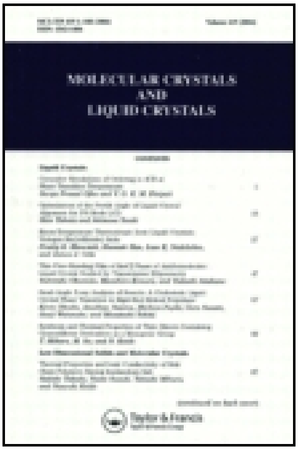

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Photochemical Modulation of the Wavelength of Lasing from a Dye-Doped Cholesteric Liquid Crystal

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This work provides reversible phototuning of the laser emission by means of photoisomerization of chiral azobenzene, causing change in the reversible helical pitch. Cholesteric liquid crystals were prepared by mixing a low molar mass liquid crystal (TKS), a laser dye (DCM), a nonphotochromic chiral compound (S811) and a chiral azobenzene compound (Azo). Lasing from the cholesteric liquid crystal was observed at longer band edge of the selective reflection. Reversible shift of the lasing was brought about by UV light irradiation and following visible light irradiation.

Keywords: cholesteric liquid crystal; laser emission; photoisomerization

INTRODUCTION

Many studies have been reported on liquid crystals containing photochromic compounds for applications to various optical devices [1–8]. Cholesteric liquid crystals (Ch LCs) have a helical structure, and selectively reflect light of a wavelength proportional to the helical pitch (p). Dissolving a chiral compound in a nematic LC provides a helical structure corresponding to the concentration of chiral compounds dissolved in the nematic LC. Here, helical twisting power (HTP) of the chiral compound is defined as the slope of 1/p versus the concentration of the chiral compound. Therefore, if one can change

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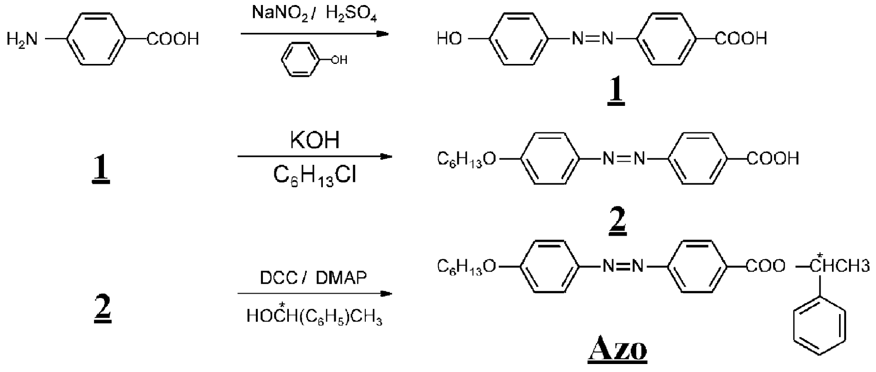
HTP of the chiral compound photochemically, a change in the helical pitch will take place, proving optical devices driven photochemically without application of any external force such as an electric field [9–12]. Recently, we have also described the reversible photochemical change in transparency as well as in the selective reflection of a Ch by photoisomerization of a chiral azobenzene compound doped in a host nematic LC [13]. The photochemical change in transparency and selective reflection can be interpreted in terms of photochemical change in HTP, resulting in a change in the helical pitch of the Ch LC.

On the other hand, much attention has been paid for the concept of the photonic crystals. Photonic crystals have the structure with a periodicity equal to optical wavelength, and exhibit a photonic bandgap in which the propagation of light is forbidden. One of interesting applications of the photonic crystals is laser emission with extremely low-threshold. Several studies have been reported on laser emission from a Ch LC, since a Ch LC having helical structure can act as a one-dimensional periodic structure [14]. Recently, Chanishvili, and Furumi independently reported on the irreversible phototunable lasing from a Ch LC doped with laser dye [15–16]. However, there is little report on reversible phototuning of the wavelength of the laser emission. Thus, an objective of this work is to provide reversible phototuning of the laser emission by means of photoisomerization of chiral azobenzene, causing change in the reversible helical pitch.

