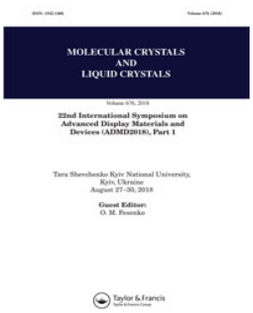

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Reversible dynamic full-color phototuning with a new chiral molecular switch containing linking group between chiral center and photosensitive group

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ABSTRACT

In this study, a new photoresponsive chiral molecular switch, where azobenzene was not directly connected to the axially chiral binaphthyl group, was successfully synthesized and used to induce helical superstructures in the achiral nematic liquid crystal (LC) host E7. Photoisomerization of the chiral molecular switch was carried out in both organic solvent and LC host upon light irradiation, contributing to the HTP difference at different photostationary states. The phototunable property of chiral molecular switch in E7 allowed dynamic, rapid and reversible tuning of the reflection color in cholesteric LC phase over the entire visible spectrum. The strategy breaks the restriction in common structures of photoresponsive chiral molecular switches, providing exciting insight into design for novel binaphthyl azobenzene derivatives with axial chirality.

KEYWORDS

Azobenzene; Cholesteric liquid crystals; Chiral molecular switch; Photoisomerization

1. Introduction

Apart from pigments and dyes, a profusion of colors in nature originate from the interaction of periodic biological structures with light, such as beetle carapaces, peacock feathers and butterfly wings [1–4]. Structural colors do not fade over time due to their unique structure-dependent property, which accordingly arouse extensive attention of scientists to exploit artificially synthesized structural colors. The self-assembled helical superstructure in cholesteric liquid crystals (CLCs) makes these materials promising for generating structural colors. The most outstanding character of CLCs is its selective reflection of light, which can be tuned through multiple external stimuli (heat [5], light [6–12], electric field [13–17], etc.). Thanks to the fast responsiveness, non-destructive property and remote precise controllability of light, phototunable CLCs are widely studied.

The most commonly used method to obtain phototunable CLCs is to dope a small amount of photoresponsive chiral molecular switches into a nematic liquid crystal (LC) host, where molecular chirality is transferred to phase chirality and the resulting helical superstructures selectively reflect light according to Bragg's law [18]. The selective reflection wavelength λ is defined by $\lambda = np$, where n is the average refraction index of LC materials and p is the pitch length of the helical superstructure. The ability of a

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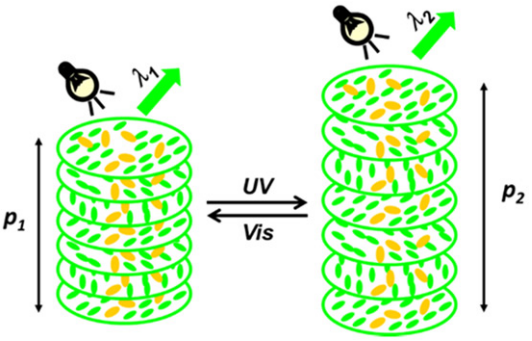

Figure 1. Schematic illustration of selective reflection of light in cholesteric liquid crystal and phototuning of pitch in helical superstructures.

chiral molecular switch to twist an achiral nematic LC is described as helical twisting power (HTP,β) following the equation $\beta = (pc)^{-1}$, where c is the molar or weight concentration of chiral molecular switches. The isomerization of chiral molecular switches under light irradiation causes change in HTP values at different photostationary states and thus controls reflection wavelength of CLCs (Figure 1), opening doors to applications in fields of tunable color reflectors and filters [12,19–21], optically addressed flexible displays [6,9,22,23], etc. The key character of those applications lies in the dynamic phototuning of reflection color over the entire visible light region, which requires photoresponsive chiral molecular switches to possess proper initial HTP values as well as HTP differences among different photostationary states.

