

Combined electric and photocontrol of selective light reflection at oblique helicoidal cholesteric doped with azoxybenzene derivative

Kamal Thapa¹², Olena S. Iadlovska¹², Hari Krishna Bisoyi¹, Daniel A. Paterson³, John M.D. Storey³, Corrie T. Imrie³, Quan Li¹⁴, Sergij V. Shiyanovskii¹⁴, and Oleg D. Lavrentovich^{124*}

¹*Advanced Materials and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA*

²*Department of Physics, Kent State University, Kent, Ohio 44242, USA*

³*Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, AB24 3UE Scotland, United Kingdom*

⁴*Materials Science Graduate Program, Kent State University, Kent, Ohio 44242, USA*

*e-mail address: olavrent@kent.edu

Abstract

An oblique helicoidal cholesteric ChOH represents a unique optical material with a single-harmonic periodic modulation of the refractive index and a pitch that can be tuned by an electric or magnetic field in a broad range from sub micrometers to micrometers. In this work, we demonstrate that the oblique helicoidal cholesteric doped with azoxybenzene molecules can be tuned by both the electric field and light irradiation. The tuning mechanism is explained by the kinetics of trans-cis photoisomerization of the azoxybenzene molecules. At a fixed voltage, UV irradiation causes a redshift of the reflection peak by more than 200 nm. The effect is caused by an increase of the bend elastic constant of ChOH under irradiation. The demonstrated principle has the potential for applications such as smart windows, sensors, tunable lasers, and filters.

I. INTRODUCTION

Cholesteric (Ch) liquid crystals (LC) are composed of chiral molecules that twist periodically in space, forming a right-angle helicoid. When the Ch pitch P is in the sub-micrometer range, a uniformly aligned Ch shows a selective reflection of light in the visible spectral range. For unpolarized light propagating along the Ch helical axis, the circularly polarized component of light with the same handedness as the Ch is reflected, and the opposite handedness is transmitted.

The selective Bragg reflection's peak wavelength $\lambda_P = \bar{n}P$ and its bandwidth $\Delta\lambda = \Delta nP$ are defined by the pitch P , the average value \bar{n} of extraordinary n_e and ordinary n_o refractive indices, and the birefringence $\Delta n = n_e - n_o$ [1]. The wavelength of the reflected light can be controlled by temperature, chemical compositions, and by the concentration of chiral dopants since these could change both the refractive indices and the pitch P . However, the most desirable electromagnetic mode to control light diffraction by Ch has been elusive. The reason is that the applied field either does not change the pitch or destroys the single-harmonic modulation of the refractive indices [2,3] thus reducing the efficiency of diffraction [4-6]. If the dielectric or diamagnetic anisotropy is negative, the director and the Ch pseudo layers align perpendicularly to the field and there is no torque that could change the pitch. If the anisotropy is positive, the helical axis aligns perpendicularly to the applied field. In this state, the regions in which the director is parallel to the field expand at the expense of the regions in which the director must be perpendicular to the field [2-5]. Although the pitch grows with the field, the uniform rate of twist is lost. The helical structure distorted by the field is no longer of a single-harmonic character and efficiency of the light diffraction is diminished, as demonstrated experimentally for various geometries, with the Ch axis in the plane of the cell [4,5] or normal to it [6]. Recent developments in the synthesis of mesomorphic compounds in the form of flexible dimers that show an anomalously low value of the bend elastic constant K_{33} led to the realization of an oblique helicoidal cholesteric (Ch_{OH}) state, in which the director twists around the helical axis while remaining tilted rather than perpendicular to it. The stability of this Ch_{OH} state, which contains both twist and bend director deformations, requires the bend elastic constant K_{33} to be smaller than the twist K_{22} modulus, as predicted theoretically by de Gennes [2] and Meyer [3]. When an electric **E** [7,8] or magnetic **H** [9] field acts along the Ch_{OH} axis, it changes the tilt angle θ of the director and the pitch of the structure but does not modify the single-harmonic character of the twist. For optical applications, it means that the efficiency of light reflection remains high in the entire range of pitch values controlled by the field. In a single Ch_{OH} cell, the wavelength of reflected (or transmitted) light can be tuned in a very broad range, from UV to near IR [8,9]. The Ch_{OH} structure is also sensitive to the torques induced by the electromagnetic field of light, which allows one to control the pitch by combining the low-frequency electric field [7,8] and the electromagnetic field at optical frequencies [10].

The responsiveness of Ch could be extended to photochemical effects by doping the chiral mixtures with photoresponsive molecules capable of photoisomerization. In the well-known phenomenon of trans-to-cis isomerization of azobenzenes and azoxybenzenes, light irradiation in the UV and visible parts of the spectrum changes the molecular shapes and interactions and affects the Ch pitch and the refractive indices, and hence the wavelength and bandwidth of selective Bragg reflection [11-18]. In various embodiments, the photocontrol could be achieved by doping a Ch with a photosensitive achiral material [11], by using a photosensitive nematic as a host for Ch with a non-photosensitive chiral dopant [15,19-22], and by using a photo-insensitive chiral dopant [12,16,17,23-31], see the recent reviews [32-34]. Photocontrol of Ch can be used to fabricate optical filters with tunable wavelength and bandwidth [35] and optically tunable lasers [36]. A UV control of optical transparency at longer wavelengths, in near-IR, can potentially be of interest in the development of smart windows [37].

In this work, we demonstrate experimentally that a combined action of the electric field and UV irradiation could continuously tune the Ch_{OH} pitch and the wavelength of selective reflection of light with longer wavelengths, in the visible part of the spectrum and potentially far beyond. To achieve the dual electric and photocontrol, the Ch_{OH} composition is prepared with flexible dimers and doped with a photosensitive achiral p,p' -diheptylazoxybenzene (D7AOB), which experiences trans-to-cis isomerization under UV irradiation and reverse transition under thermal relaxation [38], similarly to its azobenzene counterpart p,p' -diheptylazobenzene [39]. The maximum absorbance of D7AOB is at 340 nm and then decays as the wavelength of irradiation increases [38]. The presence of flexible dimers in the mixtures guarantee the smallness of K_{33} [40,41]. At a fixed voltage, UV irradiation causes a gradual redshift of the reflection wavelength by about 235 nm for the explored composition. A unique feature of Ch_{OH} is a well-defined relationship between the material parameters such as elastic moduli, birefringence, and the pitch. Using this relationship, we demonstrate that the main reason of the UV-induced redshift of the Bragg reflection wavelength is the increase of K_{33} . The dynamic scenarios of the irradiation-induced changes are described by kinetic equations. The combined action of the electric field and UV irradiation in the Ch_{OH} doped with D7AOB can find applications in smart windows, lasers, optical filters, as well as in sensors for measuring UV intensities/doses.

