

# Formation of J-Aggregates of an Alkylated Merocyanine Dye Assisted by a Fatty Acid Observed at an Air-Water Interface

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Taking the advantage of Langmuir-film system, *i.e.*, the molecules in the system are weakly immobilized on a water substrate, formation of J-aggregates in 1:*x* (molar ratio) mixtures of an alkylated merocyanine dye and a fatty acid is monitored by measuring the *in-situ* electronic absorption spectra in the period of  $\sim 10^3$  s after spreading the materials onto pure-water surfaces. A distinct J-band was detected even for *x* as small as  $10^{-2}$ , while only a trace of that was detected for *x* = 0. This phenomenon was interpreted as a drastic enhancement of the nucleation of the aggregates due to the fatty acid, on the basis of semi-quantitative spectral analysis. Transfer of the generated metal-free J-aggregates onto solid substrates was also tried.

Key words: Langmuir films, LB films, J-aggregate, nucleation, spectral deconvolution

## 1. INTRODUCTION

In recent years, J-aggregates, which are characterized by a narrow and red-shifted electronic absorption band (J-band) and strong fluorescence with a small Stokes shift, have been attracting much attention because of their potential application to information storage, energy transfer, and nonlinear optical devices.<sup>1)</sup> J-aggregates are recognized as self-organized molecular nanostructures, but their formation mechanism has not yet been fully understood.

It is known that some amphiphilic merocyanine dyes form J-aggregates<sup>2-9)</sup> when they are spread as Langmuir films<sup>10)</sup> upon the surfaces of water solutions of metal chlorides. Such Langmuir films may provide a unique system for studying the formation mechanism of the J-aggregates, because the dye molecules are quite weakly immobilized in the Langmuir-film system.

Kawaguchi and Iwata<sup>5-7)</sup> intensively studied the formation of the J-aggregates in pure Langmuir films of an alkylated merocyanine dye of DSe (Fig. 1 inset) with changing the cation species dissolved in the water subphase. Similar works were independently performed by other authors<sup>8,9)</sup> for another dye of DS (Se in DSe is replaced by S). They found that metallic cations are crucial for the J-aggregation in these pure films. In particular, Kawaguchi and Iwata thought that the intramolecular charge transfer induced by the chelation of metallic cations is generally essential for the J-aggregation of these dyes.

On the other hand, Nakahara and Möbius<sup>4)</sup> reported the development of J-aggregates in Langmuir films of a DS-arachidic acid-hexadecane ternary mixture. Furthermore, we have found that J-aggregates can be obtained in LB films of a DS-fatty acid 1:1 mixture

transferred from a nitrogen-pure water interface.<sup>11)</sup> Recently, Tachibana and Matsumoto<sup>12)</sup> also observed J-aggregates in metal-free DS-fatty acid mixed LB films.

In this context, it should be examined whether DSe forms J-aggregates without metallic cations in Langmuir films when mixed with fatty acid. And if the affirmative answer is obtained, the role played by the fatty acid in J-aggregation should be investigated. This work is devoted to these subjects.

## 2. EXPERIMENTAL

DSe and arachidic acid ( $C_{20}$ ) were purchased from the Japanese Research Institute for Photosensitizing Dyes, Co. and Fluka Co., respectively. Both compounds were used without further purification. A DSe solution with the concentration of  $5 \times 10^{-4}$  mol/l and  $C_{20}$  solutions with concentrations ranging from  $5 \times 10^{-7}$  to  $2 \times 10^{-3}$  mol/l

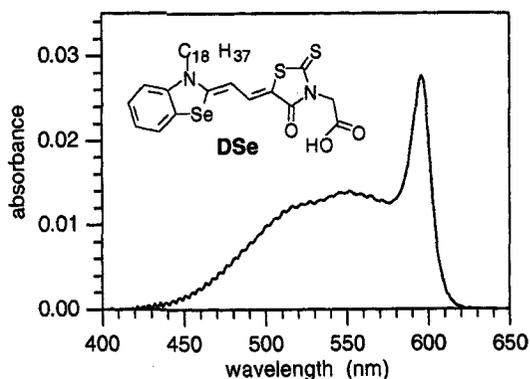


Fig.1 Electronic absorption spectrum of a Langmuir film of the 1:0.004 (molar ratio) mixture of DSe and  $C_{20}$ . The film is formed on a pure-water subphase and the spectrum is observed 600 s after spreading the material. Inset: the chemical structure of DSe.

