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Effect of Ester Moieties in Dye Structures on Photoinduced Reorientation of Dye-Doped Liquid Crystals

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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. The liquid-crystalline behavior and optical properties of these compounds were evaluated, and the effect of the dye structure on the photoinduced reorientation behavior of the dye-doped LCs was investigated. The photoinduced formation of diffraction rings was observed as a result of the self-phase modulation effect at the intensity of 11 W/cm^2, when an Ar$^+$ laser beam at 488 nm was irradiated above the threshold intensity. Comparison of the lowest threshold light intensity for the appearance of the diffraction rings revealed that the thiophene dye with ester moieties directly bound to the terminal thiophene shows a lower threshold intensity than those of any other dyes.

Introduction

The photomanipulation of liquid crystal (LC) alignment has attracted increasing attention in recent years because of 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.[1−7] On the other hand, recent researches have reported that a small amount of anthraquinone dichroic dyes dissolved in LCs can strongly enhance the photoinduced reorientational efficiency.[8] In this case, the reorientational efficiency significantly depends on the structure of doped dyes.[9] Unlike the related effects observed in azo-dye-doped materials,[10] these phenomena can neither be ascribed to photoisomerization, which does not occur in anthraquinone dyes, nor to other photochemical reactions. The accepted mechanism of the dye-induced reorientation is selective excitation of the dye molecules, followed by a consequent large change in guest−host interactions by photoexcitation of the dye molecules.[11−15]

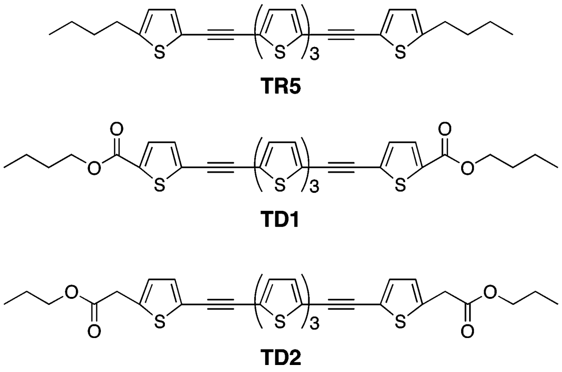

Figure 1. Chemical structures of the dyes used in this study and their abbreviations.

Recently, we reported that an oligomer-type thiophene derivative, **TR5** (Figure 1), acts as a highly efficient dye for photoinduced reorientation.[16] It is assumed that the high efficiency of **TR5** for photoinduced reorientation is mainly due to the change in the molecular polarizability between the ground and excited states, which is related to the intramolecular delocalization of π electrons along the molecular long axis.[17] However, molecular interactions responsible for the photoinduced reorientation are still unclear. Moreover, the light intensity required for reorientation of LCs is still as large as several W/cm^2 orders. Therefore, our research interest has been concentrated on the development

