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## Cholesteric Liquid Crystals with Electrically Controllable Reflection Bandwidth Based on Ionic Polymer Network and Chiral Ion

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The reflection bandwidth of cholesteric liquid crystals is typically on the order of 50-100 nm in visible region. Static bandwidths greater than 100 nm can be observed in polymer stabilized cholesteric liquid crystals (PSCLCs) that possess a pitch gradient throughout the thickness of the cell. This work presents PSCLCs based on ionic polymer networks and chiral ions, which exhibits large reflection bandwidth tunability under a small applied direct current (DC) electric field. The reflection colors dynamically switch between white, orange, red and transparent. The underlying mechanism of the electrically controllable bandwidth in PSCLCs is the redistribution of the chiral ions under DC electric fields resulting in pitch gradient variation along the optical axis. Removal of the electric field returns the PSCLC to its original optical properties due to the strong electronic attraction between the ionic polymer network and chiral ions. Moreover, the reflection bandwidth is also sensitive to the temperature.

# 1. Introduction

Cholesteric liquid crystals[1-4](CLCs) spontaneously organize into a periodic helical structure with a twist axis perpendicular to the local director and can be characterized by two structural parameters: the helical pitch and the twist sense[4-8]. The pitch length $p$ corresponding to a $360^{o}$ rotation of the rod-like molecules, is inversely proportional to the concentration $c$ and the helical twisting power $\beta$ of the chiral dopant: $p=1/ (c. \beta)$[1]. It is well known that CLC can reflect a band of incident circularly polarized light having the same sense as its helix, due to the periodic variation in refractive index, whereas the band with the opposite sense is transmitted [9]. Outside the reflection band, both polarization states are transmitted. For a single-pitch CLC, the upper ($\lambda_{max}$) and the lower ($\lambda_{min}$) boundaries of the reflection band are $\lambda_{max} = p \times n_e$ and $\lambda_{min} = p \times n_o$ respectively, where $n_o$ is the ordinary index and $n_e$ is the extraordinary index[10]. The reflection bandwidth, $\Delta\lambda$, is given by $\Delta\lambda = \lambda_{max} - \lambda_{min} = \Delta np$, where $\Delta n = n_e - n_o$ is the birefringence[2]. Since $\Delta n$ of CLC materials is typically below 0.3, the bandwidth of a single-pitch CLC in the visible region is limited to a few tens of nanometers[9]. This limits the applications in many areas such as full-color reflective polarizer-free displays, broadband polarizers, optical data storage, smart switchable reflective windows, among others[9-12].

A number of reports have introduced non-uniform pitch distributions,[13] or a pitch gradient, in CLCs for achieving broadband reflection films, as recently reviewed by Mitov[1]. Broer et al. have obtained broadband reflective polarizers with pitch gradients by controlling the kinetics of photo-polymerization reaction[14]. Polymer stabilized cholesteric liquid crystals (PSCLCs) can generate a pitch gradient across the cell gap that yields reflection bandwidths covering the entire visible spectrum[15]. The optical states of the PSCLCs[16-19] can be switched reversibly between transparent and mirror reflection by turning the electric field on and off, respectively. However, their reflection bandwidths cannot be adjusted due to the permanently solid structure. This limits the application in many fields.

Dynamic variation of the selective reflection spectra of CLCs has long been pursued[20]. Variation in the position or bandwidth can be induced by a variety of stimuli including heat[15], light[21], and electric fields[9]. Yang et al. have prepared polymer network/nematic liquid crystal/chiral dopant composites exhibiting a cholesteric phase at room temperature with a thermally controllable

reflection bandwidth[15]. TJ White[21] et al. have prepared a CLC mixture with photo-induced dynamic bandwidth broadening based on a high helical twisting power bis(azo) chiral dopant. However the heat and light tunability is limited by speed, and sensitive to environmental conditions. Since an electrically switchable device usually exhibits rapid speeds and can be operated conveniently, the ability to electrically control the reflection bandwidth is essential for numerous applications in the display and photonic communications[22, 23]. Hu et al. used a chiral ionic liquid (CIL) doped CLC material to obtain a pitch gradient with an electrically tunable reflection bandwidth[9, 24]. However due to the diffusion of the CIL, the pitch gradient gradually disappears over time, especially at high temperatures. Nemati[25] and co-workers have reported the photonic band gap of PSCLCs with negative dielectric anisotropies can be greatly broadened under DC electric fields. The bandwidth broadening is symmetric about the center of the reflection notch and completely reversible. But still the motion of the polymer network needs relatively high electric fields (4V/μm)[23].

