Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Reversible Chirality Inversion of Circularly Polarized Luminescence in a Photo-invertible Helical Cholesteric Superstructure

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## 1. General information

All the solvents and reagents were purchased from commercial sources unless otherwise noted. SLC1717 was purchased from Shijiazhuang Chengzhi Yonghua Display Materials Ltd. Right-handed chiral dopant, CD-1 was purchased from Bayi Space LCD. Column chromatography was carried out on silica gel (200-300 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh GF254 glass plates.

$^{1}$H- and $^{13}$C-NMR spectra were recorded on a Bruker AVANCE III(400 MHz $^{1}$H; 100 MHz $^{13}$C) spectrometer using $CDCl_3$ or DMSO-$d_6$ as solvent. Chemical shifts are reported as δ in unit of parts per million (ppm) with the residual solvent peak or tetramethylsilane (TMS) as the internal standard. The coupling constant (J) is reported in Hertz (Hz) and the multiplicities are designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. UV–vis absorption and fluorescence spectroscopies were carried out using a Hitachi U-3010 and a Hitachi F-4500 instrument, respectively. Circular dichroism (CD) measurement was conducted on a Jasco 810 spectropolarimeter. CPL spectra were measured and recorded at room temperature on JASCO CPL-200. Disclination line distance changes and fingerprint textures were observed using a polarizing optical microscope (POM, Leica DM2500P) mounted on a hot stage and calibrated at a temperature accuracy of 0.1 °C (Linkam, THBS-600). The blue and UV light irradiation were carried out with a 450 nm and a 365 nm LED light source. In order to estimate photoisomerization yields according to $^{1}$H-NMR spectra, the the chiral fluorescence photoswitch in solvent was irradiated for 60 s in both directions. Quantum chemical calculations on both isomers of the chiral fluorescence photoswitch were performed using density functional theory (DFT) at B3LYP/6-31G(d) level incorporated in the Gaussian 09 set of programs.

## 2. Fabrication of CLC with photo-invertible helical superstructure

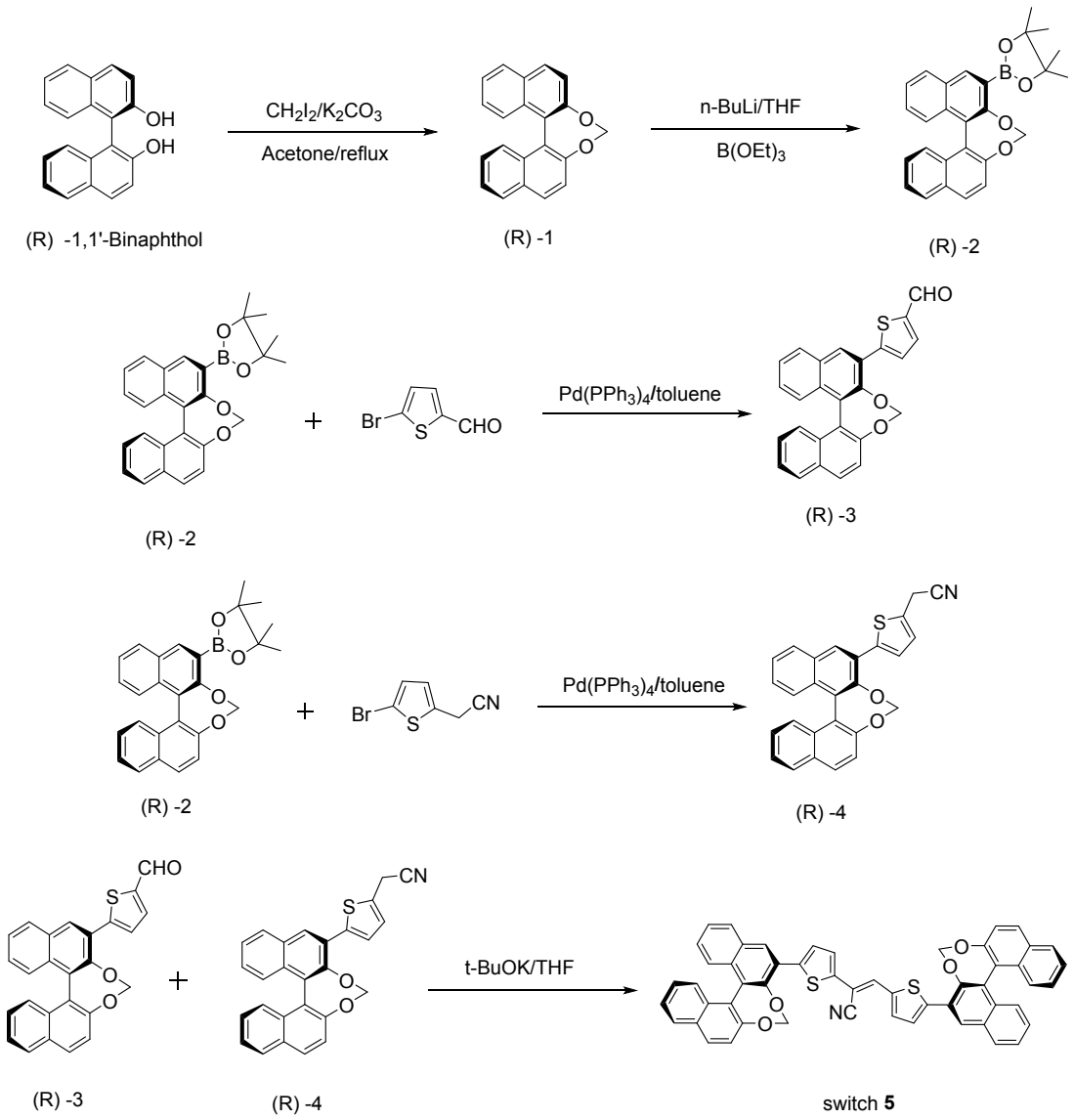
To fabricate a planar-alignment LC sample, clean glass substrates were spin-coated with an aqueous solution of polyvinylalcohol (PVA) (3.5 wt%). After curing at 80 $^{o}$C for 1 h, the PVA layers of the substrates were rubbed with rayon cloth to induce homogeneous alignment of LC molecules. Then, two substrates with rubbed PVA layer were bonded together in an anti-parallel direction, wherein the cell gap was determined by doping 10 μm polystyrene spacers into the LC mixture. Then the LC mixtures with an amount of left-handed chiral fluorescent photoswitch (switch **5**) and right-handed CD-1 were filled into the above empty cell.