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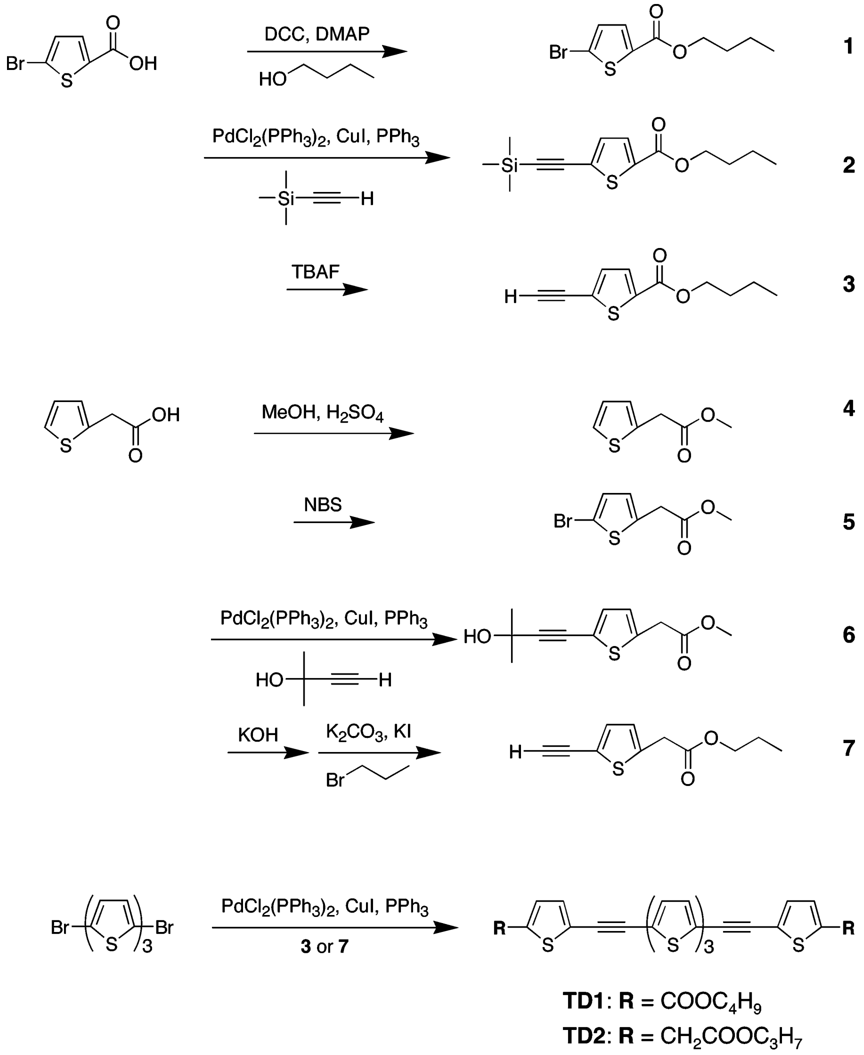
Scheme 1. Synthetic Root of the Guest Dye Molecules



of dye molecules that drive LCs very efficiently, aiming at photonic applications.

One approach to enhance the photosensitivity is to increase absorption of the dye molecule. Generally, the expansion of π conjugation and the introduction of electron donors and acceptors 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. The 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 in **5CB**, which is a representative nematic LC. For the reasons mentioned above, we have chosen an ester group on the basis of the following arguments: (1) an ester group is well-known as a weak electron acceptor group that could enhance absorption; (2) an alkyl chain that increases solubility can be substituted through the ester moiety unlike cyano and nitro groups; and (3) a carbonyl group is a polar group that might enhance the dipole−dipole interaction with the cyano group of the LC molecule. In this paper, we synthesized new oligomer-type thiophene derivatives having ester moieties and investigated the effect of the ester moiety on the photoinduced reorientation.

Experimental Section

Materials. The chemical structures of the guest dye molecules used in this study are shown in Figure 1. The synthetic routes for **TD1**, which has ester moieties directly bound to the terminal thiophene, and **TD2**, which has ester moieties indirectly bound to the terminal thiophene, are shown in Scheme 1.

5-Bromo-2-thiophenecarboxylic Acid Butyl Ester (1). 5-Bromo-2-thiophenecarboxylic acid (4.1 g, 20 mmol), 1-butanol (4.4 g, 60 mmol), and 4-(dimethylamino)pyridine (1.2 g, 10 mmol) were dissolved in dichloromethane (20 mL) under a nitrogen atmosphere, and the resulting solution was cooled at 0 °C. With stirring, *N*,*N*-dicyclohexylcarbodiimide (5.1 g, 25 mmol) dissolved in dichloromethane (10 mL) was added dropwise to the solution, and the reaction mixture was stirred at room temperature for 3 h. The resulting suspension was filtered to remove urea crystals, the filtrate was extracted with dichloromethane, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 1:2 in vol %) to give **1** as a yellowish oil (3.8 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, $J = 7.3$ Hz, 3H), 1.42 (m, $J = 7.9$ Hz, 2H), 1.69 (m, $J = 6.6$ Hz, 2H), 4.26 (t, $J = 6.6$ Hz, 2H), 7.05 (d, $J = 4.0$ Hz, 1H), 7.51 (d, $J = 4.0$ Hz, 1H).

