

Supporting Information

Electro- and Photo-Driven Orthogonal Switching of a Helical Superstructure Enabled by an Axially Chiral Molecular Switch

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S1. Synthesis and Characterization of Light-Driven Axially Chiral Molecular Switch (S)-6

The synthetic process is shown in **Scheme S1**. ^1H and ^{13}C NMR spectra with CDCl_3 as the solvent were recorded on a Bruker 400 MHz NMR spectrometer. 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 designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F254 glass plates.

Intermediate 2. Methyl 3,4,5-trihydroxybenzoate (4.00 g, 21.7 mmol), 1-bromohexane (14.34 g, 86.8 mmol), K_2CO_3 (8.99 g, 65.1 mmol), and KI (0.36 g, 2.17 mmol) were placed in a round-bottom flask. Acetone (110 mL) was added and the reaction mixture was stirred and refluxed for 72 hours. After reaction was completed, the reaction mixture was cooled down to room temperature and filtered through filter paper. The filtrate was concentrated and the obtained solid was purified by column chromatography over silica gel with an eluent of DCM/hexane to give methyl 3,4,5-tris(hexyloxy)benzoate **2**. ^1H NMR (400 MHz, CDCl_3): δ 7.25 (s, 2H), 4.03-3.99 (m, 6H), 3.88 (s, 3H), 1.84-1.70 (m, 6H), 1.51-1.44 (m, 6H), 1.36-1.30 (m, 12H), 0.90 (t, J = 7.0 Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.85, 152.83, 142.33, 124.57, 107.84, 73.37, 69.17, 52.06, 31.72, 31.37, 30.27, 29.26, 25.59, 22.60, 13.99.

Intermediate 3. To the solution of compound methyl 3,4,5-tris(hexyloxy)benzoate (1.12 g, 2.56 mmol) in methanol/THF (30 mL/5 mL) aqueous KOH (0.25 g, 1 mL H_2O) was added, the mixture was refluxed for 24 h. Then, the reaction mixture was acidified by HCl. The precipitate was then

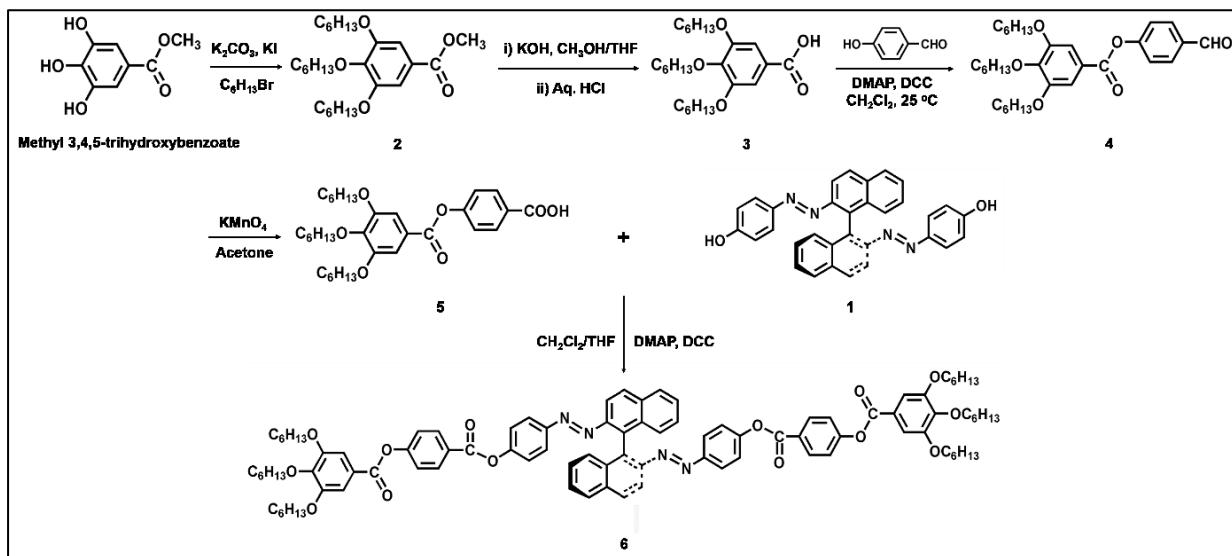
filtered, washed with deionized water and DCM, and dried under the vacuum to give **3**. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (s, 2H), 4.06-3.99 (m, 6H), 1.86-1.71 (m, 6H), 1.50-1.45 (m, 6H), 1.35-1.32 (m, 12H), 0.91 (t, *J* = 7.0 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 171.90, 152.87, 143.13, 123.66, 108.60, 73.56, 69.21, 31.72, 31.55, 30.28, 29.24, 25.74, 22.61, 14.00.

