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Photodynamic Chiral Molecular Switches with Thermal Stability: From Reflection Wavelength Tuning to Handedness Inversion of Self-Organized Helical Superstructures**

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The ability to tune and control self-organized superstructures with desired properties using an external stimulus is a major driving force in the bottom-up nanofabrication of intelligent molecular devices.[1] Light-driven chiral molecular switches or motors in liquid crystal (LC) media that are capable of self-organizing into an optically tunable helical superstructure, namely photoresponsive cholesteric LCs (CLCs), are such striking examples.[2] Helical superstructures of CLCs are characterized by both handedness and the helical pitch P. Handedness describes the direction in which the molecular orientation (director) rotates along the helical axis, and P is defined as the distance over which the director rotates by a full 360°. The most important property of CLCs is the selective reflection of circularly polarized light (CPL): When unpolarized light propagates through the CLC medium, only CPL with the same handedness as the helix is reflected, and the reflection wavelength can be determined by $\lambda = nP$, where n is the average refractive index of the LC medium. The light-induced pitch change and the resulting reflection wavelength tuning of CLCs have found widespread applications in color filters and reflectors,[3] tunable lasers,[4] and reflection displays that require no driving electronics and can be flexible.[5] Furthermore, the ability to control the chirality of CLCs with a helix inversion in response to light holds great potential for the development of stimuli-responsive materials for technological applications in areas where CPL is involved.[3–6]

Photoresponsive CLCs can be formulated by doping chiral photochromic molecules into an achiral nematic LC host. The resulting mixture can self-organize into a helical superstructure.[2] The ability of a chiral molecule to impart a twist to a nematic phase is quantified as the helical twisting power (HTP, β) and expressed by the equation $\beta_M = 1/(PC)$, where C is the molar concentration of the chiral dopant. Photoisomerization of the chiral dopant results in changes in molecular conformation and HTP, which may lead to a change in the pitch length or handedness of the CLC. Through this mechanism, the properties of CLCs can be reversibly modulated by light (Figure 1).

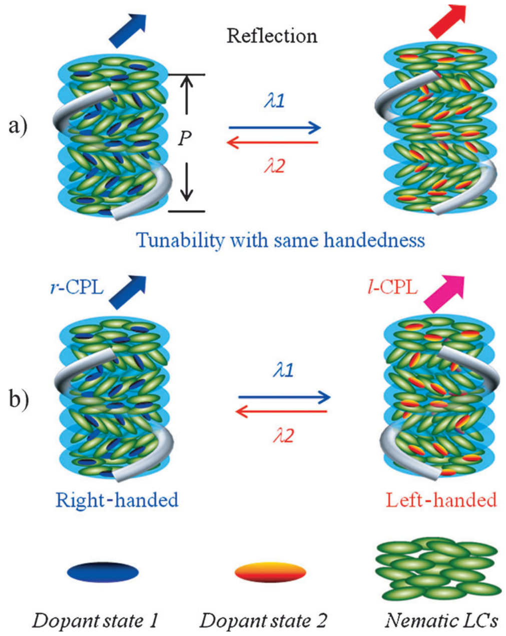

Figure 1. Pitch length tuning (a) and handedness inversion (b) of light-driven chiral molecular switches or motors in an achiral nematic LC medium that are reversibly and dynamically tuned by light.

Binaphthyl derivatives are powerful inducers of helicity in achiral nematic LCs.[7] Because of the restricted rotation along the C1−C1′ axis, binaphthyl derivatives are stable in different conformations. The dihedral angle (θ) between the two naphthalene moieties in a binaphthyl derivative plays a key role in determining their cholesteric induction ability or HTP (Figure 2).[8] Bridged binaphthyl derivatives generally exhibit a *cisoid* conformation ($\theta < 90°$), and non-bridged

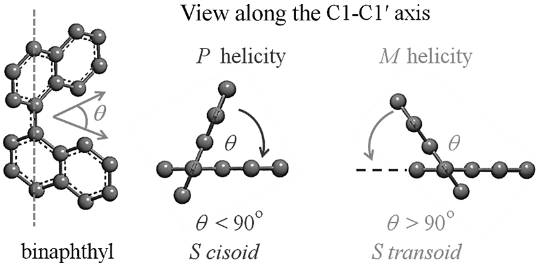

Figure 2. Different conformations of binaphthyl and handedness of induced CLCs.

