

J-Aggregates in Langmuir–Blodgett Films of a Merocyanine Dye without Metallic Cations: Using FT-IR to Observe Changes in the Electronic Structure of the Molecules upon Aggregation

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Langmuir–Blodgett films of mixtures of fatty acids (FA) and a merocyanine dye (DS), bearing one long alkyl chain and one carboxylic group, were prepared at a nitrogen–pure water interface. The films exhibit a distinct and highly anisotropic J-band near 605 nm, even though they do not contain any metallic or ammonium cations. Although an isotropic band was seen in the region of 500–550 nm, the contribution of the J-aggregates was extracted from the observed visible and IR absorption spectra by using the difference in the polarization of the bands. This analysis indicates a change in the electronic structure of DS in the J-aggregates, probably corresponding to intramolecular charge transfer. Furthermore, this analysis also suggests that in this metal-free case, the formation of the J-aggregates is strongly affected by the hydrogen bonding between the carboxylic groups in two DS and that between the carboxylic groups in DS and FA.

1. Introduction

J-aggregates in Langmuir–Blodgett (LB) films of merocyanine dyes, especially 3-carboxy-methyl-5-[2-(3-octadecylbenzothiasolin-2-ylidene)-ethylidene]rhodanine (abbreviated as DS and shown in the inset of Figure 1), have attracted much attention because of their interesting properties, such as photoconduction,^{1,2} in-plane anisotropy,^{3,4} thermo- and chemichromism,^{5,6} and nonlinear optics.^{7,8} The formation mechanism of the J-aggregates has also been studied in LB films of DS^{9–15} and other merocyanine dyes.^{10,16,17} As for the pure DS system, which bears one alkyl chain and one carboxylic group, Iriyama et al.⁹ reported that the J-band is much more distinct on a Cd-containing buffer solution than on pure water, although they could detect a small J-band on pure water. Therefore, buffer solutions containing metal or ammonium cations are commonly used as the subphase for the LB deposition of DS.^{1–15} An exception to this is the well-developed J-band that has been reported for LB films of a 1:1:1 ternary mixture of DS, fatty acids (FA), and hexadecane, prepared on pure water.¹¹ However, to our knowledge this ternary system has not been well characterized. Recently, it has been found that LB films based on simpler binary mixtures of DS and FA and prepared at a nitrogen–pure water interface show distinct J-bands.¹⁸ Because our primary interest in previous studies was restricted to in-plane anisotropy controlled by the so-called rotating-disk method,¹⁹ these metal-free J-aggregates of DS have not been suitably characterized.

As for the J-aggregates of DS with metal ions, intramolecular charge transfer in DS is indicated by Raman¹² and IR studies^{15,16} and also implied by SHG⁷ and electron-spin-resonance studies.²⁰ A correlation between this charge transfer and aggregation has

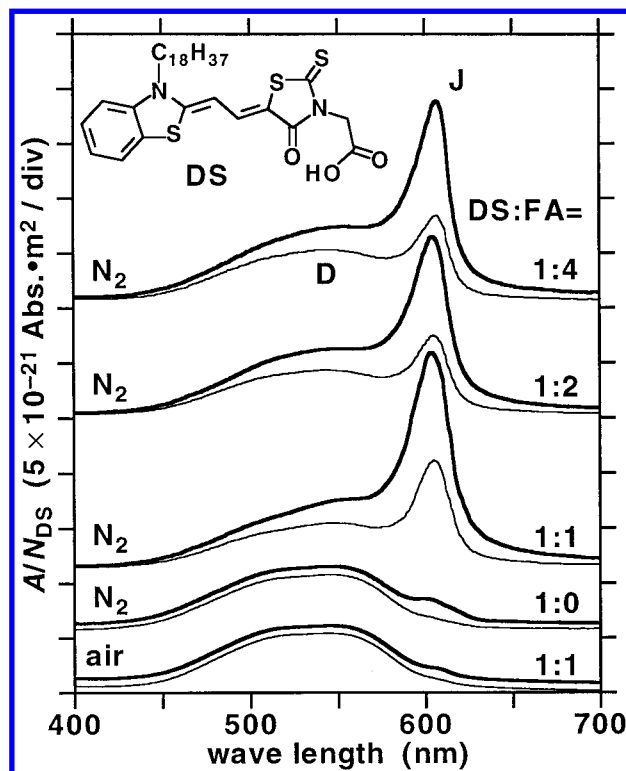


Figure 1. Polarized visible absorption spectra observed for LB films of the DS–FA mixtures prepared under nitrogen and air. The angle of incidence is 0°. The thick and thin curves are the spectra observed for the polarization of the incident light parallel and perpendicular to the dipping direction of the substrate during LB deposition, respectively. The ordinate is the absorbance (*A*) normalized by the surface density of DS (*N_{DS}*) of the films, where *N_{DS}* = (total number of monolayers on the substrate) × (molar concentration of DS)/(area per alkyl chain at 25 mN/m). The chemical structure of DS is given in the inset.

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been hypothesized.^{12,15,20} However, for metal-containing films, formation of the DS–metal chelate structure is observed, which could also cause intramolecular charge transfer.^{12,15,16} Optical characterization of metal-free J-aggregates of DS would indicate whether the intramolecular charge transfer of DS is more closely correlated with chelation or with aggregation. Along this line, we measured polarized visible and FT-IR absorption spectra of DS–FA mixed LB films prepared at a nitrogen–pure water interface. We provide these results in this paper.

As shown below, these DS–FA mixed LB films exhibit not only a J-band, but also a broad band at about 500–550 nm, indicating that not all of the DS molecules are included in J-aggregates. Therefore, the visible and IR spectra should be resolved into the contributions of aggregates and nonaggregates. In our system, because the band located at 500–550 nm is isotropic in the film plane and the J-band is highly anisotropic, due to the flow orientation effect induced by the LB deposition process,^{4,21} we used this difference in anisotropy to resolve the visible and IR spectra. Comparison of the IR spectrum corresponding to aggregated DS and that for monomeric or dimeric DS also indicated intramolecular charge transfer in these metal-free aggregates, suggesting a close correlation between the charge transfer and the aggregation. Furthermore, our experimental results imply an important role of the DS–FA complex and of intermolecular hydrogen bonding in J-aggregation.

