

Spectroscopic and AFM Studies on the Structures of Pseudoisocyanine *J* Aggregates at a Mica/Water Interface

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J aggregates of a pseudoisocyanine dye (PIC) at a mica/solution interface were in situ observed in solution for the first time by atomic force microscopy (AFM), confirming formation of the aggregates showing a narrow *J* absorption band (peak, ~ 580 nm; line width (HWHM), ~ 120 – 125 nm) at room temperature. The *J* aggregates possessed the three-dimensional island structure with the height of about 3–6 nm, consisting of at least $\sim 10^6$ PIC molecules, but not a two-dimensional monolayer structure. The growth processes of the *J* aggregates were discussed on the basis of the morphological changes of the islands with a dye concentration (i.e., Volmer–Weber type growth process), while the optical properties such as the absorption peak position, line width, or fluorescence lifetime (~ 50 ps) were unchanged. These results indicated that the physical aggregation size observed was much larger than the coherence size of the *J* aggregate.

Introduction

Self-assembling of molecules producing ordered aggregates have received widespread attention in both fundamental and applied research. *J* aggregates are specific dye assemblies discovered by Jelly and Scheibe^{1,2} and characterized by a sharp and intense absorption band: *J* band. The *J* band also shows a bathochromic shift compared to the relevant monomer band owing to a strong coupling of the molecular transition dipoles.³ On the basis of such optical characteristics, the aggregates have been often used in photographic processes.⁴ Recently, high nonlinear optical coefficients of the *J* aggregates have been also applied to modulate light signals in optical communication devices.⁵ In relation to a long-range stacking and/or coherent coupling of molecules, furthermore, a superradiant decay,⁶ a two-exciton blue shift,⁷ and a free induction decay of the aggregates⁸ have been studied both experimentally and theoretically.

It is well-known that cyanines represented by 1,1'-diethyl-2,2'-cyanine (pseudoisocyanine: PIC) produce *J* aggregates at a high dye concentration and the aggregates in aqueous solutions show an intense absorption band at ~ 572 nm at room temperature.^{1,2,9} The aggregate structure reflects highly on its spectroscopic properties,³ and it has been proposed that the *J* aggregate at ~ 572 nm (abbreviated as *J*_S) would possess a threadlike or ribbonlike structure.^{10–12} Previous studies demonstrated that PIC also produced *J* aggregates at a solid/liquid interface. In the early work by Scheibe, the *J* aggregates of PIC were observed at a mica/solution interface, as revealed by absorption spectroscopy.¹³ The peak of the *J* band was red-shifted compared to that of *J*_S in solution, and a monolayer arrangement of the dye molecules in the aggregate was proposed. On the basis of a quantum mechanical calculation and consideration by an epitaxial match between the dye and

the lattice of a mica substrate, Kuhn et al. have proposed a brick stonework arrangement of the dye molecules at a mica/solution interface.¹⁴ They explained the *J* aggregate structure by a two-dimensional monolayer adsorption model. On the other hand, we found recently that an aqueous PIC solution in an optical cell made of a soda lime glass exhibited a new absorption *J* band that shifted to the red by ~ 5 nm compared to that of *J*_S at room temperature. It is important to note that *J* aggregate formation is induced by the presence of anionic sites on a solid surface (*J*_L aggregate).¹⁵ Furthermore, total-internal-reflection (TIR) fluorescence spectroscopy of the *J*_L aggregates revealed that formation of *J*_L was confined to the vicinity of the glass/solution interface.¹⁵