For the homeotropic-alignment LC sample, the glass surface was treated with a thin DMOAP (dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride) layer to align the injected CLC mixture perpendicular to the glass substrates.

In order to induce chirality of the CLC, a blue-LED (450 nm) source was employed as a trigger for the *trans*→*cis* isomerization (20 mW/cm$^2$). A UV-LED (365 nm) source was

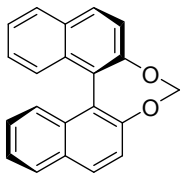
employed as a trigger for *cis*→*trans* isomerization (10 mW/cm$^2$), and it also serves as a emitted light to display fluorescence (2.0 mW/cm$^2$).

## 3. Synthesis of chiral fluorescent photoswitch




**Scheme S1.** Synthesis of chiral fluorescence photoswitch switch **5**.

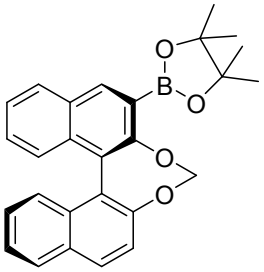
**(R)-2,2'-Methylenedioxy-1,1'-binaphthyl, (*R*)-1:**



A mixture of (R)-1,1'-Binaphthol (5.73 g, 20 mmol), diiodomethane (16.07 g, 60 mmol) and anhydrous $K_2CO_3$ (27.64 g, 200 mmol) in acetone (80 mL) was stirred magnetically and

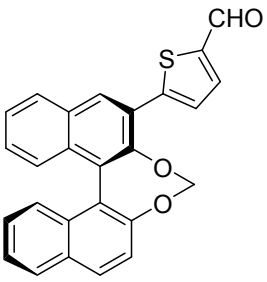
refluxed until the reaction completed as monitored by TLC. After cooling to room temperature, the mixture was extracted with trichloromethane and water. The combined organic layer was washed with water, dried over $Na_2SO_4$ and concentrated. The crude product was purified by column chromatography using trichloromethane/petroleum ether (1/1) as eluent to give a white solid (4.68 g, 78 %).$^1$H-NMR (400 MHz, $CDCl_3$, δ): 7.99 (d, 2H; Ar-H), 7.95 (d, 2H; Ar-H), 7.52–7.43 (m, 6H, Ar-H), 7.32–7.27 (m, 2H, Ar-H), 5.69 (s, 2H, -$CH_2$-).

**(R)-2-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)-4,4,5,5-tetramethyl-1,3,2-Dioxaborolane, (R)-2:**




To a THF solution (80 mL) of (R)-1 (4.47 g, 15 mmol) at -20 °C under nitrogen was added n-BuLi (5.6 mL, 2.7 M in n-pentane, 15 mmol) dropwise. The solution was then stirred at this temperature for 0.5h before 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.58 g, 30 mmol) was added dropwise. Then the reaction mixture was allowed to warm to room temperature and stirred for another 3 h. The reaction was quenched with water and extracted with dichloromethane (DCM) (2×20 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated. The resulting residue was purified by column chromatography using DCM as eluent to give a colorless solid (2.86 g, yield 45 %). $^1$H NMR (400 MHz, $CDCl_3$, δ): 8.47 (s, 1H, Ar-H), 8.01-7.94 (m, 3H, Ar-H), 7.52-7.44 (m, 5H, Ar-H), 7.36-7.29 (m, 2H, Ar-H), 5.79-5.73 (d, 2H, -$CH_2$-), 1.44 (d, 12H, -$CH_3$).

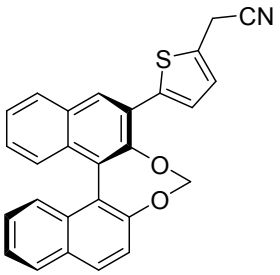
**(R)-5-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)thiophene-2-carbaldehyde, (R)-3:**




Tetrakis(triphenylphosphine)palladium(0.17g, 0.15 mmol), 5-bromothiophene-2-carbaldehyde (0.57 g, 3 mmol) and (R)-2 (1.27 g, 3 mmol) were dissolved in 30mL toluene. The mixture was then added 8 mL ethanol and 15 mL 20 % $Na_2CO_3$ solution before being stirred at 90 ℃ under nitrogen for 18 h. The mixture was extracted with DCM and the combined organic layers were

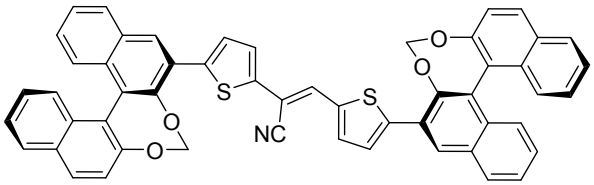
dried over $Na_2SO_4$ and concentrated. The resulting residue was purified by column chromatography (DCM:PE=1:1) to give a pale yellow solid (0.87 g, yield 71 %). $^1$H NMR (400 MHz, $CDCl_3$, δ): 9.95 (s, 1H, -CHO), 8.37(s, 1H, Ar-H), 8.03-7.95 (m, 3H, Ar-H), 7.82 (d, 1H, Ar-H), 7.78 (d, 1H, Ar-H), 7.52-7.44 (m, 5H, Ar-H), 7.34-7.30 (m, 2H, Ar-H), 5.74-5.64 (dd, 2H, -$CH_2$- ).