2. Experimental Section

2.1. LB Films Prepared under Nitrogen. The dye DS was purchased from the Japanese Research Institute for Photosensitizing Dyes, Co. and was used without further purification. For the FA we used behenic acid from Fluka Co. Spreading solutions were prepared by mixing DS and FA at a molar ratio of 1:4, 1:2, 1:1, or 1:0, adding CHCl_3 as the solvent, and adding a few drops of CH_3OH to the DS–FA mixtures. For the 1:4 mixture the concentration of DS was about 5×10^{-4} mol/L and for the other mixtures, was about 1×10^{-3} mol/L. The solution was spread on pure water contained by an ATEMETA trough. Water with a resistivity greater than $1.8 \times 10^7 \Omega \text{ cm}$ was purified by using a Millipore Milli-Q system. To minimize dissolution of carbon dioxide and oxygen into the subphase, nitrogen gas was flowed into the trough housing at a rate of 1700 L/hr. Surface-pressure isotherms were obtained by using a step-by-step compression method. Plates of CaF_2 ($3 \times 1 \times 0.2 \text{ cm}$) were used as substrates after being precoated with three layers of behenic acid. Ten to twenty layers of the DS–FA mixture were transferred by using a conventional vertical dipping method with a dipping velocity of about 2 cm/min and a surface pressure of 25 mN/m. The deposition type was recognized as Y-type with a transfer ratio near unity. To avoid aging of the monolayers, they were used within 80 min of spreading.

Visible and IR polarized absorption spectra of LB films were recorded by Perkin-Elmer 330 and Nicolet Magna-IR 750 spectrometers. Precoated substrates were used as references for these measurements. Polarized absorption spectroscopy can provide valuable information about molecular orientation.^{22–24} Although the analysis of the out-of-plane anisotropy is complex due to multiple reflections, analysis of the in-plane anisotropy is simple, because the corresponding angle of incidence is zero. Here, we denote the angle between the dipping direction of the substrate during LB deposition (i.e., x -axis) and the oscillating electric field of the incident light by φ . The angles between the transition dipole moment and the normal axis of the substrate (i.e., z -axis), and the x -axis and the projection of the moment

onto the x - y plane are represented by θ and ϕ , respectively. The optical absorbance due to this transition moment, A_φ , is given by the convolution of the inner product of the moment and the oscillating electric field, which is proportional to $\sin^2\theta\cos^2(\varphi - \phi)$ and the orientation distribution function of the moment, $p(\theta, \phi)$.²³ If $p(\theta, \phi)$ does not include cross-terms of θ and ϕ , i.e., if one can write $p(\theta, \phi) = p_1(\theta)p_2(\phi)$, the relationship between A_φ and the orientation order parameters can be expressed as

$$A_\varphi \propto \int_0^\pi \int_{-\pi}^\pi p(\theta, \phi) \sin^2\theta \cos^2(\varphi - \phi) d\phi d\theta \\ = \frac{1}{2} S_2 [1 + P_2 \cos 2(\varphi - \varphi_0)] \quad (1)$$

where

$$S_2 = \langle \sin^2 \theta \rangle \quad (2)$$

is the out-of-plane orientation order parameter and

$$P_2 = \sqrt{\langle \cos 2\phi \rangle^2 + \langle \sin 2\phi \rangle^2} \quad (3)$$

is the in-plane orientation order parameter.²⁵ Here, φ_0 describes the main orientation of the projection of the dipole onto the x - y plane

$$\tan 2\varphi_0 = \frac{\sin 2\varphi_0}{\cos 2\varphi_0} = \frac{\langle \sin 2\phi \rangle}{\langle \cos 2\phi \rangle} \quad (4)$$

and $\langle f \rangle$ denotes the averaged value of the function f

$$\langle f \rangle = \int_0^\pi \int_{-\pi}^\pi p(\theta, \phi) f(\theta, \phi) d\phi d\theta \quad (5)$$

Assuming that $p_2(\phi)$ is an even function of ϕ , as expected for normal LB films, $\langle \sin 2\phi \rangle$ is zero, so that φ_0 becomes either 0 or $\pi/2$. Hereafter, for convenience we assume that $\varphi_0 = 0$ and therefore $P_2 = \langle \cos 2\phi \rangle$ (i.e., P_2 can be either positive or negative).

2.2. LB Films Prepared under Air. For comparison, LB films of pure DS and DS–FA mixtures were prepared under air and their visible and FT-IR absorption spectra were measured. The following experimental conditions differed from those for the LB films prepared under nitrogen. For the FA, we used arachidic acid from Fluka Co. A Lauda Filmwaage trough was used for the LB deposition instead of an ATEMETA trough. Either pure water or a buffer containing 5×10^{-4} mol/L of CdCl_2 and 2×10^{-5} mol/L of KHCO_3 was used for the subphase. Plates of CaF_2 ($3.8 \times 1.3 \times 0.1 \text{ cm}$) were precoated with three layers of cadmium arachidate and used as the substrates. Perkin-Elmer Lambda-900 and Spectrum 2000 spectrometers were used for the visible and IR polarized absorption spectroscopy. Except for the intentionally introduced differences in the atmosphere and the subphase, we believe the differences in the experimental conditions imposed by technical reasons were insignificant and do not prevent comparison of the spectra observed for the two systems.

3. Results and Discussion

3.1. Occupied Area. Surface pressure–area isotherms of Langmuir films based on DS–FA mixtures at a nitrogen–pure water interface were previously reported,¹⁸ and here we briefly review only the key results from that work. For mixtures at 25 mN/m, the average area per alkyl chain increases linearly with

DS molar concentration in the concentration range of 0.2 to 0.5 (DS:FA = 1:4 to 1:1), so that the corresponding areas occupied by single DS and FA molecules can be estimated at about 43 \AA^2 and 19 \AA^2 , respectively.²⁶ The latter value coincides with the isotherm of pure FA. However, at 25 mN/m the area occupied by DS in pure Langmuir films is about 37 \AA^2 . In other words, the mixing ratio dependence of the occupied area per alkyl chain deviates from the ideal mixing behavior. This denies complete phase separation between DS and FA in 1:1 mixed films. (If DS and FA form a 1:1 complex, its area can be estimated at about 62 \AA^2 , while the molecular area of excess FA remains at 19 \AA^2 .)

3.2. Visible Spectra. Polarized visible absorption spectra of LB films of the DS–FA mixtures (1:4, 1:2, and 1:1) and pure DS, which were prepared at the nitrogen–pure water interface, are shown in Figure 1. Together with a broad band at 500–550 nm (abbreviated as band D), a distinct red-shifted band near 605 nm is observed for the mixed systems. On the other hand, the band D is dominant in the pure film and only a small J-band can be detected,⁹ similar to the spectra for either pure DS films or DS films mixed with FA and prepared at an air–“pure water” interface.^{8,11,13,14} Therefore, the atmosphere used for the LB deposition is crucial for obtaining J-aggregates of DS without metallic or ammonium cations in the DS–FA binary mixed systems.

The J-band presents a large in-plane anisotropy and is preferentially polarized in the dipping direction (i.e., x -axis), but the in-plane anisotropy of the band D is negligible. The origin of the in-plane anisotropy of the J-band is apparently a flow-orientation mechanism.^{4,21} By using this in-plane anisotropy, we can extract the spectral profile of the J-band from the observed absorption spectrum, as described below.

