Bull. Chem. Soc. Jpn. Vol. 81, No. 10, 1282–1284 (2008)

Solvent-Mediated Phase Transformation from J-aggregates of Thiacarbocyanine to H-aggregates

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It has been found that the J-aggregates of thiacarbocyanine self-assembled in solution spontaneously transform into H-aggregates. The transformation mechanism was found to be solvent-mediated phase transformation that proceeds through dissolution of the J-aggregates and subsequent aggregation into H-aggregates.

Supramolecular aggregates self-assembled from cyanine dye molecules in solution have been extensively studied from the viewpoint of both fundamental science and device applications.[1] These dye aggregates are divided into so-called J- and H-aggregates depending on their optical properties. The J-aggregates exhibit a red-shifted absorption band (J-band) with respect to the monomer absorption, while the H-aggregates exhibit a blue-shifted absorption band (H-band). The difference in optical properties is related to their internal molecular arrangement. The molecules in a J-aggregate are stacked with a large angle of slippage, and the arrangement is commonly described as "brickwork-like" or "staircase-like" arrangement. Such a molecular arrangement leads to an interaction between the transition moments of the molecules in a "tail-to-head" manner. On the other hand, the molecules in an H-aggregate are stacked with a small angle of slippage, and are commonly described as being in a "ladder-like" arrangement, leading to a "face-to-face" interaction between the transition moments. A simple exciton theory shows that the "tail-to-head" and "face-to-face" interactions of the transition moments result in the appearance of red- and blue-shifted excitonic absorption bands with respect to monomer, respectively.[2–4]

In this study, we have found that thiacarbocyanine (TCC, Figure 1a) dye molecules in a supersaturated solution initially form J-aggregates and then transform into H-aggregates on a time scale of several tens of minutes. Although the phase transformation of molecular crystals that precipitate in solution has been studied for a long time in relation to polymorphism,[5,6] few studies have been conducted on the transformation of supramolecular aggregates.[7–10] Since optical, electronic, and chemical properties of the supramolecular structures are closely related to their internal molecular arrangement, its control is a subject of essential importance in the fabrication of functional materials by molecular self-assembly. Hence, the mechanism of phase transformation that involves the rearrangement of molecules in supramolecular aggregates is particularly interesting. On the basis of in situ monitoring of the transformation by absorption spectroscopy, we demonstrate that the mechanism of the transformation is a solvent-mediated phase transformation.

