Supporting Information

Near-infrared light-controlled circularly polarized luminescence of self-organized emissive helical superstructures assisted by upconversion nanoparticles

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1. General information

All the solvents and reagents were obtained from commercial sources and used as purchased unless otherwise noted. Tetrahydrofuran (THF) and methanol were dried with 3Å molecular sieves for more than 48 hours before use. $YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $ErCl_3 \cdot 6H_2O$ (99.99%), $HoCl_3 \cdot 6H_2O$ (99.99%), $CeCl_3 \cdot 6H_2O$ (99.99%) were purchased from Beijing HWRK Chem CO., LTD. Oleic acid (technical grade, 90%) and 1-octadecene (technical grade, 90%) were purchased from Sigma-Aldrich. 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. A room temperature commercial nematic LC, SLC1717 (Shijiazhuang Chengzhi Yonghua Display Materials Ltd. $n_o = 1.519$, $n_e = 1.720$, $\Delta n = n_e - n_o = 0.201$, TN-I = 91.8 °C), was used as the host LCs.

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III (400 MHz ^1H; 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. Textures and disclination line distance changes 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). CPL spectroscopies was carried out using a JASCO CPL-200 instrument. A 520 nm green-LED source was employed as a trigger for the *trans→cis* isomerization (20 mW/cm^2). Then a 450 nm blue-LED source or 365 nm UV-LED source was employed as a trigger for the partially reverse of the *cis→trans* isomerization (30 mW/cm^2). For deduction of photoisomerization yields from ^1H NMR spectra, the sample was irradiated for 120 s in both directions. Transmission electron microscopy (TEM) images were collected on an H-800 microscope (Hitachi, Japan). The X-ray powder diffraction

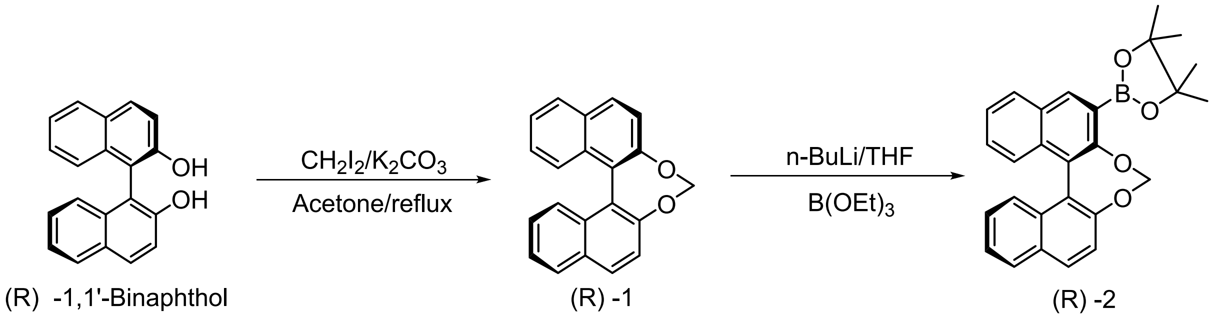
(XRD) patterns were collected on a D/MAX 2500 VB2+/PC X-ray powder diffractometer (Rigaku, Japan). Upconversion luminescence spectra of the upconversion nanoparticles (UCNPs) were collected on an F-45OO spectrofluorometer (Hitachi, Japan) equipped with an external 980 nm laser source (power, 0-10 W).

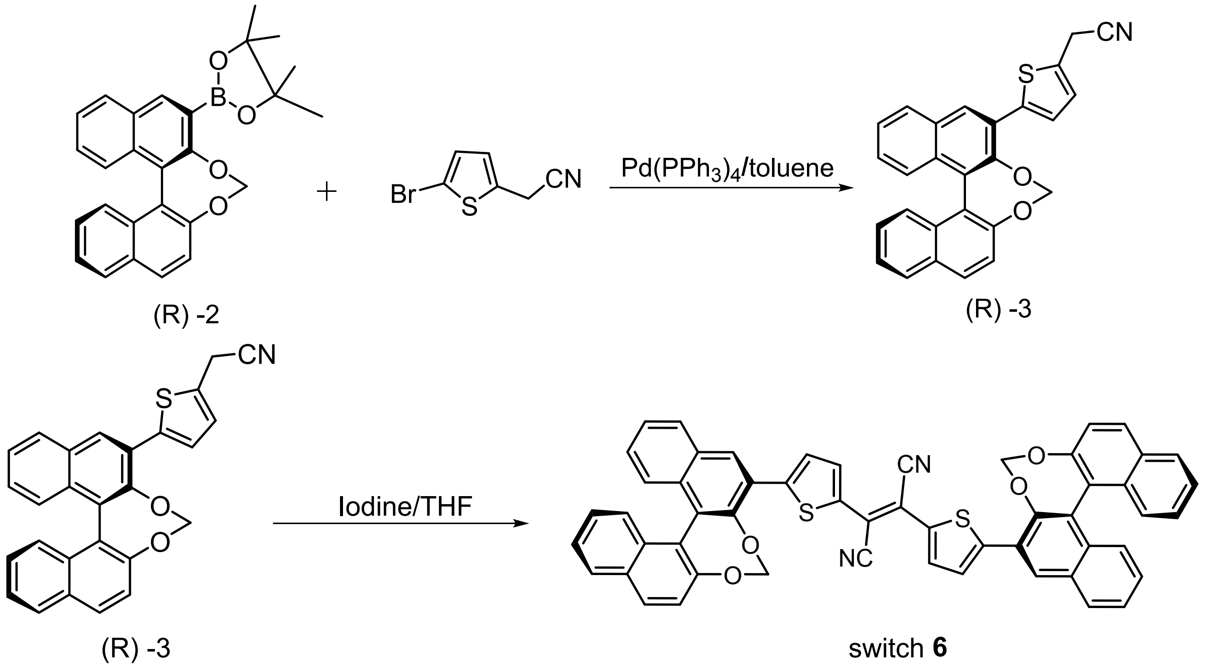
Quantum chemical calculations on both isomers of the chiral molecular switch were performed using density functional theory (DFT) at B3LYP/6-31G(d) level incorporated in the Gaussian 09 set of programs. Time-dependent density functional theory (TD-DFT) calculations were also carried out using a B3LYP/6-31G(d) method.

