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Timothy J. White
Rebecca L. Bricker
Lalgudi V. Natarajan
Vincent P. Tondiglia
Lisa Green, *Kent State University - Kent Campus*, et al.

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Timothy J. White,[1]* Rebecca L. Bricker,[1,2] Lalgudi V. Natarajan,[1,3] Vincent P. Tondiglia, [1,3] Lisa Green, [4] Quan Li, [4] and Timothy J. Bunning[1]

[1]*Air Force Research Laboratory, Materials and Manufacturing Directorate,*
Wright Patterson AFB, OH 45433, U.S.A.
[2]*Also with SOCHE Inc., 3155 Research Blvd. Suite 204, Dayton, OH 45420, U.S.A.*
[3]*Also with SAIC Inc., 4031 Colonel Glenn Highway, Dayton, OH 45431, U.S.A.*
[4]*Kent State University, Liquid Crystal Institute, Kent, OH 44242, U.S.A.*
*timothy.white2@wpafb.af.mil

Abstract: We report on the development of photoaddressable cholesteric liquid crystal (CLC) mixtures capable of large range color tuning as well as direct on-off electrical switching. The continuously photoaddressable CLC mixtures are based on a high HTP azo-containing chiral material mixed with an off-the-shelf nematic liquid crystal (QL9/E44). By polymer stabilizing the QL9/E44 mixture, it is demonstrated that the photoaddressable reflection of the notch can be switched on and off with an AC voltage. The novel combination of these effects has potential utility in lasing, dynamic notch filters, and spatial light modulators.

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1. Introduction

Numerous lifeforms in the animal and plant kingdoms utilize reconfigurable optical properties for purposes that range from defensive (camouflage, intimidation) to functional (energy harvesting). The means by which these adaptive lifeforms control their optical properties is often associated with light absorption by pigments. As recently demonstrated in the examination of iridophores in cephalopods, these lifeforms also control their reflective properties as well [1–3]. The ability of natural life to dynamically control the optical properties far outpaces man-made biomimetic efforts. To date, dynamic optical elements have seen widespread use in devices such as spatial light modulators, notch filters, or fiber modulators. Many of these devices have utilized the electro-optic properties of liquid crystals as the enabling material to accomplish their function. Liquid crystal-based reflective elements have been most commonly based on the cholesteric liquid crystal (CLC) phase, due to the spectral selectivity of the inherent reflectivity associated with the heliocoidal structure. CLCs have been screened as potential components in displays, projectors, and optical filters [4]. The position of the selective reflection of a CLC is given in Eq. (1);

$$\lambda_b = \bar{n} P \tag{1}$$

where λ_b is the center of the reflection notch (e.g. the Bragg reflection), n is the average refractive index), and P is the pitch of the helix. From Eq. (1), the color (λ_b) of the CLC can be reconfigured by changing n or changing P. Historically, most efforts have focused on electric field tuning of the CLC reflection notch to mixed success. Only a few demonstrations have been published to date [5,6] that exhibit full range visible spectrum electric field tuning in PSCLC materials. The limited number of demonstrations is indicative of the difficulties associated with changing n and/or P with electric fields.

In many ways because of these difficulties, a number of reports detail the use of light-sensitive CLC mixtures to generate color tuning [7–16]. Using light to control the reflection of CLCs also has some added benefits, due to the ease of spatial, temporal, and remote control of irradiation [10]. Tuning of light-sensitive CLCs (phototuning) have employed a number of chromophores including azobenzene, fulgides, diarylethenes, spiropyrans, and other photochromic moieties [7]. Most commonly, these efforts have utilized azo-based materials which readily undergo trans-cis isomerization to UV-light exposure and cis-trans isomerization with exposure to higher wavelength light (> 530 nm) or heat. Phototunable mixtures based on axially chiral bis(azo) materials directly affect the pitch through their conformational-dependent helical twisting power (HTP) [13,17]. The HTP of a chiral dopant effectively is a measure of the efficiency of a molecule to induce a helical twist in a given nematic liquid crystal host. Trans-cis isomerization in nearly all azo-based chiral materials decreases the HTP, which in turn increases the pitch (P) – causing a red shift.

