Photoinduced Reorientation of Liquid Crystals Doped with Thiophene having Ester Moieties

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The photoinduced reorientation behavior of dye-doped nematic liquid crystals (LCs) was investigated. Thiophene derivatives with ester moieties were newly synthesized as the guest dye molecule. Liquid crystalline behavior and optical properties of this compound was evaluated, and the effect of the dye structure on the photoinduced reorientation behavior of the dye-doped LCs was investigated. Photoinduced diffraction rings were observed according to the self-phase modulation effect when the laser beam intensity was above the lowest threshold. Comparison of the lowest threshold light intensity for the appearance of the diffraction rings revealed that the thiophene dye with ester moieties in the terminal thiophene directly shows lower threshold intensity than any other dyes.
Key words: Liquid crystal, Reorientation, Oligothiophene, Guest-host system

1. INTRODUCTION

Photo-manipulation of the liquid crystal (LC) alignment has attracted increasing attention in recent years due to its large photoinduced birefringence. It is well known that LC molecules tend to reorient parallel to the light polarization when irradiated by linearly polarized light at high intensities.[1] On the other hand, recent researches reported that a small amount of absorbing dyes dissolved in LCs might strongly enhance the photoinduced reorientational efficiency.[2] In this case the reorientational efficiency strongly depends on the structure of doped dyes.[3] The accepted mechanism of the dye-induced reorientation is a selective excitation of dye molecules and consequent large change in guest-host interaction by photoexcitation of dye molecules.[4-8]

Recently, we reported that oligomer-type thiophene derivatives TR5 (Fig. 1) act as a highly efficient dye for photoinduced reorientation.[9] It is assumed that the high efficiency of the oligothiophene for photoinduced reorientation is mainly due to the change in the molecular polarizability at ground and excited states, which is related to the intramolecular delocalization of π-electrons along the molecular long axis.[10] However, molecular interactions that are responsible for the photoinduced reorientation are still unclear. Moreover, light intensity required for reorientation of LCs is still large as several W/cm^2 orders. Therefore our research interest has been concentrated on the development of dye molecules that drive the LCs very efficiently, aiming at photonic applications.

One approach to enhance the efficiency is to increase absorption of the dye molecule. Generally, expansion of π-conjugation and introduction of electron donor and acceptor to a chromophore are effective to enhance the molar absorptivity. However an increase in aromatic rings to expand π-conjugation causes a simultaneous decrease in solubility. Introduction of a nitro or cyano group, instead of an alkyl chain also lowers the solubility even if the absorption spectra exhibit a red-

shift. For instance, TR5 without alkyl chains shows no solubility to 5CB, which is a representative nematic LC. An ester group is well known as a weak electron acceptor group that could enhance absorption. Furthermore, an alkyl chain increasing solubility can be substituted through the ester moiety unlike cyano and nitro groups. In this paper, we synthesized new oligothiophenes having ester moieties and investigated the effect of the ester moiety on photoinduced reorientation.

2. EXPERIMENTAL

The structures of the guest dye molecules used in this study are shown in Fig. 1. The compound 5,5''-bis(5-butoxycarbonyl-2-thienylethynyl)-2,2':5',2''-terthiophene (TD) that has ester moieties in the terminal thiophenes directly was synthesized according to the literature with some modifications.[11] 4-Pentyl-4'-cyanobiphenyl (5CB) was obtained from Merck Ltd., being used as a host LC without further purification, and guest dye molecules were doped at various concentrations from 0.04-0.20 mol%. The mixture was sandwiched between two lecithin-coated glass substrates with a 100-μm thick silica gel as a spacer. This cell giving homeotropic alignment was used as a sample for optical measurement.
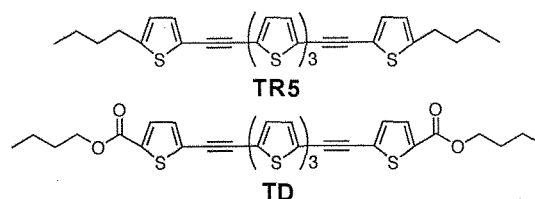

Fig. 1. Chemical structures of dyes used in this study.

