Optics Communications xxx (2008) xxx-xxx

Contents lists available at ScienceDirect

## **Optics Communications**

journal homepage: www.elsevier.com/locate/optcom

# Optical addressing in dye-doped cholesteric liquid crystals

Ko-Ting Cheng<sup>a</sup>, Cheng-Kai Liu<sup>a</sup>, Chi-Lun Ting<sup>b</sup>, Andy Ying-Guey Fuh<sup>a,b,\*</sup>

<sup>a</sup> Department of Physics, National Cheng Kung University, Tainan 701, Taiwan

<sup>b</sup> Institute of Electro-optical Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan

### ARTICLE INFO

Article history: Received 27 February 2008 Received in revised form 26 May 2008 Accepted 9 July 2008 Available online xxxx

PACS: 42.70.Df 42.79.Kr 68.43.Mn

*Keywords:* Liquid crystals Cholesteric Azo dye Adsorption

### 1. Introduction

Cholesteric liquid crystals (CLCs) have been commonly studied for use in reflective liquid crystal displays (RLCDs) [1–5] owing to their bi-stable (reflective planar and scattered focal conic states) characteristics at zero voltage. The planar cell selectively reflects a wavelength of light that is determined by the Bragg reflection condition,  $\lambda = np\cos\theta$ , where  $\lambda$  is the reflected wavelength; *n* is the mean refractive index of LC; p is the pitch length, and  $\theta$  is the angle of incidence. The reflection disappears when the device is switched to the focal conic state. Recently, Lin et al. established that a photoinduced dye adsorption layer is homogeneous and smooth, when the dye-doped CLC (DDCLC) cell is irradiated by a green laser light with an intensity of  $\sim$ 50 mW/cm<sup>2</sup>. The adsorbed dyes can change the CLC alignment of the cell from focal conic to nearly perfectly planar textures. Such a mechanism allows the micro-mirror devices to be patterned using a DDCLC cell [6]. In additions, our recent study reports that a roughly and randomly adsorbed dye layer in a DDCLC cell could apply a random alignment to change the CLC texture from planar to focal conic via guest-host effect

\* Corresponding author. Address: Department of Physics, National Cheng Kung University, Tainan 701, Taiwan. Tel.: +886 6 275 7575x65228; fax: +886 6 274 7995.

E-mail address: andyfuh@mail.ncku.edu.tw (A.Ying-Guey Fuh).

0030-4018/\$ - see front matter  $\odot$  2008 Elsevier B.V. All rights reserved. doi:10.1016/j.optcom.2008.07.028

### ABSTRACT

This study investigates a method of optical addressing in dye-doped cholesteric liquid crystals (DDCLCs). Photo-induced randomly adsorbed dyes can change the CLC textures from planar to focal conic. Such patterning can be adopted to develop a display that is initially invisible, but becomes visible upon heating above the clearing temperature, followed by cooling to room temperature. The display can also become visible upon the application of a suitable voltage, and its rapid release. Additionally, the display is thermally erasable, optically rewritable and electrically switchable. It can be applied for use as a smart card. © 2008 Elsevier B.V. All rights reserved.

without temperature control during recording, and the effect can be applied to fabricate a reflective LC Fresnel zone plate [7].

In this paper, the details of the random adsorption we reported before is studied [7]. The effectiveness of a simple and rapid optically addressing method that depends on transferring the CLC texture from planar to focal conic in a DDCLC cell is examined. Refer to our previous study [7], the proposed approach allows a pattern in a DDCLC sample to be directly recorded optically without control of the cell temperature during recording. Moreover, an interesting application using this DDCLC to pattern a logo for use as a smart card is also demonstrated. Briefly, the addressed pattern is invisible while the cell temperature is held below the clearing temperature during recording. It becomes visible after heating just over the clearing temperature and cooling to room temperature. The other method is to apply a suitable voltage and release it rapidly. Furthermore, the appeared patterns are thermally erasable, optically rewritable and electrically switchable.

