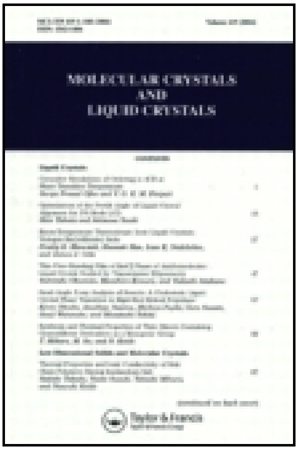

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Color Design and Adjustment of Dichroic Dyes for Reflective Three-Layered Guest-Host Liquid Crystal Displays

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Relationships between properties of dichroic dyes and performances of three layered Guest-Host Liquid Crystal Displays (GH-LCDs) with subtractive color mixing of yellow, magenta and cyan were studied by color mixing simulation.

In the case of using the dyes we developed, it was found that the color reproduction areas were as much as 1.6 times larger than in the case of using only commercially available dyes. Performances of our prototype reflective three-layered GH-LCDs were high (the luminous reflectance of the white state was 43%, and the contrast was 5.3), indicating that three-layered GH-LCDs are practical for the display of full-color images.

Keywords: color reproduction area; dichroic dyes; three-layered GH-LCDs

INTRODUCTION

Reflective Liquid Crystal Displays (LCDs) are the most suitable displays for portable information systems because of their remarkably low power consumption. Various display modes for reflective LCDs have been proposed in order to fully realize practical brightness and contrast. Among these variations, GH mode, wherein dichroic dyes are dissolved in liquid crystals, has a relatively wide viewing angle and high reflectance, and is one of the most promising display modes for future applications.

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Color Filters (CF)-type GH-LCDs using black GH liquid crystals were reported [1]. In this type of LCD, color images are created by CFs (red, green and blue) and black GH liquid crystal layers have a light-bulb function. The contrast is high and color reproduction areas are large. However, the CFs always absorb the light and light utilization efficiency becomes low. This means that images obtained from displays of this type are insufficient, with the insufficiency being particularly marked when the displays are viewed in dark places. It was reported that bright images were obtained from CF (yellow, magenta and cyan)-type GH-LCDs [2]. However, the color reproduction areas are considered to be drastically smaller than those of red, green and blue CFs.

Three-layered GH-LCDs with subtractive color mixing of yellow, magenta and cyan have been expected to lead to the development of "full-color" reflective displays [3–9] (Fig. 1). They have no CFs and polarizing plate, and light utilization efficiency is quite high.

The properties of dichroic dyes are important for the realization of bright and pure colors in GH-LCDs. In particular, absorption spectra and dichroic ratios in liquid crystals are the dominant properties with regard to the performances of displays. However, the relationships between the properties of dichroic dyes and the performances of displays are uncertain because they are too complicated to investigate by experiments. Since each dye has plural properties that have important effects on performances of displays exchanging dyes means that the plural variables are changed simultaneously.

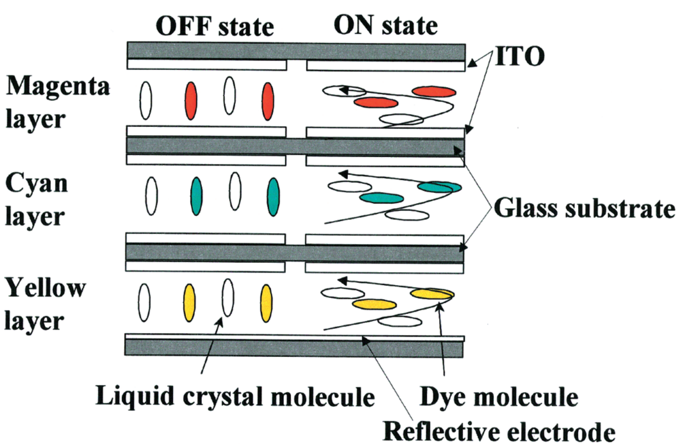

FIGURE 1 The structure of the three-layered GH-LCD.

