

Paper like cholesteric interferential mirror

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Abstract: A new type of flexible cholesteric liquid crystal mirror is presented. The simple and effective method for the deposition of a cholesteric mixture on a paper substrate and the particular design of the device give a homogeneous alignment of the cholesteric texture providing mirrors with an intense and uniform light reflectance. A desired polarization state for the reflected light, linear or circular, can be easily obtained varying the thickness and optical anisotropy of the polymer cover film. By using non-azobenzene based photosensitive materials a permanent array of RGB mirrors with high reflectivity can be obtained on the same device. Paper like reflective mirrors are versatile and they can find applications in reflective displays, adaptive optics, UV detectors and dosimeters, information recording, medicine and IR converters.

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OCIS codes: (160.3710) Liquid crystals; (230.4040) Mirrors.

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1. Introduction

The Cholesteric Liquid Crystal (CLC) phase is a nematic phase with a self-organized periodical helical arrangement that acts as a one-dimensional periodic structure. For their optical properties CLCs may be considered as one-dimensional photonic crystals. In planes perpendicular to the helical axis, the molecules have a preferred average orientation, characterized by the so-called director. Along the helical axis, the director is continuously rotated, which results in a twisted birefringent medium. In CLCs the period of the structure is equal to half the pitch p of the helix, and for light propagating along the helical axes, $p_0 = \lambda_0/n$, where λ_0 is the wavelength of the maximum reflection or the middle of the Selective Reflection Band (SRB) and n is the average of the refractive indices defined as: $n = (n_e + n_o)/2$. The extraordinary and ordinary indices of refraction are denoted by n_e and n_o respectively. The full width at half maximum of the selective reflection band equals to $\Delta\lambda = p_0\Delta n$, where $\Delta n = n_e - n_o$ is the birefringence of a nematic layer perpendicular to the helix axis. Opposite to the other photonic crystals, the SRB of the CLCs is polarization dependent. When the incident light is circularly polarized with the same handedness as the cholesteric helix, the light is totally reflected by the stop band. On the contrary, light of opposite handedness is transmitted through the CLC medium. Additionally, the SRB is very sensitive to various internal and external factors (electric, magnetic and acoustic fields, temperature, local order, etc.) [1–4]. In particular, the change in the helical pitch caused by photochemical reactions in the CLCs is of great interest [5–7]. Nowadays flexible cholesteric films have attracted particular attention as they can be easily integrated in different devices, as for example in novel reflective displays [8] solvent vapor detectors, image converters, information recording

devices, and can also be useful for the research in adaptive optics and medicine [9–14]. In this paper, we propose a new technology for the fabrication of low-cost, flexible reflective CLC mirrors with light reflectivity over the entire visible range of the optical spectrum. The proposed device shows excellent resistance to mechanical deformation, good reflection properties and easy implementation in flexible devices. Additionally, the retardation of the emitted light can also be tuned to obtain reflected light circularly or linearly polarized. Finally, for the first time we use a ester based chiral dopant that is stable upon irradiation with visible light and undergoes a non-destructive photo-isomerization upon exposure to UV light. This choice allows to create, on a monochromatic cholesteric layer, an array of multicolored reflective pixels, with the desired spectral positions of SRB, which are stable in time.

2. Materials

BL006, BL038 and MLC-6816 are used as nematic liquid crystals, ZLI-811 as optically active dopant, RM 257 as reactive monomer, (all materials from Merck), and Irgacure 2100 (Ciba, Swiss) as photo-initiator. For mixtures, all the percentage provided in the following are given in %wt. Two transparent teflon polymer sheets (Katco Ltd., UK) with thicknesses $d_1 = 15.2\mu\text{m}$, $d_2 = 30.2\mu\text{m}$ respectively, and with optical anisotropy $\Delta n = 0.01$ (when stretched) are selected. A UV photoreactive mixture is prepared using the liquid crystalline reactive monomer RM 257 with the photo-initiator Irgacure 2100 in the following concentration: 96% RM 257 + 3% Irgacure 2100. This mixture is cured and stirred at 70-80°C. The phototunable cholesteric mixture is prepared mixing in appropriate concentrations the nematic material with the optical active dopant ZLI-811. Photo-tunable CLCs, consisting of photochromic molecules such as azobenzene derivatives, are capable of large changes in the spectral position of their SRB when exposed to light. In fact, the photoinduced isomerization of azobenzene molecules can cause a change of the pitch, and thus a shift of the wavelength of the selective reflection band [15–23]. However, azobenzene molecules are chemically unstable and undergo rapid degradation when exposed to visible light [24]. In [25] for the first time the photo-isomerization of the optically active dopant ZLI-811 is reported. ZLI-811 shows high stability upon irradiation with visible light and non-damaging photo-isomerization upon exposure to UV light. The experimentally observed phenomenon of photo-transformation of ZLI-811 is explained by the photo-Fries rearrangement of its chiral molecules, which is usually observed in complex aromatic esters. The Fries rearrangement, which is irreversible, can be induced both photo-chemically or chemically [26]. When ZLI-811 is exposed to UV light with a wavelength overlapping its absorption band, its isomerization causes a rearrangement in the CLC and a change in its pitch, with a consequent shift of the SRB.

