Supporting Information

Reversible Visible-Light Tuning of Self-organized Helical Superstructures Enabled by Unprecedented Light-Driven Axially Chiral Molecular Switches

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1. Materials and Methods

All starting materials, solvents and reagents were purchased from Sigma-Aldrich Company at the highest commercial quality and used without further purification. Column chromatography was carried out on silica gel (230-400 meshes). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 meshes F_{254} glass plates. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 or a Bruker 400 spectrometer. Chemical shifts are reported in δ units (ppm) with the residual solvent peak as internal standard. UV-vis spectrum was taken by a Perkin Elmer Lambda 25 Spectrometer. CD spectrum was recorded by a Jasco-715. Mass spectrum was taken by Mass Spectrometry & Proteomics Facility of Ohio State University. Elemental analysis was performed by Robertson Microlet Inc. Textures and disclination line distance changes were observed by optical microscopy using a Leitz polarizing microscope with temperature controller or Nikon polarizing microscope. UV-vis irradiation was carried out by Xenon light source 100 W (UVGL–58, UVP Co.). The achiral nematic liquid crystal E7 was used in the study, which is a eutectic mixture of LC components commercially designed for display application.

2. Synthesis of Light-Driven Axially Chiral Switch (*S*,*S*)-6 and (*R*,*R*)-6

(*S*,*S*)-**6** was synthesized starting from (*S*)-2,2´-hydroxy-1,1´-binaphthyl [(*S*)-**1**], which was reacted with pivaloyl chloride in the presence of triethylamine to give (*S*)-2-hydroxy-2´-pivaloyloxy-1,1'-binaphthyl [(*S*)-**2**] (Figure S1). The pivaloyloxy protected (S)-**2** was nitrated to obtain the nitro-substituted binol (*S*)-**3** followed by de-protecting pivaloyloxy group with potassium hydroxide to get (*S*)-6-nitro-2,2´-dihydroxy-1,1'-binaphthyl [(*S*)-**4**]. Binaphthol (*S*)-**4** was reacted with [4-(4-propylcyclohexyl)phenyl]methanol by Mitsunobu reaction to obtain nitro product (*S*)-**5** followed by a reduction condition[1] to afford the target compound (*S*,*S*)-**6**. (*R*,*R*)-**6** was synthesized starting form (*R*)-2,2´-hydroxy-1,1´-binaphthyl [(*R*)-**1**] with the same procedure in (*S*,*S*)-**6**. (*S*,*S*)-**6**, (*R*,*R*)-**6** and all the intermediates were well identified by ^{1}H NMR, ^{13}C NMR, HRMS and elemental analysis.

