

Light-driven Chiral Molecular Switches with Tetrahedral and Axial Chirality

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1. Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ or d₆-acetone. Chemical shifts are in δ units (ppm) with the residual solvent peak as the internal standard. The coupling constant (*J*) is reported in hertz (Hz). NMR splitting patterns are designed as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60-200 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F₂₅₄ glass plates. Elemental analysis was performed by Robertson Microlet Inc. UV-vis spectrum was taken by a Perkin Elmer Lambda 19 Spectrometer. Mass spectrum was taken by Mass Spectrometry & Proteomics Facility of Ohio State University. Textures and transition temperatures were observed by optical microscopy using a Leitz polarizing microscope in conjunction with a Linkam TMS temperature controller. Calorimetric measurements were performed in a Perkin Elmer DSC using indium as a standard calibration. UV irradiation was carried out by Xenon light source 100 W through a filter at 365 nm or a handheld 4 μW/cm² UV lamp with a peak wavelength of 365 nm. Visible irradiation was carried out by Xenon light source 100 W through a filter at 440 nm. Phototuning properties of cholesteric LC was examined with an Ocean Optics UV-vis-NIR spectrometer collecting spectra from 390-1000 nm at 1 mW/cm² UV light at 365 nm. Two different commercially available achiral nematic liquid crystals were used in the study, E7 and E31, both of which are eutectic mixtures designed for display applications. The nematic, E7, is a known mixture of pure liquid crystals compounds and its molecular weight therefore known. This mixture is used in order to compare our measured values with some other chiral materials reported in the literature.

2. Synthesis of the chiral molecular switches 4a and 4b

Photoresponsive chiral switches **4** 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 reacting with cholesteryl chloroformate to get the target **4** (Fig. S1). Their structures were well identified by ¹H NMR, ¹³C NMR, MS and elemental analysis.

Synthesis of **2**: (s)-(-)-1,1'-binaphthyl-2,2'-diamine **1** (3.52 mmol) was dissolved in a solution of concentrated HCl (17 mL) and water (2 mL). A solution of NaNO₂ (7.04 mmol) in water (17 mL) was added. The resulting solution was dripped into a cooled solution of phenol (7.57 mmol) and NaOH (22.50 mmol) in water (17 mL). The resulting suspension was made acidic by the addition of 10% HCl (3 mL) and filtered. The precipitate was washed with water, dried, and purified by column chromatography to get **2** as a red solid. ¹H NMR: δ 2.90 (br s), 6.72 (d, 4H, *J* = 7.0 Hz), 7.28 (d, 4H, *J* = 8.8 Hz), 7.31 (t, 2H, *J* = 6.2 Hz), 7.37 (t, 2H, *J* = 6.4 Hz), 7.55 (m, 2H), 8.1 (d, 2H, *J* = 8.0 Hz), 8.18 (s,

4H), 8.97 (br s); ^{13}C NMR (acetone): δ 113.58, 114.80, 123.91, 125.98, 126.34, 126.54, 127.52, 128.29, 133.46, 233.53, 135.79, 145.82, 147.56, 159.58; MALDI-TOF MS ($\text{M}+\text{Na}$) calcd for $\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_2\text{Na}$: 517.1640, found: 517.1639; Anal calcd for $\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_2$: C 77.72, H 4.48, N 11.33, found: C 77.68, H 4.50, N 10.79.

