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Reversible Light-Directed Red, Green, and Blue Reflection with Thermal Stability Enabled by a Self-Organized Helical Superstructure

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Supporting Information

ABSTRACT: Adding external, remote, and dynamic control to self-organized superstructures with desired properties is an important leap necessary in leveraging the fascinating molecular subsystems for employment in applications. Here two novel light-driven dithienylethene chiral molecular switches possessing remarkable changes in helical twisting power during photoisomerization as well as very high helical twisting powers were found to experience photochemically reversible isomerization with thermal stability in both isotropic organic solvents and anisotropic liquid crystal media. When doped into a commercially available achiral liquid crystal host, the chiral switch was able to either immediately induce an optically tunable helical superstructure or retain an achiral photoresponsive liquid crystal phase whose helical superstructure was induced and tuned reversibly upon light irradiation. Moreover, reversible light-directed red, green, and blue reflection colors with thermal stability in a single thin film were demonstrated.

Controlling the dynamic nature of molecular self-organization with an external stimulus is a challenge in science and technology that, when overcome, could lead to a breakthrough in the creation of new intelligent molecular devices. Among all the stimuli such as electric field, magnetic field, mechanical stress, temperature, or chemical reaction, light is particularly fascinating due to its advantages of remote, spatial, and temporal controllability. Light-driven chiral molecular switches or motors in liquid crystal (LC) media capable of self-organizing into optically tunable helical superstructures undoubtedly represent such a striking example.[1−5] Such a system can be achieved by doping photoresponsive chiral molecules into an achiral nematic LC host to self-organize into an optically tunable helical superstructure, i.e. a photoresponsive cholesteric LC phase. The resulting macroscopic helical superstructure can selectively reflect light according to Bragg's law and be tuned by light. The central wavelength λ of the selective reflection is defined by $\lambda = np$, where p is the pitch length of the helical structure and n is the average refraction index of the LC material. The ability of a chiral dopant to twist an achiral nematic LC phase, i.e. helical twisting power (HTP, β), is expressed as $\beta = (pc)^{-1}$ where c is the chiral dopant concentration. The isomerization of dopant molecules upon light irradiation can control the HTP and reflection wavelength λ of the cholesteric phase, providing opportunities as well as challenges in fundamental science that open the door for many applications such as tunable color filters,[6] tunable LC lasers,[7] and optically addressed displays that require no driving electronics and can be flexible.[8]

It is known that color change is a key feature of modern information display technology, which is currently achieved by the employment of subpixelated color (red-green-blue) filters overlaid onto pixelated LC light valves that effectively control the transmission of light through the color filter. Much effort is devoted toward developing red, green, and blue (RGB) reflection colors in cholesteric LC thin films, since light-directed RGB color change would be a viable alternative, whereas the dimensions of a subpixelated color (R, G, or B) in a single thin film can be limited only by the dimensions of light. However, to date reversible light-directed RGB color control driven by a chiral dopant has been limited to recent reports such as those employing chiral azobenzene dopants[3,4,8d] and overcrowded alkene as dopants,[5] where all the photoresponsive dopants experienced photoisomerization but were accompanied by competing thermal back relaxation. For example, azobenzenes can transform from *trans* form to *cis* form upon UV light irradiation whereas the reverse process can occur thermally or photochemically. The slow but unavoidable thermal relaxation gives rise to the problem of lack of stability and controllability. Undoubtedly, the discovery of new light-driven chiral molecular switches capable of having good thermal stability as well as reversible phototuning of RGB reflection color and beyond in an induced helical superstructure is of great importance to practical applications. Furthermore, it is highly desirable to direct RGB color changes with only small amounts of a light-driven chiral switch since a high concentration of chiral dopant can often lead to phase separation and coloration and alter the desired physical properties of the LC host. This requires the dopant to have high HTP as well as a significant difference in HTP among the various states of the switch.

Dithienylethenes are a well-known family of photochromic compounds. Upon UV irradiation, they can transform from a colorless ring-open form to its colored ring-closed form. Their reverse isomerization process is thermally stable and occurs only photochemically by visible light irradiation. The excellent fatigue resistance and superior thermal stability of both open and closed forms make dithienylethenes especially promising candidates for technological applications. However, their applications as chiral dopants are limited by either low HTPs

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or/and minor HTP changes in photoisomerization.[9] Here we report two new enantiomeric dithienylethene switches with axial chirality, (*S*,*S*)-**1** and (*R*,*R*)-**1** (Figure 1), which not only possess very high HTPs at its initial state but also show a remarkable increase in HTP from open form to its closed form upon UV irradiation (Figure 2).