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binaphthyls are stable in *transoid* conformations ($\theta > 90°$). Both conformations can efficiently induce chirality into a nematic phase, but with opposite handedness. For example, the *cisoid* form of (*S*)-binaphthyl has *P* helicity and induces a right-handed CLC, whereas its *transoid* form has *M* helicity and results in a left-handed CLC. Vice versa, the *cisoid* and *transoid* forms of (*R*)-binaphthyl induce left-handed and right-handed CLCs, respectively.[9] The photomodulation of θ and the resulting changes in molecular conformation have been utilized to tune the reflection or handedness of CLCs by using binaphthyl-derived chiral azobenzene dopants that display *trans–cis* photoisomerization.[10] However, these systems suffer from thermal relaxation of the *cis* isomers of the azobenzenes, which gives rise to a lack of stability and controllability. Compared with azobenzenes, diarylethenes are of particular interest because of their excellent fatigue resistance and thermal stability in both states, which make them ideal candidates for functional materials for applications.[11] However, only a few chiral diarylethene dopants have been reported to date.[12] We previously developed a dithienylcyclopentene dopant that bears two methylenedioxy-bridged binaphthyl moieties.[12g] Herein, we report our new findings on related compounds that entail different bridge lengths in their binaphthyl units. Three new compounds, namely (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c**, were synthesized (Figure 3). The molecular design was based on the fact that 1) bridged binaphthyl derivatives normally exhibit higher HTPs than the non-bridged versions because of their narrow dihedral angles;[9] and that 2) an increase in bridge length may lead to relatively more-flexible structures with larger phototunabilities. Further insight into the structure–property relationships could also be gained. It was found that variations of the bridge length resulted in significantly different photoresponsive properties in LC media. Compounds (*S*,*S*)-**6a** and (*S*,*S*)-**6b** not only exhibited much higher HTPs than previously reported diarylethene dopants,[12g–i] but also experienced a dramatic decrease in HTP during photoisomerization. More importantly, with a continued increase in the bridge length to butylenedioxy, (*S*,*S*)-**6c** was found to be able to induce a reversible handedness inversion in different LC hosts with moderate to high HTPs in both states.

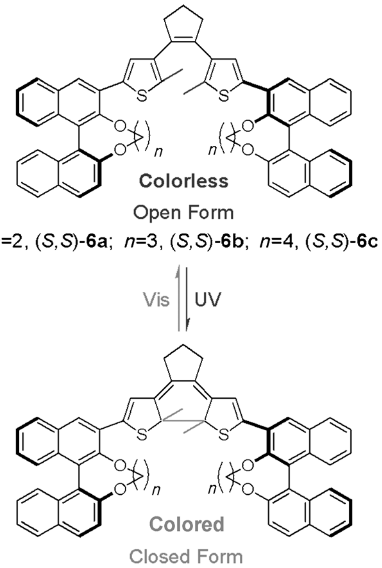

Figure 3. Molecular structures and photoisomerization of the axially chiral diarylethene dopants (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c**.

Compounds (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c** were prepared by a facile synthesis starting from (*S*)-1,1′-bi(2-naphthol) and 2-chloro-5-methylthiophene (Supporting Information, Scheme S1). As expected, all of these compounds exhibited typical photochromic behavior in organic solvents, as was confirmed by absorption spectra (Figure S1). Upon UV irradiation at 310 nm, they can transform from open forms into closed forms with the color of the solution changing from colorless to purple. NMR studies revealed that the photochemical conversions of (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c** were 93 %, 97 %, and 98 % (Figures S4, S5, and S6), respectively. The closed forms are thermally stable and can be switched back to the open forms by irradiation with 550 nm light. The reversible switching process can be repeated for many cycles without obvious degradation (Figure S3). The combination of the neat photoisomerization process with the excellent fatigue resistance is the feature that enhances the switching performance.

During photoisomerization, distinct changes in the CD spectra were also observed (Figure S2), which provides clear evidence that the chiroptical properties of these molecules can be modulated by light.[13] The photoisomerization of diarylethene molecules generates a pair of enantiomers, with *S*,*S* or *R*,*R* configurations of the two new chiral centers derived from an anti-parallel style of the open form.[11] In the presence of axial chirality on the binaphthyl units, the closed form exists as two diastereomers with configurations of *S*,*S*,*S*,*S* and *S*,*R*,*R*,*S* (Figure S4, S5, and S6). However, in the CD spectra, no Cotton effects that correspond to the absorption bands of the closed forms of all three compounds were observed in the visible region, indicating that no diastereoselective photoisomerization occurred during the photoisomerization process. Therefore, the chiroptical properties of (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c** and the related changes upon UV irradiation are mainly attributed to the conformational change of the binaphthyl units and the variation in dihedral angle.[12f]