3. Experimental results and discussion

A flexible paper-like mirror consists of three layers: a black paper substrate, a CLC layer and a polymer film. The paper substrate is suitably chosen in order to prevent the leaking of the liquid crystalline material through it and to align the CLC material uniformly to grant a perfect reflectivity of the final device. According to our investigations, the best choice for the paper substrate, is carbon paper. This substrate consists of three layers: a rear paper layer, a thin layer of black pigment and a wax layer. Carbon paper is water- and oil-resistant, slightly translucent and black. In addition, the pit-like morphology of the surface of this substrate acts as a quasi-encapsulating system which holds and stabilizes the CLC mixture. Figure 1(a), 1(b).

Small CLC droplets are then placed homogeneously on the surface of the paper substrate (Fig. 2) and a transparent polymer film is placed over them. We use a teflon film which serves simultaneously as protective layer and phase retarder. Teflon films have outstanding properties such as resistance to many chemicals, to UV irradiation and to extreme temperatures. In fact, it can temporarily withstand temperatures of 260°C and cryogenic

temperatures of -240°C and still have the same chemical properties. It has low adhesion, low coefficient of friction, low wettability and excellent optical properties.

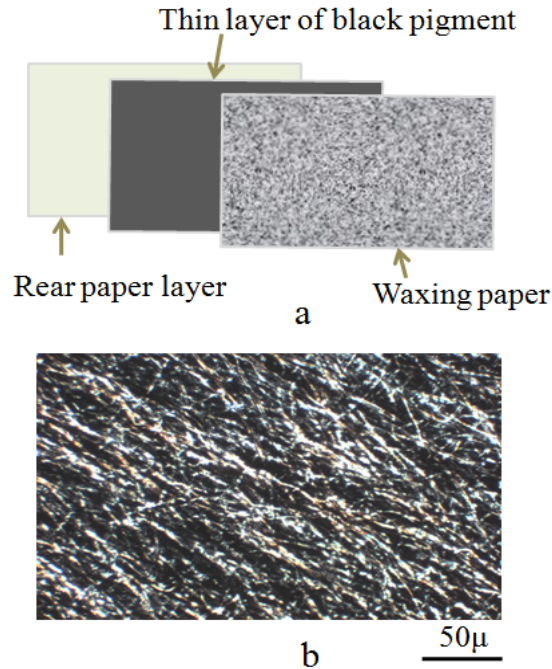


Fig. 1. a) Schematic representation of the substrate, b) optical microscope image of the paper substrate.

Once CLC droplets are sandwiched between the paper substrate and the polymer film, the three layer system is evenly and gently pressed to obtain a $3\text{-}4\mu\text{m}$ thick cholesteric layer.

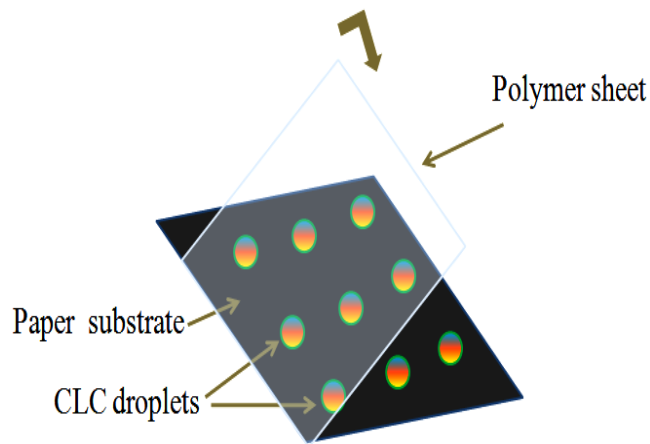


Fig. 2. Schematic representation of the flexible CLC mirror.