Here we present a -Δε polymer stabilized cholesteric liquid crystal based on a chiral ionic monomer (CIM), where the reflection bandwidth can be controlled by DC electric fields. Moreover, small DC electric field strengths can induce significant bandwidth tuning and a wideband reflection state can be obtained immediately after the electric field is turned off.
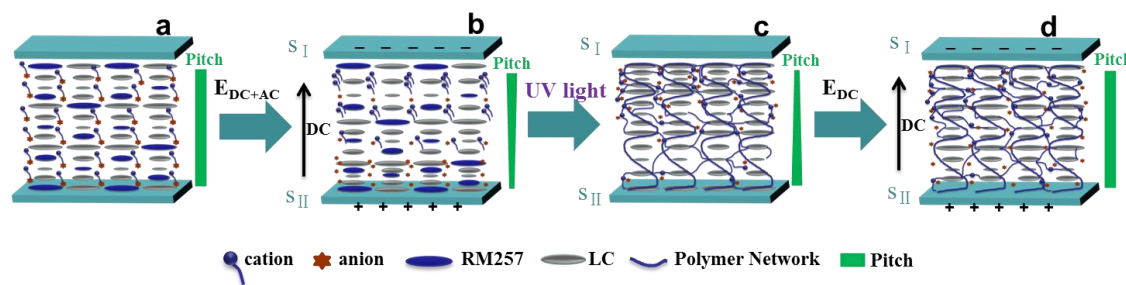
# 2. Results and Discussion



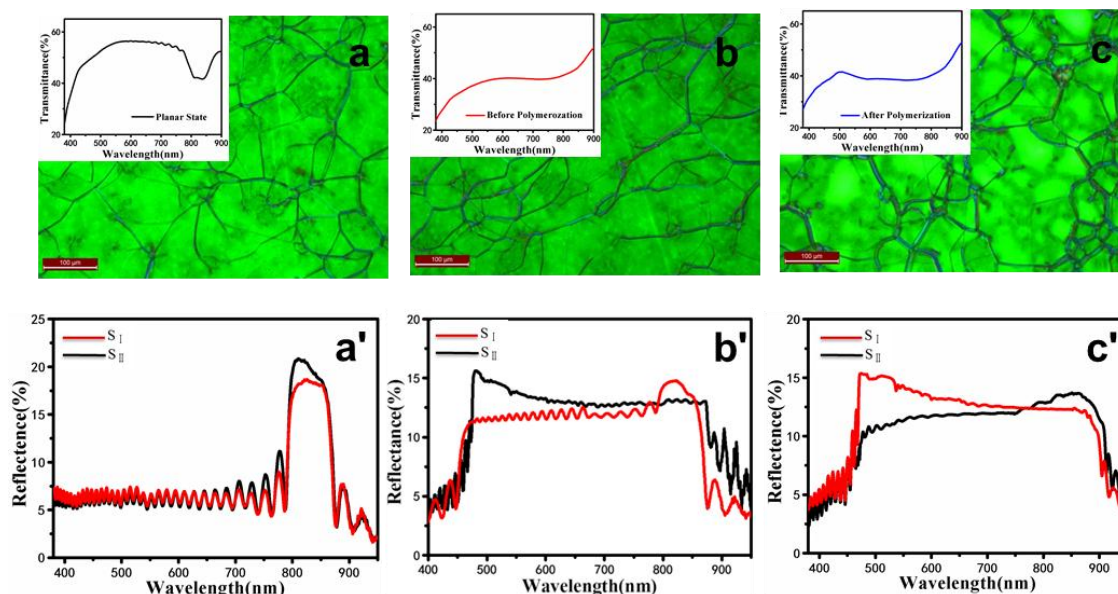**Figure 1**. Schematic illustration of the liquid molecular arrangements

**Figure 2**. The microscopy images of the textures observed under POM and the two side reflection spectra at different fabricate stages.

