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Non Polarizer Guest–Host mode based on Dyes with Negative Dichroism

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A new configuration of non polarizer "guest–host" mode, based on the liquid crystal mixture doped with black mixtures of dichroic dyes with negative dichroism, is proposed and demonstrated for the first time. Both transmissive and reflective variants are possible with either monochromatic or black/white switching. It is shown that the contrast ratio is not limited in this case. A contrast ratio of more than 5 : 1 for normal incidence and a contrast ratio of more than 3 : 1 for wide viewing angles are demonstrated in an experiment and the electrooptic response is found to be almost independent of the azimuthal angle of light incidence. [DOI: 10.1143/JJAP.42.1297]

KEYWORDS: "guest–host" effect, dichroic dye, negative dichroism, black mixture, liquid crystal display, viewing angles

1. Introduction

"Guest–host" (GH) effect in mixtures of liquid crystal (LC) and dichroic dyes is promising for applications in liquid crystal displays (LCDs).[1–4] GH-LCDs possess wide viewing angles, which make them superior to twisted (TN) or supertwisted (STN) LCDs. Black and white (B/W) and multi color images are possible.[5–7] A non polarizer GH-LC configuration markedly improves the situation, as both viewing angles and transmission becomes better. At present, most GH-LCDs are based on dyes with positive dichroism.[1–4] In this case, a polarizer is needed for a reasonable contrast, otherwise, the contrast is limited by 2 : 1, providing that the switching is made between the waveguiding mode and the homeotropic configuration. Increasing the contrast by using a double cell GH-LCD configuration[8] or normal modes of elliptically polarized light[9] has not been successful as either brightness or operating voltages were compromised.[1] A certain progress has been reported for the GH-LCD cell, based on the cholesteric-to-nematic transition (phase-change GH-LCD).[10] This configuration does not require polarizers and a contrast ratio of 4 : 1 has been obtained. However this type of GH-LCD is likely to require high operating voltages and suffer from the hysteretic behavior of the transmission versus voltage curve, which makes it inconvenient for practical applications.

The situation can be considerably improved for a reflective GH-LCD configuration by placing a quarter wave phase retarder between the mirror and LC layer to provide effective switching of the two components of natural light polarization.[11,12] However, in this case the switching takes place only for a limited part of the spectrum, as the achromatic phase retarders are not a common component of the LCD systems.[13]

In this paper, we show for the first time the possibility of obtaining color and B/W switching in the non-polarizer GH mode, using dyes with negative dichroism.[4,7,14–16] We also show how to prepare black mixtures of dyes with negative dichroism. Good assortment of these dyes was first proposed by NIOPIK in Russia.[4,7,16]

2. Advantages of GH-LCD based on Negative Dichroic Dyes

The absorption in the LC-dye mixture can be characterized by the optical density

$$D = -\log(T/T_0) = \varepsilon c d, \tag{1}$$

where T/T_0 indicates the relative decrease of the light transmission through the LC cell, ε is the extinction coefficient of the dye, c is the dye concentration and d is the LC cell thickness. Positive dichroic dyes are characterized by the dichroic ratio $N = D_\parallel / D_\perp$, where $D_\parallel$ and $D_\perp$ are optical densities measured in the directions parallel and perpendicular to the long axes of the dye molecules, respectively.[1–4] For positive dichroic dyes, the dichroic ratio N is usually 10–15 and in some cases even higher, than 20.[17] Suppose that the LC layer is switched from the waveguiding mode with one of the light polarizations always parallel to the long (absorption) axis of the dye molecule, to the perfect homeotropic LC orientation, when two basic light polarizations are perpendicular to this axis. In this case, the contrast is negative and the contrast ratio is

$$C = T_{\mathrm{on}}/T_{\mathrm{off}} = T_\perp/(T_\parallel + T_\perp)/2, \tag{2}$$

where T_{on} (T_{off}) is the GH-LCD transmission in the on (off) state, and $T_\parallel$ and $T_\perp$ are the transmissions of the LC cell with parallel and perpendicular orientation of the light polarization with respect to the long (absorption) axis of the dye molecule, respectively. Even in the ideal case of infinite dichroic ratio $N \Rightarrow \infty$ ($T_\parallel \ll T_\perp$), we have the contrast ratio $C \leq 2$, when no polarizers are used.

For negative dichroic dyes, the dichroic ratio is $N = D_\perp / D_\parallel$ and the dye absorption axis is perpendicular to the long axis of the dye molecule.[1–4] The first dyes with negative dichroism were developed in NIOPIK, Russia, where their assortment is sufficiently rich and covers the entire visible range of light.[2–4] It is easy to understand, that in this case the contrast is positive and the contrast ratio

$$C = T_{\mathrm{off}}/T_{\mathrm{on}} = (T_\parallel + T_\perp)/2T_\perp, \tag{3}$$

is not limited, even without polarizers, for high dichroic ratio N ($T_\parallel \gg T_\perp$). The bright state transmission, however, decreases with the increase of the contrast ratio and is limited by 50% in the case of the high dichroic ratio N ($T_\parallel \gg T_\perp$).