5-Trimethylsilylethynyl-2-thiophenecarboxylic Acid Butyl Ester (2). Compound **1** (3.6 g, 14 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.28 g, 0.40 mmol), copper(I) iodide

(76 mg, 0.40 mmol), triphenylphosphine (0.31 g, 1.2 mmol), and trimethylsilylacetylene (2.6 mL, 18 mmol) were added to a solution of triethylamine (20 mL) and THF (20 mL) under a nitrogen atmosphere, and the reaction mixture was stirred at 80 °C for 12 h. After being cooled to room temperature, the mixture was poured into 2 N hydrochloric acid (100 mL) and extracted with ethyl acetate, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 1:2 in vol %) to give **2** as a yellow oil (3.8 g, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.23 (s, 9H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.42 (m, $J = 7.7$ Hz, 2H), 1.69 (m, $J = 8.1$ Hz, 2H), 4.26 (t, $J = 6.6$ Hz, 2H), 7.13 (d, $J = 4.0$ Hz, 1H), 7.60 (d, $J = 4.0$ Hz, 1H).

5-Ethynyl-2-thiophenecarboxylic Acid Butyl Ester (3). A solution of 1.0 M tetra-*n*-butylammonium fluoride (5.0 mL, 5.0 mmol) in THF was added dropwise to a solution of compound **2** (3.8 g, 13 mmol) in THF (20 mL) with stirring. The reaction mixture was stirred at room temperature for 10 min. The crude product was extracted with ethyl acetate, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 1:2 in vol %) to give **3** as a yellow oil (2.2 g, 81%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.95 (t, $J = 7.3$ Hz, 3H), 1.43 (m, $J = 7.5$ Hz, 2H), 1.70 (m, $J = 7.7$ Hz, 2H), 3.42 (s, 1H), 4.27 (t, $J = 6.6$ Hz, 2H), 7.19 (d, $J = 3.9$ Hz, 1H), 7.62 (d, $J = 4.0$ Hz, 1H).

2-Thiopheneacetic Acid Methyl Ester (4). 2-Thiophene acetic acid (9.1 g, 64 mmol) and a trace amount of sulfuric acid were dissolved in methanol (100 mL), and the reaction mixture was refluxed for 30 min. Then, the solvent was removed under reduced pressure, the residue was extracted with chloroform, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 1:2 in vol %) to give **4** as a yellow oil (9.6 g, 96%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.71 (s, 3H), 3.83 (s, 2H), 6.94 (d, $J = 5.0$ Hz, 1H), 6.95 (t, $J = 3.5$ Hz, 1H), 7.20 (d, $J = 4.8$ Hz, 1H).

5-Bromo-2-thiopheneacetic Acid Methyl Ester (5). Compound **4** (9.4 g, 60 mmol) and NBS (11 g, 62 mmol) were added to a solution of chloroform (50 mL) and glacial acetic acid (20 mL), and the reaction mixture was stirred at 40 °C for 3 h. The crude product was extracted with chloroform, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 1:1 in vol %) to give **5** as a yellow oil (14 g, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.71 (s, 1H), 3.75 (s, 2H), 6.67 (d, $J = 3.7$ Hz, 1H), 6.88 (d, $J = 3.7$ Hz, 1H).

5-(3-Hydroxy-3-methyl-1-butynyl)-2-thiopheneacetic Acid Methyl Ester (6). Compound **5** (5.8 g, 25 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.53 g, 0.75 mmol), copper(I) iodide (0.17 g, 0.90 mmol), triphenylphosphine (0.66 g, 2.5 mmol), and 3-methyl-1-butyn-3-ol (2.9 g, 35 mmol) were added to a solution of triethylamine (20 mL) and THF (30 mL) under a nitrogen atmosphere, and the reaction mixture was stirred at 80 °C for 3 h. After being cooled to room temperature, the mixture was poured into 2 N hydrochloric acid (100 mL) and extracted with ethyl acetate, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: ethyl acetate/*n*-hexane 1:2 in vol %) to give **6** as a brown oil (3.8 g, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.57 (s, 6H), 3.70 (s, 3H), 3.77 (s, 2H), 6.76 (d, $J = 3.5$ Hz, 1H), 7.00 (d, $J = 3.7$ Hz, 1H).