The entire structure needs to be polymerized in order to obtain a device mechanically resistant to bending. This is achieved irradiating the sample with UV light. The experimental set up used is depicted in Fig. 3(a). A 100 W Mercury lamp and a band pass filter $\Delta\lambda = 250\text{-}310$ nm (UFS 1) are used. The distance between the lamp and the sample is 20-25 cm with a light intensity at the sample of $0.12\text{mW}/\text{cm}^2$. Once polymerized, the color reflected from the

mirror can be tuned changing the pitch of the photosensitive cholesteric mixture irradiating with light of appropriate wavelength. Further, using a mask, a pattern of reflected colors can be created on the device. The mask consists in an array of semitransparent pixels, that modulate locally the light intensity. The experimental set up is shown in Fig. 3(b), it uses the same UV lamp and an interference filter at $\lambda = 365 \text{ nm}$ (UFS 2).

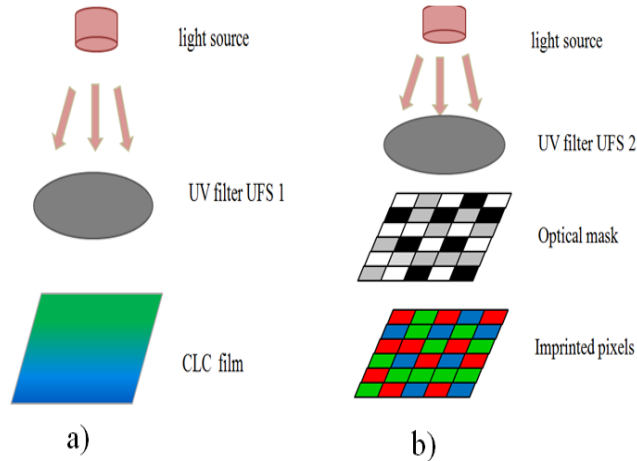


Fig. 3. a) Polymerization of the CLC film and b) patterning of RGB mirrors on the CLC Film. Reflective mirrors are patterned using a mask with interchangeable semi-transparent pixels.

3.1 CLC film polymerization

Two mirrors, reflecting two different colors, are prepared using the following two cholesteric mixtures: 96% [68% BL-038 + 32% ZLI-811] + 4% [97% RM 257 + 3% Irgacure 2100] and 96% [70% BL-006 + 30% ZLI-811] + 4% [97% RM 257 + 3% Irgacure 2100]. The mirror color, or the shift of the SRB, is obtained varying the concentration of the chiral dopant in the nematic host. The three layer mirrors are assembled and each device is placed in the set-up depicted in Fig. 3(a) for 12 min. After this polymerization procedure, each mirror shows a perfect reflectivity and homogeneity throughout its whole surface (Figs. 4(a), 4(c)). Figures 4(b) and 4(d) show the selective reflections from the two mirrors as measured using a fiber optic spectrometer (AvaSpec-2048, The Netherlands).

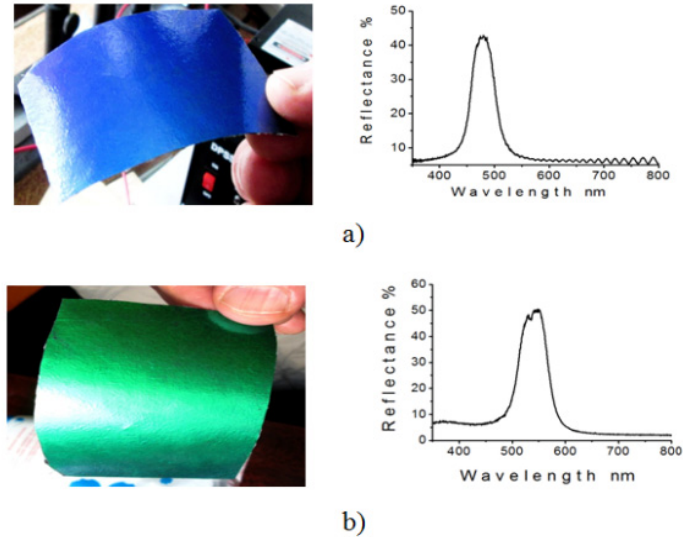


Fig. 4. Flexible CLC mirrors (a,c) and their selective reflections with peaks located at $\lambda_0 = 470$ nm (a), and $\lambda_0 = 545$ nm (b).