In this paper, we established three-layered GH-LCDs as a model and tried to clarify the effects of absorption spectra and dichroic ratios of dyes on performances of LCDs by color simulation.

EXPERIMENTAL

Fundamental Spectra Data Used in the Simulation

Dyes or dye mixtures were dissolved in negative fluorinated liquid crystals (ZLI-2806 purchased from Merck Ltd.). The chiral compound (S811, purchased from Merck Ltd) was also dissolved in the liquid crystal to construct a cholesteric-nematic phase exchange system. Dichroic dye G-232, G-202, G-239, G-471 and G-176 were purchased from Hayashibara Biochemical Laboratories Inc, and SI-497 was from Mitsui Chemicals Inc.

The dummy cell used in the experiment consisted of two glass plates, with an inner area of $1\,\mathrm{cm} \times 1\,\mathrm{cm}$, each with a transparent electrode of indium tin oxide (ITO). The oxide films were coated with a polymer layer (alignment layer) which induced a homeotropic structure in the liquid crystals.

GH-liquid crystals were injected in the cell and a voltage (10 V: saturated voltage) was applied. Spectra for both on and off states were measured with a Shimadzu UV-260 spectrophotometer in each dye and/or dye mixture.

The concentration of chiral compound was determined such that the largest contrast was achieved with no hysteresis.

The spectra of off states can be calculated by dichroic ratio ($\mathbf{D'}$) defined by formula (1) and $\mathbf{D'}$ can be determined at will in the program.

$$\mathbf{D'} = \mathbf{A(on)/A(off)} \tag{1}$$

A(on), A(off): the absorbance at the maximum absorption wavelength of on and off states.

Constitutions of Color Simulations

For three-layered GH-LCDs, we used subtractive color mixing simulation which was previously reported [6].

The calculated spectra of three-layered GH-LCD in yellow, magenta, cyan, red, green, blue, black and white states were converted into the CIE1976 $L^*a^*b^*$ color space. The light source was D65 and the CIE 1931 standard colorimetric system was used.

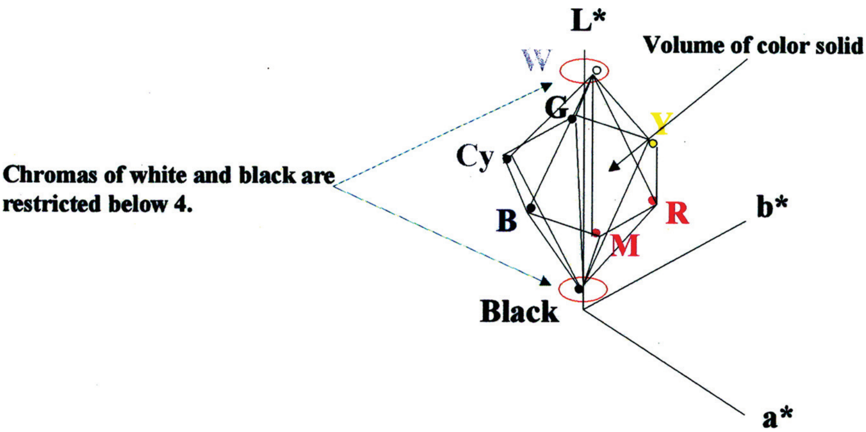

FIGURE 2 Definition of color reproduction area of three-layered GH-LCDs.

The color reproduction area of three-layered GH-LCD was defined as the volume inside the dodecahedron made by the above-mentioned eight color coordinates to simplify the calculation shown in Figure 2. In fact, real color reproduction area is the volume inside the curved surface.

Maximizing the volume of the color solid is considered to be the best way to obtain excellent performances. Color balance, especially in black and white states, can not be ignored. To adjust the color balance of the black and white states, we introduced a restrictive condition, namely, that the chromas ($\mathbf{C} = ((\mathbf{a})^2 + (\mathbf{b})^2)^{0.5}$) of the achromatic colors were below a certain value.

