

# Concentration-Dependent Structural Transition of Supramolecular Thiocyanine J-Aggregates in Solution

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String-to-sheet structural transition of mesoscopic supramolecular thiocyanine J-aggregates was demonstrated in aqueous solutions as a function of the dye concentration. Investigations by fluorescence microscopy under linearly polarized light excitation, polarizing microscopy, and atomic force microscopy revealed that the rectangular sheetlike J-aggregate consisted of a two-dimensional monomolecular layer of molecules, whose long axes lie approximately parallel to the short axis of the sheet morphology. The structural transition would be caused by the requirement where the mesoscopic aggregates are trying to stay as far apart as possible within a confined volume of solution.

Key words: J-aggregate, mesoscopic, morphology, structural transition, microscopy

## 1. INTRODUCTION

One of the well-known supramolecular dye assemblies induced by enthalpically driven attractive interactions is the J-aggregates [1]. J-aggregates were discovered by Jelley and Scheibe [2,3], and characterized by a narrow and intense absorption band that shows a bathochromic shift compared to the relevant monomer band [4]. Based on such optical characteristics, the aggregates have been often used as photographic sensitizers [5]. Recent interest has focused on the ability of J-aggregates to exhibit coherent excitation phenomena [6,7]. Therefore, there is great interest in understanding the relationships between the molecular alignment in aggregates and the spectroscopic properties such as the spectral line shape and peak energy. Although many spectroscopic properties of J-aggregates have been well-interpreted on the basis of one- or two-dimensional molecular exciton models [8-10], the knowledge of the supramolecular structure and/or morphology of the aggregates is only fragmental.

Recent structural studies of J-aggregates characterized by cryo-transmission electron microscopy (cryo-TEM) or fluorescence microscopy have proved various quasi-one-dimensional nanoscopic/mesoscopic morphologies in solution such as twisted ropes [11], rods [12,13], or strings [14]. These morphologies indicate that the J-aggregate grows anisotropically in solution. The observed morphology of these aggregates was intrinsically static, and did not change as a function of the dye concentration [15]. In this article, we report concentration-dependent string-to-sheet structural transition of mesoscopic thiocyanine J-aggregates in solution for the first time. Investigations by fluorescence microscopy, polarizing microscopy, and atomic force microscopy (AFM) will reveal the structural properties of the single sheet of the J-aggregates.

## 2. EXPERIMENTAL

Thiocyanine dye, 5,5'-dichloro-3,3'-disulfopropyl

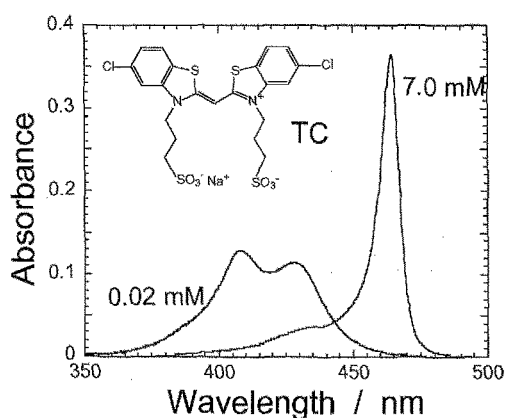
thiocyanine sodium salt (abbreviated as TC; chemical structure is shown in the inset in Fig. 1), was purchased from Hayashibara Kankoh-Shikiso Kenkyusho and used as received. Pure water was obtained by using an Aquarius GSR-200 (Avdantec Co. Ltd.) water distillation system. Sample solutions were prepared by dissolving the TC dye in water under gentle heating, followed by equilibration for 2-3 days at room temperature.