CLC mirrors are resistant to mechanical deformations, they can be bent without damaging and they maintain unchanged their reflective properties, Fig. 5.

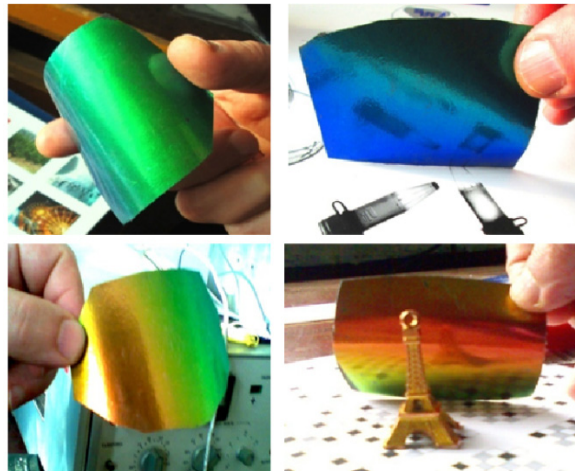


Fig. 5. CLC mirrors after photo polymerization show a strong resistance to mechanical deformation and maintain a perfect reflectance.

3.2 Mirrors array

An array of selective reflection mirrors on the same sample can be patterned using the set-up sketched in Fig. 2(b). Two CLC mixtures are prepared with the following concentrations: 96% [64% MLC-6816 + 36% ZLI-811] + 4% [97% RM 257 + 3% Irgacure 2100] and 96% [65% BL-038 + 35% ZLI-811] + 4% [97% RM 257 + 3% Irgacure 2100]. Following UV irradiation, the shape of the photoisomerizable ZLI-811 molecules changes irreversibly, providing the reflected colors of the mirrors with a good stability in time. Using a mask (Figs. 5(a), 5(b)) and varying exposure times (Fig. 5(c)), an array of mirrors with different spectral positions of the selective reflection can be patterned. In the experiments millimeter sized RGB pixels were patterned on the mirror surface as shown in Fig. 6(c).

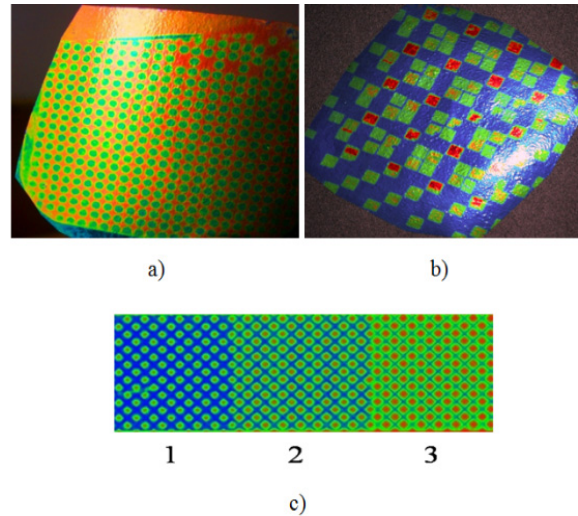


Fig. 6. CLC films with patterned arrays of reflective mirrors a) and b). In c) mirrors prepared irradiating the device with different exposure times: 1, 2 and 3 correspond to 6, 12 and 18 minutes of irradiation respectively.

As shown in Fig. 7, the Bragg peaks have symmetrical shapes and high reflectivities, very close to the maximum reflectance of perfect CLC structures.

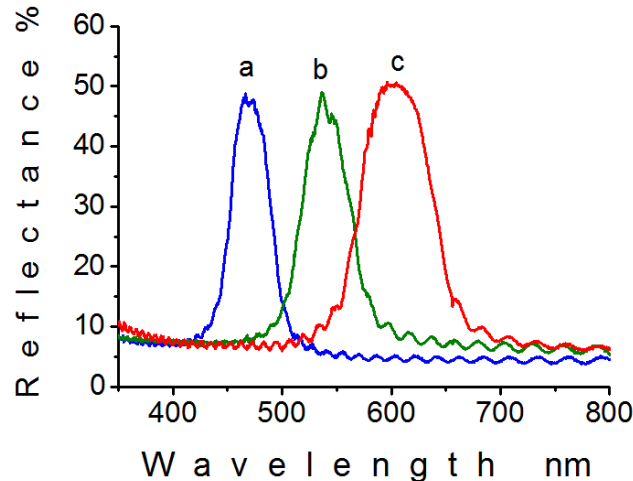


Fig. 7. Spectral positions of the selective reflections: a) before UV irradiation, b) after 9 minutes of UV exposure, c) after 18 minutes of UV exposure

