Exciton delocalization length of merocyanine J-aggregates in Langmuir–Blodgett films studied from linear and nonlinear absorption measurements

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Abstract

A delocalization length and dimensionality of Frenkel excitons in 6-methyl merocyanine J-aggregates in Langmuir–Blodgett films have been investigated by means of linear and nonlinear absorption spectroscopy. The absorption spectrum of dye molecules in an LB film shows the energy shift due to the formation of J-aggregates with respect to the transition energy of monomers. From the differential absorption spectra measured by the femtosecond pump and probe experiment, we have obtained exciton energies of the lowest and second lowest states in J-aggregates. Using both spectroscopic data and a dipole model of molecular arrangement, we have determined the exciton delocalization size of two-dimensional J-aggregates (26(±1) × 40(±9) molecules).

1. Introduction

Chemical and physical properties of J-aggregates formed by dye molecules have been extensively investigated from viewpoints of both fundamental science and technological applications. From the fundamental point of view, electron and energy transfer processes in J-aggregates have been extensively studied [1]. In a research area of biology, J-aggregates have been investigated as a model system of energy transfer processes in photosynthetic antenna complexes due to the similarities of structures and exciton states [1]. J-aggregates have been used as a photosensitizer in the photographic industry for long time, and have recently attracted much attention as a candidate for nonlinear optical materials because of their large optical nonlinearity and ultrafast response time [2–4]. Particularly, a lot of studies have been performed on dynamical properties of Frenkel excitons in J-aggregates in
conjunction with their nonlinear optical properties [5–11]. Important parameters governing optical properties of J-aggregates are a delocalization length of Frenkel excitons and a dimensionality of molecular arrangement. Such structural properties of J-aggregates have been investigated by various methods such as electron diffraction/microscopy [12,13], optical spectroscopy [5,8–11,14–16], and optical microscopy [17–20]. A transmission electron microscope/diffraction study has shown that the aggregate structure of cyanine dye molecules consists of about 30 molecules [12]. The recent work on pseudoisocyanine (PIC) has revealed that the length of J-aggregates is of the order of 350 nm corresponding to 3000 molecules, though the length is dependent on the dye concentration [13].

A lot of spectroscopic studies have reported experimental values of the exciton delocalization length from the measurement of the optical transition energies of monomers and J-aggregates (linear absorption) [15] or one- and two-exciton states (pump–probe nonlinear absorption) [8]. For PIC J-aggregates which are most intensively investigated, the reported value of the delocalization length ranges from 20 to 50,000 molecules [5,8,9,14]. One of the reasons for such a large divergence is that the length is dependent on the sample form: solution, Langmuir–Blodgett (LB) film, spin-coating film, etc. In addition, the estimation is sensitive to the theoretical model and molecular arrangement. Particularly, in two-dimensional (2D) arrangement, one of the data between linear and nonlinear absorption data yields only a lower limit of the delocalization size, and consequently we cannot accurately determine the size. Such a situation will be shown later in this Letter.

The microscopy study, on the other hand, can give more direct information on J-aggregate structures. Spin-coating films of PIC J-aggregates have been investigated by scanning near-field optical microscope (SNOM) and standard optical microscope [17–19]. The results revealed that PIC J-aggregates form fibrous structures with a length of 10–100 μm and a width of 30–160 nm. Optical microscopy study showed that J-aggregates in LB films of merocyanine dyes form island structures with an average size of 70 μm × 10 μm [20]. The observed structures are in a scale much larger than those determined by the spectroscopic methods ≤100 nm. Such a great difference in J-aggregate size between spectroscopic and microscopic methods supports a hierarchical structure model in which a J-aggregate consists of coherent aggregates on a scale of several tens nanometers (mesoaggregates), which was proposed for PIC J-aggregates by Kobayashi [21]. In this framework, the delocalization length determined by the spectroscopic method corresponds to the length of mesoaggregates.

