

Light-driven molecular switches with tetrahedral and axial chirality†

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Two light-driven molecular switches with tetrahedral and axial chirality were synthesized, which can induce a helical superstructure in an achiral liquid crystal host and dynamically phototune it to achieve reversible reflection color.

The elegance with which nature performs light-driven functions is inspiring chemists to develop smart light-driven molecular motors and switches for artificial molecular devices.¹ An important challenge is how to dynamically control mechanical motion of molecules by light. A promising solution lies in the photo-switchable chiral nematic (cholesteric) phase because its unique helical structure and physical properties can be tuned upon light irradiation. Such a phase can be achieved by doping both azo molecules and chiral molecules into a nematic liquid crystal (LC) host.² *trans*-Azobenzene is thermodynamically more stable than *cis*-azobenzene; however, irradiation with ultraviolet light leads to *trans*–*cis* isomerization. The reverse process from the *cis* to the *trans* isomer can occur thermally and/or photochemically with visible light. Since the physical and chemical properties of the azobenzene configurational isomers are different, the optically tunable switching effect has been the basis for many functional molecules and materials with applications in photonics and liquid crystal displays.^{3–6} It is also well known that when a chiral molecule is dissolved in an achiral nematic LC, its molecular chirality is transferred to the nematic solvent which then organizes into a helical superstructure that reflects light according to Bragg's law. The ability of a chiral dopant to twist a nematic phase, *i.e.* helical twisting power (HTP, β), is expressed in the equation: $\beta = (pc)^{-1}$ where p is the pitch length of the helical structure, and c is the chiral dopant concentration. If the HTP is able to be changed by light irradiation, the helical pitch will be changed, providing opportunities as well as challenges in fundamental science that are opening the door to applications such as optically addressed displays that require no drive electronics and can be made flexible.⁷ However, to date only a few developments of chiral azo molecules^{7,8,9} have been reported, compared with numerous achiral azo dyes and chiral dopants. Undoubtedly, the lack of new light-driven chiral molecular switches with satisfactory functionalities for device performance, *e.g.*, fast relaxation back to the initial state upon visible light and/or tuning the reflection color over entire visible region, has become a barrier to their applications

in color photodisplays, tunable color filters and tunable LC lasers.¹⁰

Here we report the synthesis of two novel light-driven chiral molecular switches **4a** and **4b** with tetrahedral and axial chirality, which exhibited a fast reversible response in both organic solvent and LC media upon light irradiation (Fig. 1). The material **4a** doped in an achiral LC host E31 was found to be able to phototune the reflection color of the resulting cholesteric LC thin film over the entire visible region. To the best of our knowledge, these are the first azo compounds with tetrahedral and axial chirality capable of phototuning reflection color over entire visible region to be reported. The interest behind the design of the new light-driven chiral molecular switches mainly results from 1) the axially chiral structure of 1,1'-binaphthyl group originating from the rotational barrier around the naphthyl–naphthyl bond,¹¹ 2) the mesogenic rigid-long shape of tetrahedrally chiral cholesteryl group for increasing the compatibility/solubility with LC host and extending the sphere of influence for the local photodirected changes in these molecular switches, 3) the thermal stability and distinguished absorbance of the *trans* and *cis* configurations of azobenzene, and 4) improving its solubility in the LC host by introducing a linker.¹²

