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SENSITIZING EFFECTS OF FLUORESCENT DICHROIC DYES IN NEMATIC LIQUID CRYSTAL

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Green and red fluorescence of dichroic dyes can be sensitized by adding blue fluorescent dyes in a nematic liquid crystal (LC). The excitation energy of a ultraviolet (UV) light transfers to an emitter through sensitizers and fluorescence intensity increases by 3 ∼ 13 times. Relations between absorption and emission dichroic ratios of sensitizers and emitters have been measured and discussed. The voltage dependence of fluorescence intensity is also measured in the fluorescent guest host LC cell. The brightness and contrast ratio can be enhanced by adding the sensitizer of which dichroic ratio is higher than that of the emitter.

Keywords: dichroic ratio; electro optical property; fluorescent dichroic dye; guest host mode; nematic liquid crystal; sensitizing effect

INTRODUCTION

Emissive type liquid crystal displays (LCDs) in which fluorescent guest host (GH) mode is applied to display have been proposed [1–3]. The fluorescence intensity of the fluorescent GH LC cell can be controlled by applying a voltage across the LC cell. In addition, we have studied on a multi-fluorescent-color switching in the fluorescent GH LCD in which the cell with different fluorescence colors are stacked. The GH LC cell functions as a UV shutter and/or an emitter [4–9].

We have improved the fluorescence intensity and the color switching property of the fluorescent GH LCD step by step. However, the fluorescence intensities of colors are respectively different, because dyes with different absorption spectra are excited by using, for example, a high pressure Hg lamp or a UV light emitting diode with a specific wavelength. Therefore, the color balance in the fluorescent LCD is insufficient.

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Recently, we have reported a sensitizing effect of the fluorescent LC to solve these problems [10,11]. A fluorescent nematic LC and fluorescent dyes have been used as a sensitizer and the fluorescence intensity of emitter can be increased about by 10 times. In this study, sensitizing effects by single and multiple energy transfers are investigated in the nematic LC. Electro optical properties in the fluorescence GH LC cells are measured and relations between absorption and emission dichroic ratios of the emitter and the sensitizer are discussed.

EXPERIMENTAL

Fluorescent dichroic dyes of 2,5-bis5′-tertbutyl-2′-benzoxazolyl-thiophene (BBOT), coumarin-1 (C-1), coumarin-314 (C-314), coumarin-334 (C-334) and coumarin-6 (C-6) from Aldrich and NKX-2068, NXK-4256 and NKX-2197 from Hayashibara Biochemical Lab. were used as a sensitizer and/or an emitter. A UV fluorescent lamp (Toshiba FL6BLB, $\lambda_m = 360$ nm, FWHM = 40 nm) was used as an excitation light source. ZLI-1083 of phenylcyclohexane compounds was used as a host LC, which was almost transparent in the wavelength range of the excitation UV light. The fluorescent guest dye of 0.5 wt% was dissolved in the LC host. Figure 1 shows the spectrum of the UV fluorescent lamp and absorption spectra of dichroic dyes in the LC host. Homo-

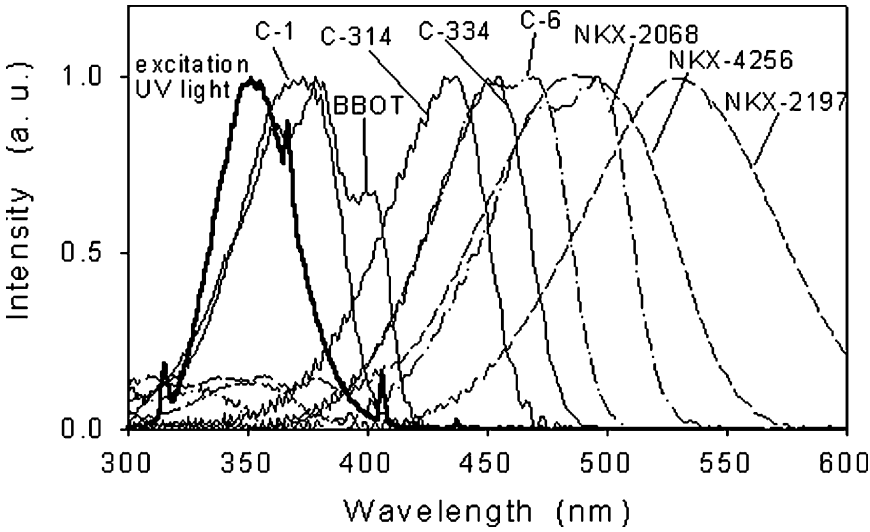

FIGURE 1 Emission spectrum of excitation UV fluorescent lamp and absorption spectra of dichroic dyes.