Currently binaphthyl azobenzene derivatives with axial chirality are a group of intensively studied photoresponsive chiral molecular switches, because the axial chirality caused by the rotational barrier around naphthyl-naphthyl bond provides significant HTP values and azobenzene leads to suitable HTP differences among various states. Nevertheless, the existing chiral molecular switches that meet the above requirements mostly share the general structure, i.e. direct connection of azobenzene to the 2, 2' positions of axially chiral binaphthyl group [6,9–12], in which it is not easy to involve diversified azobenzene structure. The monotonic structures of these chiral molecular switches make it difficult to optimize structures towards more excellent properties. Besides, relatively high cost of crude materials (i.e. 1,1'-binaphthyl-2,2'-diamine) impede the applications of CLC for it is unrealistic to synthesize these chiral molecular switches on a large scale. Therefore, it is highly necessary to explore new molecules to rich the structure of chiral molecular switches, meeting the different requirements for application.

Here we report a novel photoresponsive chiral molecular switch **4** (Figure 2) differing from the common structures mostly reported. By adding one methylene spacer and rigid benzene between axially chiral 1, 1'-binaphthyl group and azobenzene, chiral molecular switch **4** allows structural diversity of photoresponsive chiral molecular switches. The design of this chiral molecule is based on the following points: 1) the steric hindrance resulting from the rigid benzene between 1, 1'-binaphthyl group and azobenzene as well as the rotational barrier from the naphthyl-naphthyl bond (i.e. the dihedral angle θ) play an important role in transferring the axially molecular chirality to LC phase [24], 2) conformational isomers of azobenzene offers HTP differences at

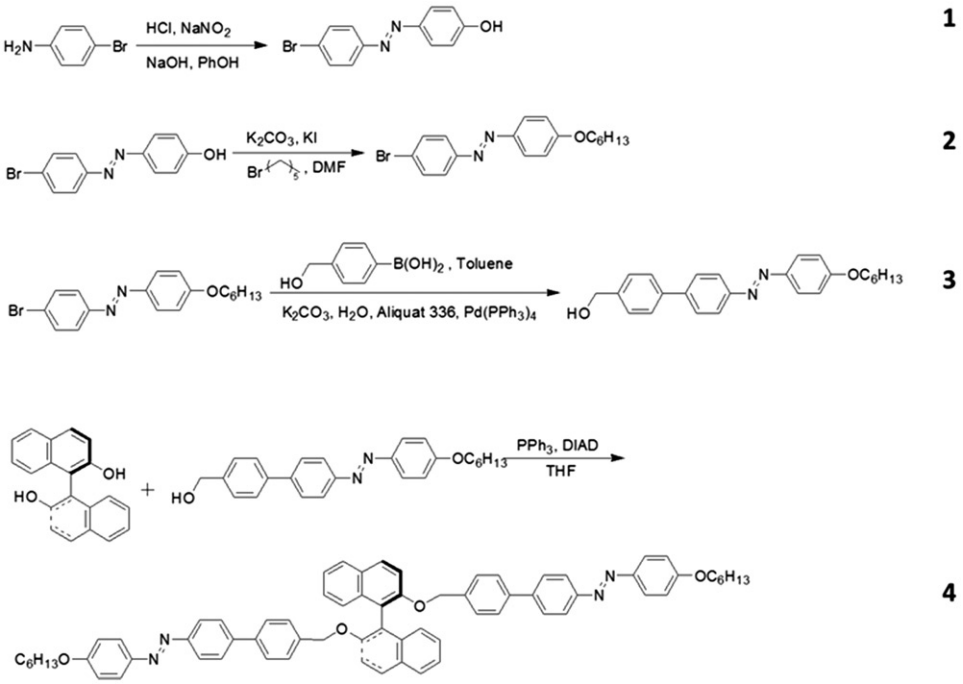

Figure 2. Synthetic route of chiral molecular switch **4**.

different photostationary states, 3) the rigid benzene between 1, 1'-binaphthyl group and azobenzene enhances geometrical variation of the chiral molecular switch under photoisomerization and hence induces larger HTP change, 4) two long methylene chains greatly improve its solubility in nematic LC host.

