

# Anisotropic Growth of J Aggregates of Pseudoisocyanine Dye at a Mica/Solution Interface Revealed by AFM and Polarization Absorption Measurements

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We investigated the J-aggregation process of pseudoisocyanine chloride at a mica/solution interface by using tapping mode atomic force microscopy (TM-AFM) and polarization absorption measurements. At a mica/solution interface, pseudoisocyanine chlorides form J aggregates that have three-dimensional leaf-like island structures. The islands are anisotropically oriented with respect to the lattice of a mica substrate. This anisotropic alignment may result from the epitaxial interaction between the positively charged N atoms of the molecules and the regularly aligned negative holes left by the dissociating  $K^+$  ions. On the basis of both the orientation of islands to the lattice of a mica and the epitaxial interaction, we proposed that in the internal structure of the J aggregate, the long axis of the dye molecules is parallel to the long axis of the islands.

## Introduction

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 a monomer band.<sup>1–3</sup> 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 because of their unique optical properties (e.g., giant oscillator strength, excitonic coherence).<sup>4</sup>

Previous studies show that pseudoisocyanine chloride (PIC-Cl), 1,1'-diethyl-2,2'-cyanine chloride, forms J aggregates with an intense absorption band at about 572 nm in aqueous solutions at room temperature.<sup>1–3,5,6</sup> Studies also show that PIC-Cl forms J aggregates at a solid/liquid interface; in an early work, Scheibe observed (from spectra) J aggregates of PIC-Cl at a mica/solution interface.<sup>7</sup> He found that the absorption band of the J aggregate was red-shifted by 7 nm compared to that of J aggregates in solution and proposed a monolayer arrangement of the dye molecules in the aggregates. On the basis of 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.<sup>8</sup> 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 that was red-shifted compared to that of J aggregates in solution.<sup>9</sup> On the basis of total internal reflection fluorescence spectroscopy, Yao et al. suggested that the formation of the J aggregates is confined to the vicinity of the glass/solution interface. These J aggregates at solid/liquid interfaces disappear when dried.<sup>9</sup>

Optical properties of J aggregates, such as the absorption line shape and spectrum shift, have been linked to the aggregate

structure, such as aggregation number, structural dimension, and dye molecular orientation.<sup>10</sup> Therefore, for a deeper understanding of their optical properties, the structure of the J aggregates at solid/liquid interfaces needs to be clarified. However, it has been difficult to access the structure of aggregates at solid/liquid interfaces ( $J_L$  aggregate)<sup>9</sup> because of the lack of suitable analytical techniques to observe in situ the structure of  $J_L$  aggregates. Although the recent advent of atomic force microscopy (AFM) now allows direct access to the real structure of J aggregates,<sup>11–15</sup> no AFM studies on the  $J_L$  aggregates in solution exist, probably because of the difficulty of in situ AFM imaging of fragile J aggregates at solid/liquid interfaces.

In previous studies, we solved this difficulty by using tapping mode atomic force microscopy (TM-AFM) and revealed for the first time the real structure of the J aggregate of PIC-Cl at a mica/liquid interface in an aqueous PIC-Cl solution.<sup>16,17</sup> Contrary to previously accepted models in which J aggregates at a mica/solution interface have two-dimensional monolayer structures,<sup>7,8</sup> our AFM images showed that the aggregates have three-dimensional leaf-like island structures. Furthermore, the morphological change revealed by AFM imaging suggests that the J aggregates grow by a Volmer–Weber type growth process.