Chiral molecular switches **4a** and **4b** were synthesized starting from (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine **1**, which was reacted with sodium nitrite in aqueous HCl to give a diazonium salt followed by coupling with phenol to obtain azo intermediate **2**. The azo intermediate was treated with bromo alcohol in the presence of K₂CO₃ to afford **3**, followed by reaction with cholesteryl chloroformate to give the target **4** as orange crystals (Fig. 1). Their structures were identified by ¹H NMR, ¹³C NMR, MS and elemental analysis (see ESI†). The materials were chemically and thermally stable, and exhibited the expected reversible photoswitchable behavior in both organic solvent and LC host. For example, incubation of a solution of **4a** in CH₂Cl₂ in the dark served to maximize the absorption at 354 nm corresponding to the (*trans,trans*)-azobenzene chromophore. Irradiation of this solution with 365 nm light resulted in clean photoisomerization to *cis*-isomers (*trans,cis*)-**4a** and (*cis,cis*)-**4a**, as evidenced by a decrease in the absorbance at 354 nm and an increase in absorbance at 458 nm (Fig. 2). Due to the molecules having two azo linkages, ultraviolet irradiation leads to reversible *trans*–*cis* isomerization of azo configurations, producing two other isomers (*trans,cis*)-**4a** and (*cis,cis*)-**4a**. The reverse process from (*cis,cis*)-**4a** → (*trans,cis*)-**4a** → (*trans,trans*)-**4a** can occur thermally and photochemically with visible light (Fig. 3). For example, a photostationary state of (*trans,trans*)-**4a** to its (*cis,cis*)-isomer was reached within approximately 50 s under UV irradiation at 365 nm (Fig. 2). Reversion of (*cis,cis*)-**4a** to its (*trans,trans*)-isomer was reached within approximately 40 s under visible irradiation at 440 nm at room temperature (Fig. 4, left). The cycle was repeated

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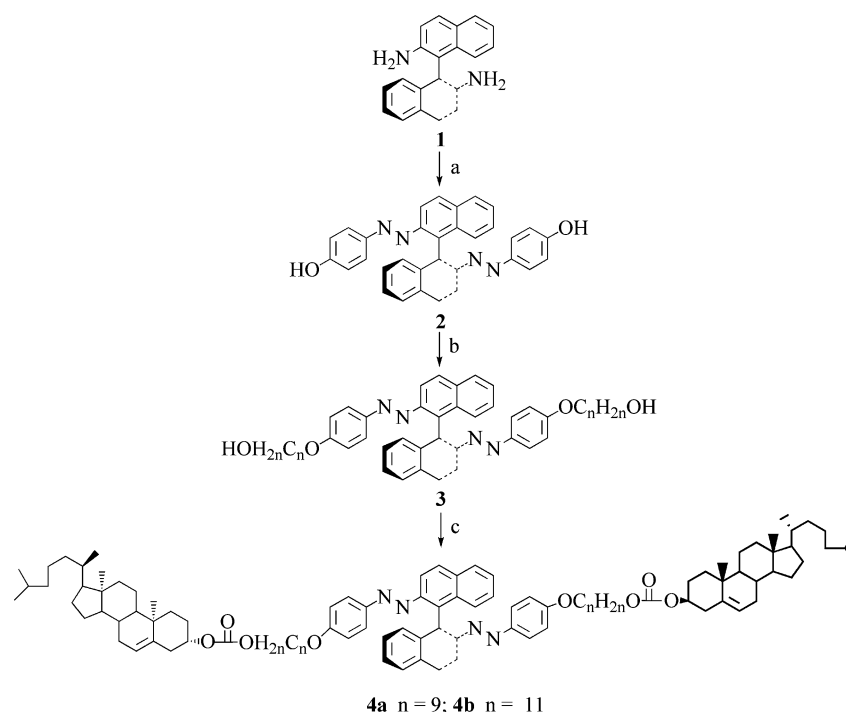


Fig. 1 Synthesis of light-driven chiral molecular switches **4a** and **4b**. Reagents and conditions: a: (i) NaNO_2 , aq. HCl , (ii) phenol, NaOH ; b: $\text{BrC}_n\text{H}_{2n}\text{OH}$, K_2CO_3 , acetone; c: cholesterol chloroformate, pyridine.

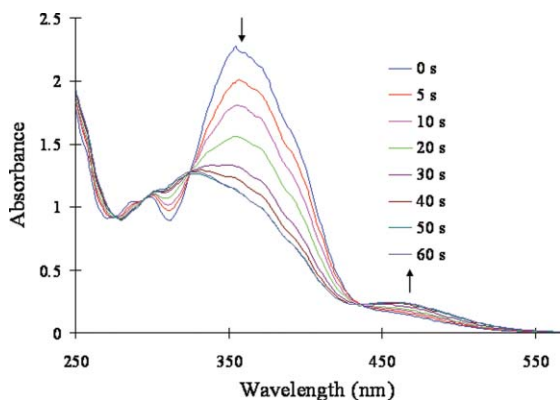


Fig. 2 UV-vis absorption spectra of **4a** ($40 \mu\text{M}$) in CH_2Cl_2 under UV irradiation (365 nm at 0 s , 5 s , 10 s , 20 s , 30 s , 40 s , 50 s and 60 s).

many times without degradation of the switches (see Fig. S2†). The thermal reversion to its (*trans,trans*)-isomer was reached within approximately 2 h at room temperature in the dark (Fig. 4, right).