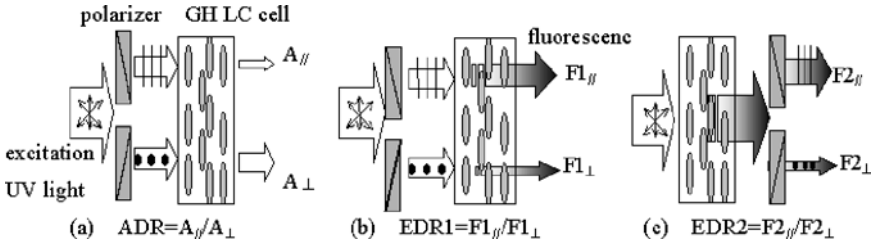

FIGURE 2 Schematic models of (a) absorption dichroic ratio ADR, (b) emission dichroic ratio EDR1 and (c) EDR2.

geneously aligned LC cells were prepared with the fluorescent GH LC and the cell thickness was 10 μm. The sensitizer of 0.5wt% was also added to the fluorescent GH LC cell.

Absorbance, $A_{//}$ and $A_{\perp}$, for the incident polarized light parallel and perpendicular to the LC alignment direction (rubbing direction in the cell) were measured and the absorption dichroic ratio ADR ($=A_{//}/A_{\perp}$) was estimated, as shown in Figure 2(a). Moreover, we measured fluorescence intensities of $F1_{//}$ and $F1_{\perp}$, when we irradiated the cell with polarized excitation lights parallel and perpendicular to the LC direction, respectively. The ratio of two fluorescence intensities, $F1_{//}/F1_{\perp}$, is defined as the emission dichroic ratio of EDR1, as shown in Figure 2(b). On the other hand, the fluorescence of the LC cell is polarized when the LC cell is irradiated with the nonpolarized excitation light. Therefore, we measured the polarized fluorescence intensities of $F2_{//}$ and $F2_{\perp}$, and estimated another emission dichroic ratio EDR2 ($=F2_{//}/F2_{\perp}$), as shown in Figure 2(c).

RESULTS AND DISCUSSION

Sensitizing Effect

Figure 3 shows fluorescence spectra of dyes in the host LC. Fluorescence intensities emitting from BBOT and C-1 are strong, since absorption spectra of BBOT and C-1 widely overlap with the emission spectrum of the excitation lamp, as shown in Figure 1. In contrast, absorption spectra of other fluorescent dyes are separate from that of the UV light source. Therefore, fluorescence intensities of those dyes are very weak. Then, we added C-1 into the C-334 GH LC to transfer the excitation energy from C-1 to C-334. As a result, the fluorescence intensity of C-334 remarkably increased by 13 times but the fluorescence of C-1 was hardly observed, as shown in Figure 4. This result strongly suggests that the energy transfer takes place from C-1 to C-334 in the host LC.

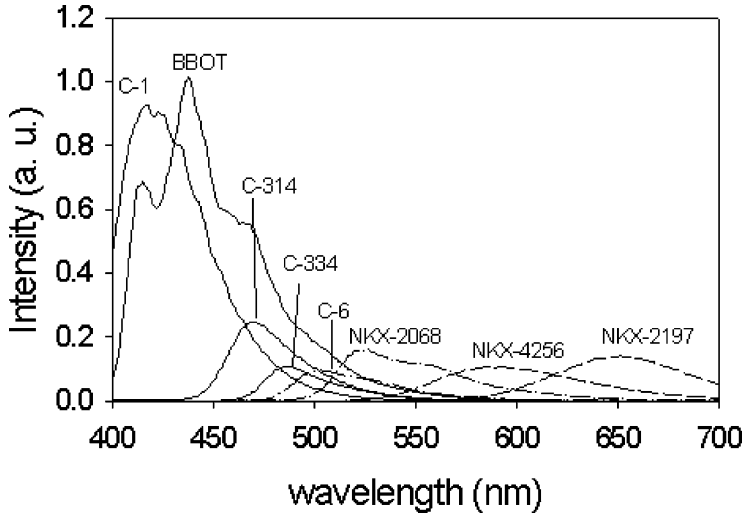

FIGURE 3 Fluorescence spectra of dyes.

