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Thermochromic Behavior of Merocyanine J-Aggregates

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J-aggregate crystallites of merocyanine dye molecules were formed in the monolayer at the solid-water interface and in methanol/water solution. The crystallites in both systems exhibited a thermochromic transition with a well-defined isosbestic point. When the systems were heated up above 30°C, the absorption band of the J-aggregate crystallites (J-band) shifted roughly from 625 to 600nm with a relaxation. The characteristic time of the transition of the J-band was investigated by varying the preparation condition of each system, and differences in transition behavior are discussed.

Key words: Thermochromism, Merocyanine, J-aggregate, Monolayer, Solution

1. INTRODUCTION

For many decades, a J-aggregate of cyanine dye molecules has been attracting the interests of the technological and scientific community due to its photosensitization effect, ultrafast nonlinear optical property and unique sharp visible absorption band (J-band) [1]. The J-aggregate is a crystallite of dye molecules and exhibits the absorption band at a longer wavelength than that of isolated (monomer) dye molecules. It is well known that amphiphilic merocyanine dye (MD) molecules* form a J-aggregate monolayer on the aqueous subphase [2,3] and a multi-layered film can be also obtained by applying the Langmuir-Blodgett (LB) method [4]. The absorption bands of the monomer and the J-aggregate state of MD molecules are around at 525 and 600nm, respectively. The cations in the subphase play an important role in J-aggregate formation. They interact with the carboxyl group of MD and form J-aggregate crystallites. The J-band position depends on the species of the cation [5]. For example, cadmium ion (Cd^{2+}) and magnesium ion (Mg^{2+}) induces the J-bands at 595nm and at 620nm, respectively.

We have previously performed microscopic observations on the MD J-aggregate monolayer by using the atomic force [6] and the multipurpose nonlinear optical microscope [7,8] and clarified the morphology of the monolayer, the formation mechanism of the crystallites, and how to control the size of the crystallites [9,10]. Recently, the first order structural phase transition of the J-aggregate crystallite was also found, when the MD monolayer was formed on an aqueous subphase containing $CdCl_2$ and $MgCl_2$ [9,10,11]. This phase transition accompanies a distinct change of J-band position (thermochromism). The J-bands of the high (HT) and the low temperature (LT) phase are at 595 and 620nm, respectively, and the band position exhibits a neat thermal hysteresis. Because the band shape of HT and LT phase corresponds to that formed by Cd^{2+} and Mg^{2+}, respectively, it is predicted that ion exchange of the carboxyl group of MD induces the thermochromic phase transition. This phenomenon should be utilized in controlling the J-band position, which determines the wavelength of the maximum photosensitization effect and nonlinear optical susceptibility.

For further application, it is better to control this phenomenon in a solid film or a liquid system than that at the monolayer on the subphase. However, the LB film did not show the transition, and the dissociation of J-aggregates was dominant on heating. In order to realize a high mobility of the cations for ion exchange, we developed an airtight cell [10] where the two MD monolayers at the solid-water interface confined the subphase, which contained $CdCl_2$ and $MgCl_2$. We also formed J-aggregate crystallites in a methanol/water solution containing $CdCl_2$ and $MgCl_2$.

In this paper, the thermochromic behavior of MD J-aggregate crystallites in an airtight cell and in methanol/water solution is investigated by varying the preparation condition of the sample, and differences in the transition manner are discussed. These studies also help us to understand the mechanism of thermochromic transition.

2. EXPERMENTAL

2.1 Airtight cell

The procedure for cell assembling is based on LB method [4]. On two hydrophobic slide glasses, an MD and arachidic acid ($CH_3(CH_2)_{18}COOH$) mixed monolayer was deposited by vertically dipping the two slide glasses into the monolayer on the subphase. During the deposition, the surface pressure of the monolayer was kept at constant (π mN/m), and the subphase temperature was 17°C. The subphase was an aqueous solution of the mixture $CdCl_2$ and $MgCl_2$. The total concentration was indicated as C_{tot} mmol/l (mM), and the molar ratio of $CdCl_2$ and $MgCl_2$ was fixed at 1:4. $NaHCO_3$ (from 0.05 to 0.1mM) was also added to adjust the pH value at ca. 6.8.

