



Photo-responsive dye-doped liquid crystals for smart windows

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Abstract: An electric field drives most dye-doped liquid crystal devices. Here, we demonstrate a new photo-responsive dye-doped self-organized cholesteric liquid crystal device. Upon UV or blue light exposure, the helical twisting power of the chiral azobenzene changes because of the *trans-cis* isomerization. As a result, the initially vertically aligned liquid crystal directors and dye molecules will change from transparent state to dark state. Such a polarizer-free photo-activated dimmer can be used for wide range of applications, such as diffractive photonic devices, portable information system, vehicular head-up displays, and as a smart window for energy-saving buildings.

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1. Introduction

Guest-host liquid crystal (LC) devices [1–4], developed in late 1960s, have found renewed interest as dimmer for see-through displays [5], diffractive photonic devices [6], portable information system [7], and smart windows for energy-saving buildings [8]. Its unique features are electrically controllable transmittance, no need for polarizer, wide viewing angle, low manufacturing cost, and possible usage of flexible plastic substrates [9,10]. A guest-host LC usually contains 2-3% absorptive dichroic dyes in a nematic host. Because of low concentration, these dichroic dye molecules follow the orientation of the LC directors. When the long axis of dichroic dyes are parallel to the incident light polarization, the absorption is strong so that the transmittance is low. As the LC directors and dye molecules are reoriented to be perpendicular to the substrates, the absorption is weak and the transmittance is high. The contrast ratio of a guest-host LC device depends on the order parameter, dyes dichroic ratio and concentration, and cell gap.

Unlike conventional voltage-driven guest-host displays, in this paper, we demonstrate a photo-sensitive dye-doped cholesteric liquid crystal (CLC) dimmer which is operated by low intensity light. CLCs are self-organized molecules which form helical structures [11,12]. To prepare a CLC, we can mix some chiral compounds into a nematic host to induce helical structures [13]. Right- or left-handedness can be chosen based on the nature of chiral dopant and interaction with the LC host, while the helical twisting power can be controlled by electromagnetic fields, temperature, and chirality of the doping materials [14]. Another way to change the helical twisting power is to irradiate the sample with UV-blue light. When a photosensitive chiral azobenzene compound is doped into a CLC host, it undergoes *trans-cis* photoisomerization upon UV-blue light exposure [15–17]. The helical twisting power of photosensitive molecule varies between rod-shaped *trans*-state and kink-shaped *cis*-state. This transformation of helical twist power of photosensitive chiral dopant would affect the helical twisting power of the combined mixture and may cause a change of helix pitch value [6]. Due to the change of helical pitch, the transformation between homeotropic and twisted state (fingerprint) happens. In our proposed guest-host LC system, we utilize this light sensitive nature of azobenzene compounds to control the transmittance of our device. At initial state, the LC directors and dye molecules are both aligned vertical to the glass substrates. Under such condition, the absorption is minimum, i.e. the transmittance is maximum. Upon UV-blue light exposure, the LCs and dye molecules turn into fingerprint state due to

photoisomerization where the helical axis is parallel to the glass substrates. Dichroic dyes absorb the same polarized light and there is light scattering due to CLC directors. Thus, the device turns into dark and the photo-switchable effect is observed. The underlying operation mechanism is similar to that of photochromic effect. One major advantage of our device is lower manufacturing cost in comparison with photochromic glass.

2. Experiment

A negative dielectric anisotropy ($\Delta\epsilon$) nematic mixture Merck ZLI-4788 was used as the LC host for this experiment. Its physical properties are listed as follows: $\Delta\epsilon = -5.7$ at $f = 1$ kHz and birefringence $\Delta n = 0.1647$ at $\lambda = 589$ nm. A right-handed photosensitive chiral azobenzene compound, PSC-01 [18,19], was doped into this LC host. The HTP of PSC-01 in *trans* and *cis* state is $64.18 \mu\text{m}^{-1}$ and $16.31 \mu\text{m}^{-1}$, respectively. Figure 1 shows the chemical structure of PSC-01.