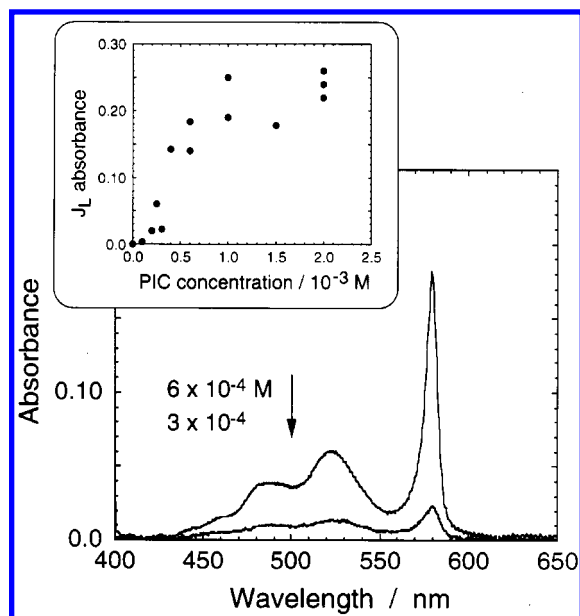
In this study, to further clarify the J-aggregation process we focused on the role of a mica surface in the formation of the J aggregates. Using both TM-AFM and polarization absorption measurements, we investigated the orientation of J-aggregate islands relative to the surface of mica at an initial growing stage of the J aggregates. We found that J-aggregate islands are anisotropically oriented with respect to the lattice of a mica substrate. This anisotropic alignment may result from the epitaxial interaction between the positively charged N atom of the molecules and the regularly aligned negative holes left by the dissociating  $K^+$  ions.

## Materials and Methods

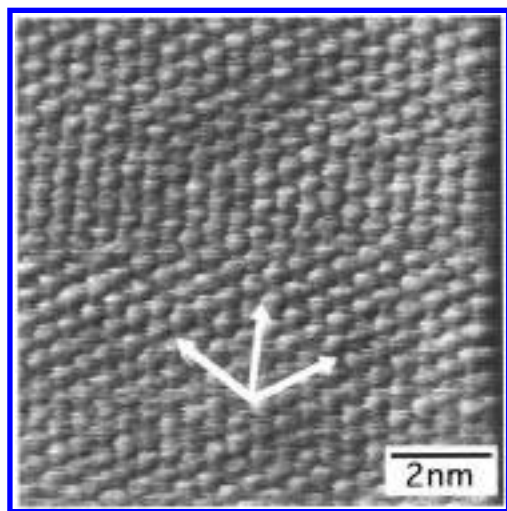
PIC-Cl (Nippon Kankoh-shikiso Kenkyusho, Co.) was used as received. Mica was purchased from Nisshin EM, Co. Ion-

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**Figure 1.** Absorption spectra of PIC-Cl J aggregate at a mica/solution interface. The inset shows the concentration dependence of the J band.

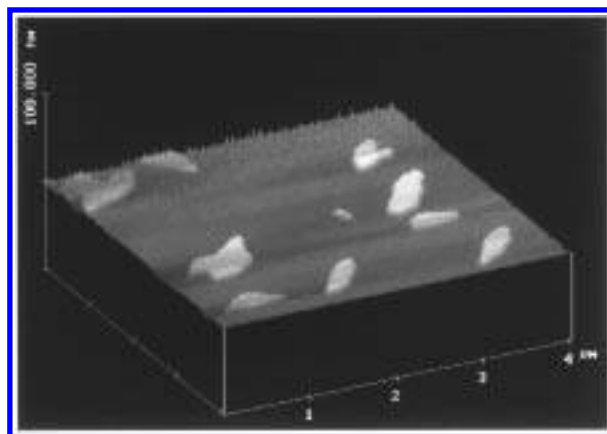


**Figure 2.** AFM image at the atomic scale of a mica surface in air. Spots correspond to alignment of holes left by the dissociating  $K^+$  ions on the surface of mica. Arrows show the periodic orientation of these holes.

exchanged water was obtained by using an Aquarius GSR-200 (Advantec Co., Ltd.).

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 magnetic steel plate by an epoxy resin and then placed in a liquid cell unit (Digital Instruments). After the mica was cleaved to expose a fresh surface, 30  $\mu$ L of an aqueous PIC-Cl solution was placed on the mica. We used triangular  $Si_3N_4$  microcantilevers (Nanoprobe, NP-S, Digital Instruments) that had a spring constant of 0.58 N/m. The drive frequency was between 8 and 10 kHz. Integral and proportional gains ranged between 0.5 and 1.2. The scan rate was between 0.5 and 1.0 Hz.

