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Determination of Third-Order Optical Nonlinearity Dispersion of 1-Methyl-1′-Octadecyl-2,2′-Cyanine Perchlorate Langmuir-Blodgett Films Using Electroabsorption Spectroscopy

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The absorption and electroabsorption (EA) spectra of 1-methyl-1′-octadecyl-2,2′-cyanine perchlorate (S120) Langmuir-Blodgett films were measured. From these results, dispersion of the third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ in the range of 1.8 to 2.7 eV was determined. In addition, the linear-polarizability difference $\Delta\alpha$ and the permanent dipole-moment difference $\Delta\mu$ between excited and ground states were evaluated. Upon comparison with the results of measurement of the S120 monomer film, it was found that the third-order nonlinear optical susceptibility of the S120 LB film is strongly enhanced by a factor of 1000. It was concluded that this strong enhancement is attributed to the fact that S120 molecules with a short methyne chain that tightly binds two quinoline rings form a rigid J-aggregate with a one-dimensional structure that hardly twists, so as to yield a sharp absorption band with a large transition moment. Finally, we evaluated the average aggregation number of the S120 LB film to be 3–4.

KEYWORDS: J-aggregate, Langmuir-Blodgett film, cyanine dye, electroabsorption spectroscopy, third-order optical nonlinearity

1. Introduction

J-aggregates of dye molecules[1,2] have attracted much attention because these systems are expected to exhibit mesoscopic properties which are a crossover between microscopic (i.e., single molecules) and macroscopic (i.e., bulk materials) properties. Moreover, they are also attractive because of their large optical nonlinearities. In each molecule, the intermolecular dipole interaction couples with electronic excitation to form an exciton state delocalized over an aggregate. As a result, the absorption spectrum of J-aggregates shows a new, very sharp and strong peak, the so-called J-band, shifted to the lower energy side with respect to a monomer absorption band. Because of the thread-like structure of the J-aggregate, significant insight into the linear and nonlinear optical properties of quasi-one-dimensional excitons is anticipated to be gained.

1-Methyl-1′-octadecyl-2,2′-cyanine perchlorate (S120), as shown in Fig. 1, is one of the materials that form J-aggregates and has the following characteristics. First, because of its short methyne chain, few stereoisomers exist. Second, the molecule is almost planar because the two quinoline rings are coupled strongly by the short methyne chain and thus shows one-dimensional (1D) confined electronic properties. Third, dye molecules have substituents and counter ions (ClO_4^-) which assist in the alignment of the molecules. Hence, S120 molecules form J-aggregates in which molecules bind more tightly to one another and become one of the typical 1D-confined Frenkel exciton systems. In contrast to this, in the case where the methyne chain is long, J-aggregates show two-dimensional electronic properties and are much more complicated to investigate. Concerning the J-aggregates of cyanine dyes, although only the origin of nonlinearity in spin-coated films[3] and nonlinearity in a disperse system[4–6] was studied, nonlinearity in LB films or dispersion of nonlinearity has not been investigated so far.

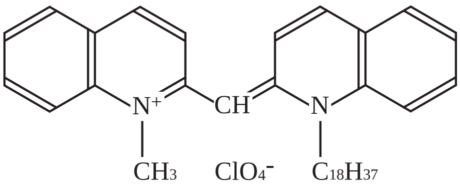

Fig. 1. Molecular structure of S120.

Modulation absorption spectroscopy using an external electric field is a powerful technique for the investigation of the subtle difference in electronic structure between aggregates and monomers. The permanent dipole moment and the linear polarizability are key parameters that govern nonlinear optical properties as well as linear optical properties. From the electroabsorption (EA) measurement, we can evaluate the change in these parameters for the electronic transition from a ground state to an excited state.[7] Moreover, we can determine the dispersion of the third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ through the Kramers-Kronig relation.[8,9] Thus, we can clarify the origin of nonlinearities of mesoscopic materials.

The purpose of the present work is to clarify the mechanism of the third-order optical nonlinearity in the S120 multilayer film fabricated by the Langmuir-Blodgett (LB) method and to evaluate the coherence size or the aggregation number of S120 molecules in the LB film from a comparison of experimental results between S120 J-aggregated and monomer samples. Finally, we determine the dispersion of the third-order nonlinearity for S120 LB film which is an ideal 1D exciton system.