Since the optical properties of the *J* aggregates are affected by the structures represented by an aggregation number, packing dimension, and dye molecular orientations,¹² the red-shift of the *J* band at a solid/liquid interface (*J*_L type aggregate) compared to the maximum wavelength of the *J*_S band is ascribed to differences in their structures or morphologies. Thus, detailed investigations of the *J*_L type aggregates are of primary importance to elucidate characteristic features of the *J* aggregates produced at a solid/solution interface. However, the structures and morphologies of the *J*_L type aggregates have been still poorly understood due to a lack of a suitable in situ analytical technique. Recently, atomic force microscopy (AFM) has been used to study both the lattice structure of Langmuir–Blodgett thin films and its *J* aggregate structure.^{16–19} Near-field scanning optical microscopy (NSOM) has been also shown to be potential for the studies along the line.²⁰ Actually, several studies have been conducted for film samples of *J* aggregates under *dry* conditions. Nonetheless, a complementary study on the *J* aggregates produced at a solid/liquid interface by AFM and spectroscopy have never been explored. In this study, we report the structures and morphologies of the PIC *J* aggregates produced at a solid/liquid interface, and the growth processes of the aggregates observed by in situ tapping-mode AFM are

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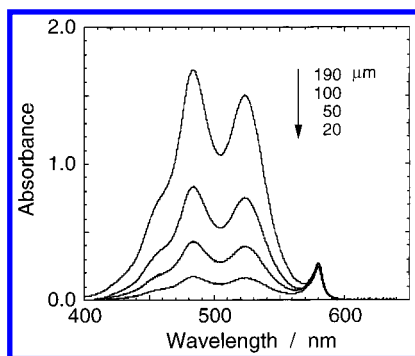


Figure 1. Optical path length dependence of the absorption spectrum measured for an aqueous PIC solution (2.0 mM) between mica and hydrophobic glass plate.

discussed. Implications of the aggregate structures with the optical properties of the aggregates (absorption, fluorescence, and fluorescence lifetime) were also discussed.

Experimental Section

Chemicals. 1,1'-Diethyl-2,2'-cyanine (pseudoisocyanine: PIC) chloride was purchased from Nippon Kankoh-Shikiso Kenkyusho Co. and used as received. Pure water was obtained by an Aquarius GSR-200 (Advantec Co. Ltd.). A hydrophobic glass plate was prepared by immersing a soda lime glass plate into a dichlorodimethylsilane/chloroform (1/10 v/v) solution for ~24 h and dried in an oven after being rinsed successively with ethanol and pure water.

Methods. Absorption measurements were carried out on a Hitachi U-3300 spectrophotometer. A sample for absorption measurements was prepared by placing an aliquot of an aqueous PIC solution between mica and hydrophobic glass plates. The path length of the cell was controlled by varying the thickness of an aluminum foil as a spacer. Fluorescence spectra were obtained by using a Hitachi F-4500 spectrofluorometer or polychromator-multichannel photodetector set (PMA-11, Hamamatsu Photonics). Fluorescence lifetimes were determined by a time-correlated single photon counting system (Hamamatsu Photonics, SPC-300) as reported previously.²¹ Briefly, regeneratively amplified (Coherent, RegA 9000) output pulses of a mode-locked Ti:sapphire laser (Coherent, Mira 900F), pumped by a solid-state green laser (Coherent, Verdi), were introduced to an optical parametric amplifier (Coherent, OPA 9400) to obtain excitation pulses at 570 nm (duration, ~150 fs; repetition, 100 kHz). For avoiding excitation-exciton annihilation in the aggregates, the excitation intensity was set as low as possible.

AFM images were recorded on a Nanoscope IIIa (Digital Instruments, Santa Barbara) operating at a tapping-mode in a liquid phase. For AFM measurements, mica was fixed on a steel plate with an epoxy resin and placed in a liquid cell unit (Digital Instruments). The mica substrate was cleaved to expose a fresh surface and then 30 μ L of an aqueous PIC solution was placed on the substrate. Triangular Si₃N₄ microcantilevers (Nanoprobe; NP-S, Digital Instruments) possessing a spring constant of 0.58 N/m were used. The drive frequency was set between 8 and 10 kHz, and integral and proportional gains ranged between 0.5 and 1.2. The scan rate was set between 0.5 and 1.0 Hz.