2. Fabrication of NIR-light triggered CLCs composite doped with UCNPs

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 °C for 1.0 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 CLC composite. The CLC mixtures with an amount of chiral fluorescent photoswitch (switch **6**) and UCNPs were filled into the above empty cell, and a self-organized helical superstructure could form in the well-planar-orientation CLC cell. In order to tune the emission and circularly polarized luminescence (CPL) of the CLC, a 980 nm laser source with tunable power of 0-10 W was employed as the excitation source for the reverisble *trans*/*cis* isomerization in our experiment.

3. Synthesis of chiral fluorescent photoswitch switch 6





Scheme S1. Synthesis of chiral fluorescence photoswitch switch **6**

Compound (R)-1. A mixture of (R)-1,1'-Binaphthol (2.86 g, 10 mmol), diiodomethane (8.04 g, 30 mmol) and anhydrous K_2CO_3 (13.82 g, 100 mmol) in acetone (60 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 (2.68 g, 90 %).^{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-).

Compound (R)-2. To a THF solution (60 mL) of (R)-1 (2.68 g, 9 mmol) at -20 °C under nitrogen was added n-BuLi (3.3 mL, 2.7 M in n-pentane, 9 mmol) dropwise. The solution was then stirred at this temperature for 0.5 h before 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.35 g, 18 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 (1.83 g, yield 48 %). ^{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, -CH2-), 1.44 (d, 12H, $-CH_3$).

Compound (R)-3. Tetrakis (triphenylphosphine) palladium (0.24g, 0.21 mmol), 2 - (5 - Bromothiophen - 2 -yl) acetonitrile (0.80 g, 4.2 mmol) and (R)-2 (1.78 g, 4.2 mmol) were dissolved in 50 mL toluene. The mixture was then added 12 mL ethanol and 20 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 (1.15 g, yield 65 %). ^{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, $-CH_2-$).

Target switch 6. Iodine (0.63 g, 2.50 mmol) and (R)-**3** (1.05 g, 2.50 mmol) were dissolved in 50 mL dry THF. Sodium methoxide methanol solution, which was prepared by adding sodium (0.118 g, 5.13 mmol) in 5 mL dry methanol, was added dropwise into the stirring solution at -70°C and stirred for 1 h under nitrogen atmosphere. The reaction was allowed to warm up to 0°C and stirred for another 3 h. The reaction was quenched with diluted hydrochloric acid 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 $CHCl_3$ as eluent to give a rufous solid (0.81 g, yield 78%). The resulting residue was purified by column chromatography using $CHCl_3$ as eluent to give a rufous solid (0.62 g, yield

75%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.39 (s, 2H, Ar-H), 8.04-7.93 (m, 8H, Ar-H), 7.79 (d, 2H, Ar-H), 7.52-7.45 (m, 10H, Ar-H), 7.35-7.30 (m, 4H, Ar-H), 5.80-5.70 (dd, 4H, $-CH_2-$).

4. Synthesis of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} / β-$NaYF_4$: 2 mol% Er^{3+}, 20 mol% Yb^{3+} / β-$NaYF^4$ UCNPs with core-shell-shell structure

The core--shell—shell nanoparticles were synthesized using a three-step solvothermal method according to previously published procedures.[1]

Synthesis of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} *core* nanoparticles.

15 mL 1-octadecene and 6 mL oleic acid were mixed in 100 mL three-necked flask. Then, 0.4219 g $YCl_3 \cdot 6H_2O$, 0.2325 g $YbCl_3 \cdot 6H_2O$ and 0.0038 g $ErCl_3 \cdot 6H_2O$ were dissolved in three-necked flask. The solution was heated up to 120 °C for 1.0 h with a gentle flow of N_2 going through the flask. After the above mixture was cooled down to room temperature, a solution of 0.2963 g NH_4F and 0.2 g NaOH dissolved in 10 mL methanol was added dropwise. Then, the solution was stir for 30 min. Afterwards, it was heated up to 50 °C for 10 min. After evaporation of methanol, the temperature was further increased to 300 °C and hold for 1 h with a gentle flow of N_2 and then cooled to room temperature. The resulting products were precipitated with ethanol, collected after centrifugation, washed for three times with ethanol and redispersed in cyclohexane.

Synthesis of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} /β-$NaYF_4$: 2 mol% Er^{3+}, 20 mol% Yb^{3+} *core-shell* nanoparticles.

15 mL 1-octadecene and 6 mL oleic acid were mixed in 100 mL three-necked flask. And 0.425 g $YCl_3 \cdot 6H_2O$, 0.1356 g $YbCl_3 \cdot 6H_2O$ and 0.0134 g $ErCl_3 \cdot 6H_2O$ were added into the system. The solution was heated up to 120 °C for 1 h with a gentle flow of N_2 going through the flask. After the above mixture was cooled down to room temperature, 10 ml cyclohexane solution of

the prepared β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} UCNPs was added into the system. Then the temperature rises to 80 ℃, removing the cyclohexane. A solution of 0.2593 g NH_4F and 0.192 g NaOH dissolved in 10 mL methanol was added dropwise. Then, the solution was stir for 30 min. Afterwards, it was heated up to 50 °C for 10 min. After evaporation of methanol, the temperature was increased to 300 °C and hold for 2 h with a gentle flow of N_2 and then cooled to room temperature. The resulting products were precipitated with ethanol, collected after centrifugation, washed for three times with ethanol and redispersed in cyclohexane.

Synthesis of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} / β-$NaYF_4$: 2 mol% Er^{3+}, 15 mol% Yb^{3+} / β-$NaYF_4$ UCNPs *core-shell-shell nanoparticle*

0.5841 g $YCl_3 \cdot 6H_2O$ was added to a 100 mL ask containing 6 mL of oleic acid and 15 mL of 1-octadecene and heated to 160°C under argon gas ow with constant stirring for 1.0 h to form a clear solution. It was then cooled to room temperature. Afterwards, β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} /β-$NaYF_4$: 2 mol% Er^{3+}, 20 mol% Yb^{3+} *core-shell* UCNPs in 10 ml of hexane was added to the above solution and stirred for 30 min. After the removal of hexane, 10 mL of methanol solution containing 0.2222 g of NH_4F and 0.152 g of NaOH was added and stirred at 50 °C for 30 min. After methanol was evaporated, the solution was heated to 300 °C under argon gas ow with vigorous stirring for 2 h and then cooled to room temperature. The obtained core–shell NCs were precipitated by addition of ethanol, collected by centrifugation at 10000 rpm for 10 min, washed with ethanol three times, and finally redispersed in hexane for further experiments.