After investigating the photoisomerization process in organic solvent, we examined the performance of the diarylethene derivatives as chiral dopants in LC hosts. At first, a mixture was fabricated by doping only 0.3 mol % of (*S*,*S*)-**6a** into commercially available nematic LC E7. With a polarized microscope, a cholesteric phase was immediately detected; the characteristic fingerprint and oily streak textures could be observed even at such a low doping concentration (Figure S7),[14] indicating that (*S*,*S*)-**6a** exhibited very high HTP in the initial state. The pitch length of the cholesteric helix and the HTPs of the dopants were measured by the method of Cano.[15] When mixtures of E7 doped with (*S*,*S*)-**6a** or (*S*,*S*)-**6b** were filled into wedge cells, the photoinduced pitch change was directly detected by broadenings of the distances between Cano's lines upon UV irradiation (Figure S8). The HTPs of

(*S*,*S*)-**6a** and (*S*,*S*)-**6b** in E7 were calculated to be 166 μm^{-1} and 139 μm^{-1}; these values decreased to 128 μm^{-1} and 94 μm^{-1} upon UV irradiation.

Inspired by the high HTPs as well as by the pronounced change in HTPs upon UV irradiation, we were determined to tune the reflection wavelength of induced CLCs in the visible region. A mixture of (*S*,*S*)-**6a** (2.0 mol %) in E7 was filled into a 5 μm thick planar cell by capillary action. The initial reflection wavelength of this cell is approximately 480 nm, and a blue reflection could be observed (Figure 4). Upon UV irradiation, the reflection wavelength was tuned to 550 nm in 20 s, and the cell exhibited green reflection. Further irradiation tuned the reflection wavelength to 620 nm with a red reflection at the photostationary state (PSS). The irradiated state was thermally stable and can be photochemically switched back by 550 nm irradiation for 240 s. The red-shift in reflection wavelength upon UV irradiation is due to an increase in pitch length and a decrease in HTP. In this system, the change is from blue to red upon UV irradiation; in our previously reported system, UV irradiation caused a red to blue color change.[12g] This tuning process here may thus provide another viable alternative for bidirectional complementary color modulation and may significantly broaden the application of diarylethene dopants.

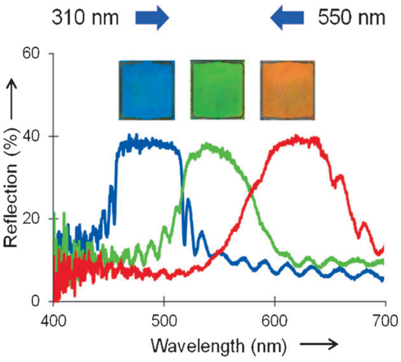

Figure 4. Phototuning of the reflection spectrum of (*S*,*S*)-**6a** (2.0 mol %) in commercially available E 7 in a 5 μm thick planar cell at room temperature. Inset: Images of the real cells that show the reflection colors corresponding to the reflection spectra.

The reversible phototuning of reflection colors was repeated many times without noticeable degradation. When this cell was stored in the dark at any irradiated state, no obvious changes in reflection wavelength or reflection color were observed after several days, which demonstrates the excellent thermal stability of the compounds. Furthermore, different reflection colors can be displayed in the same cell by masking different areas, which may also allow information to be written into the cell (Figure S9). The optically addressed images are stable in ambient environments for several days and can be erased by light irradiation when desired. The cell may be rewritten many times because of its excellent fatigue resistance.

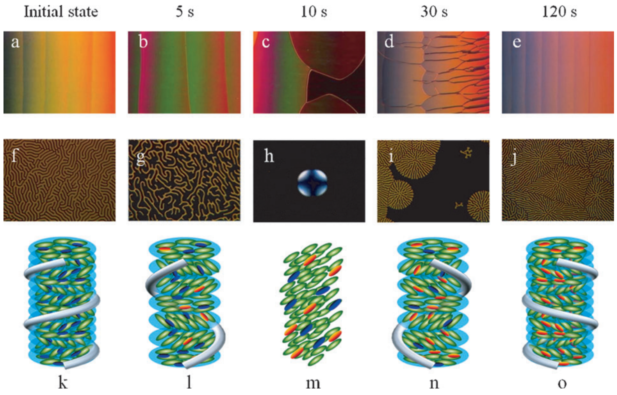

Figure 5. A change in handedness of (*S*,*S*)-**6c** (0.8 mol %) in 5 CB was observed upon UV irradiation in a wedge cell (a–e) and in a homeotropic cell (f–j; conoscopic observation for (h)); illustrations of the corresponding liquid crystal phases (k–o).

