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Azo dye adsorption effect induced by elliptically polarized light in azo dye-doped liquid crystals

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ABSTRACT

This study elucidates the azo dye adsorption effect induced by elliptically polarized light in azo dye-doped liquid crystals (ADDLCs). Experimental results reveal that the light-induced molecular reorientation that is caused by the adsorbed azo dyes declines as the absolute value of the ellipticity of the pumping beam, having a proper selectively fixed light intensity or a proper selectively fixed light component along the direction of major axis, increases. The long axes of the adsorbed dyes are found to be independent of the sign of the light ellipticity, but they do depend on the direction of the major or minor axis of the elliptically polarized light. Notably, the tilt angle in LC alignment is not observed in this experiment. Additionally, neither twist angles nor tilt angles can be induced using a circularly polarized pumping beam.

1. Introduction

Recently, light-induced molecular reorientation by the adsorption of azo dye in azo dye-doped liquid crystals (ADDLCs) has attracted much interest because of its fundamental importance and practical applications. The used materials of the azobenzene chromophore are promoted by *trans–cis* isomerization cycles. Many scientists have studied ADDLCs, including azo dye-doped nematic LCs (NLCs) [1–6], cholesteric LCs (CLCs) [7,8], polymer-dispersed LCs (PDLCs) [9–11] and ferroelectric LCs (FLCs) [12], by exploiting the adsorption of azo dye. Methyl Red (MR) is a well-known azo dye that is used in these studies. The adsorbed MR dyes align the LCs by the guest–host effect [13]. The mechanism of MR-adsorption has been extensively discussed, and can be found elsewhere [11]. Notably, adsorption effect of MR dye is dependent on the substrate surface significantly. MR-adsorption onto a substrate that is coated with a photopolymer film, fluorinated polyvinylcinnamate (PVCN-F), includes dark adsorption, light-induced adsorption and desorption [1,2]. In addition to the adsorption effect of MRs onto PVCN-F film induced by linearly polarized light, Andrienko et al. reported that induced by elliptically polarized light [3], and the effective interaction of the angular momentum of circularly polarized light with LC that was doped with azo dye [1]. Lucchetti et al. performed a detailed experimental study of the transient effects of a circularly polarized optical beam on ADDLC cells [4]. Moreover, Yeh et al. also described the circularly polarized light-induced molecular reorientation in azo dye-doped CLCs (ADDCLCs) in which the azo dyes cannot be adsorbed onto the substrate to cause permanent alignment anchoring [7]. According to the best of the authors' knowledge, only linearly polarized pumping beams have been used to illuminate the MRs to be adsorbed onto the substrates that are coated with an indium-tin-oxide (ITO) layer but not with a PVCN-F film.

This study focuses on the alignment properties of LCs with adsorbed MR dyes onto ITO-coated substrates that are excited in ADDLCs by elliptically polarized green laser beams with various ellipticities. Experimental results reveal that the permanent light-induced molecular reorientation, or the so-called twist angle, that is caused by the anisotropically adsorbed MR dyes, declines as the absolute value of the ellipticity (e) of the green laser beam increases. Fitting the measured transmission versus voltage (T–V) curves of the formed LC cell with those simulated using 1D-DIMOS software reveals that the adsorbed MR dyes cannot exert an anchoring force that aligns LC in this system with a tilt angle [5]. Additionally, the

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long axes of the adsorbed MR dyes are experimentally verified to be independent of the sign of the light ellipticity, but to depend on the direction of the major or minor axis of the elliptically polarized light. The fact that neither twist angles nor tilt angles can be generated by exciting the MR dyes by a circularly polarized green laser beam is also confirmed.