5-Ethynyl-2-thiopheneacetic Acid Propyl Ester (7). A solution of potassium hydroxide (1.7 g, 30 mmol) dissolved in methanol (10 mL) was added into a solution of compound **6** (3.2 g, 13 mmol) in toluene (120 mL). The reaction mixture was refluxed for 2 h with a Dean−Stark trap. After cooling to room temperature, the mixture was neutralized with hydrochloric acid and extracted with ether, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue, 1-bromopropane (1.1 g, 9.0 mmol), potassium carbonate (0.83 g, 6.0 mmol), and a trace amount of potassium iodide were added to DMF (20 mL). The resulting mixture was stirred at room temperature for 8 h. The crude product was extracted with ethyl acetate and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 1:2 in vol %) to give **7** as a yellow oil (0.25 g, 9.0%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.65 (m, $J = 7.3$ Hz, 2H), 3.30 (s, 1H), 3.77 (s, 2H), 4.07 (t, $J = 6.8$ Hz, 2H), 6.78 (d, $J = 2.8$ Hz, 1H), 7.11 (d, $J = 3.7$ Hz, 1H).

5,5′′-Bis(5-butoxycarbonyl-2-thienylethynyl)-2,2′:5′,2′′-terthiophene (TD1). 5,5′′-Dibromo-2,2′:5′,2′′-terthiophene (0.41 g, 1.0 mmol), which was synthesized according to the literature,[18] compound **3** (0.62 g, 2.9 mmol), dichlorobis(triphenylphosphine)palladium(II) (70 mg, 0.10 mmol), copper(I) iodide (20 mg, 0.10 mmol), and triphenylphosphine (65 mg, 0.28 mmol) were added to a solution of triethylamine (5.0 mL) in THF (30 mL) under a nitrogen atmosphere, and the reaction mixture was stirred at 80 °C for 12 h. After being cooled to room temperature, the mixture was poured into 2 N hydrochloric acid (50 mL) and extracted with chloroform, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, eluent: chloroform/*n*-hexane 2:1 in vol %). The resulting solid was recrystallized from ethanol to give **TD1** as orange crystals (0.32 g, 49%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.96 (t, $J = 7.3$ Hz, 6H), 1.43 (m, $J = 7.5$ Hz, 4H), 1.69 (m, $J = 6.6$ Hz, 4H), 4.28 (t, $J = 6.6$ Hz, 4H), 7.06 (d, $J = 3.9$ Hz, 2H), 7.09 (s, 2H), 7.18 (d, $J = 3.9$ Hz, 2H), 7.20 (d, $J = 3.9$ Hz, 2H), 7.66 (d, $J = 3.9$ Hz, 2H). ^{13}C NMR (300 MHz, CDCl$_3$): δ 13.7, 19.2, 30.7, 65.3, 87.2, 88.6, 121.0, 123.9, 125.2, 129.1, 132.2, 133.1, 133.8, 134.8, 136.1, 139.3, 161.5. LRMS (FAB+) *m*/*z*: 660 (M$^+$). Anal. Calcd for $C_{34}H_{28}O_4S_5$: C, 61.79; H, 4.27; O, 9.68; S, 24.26. Found: C, 61.87; H, 4.25; O, 9.64; S, 24.51%.