Absorption spectra were recorded with a Hitachi U-4100 spectrophotometer. Fluorescence micrographs were obtained by using a CCD camera (Flovel; HCC-600) set on an optical microscope (Olympus; BX-60). The excitation source (435 nm) was obtained by passing the light from an Hg lamp through a mirror cube unit (U-MNBV). Fluorescence micrographs under linearly polarized light excitation were obtained by using a polarizer (Olympus; U-PO or U-AN) mounted in the path of the excitation beam. Polarizing microscopy (orthoscopy) was performed with an optical microscope (Olympus; BXP) with crossed polarizers. AFM topographical images were recorded with a Nanoscope IIIa system (Digital Instruments) operating at the contact mode. Triangular  $\text{Si}_3\text{N}_4$  cantilevers that had a spring constant of 0.58 or 0.12  $\text{Nm}^{-1}$  were used. Samples for the AFM measurements were prepared by placing an aliquot of TC solution on the freshly cleaved mica. Measurements were performed at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 Spectroscopy

Fig. 1 shows the absorption spectra of aqueous TC solutions at 0.02 and 7.0 mM. At  $[\text{TC}] = 0.02$  mM, the monomer ( $\sim 430$  nm) and dimer ( $\sim 408$  nm) bands are found [14]. For a concentrated solution, the absorption spectrum showed a sharp and intense J-band at  $\sim 464$  nm [16]. The peak position and the line width ( $\sim 410$   $\text{cm}^{-1}$ ; FWHM) of the J-band were constant under the dye concentration within the range of 0.5-7.0 mM, indicating

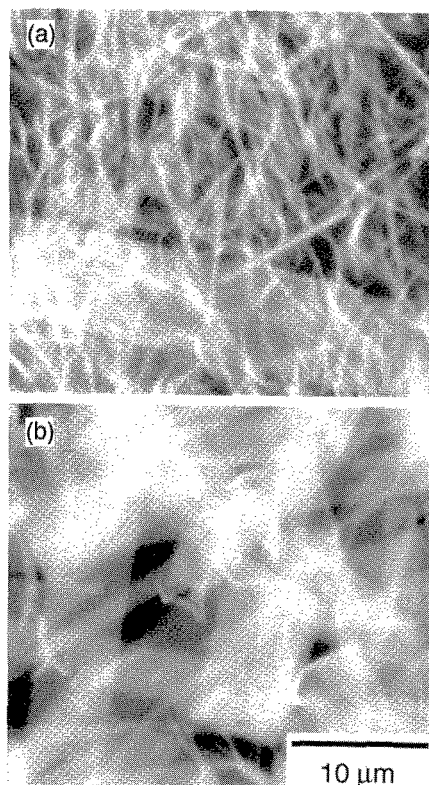


**Fig. 1** Absorption spectra of TC ([TC] = 0.02 and 7.0 mM) in aqueous solution.

that an internal structure which determines the electronic state of the J-aggregates is unchanged. Note that the observed fluorescence spectrum at [TC] = 7.0 mM did not show a Stokes shift, which is characteristic to the J-aggregate.

### 3.2 Microscopy: String-to-Sheet Structural Transition of the TC J-Aggregates in Solution

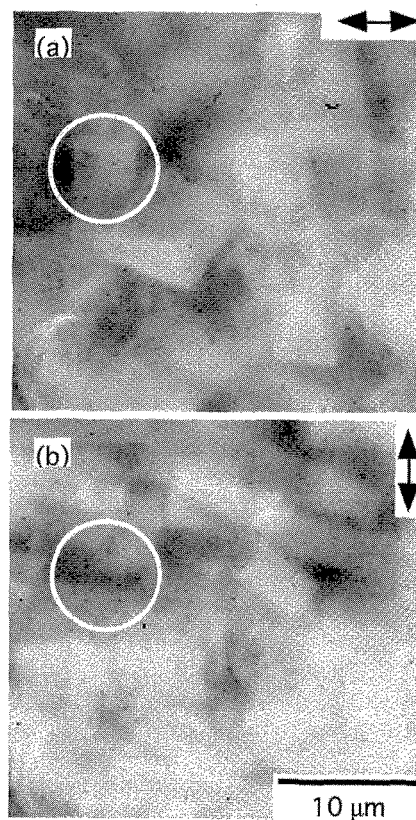
The appearance of the J-band was accompanied by a distinctive opalescence of the solution. Fluorescence microscopy was used to determine the microstructures of the TC J-aggregates in solution, because our previous studies proved that the aggregates possessed exclusively