EXPERIMENTAL

A chiral azobenzene (**Azo**) was synthesized by diazo-coupling reaction and following esterificaion with (S)-(-)-1-phenylethanol (purity: >98%) in a presence of dicyclhexylcarbodiimide (**DCC**) according to Scheme 1. In this synthesis, it was confirmed that inversion of chirality had not occured. **Azo** was found to induce left-handed helical structure when it was added in a host nematic LC (**E44**, Merck Co.). The wavelength of the selective reflection of the Ch LC was adjusted by dissolving **Azo** as well as **S811** in **E44**. Then, the Ch LC was doped with 0.4 wt% of **DCM** (Fig. 1). The Ch LC was injected into a homogeneous glass cell having 25 μm cell gap (EHC Co. Ltd). The transmittance spectra were recorded with a Simadzu UV-1600PC spectrometer. Photoirradiation was carried out using a 500 W high pressure Hg lamp (Ushio SX-UI 500H) equipped with a filter (Sigma Koki Co. UTVAF-35 for UV light or SCF-42L for visible light). The experimental setup for an emission measurement is shown in Figure 2. The emission properties of dye-doped Ch LC cells



SCHEME 1 Synthetic route of the chiral azobenzene compound, Azo.

were studied with the second harmonic light at 532 nm from a Q-switched Nd:YAG laser beam as an excitation source. The pulse repetition frequency was 10 Hz, and the pulse width was 15 ns. The laser beam was focused on the cell by using a convex lens. The Ch LC cell was irradiated with a laser beam at an incident angle of 45° from the normal of the surface. The emission spectra were recorded with an OceanOptics 2000 spectrometer, using fiber optics.

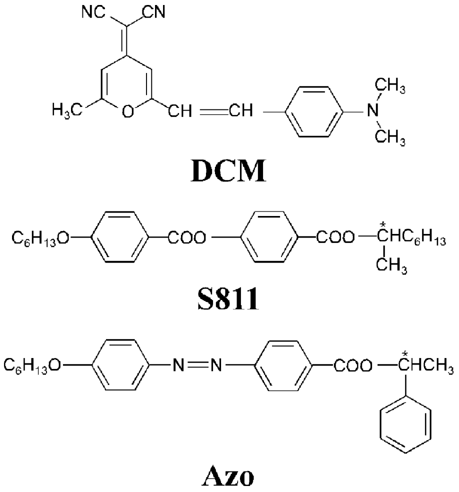


FIGURE 1 Structure of compounds in this study.

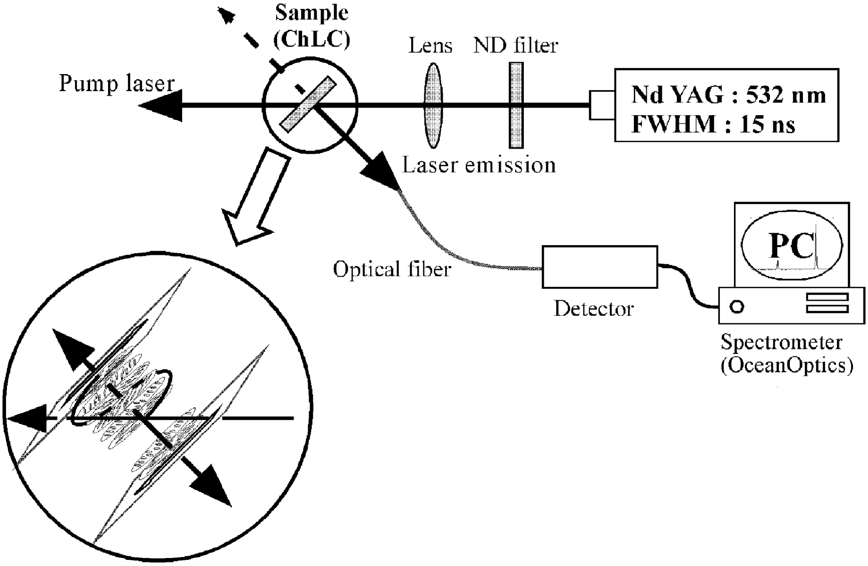


FIGURE 2 Experimental setup for measurement of emitted laser.