One drawback of CLCs as optical elements is the inability to directly switch the reflection on and off. Other approaches to CLC switching, such as surface stabilized cholesteric textures, switch between the reflective CLC phase and the scattering focal conic state. The application of a strong electric field transitions the reflection of the CLC from planar (reflective) to homeotropic (clear). Subsequent removal of the AC voltage causes the CLC helix to form a long-lived (metastable) and highly scattering focal conic state. This metastable focal conic state observed during electric field switching of CLCs has been eradicated through polymer stabilization of the CLC helix [18]. Polymer stabilization of the CLC is typically undertaken using liquid crystal monomers in concentrations around 5-10 wt%, which polymerize to effectively template the CLC helix. Like conventional CLCs, application of a

strong voltage transitions the CLC from planar (reflective) to homeotropic (clear). However, upon removal of the voltage, the templated polymer network acts as a restoring force that returns the CLC to its original spectral characteristics (transmission, reflectivity, position). Only recently have phototunable CLC mixtures been polymer stabilized, with these initial efforts focused on the effects of polymer stabilization on the dark relaxation of the azo-based PSCLC from the photodriven notch position. We demonstrate herein the novel combination of a phototunable PSCLC based on a high HTP bis(azo) chiral dopant that can be readily reconfigured and switched with application of an AC voltage. The resulting reconfigurable and switchable reflector has potential uses as a passive spatial light modulator, as a tunable/switchable optical filter, or even as a photodisplay.

2. Results and discussion

The axially chiral bis(azo) compound (QL9, structure inset into Fig. 1) was mixed with the nematic liquid crystal E44 and polymer stabilized as previously reported [7]. The HTP of QL9 has been estimated at 78 μm^{-1} in the trans/trans configuration and 20 μm^{-1} in the cis/cis configuration. Shown in Fig. 1(a) is a plot of the Bragg reflection versus time for both the phototuning and dark relaxation of the QL9 (6 wt%)/E44 PSCLC (5 μm thick). Continuous exposure to 1 mW/cm^2 of UV light (365 nm) causes the position of the QL9 (6 wt%)/E44 PSCLC to tune from 650 nm to 1000 nm in approximately 45 seconds. The second half of Fig. 1(a) shows the temporal dark relaxation of the QL9 (6 wt%)/E44 PSCLC in the dark. As is evident in Fig. 1(a) – the sample maintains the 1000 nm reflection for nearly 1 hour. After this time, the cis-trans isomerization that occurs in the dark causes a blue shift in the reflection eventually restoring the 650 nm reflection in 6 hrs. For reference, the dark relaxation of the analogous but unstabilized QL9 (6 wt%)/E44 CLC mixture regenerates the original spectral properties in 65 hours. As documented, the improvement in the dark relaxation of these materials is caused by an increase the rate of cis-trans isomerization that arises due to interactive effects between the polymer and cis-azobenzene [7].