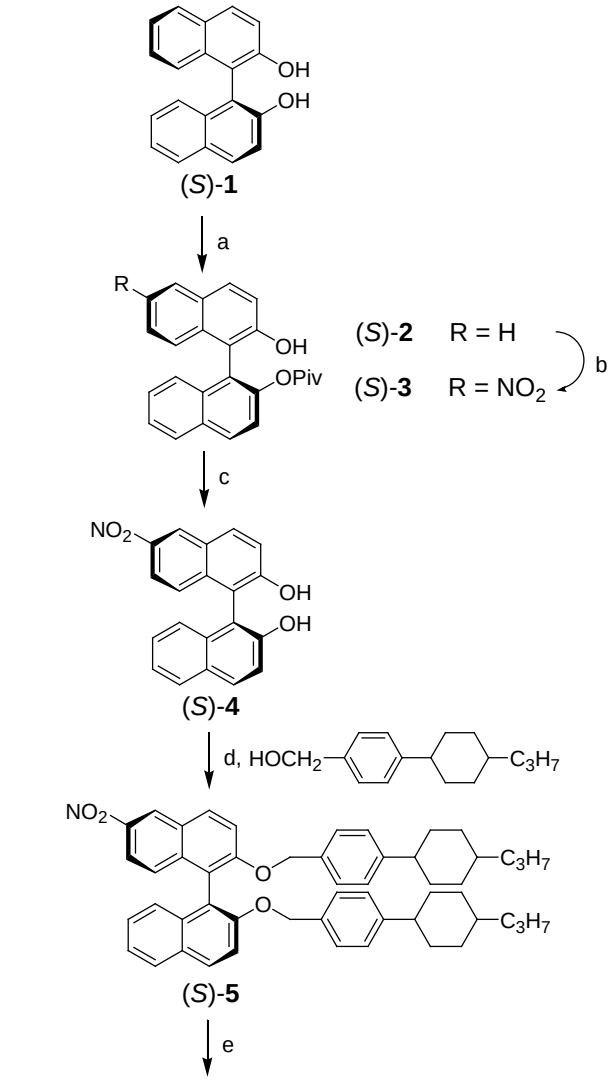

Figure S1. Synthesis of light-driven axially chiral switch (*S*,*S*)-**6** and (*R*,*R*)-**6**. Conditions: (a) Pivaloyl chloride, Et_3N; (b) concentrated HNO_3 and H_2SO_4; (c) KOH; (d) PPh_3, DIAD, THF; (e) Pb powder, HCOOH-NH_3.

2.1. (*S*)-2-Hydroxy-2'-pivaloyloxy-1,1'-binaphthyl [(*S*)-2]. To a solution of (*S*)-2,2´-hydroxy-1,1´-binaphthyl [(*S*)-**1**] (1.00 g, 3.75 mmol) and triethylamine (1.56 mL, 11.26 mmol) in acetonitrile (25 mL) was added pivaloyl chloride (0.47 mL, 3.79 mmol) dropwise slowly over 30 min at 0 ºC. The mixture was allowed to warm to room temperature and stirred for 4 h. The reaction mixture was diluted with ether (75 mL) and washed with aqueous 1N HCl (20 mL × 2), saturated aqueous $NaHCO_3$ (20 mL × 2), and brine (20 mL × 2). The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by column chromatography over silica gel with hexane/EtOAc (6:1) to give (*S*)-**2** (1.36 g, 98%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 1H, *J* = 9.2 Hz), 7.98 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 1H, *J* = 9.2 Hz), 7.82 (d, 1H, *J* = 6.8 Hz), 7.53−7.49 (m, 1H), 7.39−7.23 (m, 6H), 7.06 (d, 1H, *J* = 8.4 Hz), 5.13 (s, 1H), 0.78 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.8, 151.7, 148.3, 133.6, 133.4, 132.2, 130.7, 130.2, 129.0, 128.3, 127.9, 127.4, 126.6,

126.2, 125.6, 124.5, 123.5, 123.0, 121.8, 118.2, 114.2, 38.7, 26.4 (× 3).

2.2. (*S*)-6-Nitro-2-hydroxy-2´-pivaloyloxy-1,1´-binaphthyl [(*S*)-3]. Pivalate (*S*)-**2** (600 mg, 1.62 mmol) was added to a mixture of conc. nitric acid (1 mL), ether (15 mL) and conc. sulfuric acid (0.4 mL) at 0 ºC. The color of the reaction mixture turned yellow. After stirring for 2 h at 0 ºC, the mixture was poured into a mixture of ether (10 mL) and water (10 mL). The organic layer was washed with water (10 mL × 3) and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography over silica gel with hexane/EtOAc (4:1) to give (*S*)-**3** (606 mg, 90%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, 1H, *J* = 2.4 Hz), 8.12 (d, 1H, *J* = 8.8 Hz), 8.08 (d, 1H, *J* = 9.2 Hz), 8.03−8.00 (m, 2H), 7.56−7.53 (m, 1H), 7.47 (d, 1H, *J* = 9.2 Hz), 7.42−7.37 (m, 2H), 7.23 (d, 1H, *J* = 9.6 Hz), 7.17 (d, 1H, *J* = 9.2 Hz), 5.52 (s, 1H), 0.80 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.7, 155.3, 148.4, 143.8, 136.7, 133.0, 132.4, 132.2, 131.5, 128.6, 127.8, 127.3, 126.5, 126.0, 125.0, 124.8, 121.8, 121.3, 120.5, 120.2, 114.9, 38.8, 26.4 (× 3).