In this study, a mixture containing a $-\Delta\varepsilon$ nematic liquid crystal, chiral dopant, chiral ionic monomer (CIM), liquid crystal monomer and photoinitiator were injected into empty cells by capillarity action. The cells were fabricated with the indium tin oxide (ITO) glass substrates without any other treatment (specific details in the Experimental Section). The chemical structures of the materials are shown in Figure S1. The CIM was synthesized by a substitution reaction and acid-alkali neutralizing reaction (see Supporting Information). Figure 1 shows the schematic illustration of the molecular arrangements and the figure 2 presents the textural images observed by polarized optical microscopy (POM), and the two side reflection spectra at different fabricate stages corresponding to figure 1. After injection, in zero electric field, the CIM distributes homogeneously in the cell and the liquid crystal molecules adopt a planar orientation (Figure 1a). The cell is almost transparent due to the reflection band lying between 780 nm and 865 nm ($\Delta\lambda$=85 nm). This reflection band can be adjusted by controlling the content of chiral dopant and CIM. A broadband reflective CLC can be obtained according to the method suggested by Yang [9, 24]. The pitch gradient is obtained by sequentially applying a DC electric field (4 V/um, 3 s) followed by a high frequency AC electric field (100 KHz, 5 V/um, 0.4 s). Thus the reflection band becomes wider and the left-hand-circularly-polarized light within the visible region is reflected (Figure 2b). The mixture is then photo-polymerized by exposing side $s_I$ of the cell to UV light (specific details in the Experimental Section). After photo-polymerization, the reflection band of the PSCLC decreases slightly at

the lower boundary. The two side reflection spectra of the cell at different stages are shown in Figure 2a′, 2b′, and 2c′. There exist distinct differences in the reflection spectra depending on the polarity of the applied DC electric field before photo-polymerization. The reflection spectrum originates from a finite depth (several μm) from the sample surface due to light scatter. This finite sampling depth can be used to provide information about the CLC pitch profile through the cell thickness [23]. Before photo-polymerization, some of the anions of the CIM have moved to the side $s_{II}$ corresponding to the anode of the power supply under the applied DC fields, while some of the cations of the CIM have moved to the cathode (side $s_I$) under the influence of electrostatic forces. An increasing density gradient of the chiral anion is set up from side $s_I$ to side $s_{II}$, thereby indicating that a pitch gradient with the pitch length decreasing from side $s_I$ to side $s_{II}$. Accordingly, there are a peak located at the long wavelength regime in the reflection spectrum from side $s_I$ and a peak appearing in the short wavelength regime from the side $s_{II}$ (Figure 2b′). During the polymerization process, there is a copolymerization between the liquid crystal monomers and the cations of CIM, the cations collect with the polymer network near side $s_I$. The chiral anions should move to the side $s_I$ owing to the strong electronic attraction, which results in an opposite pitch gradient of the cell (Figure 2c′).
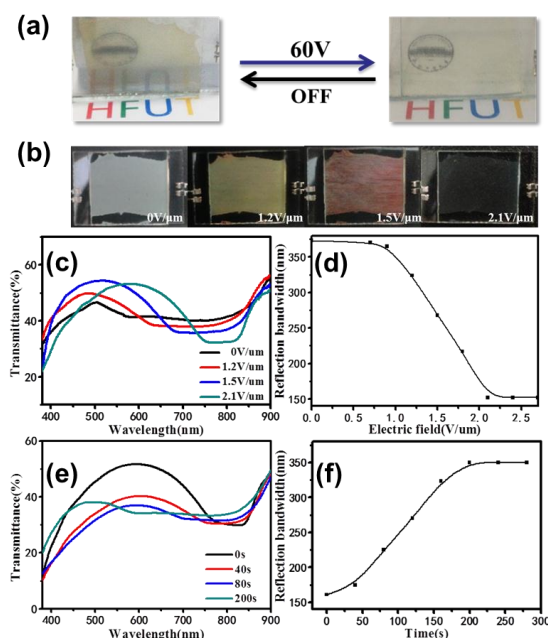


**Figure 3**. (a) Photographs illustrating the reflection/transmission of the PSCLC at 0 and 60 V (positive DC electric voltage). (b) Photographic images of color change are observed at different positive DC electric fields. (c) The transmission spectra of the PSCLC under a positive DC elec-

tric field ranging from 0-2.1 V/μm. (d) A plot of the reflection bandwidth (nm) versus the applied DC electric field strength. (e) Temporal response of the transmission spectra upon removal of the DC electric field (switch off). (f) A plot of the reflection bandwidth (nm) versus the relaxation time (s).

