Five Types of J-Aggregates in Single-Chain Merocyanine Langmuir Monolayers on an Aqueous Subphase

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The formation of J-aggregates in Langmuir monolayers of a neat merocyanine dye (3-carboxymethyl-5-[2-(3-octadecyl-2-benzothiazolinyldene)ethylidene]-2-thioxo-4-thiazolidinone) has been examined by measuring the normal incidence absorption spectra. Five types of J-aggregates were found to be formed, depending on the temperature and the concentration and type of cations present in the subphase. The shift in the absorption peak wavelength on the J-aggregates formation is accounted for in terms of the number and the geometrical arrangement of the chromophores in each J-aggregate. The spectral shifts were analyzed numerically using both a point dipole model and a transition density model. These calculations indicate that the five different J-aggregates are linear ones with aggregation numbers ranging from 2 to 6.

There have been many researches[1—11)] on the J-aggregates of single-chain merocyanine dyes with either benzothiazole (MS) or benzoselenazole ring, in view of their applications to photoelectric and optical devices. Sugi et al.[1—4)] reported highly efficient photoelectric conversion of J-aggregates in merocyanine LB films mixed with cadmium arachidate, together with enhanced lateral photoconductivity in the J-aggregate film.

The properties of the aggregates are often strongly influenced by the presense of metal ions in the subphase. Kawaguchi et al.[12—14)] succeeded in preparing two types of J-aggregates of a merocyanine dye with the benzoselenazole ring on a water surface by selecting metal ions in the subphase. One of the J-aggregates absorbing at 600—610 nm was formed on water containing Ca^{2+}, Ba^{2+}, or Cd^{2+}, and the other absorbing at 620—630 nm was formed on water containing other metal ions such as Na^+, K^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Er^{3+}, or Lu^{3+}. These results indicate the importance of a chelate structure for J-aggregate formation. Yoneyama et al.[15)] drew a similar conclusion for the MS merocyanine J-aggregates. They noted that the spectral shape depends heavily on the nature of the metal ion, but did not determine the molecular arrangement of the aggregates.

In this paper we report that the merocyanine MS J-aggregates, formed under controlled subphase temperature and the concentration of monovalent or divalent metal ions in Langmuir monolayers, can be classified into five different types of J-aggregates. Their aggregation numbers were determined using both Kasha's point dipole model[16)] and the Norland's transition density model.[17)]

Experimental

The MS dye (Fig. 1) was purchased from Nippon Kanko-Shikiso Kenkyusho Co., and was used without further purification. The synthesis of this dye was described by Iriyama et al.[7)]

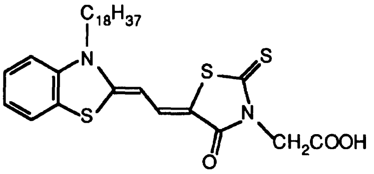

Fig. 1. Structure of the merocyanine dye.

The monolayers for absorption measurement were prepared on a Joyce–Loebl Langmuir trough Model IV. The water subphase used in the present experiment contained 0.5 mM $CdCl_2$, $CaCl_2$, or $NaHCO_3$, or 0.05 mM $NaHCO_3$ (1 M=1 mol dm^{-3}). The temperature was controlled in a range 18—29 °C. In all cases the pH was adjusted to pH 6.7 with $NaHCO_3$.

The dye was spread from a 0.4 mM solution of spectrograde chloroform onto the water surface. The monolayer was compressed to a surface pressure of 20 mN m^{-1} in 3 min. The pressure was allowed to stabilize for 2 min before optical measurements. Absorption spectra were taken under normal incidence using an Otsuka Electronics multichannel spectrophotometer Model MCPD-200.

Results and Discussion

Aggregate Formation. Figure 2 shows the normal incidence absorption spectra of the MS monolayers on a subphase containing 0.05 mM Na^+ at 21 °C. The spectrum indicates the formation of J-aggregates (λ_{max}=575 nm) when the film is initially compressed. In 10 min the 575 nm band was split into two distinct peaks at 607 and 620 nm. As will be detailed later, we attribute this spectral change to an increase in the aggregation number of the J-aggregate. On a subphase containing a higher concentration of Na^+(0.5 mM), a strong absorption peak at 620 nm is initially observed although this decayed over a period of time to leave a peak at 607 nm. These spectral changes are shown in Fig. 3.