2.3. (*S*)-6-Nitro-2,2´-dihydroxy-1,1´-binaphthyl [(*S*)-4]. A mixture of (*S*)-**3** (606 mg, 1.46 mmol), potassium hydroxide (286 mg, 5.11 mmol), THF (10 mL) and H_2O (10 mL) was refluxed for 12 h. After being cooled to room temperature, the mixture was acidified with 1 N HCl and extracted with EtOAc (20 mL × 3). The organic phase was washed with aqueous $NaHCO_3$ (20 mL), brine (20 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography over silica gel with hexane/EtOAc (2:1) to give (*S*)-**4** (479 mg, 99%) as a reddish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, 1H, *J* = 2.4 Hz), 8.17 (d, 1H, *J* = 8.4 Hz), 8.06 (dd, 1H, *J* = 9.6, 2.4 Hz), 8.03 (d, 1H, *J* = 8.8 Hz), 7.93 (d, 1H, *J* = 7.6 Hz), 7.55 (d, 1H, *J* = 9.2 Hz), 7.43−7.32 (m, 3H), 7.25 (d, 1H, *J* = 8.8 Hz), 7.06 (d, 1H, *J* = 8.4 Hz), 5.41 (s, 1H), 4.96 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.0, 152.8, 144.1, 136.7, 133.3, 133.1, 132.1, 129.5, 128.6, 127.9, 127.8, 125.8, 125.2, 124.4, 123.7, 120.9, 120.1, 117.9, 112.2, 109.5.

2.4. (*S*)-6-Nitro-2,2´-di[4-(4-propylcyclohexyl)benzyloxy]-1,1´-binaphthyl [(*S*)-5]. A mixture of (*S*)-**4** (741 mg, 2.24 mmol), [4-(4-propylcyclohexyl)phenyl]methanol (1.30 g, 5.60 mmol), triphenylphosphine (1.76 g, 6.72 mmol), DIAD (Diisopropyl azodicarboxylate) (1.40 ml, 6.72 mmol) and THF (30 mL) was stirred overnight under reflux. Then, the mixture was separated by ether (30 mL) and water (30 mL), extracted with ether (30 mL × 3) and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography over silica gel with hexane/EtOAc (5:1) to give (*S*)-**5** (728 mg, 65%) as a yellow solid.

Data of (*S*)-**5**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.83 (d, 1H, *J* = 2.2 Hz), 8.09 (d, 1H, *J* = 9.4 Hz), 7.97 (d, 1H, *J* = 9.2 Hz), 7.93 (dd, 1H, *J* = 9.2, 2.0 Hz), 7.89 (d, 1H, *J* = 7.6 Hz), 7.54 (d, 1H, *J* = 9.4 Hz), 7.46 (d, 1H, *J* = 9.0 Hz), 7.39−7.32 (m, 1H), 7.28−7.22 (m, 2H), 7.09 (d, 1H, *J* = 8.2 Hz), 6.98−6.92 (m, 6H), 6.85 (d, 2H, *J* = 8.4 Hz), 5.10 (s, 2H), 5.04 (s, 2H), 2.40−2.32 (m, 2H), 1.83−1.78 (m, 8H), 1.40−1.15 (m, 10H),

1.05−0.96 (m, 4H), 0.89 (t, 6H, *J* = 7.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.4, 154.1, 147.3, 147.2, 143.7, 137.1, 134.5, 134.0, 133.8, 131.6, 129.9, 129.4, 128.1, 127.3, 127.0, 126.8 (× 2), 126.7 (× 2), 126.6 (× 3), 126.5 (× 2), 125.0, 124.9, 123.8, 121.0, 119.6, 119.0, 117.2, 115.6, 70.9, 70.6, 44.2 (× 2), 39.7 (× 2), 37.0 (× 2), 34.2 (× 2), 33.5 (× 4), 21.6 (× 2), 20.0 (× 2), 14.4 (× 2).