Synthesis of **3a**: **2** (1.21 mmol) was dissolved in acetone. Potassium carbonate (6.06 mmol) was added with stirring. A solution of bromononanol (3.03 mmol) in acetone was then added. The reaction was refluxed overnight. An additional 250 mg of bromononanol were added in acetone (5 mL) and refluxing was continued for 3 hours. The potassium carbonate was filtered and the acetone removed. The crude product was purified by column chromatography to yield an orange solid **3a**. ^1H NMR: δ 1.28-1.69 (m, 28H), 3.60 (t, 4H, $J = 6.5$ Hz), 3.86 (t, 4H, $J = 6.6$ Hz), 6.69 (d, 4H, $J = 8.8$ Hz), 7.28 (m, 6H), 7.44 (m, 4H), 7.95 (d, 2H, $J = 8.0$ Hz), 8.02 (d, 2H, $J = 8.8$ Hz), 8.13 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3): δ 25.66, 25.87, 29.04, 29.18, 29.27, 29.41, 32.72, 62.98, 68.12, 114.39, 124.54, 26.50, 126.84, 127.78, 127.99, 128.91, 134.16, 134.28, 136.61, 147.20, 148.32, 161.20.

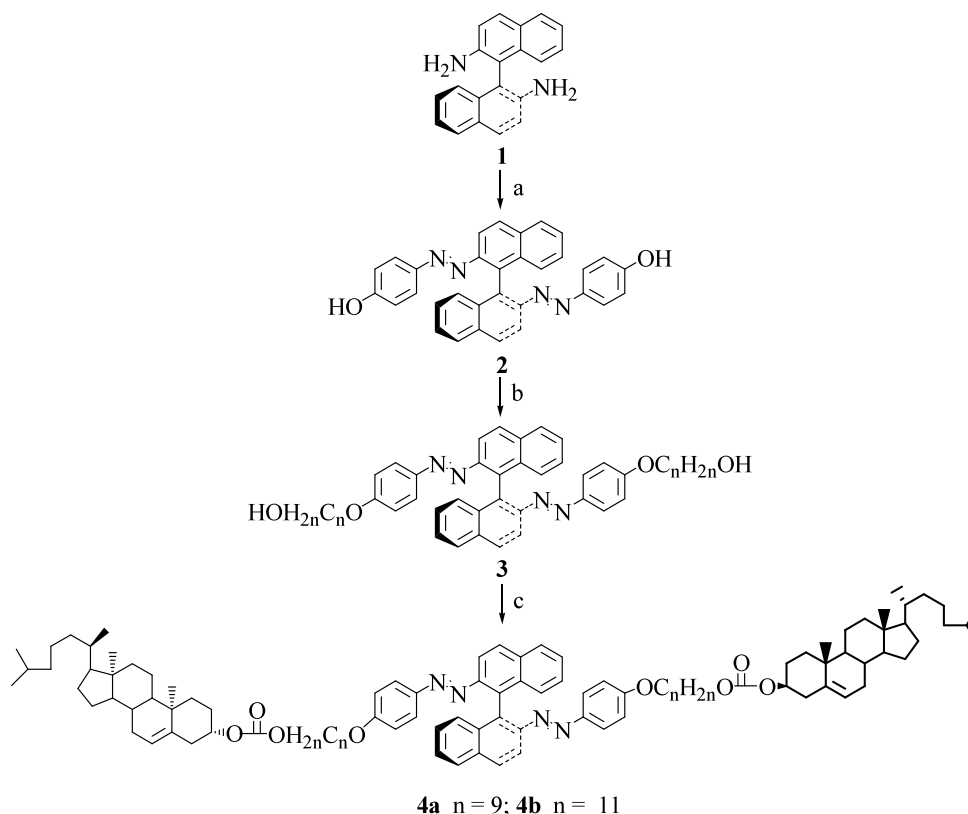


Figure S1 Synthesis of light-driven chiral molecular switches **4**.

