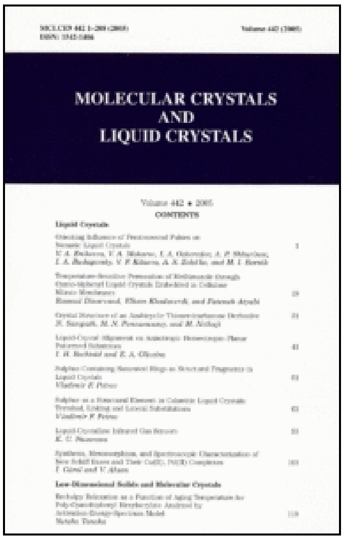

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Third-Order Nonlinear Optical Susceptibility Measurement in 1-Methyl-1'-Octadecyl-2,2'-Cyanine Perchlorate Langmuir-Blodgett Films by Means of Electroabsorption Spectroscopy

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Third-Order Nonlinear Optical Susceptibility Measurement in 1-Methyl-1'-Octadecyl-2,2'-Cyanine Perchlorate Langmuir-Blodgett Films by Means of Electroabsorption Spectroscopy

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By an electroabsorption spectroscopy technique, we determined the third-order nonlinear optical susceptibilities dispersion in 1-methyl-1'-octadecyl-2,2'-cyanine perchlorate Langmuir-Blodgett (J-aggregate) films in the range of 1.8 to 2.7 eV. In addition, from the values of the polarizability change in the monomer and aggregate films, the number of molecules in an aggregate was evaluated to be 3–4.

Keywords: J-aggregate; Langmuir-Blodgett film; cyanine dye; electroabsorption spectroscopy; nonlinear optical susceptibility

INTRODUCTION

1-methyl-1'-octadecyl-2,2'-cyanine perchlorate (S120) molecules in Langmuir-Blodgett (LB) films form J-aggregates. In each molecule, intermolecular dipole interaction couples electronic excitation and forms an exciton state delocalized over an aggregate. The excitonic transition exhibits a very sharp absorption spectrum (J-band) red-shifted from the monomer absorption. Because of thread-like form of J-aggregates, linear and nonlinear properties of quasi-one-dimensional excitons can be investigated in S120 LB films. In the present study, we measured the third-order nonlinear optical susceptibilities $\chi^{(3)}(-\omega;0,0,\omega)$ of J-aggregates in S120 LB films by use of an electroabsorption (EA) spectroscopy technique.

EXPERIMENTAL

Samples for electric-field modulation measurement were prepared as follows. While a monomer film was spin-coated on the conductive ITO (Indium Tin Oxide)-deposited glass, a 26-layer LB film of S120 (Z-type) was deposited onto a ITO-deposited glass which was coated with a single layer of arachidic acid prior to the S120 deposition, Moreover, semi-transparent aluminum was deposited on the film surface as a counter electrode. In the EA measurement, an ac electric field on the order of 10^5 V/cm was applied between the ITO glass and the electrode.

The third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega;0,0,\omega)$ can be calculated from the absorption (A') spectrum normalized by the photon energy and its Kerr-effect EA ($\Delta A'$) spectrum through the Kramers-Kronig relation. $\Delta A'$ is generally represented by a linear combination of the absorption spectrum itself and its first- and second-derivatives as[1]

$$\Delta A'(E,F) = \left|\frac{\Delta M^F}{M}\right|^2 A' + \frac{1}{2}\Delta\alpha F^2\frac{dA'}{dE} + \frac{1}{2}(\Delta\mu F)^2\frac{d^2A'}{dE^2}, \qquad (1)$$

where $E, F, \Delta\alpha$ and $\Delta\mu$ are the photon energy, the applied electric field, linear polarizability change and permanent dipole moment change, respectively. M and ΔM^F are the matrix element of transition dipole moment between the excited and ground states and its first-order change with the applied electric field, respectively.