II. MATERIALS AND METHODS

The photosensitive Ch_{OH} mixture contains a rod-like mesogen pentylcynobiphenyl (5CB), photosensitive azoxybenzene derivative p,p' -diheptylazoxybenzene (D7AOB, Fig. 1) which is also a mesogen in its pure form [42-44], flexible dimers $1'',7''$ -bis(4-cyanobiphenyl-4'-yl) heptane (CB7CB) and 1 -(4-cyanobiphenyl-4'-yloxy)- 6 -(4-cyanobiphenyl-4'-yl) hexane (CB6OCB), and left-handed chiral dopant S811 (EM Industries), in the following weight proportion: 5CB:D7AOB:CB7CB:CB6OCB:S811 = 42.0:10.0:28.5:15.5:4.0. The mixture shows a transition from an isotropic to a chiral nematic (N^*) phase at $T_{\text{I}-\text{N}^*} = 64.4$ °C and from N^* to a chiral analog of the twist-bent nematic (N_{TB}) phase at $T_{\text{N}^*-\text{NTB}} = 22.0$ °C. The flexible dimers CB7CB and CB6OCB reduce the bend elastic constant K_{33} , while other components help to keep the temperature range of a small K_{33} close to the room temperature; small K_{33} assures the stability of the Ch_{OH} state. Note that the photosensitive mesogenic dopant D7AOB shows a relatively small K_{33} in its nematic phase well above the transition temperature to the smectic A phase [44].

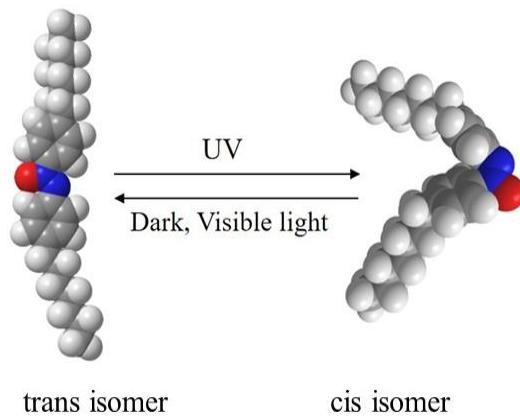


FIG. 1. Trans and cis isomers of D7AOB molecule.

In planar cells with fixed azimuthal alignment on both substrates results in a step-like behavior for azimuthal rotation of director. This affects the optical spectra, in which the discrete values of the equilibrium Ch_{OH} pitch results in discrete values of Bragg wavelength for the reflection. Although the step-like nature of optical spectra brings some disadvantages, the

equilibrium Ch_{OH} structure in the planar cell is very stable as compared to cells with the vertical orientation of the director near substrates. In homeotropic cells, the azimuthal orientation of the director is not defined on both substrates, as a result the Ch_{OH} structure easily shifts from its equilibrium by small external forces or by temperature. Therefore, in this work, photocontrol of Ch_{OH} is achieved using cells with hybrid surface anchoring, Fig. 2; the homeotropically anchored plate allows the electric field to change the rate of chiral twist in a continuous manner. The cells are assembled from two indium tin oxide (ITO) patterned glass substrates. One plate is spin-coated with a polyimide PI2555 and rubbed unidirectionally to achieve planar alignment. The other plate is coated with a silicone elastomer SE5661 for homeotropic surface anchoring. The thickness of the cells is set by spherical spacers mixed with UV-curable glue NOA 68 (Norland Products, Inc.) and measured by an interferometric technique using Lambda 18 UV/VIS spectrometer (Perkin Elmer, Inc). The cells are filled with the Ch_{OH} mixture in the isotropic phase through the capillary force action.

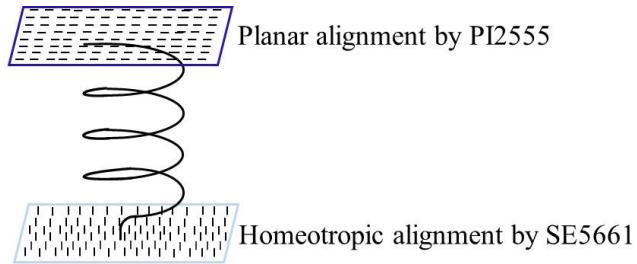


FIG. 2. A schematic representation of hybrid surface anchoring in the Ch_{OH} cell

A sinusoidal AC voltage of frequency 3 kHz from DS345 waveform generator (Stanford Research) and 7602M voltage amplifier (KROHN-HITE Co.) is applied to 5 mm \times 5 mm ITO electrodes of the Ch_{OH} cells. The selective reflection spectra are observed using a tungsten halogen light source LS-1 with a working range (360-2000) nm and a USB2000 fiber optics spectrometer (both Ocean Optics, Co.). An unpolarized light beam from LS-1 is passed through UV-VIS bifurcated fiber (200 μm diameter) and focused by the lens into a paraxial ray incident normally at the planar surface of the Ch_{OH} cells. The superimposed reflected beam is passed back through the bifurcated fiber and detected by a USB2000 spectrometer interfaced with Oceanview spectroscopy software (Ocean Optics, Co.). The light source LS-1 is switched on throughout the entire experiment. In the experiments in which the UV irradiation is absent, to avoid potential

photoisomerization caused by LS-1, a broadband filter is placed on the cells to cut off the light of wavelength below 450 nm.

An LED lamp (Thorlabs M365LP1) serves as a UV light source with an emission wavelength at 365 nm. The light intensity is measured by an S170C power meter (Thorlabs). To separate the photochemical and dielectric heating effects from the UV-induced thermal effects, the temperature of the samples during UV and electric field activation is measured by a thermocouple (accuracy ± 0.01 °C) attached to the glass plate of the cell.

The material properties important for the analysis of the UV-effect are the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, where ϵ_{\parallel} and ϵ_{\perp} are the parallel and perpendicular components of dielectric permittivity, extraordinary n_e and ordinary n_o refractive indices, and, most importantly, K_{33} . These parameters were measured before UV exposure and after 1.5 h under continuous UV exposure.

The dielectric permittivities are derived from the capacitance measurements under an applied field at the frequency 3 kHz in a planar cell formed by two ITO patterned planar glass substrates using an LCR meter 4284A (Hewlett Packard). The perpendicular component ϵ_{\perp} is determined at a low voltage that does not perturb the planar structure and ϵ_{\parallel} is measured by applying a high voltage that unwinds the Ch_{OH} state into a homeotropic N state [41].