After dipping the glasses, the subphase was sandwiched by the two slide glasses with a spacer. Then the set of glasses was taken out from the subphase, and sealed with paraffin to form the airtight cell. Finally, a cell consisting of LT phase (J-band at 620nm) was obtained. (For details of the cell preparation, see Ref.[10]) The temperature, the deposition pressure π, and the total concentration C_{tot}, were varied to investigate the thermochromic behavior.

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* 3-caboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene)-ethylidene]-2-thioxo-4-thiazolidinone

2.2 Methanol/water solution

Methanol/water (6% v/v for methanol) contained 2.0mM $MgCl_2$, 0.2mM $NaHCO_3$ and $CdCl_2$. The concentration of $CdCl_2$ was indicated as C_{Cd} μmol/l (μM). MD of 1.5μM was dissolved in this methanol/water solution. After these chemicals were put together, the solution was sonicated for 15 min. in order to achieve a uniform mixture. During this sonication, the solution showed a color change from red to blue, and the J-aggregate crystallites of LT phase were formed. In the case of the solution, the temperature and the $CdCl_2$ concentration C_{Cd} were varied to examine the transition behavior.

3. RESULTS AND DISCUSSION

3.1 Airtight cell

The cell was heated at a constant temperature and the temporal change in the visible absorption spectrum was measured. One of the typical results is indicated in Fig. 1. The cell was fabricated under the conditions of π = 30mN/m and C_{tot} = 1.5mM. The temperature of the cell was kept at 35°C. The J-band at 620nm transformed into the band at 595nm, and the isosbestic point was obtained at 604nm. The shape of the initial and final spectrum corresponds well to that of LT and HT phase, respectively, of the monolayer at the air-water interface [9,10]. However, in the case of the air-water interface, the J-band does not show a temporal change. The phase transition temperature determines the J-band position, and the transition temperatures on heating (LT to HT phase) and that on cooling (HT to LT phase) are 32 and 23°C, respectively [9,10]. Correspondingly, in the cell, the transition from LT to HT phase (shown in Fig. 1) did not occur below 32°C. After the transition to HT phase, the cell was cooled down and kept at below 23°C. Then the transition from HT to LT phase did occur. However, it took a few weeks to complete the transition and there was poor reproducibility [10].

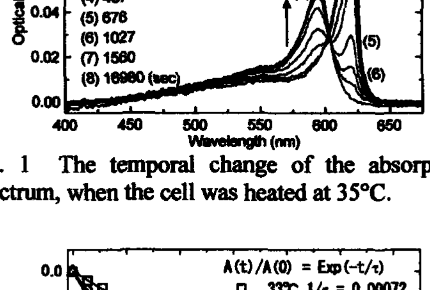

Fig. 1 The temporal change of the absorption spectrum, when the cell was heated at 35°C.

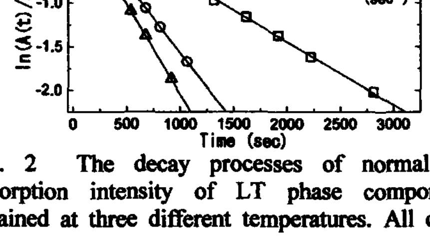

Fig. 2 The decay processes of normalized absorption intensity of LT phase component obtained at three different temperatures. All cells were prepared under the condition π = 30mN/m and C_{tot} = 1.5mM. Solid lines indicate the fitting curve of the single exponential function.

The temporal decay of the LT phase was investigated by extracting the contribution of HT phase from the spectrum in order to characterize the transition manner. The peak value of the spectrum of the LT phase component A(t) normalized by the initial value A(0) exhibited a single exponential decay. The decay process of ln[A(t)/A(0)] obtained at different heating temperatures is indicated in Fig. 2. The obtained time constant ($1/\tau$) shown in Fig. 2 indicates that the transition rate increases as the temperature increases.

