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SENSITIZED FLUORESCENCE OF DICHROIC DYE IN EMISSIVE TYPE LIQUID CRYSTAL DISPLAYS

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Sensitization effects in a fluorescent nematic liquid crystal display (LCD) have been studied using a fluorescent dichroic dye or a fluorescent liquid crystal as a sensitizer. The sensitized fluorescence intensity can be increased by ten times and a dichroic ratio of the fluorescence is also increased. Moreover, the sensitized fluorescence intensity is controlled by applying the voltage across the cell. We applied these phenomena to the emissive type LCD. The luminance can be increased and the color switching properties are improved.

Keywords: color switching; fluorescent dichroic dye; fluorescent liquid crystal display; liquid crystal; sensitization

INTRODUCTION

Light-emitting type displays, such as a cathode ray tube, electroluminescence panel and plasma display panel, show a high brightness and a wide viewing angle. On the other hand, a conventional liquid crystal display (LCD) is not light-emitting type and needs a back light or an ambient light. For emissive LCDs, guest-host modes in which fluorescent dichroic dyes are dissolved in LC have been reported [1–3]. Moreover, we have proposed multicolor fluorescent LCDs which combine the functions of the UV shutter and the emitter [4–10]. However, the solubility of the fluorescent dye in the LC is limited (<0.5 wt%), therefore we must increase the cell thickness to obtain a higher luminance of the fluorescence from the LC cell, which causes the decrease of the contrast ratio and longer decay time in the switching property. Moreover, we stack the fluorescent LC cells

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with different fluorescence colors to switch the color of the LCD. In such LCDs different dyes are excited using one excitation light source, therefore fluorescence intensities are different each other and the utilization of the excitation light is low.

In this study, the sensitized fluorescence in the LC is investigated to solve these problems. Using the sensitizer with optical anisotropy, the sensitizing effect is successfully controlled by applying the voltage across the cell and the increase both of the luminance and the contrast ratio can be attained.

EXPERIMENTAL

Fluorescent dyes of blue (BBOT: 2,5-bis5′-tertbutyl-2′-benzoxazolyl-thiophene), green (coumarin-6) and red (NKX-2197: Hayashibara Biochemical Lab.), and a fluorescent LC (5TP: Mreck Japan Limited) were prepared as an emitter and/or a sensitizer in this study. Their chemical structures are shown in Figure 1(a), (b), (c) and (d). ZLI-1083 of phenyl-cyclohexane compounds was used as a host LC, which is almost transparent in the wavelength range of the excitation UV light. Excitation and emission spectra of fluorescent substances were measured in methanol or acetone solution and are shown in Figure 2. All spectra are arbitrarily normalized to equal peak height. A UV fluorescent lamp (Toshiba FL6BLB) and a blue LED were used to evaluate the sensitization and the color switching property in fluorescent LCDs. Their spectra are shown in Figure 3.

We can see that the wavelength range of the excitation spectrum of coumarin-6 is almost coincidence with that of the emission spectrum of BBOT. Therefore, BBOT was added to the coumarin-6/LC mixture as a sensitiser. Moreover, 5TP was also be used as a sensitizer. For the red emission excited by the blue LED, coumarin-6 was used to sensitize the emission of

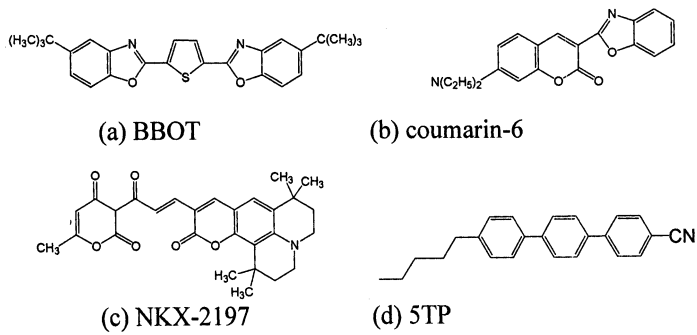

FIGURE 1 Chemical structures of fluorescent substances.