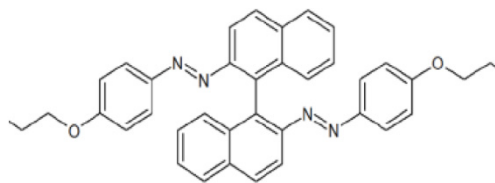


Fig. 1. Chemical structure of PSC-01.

Next, we added a left-handed chiral agent, Merck S-811, to the mixture. The concentration of PSC-01 and S-811 is 0.7 wt% and 3.8 wt%, respectively. Different concentration of black dichroic dye S428 (Mitsui, Japan) was incorporated into the mixture. After accurate weighing and mixing of components, the mixtures were heated to an isotropic phase and stirred for several minutes in order to dissolve fully. Then, the prepared sample mixture was filled into a LC cell, comprising of two glass plates. The cell gap was measured to be $9.1 \mu\text{m}$. The glass surface was spin-coated with a thin polymer layer to align the injected CLC mixture perpendicular to the glass substrates. The cell was then cooled down slowly to the room temperature ($\sim 23^\circ\text{C}$). In this experiment, we used two commercial light sources (UV and blue light) to irradiate the LC sample. The UV light source was Darkbeam UV365 LED lamp, whose central wavelength is 365 nm and FWHM (full-width at half-maximum) is 7 nm. The blue light source is a blue LED whose central wavelength is 450 nm. For the reversal process, we used a He-Ne laser beam whose wavelength is 633 nm. We used Deuterium halogen light source (DH-2000) and HR4000CG-UV-NIR spectrometer (Ocean Optics) to measure the spectrum and time dependent transmittance curve for our prepared cell before and after exposure. Microscopic images of our sample in both states were taken using Olympus BX51 polarizing optical microscope.

3. Result and discussion

The *trans*-azobenzene compounds (Fig. 1) dissolve well into ZLI-4788 without significantly disorganizing the molecular orientation of the LC host because the shape of this *trans*-molecule is similar to the nematic host. When the right-handed chiral azobenzene molecule is exposed to UV-blue light, it undergoes *trans-cis* photoisomerization. The UV-blue light exposure transforms the rod-shaped (*trans*-state) azobenzene molecule into higher energy kinked shape (*cis*-state). Such a higher energy kink-shaped *cis*-state can be transformed back to the original rod-shaped *trans*-state upon exposure to visible light or heat [20–23]. The helical twist power of this right-handed chiral compound doped LC host depends on the photoisomerization state. The *trans-cis* photoisomerization of chiral azobenzene compounds decrease the helical twist power. Chiral dopant structure and the molecular interaction between chiral dopant and nematic LC host control this helical twist power. A left-handed

chiral dopant S-811 was added to cancel the helical twisting power of *trans*-PSC-01. Therefore, in the initial state, there is no twist in the structure. Because the LC mixture is in vertical alignment, its initial state transmittance is the highest, i.e. lowest dye absorption. Upon photo-isomerization of blue/UV irradiation, a portion of *trans*-PSC-01 is promoted to *cis*-PSC-01 (lower helical twist power) while S-811 is unaffected. Thus, the overall helical twisting power is left-handed. The pitch length (P) of LC directors depends on the chiral concentration (C) and helical twisting power (β). In experiment, the pitch length can be approximated as $P = 1/(C \cdot \beta)$ [19]. The enhanced overall helical twisting power of the mixture will shorten the helical pitch value of the LC directors. In a given cell, a certain minimal pitch value can be achieved as $P_{th} = 2dK_{22}/K_{33}$ where K_{22} and K_{33} are the elastic constants for twist and bend deformations, respectively [24]. As in the photo-isomerization state, P is smaller than P_{th} , and the twisted cholesteric structure (fingerprint) is achieved due to the strong torque, which is larger than the elastic torque determined by orientational elasticity and anchoring. This leads to decreased transmittance due to dye absorption and scattering from the cholesteric directors. In the reversal process, when the sample is irradiated with a red light, *cis*-*trans* back isomerization of PSC-01 takes place and the increased helical twist power of *trans*-PSC-01 cancels out the left-handed twist power of S-811. Therefore, the overall twist power of the mixture decreases while P increases. When P is larger than the critical pitch, the chiral torque is too weak and the LC is reversed back to the initial (homeotropic) state. Thus, the cell become transparent again due to the minimal absorption and scattering.

