

# Anisotropy of third-order nonlinear optical responses in fluorescein derivatives by electroabsorption spectroscopy

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## ABSTRACT

Anisotropy of third-order nonlinear optical properties in di-*n*-butyl fluorescein derivatives was investigated by electroabsorption spectroscopy. In a series of fluoresceins, the derivatives with Cl substitution at phenyl ring presented a new intense absorption band at the wavelength range from 550 to 620nm, which is at longer wavelength side of the main absorption band in other derivatives. This new absorption band was attributed to intramolecular charge transfer transition due to Cl substitution at the phenyl ring, according to the spectral profile of electroabsorption which was proportional to the second derivative of linear absorption spectrum. Polarization dependence of normalized absorption coefficient was about 2:1 at the main absorption band in all derivatives. However, in the charge transfer transition band, the polarization dependence was about 1:1.2, suggesting that the charge transfer direction is nearly perpendicular to the optical transition. This result is consistent with structural aspect that the charge transfer direction is located along to the bond between the Cl-substituted phenyl ring and condensed ring, while the optical transition is along to the longitudinal axis of the condensed ring.

**Keywords:** Anisotropy, Third-order nonlinear optical property, Electroabsorption, Fluorescein derivatives, Charge transfer transition

## 1. INTRODUCTION

In order to design a molecule with a desired photonic function, it is essential to investigate the structure-to-property relation. Especially, the influence of peripheral substitution is important for control of solubility, aggregativeness, and electronic structure. For example, it is well known that introduction of a long alkyl chain improves solubility, and a bulky group such as a tertiary butyl prevents aggregation. Introduction of electron donor and/or acceptors at the end of main  $\pi$ -conjugated system causes intramolecular charge transfer, resulting into appearance of red-shifted charge transfer absorption band and also enhancement of optical nonlinearity. Therefore, in order to optimize properties of a molecule, it is essential to investigate a series of the molecule in which peripherals are systematically substituted.

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Having chemical stability and simple structure, fluorescein derivatives are widely used as fluorescence dyes. It can be used as a probe for molecular rotation and movement through rotational diffusion of fluorescein in the system observed by depolarization of fluorescence,<sup>1</sup> and also as a probe for pH because fluorescence decay and efficiency of fluorescein depend on pH.<sup>2</sup> Because of their extended  $\pi$ -conjugated electron system, fluoresceins are also interesting as nonlinear optical materials. It is reported that large value of  $\chi^{(3)}$  in the order of  $10^{-7}$  esu or up to 10 esu was observed in fluorescein doped boric acid glass by degenerate four-wave mixing (DFWM).<sup>3,4</sup> In this family of compounds, peripheral groups can be easily modified to tune optical and chemical properties, and also the main-chain or side-chain polymers can be easily realized. We have already reported that the absorption band of di-*n*-butyl fluorescein derivatives (Figure 1) is tunable by systematic peripheral substitution with halogens.<sup>5</sup> As shown in Figure 1,  $\lambda_{\max}$  in chloroform solution is shifted from 465 (I) to 575nm (V). Especially, the derivatives with Cl substitution at phenyl ring (IV and V) present a new intense absorption band at the wavelength range from 550 to 620nm, which we attributed to a charge transfer transition according to the profile of electroabsorption spectrum. Third-order nonlinear susceptibility  $\chi^{(3)}(-\omega; \omega, 0, 0)$  of fluorescein-doped poly(methyl methacrylate) (PMMA) film was estimated to be in the order of  $10^{-12}$  esu by electroabsorption, and an enhancement was observed at the charge transfer band of compounds IV and V.

Anisotropy of nonlinear optical response is important both in photonic applications and in fundamental research.