were made using spectrograde  $\text{CHCl}_3$  as the solvent. These solutions were mixed and spread onto pure-water subphases contained in a Lauda Filmwaage trough under air at approximately  $20^\circ\text{C}$ . (The concentrations of DSe in the spreading solution ranged from  $2.5 \times 10^{-4}$  to  $5 \times 10^{-4}$  mol/l.) Pure water with a resistivity greater than  $1.8 \times 10^7 \Omega\text{cm}$  was prepared by using a Millipore Milli-Q system. The resultant Langmuir films were compressed so that the surface pressure reached  $5 \text{ mN/m}$  in approximately 200 s.

The electronic absorption spectra of Langmuir films were recorded with a WRM-10TP polychromator of Jasco Co., Ltd. with a bundle of optical fibers as a probe. The probing light emitted from the bundle propagates into the water subphase at normal incidence, is reflected by a mirror placed on the bottom of the trough and then is collected by the bundle. A linear baseline was subtracted from each absorption spectrum so that the absorbance data at 400 and 650 nm become zero.

Conventional vertical dipping-raising method was employed for trial Langmuir-Blodgett (LB) deposition of the materials. Plates of white glass or  $\text{CaF}_2$  were used as solid substrates, after precoating of three monolayers of cadmium arachidate. The absorption spectra of the LB films were recorded with a Perkin-Elmer Lambda-900 spectrometer at normal incidence.

### 3. RESULTS AND DISCUSSION

It was easily found that DSe- $\text{C}_{20}$  1:1 (molar ratio) mixed Langmuir films on a pure-water subphase exhibit a distinct J-band at 596 nm immediately after spreading the material.<sup>13)</sup> This fact shows that metallic cations are not always necessary for J-aggregation of this dye.

On the other hand, it was confirmed that a doublet, whose peaks are located at 515 and 555 nm, is a dominant absorption component in the metal-free pure DSe films, as already reported by Kawaguchi and Iwata.<sup>5-7)</sup> Since the optical properties of the DSe- $\text{C}_{20}$  1:1 mixed films are completely different from those of the pure DSe films, those of DSe- $\text{C}_{20}$  1: $x$  ( $0 < x < 1$ ) mixed films were measured. Surprisingly, the development of the J-band could be observed even for very small  $x$ . A characteristic case ( $x = 0.004$ ) is shown in Fig. 1.

In Fig. 2, spectra observed for DSe- $\text{C}_{20}$  1: $x$  mixed films with various  $x$  values (including 0 and 1) are displayed. With decreasing  $x$ , the time when the J-band becomes most distinct (denoted as  $t_{\text{max}}$ ) increases (Fig. 2 inset) and the spectra at  $t_{\text{max}}$  are recorded. Appearance of an isosbestic point is prevented maybe due to a bleaching effect, which is notable for the spectra at long  $t_{\text{max}}$ . It should be emphasized that this kind of phenomenon is difficult to detect in the films where the molecules are tightly immobilized.

The observed spectra displayed in Fig. 2 can be analyzed in the framework of the least squares method, by assuming that they consist of only two components,

*i.e.*, the J band and the doublet. This assumption is justified by the appearance of an isosbestic point in the time dependent spectrum of the 1:1 mixed films under a relatively high surface pressure.<sup>13)</sup> Then, the absorbance datum in the  $k$ -th spectrum ( $1 \leq k \leq m$ ) at the wavelength of  $\lambda_l$  ( $1 \leq l \leq n$ ) including an experimental error of  $e_{kl}$ , defined as  $\tilde{A}_{kl}$ , can be written as

$$\tilde{A}_{kl} = p_k P_l + q_k Q_l + e_{kl}, \quad (1)$$

where  $P_l$  and  $Q_l$  are absorbance due to the J band and the doublet with the unit "concentration", respectively, and  $p_k$  and  $q_k$  are the "concentrations" of these components, respectively. Here,  $(p_k + q_k)$  is not supposed to be constant and an isosbestic point is not necessarily observed. For convenience, the spectra having the smallest  $q_k$  and  $p_k$  are chosen, respectively, as the first and last spectra. Rewriting eq. (1) as