5. Circular Dichroism Spectrum of switch 6 in solution

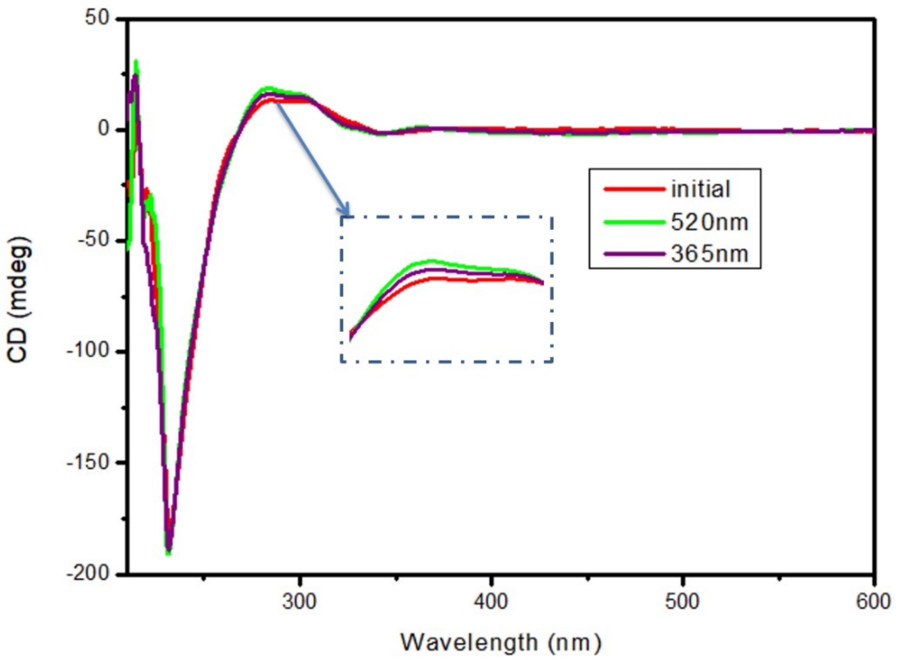
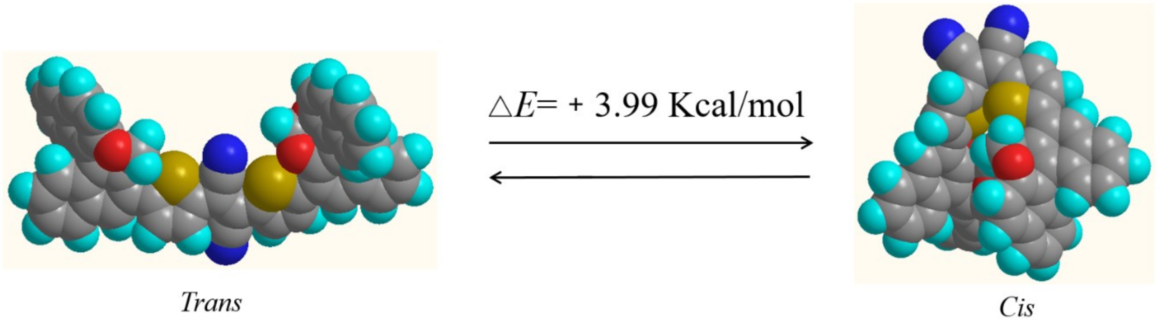


Figure S1. Variation of CD spectra of switch **6** in dichloromethane solution upon photoisomerization.

6. Computational study of the trans and cis isomers of switch 6



Trans

Cis

Figure S2. Optimized structure of switch **6** in *trans* and *cis* forms (space filling mode) obtained by Gaussian 09 calculations

The differential absorption properties of *trans* and *cis* isomers of the molecular switch **6** are discussed according to the suggestions of theoretical calculations, resulting in different photoisomer yields. For the *trans* isomer, there are four significant electronic transitions, namely, HOMO→LUMO (S1), HOMO-2→LUMO (S3), HOMO-4→LUMO (S5), and HOMO-5→LUMO (S6) transitions (Table S1). The large absorption band in green light region of the molecular *trans*-switch **6** can be assigned to the strong oscillation strengths (1.4249) of S1 at 547.80 nm. But, the absorption intensity of *cis*-switch **6** in the same region and the calculated oscillator strengths (0.1755) are rather small, indicating that green light can trigger *trans→cis* isomerization more effectively. The calculated oscillator strengths of the *cis*-switch **6** is much larger than that of the *trans* isomer in the blue and purple light region, which means the high tendency of *cis→trans* isomerization.

Table S1. Singlet transitions and corresponding energy gaps, absorption wavelengths, and oscillator strengths of the two isomers of switch **6**, obtained by TD-DFT calculations.

Isomer	Excitation	E_{cal}(eV)	$\lambda_{max,abs}$(nm)	Oscillator Strength(f)
trans	S1 HOMO→LUMO （99%）	2.2633	547.80	1.4249
	S3 HOMO-2→LUMO （95%）	2.6086	475.28	0.1905
	S5 HOMO-4→LUMO （91%）	2.9016	427.30	0.0222
	S6 HOMO-5→LUMO （90%）	3.1011	399.81	0.0333
cis	S1 HOMO→LUMO （93%）	2.4171	512.94	0.1755
	S2 HOMO-1→LUMO （94%）	2.6204	473.15	0.1911
	S5 HOMO-4→LUMO （88%）	3.0077	412.22	0.1558
	S6 HOMO-5→LUMO （93%）	3.1318	395.89	0.1489

7. Photophysical and photochemistry of switch 6 in solution

In order to demonstrate the photophysical behaviors of switch **6** in solution upon the light irradiations, UV-Vis absorption spectra of the pure *trans* isomer of switch **6** is investigated (Figure S3). The switch **6** in DMSO solution exhibits a large absorption bands with λ_{max} around 490 nm corresponding to π-π^* transition which shifts to around 450 nm with decrease in intensity after conversion from initial state to photostationary state (PSS) upon 520 nm green light irradiation (PSS_{520}) for about 90 s owing to *trans* to *cis* photoisomerization. Upon 450 nm or 365 nm light irradiations, the absorption band centered around 450 nm undergoes a red-shift with accompanied increase in its intensity until the PSS_{450} or PSS_{365} are reached in around 90 s due to *cis* to *trans* isomerization.

