

Photoinduced Hyper-Reflective Laminated Liquid Crystal Film with Simultaneous Multicolor Reflection

Gang Chen,^{†,‡} Ling Wang,^{†,§} Qian Wang,[&] Jian Sun,[‡] Ping Song,[§] Xingwu Chen,[‡] Xin Liu,[⊥] Shanghong Guan,[⊥] Xiaoguang Zhang,[⊥] Liping Wang,^{*,‡} Huai Yang,^{*,§,‡} and Haifeng Yu^{*,§}

[§]Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China

[‡]Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, P. R. China

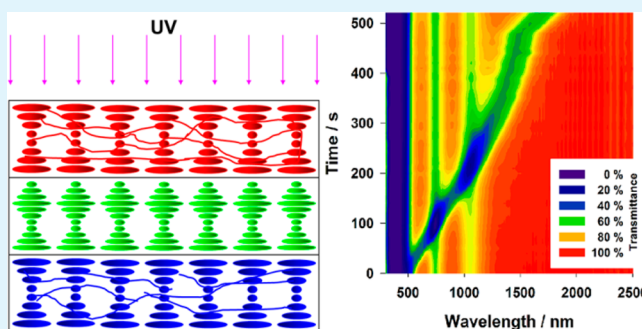
[&]School of Chemistry and Environment Science, Beijing University of Aeronautics and Astronautics, Beijing 100191, P. R. China

[⊥]Science and Technology on Electro-Optical Information Security Control Laboratory, Hebei Sanhe, 065201, P. R. China

Supporting Information

ABSTRACT: A phototunable laminated liquid crystal film with simultaneous multicolor reflection is successfully fabricated by doping a light-driven chiral molecular switch into the laminated cholesteric liquid crystal structure. Upon UV-light irradiation, the reflection notches and their hyper-reflectivity properties can be precisely tuned, and their original state can be properly returned by visible-light irradiation.

KEYWORDS: light-controllable property, hyper-reflectivity, cholesteric liquid crystal film, laminated structure, simultaneous multicolor reflection, polymer-stabilized liquid crystals



INTRODUCTION

Cholesteric liquid crystals (CLCs) have recently encouraged enormous interests in the development of soft matter materials due to their unique capability to self-organize into a helical supramolecular architecture. One of the most important optical properties of CLCs is their selective reflection of light based on the Bragg relationship. The selective reflection wavelength λ_0 is defined by $\lambda_0 = nP$, where P is the pitch length of the helical structure and n is the average refractive index of the CLCs. When unpolarized light propagates through a CLC medium, only the circularly polarized light with the same handedness as the helix is reflected. The CLCs with simultaneous multicolor reflection are extremely attractive for multicolor laser emission^{1–3} and reflective color displays without the need for back-lightening, polarizers, or color filters.^{4–6} Recently, Takezoe and his co-workers^{2,3,7–10} reported the laminated CLC films with simultaneous multicolor reflection by introducing fibonaccian phase defects. Moreover, it has been also found that a hyper-reflective notch,^{3,8,11–13} of which the reflectivity approaches 100%, can be realized by stacking two films with similar pitch lengths but opposite handedness or two films with the same handedness but separated by a half-wave phase retarder.¹¹

However, the films, thus prepared, have permanently solid structures and their reflection notch cannot be manipulated by external stimuli. As we know, CLCs can respond to external stimuli such as thermal,^{13–15} electric field,^{16,17} mechanical

stress,^{1,18} light,^{19–32} and humidity.³³ Classically, the most studied approach in this field has been focused on the light-driven CLCs for certain advantages like relatively easy spatial, temporal and remote control of irradiation. Li et al.^{24–32} have fabricated several kinds of light-driven CLCs using light-driven chiral molecular switches with azobenzene chromophore as the chiral dopants. The helical twisting power (HTP) of these chiral dopants can be changed upon light irradiation, thus tuning the selective reflection wavelength of the CLC has been obtained according to the equation $HTP = (cP)^{-1}$, where c is the chiral dopant concentration. Herein, we doped a novel light-driven chiral molecular switch into the laminated CLC structure to fabricate a phototunable film with simultaneous multicolor reflection. Interestingly, its hyper-reflective notch can be dynamically controlled by irradiating with UV or visible light. These studies will certainly provide a method to fabricate devices used for tunable multimode lasers,^{7,18} tunable optical filters,^{19,34} and liquid crystal displays.^{35–42}

EXPERIMENTAL SECTION

The fabrication process of the film is shown in Figure 1a. A CLC mixture containing photopolymerizable nematic diacrylate