Photoinduced reorientation was evaluated by self-diffraction measurement at room temperature. The optical setup is shown in Fig.2. A linearly polarized Gaussian beam at 488 nm with a diameter of 1.5 mm

from an Ar^+ laser was focused normally onto the sample cell by a lens with a focal length of 20 cm. The polarization of the laser beam was maintained as horizontal with a half-wave plate. The transmitted beam pattern created after the sample cell was observed on a screen behind the sample.
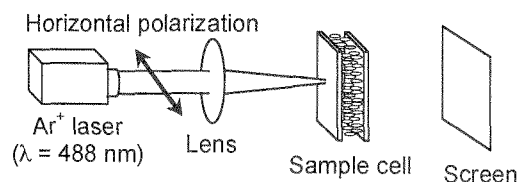
Horizontal polarization

Ar⁺ laser
(λ = 488 nm)   Lens
                        Sample cell   Screen

Fig. 2. Schematic diagram of optical setup used for evaluation of photoinduced reorientation.

3.RESULTS AND DISCUSSION

3.1 Thermal and photophysical properties of dyes

We previously reported that TR5 shows a nematic phase between 101 °C and 194 °C on heating.[11] Since the new dye has a structure similar to TR5, it can be expected that an LC phase appears. Thermal properties and LC behavior were determined by differential scanning calorimetry and polarizing optical micrography. We have found that TD shows a smectic phase between 145 °C and 209 °C on heating as shown in Table I. Although we identified the smectic phase from the texture under polarizing optical microscopy, X-ray measurement is required for more detail analysis.

Table I. Phase transition temperatures of dye molecules

Dye	Phase transition temperature (°C)
TR5[a]	K 101 N 194 I
TD	K 145 S 209 I

K: crystal; S: smectic; N: Nematic; I: isotropic
a Cited from Ref. 9

Table II summarizes the photophysical properties of dye molecules in toluene. TD shows absorption and emission properties similar to those of TR5. The absorption around 425 nm is due to a delocalized π-π transition. Compared with TR5, the absorption and emission maximum of TD was red shifted by about 9 nm. The same type of bathchromic shifts has been reported for thiophene oligomers having an electron donor and/or an acceptor as end substituents.[12] It is interpreted by an increase of the conjugation length due to the addition of two double bonds of the carbonyl groups as DiCesare et al. reported.[13]

Table II. Photophysical properties of dye molecules

Dye	λ_{abs} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (nm)
TR5[a]	423	55,000	491
TD	432	61,000	500

λ: wavelength; ε: molar absorption coefficient;
a Cited from Ref. 9

3.2 Reorientational behavior of dye-doped LCs

The TD-doped LC sample showed a red shift by about 9 nm compared with the TR5-doped sample as in the toluene solution. Absorbance at 488 nm of the sample

cells as a function of the dye concentration is plotted in Fig. 3. In each cell, absorbance increased linearly as the dye concentration increased. Especially, the values of the TD-doped cell was twice as large as that of the TR5-doped cell.
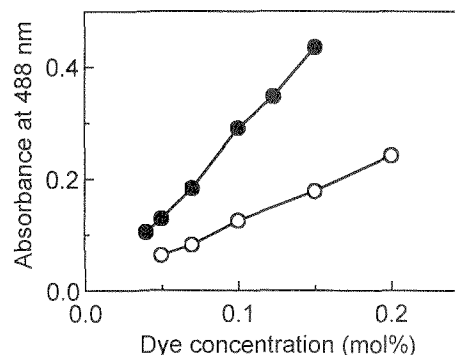

Fig. 3. Absorbance at 488 nm of sample cells as a function of dye concentration. (O) TR5; (●) TD.

When the laser beam was irradiated to the sample cell, transmitted light formed diffraction patterns on a screen depending on the light intensity. The typical diffraction pattern observed in the TD-doped cell is shown in Fig. 4. The number of diffraction rings (N) varied by the light intensity. N can be estimated from Equation 1:[1]

$$N = \frac{\Delta\psi_0}{2\pi} = \frac{1}{\lambda}\int_{-d/2}^{d/2}\Delta n(z)dz \quad (1)$$

where $\Delta\psi_0$ is the phase shift observed by the laser beam in the beam center traversing the sample thickness d, $\Delta n(z)$ is the local refractive-index change induced by the laser beam and λ is the wavelength of the laser beam. For simplicity, we assume that $\Delta n(z)$ is uniform along the propagation direction and thus the average Δn induced in the beam center can be estimated by Equation 1.
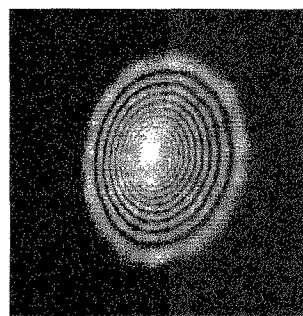

Fig. 4. Typical diffraction patterns of TD-doped 5CB formed on a screen at 22 W/cm^2.