Synthesis of **3b**: **2a** (1.21 mmol) was dissolved in acetone. Potassium carbonate was added with stirring. A solution of bromoundecanol (3.03 mmol) in acetone was then added. The reaction was refluxed overnight. An additional 300 mg of bromoundecanol were added in acetone and refluxing was continued for 3 hours. The potassium carbonate was filtered and the acetone removed. The crude product was purified by column chromatography to yield a tacky orange solid **3b**. ^1H NMR: δ 1.10-1.80 (m, 36H), 3.59 (t, 4H, $J = 5.0$ Hz), 3.86 (t, 4H, $J = 6.6$ Hz), 6.68 (d, 4H, $J = 8.4$ Hz), 7.24 (m, 6H), 7.40 (m, 4H), 7.93-8.15 (m, 6H); ^{13}C NMR (CDCl_3): δ 25.92, 26.86, 28.85, 29.09, 29.28, 29.40, 32.64, 45.15, 68.16, 114.42, 124.57, 126.52, 126.85, 127.82, 128.00, 128.91, 134.19, 134.32, 136.63, 147.25, 148.35, 161.24.

Synthesis of **4a**: **3a** (540 mg, 0.69 mmol) was dissolved in pyridine and cholesteryl chloroformate (1.73 mmol) was added. The reaction was stirred at room temperature overnight. The pyridine was removed

under reduced pressure and the crude product was redissolved in dichloromethane and washed with water three times before being dried over magnesium sulfate. The crude was purified by column chromatography with 40% hexane in dichloromethane as the eluent to afford **4a** as an orange solid. ^1H NMR (CDCl_3): δ 0.65 (s, 12H), 0.89-2.00 (m, 106H), 2.37 (d, 4H, $J = 7.0$ Hz), 3.86 (t, 4H, $J = 6.6$ Hz), 4.08 (t, 4H, $J = 6.6$ Hz), 4.42 (m, 2H), 5.36 (d, 2H, $J = 4.5$ Hz), 6.68 (d, 4H, $J = 9.2$ Hz), 7.29 (m, 6H), 7.45 (m, 4H), 7.95 (d, 2H, $J = 8.0$ Hz), 8.01 (d, 2H, $J = 8.8$ Hz), 8.13 (d, 2H, $J = 9.0$ Hz); ^{13}C NMR (CDCl_3): δ 11.88, 18.74, 19.27, 21.08, 22.55, 22.80, 23.87, 24.30, 25.71, 25.92, 27.76, 28.02, 28.22, 28.69, 29.12, 29.21, 29.34, 31.92, 35.80, 36.23, 36.59, 36.93, 38.11, 39.46, 35.79, 42.37, 50.09, 56.23, 56.76, 67.83, 68.20, 114.45, 122.87, 124.57, 126.50, 126.84, 127.84, 128.00, 128.91, 134.22, 134.36, 136.62, 139.50, 147.31, 148.38, 154.71, 161.26; MALDI-TOF MS ($\text{M}+\text{H}$) calcd for $\text{C}_{106}\text{H}_{147}\text{N}_4\text{O}_8$: 1604.11, found: 1604.28; Anal calcd for $\text{C}_{106}\text{H}_{146}\text{N}_4\text{O}_8$: C 79.36, H 9.17, N 3.49, found: C 79.61, H 9.40, N 3.49.