3. Experimental

3.1 Selection of negative dichroic dyes

Combining three dichroic dyes, which have a maximum absorption in the blue, green and red regions, we can obtain

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a black dye mixture and realize black/white switching, similar to the case of dyes with positive dichroism.[5–7] We have selected the negative dichroic dyes synthesized in NIOPIK, Russia.[4,16] The molecular structure of the dyes is based on the anthraquinone skeleton with elongated side terminal groups, which define the long molecular axis. The direction of the absorption oscillator is almost perpendicular to the long molecular axis.[4]

The dye subtractive colors covered the entire range of the visible spectrum, *e.g.*, magenta (KD261, KD33, KD36, KD327), yellow (KD266, KD208, KD291) and cyan (KD378, KD407, KD410), where we retained the original notations of the dichroic dyes, synthesized in NIOPIK, Russia.[2–4,7] The dyes were selected in groups with almost the same wavelength of the maximum absorption λ_m. The apparent colors of the dyes were complementary to their absorption spectra. We measured the spectra of all the dichroic dyes, as mentioned above. Based on the results of these measurements, we chose the most appropriate negative dichroic dyes for the black mixture (Table I). The data in Table I is based on the measurements of the dichroic spectra of the negative dichroic dyes, similar to that shown in Fig. 1. We denote the following parameters for the negative dichroic dyes: (i) subtractive color, (ii) the wavelength of the maximum absorption λ_m, (iii) the dichroic ratio $N = D_\perp/D_\parallel$ at λ_m, and (iv) the order parameter[1–4] $S = (1-N)/(1+2N)$. We should note that the order parameter in the case of ideal alignment of the dye absorption oscillator perpendicular to the direction of the light propagation is $S_m = -0.5$.

Table I. Characteristics of negative dichroic dyes*.

Dye	Color	λ_m (nm)	N	S
KD-261	Magenta	536	4.56	−0.353
KD-266	Yellow	401	1.2	−0.057
KD-407	Cyan	644	3.41	−0.308

*The cell thickness $d = 9\,\mu$m, the host mixture is ZLI-5800-100 (E. Merck), and $N = D_\perp/D_\parallel$ dichroic ratio, $S = (1-N)/(1+2N)$-order parameter at the wavelength of maximum absorption λ_m. The maximum value of the order parameter in this case is $S_m = -0.5$.

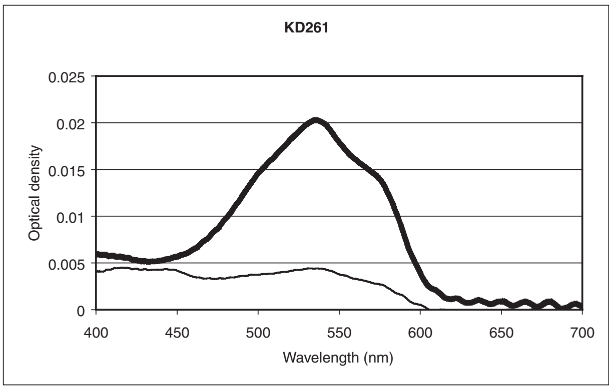

Fig. 1. Dichroic absorption spectra of magenta negative dichroic dye KD-261. The thick line indicates the optical density $D_\perp$, and the thin line $D_\parallel$, measured perpendicular and parallel to the orientation of the light polarization with respect to the long (absorption) axis of the dye molecule, respectively. The dye concentration was 2% in ZLI-5800-100 (E. Merck). The dichroic ratio $N = D_\perp/D_\parallel = 4.56$ at $\lambda_m = 536$ nm. Order parameter $S = (1-N)/(1+2N) = -0.353$.

To improve the contrast ratio C of non polarizer GH-LCD, $C = (T_\parallel/T_\perp + 1)/2 = [10^{dc(\varepsilon_\perp - \varepsilon_\parallel)} + 1]/2$, we should use the dichroic dyes with the maximum possible absorption $D_\perp$, see eq. (3). The extinction coefficient $\varepsilon_\perp$ is defined by the dye molecular structure, thus the only way to increase $D_\perp$ is to use a large thickness d of the LC cell or a higher solubility c of the dichroic dye (''guest'') in LC (''host''). The latter can be attained using homologues of the same dye, which possess similar basic molecular structures differing only in the number of hydrogen atoms in the terminal groups. Combining the homologues, we can considerably improve the solubility of the dyes in the host mixture.[4] The LC host mixture should have the highest possible value of dielectric anisotropy, which can also contribute to the better dye solubility. The layer thickness d was 50 µm in our case. The larger thickness of the LC cell will considerably deteriorate the LC response time in the GH mode.