Intermediate 4. 3,4,5-tris(hexyloxy)benzoic acid (0.597 g, 1.41 mmol), 4-hydroxybenzaldehyde (0.258 g, 2.12 mmol) and DMAP (0.169 g, 1.38 mmol) were dissolved in dry dichloromethane. DCC (0.335 g, 1.62 mmol) was added all at once. The mixture was stirred overnight at room temperature. The reaction mixture was hot filtered to remove DCU and the filtrate was washed with water. The organic layer was dried and purified by column chromatography using a mixture of ethyl acetate:hexane to afford **4**. ¹H NMR (400 MHz, CDCl₃): δ 10.02 (s, 1H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.41-7.36 (m, 4H), 4.09-4.03 (m, 6H), 1.87-1.73 (m, 6H), 1.53-1.46 (m, 6H), 1.37-1.30 (m, 12H), 0.90 (t, *J* = 7.1 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 170.88, 164.47, 155.31, 153.04, 143.56, 131.90, 126.81, 123.33, 122.01, 108.71, 73.63, 69.22, 33.52, 31.61, 30.29, 29.25, 25.69, 22.60, 14.00. Anal. calcd.: C 72.97, H 8.80; found: C 73.17, H 9.03.

Intermediate 5. In a round bottom flask, KMnO₄ (0.484 g, 3.06 mmol) was added to a solution of the aldehyde **4** (0.54 g, 1.02 mmol) dissolved in acetone (45 mL). The mixture was stirred overnight at room temperature. Then, aqueous NaHSO₃ (0.76 g, 3.06 mmol) was added to the mixture and the mixture was stirred for additional 1 hour. After this time, the mixture was poured into 5 mL of aqueous 2N HCl. The resulting white precipitate was filtered, washed with water, and dried to give **5**. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.41 (s, 2H), 7.33 (d, *J* =

8.7 Hz, 2H), 4.09-4.04 (m, 6H), 1.88-1.74 (m, 6H), 1.54-1.47 (m, 6H), 1.37-1.32 (m, 12H), 0.91 (t, J = 6.8 Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.88, 164.47, 155.31, 153.04, 143.56, 131.90, 126.81, 123.33, 122.01, 108.71, 73.63, 69.22, 33.52, 31.61, 30.29, 29.25, 25.69, 22.60, 14.00. Elemental analysis calcd.: C 72.97, H 8.80; found: C 73.17, H 9.03.