2. Experiment and Analysis

The cyanine dye S120 used in this work was purchased from Hayashibara Biochemical Laboratories Inc. (NK-3025). Conductive indium tin oxide (ITO) coated quartz glass was employed as the substrate. Cyanine dye S120 J-aggregated samples for measurement were prepared by the Langmuir-

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Blodgett method; S120 monolayers were transferred onto the substrate after coating with cadmium arachidate to render the substrate surface hydrophobic. The fabricated sample has 26 layers and forms a Z-type LB film. For the S120 monomer sample, S120-doped tetraethyl orthosilicate thin film was fabricated by the spin-coating method. Semi-transparent aluminum was deposited over the film surface as a counter electrode. The thickness of the J-aggregated sample was about 0.07 μm, which was measured using a multiple-beam interferometer (Mizojiri BM-4).

EA spectroscopy was carried out at room temperature using the previously employed system[10] with the introduction of a vacuum chamber in order to avoid sample degradation in air. The spectral range for EA measurement was from 1.80 to 2.70 eV for the J-aggregated sample and from 2.00 to 3.00 eV for the monomer sample.

When an electric field is applied to the sample, the change in the absorption spectrum is described by a linear combination of the absorption spectrum and its first- and second-derivatives as follows:[7,11,12]

$$\Delta A(E,F)/E = \left[a_0\left(\frac{A}{E}\right) + a_1\frac{d}{dE}\left(\frac{A}{E}\right) + a_2\frac{d^2}{dE^2}\left(\frac{A}{E}\right) + \cdots\right] R(\theta)[L(0)F]^2, \tag{1}$$

where E is the photon energy $\hbar\omega$. a_0, a_1 and a_2 are, respectively, given by

$$a_0 = \frac{X^2}{\mu^2} + \frac{2Y}{\mu}, \tag{2}$$

$$a_1 = \frac{2X}{\mu}\Delta\mu + \frac{1}{2}\Delta\alpha, \tag{3}$$

$$a_2 = \frac{1}{2}(\Delta\mu)^2. \tag{4}$$

Here, μ, X, Y, $\Delta\alpha$ and $\Delta\mu$ are the transition-dipole moment, the transition-dipole-moment polarizability, its hyperpolarizability, the linear-polarizability difference and the permanent dipole-moment difference between excited and ground states, respectively. They generally have a relationship expressed in the dyadic notation:

$$\boldsymbol{\mu}(\boldsymbol{F}_{\text{int}}) = \boldsymbol{\mu} + \mathsf{X}\cdot\boldsymbol{F}_{\text{int}} + \boldsymbol{F}_{\text{int}}\cdot\mathsf{Y}\cdot\boldsymbol{F}_{\text{int}} + \cdots, \tag{5}$$

where $\boldsymbol{F}_{\text{int}}$ is the internal electric field,

$$\boldsymbol{F}_{\text{int}} = L(0)\boldsymbol{F}, \tag{6}$$

and where $L(\Omega)$ is the Lorentz local-field factor given by

$$L(\Omega) = \frac{\epsilon(\Omega)+2}{3}, \tag{7}$$

where $\epsilon(\Omega)$ is a dielectric constant at an angular frequency of the applied field. For J-aggregates, molecules are aligned parallel to each other; thus, vectors $\boldsymbol{\mu}$ and $\Delta\boldsymbol{\mu}$, and tensors X, Y and $\Delta\alpha$ are reduced to scalars μ, $\Delta\mu$, X, Y and $\Delta\alpha$, respectively. $R(\theta)$ is a general sensitivity function given by

$$R(\theta) = \frac{1}{15}[5 + (3\cos^2\xi - 1)(3\cos^2\theta - 1)], \tag{8}$$

where ξ is the angle between the directions of $\Delta\boldsymbol{\mu}$ and $\boldsymbol{\mu}$, and θ is the angle between the directions of the applied electric field and the polarization vector of the incident light.

The first, second and third terms in eq. (1) correspond to the change in oscillator strength, the spectral shift and the spectral broadening induced by the applied electric field, respectively. When the change in linear polarizability is significant, the first derivative of the absorption spectrum is dominant in the EA spectrum. In contrast, when the permanent dipole-moment difference is significant, the second derivative is dominant. This formula is valid for an isolated absorption band due to a single electronic transition.