2. Experimental

Materials and Methods

In the syntheses of chiral molecular switch, common reagents and solvents were commercially available and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on 500 MHz Liquid NMR (AVANCE III HD) spectrometer in $CDCl_3$ or DMSO. Mass spectra were taken by Bruker McriOTOF11 Mass Spectrometer and Voyager-DE STR Mass Spectrometer. DSC (TA Q2000 Differential Scanning Calorimetry) was used to measure melting points, where heating and cooling rates were both 5 °C min^{-1}. UV-Vis absorption spectrum was measured by Perkin Elmer Lambda 650 Spectrometer. Circular dichroism (CD) spectra were measured by MM-450 CD spectrophotometer. Disclination lines, fingerprint texture and reflection color were recorded by Leika DM2500p Polarized Optical Microscopy. Reflection spectra and thermal relaxation were carried out by PG2000 PRO/NIR 2500 reflection spectroscopy.

Synthesis of chiral molecular switch 4

4-Bromoaniline (5g, 29 mmol) was dissolved in a solution of 6 mL concentrated HCl and 40 mL H_2O. A solution of sodium nitrite (2.07g, 29 mmol) in 40 mL H_2O was

added dropwise and stirred at 0 °C for 2 h. Then a solution of phenol (2.82 g, 29 mmol) and NaOH (1.2 g, 30 mmol) in 40 mL H_2O was added dropwise. The solution was stirred at 0 °C for 2 h. The suspension was then acidified with HCl solution and filtered. The precipitate was washed and dried over magnesium sulfate to get crude intermediate **1**. The mixture of crude intermediate **1**, 1-bromohexane (4.79 g, 29 mmol) and potassium carbonate (4.81g, 34.8 mmol) were dissolved in 100 mL DMF and heated to reflux at 110 °C for 4 h. The resulting mixture was cooled to room temperature (25 °C) and added great amount of H_2O to obtain precipitate. The precipitate was purified by chromatography (petroleum ether: dichloromethane = 4:1) to yield intermediate **2** as an orange solid (6.6 g, 18.33 mmol, yield 63.2%). m.p. 92.75 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, $J = 9.0$ Hz, 2H), 7.75 (d, $J = 9.0$ Hz, 2H), 7.62 (d, $J = 9.0$ Hz, 2H), 7.00 (d, $J = 9.0$ Hz, 2H), 4.04 (t, $J = 13.0$ Hz, 2H), 1.82 (m, 2H), 1.48 (m, 4H), 1.36 (m, 2H), 0.92 (t, $J = 14.0$ Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 162.04, 151.55, 146.72, 132.23, 124.92, 124.47, 124.07, 114.80, 68.44, 31.57, 29.16, 25.70, 22.60, 14.02; MALDI-TOF MS (M + H) calcd for $C_{18}H_{21}BrN_2O$: 361.1, found: 361.1

The mixture of intermediate **2** (2.12 g, 5.89 mmol) and 4-(hydroxymethyl)phenylboronic acid (1.34 g, 8.83 mmol) in 20 mL toluene was added a solution of potassium carbonate (4.88 g, 35.34 mmol) in 10 mL H_2O. The heterogeneous mixture was stirred at room temperature (25 °C) under an atmosphere of nitrogen. Then 10 droplets of methyltrioctylammonium and tetrakis(triphenylphosphine)palladium(0) (0.68g, 0.59 mmol) were added. The reaction was heated to reflux at 90 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified by chromatography (dichloromethane) to yield intermediate **3** as a yellow solid (1.61 g, 4.14 mmol, yield 70.3%). m.p. 91.37 °C; ^{1}H NMR (500 MHz, DMSO): δ 7.90 (d, $J = 9.0$ Hz, 2H), 7.88 (d, $J = 9.0$ Hz, 2H), 7.85 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.11 (d, $J = 9.0$ Hz, 2H), 4.55 (s, 2H), 4.08 (t, $J = 13.0$ Hz, 2H), 1.74 (m, 2H), 1.44 (m, 2H), 1.32 (m, 4H), 0.88 (t, $J = 14.5$ Hz, 3H); ^{13}C NMR (500 MHz, DMSO): δ 162.04, 151.69, 146.81, 143.05, 142.73, 137.97, 127.85, 127.59, 126.97, 125.02, 123.33, 115.62, 68.62, 63.14, 31.42, 29.05, 25.57, 22.47, 14.28; MALDI-TOF MS (M + H) calcd for $C_{25}H_{28}N_2O_2$: 389.2, found: 389.2