With respect to the substrate, the out-of-plane and in-plane orientation order parameters of the X-band ($X = J$ or D) can be defined as $S_2(X0|\text{substrate}) = \langle \sin^2 \theta_{X0} \rangle$ and $P_2(X0|\text{substrate}) = \langle \cos^2 \phi_{X0} \rangle$, respectively. As shown in section 2, $\langle \sin^2 \phi_{X0} \rangle = 0$, so this term does not appear in these definitions. Here, θ_{X0} is the angle between the axis normal to the substrate (i.e., z -axis) and the transition dipole moment of the X-band, and ϕ_{X0} is the angle between x and the projection of the moment onto the substrate plane. Then, writing the spectral profile of the X-band as $A_{X0}(\lambda)$, the absorption spectra of the film with the polarization parallel and perpendicular to x is denoted by $A_+(\lambda)$ and $A_-(\lambda)$, respectively, and expressed as

$$A_{\pm}(\lambda) = \frac{1}{2} \sum_{X=D,J} [1 \pm P_2(X0|\text{substrate})] N_X S_2(X0|\text{substrate}) A_{X0}(\lambda) \quad (6)$$

where λ is the wavelength and N_X is the number of molecules contributing to the X-band. Therefore, if $|P_2(D0|\text{substrate})| \ll P_2(J0|\text{substrate})$, the difference between $A_+(\lambda)$ and $A_-(\lambda)$ is approximately proportional to $A_{J0}(\lambda)$ and can be expressed as

$$\begin{aligned} A_+(\lambda) - A_-(\lambda) &= \sum_{X=D,J} P_2(X0|\text{substrate}) N_X S_2(X0|\text{substrate}) A_{X0}(\lambda) \\ &\approx P_2(J0|\text{substrate}) N_J S_2(J0|\text{substrate}) A_{J0}(\lambda) \\ &\propto A_{J0}(\lambda) \end{aligned} \quad (7)$$

Because the condition $|P_2(D0|\text{substrate})| \ll P_2(J0|\text{substrate})$ is satisfied in our system, eq 7 can be applied to our observed

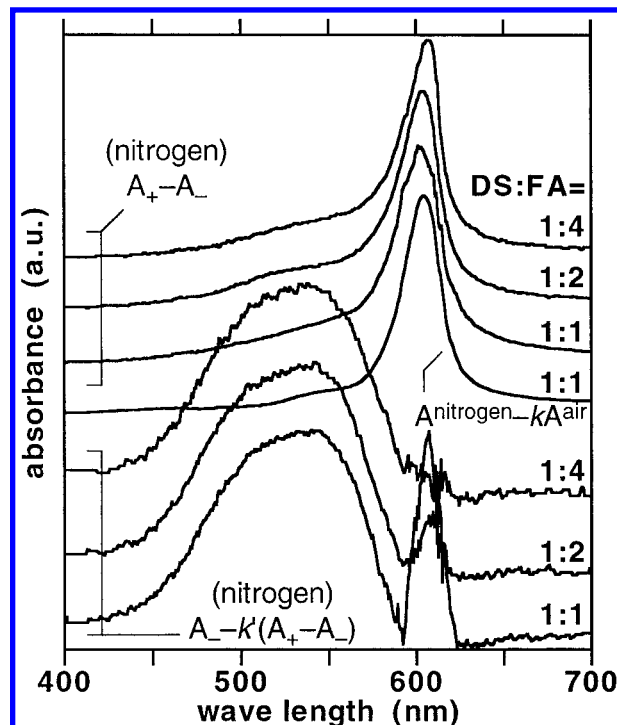


Figure 2. Difference spectra described by eq 7 for the DS–FA mixed (molar ratios of 1:4, 1:2, 1:1) films prepared under nitrogen, difference spectrum described by eq 8 for the DS–FA mixed (1:1) films prepared under nitrogen and air with $k = 0.74$, and difference spectra described by eq 9 for the DS–FA mixed films prepared under nitrogen with $k' = 0.77$. See the text for detailed explanation.

spectra. Figure 2 shows the difference between the spectra, $A_+(\lambda) - A_-(\lambda)$. As for the DS–FA mixed LB films prepared under nitrogen, the shape of the J-band appears to be approximately independent of the mixing ratio of FA. For the 1:4, 1:2, and 1:1 DS–FA mixtures, the peaks occur at about 607, 604, and 602 nm, respectively, and the full widths at half-maximum (fwhm) of these peaks are 730 , 830 , and 890 cm^{-1} , respectively. The small shift of the peak suggests a slight decrease in the average number of molecules in an aggregate with decreasing FA mixing ratio, and the increase of the fwhm indicates an increase in the number of defects. Here, we assumed that the “monomer shift”²⁷ and the dipole interactions in the aggregates are independent of the mixing ratio for the DS–FA mixed films prepared under nitrogen. The analysis on the IR spectra described in section 3.3 supports this assumption. In addition, $A_+(\lambda) - A_-(\lambda)$ for the pure film can also be considered as a J-band, although the J-aggregate is a minor component in this film.⁹

Because $P_2(X0|\text{substrate})$ disappears in $A(\lambda) = A_+(\lambda) + A_-(\lambda)$, if the shape of the band D is independent of the atmosphere used, the difference between $A(\lambda)$ of the films prepared under nitrogen, $A^{\text{nitrogen}}(\lambda)$, and $A(\lambda)$ of the films prepared under air, $A^{\text{air}}(\lambda)$, also provides the shape of the J-band

$$\begin{aligned} A^{\text{nitrogen}}(\lambda) - k A^{\text{air}}(\lambda) &= \sum_{X=D,J} (N_X^{\text{nitrogen}} S_2^{\text{nitrogen}}(X0|\text{substrate}) - k N_X^{\text{air}} S_2^{\text{air}}(X0|\text{substrate})) A_{X0}(\lambda) \\ &\propto A_{J0}(\lambda) \left[\text{for } k = \frac{N_D^{\text{nitrogen}} S_2^{\text{nitrogen}}(D0|\text{substrate})}{N_D^{\text{air}} S_2^{\text{air}}(D0|\text{substrate})} \right] \end{aligned} \quad (8)$$

in the DS–FA 1:1 mixed case. In this subtraction, we can adjust

the parameter k by minimizing the contribution of the band D in the calculated spectrum, even though we do not know the ratio of $N_{\text{D}}^{\text{nitrogen}}/N_{\text{D}}^{\text{air}}$. From the observed spectra of the 1:1 mixed films prepared under nitrogen and air, the difference spectrum described by eq 8 was obtained by setting $k = 0.74$ (Figure 2). The calculated spectrum is compatible with the difference spectrum based on eq 7 for the 1:1 film prepared under nitrogen. This result shows that the deviations of the difference spectra based on eqs 7 and 8 from the real $A_{\text{J0}}(\lambda)$ are, respectively, negligible, because those deviations are determined by different factors. Indeed, the deviation of the difference spectra based on eq 7 from $A_{\text{J0}}(\lambda)$, which could not directly be observed, is caused by a possible nonzero $P_2(\text{D0}|\text{substrate})$ value. In contrast, the deviation of the difference spectra based on eq 8 from $A_{\text{J0}}(\lambda)$ is caused by a possible difference in the shapes of the band D due to the difference in the atmosphere used for the film preparation. Moreover, the value of k obtained here is required for the analysis of the IR spectrum, which is given in section 3.3.