$$\tilde{A}_{kl} = p'_k P'_l + q'_k Q'_l + e_{kl}, \quad (2)$$

with defining

$$P'_l = p_l P_l + q_l Q_l, \quad Q'_l = p_m P_l + q_m Q_l, \quad (3)$$

$$p'_k = \frac{p_k q_m - p_m q_k}{p_l q_m - p_m q_l} \quad \text{and} \quad q'_k = \frac{p_k q_l - p_l q_k}{p_m q_l - p_l q_m}, \quad (4)$$

the number of unknowns is found to be  $2n+2m-4$ , because  $p'_1 = q'_2 = 1$  and  $p'_2 = q'_1 = 0$ . As explained in Appendix, the unknowns  $P'_l$ ,  $Q'_l$ ,  $p'_k$ , and  $q'_k$  ( $1 \leq l \leq n$ ,  $2 \leq k \leq m-1$ ) can be estimated by minimizing the residual

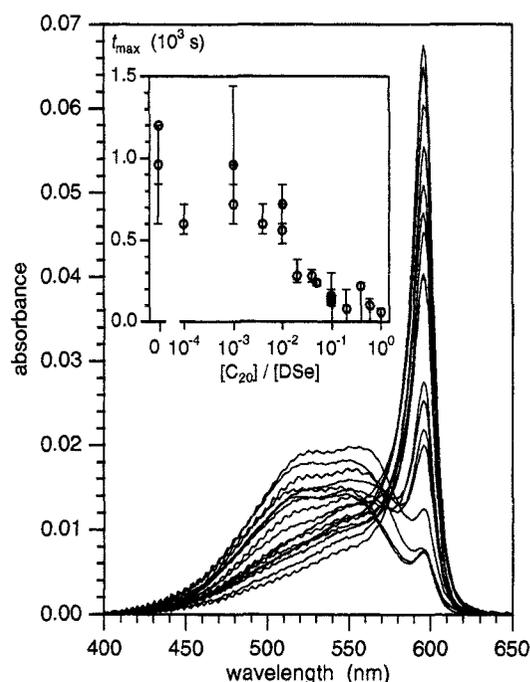


Fig. 2 Absorption spectra of DSe- $\text{C}_{20}$  mixed Langmuir films formed on pure-water subphases observed at  $t_{\text{max}}$ . Inset: the mixing-ratio dependence of  $t_{\text{max}}$ .

sum of squares,

$$S = \sum_{i=1}^m \sum_{j=1}^n (e_{ij})^2, \quad (5)$$

if  $nm > 2n+2m-4$ . Solid lines in Fig. 3 indicate  $P'_i$  and  $Q'_i$  obtained by applying the above method to the spectra displayed in Fig. 2.

Subtraction of  $sQ'_i$  from  $P'_i$  with a positive constant  $s$  brings about an unnatural downward peak around 515 nm, suggesting that  $P'_i$  corresponds to the pure J band, i.e.,  $q_1/q_m = s = 0$ . On the contrary,  $Q'_i$  contains the J band to a certain extent. The pure spectrum of the doublet can be obtained by subtracting  $tP'_i$  from  $Q'_i$ , where  $t \equiv p_m/p_1$ . A satisfactory result (Fig. 3 dotted line) is obtained by adjusting  $t = 0.07$ .

Now, a quantity indicating the predominant component can be evaluated as

$$\Delta_k = \frac{(p_k/p_1) - (q_k/q_m)}{(p_k/p_1) + (q_k/q_m)} = \frac{(1-s)p'_k + (t-1)q'_k}{(1+s)p'_k + (t+1)q'_k}. \quad (6)$$

If  $p_1 \approx q_m$ ,  $\Delta_k \approx +1$  and  $\Delta_k \approx -1$  when  $p_k \gg q_k$  and  $p_k \ll q_k$ , respectively, and  $\Delta_k \approx 0$  when  $p_k \approx q_k$ .  $\Delta_k$  is plotted against  $x$  in the inset of Fig. 3. The fact that  $\Delta_k \approx 0$  for  $x \approx 10^{-2}$  implies that one  $C_{20}$  molecule can assist  $10^2$  DSe molecules in the formation of J-aggregate(s). [This does not deny the possibility that one  $C_{20}$  molecule can assist more than  $10^2$  DSe molecules in the formation of J-aggregate(s).]