RESULTS AND DISCUSSION

The System of Three-layered GH-LCD

Three-layered GH-LCDs (the model LCD of calculation) shown in Figure 1 involves negative GH-liquid crystals in each layer. When voltage is applied to the cell, the helical structure (on states) is realized and dichroic dyes absorb a large quantity of light. In off states, liquid crystals are aligned vertically to the substrate and dichroic dyes absorb a small quantity of light. Each layer is controlled independently and full color images are realized. Cholesteric-nematic phase transition system using negative liquid crystals were selected to obtain large reflectance because of small anchoring energy and wide viewing angle.

The Relationship Between Absorption Spectra and Color Reproduction Areas

We tried to estimate the effects of absorption spectra and dichroic ratio (D′) individually by subtractive color mixing simulation.

At first, to determine the effects of absorption spectra of dichroic dyes on the color reproduction areas (volume of color solid), dichroic ratio of three layers was set equal and only absorption spectra were changed. We set $D' = 3.9$ (measured value of cyan dye **SI-497** in ZLI-2806). Other calculation conditions are so determined that reflectance of white state was above 30%, reflectance of black states was above 5%, and metric chroma C^* was below 4. In the case that no solution exists capable of fulfilling the conditions, volume of color solid was described to be 0.

Several anthraquinone, azo and coumarin dyes were prepared. Yellow dyes were **G-232** (azo), **1** (anthraquinone) and **2** (coumarin). Magenta dyes were **G-202** (azo), **G-239** (azo), **G-471** (azo), **G-176** (anthraquinone) and **3**. Cyan dyes were fixed with **SI-497** (anthraquinone). The molecular structures of dyes **1**, **2** and **3** are shown in Figure 3.

The calculated volumes of color solids of three-layered GH-LCDs are shown Figure 4.

When the anthraquinone dyes and/or coumarin dyes (**1**, **2**, **3**, **G-176**) were used in yellow and magenta layers, the volumes of color

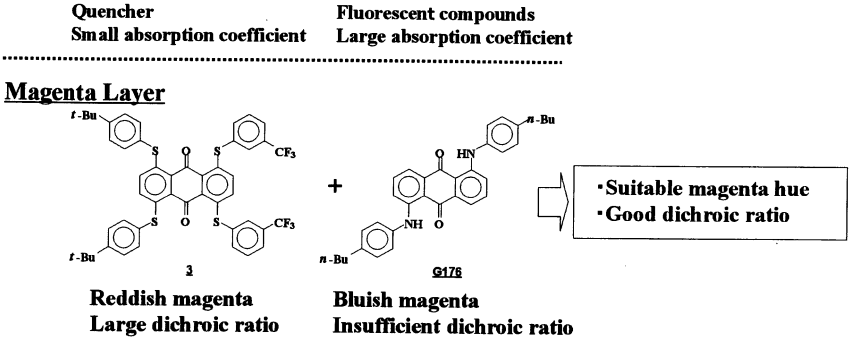

FIGURE 3 Molecular structures of the novel dichroic dyes and dye mixtures.