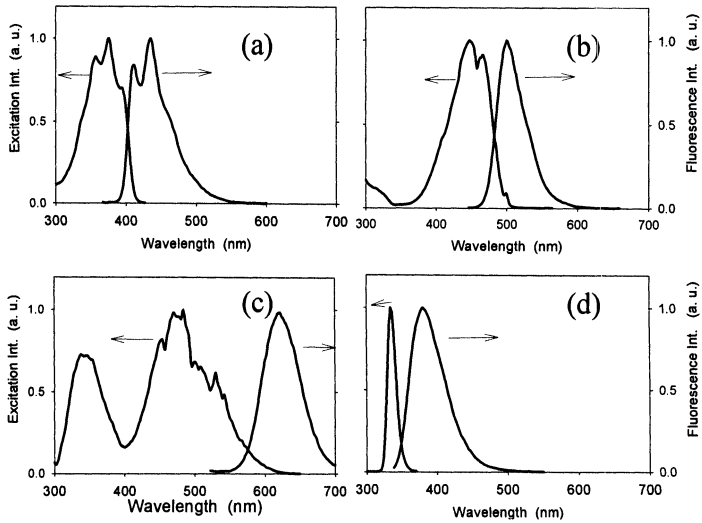

FIGURE 2 The normalized excitation and emission spectra of (a) BBOT in methanol solution, (b) coumarin-6 in methanol solution, (c) NKX-2197 in acetone solution and (d) 5TP in acetone solution.

NKX-2197. The cell thickness was controlled by spherical spacers of 11 μm diameter in all LC cells.

RESULTS AND DISCUSSION

Homogeneously aligned LC cells were prepared by adding each fluorescent dye of 0.5 wt% or 5TP of 15 wt% to the LC host. The cell was irradiated

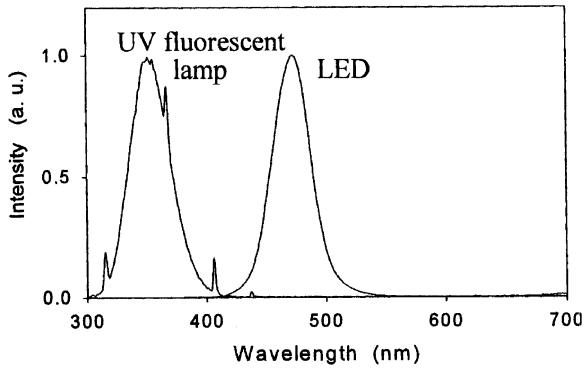

FIGURE 3 The normalized spectra of the UV fluorescent lamp and LED.

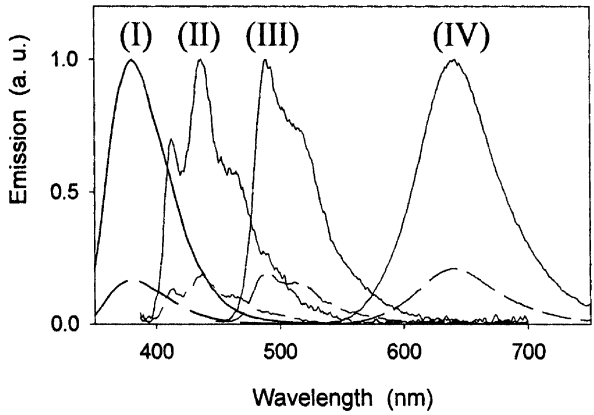

FIGURE 4 The normalized emission spectra of (I) 5TP, (II) BBOT, (III) coumarin-6 and (IV) NKX-2197 in homogeneously aligned LC cell. Solid and broken lines show the polarized spectra parallel and perpendicular to the LC direction, respectively.

with non-polarized UV light and polarized emission parallel and perpendicular to the LC direction were measured. Figure 4 shows that their peak wavelengths are almost same as those in methanol or acetone solution, except for NKX-2197 of which peak is at 650 nm in the LC and at 622 nm in the acetone solution.

Figure 5(a) shows the fluorescent spectra of the coumalin-6 of 0.5 wt% in the LC cell where the concentration of BBOT is varied (0–0.5 wt%). The fluorescence intensity of coumarin-6 directly excited with the UV light is very small, compared to that of BBOT, since the absorptivity of coumarin-6 in the wavelength of the UV light from the UV fluorescent lamp is very low. When BBOT is added to the coumarin-6/LC mixture, the peak