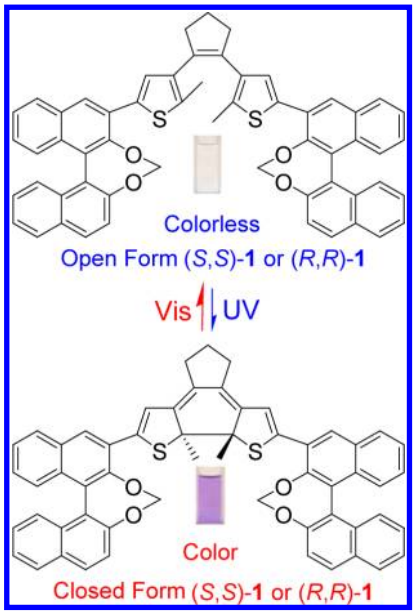

Figure 1. Photoisomerization of dithienylcyclopentene chiral switches (*S*,*S*)-**1** or (*R*,*R*)-**1**. Note: The photoisomerization generates two diastereomers with (*S*,*S*) and (*R*,*R*) configuration of the two new chiral centers (see Supporting Information Figure S7). Inset: color change from colorless to purple upon UV irradiation.

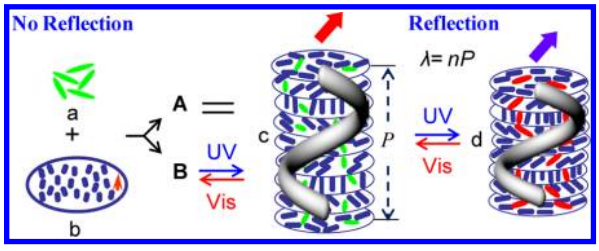

Figure 2. A schematic mechanism of the reflection wavelength of light-driven chiral molecular switch (*S*,*S*)-**1** or (*R*,*R*)-**1** in an achiral nematic LC media reversibly tuned by light. (a) Light-driven chiral switch; (b) achiral nematic host; (c and d) photoresponsive chiral nematic phase with pitch length decrease from c to d. (A) Immediately induce helical superstructure c and (B) retain a photoresponsive achiral phase whose helical superstructure is induced and tuned reversibly with light irradiation.

The chiral switch (*S*,*S*)-**1** and its enantiomer (*R*,*R*)-**1** were prepared in a facile synthesis. Their chemical structures were identified by ^{1}H and ^{13}C NMR, high resolution MS, and elemental analysis (see Supporting Information). They exhibited photochemically reversible but thermally stable behavior in both organic solvents and liquid crystal media. For example, the solution of (*S*,*S*)-**1** in hexane was colorless, which is consistent with its UV−vis spectrum, i.e. no absorption in the visible region at the initial state (see Supporting Information Figure S8). Upon UV irradiation at 310 nm, the solution color changed immediately from colorless to fresh purple due to its photoisomerization from the open form to closed form. Accordingly, there was a gradual decrease seen in the maximum absorption at 282 nm with a concomitant appearance of a new absorption band around 550 nm. The photostationary state ($PSS_{310\ nm}$) was reached in 60 s. The irradiated state was thermally stable and was able to photochemically switch back to its initial state by visible light irradiation at 550 nm for 15 min (see Supporting Information Figure S9). The excellent fatigue resistance was confirmed by repeated irradiation of the solution with UV and visible light. No obvious degradation was observed after many cycles (see Supporting Information Figure S10).

As expected, the CD spectra of (*S*,*S*)-**1** and (*R*,*R*)-**1** exhibited a mirror image relationship (Figure 3). The strongest

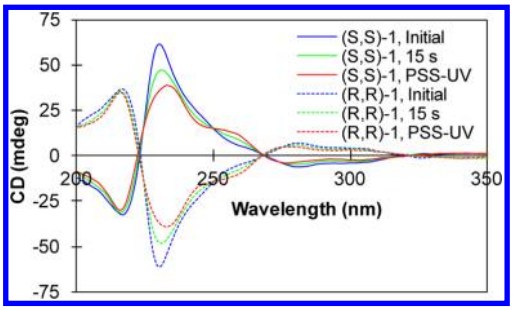

Figure 3. CD spectra changes of (*S*,*S*)-**1** and (*R*,*R*)-**1** (3 μM in hexane) upon UV irradiation at 310 nm.

bisignated exciton couplet between 200 and 240 nm is due to the coupling of the two $^{1}B_{b}$ transitions located on distinct naphthalene rings, while the couplet at around 280 and 310 nm is related to the $^{1}L_{a}$ and $^{1}L_{b}$ transitions of naphthalene.[10] Upon UV irradiation, the exciton couplet at 230 nm weakened significantly while a shoulder exciton developed at 260 nm. The distinct changes gave clear evidence that the chiroptical properties of this compound can be modulated by light.