The mixture of intermediate **3** (0.5 g, 1.28 mmol) and diisopropyl azodicarboxylate (0.62 g, 3.09 mmol) was added dropwise to a mixture of (S)-(-)-1,1'-Bi-2,2'-naphthol (0.15 g, 0.52 mmol) and triphenylphosphine (0.81 g, 3.09 mmol) in THF at 50 °C under an atmosphere of nitrogen. Then the reaction was heated to reflux at 90 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified by chromatography (petroleum ether: dichloromethane = 1:4) to yield chiral molecular switch **4** as an orange solid (0.35 g, 0.34 mmol, 66.0%). m.p. 119.49 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (m, 8H), 7.94 (d, $J = 9.0$ Hz, 2H), 7.89 (d, $J = 8.5$ Hz, 4H), 7.65 (d, $J = 8.5$ Hz, 4H), 7.50 (d, $J = 9.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 4H), 7.39 (d, $J = 8.5$ Hz, 4H), 7.12 (d, $J = 8.0$ Hz, 4H), 7.03 (d, $J = 8.5$ Hz, 4H), 5.15 (m, 4H), 4.06 (t, $J = 13.5$ Hz, 4H), 1.83 (m, 4H), 1.49 (m, 4H), 1.36 (m, 8H), 0.92 (t, $J = 14.0$ Hz, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 161.77, 154.94, 151.97, 147.02, 142.50, 139.70, 136.51, 134.10, 133.87, 130.93, 129.89, 127.60, 127.47, 127.07, 126.44, 125.10, 124.77, 123.28, 123.01, 117.54, 116.03, 114.76, 71.00, 68.42, 31.59, 29.19, 25.71, 22.61, 14.03; MALDI-TOF MS (M + H) calcd for $C_{70}H_{66}N_4O_4$: 1027.5, found: 1027.5

3. Results and Discussion

Chiral molecular switch **4** was prepared in a facile synthesis route (Figure 2) starting from 4-bromoaniline which first reacted with phenol to give the azobenzene intermediate **1**, followed by coupling with 1-bromohexane to afford intermediate **2**. Intermediate **2** was then coupled with 4-(hydroxymethyl)phenylboronic acid through Suzuki Cross-coupling Reaction [25] to obtain intermediate **3**. Intermediate **3** was treated with the cheap axially chiral binaphthyl source (S)-(-)-1,1'-bi-2,2'-naphthol to yield the target molecule **4** by Mitsunobu Reaction [26]. These molecules were well-identified by ^{1}H NMR, ^{13}C NMR and high resolution MS.

Containing azobenzene groups in the structure, chiral molecular switch **4** exhibited fast and reversible photoresponsive behavior in both organic solvent and nematic LC host. A solution of chiral molecular switch **4** in CH_3Cl underwent fast *trans-cis* photoisomerization upon 365 nm light irradiation (3 mW cm^{-2}), transferring from the initial state ((*trans*, *trans*)-**4** in dominant ratio) to the 365 nm photostationary state ((*cis*, *cis*)-**4** in dominant ratio) in 24 seconds (Figure 3(a)). This was evidenced by the decrease in the maximum absorption around 365 nm indicating π-π^* transition together with the increase in the absorption around 450 nm representing n-π^* transition. Similarly, the reverse *cis-trans* isomerization process from the 365 nm photostationary state to the 530 nm photostationary state was achieved through 530 nm visible light irradiation