**(R)-2-(5-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)thiophen-2-yl)acetonitrile, (R)-4:**




Tetrakis ( triphenylphosphine ) palladium ( 0.17g, 0.15 mmol ), 2 - (5 - Bromothiophen - 2 -yl ) acetonitrile (0.61 g, 3 mmol) and (R)-2 (1.27 g, 3 mmol) were dissolved in 30 mL toluene. The mixture was then added 8mL ethanol and 15 mL 20% $Na_2CO_3$ solution before being stirred at 90 ℃ under nitrogen for 18 h. The mixture was extracted with DCM and the combined organic layers were dried over $Na_2SO_4$ and concentrated. The resulting residue was purified by column chromatography (DCM:PE=1:1) to give a pale red solid (0.76 g, yield 60 %). $^1$H NMR (400 MHz, CDCl3, δ): 8.25 (s, 1H, Ar-H), 8.02 (d, 1H, Ar-H), 7.96-7.93 (dd, 2H, Ar-H), 7.55-7.42 (m, 6H, Ar-H), 7.34-7.28 (m, 2H, Ar-H), 7.12 (d, 1H, Ar-H), 5.71-5.62 (dd, 2H, -$CH_2$-), 3.96 (s, 2H, -$CH_2$-).

**Switch 5:**




(R)-3 (0.735g, 1.8 mmol), (R)-4 (0.755g, 1.8 mmol) and t-BuOK (0.81g, 0.72 mmol) were dissolved in THF (50 ml). Two drops of t-BuOH was added as the catalyst and the solution was heated at 60 ℃ and reflux. After 3 h the reaction mixture was cooled to room temperature. Then check for the acidity and alkalinity, with a PH between 7 and 8. The product was purified by column chromatography using trichloromethane as eluent to give a red solid (0.73 g, yield 50 %). The whole operation took place in the dark. $^1$H NMR (400 MHz, $CDCl_3$, δ): 8.36 (s, 1H, Ar-H), 8.31 (s, 1H, Ar-H), 8.02-7.94 (m, 6H, Ar-H), 7.74-7.65 (m, 3H, Ar-H), 7.51 (s, 1H, -CH=CCN), 7.50-7.40 (m, 11H, Ar-H), 7.34-7.29 (m, 4H, Ar-H), 5.77-5.75 (dd, 2H, -$CH_2$-), 5.69-5.67 (dd, 2H, -$CH_2$-). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 151.25, 151.20, 147.40, 147.30,

143.30, 139.58, 139.23, 138.23, 132.52, 132.17, 131.88, 131,81, 131.68, 131.54, 131.49, 131.31, 130.65, 128.68, 128.53, 128.48, 128.22, 127.79, 127.55, 127.49, 127.32, 127.22, 127.16, 126.81, 126.69, 126.51, 126.26, 125.89, 125.73, 125.66 125.13, 120.75, 120.72, 117.02, 102.81, 102.63.

**4. Photochemistry behavior of switch 5**

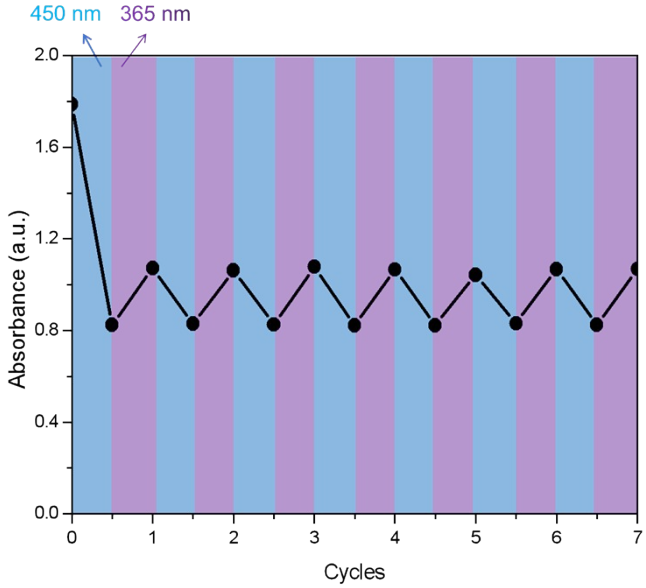



**Figure S1.** Fatigue resistance of UV absorption spectrum of switch **5** in THF solution upon alternating irradiations with 450 nm visible light and 365 nm UV light in seven cycles.

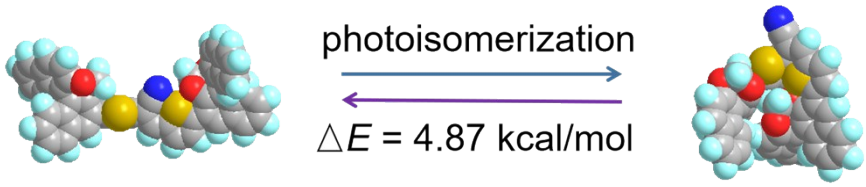



**Figure S2.** Optimized structure of switch **5** in trans and cis forms (space filling mode) obtained by Gaussian09 calculations

**5. Measurement of helical twisting power (HTP) of the chiral dopant**

Grandjean-Cano wedge method is used here to measure pitch length and the procedures are mentioned in previous paper[3]. We can see disclination lines of the Ch-LC in the wedge cell through a polarizing optical microscope (POM). The pitch length was calculated based on the equation $p$=2Rtanθ, where R represents the distance between two adjacent lines and θ is the angle of wedge cells (EHC, KCRK-07, tanθ = 0.0183). The helical twisting power (HTP) can

be defined as the ability of chiral dopants to induce a helical superstructure in nematic host and the HTP value is related to the pitch of the cholesteric liquid crystal as $\beta=(pc)^{-1}$, where $p$ is the helical pitch length and $c$ is the concentration of the chiral dopants.

