1, Part IIIB, p 577.
2. M. Sugi and S. Iizima, Thin Solid Films, 68 (1980) 199
3. T. Inoue, Thin Solid Films, 132 (1985) 21
4. S. Kuroda, Colloids and Surfaces, A72 (1993) 127
5. K. Murata, S. Kuroda and K. Saito, Thin Solid Films, in press.
6. T. L. Penner and D. Möbius, Thin Solid Films, 132 (1985) 185