Supporting Information

Induction of a Helical Superstructure in Photoresponsive Liquid Crystals: Switching from Linearly Polarized to Circularly Polarized Luminescence

Yanrong He,[a] Qingyan Fan,[a] Jingjing Gao,[a] Hong Chen,[a] and Jinbao Guo*[a]

Key Laboratory of Carbon Fibers and Functional Polymers, Ministry of Education, and College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029 (China).
E-mail: guojb@mail.buct.edu.cn

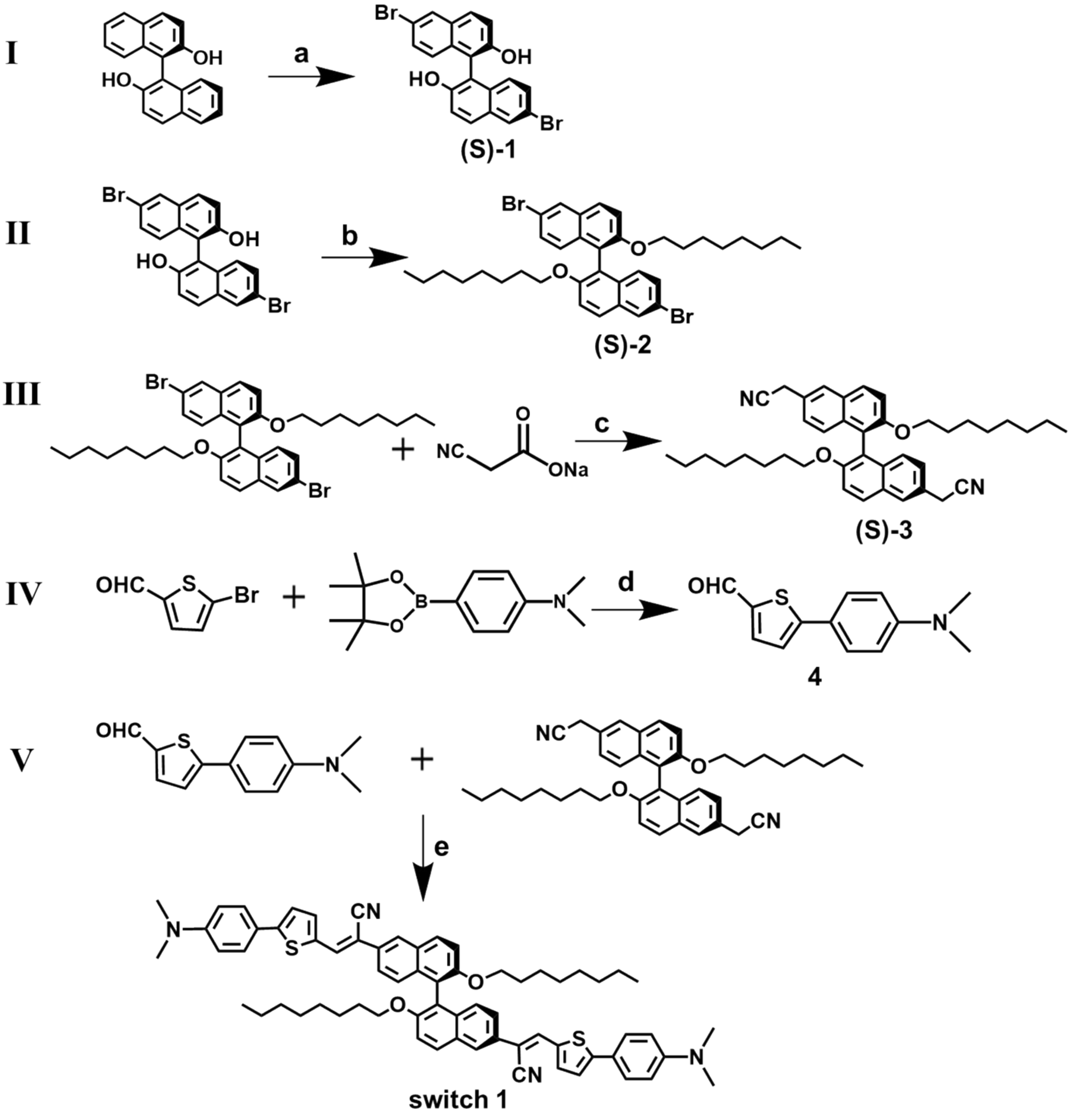
1. Materials and measurements

Materials: In this work, all the chemicals, solvents, and reagents were acquired from commercial sources and used without further purification unless otherwise mentioned. 5CB was purchased from Jiangsu Hecheng Display Technology Co., Ltd.. Super dry tetrahydrofuran (THF) was purchased from Beijing Huawei Ruike Chemical Co., Ltd., and SD1 was bought from Nanjing Murun company. Xylene was dried with 3Å molecular sieves for more than 48 hours before use. Column chromatography was performed on silica gel (200-300 mesh). Commercially coated 60 mesh GF254 glass plates were selected as analytical thin-layer chromatography (TLC). Spots on the TLC plates were rendered visible by exposure to UV light.

Measurements: ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AVANCE III (400 MHz ^{1}H; 100 MHz ^{13}C) spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported as δ in a 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. Mass spectra data were obtained with XEVO-G2QTOF (ESI) (Waters, USA) in positive ion mode. UV-Vis absorption and fluorescence spectroscopies were carried out using a Hitachi U-3010 and a Hitachi F-4500 instrument, respectively. Circular dichroism (CD) spectra were conducted on a Jasco 810 spectropolarimeter. CPL spectra were examined at room temperature on JASCO CPL-200. Textures and Cano line distance changes were observed by a polarizing optical microscope (POM, Leica DM2500P) equipped with a hot stage and calibrated at a temperature accuracy of ±0.1 °C (Linkam, THMS-600) under the transmission mode. The two photostationary states of switch **1** in solution or liquid crystal (LC) mixture were obtained by the irradiation of 365 nm light (14.0 mW/cm^2) for 30 s or 2 min, and 450 nm light (15.0 mW/cm^2) LED light for 30 s or 2 min, respectively. Quantum chemical calculations on all isomers of switch **1** were executed using density functional theory (DFT) at the 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.