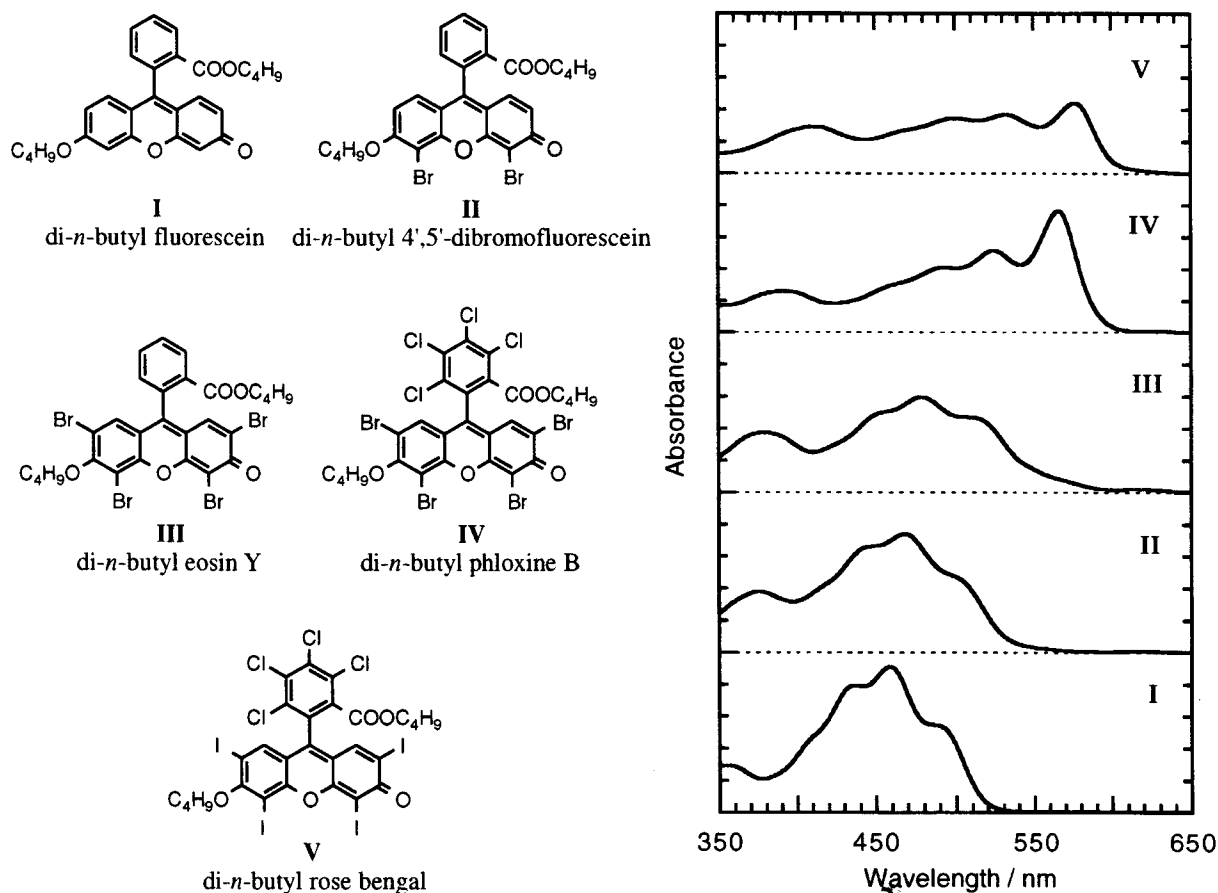


Figure 1 : Chemical structure and linear absorption spectra of di-*n*-butyl fluorescein derivatives.

In applications, polarization dependence of optical switches and electrooptic modulators are governed by this anisotropy. From the fundamental point of view, anisotropy of nonlinear optical response reflects arrangement of transitions, polarizability change, and state dipole change (charge transfer).<sup>6,7</sup> Therefore, it is of great significance to investigate anisotropy of nonlinear optical response.

In this paper, we report anisotropy of electroabsorption response in the series of di-*n*-butyl fluorescein derivatives, in terms of the nature of the transitions and the direction of polarizability change and charge transfer.

## 2. THEORY

Electroabsorption spectroscopy is a unique technique to measure third-order nonlinear susceptibility as a spectrum, and a useful method to investigate the nature of the transition whether it is polar (charge transfer excitons) or neutral (Frenkel excitons). In order to estimate the nature of the transition by electroabsorption spectrum, it is necessary to define the change in absorption coefficient due to external electric field, theoretically.<sup>8</sup> The field-induced change in absorption coefficient  $\Delta\alpha$  is described as a function of transition energy change  $\Delta E$  due to external electric field  $F$  using Maclaurin's expansion :

$$\Delta\alpha = \frac{\partial\alpha}{\partial E} \Delta E + \frac{1}{2} \frac{\partial^2\alpha}{\partial E^2} \Delta E^2 \quad (2.1)$$