Target chiral molecular switch 6: Compound **1** was synthesized from the chiral (*S*)-(−)-1,1'-Binaphthyl-2,2'-diamine as the raw material according to our previously published procedure.^[1] Compound **1** (0.15 g, 0.310 mmol), compound **5** (0.399 g, 0.737 mmol), DMAP (0.036 g, 0.295 mmol), and DCC (0.304 g, 1.474 mmol) were dissolved in 20 mL/10 mL dry dichloromethane/THF. The reaction mixture was refluxed overnight. Then, the mixture was filtered to remove DCU. The filtrated was evaporated in a rotary evaporator and dried at vacuum oven. The product was recrystallized in a mixture of dichloromethane and ethanol to give an orange product (*S*)-**6**. ^1H NMR (400MHz, CDCl_3): δ 8.22 (d, J = 8.8 Hz, 4H), 8.18 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.42-7.38 (m, 8H), 7.34-7.31 (m, 6H), 7.10 (d, J = 8.9 Hz, 4H), 4.08-4.03 (m, 12H), 1.87-1.73 (m, 12H), 1.53-1.46 (m, 12H), 1.37-1.31 (m, 24H), 0.90 (t, J = 8.0 Hz, 18H). ^{13}C NMR (100MHz, CDCl_3): δ 164.49, 164.07, 155.39, 153.06, 152.45, 150.61, 148.22, 143.32, 137.60, 134.56, 134.24, 131.88, 129.27, 127.90, 127.47, 126.85, 126.80, 124.08, 123.30, 122.18, 122.05, 114.24, 108.64, 73.64, 69.31, 31.75, 31.57, 30.32, 29.27, 25.77, 25.73, 22.71, 22.65, 14.13, 14.06. Elemental analysis calcd.: C 74.68, H 7.18, N 3.63; found: C 74.89, H 7.12, N 3.56.



Scheme S1. Synthesis route of the light-driven axially chiral molecular switch (*S*)-6.

S2. UV-vis Absorption of Light-Driven Axially Chiral Molecular Switch (*S*)-6 upon Irradiation with Two Different Wavelengths of Light

The photoisomerization of light-driven axially chiral molecular switch (*S*)-6 was studied in organic solvent (10^{-5} M hexane). UV-vis absorption spectra are shown in **Figure S1**.

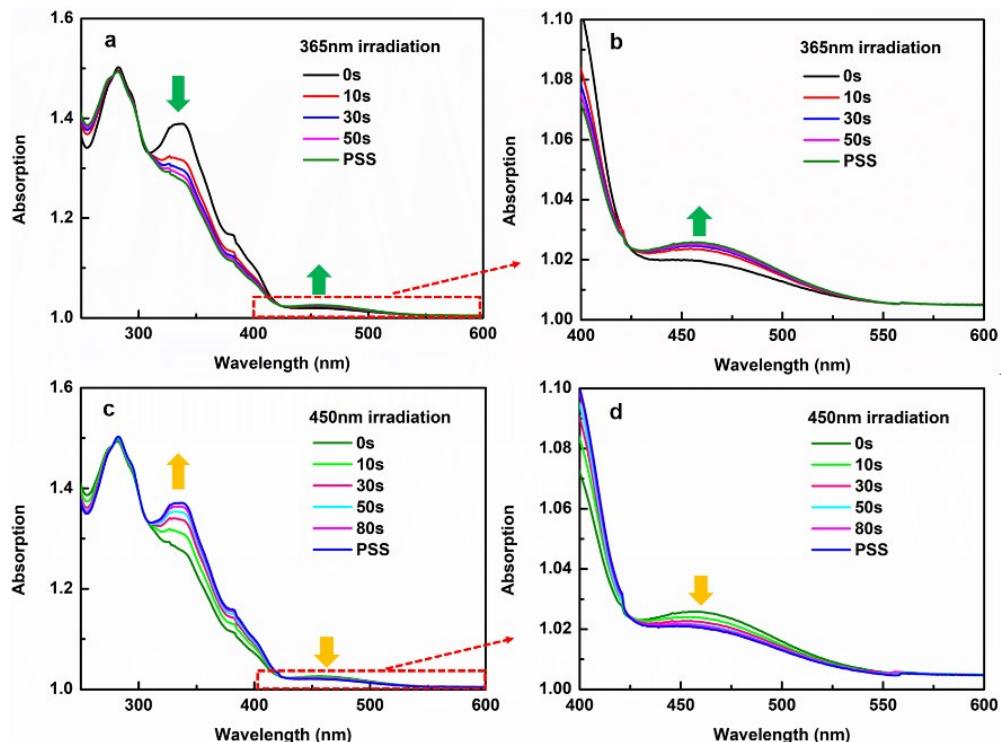


Figure S1. UV-vis absorption spectra of chiral switch (*S*)-**6** in 10^{-5} M hexane upon a, b) UV (365 nm, 1.5 mW/cm²) and c, d) blue (450 nm, 1.5 mW/cm²) light irradiation. PSS: Photostationary state.