#### 2. Experiments

The LC and right-handed chiral agent adopted in this experiment were, respectively, E7 (Merck) and CB15 (Merck). A CLC material was prepared by mixing E7 with CB15 in a weight ratio of 16:9. The reflection band of the mixed CLC was between 615 and 665 nm. The azo dye employed herein was methyl red (MR, Aldrich), whose absorption band in the *trans*-state spanned from 440



to 550 nm, peaking at about 530 nm [7]. The quantity of MR in a DDCLC sample was 2% by weight. The clearing temperature of the DDCLC compound decreased from ~61 °C for pure E7 to ~30.7 °C when chiral dopant and azo dye were added [9]. Two indium-tin-oxide- (ITO-) coated glass slides, separated by two 11 µm-thick plastic spacers, were utilized to form an empty cell. Each ITO glass substrate was coated with a homogeneous alignment film of poly(vinyl alcohol) (PVA) and rubbed in the direction *R*. Then, the homogeneously mixed compound was injected into the empty cells to form a planar DDCLC sample. Finally, the edges of the cell were sealed with epoxy.

Fig. 1a and b present the experimental setups for measuring the reflection spectra of, and for recording the patterns onto the DDCLC sample, respectively. In Fig. 1, the abbreviations, P, M, BE, and AP, represent polarizer, mirror, beam expander, and aperture, respectively. Notably, BE, made up of two convex lenses separated with a distance of the summation of the focal lengths of these two lenses, is used to expand the beam size of the DPSS laser light, and AP is used to block the undesired light. Refer to Fig. 1a and b, a planar DDCLC sample was irradiated with a linearly polarized green laser beam ( $E_G$ , 90 mW/cm<sup>2</sup>, from a diodepumped solid state laser, DPSS laser,  $\lambda = 532$  nm), which was expanded and collimated to a diameter of 1 cm by BE to study the changes of the surface alignment property and the textures of the DDCLC that followed from the randomly adsorbed dyes. A broadband light source from a mercury lamp through an aperture was incident onto the DDCLC sample to measure the reflectance of the sample after being illuminated with the DPSS laser at a designed duration. A spectrum meter was used to collect the reflected light from the DDCLC sample. In Fig. 1b, a home-made mask having two transparent letters "KT" was placed in contact with a DDCLC sample. A DPSS laser beam, propagating through a polarizer, beam expander, aperture, and the "KT" mask, was incident onto the DDCLC sample to record the pattern. Notably, the polarization of the green laser light,  $E_G$ , could be set arbitrarily relative to the rubbing direction, **R**, since the absorptions were always equal in all polarization directions in a planar DDCLC cell. In this study,  $E_{\rm C}$  and **R** were set parallel. The scanning electron microscopy (SEM) images (not shown) of the adsorbed dyes reveal that the MR molecules were randomly (homogeneously) adsorbed onto



**Fig. 1.** Experimental setups; (a) measurement of reflection spectra, (b) writing pattern onto a DDCLC sample. P, M, AP, and BE represent polarizer, mirror, aperture and beam expander. The home-made mask is a transparent mask of the two letters, "KT".

the substrate as the DDCLC sample was excited by a strong (weak) DPSS laser with an intensity of 90 (50) mW/cm<sup>2</sup>. Restated, the homogenously adsorbed dye layer changed the CLC alignment in a DDCLC cell from focal conic to nearly perfectly planar [6], while the randomly adsorbed dyes on the homogeneous PVA alignment film eliminated the ability of the homogeneous PVA alignment film, thus altering the CLC alignment from planar to focal conic [7]. Notably, however, the thermal effect of the absorption by dyes of DPSS laser light also affects the CLC alignment that is described above. The thermal mechanism should be considered and be discussed later.