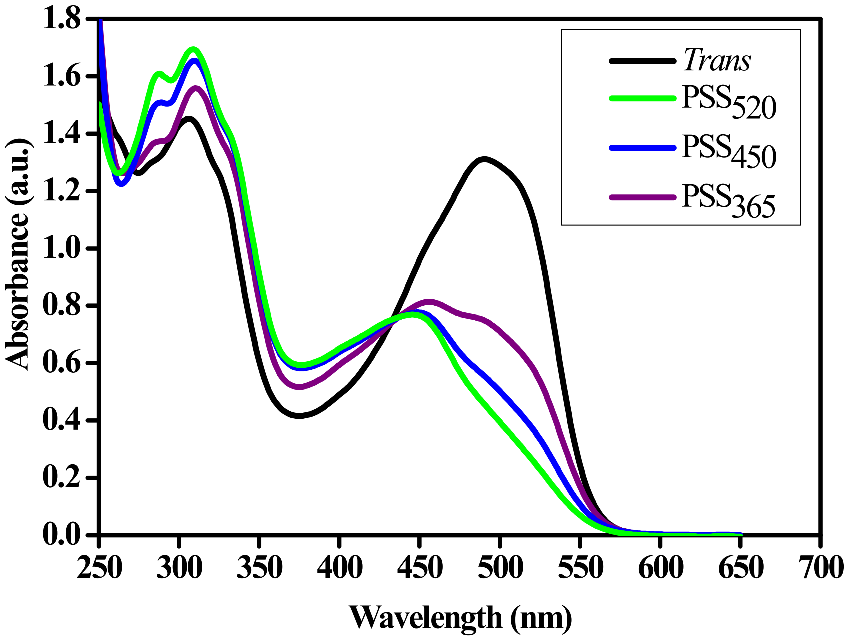


Figure S3. UV-vis spectrum of switch **6** (10^{-6} M in DMSO) at different PSS at room temperature

As shown in Figure S4, switch **6** emits orange-red light in DMSO under 520 nm excitation. A large fluorescence intensity variation (about 3.5 times at 581 nm) between initial state and PSS_{520} could be clearly observed. The fluorescence intensity recovers to an intermediate level upon *cis* to *trans* isomerization Such characteristics can be explained by differences in molecular geometries between *trans* and *cis* isomers.

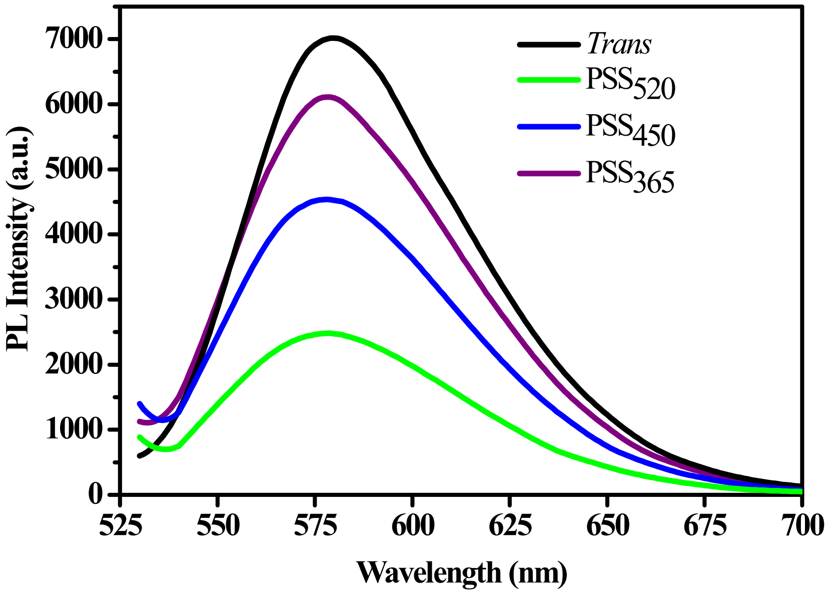


Figure S4. Fluorescence spectrum of switch **6** (10^{-6} M in DMSO) at different PSS at room temperature