In this Letter, we have investigated a delocalization length, dimensionality, and relaxation dynamics of excitons in 6-methyl merocyanine J-aggregates in LB films by means of both the absorption measurement and the femtosecond pump–probe spectroscopy. Using experimental data taken by both methods, we have determined the exciton delocalization length. The J-aggregate structure is 2D, and the exciton state is extended over 26(±1) × 40(±9) molecules. Relaxation processes of excitons are also discussed.

2. Experimental

A molecular structure of merocyanine dye used in this study is shown in inset of Fig. 1. The dye
molecule has a structure in which a proton at the 6-position in benzothiazole of 3-carboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene) ethylidene]-2-thioxo-4-thiazolidinone (DS) is substituted by a methyl group, and is abbreviated as 6Me-DS. J-aggregates of 6Me-DS were prepared using an LB method [22]. Y-type LB films consisting of 24 molecular layers were fabricated on glass substrates using a standard vertical dipping method. The aqueous solution of 0.4 mmol/l CdCl₂ with a surface pressure of 30 mN/m during the dipping process. A pH value of the subphase was adjusted to 6.0–6.3. Linear absorption spectra were recorded using a double-beam spectrophotometer (Hitachi U3500). Femtosecond transient absorption spectra were measured by a pump and probe method using an amplified Ti:sapphire laser operated at 1 kHz. The pulse duration, photon energy, and pulse energy of the output were 150 fs, 1.55 eV, and 1 mJ, respectively. 70% of the output power was used for an optical parametric amplifier (OPA) system which generated a pump pulse with the photon energy of 2.08 eV. The Ti:sapphire laser beam with the residual power was focused onto a 10 mm cell containing water to generate a white-continuum probe pulse by a self-phase modulation. 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.

3. Results and discussion

A linear absorption spectrum measurement was carried out to investigate a delocalization size of Frenkel excitons in J-aggregates of 6Me-DS merocyanine dyes. We show in Fig. 1 absorption spectra of a 6Me-DS LB film (solid curve) and a dilute ethanol solution of 6Me-DS (dashed curve) at room temperature. The absorption band peaked at 2.366 eV in the spectrum for the solution is ascribed to the S0–S1 transition of 6Me-DS monomers. In the spectrum of the LB film, a sharp absorption band appears at 2.045 eV due to the formation of J-aggregates, and this band (J-band) is assigned to the Frenkel exciton transition. The spectral width (FWHM) of the J-band is 84 meV and the energy shift of the J-band from the monomer band is −0.321 eV. The J-band shifted to 2.064 eV as cooling the LB film down to 4.2 K, while the width of the J-band was unchanged. The energy shift from the monomer absorption band and the spectral width depend on the arrangement of dye molecules in a J-aggregate [23,24]. If a size distribution of J-aggregates is rather small, we can estimate a J-aggregate size from the spectral width. However, the observed J-band width is much larger than the homogeneous width measured for J-aggregates of typical dye molecules (0.1–1.3 meV) [21,25] and does not change over wide temperature range between 4.2 K and room temperature, which suggests a large inhomogeneity of J-aggregates in the 6Me-DS LB film. In such a case, the spectral width does not yield an accurate estimation of a J-aggregate size.