Interestingly, when a LC mixture of (*S*,*S*)-**6c** (0.8 mol %) in 5CB was filled into a wedge cell and irradiated with UV light, the Cano's lines moved outwards, which indicates an increase in pitch length (Figure 5 a,b); the lines disappeared within 10 s, and an apparently nematic phase (infinite-pitch CLC) was observed in the wedge cell as a result of the destruction of the induced cholesteric phase (Figure 5 c). Upon further irradiation with UV light, an oily streak texture of the CLC was observed (Figure 5 d), and Cano's lines were re-formed at PSS within 2 min (Figure 5 e). The same phase-transition behavior was also observed in a homeotropic cell. When the same mixture was filled into a homeotropic cell, the typical fingerprint texture of a cholesteric phase was clearly observed for the initial state with a polarized optical microscope (Figure 5 f). Upon UV irradiation at 310 nm, the fingerprint texture gradually disappeared (Figure 5 g), and the appearance of a transient nematic phase was confirmed by conoscopic observation (Figure 5 h). Continued irradiation resulted in the reappearance of the fingerprint texture (Figure 5 i,j), which indicates the formation of another cholesteric phase with opposite handedness. This cholesteric–nematic–cholesteric phase-transition sequence is actually a sign of the inversion of the cholesteric handedness.[16] Helix inversion occurs when the helix of one handedness unwinds, with a helicity of zero at a certain point, and then forms a helix of the opposite handedness (Figure 5 k–o). The phase-transition sequence observed is reversible upon visible-light irradiation at 550 nm as a result of the reverse isomerization of (*S*,*S*)-**6c** from its closed into its open form.

To observe the opposite helicity of two states, the handedness of CLCs was examined by the contact method,[17] which is based on the miscibility of two CLCs, and the observation of the mixing boundary of two CLCs. In our experiment, (*S*)-2,2′-methylenedioxy-1,1′-binaphthyl (MDB) was used as the standard dopant, as it is known to induce a right-handed CLC in nematic LC5CB owing to a *cisoid* conformation of the bridged binaphthyl.[8] The mixing area of CLCs induced by (*S*,*S*)-**6c** and MDB exhibited a continuous pattern (Figure S10), indicating that (*S*,*S*)-**6c** induced a right-handed CLC in its initial state. By using this method, the handedness of (*S*,*S*)-**6c** in the UV-irradiated state was determined to be left-handed by the appearance of a discontinuous boundary. These results provide direct evidence that the handedness of a CLC induced by (*S*,*S*)-**6c** inverted upon UV irradiation as a result of the photoisomerization of the open form into the closed form.

The HTPs of all three compounds in different states were measured with three commercially available LC hosts (Table 1). The positive and negative signs represent right-handedness and left-handedness, respectively. Compounds (*S*,*S*)-**6a** and (*S*,*S*)-**6b** were found to exhibit very high HTPs in their initial state in all three nematic LCs, with a decrease in HTP during photoisomerization. For example, the HTP of (*S*,*S*)-**6a** in 5CB is 228 μm^{-1} in the initial state; this is the highest HTP value for a diarylethene dopant reported thus far. All of the CLCs that were induced by (*S*,*S*)-**6a** and **6b** are right-handed, and no handedness inversion was observed. Compound (*S*,*S*)-**6c** induced a right-handed CLC in its initial state, but experienced handedness inversion to left-handed in all three LC hosts with moderate to high HTPs upon UV light irradiation.

Table 1: Helical twisting power (HTP) of (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c** in different nematic LC hosts and changes observed upon light irradiation.[a]

Dopant	NLC	HTP β_M [μm^{-1}]		$\Delta\beta_M/\beta_M$[b]
		initial	PSS_{UV}	
(*S*,*S*)-**6a**	E 7	+166	+128	−23%
(*S*,*S*)-**6a**	5 CB	+228	+179	−22%
(*S*,*S*)-**6a**	ZLI-1132	+200	+152	−24%
(*S*,*S*)-**6b**	E 7	+139	+94	−33%
(*S*,*S*)-**6b**	5 CB	+188	+136	−28%
(*S*,*S*)-**6b**	ZLI-1132	+124	+63	−49%
(*S*,*S*)-**6c**	E 7	+37	−57	−254%
(*S*,*S*)-**6c**	5 CB	+54	−75	−239%
(*S*,*S*)-**6c**	ZLI-1132	+6	−25	−517%

[a] Positive and negative signs represent right- and left-handed helical twists, respectively. [b] Percentage change in β observed on going from the initial state to PSS_{UV}.