$\Delta E$  is given by

$$\begin{aligned} \Delta E &= E(F) - E(0) = (E_f(F) - E_f(0)) - (E_i(F) - E_i(0)) \\ &= \left( -\mathbf{m}_f \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \mathbf{p}_f \mathbf{F} \right) - \left( -\mathbf{m}_i \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \mathbf{p}_i \mathbf{F} \right) \\ &= -(\mathbf{m}_f - \mathbf{m}_i) \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot (\mathbf{p}_f - \mathbf{p}_i) \mathbf{F} \\ &= -\Delta\mathbf{m} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \Delta\mathbf{p} \mathbf{F} \end{aligned} \quad (2.2)$$

where  $i$  and  $f$  stand for initial and final state, and  $\mathbf{m}$  and  $\mathbf{p}$  for state dipole moment and polarizability, respectively.  $\Delta\mathbf{p}$  and  $\Delta\mathbf{m}$  are polarizability change and dipole moment change, respectively, due to photoexcitation. From equations (2.1) and (2.2),  $\Delta\alpha$  is given by following equation :

$$\begin{aligned} \Delta\alpha &= \frac{\partial\alpha}{\partial E} \left( -\Delta\mathbf{m} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \Delta\mathbf{p} \mathbf{F} \right) + \frac{1}{2} \frac{\partial^2\alpha}{\partial E^2} \left( -\Delta\mathbf{m} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \Delta\mathbf{p} \mathbf{F} \right)^2 \\ &= \frac{\partial\alpha}{\partial E} \left( -\Delta\mathbf{m} \cdot \mathbf{F} \right) + \left\{ \frac{\partial\alpha}{\partial E} \left( -\frac{1}{2} \mathbf{F} \cdot \Delta\mathbf{p} \mathbf{F} \right) + \frac{1}{2} \frac{\partial^2\alpha}{\partial E^2} \left( -\Delta\mathbf{m} \cdot \mathbf{F} \right)^2 \right\} + O(F^3) + O(F^4) \end{aligned} \quad (2.3)$$

where  $O(F^3)$  and  $O(F^4)$  are the terms proportional to the cubic and the fourth power of  $F$ , respectively. In our measurement, we extract the component proportional to  $F^2$  by detecting the double-frequency component using lock-in amplifier. Thus, the actual signal we detect is described as follows :

$$\langle \Delta\alpha \rangle = \left\langle \frac{\partial\alpha}{\partial E} \left( -\frac{1}{2} \mathbf{F} \cdot \Delta\mathbf{p} \mathbf{F} \right) + \frac{1}{2} \frac{\partial^2\alpha}{\partial E^2} \left( -\Delta\mathbf{m} \cdot \mathbf{F} \right)^2 \right\rangle \quad (2.4)$$

where  $\langle \rangle$  means ensemble average for random orientation. The orientationally averaged values are

$$\langle \mathbf{F} \cdot \Delta \mathbf{p} \mathbf{F} \rangle = \overline{\Delta p} F^2 \quad , \quad (2.5)$$

and

$$\langle (-\Delta \mathbf{m} \cdot \mathbf{F})^2 \rangle = \frac{1}{3} \Delta m F^2 \quad , \quad (2.6)$$

where  $\overline{\Delta p}$  stands for the average change in polarizability. Finally, the field-induced change in absorption coefficient is expressed as

$$\langle \Delta \alpha \rangle = \left( -\frac{1}{2} \overline{\Delta p} F^2 \right) \frac{\partial \alpha}{\partial E} + \left( -\frac{1}{6} \Delta m^2 F^2 \right) \frac{\partial^2 \alpha}{\partial E^2} \quad . \quad (2.7)$$

The term proportional to  $\frac{\partial \alpha}{\partial E}$  originates from polarizability change due to photoexcitation, and the term proportional to  $\frac{\partial^2 \alpha}{\partial E^2}$  originates from state dipole change due to photoexcitation. If the transition is charge transfer one and thus polar, the second term is dominant. On the other hand, if the transition is almost neutral which is the case of Frenkel exciton, the first term is dominant. Therefore, it is possible to estimate the nature of the transition by comparing electroabsorption spectrum with the first- and second-derivatives of linear absorption spectrum.

Anisotropy of electroabsorption response is derived from two projection factors : one is for the external electric field ; the other is for the optical polarization. The former is expressed as the square of the projection factor between  $\mathbf{F}$  and  $\overline{\Delta p}$  or  $\Delta \mathbf{m}$ . The latter is expressed as the square of the projection factor between the optical polarization and the transition. In a perfect one-dimensional molecule, in which optical transition and  $\overline{\Delta p}$  or  $\Delta \mathbf{m}$  are parallel to each other, the polarization ratio is 3:1, assuming random orientation. Here the polarization ratio stands for the ratio of the electroabsorption response in a polarization parallel to the external electric field to the response in a polarization perpendicular to the external electric field. If  $\overline{\Delta p}$  or  $\Delta \mathbf{m}$  is perpendicular to the optical transition, the polarization ratio is 1:2.