Data of (*R*)-**5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, 1H, *J* = 2.0 Hz), 8.08 (d, 1H, *J* = 8.8 Hz), 7.96 (d, 1H, *J* = 8.8 Hz), 7.92 (dd, 1H, *J* = 9.6, 2.4 Hz), 7.89 (d, 1H, *J* = 8.0 Hz), 7.53 (d, 1H, *J* = 9.2 Hz), 7.45 (d, 1H, *J* = 8.8 Hz), 7.37−7.33 (m, 1H), 7.26−7.22 (m, 2H), 7.09 (d, 1H, *J* = 8.8 Hz), 6.96−6.90 (m, 6H), 6.85 (d, 2H, *J* = 8.4 Hz), 5.09 (s, 2H), 5.03 (s, 2H), 2.38−2.31 (m, 2H), 1.83−1.77 (m, 8H), 1.39−1.16 (m, 10H), 1.04−0.95 (m, 4H), 0.89 (t, 6H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 154.1, 147.3, 147.2, 143.7, 137.1, 134.5, 134.0, 133.8, 131.6, 129.9, 129.4, 128.1, 127.3, 127.0, 126.8 (× 2), 126.6 (× 2), 126.6 (× 3), 126.5 (× 2), 125.0, 124.9, 123.8, 121.0, 119.6, 119.0, 117.2, 115.6, 70.9, 70.6, 44.2 (× 2), 44.2 (× 2), 39.7 (× 2), 37.0 (× 2), 34.2 (× 2), 33.5 (× 4), 20.0 (× 2), 14.4 (× 2).

2.5. (*S*,*S*)-2,2′,2′′,2′′′-tetra[4-(4-propylcyclohexyl)benzyloxy]-6,6′-azo-dibinaphthyl [(*S*,*S*)-6]. A suspension of (*S*)-**5** (100 mg, 0.13 mmol) and lead powder (273 mg, 1.30 mmol) in methanol/THF was stirred with triethylammonium formate (230 μL, 1.3 mmol) under a nitrogen atmosphere. The resulting reaction mixture was filtered through a Celite pad and washed with solvent. The combined filtrate and washings were concentrated under vacuum. The residue was taken up in ether (10 mL), and washed with water (10 mL × 2). The organic layer was dried over Na_2SO_4, evaporated the organic solvent, and the residue was purified by column chromatography over silica gel with hexane/EtOAc to give (*S*,*S*)-**6** (89 mg, 61%).