5,5′′-Bis(5-propoxycarbonylmethyl-2-thienylethynyl)-2,2′:5′,2′′-terthiophene (TD2). TD2 was synthesized by a procedure similar to that for **TD1** using **7** (0.25 g, 1.2 mmol) and was obtained as orange crystals (0.15 g, 45%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.93 (t, $J = 7.3$ Hz, 6H), 1.65 (m, $J = 7.2$ Hz, 4H), 3.80 (s, 4H), 4.08 (t, $J = 6.6$ Hz, 4H), 6.83 (d, $J = 3.3$ Hz, 2H), 7.04 (d, $J = 3.7$ Hz, 2H), 7.07 (s, 2H), 7.12 (d, $J = 3.7$ Hz, 2H), 7.14 (d, $J = 3.7$ Hz, 2H). ^{13}C NMR (300 MHz, CDCl$_3$): δ 10.4, 21.9, 35.8, 67.0, 86.1, 87.7, 121.1, 122.3, 123.7, 124.9, 127.0, 132.1, 133.0, 136.0, 137.8, 138.5, 169.9. LRMS (FAB+) *m*/*z*: 660 (M$^+$). Anal. Calcd for $C_{34}H_{28}O_4S_5$: C, 61.79; H, 4.27; O, 9.68; S, 24.26. Found: C, 62.06; H, 4.30; O, 9.70; S, 24.11%.

Characterization of the Dye Molecules. LC behavior and phase transition behavior were evaluated on a polarizing optical microscope (POM; Olympus, BX50) equipped with a hot stage (Mettler, FP-90 and FP-82HT). Thermotropic properties of the dye molecules were determined with a differential scanning calorimeter (DSC; Seiko I&E, SSC-5200 and DSC220C) at heating and cooling rates of 2−10 °C/min and thermogravimetry and differential thermal analysis (Seiko I&C, SSC-5200 and TG/DTA6200) at a heating rate of 5 °C/min under a nitrogen atmosphere. At least three scans

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Table 1. Thermal Properties of the Guest Dye Molecules

dye	phase transition temperature (°C)	thermal decomposition temperature (°C)[a]
TR5[b]	I 191 N 90 S 54 K	n.d.
TD1	I 201 S 130 K	361
TD2	I 141 N 114 K	331

[a] Temperature at which a sample loses its weight by 3 wt % from its initial weight. [b] Cited from ref 14. n.d., not determined; K, crystal; S, smectic; N, nematic; I, isotropic.

were performed in each sample to verify reproducibility of the DSC measurement. The absorption spectra were measured with a UV−vis spectrometer (JASCO, V-550).

Sample Preparation. 4-Pentyl-4′-cyanobiphenyl (**5CB**) was obtained from Merck Ltd., being used as a nonphotosensitive host LC, without further purification. Guest dye molecules and **5CB** were dissolved separately in toluene, and the solutions were mixed together at dye concentrations from 0.04 to 0.20 mol %. After the solvent was removed completely under a vacuum, the LC mixture was sandwiched between two lecithin-coated glass substrates with a 100-μm-thick silica particle as a spacer. This cell with a homeotropic alignment of LCs was used as a sample for optical measurement.

Photoinduced Reorientation. Photoinduced reorientation of dye-doped LCs was evaluated by self-diffraction measurements at room temperature. The optical setup was illustrated elsewhere.[19] A linearly polarized Gaussian beam at 488 nm with a diameter of 1.5 mm from an Ar^+ laser (NEC, GLG3280) 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.

Results and Discussion

We previously reported that **TR5** shows a nematic phase between 191 and 90 °C and a smectic B phase between 90 and 54 °C on cooling.[20] Since the new dye has a structure similar to that of **TR5**, it can be expected that an LC phase appears. We have found that **TD1** shows a smectic phase between 201 and 130 °C and **TD2** exhibits a nematic phase between 141 and 114 °C on cooling (Table 1). It is interesting to note that **TD1** and **TD2** possess a very similar structure; the only difference is the position of the carbonyl moiety. In **TD1**, the carbonyl moieties are directly bound to the terminal thiophene rings, whereas in **TD2**, the carbonyl moieties are bound to the thiophene rings through a methylene spacer. Insertion of the methylene spacer between the carbonyl moiety and the thiophene ring significantly affected the thermal properties of the dye molecule: the decomposition temperature of **TD2** was lower than that of **TD1**, and the temperature range of the LC phase was found to be much narrower in **TD2** than that in **TD1**. Although we identified the smectic phase for **TD1** from the texture under POM, X-ray measurement is needed for more detail analysis.