### 3. EXPERIMENTAL

Thin film samples of fluoresceins were prepared as follows. A series of di-*n*-butyl fluorescein derivatives was doped in PMMA at the concentration of 0.1, 1.0 and 10wt%, and the solutions were spin-coated or casted on ITO-coated glass substrates. Thicknesses of the films were *ca.* 20, 6 and 2 $\mu$ m at the concentrations of 0.1, 1.0 and 10wt%, respectively. The films were dried in vacuum at 100°C for 12 hours. Semitransparent gold electrodes were evaporated on them to form a sandwich structure. Figure 2 shows the experimental setup and the structure of the sample for electroabsorption spectrum measurement. The light from a tungsten-halogen lamp is monochromated and focused onto the sample. The transmitted light goes through a polarizer to select *s*- or *p*- polarization, and is detected by a photodiode, and the signal is extracted by a lock-in amplifier. In order to obtain absorption change, the light intensity *I* and its change by applied field  $\Delta I$  are measured separately. *I* is measured by chopping the light at a low frequency *f* (=137.5Hz) and detecting the *f* component by the lock-in amplifier.  $\Delta I$  is measured by applying AC electric field of  $\sim 10^5$ V/cm at *f* normal to the film, and detecting 2*f* component by the lock-in amplifier.

The field-induced change in absorption coefficient  $\Delta \alpha$  is given by

$$\Delta \alpha = -\frac{\Delta I I}{d} \quad , \quad (3.1)$$

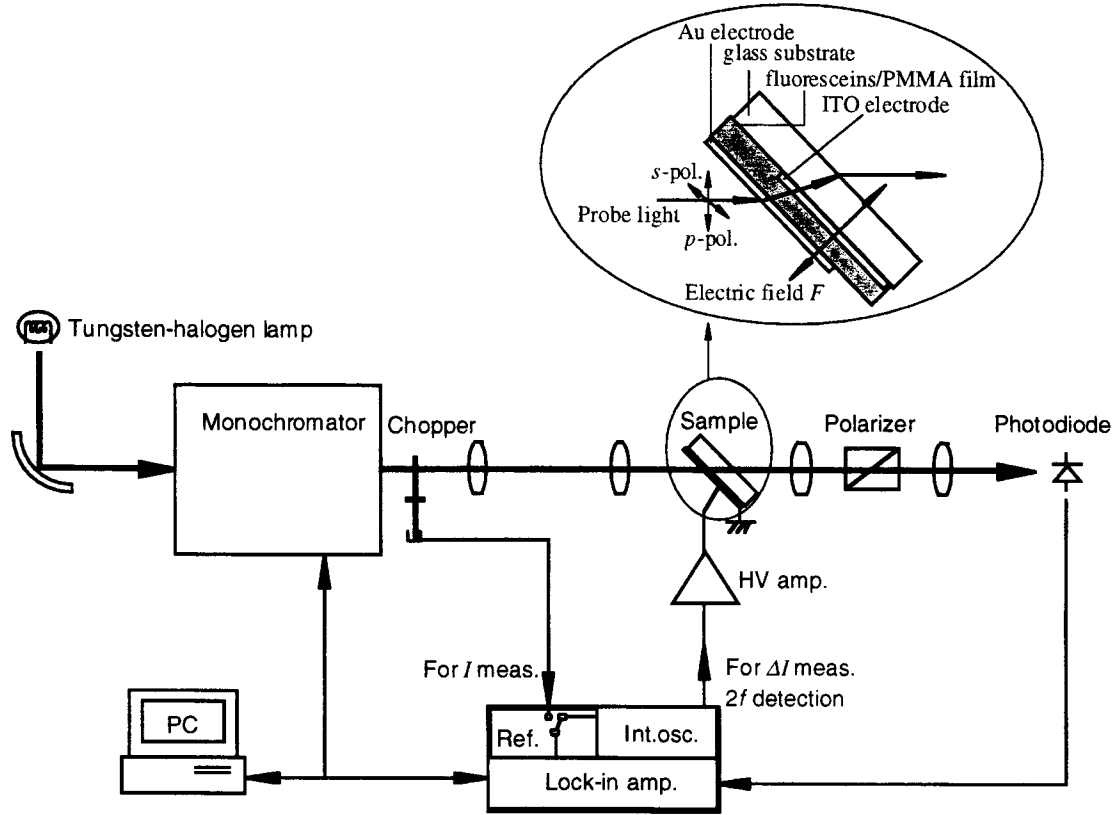


Figure 2 : Sample structure and experimental setup for electroabsorption spectra measurement.