S3. Measurement of Pitch (*P*) and Helical Twisting Power (HTP, β)

The pitch (*P*, μm) of the sample mixture (0.42 wt% (*S*)-**6** in E7) was measured by the traditional Grandjean-Cano wedge cell.^[2-4] The wedge cell (EHC, KCRK-07, $\tan\theta = 0.0196$) has an opening angle θ , made by applying two differently sized spacers at each end of the cell, with anti-parallel rubbing direction of the substrates. Thus, at certain temperature and boundary conditions, the CLC phase organizes as shown in **Figure. S2**. There are disclination lines formed between different number of layers which can be seen by POM and the thickness difference can be considered as an integer multiple of *P*/2.

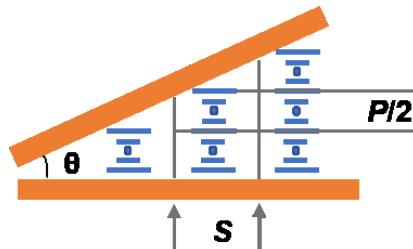


Figure S2. Schematic illustration of a Grandjean-Cano wedge cell. *S* is the distance between two disclination lines donated with arrows. *P*/2 is the thickness difference between two domains.

The relationship between *S* and *P*/2 can be expressed by the equation $P/2 = S \cdot \tan\theta$. Based on the pitch value, the helical twisting power (HTP, μm^{-1}), the ability of a chiral dopant to twist a nematic LC, can be calculated by the equation $HTP(\beta) = 1/(c \cdot P)$, where *c* (mol% or wt%) is the concentration of the chiral dopant in the sample mixture.

S4. Formation of Cholesteric Grating

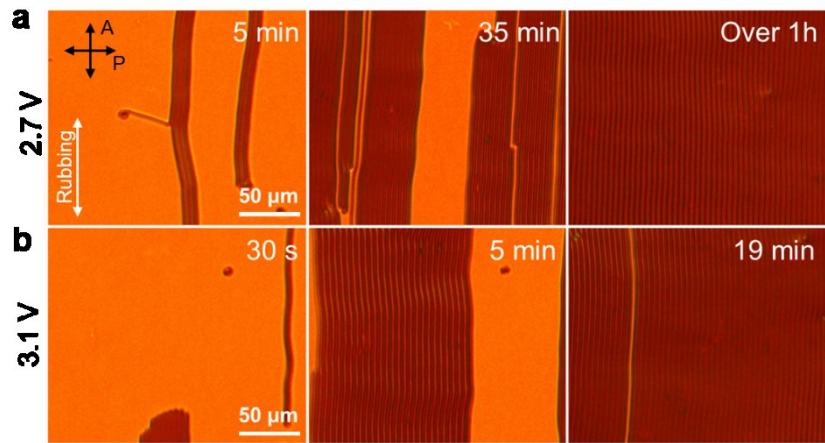


Figure S3. The formation process of the CLC grating by transitioning from standing helix (planar state) to lying helix state under (a) 2.7 V and (b) 3.1 V before irradiating at the wavelength of 365 nm.