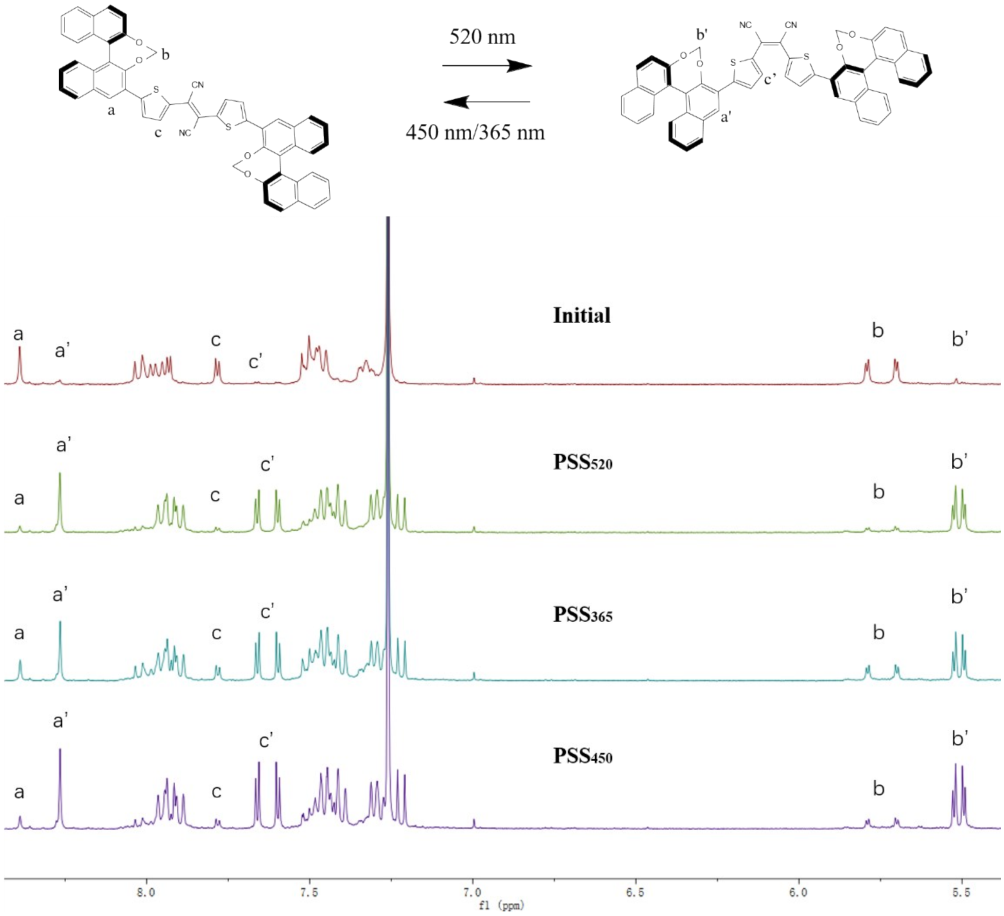


Figure S5. Photoisomerization yields of switch **6** at different states as deduced from the aromatic region of its ^{1}H-NMR spectra.

8. Measurement of helical twisting power (HTP) of switch 6

The pitch value is determined by a recognized grandjean-cano wedge method. As shown in Figure S6, we can see disclination lines of the CLC 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, tan θ = 0.0183). The helical twisted power (HTP) value can be used to represent the ability of chiral dopants for twisting cholesteric mesophase which is defined as the value of *β* and expressed by following equation: *β*=1/*pc*, where *p* is the helical pitch and *c* is the concentration of the chiral dopants.

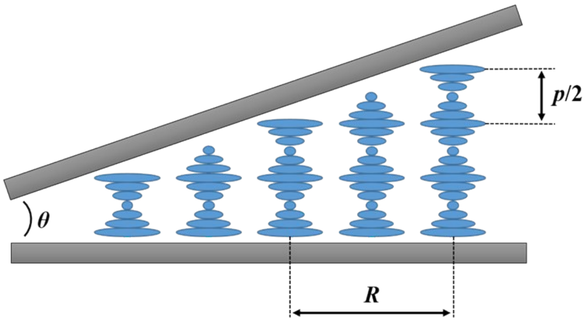


Figure S6. Schematic diagram of the HTP value measurement using the Grandjean-Cano wedge method.

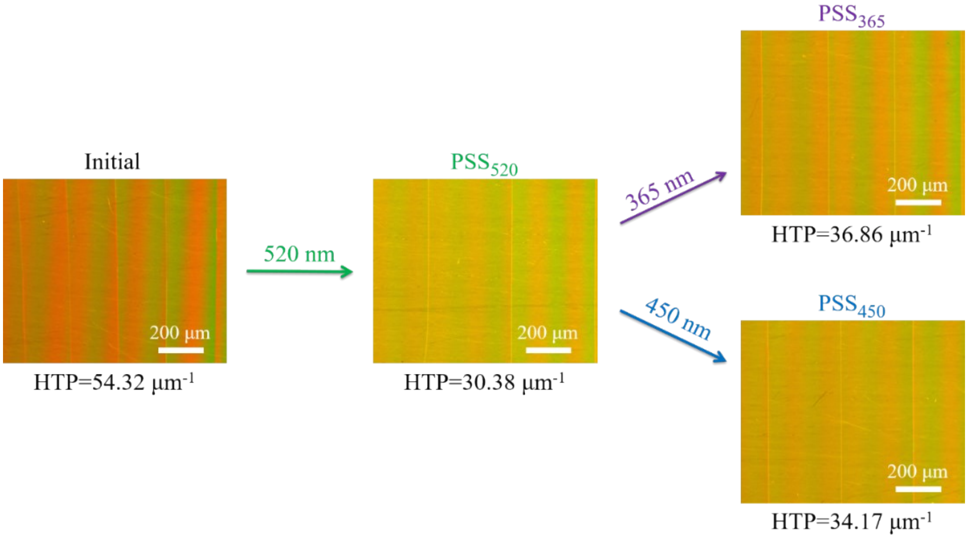


Figure S7. Variations of Cano lines observed by using POM of switch **6** in different states. The scale bars are 200 μm.