Although our main purpose is to obtain information about the formation mechanism of the J-aggregates, we also discuss about the origins of the band D, because their formation may compete with J-aggregation. Because $A_+(\lambda) - A_-(\lambda)$ is proportional to $A_{\text{J0}}(\lambda)$, as discussed above, by properly choosing the constant k' , $A_{\text{D0}}(\lambda)$ can be approximated by subtracting $k'[A_+(\lambda) - A_-(\lambda)]$ from $A_-(\lambda)$ as

$$A_-(\lambda) - k'[A_+(\lambda) - A_-(\lambda)] = \frac{1}{2} \sum_{X=\text{D,J}} [1 - (1 + 2k')P_2(X|\text{substrate})]N_X S_2(X|\text{substrate})A_{X0}(\lambda) \propto A_{\text{D0}}(\lambda) \quad [\text{for } k' = 1/2P_2(\text{J0}|\text{substrate}) - 1/2] \quad (9)$$

Although we do not know the exact P_2 values, we can adjust the parameter k' by minimizing the contribution of the J-band in the calculated spectrum. The corresponding results of the subtraction for films prepared from DS-FA molar ratios of 1:4, 1:2, and 1:1 under nitrogen are shown in Figure 2 with $k' = 0.77$, 0.77, and 0.77, respectively.²⁸ Although the contribution of the J-band could not be completely canceled, these spectra are approximately identical to each other. Furthermore, these spectra for pure films prepared under nitrogen are nearly identical to the spectra observed for the 1:1 films prepared under air (Figure 1). This implies that $A_{\text{D0}}(\lambda)$ can be extracted by using this method.

The spectral shape of $A_{\text{D0}}(\lambda)$ shows that this band is a convolution of peaks centered around 545 and 510 nm. These peaks at the longer and shorter wavelengths were once assigned to the monomer and blue-shifted dimer bands, respectively.²⁹ This assignment is consistent with the face-to-face stacking structure of dimers reported for a merocyanine derivative, 3-ethyl-5-[2-(3-ethylbenzothiasolin-2-ylidene)-ethylidene]rhodanine, in a crystal.³¹ However, the relative contributions of these peaks to the band D are not modified by changing the mixing ratio of FA. Moreover, they are not significantly affected by the atmosphere used during LB deposition. This may indicate that the origins of these peaks are identical. Indeed, the shape of the band D resembles that of the absorption band of dimeric Rose Bengal,³² which shows Davidov splitting^{33,34} when the monomer spectrum of DS in the CHCl_3 solutions³⁰ resembles the monomer band of Rose Bengal.³² Preliminary measurements of the out-of-plane anisotropy of the visible absorption of the

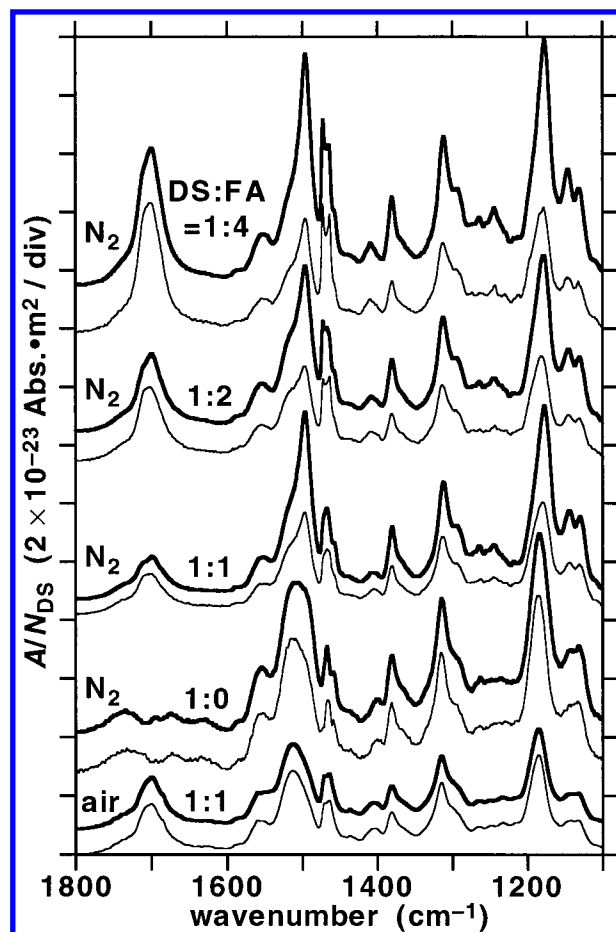


Figure 3. Polarized FT-IR absorption spectra observed for the DS-FA mixed films prepared under nitrogen and air. The angle of incidence is fixed at 0°. The thick and thin curves are the spectra observed for the polarization of incident light parallel and perpendicular to the dipping direction of the substrate, respectively.

films (data not shown) suggest that the polarizations of the peaks at 545 and 510 nm are different from each other. (The latter peak is larger than the former in the p-polarized spectrum with an angle of incidence of 60°.) For these reasons, at the present stage, we attribute the band D mainly to a dimeric form of DS with Davidov splitting, although further characterization of this band is clearly needed for the concrete assignment. The dimer structures of DS and 3-ethyl-5-[2-(3-ethylbenzothiasolin-2-ylidene)-ethylidene]rhodanine could be different from each other, because the latter dye bears neither long alkyl chains nor carboxylic groups. The formation of the DS dimer may be driven by hydrogen bonding between the carboxylic groups in the two molecules. Possible formation of dimers via hydrogen bonding between the carboxylic groups was noted by Fujimoto et al.³⁵ for merocyanine molecules, which are similar to DS but bear shorter alkyl chains (C_4H_9 to $\text{C}_{10}\text{H}_{21}$) instead of the octadecyl group.