Results and Discussion

Absorption Spectroscopy. Figure 1 shows an optical path length dependence of the absorption spectrum of an aqueous PIC solution (2.0 mM). The spectrum showed a sharp (line width (HWHM): ~120–125 cm⁻¹) and intense *J* band (580 nm) in

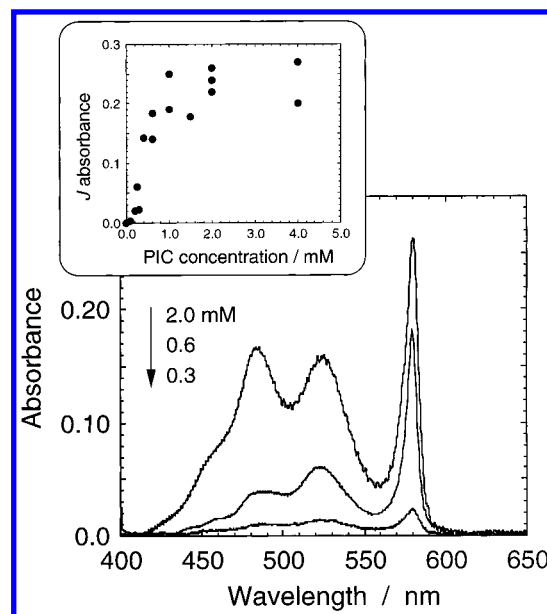


Figure 2. Absorption spectra of the PIC *J* aggregate produced at a mica/solution interface. The inset shows the concentration dependence of the *J* band.

addition to the superposition of monomer and dimer spectra. The peak observed at 525 or 480 nm is mainly ascribed to the monomer or dimer band, respectively.^{22,23} The peak wavelength of the *J* band was red-shifted compared to that of the well-known *J*_S aggregate observed in a solution phase. It is worth noting that no *J* band can be observed when absorption measurements are conducted using a hydrophobic glass cell at the same concentration, since the PIC concentration is too low to generate the *J*_S aggregate in solution.⁹ Thus, *J* aggregate formation (*J*_L type) is originated from the interactions between PIC molecules and the mica surface, as reported previously.¹³ It is clear from Figure 1 that the absorbance of the monomer or dimer band increases with increasing optical path length, while that of the *J* band is independent of the path length. Therefore, *J* aggregate formation is concluded to be confined to the vicinity of the mica/solution interface, which is very similar to that at a soda lime glass/solution interface.¹⁵

A concentration dependence of the absorption spectrum of PIC was studied to examine the growth of the *J* aggregate. Figure 2 shows the absorption spectrum of an aqueous PIC solution at a different concentration (2.0, 0.6, or 0.3 mM). The absorption peak wavelength and line width of the *J* band were constant at any concentration (0.1–4.0 mM), indicating that the delocalization size of the *J* aggregate determining the optical properties is unchanged.^{24,25} The concentration dependence of the spectrum at 580 nm showed a quasi-adsorption behavior (inset in Figure 2); the *J* band appeared at above 0.1 mM, and the absorbance increased with increasing PIC concentration and saturated at >~1.0 mM. The results also support that *J* aggregate formation takes place at the mica/solution interface. Comparing with the *J* aggregates produced at a soda lime glass/water interface, the saturated absorbance of the *J* band at a mica/solution interface was nearly twice that at the glass/solution interface with a similar bandwidth,¹⁵ indicating the amount of adsorbed PIC in the former system is larger than that in the latter.