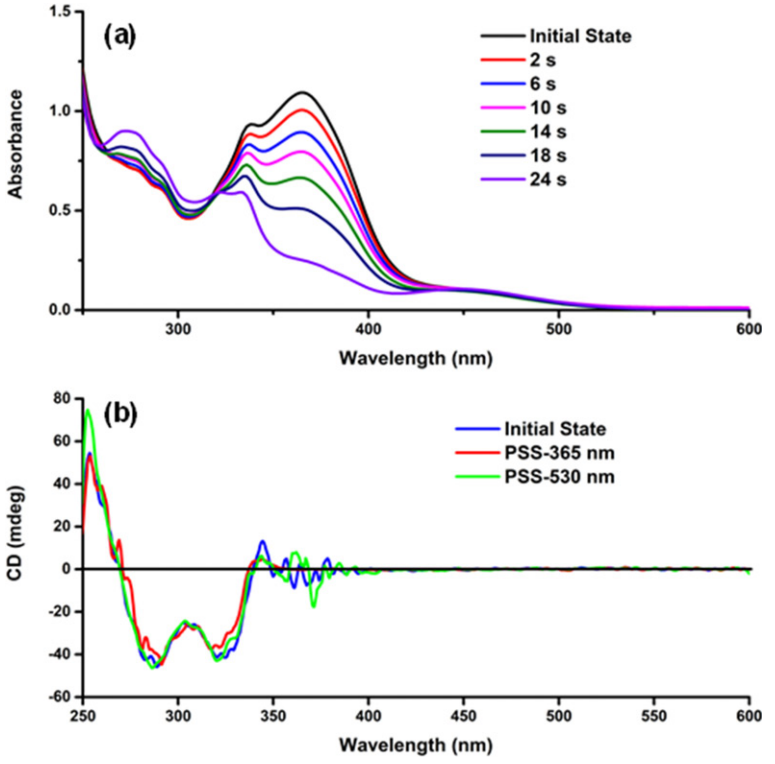

Figure 3. (a) Changes in UV-Vis absorption spectra of chiral molecular switch **4** in CH_3Cl (2×10^{-5} mol L^{-1}) under 365 nm light irradiation (3 mW cm^{-2}); (b) Changes in CD spectra of chiral molecular switch **4** in CH_3Cl (1×10^{-4} mol L^{-1}) under 365 nm light and 530 nm light irradiation.

(10 mW cm^{-2}) within 210 seconds. Apart from π-π^* and n-π^* transition bands of azobenzene chromophore, the bands between 250-350 nm represented short-axis polarizations (^1L_b and ^1L_a) of the 1, 1'-binaphthyl group. Circular dichroism (CD) spectroscopy was also used to identify the conformation of chiral molecular switch **4** and the effect of photoisomerization on conformational change. As shown in Figure 3(b), the positive cotton effect in CD spectrum proved the absolute S configuration of chiral molecular switch **4**. The CD spectrum showed two main regions of absorption: a) 250-350 nm with strong Cotton effect and b) over 350 nm with relatively weak Cotton effect. The former represented short-axis polarizations (^1L_b and ^1L_a) of the 1, 1'-binaphthyl group and the latter was caused by π-π^* and n-π^* transition of azobenzene chromophore, which was also indicated in UV-Vis spectrum as well. Upon 365 nm light irradiation, the absolute S configuration did not change, but intensity changed in both two main regions. CD band changes between 250-350 nm clearly indicated dihedral angle change in 1, 1'-binaphthyl group, while excitations of azobenzenzene over 350 nm in the CD spectrum illustrated *trans-cis* photoisomerization. In other words, light irradiation cannot change the overall configuration of chiral molecular switch **4**, but dihedral angle change upon photosiomerization is essential for creating HTP differences at different photostationary states [21,24,27].

When doped in a commercially available achiral nematic LC host E7 at a low concentration, chiral molecular switch **4** can induce self-organization of helical superstructures and formation of cholesteric LC phase. The HTP values were measured by Grandjean-Cano method [28]. Disclination lines were observed under polarized optical microscope and distance between them was measured for further calculation of HTP values. The initial HTP of chiral molecular switch **4** was 67 μm^{-1} and decreased by 29 μm^{-1} upon 365 nm light irradiation, indicating the enlargement of helical pitch in CLC phase. After exposure to 530 nm light, the helical pitch decreased and the HTP value of chiral molecular switch **4** returned to 66 μm^{-1}, which was almost equal to its initial value (Figure 4). Though the initial HTP of chiral molecular switch **4** is not very high, it didn't hinder the excellent phototuning performance of the chiral switch in LC phase. And this problem could be solved conveniently by introducing rod-like cyclohexyl-phenyl moieties that resemble the LC host structure, since they have better interaction with LC host and may bring about higher HTP values [29]. The reversible phototuning of pitches in helical superstructures as well as HTP values of chiral molecular switch **4** lay foundations for phototunable reflection color change.