9. Characterizations of UCNPs

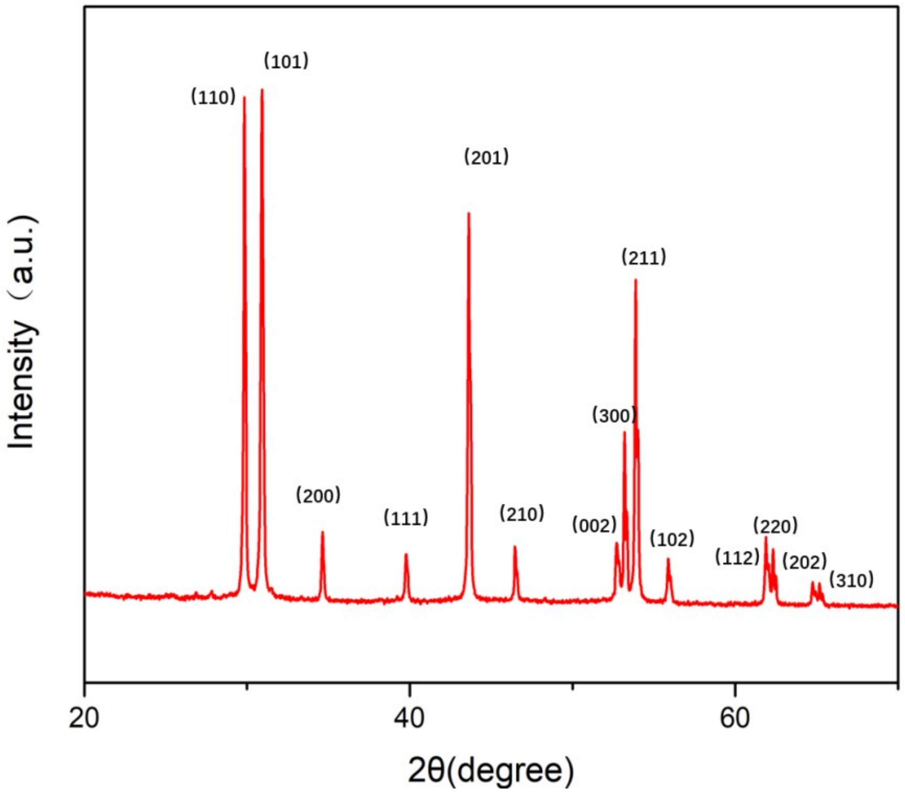


Figure S8. X-ray diffraction (XRD) patterns of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol % Yb^{3+} @ β-$NaYF_4$: 2mol % Er^{3+}, 15 mol % Yb^{3+} @β-$NaYF_4$ core-shell-shell UCNPs.

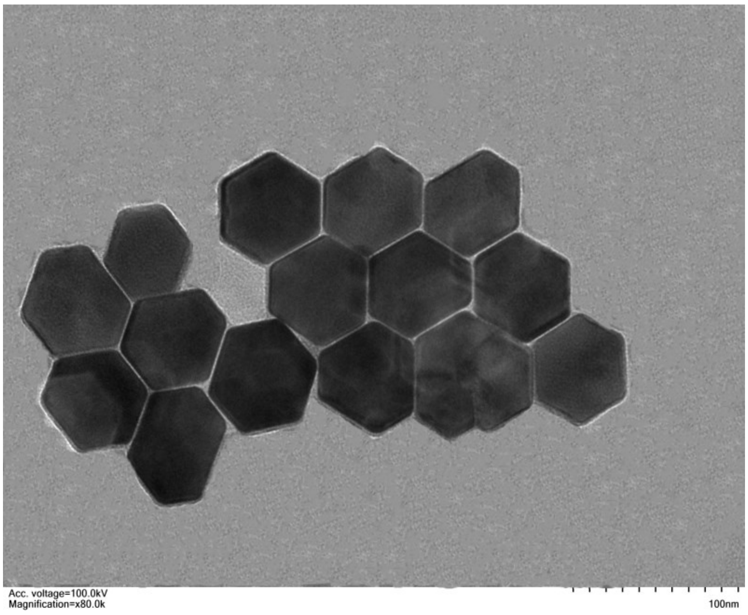


Figure S9. β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol % Yb^{3+} @ β-$NaYF_4$: 2mol % Er^{3+}, 15 mol % Yb^{3+} @β-$NaYF_4$ core-shell-shell UCNPs.

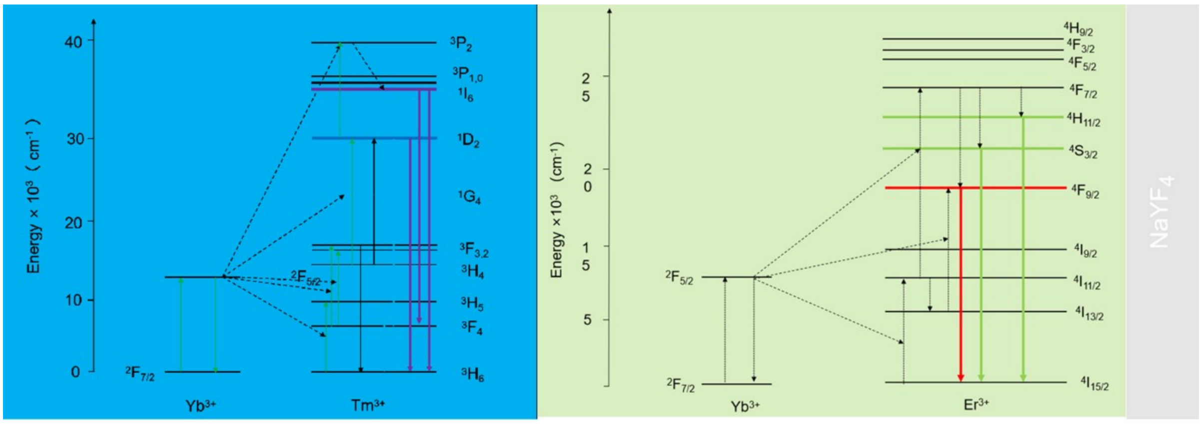


Figure S10. The energy level diagrams of UCNPs. Arrows shows radiative and nonradiative energy transfer and multiphonon relaxation processes.