***Fabrication of LC Cells*:** Glass substrates were spin-coated with 3.5 wt% polyvinyl alcohol (PVA) in water and subsequently dried at 80 °C for 2 h. Then the PVA layer was rubbed with a rayon cloth to obtain homogeneous alignment. The planar alignment LC cells with anti-parallel rubbing directions were fixed by glue and their cell gap was regulated as 10 μm by embedding polypropylene strips between the edge sides of two glass substrates. In addition, the glass sheets that were immersed in the aqueous solution of dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride for 2 h could be employed to fabricate the vertically oriented LC cells. Finally, the LC mixture was filled into the empty cells. More importantly, the concentration of switch **1** in 5CB remained 0.2 wt% in all measurements unless otherwise stated.

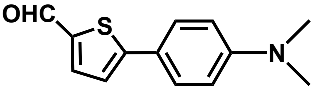
2. Synthesis of chiral fluorescent switch 1



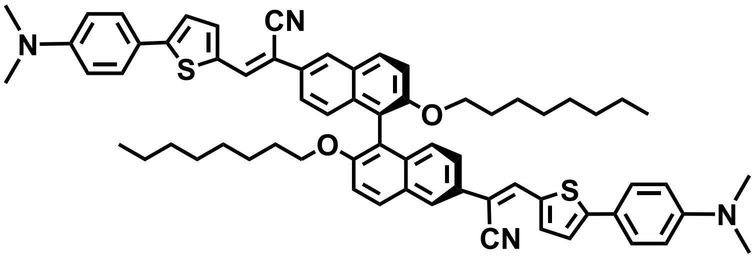
Scheme S1. Synthetic routes of switch **1**. *Reagents and reaction conditions:* (a) Br$_2$, CH$_2$Cl$_2$, 0 °C to rt; (b) 1-bromooctane, acetonitrile, K$_2$CO$_3$, 80 °C; (c) Pd$_2$Cl$_2$(allyl)$_2$, xylene, 4,5-bis(diphenylphosphino)-

9,9-dimethylxanthene, 140 °C; (d) Pd[P(Ph)$_3$]$_4$, Toluene, 90 °C; (e) *t*-BuOK, THF, 60 °C.

Compounds **(S)-1, (S)-2, (S)-3,** and sodium 2-cyanoacetate were synthesized according to our previous work.[1] Herein, it should be noted that we choose **(S)**-[1,1'-binaphthalene]-2,2'-diol as raw material.



5-(4-(dimethylamino)phenyl)thiophene-2-carbaldehyde, 4: N,N-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3.0 g, 12.1 mmol), 5-bromothiophene-2-carbaldehyde (2.3 g, 12.1 mmol) and Tetrakis- (triphenylphosphine) palladium (0) (0.7 g, 0.05 eq) were dissolved in 65 ml toluene. Meanwhile, 30 ml Na_2CO_3 solution (2 M) and 20 ml normal propyl alcohol were poured into the mixture, and they were stirred and refluxed for 18 h at 90 °C under the protection of nitrogen. When the reaction was over, the mixture was extracted with DCM and saturated NaCl solution three times, washed twice with deionized water, and purified by column chromatography with (DCM: PE=10:1). Finally, pure golden solid (2.3 g, yield 82.1%) was obtained successfully. ^{1}H-NMR (400 MHz, Chloroform-d) δ 9.83 (s, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.58 (d, J = 8.9 Hz, 2H), 7.25 (s, 1H), 6.78 (d, J = 8.1 Hz, 2H), 3.04 (s, 6H).



Switch 1: Both compound **4** (1.57 g, 6.8 mmol) and compound **(S)-3** (1.00 g, 1.7 mmol) were dissolved into the dry THF (50 ml), then KTB (0.19 g, 1.7mmol) was slowly added into the mixture during stirring. The mixture was heated up to 55 °C to reflux for 6 h under nitrogen. Afterwards, adding dilute HCl solution into above mixture was used to quench the reaction and adjust pH to be neutral. The crude product was extracted with DCM and deionized water for three times, and purified by column chromatography with DCM and PE to obtain the red solid (1.1 g, yield 63.6%). The whole operation

took place in the dark. ^{1}H-NMR (400 MHz, Chloroform-d) δ 8.15 (d, J = 1.6 Hz, 2H), 7.99 (d, J = 9.1 Hz, 2H), 7.60 (s, 2H), 7.54 (d, J = 8.8 Hz, 4H), 7.48-7.42 (m, 6H), 7.20 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 3.9 Hz, 2H), 6.70-6.65 (m, 4H), 3.98 (dt, J = 13.2, 6.4 Hz, 4H), 2.97 (s, 12H), 1.44 (dd, J = 10.4, 6.5 Hz, 4H), 1.29-1.20 (m, 4H), 1.04 (t, J = 30.6 Hz, 16H), 0.87 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (101 MHz, Chloroform-d) δ 155.40, 150.57, 135.20, 134.42, 133.87, 133.42, 129.87, 129.20, 127.16, 126.34, 125.80, 122.34, 121.15, 120.05, 118.84, 116.17, 112.29, 105.71, 69.52, 40.30, 31.79, 29.18, 25.77, 22.73, 14.19. HRMS (ESI) calcd for $C_{66}H_{70}N_4O_2S_2$ $(M+H)^+$: 1015.5013; found: 1015.4955.

3. Reversible photoisomerization process of switch 1

Switch 1:

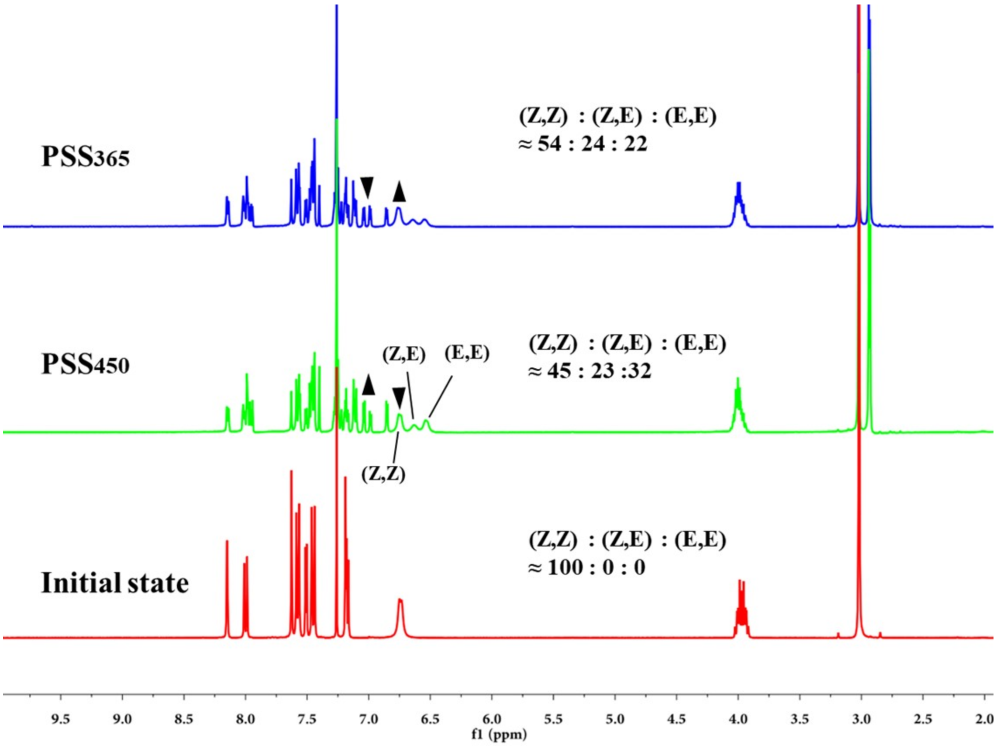


Figure S1. Partial ^{1}H-NMR spectra of switch **1** in $CDCl_3$ at different states.

Generally, every photostationary state in chloroform can be achieved by illumination within 30 s. However, to ensure that the three states realized complete photoisomerization, we have extended the irradiation time up to 50 min and collected data every 5 min, as a result, there was no change after 30 min. It should be noted that PSS_{450} was obtained from the initial state, while PSS_{365} can be acquired by the subsequent irradiation of 365 nm light for 30 min from PSS_{450}.

4. UV-Vis absorption spectra of switch 1

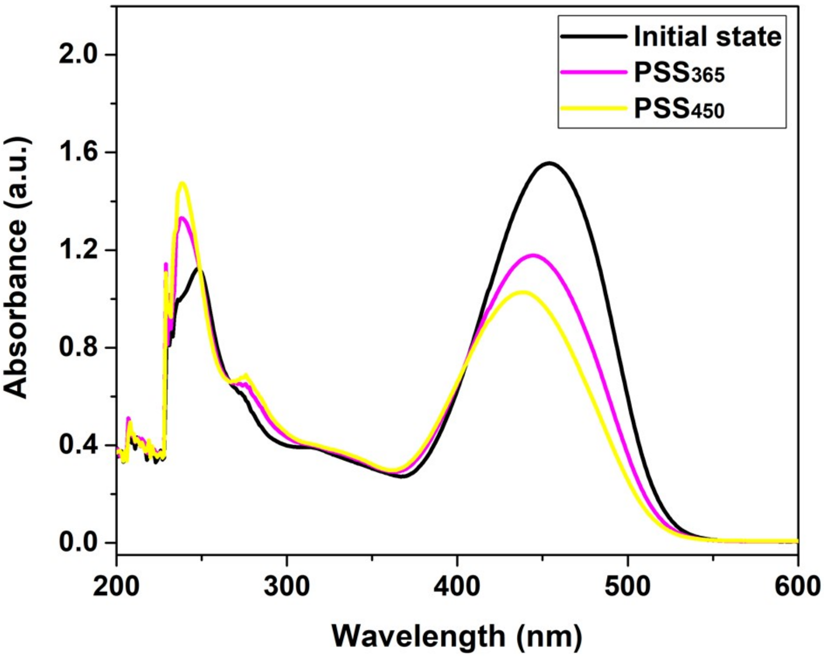


Figure S2. UV-Vis spectra of switch 1 in three states (10^{-6} M in THF, λ_{ex}= 365 nm) upon the irradiation of 365 nm light (30 s) and subsequent 450 nm light (30 s).

5. Fluorescence fatigue resistance of switch 1

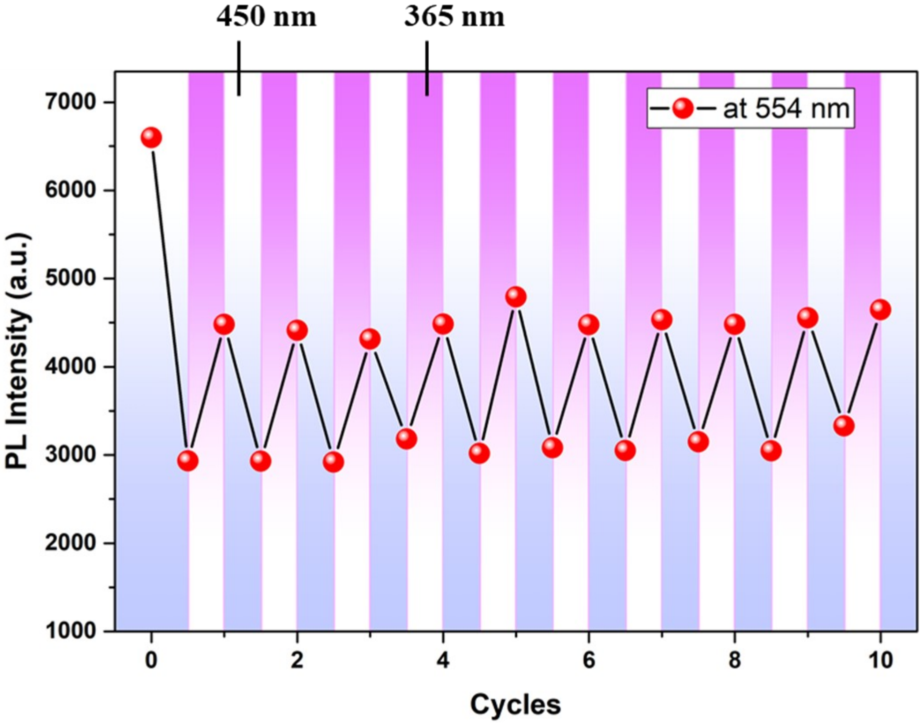


Figure S3. Fluorescence fatigue resistance (λ_{ex}= 365 nm) between the PSS_{450} and PSS_{365} for switch **1** in

THF solution. PSS_{450} and PSS_{365} can be obtained upon the irradiation of 450 nm and 365 nm lights for 30 s, respectively.