where  $d$  is the thickness of the film. Refractive index  $n$  and extinction coefficient  $k$  were determined by ellipsometry combined with Kramers-Krönig transformation<sup>9</sup> of absorption coefficient. Electroabsorption response was measured using  $s$ - or  $p$ -polarized light at  $45^\circ$  incident angle, and electroabsorption response in polarization parallel and perpendicular to the applied electric field was obtained through the following equations :

$$\Delta\alpha_s = \Delta\alpha_{\perp} \quad (3.2)$$

$$\Delta\alpha_p = \Delta\alpha_{\perp}\cos^2\theta + \Delta\alpha_{\parallel}\sin^2\theta \quad , \quad (3.3)$$

where  $s$  and  $p$  stand for  $s$ - and  $p$ -polarizations,  $\perp$  and  $\parallel$  for polarizations perpendicular and parallel to the applied electric field, respectively, and  $\theta$  for angle of refraction in the film. Finally, absorption coefficient normalized by the number density of chromophore  $N$ , namely  $\Delta\alpha/N$ , was evaluated in each polarizations parallel ( $\Delta\alpha_{\parallel}$ ) and perpendicular ( $\Delta\alpha_{\perp}$ ) to the applied electric field .

## 4. RESULTS

### 4.1. di-*n*-butyl fluorescein (I)

Figure 3 shows linear absorption, electroabsorption response for *s*- and *p*-polarizations, anisotropic electroabsorption response for polarizations parallel and perpendicular to the applied electric field, and polarization ratio of di-*n*-butyl fluorescein (I). Electroabsorption responses of I presented as transmission change,  $\Delta I/I$ , were almost proportional to the first derivative of linear absorption spectrum, revealing Frenkel exciton-like nature of the excitation. Polarization dependence presented as normalized absorption coefficient,  $\Delta\alpha/N$ , was about 2:1 at main absorption band between 350 and 550nm. This is a value very often observed in one-dimensional molecules and close to the value for the ideal one-dimensional molecule, 3:1.

It was already reported that no significant concentration dependence was observed in linear absorption spectra of I.<sup>10</sup> However, in electroabsorption spectra, I showed significant concentration dependence. With increase of concentration, the spectral profile and magnitude of the normalized third-order nonlinear susceptibility  $\chi^{(3)}/N$  changed, suggesting intermolecular interaction due to aggregation. Anisotropy of electroabsorption responses presented some change with concentration, although it might be not significant.

### 4.2. di-*n*-butyl 4',5'-dibromofluorescein (II) and di-*n*-butyl eosin Y (III)

Electroabsorption responses of II and III presented same tendency as I. The spectral profile of electroabsorption was also proportional to the first derivative of linear absorption spectrum, and the polarization dependence was about 2:1 as

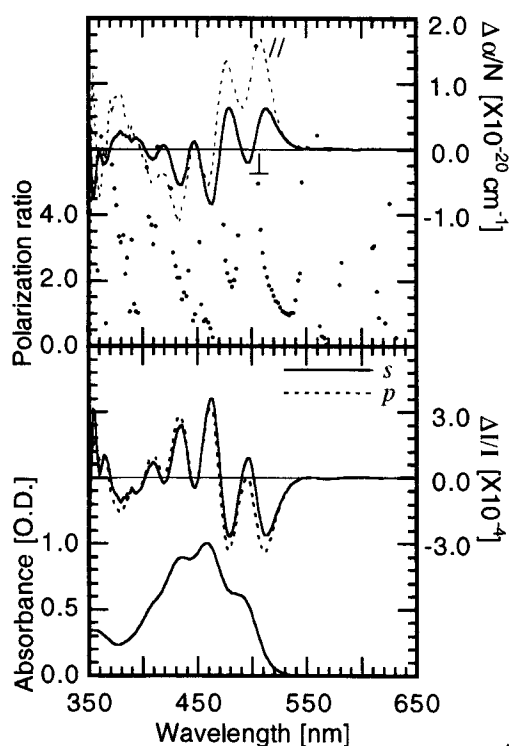


Figure 3 : Electroabsorption responses of di-*n*-butyl fluorescein (I) thin films (10wt%). From the bottom part. linear absorption spectrum, electroabsorption spectra presented as transmitted light intensity change for *s*- (dotted line) and *p*- (full line) polarizations, polarization ratio, and normalized absorption coefficient for polarizations parallel (//, dotted line) and perpendicular (⊥, full line) to the applied field.

shown in Figure 4. However, in contrast with **I**, the concentration dependence of **II** and **III** was insignificant, indicating that halogen (Br) disubstitution at 4'- and 5'- position on condensed ring prevents aggregation. According to the linear absorption spectra, halogen disubstitution at 4'- and 5'- position does not affect the electronic structure of this series of derivatives, except for slight red-shift in  $\lambda_{\max}$  in absorption spectra. The electroabsorption spectra and their anisotropy which are also fundamentally same as those of **I** also support this feature, indicating that halogen (Br) disubstitution at 4'- and 5'- position on condensed ring does not affect electronic structure of molecule.