Doping (*S*,*S*)-**1** into an achiral nematic LC host E7 even at a very low concentration (0.7 wt %) can immediately induce a chiral nematic mesophase with a characteristic fingerprint texture (Figure 4A). Interestingly, when doped at a lower

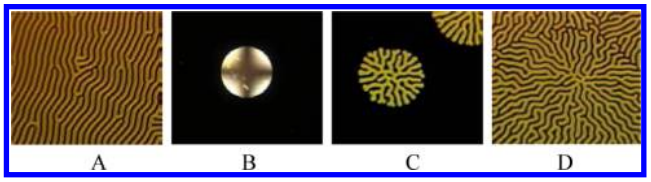

Figure 4. Crossed polarized optical textures of 0.7 wt % (A) and 0.4% (B, C, and D) (*S*,*S*)-**1** in E7 in a 5 μm thick homeotropic aligned cell. Upon UV irradiation at 310 nm with different time: 0 s (A, B), 5 s (C), and 30 s (D). Inset: Conoscopic texture (B).

concentration (0.4 wt %), the resulting mixture retained an achiral nematic phase, as evidenced by the characteristic black texture in a homeotropic aligned cell with the inset conoscopic observation (Figure 4B). Upon irradiation at 310 nm, the fingerprint texture gradually appeared (Figure 4C and 4D), indicating the formation of a cholesteric phase and the increase in HTP. The reverse process happened upon visible light irradiation at 550 nm.

The HTPs of (*S*,*S*)-**1** and (*R*,*R*)-**1** in two commercially available nematic LC hosts and the changes in HTP upon light irradiation were determined by the Grandjean−Cano method[11]

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and summarized in Table 1. (*S*,*S*)-**1** induced a right-handed helix whereas (*R*,*R*)-**1** induced a left-handed helix. Upon UV

Table 1. HTPs of Chiral Dopants (*S*,*S*)-1 and (*R*,*R*)-1 at Different States in Nematic LC Host

		HTP β_M (μm^{-1})			
dopant	LC host	initial	PSS_{UV}	PSS_{vis}	$\Delta\beta/\beta$
(*S*,*S*)-**1**	E7	+104	+153	+105	47%
(*S*,*S*)-**1**	5CB	+109	+156	+113	43%
(*R*,*R*)-**1**	E7	−104	−153	−105	47%
(*R*,*R*)-**1**	5CB	−109	−156	−113	43%

irradiation, the HTP of (*S*,*S*)-**1** in E7 increased from 104 to 153 μm^{-1} which could be almost switched back to its initial state with 105 μm^{-1} HTP upon visible light irradiation at 550 nm. Of significance are the unusually high HTP values and the remarkable increase in HTP upon UV irradiation that (*S*,*S*)-**1** and its enantiomer (*R*,*R*)-**1** exhibited in the two LC hosts.

It is established that the dihedral angle (θ) of two naphthalene rings in binaphthyl derivatives plays a key role in their cholesteric induction abilities. The unusual high HTPs of these two compounds might originate from the bridged binaphthyl unit, which is significantly more efficient for helicity induction than unbridged ones due to its rigid structure and quite narrow dihedral angle (around 60°).[12] The handedness of the cholesteric phase observed for (*S*,*S*)-**1** is also in accordance with the fact that *S* configuration binaphthyl derivatives normally induced a left-handed helix in CLCs with $\theta > 90°$, while right-handedness is only observed when $\theta < 90°$. As indicated by CD spectra changes (Figure 3), although the binaphthyl units are fixed with a methylene tether and thus have less flexibility, a slight variation of the dihedral angle is also possible ($\Delta\theta \sim 5°$).[13] The dramatic increase in HTP upon UV irradiation can be ascribed to this dihedral angle change and the possible overall conformation change of the molecule caused by photoisomerization.

Encouraged by the high HTPs as well as the remarkable variation in HTP value upon light irradiation, a mixture of 7.7 wt % of (*S*,*S*)-**1** in LC E7 was capillary-filled into a 5 μm thick planar aligned cell which was painted black on one side. Surprisingly, reversible light-directed RGB reflection colors with thermal stability were achieved in the cell (Figure 5 top). The reflection central wavelength was around 630 nm at the initial state. Upon UV irradiation, its reflection wavelength was tuned to 530 nm in only 10 s and further reached a photostationary state in 25 s with a reflection central wavelength at 440 nm (Figure 5 bottom). This photostationary state was thermally stable and was able to photochemically switch back to a nearly initial state by visible light irradiation at 550 nm within 2 min. The reversible tuning of reflection across RGB reflection colors was repeated many times without noticeable degradation. When this cell was stored in the dark at any irradiated state, no observable change was found in both reflection color and reflection wavelength, even after one week, which results from the excellent thermal stability of (*S*,*S*)-**1**. Furthermore, three primary RGB colors can be observed simultaneously in a single thin film based on different UV irradiation times (Figure 6 D and E) facilitated by masking at different areas: red, no irradiation; green, irradiated for 10 s; blue, irradiated for 25 s. After driving the background color to blue by UV irradiation, the red and green reflection colors can be recorded through visible light irradiation for different times