To gain further insight into the structure–property relationships, we evaluated the optimized geometries of (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c** by using DFT calculations at the B3LYP level of theory (Gaussian09 software). The dihedral angles of the binaphthyl moieties in these compounds in their open and closed forms (including two isomers) were then calculated (Figures S12 and S13). As expected, the binaphthyls in all three compounds exist as *cisoid* forms in the initial state, with dihedral angles of less than 90° (73° for (*S*,*S*)-**6a**, 86° for (*S*,*S*)-**6b,** and 76° for (*S*,*S*)-**6c**), which is consistent with the right-handedness of the induced CLCs shown in Table 1. For compounds (*S*,*S*)-**6a** and (*S*,*S*)-**6b**, the dihedral angles increased in this initial state because of the structural rigidity and an increase in bridge length. However, the dihedral angle of (*S*,*S*)-**6c** is narrower than that of (*S*,*S*)-**6b**; this might be the result of structural flexibility of compound (*S*,*S*)-**6c**. For the closed forms, slight increases in θ (ca. 2°) were observed for (*S*,*S*)-**6a** and **6b**, but the binaphthyls are still present in the *cisoid* forms, which is in accordance with the handedness retention of CLCs induced by these two compounds. As the HTP is very sensitive to the dihedral angles, changes in the HTP of these compounds are attributed to changes in the dihedral angles of the binaphthyl units and corresponding variations in molecular shape. Interestingly, for compound (*S*,*S*)-**6c**, the binaphthyl in the open isomer was in the *cisoid* form with a θ value of approximately 76°, which was transformed into a *transoid* form in the closed isomer with $\theta > 90°$ (93° and 94°; Figure 6). Compared with (*S*,*S*)-**6a** and (*S*,*S*)-**6b**, the significant increase in the θ value of (*S*,*S*)-**6c** can be ascribed to the relatively longer bridge length and increased molecular flexibility. The results of these calculations matched the experimental observations and substantiated that the handedness changes in CLCs induced by (*S*,*S*)-**6c** are due to a conformational change of the binaphthyl unit from a *cisoid* into a *transoid* form. These results also reveal that the bridge length is crucial for a change in conformation and the photoresponsive properties. The ethylenedioxy- and propylenedioxy-bridged binaphthyl derivatives are quite rigid, and a minor change in conformation and HTP variations were observed. Butylenedioxy-bridged binaphthyl compounds, however, are more flexible, which facilitates the substantial change in conformation and results in handedness inversion in CLCs.

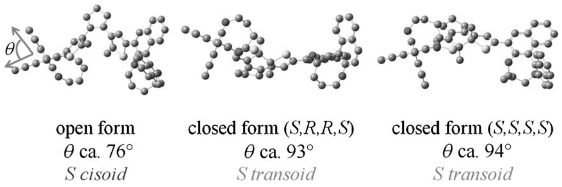

Figure 6. Optimized structures of (*S*,*S*)-**6c** in its open and closed forms.

In conclusion, the three new dithienylcyclopentene compounds (*S*,*S*)-**6a**, (*S*,*S*)-**6b**, and (*S*,*S*)-**6c** that bear two axially chiral bridged binaphthyl units with different bridge lengths were designed and synthesized. When used as a chiral dopant for nematic LCs, compound (*S*,*S*)-**6a** exhibited unusually high HTPs in both states, which are significantly larger than those of chiral diarylethene dopants developed thus far. Reversible phototuning of the reflection wavelength in the visible region was demonstrated by using this dopant. More interestingly, with an increase in bridge length from ethylenedioxy to butylenedioxy, the dihedral angle of (*S*,*S*)-**6c** could be modulated to switch the binaphthyl units from a *cisoid* to *transoid* form, which resulted in handedness inversion of the induced CLCs in different LC hosts with moderate to high HTPs in both states. The novel structures, high HTPs, and helix inversion may significantly broaden the applications of CLC materials, including all-optical displays and in areas in which CPL is involved. The structure–property relationships of the series should assist the future design of chiral diarylethene molecules for different application purposes.

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