2. Experiments

The used LC/azo dye mixture comprised 99 wt% LC, E7 (from Merck) and 1 wt% azo dye, MR (from Aldrich). The dichroic ratio D, defined as $A_{//}/A_{\perp}$, of MR is approximately six for visible light, where $A_{//}$ and $A_{\perp}$ are the absorbances when the polarization of the incident light is, respectively, parallel and perpendicular to the optical axis of the dye molecules. The homogeneous mixture in the nematic phase was used to fill an empty cell, which was fabricated from two ITO-coated glass slides, one of which was coated with an alignment film of poly(vinyl alcohol) (PVA) on its inner-surface, which was rubbed in the direction **R** (along the ***y***-axis in Fig. 1), while the other was left untreated. The cell gap was fixed at ~12 μm using plastic ball spacers. The edges of the ADDLC sample were sealed by epoxy. The surface with (without) a rubbed PVA film is denoted S_{PVA} (S_{ITO}). An S_{PVA} with a strong anchoring force can align LCs in a cell parallel to **R**, according to continuum elastic theory [14], even if S_{ITO} is not rubbed. Fig. 1(a) presents the experimental setup that was used to illuminate the ADDLC sample by an elliptically polarized light beam. A green laser beam from a diode-pumped solid-state (DPSS) laser ($\lambda = 532$ nm), propagating through a polarizer and a quarter-waveplate, was normally incident (along the ***x***-axis in Fig. 1) onto S_{ITO} of the sample. The polarizer and the quarter-waveplate were used to determine the ellipticity of the green laser beam by rotating the transmissive axis of the polarizer. The ellipticity of the green laser beam is defined as the square root of the ratio of the light intensity along minor axis to that along major axis. In detail, the ratio of the light intensity is the value of intensity that is measured behind a polarizer with its transmissive axis parallel to the minor axis of the green laser beam, divided by that measured behind a polarizer with its transmissive axis parallel to the major axis of the green laser beam. Fig. 1(b) shows the experimental setup for measuring the twist angles of the LCs in an ADDLC sample. A red He–Ne laser beam ($\lambda = 632.8$ nm) that was linearly polarized ($\boldsymbol{E_R}$) along **R** was used as a probe beam.

3. Results and discussion

Fig. 2 displays the measured distribution of the light power of each elliptically polarized light beam as a function of the angle of the transmissive axis of the light from **R**. The chosen ellipticities are −0.98 (circularly polarized light), −0.93, −0.87, −0.8, −0.71, −0.61, −0.49, and −0.11 (almost linearly polarized light). A positive (negative) ellipticity represents right- (left-) hand elliptically

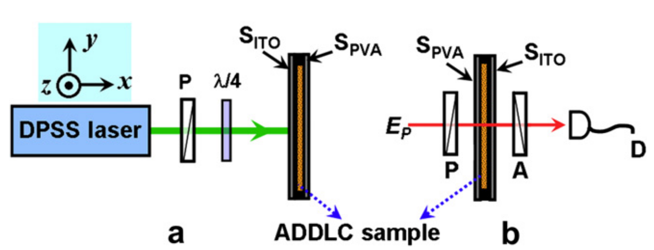

Fig. 1. Schematic experimental setups for, (a) generating adsorbed layer under elliptically polarized light beam; (b) measuring twist angles. P, A, λ/4, and D represent polarizer, analyzer, quarter-waveplate, and detector, respectively.

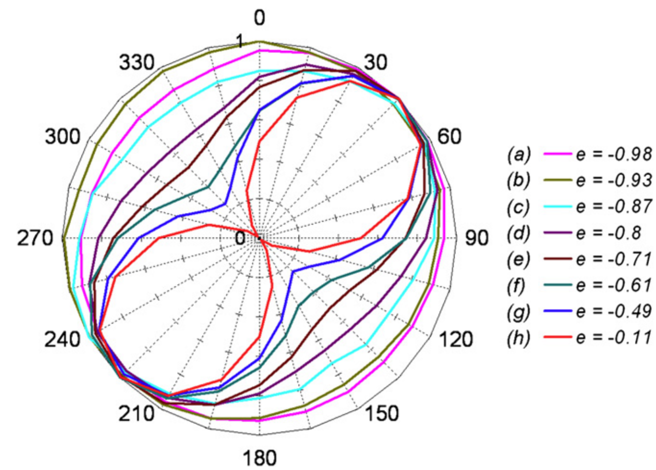

Fig. 2. Measured light power of each elliptically polarized light beam against of the angle between the transmissive axis of the light from **R**. These chosen ellipticities are −0.98, −0.93, −0.87, −0.8, −0.71, −0.61, −0.49, and −0.11.