The third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ is obtained from the absorption spectrum $A(\omega)$, the Kerr-effect EA spectrum $\Delta A(\omega)$, the refractive index $n(\omega)$ and the refractive index change $\Delta n(\omega)$.[8,9] The refractive index $n(\omega)$ is related to the absorption coefficient through the Kramers-Kronig (K-K) relation, and the refractive index change $\Delta n(\omega)$ due to electromodulation is calculated using the following derivative form of the K-K relation:

$$\Delta n(\omega) = \frac{c}{\pi}\mathcal{P}\int_0^\infty \frac{\Delta A(\omega')}{\omega'^2 - \omega^2}d\omega', \tag{9}$$

where $\mathcal{P}$ denotes the Cauchy principal value of the integral and c is the velocity of light. This relation is valid for the case where the frequency Ω of the applied electric field is sufficiently low compared with the optical frequency ω, and the system is regarded to be in the steady state. The third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ is expressed as

$$\chi^{(3)}(-\omega; 0, 0, \omega) = \frac{1}{6\pi F^2}\left[(n(\omega)\Delta n(\omega) - k(\omega)\Delta k(\omega)) + i(n(\omega)\Delta k(\omega) + k(\omega)\Delta n(\omega))\right], \tag{10}$$

where F is the amplitude of the applied electric field, and k and Δk are the extinction coefficient and its change due to electromodulation, respectively, represented by

$$k(\omega) = \frac{\lambda}{4\pi}A(\omega), \tag{11}$$

$$\Delta k(\omega) = \frac{\lambda}{4\pi}\Delta A(\omega), \tag{12}$$

where λ is the wavelength.

3. Results and Discussion

Figure 2(a) shows the absorption spectrum of the S120 LB film together with that of the S120/acetone solution. The S120 LB film has a new absorption band in the low-energy side of the lowest absorption band of the S120 solution. The fact that the new absorption band is extremely strong and sharp indicates that S120 molecules form stable J-aggregates, and that the S120 molecule has a short methyne chain. Figures 2(b) and 2(c) show the first and second derivatives of the absorption spectrum, respectively. The EA spectrum of the S120 LB film and its fit using eq. (1) are shown in Fig. 2(d). It is found that the EA spectrum has a simple profile dominated by the second-derivative of the absorption spectrum, that is, the third term of eq. (1). Thus, we conclude that the spectral change in the presence of the electric field is mainly due to the permanent dipole-moment difference $\Delta\mu$. Here, we assume that the component proportional to the absorption spectrum in the measured EA spectrum is negligible, that is, $a_0 = 0$ in eq. (1). Decomposing the EA spectrum into the

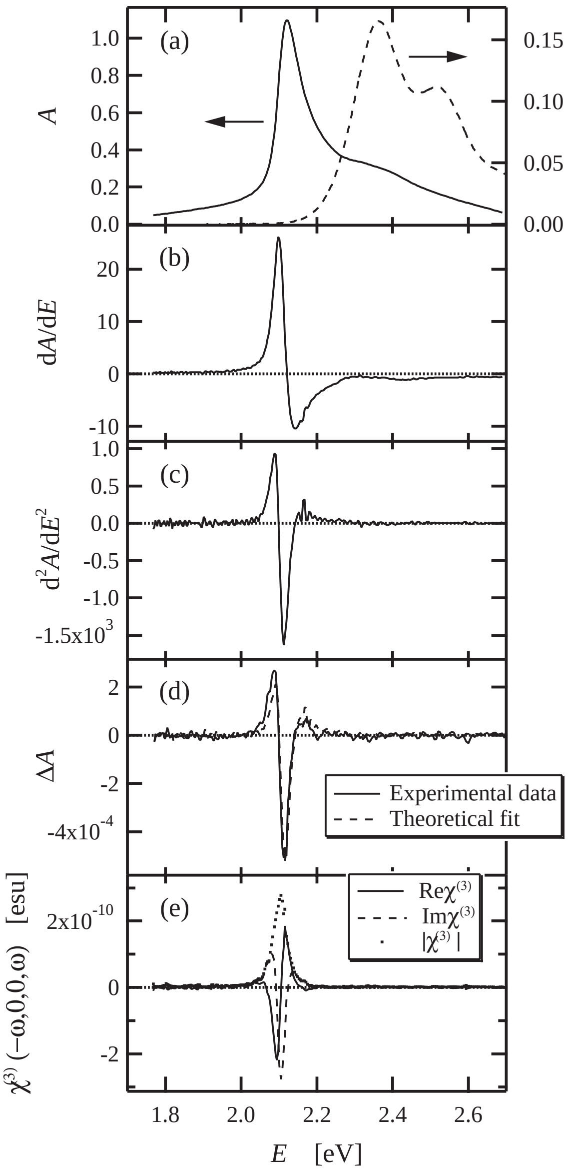

Fig. 2. (a) Absorption spectrum of the S120 LB film (J-aggregated sample, solid line) together with that of the S120/acetone solution (monomer sample, broken line), and its (b) first and (c) second derivatives. (d) EA spectra of the S120 LB film [solid line: experimental result, broken line: fit by eq. (1)]. (e) Dispersion of $\chi^{(3)}(-\omega; 0, 0, \omega)$ for the S120 LB film (solid line: real part of $\chi^{(3)}$, broken line: imaginary part of $\chi^{(3)}$, dotted line: $|\chi^{(3)}|$).