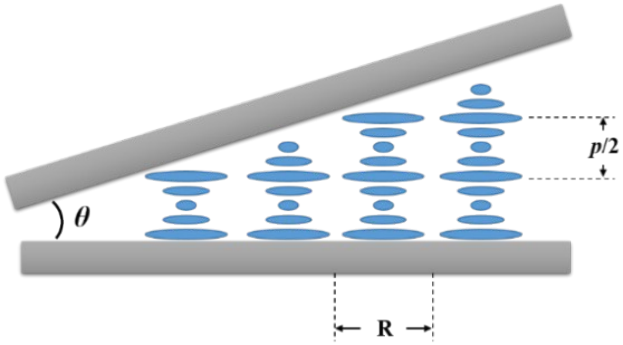



**Figure S3.** Schematic diagram of the HTP value measurement using the Grandjean-Cano wedge method.

As listed in Figure S4 and Table S1, upon irradiation with 450 nm visible light, the HTP value of switch **5** in SLC1717 dramatically decreased from 65.79 to 34.36 $\mu m^{-1}$. Then irradiation with 365 nm UV light, the HTP value of switch **5** in SLC1717 dramatically increased from 34.36 to 50.51 $\mu m^{-1}$. The above results demonstrate that switch **5** exhibits high HTP values and moderate HTP changes upon the light irradiations.

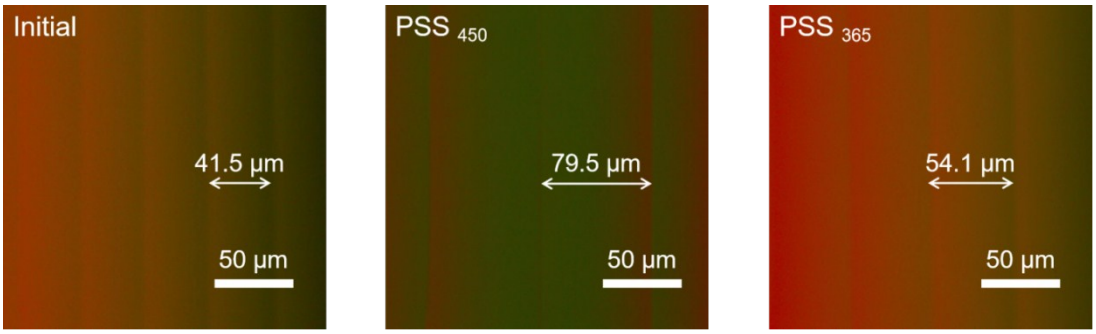



**Figure S4.** Variations of Cano lines observed by using POM of LC cell with 1.0 wt% switch **5** in SLC1717.

**Table 1.** The changes in HTP values of LC cell with 1.0 wt% switch **5** in SLC1717.

| Dopant | P(μm) | | | HTP(wt%/$\mu m^{-1}$) | | | $\triangle HTP^a$ [$\mu m^{-1}$] | $\triangle HTP^b$ [$\mu m^{-1}$] |
|---|---|---|---|---|---|---|---|---|
| | Initial | $PSS_{450}$ | $PSS_{365}$ | Initial | $PSS_{450}$ | $PSS_{365}$ | | |
| switch **5** | 1.52 | 2.91 | 1.98 | 65.79 | 34.36 | 50.51 | 31.43 | 16.15 |

[a]The change of HTP value between the initial state and the $PSS_{450}$. [b]The change of HTP value between $PSS_{450}$ and $PSS_{365}$.

## 6. Photoluminescence properties of the photo-invertible CLC sample

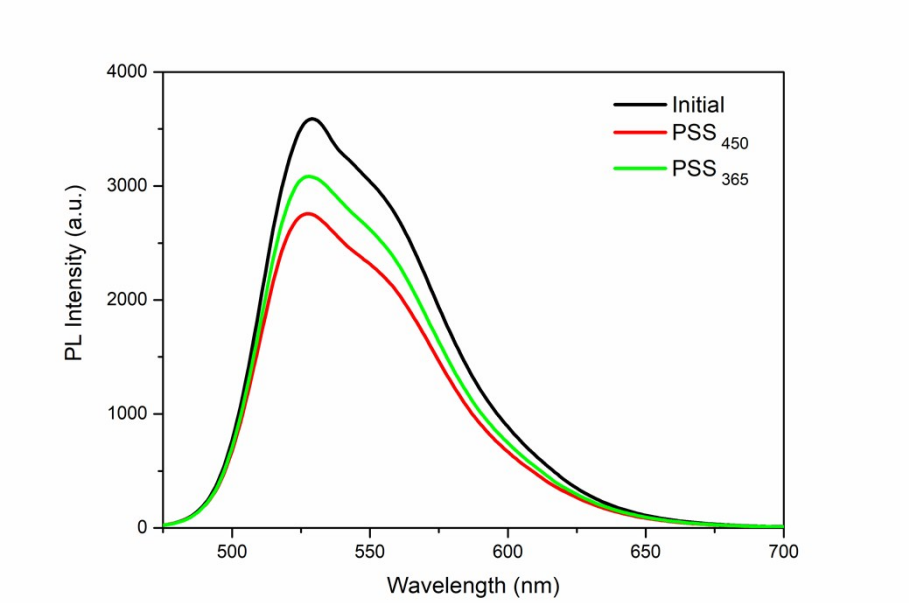



**Figure S5.** PL spectra of photo-responsive CLC doping 1.2 wt% of switch **5** and 1.1 wt% CD-1 into SLC1717 tuned by 450 nm visible light and 365nm UV light.