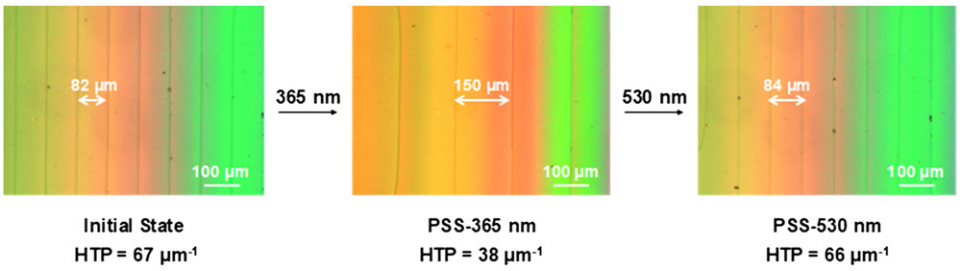

Figure 4. Polarized optical microscopy images of 0.47 mol% chiral molecular switch **4** in E7 in wedge cells, showing disclination lines and pitch changes upon light irradiation. (a) Initial state; (b) 365 nm photostationary state; (c) 530 nm photostationary state.

A mixture of 6.0 mol% chiral molecular switch **4** in nematic LC host E7 was capillary-filled in a 5 μm thick cell with planar alignment layer to induce the formation of homogenous aligned CLC phase. A black board was introduced on one side of the LC cell in order to avoid background light interference. Measured by reflection spectra, the wavelength of refection light ranged from blue light region across the entire visible spectrum to near infrared region after 365 nm light irradiation at 3 mW cm^{-2} light intensity (Figure 5). The reverse process from near infrared region to blue light region was achieved by 530 nm light irradiation at the same light intensity within several seconds, or it was realized by thermal relaxation in the dark at room temperature in approximately 28 h. As is shown in Figure 5, the reflection spectra have no palpable drawbacks such as fluctuation in peak intensity or distortion of peak shape. The cycle was repeated many times without obvious fatigue.

In addition, color change of the resulting CLC film induced by light irradiation was observed and recorded. When a mixture of 5.9 mol% chiral molecular switch **4** in nematic LC host E7 was capillary-filled in a 5 μm thick planar anchoring cell, reflection color of the resulting CLC film shifted rapidly between blue and red upon UV or visible light irradiation, covering the whole visible spectrum (Figure 6). The entire process was easily captured by a polarized optical microscope in reflective mode and no phase separation or coloration was observed. By carefully controlling the irradiation time, ratio of trans/cis isomers in chiral molecular switch **4** could be tuned continuously. Accordingly, color almost changed sequentially from blue to red in 18 seconds upon 365 nm light irradiation at intensity of 3 mW cm^{-2}, while the reverse process was achieved in 35 seconds upon 530 nm light irradiation at the same light intensity. Phototunable reflection color change over the visible spectrum is an ideal property for