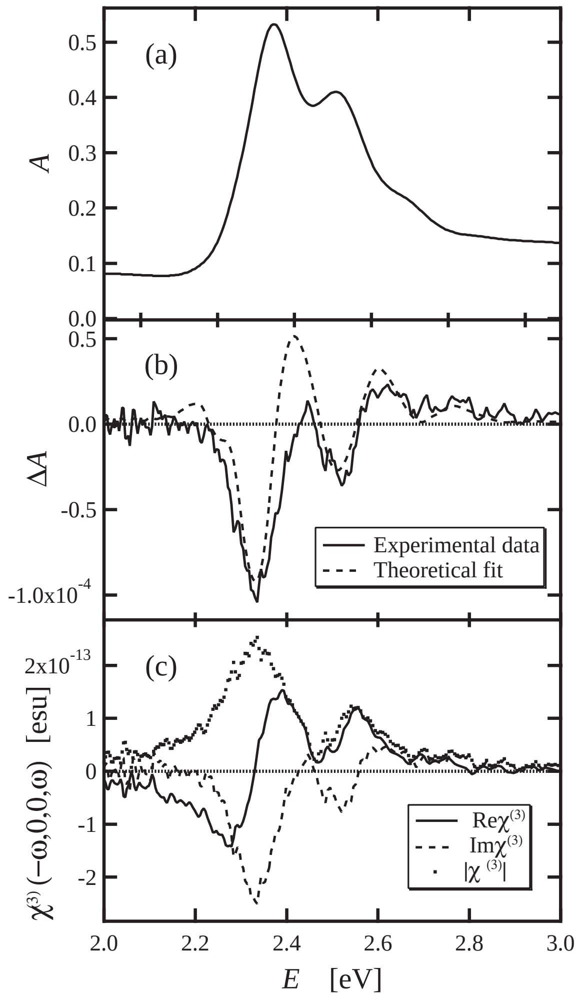

Fig. 3. (a) Absorption spectrum of the S120 monomer film, and its (b) EA spectra [solid line: experimental result, broken line: fit by eq. (1)]. (c) Dispersion of $\chi^{(3)}(-\omega; 0, 0, \omega)$ for the S120 monomer film (solid line: real part of $\chi^{(3)}$, broken line: imaginary part of $\chi^{(3)}$, dotted line: $|\chi^{(3)}|$).

linear combination expressed as eq. (1), we evaluate the $\Delta\alpha$ and $\Delta\mu$ values to be -1.5×10^{-22} cm^3 and 1.6 D, respectively. Fig. 2(e) shows the dispersion of the real and imaginary parts of $\chi^{(3)}(-\omega; 0, 0, \omega)$ in the range of 1.80 to 2.70 eV obtained from the absorption and EA spectra using eq. (10). The $\chi^{(3)}$ value also changes markedly around the J-band. The maximum value of $|\chi^{(3)}(-\omega; 0, 0, \omega)|$ of the S120 LB film is 2.8×10^{-10} esu at 2.10 eV where the J-band is.

The absorption and EA spectra of the S120 monomer film are shown in Figs. 3(a) and 3(b), respectively. We evaluate the $\Delta\alpha$ and $\Delta\mu$ values for the S120 monomer film to be $-(4.0\text{–}5.2) \times 10^{-23}$ cm^3 and 0.70–0.83 D in a manner similar to the S120 LB film, respectively, with a lower signal-to-noise ratio. Figure 3(c) shows the dispersion of the real and imaginary parts of $\chi^{(3)}(-\omega; 0, 0, \omega)$ in the range of 2.00 to 3.00 eV. The maximum value of $|\chi^{(3)}(-\omega; 0, 0, \omega)|$ is 2.7×10^{-13} esu at 2.34 eV.