The dependence on the conditions of cell assembly was also investigated. Fig. 3 shows the transition process of the cell prepared at π = 7mN/m and C_{tot} = 1.5mM. The heating temperature was 34°C. The spectral shape of LT and HT phase corresponds well to that of the cell prepared at π = 30mN/m (Fig. 1). The decay of the LT phase was fitted with a single exponential function, and $1/\tau$ was determined to be 0.00190sec^{-1}. According to the results indicated in Fig. 2, it can be said that $1/\tau$ does not show a remarkable dependence on the deposition pressure π. In other words, the transition rate does not depend on the area density of the MD molecule. Therefore, it is reasonably predicted that the molecular density of the J-aggregate crystallite of the LT phase is the same or larger than that of the HT phase.

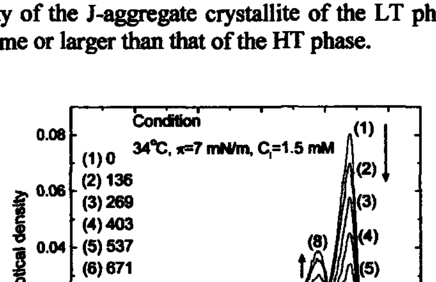

Fig. 3 The temporal change of absorption spectrum of cell prepared at π = 7mN/m.

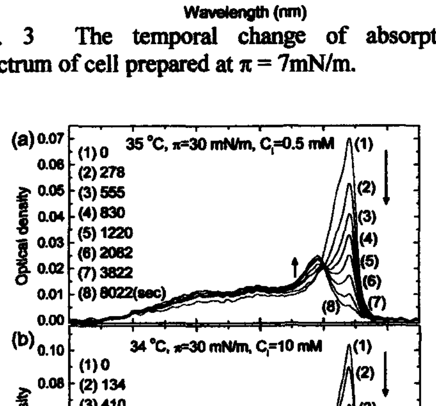

Fig. 4 The temporal change in the absorption spectrum. (a) indicates the result obtained from the cell prepared at C_{tot} = 0.5mM, and (b), at C_{tot} = 10.0mM.

The dependence on C_{tot} is shown in Fig. 4. Cells of C_{tot} = 0.5, 2.5, 5.0 and 10.0mM were prepared. π was fixed at 30mN/m. The heating temperature was between 34 and 35°C. The spectrum shape of the cells prepared at C_{tot} = 2.5 and 5.0mM corresponded well to that shown in Fig. 1. In the case of C_{tot} = 0.5 and 10.0mM, the J-band of LT phase exhibited a shoulder at 605nm and the isosbestic point became dim (Fig. 4). The temporal change in the LT phase component obeyed a single exponential decay irrespective to C_{tot} value. The obtained $1/\tau$ distributed around 0.00130sec^{-1}, and it was revealed that there was no specific dependence of the transition behavior on C_{tot}.

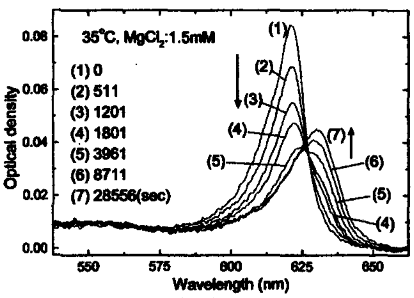

Fig. 5 The temporal change in the absorption spectrum observed from the cell whose subphase consisted of aqueous solution of 1.5mM $MgCl_2$. The cell was heated at 35°C.