Here, a new question arises: does  $C_{20}$  work as a catalyst or assist nucleation of the J-aggregates? The time dependence of the absorption spectra provides the

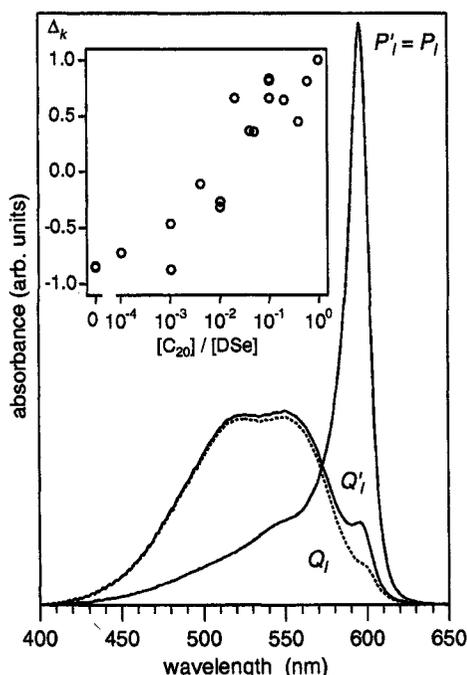


Fig. 3 Deconvoluted spectra (See text). Inset: the mixing-ratio dependence of  $\Delta_k$ .

answer to this question, as discussed below. Development of the J-aggregates in the initial stage is rapid for  $x \approx 1$  and gradual for  $x \ll 1$ . After  $t_{\max}$ , the J-band diminishes gradually. This diminishment of the J-band is not associated with development of any absorption bands, implying that the dye molecules are decomposed or isomerized. On the contrary, the doublet survive a long time ( $> 10^3$  s) after the complete disappearance of the J-band. This phenomenon cannot be explained if we assume that  $C_{20}$  works as a catalyst to convert non-J-aggregated DSe to J-aggregated DSe. Therefore, it can be concluded that  $C_{20}$  assists nucleation of the J-aggregates. The J-aggregates grow quasi one-dimensionally and stop growing when their endpoints reach other J-aggregates or isomerized DSe molecules. Consequently, non-J-aggregated DSe can remain even after all the J-aggregates stop growing, if the density of the J-aggregate nuclei is much smaller than that of the DSe molecule.

LB deposition of DSe- $C_{20}$  mixed Langmuir films containing the metal-free J-aggregates was found not easy. Two drawbacks were recognized. Firstly, the aggregates are not stable at surface pressures suitable for LB deposition (e.g., 25 mN/m). Secondly, the layers transferred during the raising process are easily cleaved during the successive dipping process, if they are not dried enough. On the other hand, drying the transferred layers too rapidly may destroy the J-aggregates in them. Anyway, however, a DSe- $C_{20}$  mixed LB film deposited under compromised conditions holds the metal-free J-aggregate to a certain extent (Fig. 4 (a)). In addition, those J-aggregates are preferentially aligned along the dipping-raising direction of the substrate. Further optimization of the deposition conditions is desired to prepare LB samples for characterization techniques other than electronic absorption spectroscopy. Note that

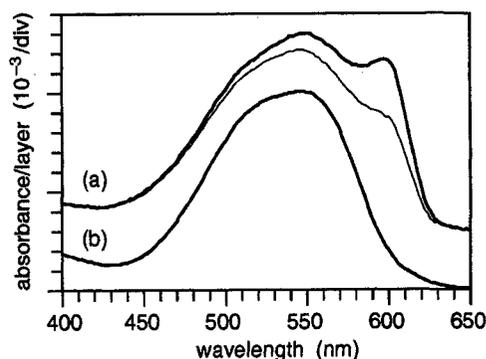


Fig. 4 (a) Polarized electronic absorption spectra observed for a metal-free LB film containing 2 layers of the 1:0.04 mixture of DSe and  $C_{20}$ . (b) Those observed for a metal-free LB film containing 12 layers of pure DSe. The light is polarized parallel to the film plane and parallel (thick lines) or perpendicular (thin lines) to the dipping-raising direction of the substrate. (For (b), the two spectra are not distinguishable from each other.)

neither J-band nor in-plane anisotropy was detected in the absorption spectrum of pure DSe LB films deposited from pure-water surfaces (Fig.4 (b)).