Figure 2 shows absorption spectra of dye-doped LC samples. **TD1** and **TD2** show absorption property similar to that of **TR5**, and all spectra in **5CB** were red shifted by about 10 nm compared with those in toluene solution.[19] The absorption around 440 nm is due to a delocalized $\pi-\pi$ transition. Compared with **TR5**, the absorption maximum of **TD1** was red shifted by about 8 nm. The same type of bathchromic shift has been reported for thiophene oligomers having an electron donor or acceptor as end substituents.[21] 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.[22] On the other hand, the absorption maximum of **TD2** was almost the same as that of **TR5** despite having ester moieties at both ends. This indicates clearly that the conjugation is interrupted by the introduction of a methylene spacer between thiophene and the ester moiety.

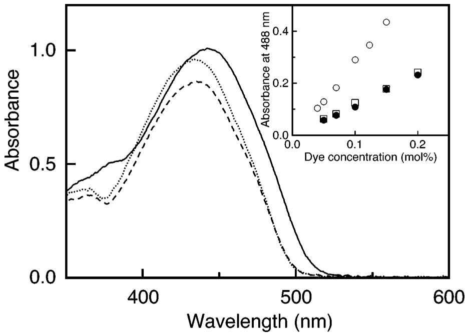

Figure 2. UV−vis absorption spectra of the dye-doped LC cells ([dye] = 0.15 mol %). (- - -) **TR5**; (—) **TD1**; (···) **TD2**. The inset shows absorbance at 488 nm of sample cells as a function of dye concentration. (□) **TR5**; (○) **TD1**; (●) **TD2**.

Absorbance at 488 nm of the sample cells is plotted as a function of the dye concentration and shown in the inset of Figure 2. In each cell, the absorbance increased linearly as the dye concentration increased. The values of the **TD1**-doped cell were twice as large as those of the **TR5**-doped cell, and the **TD2**-doped cell showed almost the same values as those of the **TR5**-doped cell.

Photoinduced reorientation of dye-doped LCs has been evaluated most conveniently by self-diffraction ring measurements thanks to the extremely large self-phase modulation of the dye-doped LCs.[9,16,19,23,24] When the refractive index is changed and the maximum phase increment is much larger than 2π, the number of bright rings is related to such factors as the LC cell thickness and the wavelength of the laser beam.[1] When LC molecules are reoriented, the diffraction rings appear in proportion to the change in refractive index, while no diffraction ring is formed when the LC molecules are in the initial state or with only little reorientation. Upon photoirradiation of the laser beam, transmitted light formed diffraction patterns on a screen. The typical diffraction pattern observed in the **TD1**-doped cell is shown in Figure 3. Depending on the light intensity, the time needed for the appearance of the diffraction rings was varied from several seconds to several minutes. The diffraction rings were clear and in high contrast but slightly fluctuating on the

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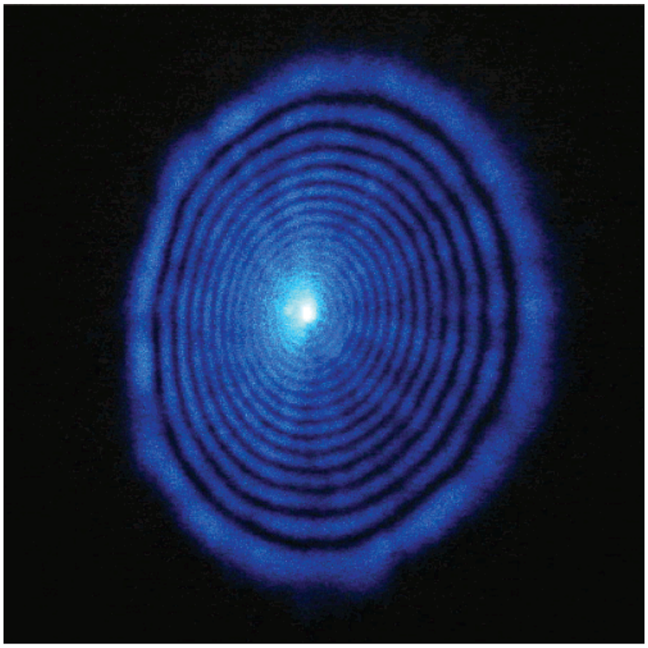