Time-Resolved Fluorescence Spectroscopy. The *J* aggregates produced at a mica/solution interface showed a sharp fluorescence spectrum (HWHM: ~115–120 cm⁻¹), as shown in Figure 3a ([PIC] = 2 mM), whose bandwidth was narrowed

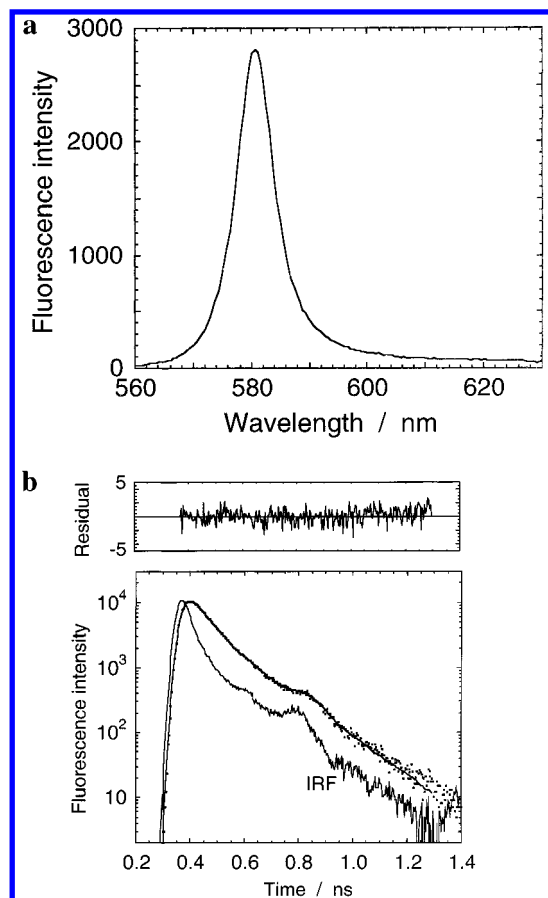


Figure 3. (a) Fluorescence spectrum of the *J* aggregate at a mica/solution interface ([PIC] = 2.0 mM). (b) Fluorescence decay profile of the *J* aggregate excited at 570 nm. The double exponential fit is also shown.

slightly compared to that of the absorption spectrum. The fluorescence spectrum does not show a Stokes shift, as is characteristic of the *J* aggregate, and tracks the absorption spectrum profile except for the blue edge of the band. So, the characteristics of the fluorescence spectrum are ascribed to fast relaxation to the lowest energy sites in the excitonic state of the *J* aggregate.²⁵ To examine the effects of the growth of the *J* aggregates on the excitonic state, fluorescence lifetime measurements were explored at various PIC concentrations. Figure 3b shows a typical fluorescence decay profile (2.0 mM) together with an instrumental response function (IRF). Although a very fast component was dominant in the decay, the profile was best fitted by a double exponential function probably due to the inhomogeneity in interactions between the *J* aggregates and the mica surface. Thus, we estimated an average fluorescence lifetime ($\langle\tau\rangle$), as often used for fluorescence decay analysis of a molecule in an inhomogeneous adsorbed state:

$$\langle\tau\rangle = \frac{\sum_i a_i \tau_i^2}{\sum_i a_i \tau_i}$$

where a_i and τ_i are the preexponential factor and the fluorescence lifetime of the i th component, respectively. The present approach is advantageous in determining $\langle\tau\rangle$ with a very high reproducibility even when a_i or τ_i is somewhat scattered from one measurement to the another.²⁶ The solid curve in Figure 3b is the best fit of the decay profile with the parameters of $a_1 = 30.5$, $\tau_1 = 44$ ps, $a_2 = 4.0$, and $\tau_2 = 96$ ps (2.0 mM). The average fluorescence lifetime $\langle\tau\rangle$ was then calculated to be 55 ps. A short fluorescence lifetime compared to that in solution

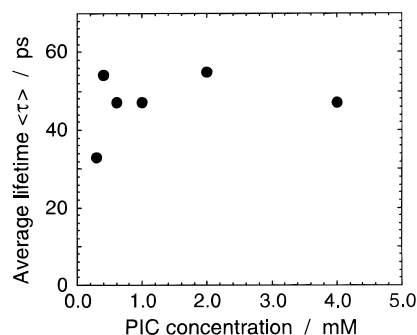


Figure 4. Concentration dependence of the average fluorescence lifetime $\langle\tau\rangle$.

