X-ray analysis on the size and shape of J-aggregates formed at the air-water interface

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Abstract. The X-ray analysis on the J-aggregate monolayer formed by amphiphilic merocyanine dye (MD) molecules at the air-water interface was carried out. For the analysis, a grazing incidence X-ray diffraction method was applied by using monochromatic synchrotron radiation. After deconvolution of the instrumental broadening factor from the obtained diffraction peaks, the pure widths of the diffraction peaks were substituted for the Scherrer formula, and the size and shape of the MD J-aggregate were evaluated. It was found that the MD J-aggregate had oval or elliptical shape with the long axis of submicrometer.

1. Introduction
Molecular assemblies and supramolecules are expected to play an important role for opto-electronic and optical devices, and an extensive effort has been made to synthesize them using various organic dye molecules [1, 2]. J-aggregates are one of the supramolecules of the organic dye molecules having specific molecular orderings, and form a narrow excitonic absorption band (J-band) located in a lower energy side from the band of the isolated molecules [3]. Mainly, cyanine dye molecules are used as J-aggregate forming molecules [4]. Due to this characteristic absorption band based on the interaction of transition moments, the J-aggregates exhibit variety of optical properties that contribute to photosensitizing effects [5], ultrafast nonlinear optical responses [6, 7] and efficient energy transfers in solar cells [8, 9] and photosynthetic bacteria [10].

So far, we have focused on the J-aggregates formed by amphiphilic merocyanine dye (MD) molecules (see figure 1). Due to the amphiphilic structure, the MD molecules form the J-aggregate monolayer at the air-water interface, and the monolayer can be deposited into a multi-layered film on the substrates (Langmuir-Blodgett film) [11, 12]. By microscopic observations, we have shown that they form randomly oriented mesoscopic domains in the monolayer [13, 14, 15, 16]. Recently, our grazing incidence X-ray diffraction (GIXD) measurements revealed a quantitative relation between the molecular arrangement and the energy shift of the J-band upon aggregation [17]. The MD J-aggregates show polymorphism accompanied by the change in the J-band wavelength on changing the subphase temperature (thermochromism) [13, 16]. It was also shown that the J-aggregates having different J-band wavelengths exhibit different molecular arrangements [18, 19].

Here, I report a two-dimensional domain size and shape of the MD J-aggregates formed at the air-water interface. The size and shape of the aggregates were investigated by the GIXD method. After evaluating the instrumental broadening of the diffractometer, the pure widths of the diffraction peaks were obtained. The peak widths were converted into the dimensions of the J-aggregate domain with the aid of the Scherrer formula [20].
Figure 1. Absorption spectra of the MD J-aggregate monolayer on the aqueous subphase consisting of MgCl$_2$, and the molecular structure of the MD molecule. Since the electric and transition dipole moments of the MD molecule are almost in the same direction, one arrow represents their direction [17].

2. Experimental Details

2.1. Materials
The MD molecule was purchased from Hayashibara Biochemical Laboratory, Inc. and chloroform, MgCl$_2$ and NaHCO$_3$ were from Kanto Kagaku. 1 mM chloroform solution of the MD molecule was prepared for a spreading solution. The solution exhibited a typical monomeric absorption maximum at 525 nm. Pure water used for aqueous subphase solutions was prepared in a Milli-Q system. 0.5 mM aqueous solution of MgCl$_2$ was prepared for the subphase to supply the counter-ions (Mg$^{2+}$) of the MD molecules, and NaHCO$_3$ was added to keep the pH of the subphase ca. 6.8.

2.2. Monolayer preparation
On the MgCl$_2$-containing subphase at the temperature of 17 °C, the J-band of the MD J-aggregates was located at 618 nm as shown in figure 1. The MD spreading solution was dripped on the aqueous subphase in the trough, which was designed for the GIXD measurements, until the monolayer covered the whole surface of the subphase, and the surface pressure was less than 5 mN/m. It should be noted that, after being spread on the subphase, the MD molecules form J-aggregates within a second even at fairly low surface pressure (<5 mN/m), i.e., the MD monolayer is classified in a condensed monolayer [21]. The temperature of the subphase was kept 17 ± 0.25 °C for all measurements.