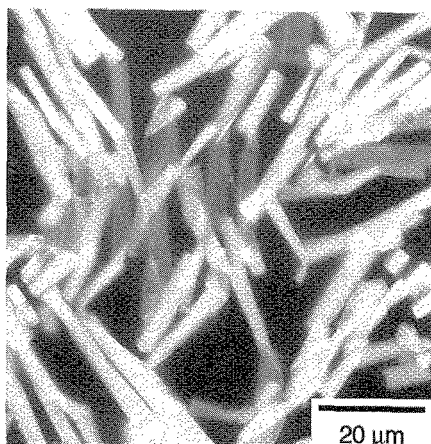
**Fig. 2** Fluorescence micrographs of the TC J-aggregates. (a) and (b) show images at [TC] = 1.0 and 4.0 mM, respectively.

mesoscopic-size morphology with highly emissive property [13,14]. Figs. 2 and 3 show typical fluorescence micrographs of the J-aggregate at different TC concentrations ([TC] = 1.0, 4.0, and 7.0 mM), clearly showing string or sheet mesophases. The sheet had an elongated rectangular shape, and its short-axis length was about 4–9  $\mu\text{m}$ . When the concentration of TC is  $\leq 0.7$  mM, only string morphologies were observed. At [TC] = 1.0 mM (Fig. 2a), a sheetlike morphology of the J-aggregate appeared in the solution along with a large number of the strings. With increasing [TC], the number of the sheet increased accompanying with a decrease in that of the string (Fig. 2b). The sheetlike J-aggregates coexisted with the strings at the concentration range between 1.0 and 5.0 mM. When the concentration of TC was higher than  $\sim 5.0$  mM, we could detect the sheet morphology alone (Fig. 3; [TC] = 7.0 mM). The results indicate that mesoscopic string-to-sheet structural transition occurred as a function of the dye concentration. To the best of our knowledge, this is the first in situ observation of concentration-dependent structural transition of supramolecular J-aggregates in solution.

The direction of the molecular alignment in the sheetlike aggregates can be evaluated by examining the fluorescence image taken under linearly polarized light excitation, because excitation efficiency depends on the direction of electronic transition moments of the J-



**Fig. 3** Fluorescence micrographs of the TC J-aggregates at [TC] = 7.0 mM. (a) and (b) show images (same view area) obtained with linearly polarized light excitation. The direction of excitation polarization is indicated by the black arrow at the top right in each figure.



**Fig. 4** Polarizing microscope images of the TC J-aggregate sheets in solution with crossed polarizers.

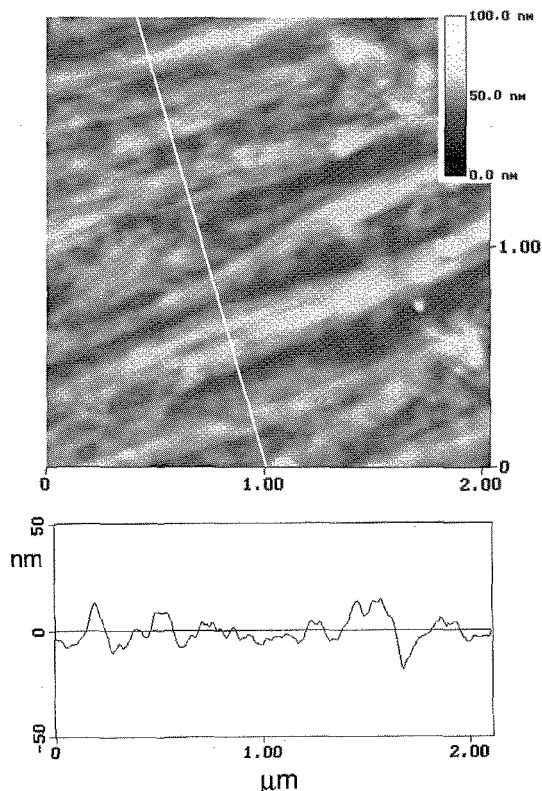
aggregate and this direction relates to that of the molecular alignment [17]. Figs. 3a and 3b represent typical fluorescence micrographs of the sheetlike aggregates at  $[TC] = 7.0$  mM obtained by an excitation with linearly polarized light at the same view area. The direction of the excitation polarization is indicated by the black arrow in each figure. Interestingly, a bright fluorescence image was obtained when the direction of excitation polarization was approximately perpendicular to that of the long axis of the sheet, whereas a dark image was obtained when it was parallel to the long axis of the sheet (see the region indicated by a circle in each figure). With respect to the molecular arrangement in the sheet, these results indicate that the long axis (molecular axis) of each of the TC molecules was approximately perpendicular to that of the sheet. We previously revealed that the stringlike J-aggregates had molecular alignment in which the long axis of the constituent TC molecules was approximately parallel to that of the string [14]. Therefore, the sheet is not the agglomerate of the strings. It should be noted that a small number of sheets showed a reverse polarization behavior of the fluorescence under linearly polarized light excitation.

