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Dual electrically and thermally responsive broadband reflectors based on polymer network stabilized chiral nematic liquid crystals: the role of crosslink density†

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A broadband reflector based on a polymer stabilized chiral nematic liquid crystal has been fabricated. The reflection bandwidth can be manually controlled by an electric field and autonomously by temperature.

Stimuli-responsive photonic reflectors are the subject of widespread research.^{1,2} In such systems the reflection and transmission of light can be altered by exposure to stimuli including temperature,³ light,^{4–8} electricity,⁹ mechanical stress¹⁰ or chemicals.¹¹ This makes these reflectors interesting for a variety of applications ranging from battery-free optical sensors to smart windows for energy management.^{12–16} For certain applications, however, it would be desirable to fabricate materials in which the reflection properties can be adjusted manually depending on user needs or autonomously upon environmental changes. Such dual responsive photonic reflectors have been rarely reported.

Self-organised chiral nematic (cholesteric) liquid crystals (Ch-LCs) are well-known responsive photonic reflectors.¹⁷ Ch-LCs are able to reflect light due to their helical structure and the colour of the reflected light depends on the helical pitch. The bandwidth ($\Delta\lambda$) of the reflected light depends on birefringence (Δn) of the nematic LC host and concentration and helical twisting power (HTP) of the chiral dopants. Generally, the bandwidth is limited to between 30 nm to 120 nm, depending on the wavelength of the reflection notch. Ch-LC narrowband reflectors have been reported which can broaden their bandwidth in presence of stimuli including electric fields,^{18–20} temperature,²¹ and light.²² Few dual responsive narrowband reflectors which change their reflection position have been shown in the literature.^{23–25} Recently, Lu *et al.*

have shown that the bandwidth of a broadband ionic polymer reflector can be adjusted by applying both DC electric fields and temperature.²⁶ Diffusion of the chiral ionic polymer in presence of stimuli was used to create such a dual responsive broadband reflector.

Recently, we fabricated a broadband infrared reflector using a flexible polymer stabilized Ch-LC that can be switched from a broadband reflective (planar) state to a transparent (homeotropic) state by applying an AC electric field.²⁷ We now report a dual responsive broadband reflector ($\Delta\lambda = 620$ nm) using a similar method. We show that using a specific polymer crosslink density a broadband reflector can be fabricated whose reflection bandwidth can be reduced by more than 500 nm upon application of both an AC electric field as well as exposure to elevated temperature. The polymer network was used to create the broadband reflector and stabilize the planar orientation of the nonreactive LC component.^{28,29} It is shown that the crosslink density is crucial for making dual responsive broadband reflectors.

For the fabrication of our dual responsive bandwidth tunable broadband reflector, we have used a similar chemical composition reported earlier,²⁷ but with increased concentration of the crosslinker (Fig. 1a). The Ch-LC mixture consists of the nematic liquid crystal E7 (69.5 wt%), polymerizable chiral dopant CD-267 (13.7 wt%), non-polymerizable chiral dopant CB-15 (12.1 wt%), crosslinker RM-82 (2.0 wt%), photoinitiator Irgacure-651 (1.2 wt%) and UV absorbing dye Tinuvin-328 (1.5 wt%). This mixture was used to fill ITO coated glass cells covered with oppositely-rubbed polyimide layers with a cell-gap of 20.4 μm . This resulted in a reflection notch centered at $\lambda = 980$ nm with a bandwidth of $\Delta\lambda = 118$ nm (Fig. 1c). The broadband reflector was fabricated by generating a gradient in chiral dopant through photo polymerizing the mixture using low intensity of UV light for one hour at room temperature (Fig. 1b).^{27,30,31} Due to absorption of UV by Tinuvin-328, a gradient of light was created throughout the thickness of the cell, with the intensity of UV light higher at the top side closest to the lamp compared to the bottom side. This causes the reactive mesogens (CD-267 and RM-82) to polymerize faster at the top than at the bottom side of the cell, causing

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Fig. 1 (a) Molecular structure of the chemicals used for the fabrication of the broadband reflector (b) schematic diagram showing the change in pitch and crosslinking density upon polymerization; transmission spectrum of a cell (c) before and (d) after photopolymerization (inset: photograph of the sample after polymerization).

depletion of these mesogens at the top, which resulted in diffusion of these mesogens from the bottom to the top of the cell. Hence, a concentration gradient of chiral dopant CD-267 and crosslinker RM-82 was created. This also leads to generation of a pitch gradient throughout the thickness of the cell (Fig. 1b) with shorter pitch at the top, resulting in a broadband reflector with a reflection bandwidth of 620 nm (Fig. 1d).

