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Formation of J-aggregates of mixed merocyanine dyes in Langmuir–Blodgett films

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Abstract

The formation and stability of J-aggregates of a $[\text{6Me-DS}]_{1-x}[\text{DO}]_x$ mixed dye system in Langmuir–Blodgett films have been investigated using absorption and photoluminescence measurements. The variations of the spectral weights of the J-aggregate and DO monomer bands with DO content x allowed us to find that there exist two different regions: phase separation and solid solution. For $0 \leq x \leq 0.3$, J-aggregates are formed from 6Me-DS molecules, and DO molecules exist as a monomer. In the range $0.4 \leq x \leq 0.8$, J-aggregates are stably formed from both 6Me-DS and DO molecules. We have also found that the quantum efficiency of the J-aggregate emission for $x = 0.6$–0.7 is higher than for the pure 6Me-DS dye system.

Keywords: J-aggregate; Merocyanine dye; LB film; Absorption; Photoluminescence

1. Introduction

Molecular assemblies such as J-aggregates and dendrimers have attracted much attention from the viewpoint of chemistry and physics of molecular nanostructures [1–3]. In J-aggregates highly ordered molecular arrangements are accomplished, and ordering of transition dipole moments generates collective excitation states (Frenkel exciton). Such Frenkel exciton states govern various photophysical and photochemical properties of J-aggregates [4–8].

J-aggregates have been known to form a hierarchical structure in which a J-aggregate domain with a size of 1–100 μm consists of coherent aggregates on a scale of several tens nanometers [9]. In pseudoisocyanine (PIC) dye films J-aggregates form a fibrous structure with a length of 10–100 μm and a width of 30–160 nm [10–12], and such a domain structure is composed of small coherent aggregates. Our previous study has shown that the size and shape of the domain structure in merocyanine dye films depend on the concentrations of merocyanine and arachidic acid, and the domain shape changes from the grain-shape into the fiber-shape [13,14].

A mixture of different dye molecules is also an interesting system to investigate the formation and stability of J-aggregates. In merocyanine dyes, 3-carboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone (abbreviated as DS) and its derivatives of DSe and 6Me-DS form J-aggregates in Langmuir–Blodgett (LB) films, while DO does not form aggregates. Several studies on mixed merocyanine dye systems have already been done for LB films, and have found that J-aggregates are formed in LB films of mixed dyes containing DO molecules [15–17]. In this paper, we report on a systematic study of the formation and stability of J-aggregates in a mixed dye system of 6Me-DS and DO molecules($[\text{6Me-DS}]_{1-x}[\text{DO}]_x$). Optical absorption and photoluminescence measurements have been performed for LB films with different DO contents x.

2. Experimental

Molecular structures of merocyanine dyes used in this study are shown in Fig. 1. The dye molecule abbreviated as 6Me-Ds has a structure in which a proton at the 6-position

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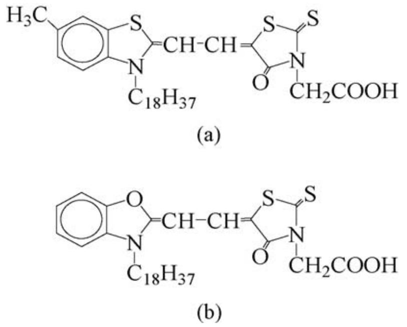

Fig. 1. A. Nakamura et al., Formation of J-Aggregates of Mixed Merocyanine Dyes in Langmuir-Blodgett Films.

in benzothiazole of 3-arboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone (abbreviated as DS) is substituted by a methyl group. A derivative of DS, in which S in DS is substituted by O, is abbreviated as DO. J-aggregates of the mixed dye system of 6Me-DS and DO molecules were prepared with a LB method [18,19]. LB films consisting of eight molecular layers were fabricated on silica glass substrates using a standard vertical dipping method from a mixed solution of $[\text{6Me-DS}]_{1-x}[\text{DO}]_x$ and arachidic acid with a molar ratio of 1:2. The aqueous subphase was prepared by adding 3×10^{-4} M $CdCl_2$ and 5×10^{-5} M $KHCO_3$. The subphase temperature was kept at 20.5 °C, and pH was between 5.8 and 6.0.

We measured pressure–area (π–A) isotherms at the air–water interface of monolayer films. Plots of surface pressure (π) versus molecular area per arachidic acid molecule (A) are shown in the inset of Fig. 2. The surface pressure exhibits an abrupt increase in the range of 0.45–0.65 nm^2 depending on the DO content x. The decrease in the molecular area with x is ascribed to the small size of the DO molecule compared with the 6Me-DS molecule. During the dipping process the surface pressure was kept at 30 mN/m.

