

Lattice Structure of Mesoscopic Rod-like *J* Aggregates of Thiocyanine Dye Characterized by Atomic Force Microscopy

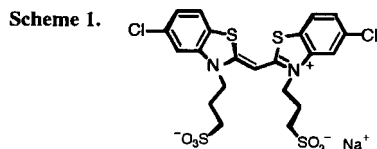
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(Received June 12, 2001; CL-010552)

We characterized the lattice structure of mesoscopic rod-like *J* aggregates of thiocyanine dye on mica possessing similar morphological and spectroscopic characteristics with those in bulk solution. The structure showed a staircase molecular arrangement.

Self-assembling of functional molecules is extensively studied owing to their involvement in many fundamental physical as well as biological processes such as bacterial light harvesting and energy transport.^{1,2} Cyanine dyes form highly ordered self-assemblies commonly known as *J* aggregates,^{3,4} which are characterized by a narrow excitonic absorption band that shows a bathochromic shift with respect to the relevant monomer band.⁵ Recent interest has centered on the ability of *J* aggregate to exhibit coherent excitation phenomena,⁶ which can lead to wide applications in such as molecular electronics and nonlinear optical devices. The aggregate internal structure (molecular packing) has been so far theoretically linked to its spectroscopic properties, however, an exact description is still little known.⁷ Consequently, there is growing much interest in high-resolution imaging of these assemblies.

Scanning probe microscopy (SPM) is an outstanding tool for molecular imaging of the aggregate structures, and several groups have reported molecular images of *J* aggregate thin films by using STM (Scanning Tunneling Microscopy) and AFM (Atomic Force Microscopy).⁸⁻¹¹ Because the aggregates in films are induced by the lattice of a substrate such as silver halides,^{10,11} optical properties and/or morphologies of the aggregates are generally different between the film and bulk solution. Therefore, it is difficult to infer the molecular packing of *J* aggregates produced in solution. We have recently observed that a 5,5'-dichloro-3,3'-disulfopropyl thiocyanine dye (abbreviated as TC; chemical structure is shown in Scheme 1) forms mesoscopic rod-like *J* aggregates in aqueous solutions under prolonged equilibrium, which were several tens of



micrometers in length and sub-micrometers in width.^{12,13} If the mesoscopic aggregates would be fixed on a substrate without morphological and spectroscopic changes, we can analyze the molecular arrangements within the aggregate, and make progress in the elucidation of internal structures of the aggregates existed in a solution phase. In this letter, we characterize the lattice structure of the TC *J* aggregate on mica keeping similar mesoscopic morphologies and optical characteristics with those in bulk solution.

The *J* aggregate solutions were prepared by dissolving a TC dye (0.05 mM) in an aqueous NaCl (5.0 mM) solution under mod-

erate heating followed by prolonged equilibration at room temperature. After a drop of the aqueous TC solution was placed on a mica substrate, a piece of filter paper was dipped in the solution, leaving only a small amount of solution on the substrate. Rod-like TC *J* aggregates were then fixed on mica when this small amount of solution was quickly dried by flowing N₂ gas over the substrate. Fluorescence micrographs were obtained by using a color CCD camera (HCC-600; Flovel) set on an optical microscope (BX-60; Olympus). An Hg lamp being passed through a mirror cube (U-MNBV; Olympus) was used as an excitation source. Fluorescence microspectroscopy was conducted by using a multi-channel photodetector (PMA-11; Hamamatsu Photonics) mounted on the microscope. High-resolution AFM images were recorded with a Nanoscope IIIa (Digital Instruments) operating at the force-constant contact mode with Si₃N₄ cantilevers that had a spring constant of 0.58 N/m. The measurements were performed at ambient conditions in air repeatedly.

A fluorescence micrograph of a TC bulk solution (inset in Figure 1a) shows mesoscopic rod structures. Fluorescence spectrum (Figure 1a) for a single rod obtained under the microscope shows a narrow and intense band at 467 nm which is

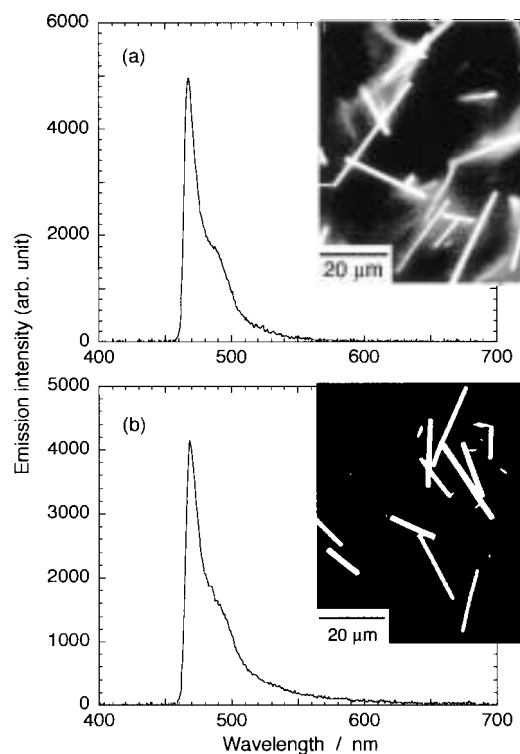


Figure 1. Fluorescence spectra for a single rod of TC *J* aggregates in solution (a) and on mica (b) observed under a microscope. Fluorescence micrographs of the *J* aggregates are also shown in the insets in each figure.

assigned to the TC *J* aggregates.^{12,13} Since a characteristic emission was not observed at around the outer periphery of the rod, TC in an aqueous solution exclusively forms mesoscopic *J* aggregates. A fluorescence micrograph of a mica surface for the sample in air (inset in Figure 1b) also shows similar mesoscopic rod morphologies with those in solution.¹⁴ This similarity implies that the observed rod morphology in air corresponds to that of the TC *J* aggregates in solution. Figure 1b shows the fluorescence spectrum for a single rod on mica. The spectrum of the rods was also quite similar to that in a solution phase,^{12,13} indicating that molecular arrangements within the aggregate, which directly relate to the spectroscopic characteristics of *J* band, are almost unchanged through drying processes.