Figure 2 depicts the structures and mechanism of our proposed photosensitive device. Figure 2(a) shows the distribution of LC directors and dichroic dyes in the structure when unexposed to UV-blue light. At this state, the LC directors and dyes are perpendicularly aligned to the glass substrate. For a dichroic dye, if the incident light polarization is parallel to the longer molecular axis, such a polarized light would be absorbed strongly. On the contrary, if the light's polarization is perpendicular to the dyes long axis, the absorption is much weaker. Hence, the transmittance is high. In our experiment, when the prepared cell is exposed to UV-blue light, isomerization takes place and the LC directors are reoriented from homeotropic state to fingerprint state, as Fig. 2(b) shows. Because of the doped chiral agent S811, the LC directors and dye molecules form cholesteric helical structure, where the helical axis is parallel to the substrate. Under such a condition, the dye molecules can absorb light polarized along the same axis. In addition, the light polarized perpendicular to the LC directors will still be absorbed slightly because the limited dichroic ratio of the dye molecules. In the cholesteric state, the orientation, which allows part of the directors to be perpendicular to the boundary, is the texture where the helix axis is parallel to the surface. In this state, the device not only absorbs (by the dye molecules) but also scatters the incident light (by the LC directors), resulting in a low transmittance. Unlike a traditional guest-host system, our proposed photo-switchable device only consumes power during dynamic switching and is stable in the absence of irradiation.

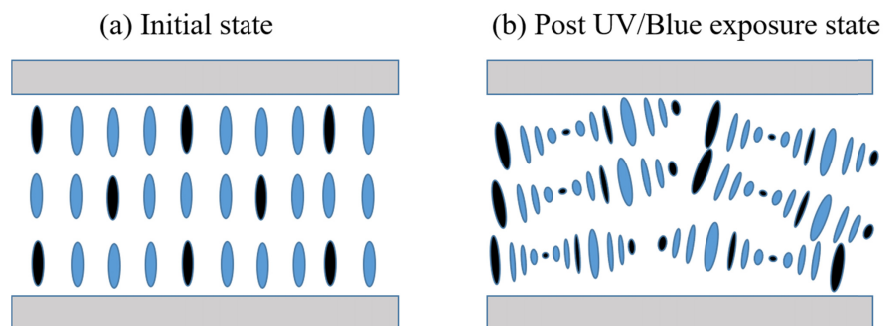


Fig. 2. LC director and dye orientations of the proposed photo-sensitive dimmer.

The reversal process from fingerprint state to vertical state can be carried out either by a longer wavelength light exposure or by heat. We measured the transmission spectra of our sample from 400 nm to 700 nm at the room temperature (23°C). Results are depicted in Fig. 3 for the sample containing 2wt% dichroic dye before and after UV exposure. At initial state (Fig. 2(a)), a relatively high transmittance (60-70%) is obtained in the visible spectral region because the absorption loss is minimal. The remaining optical loss is due to limited dichroic ratio of the employed dyes and order parameter, and surface reflections. As shown in Fig. 3, transmittance decreases significantly in the visible region after UV exposure. At $\lambda = 550$ nm, transmittance drops from 65.6% to 17.4% when the UV lamp was turned on. The LC directors and dyes are in fingerprint state at post exposure state as Fig. 2(b) depicts. As dichroic dye and LC directors are in fingerprint state, the LC cell turned into dark due to the absorption and scattering. The measured contrast ratio is about 4:1, which is quite typical for a guest-host display.