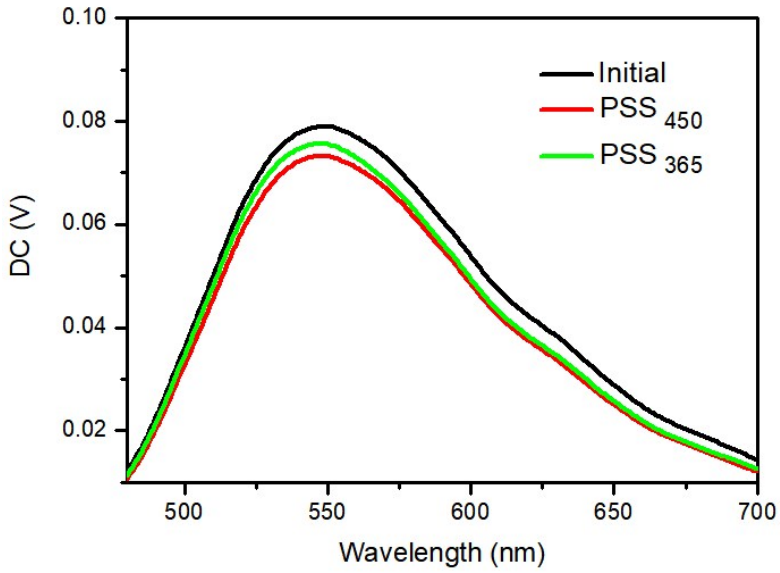



**Figure S6.** DC spectra of photo-responsive CLC doping 1.2 wt% of switch 5 and 1.1 wt% CD-1 into SLC1717 tuned by 450 nm visible light and 365nm UV light.

### 7. CD spectra of the photo-invertible CLC sample

To obtain the CD spectrum of photo-invertible CLC sample, the initial CLC sample was diluted 5 time with SLC1717. From the CD spectra results, it is further confirmed that the reversible chiral inversion of the CLC superstructure happened upon the 450 nm blue light and 365 nm UV light irradiations.

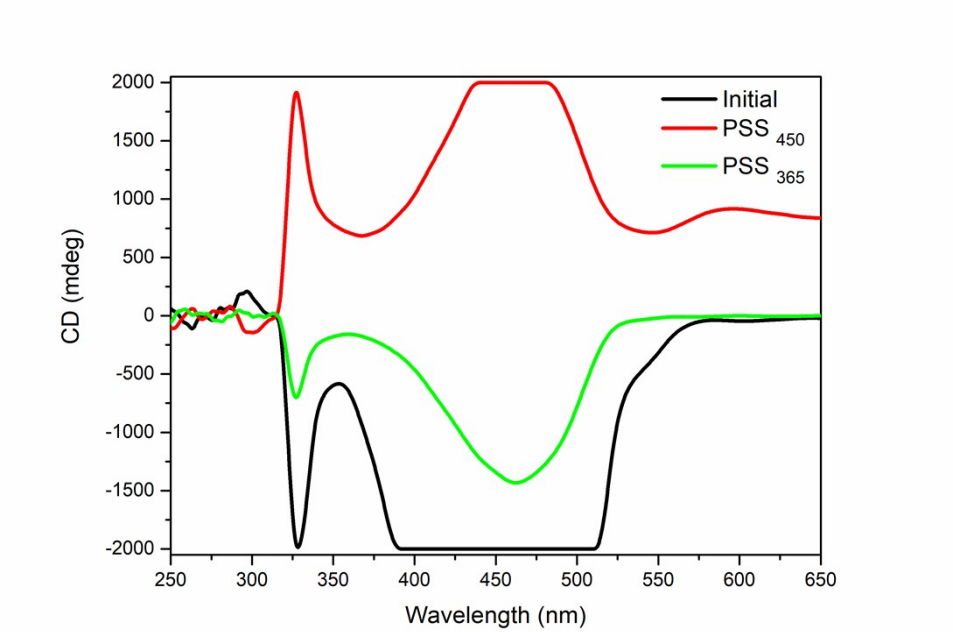
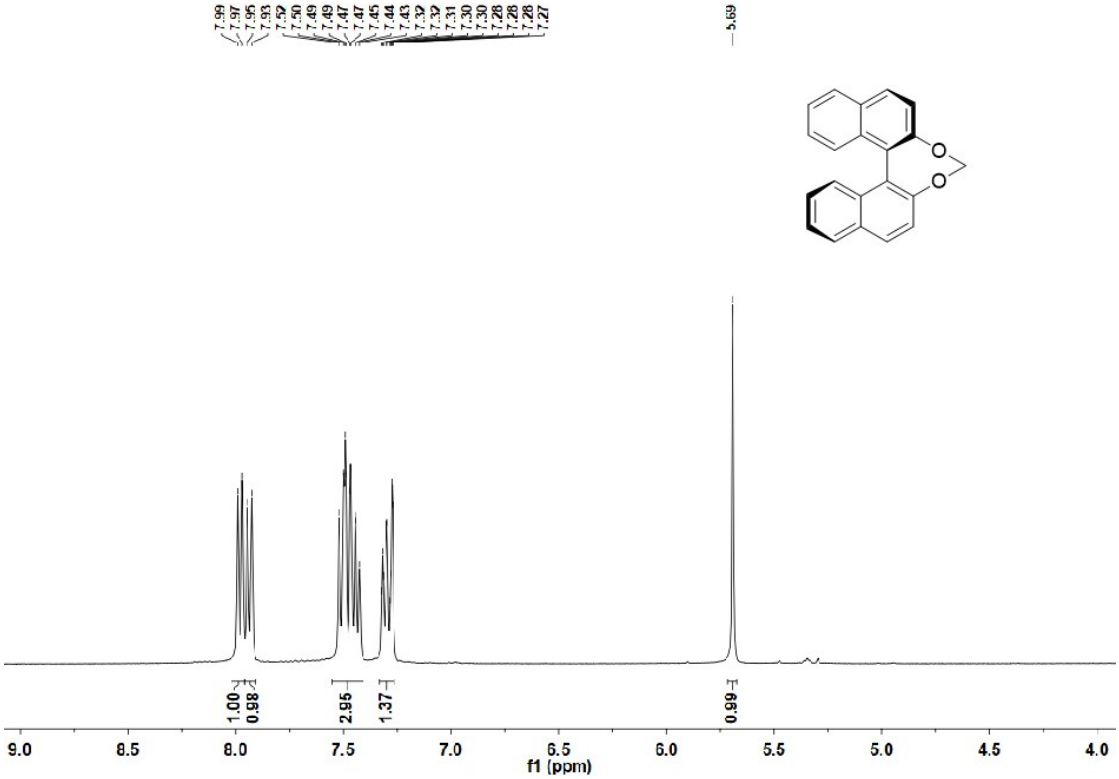