Figure 4 shows the absorption spectra of monolayers on a subphase containing 0.5 mM Ca^{2+}. In this case only a single absorption peak characteristic of a J-aggregate is observed at 606 nm. No change in the absorption peak was observed as a function of time.

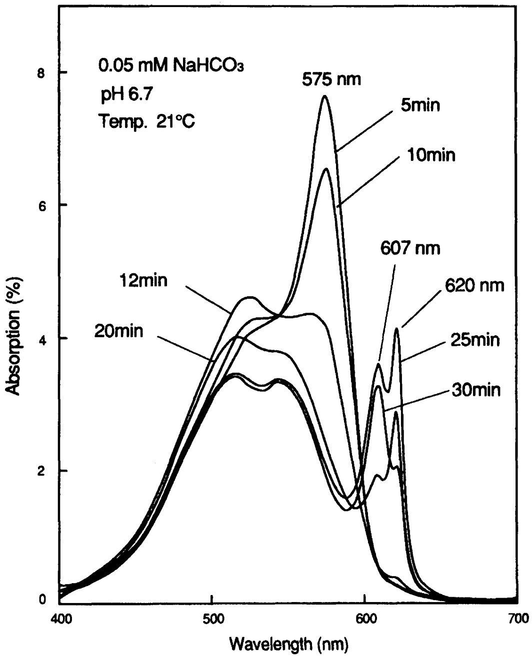

Fig. 2. Spectral change for the merocyanine monolayer on water containing 0.05 mM $NaHCO_3$.

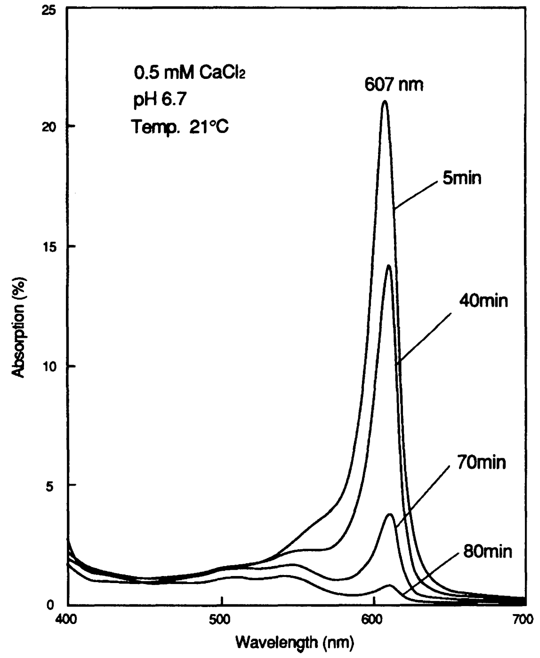

Fig. 4. Spectral change for the merocyanine monolayer on water containing 0.5 mM $CaCl_2$.

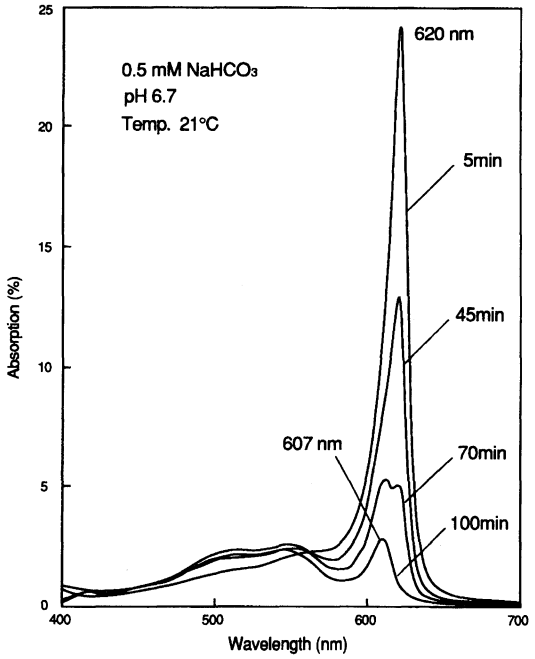

Fig. 3. Spectral change for the merocyanine monolayer on water containing 0.5 mM $NaHCO_3$.

