

# Light Amplification in Photorefractive Ferroelectric Liquid Crystal Blends Containing Quarter-Thiophene Photoconductive Dopant

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**Abstract** Ferroelectric liquid crystal blends containing a photoconductive chiral dopant and an electron trap reagent exhibit a large photorefractivity and fast response. They can be utilized in dynamic amplification of moving optical signals. In the present study, the enhancement of working wavelength to a longer wavelength regions was investigated. A series of photoconductive chiral dopants was prepared and the photorefractive properties were examined.

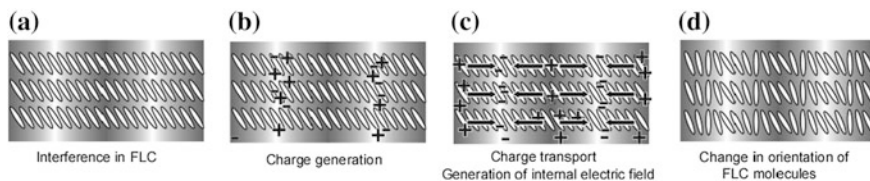
## 1 Introduction

A ferroelectric liquid crystal (FLC) mixture composed of liquid crystal compounds and photoconductive chiral dopant exhibits a large photorefractivity. Blends of liquid crystalline compounds and photoconductive chiral compounds are used to achieve a high photorefractivity since it is difficult to obtain high transparency and high performance using a single compound. We have investigated the amplification of moving optical signals by photorefractive FLC blends [1]. The photorefractive effect forms a refractive index grating within a medium, based on a change in the refractive index of the medium resulted from photoinduced electric field and an electro-optic effect. The mechanism of the photorefractive effect in FLC blends containing photoconductive compounds is shown in Fig. 1.

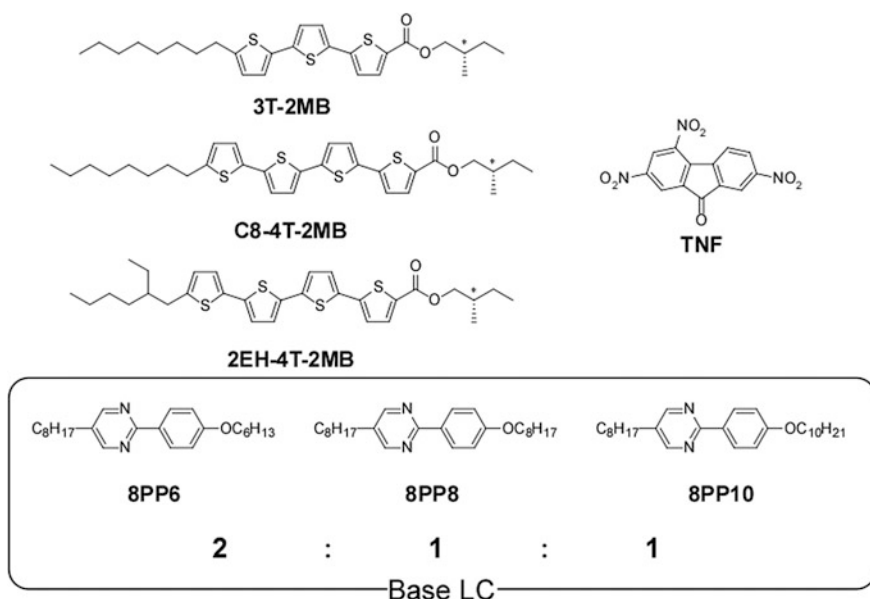
The most characteristic phenomena of the photorefractive effect is the asymmetric energy exchange, in which the energy of one of the interfering laser beams transfer to the other. The asymmetric energy exchange can be utilized in optical signal amplification. The ferroelectric liquid crystals used for practical application are mixtures of several liquid crystalline compounds and chiral dopants. In order to obtain a photorefractive FLC, a photoconductive compound is also added to the FLC mixture. However, in the most case, the photoconductive compounds are not

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**Fig. 1** Mechanism of the photorefractive effect in an FLC. **a** Two laser beams interfere in the SS state of the mixture of a FLC and a photoconductive compound, **b** positive and negative charges are generated at the bright areas of the interference fringes, **c** while electrons are trapped at trap sites in the bright areas, positive charges (holes) migrate by diffusion or drift in the presence of an external electric field to generate an internal electric field between the bright and dark positions, and **d** a change in orientation of the spontaneous polarization vector is induced by the internal electric field