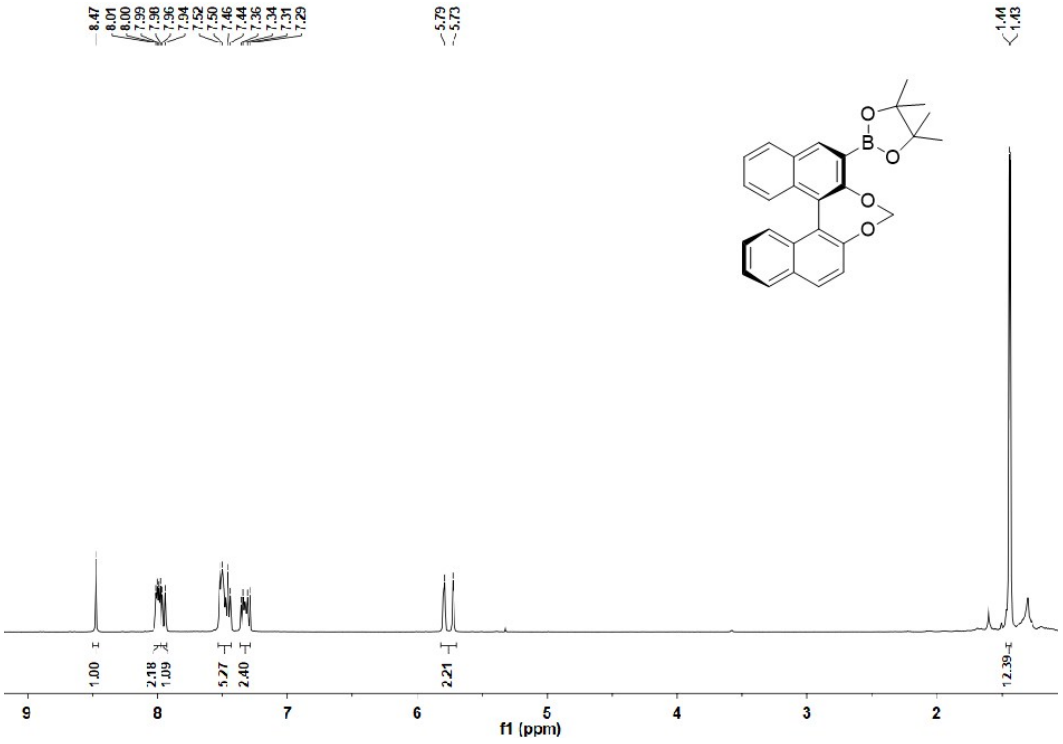

**Figure S7.** CD spectra of the photo-invertible CLC doping 0.24 wt% of switch **5** and 0.22 wt% CD-1 into SLC1717 tuned by 450 nm visible light and 365 nm UV light.

