Hierarchical structure of merocyanine J-aggregates prepared by Langmuir–Blodgett and spin-coating methods

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Abstract

We have investigated structures of 6-methyl merocyanine (6Me-DS) J-aggregates self-assembled in Langmuir–Blodgett (LB) films and spin-coated polyvinyl alcohol (PVA) films prepared from a mixed solution of 6Me-DS and arachidic acid (AA). The coherent size of J-aggregate depends on the fabrication method. The coherent sizes in the LB and spin-coated film for the same concentration ratio of 6Me-DS:AA = 1:2 are $26\,(\pm 1) \times 40\,(\pm 9)$ molecules and $31\,(\pm 1) \times 22\,(\pm 3)$ molecules, respectively. This result indicates that the well-defined molecular arrangement in the LB film provides a larger coherent size. Microscopy observation shows that J-aggregates in spin-coated film form domains with sizes on a submicron scale. Domain shape is a grain-type if the molar concentration ratio of 6Me-DS to AA is less than 1:8 for 6Me-DS:PVA = 1:6. Increasing AA concentration to 6Me-DS:AA = 1:12, the domain shape drastically changes to a fiber type, indicating that the concentration of AA is a key parameter determining the shape of J-aggregate domain.
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1. Introduction

Recently, much attention has been paid to molecular assemblies for their application potential to novel functional materials. In particular, J-aggregates of cyanine dyes have attracted special interest as a candidate for nonlinear optical materials because of their large optical nonlinearity and ultrafast response time [1–3]. Dynamical properties of Frenkel excitons in J-aggregates have been intensively studied in conjunction with the nonlinear optical properties [4–6]. Fundamental parameters governing optical properties of J-aggregates are a delocalization length of Frenkel excitons and a molecular arrangement. Such structural properties of J-aggregates have been investigated by optical spectroscopy and microscopy [7–12]. J-aggregate structure estimated from spectroscopic data corresponds to the area in which the exciton is coherently extended, while the microscopy study gives an insight into morphologies of J-aggregates on a submicron scale.

J-aggregates of pseudoisocyanine (PIC) have been most intensively studied. The coherent length of the one-dimensional molecular chain structure of PIC J-aggregates has been determined by a spectroscopic method [4,7,9]. Molecule numbers in the coherent area range from 20 to 50 000, depending on the sample form, the theoretical model used in the analysis and the molecular arrangement assumed in the analysis. Recently, Hamanaka et al. have developed the method for precisely determining the coherent size and dimensionality of molecular arrangements in J-aggregates by analyzing both the linear and nonlinear absorption spectra [13,14]. The molecular arrangement for 6-methyl merocyanine J-aggregates fabricated by the Langmuir–Blodgett (LB) method is two-dimensional, and the coherent size is about 26×40 molecules. Optical microscope studies have shown that the PIC J-aggregates in polymer films form fiber-shaped structures with a length of 10–100 μm and a width

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of 30–160 nm [10–12]. Merocyanine J-aggregates have been also studied by a microscopic technique. Merocyanine J-aggregates prepared by the spin-coating method form a grain structure with a diameter of 1 μm, and J-aggregates in LB film form a cigar-shaped structure of several tens micrometeres [11,15]. The LB method provides molecular layers in which an orientation of molecules is well controlled, which is in contrast to the spin-coating method. Consequently, we expect that there is a difference in coherent size of J-aggregates between the LB and spin-coating methods.

In this paper, we report on the coherent size and the domain structure of 6-methyl merocyanine J-aggregates prepared by LB and spin-coating methods with various concentrations of merocyanine and arachidic acid in films to investigate parameters determining the shape and size of 6-methyl merocyanine J-aggregate. A transformation of J-aggregate morphology caused by fatty acid introduced in a spin-coated film is also investigated.