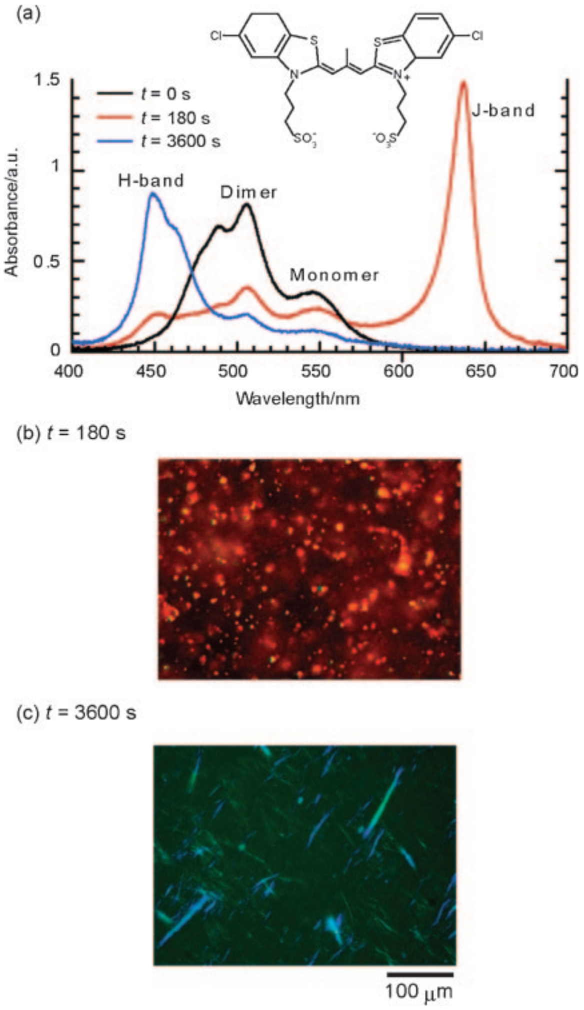

Figure 1. (a) Absorption spectra of the solution prepared by the addition of NaCl solution to 0.05 mM TCC-aqueous solution at $t = 0$ s. The inset shows the chemical structure of TCC. Polarized microscope images of the solution at $t = 180$ s (b) and at $t = 3600$ s (c).

It has been reported that TCC in an aqueous solution forms both J- and H-aggregates depending on the concentration of the solution.[11] Only J-aggregates are formed in a 10 mM ($M = \mathrm{mol\,dm^{-3}}$) solution, while only H-aggregates are formed in a 1 mM solution. Both J- and H-aggregates are formed in a 4 mM solution. We used low concentration solutions (<1 mM) as starting solutions in which neither the J- nor H-aggregates are formed. To start the aggregation process in a controlled manner, an aqueous solution of NaCl (60 mM) was added to the starting solutions at a volume ratio of 1:1 to induce supersaturation by providing counter ions.[12]

Figure 1a shows the absorption spectra of a solution pre-

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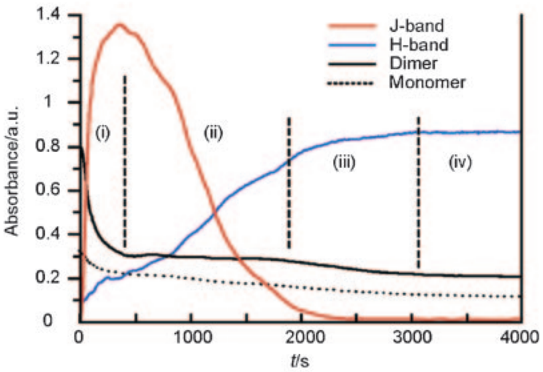
(a) 0.05 mM TCC + NaCl solution



(b) 0.04 mM TCC + NaCl solution

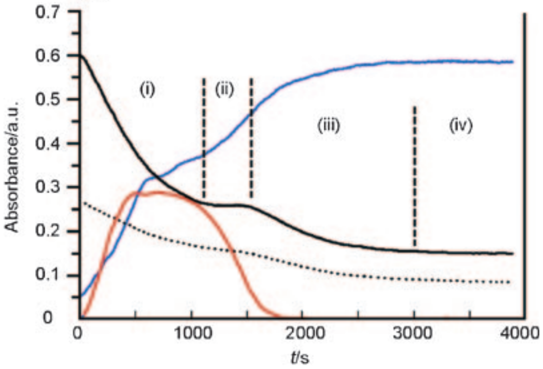


Figure 2. Time evolutions of J-, H-, dimer, and monomer band intensities for solutions prepared using starting solutions of 0.05 mM (a) and 0.04 mM (b).

pared by the addition of the NaCl solution to a 0.05 mM starting solution at $t = 0$ s. The spectrum at $t = 0$ showed monomer and dimer absorption bands at 545 and 505 nm, respectively.[11,13] The spectrum measured at $t = 180$ s showed the J-band at 640 nm. However, at $t = 3600$ s, the J-band entirely disappeared, whereas the H-band appeared at 450 nm. The polarized microscope image of the solution at $t = 180$ s exhibited grain-shaped aggregates with a diameter of a few micrometers (Figure 1b), whereas that at $t = 3600$ s showed fiber-shaped aggregates with a length of up to $\approx 200\,\mu m$ (Figure 1c). On the basis of the absorption spectra and the polarized microscope observations, it can be concluded that the grain-shaped J-aggregates transformed into fiber-shaped H-aggregates. The transformation was observed for a concentration range of the starting solution 0.03–0.15 mM at 20 °C. In the solution with a concentration of less than 0.03 mM, the H-aggregates were formed a few minutes after the addition of the NaCl solution without the prior formation of J-aggregates.