The samples for the 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  $\sim 25 \mu$ m). Absorption spectra measurements were taken using a Hitachi U-3300 spectrophotometer. Polarization absorption measurements were taken using linearly polarized light (s- and



**Figure 3.** Top-view AFM image of a mica surface at  $[PIC-Cl] = 0.1$  mM. The leaf-like three-dimensional islands correspond to J aggregates at the mica/solution interface.

p-polarized lights) and taken at the same position of the sample cell by attaching a polarizer film (HNP'B, Polaroid) in front of the hydrophobic glass side of the cell.

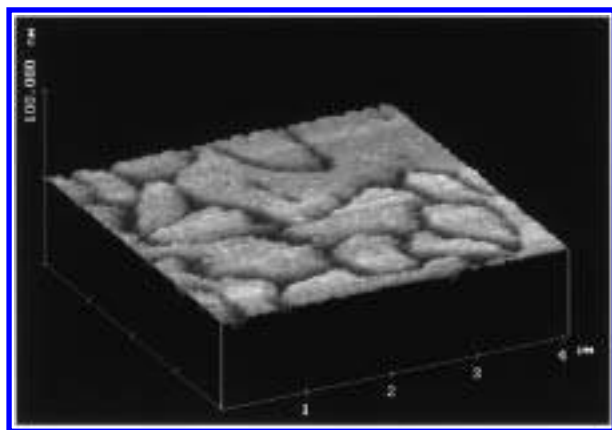
The orientation of the J-aggregate islands relative to the surface structure of mica was analyzed as follows. First, we imaged the atomic structures of the surface of mica in air. Then, we imaged the same surface of mica in a PIC-Cl solution at a PIC-Cl concentration region where the J-aggregate islands form, and measured the angle ( $\theta$ ) between the long axis of the islands and the line connecting the two holes (i.e., spots in Figure 2) left by dissociating  $K^+$  ions (Figure 6b). The AFM images were obtained for three separate specimens at the same PIC-Cl concentration. The measured angles ( $\theta$ ) were plotted in a histogram.

## Results and Discussion

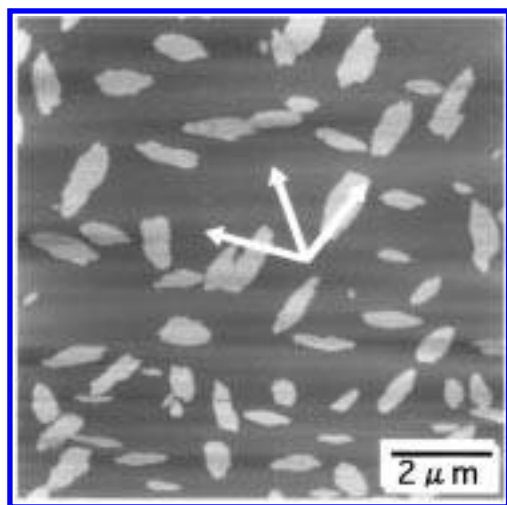
Previous reports state that PIC-Cl forms J aggregates at a mica/solution interface when the concentration of PIC-Cl exceeds  $1.0 \times 10^{-4}$  M.<sup>16,17</sup> We examined the growth process of these J aggregates in detail. Figure 1 shows typical absorption spectra of aqueous PIC-Cl solutions.<sup>16</sup> The spectra showed quasi-adsorption behavior (Figure 1, inset).