The ability of dynamic switching between a broadband reflection (white) and a selective reflection (transparent) is shown in Figure 3a. A paper with the image of a school badge of HFUT was put under the cell to characterize the transmission performance. A pattern of "HFUT" containing RGB colors was put above the cell to characterize the reflection band in the visible region. In the initial state, the reflection band of the PSCLC was broadened covering the entire visible wavelength range. Accordingly, the image is visible behind the PSCLC and the letters "HFUT" are reflected. Upon application of a 60 V positive DC bias, the letters "HFUT" could no longer be reflected by the PSCLC and the image could be observed clearly due to the reflection band shifting out of the visible wavelength range. It is worth noting that the positive DC electric field means the same direction as the field was applied before polymerization, while the negative DC electric field means the opposite direction. The colored appearance at intermediate bandwidths is depicted in Figure 3b. Initially, the PSCLC exhibits a white reflection. With application of a DC electric field (1.2 V/μm and 1.5 V/μm) the color changes from white to orange to red. When the electric field is applied above 2.1V/μm, the PSCLC is transparent to the visible light. After the DC electric field is removed, the optical properties restore to the initial state. Figure 3c shows the transmission spectra under various electric field strengths. A plot of the reflection bandwidth as a function of the electric field strength is shown in Figure 3d. Above the threshold voltage ($V_{th}$= 0.75 V/μm), the reflection bandwidth decreases from 373 nm to 153 nm. When the electric field surpasses the saturation voltage ($V_{sat}$= 2.1 V/μm), the reflection bandwidth of PSCLC remains at 153 nm. The reflection band can be reversibly modified up to 60% (Figure S3a). Another important consideration for practical utility is the response time. The bandwidth quickly decreases upon application of 60 V with a switch on the time of 20 ms to reach the selective reflection state. When the DC electric field is removed, the bandwidth increases gradually and relaxes back to the initial state. A plot of the transmission spectra as a function of relaxation time is shown in Figure 3e. The bandwidth returns to the original value in approximately 200 s (Figure 3f). Compared to other approaches[9, 24, 25], the PSCLCs demonstrate heat stability and need relatively low tuned field, which is on account of the stable polymer network structure and the

strong electric attraction between the chiral anion and the ionic polymer network.
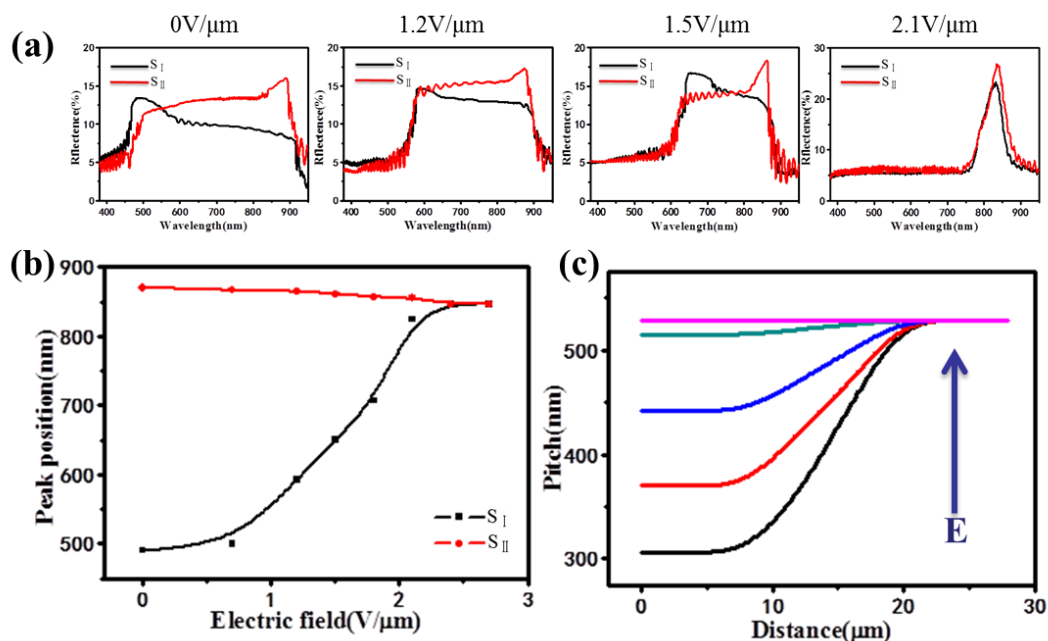


**Figure 4.** (a) The reflection spectra of the PSCLC from two sides at various electric fields. (b) A plot of the reflection peak position versus the applied field strength. (c) The empirically predicted plot of the relative pitch length versus the distance from the side $s_I$.