**Fig. 2** Structures of the photoconductive chiral dopants smectic LCs, and the electron trap reagent (TNF)

liquid crystalline materials, addition of the photoconductive compound to the FLC mixture disturbs the alignment of FLC molecules. Thus the light scattering in the FLC medium increases. In order to avoid this problem, photoconductive compounds that also possess chiral structure were synthesized. One can obtain a photorefractive FLC just by mixing of the photoconductive chiral compound with a FLC mixture. We have reported that photorefractive FLC blends containing photoconductive chiral dopants exhibit a large photorefractivity and a fast response [2]. The photoconductive chiral dopants used in the previous study were terthiophene compounds (Fig. 2, 3T-2MB). The absorption of terthiophene is shorter than

500 nm so that 488 nm lasers were used to induce the photorefractive effect. In the present study, quarter-thiophenes (Fig. 2, C8-4T-2MB and 2EH-4T-2MB) were synthesized and mixed with a smectic liquid crystal to form a ferroelectric liquid crystals. The photorefractive properties in longer wavelength region were investigated.

## 2 Experimental

### 2.1 Samples

The structures of the compounds used in this study are shown in Fig. 2. A mixture of phenylpyrimidine type smectic liquid crystalline compounds, 8PP8, 8PP10 and 8PP6, was used as a host liquid crystal (base-LC). The mixing ratio of 8PP6, 8PP8 and 8PP10 was set to 2:1:1. Photoconductive chiral dopants possessing quaterthiophene chromophore were synthesized. The photoconductive chiral dopant was mixed with host liquid crystal and electron trap reagent TNF. The mixture of the base-LC, TNF and a photoconductive chiral dopant was injected into a glass-cell equipped with ITO electrode and polyimide alignment layer. The thickness of the FLC was adjusted to 10  $\mu\text{m}$ .

### 2.2 Measurement

Phase transition temperatures were measured by differential scanning calorimetry (DSC; DSC822, Mettler) and by microscopic observations (FP-80, FP-82, Mettler; DM2700 polarizing microscope, Leica). Spontaneous polarization ( $P_s$ ) was measured by the spontaneous polarization measurement system for ferroelectric liquid crystals (TS-LCM-6254C, Toyo Technica). The photorefractive effect was evaluated by two-beam coupling experiments. A linearly polarized 488 nm beam from a diode-pumped solid state laser (DPSS laser, Spectra Physics, Cyan) was divided in two by a beam splitter, and interfered within the sample film. The laser intensity was 2 mW for each beam and the diameter of each beam was 0.5 mm. The incident angles of the beams to the glass plane were  $30^\circ$  and  $50^\circ$ . The interference fringe interval was 1.87  $\mu\text{m}$ . The measurement was conducted at room temperature ( $26^\circ\text{C}$ ). An electric field (0–10 V/ $\mu\text{m}$ ) was applied to the sample from a regulated DC power supply (Kenwood DW36-1). The transmitted beam intensity was monitored by photodiodes (ET-2040, Electro-Optics Technology, Inc.). The time required to form the refractive index grating in the FLC was ascertained based on the simplest single-carrier model of photorefractivity, in which the gain transient is exponential. The rising signal of the diffracted beam was fitted using a single exponential function:

$$\gamma(t)-1 = (\gamma-1)[1 - \exp(-t/\tau)]^2, \quad (1)$$

$\gamma(t)$  represents the transmitted beam intensity at time  $t$  divided by the initial intensity ( $\gamma(t) = I(t)/I_0$ ), and  $\tau$  is the formation time. the two-beam coupling gain coefficient  $\Gamma$  was calculated assuming Bragg diffraction [1–5].

$$\Gamma = \frac{1}{D} \ln \left( \frac{gm}{1+m-g} \right), \quad (2)$$

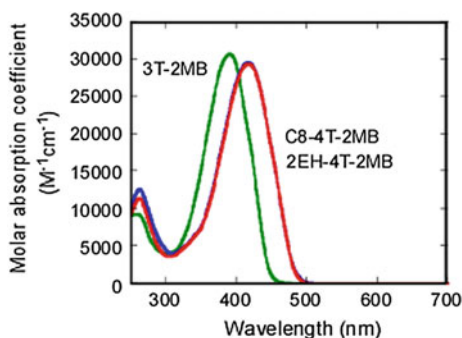
$D = L/\cos(\theta)$  is the interaction path for the signal beam ( $L$  = thickness of the sample,  $\theta$  = propagation angle of the signal beam in the sample),  $g$  is the ratio of the signal beam intensities behind the sample with and without a pump beam, and  $m$  is the beam intensity ratio (pump/signal) in front of the sample.