When the sheet is composed of regularly aligned TC molecules, observation of birefringence for a single sheetlike J-aggregate can be expected. Fig. 4 shows a typical polarizing microscope image with crossed polarizers. The bright image clearly showed elongated rectangular sheetlike morphologies of the J-aggregate with strong birefringence. The size of the sheet was 20–50  $\mu\text{m}$  in length and 4–15  $\mu\text{m}$  in width, indicating that the morphology observed with polarizing microscopy corresponds to that with fluorescence microscopy. The sheetlike J-aggregates showed a straight extinction; namely, a dark image was obtained when the long axis of the sheet was parallel to the direction of polarization of the analyzer (extinction direction, the image  $y$ -axis in Fig. 4). This property indicates that the sheet aggregates possess a uniaxial crystalline nature.

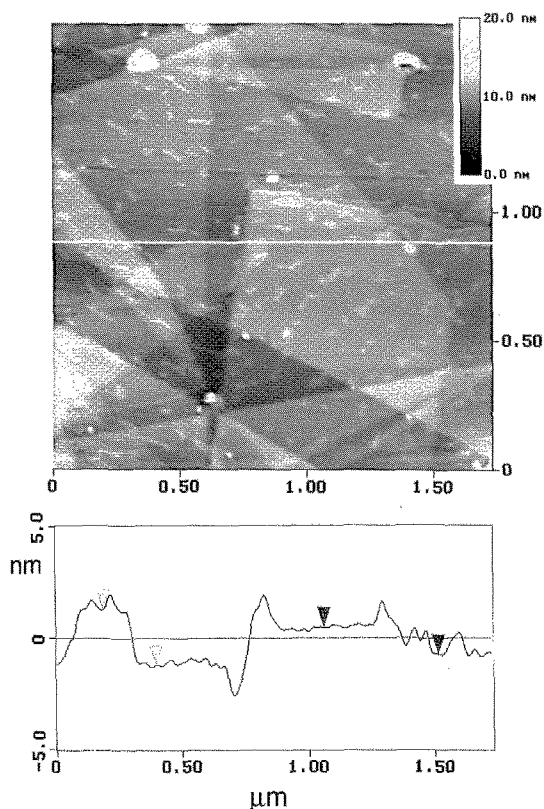
AFM measurements were conducted at ambient conditions to clarify the string or sheet structure of the J-aggregate. We prepared the sample in which a drop of solution on a mica substrate was dried in vacuo. Rapid evacuation of the sample would prevent the structural

transition of the stringlike J-aggregates. Before the measurements, we confirmed that the observed fluorescence microscope image was similar to that obtained in solution. Fig. 5 or 6 shows a typical AFM image and its cross-sectional profile of the stringlike or sheetlike J-aggregates, respectively. Fig. 5 indicates that a thick string J-aggregate ( $\sim 100$ – $300$  nm thick) was a bundle of thin strings of  $\sim 10$ – $30$  nm. This can be confirmed by the fluorescence micrographs because some of the tips of the strings were branched in Fig. 2. For the J-aggregate sheets (Fig. 6), the cross-sectional profile clarifies that the sheets were 1–2 nm high, indicating a monomolecular layer structure (Note that a TC molecule possesses  $\pi$ -electron chromophore of about 0.5 nm and sulfopropyl groups of about 0.6 nm.). The thicker region shows a turn up of a single sheet. Therefore, we conclude that the sheetlike J-aggregates consist of a two-dimensional monomolecular layer of TC molecules, whose long axes lie approximately parallel to the short axis of a sheet morphology.