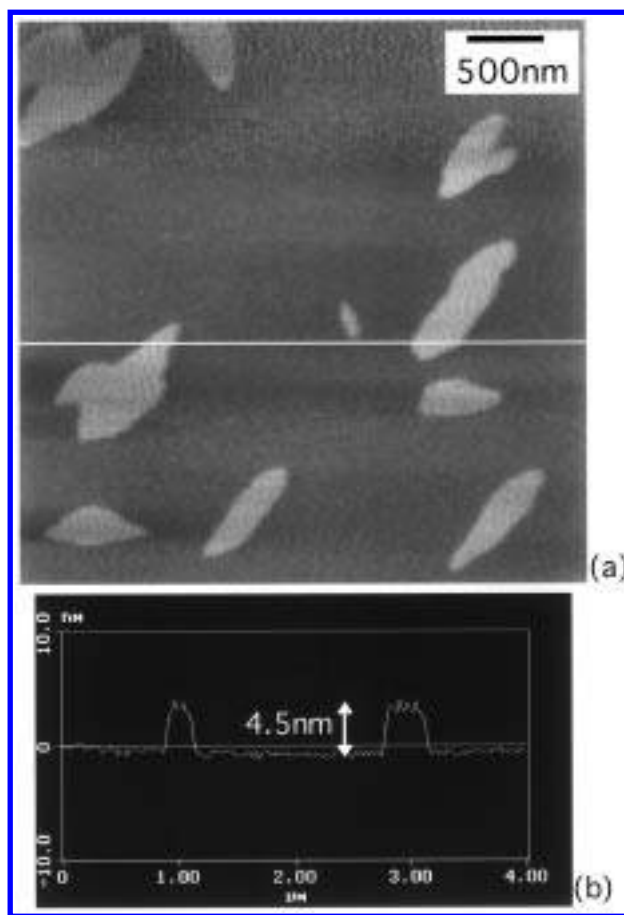


Figure 5. (a) AFM top-view image at [PIC] = 0.1 mM. The leaf-like islands correspond to the *J* aggregate at a mica/solution interface. (b) Cross-sectional profile along the line indicated in (a).

has been generally observed for the *J* aggregate adsorbed on surfaces.²⁷ Figure 4 shows a PIC concentration dependence of $\langle\tau\rangle$. The fluorescence lifetime was almost constant at 45–50 ps at any concentration.²⁸ The results indicate that the coherency in the exciton state of the *J* aggregate does not change even upon the growth of the aggregates.

Atomic Force Microscopy. Since the *J* aggregates were confined to the vicinity of a mica/water interface as described above, atomic force microscopy (AFM) was conducted to examine the microstructures of the *J* aggregates and their roles in deciding the absorption and fluorescence characteristics of the *J* aggregates. Figures 5–7 show AFM images at the concentration region where the absorbance of the *J* band increases drastically. No scan damage was confirmed under the present experimental conditions. The surface of mica remained unchanged and was atomically flat until the *J* band appeared