The refractive indices are measured by an interference technique [45] using a wedge cell filled with the nematic analog of the Ch_{OH} mixture. The nematic mixture preserves the same fraction of D7AOB as the Ch_{OH} mixture, namely, 5CB:D7AOB:CB7CB:CB6OCB = 41.8:10.0:31.3:16.9 ($T_{\text{I-N}} = 75.1$ °C, $T_{\text{N-NTB}} = 19.4$ °C). The nematic fills a wedge sample with a small wedge angle 0.00675 radians, formed by two planar ITO-PI 2555 glass substrates with the rubbing direction perpendicular to the thickness gradient, in order to avoid director deformations. The measurements are performed at three different wavelengths 432, 532, and 632.8 nm using laser line color filters (Thorlabs) of 1 nm central bandwidth. The thickness of the thick end is fixed by 100 μm spacers mixed with a glue NOA68; there are no spacers at the glued thin end.

The bend elastic constant K_{33} is measured in hybrid aligned Ch_{OH} cells using the dependence of the Bragg reflection wavelength λ_P on the applied electric field E [41], $\lambda_P/n_o(\lambda_P) = a_1 E^{-1} + a_2 E^{-2}$, where the ordinary refractive index should be evaluated at the

corresponding wavelength, $n_o = n_o(\lambda_p)$; a_1 and a_2 are the fitting parameters. Using the three measured values of the ordinary refractive index, we find the polynomial coefficients of the Cauchy dispersion relation $n_o(\lambda) = A + B\lambda^{-2} + C\lambda^{-4}$ and calculate the ratio $\lambda_p/n_o(\lambda_p)$. The field dependency of $\lambda_p/n_o(\lambda_p)$ is fitted with a polynomial $a_1E^{-1} + a_2E^{-2}$ to find a_1 and a_2 . The slope $a_1 = 2\pi \sqrt{\frac{K_{33}}{\varepsilon_o \Delta \varepsilon}}$ is used to determine K_{33} ; the correction a_2E^{-1} is negligibly small as compared to a_1 ; similar results were obtained for other Ch_{OH} materials, see Ref. [41].

III. RESULTS AND DISCUSSION

The field dependence of the selective Bragg reflection of light by a mixture that is not exposed to UV irradiation is shown in Figure 3, as measured in a hybrid cell of the thickness $d = (9.25 \pm 0.02) \mu\text{m}$ at a constant temperature $T = T_{\text{N}^*-\text{NTB}} + 2 \text{ }^\circ\text{C} = 24 \text{ }^\circ\text{C}$. The peak wavelength λ_p is calculated as the coordinate of the middle of the width at the half-amplitude of the Bragg peak. The field is first raised to $4.0 \text{ V}/\mu\text{m}$ at which the Ch is completely unwound and the director is aligned uniformly along the electric field and then reduced to form Ch_{OH} and measure the reflection spectra, Fig. 3. As the electric field increases, the Ch_{OH} pitch, λ_p and conical angle θ decrease, similarly to previous results [8,41,45,46] on Ch_{OH} without photosensitive dopants according to the following relations,

$$\lambda_p = \frac{2\pi}{E} \sqrt{\frac{K_{33}}{\varepsilon_o \Delta \varepsilon}}, \quad (1)$$

$$\sin^2 \theta = \frac{K_{33}}{K_{22} - K_{33}} \left(\frac{E_{\text{NC}}}{E} - 1 \right), \quad (2)$$

here ε_o is the dielectric constant, $\Delta \varepsilon$ is the dielectric anisotropy, $E_{\text{NC}} = \frac{2\pi K_{22}}{P_o \sqrt{\varepsilon_o \Delta \varepsilon K_{33}}}$ is a critical field above which the Ch structure unwinds into a uniaxial state N and P_o is the intrinsic pitch of Ch state in the absence of field.

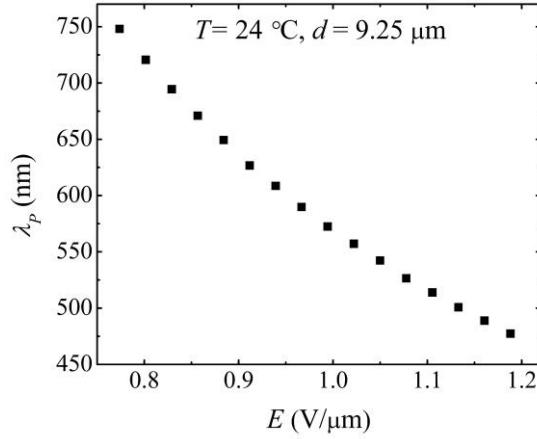


FIG. 3. Electric field dependence of the peak wavelength λ_p measured at the planar side of the hybrid Ch_{OH} cell with thickness $d = (9.25 \pm 0.02)$ μm at temperature $T = 24.0$ $^\circ\text{C}$.

To explore whether the UV irradiation could independently control the structural color of Ch_{OH}, we used the same cell at the same temperature $T = 24.0$ $^\circ\text{C}$, under a fixed electric field, of the RMS amplitude $E = 1.15$ V/ μm . The single value of the electric field is chosen in such a way that the redshift of Bragg reflection due to continuous UV irradiation is in the visible covering blue, green, and red colors. Continuous irradiation with non-polarized UV light ($\lambda = 365$ nm) of low intensity ($I_{\text{UV}} = 0.3$ mW/cm²) causes a continuous redshift of the reflection band from $\lambda_p^0 = 473$ nm to $\lambda_p^{\text{on}} = 708$ nm after 1.5 h of irradiation, Fig. 4(a). The redshift starts to saturate after about 40 min of UV irradiation. Once the UV is switched off, λ_p gradually relaxes back to the shorter values, at a rate that is much slower than the redshift rate under the UV, coming close to the initial pre-UV wavelength of 473 nm, but remaining a few nm above it even after 80 h, Fig. 4(b). This slow relaxation is a common property of azo- and azoxy-benzene compounds [16,47].

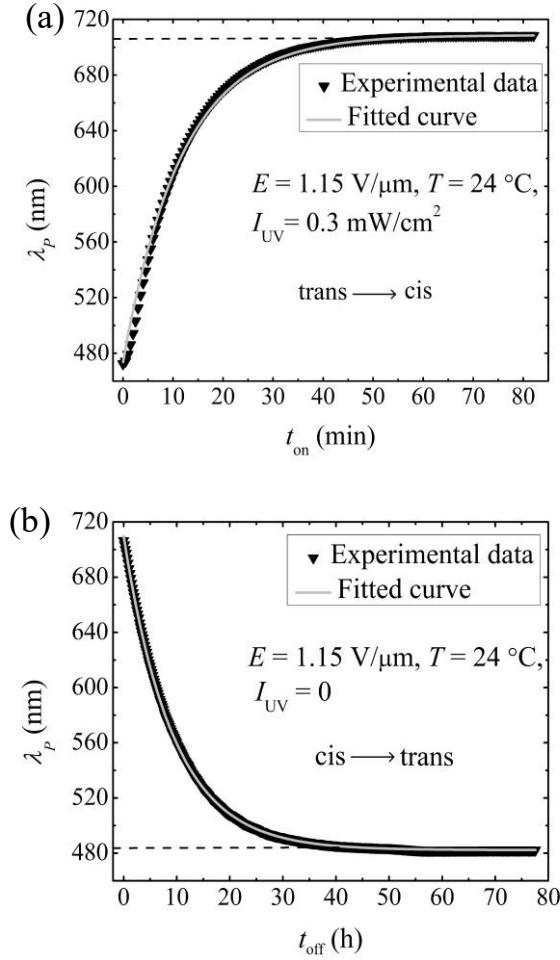


FIG. 4. Dynamics of the peak wavelength λ_p shifts for a ChOH cell with thickness $d = (9.25 \pm 0.02) \mu\text{m}$: (a) λ_p as a function of the UV exposure time t_{on} for UV irradiation at 365 nm, $0.3 \text{ mW}/\text{cm}^2$; (b) λ_p as a function of the relaxation time t_{off} after UV is switched off. In both cases, the electric field is fixed at $E = 1.15 \text{ V}/\mu\text{m}$.