RESULTS AND DISCUSSION

Absorption and EA spectra (normalized by the photon energy) of S120 LB films are shown in Figure 1 (a) and (b), respectively. It is found that the EA spectrum has a similar profile to the second-derivative of the absorption spectrum, that is, the third term of Equation (1). Thus we conclude that the spectral change in the presence of the electric field is mainly due to the permanent dipole change. Decomposing the EA spectrum into the linear combination expressed as Equation (1), we evaluated the $\Delta\alpha$ and $\Delta\mu$ values to be -1.5×10^{-22} cm^3 and 1.6 D, respectively. Absorption and EA spectra of S120 monomer films are shown in Figure 1 (c) and (d), respectively. In the similar manner, but in less S/N ratio experimental condition, $\Delta\alpha$ and $\Delta\mu$ values for the monomer were evaluated to be $-(4.0\text{-}5.2) \times 10^{-23}$ cm^3 and 0.70-0.83 D, respectively. From the ratio between $\Delta\alpha$ values for the monomer and aggregate, the number of molecules in an aggregate was evaluated to be 3-4.

Besides, the dispersion of real and imaginary parts of $\chi^{(3)}(-\omega; 0, 0, \omega)$ in the range of 1.8 to 2.7 eV were also determined, as shown in Figure 2. S120 LB films have a large $|\chi^{(3)}(-\omega; 0, 0, \omega)|$ value of 2.8×10^{-10} esu at 2.10 eV corresponding to the J-band.

CONCLUSION

We determined the third-order nonlinear optical susceptibilities dispersion of in 1-methyl-1'-octadecyl-2,2'-cyanine perchlorate Langmuir-Blodgett (J-aggregate) films in the range of 1.8 to 2.7 eV, by use of an electroabsorption spectroscopy technique. From the values of the polarizability change in the monomer and aggregate, the number of molecules in an aggregate was evaluated to be 3-4.

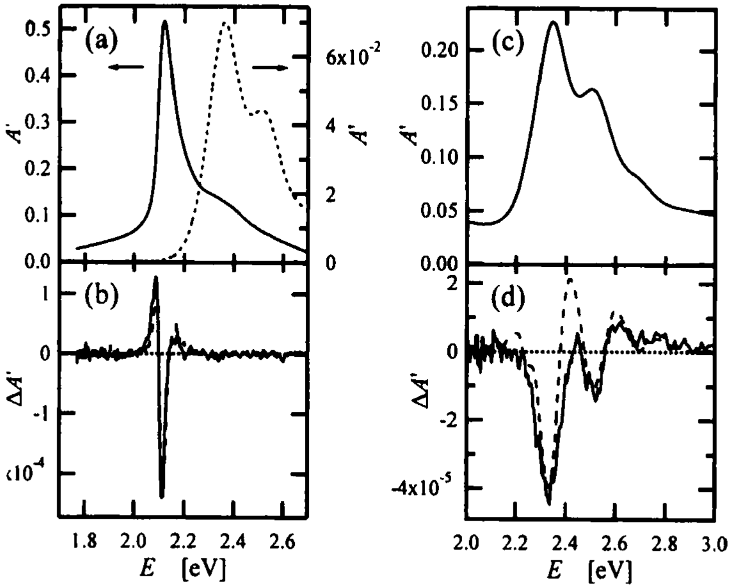

FIGURE 1 (a) Absorption spectra of the S120 LB film (solid line) and S120/acetone solution (broken line), and its (b) electroabsorption spectrum (solid line: experimental result, broken line: theoretical fit). (c) Absorption spectrum of the S120 monomer film, and its (d) electroabsorption spectrum (solid line: experimental result, broken line: theoretical fit).

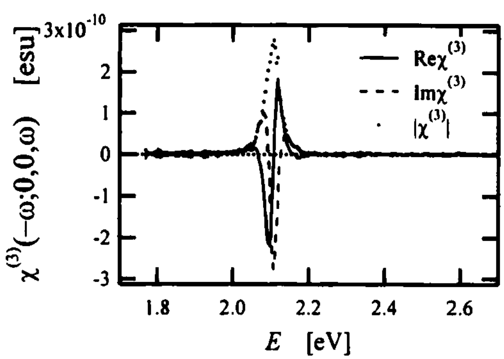

FIGURE 2 Dispersion of $\chi^{(3)}(-\omega; 0, 0, \omega)$ for S120 LB films.

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