Fluorescence intensities of C-314, C-6 and NKX-2068 were also increased by adding C-1. Peak intensities without the sensitizer are normalized to 1 and spectra of the sensitized fluorescence are shown in Figure 5. In the case of NKX-4256, C-1 and C-334 were added as sensitizers, since

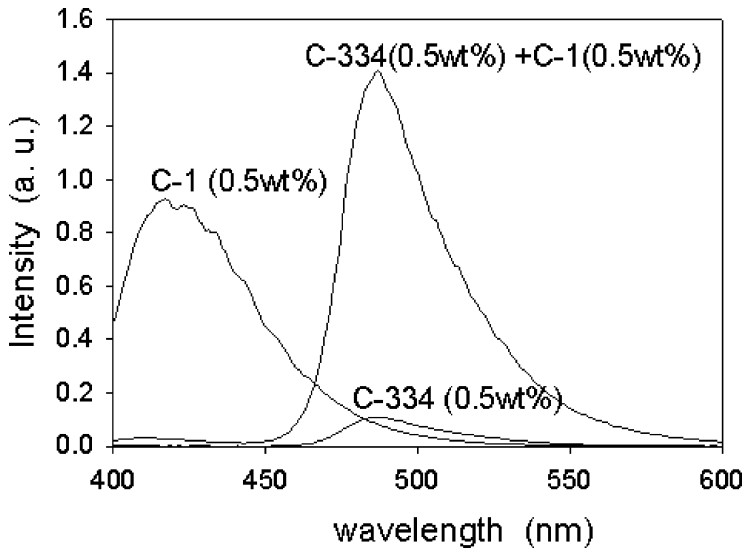

FIGURE 4 Fluorescence spectra of C-1 and C-334.

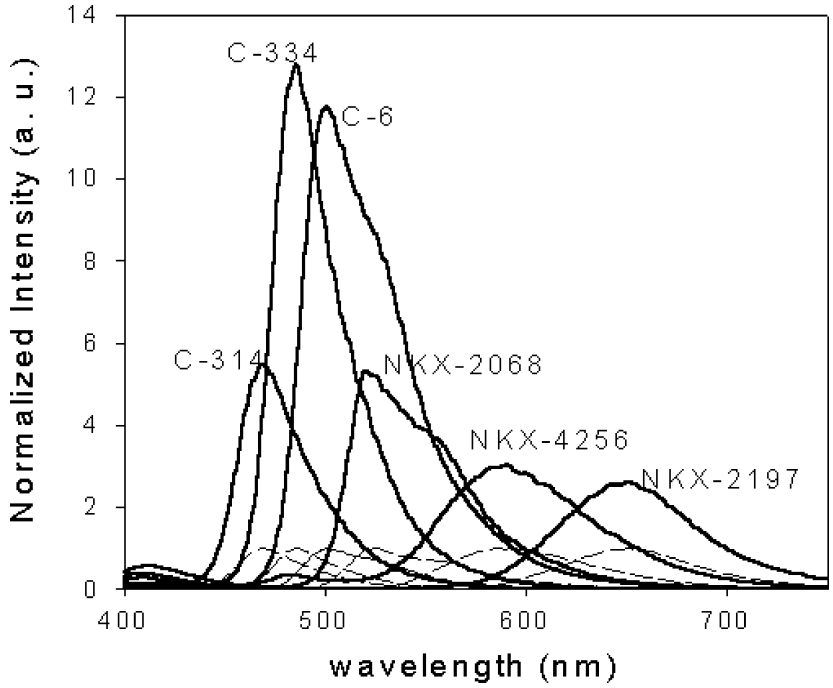

FIGURE 5 Normalized fluorescence spectra of dyes with the sensitizer of C-1.