6. The theoretical calculation for switch 1

Switch **1**:

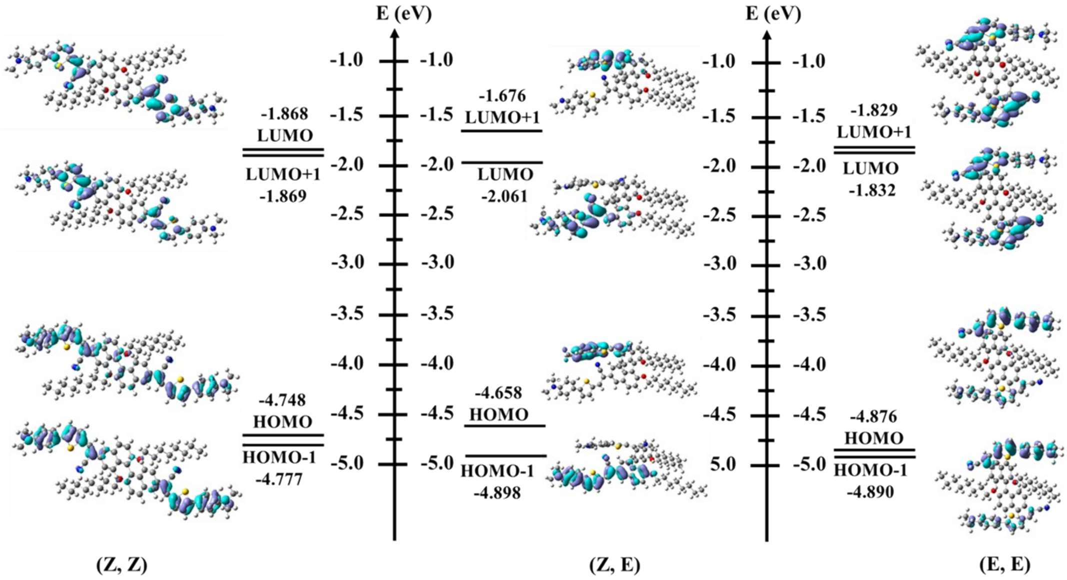


Figure S4. Energy levels and corresponding frontier molecular orbitals of switch **1** in its three conformations calculated by DFT theory at the B3LYP/6-31G (d) level.

To explore the photoisomerization process of switch **1** more clearly from a micro perspective, energy levels and corresponding frontier molecular orbitals of its three isomers were simulated and calculated under the environment of B3LYP/6-31G(d). As shown in Figure S4, in terms of the HOMO orbitals of switch **1**, the electron cloud is mainly concentrated on the C=C double bonds and the linked thiophene aniline, while the electron distribution of its LUMO orbitals is mostly located near the cyano groups. The electronic push-pull effect between the electron-donating aromatic units and electron-withdrawing cyano groups could stimulate the electronic π-π* transition leading to the occurrence of the photoisomerization of switch **1** upon the light irradiation.

Generally, different absorption characteristics of the three isomers of switch **1** often generate dissimilar photoisomerization yields. To predict the photophysical properties of the three isomers for switch **1**, the data of their singlet transitions and corresponding energy gaps, absorption wavelengths, and oscillator strengths were simulated through theoretical calculations and summarized in Table S1. Notably, it should be particularly emphasized here is that *Z, E* isomer is the necessary intermediate state from *Z, Z* (*E, E*) to *E, E* (*Z, Z*) conformational transition and the difference of their oscillator strengths influences the degree of difficulty of photoisomerization. In terms of the *Z, Z* isomer of switch **1**, there are three important electronic transitions including HOMO→LUMO (S1), HOMO-1→LUMO (S4), and HOMO→LUMO+2 (S9). The maximum absorption peak appears in the cyan light region at 474.63 nm, which mainly comes from the contribution of the S1 transition with high oscillator strength (1.8331). Compared with that of *Z, Z* isomer, *Z, E*, and *E, E* isomers exhibit the smaller absorption in this area. In addition, there is another intense absorption peak at the position of 457.82 nm for *Z, Z* isomer, which indicates that this isomer possesses a wide characteristic absorption in the cyan and blue light region and the lights in this area could effectually trigger *Z, Z* to *Z, E* or *E, E* photoisomerization. However, *E, E* isomer has the relatively largest oscillator strengths among three isomers in the ultraviolet region, which is about 2.6 times higher than that of *Z, Z* isomer leading to a tendency

Table S1. Simulated UV-Vis absorption spectra data of switch **1** in three conformations obtained by TD-DFT calculations.

Switch	Excitation	Energy (eV)	$\lambda_{max, abs}$ (nm)	Oscillator Strength (f)
Z, Z	S1 HOMO→LUMO (74.4%)	2.6122	474.63	1.8331
	S4 HOMO-1→LUMO (87.7%)	2.7082	457.82	0.6807
	S9 HOMO→LUMO+2 (81.6%)	3.4779	356.49	0.0430
Z, E	S1 HOMO→LUMO (99.6%)	2.2344	554.89	0.0056
	S3 HOMO→LUMO+1 (92.4%)	2.7330	453.66	1.0843
	S8 HOMO→LUMO+2 (79.7%)	3.3594	369.07	0.0473
E, E	S1 HOMO→LUMO+1 (64.1%)	2.7489	451.03	0.6819
	S2 HOMO→LUMO (78.9%)	2.7624	448.83	0.2811
	S9 HOMO→LUMO+2 (77.2%)	3.5102	353.21	0.1128

of antidromic photoisomerization. But this process is incomplete and gives a low conversion rate. There may be two reasons as follows: on the one hand, there is a chemical equilibrium among three isomers due to the similar oscillator strengths between *E, E* and *Z, E* isomers; on the other hand, the absorption of three isomers in the ultraviolet region is relatively weak; both of them make the reverse reaction hard to carry out thoroughly.

In fact, the experimental results of UV-Vis absorption and ^{1}H-NMR spectra are well in accordance with the above theoretical calculation.

7. HTP determination by using Grandjean-Cano method

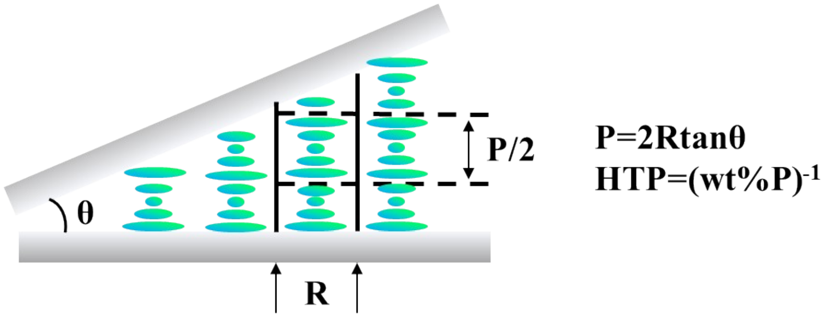


Figure S5. Mechanism diagram of the HTP value calculation by adopting the Grandjean-Cano method[2].