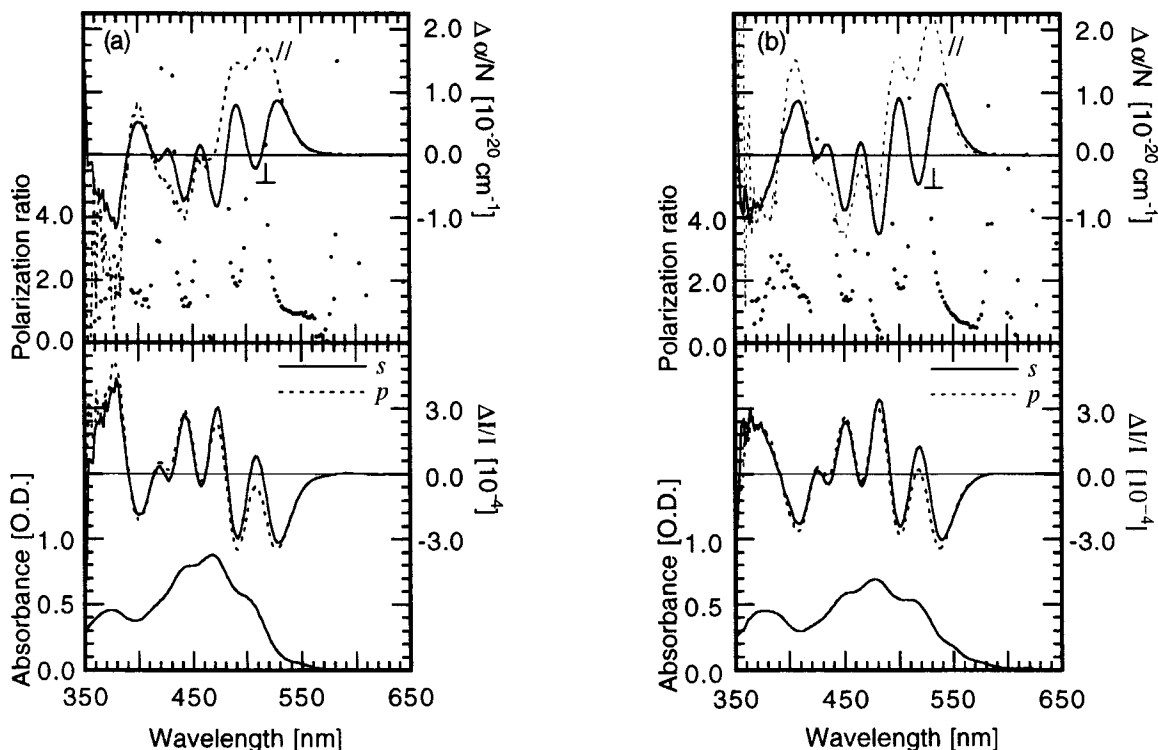


Figure 4 : Electroabsorption responses of di-*n*-butyl 4',5'-dibromofluorescein (**II**, (a)) and di-*n*-butyl eosin Y (**III**, (b)) thin films (10wt%). From the bottom part of each compound, linear absorption spectrum, electroabsorption spectra for *s*- (full line) and *p*- (dotted line) polarizations, polarization ratio, and normalized absorption coefficient for polarizations parallel (//, dotted line) and perpendicular (⊥, full line) to the applied field.

#### 4.3. di-*n*-butyl phloxine B (**IV**) and di-*n*-butyl rose bengal (**V**)

Compared with **I**, **II** and **III**, the derivatives with Cl substitution at the phenyl ring presented a new intense absorption band at the wavelength range from 550 to 620nm which is at longer wavelength side of the main absorption band. This new absorption band presented a spectral profile of electroabsorption almost proportional to the second derivative of the linear absorption spectrum as shown in Figure 5, revealing the polar (charge transfer) nature of the transition. Thus, it is clear that Cl substitution at the phenyl ring introduces intramolecular charge transfer transition.

Anisotropy of electroabsorption response at main absorption band between 350 and 550nm was about 2:1, showing an ordinary one-dimensional nature as in **I**, **II** and **III**. However, the polarization dependence in the charge transfer band was about 1:1.2, suggesting that the arrangement of the charge transfer direction and the optical transition is significantly

different from that of the polarizability change and the optical transition at the main band. The concentration dependence of these derivatives was insignificant both in electroabsorption spectra and in polarization dependence.