Absorption spectra were measured using a double-beam spectrophotometer. Photoluminescence (PL) spectra were detected with a spectrometer equipped with a charge-coupled device (CCD) detector. A cw-Nd:YAG laser with a wavelength of 532 nm was used as an excitation source.

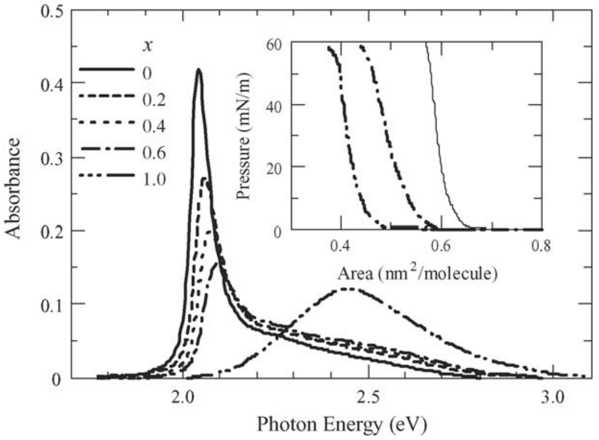

Fig. 2. Absorption spectra of $[\text{6Me-DS}]_{1-x}[\text{DO}]_x$ LB films with different DO contents x. Surface pressure-area isotherms for $x = 0$, 0.6 and 1 are shown in the inset.

3. Results and discussion

Fig. 2 shows absorption spectra of LB films with different DO contents. A sharp absorption band peaked at 2.043 eV for $x = 0$ is assigned to the Frenkel exciton transition (J band) in J-aggregates. For $x = 1$, the broad absorption band is observed at 2.450 eV, and is assigned to the S_0–S_1 transition of DO monomers, which indicates that there is no J-aggregate in the pure DO dye system. With increasing DO content in the mixed dye system the peak absorbance of the J band decreases, and the peak shifts to the higher energy side, suggesting the formation of J-aggregates.

To discuss quantitatively the formation of J-aggregates we derived spectral weights of the J and monomer bands from the spectral analysis of the observed spectra. The absorption spectra were analyzed in the following way. For $x = 0$, the J band was fitted to two Gauss functions to reproduce the asymmetric shape, and the spectral shape in the photon energy range 2.2–2.7 eV was fitted to two Gauss functions which were assigned to optical transitions of dimmers [20]. Ikegami reported that the absorption bands observed at 2.282 and 2.443 eV in 6Me-DS Langmuir films are due to dimmers, showing the Davidov splitting [20]. In our study, such absorption bands were also observed as more pronounced peaks at 2.236 and 2.420 eV in the LB film in which the J band absorption was relatively weak because the film was not well stacked. For $x = 1$, the spectrum was analyzed by using two Gauss functions to reproduce the asymmetric shape of the DO monomer band. Keeping the peak energies and the widths of the 6Me-DS dimmer band and the DO monomer band constant, we analyzed the absorption spectra in the LB films with different DO contents. The error of determination of the spectral weight was about 10%.

Fig. 3(a) shows the spectral weight of the J band, and the straight line in the figure depicts the relative number of 6Me-DS molecules. The spectral weight is proportional to the number of molecules contained in the J-aggregates if the oscillator strength is kept constant with the variation of the DO content. For $0 \leq x \leq 0.3$, the spectral weight decreases linearly with x, and is proportional to the number of 6Me-DS molecules. In the range between 0.4 and 0.8, however, the spectral weight is larger than that expected from the relative number of 6Me-DS molecules contained in the J-aggregates. This deviation from the proportionality suggests that there is an additional contribution to the J band absorption. For $x \geq 0.9$, the J band cannot be observed. As shown in Fig. 3(b) the spectral weight of the DO monomer band increases linearly with x for $0 \leq x \leq 0.3$. For $0.4 \leq x \leq 0.8$, however, the deviation of the spectral weight from that expected from the relative number of DO molecules in the LB film is observed. For $x > 0.9$, the spectral weight of the DO monomer band is proportional to x.

The variations of the spectral weights observed in the range $0 \leq x \leq 0.3$ indicate that the J-aggregates are formed from only 6Me-DS molecules, and DO molecules exist as a monomer. By contrast, for $0.4 \leq x \leq 0.8$ DO molecules are contained in