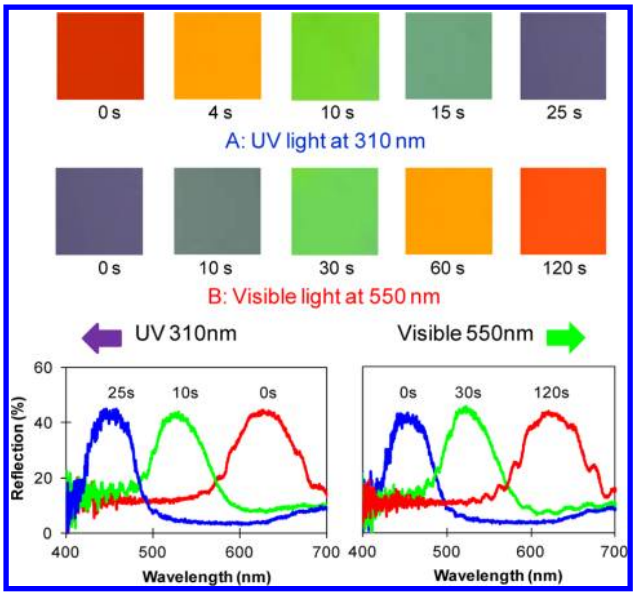

Figure 5. (Top) Reflection color images of 7.7 wt % (*S*,*S*)-**1** in E7 in a 5 μm thick planar cell taken from a polarized reflective mode microscope. (A) Upon UV irradiation at 310 nm (30 mW/cm^2) and followed by (B) upon visible irradiation at 550 nm (30 mW/cm^2). (Bottom) Reflective spectra of 7.7 wt % (*S*,*S*)-**1** in E7 in a 5 μm thick planar cell at room temperature. (Left) Upon UV irradiation at 310 nm (30 mW/cm^2) for different times. (Right) Upon visible light irradiation at 550 nm (30 mW/cm^2) for different times.

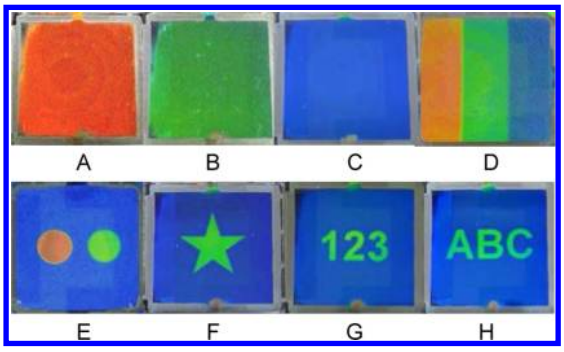

Figure 6. Real cell images of a 8 μm thick planar cell (2.1 cm ×2.5 cm) filled with 7.7 wt % (*S*,*S*)-**1** in E7.

respectively. Moreover, the optically addressed images can be erased by light irradiation when desired, and the cell is rewritable for many times due to the excellent fatigue resistance.

In conclusion, two novel enantiomeric light-driven dithienylethene chiral switches with axial chirality were designed and synthesized. They possessed a remarkable change in HTP during photoisomerization as well as an unusually high HTP, which are significantly larger than the HTPs previously reported for chiral dithienylethenes. The switches exhibited photochemically reversible switching between open and closed forms with good thermal stability in both isotropic organic solvents and anisotropic LC media. When doped in an achiral nematic LC with a larger concentration, the switch was able to immediately induce a helical superstructure that was reversibly tunable upon light irradiation. However, when doped in an achiral nematic LC with a lower concentration, it retained an achiral LC phase whose helical superstructure was induced upon light irradiation and vice versa. Furthermore, reversible

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light-directed red, green, and blue reflection colors with thermal stability in a single thin film were demonstrated. Of significance are the superior thermal stability and excellent fatigue resistance of the light-directing tuning of the self-organized helical superstructure in a controllable way, which are important for practical applications.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis, chemical data, 3D molecular structures at open and closed forms, measurement of pitch and HTP, ^{1}H NMR changes before and after UV irradiation, and copies of ^{1}H and ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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