#### 3. Results and discussion

Based on the experimental setup in Fig. 1a, with the use of a broadband white light having a weak intensity of ~0.8 mW/cm<sup>2</sup> as a probe, the reflection spectra of the DDCLC sample irradiated for various durations with a DPSS laser beam  $(90 \text{ mW/cm}^2)$  were obtained without controlling the temperature of the cell. Subtracting the surface reflections from the glass substrates yielded the measured reflection spectra in Fig. 2. The initial measured reflection spectrum indicates that the texture of the DDCLC sample is planar and its reflectivity is about 46%. Notably, the reflection spectra were measured when the DDCLC textures were in stable states after the DPSS laser was switched off ( $\sim$ 3 min). The results show that the longer illumination with the DPSS laser corresponds to the lower reflectivity. The reflectivity was lowest after approximately 10 min of illumination. Fig. 2 indicates that the cell exposed for 1, 2, and 3 min remains high reflectivity about 30%, suggesting that the generated MR-adsorption does not suffice to transit the CLC texture from planar to focal conic. The mechanisms of MRadsorption have been reported on elsewhere [10–12]. They are summarized briefly herein. When MR molecules are excited by the absorption of blue-green light, they undergo a series of transformations, including photoisomerization, three-dimensional (3-D) reorientation, diffusion and finally adsorption on the substrate that faces the incident beam [8]. It should be noted that the homogeneous or random MR-adsorption in DDCLC depends only on the intensity, illumination duration of the pumped beam, independently of the CLC phase in the sample, because the absorbances of DPSS laser light by dyes are always equal in planar and isotropic DDCLC cells. However, the CLC phase and illumination duration may affect the thickness of the adsorption layer on the substrate. The thermal effect as well as the MR-adsorption effect must be considered. The chiral dopant and azo dye impurities reduce the clearing temperature of LC from  $\sim$ 61 °C to  $\sim$ 30.7 °C. Such a low clearing temperature corresponds to a low threshold for changing



**Fig. 2.** Variations of reflection spectrum with a planar DDCLC cell irradiated for various durations; (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, and (f) 10 min.

the cell texture from planar to isotropic by the thermal effect. Therefore, when it is illuminated by the DPSS laser for over 5 min, the texture of the DDCLC cell finally changes from planar to focal conic, by the roughly and randomly adsorbed dye layer in the isotropic phase of CLC due to thermal effect. The induced phase transition was verified from the observation that a DDCLC sample was transparent (isotropic texture) immediately after the DPSS laser was switched off, and became increasingly opaque (focal conic texture) upon cooling. The relaxation time from the isotropic texture to final focal conic texture is dependent on the illumination duration, and was found to be less than 3 min after switching off the DPSS laser. The MR-adsorption process in isotropic state caused by the absorption by dyes of DPSS laser light is the key in the present work and the mechanism will be described below.

Fig. 3 presents the textures of DDCLCs that have been illuminated for various durations without controlling the temperature. observed under a crossed-polarizer optical microscope. Since the probing light is linearly polarized, it is decomposed into rightand left-handed circularly polarized components. The former is reflected and the latter is transmitted through the planar textures, while both are scattered by the focal conic textures. Accordingly, the bright (dark) patterns represent the regions of the planar (focal conic) textures. Fig. 3a indicates that the DDCLC is in its initial planar texture before exposure. The total size of the regions in which the texture is induced to become focal conic from planar increases with the duration of irradiation with a green laser having an intensity of 90 mW/cm<sup>2</sup>. Fig. 3b-f present the observed textures of DDCLCs that have been exposed for 1, 2, 3, 5, and 10 min, respectively, and clearly reveal that the focal conic textures become more dominant in the sample as the illumination duration increases. These results are consistent with those presented in Fig. 2.

Fig. 4 depicts the optically patternable, thermally erasable and optically rewritable DDCLC samples. They were obtained using

