Abstract

The effect of humidity treatments on the surface morphology of spin-coated pseudoisocyanine (PIC) dye films on mica was investigated by absorption spectroscopy, fluorescence microscopy, and atomic force microscopy (AFM). We demonstrated that the humidity treatment caused dynamic changes of mesoscopic J aggregate morphology due to the mobile nature of PIC molecules on mica surface. Under dry condition, lots of microcrystalline PIC J aggregates were isolatedly distributed on mica. In a low-humidity treatment (32% relative humidity (RH)), characteristic branch-like and patchy leaf-like J aggregate islands could be observed together with non-emissive disordered aggregates. The J aggregate islands grew to possess large patchy leaf-like morphology in a high-humidity treatment of 65% RH. The mobile properties of PIC on a mica surface under humid environments can be explained by capillary condensation of water around hydrophilic microcrystals on the surface and consequent disjoining pressure.

1. Introduction

Organic thin films on a large variety of substrates have attracted a great deal of attention because of numerous promising industrial applications such as solar cells [1] and photonic/electronic devices [2,3]. For fabricating such devices, physico-chemical properties of the surface materials (e.g. durability, interfacial bonding, molecular order, structure, and morphology) have to be optimized to achieve superior electrical and optical parameters. Uniform thin films consisting of physisorbed monolayers are usually prepared by adsorption of functional molecules from solution (self-assembly) or by a Langmuir-Blodgett technique [4,5]. Spin- or dip-coating is also frequently applied for preparing such thin films of a specific thickness [6,7]. Unlike chemisorbed layers that are covalently bonded to surfaces, they are bound to surface via weak interactions such as electrostatic, hydrogen bonding, or van der Waals interactions. Therefore, physical characteristics of the films are readily subject to ambient conditions.

We previously revealed that a cationic pseudoisocyanine (PIC) dye adsorbed at a mica/aqueous solution interface electrostatically forms J aggregates [8,9]. J aggregates are ordered supramolecular dye assemblies discovered by Jelley [10,11] and Scheibe [12,13], and characterized by a narrow and intense absorption band that shows a bathochromic shift compared to the relevant monomer band [14]. Recent interest has focused on the ability of J aggregates to exhibit coherent excitation phenomena that provide large optical nonlinearities [15]. The PIC J aggregates at the mica/solution interface had a three-dimensional island structure in mesoscopic size, and exhibited different spectroscopic properties from those produced in concentrated bulk aqueous solution [8,9].

If water is removed from the interface to prepare thin solid films of the J aggregate, large optical, structural, and/or morphological changes of the aggregate are expected [16], and would be surely affected by environmental humidity. However, only little is known about the properties of such thin films consisting of the supramolecular aggregates. Therefore, detailed investigations of the supramolecular film on
mica surface and the effect of humidity treatment on the structural/morphological characteristics of the film are of prime importance in view of their future device applications. In this study, we report the effect of humidity treatments on the mesoscopic morphology of supramolecular PIC J aggregates on a mica surface manifested by fluorescence microscopy and atomic force microscopy (AFM). We found that the morphology of the J aggregate was dynamically altered by humidity treatments due to a mobile nature of PIC molecules under the humid environments. These dynamic morphologies will be discussed by capillary condensation of water around dye microcrystals on a mica surface and subsequent disjoining pressure effect.

2. Experimental

2.1. Chemicals and sample preparation

Pseudoisocyanine bromide, whose chemical structure and molecular size are shown in Fig. 1a, was purchased from Hayashibara Research Institute for Photosensitizing Dyes and used as received. Mica was purchased from Nilaco Co. Pure water was obtained by using an Aquarius GSR-200 (Advantec Co. Ltd.).

Thin films of PIC were prepared by a vertical spin-coating method [17]. Briefly, a mica substrate was first cleaved to expose a fresh surface, and attached to the shaft of a handy motor (Iuchi, Pencil Mixer DX). After the mica sheet was immersed into an aqueous PIC solution (0.8 mM) for 10 min, we performed spinning with high acceleration of the spinning rate (6000 rpm) for 30 s in the direction normal to the surface plane. During the spinning, the solution left on mica was spread over along the surface in the radial direction of the rotational motion by centrifuge force.