3.3 Reflected light polarization

The polarization of light reflected from the flexible mirrors can be tuned and a key role in this operation is played by the transparent polymer film. As previously stated, circularly polarized light with the same handedness as the CLC helix, is totally reflected in the frequency range $q_0/n_e < \omega/c < q_0/n_o$, where, $q_0 = \pm 2\pi/p_0$, (\pm sign determines the handedness of the CLC helix). It is well known that, for applications, the circular polarized light obtained from CLC polarizers should be converted into linear polarized light [27]. Retarders are inevitably necessary to this end. A polymer film, as teflon with a quarter-wave retardation value for a reference wavelength, can be used to obtain linear polarized light [28]. An expression for the

phase retardation ϕ that varies strongly with the wavelength λ is given by the following equation:

$$\phi = 2\pi\Delta nd / \lambda. \quad (1)$$

From a practical point of view, it is important to investigate phase retardation within the entire reflection band of the CLC mirror. A left-handed CLC mixture: 96% [76%BL-006 + 24% ZLI-811] + 4% [97% RM257 + 3% Irgacure 2100] is prepared and a CLC mirror is assembled. A spectral analysis of the reflected light (Fig. 8) shows a reflection peak at $\lambda_0 = 0.605\mu\text{m}$ while the half-width of the SRB is $\Delta\lambda = \lambda_2 - \lambda_1 = (0.650 - 0.560)\mu\text{m} = 0.09\mu\text{m}$.

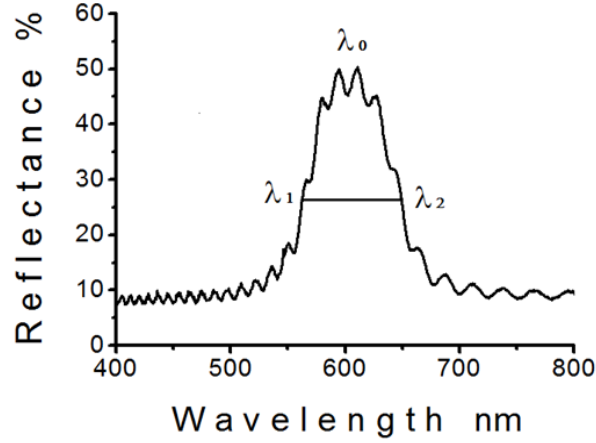


Fig. 8. Selective reflection of the CLC film, λ_0 is the maximum middle point of the selective reflection, λ_1 and λ_2 the borders of the FWHM interval of selective reflection.

The thickness of the polymer film affects, as expected, the state of the polarized light. In the following a calculation of the phase retardation for three different wavelengths, were found $\lambda' = 0.560\text{nm}$, $\lambda'' = 0.605\text{nm}$ and $\lambda''' = 0.650\text{nm}$.

For a polymer film $15.2\mu\text{m}$ thick, the phase retardation values are the following:

$$\begin{aligned} \phi &= 2\pi\Delta nd / \lambda' = 2\pi \times 0.01 \times \frac{15.2}{0.560} = 0.54\pi \approx \frac{\pi}{2} \approx \lambda / 4 \\ \phi &= 2\pi\Delta nd / \lambda'' = 2\pi \times 0.01 \times \frac{15.2}{0.605} = \frac{\pi}{2} = \lambda / 4 \\ \phi &= 2\pi\Delta nd / \lambda''' = 2\pi \times 0.01 \times \frac{15.2}{0.650} = 0.47\pi \approx \frac{\pi}{2} \approx \lambda / 4. \end{aligned} \quad (2)$$

When the thickness of the polymeric cover film doubles, $d = 30.2\mu\text{m}$, the phase retardation values change:

$$\begin{aligned} \phi &= 2\pi\Delta nd / \lambda' = 2\pi \times 0.01 \times \frac{30.2}{0.560} = 1.07\pi \approx \pi \approx \lambda / 2 \\ \phi &= 2\pi\Delta nd / \lambda'' = 2\pi \times 0.01 \times \frac{30.2}{0.605} = 1.0\pi = \lambda / 2 \\ \phi &= 2\pi\Delta nd / \lambda''' = 2\pi \times 0.01 \times \frac{30.2}{0.650} = 0.93\pi \approx \pi \approx \lambda / 2. \end{aligned} \quad (3)$$