To know the pitch distribution under various DC electric fields, the reflection spectra taken from both the side $s_I$ and side $s_{II}$ are presented in Figure 4a. The differences in reflection spectra depend on the cell surfaces due to the pitch gradient. Below the saturation point of 50% reflection ($>$10 pitches), the reflectance is an indication of the number of pitch with a particular pitch length. The reflection peak from side $s_{II}$ has a higher reflectance than that from side $s_I$ (Figure 4a), which indicates that there are more pitches associated with the longer pitch length near side $s_I$. There is also significantly more volume associated with that pitch. Figure 4b depicts the reflection peak shifting from both sides as a function of electric field strength. Upon slowly ramping the DC field strength from 0 to 2.1 V/μm, the reflection peak from side $s_I$ is red shifted due to the movement of chiral anions to side $s_{II}$, which elongates the pitch length near the side $s_I$. At the same time the reflection peak from side $s_{II}$ is blue shifted. Above 2.1 V/μm, the reflection peaks superimpose at 850 nm. The relatively high reflectance from side $s_{II}$ is attributed to relatively lower scattering. The tuning rate of the peak from side $s_I$ is larger than the blue-tuning peak from side $s_{II}$. Thus, the pitch change through the thickness can be described with a rotational symmetry curve (Figure 4c).
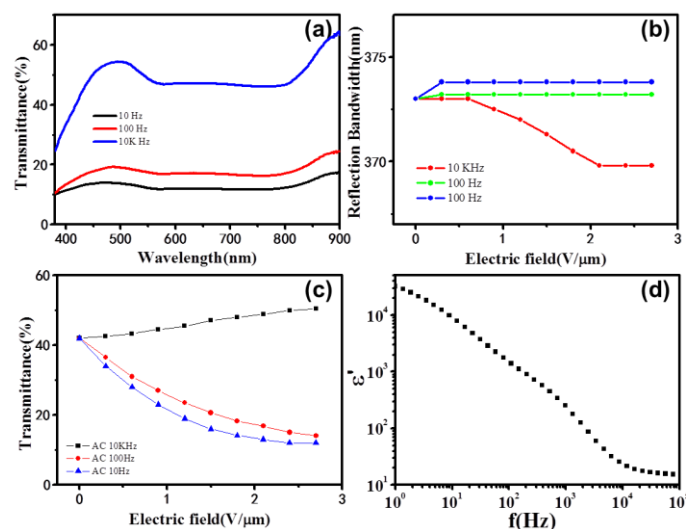
**Figure 5.** Comparisons of the response of the PSCLC to applied AC electric field. (a) The transmission spectra under AC electric field ($E$=2.1 V/μm) with different frequencies (10 KHz, 100 Hz, and 10 Hz). (b) A plot of the reflection bandwidth versus the applied field strength. (c) A plot of the transmittance versus the applied field strength. (d) The dielectric constant of the PSCLC at different frequencies.