2.3. GIXD measurements
For the in-plane diffraction measurements of the monolayer at the air-water interface, a synchrotron radiation source is required due to a low X-ray scattering rate of organic monolayers [22]. In the present GIXD measurements, the synchrotron radiation source of BL46XU at SPring-8 (Hyogo, Japan) was used. The photon flux of the beam was the order of 10$^{12}$ photons/sec in 0.1% of the beam-width. Optical setup is illustrated in figure 2. The X-ray radiation emitted by the hybrid undulator was monochromatized at the energy of 12 keV ($\lambda = 0.103$ nm), and the cross-section of the beam was collimated into 1 mm width and 0.1 mm height by the divergence slits (DS1 and DS2). The incident angle $\theta_{\text{in}}$ was adjusted by the two Si-mirrors at 0.09°, which is below the critical angle of the total reflection for water. The trough was mounted on the HUBER 5020 eight-axis diffractometer. Their photographs are shown in figure 3. The take-off angle $\theta_{\text{out}}$ was also set to be 0.09°. The receiving slits (RS1 and RS2) were set at 4 mm width and 10 mm height, and the Soller slit was equipped between RS1 and RS2. After the receiving slits, a scintillation counter was mounted for the detection. Because the J-aggregate crystallites were oriented in a random direction on the subphase, the 2$\theta$ scan enabled
us to observe the two-dimensional powder diffraction of the monolayer. The signal was accumulated for 15–30 sec on each scan step.

![Side View and Top View of the Optical Setup](image)

**Figure 2.** Optical setup for grazing incidence X-ray diffraction measurements.

![Figure 3a and 3b](image)

**Figure 3.** (a) Photograph of the diffractometer. The X-ray beam propagates from right-hand side trough the evacuated polyvinyl chloride tubes. The evacuated tubes are placed from DS2 to DS3, from DS3 to the trough, from the trough to RS1, and from RS2 to the scintillation counter to reduce the X-ray scattering induced by air. The housing of the Soller slit is also evacuated. The orange part on the diffractometer corresponds to the trough. (b) Photograph of the home-built trough. The trough is mounted on the diffractometer. The housing of the trough is made by duralumin. The X-ray windows of the housing are sealed with Kapton foil (orange foil), and air is purged from the housing by He gas flow. Through the Kapton window, a white frame of the Teflon trough, where the aqueous subphase is loaded, can be seen. The temperature of the subphase is contorted by the Peltier devices equipped underneath the trough.

3. Results and Discussion

3.1. Instrumental broadening

To evaluate the peak broadening due to the instrumental factor, the diffraction from the silicon (222) plane was observed in the same setup using the Si(111) plate. As shown in figure 4, the obtained diffraction peak was fitted well by the Lorentz function, and its full width at half maximum (FWHM) was 0.146° in 2θ. Since the Si wafer has nearly ideal crystalline, the Lorentz function having the
FWHM of 0.146° was employed as the instrumental weight function of the diffractometer that should be deconvoluted from the observed peaks to have pure peak widths.

**Figure 4.** Diffraction peak of Si(222) plane obtained from the Si(111) plate. Open circles show the experimental data, and the solid line, the Lorentz function.

**Figure 5.** In-plane diffraction pattern of the MD J-aggregate monolayer at the air-water interface. $Q = 4\pi \sin \theta / \lambda$, where $\lambda = 0.103$ nm is the X-ray wavelength and $2\theta$ is the diffraction angle. The inset shows the two lattice structure and the molecular arrangement. Each arrow showing the electric and transition dipole moments corresponds to one MD molecule (see figure 1). The Miller indices shown are based on this lattice structure. The lattice parameters of the monolayer are $a = 0.771$ nm, $b = 1.572$ nm and $\gamma = 78.21°$ (1.365 rad) [17].
3.2. Monolayer observation
The obtained GIXD pattern was fitted by polynomial and Lorentz functions for the background and diffraction peaks, respectively. The diffraction pattern after extraction of the background and correction of the Lorentz factor is shown in figure 5 together with the Lorentz functions. Four clear diffraction peaks [(0 2), (1 1), (1 3) and (2 0)] and four weak peaks [(1 4), (1 3), (0 4) and (2 2)] were observed. To obtain this pattern, the range of the 2θ scan was divided in four ranges, and the four patterns were connected after the observations. In each scan, the monolayer was freshly prepared on the subphase having the same content and temperature.