3.2 *Black mixture of negative dichroic dyes*

To prepare the black (neutral) mixture of the dyes with negative dichroism we must determine the appropriate concentration c_i of the dye components. This is easy to accomplish, using the Newton–Raphson procedure.[5,6] The total optical density of the mixture with n components is

$$D = d \sum_{i=1}^{n} \varepsilon_i c_i, \tag{4}$$

where ε_i and c_i are the extinction and concentration of the i-th component, respectively, to be taken separately for the directions parallel ($\parallel$) and perpendicular ($\perp$) to the long axis of the dichroic dye molecule. The Newton–Raphson procedure[5,6] allows us to obtain the black (neutral) state for both the background ($T_{\text{off}} = (T_\parallel + T_\perp)/2$) and the image ($T_{\text{on}} = T_\perp$) of the GH mode in the LC cell. We consider that the perfect dark image is preferable for achieving a higher contrast of GH-LCD, thus we chose, for the optimization the value of $D_\perp$ in eq. (4). The dye ratio of KD261 : KD266 : KD407 = 3.161 : 1.5595 : 1.3993 was obtained and 3.5% of the dyes was mixed with the LC host (ZLI-5800-100, E. Merck) in a 50 µm cell. The transmittance of the LC cell in the GH mode using this mixture of negative dichroic dyes is shown in Fig. 2. The brightness and contrast should be improved in the ''blue'' part of the spectrum by synthesizing ''yellow'' dyes with a higher dichroic ratio $N = D_\perp/D_\parallel$ ($N = -0.057$ for KD-266, Table I).

3.3 *GH-LCDs based on black mixture of negative dichroic dyes*

We have shown the possibility to use our GH-LCD not only in the transmissive mode, but also in the reflective mode. A 50-µm-thick and 240° twisted STN LC cell without a polarizer was used in experiment. The electrooptic mode provides the switching between STN and almost homeotropic LC alignment. The contrast in the latter case is highly dependent on the quality of the reflective mirrors. In the case of an ideal mirror, the contrast ratio is:

$$C = T_{\text{off}}/T_{\text{on}} = [(T_\parallel/T_\perp)^2 + 1)/2, \tag{5}$$

where $T_{\text{off}} = (T_\parallel^2 + T_\perp^2)/2$ and $T_{\text{on}} = T_\perp^2$. For high dichroic

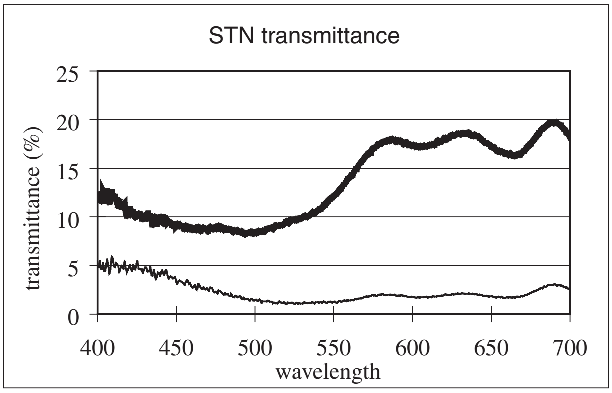

Fig. 2. The transmittance of LC cell in GH mode using this mixture of the negative dichroic dyes. The dye ratio (KD261 : KD266 : KD407 = 3.161 : 1.5595 : 1.3993) was obtained and 3.5% of the dyes was mixed with LC host (ZLI-5800-100, E. Merck) in a 50 µm cell. The thick line is the transmittance of the "off" state and the thin line the transmittance of the "on" state.

absorption $T_{\parallel} \gg T_{\perp}$, the contrast of non polarizer reflective GH-LCD is not limited similar to the transmissive case. The contrast ratio for reflective LCDs based on the GH mode can be higher than that in the transmissive case, as the effective LCD thickness is increased twice. The latter is taken into account in the estimations of the contrast using eqs. (3) and (5). However the maximum reflectance in this ideal case cannot exceed 50%, similar to the above-mentioned transmissive GH-LCD.

The experimental data for the transmission and reflectance of GH-LCD based on the black mixtures of negative dichroic dyes are shown in Figs. 3 and 4, respectively. The upper parts of the Figs. 3 and 4 indicate the transmission (reflectance) for the normal light incidence. It is clear that the contrast ratio is more than 5 : 1 in this case. The lower parts of the Figs. 3 and 4 provide the dependence of the contrast on the GH-LCD viewing angle. A contrast ratio of 3 : 1 is observed for wide viewing angles and the electro-optic response is almost independent of the azimuthal angle of the light incidence.
We used the black/white mixture of the negative dichroic dyes to produce the 240° STN-LCD having 16 × 16 elements and a duty ratio of 16 : 1. The contrast ratio was 3 : 1 up to the light incidence angles of 30°, which was almost uniform for various azimuthal directions of the light incidence.