Here, we estimate a J-aggregate size from the energy shift using an extended dipole model proposed by Kuhn and co-workers [23]. In this model, the transition dipole moments of the dye molecules are replaced by classical dipoles with a length l and charges +q and −q as shown in Fig. 2a. We assume a 2D arrangement of 6Me-DS molecules in a J-aggregate, because the long axis of dye chromophores is parallel to the LB film and a long alkyl chain in the molecule is perpendicular to the film [26,27]. The distance between dye molecules in each LB monolayer is much larger than that within a monolayer. We assume that a J-aggregate consists of M × N molecules with the slip angle of x, and the dipole direction of each molecule is parallel to each other. The length r and thickness d of the dye chromophore are taken as r = 1.58 nm and d = 0.36 nm, respectively [28]. The occupied area per 6Me-DS molecule estimated from the above parameters (r × d ≈ 0.589 nm²) agrees well with the value which was estimated from the surface pressure-area isotherm measured during preparation of a LB film (≈ 0.586 nm²) [22]. In the Y-type LB film, some of the chromophores contact directly with those in adjacent layers. However, such a stack is not a dominant structure because each layer contains arachidic acid with the density of 6Me-DS twice as much. Even if it is the case, the...
interaction between adjacent dye molecules within a layer is stronger than that in the stacking direction, because the interlayer distance is larger than $d$ considering the chromophore size [28]. Therefore, we neglected the interlayer interaction within an approximation.

The transition energy $E_J$ of a $J$-aggregate is approximately given by the following equation in terms of the transition energy $E_m$ of the monomer and the interaction integral $J_{ij,xy}$ [23],

$$E_J = E_m + \frac{2}{MN} \sum_{i=1}^{M} \sum_{j=1}^{N} \sum_{x=1}^{M} \sum_{y=1}^{N} J_{ij,xy},$$

\[(i \neq x, j \neq y)\] (1)

Here, $E_J$ and $E_m$ correspond to the peak photon energies of the $J$-band and monomer absorption band, respectively. $J_{ij,xy}$ represents interactions between any two dipoles in an aggregate. In the calculation of $J_{ij,xy}$ values, we used the following parameters. The dielectric constant is 2.5 which is the typical value for hydrocarbons [15], and $\alpha \approx 28^\circ$ which was estimated for $J$-aggregates of DS dyes in LB film by ESR measurements [26]. The length $l$ of the dipole is estimated to be 0.6 nm using the values of the charge $q = 4.49 \times 10^{-20}$ C and the dipole moment $\mu = 8.256$ D [15].

Using the parameters described above, numbers of molecules in a $J$-aggregate were calculated. We derive values of $M$ and $N$ which reproduce the observed energy shift $\Delta E = E_J - E_m = -0.302$ eV. The obtained result ranges between $M = 60$, $N = 18$ and $M = 23$, $N = 50$. All the sets of $M$ and $N$ which can reproduce the observed energy shift $\Delta E$ are shown by the solid curve in Fig. 3. Dashed curves indicate the lower and upper limits of errors due to the experimental accuracy of the absorption peak energy. Although we cannot uniquely determine the values of $M$ and $N$ from this analysis based on the absorption spectra, we will more accurately determine them using a transition energy of one-exciton to two-exciton states.

Now, we carried out a pump and probe experiment to measure an exciton transition energy in the presence of a one-exciton state in a $J$-aggregate. Transient absorption spectra after the excitation with the pump pulse of 2.08 eV were measured at 4.2 K. Shown in Fig. 4a are the ab-
sorption spectrum of the LB film (solid curve) and the spectrum of the pump pulse (dashed curve). The photon energy of the pump pulse coincides approximately with the peak energy of the J-band, and consequently the pump pulse predominantly creates one-exciton states in aggregates. Differential absorption spectra $\Delta$OD measured for the pump fluence of 12 $\mu$J/cm$^2$ are shown in Fig. 4b. Bleaching of the J-band and induced absorption at the high energy side of the J-band are observed in the differential spectra for any delay time shown here. In addition, an oscillatory structure is observed for negative delay times. A similar oscillation was observed for J-aggregates of PIC dyes [9,29], and interpreted in terms of free-induction decay. We briefly describe dynamical properties of excitons generated by the pump pulse. The inset in Fig. 4a shows a time-evolution of the differential absorption measured at the probe photon energy of 2.05 eV. The absorption change $\Delta$OD exhibits a two-component decay. Assuming exponential decay behaviors, the decay times of the fast and slow components are obtained to be 0.7 and 400 ps, respectively. The fast component decay is shortened to 0.5 ps when the pump pulse energy is increased to 65 $\mu$J/cm$^2$. Therefore, the fast decay component is ascribed to an exciton–exciton annihilation process [5,7,8,10]. The slow component corresponds to the recombination decay process of the one-exciton states. These results indicate that the pump pulse under the condition studied here generates multi-exciton states lasting a few picoseconds.