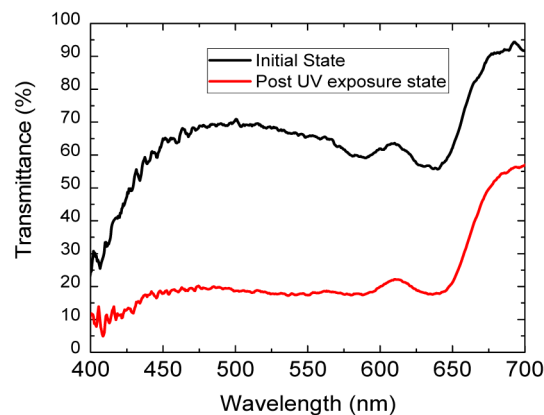


Fig. 3. Measured transmission spectra of our LC sample before and after UV exposure.

Figure 4 shows the images behind our photosensitive LC device before and after UV exposure. The dynamic transition is recorded in [Visualization 1](#). The images were taken under the lab yellow lighting environment. When the sample is not exposed to UV light (Fig. 4(a)), we can easily recognize the colored “UCF” because our dimmer is a broadband device. After UV exposure (Fig. 4(b)), the transmittance decreases but the image of “UCF” remains distinguishable because the transmittance stays at about 15-20%. The intermediate transmittance state can be achieved by controlling the UV dosage. Thus, this passive dimmer does not need an adaptive sensor and this is an important advantage of our device. Under strong UV light illumination, it gets darker. When the UV light is weak, the device becomes transparent. No sensor is needed which is similar to a photochromic glass.

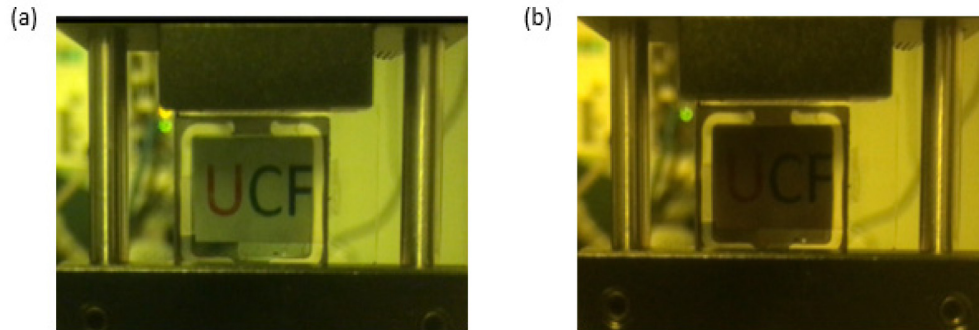


Fig. 4. See-through image of our smart dimmer: (a) before and (b) after UV exposure. The dynamic transition is recorded in [Visualization 1](#).

The switching time of our photosensitive guest-host device depends on the light dosage. Figure 5 shows the measured transmittance change ($\lambda = 550$ nm) as the UV exposure time increases. In Fig. 5, the red line represents the measured transmittance when the sample is exposed to a weak UV light ($\lambda = 365$ nm and intensity ≈ 0.12 mW/cm²), whereas black line shows the measured result using a strong UV light (intensity ≈ 0.5 mW/cm²). As the black line depicts, the transmittance declines from $\sim 65.6\%$ to $\sim 23\%$ at about 8s. Although slow, this result is comparable with commercial photochromic transition glass [5,25]. But when the sample is exposed to a weak UV light, the response time becomes slower, which takes 13.5s to drop to $\sim 23\%$ transmittance. As the UV light intensity increases, the number of photons increases, so does the probability of photo-chemical reaction. As a result, the turn-on time is faster. The response time can be further improved by using a faster azobenzene material [26].

