Thermochromic Phase Transition on 2 dimensional organic dye crystallites

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When organic dye molecules form crystals or aggregates, visible absorption bands generally split or shift from those of isolated (monomeric) dye molecules. Such spectral changes are described under the concept of molecular excitons in the crystals or the aggregates, i.e., optical transition moment and electric dipole moment interactions among the molecules induce shifts and splits of the bands, and the interactions depend on the molecular arrangement in the crystal or the aggregate. [1] When the absorption band shifts to a lower energy, such an aggregate and the shifted band are called J-aggregate and J-band, respectively. [2] J-aggregates have been utilized as spectral sensitizers for silver halides in conventional photography, and they are attracting much attention as candidates for nonlinear optical materials for ultra-fast optical devices and sensitizers for solar cells.

Amphiphilic merocyanine dye (MD) molecules (Fig. 1) self-organize 2 dimensional crystallites at the air-water interface, and the MD crystallites classified into J-aggregates. Recently, we found a thermochromic phase transition of the MD J-aggregates. [3] For an example, the J-band at 618 nm shifts to 595 nm reversibly by changing the water temperature, and the low and the high temperature phases exhibit the J-band at 618 and 595 nm, respectively (Fig. 2). This phenomenon is important for practical applications, because the J-band wavelength, where the susceptibilities of the sensitization and the optical nonlinearity are maximized, can be contorted by the temperature. From the viewpoint of fundamental materials science, the mechanism of this phase transition and the relationship between the molecular arrangement in the J-aggregate and the J-band wavelength are also interesting.

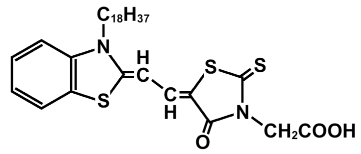

Fig. 1 Molecular structure

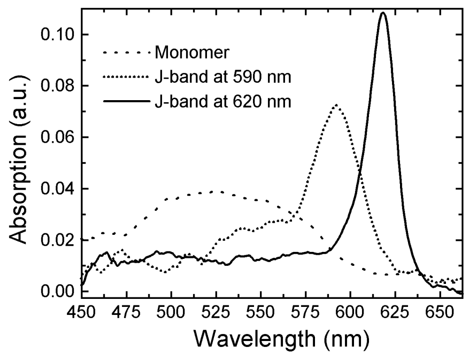

Fig. 2 Visible absorption Spectra

In the seminar, the details of the thermochrmic behavior of the MD J-aggregates under different conditions will be reported with showing thermal hysteresis loops of J-band wavelength and a phase diagram. The results of grazing incidence X-ray diffraction measurements, indicating that the phase transition is a structural phase transition, will be also shown, and the relationship between the determined crystallographic structure of the MD J-aggregate and the J-band wavelength will be discussed.

[1] A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill, New York, 1962).
[2] *J-Aggregates*, edited by T. Kobayashi (World Scientific, Singapore, 1996).
[3] N. Kato *et al.*, J. Phys. Chem. B **107**, 11917 (2003).