Synthesis of **4b**: **3b** (0.40 mmol) was dissolved in pyridine and cholesteryl chloroformate (1.38 mmol) was added. The reaction was stirred at room temperature overnight. The pyridine was removed under reduced pressure and the crude product was redissolved in dichloromethane and washed with water three times before being dried over magnesium sulfate. The crude was purified by column chromatography with 50% hexane in dichloromethane as the eluent to afford **4b** as an orange solid. ^1H NMR (CDCl_3): δ 0.65 (s, 12H), 0.86-1.96 (m, 114H), 2.37 (d, 4H, $J = 8.2$ Hz), 3.86 (t, 4H, $J = 6.6$ Hz), 4.08 (t, 4H, $J = 6.8$ Hz), 4.45 (m, 2H), 5.39 (d, 2H, $J = 3.7$ Hz), 6.68 (d, 4H, $J = 9.2$ Hz), 7.24 (m, 6H), 7.44 (m, 4H), 7.95 (d, 2H, $J = 7.8$ Hz), 8.00 (d, 2H, $J = 8.8$ Hz), 8.13 (d, 2H, $J = 9.0$ Hz); ^{13}C NMR (CDCl_3): δ 11.86, 18.73, 19.25, 21.07, 25.72, 25.94, 27.75, 28.01, 28.21, 28.70, 29.18, 29.29, 29.42, 31.90, 35.79, 36.22, 36.57, 36.92, 38.10, 39.54, 39.78, 42.35, 50.07, 56.21, 56.74, 67.85, 68.21, 114.44, 122.86, 124.57, 126.49, 126.82, 127.82, 127.99, 128.89, 134.20, 134.35, 136.62, 139.48, 147.29, 148.38, 157.70, 161.26; MALDI-TOF MS ($\text{M}+\text{H}$) $\text{C}_{110}\text{H}_{155}\text{N}_4\text{O}_8$ calcd: 1660.18, found: 1660.31; Anal calcd for $\text{C}_{110}\text{H}_{154}\text{N}_4\text{O}_8$: C 79.57, H 9.35, N 3.37, found: C 79.70, H 9.59, N 3.35.

3. Reversible photoswitchable experiment.

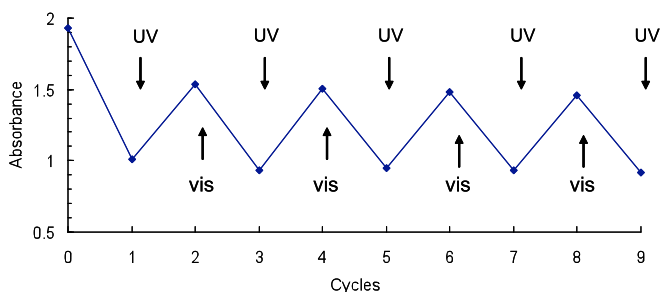


Figure S2 Cycles of absorbance at 354 nm as the solution of **4a** in CH_2Cl_2 is irradiated with UV light at 365 nm for 2 minutes and then with visible light at 440 nm for 2 minutes.

4. Measurement of pitch and helical twisting

A conventional technique for pitch measurement is the so-called Grandjean-Cano wedge method. Such wedge cell with an opening angle θ is made by applying two differently sized spacers at each end of the cell (Figure S3). If the alignment of the substrates is planar (the director lies parallel to the surface) and the rubbing directions of the substrates are parallel to one another, the cholesteric becomes discrete. Because the value of the pitch is fixed, and the alignment is also fixed, the cholesteric arranges itself as in Figure S3. This arrangement produces disclination lines between areas that contain a different number of layers. The difference in thickness between each domain must be $p/2$ in order to satisfy the alignment boundary condition.

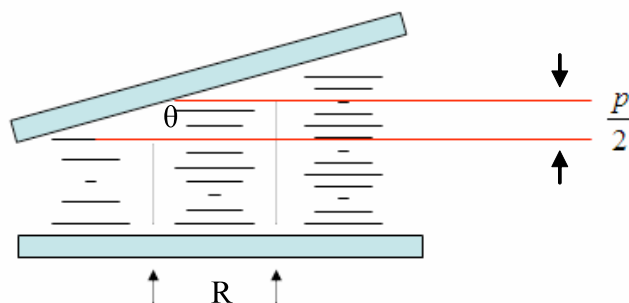


Figure S3 Schematic illustration of a Grandjean-Cano wedge cell for pitch measurement of cholesteric liquid crystal. Disclination lines are pointed out with arrows and the thickness change between two domains is marked $p/2$.

The pitch was determined according to the equation $P = 2R \tan\theta$, where R represents the distance between the Grandjean lines and θ is the wedge angle of wedge cells (EHC, KCRK-07, $\tan\theta = 0.0196$). Once the pitch is known, the helical twisting power β can be calculated from $\beta = (pc)^{-1}$ where c is the chiral dopant concentration in liquid crystal host (Figure S4). More information about the measurement can be found in Dierking, I. Textures of Liquid Crystals, Wiley-VCH, Weinheim, 2003.