In order to understand the fundamental mechanism of this electrically controllable reflection bandwidth, we explored the response of PSCLC films to AC electric fields with different frequencies and DC electric fields with different polarity. Figure 5a shows the transmission spectra of the PSCLC under a high electric field (2.1 V/μm) with different frequencies. AC electric fields have little effect on the reflection bandwidth. A slight broadening (≤5 nm) can be observed at lower frequencies (10 Hz, 100 Hz), which is attributed to the disturbed arrangement of the liquid crystal molecules (Figure S4). AC electric fields at lower frequencies introduce disorder into the orientation of the liquid crystal molecules due to the movement of the ions, which result in a low transmittance (Figure 5c). Under a high frequency (10 KHz) electric field, the liquid crystal molecules inherit a regular planar orientation resulting from the nematic liquid crystal with negative dielectric anisotropy. This ordering can slightly decrease the reflection bandwidth (≤5 nm) and increase the transmittance as shown in Figure 5b and 5c. This behavior is in agreement with the dielectric constant measurements at different frequencies (Figure 5d).
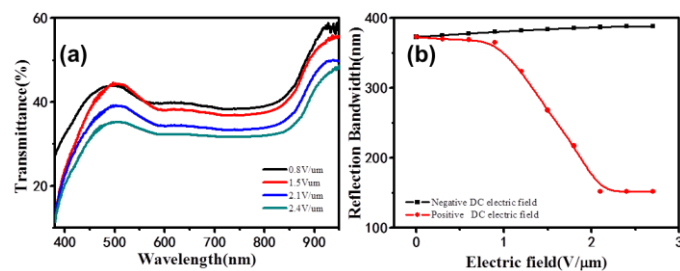
**Figure 6**. (a) The transmission spectra of the PSCLC under negative DC electric fields. (b) A plot of the reflection bandwidth versus the applied electric field strength.

Figure 6 shows the response of the PSCLC to a DC electric field. In contrary to a positive DC electric field, the negative DC field (the polarity is contrast to the applied DC field before polymerization) induces broadening of the reflection bandwidth (~15 nm at 2.7 V/μm), which is larger than the broadening induced under lower frequency AC electric fields. The DC electric field also introduces disorder into the orientation of the liquid crystal molecules, although the disorder is lower than lower frequency electric fields (Figure S5). Thus it indicates that the expansion of the pitch gradient, besides the disturbed arrangement of molecules, results in such broadening of the reflection bandwidth.
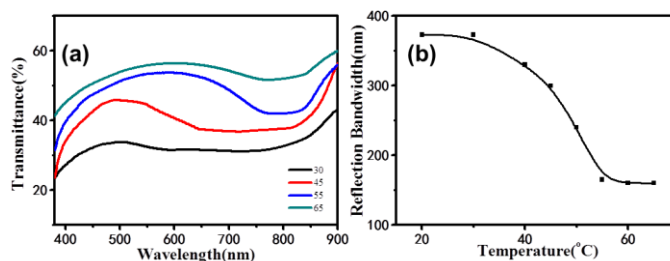


**Figure 7**. (a) The transmission spectra of the PSCLC at temperature's ranging from 30~65 °C. (b) A plot of the reflection bandwidth (nm) versus temperature.

Based on these studies, we propose that the tunability of the reflection bandwidth by DC fields is caused by a redistribution of the chiral ions. This postulate is supported by the temperature response of the PSCLC. As shown in Figure 7a, high temperatures result in a relatively narrow bandwidth. A plot of the reflection bandwidth as a function of temperature is shown in Figure 7b. The reflection bandwidth of the PSCLC decreases from 373 nm to 160 nm when the temperature increases from room temperature to 55 °C respectively. When the temperature is higher than 55 °C, the reflection bandwidth stabilizes at 160 nm, which is a similar response to when the system is under a high positive DC electric field. Higher temperatures decrease electric attraction between the

chiral anions and the ionic polymer network, and increase the dispersion of chiral anions, which decreases the pitch gradient and results in narrower reflection bandwidth. Thus, the tunability of the reflection bandwidth is caused by a redistribution of the chiral ions other than the motion of the polymer network [22, 23, 25].
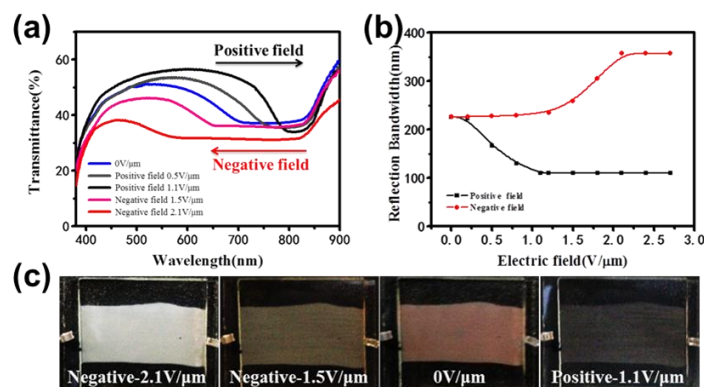


**Figure 8.** (a) The transmission spectra of sample 2 under DC electric fields. (b) A plot of the reflection bandwidth versus DC field strength. (c) The photographic image color of sample 2 under DC electric fields.