As expected, doping **4a** and **4b** in an achiral nematic LC host even at a low concentration can induce a chiral nematic mesophase with characteristic fingerprint texture (Fig. 5, left). For example, a mixture of 1 wt% **4a** in a commercially available nematic LC host E7 was capillary-filled into a $5 \mu\text{m}$ thick cell coated with polyimide. A homogenous aligned chiral nematic mesophase was observed at room temperature under a crossed polarized microscope (Fig. 5, middle). Upon UV irradiation at 365 nm , the color changed from red to green within approximately 30 s (Fig. 5, right). Upon visible light irradiation at 440 nm , the green color changed back to red within approximately 60 s. Their helical twist powers were measured by using Grandjean-Cano method.¹³

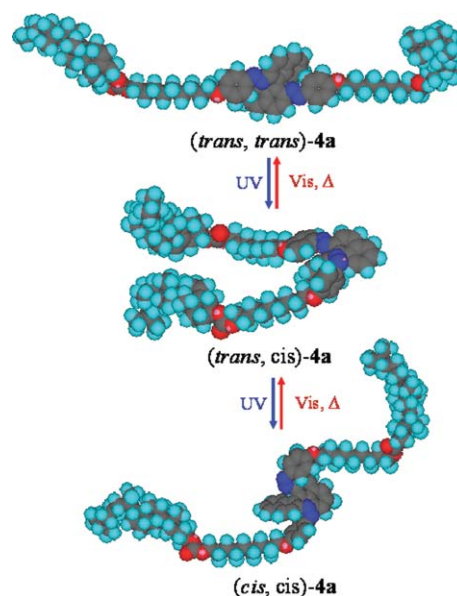


Fig. 3 *trans*–*cis* Isomerization of light-driven chiral molecular switch **4a** (3D-ChemDraw space-filling model).

A wedge cell produces disclination lines in the cholesteric LC and can be seen clearly through a polarizing optical microscope. The inverse of pitch proportionally increases with increase in the switch concentration (see Fig. S4†). Their HTP values, *i.e.* $\beta = (pc)^{-1}$, are shown in Table 1. A red-shifted change in pitch of 2 wt% **4a** in E7 in a wedge cell upon UV irradiation can be clearly seen as the change in distance between the Cano lines when observed under the polarizing optical microscope (Fig. 6), whereas the pitch of the resulting excited mixture was blue-shifted back upon visible

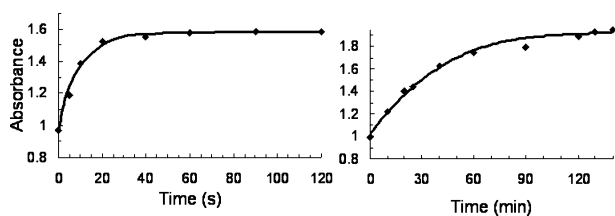


Fig. 4 Absorbance at 354 nm of **4a** in CH_2Cl_2 at room temperature under visible light at 440 nm (left) and in the dark (right) after UV irradiation at 365 nm for 2 min.



Fig. 5 Crossed-polarized optical texture micrograph of the mixture of 1 wt% **4a** in achiral nematic LC host E7 at room temperature in a 5 μm homeotropic cell (left) and in a 5 μm anti-parallel cell (middle: before UV irradiation; right: after UV irradiation at 365 nm for about 30 s).

