

MOLECULAR ARRANGEMENT IN ORGANIC DYE MONOLAYER AT AIR-WATER INTERFACE AND ITS VISIBLE ABSORPTION BAND

When organic dye molecules form a crystal or an aggregate, their color becomes different from that of isolated molecules. Due to the close packing in a crystal, the interaction of optical transition dipole moments (TDM[#]) among molecules splits the degenerated state of the ensemble of the molecules and induces a splitting of the molecular energy levels into energy bands. The energy levels in the energy bands, where optically allowed transitions from the ground state take place, are often different from those of an isolated molecule, resulting in a shift of the visible absorption band upon crystallization or aggregation (E_{Shift}). This is a usual interpretation of E_{Shift} . However, in dye aggregates, we have found that not only TDM interaction but also electric dipole moment (EDM^{##}) interaction plays an important role in E_{Shift} [1,2].

When the energy levels, where optically allowed transitions from the ground state take place, are localized at the bottom edge of the first energy band, the aggregates are classified into J-aggregates [3]. Amphiphilic merocyanine dye (MD) molecules (Fig. 1(a)) form J-aggregates at the air-water interface. Figure 1(a) indicates the visible absorption spectra of the monomer and J-aggregate states of the MD monolayer at the air-water interface. Since the former has an absorption band at 524 nm (2.366 eV) and the latter at 618 nm (2.006 eV), MD J-aggregates exhibit $E_{\text{Shift}} = -0.36$ eV and their colors differ as shown in Fig. 1(b). To evaluate the contribution of TDM and EDM interaction energies to E_{Shift} quantitatively, a structural analysis of MD J-aggregates was carried out and E_{Shift} calculations, where the TDM and EDM

interaction energies were rigorously accounted for, were performed on the determined structure [1,2].

For structural determination, the grazing incidence X-ray diffraction of the MD monolayer was observed at beamline BL46XU. Figure 2 shows the optical setup. A 12 keV X-ray beam was irradiated on the monolayer at the air-water interface. Using Si mirrors, θ_{in} was set at 0.09° , which was below the critical angle of the total reflection for the water surface. The DS2 and DS3 slits were 1 mm wide and 0.15 mm high. Incidence intensity was monitored using an ion chamber to normalize detected intensity. A trough for the monolayer was mounted on an 8-axis diffractometer and θ_{out} was also set at 0.09° . The RS1 and RS2 slits were 4 mm wide and 10 mm high. A $2\theta_z$ scan was performed to obtain an in-plane diffraction pattern of the monolayer, and the Soller slit ensured a $2\theta_z$ resolution better than 0.2° . Since the monolayer consisted of randomly oriented J-aggregate crystallites, the observed diffraction corresponds to the two-dimensional powder diffraction.

Figure 3 shows the obtained diffraction pattern, where the Lorentz factor and the background were corrected. Red solid lines are fitting curves for the diffraction peaks. The Miller indices were based on the unit cell in Fig. 3. Structure analysis was carried out by calculating the R-factor. For simplicity, the Debye-Waller factor and water molecules were neglected and the molecular structure obtained by an *ab initio* calculation was used. By changing the molecular orientation while keeping the plane of the planar dye group normal to the lattice plane, and by

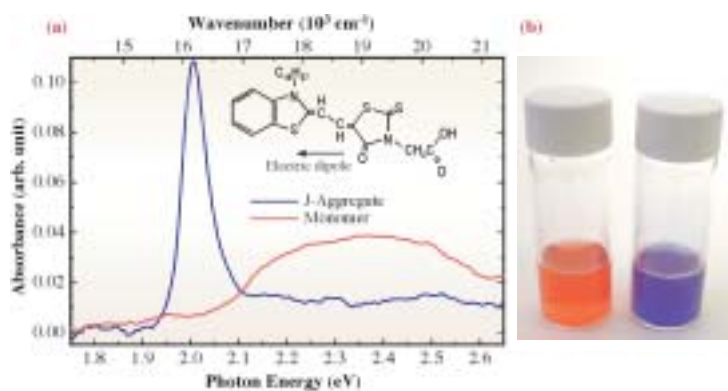


Fig. 1. (a) Chemical structure of amphiphilic merocyanine dye (MD) and visible absorption spectra of MD monolayer in monomer (isolated) and J-aggregate states. (b) Photograph of aqueous dispersions of monomers (left) and J-aggregates (right) prepared with lipids.

[#] A charge distribution in a molecule changes on a transition from its initial to final states. The TDM is related to an overlap between the charge distributions of the initial and final states. The square of the absolute value of the TDM is proportional to the transition probability.

^{##} The EDM is related to an asymmetry of the charge distribution in a molecule. Polar molecules have finite EDMs.