10. Photo-responsive behaviors of CLC composite sample

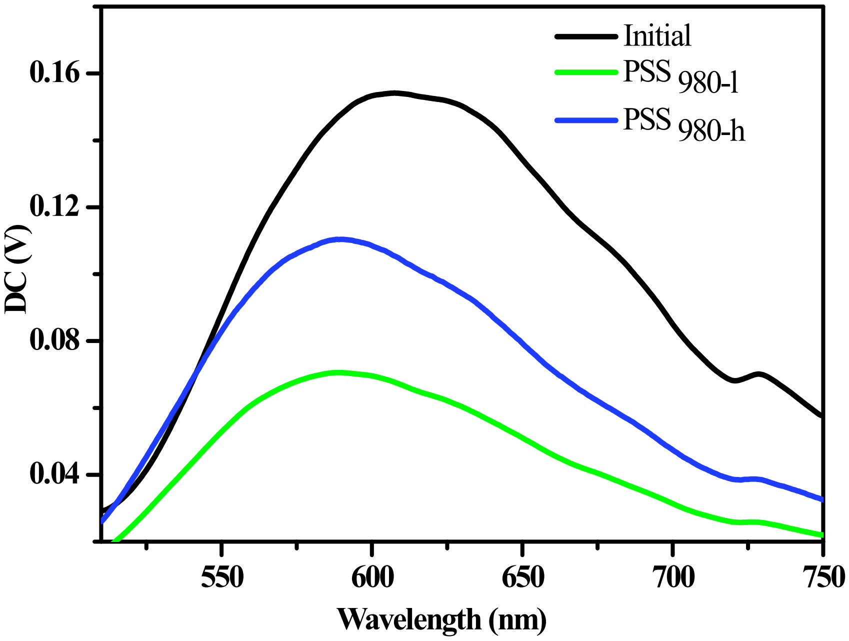
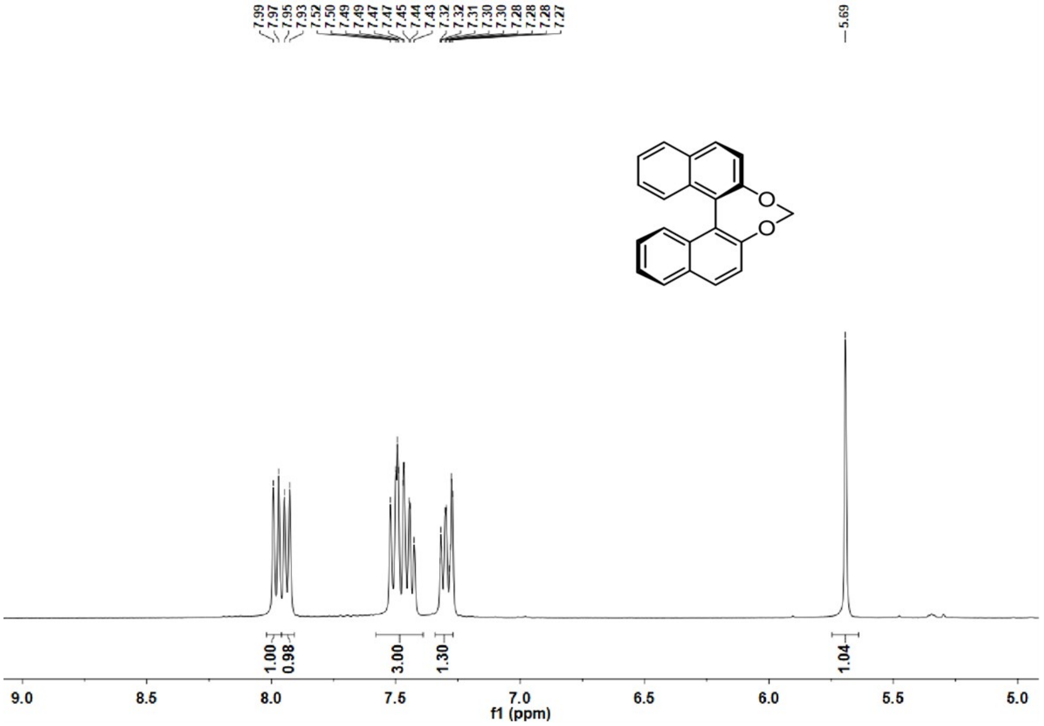


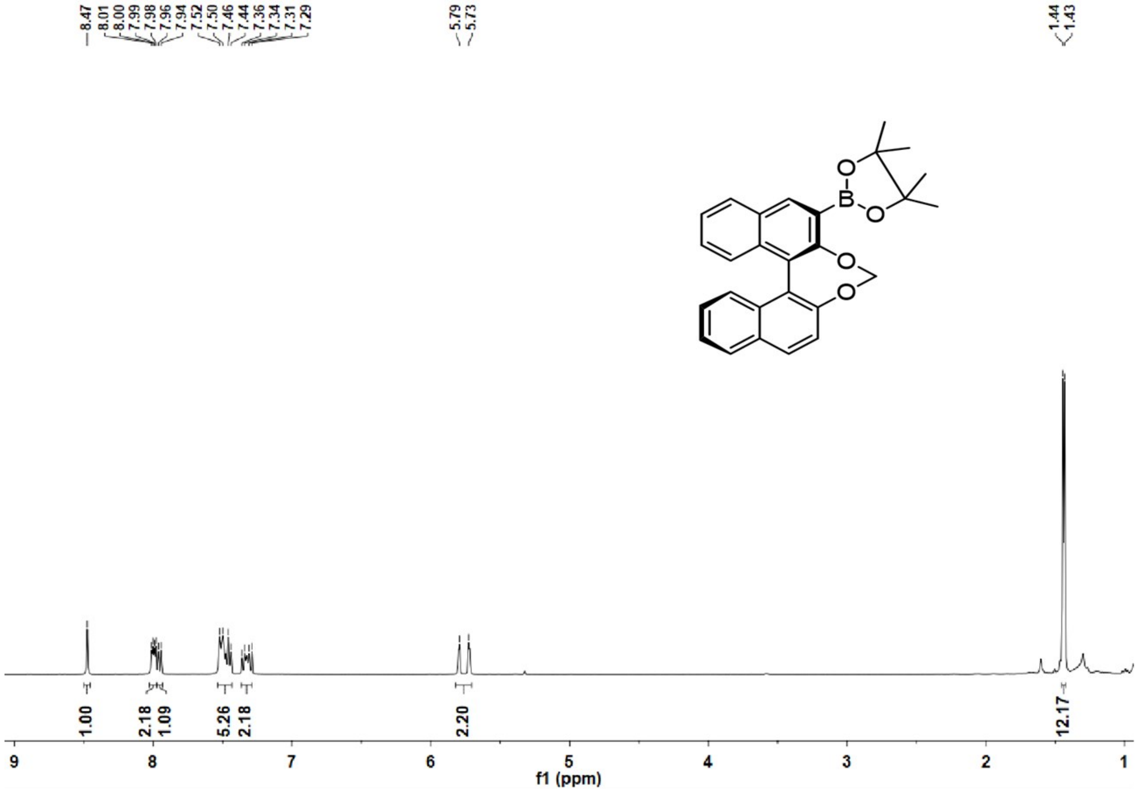
Figure S11. DC spectra of photo-responsive CLC doping 1.0 wt% of switch **6** and 0.5 wt% UCNPs into SLC1717 tuned by 980 nm NIR laser light.