Figure 3. Typical diffraction pattern of **TD1**-doped **5CB** formed on a screen at 24 W/cm^2. Dye concentration: 0.15 mol %.

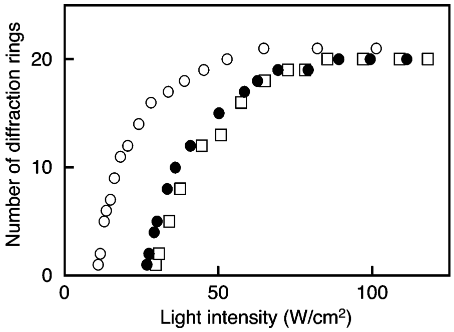

Figure 4. The number of observed diffraction rings as a function of light intensity. (□) **TR5**; (○) **TD1**; (●) **TD2**. Dye concentration: 0.15 mol %.

screen. The number of diffraction rings (N) varied by the light intensity. N can be estimated from eq 1:[1]

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

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 eq 1.

The number of diffraction rings observed on the screen in the dye-doped cell is shown in Figure 4. When the light intensity was low, no rings could be observed. Above the threshold intensity, the rings appeared, and the number of rings increased with the light intensity. Then, the growth of the rings 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 the **TR5**-, **TD1**-, and **TD2**-doped samples were 20, 21, and 20, respectively. According to eq 1, these values correspond to Δn values of 9.8×10^{-2}, 0.10, and 9.8×10^{-2}, respectively, which are almost the same as those of the pure LC host.[1] It is inferred from the value of birefringence of **5CB** (0.194)[25] that LC molecules are aligned parallel to the glass substrates in the central part of the irradiated spot. We assume that there is no large difference in the reorientational behavior among the three dye molecules on the basis of their structure. We defined the threshold intensity as the light intensity at which the first ring appears. The threshold intensity was 30 W/cm^2 for the **TR5**-, 11 W/cm^2 for the **TD1**-, and 27 W/cm^2 for the **TD2**-doped samples. The introduction of ester moieties to **TR5** effectively reduces the threshold intensity by about 3 times in the **TD1**-doped cell.

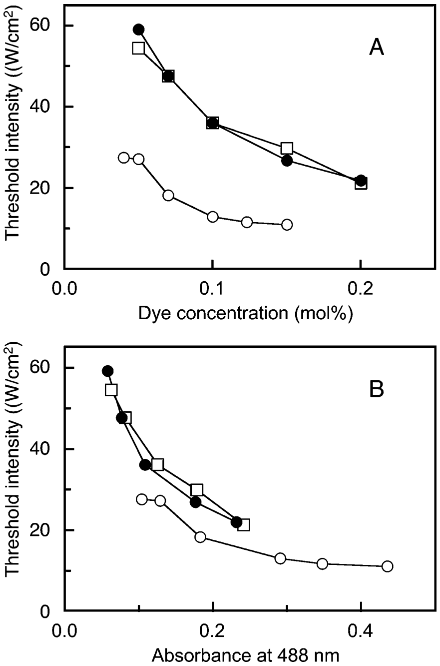

Figure 5. Change in the threshold intensity as a function of dye concentration (A) and as a function of absorbance at 488 nm of the sample cell (B). (□) **TR5**; (○) **TD1**; (●) **TD2**.