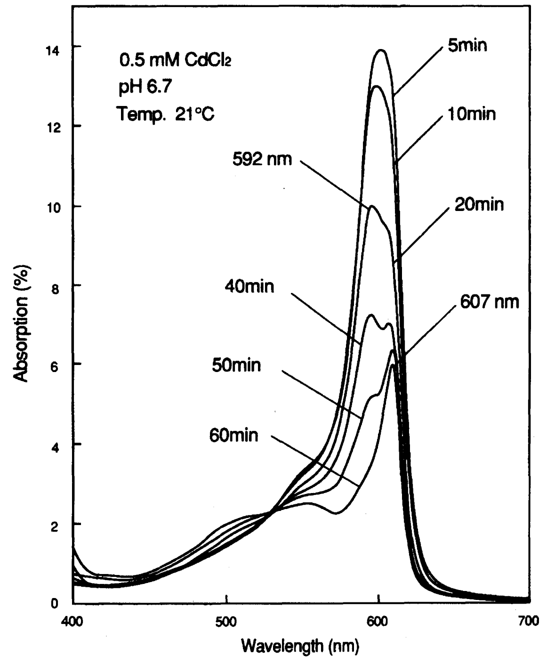

Fig. 5. Spectral change for the merocyanine monolayer on water containing 0.5 mM $CdCl_2$.

In previous work[18] we showed that it is possible to selectively control the formation of aggregates by changing the subphase temperature. In the case of the MS dye on a 0.5 mM Cd^{2+} subphase, J-aggregates with absorption peaks at 592 and 607 nm are formed depending on the temperature. At 21 °C the 592 nm peak is dominant although this slowly changes to the 607 nm peak with time as shown in Fig. 5. At a higher temperature, 29 °C, the 607 nm peak is dominant (Fig. 6). The longer wavelength peak is characteristic of an aggregate containing a larger number of chromophores and thus the aggregate size is found to increase with time and temperature.

Separately Yoneyama et al.[15] prepared 615—617 nm J-aggregates using 0.1 mM Mg^{2+}, Zn^{2+}, and Mn^{2+}, and 607 nm J-aggregates at a lower metal concentration

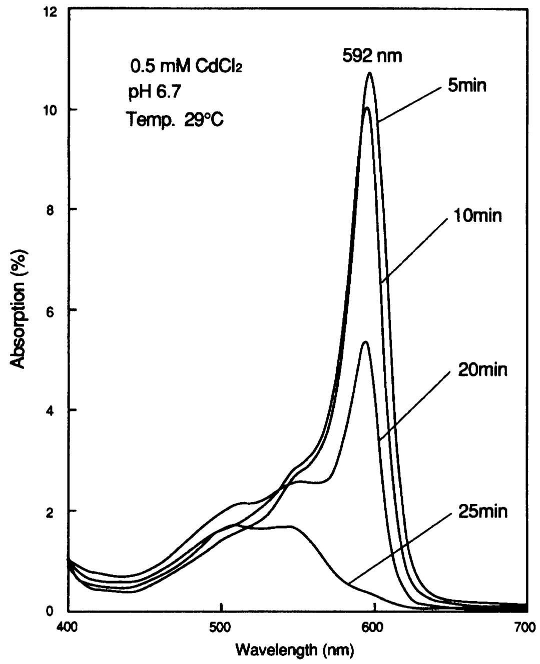

Fig. 6. Same as Fig. 5 but at a temperature of 29 °C.

(0.01 mM).

The J-aggregate absorption wavelengths and their preparation conditions are summarized in Table 1. It is seen that the merocyanine dye forms five types of J-aggregates depending on the nature of cation present in the subphase and on the subphase temperature.

Aggregation Numbers. The absorption shifts caused by the interaction of charge densities in aggregates can be analyzed numerically by a simple point-dipole cyclic model such as that proposed by McRae and Kasha.[16] This model includes only the nearest-neighbor interaction between molecules in an aggregate. In this method the frequency shift of the aggregate's absorption band compared to the monomer's peak absorption is defined by:

$$\Delta\nu_N = 2h^{-1}[(N-1)/N]M^2(1-3\cos^2\alpha)/r^3, \qquad (1)$$

where h is the Planck's constant, N the number of monomers in the aggregate, r the separation distance between molecules, α the slip angle between the transition dipole moment and the molecular axis, and M the transition dipole moment which is related to the molecular extinction coefficient of the monomer. It can be shown that when the slip angle is smaller than 54.7° then red shifted J-aggregate bands appear. The slip angle (α) can be assumed to be constant for a particular material; the above equation can then be written in the form

$$\Delta\nu_N = [(N-1)/N]\Delta\nu_\infty, \qquad (2)$$

where $\Delta\nu_\infty$ is a constant and refers to the frequency shift for an infinitely large aggregate. For example, similar assignments of aggregation numbers have been reported by Rosenoff et al.[19,20] for bulk solution of cyanine dye H-aggregates. The H-aggregates consisted of the trimer, tetramer, and pentamer in their case.