Humidity treatment was conducted as follows: immediately after spin-coating, the film samples were stored at ~20 °C under dark at a different relative humidity (RH) level (65%, 32% or dry) for 48 h. Note that the term “dry” denotes the condition for the sample stored at ~20 °C under vacuum by using a rotary pump for 48 h; the RH was lower than 20%. RH of 65 or 32% was maintained in a closed vessel which contains a saturated Mg(CH3 COO)2·4H2O or CaCl2·6H2O solution, respectively.

2.2. Measurements

Absorption spectra were recorded with a Hitachi U-3210 spectrophotometer, and fluorescence spectra with a Hitachi F-4500 spectrofluorometer.

Fluorescence micrographs were obtained by using a CCD camera (Flovel; HCC-600) set on an optical microscope (Olympus; BX-60). The excitation beam (~546 nm) was obtained by passing the light from an Hg lamp (Ushio; USH102D, 100W) through a mirror cube unit (U-MWIG).

AFM topographical images were recorded with a Nanoscope IIIa system (Digital Instruments). For tapping mode operation at an ambient condition, square-pyramidal Si

![Fig. 1. (a) Chemical structure of a pseudoisocyanine (PIC) dye. The molecular size is also shown. (b) Fluorescence micrograph of PIC J aggregates formed at an mica/aqueous solution interface. The concentration of PIC is 0.8 mM. (c) Topographical AFM image of the PIC J aggregates at the mica/solution interface.](image-url)
films treated at different RH. The spectra showed a sharp
3.2. Surface morphology of spin-coated PIC solid films


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...microcantilevers that had a spring constant of 30–100 N m\(^{-1}\) (TESP; Digital Instruments) were used. The drive frequency was \(\sim 270\) kHz. For the measurements in a liquid phase, triangular Si\(_3\)N\(_4\) microcantilevers (NP-S; Digital Instruments) with a spring constant of 0.58 N m\(^{-1}\) were used for tapping mode operation. The drive frequency was set between 7 and 9 kHz.

Relative humidity was measured with a hygrometer (Testo, 605-H1). Spectroscopic and fluorescence microscopic data were obtained under ambient air conditions (\(\sim 20^\circ\text{C}, \sim 30–35\%\ \text{RH}\)) within \(\sim 10\) min immediately after taking out the samples from the constant humidity vessels. AFM measurements were performed under the same ambient conditions within \(\sim 30\) min immediately after taking out the samples from these vessels. Because similar images between fluorescence microscopy and AFM could be obtained in the same humidity treatment, we concluded that large morphological changes of the aggregates did not occur during these measurements.

3. Results and discussion

3.1. Morphology of PIC J aggregates at a mica/aqueous solution interface

At [PIC] = 0.8 mM, the dye molecules do not form J aggregates in an aqueous bulk solution whereas produce self-assembled J aggregates at a mica/solution interface. The facts have been confirmed by experiments of an optical path length dependence of the absorption spectrum of the J aggregates [8,9]. Hence, we first studied morphological properties of the J aggregates at the mica/solution interface.

Fluorescence microscopy was used to determine the microstructures of the J aggregates, because the J aggregates show high emissivity whereas molecular (or monomeric) PIC scarcely exhibits any emission. Fig. 1b shows a typical fluorescence micrograph of the J aggregate at a mica/solution interface. All of the interfacial region were brightly emissive. The fluorescence micrograph indicates that the interface was completely covered with PIC J aggregates constituting of small domains.

Fig. 1c shows a topographical AFM image of the mica/solution interface. We revealed that the mica surface was completely covered with islands of J aggregates in an aqueous PIC solution, consistent with the result obtained by the fluorescence microscopic observation (Fig. 1b). The island had a three-dimensional mesoscopic structure (\(\sim 0.5–1\) \(\mu\)m wide, \(\sim 1–4\) \(\mu\)m long, and \(\sim 3\) nm high) possessing a complex shape.

3.2. Surface morphology of spin-coated PIC solid films treated at different RH

Fig. 2 shows absorption spectra of spin-coated PIC solid films treated at different RH. The spectra showed a sharp band (J band) at around 580 nm that was red-shifted with respect to the PIC monomer band (525 nm) [8], as is a characteristic of the J aggregates. All of the spectra are quite similar indicating similarities in the aggregate structures. A broad band at around 520 nm is attributed to the monomer adsorbed on a mica surface and a vibrational structure of the J aggregates [18].