RESULTS AND DISCUSSION

A Ch LC sample was prepared by mixing **Azo**, **S811**, **DCM** and **E44** (4.3/24.2/0.4/71.1 wt%). This LC mixture showed a cholesteric phase in a temperature range from room temperature to 50°C. The helical structure was left-handed.

Changes in transmission spectra of the Ch LC by UV irradiation at 25°C are shown in Figure 3. The selective reflection band was shifted to longer wavelength by UV irradiation. In order to clarify the thermal effect due to UV light, the helical pitch was measure by varying temperature.

The photochemical shift of the selective reflection can be interpreted to difference in HTP between trans-form and cis-form: HTP of trans-form was larger than that of cis-form.

Figure 4 shows the emission intensity and its spectral bandwidth as a function of the pumping energy of Nd:YAG laser pulse. An abrupt increase in the emission intensity was observed higher than 6 μJ/pulse of the pumping energy. In addition, the bandwidth became extremely sharp from 15 nm to 1.5 nm at the same pumping energy. These results indicate that the threshold for lasing is approximately 6 μJ/pulse. The selective reflection band and laser emission are shown

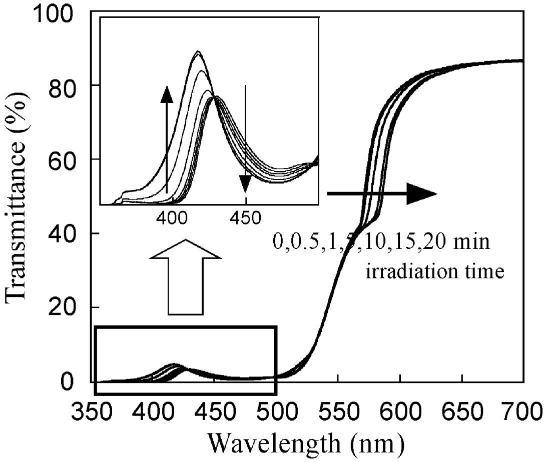


FIGURE 3 Changes in transmittance spectra of the Ch LC mixture on UV irradiation (366 nm, 20 mW/cm^2).

in Figure 5. The laser emission was observed at longer edge of the reflection band of the Ch LC, corresponding to the lower-energy-edge of the reflection band.

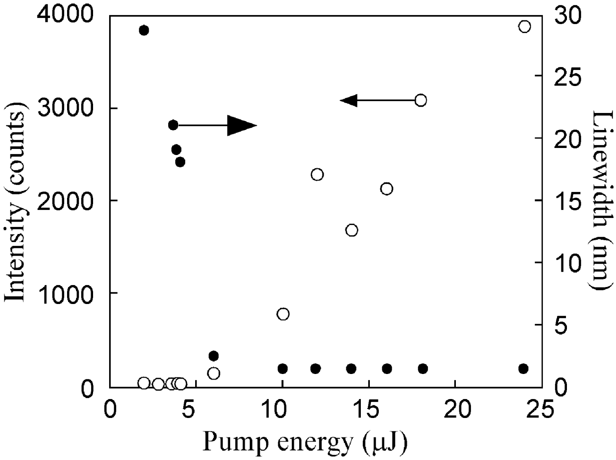


FIGURE 4 Changes in emission intensity and spectral linewidth as function of pump energy at room temperature.