the experimental setup presented in Fig. 1b. Fig. 4a displays the initial unexposed planar DDCLC sample, which reflects the incident probe beam. Then, a home-made mask with two transparent letters "KT" was placed in contact with a DDCLC sample. A linearly polarized DPSS laser light with an intensity of ~90 mW/cm<sup>2</sup> was applied to illuminate the sample through the transparent letters "KT" for 5 min without controlling the temperature (Fig. 4b). The results in Fig. 2 (curve e) demonstrate that the texture of the illuminated "KT" becomes focal conic. Thus, "KT" is patterned and displayed in the reflective background, and the contrast ratio evaluated from Fig. 2 (curves a and e) is about 10. Additionally, Fig. 4c photographed by a digital camera presents the DDCLC cell after being thermal treatment. The DDCLC sample was heated to  $\sim$ 80 °C, which temperature was held for 10 min. Then, it was cooled naturally to room temperature. Finally, the recorded "KT" patterns with randomly adsorbed dyes were erased by thermal disturbance, and the initially homogeneous PVA alignment film switched the texture of the cell back to planar [7–8,13]. Moreover, the thermally treated sample is optically rewritable using the setup presented in Fig. 1b. Fig. 4d depicts the results. A separate experiment reveals that the photo-addressing patterns are electrically switchable. When an AC voltage (1 kHz, 50 V) is applied, the texture of the cell becomes homeotropic. As soon as the applied voltage is switched off rapidly, the LCs of the unexposed and exposed regions return to their original states, which are planar and focal conic textures, respectively. Finally, the pattern reappears.

Fig. 5a presents the image of the fabricated "KT" patterns under two fluorescent tubes. The edge portions of "KT" were observed under a crossed-polarizer optical microscope to investigate the texture of the patterned "KT" as shown in Fig. 5b and c. Clearly, the exposed (unexposed) regions have a scattered focal conic (reflective planar) texture. Hence, the exposed regions are verified again to have focal conic textures, and the edges of the patterned letters in Fig. 5b and c are sharp.



Fig. 3. Microscopic textures of photo-alignment DDCLC observed under a crossed-polarizer optical microscope, after illumination for (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, and (f) 10 min.

K.-T. Cheng et al./Optics Communications xxx (2008) xxx-xxx



Fig. 4. Images of fabricated optically patternable, thermally erasable and optically rewritable DDCLC samples photographed using a digital camera; (a) before and (b) after the DDCLC sample was exposed to DPSS laser light without controlling the temperature; (c) and (d) images of cell after it is thermally erased and optically rewritten, respectively.



**Fig. 5.** (a) Image of fabricated "KT" patterns without controlling the temperature observed under two electrified fluorescent tubes; (b) and (c) images of edge portions in (a) observed under a crossed-polarizer optical microscope. *P* and *F* represent the planar and focal conic texture regions, respectively.

Please cite this article in press as: K.-T. Cheng et al., Opt. Commun. (2008), doi:10.1016/j.optcom.2008.07.028

4

Following the mechanism described above, a process was designed for recording a pattern in this DDCLC sample, which was initially invisible, but became visible following the treatment described below. The key to this device is to maintain the cell temperature below its clearing temperature (~30.7 °C) during illumination through a mask-"KT" by a linearly polarized DPSS laser light with an intensity of 90 mW/cm<sup>2</sup> for 5 min. Herein, the cell is maintained at  $\sim$ 20 °C. Fig. 6a and b show images photographed using a digital camera of a DDCLC sample before and after being exposure, respectively. Notably, Fig. 6b indicates that the cell retains the planar texture such that no pattern is observed under a microscope. Afterwards, the recorded patterns appear when the sample is heated to about 35 °C, just above the clearing temperature, and cooled naturally back to room temperature (Fig. 6c), or a voltage of 50 V is applied and rapidly released (Fig. 6d). The patterns were also examined using a crossed-polarizer optical microscope. The observed image is similar to that depicted in Fig. 5. Therefore, the results in Fig. 6 imply that the device can be used as a smart card. Notably, the pattern is thermally erasable, optically rewritable and electrically switchable as well. The recorded patterns exhibit no significant age effect after more than two months. Based on the results described above, we conclude that controlling the cell temperature, the intensity of the pumped beam, and the duration of illumination are the keys to realize the smart card application of a DDCLC cell.