According to the previous calculations, a polymer film with thickness $15.2\mu\text{m}$ acts as a quarter wave plate, that introduces a 90° phase shift of the reflected light, whereas a polymer sheet with thickness $30.2\mu\text{m}$ acts as a half wave plate, introducing a 180° phase shift. The state of polarization of the light reflected by the cholesteric mirror is fully investigated using

an optical fiber spectrometer and appropriate polarizers. A schematic presentation of the polarization conversions is given in Fig. 9.

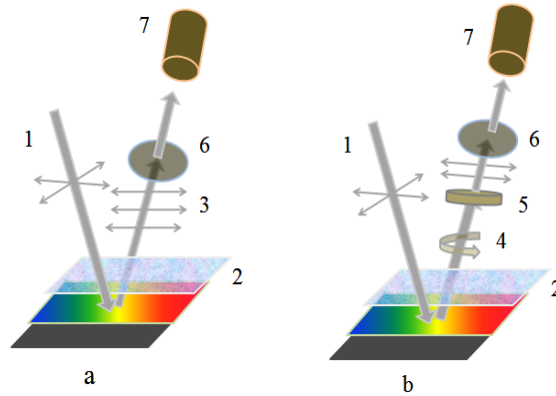


Fig. 9. Polarization conversions of the light beam reflected from the mirror, a) polymer layer thickness $d = 15.2 \mu\text{m}$ and b) polymer layer thickness $d = 30.2 \mu\text{m}$. The experimental set up used to analyze the light reflected from the mirrors is also shown: 1-unpolarized light, 2-polymer sheet, 3-linearly polarized light, 4-circularly polarized light, 5- $\lambda/4$ plate, 6-linear polarizer (analyzer), 7-spectrometer.

In Fig. 10 it is shown the variation of the intensity of the reflected light from the mirror with the $15.2 \mu\text{m}$ thick teflon film 1. and the $30.2 \mu\text{m}$ thick teflon film 2. as a function of the analyzer rotation. The experimental set up, that uses a spectrometer, is shown in Fig. 9.

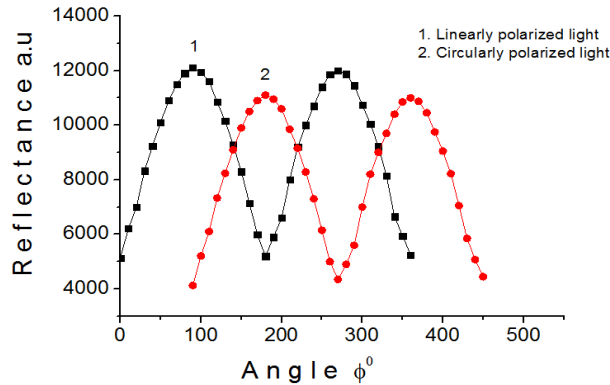


Fig. 10. Orientational dependence of the reflected light intensities as a function of the analyzer rotation for a mirror prepared with the 15.2 mm thick teflon film 1. and the 30.2 mm thick teflon film 2.

4. Conclusions

We report on a novel technology to fabricate reflective CLC mirrors on flexible paper like substrates. The not encapsulated design and the peculiar architecture of the device significantly reduce the light scattering and provide a uniform reflection of the incident light. Depending on its thickness, the cover polymer film acts as half-wave or quarter-wave plate, which provides the desired state of polarization for the reflected light. Due to its low cost, light weight, flexibility, durability, easy technology and high reflectivity, the proposed paper based cholesteric mirror offers a novel engineering solution in applications such liquid crystals displays. As an example, they may be used as selective reflectors in guest host displays, where the guest-host system can contain a complementary colour with respect to the

selective reflection of the cholesteric mirror. Additionally, the patterning of the reflector also opens up a way to make cheaper reflectors than the silver coated ones used nowadays in the display technology, with more flexibility, for any backlight or reflective display application [29]. Flexible mirrors may also find applications in optoelectronics, e-readers, smart credit cards and labels, adaptive optics, astronomy, medicine, defectoscopy, UV dosimetry.

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