The number of diffraction rings observed on the screen in the dye-doped cell is shown in Fig. 4. When the light intensity was low, no ring could be observed. Above the threshold intensity, the ring appeared and the number of the ring increased with the light intensity. Then the growth of the ring ceased at a certain intensity. Further irradiation with a high-intensity laser beam brought about oscillation and distortion of the rings on the screen due to a thermal effect of dye molecules absorbing light of high intensity. The maximum number of the stable diffraction rings induced in TR5 and TD-doped samples was 22 and 23, respectively. According

to Equation 1, these values correspond to Δn of 0.11 and 0.11, respectively, which are almost the same as those of the pure LC host.[1] We consider that there is no large difference in the behavior of reorientation based on the structure between the two dye molecules. We defined the threshold intensity as the light intensity at which the first ring appears. The threshold intensity was 36 W/cm^2 for TR5 and 13 W/cm^2 for the TD-doped samples. The introduction of ester moieties to TR5 effectively reduced the threshold intensity by about 3 times in the TD-doped cell.
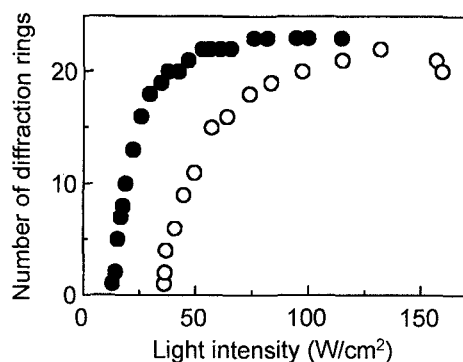

Fig. 5. The number of observed diffraction rings as a function of light intensity. (O) TR5; (●) TD. Dye concentration: 0.10 mol%.

Fig. 6A shows the threshold intensity as a function of the dye concentration. The threshold intensity decreased with an increase in the dye concentration, indicating that the reorientation of LCs is accelerated at higher concentrations. Compared to TR5, at the same dye concentration, the threshold intensity of the TD-doped sample was lower by about 3 times at any concentration. This can be attributed to larger absorption of the TD dye at 488 nm. Therefore, to investigate the genuine effect of the dyes on the reorientational behavior, we normalized threshold intensities by absorbance at 488 nm. The result is shown in Fig. 6B. Even at the same absorbance at 488 nm, the threshold intensity of the TD-doped cells was still lower than that of the TR5-doped cells. It suggests that the dye possesses substantially higher ability to induce reorientation of host LCs than TR5 dye.

Marrucci et al. reported that polar host LCs enhance the dye-induced torque effect compared to nonpolar hosts. It is suggested that polar interactions in local site, such as dipole-dipole interactions and hydrogen bonds, contribute to the dye-induced torque effect in their LC system.[8] The compound TD has no dipole moment along the long axis, but two carbonyl groups (polar group) in the terminal thiophene. We also consider that in our results the reorientational efficiency was improved by polar interactions such as dipole-dipole interactions between a cyano moiety in the host LC molecule and a carbonyl moiety in the dye molecule.

4. CONCLUSION

We synthesized a liquid crystalline oligomer-type thiophene derivative having ester moieties in the terminal thiophene TD as a guest dye molecules for dye-doped LCs. The compound TD decreased the reorientational threshold intensities about 3 times compared to the thiophene dye with no ester moiety at
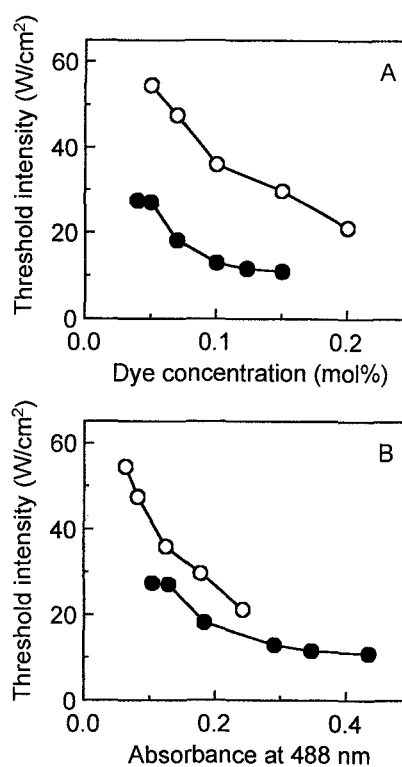

Fig. 6. Change in the threshold intensity as a function of dye concentrations (A) and as a function of absorbance at 488 nm of the sample cell (B). (O) TR5; (●) TD.

the same doping concentration. It is considered that an interaction of ester group enhance dipole-dipole interactions between the dye molecule and the host LC, resulting the increase in the reorientational efficiency.

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