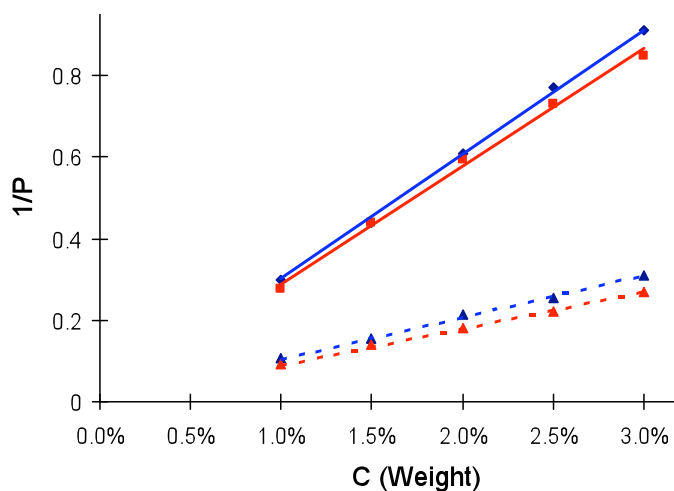


Figure S4 Reciprocal helical pitch as a function of concentration of chiral molecular switches **4a** (blue line) and **4b** (red line) in a chiral nematic host E7 (solid line: initial state; dash line: UV irradiated state)

5. Relaxation back upon visible light at 440 nm.

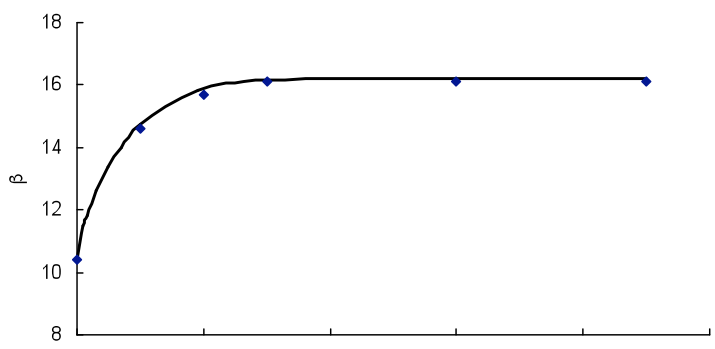


Figure S5 Plot of helical twisting power of **4a** under visible light (440 nm) with different time after UV irradiation at 365 nm of the mixture of 2 wt% **4a** in an achiral nematic LC host for 2 min

6. Schematic mechanism of reflection color of cholesteric LC tuned by light.

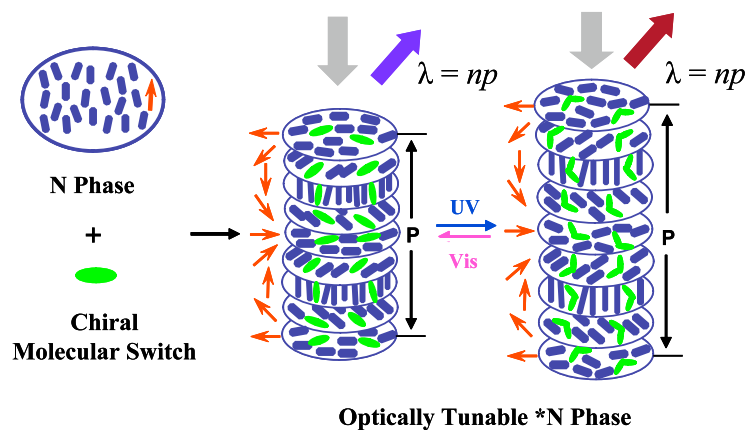


Figure S6 A schematic mechanism of reflection wavelength of cholesteric LC tuned by light over entire visible region.