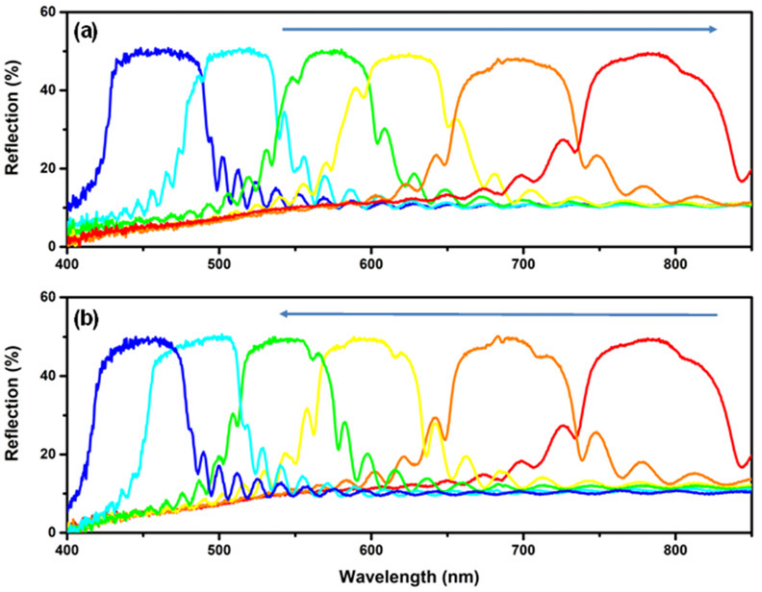

Figure 5. Reflection spectra of 6.0 mol% chiral molecular switch **4** in nematic LC host E7 in a 5 μm thick planar anchoring cell. (a) Upon 365 nm light irradiation at intensity of 3 mW cm^{-2}; (b) Upon 530 nm light irradiation at the same light intensity.

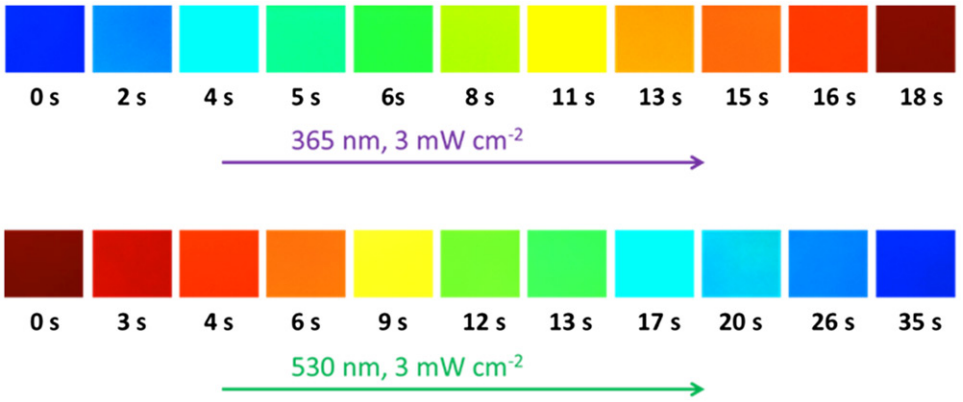

Figure 6. Reflection color change of 5.9 mol% chiral molecular switch **4** in nematic LC host E7 in a 5 μm thick planar anchoring cell under polarized optical microscope. (Top) Color change from blue to red in 18 seconds upon 365 nm light irradiation at intensity of 3 mW cm^{-2}; (Bottom) The reverse process achieved in 35 seconds upon 530 nm light irradiation at the same light intensity. (Bottom) Upon 530 nm light irradiation at the same light intensity.

optical devices. This rapid and reversible phototunable behavior could be mainly attributed to the excellent solubility of chiral molecular switch **4** in E7 and proper HTP difference between two photostationary states. The excellent solubility of chiral molecular switches is also a property urgently demanded for display applications.

4. Conclusions

In conclusion, we have successfully synthesized a novel photoresponsive chiral molecular switch **4** that can phototune reflection color reversibly and rapidly over visible spectrum. The unique structure of chiral molecular switch **4** broke through restriction in the classic structure of photoresponsive chiral molecular switches where azobenzene was directly connected to axially chiral binaphthyl group. Chiral molecular switch **4** was able to induce helical superstructures in the achiral nematic LC host E7 and thus form the cholesteric LC phase. Photoisomerization of chiral molecular switch **4** was carried out in both organic solvent and LC host upon light irradiation, contributing to the HTP difference at different photostationary states. The phototunable property of chiral molecular switch **4** in E7 allowed dynamic, rapid and reversible phototuning of the reflection color in CLC phase over the entire visible light region. These results provide exciting insight into design for novel binaphthyl azobenzene derivatives with axial chirality and widen applications of CLCs in optical displays.

Funding

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