Fig. 3 shows typical fluorescence micrographs of the spin-coated PIC films on mica treated at different RH, along with the image obtained immediately after spin-coating. These images are quite different from that obtained for the mica/solution interface (Fig. 1b). When the film sample was stored in a dry vessel (namely, <20% RH), microcrystalline PIC J aggregates (1–2\(\mu\)m) were precipitated isolatedly on mica (Fig. 3a). We confirmed that a similar microscope image could be taken for the film immediately after spin-coating (inset in Fig. 3a). Note that the size of the microcrystals seemed to be slightly larger (2–4 \(\mu\)m) than that obtained in the dry treatment, indicating that PIC molecules were about to expand in the vicinity of microcrystals.

On the other hand, humid air treatments caused remarkable changes in the J aggregate morphology. For the film in a 32% RH treatment, patchy leaf-like and branch-like J aggregate islands appeared on mica, while the microcrystalline J aggregates disappeared (Fig. 3b). The leaf-like (anisotropic) shape implies the anisotropic growth toward the long axis of the islands [9]. At high-humidity level (65% RH), the J aggregate grew to be a larger patchy leaf-like island (Fig. 3c). The island domain was about 50–60\(\mu\)m long and about 20–30\(\mu\)m wide. Therefore, the observed dynamic morphology of the J aggregate islands suggests a highly mobile nature and strong self-aggregation (dipole–dipole) interaction of PIC molecules [16] on mica surface under humid conditions.

Fluorescence micrographs do not clarify whether molecules are distributed or not on mica surface where the J aggregates are not produced (namely, the dark regions in
Fig. 3. Fluorescence micrographs of the PIC J aggregates on mica treated at different RH: (a) dry; (b) 32% RH; and (c) 65% RH. Inset in (a) shows a typical fluorescence micrograph taken immediately after spin-coating.

AFM measurements allow direct access to the real morphology of the surface of mica. Fig. 4 shows topographical AFM images (4 μm x 4 μm) of a surface of mica treated at different RH where J aggregate domain islands are distributed. Fig. 5 shows topographies of the mica surface for the outside region of each J aggregate island. The J aggregate island was determined by comparing the AFM images with those of fluorescence microscopy. Table 1 summarizes the height (thickness) of each island observed in Figs. 4 and 5.

Table 1

<table>
<thead>
<tr>
<th>Height (thickness in nm)</th>
<th>&lt;20°</th>
<th>32°</th>
<th>65°</th>
</tr>
</thead>
<tbody>
<tr>
<td>J aggregate domains</td>
<td>50-80 (microcrystals)</td>
<td>1.5-2.0</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>Regions outside the J aggregates</td>
<td>0.2-0.3</td>
<td>0.5-0.8</td>
<td>0.5-1.1</td>
</tr>
</tbody>
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aHumidity treatment (relative humidity in %).

In Figs. 4a and 5a (dry treatment), very thin strings are randomly distributed in the vicinity of a PIC microcrystal. The string is not a J aggregate but a disordered aggregate, because no emission could be detected from the string. The height of the string is 0.2-0.3 nm, showing that the string is composed of disorderly adsorbed PIC molecules lying down on the mica surface. Fig. 4b (32% RH) shows branch-like islands of J aggregates constituting of linear aggregate domains. The linear morphology of J aggregates might suggest the nature of anisotropic growth of PIC J aggregates on mica surface. Fig. 4c shows the topographical image inside the patchy leaf-like J aggregate domain formed by the 65% RH treatment. The "holes" (dark regions in the absence of molecules) in the leaf-like island also showed leaf-like shapes aligning in one direction, reflecting that the J aggregate domain grew anisotropically under humidified conditions.

The J aggregate islands shown in Fig. 4b and c had a multi-layered structure. In both cases (humidity treatments at 32 and 65% RH), the height of the islands is 1.5-2.0 nm (Table 1). Note that the height of the J aggregate produced at the mica/solution interface was ∼3 nm. The results suggest that the molecular interactions among PIC layers along normal to a mica surface brought about the multi-layered structure under humidified or aqueous environments.