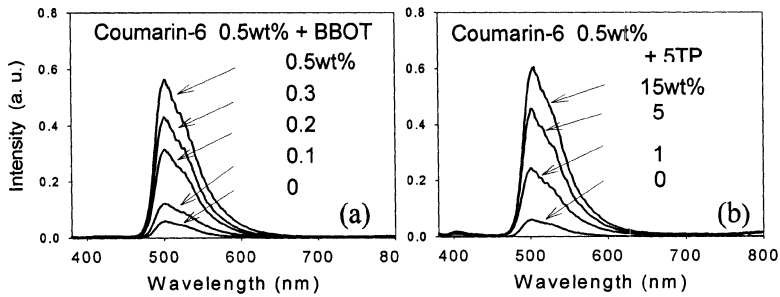

FIGURE 5 Emission spectra of coumarin-6 by adding (a) BBOT and (b) 5TP as a sensitizer.

intensity remarkably increases with increasing the BBOT concentration, and is about by 10 times by adding BBOT of 0.5 wt%. In this case, the emission spectrum of BBOT is hardly observed. This result strongly suggests that the excitation energy would be transfered from BBOT to coumarin-6.

The same phenomena were also observed when the 5TP was used as a sensitizer for the coumarin-6/LC mixture, as shown in Figure 5(b). The absorption spectrum of coumarin-6 is not completely coincident with the emission spectrum of 5TP. However, since 5TP can be dissolved in the LC host up to 15 wt%, the same peak intensity level can be obtained as that sensitized by BBOT of 0.5 wt%.

Dichroic ratios (DRs) of fluorescences were measured in the coumarin-6/LC/sensitizer mixture cell by irradiating with the non-polarized UV light. Figure 6 shows DR as a function of the concentration of the sensitizers. The DR in the LC cell sensitized by BBOT decreases with increasing the BBOT concentration. On the other hand, that sensitized by 5TP increases with the 5TP concentration. The DR of the fluorescence of 5TP itself in the LC host also increases with increase its concentration. Therefore, it is expected that the order parameter of the LC molecular alignment increases with the 5TP concentration.

Next we assembled the LCD with the homogeneously aligned BBOT/LC cell and the coumarin-6/LC TN cell, as shown in Figure 7(a). The homogeneous cell is exposed with the non-polarized UV light and BBOT molecules absorb the UV light polarized parallel to the LC director and

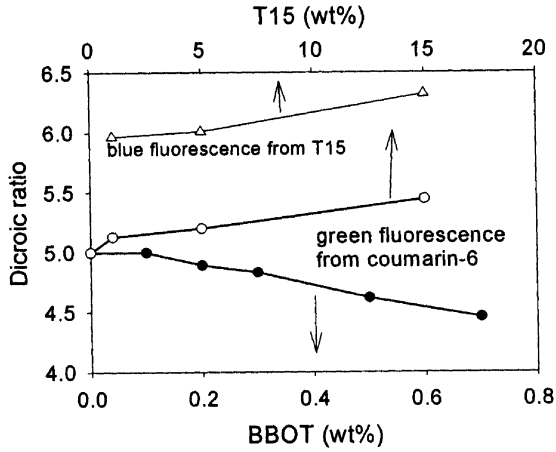

FIGURE 6 Dichroic ratios of fluorescences as a function of the concentration of the sensitizer.

emits the blue fluorescence polarized parallel to that director. Moreover, that polarizing direction rotates by 90° after passing through the TN cell. On the other hand, the UV light polarized perpendicular to the director reaches to the TN cell and excites coumarin-6 molecules dissolved in the TN cell. Therefore, we can obtain bright two fluorescences of which polarization directions are perpendicular to each other, and the green fluorescence can only pass through the polarizer. When the voltage is applied to the TN cell, the fluorescence emitted from the homogeneous cell passes through the TN cell without the rotation of its polarization direction. The fluorescence intensity emitted from the TN is weak. Therefore, we can observe the blue color fluorescence.