the absorption spectrum of NKX-4256 nearly overlaps with the fluorescence spectrum of C-334 and C-334 is strongly sensitized by C-1. The excitation energy of UV light transferred successively to the emitter of NKX-4256 through C-1 and C-334, and the fluorescence intensity increased about 3 times compared to that without the sensitizers. The fluorescence intensity of NKX-2197 can also be increased by adding C-1 and C-6. Moreover, we tried to attain the energy transfer of the triple cascade process in the host LC. We mixed C-1, C-314, NKX-2068 and NKX-2197 in the host LC. When the GH LC was excited with the UV light, only the fluorescence of NKX-2197 was observed and the intensity increased by 2.7 times, comparing to that without those sensitizers. If BBOT was utilized instead of C-1, almost the same or slightly lower intensities of the sensitized fluorescence were obtained in each LC cells.

Dichroic Ratio

Table 1 shows absorption and emission dicroic ratios of fluorescent dyes, ADR, EDR1 and EDR2, in the LC host. The uncertainties for all data in this

TABLE 1 Dichroic Ratios for Absorption and Emission

Emitter	Sensitizer	ADR	EDR1	EDR2
C-1		2.2	1.5	2.2
BBOT		4.8	2.3	4.7
C-6		4.4	2.1	4.2
C-6	C-1		1.5	4.3
C-6	BBOT		2.3	4.3
NKX-4256		2.2	1.3	2.2
NKX-4256	C-1 + C-6		1.4	2.1
NKX-4256	BBOT + C-6		1.7	2.2

table are within ±5%. EDR1 is different from EDR2 in all fluorescent LC cells. EDR1 is smaller than ADR and EDR2 approximately coincides with ADR. EDR1 of the sensitized fluorescence is also smaller than EDR2 in all cases. For the sensitizer, dichroic ratios of BBOT are about twice higher than those of C-1. When the sensitizer is added to C-6/LC mixture, EDR1 of C-6 emission changes and it is clarified that their values correspond to values of the sensitizer used.

On the other hand, EDR2 of C-6 fluorescence sensitized by BBOT is same as that sensitized by C-1. We compared EDR2 of other dyes sensitized by C-1 and BBOT, as shown in Figure 6. EDR2 does not change before and after adding the sensitizer, which indicates that the EDR2 of sensitized fluorescence is independent of the dichroic ratio of the sensitizer. In the case of sensitized NKX-4256 fluorescence, the excitation energy transfers to the emitter through two dyes. EDR1 depends on the sensitizer and EDR2 is independent of the sensitizer, as well as those in the GH LC cell of the single energy transfer.

Electro Optical Property

The fluorescence intensity in the fluorescent GH mode can be controlled by applying an external voltage, as well as the transmission intensity in the conventional GH LC cell. We measured the voltage dependence of the fluorescence intensity in the LC cell with BBOT guest. $F1_{//}$ decreased as increasing the applied voltage above the threshold, as shown in Figure 7(a), because the absorbance of the excitation light decreased due to the reorientation of LC and dye molecules. Moreover, $F1_{//}$ under the high voltage application became smaller than $F1_{\perp}$ under the no voltage application. $F1_{//}$ of other dichroic dyes also became lower than $F1_{\perp}$ by applying the voltage. In addition, we measured $F1_{\perp}$ of BBOT in the LC cell as a function of an applied voltage and the electro optical property is also shown in Figure 7(a). $F1_{\perp}$ also decreased with increasing the voltage.