3.3. IR Spectra. Polarized FT-IR absorption spectra recorded for the LB films of DS-FA mixtures (1:4, 1:2, and 1:1) and pure DS, prepared under nitrogen, are shown in Figure 3. For the mixed films, the C=O stretching mode of the intermolecular hydrogen-bonded carboxylic groups in dimeric FA dominates the contribution to the band near 1700 cm^{-1} , as in the case of pure FA films. The band near 1733 cm^{-1} seen in the pure film spectrum is assignable to either the intra-³⁵ or intermolecular hydrogen bonded carboxylic group in DS. This band is also seen as a shoulder in the mixed film spectra. As reported in pure DS solid (powder)³⁵ and LB films^{12,15} of DS with metallic

TABLE 1. Peak Positions of IR Absorption Due to DS (cm⁻¹)

metal-free LB films		Cd ²⁺ -containing LB films	
dimer	J-aggregate	dimer	J-aggregate
(1635)		(1585)	(1606)
1558	1553		1558
1515	1496	(1512)	1488
1382	1380	1381	1380
1316	1311	1317	1313
	1264		(1262)
	1244		1240
1186	1176	1190	1183
	1144		1145
1130	1129	1130	1130

cations, the absorption bands attributed to the DS chromophore are seen in the 1600–1100 cm⁻¹ range (Table 1).³⁶ A broad band resulting from the stretching mode of hydrogen-bonded OH groups is observed in the region of 3300–2500 cm⁻¹.

To obtain information about the possible modifications of the electronic structure of DS forming J-aggregates, the contribution due to these molecules should be extracted from the observed IR spectrum. This can be done by using the subtraction method based on the in-plane anisotropy, similar to that for the visible spectra. However, eq 6 should be modified to make it applicable to the IR spectra, which contain many transition moments with different order parameters. Therefore, the orientation order parameters of the *n*th (*n* ≥ 1) transition moment associated with X (X = J-aggregate or Dimer), $S_2(Xn|substrate) = \langle \sin^2 \theta_{Xn} \rangle$, and $P_2(Xn|substrate) = \langle \cos 2\phi_{Xn} \rangle$ are introduced. Then, writing the spectral profiles due to the moment as $A_{Xn}(\lambda)$, the absorption spectrum of the film can be expressed as

$$A_{\pm}(\lambda) = \frac{1}{2} \sum_{X=D,J} N_X \sum_n [1 \pm P_2(Xn|substrate)] S_2(Xn|substrate) A_{Xn}(\lambda) \quad (6')$$

Because $P_2(Xn|substrate)$ can be written as a simple product of two parts,¹⁸ one describing the orientation of the aggregate (or dimer) with respect to the substrate, $P_2(X|substrate)$, and one describing the orientation of the transition moment with respect to the aggregates, $P_2(n|X)$, when $P_2(D|substrate)$ is negligible, eq 7 can be rewritten as

$$\begin{aligned} A_+(\lambda) - A_-(\lambda) &= \sum_{X=D,J} N_X \sum_n P_2(n|X) P_2(X|substrate) S_2(Xn|substrate) A_{Xn}(\lambda) \\ &\approx N_J P_2(J|substrate) \sum_n P_2(n|J) S_2(Jn|substrate) A_{Jn}(\lambda) \quad (7') \end{aligned}$$

This method was applied to the DS–FA mixed films as well as to pure DS films prepared under nitrogen. As expected, no significant dependence on the mixing ratio was observed, implying that the electronic structure of DS in the J-aggregates in these films is identical. The difference spectrum obtained for the 1:1 film (as a representative of the mixed films) is given in Figure 4. The strong band around 1700 cm⁻¹ and the shoulder around 1733 cm⁻¹ disappeared in these difference spectra, showing that $P_2(n|J) \approx 0$ or $S_2(Jn|substrate) \approx 0$ for the C=O stretching mode of the aggregated DS.

Application of another subtraction method to the IR region, similar to eq 8, may be able to determine which order parameter, P_2 or S_2 , is zero for the C=O stretching mode of the aggregated DS. To do this we rewrite eq 8 as

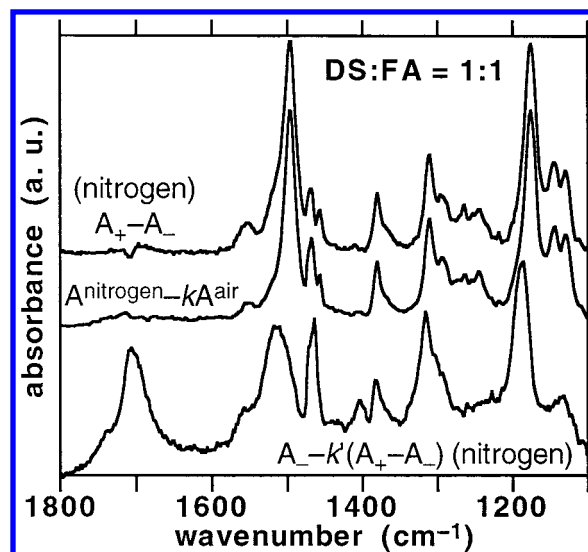


Figure 4. Difference spectrum described by eq 7' for the DS–FA mixed films prepared under nitrogen, that by eq 8' for the DS–FA mixed films prepared under nitrogen and air with $k = 0.74$, and that by (modified) eq 9 for the DS–FA mixed films prepared under nitrogen with $k' = 0.77$. See the text for detailed explanation.

$$\begin{aligned} A^{\text{nitrogen}}(\lambda) - k A^{\text{air}}(\lambda) &= \sum_{X=D,J} [N_X^{\text{nitrogen}} S_2^{\text{nitrogen}}(Xn|substrate) \\ &\quad - k N_X^{\text{air}} S_2^{\text{air}}(Xn|substrate)] A_{Xn}(\lambda) \\ &\propto \sum_n S_2(Jn|substrate) A_{Jn}(\lambda) \quad (8') \end{aligned}$$

Although we assumed $S_2^{\text{nitrogen}}(Xn|substrate) = S_2^{\text{air}}(Xn|substrate)$, we believe that this assumption causes no serious artifacts in the resultant difference spectrum. Then, the k parameter is determined by the analysis of the visible spectra. Another problem is the contribution from FA, but this problem disappears in the 1:1 case,³⁷ if the aggregates are based on the DS–FA 1:1 complex as proposed in section 3.5. In the difference spectrum for the DS–FA 1:1 films prepared under nitrogen and air, shown in Figure 4, both the bands near 1733 and 1700 cm⁻¹ are also weak. This may indicate that $S_2(Jn|substrate) \approx 0$ for the C=O stretching mode of the aggregated DS.