Figures 7(b), (c) and (d) show switching properties in the LCDs. When the sensitizer is not added in the TN cell, the intensity of the green fluorescence in the off-state is much weaker than that on the blue fluorescence in the on-state, as shown in Figure 7(b). If BBOT of 0.5 wt% or 5TP of 15 wt% is added to the TN cell, the intensity of the green fluorescence increases about by three times. We also see that the peak intensity at 500 nm of the fluorescence spectra in the on-state slightly increases. The color switching is evaluated in the chromaticity diagram, as shown in

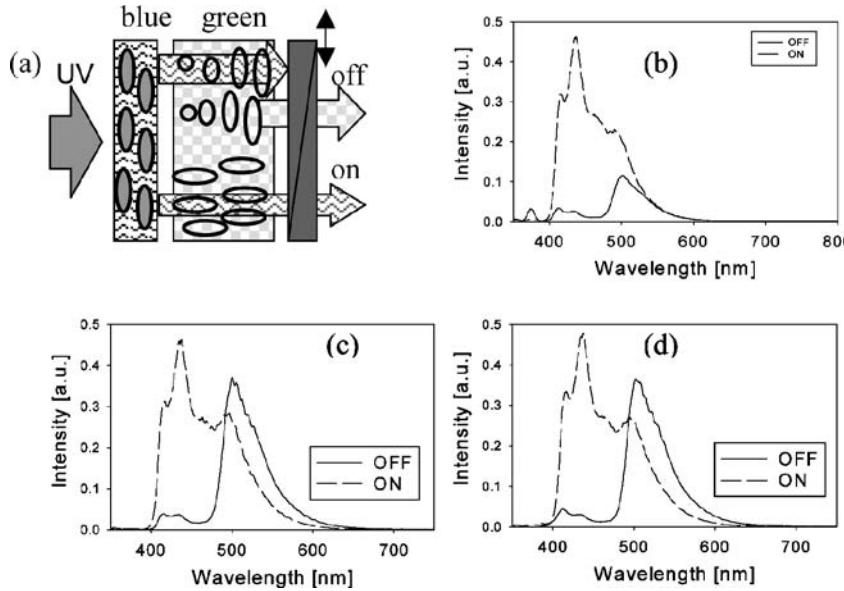

FIGURE 7 (a) Schematic switching model of the LCD with stacked fluorescent LC cell, and switching properties of LCDs (b) without the sensitizer and with sensitizers of (c) BBOT and (d) 5TP.

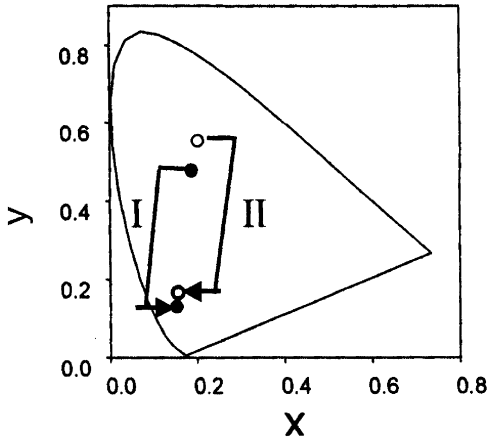

FIGURE 8 The chromaticity coordinates of fluorescence colors in LCDs (I) without and (II) with the sensitizer.

Figure 8. The hue and the chroma of the green fluorescence in the off-state is improved.

The red fluorescence intensity can also be increased by dissolving the sensitizer in the LC host when the blue excitation light is used. Figure 9 shows the polarized absorption and emission spectra of the fluorescent LC cell with coumarin-6 of 0.5 wt% and NKX-2197 of 0.5 wt%. We can see that the absorption spectrum consists of the composition of the

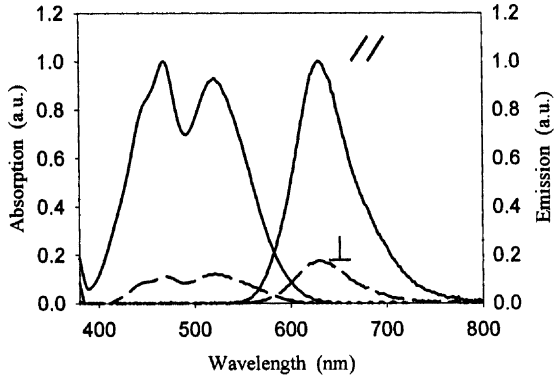

FIGURE 9 Polarized absorption and emission spectra of the LC cell with coumarin-6 of 0.5 wt% and NKX-2197 of 0.5 wt%.

absorption spectrum of coumarin-6 and NKX-2197. However, only the emission from NKX-2197 is observed.

The color switching principle using the visible excitation light source and the fluorescent LC cell is shown in Figure 10(a). When the homogeneously aligned LC cell is irradiated with the blue LED, dye molecules absorb the blue light polarized parallel to the LC director and emit the fluorescence polarized parallel to that director. On the other hand, the blue light passing through the cell is polarized perpendicular to the director. Therefore, the fluorescence from the LC cell can be seen out of the polarizer. When the voltage is applied to the LC cell, the blue light from the LED passes through the polarizer due to the less absorption in the LC cell.