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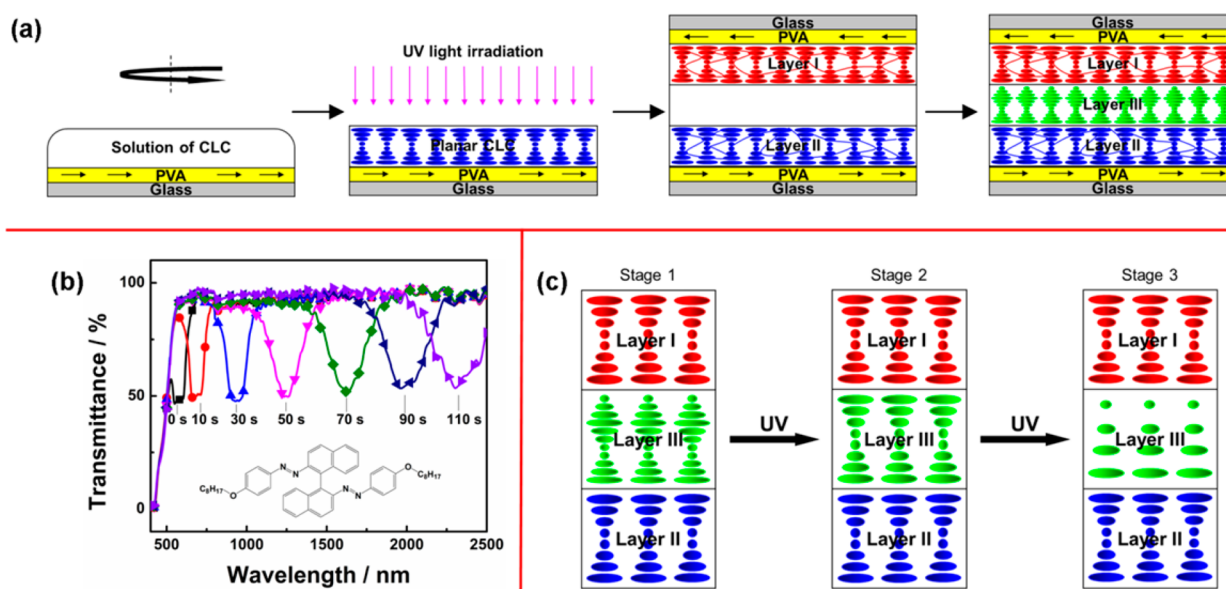


Figure 1. (a) Schematic representation of the fabrication process of the laminated CLC film. (b) Transmittance curves of the CLC that is composed of 5 wt% CD1 and 95 wt% SLC1717 after different UV exposure times (365 nm, 3 mW/cm²) and the molecular structure of CD1 (the inset). (c) Basic principle of the light-driven property of the phototunable laminated CLC film.

Table 1. Composition, Center Reflection Wavelength, and Handedness of the CLCs Used in This Paper

CLC	composition of the CLC (wt%)						reflection notch		sample		
	SLC1717	C6M	S811	R811	Irg651	CD1	center wavelength ^a (nm)	handedness	A	B	C
A	94.0					6.0	400–2000 (light-tunable)	right	layer III	layer III	layer III
B _L	54.0	30.0	15.0		1.0		700	left	layer I and layer II	layer I	layer I
C _R	59.0	30.0		10.0	1.0		1020	right		layer II	
C _L	59.0	30.0	10.0		1.0		1020	left			layer II

^aThe center reflection wavelengths of CLC B_L, CLC C_R, and CLC C_L were measured after polymerization.

monomer (C6M, synthesized by our laboratory), chiral dopant (left-handed S811 or right-handed R811, Merck), nematic liquid crystal (SLC1717, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd.) and photoinitiator (Irgacure 651, Aldrich) was deposited by a spin coating at 2500 rpm to give the required thickness on a glass substrate which has been covered by a prerubbed PVA layer (see the Supporting Information). Then it was cured upon UV-light irradiation (365 nm, 25 mW/cm²) for 30 min in an inert argon environment. Thus a polymer-stabilized CLC (PSCLC) layer was achieved. Two PSCLC layers (layer I and layer II) were attached together to form a liquid crystal cell and an untemplated region in between (about 20 μm). Finally, a light-driven CLC was drawn into the untemplated region as layer III by capillary filling.