8. Aggregation-induced emission enhancement (AIEE) effect of switch 1

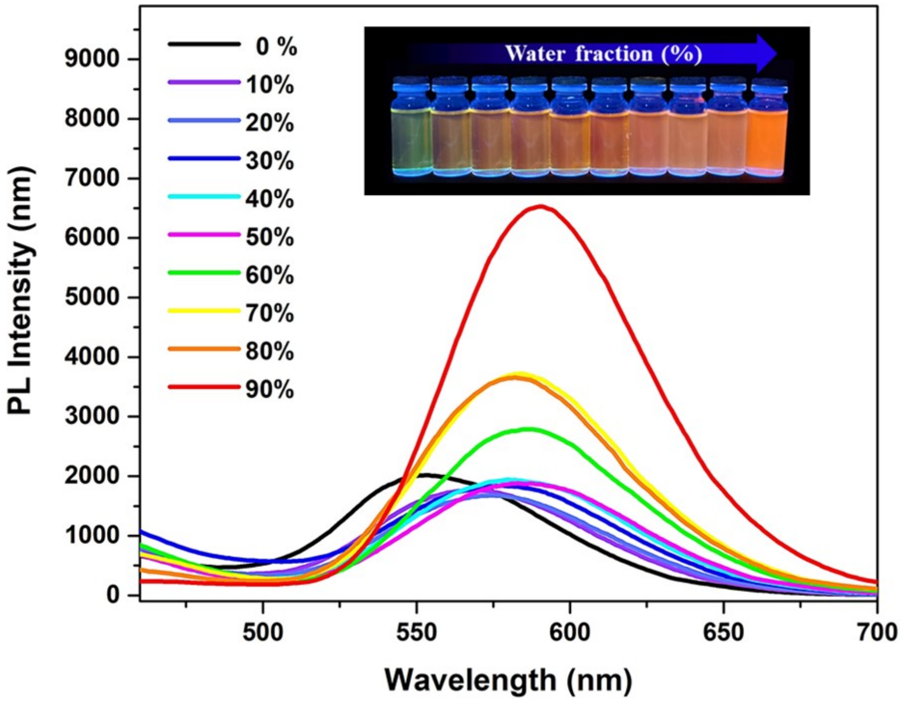


Figure S6. Comparison in emission intensity (λ_{ex}= 365 nm) of switch **1** in the mixture (THF and water) with the gradual increase of water content (volume). The insets give the real fluorescent images of solutions with different water fractions.

9. The fluorescence property of switch 1 in LC

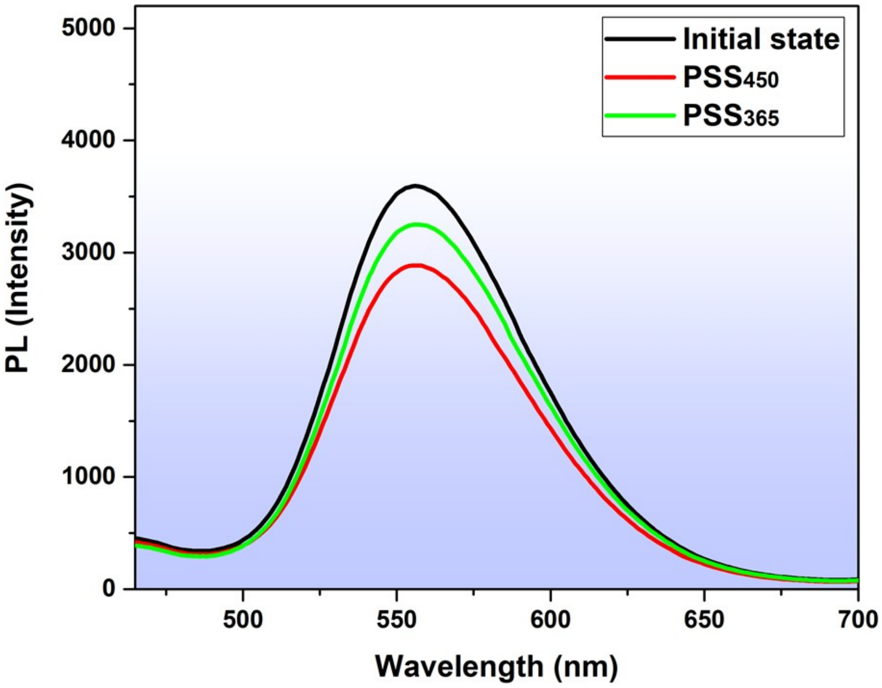


Figure S7. Changes in emission intensity (λ_{ex}= 365 nm) of switch **1** in 5CB upon the irradiation of 450 nm and 365 nm lights for 2 min, respectively.

10. Photo-regulation of CPL for switch 1

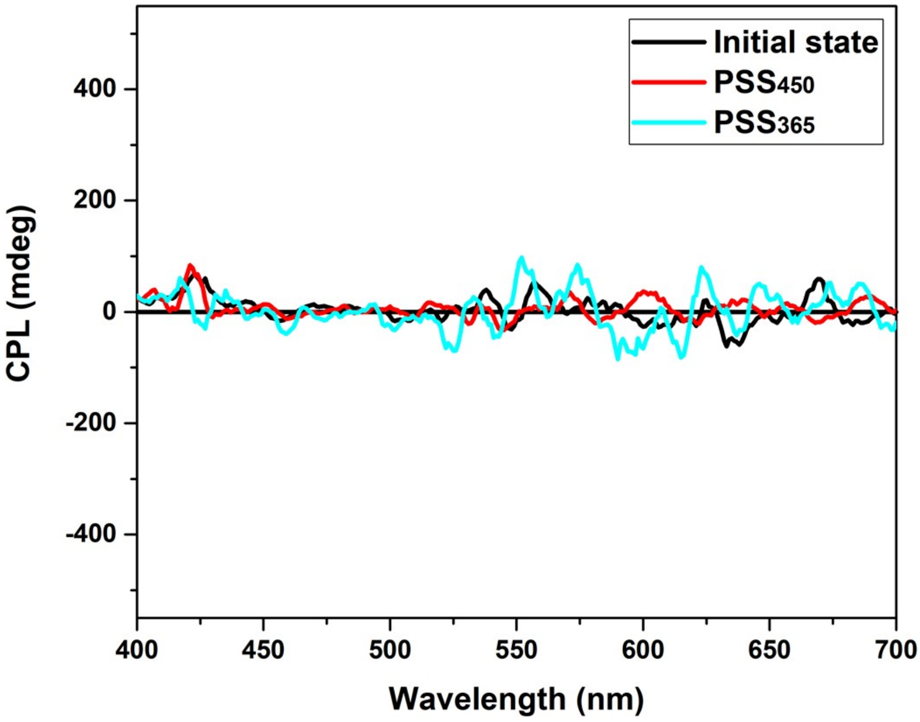


Figure S8. CPL spectrum of switch **1** (10^{-6} M) in THF solution at different states.