### 3 Results and Discussions

Figure 3 shows the UV-visible absorption spectra of the photoconductive chiral dopants used in this study. The quarter-thiophene moiety absorbs longer wavelength than ter-thiophene moiety because of the expanded  $\pi$ -conjugation structure. It was confirmed that the quarter-thiophene dopants can be used for the writing beam wavelength of 532 nm.

The textures of the FLC blends containing C8-4T-2MB in 10- $\mu\text{m}$  gap LC cell observed under polarizing microscope. C8-4T-2MB was soluble to the base-LC at the concentration of 4 wt%, however, precipitation of C8-4T-2MB crystals was observed at concentrations higher than 6 wt%. The size of the quarter-thiophene moiety is larger than that of the ter-thiophene moiety, so that the quarter-thiophene compound is more likely to crystallize. In order to prevent the quarter-thiophene dopants from crystallization in a LC medium, we made a modification to the molecular structure of the quarter-thiophene dopants. The flexible alkyl chain (tail unit), which is attached to the quarter-thiophene moiety, is necessary to achieve a

**Fig. 3** UV-visible absorption spectra of the photoconductive chiral dopants measured in chloroform solution



high miscibility to a liquid crystalline medium. The tail unit is responsible for the lowering of the melting point and make the molecular structure more resemble to that of base LC. The quarter-thiophene dopant introduced with branched tail (2EH-4T-2MB) was synthesized.

The phase diagrams of the FLC blends mixed with quarter-thiophene chiral dopants are shown in Fig. 4. The temperature range of the SmC\* phase was widened in the FLC blend with 2EH-4T-2MB. The textures of the FLC blend containing 2EH-4T-2MB in 10  $\mu\text{m}$ -gap LC cells were observed under polarizing microscope.

No crystallization of the dopant was observed at the dopant concentration of 4 and 6 wt%. Thus, the miscibility of the quarter-thiophene dopant was improved by the introduction of branched tail structure. The transmittance of 633 nm laser through the FLC sample was investigated. Figure 5a shows the transmitted intensity of the laser beam through the FLC sample plotted as a function of the concentration of the quarter-thiophene dopants. The FLC sample containing 2EH-4T-2MB exhibited a higher transparency. The photoconductivities of the FLC samples were investigated as shown in Fig. 5b. No currents were observed in the FLC blends in the dark. When the 488 nm laser was irradiated to the sample, photocurrents were observed. The photocurrent of FLC blends with quarter-thiophene dopants were much larger than that of the FLC blend with ter-thiophene dopant. The photoconductivity was enhanced in the larger  $\pi$  conjugate system. No difference in photoconductivity was observed in FLC samples with C8-4T-2MB and 2EH-4T-2MB.

The photorefractive effects of the FLC blends were investigated by two-beam coupling method. Figure 6a shows the typical example of the asymmetric energy exchange observed in a FLC sample containing 2EH-4T-2MB. The asymmetric energy exchange was clearly observed at the writing beam wavelength of 532 nm. The photorefractive effect was observed only in the SmC\* phase (ferroelectric phase). The result shows that the photorefractive effect of the FLC is caused by the response of the spontaneous polarization (Fig. 1). The magnitude of the gain