| Miller Indices | $W$ (nm$^{-1}$) | $D$ (nm) |
|---------------|---------------|---------|
| (0 2)         | 0.007         | 796     |
| (1 1)         | 0.021         | 266     |
| (1 3)         | 0.025         | 223     |
| (2 0)         | 0.042         | 133     |

3.3. Size and shape of the J-aggregate domain
From the FWHM of the diffraction peaks, the Scherrer formula $D = 0.89 \cdot 2\pi/W$ gives the approximate crystallite dimensions [20]. We focused on the four clear peaks having the Miller indices of (0 2), (1 1), (1 3), and (2 0) (figure 5). The pure FWHMs of these peaks $W$, which are obtained after the deconvolution of the instrumental weight function of the diffractometer (figure 4), are listed in table 1. From these FWHMs, the crystallographic coherent lengths $D$ were calculated using the Scherrer formula (table 1). Since we had revealed that the monolayer consists of the MD J-aggregate domains [13, 14, 15, 16], the calculated crystallographic coherent lengths $D$ correspond to the domain dimensions of the J-aggregate.

Figure 6. Polar plot of the J-aggregate dimensions obtained by the Scherrer formula. The vertical axis of the polar plot is parallel to the b axis of the lattice.

In figure 6, the polar plot of the $D$ values is shown together with the lattice structure of the MD J-aggregate. The $D$ values are divided by 2 to give the radii. The vertical direction of the polar plot is set to be parallel to the b axis of the lattice, i.e., the $D$ value of 133 nm obtained by the (2 0) diffraction
and that of 796 nm obtained by the (0 2) diffraction orient perpendicular to the b and a axes, respectively. The plot shows that the shape of the J-aggregate domain is oval or elliptical. When we treat the domain shape as an ellipse, the length of the major and minor axes are submicrometer (ca. 800 nm) and several hundreds nanometer (ca. 200 nm), respectively. Since the direction of the dipole moment of the MD molecule is parallel to the b axis (see inset of figure 5), it is found that the MD molecules orient along the major axis of the elliptical domain.

Previous observations by using an atomic force microscope (AFM) had revealed that the domain shape was ellipse [13, 14, 15]. From these AFM observations, it had been also shown that the average ratio of the major and minor axes of the domain in the monolayer prepared using the MgCl₂ subphase was ca. 4 and the average area of the elliptical domain was ca. 0.2 µm² [13]. These values coincide well with the results shown in figure 6. Moreover, by our nonlinear optical microscope based on a second harmonic generation, the orientation of the electric dipole moments of the MD molecules is almost parallel to the major axis of the elliptical domain. This was observed in the monolayer having the same J-band, but the monolayer was prepared on the aqueous ammonia instead of the aqueous MgCl₂ solution [13]. This anisotropic arrangement of the MD molecules in the elliptical domain also exhibits a good agreement with the results shown in figure 6.

4. Summary
The GIXD pattern of the MD J-aggregates in the monolayer at the air-water interface was observed (figure 5), and the size and shape of the J-aggregate domain were evaluated from the widths of the diffraction peaks by using the Scherrer formula (table 1 and figure 6). It is found that the shape of the domain is elliptical, and lengths of the major and minor axes of the ellipse domain are ca. 0.8 µm and ca. 200 nm, respectively. These results evaluated by the X-ray diffraction show good agreements with the previous results obtained by the AFM and the nonlinear optical microscope [13].

Acknowledgments
The GIXD experiments were performed with the approval of the Japan Synchrotron Radiation Research Institute (2003B0222-ND1d-np, 2004A0247-ND1d-np and 2006A1259). This work was supported by the Grant-in-Aids for Young Scientists (B) 17760015, 2005 from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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