The dependence of λ_p on the duration t_{on} of UV irradiation in Fig. 4(a) is well fitted by an exponential dependence

$$\lambda_p(t_{\text{on}} \geq 0) = \lambda_p^{\text{on}} + (\lambda_p^0 - \lambda_p^{\text{on}}) e^{-\frac{t_{\text{on}}}{\tau_{\text{on}}}}, \quad (3)$$

where t_{on} is the UV exposure time measured from the moment the UV irradiation is switched on, $\lambda_p^0 = 473 \text{ nm}$ and $\lambda_p^{\text{on}} = 708 \text{ nm}$ are the stationary peak wavelengths when UV is off and on,

respectively, and the fitting parameter $\tau_{\text{on}} = 11.7$ min is the characteristic time of the Ch_{OH} reflection wavelength response to the continuous UV irradiation. Similarly, the blueshift during the relaxation, Fig. 4(b), is well described by

$$\lambda_P(t_{\text{off}} \geq 0) = \lambda_P^{\text{off}} + (\lambda_P^{\text{on}} - \lambda_P^{\text{off}}) e^{-\frac{t_{\text{off}}}{\tau_{\text{off}}}}, \quad (4)$$

where t_{off} is the time measured from the moment the UV irradiation is switched off, $\tau_{\text{off}} = 9.25$ h is the fitted value of the relaxation characteristic time and $\lambda_P^{\text{off}} = 482$ nm is the peak wavelength at the stationary relaxed state in the dark.

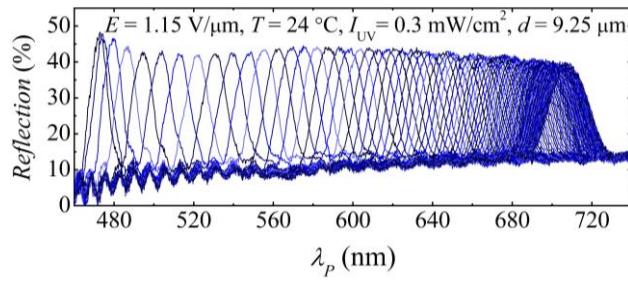


FIG. 5. Bragg reflection spectra during 1.5 h of UV irradiation 365 nm, 0.3 mW/cm² recorded at the planar side of the hybrid Ch_{OH} cell with thickness $d = (9.25 \pm 0.02)$ μm at fixed temperature $T = 24.0$ $^{\circ}\text{C}$ and electric field $E = 1.15$ V/ μm .

The reflection spectra over the entire 1.5 h of UV irradiation corresponding to each value of the experimental data points of Fig. 4(a) are shown in Fig. 5. The time interval between each reflection spectrum is 30 s. Note that the efficiency of reflection decreases in the red and near-infrared regions. One reason is that the pitch increase implies that the Bragg reflection is less effective since it involves a smaller number of Ch_{OH} pseudo layers. The second reason is that as the UV irradiation progresses with time and more cis-isomers form, the structure becomes slightly nonuniform, as evidenced by textural observation discussed below.

The three different colors reflected by the planar side of the hybrid Ch_{OH} cell at the beginning of UV exposure, $t_{\text{on}} = 0$ min, and during the exposure, $t_{\text{on}} = 4.4$ min and $t_{\text{on}} = 11.6$ min of continuous UV irradiation are shown in figures 6(a), 6(b), and 6(c) respectively. The change of the pitch often involves the formation of slow-relaxing defects, such as edge dislocations, as described previously for both Ch [48] and Ch_{OH} [7,46] structures. These metastable defects cause

some light scattering and small variations of the structural colors within the plane of the cell, some of these could be seen in Fig. 6(c). Nonuniformity of the samples after a prolonged UV exposure and decrease in the number of pseudo layers explain the decrease of reflection efficiency observed in the red and near infrared part of the spectra in Fig. 5.

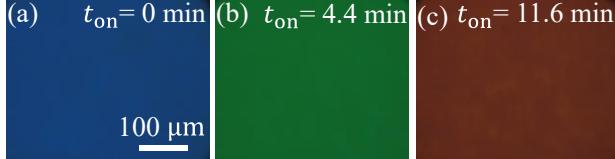


FIG.6. (a) Blue, (b) green, and (c) red colors reflected by the planar side of the hybrid Ch_{OH} cell with thickness $d = (9.25 \pm 0.02) \mu\text{m}$ at fixed temperature $T = 24.0 \text{ }^{\circ}\text{C}$ and electric field $E = 1.15 \text{ V}/\mu\text{m}$ at three different instances of UV irradiation of UV irradiation 365 nm, 0.3 mW/cm².

There are two potential reasons for the redshift of the reflection peak during UV irradiation: (1) heating of the cell caused by both UV and the electric field and (2) UV-photoisomerization of D7AOB molecules. The Ch_{OH} state is indeed temperature-sensitive, but this sensitivity cannot explain the effects presented in Figures 4, 5, and 6. To demonstrate this, we measured the temperature dependence of the peak wavelength λ_p , Fig. 7. Figure 7 shows that the reflection peak wavelength increases monotonously with the increase in temperature, with the rate of 55 nm/ $^{\circ}\text{C}$. However, the direct measurement of sample temperature by the thermocouple for an hour during UV irradiation at a constant electric field indicates that the temperate changes are smaller than 0.01 $^{\circ}\text{C}$. If there is no UV irradiation, the temperature of the cell under a continuous electric field activation varied by 0.27 $^{\circ}\text{C}$ over a 35 h period of observation; this change is most likely caused by fluctuations in the room temperature. Even with the overestimated temperature change of 0.27 $^{\circ}\text{C}$, the spectral shift would be about 15 nm, much smaller than the observed 235 nm shifts in Fig.4 (a). Therefore, the thermally-induced shift of the reflection wavelength is negligibly small as compared to the UV-induced shifts in Fig.4 (a). Furthermore, the idea that the wavelength shift could be caused by the electric field heating is also contradicted by the experimental data in Fig. 4(a), since the characteristic time of electric field heating effects is ~ 1 second [49], while the experiment shows a much longer time $\tau_{\text{on}} \sim 12$ min. Note here that we do not exclude the possibility of some temperature increase by UV irradiation, but this thermal effect

is expected to be of the same short characteristic time as the heating effects caused by the electric field; it does not influence the dynamics on the time scales of τ_{on} . We conclude that the spectral shifts caused by switching the UV irradiation on and off are caused primarily by the photoisomerization of D7AOB.