Using a spectral fitting analysis, we deduce the energy difference $\delta E$ between the bleaching and induced absorption components. The pump pulse creates a one-exciton state which is in the lowest level of the exciton band, and the probe pulse delayed from the pump pulse creates another exciton in the second lowest level because the lowest level is already occupied [6]. In the differential spectrum, the negative contribution (bleaching component) is due to the transition from the ground states to the one-exciton states, and the positive contribution (induced absorption component) is due to the transition from the one-exciton to two-exciton states [6]. In our experimental conditions, this situation is achieved after the decay due to the exciton-exciton annihilation: $\geq$2 ps. The lineshape of each component is taken as the J-band lineshape, and the energy separation between the bleaching and induced absorption components is a fitting parameter. An example of the fitted spectra is shown in Fig. 5a. The observed differential spectrum at the delay time of 5.0 ps (open circles) is well reproduced by a superposition of the bleaching component and the induced absorption component (solid curve) when the blue shift $\delta E$ is taken to be 8.4 meV. The spectral components for the bleaching and induced absorption obtained by the fitting analysis are shown in Fig. 5b. The
differential spectra measured at different delay times in the range 2–200 ps were also reproduced by the same parameter. At the early stage of the delay time (<2 ps), we observed the large blue shift depending on the pump fluence. This result suggests that the differential absorption spectra in these delay times are affected by the multi-exciton state in which two or three excitons are created in a J-aggregate by the pump pulse. To avoid the multi-exciton effect, we used the energy shift observed at the late stage (>2 ps) for determination of the two-exciton state energy.

As the energy difference between the one-exciton and two-exciton transitions depends on the exciton delocalization length, we can calculate numbers of molecules which reproduce the observed blue shift \( \delta E \). Here, we mention the validity of such analysis when there exists an inhomogeneity of J-aggregates. Bakalis and Knoester [30] have carried out a numerical calculation to examine the model analysis assuming a J-aggregate as a linear chain of two-level molecules. They showed that the exciton delocalization length is underestimated if there exists an inhomogeneity due to energetic disorder between molecules in an aggregate. However, the delocalization length can be correctly determined as long as the delocalization length is shorter than \( \sim 60 \) molecules [30]. As will be discussed later, the molecule number studied here is less than 50 in each direction, and thus such a condition is fulfilled.

Let us calculate a delocalization size using a point dipole model in which one-exciton and two-exciton states within a J-aggregate are taken into account. For the simplicity, the transition dipole of the dye molecule is regarded as a point dipole with a moment \( \mu \) placed in the center of each molecule as shown in Fig. 2b. If a nearest-neighbor interaction is taken into account [31], the transition energy \( E_k \) of Frenkel excitons with the wave vector \( k \) is given by

\[
E_k = E_m + 2J(k).
\]

As the LB film gives a well-defined 2D monolayer of dye molecules, the aggregate structure is regarded as 2D. In this case, \( J(k) \) is written as

\[
J(k) = J_1 \cos \left( \frac{2\pi k_1}{N} \right) + J_2 \cos \left( \frac{2\pi k_2}{M} \right) + J_3 \cos \left( \frac{2\pi k_1}{N} - \frac{2\pi k_2}{M} \right)
\]

by considering interactions with eight neighboring molecules, where

\[
J_1 = \mu^2 \frac{2}{a_1^3},
\]

\[
J_2 = \mu^2 \frac{1 - 3 \cos^2 \alpha}{a_2^3},
\]

\[
J_3 = \mu^2 \frac{a_1^2 - 3[a_1 - a_2 \cos \alpha]^2}{a_3^5}.
\]