RESULTS AND DISCUSSION

The light-driven CLC used here is composed of SLC1717 and right-handed CD1 (Figure 1b), a light-driven chiral molecular switch synthesized according to Li's work.²⁷ Upon irradiation at 365 nm, the HTP of CD1 decreases for the *trans*–*cis* isomerization of azobenzene configurations, resulting in the red-shift of reflection notch (Figure 1b). On the other hand, the blue-shift of the reflection notch occurs upon irradiation at 458 nm (see Figure S2 in the Supporting Information). Thus the layer III has a dynamic reflection notch. But layer I and layer II only have a static reflection notch for the nonlight driven chiral dopant. Upon UV-light irradiation, the relative position of the dynamic reflection notch and the static reflection notch enables

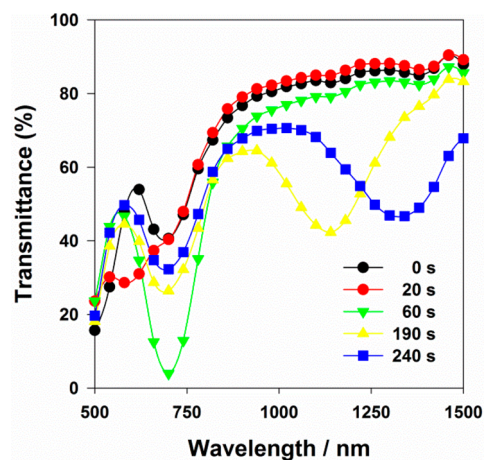


Figure 2. Transmittance curves of sample A after different UV exposure times (365 nm, 3 mW/cm²). The transmittance changing at 600 nm upon UV-light irradiation results from the partial overlap of the static reflection notch and the dynamic reflection notch.

the laminated CLC film to show several interesting characteristics. More specifically, it was assumed that layer I and layer II have the same reflection notch here (both of their handedness and reflection wavelength are the same). When the dynamic reflection notch has different pitch length from the static reflection notch, the film will have two 50% reflection notches (called conventional reflection notch), as shown in stage 1 and

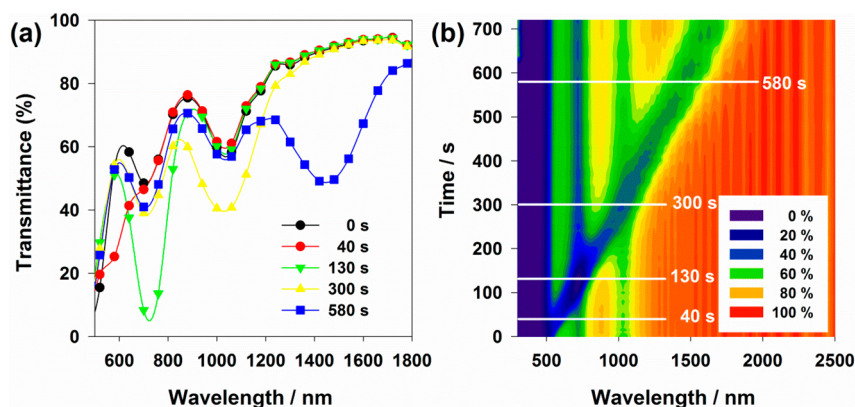


Figure 3. (a) Transmittance curves of sample B after different UV exposure times (365 nm, 1 mW/cm²). (b) Reflection notch dispersion image of sample B recorded at different UV exposure times. The transmittance is represented by the color.

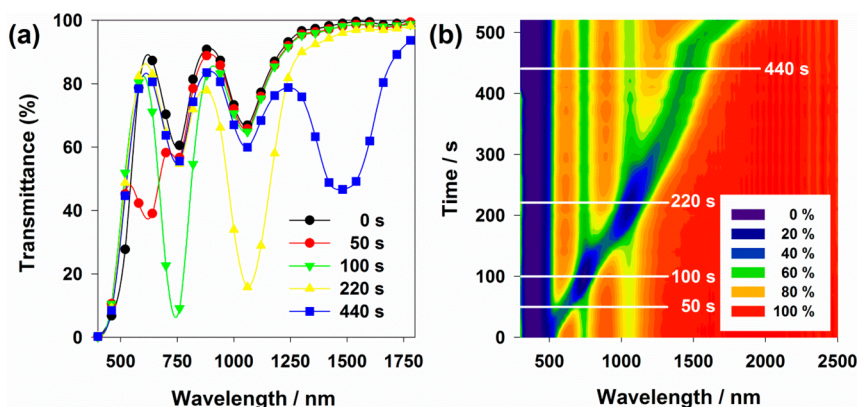


Figure 4. (a) Transmittance curves of sample C after different UV exposure times (365 nm, 1 mW/cm²). (b) Reflection notch dispersion image of sample C recorded at different UV exposure times.

