Studies on Aggregation of Fluorescein Derivatives by Electroabsorption Spectroscopy

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Concentration dependence of linear and nonlinear optical property in a series of di-*n*-butyl fluorescein derivatives was investigated by absorption and electroabsorption measurements, in order to examine the aggregativeness of them. It was found that Br substitution prevents molecular aggregation which affects the third-order nonlinearity.

Keywords: molecular aggregation; electroabsorption spectroscopy; fluorescein derivatives; third-order nonlinear susceptibility

INTRODUCTION

Fluorescein derivatives are chemically stable and thus widely used as fluorescence dyes. They are also attracting a lot of attention as nonlinear optical materials because of their extended π-conjugation. Flexible tunability of chemical and optical properties by peripheral substitution makes this family model compounds to investigate the structure-property relationship. For example, Cl substitution at phenyl group introduces intramolecular charge transfer which enhances third-order optical nonlinearity as already reported[1]. The peripheral groups also govern the

aggregativeness. It is well known that the aggregation affects seriously to linear and nonlinear optical properties especially in heavily doped film samples.[2,3] In this paper, the influence of halogen substitution to molecular aggregativeness is investigated in a series of di-*n*-butyl fluorescein derivatives by means of concentration dependence of electroabsorption spectra.

EXPERIMENTAL

Films for electroabsorption measurement were prepared as follows. A series of di-*n*-butyl fluorescein derivatives (Fig. 1) were doped in poly(methyl methacrylate) (PMMA) at various concentrations, and spin-coated or casted on ITO-coated glass substrates. Semitransparent gold electrodes were evaporated on them to form a sandwich structure. AC electric field at a low frequency ($f = 137.5$Hz) was applied normal to the film, and $2f$ component of the light intensity modulation , ΔI, was detected by a lock-in amplifier. This $2f$ component is proportional to the square of applied electric field, F, representing the third-order optical nonlinearity. The field-induced change in absorption coefficient, $\Delta\alpha$, was obtained from transmission change, $\Delta I/I$, and Kramers-Krönig transformation was applied to calculate field-induced refractive index change, Δn, and extinction

Compounds
I   : $X_1 = X_2 = X_3 = H$
II : $X_1 = Br, X_2 = X_3 = H$
III : $X_1 = X_2 = Br, X_3 = H$
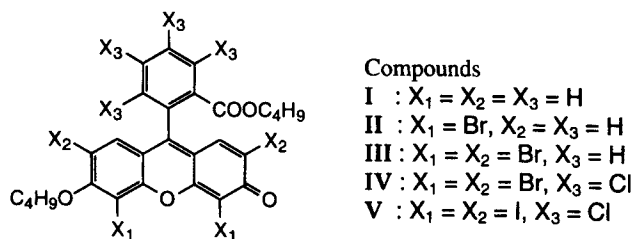IV : $X_1 = X_2 = Br, X_3 = Cl$
V   : $X_1 = X_2 = I, X_3 = Cl$

FIGURE 1 Molecular structure of di-*n*-butyl fluorescein derivatives investigated in this paper.

coefficient change, Δk. Linear refractive index, n, and extinction coefficient, k, were determined by ellipsometry combined with Kramers-Krönig transformation of absorption coefficient, α. Third-order nonlinear susceptibility, $\chi^{(3)}(-\omega; \omega, 0, 0)$, was evaluated from these values, Δn, Δk. n, k, and F.[4] In order to compare molecular nonlinearity at different concentrations, $\chi^{(3)}$ was normalized by the number density of chromophore N, namely $\chi^{(3)}/N$. Dilute chloroform solutions at various concentration were also prepared for linear absorption measurement to compare with the solid state films.

RESULTS AND DISCUSSION

In linear absorption spectra, no significant concentration dependence was observed in all of the compounds. Insignificant difference in absorption spectra between dilute solutions and films suggests rather nonaggregative character of this family of compounds. However, in electroabsorption spectra, di-n-butyl fluorescein (compound **I**) showed a significant concentration dependence, as shown in Fig. 2 (a). With increase of concentration, Im[$\chi^{(3)}/N$] was reduced except for the peak at 465nm, suggesting intermolecular interaction due to aggregation. On the other hand, concentration dependence in Br and I substituted derivatives such as di-n-butyl 4',5'-dibromofluorescein (**II**), di-n-butyl eosin Y (**III**), di-n-butyl phloxine B (**IV**) and di-n-butyl rose bengal (**V**) was insignificant, indicating no aggregation at up to 10wt% concentration. Fig. 2 (b) shows third-order nonlinear susceptibility spectra of di-n-butyl eosin Y (**III**) as an example, showing coincidence of Im[$\chi^{(3)}/N$] values on each concentration.

These results indicate that halogen disubstitution at 4'- and 5'-positions (X_1) is enough to prevent aggregation. According to the linear absorption spectra (not shown), halogen substitution at 4'- and 5'- positions (X_1) and at 2'- and 6'- positions (X_2) does not affect the electronic structure of this series of compounds, except for slight red-shift in the λ_{max}. It is in contrast with Cl substitution at phenyl ring (X_3) as in compounds **IV** and

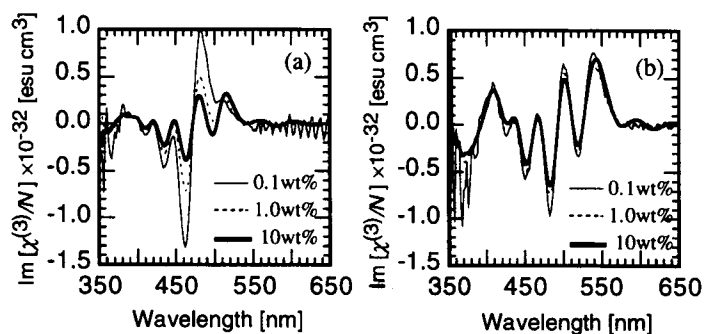FIGURE 2   Imaginary part of normalized third-order nonlinear susceptibility, Im[$\chi^{(3)}(-\omega; \omega, 0, 0)/N$], of (a) di-$n$-butyl fluorescein (I) and (b) di-n-butyl eosin Y (III).

V, which introduces a charge-transfer transition at the lower energy side of absorption band[1]. These features are useful for molecular design to control electronic structure and aggregativeness independently.

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