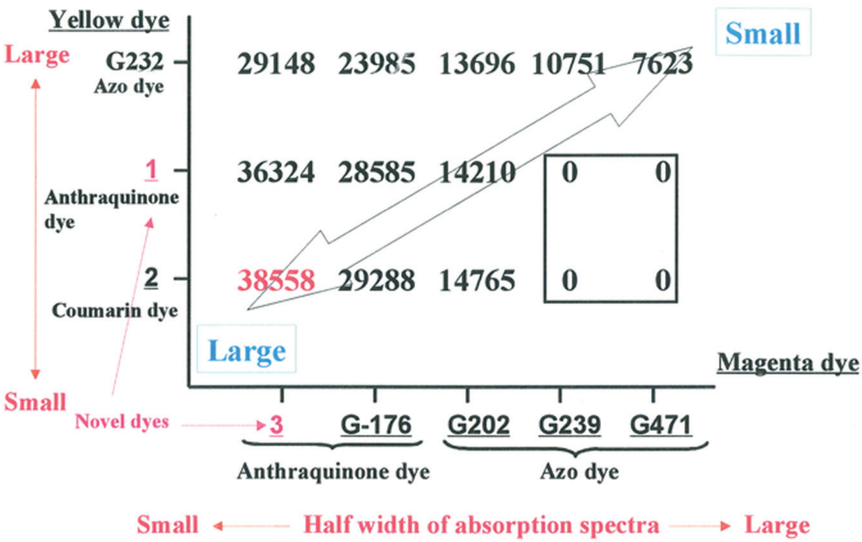

FIGURE 4 Calculated volume of color solid when dichroic ratios were set equal ((D′) = 3.9).

solids were markedly larger than those in the case of azo dyes. The largest volume of color solid was 38558. This was realized when **2** (coumarin) was used in yellow layer and **3** (anthraquinone) was used in magenta layer.

Regarding the comparison of anthraquinone dyes in magenta layer, dye **3** was found to realize volume of color solid 1.2–1.3 times larger than that of **G-176**. In comparison with half width of dye **G-176** (117 nm), that of dye **3** (84 nm) is smaller.

On the other hand, the half widths of azo dyes are markedly larger than those of anthraquinone and coumarin dyes and volumes of color solids are small. These results are considered to be strongly related to the half widths of absorption spectra.

The combinations of anthraquinone and azo dyes or coumarin and azo dyes in yellow and magenta layer include no solution capable of fulfilling the condition. The valence of half width may be another important factor to realize large volume of color solid.

When half width of absorption spectrum is small, saturation of color and volume of color solid are large, but color balance (condition of metric chroma) is considered to be hard to fill (volume of color solid become 0) and contrast is reduced because of the leak of light that is in the wavelength region between absorption spectra. On the other hand, when it is large, volume of color solid is small, but color balance is easy to fill and contrast is large. From the results shown in Figure 4, half widths of anthraquinone and coumarin dyes are found to be suitable for three-layered GH-LCDs.

Color Adjustment of Yellow and Magenta Layer

From the results of Figure 4, coumarin dye **2** was the best one to obtain large volume of color solid. Moreover, coumarin dye **2** has large molar absorption coefficient. However, strong fluorescence of coumarin dye adversely affects the hues it exhibits, and this effect is especially marked in the case of three-layered GH-LCDs which are based on the subtractive color-mixing system. The effects of fluorescence were not considered in the calculation.

We have already reported that anthraquinone dye **1** behaves as an efficient fluorescence quencher for coumarin dyes [10]. Above all, the mixture of anthraquinone dye **1** and coumarin dye **2** is considered to have a large absorption coefficient, pure yellow color and no fluorescence.

The solubility of anthraquinone dye **1** was the key point to realize the above-mentioned yellow GH liquid crystals. Anthraquinone dyes have been the subject of intensive study due to their excellent photostabilities and good hues [11–16]. However, further extensive experiments are required in order to apply them to Thin Film Transistor Liquid Crystal Displays (TFT-LCDs), which require fluorinated liquid crystals with high resistance values. We found that solubilities of guest dyes in fluorinated liquid crystals were much smaller than those in cyanobiphenyl liquid crystals [17]. High solubilities of dyes in fluorinated liquid crystals are one of the most important requirements for realizing GH-LCDs with high contrast and large color reproduction areas. We developed dyes **1** and **3**. Fluorinated groups are introduced in phenylthiogroup at specific position and high solubilities are realized [17].

Compared with previous dyes, the novel dichroic dye can be used in a cell with a narrower gap while keeping adequate absorbance, because a higher concentration of dye is possible. Figure 4 shows that in the case that dye **3** was used as magenta dye, the largest volume of color solid was predicted to be obtained. The magenta layer is the most important one for the contrast (defined by the ratio of luminous reflectance in black and white states), the color reproduction areas and color balance of three-layered GH-LCDs. However, the hue of the color of dye **3** is shifted to red. On the other hand, the hue of the color of

G-176 is shifted to blue. We adjusted the mixture of dye **3** and **G-176** for magenta layer.