stage 3 in Figure 1c. But when the dynamic reflection notch is tuned to overlap to the static reflection notch, the film will have a single reflection notch (stage 2 in Figure 1c). Interestingly, the single reflection notch is hyper-reflective if the dynamic reflection notch has opposite handedness with the static reflection notch. In other words, a hyper-reflective CLC film has been achieved. According to Figure 1c, sample A was made with CLC B_L and CLC A (Table 1). Upon UV-light irradiation for 60 s, a hyper-reflective notch appears that is due to the opposite handedness and equal pitch length of CLC B_L and CLC A (Figure 2). Besides, sample A has two conventional reflection notches.

To take full advantage of CLCs in layer I and layer II that can have different pitch lengths, sample B with two static reflection notches has been fabricated by CLC B_L, CLC C_R, and CLC A (Table 1). As shown in Figure 3a, the two evident static reflection notches are centered at 700 and 1020 nm, respectively, with the former reflecting only left circularly polarized light and the latter reflecting only right circularly polarized light. Initially, the dynamic reflection notch, centered at 455 nm (calculated according to the HTP of CD1), is invisible because of the strong absorbance of CD1 molecule below 550 nm (see Figure S2 in the Supporting Information). Upon UV-light irradiation for 40 s, the dynamic reflection notch is tuned to 600 nm, thus the film has three conventional reflection notches. Further irradiation for 90 s redshifts the dynamic notch to overlap with the static reflection notch at 700 nm, inducing a hyper-reflective notch at 700 nm due to the

opposite helicity senses of layer I and layer III. Thus the film has one hyper-reflective notch and another conventional reflection notch at the same time. Upon continuous irradiation for 170 s, the two reflection notches of layer II and layer III overlap, inducing that sample B has two reflection notches, and no hyper-reflective notch appears due to the same helicity sense of layer II and layer III. Additional irradiation causes the dynamic notch to redshift in wavelength, and sample B has three conventional reflection notches again.

Sample B not only has different reflecting characters after different UV exposure times, but the dynamic reflection notch can be precisely controlled by UV exposure time. As shown in Figure 3b, throughout the UV-light irradiation, either static reflection notch keeps constant transmittance unless it overlaps with the dynamic reflection notch. And the center wavelength of the dynamic reflection notch has an approximately linear relationship with the UV exposure time. In other words, the switch from one condition to another can be precisely controlled by UV-light irradiation. Here the decrease in reflection of the dynamic notch and the notch broadening is caused by the increase in pitch length. And the lower reflectivity of CLC C_R results from finite units of the pitch¹⁰ in the maximum thickness of layer that can keep the CLC in planar texture.

If CLC C_R in sample B was replaced by CLC C_L, sample C (Table 1 and Figure 4) with two left-handed static reflection notches was fabricated. For the opposite helicity sense of the dynamic reflection notch and the static reflection notches, a

hyper-reflective notch appears when the dynamic reflection notch is tuned to overlap with one of the static reflection notches, and the other static reflection notch remains unchanged, as shown by the transmittance curves for 100 and 220 s in Figure 4. Except these, sample C can also show three conventional reflection notches.

CONCLUSION

We have presented a novel method to fabricate a photoinduced hyper-reflective laminated liquid crystal film with simultaneous multicolor reflection by doping a novel light-driven chiral molecular switch into the laminated CLC structure. This technique allows for the realization of changing a conventional reflection notch at a certain wavelength into a hyper-reflective one without influencing on others under the precise control of UV-light irradiation condition. Moreover, the original state can be properly returned by visible light irradiation, thus the hyper-reflective notch can be reversibly switched to a conventional one. Our design is expected to suggest a new direction for developing the novel materials in areas of tunable multimode lasers, tunable optical filters, optical switches, and liquid crystal displays. This work will also pave a way for regulating the promising nanostructures by the external stimuli and exploring the relationship between the nanostructured devices and the properties of the used materials.

ASSOCIATED CONTENT

Supporting Information

The molecular structures and synthesis of compounds (CD1, C6M, R811, S811, and Irg651), the UV-vis absorption spectra of CD1, the fabrication of layer I/layer II, several other laminated CLCs films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yanghuai@coe.pku.edu.cn.

Author Contributions

†Authors G.C. and L.W. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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