#### 4. CONCLUDING REMARKS

Metal-free J-aggregates of DSe are obtained in DSe-C<sub>20</sub> mixed Langmuir films, even with very small mixing ratio of C<sub>20</sub>, although the generation of such aggregates in pure DSe films is highly restricted. The time dependence of the absorption spectra of the films indicates that C<sub>20</sub> assists the nucleation of the J-aggregates. Furthermore, it is implied that one J-aggregate can contain 10<sup>2</sup> DSe molecules (or more). LB deposition of these metal-free J-aggregates is not very easy, but seems possible, which may invoke further characterization of them.

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#### APPENDIX

In this appendix, the method to estimate the unknowns in eq. (2) is explained. Hereafter, primes are omitted for simplicity. Firstly, a vector containing the true values of the unknowns is introduced:

$$\alpha_i = \begin{cases} P_i & (i = 1, \dots, n) \\ Q_{i-n} & (i = n+1, \dots, 2n) \\ P_{i-2n+1} & (i = 2n+1, \dots, 2n+m-2) \\ q_{i-2n-m+3} & (i = 2n+m-1, \dots, 2n+2m-4) \end{cases} \quad (\text{A1})$$

We also define the next function based on the true values and the true absorbance,  $A_{kl}$ , which cannot be obtained by experiments, as

$$f(k, l; \mathbf{A}, \boldsymbol{\alpha}) = A_{kl} - p_k P_l - q_l Q_l. \quad (\text{A2})$$

To evaluate eqs. (A2), they must be developed around the estimators of the unknowns (variables with tildes):

$$f(k, l; \mathbf{A}, \boldsymbol{\alpha}) \approx f_{kl} = \tilde{f}_{kl} - e_{kl} - \sum_{i=1}^{2n+2m-4} \tilde{f}_{kl;i} \tilde{\alpha}_i, \quad (\text{A3})$$

where  $\mathbf{a}$  is the correction of  $\tilde{\boldsymbol{\alpha}}$ , i.e.,  $\mathbf{a} = \tilde{\boldsymbol{\alpha}} - \boldsymbol{\alpha}$ ,

$$\tilde{f}_{kl} = \begin{cases} \tilde{A}_{1l} - \tilde{\alpha}_l & (k=1) \\ \tilde{A}_{kl} - \tilde{\alpha}_{k+2n-1} \tilde{\alpha}_l - \tilde{\alpha}_{k+2n+m-3} \tilde{\alpha}_{l+n} & (1 < k < m) \\ \tilde{A}_{ml} - \tilde{\alpha}_{l+n} & (k=m) \end{cases} \quad (\text{A4})$$

and

$$f_{kl;i} = \left. \frac{\partial f}{\partial \alpha_i} \right|_{\mathbf{A}=\tilde{\mathbf{A}}, \boldsymbol{\alpha}=\tilde{\boldsymbol{\alpha}}} \quad (\text{A5})$$

The unknowns can be estimated by minimizing  $S$  defined by eq. (5) under the constraints of  $f_{kl} = 0$ . This constrained minimization of  $S$  is equivalent to the unconstrained minimization of the next value:

$$g = \frac{1}{2} S - \sum_{k,l} \mu_{kl} f_{kl}, \quad (\text{A6})$$

where  $\mu_{kl}$  are Lagrangian multipliers. Then,  $\mathbf{a}$  can be obtained as

$$\mathbf{a} = \mathbf{H}^{-1} \mathbf{Z}, \quad (\text{A7})$$

where

$$H_{ij} = \sum_{k,l} f_{kl;i} f_{kl;j} \quad \text{and} \quad Z_i = \sum_{k,l} \tilde{f}_{kl} f_{kl;i}. \quad (\text{A8})$$

The correction for  $\tilde{\boldsymbol{\alpha}}$  should be iterated until the change in  $S$  becomes negligible. Note that modification of this method for multi-component systems is straightforward.

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