At the atomic scale, the lattice structure of the mica surface in air (Figure 2) can be recognized and corresponds to the alignment of holes left by the dissociating  $K^+$  ions on the mica surface.<sup>18,19</sup> When a mica was cleaved, interlayer  $K^+$  ions were divided onto two mica surfaces, resulting in the formation of negative holes left by  $K^+$  ions dissociating. As the ordering of the  $K^+$  ions is hexagonal between silicate layers in mica, the ordering of the induced negative holes is also hexagonal.<sup>8,19</sup> Spots in Figure 2 have been interpreted as hexagonal rings of oxygen ions corresponding to the position of  $K^+$  ions.<sup>20</sup> The mica surface remained unchanged (i.e., atomically flat) until the J band appeared ( $< 1.0 \times 10^{-4}$  M). Figures 3 and 4 show AFM images at the concentration region between  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-3}$  M, where the intensity of the J band increased drastically. At the concentration where the J band started to appear ( $1.0 \times 10^{-4}$  M), leaf-like islands of the J aggregates suddenly appeared. The average size of these islands ranged between about 400–600 nm long, about 80–100 nm wide, and 3–6 nm high. The number density of the leaf-like islands increased with increasing PIC-Cl concentration, and then when the PIC-Cl concentration reached  $3.0 \times 10^{-4}$  M, these islands coalesced into larger islands about 2–4  $\mu$ m<sup>2</sup> in area.

These AFM images showing the concentration dependence reveal the growth scenario of the J aggregates. An adsorption–



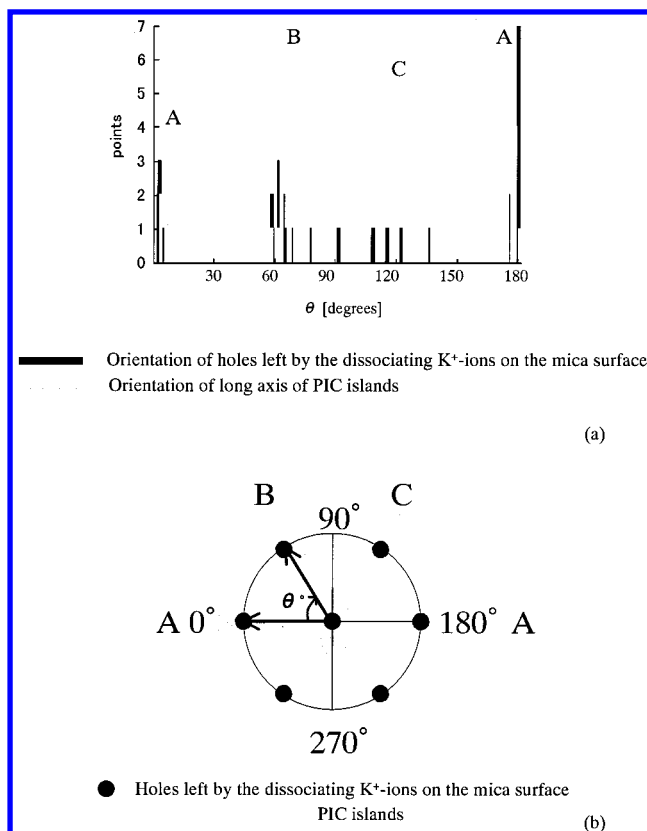
**Figure 4.** Top-view AFM image of a mica surface at [PIC-Cl] = 0.3mM.



**Figure 5.** Anisotropic growth of PIC-Cl islands. Top-view AFM image of a mica surface at [PIC-Cl] = 0.2mM. Arrows show the periodic orientation of negative holes as shown in Figure 2.

desorption equilibrium of the dye, molecules may exist on the mica surface. This equilibrium means that dye molecules are actually present on the mica surface at concentrations even below  $10^{-4}$  M, although the AFM images show no change in this concentration region. The reason for no detected change is that the rate of adsorption-desorption of the dye molecules is faster than the scanning rate of the AFM tip, and thus the dye molecules cannot be imaged. Furthermore, the lack of any J band that is characteristic for the J aggregates means that no J aggregates were present. Critical nuclei are probably controlled by parameters such as adsorption/aggregation and dissolution energy.<sup>17</sup> When adsorption/aggregation energy exceeds the dissolution energy, nuclei are formed, resulting in the island formation. In the concentration region below  $10^{-4}$  M, adsorption/aggregation energy is less than dissolution energy, and therefore nuclei cannot be formed. On the contrary, at the concentration region above  $10^{-4}$  M, adsorption/aggregation energy exceeds the dissolution energy, resulting in the formation of nuclei followed by their growth to islands.