polarized light. According to our previous studies [8,15], a smooth and rough layer of adsorbed dyes may be developed using weak- and strong-intensity light, respectively. The former can provide a homogeneously anisotropic alignment anchoring, while the latter disturbs the LC alignment. Restated, the orientations of the adsorbed dyes are perpendicular to the polarization of the pump beam in smooth layers, but random in rough layers. In this study, the selective intensities of the used green light beam herein were classified as weak intensities. The alignment properties of the adsorbed MR generated by illuminating elliptically polarized green laser beams with various ellipticities having a proper selectively fixed light intensity or a proper selectively fixed light component along the direction of major axis were studied. First, the intensity ($\mathbf{I_{major}}$) of the elliptically polarized green laser beam through a polarizer whose transmissive axis was along the major elliptical axis of the green light beam was fixed at 28.65 mW/cm^2. The fixed $\mathbf{I_{major}}$ was employed to fix the alignment capability of the adsorbed MR along the direction perpendicular to the major axis, and to examine the effect of alignment resulted from the light component along the direction of minor axis. Notably, the fixed $\mathbf{I_{major}}$ for each elliptically polarized light beam can be achieved by rotating the transmissive axis of the polarizer and tuning the power of the DPSS laser source in Fig. 1(a). The total intensities (**I**) of the green laser beams with various ellipticities varied, increasing with the absolute value of ellipticity, |*e*|. Second, the total intensity (**I**) of the elliptically polarized green laser beam was fixed at 41 mW/cm^2. In this case, it can be used to prove that the permanent elliptically light-induced molecular reorientation is dependent on the ellipticity of light without the consideration of total intensity of light. The intensities ($\mathbf{I_{major}}$) of the green laser beams through a polarizer with its transmissive axis along the major elliptical axes of the green light beams with their various ellipticities varied, increasing as the absolute value of ellipticity, |*e*|, decreased. Notably, the fast and slow axes of the quarter-waveplate were set at +45°/−45° from **R** in this experiment. After the ADDLC sample had been irradiated under green laser beams with various ellipticities from S_{ITO} at room temperature (~25 °C), different adsorbed dye layers formed on S_{ITO}. Notably, the authors previously examined that the adsorption of MR dyes can be made onto both of S_{ITO} and S_{PVA}, which is called double-side photoalignment, if the ADDLC sample is optically excited at a temperature just above the clearing temperature of the used LC materials [16]. Accordingly, in this study, the excited dyes were adsorbed onto the S_{ITO} but not onto S_{PVA} since the temperature of ADDLC sample was below its clearing temperature. Additionally, the illumination periods (>500 s) of the ADDLC sample

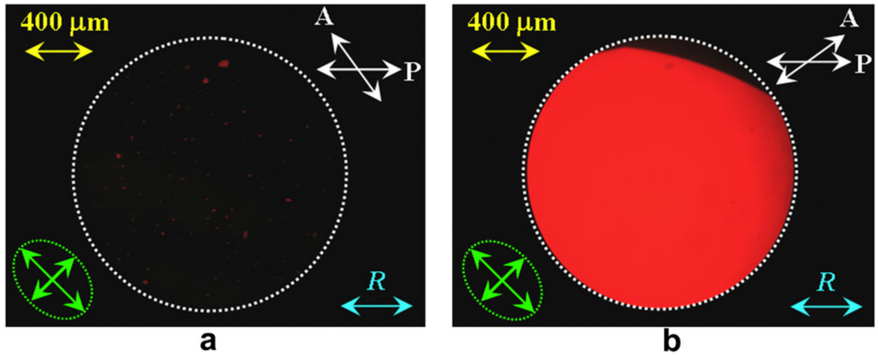

Fig. 3. Illuminated region observed under a POM, in which the transmissive axis of the polarizer is set parallel to **R** and the transmissive axes of the analyzer are set at angles of (a) 126° and (b) 36° with respect to **R** (counting counterclockwise from **R**). P and A denote the transmissive axes of the polarizer and analyzer, respectively. **R** is direction of rubbing. The ellipticity of the pumping beam is −0.71.

for various ellipticities were different. Experimentally, the twist angles increase with the illumination duration, and eventually reach their maxima. In this study, the green laser beam was blocked as the dynamic transmittances, monitored by the experiment setup of the combination of Fig. 1(a) and (b), reached the stable values. Restated, each measured twist angle herein was the maximum value achieved by the selective elliptically polarized light with weak intensity. The twist angles and the transmittance versus voltage (T–V) curves of the samples were also experimentally studied using the setup elucidated below. A red probe He–Ne laser beam with linear polarization ($\boldsymbol{E_R}$) at an angle of 45° from the direction of rubbing, **R**, was normally incident onto the S_{PVA} of the sample. The transmissive axis of the analyzer was set perpendicular (−45° with respect to **R**) to that of the polarizer. The transmission through the illuminated region under an applied AC (1 kHz) voltage was measured. Finally, the measured T–V curves were compared the simulated results to determine the tilt angles [5].