Data of (*S*,*S*)-**6**: IR (film) 2954, 2920, 2850, 1619, 1592, 1509, 1269, 1087 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, 2H, *J* = 1.6 Hz), 8.06 (d, 2H, *J* = 9.2 Hz), 7.94 (d, 2H, *J* = 9.2 Hz), 7.87 (d, 2H, *J* = 8.0 Hz), 7.83 (dd, 2H, *J* = 9.2, 1.6 Hz), 7.44 (d, 4H, *J* = 9.2 Hz), 7.35−7.31 (m, 2H), 7.25−7.19 (m, 6H), 6.95−6.88 (m, 16H), 5.04 (d, 4H, *J* = 8.0 Hz), 5.03 (d, 4H, *J* = 7.6 Hz), 2.38−2.29 (m, 4H), 1.83−1.76 (m, 16H), 1.51−1.12 (m, 20H), 1.04−0.94 (m, 8H), 0.88 (t, 6H, *J* = 7.6 Hz), 0.86 (t, 6H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6 (× 2), 154.2 (× 2), 149.0 (× 2), 147.0 (× 2), 147.0 (× 2), 135.6 (× 2), 134.8 (× 2), 134.6 (× 2), 134.1 (× 2), 130.7 (× 2), 129.4 (× 2), 129.2 (× 2), 127.9 (× 2), 127.6 (× 2), 126.7 (× 4), 126.6 (× 4), 126.6 (× 4), 126.4 (× 2), 125.4 (× 2), 123.7 (× 2), 121.1 (× 2), 120.4 (× 2), 117.7 (× 2), 116.2 (× 2), 116.1 (× 2), 71.1 (× 2), 70.8 (× 2), 44.2 (× 2), 44.2 (× 2), 39.7 (× 4), 39.7 (× 4), 37.0 (× 2), 37.0 (× 2), 34.3 (× 2), 34.2 (× 2), 33.5 (× 4), 33.5 (× 4), 20.0 (× 2), 20.0 (× 2), 14.4 (× 4); HRMS (MALDI$^+$) calcd for $C_{104}H_{114}N_2O_4^+$ (M^+) 1454.878, found 1455.863; Elemental analysis calcd for $C_{104}H_{114}N_2O_4$: C 85.79, H 7.89, N 1.92, Found: C 85.52, H 7.95, N 1.85.

Data of (*R*,*R*)-**6**: IR (film) 2956, 2920, 2849, 1619, 1592, 1509, 1268, 1086 cm^{-1}; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.38 (d, 2H, *J* = 2.4 Hz), 8.00 (d, 2H, *J* = 8.8 Hz), 7.86 (d, 2H, *J* = 9.2 Hz), 7.80 (d, 2H, *J* = 8.0 Hz), 7.75 (dd, 2H, *J* = 9.2, 2.4 Hz), 7.37 (d, 4H, *J* = 9.2 Hz), 7.28−7.24 (m, 2H), 7.17−7.14 (m, 6H), 6.87−6.80 (m, 16H), 4.96 (d, 4H, *J* = 8.0 Hz), 4.96 (d, 4H, *J* = 8.4 Hz), 2.30−2.21 (m, 4H), 1.75−1.69 (m, 16H), 1.29−1.06 (m, 20H), 0.98−0.87 (m, 8H), 0.81 (t, 6H, *J* = 7.2 Hz), 0.78 (t, 6H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6 (× 2), 154.2 (× 2), 149.0 (× 2), 147.0 (× 2), 147.0 (× 2), 135.6 (× 2), 134.8 (× 2), 134.6 (× 2), 134.1 (× 2), 130.7 (× 2), 129.4 (× 2), 129.2 (× 2), 127.9 (× 2), 127.6 (× 2), 126.7 (× 4), 126.6 (× 4), 126.6 (× 4), 126.4 (× 2), 125.4 (× 2), 123.7 (× 2), 121.1 (× 2), 120.4 (× 2), 117.7 (× 2), 116.3 (× 2), 116.1 (× 2), 71.2 (× 2), 70.8 (× 2), 44.2 (× 2), 44.2 (× 2), 39.7 (× 4), 39.7 (× 4), 37.0 (× 2), 37.0 (× 2), 34.3 (× 2), 34.2 (× 2), 33.5 (× 4), 33.5 (× 4), 20.0 (× 2), 20.0 (× 2), 14.4 (× 4); HRMS (MALDI$^+$) calcd for $C_{104}H_{114}N_2O_4^+$ (M^+) 1454.878, found 1455.860; Elemental analysis calcd for $C_{104}H_{114}N_2O_4$: C 85.79, H 7.89, N 1.92, Found: C 85.53, H 7.97, N 1.94.