AFM images (Figure 5) clearly show the anisotropic growth of these islands. We clarified the anisotropic growth of J aggregates by determining the orientation of the long axis of the islands. Although the histogram of  $\theta$  between 0 and  $180^\circ$  (Figure 6a) shows some scatter, it clearly shows that the long axes of the islands are anisotropically oriented relative to the alignment of the holes formed by dissociating  $K^+$  ions. The long axis of each island is oriented to one of three directions



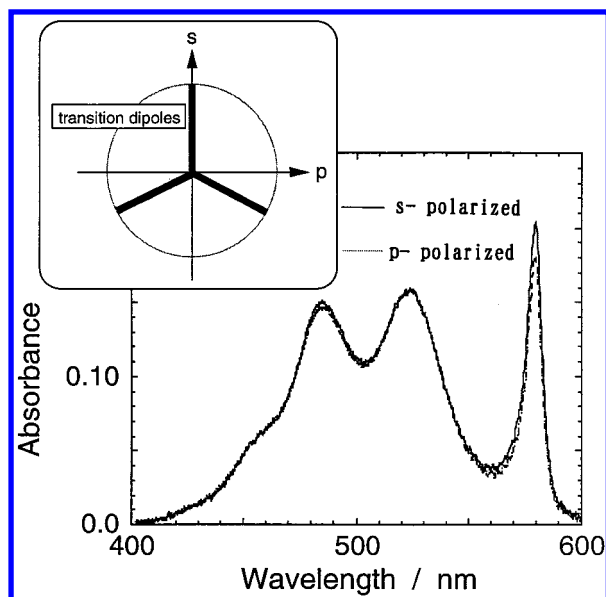
**Figure 6.** (a) Histogram of the angles  $\theta$  between 0 and  $180^\circ$ . (b) Schematic of the relation between the lattice structure of a mica surface and J-aggregate islands.

(labeled A, B, and C in Figure 6) whose respective peak maximum is at 0, 60, and  $120^\circ$ , respectively. These three directions coincide well with the directions to neighboring holes (see model in Figure 6b).

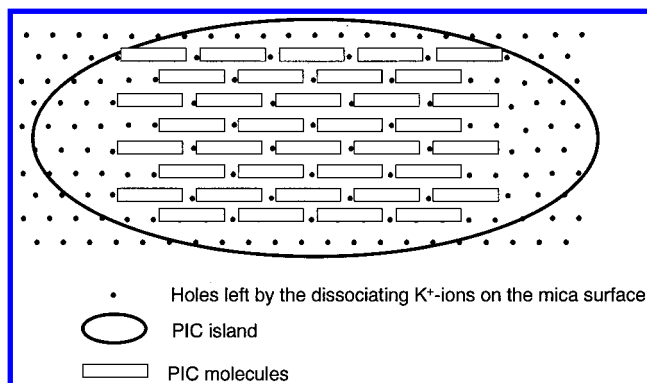
The orientation of the grown J aggregates possessed triangular symmetry on a mica substrate. Thus, differences in absorption spectra measured with linearly polarized light can be expected.<sup>21</sup> Figure 7 shows absorption spectra of an aqueous PIC solution ( $2.0 \times 10^{-3}$  M) in the mica/hydrophobic cell obtained by using s- and p-polarized lights. Small differences in absorption at the J band were observed between the spectra measured by the s- and p-polarized lights. Furthermore, the absorbance ratio at the J band was reproducible,  $\sim 1.15$ . These results indicate anisotropy of the transition dipoles of the J aggregate and thus show the anisotropic growth of the J aggregates. The absorption spectra in the short wavelength region ( $\lambda < 550$  nm) were similar to each other, suggesting that Davydov-type splitting does not exist in the plane of mica.<sup>21</sup>