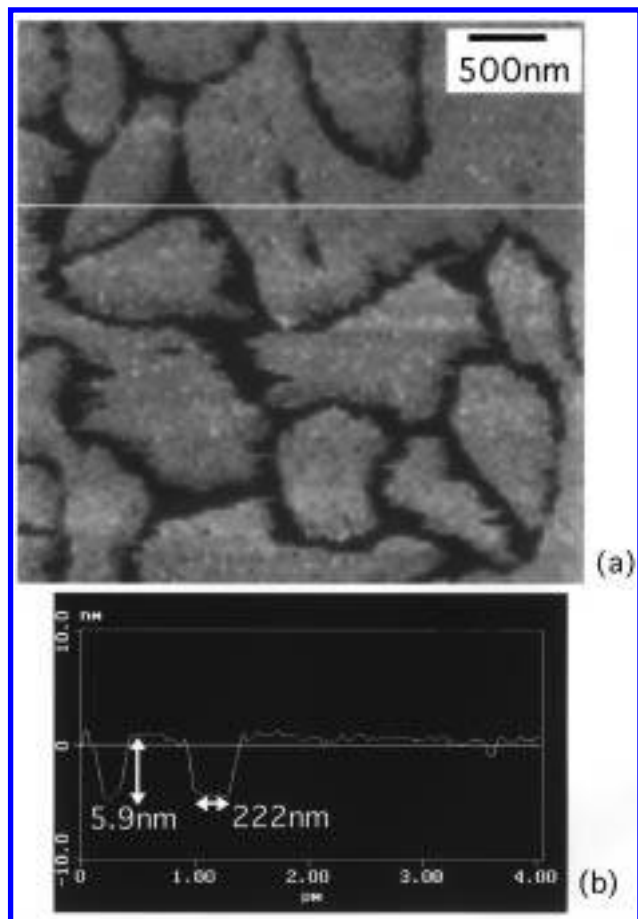


Figure 6. (a) AFM top-view image at $[PIC] = 0.3$ mM. (b) Cross-sectional profile along the line indicated in (a).

(<0.1 mM). At the concentration where *J* aggregate formation took place ($=0.1$ mM), leaf-like islands appeared abruptly (Figure 5a). Thus, the islands were considered to be the *J* aggregates. The size of these islands ranged ~ 400 – 600 nm long, ~ 80 – 100 nm wide, and 3–6 nm high (cross-sectional profiles; Figure 5b). Our AFM images revealed that the *J* aggregates produced at a mica/solution interface have a three-dimensional disk structure, but not a two-dimensional monolayer structure, as has been proposed so far. In Figure 5a, anisotropic growth of the long axis of the islands can be recognized, suggesting that there is a specific interaction between PIC and mica, although the details are reported elsewhere.²⁹ Under the assumption of the edge-on arrangement of PIC molecules on mica, the height of the islands corresponds to several molecular layers. Also, assuming that the positively charged N atoms in a PIC molecule are adsorbed on the negative sites on mica (owing to the dissociation of K^+ ions)¹⁴ and PIC are stacked in a layer-by-layer structure including interstitial Cl^- ions,³⁰ $\sim 10^6$ PIC monomers are approximately included in the leaf-like, three-dimensional *J* aggregate. Such a structure of the J_L type aggregates produced by the interactions between the substrate and PIC molecules may cause different optical properties (red-shifted and/or broad *J* band) compared to those of the J_S aggregates produced in solution, possessing a threadlike structure with the size of several hundreds of nanometers.¹²

The number density of the leaf-like islands increased with increasing PIC concentration (0.3 mM; Figure 6a), and then they coalesced into larger domains with the apparent surface area of ~ 2 – $4 \mu m^2$. In contrast, the height of the islands was independent of the solution concentration, ~ 3 – 6 nm (Figure 6b). At 3.0 mM, the surface of mica was almost completely