Shown in Fig. 1(b) and 1(c) is the response of QL9(8 wt%)/E44 CLC and PSCLC to AC voltages from 0 to 210 V (at 1 kHz frequency). In both the QL9/E44 CLC and PSCLC, the original ~500 nm (blue-green) transitions to a focal conic state with application of low voltage AC. Thereafter, application of 125 and 210 V (respectively) AC transition the focal conic state to the homeotropic state (clear). It should be noted, that direct application of 125 and 210 V AC directly convert the reflective CLC or PSCLC to the clear, homeotropic state. In both the CLC and PSCLC, switching times were less than 500 ms. The benefit of polymer stabilization is observed in Fig. 1(b) and 1(c) by comparing the spectra after the AC voltage has been removed. Removal of the 125 V AC voltage from the QL9 (8 wt%)/E44 CLC causes the spectrum to shift from the homeotropic state (iv) to the focal conic state (ii). Opposingly, removal of the 210 V AC voltage from the QL9 (8 wt%)/E44 PSCLC transitions from the
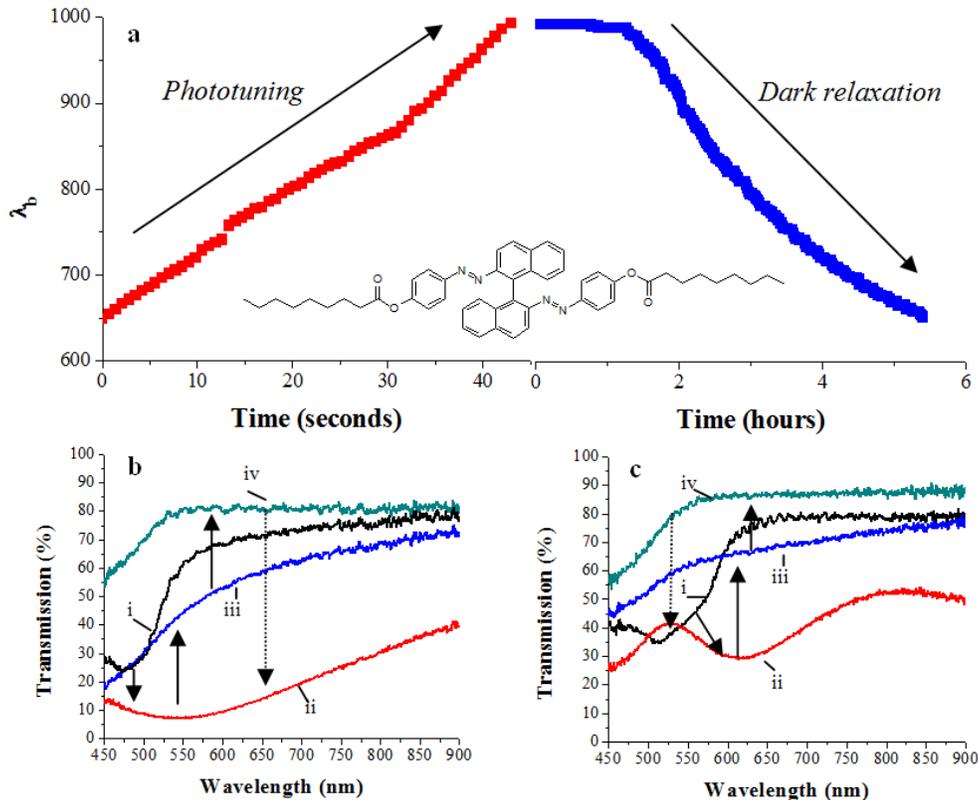
Fig. 1. a) Phototuning and dark relaxation for a polymer stabilized CLC mixture based on the high HTP chiral dopant QL9 (inset) and the nematic liquid crystal E44. The temporal dependence of the Bragg reflection during UV-directed tuning (1 mW/cm^2). b) and c) AC switching of QL9/E44 CLC (b) and PSCLC (c). Original spectrum (i) is driven to focal conic texture (ii) with application of low voltage AC. Increasing AC voltage shifts from focal conic texture to an increasingly homeotropic (iii) alignment. Application of a sufficient AC voltage (210 V AC – PSCLC, 125V AC – CLC) drives the sample from planar (i) to homeotropic state (iv). With removal of the AC voltage, the CLC transitions back to the focal conic state (b-ii) while the PSCLC sample returns to the reflective state (c-i).

homeotropic state (iv) to the reflective state (i), which occurs in 1-2 seconds. In simple terms, polymer stabilizing the CLC helix enables direct switching from the reflective to the clear state. The polymer network enables switching to applied AC voltage through elastic interaction that guides the CLC from the homeotropic state back to the planar state, as has been documented [18].