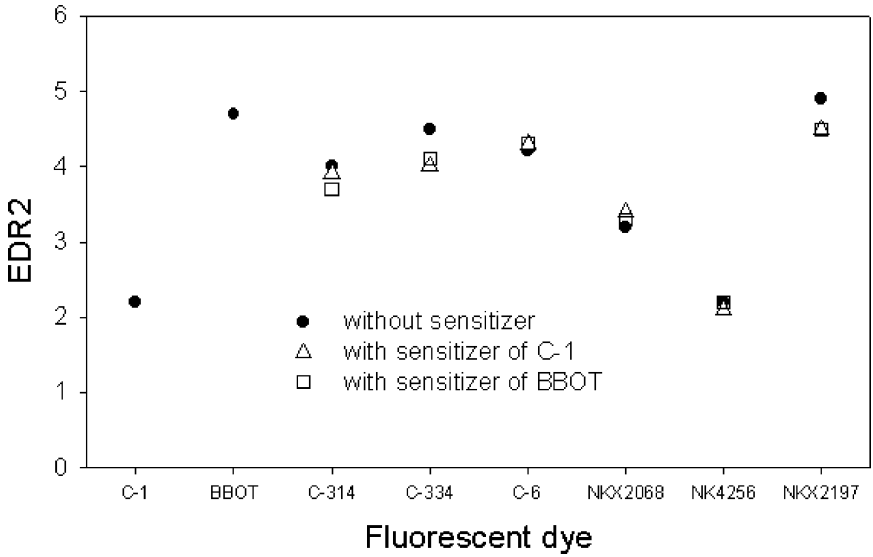

FIGURE 6 EDR2 of dyes before and after adding sensitizers of C-1 and BBOT.

In electro optical properties of $F2_{//}$ and $F2_{\perp}$ shown in Figure 7(b), almost same phenomena were observed as well as $F1_{//}$ and $F1_{\perp}$, respectively. Therefore, the contrast ratio of the $F1|_{//}$ signal for voltage-off to the same signal for voltage-on in the fluorescent GH LC cell is higher than the ADR ratio. In conventional GH cells, the contrast ratio does not become smaller than ADR, since LC and dye molecules near the substrate are still adsorbed on the alignment surface and do not reorient parallel to the electric field. In the fluorescent GH LC cell, higher contrast ratio is attributed to the decrease of $F2_{\perp}$ by applying the voltage.

Figure 8 shows electro optical properties of sensitized fluorescence. Fluorescence intensities of $F2_{//}$ without the voltage are normalized to 1. When C-1 was added to C-6 GH LC cell, normalized intensity under the high voltage application was higher than that without the sensitizer. Therefore, the contrast ratio becomes lower by using the sensitizer of C-1. If the sensitizer of BBOT was added, almost the same property was obtained. On the other hand, normalized intensity under the high voltage application was lower than that without the sensitizer and the contrast ratio increased by adding BBOT and C-6 to NKX-4256 GH LC cell, as shown in Figure 8(b). This indicates that both the brightness and the contrast ratio can be enhanced by using the sensitizer of which dichroic ratio is larger than that of the emitter.