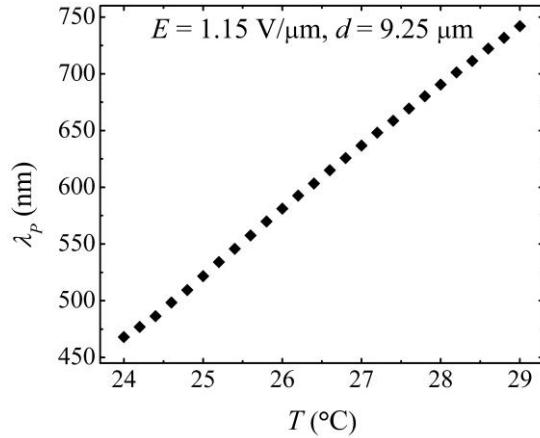


FIG.7. Temperature dependence of the reflection peak λ_P at a constant electric field $E = 1.15 \text{ V}/\mu\text{m}$ in a Ch_{OH} cell with $d = (9.25 \pm 0.02) \mu\text{m}$.

UV irradiation causes a shift in the phase transition temperatures. After 1.5 h of continuous UV irradiation, $T_{\text{N}^*-\text{NTB}}$ of the chiral mixture decreases by 2.8 °C and $T_{\text{N}-\text{NTB}}$ of the non-chiral mixture decreases by 3.2 °C. There is no effect of UV on the clearing temperatures $T_{\text{I}-\text{N}}$ and $T_{\text{I}-\text{N}^*}$, apparently, because heating facilitates cis-to-trans isomerization [38]. These changes should be attributed by modifications of the molecular interactions triggered by the appearance of the cis isomers of D7AOB. Discussion of light-induced effects in liquid crystals caused by trans-cis isomerization usually ends at the statement that the isomers somehow change the molecular interactions. The unique structure of Ch_{OH} allows us to explore the mechanism at a deeper level and connect it to the concrete material parameter, namely, the modification of the bend elastic constant, as described below.

The wavelength of the selective reflection of light

$$\lambda_P = \bar{n}_{\text{eff}} P, \quad (5)$$

depends on the Ch_{OH} pitch P and the effective refractive index $\bar{n}_{\text{eff}} = (n_o + n_{e,\text{eff}})/2$, where $n_{e,\text{eff}} = n_o n_e / \sqrt{n_e^2 \cos^2 \theta + n_0^2 \sin^2 \theta}$, θ is the cone angle made by the director $\hat{\mathbf{n}}$ with respect to the helicoidal axis [47]. We first analyze whether the UV-induced isomerization could change the effective refractive index.

Before UV exposure, $n_o = 1.519$, $n_e = 1.726$, and $\Delta n = 0.207$, as measured at 532 nm and $T = T_{\text{N-NTB}} + 2.0 \text{ }^{\circ}\text{C} = 21.4 \text{ }^{\circ}\text{C}$. After 1.5 h of continuous UV exposure, these values change very little: $n_o = 1.522$, $n_e = 1.728$, and $\Delta n = 0.196$, which indicate that the dramatic shift of λ_P cannot be attributed to the UV-induced change of the refractive indices. The main effect of the UV irradiation is thus the change of the Ch_{OH} pitch P , Eq. (1), which is defined by the electric field, dielectric anisotropy $\Delta\epsilon$, and the bend elastic modulus K_{33} [2,7,50]. The only parameters on the right-hand side of Eq. (1) that could change as a result of isomerization are two material parameters, $\Delta\epsilon$ and K_{33} .

The values of the dielectric anisotropy $\Delta\epsilon$ measured in a planar cell with the thickness $(4.66 \pm 0.01) \text{ } \mu\text{m}$ at temperature $T = 24 \text{ }^{\circ}\text{C}$ before the UV exposure and after 1.5 h of continuous UV irradiation at 365 nm, 0.3 mW/cm^2 , are found to be 7.18 and 6.90, respectively. The UV-induced decrease of $\Delta\epsilon$ is 0.28, too small to explain the spectral shifts.

The bend elastic constant K_{33} is calculated from the dependency $\lambda_P/n_o(\lambda_P) = a_1 E^{-1} + a_2 E^{-2}$, as described in the Materials and Methods section and Ref. [41], using a hybrid aligned cell of the thickness $d = (9.25 \pm 0.02) \text{ } \mu\text{m}$ at a fixed temperature $T = 24 \text{ }^{\circ}\text{C}$. Before the UV exposure, n_o equals 1.528, 1.519, and 1.509 at 488 nm, 532 nm, and 632.8 nm, respectively. These values of n_o are extrapolated by the Cauchy dispersion relation $n_o(\lambda) = A + B\lambda^{-2} + C\lambda^{-4}$ with $A = 1.505$, $B = -4.038 \times 10^{-3} \text{ } \mu\text{m}^2$, $C = 2.270 \times 10^{-3} \text{ } \mu\text{m}^4$. The dependence $\lambda_P/n_o(\lambda_P)$ vs E^{-1} is linear, Fig. 8(a), which implies that its slope a_1 could be used to determine $K_{33} = \epsilon_0 \Delta\epsilon a_1^2 / 4\pi^2$ as $K_{33} = 0.19 \text{ pN}$. After 1.5 h of continuous UV irradiation, the values of n_o are 1.529, 1.522, and 1.513 at 488 nm, 532 nm, and 632.8 nm, respectively, yielding $A = 1.501$, $B = 2.220 \times 10^{-3} \text{ } \mu\text{m}^2$, $C = 1.073 \times 10^{-3} \text{ } \mu\text{m}^4$, and $K_{33} = 0.42 \text{ pN}$, Fig. 8(b). We conclude that the UV irradiation causes a dramatic increase of K_{33} by a factor larger than 2, from 0.19 pN in the dark to 0.42 pN after 1.5 h of continuous exposure.