3. Reversible Photoisomerization.

Many different wavelength lights (Light source: Xenon light source 100 W, Intensity: 30 mW/cm^2) were attempted to irradiate (*S*,*S*)-**6** and (*R*,*R*)-**6** for seeking appropriate wavelength which could give the largest change upon its irradiation, and the visible-light irradiation at 440 nm light showed the biggest change from initial state to the photostationary state (PSS) (*trans*↔*cis* equilibrium). Irradiating (*S*,*S*)-**6** or (*R*,*R*)-**6** to PSS_{440} upon 440 nm light followed by using some different wavelength lights to irradiate them, it was observed that 550 nm wavelength was the appropriate wavelength which made the excited state isomer have the greatest-scaled transformation towards its initial state isomer. The reversible photoisomerization process, either initial state to excited state or excited state to initial state transformation, can be happened just by visible light irradiation at 440 nm or 550 nm wavelength, which brings a different vision from the normal form, *trans*→*cis* by UV light and *cis*→*trans* by visible light. Using visible light instead of UV light opens a new and exciting avenue and provides a wider application.

17.0 μM solution of (*S*,*S*)-**6** in CH_2Cl_2 irradiated with visible light at 440 nm takes approximately 40 s to reach PSS_{440} (Figure 3A) whereas its reverse process irradiated with visible light at 550 nm takes approximately 70 s to PSS_{550} (Figure 3B). Compared with most azo compounds, it exhibited a very short time to perform the reversible photoisomerization. Figure S2 showed the cycle of the absorbance of (*S*,*S*)-**6**. The maximum absorption wavelengths upon 440 nm and 550 nm irradiation were chosen to confirm the change cycles. Our experiment result showed that the photoisomerization of (*S*,*S*)-**6** is reversible and has a pretty good repeatability.

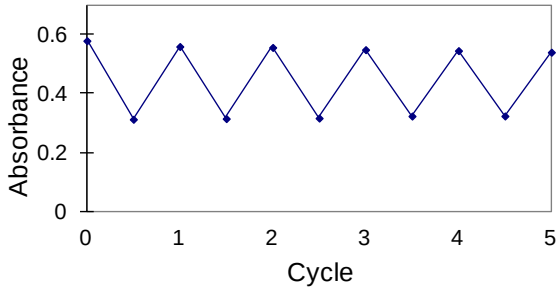

Figure S2. Cyclic absorbance of (*S*,*S*)-**6** in CH_2Cl_2 (17 μM) at 407 nm as the solution was irradiated with visible light at 440 nm for 45 s and then with visible light at 550 nm for 75 s.

The effects of photoisomerizations on the chirality of these two isomers were studied by CD spectroscopy. The CD spectra show two main regions (Figure 4). The intense negative excitations at 210-240 nm due to the long-axis-polarized transition of the naphthalene reflect the absolute *S*-configuration of the binaphthyl moieties. However, the chirality changes of *trans*↔*cis* photoisomerization are clearly revealed at 240-300 nm in the CD spectra, which shows the chirality of the two isomers of the azo moieties changes along with the *trans*↔*cis* photoisomerization. The optical activity of (*S*,*S*)-**6** and (*R*,*R*)-**6** at initial state were characterized by CD spectra shown in Figure S3. Their CD spectra exhibited a mirror image relationship with a strong sharp peak at about 230 nm which means the system existed an enantiomeric binaphthyl.