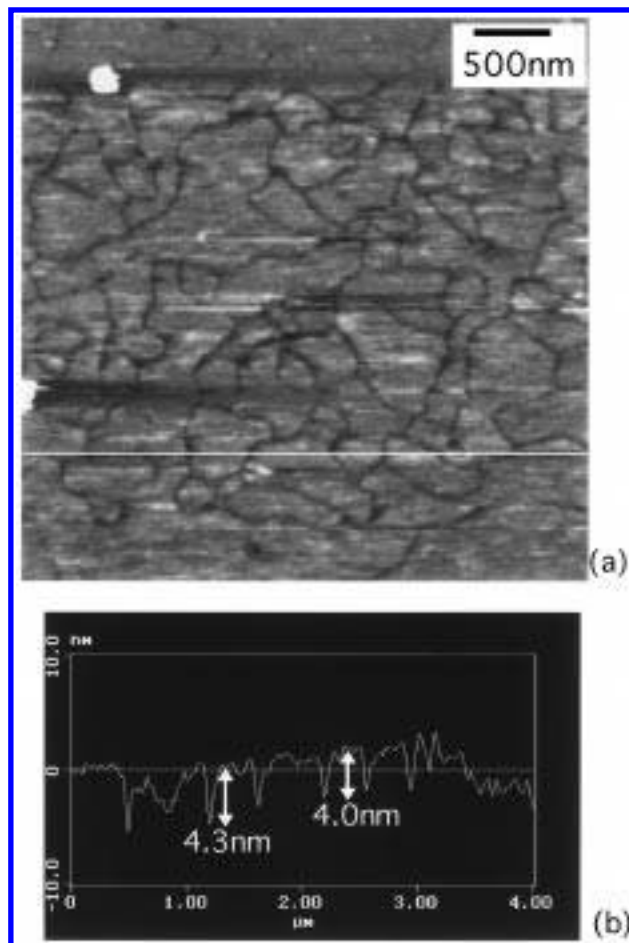


Figure 7. (a) AFM top-view image at $[PIC] = 3.0$ mM. (b) Cross-sectional profile along the line indicated in (a).

covered with the islands while the height of the islands remained unchanged (Figure 7).³¹ The results in Figures 5–7 would support the quasi-adsorption behavior of the absorbance of the *J* band in Figure 2. Moreover, Figure 7a shows that many smaller-sized domains of the *J* aggregate compared to those at lower concentrations (0.3 mM) were observed, and the domain area distribution became broader (~ 0.5 – $4 \mu m^2$). This would be caused by frequent nuclei formation for *J* aggregation at higher concentrations.³² These morphological changes suggest that the *J* aggregates are grown at the mica/solution interface by a Volmer–Weber type growth process: spatially discrete nucleation on mica and successive growth to the islands.³³ The growth process indicates that flocculation of the molecules at the anion sites on mica could increase the adsorption energy, leading to formation of discrete nuclei and successive growth to larger *J* islands.^{32,33} The constant height of the *J* aggregates (3–6 nm) would be determined by the balance between the adsorption/aggregation and dissolution energies.

The absorbance of the *J* band increases in accordance with the growth of the aggregates at a mica/solution interface. However, the absorption properties of the *J* aggregate such as the peak wavelength and line width were almost unchanged upon the growth of the aggregates, as described in the preceding sections. The results indicate that a single leaf-like island observed by AFM at room temperature involves some disorder and the size of coherently coupled molecules is below that of the island;²⁵ the physical size of the *J* aggregate. The bandwidth of the fluorescence spectrum of the *J* aggregate was slightly narrower than that of the absorption spectrum, and the lifetime was also unchanged upon the growth of the aggregates. The

results also prove that the coherence size of the *J* aggregate is much smaller than the physical size of the single leaf-like island. Therefore, the observed aggregates are considered to be composed of an incoherent ensemble of coherent aggregates, similar to those proposed recently for the aggregates in bulk solution.¹²

Conclusions

The *J* aggregates of a pseudocyanine (PIC) dye were shown to be produced at a mica/water interface and showed characteristic optical features: a sharp and narrow absorption band at ~580 nm. The *J* aggregates at various dye concentrations were in situ observed in solution by atomic force microscopy (AFM), and they were elucidated to possess *three-dimensional* island structures for the first time. The growth of the *J* aggregates was shown to proceed via a Volmer–Weber type process, while the height of the islands was unchanged. Since the absorption peak wavelength, line width, or fluorescence lifetime was independent of the growth of the aggregates, the physical aggregation size ($> \sim 10^6$ molecules) is suggested to be much larger than the coherence size at room temperature. Further investigations are necessary for determining the molecular structures of the *J* aggregate, *J* aggregation processes, and optical properties in the single *J* domains (single leaf-like islands), which are in progress in our groups.

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