\( a_1, a_2, \) and \( a_3 \) are the distance between the neighboring point dipoles as shown in Fig. 2b. Assuming the same arrangement of molecules as used for the LB film of DS merocyanine dyes, \( a_1, a_2, \) and \( a_3 \) are 1.58, 0.42, 1.24 nm, respectively. The lowest energy \( E_{k=(0,0)} \) corresponds to the peak energy of the J-band, and \( E_{k=(0,1)} - E_{k=(0,0)} \) corresponds to \( \delta E \). Taking molecule numbers \( M \) and \( N \) as adjustable parameters, we calculate a value of \( E_{k=(0,1)} - E_{k=(0,0)} \) that corresponds to the experi-
mentally obtained value of $\delta E$ (8.4 meV). The obtained values of $M$ and $N$ are shown in Fig. 3 by the dotted curve. The values range between $M = 60$, $N = 8$ and $M = 26$, $N = 50$, and the curve does not exactly coincide with the solid curve which was obtained from the absorption peak energies of the $J$- and monomer-bands. However, there exists a crossed area including experimental errors, and this area (hatched area) gives us values of $M$ and $N$ that can reproduce both experimental data. The obtained size is $M \times N = 26(\pm 1) \times 40(\pm 9)$ molecules. It is worthy to mention that any value calculated using a model based on the one-dimensional (1D) arrangement of chromophores was in disagreement with the experimental values obtained in this study.

The model used in the analysis assumed the homogeneous $J$-aggregates. In the samples studied here, however, there exists an inhomogeneous broadening of the $J$-band due to a distribution of the delocalization size. Accordingly, the obtained size is a most probable value within the distribution. Although the inclusion of the inhomogeneity in the model may improve the precision of the delocalization size, we focus this study on a demonstration of the size determination based on both the linear absorption data and the femtosecond pump-probe data for 2D $J$-aggregates. Indeed, by using the method proposed in this study, we can reduce an uncertainty range compared to the method based on one of these data.

Finally, we discuss the exciton delocalization size determined from the spectroscopic data comparing with the size observed by the optical microscope. Taking account of the molecular size of 6Me-DS dyes, we estimate the delocalization size to be about 9 nm $\times$ 60 nm from $M \times N = 26(\pm 1)$ $\times$ 40(±9). Although the $J$-aggregate size of 6Me-DS LB films has not been measured by the microscopy, that of DS merocyanine LB films observed by the optical microscope has been known as $\sim 70 \mu m \times 10 \mu m$ [20]. Our preliminary SNOM observation for the LB film consisting of 6Me-DS dye and arachidic acid with the molar ratio of 1:2 shows that the size is of the order of 10 μm which is similar to that for DS merocyanine LB films. This result suggests the hierarchical structure where the macroscopic aggregate is composed of many small aggregates, that is, the delocalization areas with the size of 9 nm $\times$ 60 nm [21].

4. Summary

We have investigated a delocalization length, dimensionality, and relaxation dynamics of excitons in 6Me-DS merocyanine $J$-aggregates prepared by the LB method. The exciton delocalization length and their dimensionality were obtained by analyzing the energy shift of the $J$-band from the monomer absorption band in the absorption spectrum and the energy difference in the transient absorption spectrum between the bleaching and induced absorption bands. We have found that the $J$-aggregate structure is 2D, and the exciton delocalization area consists of 26(±1) $\times$ 40(±9) molecules. In the hierarchical structure model, there may exist a large aggregate consisting of the exciton delocalization area. A microscopic study using the SNOM is in progress to elucidate this situation. Transient absorption spectra of the $J$-band have shown a two-component decay behavior. The fast and slow components are ascribed to the exciton–exciton annihilation process and the recombination process, respectively.

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