The novel combination of phototunable and electrically switchable QL9 (8 wt%)/E44 PSCLC is demonstrated in the transmission spectra in Fig. 2(a) and pictorially in Fig. 2(b). The original spectral position (blue) of the QL9/E44 PSCLC can be turned on and off with applied AC voltage. Subsequent exposure to UV light red shifts the color of the PSCLC reflection from blue to green. At this point, application of 210 V AC also switches the reflection on and off. Additional exposure to UV light can transition the PSCLC reflection of this mixture to the red or into the infrared, where the reflection can also be switched on and off with application of 210 V AC. While not shown here, it is possible to blue shift the PSCLC reflection with exposure to higher wavelength light or heat. Regardless of the spectral position, the PSCLC reflection can be turned on and off with application of an AC voltage irrespective of the previous exposure history. LG9/E44 PSCLC cells have been repeatedly
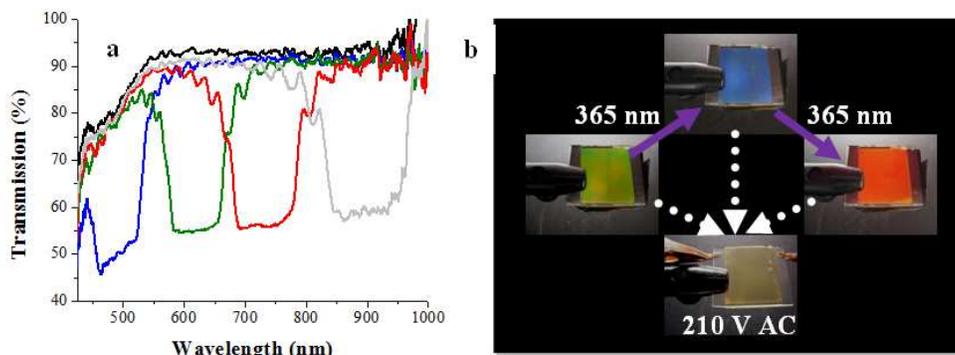
Fig. 2. a) Transmission spectra and b) pictorial demonstration of the phototuning and switching of a QL9 (8 wt%)/E44 PSCLC. In both, the QL9/E44 PSCLC is tuned with UV light shifting the reflection from the blue to the infrared. From each spectral position, the reflection can be driven to the clear state by application of a 210 V AC. Removal of the 210 V AC returns the PSCLC from the clear state (— in a, "210 V AC" in b) to the spectrum observed before applied voltage.
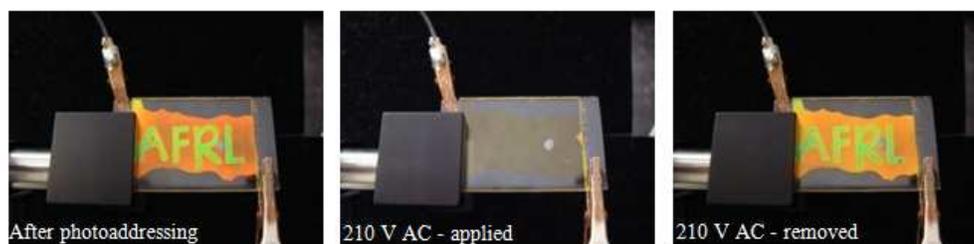

Fig. 3. Using a photomask, the letters "AFRL" are written into the QL9/E44 PSCLC (originally reflecting green). The area outside the "AFRL" mask is tuned to reflect orange-red. Application of 210 V AC switches the entire cell on and off. With removal of the voltage, the image is restored retaining its content. See also MOVIE1.

photoaddressed and switched numerous times in a period of months, with no discernable degradation in switching speed or other performance measures.

The phototunable and electrically switchable characteristics of the QL9/E44 PSCLC are combined with the spatial control of light to selectively photoaddress the PSCLC reflection using a photomask (Fig. 3). UV light exposure of the cell outside the mask tunes the originally green-reflecting CLC to red-reflecting, leaving the letters AFRL written in green. Application of 210 V AC switches the reflection of the entire cell off, clearing the light-written content. Upon removal of the voltage, the PSCLC reflection returns in less than a second, still retaining the information content written into the cell. The ability to selectively address the LG9/E44 PSCLC could be extended to laser rastering to write complex patterns, as has been demonstrated [10].

3. Conclusion

A polymer stabilized, phototunable cholesteric liquid crystal (PSCLC) mixture based on a high HTP light-sensitive chiral dopant is examined. It is demonstrated that this mixture can be continuously addressed with light to change the color of the reflector and it is demonstrated that by masking, the reflection of the PSCLC can be patterned. Due to the polymer stabilized CLC helix, the photoaddressable PSCLC can switched on and off with applied AC voltage. As presented (Fig. 2) the tunable and switchable properties of these PSCLC reflectors open up a wide range of possibilities – as color-changeable light valves, lasing elements, or dynamic filters.

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