We first observed the rod structure of the *J* aggregates on mica by tapping-mode AFM. Figure 2 shows a typical AFM image of a rod aggregate. The morphology observed by AFM was similar to that observed by fluorescence microscopy as shown in Figure 1b. The rods were $\sim 1 \mu\text{m}$ wide and $\sim 3 \text{ nm}$ high, indicating a flat multilayer structure at the molecular level. Note that all the rods were several nanometers high. It is possible that the removal of water by evaporation would cause a decrease in the height of these rods without changing the spectroscopic nature of the *J* aggregates.

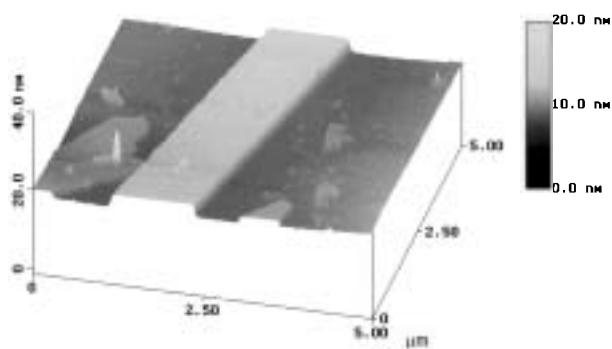


Figure 2. AFM image of the rod-like *J* aggregate on mica.

To observe the molecular packing, contact-mode AFM measurements were conducted. We primarily checked high-resolution images of a bare mica surface where the rods were not distributed. After confirming the appearance of the bright spots hexagonally arranged in the images which represent the oxygen atoms in the lattice of mica,¹⁵ we observed the surface structures of the rod-like *J* aggregate. Figure 3a shows an AFM image obtained for the rod on mica. Bright intermittent striations were observed from top-right to bottom-left, suggesting that molecules would be aligned along these striations. A molecular model of TC is drawn to scale on top left in Figure 3a. Comparing the AFM image with the model, the striated patterns correspond in size with the molecular length and to the arrangements in a staircase style.⁵ To clarify the structure statistically, the AFM image was subjected to two-dimensional Fourier transform (FT).⁸ Figure 3b shows the FT pattern derived from the image, representing three bright spots (7.5, 4.5 and 3.1 Å: the distance of the spot from the DC center) and their symmetries.¹⁶ The brighter two spots (7.5 and 4.5 Å) and their symmetries essentially determined the lattice structure for the staircase with a slip angle (angle between the long molecular axis and the row direction) of $\sim 35^\circ$, which is schematically illustrated in Figure 3c. The remaining spots corresponding to 3.1 Å were confirmed to contribute to the emphasis of the striated pattern, suggesting that the slip angle might be smaller than $\sim 35^\circ$. In conclusion, we determined the lat-

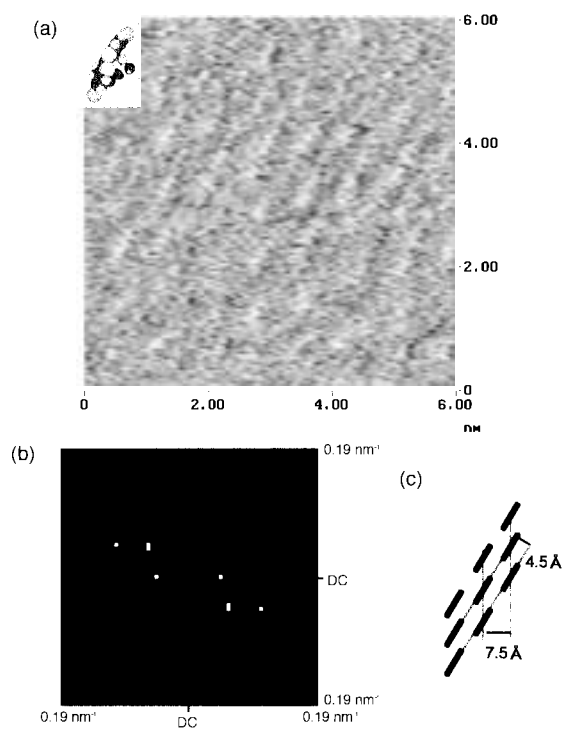


Figure 3. (a): High-resolution AFM image of the surface of a rod-like TC *J* aggregate on mica. The inset in top-left shows a TC molecule drawn to scale. (b): Fourier transform pattern derived from the image (a). "DC" corresponds to frequency zero (direct current). (c): Schematic illustration of molecular arrangements of TC.

tice structure of mesoscopic rod-like TC *J* aggregates possessing similar morphological and spectroscopic properties with those in bulk solution to be staircase molecular packing.

H.Y. gratefully acknowledges the Hyogo Science and Technology Association, and a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology (12640563) for financial support.

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- A dim spot and its symmetry observed in the FT image would be due to a mica substrate.