On the contrary, the absorption bands due to the antisymmetric and symmetric CH₂ stretching modes in the region of 3000–2800 cm⁻¹ are observed in the difference spectrum described by eq (8'), whereas they are canceled in the difference spectrum described by eq (7'). The disappearance of these bands in the latter spectrum is caused by small $P_2(n|J)$ values of their moments. The peaks of these bands in the former spectrum are located near 2916 (antisymmetric) and 2848 cm⁻¹ (symmetric), reflecting the *trans*-rich state of the alkyl chain associated with the J-aggregates.¹⁸

For the DS–FA mixed films, the IR spectrum of the dimeric DS was extracted by subtracting $k'[A_+(\lambda) - A_-(\lambda)]$ from $A_-(\lambda)$, while using the same value for k' as used for the visible case. (We modified eq 9 explicitly for this purpose, but we do not show the modified equation here.) As expected, with increasing mixing ratio of FA no significant dependence could be observed, except for the increase in the contribution of FA, especially in the bands near 1700 and 1470 cm⁻¹. The resultant spectrum for the 1:1 film is shown in Figure 4. As for the bands due to the DS chromophore, this spectrum is compatible with the spectrum observed for the pure film prepared under nitrogen and with the spectrum for the 1:1 film prepared under air (Figure 3). The bands due to the J-aggregates with $P_2(n|J) = 0$ cannot

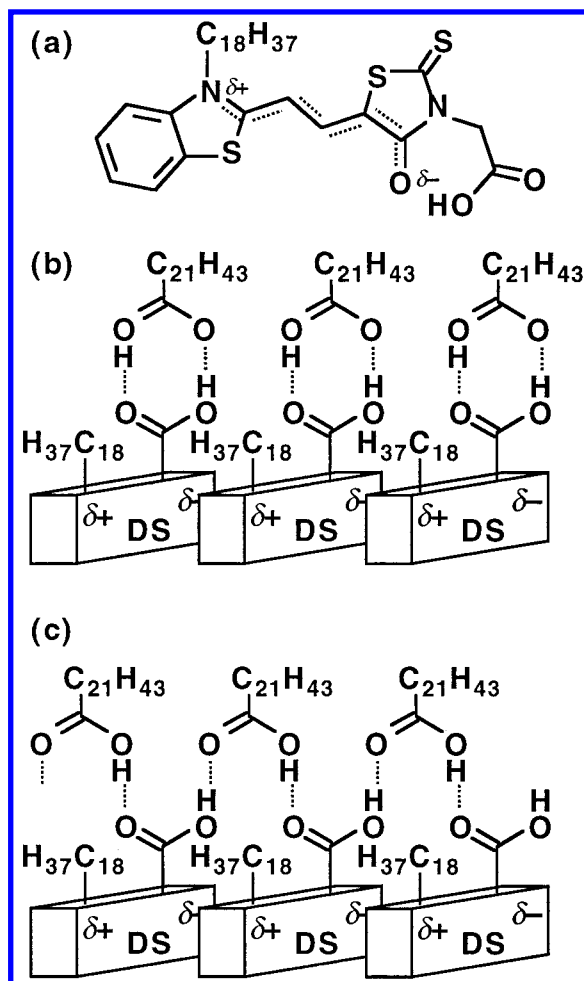


Figure 5. Schematic illustrations of (a) intramolecular charge transfer in DS and (b) possible complexes of DS and FA with "capping" and (c) with "bridging".

be canceled by this method, unfortunately. However, the bands with $S_2(Jn|\text{substrate}) = 0$, such as the C=O stretching mode in the J-aggregates, do not appear in these difference spectra. Therefore, the strong band near 1700 cm^{-1} could be entirely attributed to the excess dimerized FA. The C=O stretching mode of the carboxylic group in DS is observed as a shoulder near 1733 cm^{-1} .

Comparing the resolved spectra for J-aggregates and for dimers of DS (Table 1), red shifts of the bands assigned to the conjugated system of DS seen in the $1600\text{--}1100\text{ cm}^{-1}$ region are clearly observed. Furthermore, several peaks are much more pronounced in the aggregates. These results show the difference in the electronic structure between J-aggregated and dimeric DS. In particular, the red shifts of the IR absorption bands near 1550 and 1500 cm^{-1} indicate the delocalization of the π electrons in the butadiene group related to the intramolecular charge transfer from the rhodanine group to the benzothiazolylidene group (Figure 5a). For the metal-ion-containing LB films, intramolecular charge transfer in the J-aggregated merocyanine dyes was already indicated by other authors using resonance Raman,¹² FT-IR,^{15,16} electron spin resonance,²⁰ and SHG.⁷ The fact that the intramolecular charge transfer in DS was indicated in both the metal-containing and metal-free cases suggests close correlation between this charge transfer and J-aggregation of DS.

3.4. Comparison with Cd²⁺-Containing Films. To compare the results described in section 3.3 with the optical properties of the LB films of DS with metallic ions, LB films of DS

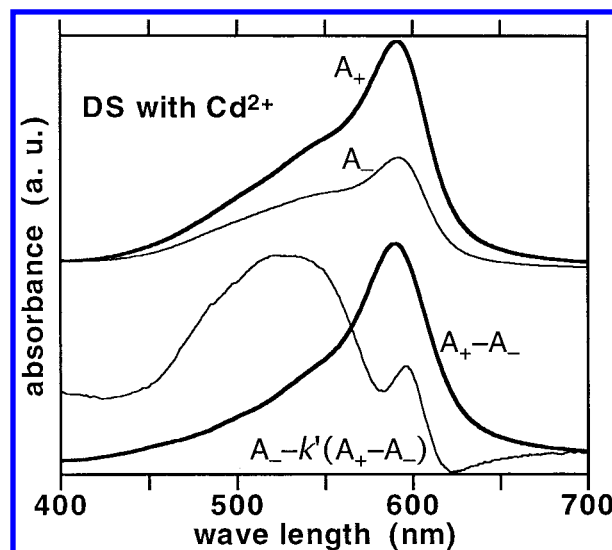


Figure 6. Polarized visible absorption spectra observed for a pure DS film, prepared by using a Cd²⁺-containing subphase, and difference spectra described by eq 7 and eq 9 with $k' = 0.9$.