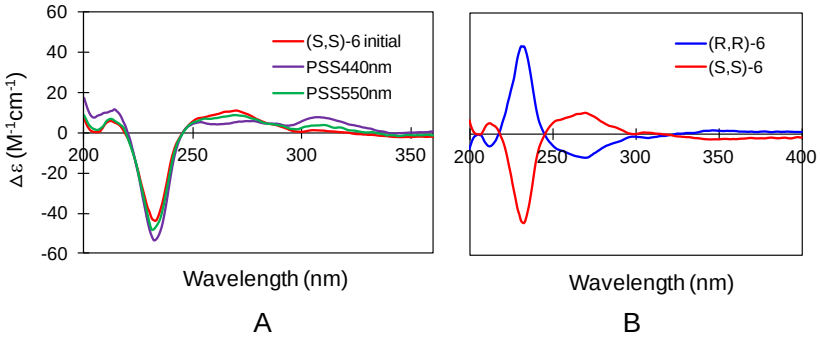

Figure S3. A: CD spectra of (*S*,*S*)-**6** from initial to PSS_{440} upon visible light at 440 nm irradiation, then back to PSS_{550} upon visible light at 550 nm. B: CD spectra of (*S*,*S*)-**6** and (*R*,*R*)-**6** (9.6 μM in CH_3CN) in their initial state.

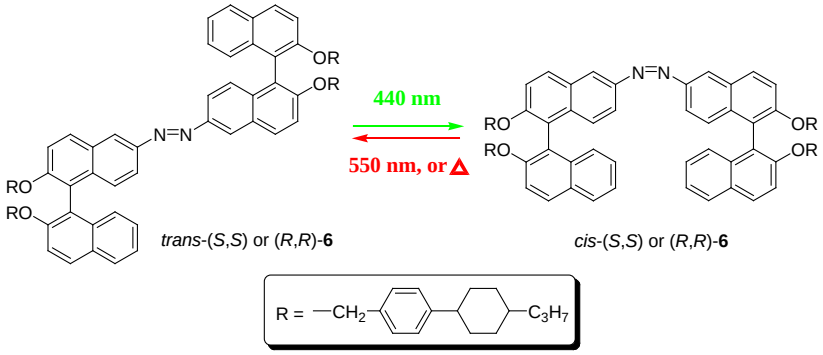

Figure S4. Schematic representation of proposed photoisomerization of chiral azo molecule (*S*,*S*)-**6** and (*R*,*R*)-**6**.

3. Measurement of Helical Twisting Power.

Doping chiral switch (*S*,*S*)-**6** and (*R*,*R*)-**6** in an achiral nematic LC host E7 at a proper concentration can induce left handedness and right-handedness optically tunable helical superstructure, i.e. cholesteric phase, respectively. The helical twisting powers (HTPs, β) were calculated following the equation, $\beta = (pc)^{-1}$. c is the concentration. The induced helical pitches (p) were measured by using the Grandjean-Cano method, $p = 2R\tan\theta$, where R represents the distance between Grandjean lines as shown in Figure S5, and θ is the wedge angle of wedge cells (KCRK-07, $\tan\theta = 0.0196$). The corresponding HTP values at different states were calculated on the basis of the above equations.

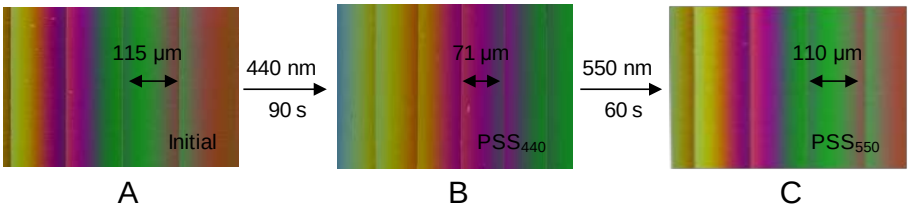

Figure S5. Crossed polarized textures of 2.1 wt% (*S*,*S*)-**6** in an achiral LC E7 at room temperature in a stripe-wedge Grandjean-Cano cell upon visible light at 440 nm under 0 s (A) and 90 s (B) followed by visible light irradiation at 550 nm with 60 s (C).