## 8. $^{1}$H-NMR and $^{13}$C-NMR spectra:

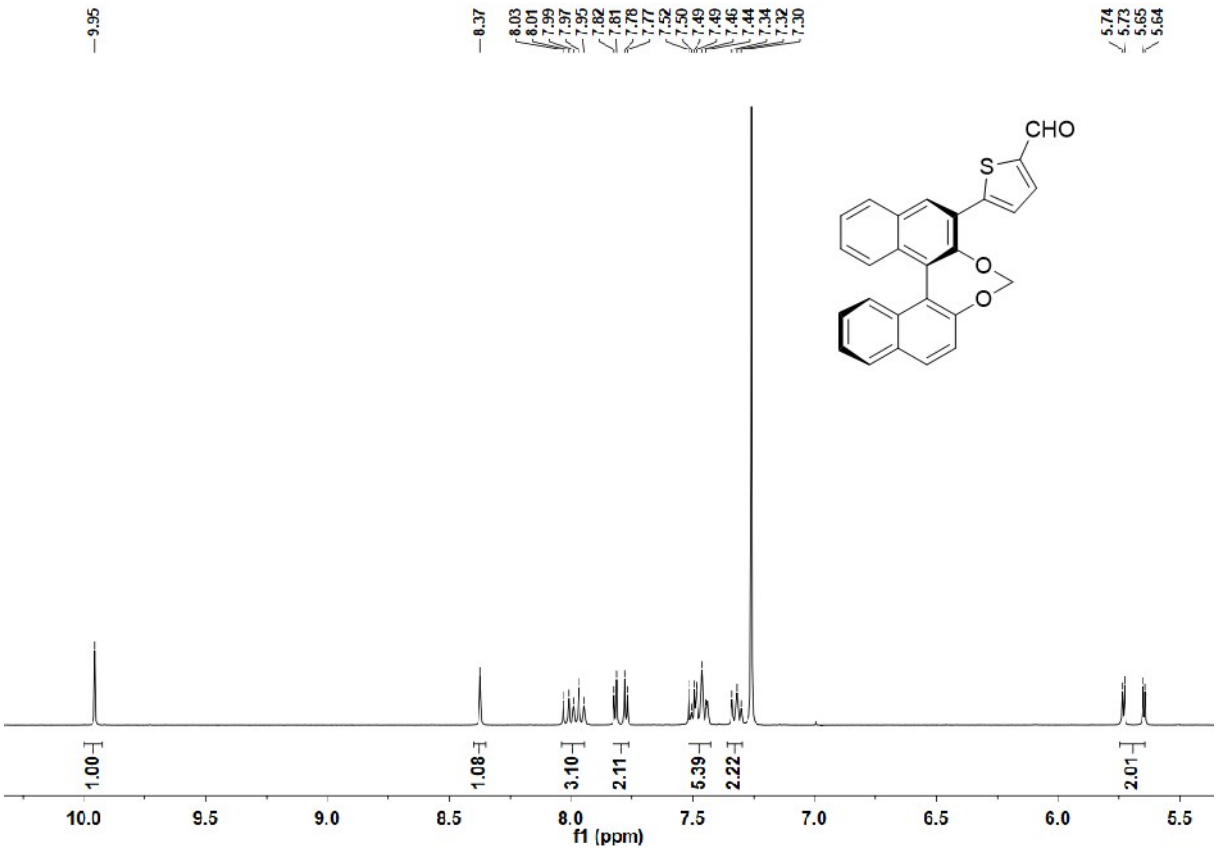
### $^{1}$H-NMR of (R)-1:



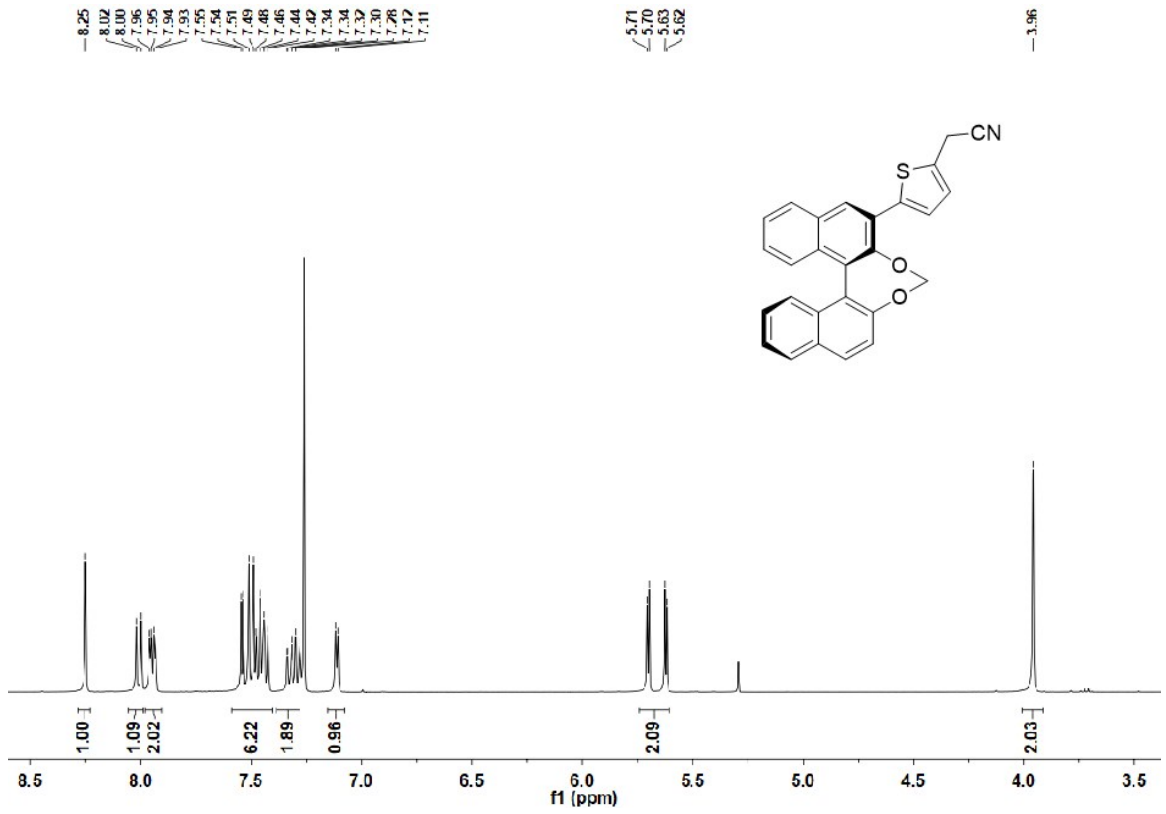
**$^1$H-NMR of (R)-2:**



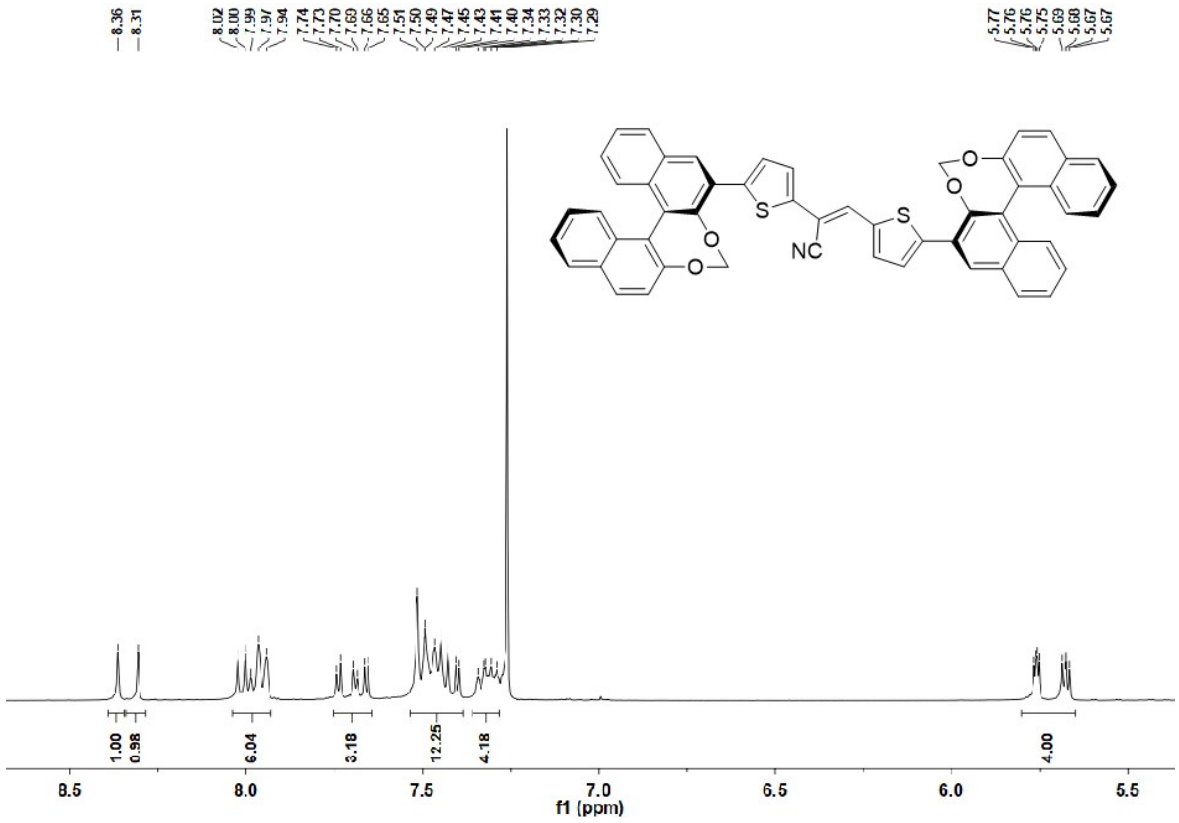

**$^1$H-NMR of (R)-3:**



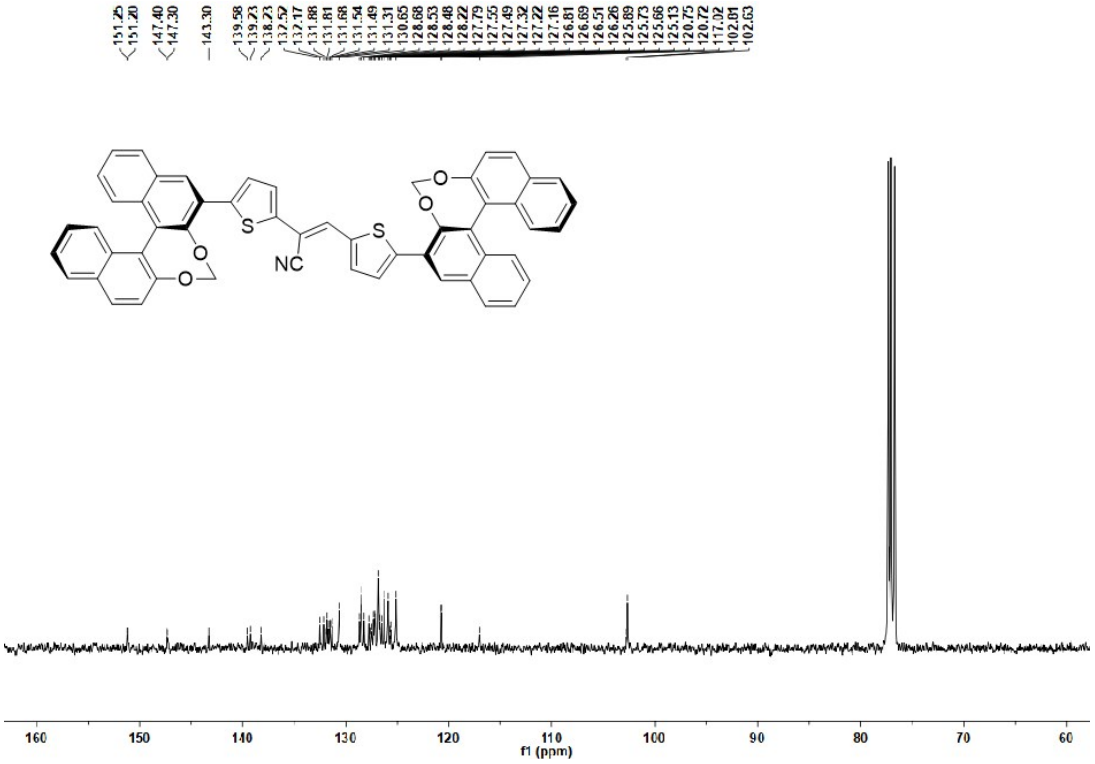
**$^1$H-NMR of (R)-4:**




**$^1$H-NMR of switch 5:**



**$^{13}$C-NMR of switch 5:**




**$^{1}$H-NMR of CD-1:**