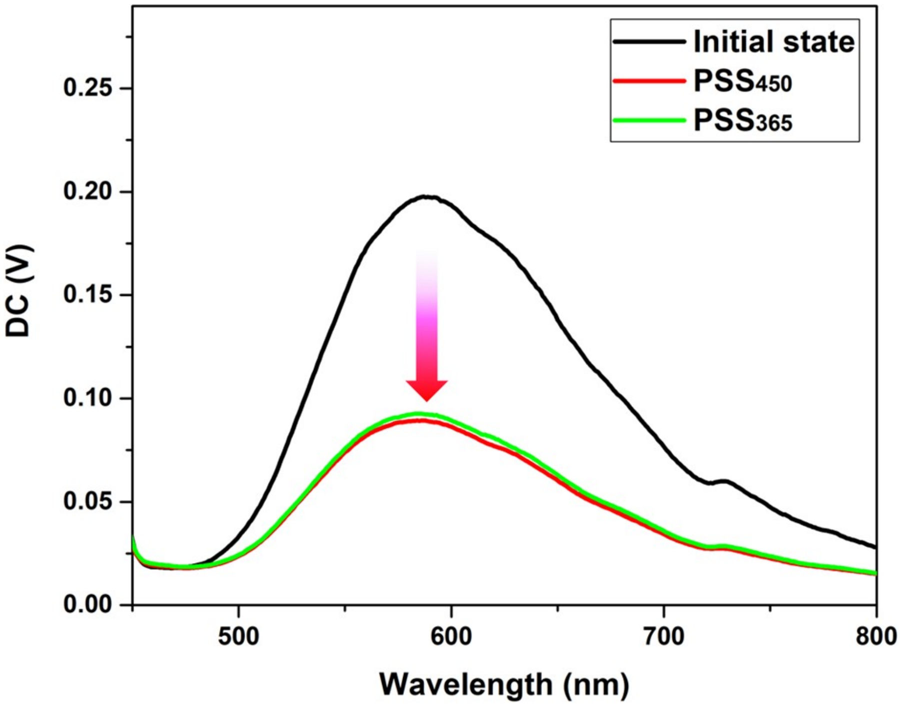


Figure S9. DC spectrum of switch **1** (10^{-6} M) in 5CB at different states.

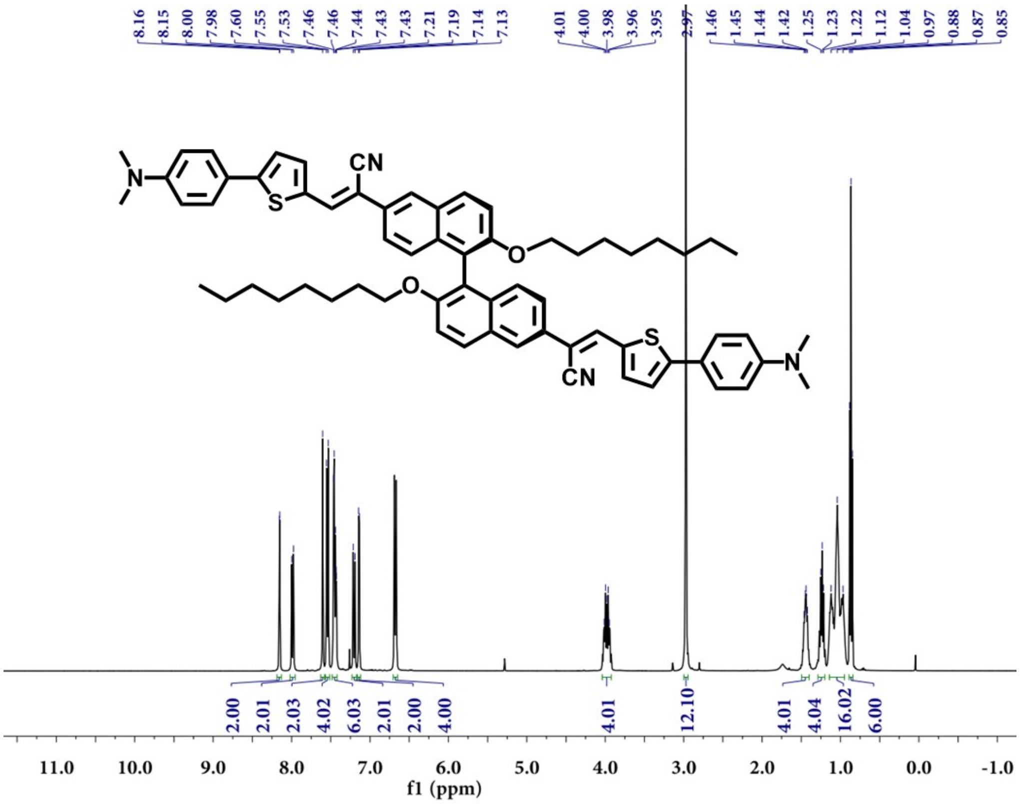
The dissymmetry factor of luminescence (g_{lum}) is an important parameter to evaluate the performance of CPL materials, and it can be calculated by the following equation:

$$g_{lum} = \Delta I/I = 2(IL - IR) / (IL + IR),$$

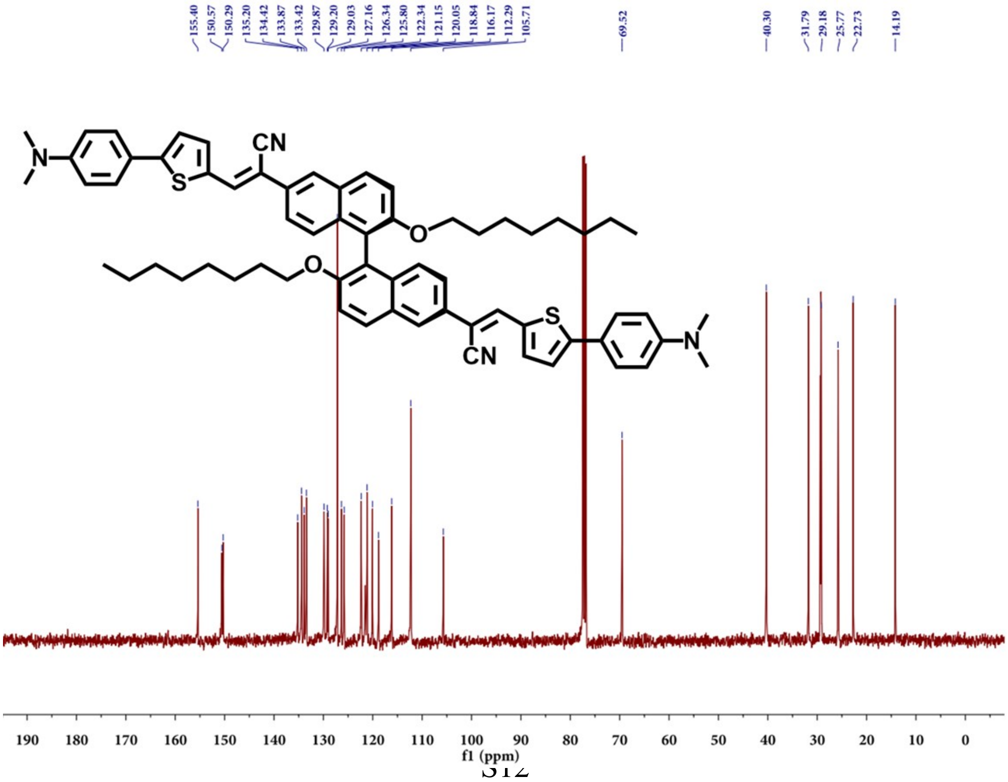
where IL and IR are the intensities of the pure left- and right-handed circularly polarized luminescence, respectively.

