Three-dimensional Structure of *J* Aggregates of Pseudoisocyanine Chloride Dyes at a Mica/Solution Interface Revealed by AFM

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By using tapping-mode atomic force microscopy (AFM), we revealed for the first time the structure of *J* aggregates of pseudoisocyanine chloride(PIC-Cl) dyes at a mica/solution interface in an aqueous PIC-Cl solution. The *J* aggregates were leaf-like islands in multilayers of PIC-Cl molecules. The minimal size of the aggregate necessary for the *J* band was also revealed. Dye molecules grow into the *J* aggregates at a mica/solution interface by a Volmer-Weber type growth process.

It is well known that cyanine dyes form so-called *J* aggregates, which are characterized by a sharp, intensive absorption band with a bathochromic shift compared to the monomer band.[1-3] Recently, *J* aggregates have attracted considerable attention as molecular assemblies in systems that can bridge the gap between the physics of a single molecule and structurally-ordered crystals and in systems for optical communications based on the high nonlinear optical coefficients of these aggregates.[4]

Previous studies demonstrated that pseudoisocyanine chloride (PIC-Cl), 1,1'-diethyl-2,2'-cyanine chloride, form *J* aggregates with an intense absorption band at ~572nm in aqueous solutions at room temperature.[1-3, 5, 6] These *J* aggregates (J_S aggregates) may possess a thread-like or ribbon-like structure.[5, 6] Studies also show that PIC-Cl forms *J* aggregates at a solid/liquid interface; in an early work, Scheibe observed (by using spectroscopy) *J* aggregates of PIC-Cl at a mica/solution interface.[7] He found that the band of the *J* aggregate was red-shifted by 7 nm compared to that of J_S, and proposed a monolayer arrangement of the dye molecules in the aggregates.[7] Based on a quantum mechanical calculation, Kuhn *et al.* later proposed a brick-stonework arrangement of the dye molecules in *J* aggregates of PIC-Cl at a mica/solution interface.[8] These models are based on two-dimensional monolayer adsorption of the dye molecules. Recently, Yao *et al.* observed that an aqueous PIC-Cl solution in optical cells made of soda lime glass exhibited a new absorption band of a *J* aggregate (J_L aggregates) that was also red-shifted compared to that of J_S at room temperature.[9] Based on total-internal-reflection (TIR) fluorescence spectroscopy, Yao *et al.* suggested that the formation of J_L is confined to the vicinity of the glass/solution interface in solution.

The structure and morphology of *J* aggregates at a solid/liquid interface (J_L type aggregates) are still controversial, as mentioned above. Optical properties of *J* aggregates, such as the absorption line shape and spectrum shift, are determined by the structure of the aggregates, such as aggregation number, structural dimension, and dye molecular orientation.[8] Therefore, for deeper insight into the optical properties of J_L type aggregates and the difference in optical properties between J_S and J_L type aggregates, the structure and morphology of J_L type aggregates need to be clarified. The lack of suitable analytical techniques has made it difficult to observe in-situ the structure of J_L type aggregates. Recent advances in atomic force microscopy (AFM) have made possible the in situ observation of the structure of *J* aggregates. Several such studies have been done for films of *J* aggregates under dry conditions.[10-14] However, no AFM studies on *J* aggregates at a solid/liquid interface in solution exist probably due to the difficulty of in-situ AFM imaging of fragile *J* aggregates at a solid/liquid interface. In this study, we focused on clarifying the structure and morphology of J_L type aggregates by in-situ tapping-mode AFM imaging.

We used mica as a solid that forms the J_L type aggregates because mica has an atomically flat surface that makes AFM imaging easier. AFM images were recorded on a Nanoscope III a (Digital Instruments, Santa Barbara, CA) operating at the tapping mode in liquid phase. For the AFM measurements, mica was fixed on a steel plate by an epoxy resin and then placed in a liquid cell unit (Digital Instruments). The mica was cleaved to expose a fresh surface and then 30 μl of an aqueous PIC-Cl solution (Nippon Kankoh-shikiso Kenkyusho Co.) was placed on the mica. We used triangular Si_3N_4 microcantilevers (Nanoprobe, NP-S, Digital Instruments) that had a spring

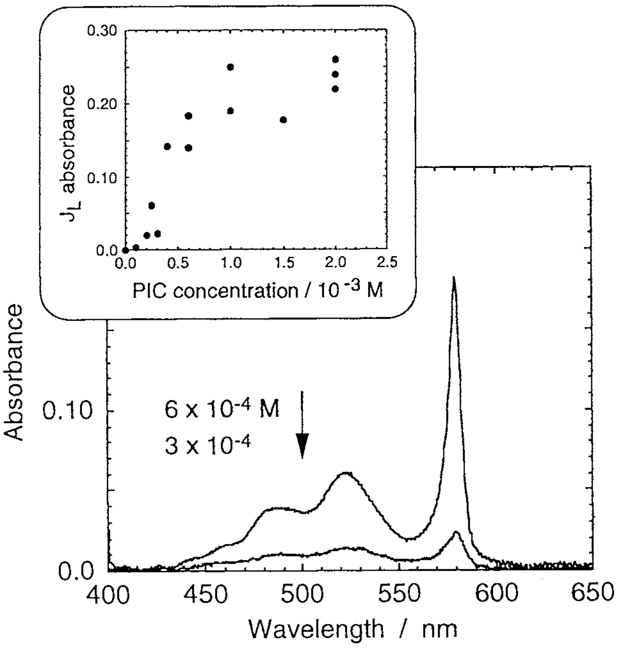

Figure 1. Absorption spectra of aqueous PIC-Cl at a mica/solution interface. The inset shows a PIC-Cl concentration dependence on the J_L absorbance.

constant of 0.58 N/m. The drive frequency was between 8-10kHz. Integral and proportional gains ranged between 0.5-1.2. The scan rate was between 0.5 and 1.0 Hz. The samples for absorption measurements were prepared by placing an aliquot of the aqueous PIC-Cl solution between a mica film and a hydrophobic glass plate (optical path length ~25 μm).