Relation Between Dichroic Ratios of Dyes and Color Reproduction Areas

To find out the effects of dichroic ratios (D′) of dyes on the volume of color solid, the dichroic ratios were changed by simulation in three combinations of dyes (combination **A**: Y = dye **4** (1-(4-*t*-butylphenylthio)-5-phenylthioanthraquinone, the absorption spectrum is almost same as dye **1**), M = **G-176** and Cy = **SI-497**, combination **B**: Y = **1** + **2**, M = **G-176** + **3** and Cy = **SI-497** combination **C**: Y = **G-232**, M = **G-202**, and Cy = **SI-497**). Combination **A** is the combination of dyes which realizes the largest volume of color solid only using commercially available dyes, and combination **B** is the combination of dyes which realizes the largest volume of color solid using dyes suitable for three-layered GH-LCDs obtained by our original dye technology. Combination **C** is the combination of only azo dyes. Calculated results of the relation between D′ and volumes of color solids are shown Figure 5.

By increasing dichroic ratios, volumes of color solids are enlarged monotonously in every combination. However, differential coefficients

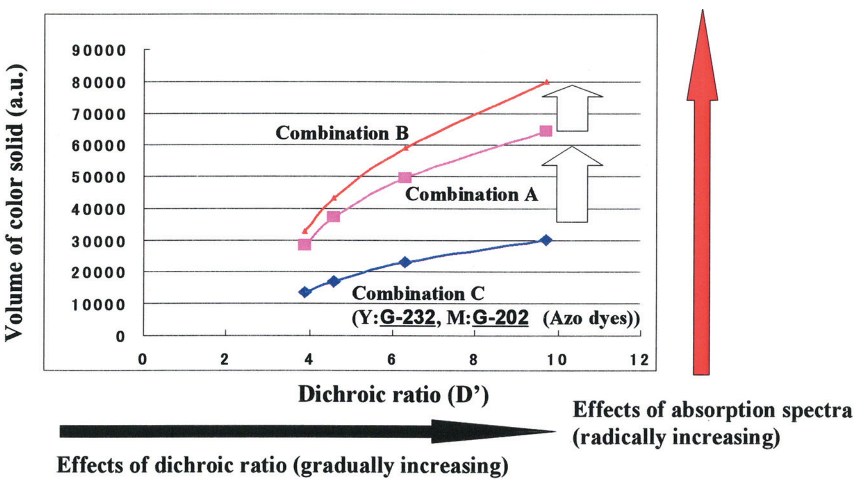

FIGURE 5 Calculated effects of magenta dyes on chromaticity coordinates of red, green and blue states of three-layered GH-LCDs.

TABLE 1 Volume of Color Solid of Combination A and B (Using Measured D′)

Combination	Yellow	Magenta	Cyan	Volume of color solid
A	**4**[*]	**G-176**	**SI-497**	17423
B	**1** + **2**	**G-176** + **3**	**SI-497**	27326

[*]1-(4-t-butylphenylthio)-5-phenylthioanthraquinone.

(dV/dD′) are quite different among dye combinations. The differential coefficient of combination **B** is the largest and this indicates that absorption spectra are key factors to draw the effects of enlarged dichroic ratios.

On the other hand, sudden increases in the volume of color solid due to improvement of absorption spectra appeared in combination **B**. As for combination **C**, large volume of color solid cannot be obtained by increasing dichroic ratio.

The Volume of Color Solid Based on Measured Dichroic Ratio

Dichroic ratios (D′) of dyes were measured by dummy cell as described in the experimental section. Volumes of color solids were calculated by using these data on the condition that other parameters were all equal to calculations described previously (Table 1).