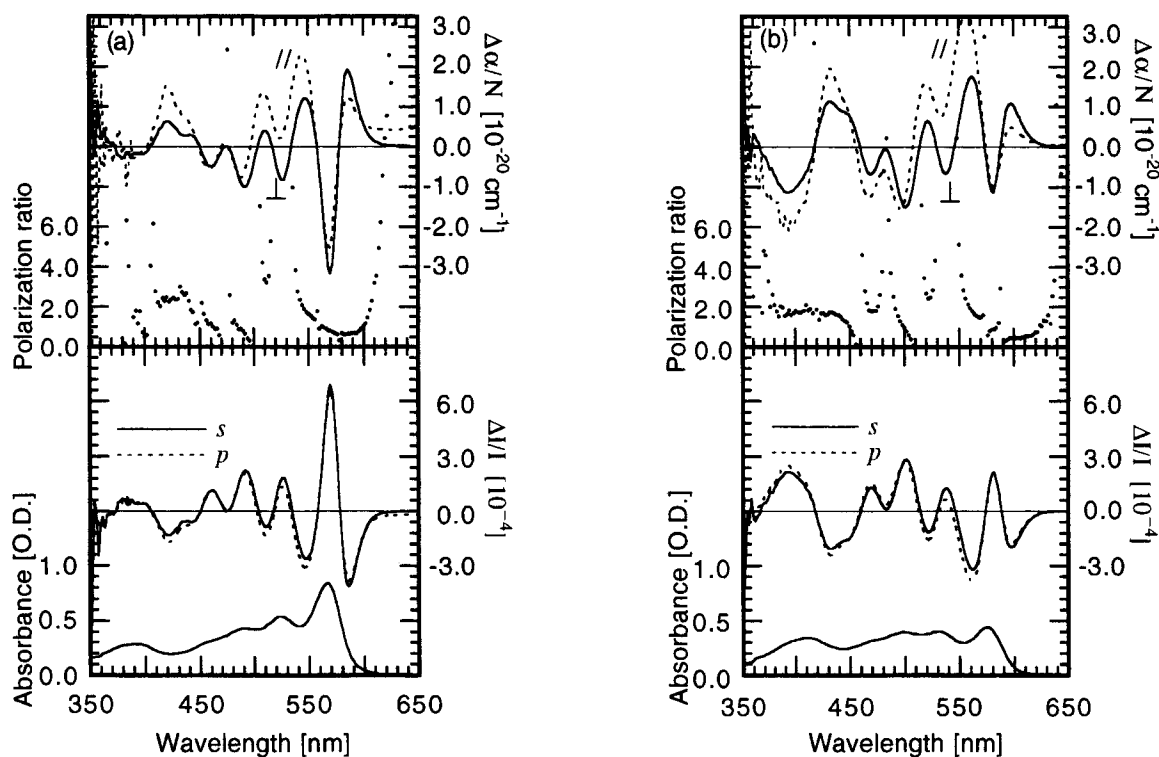


Figure 5 : Electroabsorption responses of di-*n*-butyl phloxine B (IV, (a)) and di-*n*-butyl rose bengal (V, (b)) thin films (10wt%). From the bottom part of each compound, linear absorption spectrum, electroabsorption spectra for *s*- (full line) and *p*- (dotted line) polarizations, polarization ratio, and normalized absorption coefficient for polarizations parallel (//, dotted line) and perpendicular (⊥, full line) to the applied field.

## 5. DISCUSSION

As already described in chapter 2, polarization dependence of electroabsorption response can be derived through consideration on projection factors. In two extreme cases that  $\overline{\Delta p}$  or  $\Delta m$  is parallel and perpendicular to the optical transition, the polarization ratio is 3:1 and 1:2, respectively. In an actual molecule, an intermediate arrangement is possible. Calculating the projection factors for random orientation, polarizability dependence is expressed as,

$$\frac{\Delta\alpha_{//}}{\Delta\alpha_{\perp}} = \frac{2 \cos^2 \Theta + 1}{\sin^2 \Theta + 1} \quad (5.1)$$

where  $\Theta$  is the angle between the optical transition and the charge transfer direction ( $\Delta m$ ) or polarizability change ( $\overline{\Delta p}$ ), as shown in Figure 6.