The concentration-dependent string-to-sheet structural transition of supramolecular J-aggregates is a similar phenomenon to that observed for surfactant or lipid dispersion [18]. This type of phase transition arises from repulsive interactions between aggregates, where the aggregates are trying to stay as far apart as possible within a confined volume of solution [19]. The repulsive electrostatic interactions between stringlike aggregates might be justified by negatively-charged sulfopropyl groups of TC molecules within the aggregate. Under the repulsive interactions between the strings, it is



**Fig. 5** AFM topographical image of the J-aggregate strings on mica. Cross-sectional profile along the line is also shown.



**Fig. 6** AFM topographical image of the J-aggregate sheets on mica. Cross-sectional profile along the line is also shown.

energetically unfavorable to make the aggregates come closer together in solution at high concentrations. To keep their surfaces away from each other and to reduce the internal energy, the stringlike aggregates will rearrange to form a two-dimensional layer or sheet as observed in Fig. 2 or 3. Further clarification of higher-order structures of concentrated sheetlike J-aggregates are now in progress in our research group [20].

In summary, we observed string-to-sheet structural transition of mesoscopic thiocyanine J-aggregates in solution as a function of the dye concentration. At a high dye concentration, the transition would be caused by the requirement to keep the aggregate surfaces away from each other under the repulsive interactions between mesoscopic aggregates. Polarizing microscopy and AFM have revealed that the rectangular single sheetlike aggregate consisted of a monomolecular layer of thiocyanine molecules, whose long axes lie approximately parallel to the short axis of the sheet morphology.

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#### REFERENCES

- [1] D. Möbius, *Adv. Mater.*, **7**, 437-444 (1995).
- [2] E. E. Jelley, *Nature*, **138**, 1009-1010 (1936); **139**, 631-632 (1937).
- [3] G. Scheibe, *Angew. Chem.*, **49**, 563 (1936); **50**, 212 (1937).

- [4] K. Norland, A. Ames and T. Taylor, *Photogr. Sci. Eng.*, **14**, 296-307 (1970).
- [5] A. H. Herz, in *The Theory of the Photographic process*, 4th Ed., ed. T. H. James, Macmillan, New York, 1977, chapter 10.
- [6] E. Hanamura, *Phys. Rev. B*, **47**, 2019-2030 (1988).
- [7] F. C. Spano, J. R. Kuklinski and S. Mukamel, *J. Chem. Phys.*, **94**, 7534-7544 (1991).
- [8] P. O. J. Scherer and S. F. Fisher, *Chem. Phys.*, **86**, 269-283 (1984).
- [9] V. Czikkely, H. D. Förstling and H. Kuhn, *Chem. Phys. Lett.*, **6**, 207-210 (1970).
- [10] J. Knoester, *J. Chem. Phys.*, **99**, 8466-8479 (1993).
- [11] H. von Berlepsch, C. Böttcher, A. Ouart, C. Burger, S. Dähne and S. Kristein, *J. Phys. Chem. B*, **104**, 5255-5262 (2000).
- [12] H. von Berlepsch, C. Böttcher and L. Dähne, *J. Phys. Chem. B*, **104**, 8792-8799 (2000).
- [13] H. Yao and K. Kimura, *Chem. Phys. Lett.*, **340**, 211-216 (2001).
- [14] H. Yao, S. Kitamura and K. Kimura, *Phys. Chem. Chem. Phys.*, **3**, 4560-4565 (2001).
- [15] H. von Berlepsch and C. Böttcher, *J. Phys. Chem. B*, **106**, 3146-3150 (2002).
- [16] For absorption measurements of a highly concentrated TC solution, samples were prepared by placing a small droplet of the solution between a microscope slide and a cover slip without any spacers.
- [17] A. P. Marchetti, C. D. Salzberg and E. I. P. Walker, *J. Chem. Phys.*, **64**, 4693-4698 (1976).
- [18] K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, *Colloidal Surfactants*; Academic Press: London, 1963.
- [19] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press: London, 1985.
- [20] H. Yao, Y. Kagoshima, S. Kitamura, T. Isohashi, Y. Ozawa and K. Kimura, *Langmuir*, **19**, 8882-8887 (2003).

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