Table 1. Spectral Properties of Merocyanine Langmuir Films Formed on Water Subphase Containing Metal Ions[a]

Metal ion	J-Band peak wavelength nm
None	523 (in Chloroform)
Na^+	575, 592, 620
Ba^{2+}	590[b]
Cd^{2+}	592,[c,d] 607[c]
Pb^{2+}	595[b]
Ca^{2+}	606
Zn^{2+}	607, 615[b]
Mg^{2+}	607, 617[b]
Mn^{2+}	607, 617[b]

a) pH was adjusted to 6.7 with $NaHCO_3$; Temperature of the subphase, 21 °C. b) See Ref. 15. c) See Ref. 18. d) pH 6.7; Temperature of the subphase, 29 °C.

The absorption peak wavenumbers of the various J-aggregates are plotted against $(N-1)/N$ in Fig. 7, where a linear relationship is clearly noted. The frequency shift proportional to $(N-1)/N$ may thus be taken as an approximate empirical law and may be used to classify the sizes of aggregates.

An alternative approach is that proposed by Norland et al.[17] based on a transition density model and includes not only the nearest-neighbor interaction but the next-nearest-neighbor and more distant interactions between molecules in an aggregate. We have used this model in order to estimate the number of molecules in

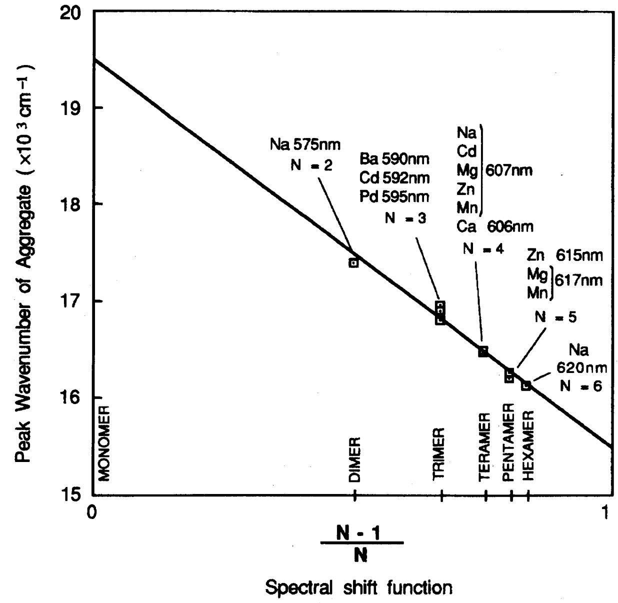

Fig. 7. Plot of absorption maxima on peak wavenumber against the theoretical spectral shift function.

the J-aggregates. Using the Hückel molecular orbital method we first calculated the electronic transition density associated with each atom, which corresponds to the first allowed transition of this molecule. The results are shown in Fig. 8(a) for the merocyanine dye. The calculated transition dipole moment is 13.134 debye (1 debye=3.33564×10^{-30} C m).

The excitation energy $\Delta E'$ of a dye aggregate is given by the sum of the excitation energies for the monomer, ΔE_m, and the interaction integral $2J$, where J is given by:

$$J=\sum_{i,j} q(i)q(j)/r(i,j). \qquad (3)$$

Here $q(i)$ and $q(j)$ are the transition densities of the i th and j th atom, respectively, and $r(i,j)$ is the distance between atoms i and j. For the calculation of the interaction energy, the transition density at each atom was split into equal parts located ±0.84 Å above and below the molecular plane. The Coulombic interaction was calculated between a point on one molecule and each of the 18 pairs of transition density points on another molecule. The cycle of the interaction is then repeated for all the 36 points on the molecule and summed. The total interaction energy is divided by the aggregation number. The perpendicular separation distance between adjacent molecules is estimated to be 3.6 Å.