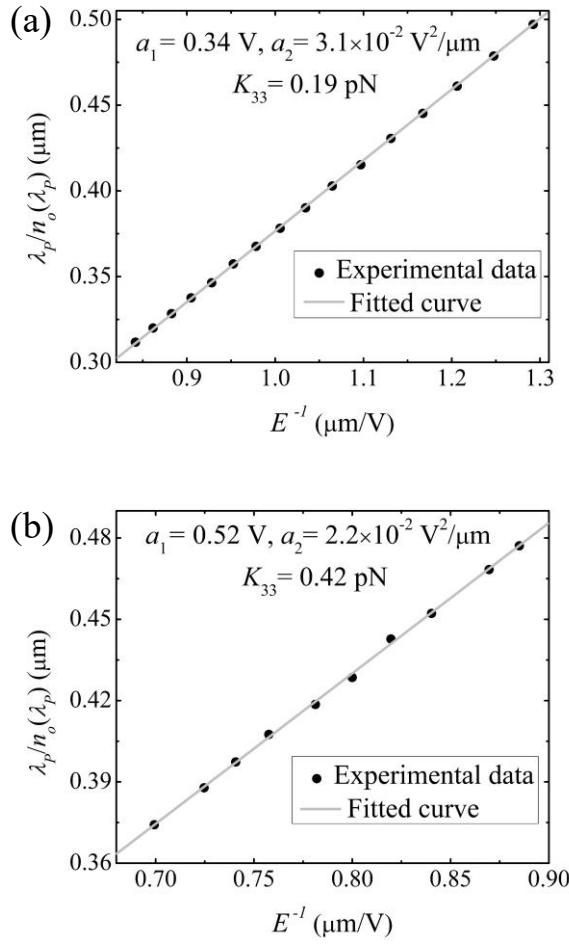


FIG.8. Dependencies $\lambda_p/n_o(\lambda_p)$ vs E^{-1} fitted to a polynomial $a_1E^{-1} + a_2E^{-2}$ and the calculated bend elastic constant (a) $K_{33} = 0.19 \text{ pN}$ before UV irradiation and (b) $K_{33} = 0.42 \text{ pN}$ after 1.5 h of continuous UV irradiation.

It is known that the bend elastic constant K_{33} in flexible dimer nematics and cholesterics shows a complicated non-monotonous behavior as a function of temperature [40,41,53]. Upon cooling from the isotropic phase, K_{33} first increases and then decreases, reaching a minimum at about 1 °C above the transition into the twist-bend state. [40,41]. Experiments by Aronzon et al. [38] show that UV-generation of cis-isomers in azoxybenzenes reduces the scalar order parameter and birefringence, a behavior that mimics the effect of heating. Direct evidence of the UV-induced weakening of dielectric anisotropy in azoxybenzene nematics was presented by Lisetski et al. [51]. The decrease of $T_{\text{N}^*-\text{NTB}}$ and $T_{\text{N}-\text{NTB}}$ during UV irradiation could be similarly treated as the

effective temperature increase. However, the most important point is that the trans-to-cis isomerization dramatically increase the bend elastic constant K_{33} , while Δn and $\Delta \varepsilon$ remain practically unchanged. The increase of K_{33} and of the Ch_{OH} pitch $P \propto \sqrt{K_{33}/\Delta \varepsilon}$ explains the UV-induced redshift of the reflection wavelength λ_P . In the next section, we present a kinetic model of the UV effect in order to substantiate the exponential processes revealed by the fitting of the experimental data, Eqs. (3),(4).

The sensitivity of the structure to UV irradiation is remarkably strong. The concentration of D7AOB in the mixture is 10 wt.%. The maximum concentration of cis-isomers created by UV irradiation at 366 nm is expected to be 50% [38], thus the observed spectral shift of λ_P by about 235 nm is triggered by transformations of only about 5 wt.% of all the molecules in the mixture. Usually, the mechanisms of the UV-induced changes in liquid crystals doped with azoxybenzenes and azobenzenes are associated with the fact that the rod-like trans-isomers fit well in the orientationally ordered environment, while the cis-isomers do not [11-16,18,38,47,52]. In the case of photoresponsive conventional Ch, isomerization transitions of photosensitive achiral dopants such as D7AOB change both the intrinsic (field-free) pitch P_0 and the refractive indices, although the detailed molecular mechanisms remain difficult to uncover [11]. Peculiar properties of Ch_{OH} allow one to draw a concrete connection between the material properties such as the bend elastic constant and photoisomerization.

III. KINETIC MODEL OF TRANS-CIS PHOTOISOMERIZATION

The kinetic model of trans-cis photoisomerization explains the experimentally observed temporal behavior of the reflection peak and hence the fitted equations (3) and (4). The photoisomerization of D7AOB is modeled by the standard kinetic equations that control the dynamics of transitions between trans and cis-isomers [53].

Under the irradiation by a monochromatic source with intensity $I(\lambda_{\text{irr}}, t)$ at the wavelength λ_{irr} , the relative concentrations of D7AOB molecules in the trans-state $n_t(t)$ and in the cis state $n_c(t)$ obey the following kinetic equations

$$dn_c(t)/dt = -k(t)n_c(t) + k'(t)n_t(t), \quad (6)$$

$$dn_t(t)/dt = k(t)n_c(t) - k'(t)n_t(t),$$

where $k'(t) = A' + B'(\lambda_{\text{irr}})I(\lambda_{\text{irr}}, t)$ and $k(t) = A + B(\lambda_{\text{irr}})I(\lambda_{\text{irr}}, t)$ are the transition rates from trans- to cis-isomer and vice versa, respectively, A' and A are the transition rates without irradiation, $B'(\lambda_{\text{irr}})$ and $B(\lambda_{\text{irr}})$ are the photoisomerization coefficient [54]. For azoxybenzene derivatives, such as D7AOB, $B'(\lambda_{\text{irr}})$ and $B(\lambda_{\text{irr}})$ exhibit a strong dispersion, resulting in $B'(\lambda_{\text{irr}}) > B(\lambda_{\text{irr}})$ for UV irradiation, but $B'(\lambda_{\text{irr}}) < B(\lambda_{\text{irr}})$ for irradiation in the visible range. Thus, for a broadband irradiation source $k'(t)$, and $k(t)$ should contain integrals over λ_{irr} .