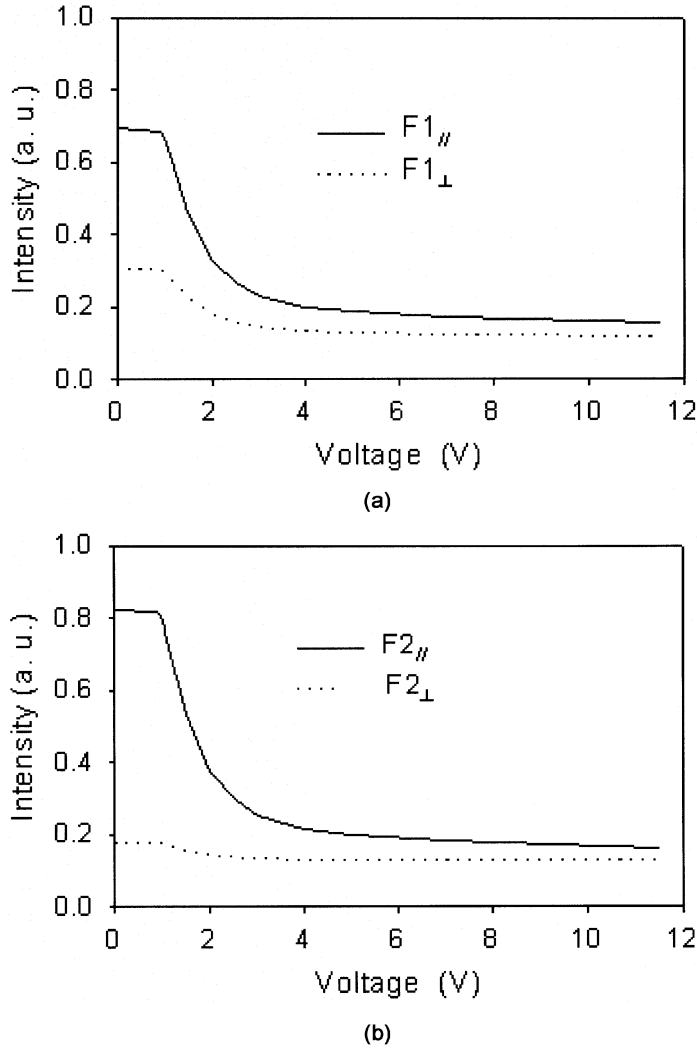

FIGURE 7 Electro optical properties of BBOT in the LC cell. (a) $F1_{\perp}$ and $F1_{//}$, (b) $F2_{//}$ and $F2_{\perp}$.

SUMMARY

The increase of the green and red fluorescence intensity from the dichroic dyes in the LC host can be obtained by the sensitizing effect. Relations between absorption and emission dichroic ratios are measured in the homogeneously aligned GH LC cell with and without the sensitizer.

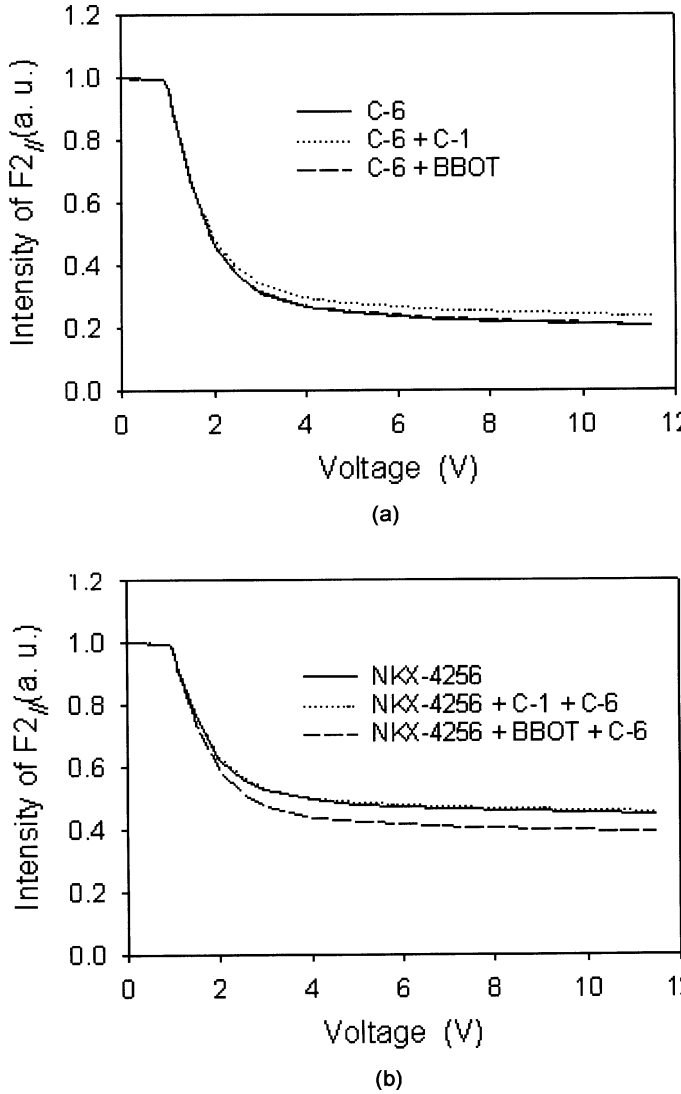

FIGURE 8 Electro optical properties of (a) C-6 and (b) NKX-4256 in the LC cell with and without sensitizers.

Fluorescence intensity are also investigated as a function of the applied voltage. When the LC cell is irradiated with the polarized UV light parallel and perpendicular to the LC direction, both fluorescence intensities decrease above the threshold with increasing the voltage. When the cell

is irradiated with the nonpolarized UV light, both intensities of polarized fluorescence parallel and perpendicular to the LC direction also decrease and the contrast ratio is higher than ADR in the GH LC cell. Moreover, the brightness and the contrast ratio can be enhanced, if the dichroic ratio of the sensitizer is larger than that of the emitter.

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