In order to understand the mechanism of the smart card application of a DDCLC cell, the surface morphologies of adsorbed dyes in the exposed regions were studied using a SEM and an AFM to examine the behaviors of the devices fabricated with and without temperature control during illumination. For reference, Fig. 7a gives the surface SEM morphology of the substrate coated with PVA alignment film before photo-induced dye adsorption (its optically patterned image is shown in Fig. 4a or Fig. 6a). Fig. 7b and c display the SEM images of the dye-adsorbed morphologies for the sample after being illuminated 5 (its optically patterned image is shown in Fig. 4b) and 10 min without controlling the tempera-

ture of the cell, respectively. It is obvious and reasonable to see that the adsorbed dyes in Fig. 7c is denser than that in Fig. 7b. Restated, the longer the illumination of green light is, the more dyes are adsorbed onto the surface. Experimentally, the substrates should be treated with a homogeneous alignment film, such as rubbing-polyimide, rubbing-PVA films to fabricate a planar CLC sample. However, if the alignment ability of the homogeneous film is disturbed, the planar CLC should be transferred to focal conic CLC. In additions, Fig. 7d presents the SEM image of the dye-adsorbed morphology of the sample illuminated for 5 min with green light, and with the temperature being kept at 20 °C (its optically patterned image is shown in Fig. 6b). It is seen from Fig. 7b and d that ball-like adsorption structures instead of rough and inhomogeneous ribbon-like adsorption are formed, as reported in our previous investigation [10]. The images reveal that the homogeneous PVA alignment film is covered with ball-like adsorbed dves. Considering the relative depth of the adsorption layer, the average depths of Fig. 7b and d are, respectively, about 80 and 35 nm, measured using an AFM. Notably, the adsorbed ball-like dyes in Fig. 7b are random and thick; while those in Fig. 7d are rare and thin, and have a roughly periodic pattern. The pattern with a spacing of  $\sim$ 340 nm is the laser-induced periodic surface structure (LIPSS), which was described in our earlier study [10,14]. The MR-adsorption in Fig. 7b is denser than that in Fig. 7d because the diffusion of dyes in the isotropic state exceeds that in the liquid crystal state. Therefore, random and dense adsorbed dyes were responsible for the transition of the texture of the CLC cell from planar to focal conic, and the results in Fig. 4b are reasonable. When the cell is temperature-controlled during illumination (Fig. 6), the adsorbed ball-like dyes are too rare and too thin to generate a high enough light-induced anchoring energy [10] for eliminating the alignment ability of the PVA film and for transferring the LC texture from planar to focal conic, after the incident beam is switched off. Yet, the adsorbed dyes on the PVA film suffice to eliminate the alignment ability of the homogeneous PVA film to align the LCs from isotropic or homeotropic to planar textures after a thermal or an AC field



Fig. 6. Images of DDCLC sample photographed using a digital camera; (a) before and (b) after being exposure at controlled temperature of 20 °C; (c) and (d) images of exposed DDCLC sample after thermal and electrical treatment, respectively, which change the LC alignment. Finally, the recorded patterns appear.



**Fig. 7.** SEM images of dye-adsorbed morphologies in exposed regions after DDCLC cell is irradiated under a green light with intensity of 90 mW/cm<sup>2</sup> for (a) 0 min; (b) 5 min and (c) 10 min without controlling cell temperature; (d), (e), and (f) illumination for 5, 10, and 30 min with controlling cell temperature.

disturbance is applied. Hence, the final textures of the pattern, "KT", in Fig. 6c and d are focal conic. A separate experiment demonstrates that the pattern, "KT", recorded under the same condition of Fig. 6b, except when the illumination duration was changed to 10 and 30 min, with the corresponding SEM images of the adsorbed dyes shown in Fig. 7e and f, respectively, can be observed under an optical microscope. It reveals that the adsorbed dyes become more random and sufficiently thick to induced a high enough anchoring energy to change the texture of the CLC from planar to focal conic without any external disturbances, such as heat or voltage. It means that the recording pattern is visible after 10 or 30 min illumination under the conditions described above. Similarly, the longer illumination causes the more random and thicker adsorbed dyes, which can directly realign the planar CLCs to focal conic texture. Comparing the surface morphologies shown in Fig. 7a-f, we conclude that the morphology of the adsorbed dyes on the substrate is the key to change the CLC texture after the cell was irradiated with a green light. The morphology can be controlled by controlling the illumination duration of the laser beam and/or the cell temperature. In additions, another DDCLC cell with the used LC (BL006, Merck) and chiral dopant (CB15, Merck), having a clearing temperature of ~72.8 °C, was used in repeated experiments under the same conditions, yielding the results of Fig. 6. The experimental results indicate that the smart card can be achieved without controlling the cell temperature. This result is reasonable since thermal heating does not push the cell over its clearing temperature. The MR molecules are adsorbed in liquid crystal state. This experiment establishes that the thermal effect is important in this case.