In the NKX-2197/LC mixture cell, NKX-2197 molecules absorb only a part of the blue light and emit the weak red fluorescence. Therefore, in the off-state, the blue light intensity is large and that of red fluorescence is small, as shown in Fig. 10(b). This results in the very narrow color change. When coumalin-6 is added to the LC cell, coumarin-6 molecules absorb the blue light and the excitation energy transfers to NKX-2197 molecules. Therefore, the red fluorescence intensity increases by two times and the blue light out of the LC cell decreases, as shown in Figure 10(b). As

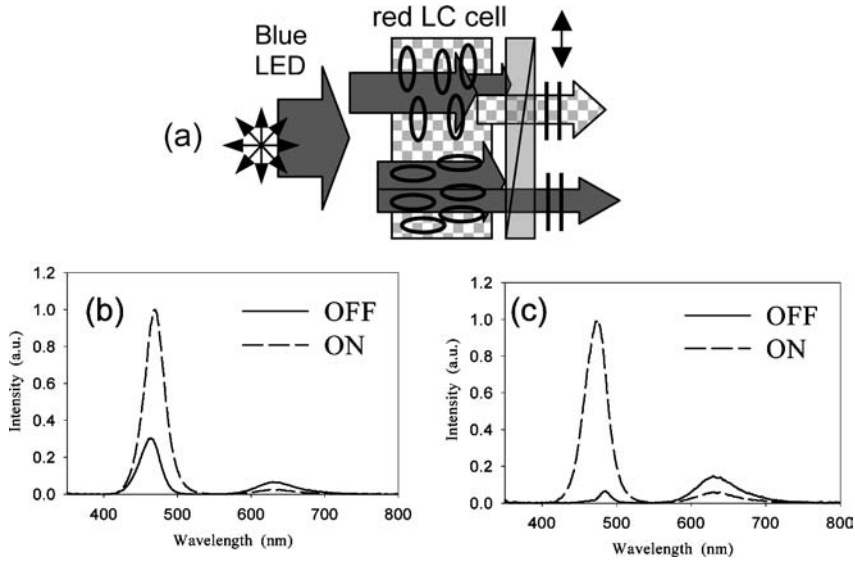

FIGURE 10 (a) Schematic switching model of the LCD using an LED as an excitation light source and switching properties of LCDs (b) without and (c) with the sensitizer of the coumarin-6.

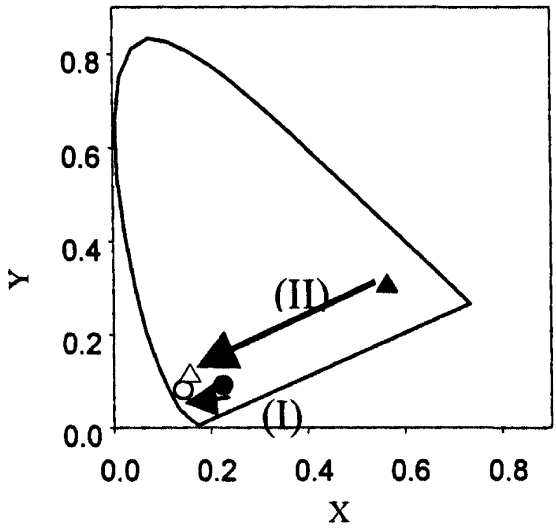

FIGURE 11 The chromaticity coordinates of LCDs (I) without and (II) with the sensitizer.

a result, the color change property from red to blue can be dramatically improved, as shown in Figure 11.

CONCLUSIONS

The remarkable increase of the green fluorescence intensity from the coumarin-6 in the LC host can be obtained by adding the blue fluorescent dichroic dye (BBOT) or the fluorescent liquid crystal (5TP) as a sensitizer. The dichroic ratio of the fluorescence can also be increased when using the 5TP. Applying the sensitization to the emissive type LCD of which color is switched from green to blue, the luminance of the green fluorescence and the color switching property are improved. The color switching between blue to red in the LCD assembled with the blue LED and the red (NKX-2197) fluorescent LC cell is also improved by using the coumarin-6 as a sensitizer.

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