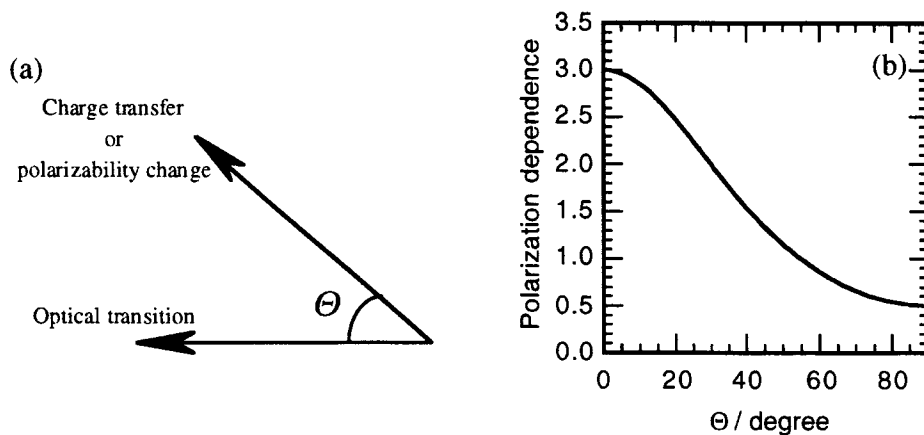


Figure 6 : (a) Description of the arrangement of optical transition and charge transfer or polarizability change, and (b) polarization ratio depending on the angle  $\Theta$  between optical transition and charge transfer direction.

From the results of the anisotropy of electroabsorption responses of **I**, **II** and **III**, it was found that the direction of polarizability change is less than  $30^\circ$  from the optical transition. On the other hand, Cl-substituted derivatives at phenyl ring (**IV** and **V**) showed the polarization dependence of 1:1.2 at charge transfer band between 550 and 620nm, suggesting that the angle between the charge transfer and the optical transition is larger than  $65^\circ$ . This is consistent with the structural consideration that the charge transfer axis is located along to the bond between the Cl-substituted phenyl ring and condensed ring, while the optical transition is along to the longitudinal axis of the condensed ring, as shown in Figure 7.

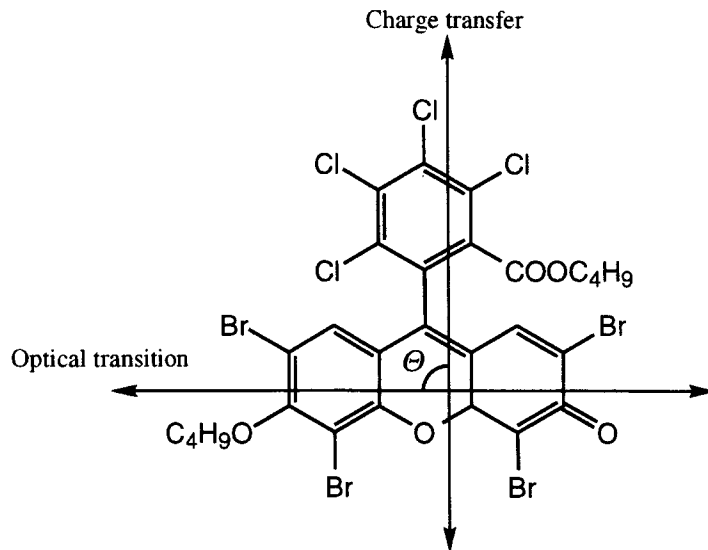


Figure 7 : Schematic arrangement of optical transition and charge transfer of di-*n*-butyl phloxine B (**IV**).

## 6. CONCLUSION

Fluorescein derivatives with systematic peripheral substitution were characterized by polarization-dependent electroabsorption spectroscopy in terms of anisotropy of electroabsorption response. The derivatives with Cl substitution at phenyl ring (IV and V) presented a new intense absorption band at the wavelength range from 550 to 620nm, which is at longer wavelength side of the main absorption band in fluorescein. This new absorption band presented a spectral profile of electroabsorption almost proportional to the second derivative of the linear absorption spectrum and attributed to intramolecular charge transfer transition due to Cl substitution. This charge transfer band showed enhanced  $\chi^{(3)}/N$ . Electroabsorption responses of I, II and III were almost proportional to the first derivative of linear absorption spectrum, and polarization dependence of normalized absorption coefficient,  $\Delta\alpha/N$ , was 2:1 at main absorption band between 350 and 550nm, showing ordinary one-dimensional nature. Polarization dependence of IV and V at main absorption band was same as I, II and III. However, the polarization dependence in the charge transfer band was about 1:1.2, indicating that charge transfer direction is nearly perpendicular to the optical transition. This is elucidated as follows: the charge transfer direction is located along to the bond between the Cl-substituted phenyl ring and condensed ring, while the optical transition is along to the longitudinal axis of the condensed ring.

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