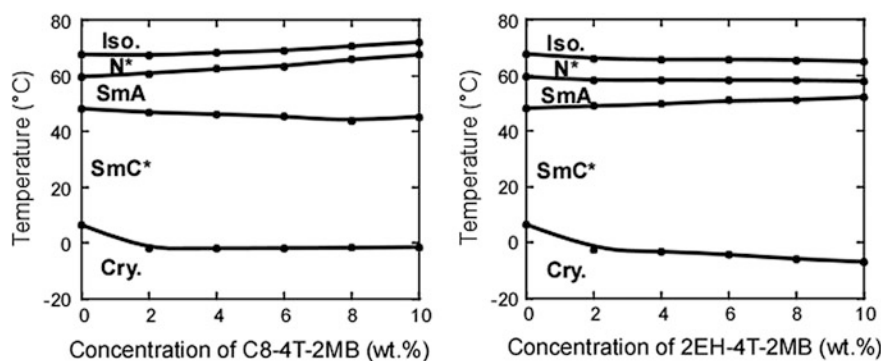
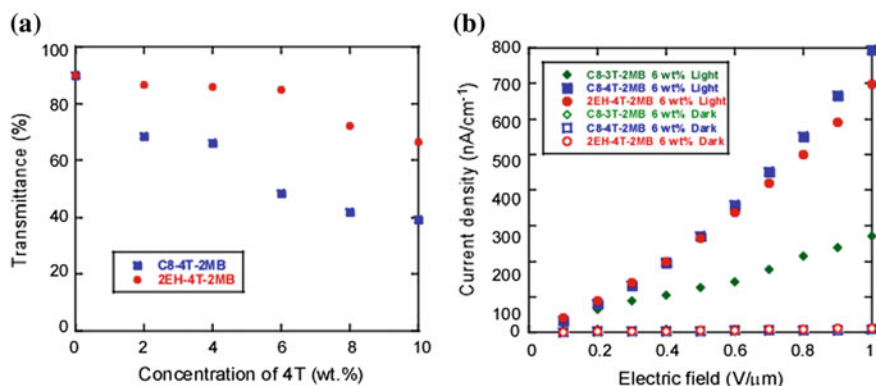
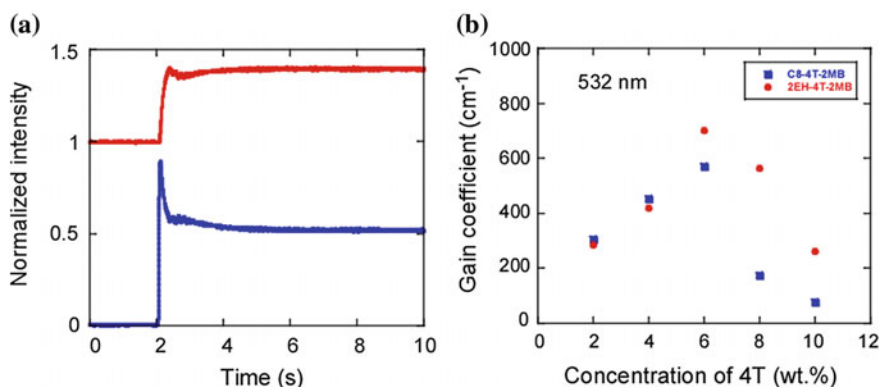


Fig. 4 Phase diagrams of base-LC and photoconductive chiral dopants



**Fig. 5** **a** Transmitted beam intensities through FLC samples. The wavelength of the laser was 633 nm. The concentration of the photoconductive chiral dopant was set to 6 wt%. **b** The photoconductivities of the photorefractive FLC blends containing photoconductive chiral dopants. Current densities are plotted as a function of the applied electric field. The concentration of the photoconductive chiral dopants was kept at 6 wt%. A 488 nm laser (10 mW/cm<sup>2</sup>, 1 mm diameter) was used as the irradiation source



**Fig. 6** **a** Typical example of the asymmetric energy exchange observed in two-beam coupling experiments for a FLC blend composed of a ternary mixture base LC, 2EH-4T-2MB, and TNF measured at 30 °C. The pump beam was incident to the sample at 2 s. **b** The magnitude of two-beam coupling gain coefficient of FLC blends are plotted as functions of the concentrations of the photoconductive chiral dopants. The wavelength of the laser was 532 nm. The measurement was conducted at 30 °C

coefficient measured at 532 nm are plotted as a function of the concentration of the quarter-thiophene dopants in Fig. 6b. The maximum gain coefficients were obtained at the photoconductive chiral dopant concentration of 6 wt%. It was considered that the sample kept transparent while exhibiting a large photoconductivity at this concentration. The gain coefficient was larger in the FLC blend

with 2EH-4T-2MB than that with C8-4T-2MB because of the higher transparency in the 2EH-4T-2MB sample.

## 4 Conclusion

The photorefractive effects of FLC blends containing ter-thiophene and quarter-thiophene photoconductive chiral dopants were investigated. The low miscibility of the quarter-thiophene moiety into the liquid crystalline medium was improved by the introduction of branched chain into the tail unit of the quarter-thiophene chiral dopant. The FLC blend with branched tail quarter-thiophene compound exhibit a higher photoconductivity and longer absorption wavelength. The two-beam coupling experiment was conducted using a 532 nm laser. A large photorefractivity at 532 nm was observed in a FLC blend containing quarter-thiophene photoconductive chiral dopant.

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