On the basis of our AFM observations, if the direction of transition dipoles is parallel to that of the long axis of the J-aggregate islands, then the transition dipoles are oriented to three directions ( $\theta = 0, 60, 120^\circ$  labeled by A, B, C, respectively) in equal numbers ( $m$ ). For simplicity, if we assume that the axes of s- and p-polarized lights are set to  $\theta = 0$  and  $90^\circ$ , respectively, then the absorbance of the J band measured by using s-polarization corresponds to the sum of dipoles oriented to  $\theta = 0^\circ$ , namely, those of direction A, which is  $\cos 60^\circ$  of directions B and C ( $2m$ ). Similarly, for the measurement involving p-polarization, the sum of the dipoles oriented to  $\theta = 90^\circ$  of  $\sin 60^\circ$  of directions B and C ( $\sqrt{3}m$ ) is expected to contribute  $2/\sqrt{3}$  (i.e., 1.154) to the J band. The directions of s- and p-polarizations are arbitrary, and therefore the results indicate that transition dipoles are oriented to three directions





**Figure 7.** Absorption spectra of an aqueous PIC-Cl solution (2.0 mM) in the cell composed of mica and hydrophobic glass plates with s- and p-polarized lights. The inset shows three-direction orientation of transition dipoles relative to s- and p-polarized light.



**Figure 8.** Model of the alignment of PIC-Cl molecules in a J-aggregate island.

as a result of the anisotropic growth of the J aggregate at a mica/solution interface. It should be noted that the polarization absorption measurements were performed at a higher concentration of PIC, while the angle dependence of the islands by AFM was examined at 0.2 mM. In our previous study,<sup>17</sup> we revealed that optical properties of the J aggregates were determined by the smaller domains included in the leaf-like islands. Since the J aggregates observed at 2.0 mM consisted of the grown islands,<sup>17</sup> the polarization absorption supports the results. Furthermore, the role of the leaf-like island observed by AFM would correspond to a "macroaggregate" proposed by Kobayashi et al. for J aggregates of PIC-Br.<sup>22-24</sup>

This anisotropic growth suggests the existence of epitaxial interaction between the dye molecules and the lattice of a mica substrate during the aggregation process. The highly probable epitaxial interaction is the one proposed by Scheibe, namely, that the positively charged N atoms of the dye molecules are placed at the negative holes left by the dissociating  $K^+$  ions.<sup>25</sup> According to this epitaxial interaction, there are two possible alignments of the dye molecules in the islands: the long axes of the dye molecules are either parallel or  $60^\circ$  relative to the long axes of the islands. Spano and Mukamel<sup>5</sup> and Scherer and Fischer<sup>6</sup> proposed that J aggregates of PIC-Cl in solution possess a one-dimensional threadlike structure. Higgins et al. found that J aggregates form by combining the dye molecules

with polymer chains.<sup>14</sup> All of these studies showed that dye molecules are in a brick-stonework structure and are parallel to the long axis of the threadlike structure or of the polymer chains. In terms of energy, this means that this is the preferred alignment for producing the J aggregates. Thus, dye molecules may grow so that the long axis of dye molecules is parallel to the long axis of the islands (Figure 8). This structure is different from that of bulk crystal<sup>26,27</sup> and inherent to a mica/solution interface.

To validate this structure model, we need more details of the internal structure of the J aggregate. Future research in our laboratory includes investigating such detail by using TM-AFM and near-field scanning optical microscopy.

## Conclusion

We clarified the anisotropic growth of J aggregates of pseudoisocyanine chloride dyes at a mica/solution interface. This anisotropy probably originates from the epitaxial interaction between the dye molecules and the regularly aligned negative holes left by the dissociating  $K^+$  ions. For further clarification of the anisotropic J-aggregation process, details are needed on the internal structure of the J aggregates.