4. Conclusions

A new configuration of the non polarizer guest–host liquid crystal mode, based on dyes with negative dichroism, is proposed. The contrast ratio of GH-LCD is not limited in this case and the viewing angles are perfect. The rich assortment of the negative dichroic dyes from NIOPIK (Russia) covering the entire visible spectrum was used in the experiment. The possibility of preparing effective black mixtures of negative dichroic dyes was shown. GH-LCD with a contrast ratio of more than 5 : 1 for transmissive and reflective LC cells was fabricated. A contrast ratio of more than 3 : 1, which is almost independent on the azimuthal angle of the incident light, was demonstrated in both cases. A 240° supertwist nematic STN-LCD having 16 × 16

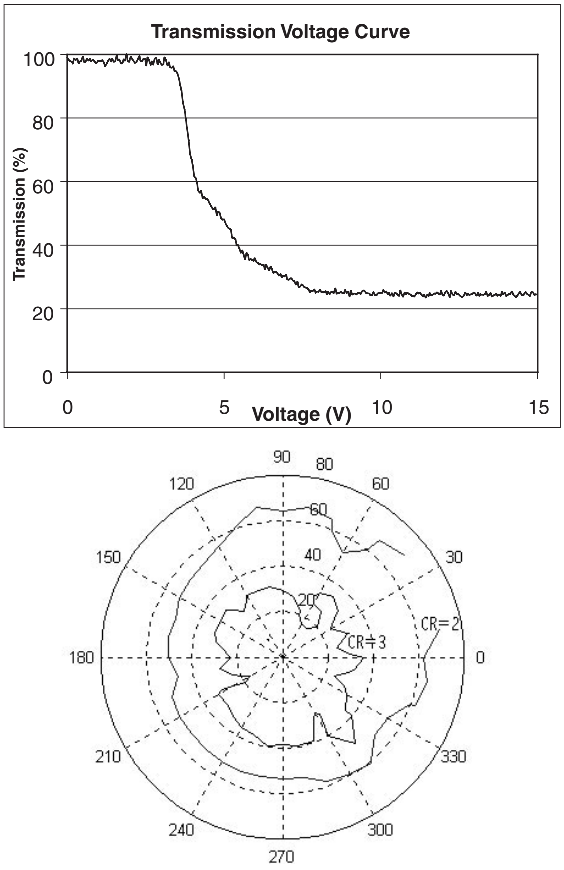

Fig. 3. The transmission of GH-LCD versus voltage. Upper part: normal light incidence; lower part: viewing angle dependence of the contrast ratio.

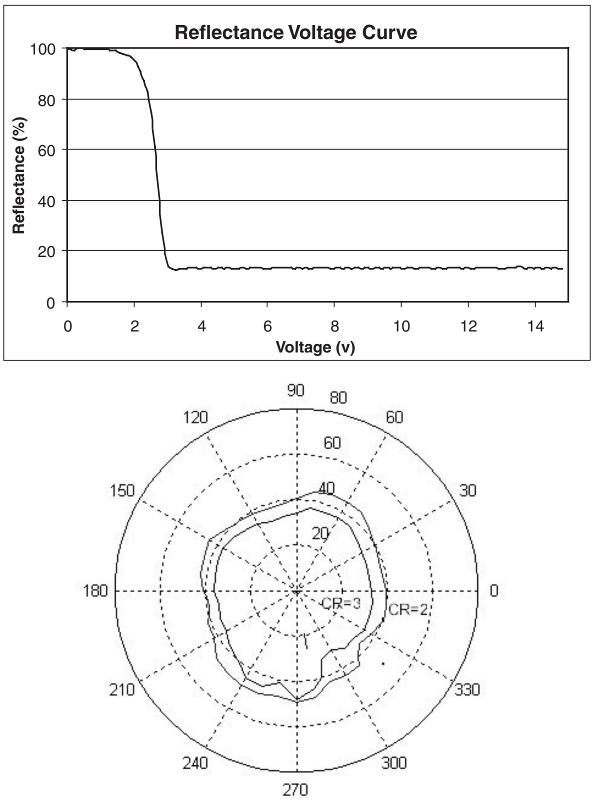

Fig. 4. The reflectance of GH-LCD versus voltage. Upper part: normal light incidence; lower part: viewing angle dependence of the contrast ratio.

elements and a duty ratio of 16 : 1 operating in the above mode was also produced. The described GH mode can be successfully applied for portable LCDs with wide viewing angles.

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