As noted previously, the J aggregate island in a humid treatment of 65% RH grew to be larger than that in 32% RH treatment. The fact implies that PIC molecules which do not form J aggregates are present at the outside regions of the J aggregate island. Fig. 5b and c show the AFM images outside the J aggregate island obtained in 32 and 65% RH treatments, respectively. Because no brightly emitted fluorescence images could be obtained outside the branch-like or patchy leaf-like regions as shown in Fig. 3, these AFM images correspond to the disordered PIC aggregates different from the J aggregate domains. Therefore, a binary phase constituting both J and disordered aggregates was revealed for spin-coated PIC solid films. The height of the disordered aggregates was 0.5-0.8 nm (Table 1), suggesting that PIC molecules randomly adsorb on a mica surface in a side-on style. These disordered aggregates could contribute to the growth of J aggregate islands under humid conditions as a reservoir.

According to the fluorescence micrographs and the AFM images, we can roughly estimate the amount (volume in a
unit surface area) of PIC molecules on mica which form J aggregates. From Fig. 3a, a microcrystalline J aggregate covered the surface area of ~7%. By knowing that the height of the crystals, which was about 50 nm (Table 1), the volume ($V$) of the PIC J aggregates present in a surface area of 1 µm$^2$ was estimated to be $\sim 3.5 \times 10^{-4}$ µm$^3$. Similarly, we can determine $V$ values from Fig. 3b and c, and Table 1.

In case of the 32 and 65% RH treatments, the J aggregate covered the surface area of ~40 and ~50%, respectively. In both the treatments, the height of the J aggregate islands was ~2.0 nm. Therefore, the $V$ value was estimated to be $\sim 8.2 \times 10^{-4}$ and $\sim 1.0 \times 10^{-3}$ µm$^3$ in the 32 and 65% RH treatment.
3.3. Mobile nature of PIC molecules on a mica surface under humid environments

In the humidity treatments, a highly mobile nature of PIC molecules on mica was revealed to form characteristic mesoscopic structures of J aggregates. The increase in mobility of PIC under humid environments can be related to the...
formation of water films on the mica surface. It is well-known that a two-dimensional monolayer water film forms on mica surface at RH $\leq 40\%$ [19]. With an increase in RH, more water adsorbs on the surface, forming thicker films or droplets in a liquid character at RH $> 40\%$ [19]. However, these structures of the water films on mica are locally disturbed by contact with a hydrophilic material [20]. According to scanning polarization force microscopic studies and pull-off force measurements between a hydrophilic AFM tip and the mica surface as a function of RH [20], capillary condensation brought about water to form droplets around the contact point at intermediate relative humidity ($\sim 20\% < \text{RH} < 40\%$), whereas capillary force did not play an important role at low RH ($< \sim 20\%$).

In the case of our system, we consider the PIC microcrystals on the mica surface as a contact point of a hydrophilic material. In a treatment of 32% RH (intermediate RH region), the PIC microcrystal on mica gives rise to the condensation of water vapor which forms a capillary meniscus around the contact point (namely, PIC microcrystal). Consequently, the microcrystal will dissolve into condensed water to form PIC cations, which forms an electric double-layer at the mica/water film interface. The pressure present in the water thin film on a charged solid surface is defined as “disjoining pressure”, and the double-layer force depending on the surface density of counterions becomes the origin of the disjoining pressure that stabilizes and develops the water thin film on a charged solid surface under humid environments (32 and 65% RH), resulting in the formation of characteristic branch-like or patchy leaf-like J aggregate morphologies along with disordered non-emissive aggregates. Diffusion of the dye molecules on mica under humid environments could be explained by capillary condensation of water around hydrophilic dye microcrystals on mica surface and consequent disjoining pressure due to the electric double-layer force brought by the PIC cations.

4. Conclusion

The mesoscopic morphology of PIC J aggregate films on mica prepared by spin-coating was quite different from that produced at a mica/aqueous solution interface. We demonstrated that dynamic morphological changes of the aggregate were caused by the humidity treatments. The behaviors were dependent on a highly mobile nature of PIC molecules on a mica surface under humid environments (32 and 65% RH), resulting in the formation of characteristic branch-like or patchy leaf-like J aggregate morphologies along with disordered non-emissive aggregates. Diffusion of the dye molecules on mica under humid environments could be explained by capillary condensation of water around hydrophilic dye microcrystals on mica surface and consequent disjoining pressure due to the electric double-layer force brought by the PIC cations.

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References