11. ^{1}H-NMR and ^{13}C-NMR spectra

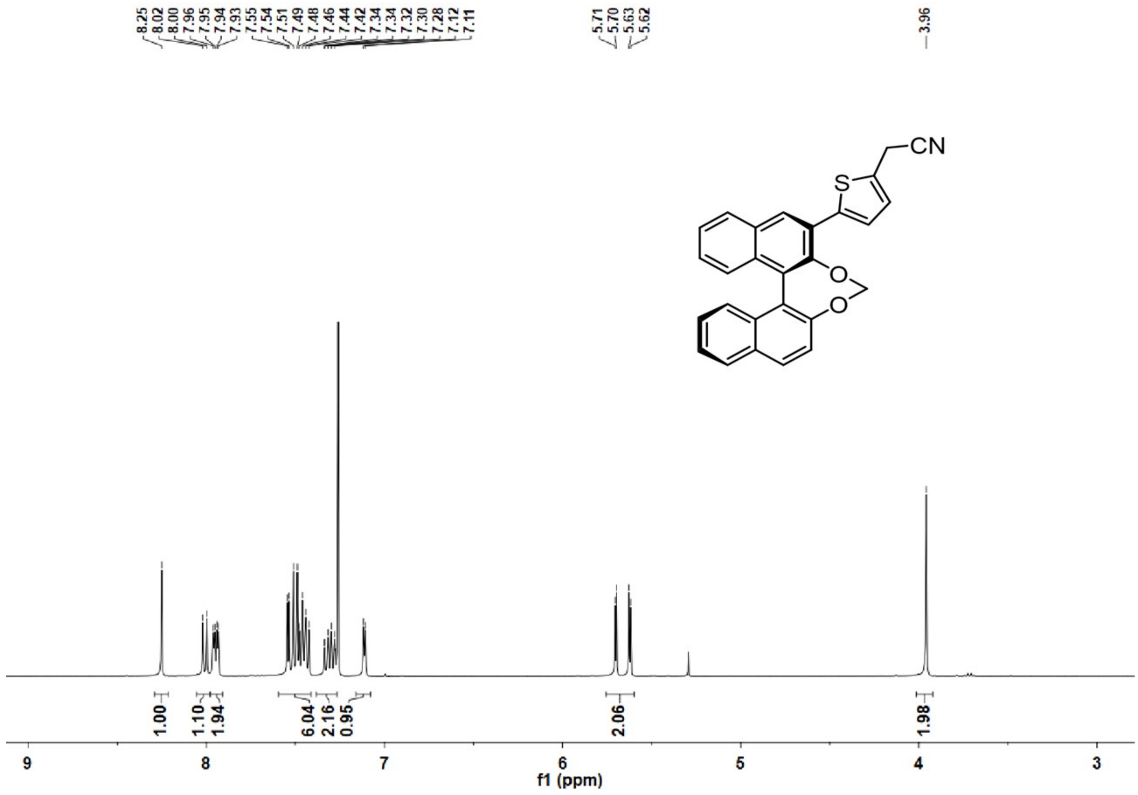
^{1}H-NMR of (R)-1:



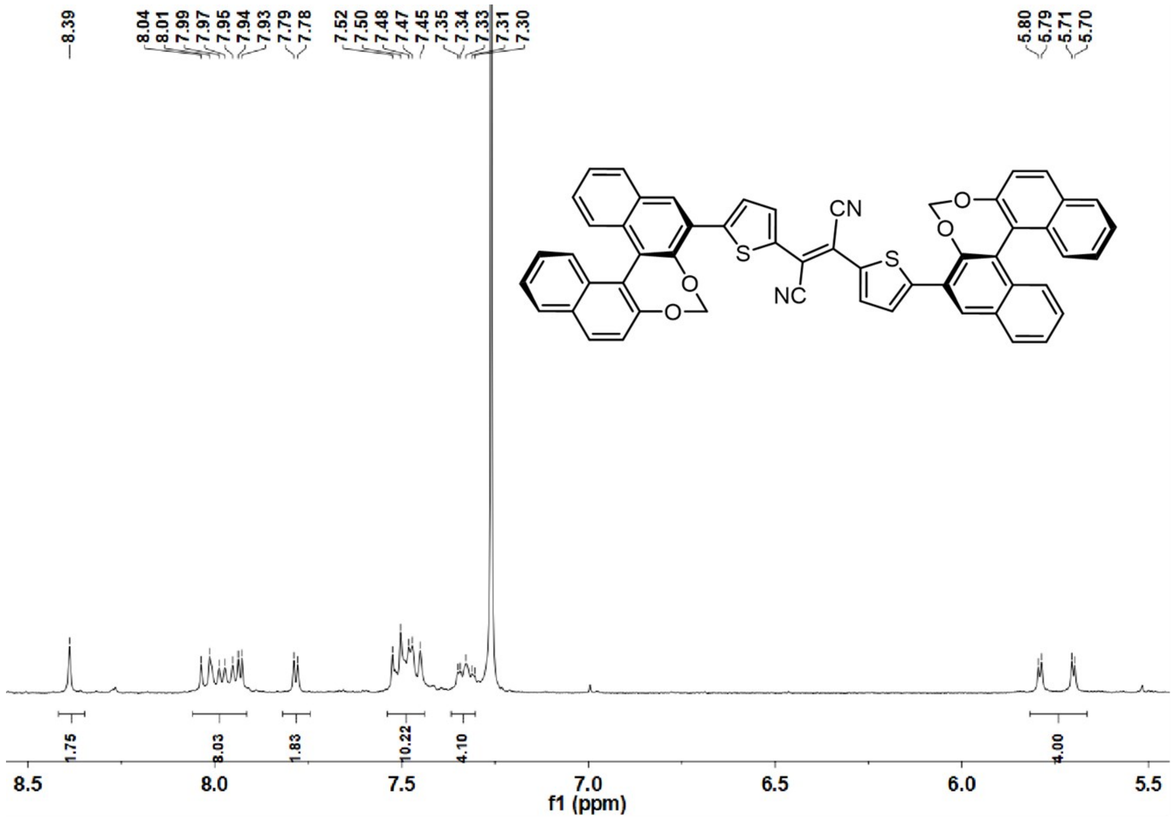
^{1}H-NMR of (R)-2:



^{1}H-NMR of (R)-3:



^{1}H-NMR of switch 6:



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1 J.-C. Boyer, C.-J. Carling, B. D. Gates and N. R. Branda, *J. Am. Chem. Soc.*, 2010, **132**, 15766.