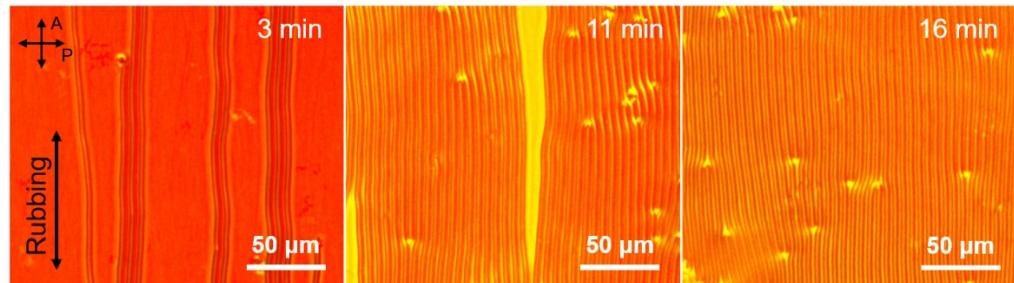


Figure S4. The formation process of the CLC grating by transitioning from standing helix (planar state) to lying helix state after irradiating at the wavelength of 450 nm under 2.8 V.

S5. Effect of Electric Field on Diffraction Angle

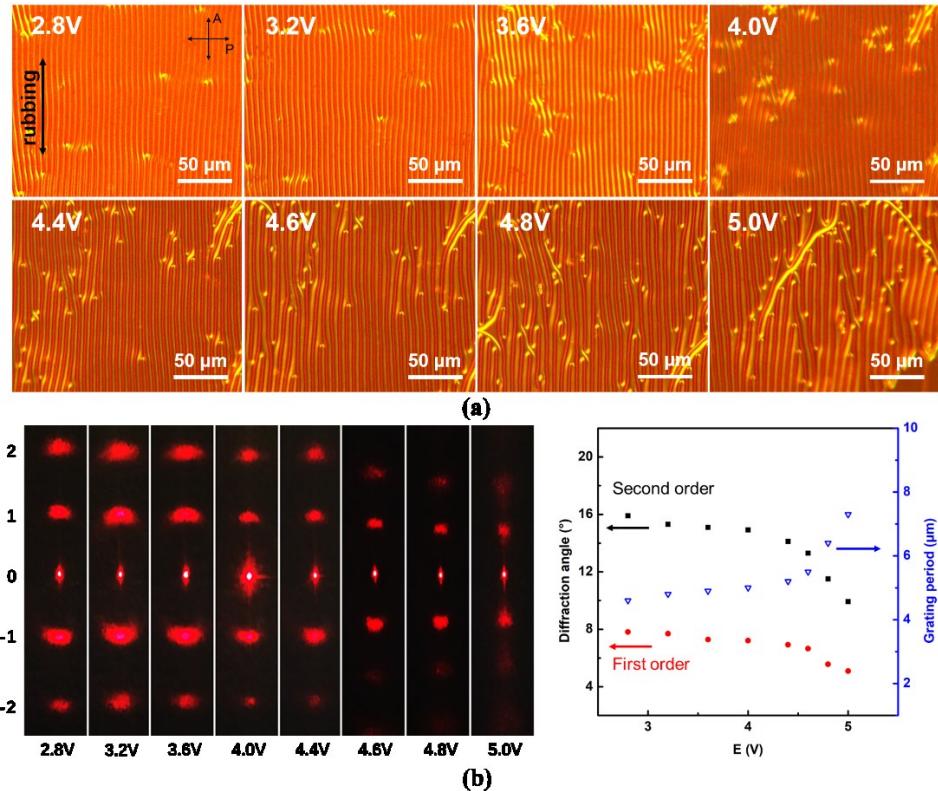


Figure S5. The CLC gratings with stripe direction parallel to the rubbing direction under different voltages. a) POM images and b) corresponding diffraction patterns (left), and corresponding diffraction angle and grating period (right) varying with electric field strength.