Equations (6) obey the conservation law, $n_t(t) + n_c(t) = 1$, and can be reduced to

$$\frac{dn_c(t)}{dt} = k'(t) - (k'(t) + k(t))n_c(t). \quad (7)$$

When the irradiation is of a constant intensity or absent, both $k'(t)$ and $k(t)$ are constant, and equation (7) has the solution

$$n_c(t > t_o) = \bar{n}_c + (n_c(t_o) - \bar{n}_c)e^{-(k' + k)t}, \quad (8)$$

where t_o can be any time moment provided the intensity is constant and $\bar{n}_c = k/(k' + k)$ is the stationary relative concentration of the cis molecules that establishes itself after a sufficiently long time $t - t_o \gg \tau = (k' + k)^{-1}$. When the irradiation is off, $\bar{n}_c = \bar{n}_c^{\text{off}} = A'/(A' + A)$ and $\tau_{\text{off}} = (A' + A)^{-1}$, and when the irradiation is on, $\bar{n}_c = \bar{n}_c^{\text{on}} = (A' + B'I)/(A' + A + (B' + B)I)$ and $\tau_{\text{on}} = (A' + A + (B' + B)I)^{-1}$. We assume proportionality between the photoinduced shift of Bragg reflection peak $\lambda_P - \lambda_P^{\text{off}}$ and the photoinduced change of the relative concentration of cis molecules $n_c(t) - \bar{n}_c^{\text{off}}$ [11],

$$\lambda_P - \lambda_P^{\text{off}} = K(n_c(t) - \bar{n}_c^{\text{off}}), \quad (9)$$

where K is a positive proportionality constant. Now, the fitted equations (3) and (4) can be combined as

$$\lambda_P(t > t_o) = \bar{\lambda}_P + (\lambda_P(t_o) - \bar{\lambda}_P)e^{-\frac{t}{\tau}}, \quad (10)$$

The experiment explores two regimes:

- (1) continuous UV irradiation with $\tau_{\text{on}} = (A' + A + (B' + B)I_{\text{UV}})^{-1} = 11.71 \text{ min}$, $\lambda_P(t_o) = \lambda_P(0) = 473 \text{ nm}$ and $\bar{\lambda}_P = \lambda_P^{\text{on}} = 708 \text{ nm}$;
- (2) relaxation in the dark after UV radiation is switched off, with $\tau_{\text{off}} = (A' + A)^{-1} = 9.25 \text{ h}$, $\lambda_P(t_o) = \lambda_P(0) = 708 \text{ nm}$ and $\bar{\lambda}_P = \lambda_P^{\text{off}} = 482 \text{ nm}$.

This model (9) explains the dynamics of λ_P by connecting the spectral changes to the instantaneous concentration of molecules in the cis state. Because of the difference in the characteristic times, the thermal relaxation process can easily be neglected during the UV photoisomerization: $A + A' \ll I_{\text{UV}}(B + B')$.

III. CONCLUSION

Our study demonstrates that the pitch of the oblique helicoidal cholesteric can be tuned by simultaneous action of the electric field and low-intensity UV irradiation. Photoinduced transformations could be used as yet another external cue tuning the diffractive properties of Ch_{OH} , adding to the list of static electric [7,8] and magnetic [9] fields, optical torques [10], composition, and temperature [8,46]. The underlying principle is trans-cis photoisomerization of an achiral azoxybenzene dopant, the dynamics of which is described by a kinetic model. Direct measurements of the material parameters show that the trans to cis photoisomerization mainly causes the increase of the bend elastic constant. This effect explains the experimentally observed redshift of Ch_{OH} reflection spectra under UV irradiation. The increase of the bend elastic constant is associated with the fact that trans to cis photoisomerization leads to a decrease of transition temperature from the cholesteric (or nematic) to the twist bend nematic phase, mimicking the heating effect. However, we cannot neglect the effect of change in molecular curvature of D7AOB molecule during trans-cis photoisomerization on bend elastic constant [57]. The sensitivity of the Ch_{OH} to the UV irradiation is strong, as the spectral shift of the Bragg reflection maximum by about 235 nm is achieved by photoisomerization of only about 5 wt. % of achiral molecules in the mixture. The sensitivity could be further increased if the photosensitive functionality is assigned to the chiral azo-dopant [16,29-31]. Hybrid surface anchoring allows one to change the pitch and thus the wavelength of selective reflection/transmission of light in a continuous manner. The proof-of-concept of the phototunable Ch_{OH} structures is demonstrated with the azoxybenzene

derivative D7AOB. The azoxybenzene compounds such as this one show a relatively slow relaxation when the UV is switched off. In practical applications that require a faster response, one can use other photosensitive materials with a quicker response [55,56] and a wide tunable range [16,55]. In the explored case, the UV irradiation was of fixed intensity. It would be of interest to explore whether the variable intensity of irradiation could be used to control dynamically the rate of the wavelength shifts. Photoelectrooptical effects in Ch_{OH} could be improved further by using flexible dimers that are photosensitive [57] and photosensitive chiral dopants [29-31]. This work is in progress.

Acknowledgements

The work was supported by the National Science Foundation grant ECCS-1906104. We thank Dr. Hao Wang for the help with Figure 1.

References

- [1] D.-K. Yang and S.-T. Wu, *Fundamentals of Liquid Crystal Devices* (John Wiley & Sons, Chichester, England, 2006).
- [2] P. G. de Gennes, Solid State Commun **6**, 163 (1968).
- [3] R. B. Meyer, Appl Phys Lett **12**, 281 (1968).
- [4] D. Subacius, S. V. Shiyanovskii, Ph. Bos, and O. D. Lavrentovich, Appl Phys Lett **71**, 3323 (1997).
- [5] S. V. Shiyanovskii, D. Voloschenko, T. Ishikawa, and O. D. Lavrentovich, Mol Cryst Liq Cryst **358**, 225 (2001).
- [6] H. Q. Xianyu, S. Faris, and G. P. Crawford, Appl Optics **43**, 5006 (2004).
- [7] J. Xiang, S. V. Shiyanovskii, C. T. Imrie, and O. D. Lavrentovich, Phys. Rev. Lett. **112**, 217801 (2014).
- [8] J. Xiang, Y. Li, Q. Li, D. A. Paterson, J. M. D. Storey, C. T. Imrie, and O. D. Lavrentovich, Adv Mater **27**, 3014 (2015).
- [9] S. M. Salili *et al.*, Phys Rev E **94**, 042705 (2016).
- [10] G. Nava, F. Ciciulla, O. S. Iadlovska, O. D. Lavrentovich, F. Simoni, and L. Lucchetti, Physical Review Research **1**, 033215 (2019).