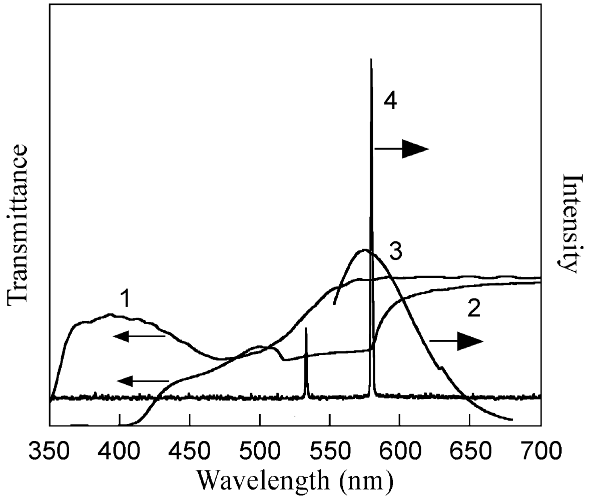


FIGURE 5 1) Transmission spectrum of NLC/DCM mixture. 2) Transmission spectrum of NLC/S811/Azo mixture. 3) Fluorescence emission spectrum of NLC/S811/Azo/DCM mixture. 4) Emission spectrum of NLC/S811/Azo/DCM mixture. (Pump light wavelength: 532 nm).

Figure 6 shows changes in laser emission spectra of the Ch LC by UV irradiation. It is clear that the laser emission was shifted to longer wavelength by UV irradiation. The shift of the reflection band was caused by UV irradiation as can be seen in Figure 3, due to photochemical decrease in HTP of **Azo** dye. It was reported that the laser action of the Ch LC arises from the internal distributed feedback effect of the Ch LC. Therefore, the change in laser emission shown in Figure 6 may be related closely to the photochemical change in helical pitch. In addition, UV irradiation caused a decrease in the emission intensity as well as slight increase in the linewidth. Azo dyes are well known to an isothermal phase transition of LC materials from LC phase to an isotropic phase owing to the disorganization effect which arises from the difference in the molecular shape between trans-from with rod-shape and cis-form with bent shape. Besides the dependence of threshold excitation energy on the wavelength due to overlapping of fluorescence of the laser dye with the reflection band of the Ch LC, the disorganization effect may be contributed to the change in the emission spectra by UV irradiation. The emission spectra were restored to the initial state by visible light irradiation or thermally in the dark.

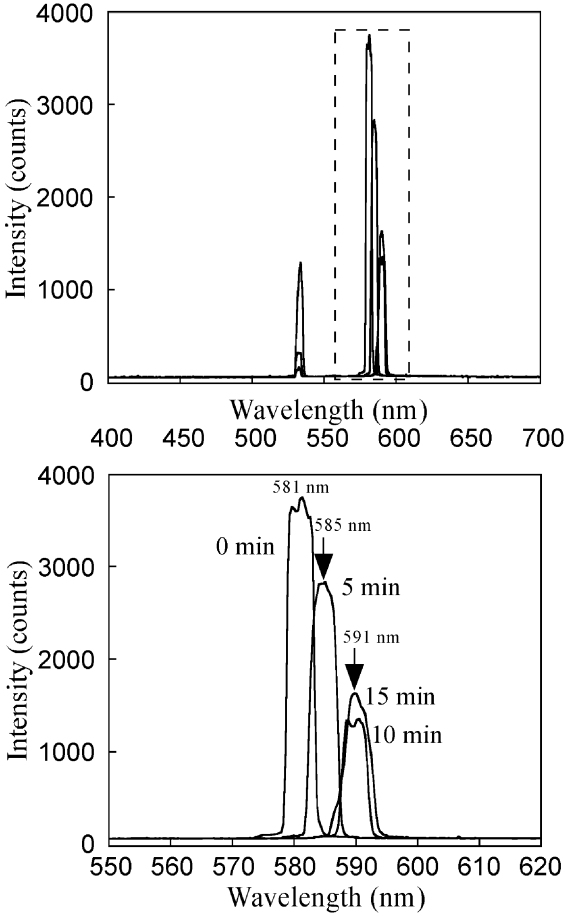


FIGURE 6 Changes in wavelength of lasing Ch LC mixture by UV irradiation.

CONCLUSION

We demonstrated the reversible photochemical modulation of laser emission by the use of the Ch LC containing chiral azobenzene compound. The Ch LC showed lasing at the longer edge wavelength of the selective reflection. Reversible shift of the lasing was brought about by UV light irradiation and following visible light irradiation. However, the lasing was labilized by UV irradiation. Synthesis of new chiral azobenzene compounds is in progress in order to improve the response and the stability of the lasing.

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