Having fabricated the broadband reflector, we studied the effect of electric field on the transmission spectrum (Fig. 2a). No significant change in transmission was observed until a threshold voltage $2.2 \text{ V } \mu\text{m}^{-1}$. Upon increasing the voltage from $2.2 \text{ V } \mu\text{m}^{-1}$ to $8.5 \text{ V } \mu\text{m}^{-1}$, the reflection% in the long wavelength region (around 1000–1400 nm) diminishes continuously. At $10.6 \text{ V } \mu\text{m}^{-1}$, the long wavelength reflection disappeared completely, resulting in a narrowband reflector with a reflection bandwidth of 108 nm centered around 800 nm (Fig. 2b). Thus, we have fabricated a broadband which can systematically reduce its reflection bandwidth from 620 nm to 108 nm on application of voltage from $0 \text{ V } \mu\text{m}^{-1}$ to $10.6 \text{ V } \mu\text{m}^{-1}$ (Fig. 2c). Moreover, the switching from broadband to narrowband can be

Fig. 2 (a) Transmission spectrum of the cell as a function of applied voltage at room temperature; (b) broadband to narrowband switching by applying $10.6 \text{ V } \mu\text{m}^{-1}$; (c) change in the reflection bandwidth with increase in voltage from $0 \text{ V } \mu\text{m}^{-1}$ to $10.6 \text{ V } \mu\text{m}^{-1}$; (d) reversibility data showing the reflection bandwidth during on ($0 \text{ V } \mu\text{m}^{-1}$) and off ($10.6 \text{ V } \mu\text{m}^{-1}$) states over ten switching cycles; and (e) schematic diagram showing the proposed mechanism for the electrically bandwidth tunable broadband reflector.

done multiple times without significant change in the transmission spectrum (Fig. 2d).

The narrowing in the reflection band on application of electric field can be attributed to a non-uniform distribution of the polymer density. As shown in Fig. 2e(i), the polymer density is higher at the short pitch side (top side) compared to longer pitch side (bottom of the cell) due to the polymerization induced diffusion. On application of $V_1 = 6.4 \text{ V } \mu\text{m}^{-1}$, the Ch-LC with lower polymer density (at the longer pitch side) undergoes homeotropic reorientation, whereas Ch-LC embedded in the region with high polymer density remains unchanged (Fig. 2e(ii)). This causes reduction in the reflection% in the longer wavelength region whereas the shorter wavelength reflection region remains undisturbed. On further increasing the voltage to $V_2 = 10.6 \text{ V } \mu\text{m}^{-1}$, most of the polymer stabilized Ch-LC undergoes homeotropic reorientation, except in the most highly crosslinked Ch-LC side (shorter pitch length) (Fig. 2e(iii)). This leads to disappearance of the longer wavelength reflection entirely and formation of a narrowband reflector at the shorter reflection edge. It is important to note that upon further increasing the crosslinker concentration (RM-82, 3 wt%), the modification in the transmission spectrum is no longer as pronounced, as higher crosslinked density requires higher electric fields ($>10.6 \text{ V } \mu\text{m}^{-1}$) to attain homeotropic orientation (Fig. S1a, ESI†). On the other hand, as reported earlier, lowering the crosslinker concentration (RM-82, 0.7 wt%) results in the switching of the broad reflection band to a completely transparent state at $8.6 \text{ V } \mu\text{m}^{-1}$, as the entire polymer network is flexible (Fig. S1b, ESI†).²⁷

Fig. 3 (a) Transmission spectrum of the cell at different temperatures; (b) broadband to narrowband switching at 48 °C; (c) change in the reflection bandwidth on increasing the temperature from 20 °C and 80 °C; (d) reversibility data showing the reflection bandwidth can be switched multiple times between 30 °C and 50 °C; and (e) schematic diagram showing the proposed mechanism for thermal bandwidth tunable broadband reflector.