- [11] E. Sackmann, *J. Am. Chem. Soc.* **93**, 7088 (1971).
- [12] V. Vinogradov, A. Khizhnyak, L. Kutulya, Yu. Reznikov, and V. Reshetnyak, *Mol Cryst Liq Cryst* **192**, 273 (1990).
- [13] S. Kurihara, T. Kanda, T. Nagase, and T. Nonaka, *Appl Phys Lett* **73**, 2081 (1998).
- [14] S. V. Serak, E. O. Arikainen, H. F. Gleeson, V. A. Grozhik, J.-P. Guillou, and N. A. Usova, *Liquid Crystals* **29**, 19 (2002).
- [15] U. A. Hrozhik, S. V. Serak, N. V. Tabiryan, and T. J. Bunning, *Advanced Functional Materials* **17**, 1735 (2007).
- [16] T. J. White, R. L. Bricker, L. V. Natarajan, N. V. Tabiryan, L. Green, Q. Li, and T. J. Bunning, *Advanced Functional Materials* **19**, 3484 (2009).
- [17] T. J. White, A. S. Freer, N. V. Tabiryan, and T. J. Bunning, *Journal of Applied Physics* **107**, 073110 (2010).
- [18] Y. Wang and Q. Li, *Adv Mater* **24**, 1926 (2012).
- [19] A. Chanishvili, G. Chilaya, G. Petriashvili, and D. Sikharulidze, *Mol Cryst Liq Cryst* **409**, 209 (2004).
- [20] G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, R. Bartolino, M. P. De Santo, M. A. Matranga, and P. Collings, *Mol Cryst Liq Cryst* **453**, 123 (2006).
- [21] G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla, and P. V. Shibaev, *Advanced Materials* **19**, 565 (2007).
- [22] U. A. Hrozhik, S. V. Serak, N. V. Tabiryan, and T. J. Bunning, *Advanced Materials* **19**, 3244 (2007).
- [23] M. Aronishidze, A. Chanishvili, G. Chilaya, G. Petriashvili, S. Tavzarashvili, L. Lisetski, I. Gvozdovskyy, and I. Terenetskaya, *Mol Cryst Liq Cryst* **420**, 47 (2004).
- [24] T. Yamaguchi, T. Inagawa, H. Nakazumi, S. Irie, and M. Irie, *Mol Cryst Liq Cryst* **365**, 1817 (2001).
- [25] T. Yamaguchi, T. Inagawa, H. Nakazumi, S. Irie, and M. Irie, *J. Mater. Chem.* **11**, 2453 (2001).
- [26] S. Pieraccini, S. Masiero, G. P. Spada, and G. Gottarelli, *Chem Commun*, 598 (2003).
- [27] S. Pieraccini, G. Gottarelli, R. Labruto, S. Masiero, O. Pandoli, and G. P. Spada, *Chem-Eur J* **10**, 5632 (2004).

[28] Q. Li, L. Green, N. Venkataraman, I. Shiyanovskaya, A. Khan, A. Urbas, and J. W. Doane, *J Am Chem Soc* **129**, 12908 (2007).

[29] H. Wang, H. K. Bisoyi, M. E. McConney, A. M. Urbas, T. J. Bunning, and Q. Li, *Adv Mater* **31**, 1902958 (2019).

[30] H. Wang, H. K. Bisoyi, A. M. Urbas, T. J. Bunning, and Q. Li, *J Am Chem Soc* **141**, 8078 (2019).

[31] H. Wang, H. K. Bisoyi, B.-X. Li, M. E. McConney, T. J. Bunning, and Q. Li, *Angew Chem Int Edit* **59**, 2684 (2020).

[32] L. Wang and Q. Li, *Chem Soc Rev* **47**, 1044 (2018).

[33] R. S. Zola, H. K. Bisoyi, H. Wang, A. M. Urbas, T. J. Bunning, and Q. Li, *Adv Mater* **31**, 1806172 (2019).

[34] M. E. McConney, M. Rumi, N. P. Godman, U. N. Tohgha, and T. J. Bunning, *Advanced Optical Materials* **7**, 1900429 (2019).

[35] A. Y.-G. Fuh, S.-J. Ho, S.-T. Wu, and M.-S. Li, *Appl Optics* **53**, 1658 (2014).

[36] J.-D. Lin, M.-H. Hsieh, G.-J. Wei, T.-S. Mo, S.-Y. Huang, and C.-R. Lee, *Opt Express* **21**, 15765 (2013).

[37] N. C. Davy, M. Sezen-Edmonds, J. Gao, X. Lin, A. Liu, N. Yao, A. Kahn, and Y.-L. Loo, *Nat Energy* **2**, 17104 (2017).

[38] D. Aronzon, E. P. Levy, P. J. Collings, A. Chanishvili, G. Chilaya, and G. Petriashvili, *Liquid Crystals* **34**, 707 (2007).

[39] W. R. Folks, Yu. A. Reznikov, S. N. Yarmolenko, and O. D. Lavrentovich, *Mol Cryst Liq Crys A* **292**, 183 (1997).

[40] G. Babakhanova, Z. Parsouzi, S. Paladugu, H. Wang, Yu. A. Nastishin, S. V. Shiyanovskii, S. Sprunt, and O. D. Lavrentovich, *Phys Rev E* **96**, 062704 (2017).

[41] O. S. Iadlovska *et al.*, *Physical Review Research* **2**, 013248 (2020).

[42] J. van der Veen, W. H. De Jeu, A. H. Grobben, and J. Boven, *Mol Cryst Liq Cryst* **17**, 291 (1972).

[43] W. H. de Jeu, Th. W. Lathouwers, and P. Bordewijk, *Phys Rev Lett* **32**, 40 (1974).

[44] W. H. de Jeu and W. A. P. Claassen, *J Chem Phys* **67**, 3705 (1977).

[45] O. S. Iadlovska, G. R. Maxwell, G. Babakhanova, G. H. Mehl, C. Welch, S. V. Shiyanovskii, and O. D. Lavrentovich, *Opt Lett* **43**, 1850 (2018).

- [46] M. Mrukiewicz, O. S. Iadlovska, G. Babakhanova, S. Siemianowski, S. V. Shiyanovskii, and O. D. Lavrentovich, *Liq Cryst* **46**, 1544 (2019).
- [47] W. R. Folks *et al.*, *Mol Cryst Liq Crys A* **320**, 77 (1998).
- [48] I. I. Smalyukh and O. D. Lavrentovich, *Phys Rev E* **66**, 051703 (2002).
- [49] Y. Yin, S. V. Shiyanovskii, and O. D. Lavrentovich, *J Appl Phys* **100**, 024906 (2006).
- [50] R. B. Meyer, *Appl Phys Lett* **14**, 208 (1969).
- [51] L. N. Lisetski, A. N. Samoilov, S. S. Minenko, A. P. Fedoryako, and T. V. Bidna, *Functional Materials* **25**, 681 (2018).
- [52] Y. Lansac, M. A. Glaser, N. A. Clark, and O. D. Lavrentovich, *Nature* **398**, 54 (1999).
- [53] P. Atkins, J. de Paula, and J. Keeler, *Atkins' Physical Chemistry* (Oxford University Press, 2018).
- [54] P. Arya, J. Jelken, N. Lomadze, S. Santer, and M. Bekir, *J Chem Phys* **152**, 024904 (2020).
- [55] T. J. White, S. A. Cazzell, A. S. Freer, D.-K. Yang, L. Sukhomlinova, L. L. Su, T. Kosa, B. Taheri, and T. J. Bunning, *Adv Mater* **23**, 1389 (2011).
- [56] T. V. Mykytiuk, I. P. Ilchishin, O. V. Yaroshchuk, R. M. Kravchuk, Y. Li, and Q. Li, *Opt Lett* **39**, 6490 (2014).
- [57] D. A. Paterson *et al.*, *J Am Chem Soc* **138**, 5283 (2016).