#### 4. Conclusion

In conclusion, a photo-addressing liquid crystal device based on MR-adsorption in DDCLC is realized. Illuminating a DDCLC sample with a suitable DPSS laser beam causes the homogeneous PVA alignment film in the front substrate to be covered with a sufficiently thick layer of randomly adsorbed dyes, and to lose its alignment effect on LCs; then, the recorded patterns appear. If the cell is maintained below the clearing temperature of the LC used during the recording process, then the patterns are initially invisible. The recorded patterns, however, appear when the sample is heated over the clearing temperature, and cooled naturally to room temperature, or a voltage is applied and released rapidly. Additionally, such a device is thermally erasable, optically rewritable, electrically switchable and extremely simple to fabricate. Therefore, it can be applied for use as a smart card.

### Acknowledgements

The authors would like to thank the National Science Council (NSC) of the Republic of China (Taiwan) and the National Cheng Kung University (NCKU) for financially supporting this research under Grant No. NSC 95-2112-M-006-022-MY3, and the NCKU Landmark project Grant No. B0055. Ted Knoy is appreciated for his editorial assistance.

#### References

- [1] D.-K. Yang, J.-L. West, L.-C. Chien, J.-W. Doane, J. Appl. Phys. 76 (1994) 1331.
- [2] M.-H. Lu, J. Appl. Phys. 81 (1997) 1063.
- [3] S.-T. Wu, D.-K. Yang, Reflective Liquid Crystal Displays, Wiley, New York, 2001.
- [4] I. Shiyanovskaya, A. Khan, S. Green, G. Magyar, J.W. Doane, SID Symposium Digest 36 (2005) 1556.
- [5] K. Chari, C.M. Rankin, D.M. Johnson, T.N. Blanton, R.G. Capurso, Appl. Phys. Lett. 88 (2006) 043502.
- [6] T.-H. Lin, Y. Huang, Y. Zhou, Andy Y.-G. Fuh, S.-T. Wu, Opt. Express 14 (2006) 4479.
- [7] K.-T. Cheng, C.-K. Liu, C.-L. Ting, Andy Y.-G. Fuh, Opt. Express 15 (2007) 14078.

K.-T. Cheng et al./Optics Communications xxx (2008) xxx-xxx

- [8] C.-R. Lee, T.-S. Mo, K.-T. Cheng, T.-L. Fu, Andy Y.-G. Fuh, Appl. Phys. Lett. 83 (2003) 4285.
- [9] H.-K. Lee, K. Doi, H. Harada, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, J. Phys. Chem. B 104 (2000) 7023.
- [10] C.-R. Lee, T.-L. Fu, K.-T. Cheng, T.-S. Mo, Andy Y.-G. Fuh, Phys. Rev. E 69 (2004) 031704.
- [11] F. Simoni, O. Francescangeli, J. Phys. Condens. Matter. 11 (1999) R439.
  [12] L.-C. Lin, H.-C. Jau, T.-H. Lin, Andy Y.-G. Fuh, Opt. Express 15 (2007) 2900.
- [13] Andy Y.-G. Fuh, K.-T. Cheng, C.-R. Lee, Liq. Cryst. 34 (2007) 389.
- [14] Andy Y.-G. Fuh, K.-T. Cheng, C.-R. Lee, Jpn. J. Appl. Phys. 45 (2006) 7024.