With a mechanism as described above, the PSCLCs (sample 2) with suitable reflection bandwidth can be prepared, where the reflection bandwidth can be modulated dual-directionally based on chiral ion redistribution by the DC electric field. Figure 8 shows the DC electric field dependence of the transmission spectra and reflection color of sample 2. In the initial state, by adjusting the DC electric field (1.1 V/μm) applied before polymerization, the reflection band of sample 2 is between 647 nm to 860 nm ($\Delta\lambda$=213 nm) (Figure 8a) and the cell shows a reflective red color. Under a positive DC electric field of 1.1 V/μm, the bandwidth of sample 2 decreases to 108 nm and the cell appears transparent. The negative DC electric fields broaden the reflection bandwidth with the reflection color varying from light red to light orange to white (Figure 8c).

# 3. Experimental

*Sample Preparation*: The cells were fabricated with the indium tin oxide (ITO) glass substrates without any treatment. The thickness was controlled by a dispersion of 28μm spacer beads. The ultraviolet curing adhesive was used to seal the cells by irradiating with UV light for about 20 s. Cells were filled with a mixture containing 77.2 wt% -$\Delta\varepsilon$ nematic liquid crystal HNG715600-100 [10, 26] (HCCH, China), 15.5 wt% chiral dopant S811 (HCCH, China), 4.3 wt% chiral ionic mono-

mer (CIM), 2.7 wt% liquid crystal monomer RM257 (HCCH, china), and 0.3% photoinitiator benzoin methyl ether (BME). The mixture was injected into empty cells by capillarity action. After a static electric field (4V/μm) was applied to the cell followed by a high-frequency AC electric field (100 KHz, 5V/μm), CLC with wide reflection bandwidth was prepared. Then the cell was photo-polymerized by exposing the side $s_I$ to 1.25 mW cm$^{-2}$ of UV light (365 nm) at 20 $^{\circ}$C for 2h.

*Measurements*: The textures of the cells were observed under crossed polarizers using a polarized optical microscope (Leica DM2500M). The optical properties of the cells were measured by ultraviolet spectrophotometer (Shimadzu UV2550). The DC electric field was applied by SourceMeter (Keithley 2400). The AC electric field was applied by 20MHz Function/Arbitrary Waveform Generator (Agilent 33220A) with High Speed Bipolar Amplifier (NF BA4825). The response time was measured by test system including High Performance Mixed Oscilloscope (Agilent MS09104A), LED backlight source (Luminus PT121), and detector (Thorlabs PDA36A-EC).

# 4. Conclusion

A new approach to large scale tuning of the reflection bandwidth of polymer stabilized cholesteric liquid crystals with an applied DC electric field has been presented. Due to the stable polymer network structure and the strong electronic attraction between the chiral anion and the ionic polymer network, the PSCLCs stabilize in a planar texture under DC electric fields. The movement of the chiral anions under DC electric fields results in a variation in pitch gradient, which is observable as the tuning of the reflection bandwidth. The reflection bandwidth can be tuned arbitrarily in the visible wavelength regime with a reflection color varying between white, orange, red, and transparent. Moreover, the reflection bandwidth can also be controlled by the temperature.

# Acknowledgments

# Notes and references

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## Footnote

†Electronic supplementary information (ESI) available. See DOI: 10.1039/ ((please add manuscript number))

**Table of contents entry**

**Title (**Cholesteric Liquid Crystals with Electrically Controllable Reflection Bandwidth Based on Ionic Polymer Network and Chiral Ion**)**

*Hongbo Lu\*, Jinliang Hu, Yutian Chu, Wei Xu, Longzhen Qiu, Xianghua Wang, Guobing Zhang, Juntao Hu, Jiaxiang Yang*
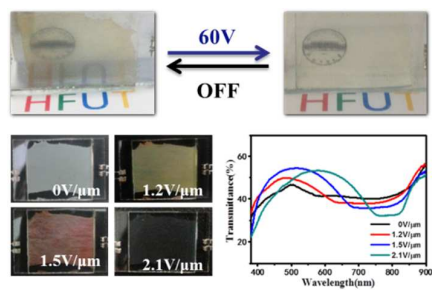


The reflection bandwidth can be tuned dynamically by electric fields in the visible wavelength regime.