Fig. 3(a) and (b) present the regions of adsorbed MR dyes, observed under a polarized optical microscope (POM), with the transmissive axis of the polarizer set parallel to **R** (along the ***y***-axis in Fig. 1) and the transmissive axes of the analyzer set at angles of 126° and 36° with respect to **R** (counting counterclockwise from **R**). Based on the dark [Fig. 3(a)] and bright [Fig. 3(b)] states, the configuration of the ADDLC after it was irradiated under an elliptically polarized DPSS laser beam ($e \sim -0.71$) was ∼36° TN structures (polarization rotation mode).

Fig. 4(a) displays the polarization characteristics of the probe beam that propagated through the ADDLC sample following irradiation with an elliptically polarized DPSS laser beam ($e \sim -0.71$) using the experimental setup that was shown in Fig. 1(a). It clearly reveals that the homogeneously aligned ADDLCs became twisted nematics (TN) because the LCs close to S_{ITO} (S_{PVA}) were aligned by adsorbed MR dyes (homogeneous alignment film of PVA). The measured twist angle of the LCs in this ADDLC sample was about 36°. The polarization rotation properties of the 36° TN structure were clearly observed and repeatedly verified. Fig. 4(b) plots the measured (blue line) and the 1D-DIMOS-simulated (pink line) T–V curves of the above ADDLC sample. Notably, the experimental data qualitatively fit the simulated results, obtained using the measured cell gap, measured twist angle and fitted tilt angles as input parameters. The LC tilt angle can be obtained by comparing these two curves with each other.

Fig. 5 plots the measured twist angle against the ellipticity of the green laser beam with fixed $\mathbf{I_{major}}$ (pink, 28.65 mW/cm^2) and **I** (blue, 41 mW/cm^2), respectively. Since the angle between the major elliptical axis and **R** was set to 45° in this experiment, the twist angle measured using the experiment setup shown in Fig. 1(b) ranged from 0° to 45°. Refer to ref. [5], the molecules of MR are excited by a linearly polarized ($e \sim 0$) green laser beam of suitable intensity and period, and are then anisotropically adsorbed onto the substrates with their long axes perpendicular to both the directions of polarization and propagation of the green laser beam. The experimental twist angle that was generated by the green laser beam with $|e| \sim 0.1$ (linearly polarized) is consistent with the MR-adsorption, as described above. Experimentally, the LC twist angle declines as the absolute ellipticity of the pumping beam increases. Additionally, in this study, tilt angles in LC, measured by fitting the measured T–V curves to the simulated (1D-DIMOS software) curve, cannot be generated by MR-adsorption by elliptically polarized light in ADDLCs. In other words, the long axes of the adsorbed MRs were perpendicular to the propagation direction of the impinging light beam (***y***–***z*** plane in Fig. 1).

The experimental results described above will be discussed as follows. The optical properties of the MR-adsorption that are

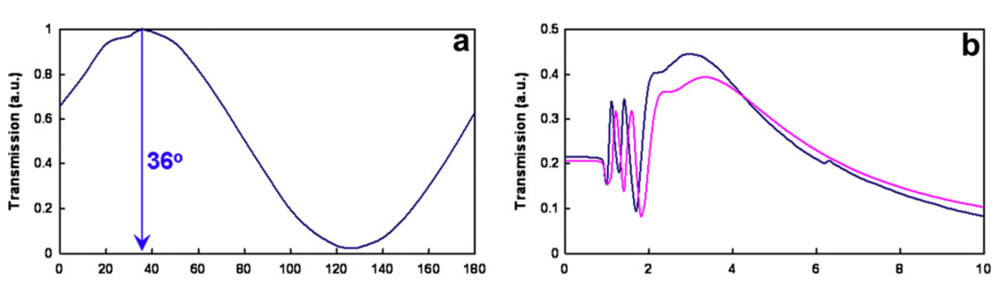

Fig. 4. (a) Transmittances of illuminated region against direction of polarization of probe light; (b) measured (blue line) and simulated (pink line) T–V curves for illuminated region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