Figure 5A 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 by an increase in the number of the photoexcited dye molecules. Compared to the **TR5**-doped sample, at the same dye concentration, the threshold intensity of the **TD1**-doped sample was lower by about 3 times at any concentration. This can be attributed to a larger absorption of the **TD1** dye at 488 nm. Therefore, to investigate the genuine effect of the dyes on the reorientational behavior, we normalized the threshold intensities by absorbance at 488 nm. The result is shown in Figure 5B. Even at the same absorbance, at 488 nm, the threshold intensity of the **TD1**-doped cells was still lower than that of the **TR5**-doped cells. It suggests that **TD1** possesses a substantially higher ability to induce reorientation of host LCs than **TR5**.

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(25) Dunmur, D.; Toriyama, K. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, p 215.

Marrucci et al. reported that polar interactions, such as dipole–dipole interactions and hydrogen bonds, account for the dye-induced reorientation rather than dispersive interactions in their LC system.[15] In fact, it is possible that the reorientational efficiency is improved by the dipole–dipole interaction between a cyano moiety in the host LC molecule and a carbonyl moiety in the dye molecule. We will now examine dipole–dipole interactions due to the carbonyl moiety in detail. Compound **TD2** has ester moieties that are not directly bound to the terminal thiophene, and it showed almost the same optical property as **TR5**, as mentioned above. Therefore, we assume that if there is any dipole–dipole interaction between the cyano moiety and the carbonyl moiety, we could see any difference on the threshold intensity between the **TR5**- and **TD2**-doped samples. However, at the same dye concentration or the same absorbance at 488 nm, the threshold intensity of the **TD2**-doped sample was comparable to that of the **TR5**-doped sample at any condition in Figure 5. These results indicate that dipole–dipole interaction between the cyano moiety and the carbonyl moiety hardly influences the threshold intensity for reorientation under the present experimental conditions. Hence, we may assume that the improvement of the reorientational efficiency in the **TD1**-doped sample results from the photophysical excitation state of the dye molecule instead of the ground-state interactions between the dye molecule and the host LCs.

Chakraborty et al. performed the molecular orbital analysis of oligothiophene and its cyano derivative.[26] They have reported that an introduction of an electron accepting group (cyano group) into the backbone influences the highest occupied molecular orbital (HOMO) to the least extent but affects the lowest unoccupied molecular orbital (LUMO) significantly, in such a way that it is localized in the cyano substituent to more of an extent than the unsubstituted parent oligomer. On the basis of their results, we interpret our results as follows. We can assume that the HOMO and LUMO are the electronic states of the ground state and the photoexcited state of the dye molecule, respectively. Then, we would expect that an introduction of the ester group into the terminal thiophene could strongly affect the electronic state of the photoexcited state of **TD1**. The electronic states of **TR5**, which has no ester moieties, and **TD2**, which has ester moieties bound to the thiophene rings through a methylene spacer, would be the same at the photoexcited state. This can also be expected from the absorption spectra described above. On the contrary, with the electronic state of the photoexcited state of **TD1**, which has ester moieties bound to the thiophene rings directly, we consider that π electrons tend to localize at the terminal thiophenes by the electron acceptor effect of the ester moieties. This could expand the intramolecular delocalization of π electrons along the molecular long axis, and the resulting electronic state could enhance the molecular polarizability of the excited states in comparison to those of the other two dye molecules. This consideration could explain the result that **TD1** possesses a substantially high ability to induce reorientation of host LCs.

Conclusion

We newly synthesized LC oligomer-type thiophene derivatives having ester moieties directly bound to the terminal thiophene (**TD1**) and indirectly bound to the terminal thiophene (**TD2**) as a guest dye molecule for dye-doped LCs. Compound **TD1** lowered the reorientational threshold intensities by about 3 times compared to that of the thiophene dye with no ester moiety at the same doping concentration. This result could be interpreted in terms of extended delocalization due to ester moieties directly bound to the thiophene rings in the excited state.

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(26) Chakraborty, D.; Lagowaki, J. B. *J. Chem. Phys.* **2001**, *115*, 184–194.