Dye combination **B** in Table 1 is the result of our novel techniques respecting yellow and magenta layer. The volume of color solid using dye combination **B** (V = 27326) is 1.6 times larger than that of dye

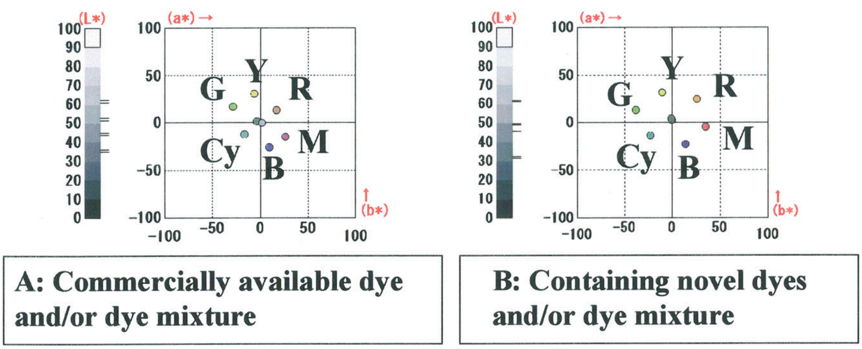

FIGURE 6 Calculated color coordinates of combinations A and B using measured dichroic ratio.

TABLE 2 Measured Dichroic Ratios (D′) of Dummy Cell (Combination B)

Layer	Dyes and concentrations	D′ (A(ON)/A(OFF))
Y	**1**: 0.46 Wt% + **2**: 0.19 Wt%	3.9
M	**3**: 1.0 Wt% + **G-176**: 0.31 Wt%	3.5
Cy	**SI-497**: 2.4 Wt%	3.7

ZLI-2806 (negative liquid crystal purchased from Merck Ltd.) and S811 (chiral compound purchased from Merck Ltd.) were used in this study.
Thickness Dummy cell: 10 μm
Applied voltage: 10 V
Alignment layer: polymer which induced a homeotropic structure in liquid crystal.

combination **A** (V = 17423), simply as a result of selecting dyes for each layer.

The color coordinates of combinations **A** and **B** are shown in Figure 6. Marked improvement of color reproduction area is observed in combination **B**. In particular, the chroma of red is drastically increased.

FIGURE 7 A color image of the reflective three-layered GH-LCDs.

TABLE 3 Performances of Prototype Reflective Three-Layered GH-LCDs

Size of Panel	3.4 inches (diagonal)
Number of Pixels	240 (H) $\times$ 160 (V)
Size of Pixels	0.3 mm $\times$ 0.3 mm
CR	5.3
Reflectance in White State	43%

Prototype of Three-layered GH-LCD Using Combination B and its Performance

The prototype of the three-layered GH-LCD shown in Figure 1 was produced. The cell gap of each layer was 10 μm. Each substrate has a TFT array, and liquid crystal layers can be driven independently. With active matrix driving, high-contrast images can be achieved. The composition of dyes in each layer and dichroic ratio (measured in dummy cell) are shown in Table 2.

A color image of our three-layered GH-LCD is shown in Figure 7. These values show that the three-layered GH-LCD is practical for full color display. The performances of the prototype reflective three-layered GH-LCD are summarized in Table 3.

The reflectance in white state is 43% and contrast is 5.3. Contrast is not large but large color reproduction area fully covers negative factor. We realized high performance GH-LCDs with pure colors and bright image.

CONCLUSION

The relationship between properties of dichroic dyes and performances of reflective GH-LCDs were predicted by color simulation. The effects of absorption spectra and dichroic ratios of dyes were separated and estimated.

Dyes with small half widths of absorption spectra, such as anthraquinone and/or coumarin dyes were found to be suitable for realizing three-layered GH-LCDs with large color reproduction area. We adjusted the dyes for three-layered GH-LCD by using novel techniques for yellow and magenta layers. The color reproduction area of three-layered GH-LCDs can be as much as 1.6 times larger than that of the combination A, simply as a result of selecting commercially available dyes for each layer. The performances of our reflective three-layered GH-LCDs were high (the luminous reflectance of the white state was 43%, and the contrast was 5.3), indicating that three-layered GH-LCDs are practical for the display of full-color images.

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