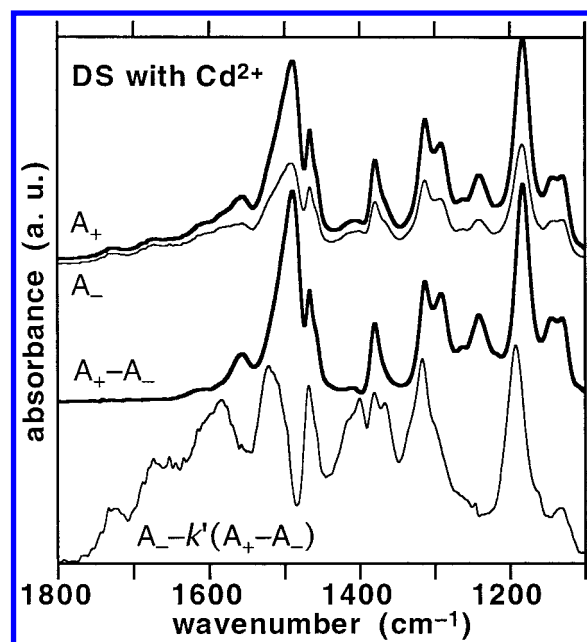


Figure 7. Polarized IR absorption spectra observed for a pure DS film, prepared by using the Cd²⁺-containing subphase, and difference spectra described by eq 7' and (modified) eq 9 with $k' = 0.9$.

containing Cd²⁺ were made and their anisotropic visible and IR spectra were measured (Figures 6 and 7). In contrast to the metal-free case, with metallic ions the J-band is observed not only for DS-FA mixed films but also for pure DS films. Moreover, the spectra observed for those films are essentially identical to one another. Compared with the metal-free case, another difference is that the band D appears somewhat anisotropic. This decreases the reliability of the spectral resolution based on the in-plane anisotropy, especially using eqs 7 and 7'. This may be one of the reasons that, although this system has been extensively studied, such analysis of the visible and IR spectra has not been previously reported. Despite the insufficient reliability of our method in this case, we applied it to the Cd²⁺-containing system.

The visible difference spectrum of the Cd²⁺-containing DS film described by eq 7 and shown in Figure 6 is nearly identical to those obtained for the Cd²⁺-containing DS-FA films. The

J-band peak is observed near 592 nm for the DS film and the fwhm is 1970 cm^{-1} . The corresponding IR difference spectra (Figure 7) are also approximately identical to those obtained for the Cd^{2+} -containing DS–FA films, except that a peak near 1542 cm^{-1} ($\text{Cd}(\text{COO})_2$) appears in the DS–FA films. Peak positions of some IR bands are different between the metal-free and Cd^{2+} -containing LB films (Table 1). The magnitude of these differences is greater than the magnitude of the experimental errors. This suggests that the electronic structure of DS is modified by the presence of Cd^{2+} . Therefore, the difference in the peak wavelength of the J-band in these films is not only related to the difference in the average number of molecules in the aggregates, but it can also be caused by the difference in the “monomer shift”²⁷ between these systems. Both the visible J-band and the IR absorption bands associated with the J-band exhibit smaller line width for the metal-free films than for the Cd-containing films, reflecting better organization of the aggregates in the former films compared with the latter films.

The difference spectra described by eq 9 of the Cd^{2+} -containing pure DS films with $k' = 0.9$ (Figure 6) are nearly identical to those obtained for the Cd^{2+} -containing DS–FA films. The corresponding IR difference spectra are shown in Figure 7 and are compatible to those obtained for the Cd^{2+} -containing DS–FA films, except that the latter are dominated by the large band near 1545 cm^{-1} ($\text{Cd}(\text{COO})_2$). In contrast to the J-aggregates, the visible and IR spectra of the dimeric DS in the metal-free and in the Cd^{2+} -containing films are close to each other, suggesting that the electronic structure and the molecular arrangements in these dimers are not significantly different. Note that DS with singly charged carboxylic groups cannot be in the monomeric state when it makes salt with Cd^{2+} .

3.5. J-Aggregates. From these experimental results we make the following discussion of the J-aggregates in metal-free LB films of DS–FA systems.

In the LB films of pure DS, the band D, which could be attributed to the absorption associated with dimeric DS with a Davydov splitting, is dominant in the visible spectra. The intermolecular hydrogen bonding between the carboxylic groups may be the driving force of the dimerization. (Although the IR spectra do not clearly indicate intermolecular hydrogen bonding between two DS, visible spectra for the pure film with Cd^{2+} support the suggested assignment of the band D to dimeric DS.) In this case, the two chromophores in the dimer may not be parallel to each other, because such molecular arrangement is difficult. Then, the formation of the dimer may prevent the formation of J-aggregates, because in such aggregates the transition moments of the chromophore should be parallel to one another. Note that a merocyanine derivative bearing no carboxylic group forms well-developed J-aggregates at an air–“pure water” interface without mixing with FA.¹⁷

When DS is mixed with FA, the situation changes: the carboxylic group of FA can “cap” or “bridge” the carboxylic group in DS as illustrated by Figure 5b and c, respectively. The areas occupied by the molecules in Langmuir films of the DS–FA mixtures under nitrogen also suggest the formation of complexes of DS and FA, because its behavior deviates from that associated with ideal mixing. If such a complex is formed, the transition moments of the DS chromophore can orient parallel to one another and the formation of the J-aggregates is possible. This may be the reason the J-band appears in the visible spectra for the mixed films prepared under nitrogen. The potential importance of DS–FA complexes for J-aggregation is also suggested by a result reported in ref 11: LB films of a

ternary mixture of DS, eicosylamine, and hexadecane (HD) prepared with an air–“pure water” interface do not show the J-band, although those of DS–FA–HD exhibit a well developed J-band. The IR spectra of the J-aggregates (Figure 4) suggest $S_2(\text{Jn}|\text{substrate}) \approx 0$ for the antisymmetric stretching mode of $(\text{COOH})_2$, suggesting that the axis connecting the two carbons in this $(\text{COOH})_2$ is nearly perpendicular to the film plane.

However, the J-aggregates may not be strongly stabilized by the presence of FA. The visible spectra observed for the films prepared with the air–“pure water” interface (Figure 1) show that the dimer is more stable under this condition. In this case, carbon dioxide in air decreases the pH value of the subphase and may change the energies of the dimer and of the aggregates. Further, HD apparently stabilizes DS–FA complexes even at an air–“pure water” interface.¹¹

Intramolecular charge transfer is indicated for DS in metal-free J-aggregates by the red shifts of IR bands near 1550 and 1500 cm^{-1} . In the metal-containing case, ref 16 assumed that the formation of the chelate structure induces intramolecular charge transfer. In contrast to the chelating structure, however, the hydrogen bonding between the carboxylic groups in DS and FA itself may not be responsible for the intramolecular charge transfer. In the metal-free case, the J-aggregation must be correlated with the intramolecular charge transfer, as discussed below.