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## References and Notes

- (1) Jelley, E. E. *Nature*, **1936**, *138*, 1009; **1937**, *139*, 631.
- (2) Scheibe, G. *Angew. Chem.* **1936**, *49*, 563; **1937**, *50*, 212.
- (3) De Boer, S.; Vink, K. J.; Wiersma, D. A. *Chem. Phys. Lett.* **1987**, *137*, 99.
- (4) Spano, F. C.; Mukamel, S. *Phys. Rev. A* **1989**, *40*, 5783.
- (5) Scherer, P. O.; Fischer, S. F. *Chem. Phys.* **1984**, *86*, 269.
- (6) Dalozzo, E.; Scheibe, G.; Gschwind, K.; Haimel, F. *Photo. Sci. Eng.* **1974**, *18*, 441.
- (7) Scheibe, G. *Angew. Chem.* **1939**, *52*, 631.
- (8) Czikkely, V.; Foersterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 11.
- (9) Yao, H.; Ikeda, H.; Kitamura, N. *J. Phys. Chem.* **1998**, *102*, 7691.
- (10) Kobayashi, T., Ed. *J. Aggregates*; World Scientific: Singapore, 1996.
- (11) Wolthaus, L.; Schaper, A.; Moebius, D. *Chem. Phys. Lett.* **1994**, *225*, 322.
- (12) Saijo, H.; Shiojiri, M. *J. Imaging Sci. Technol.* **1996**, *40*, 111.
- (13) Saijo, H.; Shiojiri, M. *J. Cryst. Growth* **1996**, *166*, 930.
- (14) Higgins, D. A.; Kerimo, J.; Bout, D. A. V.; Reid, P. J.; Barbara, P. F. *J. Am. Chem. Soc.* **1996**, *118*, 4049.
- (15) Daehne, L.; Tao, J.; Mao, G. *Langmuir* **1998**, *14*, 565.
- (16) Sugiyama, S.; Yao, H.; Matsuoka, O.; Kawabata, R.; Kitamura, N.; Yamamoto, S. *Chem. Lett.* **1999**, 37.
- (17) Yao, H.; Sugiyama, S.; Kawabata, R.; Ikeda, H.; Matsuoka, O.; Yamamoto, S.; Kitamura, N. *J. Phys. Chem. B* **1999**, *103*, 4452.
- (18) Schmidt, H. *J. Vac. Sci. Technol. A* **1990**, *8*, 388.
- (19) Drake, B.; Prater, C. B.; Weisenborn, A. L.; Gould, S. A. C.; Albrecht, T. R.; Quate, C. F.; Cannell, D. S.; Hansma, H. G.; Hansma, P. K. *Science* **1989**, *243*, 1586.
- (20) Hartman, H.; Sposito, G.; Yang, A.; Manne, S.; Gould, S. A. C.; Hansma, P. K. *Clays Clay Mineral* **1990**, *38*, 337.
- (21) Marchetti, A. P.; Salzberg, C. D.; Walker, E. I. P. *J. Chem. Phys.* **1976**, *64*, 4693.
- (22) Misawa, K.; Minoshima, K.; Ono, H.; Kobayashi, T. *Chem. Phys. Lett.* **1994**, *220*, 251.
- (23) Kobayashi, T.; Misawa, K. *J. Lumin.* **1997**, *72-74*, 38.
- (24) Kobayashi, T. *Supramol. Sci.* **1998**, *5*, 343.
- (25) We propose that the driving force for the formation of J aggregates would be the interactions between regularly aligned negative holes and positively charged N atoms of dye molecules. However, counterions might become important in stacking the dye molecules in three dimensions.
- (26) Dammeier, Von B.; Hoppe, W. *Acta Crystallogr.* **1971**, *B27*, 2365.
- (27) Daehne, L.; Horvath, A.; Weiser, G. *Chem. Phys.* **1995**, *196*, 307.