2. Experimental

J-aggregates of 6-methyl merocyanine (3-carboxymethyl-5-[2-(6-methyl-3-octadecyl-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone (abbreviated to 6Me-DS) were prepared by the LB and spin-coating methods. The details of the J-aggregate preparation are described in our previous papers of References [14,16]. A molecular structure of 6Me-DS merocyanine is shown in the inset of Fig. 1. Y-type LB films consisting of 24 molecular layers were fabricated on glass substrates using a standard vertical dipping method from the mixed solution of 6Me-DS and arachidic acid (AA) with the molar ratio of 1:2. A plot of surface pressure (π) of a monolayer versus molecular area
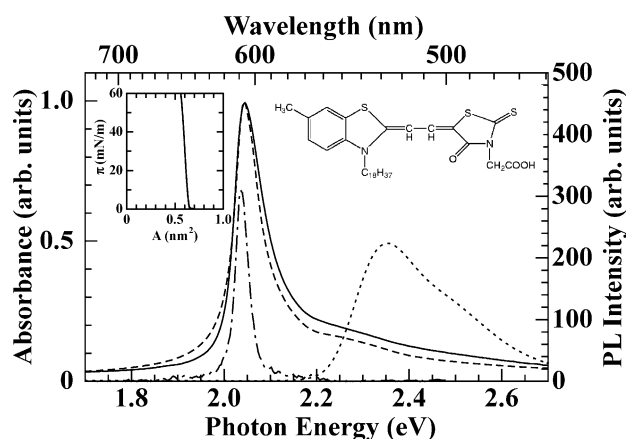

Fig. 1. Absorption spectra of 6Me-DS merocyanine J-aggregates in the LB film for 6Me-DS:AA = 1:2 (solid curve) and spin-coated film for 6Me-DS:AA:PVA = 1:2:2 (dashed curve). Absorption spectrum of the dilute solution of 6Me-DS is shown by the dotted curve. A dot–dashed curve indicates a photoluminescence spectrum of the spin-coated film. A molecular structure of 6Me-DS merocyanine dye is shown in the inset. A surface pressure-area isotherm for the LB film is also shown in the inset.

(*A*) is also shown in the inset of Fig. 1. The monolayers consisting of 6Me-DS and AA were transferred onto glass substrates at $\pi = 30$ (± 0.5) mN/m. J-aggregates in polyvinyl alcohol (PVA) films were prepared on glass substrates by the spin-coating method from a mixed solution of 6Me-DS, AA and PVA. The molar ratio of 6Me-DS to AA was varied from 1:0 to 1:100 and the molar ratio of 6Me-DS to PVA was fixed at 1:2 or 1:6.

Linear absorption spectra were measured using a standard double-beam spectrophotometer. Nonlinear absorption spectra were measured by a pump and probe method [13,14]. An optical parametric amplifier (OPA) based on an amplified Ti:sapphire laser was used for generation of a pump pulse with a pulse duration of 150 fs. A white continuum probe pulse was generated by a self-phase modulation in a water cell. A pump laser fluence was kept below 65 μJ/cm², and the sample was placed in the cryostat at 4.2 K to avoid degradation by laser irradiation.

Photoluminescence (PL) images of J-aggregates were measured by scanning near-field optical microscope (SNOM). The sample was excited by the near-field component of the 488 nm line of a CW argon ion laser from the small aperture with a diameter of ≥50 nm of the fiber probe tip. The PL signal was collected by the microscope objective and detected by the photo-multiplier tube. PL images were recorded by scanning the probe tip by shear-force control. The spatial resolution of the SNOM was about 90 nm. All the measurements were made on fresh samples within a week after the preparation to avoid the degradation of J-aggregate structures.

3. Results and discussion

In Fig. 1, we show linear absorption spectra of a LB film (solid curve) and a spin-coated film (dashed curve) for 6Me-DS:AA = 1:2, together with an absorption spectrum of a dilute ethanol solution of 6Me-DS (dotted curve). A concentration ratio of 6Me-DS to PVA in the spin-coated film is 1:2. The absorption band of 6Me-DS monomers is observed at 2.366 eV in the spectrum for the solution. Sharp absorption bands at 2.045 and 2.043 eV for the LB and spin-coated films are assigned to the Frenkel exciton transition due to the formation of J-aggregates (J-band). The energy shift ΔE of the J-band from the monomer absorption band depends on the number of dye molecules in a coherent area and the molecular arrangement. Absorbance of the J-band of the LB film stored in the air decreased by 10–20% in a month after the preparation, but the absorbance of the spin-coated film did not change for more than 6 months.

A coherent size of 6Me-DS J-aggregates was determined from the observed exciton energy assuming a two-dimensional molecular arrangement shown in Fig. 2. In this model, a coherent area consists of $M \times N$ molecules with the slip angle of α and the dipole direction of each molecule is parallel to each other. Numbers of molecules in a coherent