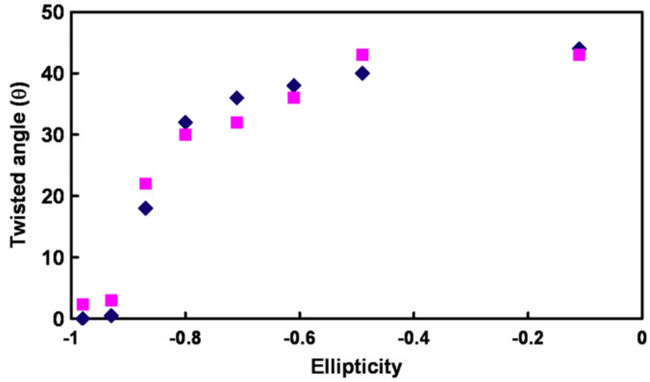

Fig. 5. Twist angle against ellipticity of green laser beam with fixed $\mathbf{I_{major}}$ (pink, 28.65 mW/cm^2) and **I** (blue, 41 mW/cm^2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

generated by elliptically polarized light are similar to those that are generated by linearly polarized light. This result can be easily understood because the total electric field of elliptically polarized light is the vector sum of the two component fields with different phases, such as $\mathbf{E}_{major}\cos(kx-\omega t)$ and $\mathbf{E}_{minor}\sin(kx-\omega t)$ where $\mathbf{E}_{major}\neq\mathbf{E}_{minor}$. These two vector component fields are two linearly polarized fields with their polarization along the major (+45° with respect to **R**) and minor axes (−45° with respect to **R**) of the light. Therefore, the contribution of the elliptically polarized light can be divided into two parts. As is well-known, MRs that are excited by the absorption of green light, can be transformed from *trans*-isomers to *cis*-isomers, and then be adsorbed onto substrates, which apply a torque to align LCs [1–11]. Hence, the light component field along the major axis (+45°) generates a torque of Γ_M (from +45° to 0°), while that along the minor axis (−45°) generates another torque of Γ_m (from −45° to 0°). Notably, one of the torques (Γ_M and Γ_m) is positive, while the other is negative. Hence, the effective torque (Γ) can be written simply as $\Gamma=\Gamma_m+\Gamma_M$.

In the first case (fixed $\mathbf{I_{major}}\sim 28.65$ mW/cm^2), the absolute value of Γ_M, $|\Gamma_M|$, is a constant, while that of Γ_m, $|\Gamma_m|$, increases with the absolute value of the ellipticity of the pumping beam. Accordingly, the effective torque declines as $|e|$ increase. In particular, $|\Gamma_M|$ equals $|\Gamma_m|$ when $|e|$ equals one. Restated, the effective torque (angle of twist) becomes zero when $|e|$ equals one (circularly polarized light). Experimentally, the twist angle that is generated by the adsorbed MR dyes that are exited by a green laser beam increases as $|e|$ decreases. In the second case (fixed $\mathbf{I}\sim 41$ mW/cm^2), the absolute value of Γ_M exceeds that of Γ_m at the selected ellipticities, and increases as $|e|$ declines. Experimentally, the generated twist angle increases as $|e|$ declines in this case as well. Therefore, the variations of the twist angle in cases of fixed $\mathbf{I_{major}}$ and **I** are identical. Additionally, the long axes of the adsorbed dyes are found to be independent of the sign of the ellipticity of light in both cases.

A separate experiment (not described) also indicated that the long axes of the adsorbed dyes are dependent on the directions of the major and minor axes of the elliptically polarized light, regardless of its sign of the light ellipticity. Restated, the long axes of the adsorbed MR dyes excited by right- and left-hand elliptically polarized light beams with identical intensity and ellipticity are the same. Accordingly, the effective torque (Γ) determines the eventual direction of the anchoring resulted from the adsorbed MR dyes. In the case of circularly polarized light ($|e|=1$), which is a special case of elliptically polarized light, neither a twist angle nor a tilt angle can be generated by the randomly adsorbed MR dyes that are exited by a circularly polarized green laser beam. The experimental results are consistent with the theoretical prediction according to the effective torque, as described above. The experimental results in another investigation reveal that the circularly polarized green laser beam stimulates the azo dye-doped cholesteric LCs by *trans–cis* isomerization, causing reorientation parallel to the direction of propagation of the green light beam [7]. Notably, the used material, azo dye (D2), cannot be adsorbed onto the substrate following irradiation under a green laser beam.