The intramolecular charge transfer should induce large static dipoles in the aggregated DS molecules. In the chelate model,¹⁶ the electrostatic interaction between these static dipoles causes the J-aggregation. The electrostatic interaction between static dipoles is, however, not always favorable for the formation of the J-aggregates. In fact, it is easy to show that NaCl-like arrangements of the charges have the lowest electrostatic energy in the two-dimensional system, i.e., face-to-face H-like aggregates should be formed if the electrostatic interaction dominates the aggregation.³⁸ Indeed, NaCl-like arrangements of the charges are realized in the crystal of the merocyanine dye derivative, 3-ethyl-5-[2-(3-ethylbenzothiasolin-2-ylidene)-ethylidene]rhodanine.³¹ Then, other interactions between the DS molecules must dominate in this system. The π – π interaction is a candidate, but it might be more favorable for the formation of face-to-face aggregates. Another candidate is intermolecular hydrogen bonding, which is known to be the driving force in the formation of some self-organized supramolecular networks.³⁹ For example, the ladder structure shown in Figure 5c could stabilize the J-aggregates. Moreover, once the head-to-tail structure is produced, the intramolecular charge transfer could decrease the total energy. Therefore, the formation of head-to-tail aggregates may induce the intramolecular charge transfer.

Under the presence of metal cations, J-aggregates of DS can be formed without FA. Other authors^{12,15,16} indicated that the chelate structure is important for the J-aggregation. Because chelating destroys the hydrogen bonds, this picture is consistent with our hypothesis: dimerization of DS via hydrogen bonding between carboxylic groups prevents the J-aggregation.

4. Conclusions

It is known that the formation of the J-aggregates of a merocyanine dye (DS) in Langmuir–Blodgett (LB) films is strongly affected by the preparation conditions of the films. Normally, the presence of metallic or ammonium cations is required to get well developed J-aggregates of this dye, which contains a carboxylic group. However, recently it was found that LB films of DS–fatty-acid (FA) binary mixtures prepared at a nitrogen–pure water interface show a distinct J-band near

605 nm.¹⁸ To provide new insights into the formation of the J-aggregates of DS, visible and IR absorption spectra were measured for these new LB films. The broad band in the range of 500–550 nm, which could be attributed to dimeric DS, was also seen in the visible absorption spectra of these films. The observed J-band is highly anisotropic in the film plane due to the flow orientation effect,^{4,21} while the dimer band is isotropic. By using this difference in the polarization, we resolved the observed visible and IR absorption spectra into the contribution of the J-aggregates and that of the dimers. Note that to resolve the IR spectra of a sample, information obtained from the resolving process of the visible spectra of the same sample is required. A comparison of the IR absorption spectra of the aggregated and dimeric DS indicates a change in the electronic structure related to the intramolecular charge transfer, suggesting close correlation between charge transfer and aggregation. Infrared analysis also suggested that the carboxylic group of the aggregated DS is oriented preferentially along the normal axis of the substrate, although further measurements such as those using reflection–absorption spectroscopy are required to confirm this. Furthermore, our results suggest that DS–FA complexes and intermolecular hydrogen bonding play a critical role in metal-free J-aggregation.

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- The surface pressure–area isotherms given by Figure 3 in ref 18 are correct, but the value of the occupied area of DS given in the text, 23 Å², is incorrect: the correct value is 43 Å². This error does not affect the discussion in ref 18, because it is related to the rotating-disc method, not to the characterization of DS–FA films.
- Aggregation generally changes the electronic structure of both the ground and the excited states. Therefore, the excitation energy, which is the difference between the energies of these states, can vary between the monomeric and the aggregated molecules, even when dipole–dipole interactions between the transition moments are neglected. What we abbreviate to “monomer shift” in this paper corresponds to this effect.
- The k' parameter depends on deposition conditions, but its value of 0.77 corresponds to the practical maximum of the $P_2(J)$ /substrate parameter (0.4) of the films formed in this study (See ref 18).
- In refs 1 and 9, by comparing the absorption spectra of DS in acetone and aqueous acetone solutions to that of cast films of pure DS and DS–FA mixtures, the authors assigned the absorption peaks near 504 and 540 nm to the dimeric and monomeric bands, respectively. However, the shoulder near 500 nm seen in the acetone solution spectrum may not correspond to the dimer, as for CHCl₃ solutions described in ref 30. For the aqueous–acetone solution and cast films, the development of J-bands in their spectra complicates the situation, making correlation between their and our results unclear.
- To confirm the absorption of monomeric DS, we measured the visible spectra of dilute solutions. In CHCl₃, the main absorption peak was observed near 527 nm. Although a shoulder was observed for an energy about 1400 cm^{−1} higher than this main peak, no clear concentration dependence of the spectral shape was detected when the concentration of DS was between 5×10^{-3} and 10^{-8} mol/L. For 10^{-6} mol/L C₂H₅OH and CH₃CN solutions, blue shifts of about 300 and 400 cm^{−1}, respectively, were observed. However, the difference in energy between the main peak and the shoulder of about 1400 cm^{−1} did not change in these solutions. These results indicate that the observed spectra are due to the monomeric DS and that the shoulder at the higher energy side is a vibronic structure.
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- This phenomenon may be summarized as following. In a dimer of dye molecules, the dipole–dipole interaction between the transition moments creates two new transition moments, whose excitation energies are split. When the molecules in the dimer are not parallel to each other, the orientation of these new transition moments becomes different and therefore both of them are allowed.
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- The following bands are not relevant with the DS chromophore. The narrow bands at 1473, 1468, and 1463 cm^{−1} correspond to scissoring of CH₂ groups, which is observed at 1473 and 1463 cm^{−1} in pure FA films. A medium band near 1405 cm^{−1} is attributed to the COH in-plane bending mode, because this band is also observed in the pure FA films. The C–O stretching mode can be detected as a shoulder near 1300 cm^{−1}. Very weak bands due to C–C stretching modes of the alkyl chains are detected in the region of 1280–1210 cm^{−1}. The COH out-of-plane bending mode is seen near 950 cm^{−1}.
- In films prepared under either nitrogen or air, the number of FA molecules associated with the J-aggregates is equivalent to either N_J^{nitrogen} or N_J^{air} , and then the number of FA molecules not associated with the J-aggregates is equivalent to either N_D^{nitrogen} or N_D^{air} , because the total number of FA molecules is the same as that of DS ($N_J + N_D$). Therefore, the contribution from FA not associated with the aggregates is canceled by the subtraction described by eq 8'.
- Unfortunately, in ref 16 the static dipoles due to the intramolecular charge transfer and the transition dipoles related to the optical absorption were confused, and the application of the extended dipole model resulted in a questionable conclusion. The application of the extended dipole model to the transition moments is effective for calculating the absorption shifts due to the aggregation. In that case, only the in-phase arrangements of the dipoles (all of the dipoles have the same direction) should be considered, because the oscillator strength associated with the out-of-phase arrangement (half of the dipoles have direction opposite to the others) is zero. However, minimizing the excitation energy (maximizing the red shift) is useless for the estimation of the molecular arrangements, which is determined by the ground-state energy. To minimize the electrostatic energy of the ground state, the model should be applied to the static dipoles with both in-phase and out-of-phase arrangements. Otherwise, structures such as the one presented in ref 31 are automatically eliminated.
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