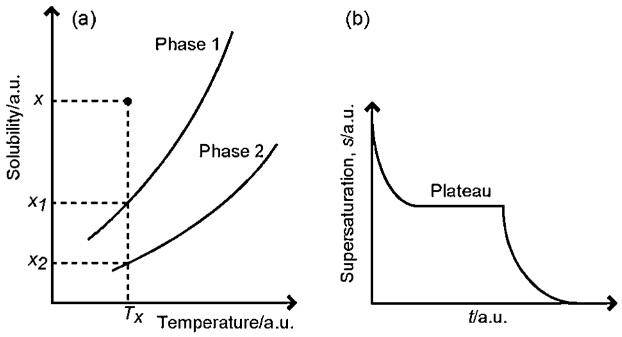


Figure 3. (a) Generalized phase diagram of monotropic system with two crystal phases. (b) Time evolution of supersaturation in the solvent-mediated phase transformation.

In order to investigate the mechanism of the transformation, the absorbances of the monomer, dimer, J-, and H-bands were plotted as a function of time. Figures 2a and 2b show the plots for the solutions prepared using 0.04 and 0.05 mM starting solutions, respectively. The curves show that the transformation process can be divided into four stages, although the duration of each stage varies depending on the solution concentration: In stage (i), the formation of the J-aggregates is induced by the addition of the NaCl solution at $t = 0$ s and the dimer (monomer) concentration decreases as the J-band intensity increases. In stage (ii), the J-band intensity decreases, while the H-band intensity begins to increase. It should be noted that the dimer (monomer) concentration is nearly constant during this stage. In stage (iii), the J-band entirely disappears, while the H-band intensity continues to increase gradually. The dimer (monomer) concentration starts decreasing again in this stage. In stage (iv), the transformation is complete and the system reaches equilibrium.

The observed time evolutions are well interpreted by the mechanism of the solvent-mediated phase transformation, which has been observed in the crystallization of polymorphic substances in solution. In this transformation, metastable crystals initially precipitate and then transform into stable crystals through dissolution and recrystallization. A theoretical analysis of the solvent-mediated transformation was conducted by Cardew, Davey, et al.[14,15] A generalized phase diagram of a monotropic system with two crystal phases, i.e., a metastable phase 1 and a stable phase 2, is shown in Figure 3a to illustrate the transformation kinetics according to Cardew and Davey. A solution of composition x at temperature Tx is supersaturated with respect to both phase 1 and phase 2. Thus, precipitation can yield both phases. However, in this situation, the metastable phase 1 appears as the initial precipitate. This is an empirical law known as Ostwald's law of stage.[16] As phase 1 grows, the solution composition drops below x_1, which is the saturated solubility of phase 1, and the solution becomes undersaturated with respect to phase 1. Thus, the crystals of phase 1 dissolve, leading to supersaturation for the continued growth of phase 2. This dissolution–growth process continues until phase 1 disappears entirely and the transformation is complete. A characteristic feature of the solvent-mediated phase transformation appears in the time evolution of the supersaturation, which is defined by $s = (x - x_2)/x_2$ (x_2: saturated solubility of phase 2). Since the growth and dissolution rates of the two phases must be balanced at least during some period in the transformation, the supersaturation curve exhibits a plateau as schematically illustrated in Figure 3b.[14,15] Such plateaus in the supersaturation curve have been observed in the solvent-mediated phase transformation of polymorphic crystals by the in situ monitoring of solution compositions by Raman spectroscopy.[17]

The constant dimer (monomer) concentration in stage (ii) strongly suggests that J-aggregates are transformed into H-aggregates by the solvent-mediated phase transformation that