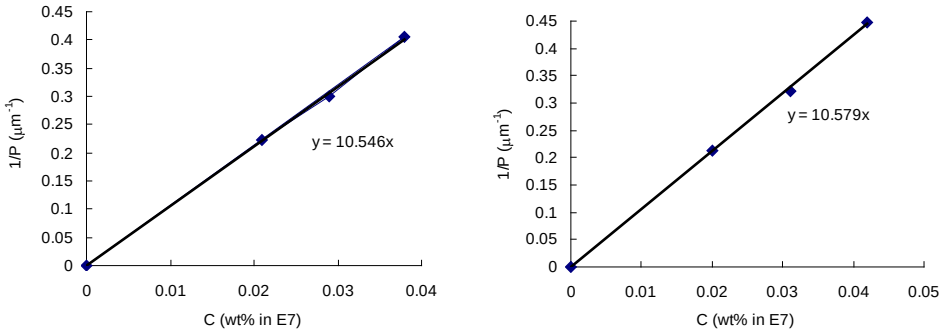

Figure S6. The plots of 1/P *vs.* C showed the HTP values of (*S*,*S*)-**6** (left) and (*R*,*R*)-**6** (right) at their initial state.

4. Fluorescence Spectrum of (*S*,*S*)-6

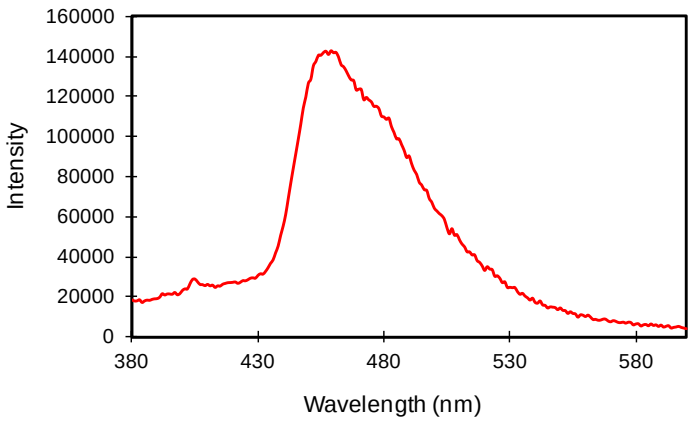

Figure S7 Fluorescence spectrum of (*S*,*S*)-**6** in CH_3CN (15 μM) with excitation wavelength at 361 nm.

5. Thermal relax of (*S*,*S*)-6 in CH_2Cl_2 Solvent

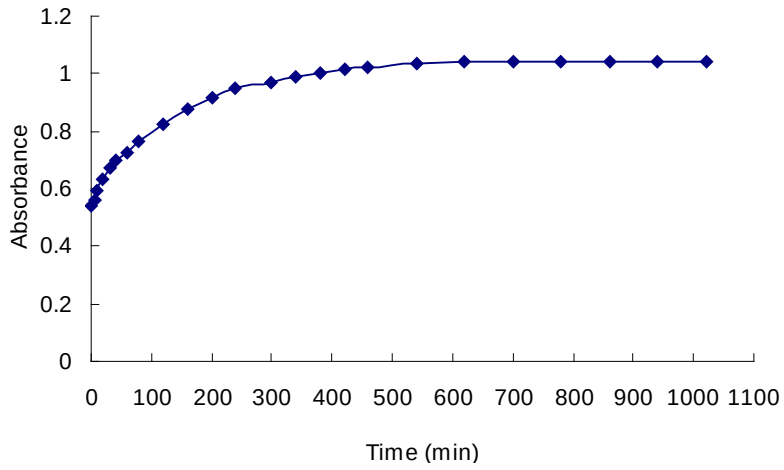

Figure S8 The plots of thermal relax of (*S*,*S*)-**6** in CH_2Cl_2 (17 μM) starting from PSS_{440nm}. For the process of (*S*,*S*)-**6** from PSS_{440nm} to initial state, it took approximately 10 h in CH_2Cl_2.

Reference

1. Srinivasa, G. R.; Abiraj, K.; Channe Gowda, D. *Tetrahedron Lett.* **2003**, *44*, 5835-5837.