Considering that the linear polarizability is proportional to the occupied volume of a molecule,[13)] from the ratio of the linear-polarizability difference between the S120 monomer film and the LB film, we evaluate the average aggregation number to be three to four molecules.

We would like to emphasize that the maximum value of $|\chi^{(3)}(-\omega; 0, 0, \omega)|$ of the S120 LB film is about 1000 times larger than that of the S120 monomer film. It is clear that this extremely large $\chi^{(3)}$ enhancement is caused by the formation of a J-aggregate by S120 molecules in the LB films. This enhancement can be explained as follows.

For the two-level model, the third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ under the resonant condition is represented by the following equation based on the quantum-mechanical perturbation theory:[14)]

$$\chi^{(3)}(-\omega; 0, 0, \omega)_{\text{reso}} \propto \frac{1}{\hbar^3} \frac{|\mu|^2(\Delta\mu)^2}{(\omega_{\text{eg}} - \omega - i\Gamma_{\text{eg}})^3}, \qquad (13)$$

where Γ_{eg} is the relaxation rate between the excited state and the ground state. $\hbar\omega_{\text{eg}}$ is the energy difference between the excited state and the ground state. From eq. (13), it is found that there are three possibilities for the $\chi^{(3)}$ enhancement of the J-aggregate sample. They are: 1) an increase in $\Delta\mu$, 2) an increase in μ and 3) a decrease in Γ_{eg}. The experiment showed that the $\Delta\mu$ value of the S120 LB film slightly increases compared with that of the S120 monomer film. In contrast, the μ value is large (corresponding to the strong absorption intensity and hence the large absorption cross section) and the Γ_{eg} value is small (corresponding to the very sharp absorption spectrum). This suggests that the significant $\chi^{(3)}$-enhancement of the S120 LB film is due to the latter points, 2) and 3). This finding is based on the fact that the formed aggregate has a hardly twisting and rigid 1D structure because S120 molecules with the short methyne chain bind tightly with one another unlike the other aggregates. That is, this aggregate yields the well-behaved 1D Frenkel exciton that delocalizes over the N-independent molecular sites of one J-aggregate due to the intermolecular dipole-dipole interaction during optical excitation. As a result, the typical 1D exciton produces a strong absorption band on the lower energy side and its coherent delocalization causes the decrease in Γ_{eg}. In spite of the rigid 1D structure, the $\chi^{(3)}$ value of S120 LB film is smaller than those of previously reported pseudoisocyanines or cyanine J-aggregates.[4–6] This is ascribed to the following two reasons. One is that the aggregation number is limited by the long alkyl chain which is introduced to form the LB film configuration. The longer the alkyl chain, the lower the aggregation number. The other reason is that while the $\chi^{(3)}_{iiii}$ component was measured using the four-wave mixing[4,5] or the Z-scan[6] technique in previous works, a comparatively small $\chi^{(3)}_{ijji}$ $(i \neq j)$ component was measured for S120 LB films since the direction of the applied electric field to S120 molecules in LB film was perpendicular to the transition dipole moment of S120 molecules in our configuration. Therefore, the absolute value in our measurement cannot be directly compared with those in previous measurements. However, the comparison of the relative value, that is, the comparison of the magnitude of the $\chi^{(3)}$ enhancement between our result and the previous one is reasonable even if the measurements were carried out in different ways. In fact, our result that $\chi^{(3)}$ is enhanced by a factor of 1000 is comparable to the previous result[4] of the H-aggregate which has the same origin of $\chi^{(3)}$ enhancement as the J-aggregate, which is due to the near-resonant effect and the delocalized exciton in an aggregate unit.

4. Conclusion

We measured the absorption and EA spectra for 1-methyl-1′-octadecyl-2,2′-cyanine perchlorate Langumuir-Blodgett films and monomer films. From these results, we evaluated the linear-polarizability difference $\Delta\alpha$ and the permanent dipole-moment difference $\Delta\mu$. In addition, we determined the dispersion of the third-order nonlinear susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ through the Kramers-Kronig relation. Consequently, it was found that the $\chi^{(3)}$ value is extremely enhanced, i.e., the maximum value of $|\chi^{(3)}(-\omega; 0, 0, \omega)|$ of the S120 LB film is about 1000 times larger than that of the monomer film. This result is ascribed to the fact that S120 molecules, possessing the short methyne chain, bind tightly to form a rigid J-aggregate. Finally, from the ratio of the values of the linear-polarizability difference between the monomer and the J-aggregate, we evaluated the average aggregation number of the S120 molecules to be 3–4.

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