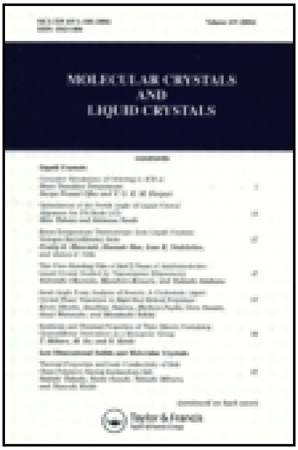

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Electroabsorption Studies on Fluorescein Derivatives

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Electroabsorption Studies on Fluorescein Derivatives

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Absorption and electroabsorption spectra of di-n-butyl fluorescein derivatives were obtained in order to investigate influence of substituted peripheral groups. It was found that substitution by Cl at phenyl ring introduces intramolecular charge transfer transition, resulting into enhancement of third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega: \omega, 0, 0)$.

Keywords: electroabsorption spectroscopy; fluorescein derivatives; intramolecular charge transfer; third-order nonlinear optical properties

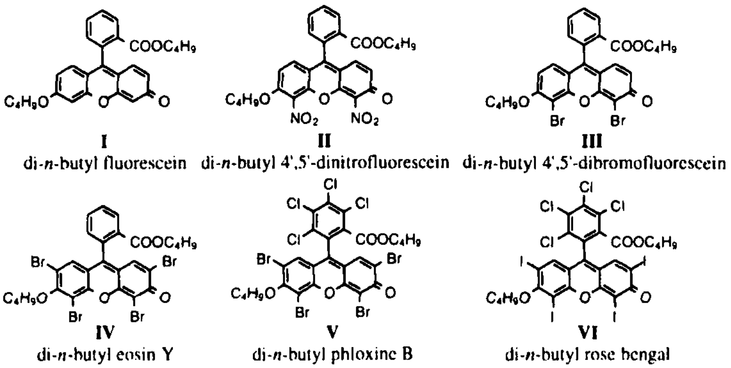
INTRODUCTION

Fluorescein derivatives are widely used fluorescence dyes because of their chemical stability. In this family of compounds, peripherals can be easily modified to tune optical and chemical properties, and main-chain or side-chain polymers can be easily realized. They are also expected to have a large optical nonlinearity due to their extended π-conjugated electron system.

Electroabsorption (EA) spectroscopy is a unique technique to determine the nature of excitons [1], and also a useful method to obtain third-order nonlinear susceptibility $\chi^{(3)}(-\omega; \omega, 0, 0)$ as a spectrum. [2, 3] In this paper, the influence of peripherals in di-*n*-butyl fluoresceins on their linear and nonlinear optical properties was investigated by absorption and EA measurements.

EXPERIMENTAL

A series of di-*n*-butyl fluorescein derivatives shown in Figure 1 has been synthesized. For EA measurement, poly(methyl methacrylate) (PMMA) films doped with fluorescein derivatives at 10wt% were prepared by spin-coating on ITO-coated glass substrates. Thickness of the films was *ca.* 2μm. Sandwich structure was formed with semitransparent gold electrodes on these films by vacuum evaporation. Dilute chloroform solutions with ~10^{-5}M were also prepared for linear absorption measurement to compare with the solid state films.



I di-*n*-butyl fluorescein
II di-*n*-butyl 4',5'-dinitrofluorescein
III di-*n*-butyl 4',5'-dibromofluorescein
IV di-*n*-butyl eosin Y
V di-*n*-butyl phloxine B
VI di-*n*-butyl rose bengal

FIGURE 1. The chemical structure of fluorescein derivatives investigated in this work.

In EA measurement, AC electric field of ~ 10^5V/cm at a low frequency (f=137.5Hz) was applied normal to the film, and $2f$ component of the light intensity modulation was detected by a lock-in amplifier. Refractive index and extinction coefficient were determined by ellipsometry combined with Kramers-Krönig transformation of absorption coefficient. Third-order nonlinear susceptibilities $\chi^{(3)}$ $(-\omega; \omega, 0, 0)$ of each samples were evaluated by the procedure described in references [2] and [3]. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

In absorption spectra, λ_{max} of fluorescein derivatives was shifted from 465nm (compound **I**) to 575nm (compound **VI**) by peripheral groups. Especially, significant difference in absorption spectrum was observed between compounds without Cl at phenyl ring (**I**~**IV**) and those with it (**V** and **VI**). The most distinct difference was found in **IV** and **V** as shown in Figure 2.

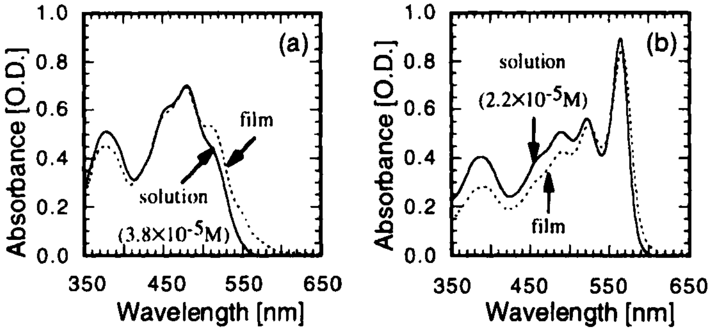


FIGURE 2. Absorption spectra in solution (full line) and PMMA film (10wt%, dotted line) of **IV** (a) and **V** (b).

Figure 3 shows EA spectra of **IV** and **V**. It should be noted that **V** presented EA and absorption spectra similar to **IV** except for the peak at 567nm as shown in Figure 2 and 3. In the EA peak of **V** at 567nm, the second-derivative component of linear absorption spectrum was dominant, reflecting the polar character of this transition. These results suggest that the intense absorption peak at 567nm in **V** is due to an intramolecular charge transfer transition caused by Cl substitution.

Third-order nonlinear susceptibility $\chi^{(3)}$ $(-\omega; \omega, 0, 0)$ of **IV** and **V** was 0.8×10^{-12} and 1.5×10^{-12} esu, respectively. Dividing by the number density of molecule N, normalized third-order nonlinear susceptibility $\chi^{(3)}/N$ of **V** was 1.9×10^{-32} esu cm^3, almost three times larger than that of **IV** (0.6×10^{-32} esu cm^3).

In summary, a series of di-*n*-butyl fluorescein derivatives was investigated by linear absorption and EA measurements, and it was found that the substitution by Cl at phenyl ring provides intramolecular charge transfer transition which results into enhancement of $\chi^{(3)}$.

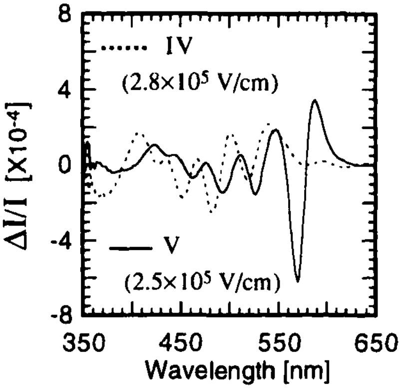


FIGURE 3. Electric field-induced transmission changes of **IV** (dotted line) and **V** (full line).

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