Figure 1 shows typical absorption spectra of aqueous PIC-Cl solutions (3.0 and 6.0 x 10^{-4}M; 1M=1mol dm^{-3}). The spectra showed a sharp, intense *J* band (580 nm) in addition to monomer bands (525 and 490 nm) and dimer bands (480 nm). The peak position of the *J* band was red-shifted compared to that of J_S (~572 nm).[6] The spectra showed quasi-adsorption behavior (Figure1, inset): the *J* band appeared when the PIC-Cl concentration exceeded 1.0 x 10^{-4} M, and the absorbance of the *J* band increased with increasing PIC-Cl concentration and saturated at about 1.0 x 10^{-3} M, though the absorbance of the J band was somewhat scattered. For the same PIC-CL concentration, *J* aggregation was not observed between two hydrophobic glass plates, indicating that the origin of the band is the interaction between PIC-Cl and mica. The J_L aggregates at a soda lime glass/solution interface showed similar results, thus suggesting that J_L type aggregates are also produced at a mica/solution interface.

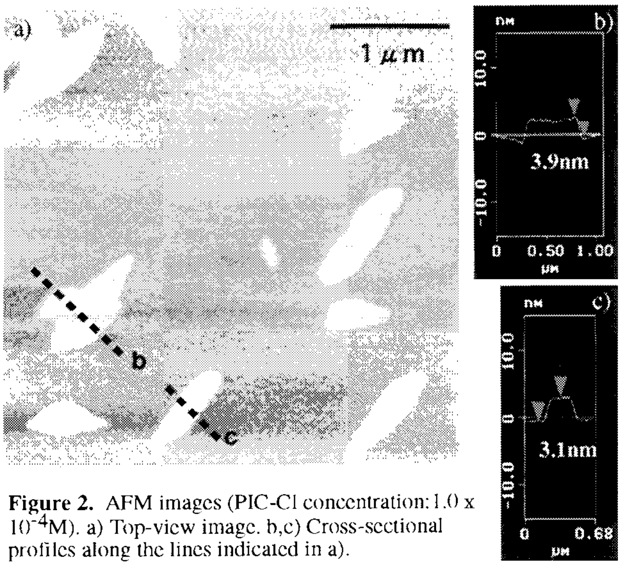

Figure 2. AFM images (PIC-Cl concentration: 1.0 x 10^{-4}M). a) Top-view image. b,c) Cross-sectional profiles along the lines indicated in a).

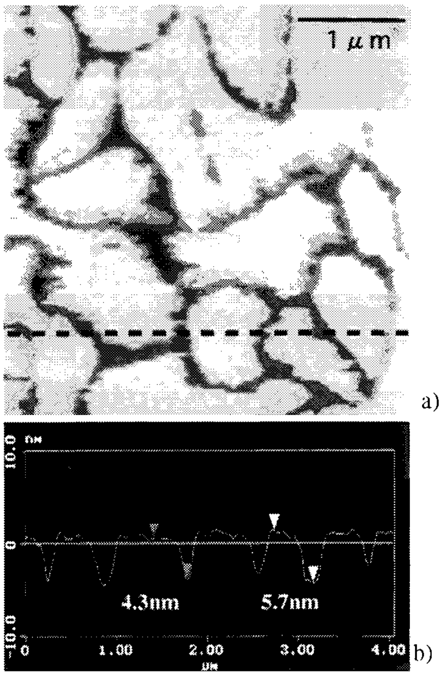

Figure 3. AFM images (PIC-Cl concentration: 3.0 x 10^{-4}M). a) Top-view image. b) Cross-sectional profile along the line indicated in a).

Figures 2 and 3 show AFM images at the concentration region where the intensity of the *J* band increased drastically. The surface of mica remained unchanged, (i.e., atomically flat) until the *J* band appeared (<1.0 x 10^{-4} M). At the concentration where the *J* band started to appear (1.0 x 10^{-4} M), leaf-like islands suddenly appeared (Figure 2). The average size of these islands ranged between about 400-600 nm long, about 80-100 nm wide and 3-6nm height. The structure of J_L type aggregates significantly differs from the thread-like or ribbon-like one-dimensional structure of J_S.[5, 6] This structural difference may cause the difference in optical properties between J_L and J_S aggregates. Because the *J* bands started to appear at this concentration, this size corresponds to the minimal size of the aggregate necessary for the characteristic *J* band.

So far, the *J* aggregates of PIC-Cl at a mica/solution interface supposedly have two-dimensional monolayer structure.[7, 8] However, our AFM images revealed for the first time that these aggregates have three-dimensional leaf-like island structure. The density of the leaf-like islands increased with increasing PIC-Cl concentration, and then when the PIC-Cl concentration reached 3.0 x 10^{-4} M, these islands coalesced into larger islands about 2-4 μm^2 in area. In contrast, the height of the islands was independent of PIC-Cl concentration (Figure 3), about 3-6nm. Assuming that the molecules have an edge-on arrangement, this height corresponds to several layers of PIC-Cl molecules. The height of 3-6 nm is probably determined by the energy of adsorption and aggregation of PIC molecules on mica. At a distance higher than 3-6nm, PIC-Cl would dissolve because of the solubility of the PIC-Cl at concentrations where the AFM imaging were done. The morphological change revealed by AFM imaging suggests that the J_L type aggregates grow at a mica/solution interface by a Volmer-Weber type growth process, namely, discrete nucleation on mica and successive growth by the aggregates into islands.[15]

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