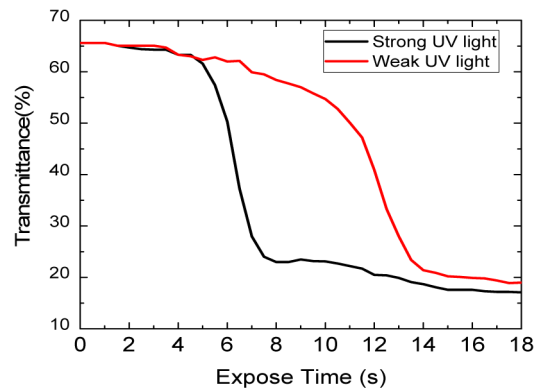


Fig. 5. Measured transmission vs. exposure time (UV light).

In addition to UV light, we also irradiated blue light to our guest-host CLC sample and measured the dynamic response. Results are plotted in Fig. 6, where the black line corresponds to the measured result for a strong blue light irradiation ($\lambda \approx 450$ nm and intensity = 2.57 mW/cm²) and red line represents a weak blue light exposure (intensity = 0.57 mW/cm²). From Fig. 6, it takes 16s to decrease the transmittance from $\sim 65.6\%$ to $\sim 23\%$ for a strong blue light exposure. This response time is longer than the corresponding UV light. For a weaker blue light exposure, the response time is even longer (~ 21 s). This means, our smart dimmer can be activated by either UV light or blue light, depending on the application needs. This is particularly important for vehicle displays because the majority of UV light is blocked by the windshield. Therefore, the commercial transition glass does not function well inside a car. Our CLC dimmer can be activated by blue light. Thus, it works inside a vehicle.

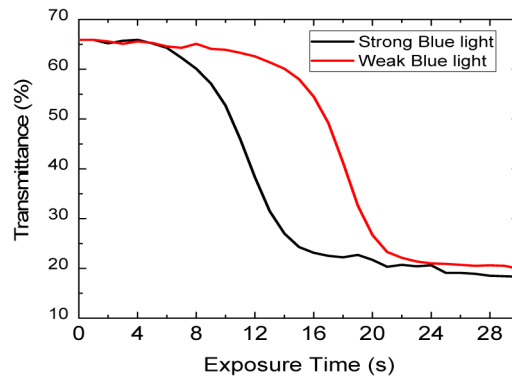


Fig. 6. Measured transmission vs. exposure time using a blue light $\lambda=450$ nm.

In order to measure the reversal time, we exposed our guest-host device using a red He-Ne laser beam ($\lambda = 633$ nm and intensity = 6.8 mW/cm²) at the post UV exposure state. In Fig. 7, we plot the transmittance change with respect to the laser exposure time. From Fig. 7, it takes ~ 42 s to change the transmittance from $\sim 20.7\%$ to $\sim 53.8\%$. Such a sluggish response time is due to the slow cis-trans transition of the employed chiral azobenzene molecules.

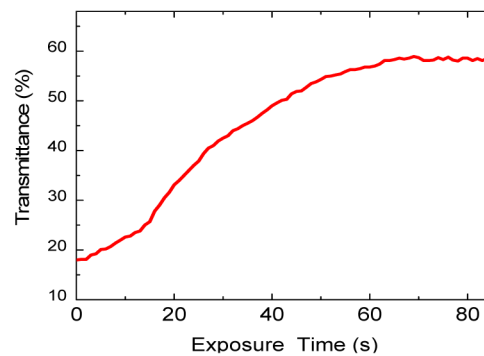


Fig. 7. Measured transmission vs. exposure time of reversal process using a red HeNe laser beam.

Next, we investigate how the dichroic dye concentration affects the transmittance and contrast ratio of our samples. To do so, we prepared four samples, S1-S4, by varying the S428 dye concentration from 2% to 3.5%. Table 1 lists the detailed concentration of each compound.