In order to investigate the role of the cations (Mg^{2+} and Cd^{2+}), the cell whose subphase contained 1.5mM $MgCl_2$ and no $CdCl_2$ was fabricated, and heated at 35°C. In this case, the 620nm J-band shifted to 630nm (Fig. 5). This suggests that, in the case of the cell, both Mg^{2+} and Cd^{2+} are needed to induce the transition, as in the case of the monolayer at the air-water interface [10]. However, in the case of the monolayer at the air-water interface, the J-aggregate crystallites on the subphase without $CdCl_2$ show dissociation to the monomer at 63°C, and there is no transition below this temperature. Thus the new transition shown in Fig. 5 is unique for the cell (the monolayer at the solid–water interface).

3.2 Methanol/water solution

By heating the solution, a similar transition from LT to HT phase also occurred. In the case of the solution, the J-band of the LT phase was observed at 630nm, and that of HT phase was at 605nm. The isosbestic point was at 613nm. The small red-shift of the J-band should be attributed to the solvent effect [12]. At room temperature, the solution did not show the transition from LT to HT phase. This suggests that there should be a certain temperature which corresponds to the transition temperature of the monolayer at the air-water interface. However, we could not obtain a solution which shows reversible transition.

The temporal changes of absorption spectrum are indicated in Fig. 6. The solution at C_{Cd} = 6.0 and 0.0μM was heated at 58 and 67°C, respectively. It is surprising that the solution without $CdCl_2$ exhibited the same thermochromic transition. The decay process of the LT phase component at different C_{Cd} is summarized in Fig. 7(a). The observed data matched well again to a single exponential function irrespective of C_{Cd} value. The obtained $1/\tau$ was plotted as a function of C_{Cd} (Fig. 7(b)). It was found that the transition rate increases steeply as the concentration of $CdCl_2$ increases.

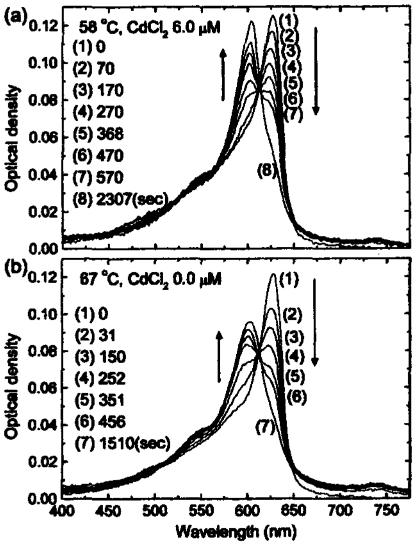

Fig. 6 The temporal change in the absorption spectrum. (a) indicates the result when C_{Cd} = 6.0μM and the temperature was 58°C, and (b), when C_{Cd} = 0.0μM and the temperature was 67°C.

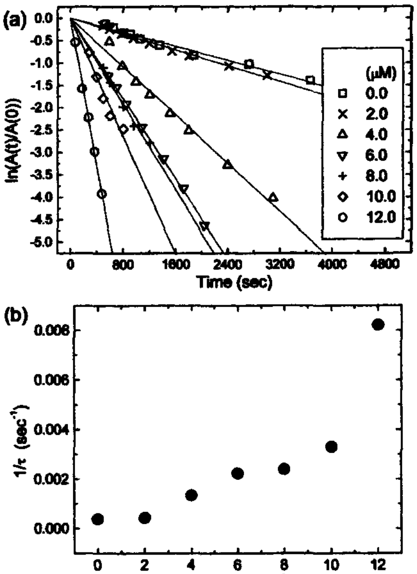

Fig. 7 The dependence of the decay process on C_{Cd}. (a) indicates the decay of the absorption spectrum of LT phase at different C_{Cd} value. The solution was heated at 58°C. The fitted curves of a single exponential function are indicated as a solid line. (b) indicates $1/\tau$ as a function of C_{Cd}. The values of $1/\tau$ were obtained from the fitting curves indicated in (a).