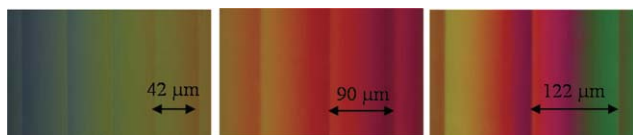


Fig. 6 Crossed polarized textures of 2.0 wt% **4a** in E7 at room temperature in a stripe-wedge Grandjean-Cano cell upon UV irradiation at 365 nm under 0 s (left), 30 s (middle) and 90 s (right). (The distance between the Cano lines is R , pitch $P = 2R \tan\theta$).

light irradiation. The red-shift of its pitch upon UV irradiation at 365 nm was reached within approximately 90 s, and its blue-shifted reversion upon visible light at 440 nm was reached within approximately 40 s at room temperature (see Fig. S5 and S6†). The cycle from UV irradiation at 365 nm for 2 min to visible light irradiation at 440 nm for 2 min was repeated many times without fatigue. It is worth noting here that the relaxation time of the two switches upon visible light is much shorter than our previous reported axially chiral molecules for the thermally driven system,⁷ which might result from the introduction of the second bulky mesogenic chiral cholesteryl group, making the chiral moiety spread over a large area of the molecule and therefore resulting in the light-driven change in the molecules have a larger sphere of influence.

A mixture of 15 wt% **4a** in a commercially available nematic LC host E31 was capillary-filled into a 5 μm cell with polyimide. The cell was covered with black paint on one side and the resulting cell was placed under a UV lamp at 365 nm for about 1 min, resulting in the expected red-shift of the exposed region. As expected, the



Fig. 7 Pictures of the 5 μm cell with 15 wt% **4a** in E31 taken by a microscope in the crossed-polarized reflective mode from a dark state to the excited state under UV irradiation at 365 nm for different times: 6 s, 20 s, 30 s, 40 s, 50 s, 60 s and 70 s.

Table 1 HTP (β) of the chiral molecular switches **4a** and **4b** in E7 nematic host measured by Grandjean-Cano wedge cell

Switch	β (mol%)/ μm^{-1}		β (wt%)/ μm^{-1}	
	Initial	UV-irradiated	Initial	UV-irradiated
4a	176.1	60.1	30.4	10.4
4b	173.1	54.0	28.9	9.0

irradiated region shows reflection of very deep red wavelength that was difficult to capture on camera but easy to capture on a microscope in the crossed-polarized reflective mode. The cell was left overnight in the dark, in order to achieve the completely relaxed dark state, which reflected a very deep blue. When the cell in the dark state is irradiated in approximately 10 s increments, the reflection band is slowly red-shifted, and the resulting reflection can be seen through the full-range visible region and almost into the infrared, as in Fig. 7. This figure is an impressive display of these switches in action. An amazing feature of this system is the quick relaxation. After 1 min of exposure to bright white light, it surprisingly returned to the original ambient color. Its ability to phototune reflection color over entire visible region is further evidenced in Fig. 8. Research into developing light-driven chiral molecular switches with satisfactory functionalities for device applications, *e.g.* much higher helical twisting power and good solubility, is underway.

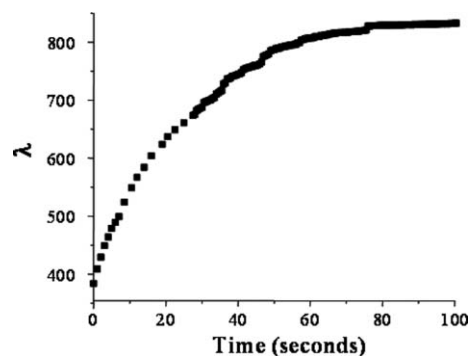


Fig. 8 Phototuning of 15 wt% **4a** in achiral nematic host E31 in a 9 μm thick cell under 1 mW/cm^2 UV light at 365 nm.

In conclusion, two novel light-driven chiral molecular switches with tetrahedral and axial chirality were synthesized. These chiral molecular switches were able to induce a helical superstructure in an achiral nematic LC host to form the so-called cholesteric LC, and dynamically tune it upon light irradiation. Their reversible photoresponsive properties in both organic solvent and liquid crystal host were demonstrated. Chiral molecular switch **4a** doped in an achiral LC host was found to be able to phototune the reflection color of the resulting cholesteric LC over the entire

visible region. To the best of our knowledge, these are the first azo compounds to be synthesized with tetrahedral and axial chirality capable of full range tunable reflection color. This research should provide new insights into developing light-driven chiral molecular switches with satisfactory functionalities for device applications.

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