Table 1. Prepared 4 samples using different dichroic dye (S428) concentration (in wt. %)

Sample	S428	ZLI-4788	S-811	PSC-01
S1	2.0%	93.4%	3.8%	0.8%
S2	2.5%	92.9%	3.8%	0.8%
S3	3.0%	92.4%	3.8%	0.8%
S4	3.5%	91.9%	3.8%	0.8%

We characterized the transmittance of these four samples (S1-S4) before and after UV exposure. Figure 8(a) shows the measured transmittance (at $\lambda = 550$ nm) versus S428 concentration before and after UV exposure. As expected, transmittance decreases as the dichroic dye concentration increases in both pre and post UV exposure states. A higher concentration means more dyes in a given area, which in turn absorbs more light. In Fig. 8(b),

we plot the contrast ratio (CR) versus dichroic dyes concentration. As the dye concentration increases, CR increases. However, the trade-off is compromised transmittance.

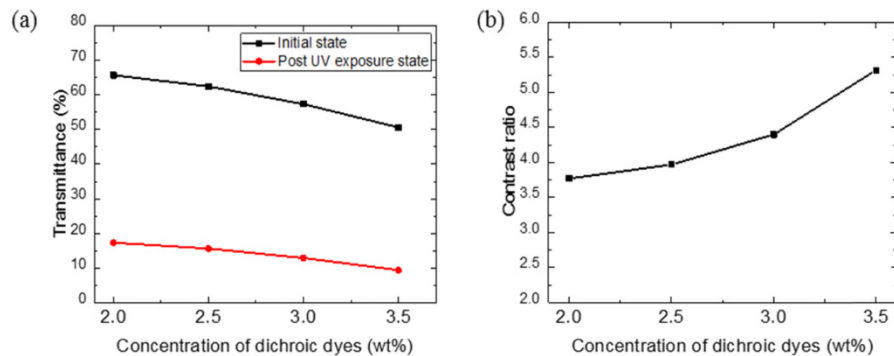


Fig. 8. (a) Measured transmittance vs. dye concentration before and after UV exposure. (b) Measured contrast ratio vs. dye concentration.

Finally, we inspected the CLC sample 1 (2% dye) under a polarizing optical microscope between crossed polarizers. Figure 9 depicts the microscopic images at pre and post UV exposure state. Before UV exposure (Fig. 9(a)), the LC directors and dye molecules are all perpendicular to the substrate surface. As a result, the image appears black. Figure 9(b) shows the post UV exposure state where the LC molecules and dyes are switched to fingerprint state (Fig. 2(b)). In this state, helical axis is parallel to the cell surface. The dark lines in Fig. 9(b) are the oil streaks where the cholesteric layers are bent [27].

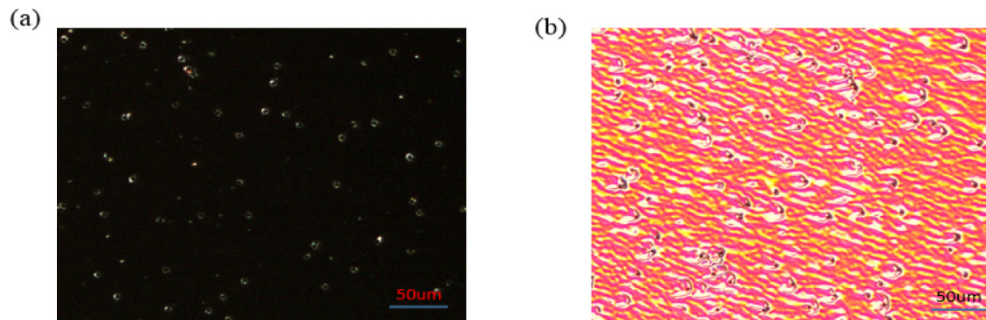


Fig. 9. Microscopic images of sample 1: (a) initial state, and (b) post UV exposure state.

4. Conclusion

We have demonstrated a dimmer using a photoresponsive azobenzene and dye-doped cholesteric liquid crystal. Unlike a commercial photochromic transition glass which can only be activated by UV light, our device can be activated by UV or blue light. The reversal process can be carried out by a longer wavelength light (red light) or by thermal effect. The dynamic response time is comparable with transition glass. Potential applications of such a dimmer for smart windows and automotive displays are foreseeable.

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Disclosures

The authors declare that there are no conflicts of interest related to this article.

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