$1/\tau$ was measured at different temperatures. The range of the heating temperature for the solution at C_{Cd} = 0.0 and 10.0μM was 58 ~ 66°C and 49 ~ 58°C, respectively. The results were summarized as an Arrhenius' plot (Fig. 8). Arrhenius' equation relates $1/\tau$, activation energy (E)

and temperature (T) as indicated below.

$$\ln(1/\tau) = \ln(1/\tau_0) - \frac{E}{RT}, \qquad (1)$$

where R and $1/\tau_0$ are gas constant and frequency factor, respectively. $\ln(1/\tau)$ at different temperatures was fitted by using Eq. (1) and the obtained activation energy and frequency factor are indicated in Table I. It was found that the presence of $CdCl_2$ contributes to the increment of the frequency factor and there is almost no influence on the activation energy.

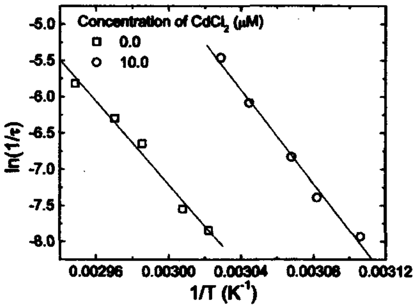

Fig. 8 Arrhenius' plot of the decay rate of LT phase obtained from the solution. Square plots indicate the result when C_{Cd} = 0.0μM, and circle plots, when C_{Cd} = 10.0μM. Solid lines are fitting curves based on Arrhenius' equation (Eq. (1)).

Table I. Activation energies and frequency factors of the transition from LT to HT phase observed in the solution.

Concentration of $CdCl_2$ (μM)	Activation energy (eV)	Frequency factor (s^{-1})
0.0	2.5	1.0×10^{35}
10.0	2.6	3.1×10^{37}

In the case of the airtight cell, we also performed an Arrhenius' plot. The cell was prepared under the same condition indicated in Fig. 1, and the heating temperature was varied within the range from 33 to 36°C. Though the obtained $\ln(1/\tau)$ did not align in linear relationship with $1/T$, we forced the fit by using Eq. (1), and the obtained activation energy was ca. 5.5eV. This is too high energy for organic compounds. This fact suggests that the transition manner cannot be explained by Arrhenius' equation and the mechanism of the transition exhibited by the J-aggregate crystallites in the cell is different from that in the solution.

4. CONCLUSIONS

In this work, we have investigated the thermochromic behavior of MD J-aggregate crystallites formed in an airtight cell and in methanol/water solution. The transition corresponded to the phase transition from LT to HT phase, which is observed in the monolayer at the air-water interface on heating. It was found that there are differences in the transition behavior between the monolayer at the air-water interface, the monolayer at the solid-water interface (airtight cell) and the solution. The differences are summarized by the following three points. (i) The reversibility of the transition. In the case of the monolayer at the air-water interface, the transition is reversible and behaves as a first order structural phase transition [9,10,11]. In the case of the airtight cell, the reproducibility of the transition from LT to HT phase is good, while that of the transition from HT to LT phase is very poor. Though the cells were prepared under the same condition, we have obtained only a few cells which showed the transition from HT to LT phase, and the transition took a few weeks [10]. In the case of the solution, the transition from LT to HT phase occurs successfully. However, we could not obtain a solution which showed the transition from HT to LT phase. (ii) The transition manner of the J-band. In the case of the monolayer at the air-water interface, the J-band changes at the well-defined phase transition temperature. Correspondingly, in the case of the cell and the solution, there is a certain temperature that we have to heat the system above to induce the transition. However, the J-band changes with a relaxation. The decay manner of LT phase is expressed by a single exponential function, and the transition rate increases as the temperature increases. Specifically, in the case of the solution, the relaxation rate obeys Arrhenius' law. (iii) The role of $CdCl_2$ for the transition. In the case of the monolayer at the air-water interface and the cell, $CdCl_2$ and $MgCl_2$ are needed in the subphase for the transition. However, in the case of the solution, the transition occurs without $CdCl_2$. These differences suggest that the transition mechanism is not simple like an ion exchange reaction. To explain the mechanism of the transition, we have to take into account temperature-dependent free energy of the LT and HT phase.

5. ACKNOWLEGEMNTS

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