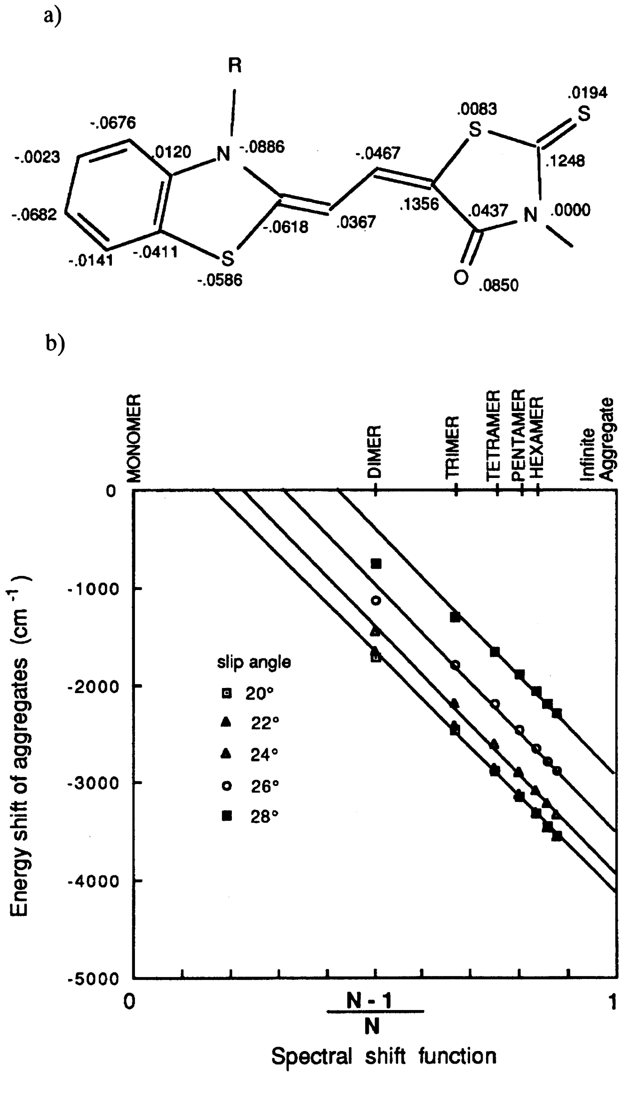

Fig. 8. (a) Calculated transition density map for merocyanine dye. (b) Slip angle dependence of the calculated energy shifts ($2J$).

Using this method we calculated the interaction energies for an aggregate of the merocyanine dye as a function of the slip angle. The relationship between the aggregation number and the energy shift was then calculated. Figure 8(b) shows the spectral shifts ($2J$) which occur in simple linear aggregates containing N chromophores. The relationship between the aggregation number and the energy shift is linear with slip angles close to 20°. The calculated energy shift $2(J_\infty-J_2)$ at 2390 cm^{-1} between a dimer and an infinite aggregate at the slip angle of 20° corresponds to the experimental shift in frequency at 2020 cm^{-1} from absorption of the dimer to that of an infinite aggregate (Fig. 7).

Analyzing the results discussed in this paper the aggregation number appears to depend on both the size and charge of the cation. Cations of smaller radius give rise to aggregates of larger aggregation numbers. Merocyanine dyes coordinated to monovalent Na^+ form J-aggregates composed of dimer, tetramer, and hexamer, by two-molecule association depending on the ionic strength. For divalent cations, the dye exhibits a tendency to form J-aggregates with smaller aggregation number than the case of Na^+. The dyes coordinated to Cd^{2+} form the 607 and 592 nm aggregates assignable to a tetramer and a trimer, respectively. The tetramer formation is more effective with Ca^{2+} than with Cd^{2+}. Mg^{2+}, Zn^{2+}, and Mn^{2+}, with radii between those of Na^+ and Ca^{2+}, promote the formation of 615—617 nm aggregates assignable to a pentamer in addition to the 607 nm aggregate (tetramer). It has been confirmed that the unit of the morocyanine J-aggregates is a pair of molecules.

In conclusion, the merocyanine dye can exist in five different of aggregate states. The aggregation numbers of these states are 2, 3, 4, 5, and 6, depending on the preparation conditions of the film, i.e. pH, temperature, the concentration, and type of the cation. The J-aggregates are formed when small groups of strongly bonded chromophores join in a loosely bonded structure. In the case of the merocyanine dye the structure of aggregates is influenced by the bonding between the carboxyl group and the metal cation. Our results support this hypothesis. Further work is currently under way as to why the selective interactions between the carboxyl group and the cations lead to the formation of different J-aggregates.

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