We studied the temperature response of the electrically responsive bandwidth tunable broadband Ch-LC reflector as well (Fig. 3a). At room temperature (20 °C), the Ch-LC broadband reflector has a bandwidth of 620 nm. As the temperature increases to 44 °C, the reflection% at the longer wavelength edge decreases whereas in the shorter wavelength region it remains the same. On increasing the temperature to 46 °C there is a sudden jump from broadband to narrowband at the shorter wavelength edge; a bandwidth of 170 nm centered around 820 nm was observed. On further increasing the temperature, the reflection band continues to narrow: a reflection bandwidth of only 80 nm is observed at 50 °C. The reflection band completely disappears at 100 °C. On cooling from 100 °C to room temperature, similar transmission behavior, as seen during heating, was observed (Fig. S2, ESI†). Interestingly, this bandwidth change from 620 nm to ~80 nm on increasing the temperature from 20 °C to 80 °C (Fig. 3c) is similar to the electric field response (Fig. 3b *versus* Fig. 2b). The reflection bandwidth can be changed reversibly from approximately 588 nm to 80 nm on increasing the temperature from 30 °C to 50 °C without significantly changing in the transmission behavior (Fig. 3d).

In order to better understand the temperature response of the broadband reflector, the effect of temperature on transmission spectrum of the uniformly distributed polymer stabilized narrowband reflector was investigated (Fig. S3, ESI†). To obtain the

uniform distribution of the polymer network in the narrowband reflector, we polymerized the same LC mixture, but this time excluded the UV absorbing dye and photopolymerized using high intensity UV-light so that diffusion of the chiral dopant (CD-267) and crosslinker (RM-82) is minimized. Upon heating up the narrowband reflector, we only observed some narrowing in the reflection band from both the long and short wavelength edges which might be due to decrease in the birefringence of the Ch-LCs.³² On further heating the sample, the reflection band completely disappears at 80 °C. These findings reveal that a homogenous polymer network having 2 wt% crosslinker is able to uniformly stabilize the orientation of the non-polymerized LCs. The effect of change in HTP of CB-15 and CD-267 at elevated temperature can be neglected,³³ as we did not observe a change in the position of the reflection notch upon heating (Fig. S3, ESI†). Therefore, for the broadband reflector, the non-uniform distribution of polymer density could be the main reason for narrowing in the reflection band at short wavelength region.

As the temperature response is similar to the electrical response, we propose the following underlying mechanism behind the observed narrowing of bandwidth of the broadband reflector at elevated temperatures (Fig. 3e). At higher temperatures ($T_1 = 48$ °C), the least crosslinked Ch-LC region (at the bottom of the cell, cross link density < 2 wt%), becomes isotropic, whereas higher crosslinked region (top of the cell, cross link density > 2 wt%) remains in their LC phase (Fig. 3e(ii)). This results in the appearance of a narrowband reflector at the shorter wavelength side with simultaneous disappearance of the long wavelength reflection band. On further increasing the temperature ($T_2 = 100$ °C), the Ch-LC region with higher polymer density also undergoes phase change into the isotropic state (Fig. 3e(iii)) resulting in the complete disappearance of the reflection band. The non-uniform clearing temperature of the LC mixture throughout the thickness of the cell could be due to the difference in crosslink density between the top and bottom of the cell. The LC with high polymer network density provides stronger anchoring to the non-reactive LC, causing an increase in the local isotropic transition temperature. This was confirmed with a narrowband reflector with 3 wt% crosslinker which was found to have a higher isotropic transition temperature compared to the narrowband reflector with 2 wt% crosslinker (Fig. S4, ESI†).

In conclusion, we have fabricated a dual responsive broadband cholesteric reflector which can reduce its reflection bandwidth by more than 500 nm either upon application of an electrical field or by changes in temperature. A novel method has been developed by optimizing the concentration of the crosslinker where the reflection bandwidth of the broadband can be systematically reduced. Such findings can be used with other polymer stabilized liquid crystals to prepare dual responsive tunable photonic materials. The unprecedented manual or autonomous change in the infrared reflection makes these reflectors interesting for application in heat controlling smart windows to maintain more comfortable climates within automobiles and buildings and improved growing conditions within greenhouses.³⁴

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