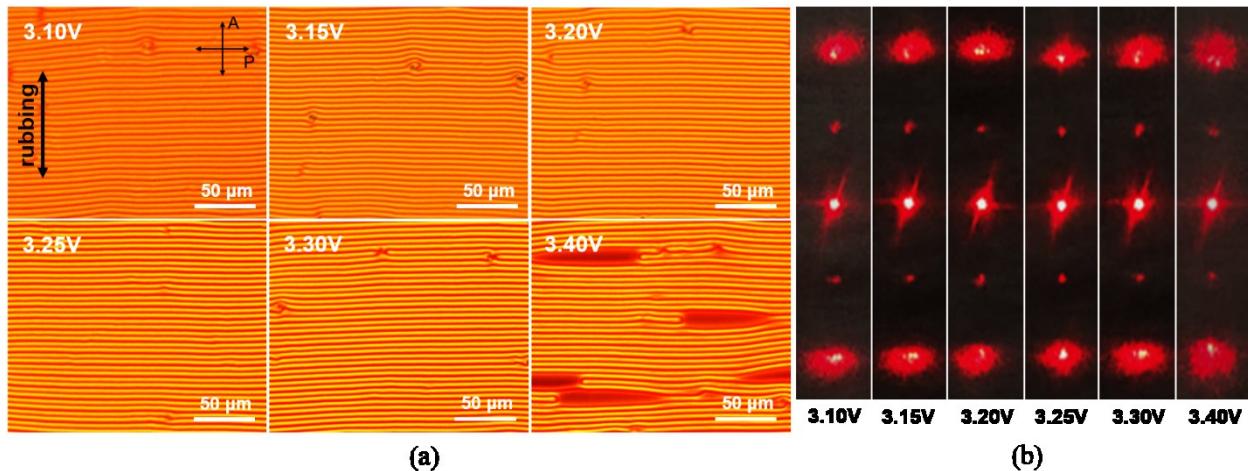


Figure S6. The CLC gratings with stripe direction perpendicular to the rubbing direction. a) POM images and b) corresponding diffraction patterns varying with electric field strength.

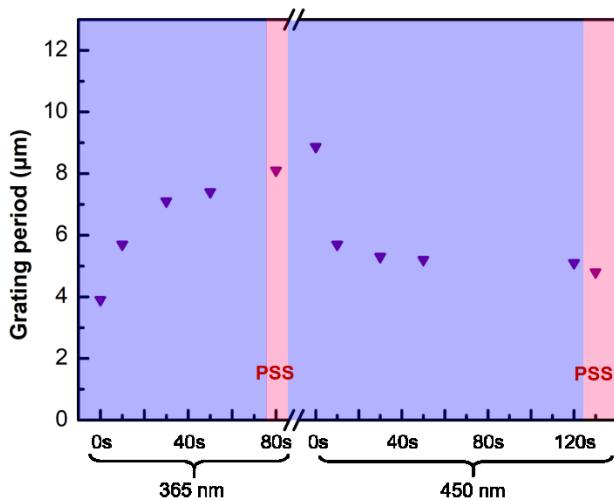


Figure S7. Variation of the grating period as a function of exposure time of two different wavelengths (365 nm and 450 nm) of light based on the diffraction patterns in Figure 7. Note that the electric field was increased from 2.7 V to 2.9 V at PSS of 365 nm irradiation.

References

- [1] Wang, H.; Bisoyi, H. K.; Wang, L.; Urbas, A. M.; Bunning, T. J.; Li, Q. Photochemically and Thermally Driven Full-Color Reflection in a Self-Organized Helical Superstructure Enabled by a Halogen-Bonded Chiral Molecular Switch. *Angew. Chem. Int. Ed.* **2018**, *57*, 1627.
- [2] Li, Q.; Li, Y.; Ma, J.; Yang, D.; White, T. J.; Bunning, T. J. Directing Dynamic Control of Red, Green, and Blue Reflection Enabled by a Light-Driven Self-Organized Helical Superstructure. *Adv. Mater.* **2011**, *23*, 5069.
- [3] Cano, R. Interprétation Des Discontinuités De Grandjean. *Bull. Soc. Fr. Mineral.* **1968**, *91*, 20.
- [4] Li, Y.; Wang, M.; White, T. J.; Bunning, T. J.; Li, Q. Azoarenes with Opposite Chiral Configurations: Light-Driven Reversible Handedness Inversion in Self-Organized Helical Superstructures. *Angew. Chem. Int. Ed.* **2013**, *52*, 8925.