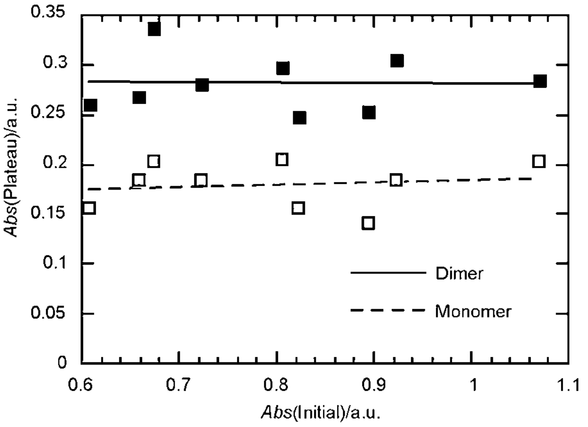


Figure 4. Plots of dimer and monomer absorbances in stage (ii) (Abs(Plateau)) against those at $t = 0$ s (Abs(Initial)).

proceeds through the dissolution of metastable J-aggregates into dimer (monomer) and subsequent aggregation into stable H-aggregates. The dimer and monomer absorbances exhibited similar time evolution curves (Figure 2), indicating that the exchange between them is in equilibrium throughout the transformation. When the transformation proceeds through this mechanism, the solution concentration, i.e., dimer (monomer) concentration, in stage (ii) can be considered as the saturated solubility of the J-aggregate, which corresponds to x_1 in the phase diagram shown in Figure 3a. Therefore, the dimer (monomer) concentration in stage (ii) should be independent of that at $t = 0$ s, which corresponds to x in Figure 3a. To confirm the independence, the absorbance of the dimer (monomer) in stage (ii) was plotted against that at $t = 0$ s for solutions with different concentrations (Figure 4). The plot shows that the absorbances in stage (ii) are nearly constant regardless of those at $t = 0$ s, further supporting that the transformation mechanism is the solvent-mediated phase transformation. These results demonstrate that phase transformation with molecular rearrangement can occur in supramolecular aggregates as well as molecular crystals through solvent-mediated phase transformation and that such transformation can lead to a striking change in the properties of the aggregates. In addition, this system can be suitable to conduct a detailed investigation of the transformation kinetics, since the solution composition can be easily monitored by simple absorption spectroscopy due to the largely separated absorption bands of the aggregates, dimer, and monomer.

In summary, it was found that the J-aggregates of TCC self-assembled in supersaturated solution transform into H-aggregates in the time scale of several tens of minutes. The transformation was monitored by absorption spectroscopy. On the basis of the time evolution of the absorption spectrum, it was concluded that the transformation was a solvent-mediate phase transformation that proceeded through dissolution of the metastable J-aggregates and subsequent aggregation into stable H-aggregates.

Experimental

TCC (3,3′-disulfopropyl-5,5′-dichloro-9-methylthiacarbocyanine triethylamine [=3-(5-chloro-2-{3-[5-chloro-3-(triethylammoniosulfonatopropyl)-2,3-dihydrobenzothiazol-2-ylidene]-2-methyl-1-propenyl}-3-benzothiazolio)propane-1-sulfonate]) was obtained from Hayashibara Corporation and was used without further purification. The mixing of the starting TCC and NaCl solutions was conducted in a glass cuvette (optical path length: 3 mm). The absorption spectrum of the mixed solution was continuously measured by a spectrometer (Ocean Optics, USB2000). A halogen lamp coupled to an optical fiber was used for excitation. The measurement was conducted at room temperature (≈20 °C).

The fraction of the solution dropped on a slide glass was placed between crossed polarizers. The aggregates in the solution were observed by a polarized microscope (Olympus, BX-60), and the image was recorded by a CCD camera (JENOPTIK, ProgRes C10 plus).

This work was supported by a Grant-in-Aid for Scientific Research (No. 18550135), Japan Society for the Promotion of Science.

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