4. Conclusion

In conclusion, this study demonstrates the properties of MR-adsorption that are induced by elliptically polarized light in azo dye-doped liquid crystals (ADDLCs). The alignment properties of the adsorbed MR generated by illuminating elliptically polarized green laser beams with various ellipticities having a proper selectively fixed total intensity of light or a proper selectively fixed light component along the direction of major axis were studied. According to the experimental results, it clearly reveals that the twist angle increases as $|e|$ declines, and no tilt angle of LC alignment can be generated by the adsorbed MR dyes exited by elliptically/circularly polarized green laser. The long axes of the adsorbed MRs are independent of the sign of the light ellipticity, but depend on the direction of the major or minor axis of the elliptically polarized light. Additionally, neither a twist angle nor a tilt angle can be produced using a circularly polarized pumping beam. Therefore, the experimental results completely explain the fabricated structures of the polarization holographic grating based on azo dye-doped polymer-ball-type polymer-dispersed liquid crystals [9,10].

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References

[1] Andrienko D, Fedorenko D, Reznikov Y, Slussarenko S, Francescangeli O, Simoni F. Photoalignment effect induced by angular momentum of light in dye-doped liquid crystals. Mol Cryst Liq Cryst 1999;329:1–10.
[2] Andrienko D, Fedorenko D, Uskova O, Reshetnyak V, Reznikov Y, Slussarenko S, et al. Light-induced alignment and reorientation effects in liquid crystals doped with azo-dyes. Ukr Jorn Fiz 1999;44:149–57.
[3] Andrienko D, Reshetnyak V, Reznikov Y, Sluckin TJ. Nematic director slippage: role of the angular momentum of light. Phys Rev E 2000;63:011701.
[4] Lucchetti L, Tifi L, Simoni F. Director sliding induced by a circularly polarised light in dye-doped liquid crystals. Opt Commun 2008;281:4363–9.
[5] Fuh AY-G, Liu C-K, Cheng K-T, Ting C-L, Chen C-C, Chao PC-P, et al. Variable liquid crystal pretilt angles generated by photoalignment technique in dye-doped liquid crystals. Appl Phys Lett 2009;95:161104.
[6] Fuh AY-G, Chen J-C, Huang S-Y, Cheng K-T. Binary liquid crystal alignments based on photoalignment in azo dye-doped liquid crystals and their application. Appl Phys Lett 2010;96:051103.
[7] Yeh H-C, Chen G-H, Lee C-R, Mo T-S. Optically switchable biphotonic gratings based on dye-doped cholesteric liquid crystal films. Appl Phys Lett 2007;90:261103.
[8] Cheng K-T, Liu C-K, Ting C-L, Fuh AY-G. Electrically switchable and optically rewritable reflective Fresnel zone plate in dye-doped cholesteric liquid crystals. Opt Express 2007;15:14078–85.
[9] Fuh AY-G, Lee C-R, Mo T-S. Polarization holographic grating based on azo-dye-doped polymer-ball-type polymer-dispersed liquid crystals. J Opt Soc Am B 2002;19:2590–4.
[10] Fuh AY-G, Lee C-R, Cheng K-T. Fast optical recording of polarization holographic grating based on an azo-dye-doped polymer-ball-type polymer-dispersed liquid crystal film. Jpn J Appl Phys 2003;42:4406–10.
[11] Fuh AY-G, Chen C-C, Liu C-K, Cheng K-T. Polarizer-free, electrically switchable and optically rewritable displays based on dye-doped polymer-dispersed liquid crystals. Opt Express 2009;17:7088–94.
[12] Fuh AY-G, Mo T-S. Holographic grating based on dye-doped surface-stabilized ferroelectric liquid crystal films. Jpn J Appl Phys 2002;41:2122–7.

[13] Heilmeier GH, Zanoni L. Guest–host interactions in nematic liquid crystals: a new electro-optic effect. Appl Phys Lett 1968;13:91–2.
[14] Berreman DW. Elastic continuum theory cutoffs and order in nematics and solids. J Chem Phys 1975;62:776–8.
[15] Lee C-R, Fu T-L, Cheng K-T, Mo T-S, Fuh AY-G. Surface-assisted photo-alignment in dye-doped liquid crystal films. Phys Rev E 2004;69:031704.
[16] Lin L-C, Jau H-C, Lin T-H, Fuh AY-G. Highly efficient and polarization independent Fresnel lens based on dye-doped liquid crystal. Opt Express 2007;15:2900–6.