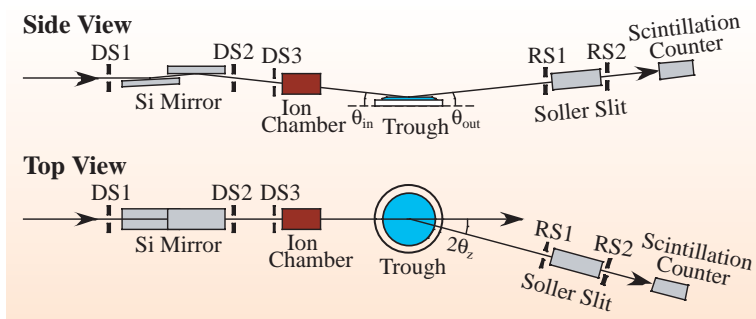


Fig. 2. Optical setup of grazing incidence X-ray diffraction measurements.

rotating the alkyl chain around the N-C bond on the benzothiazole group, the R-factor was investigated. The minimum R-factor (13%) was achieved using the arrangement in Fig. 4. Since the long axis of the dye group, where π electrons are delocalized, is almost parallel to the b -axis, the TDM and EDM are reasonably considered to be parallel to the b -axis.

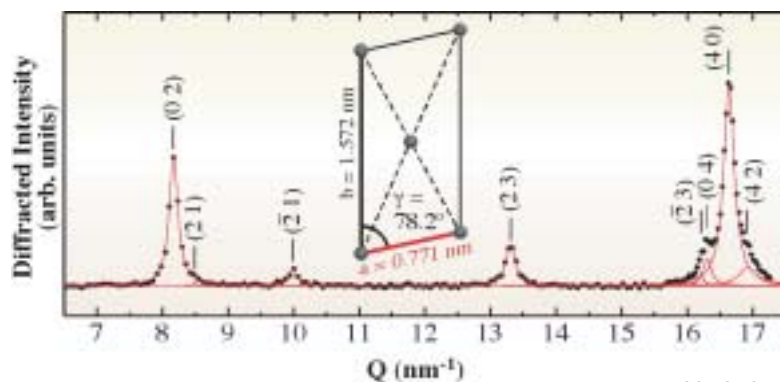


Fig. 3. Diffraction pattern of MD J-aggregate monolayer at air-water interface ($Q = 4\pi \sin\theta_z / \lambda$ with $\lambda = 0.103$ nm) and two-dimensional unit cell.

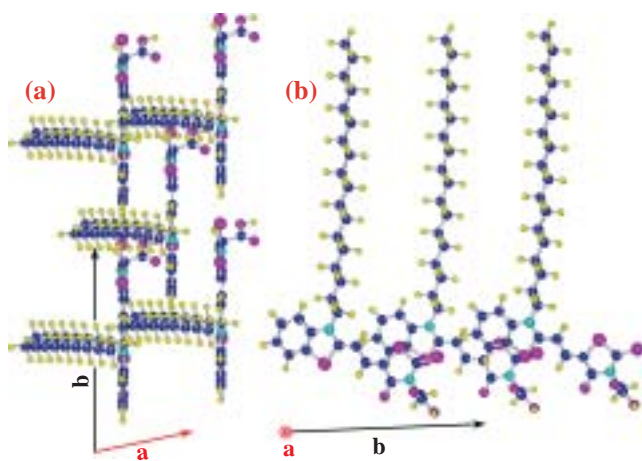


Fig. 4. Molecular arrangement illustrated in direction normal to lattice plane (a) and in the direction along the a -axis of unit cell (b). Due to overlaps, two molecules are hidden in (b).

Taking into account the electrostatic interaction among the molecules in a perturbative way, the eigenvalue equation of E_{Shift} for an infinitely large aggregate was driven [4]. The selection rule for the optical transition permits the aggregate to be optically excited to only one of the eigenstates in the present case, and the eigenvalue is calculated by $E_{\text{Shift}} = J + K$, where J and K represent the TDM and EDM interaction energies, respectively. The latter originates from the difference between the EDMs in the ground and excited states of the molecule. According to the determined arrangement (Fig. 4), all the dipole moments were set to be parallel to the b -axis, and J and K were calculated using formulas simplified by extended dipole approximation. It was clearly shown that J could not explain the observed E_{Shift} solely. Our quantitative analysis revealed that J and K contributed to 44% and 56% of E_{Shift} , respectively, indicating the importance of EDM interaction.

The determination of the aggregate structure led to a deeper understanding of the physics of color change upon dye crystallization, and clarified the contribution of EDM interaction to E_{Shift} , which has not duly been discussed so far, can be significant when the aggregate is formed by polar dye molecules.

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