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

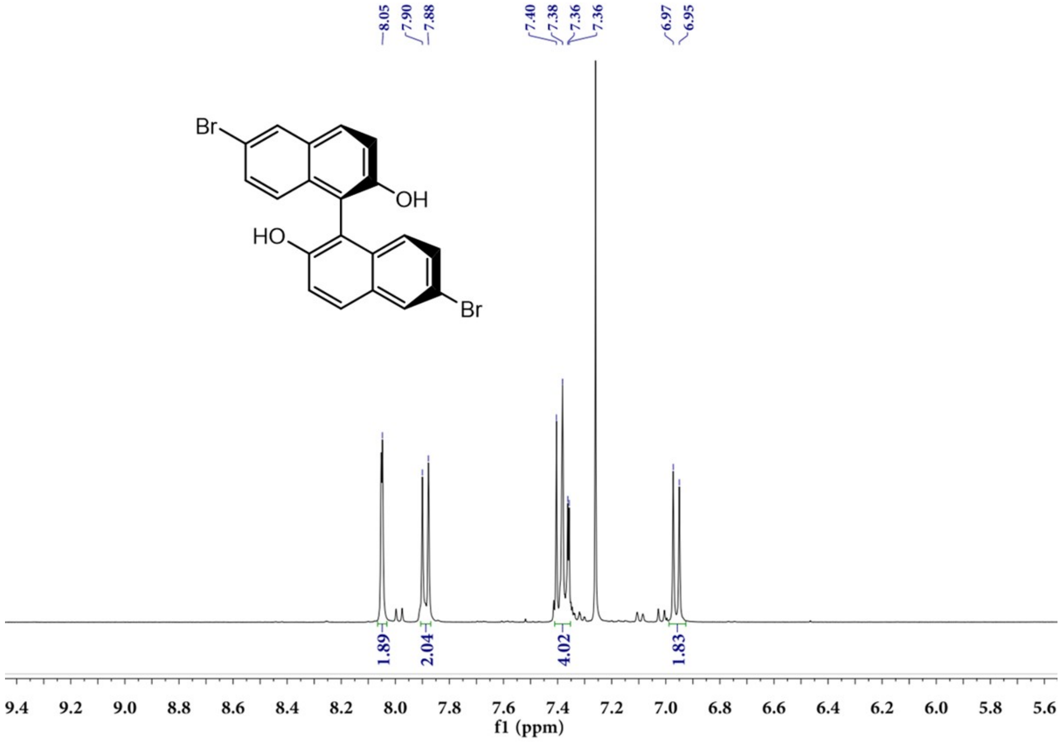
^{1}H-NMR of switch **1:**



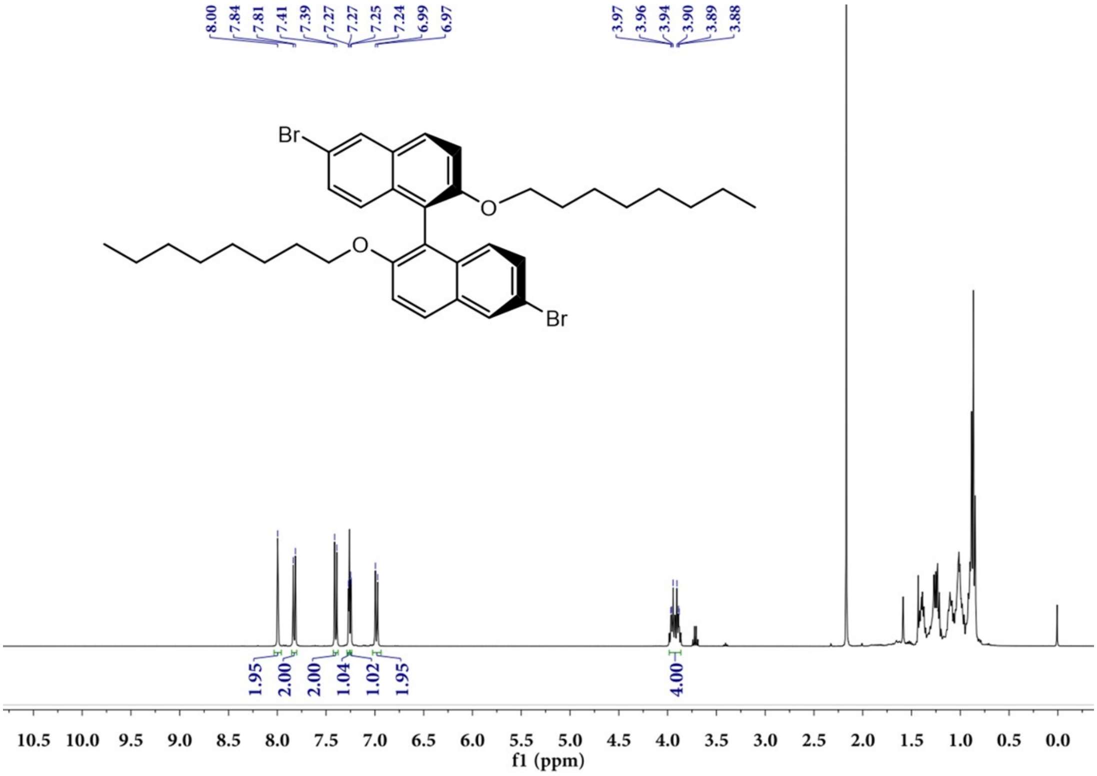
^{13}C-NMR of switch **1:**



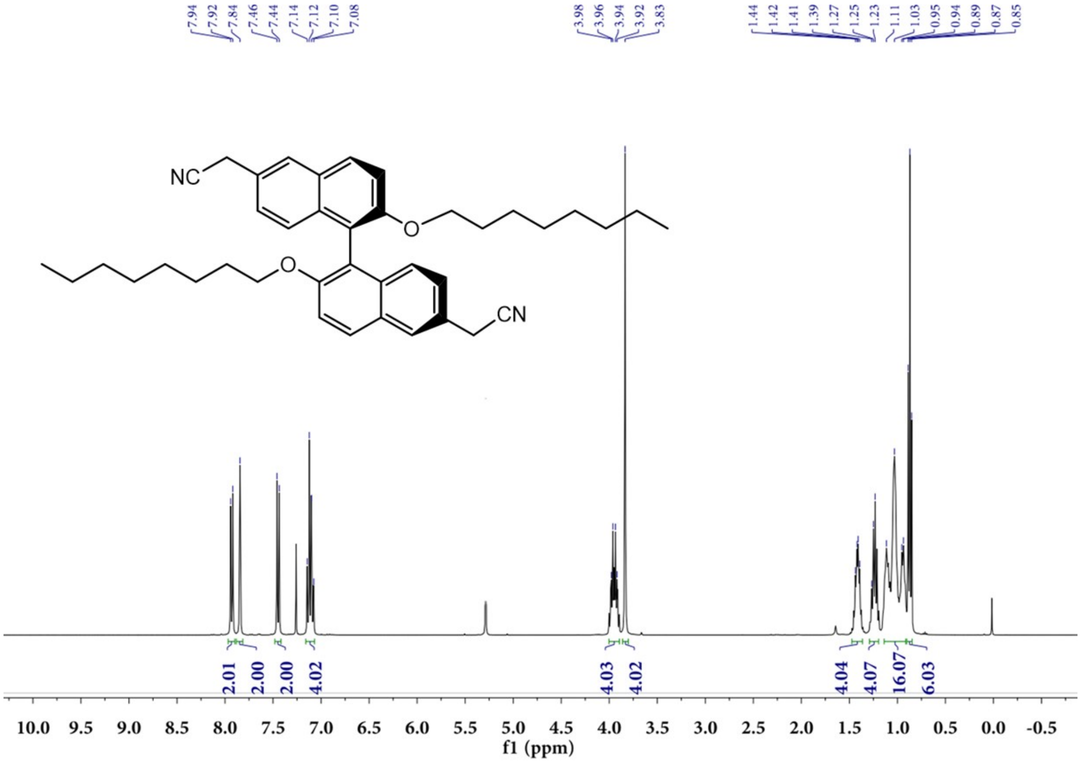
^{1}H-NMR of **Compound (S)-1:**



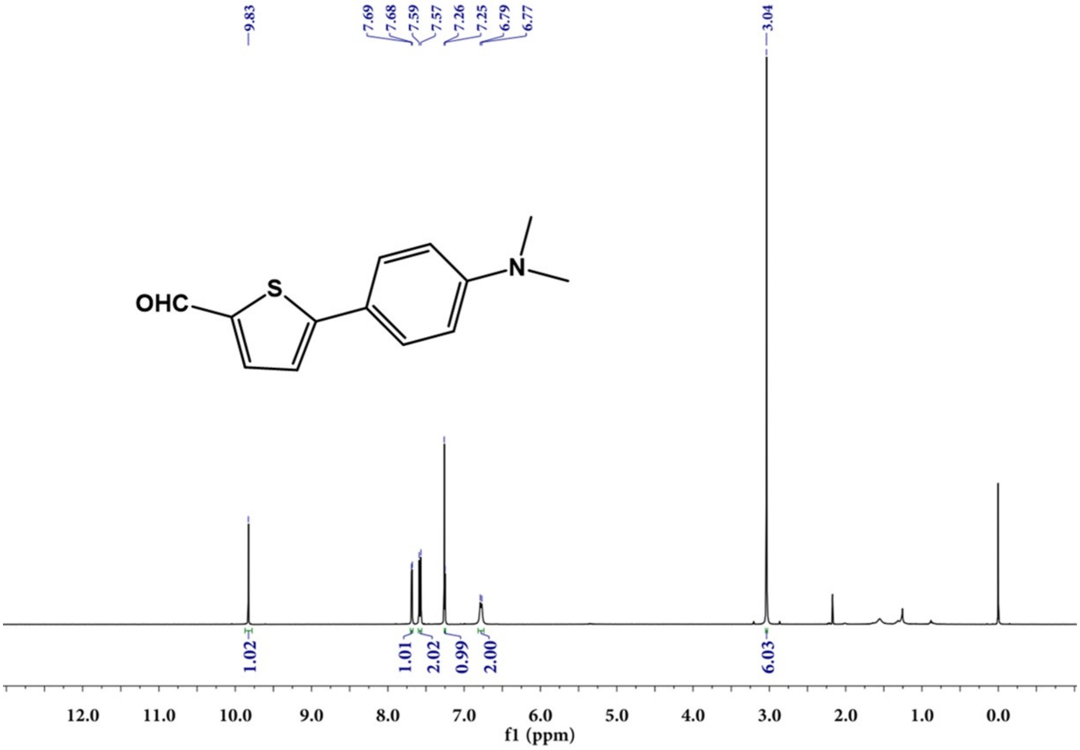
^{1}H-NMR of **Compound (S)-2:**



^{1}H-NMR of **Compound (S)-3:**

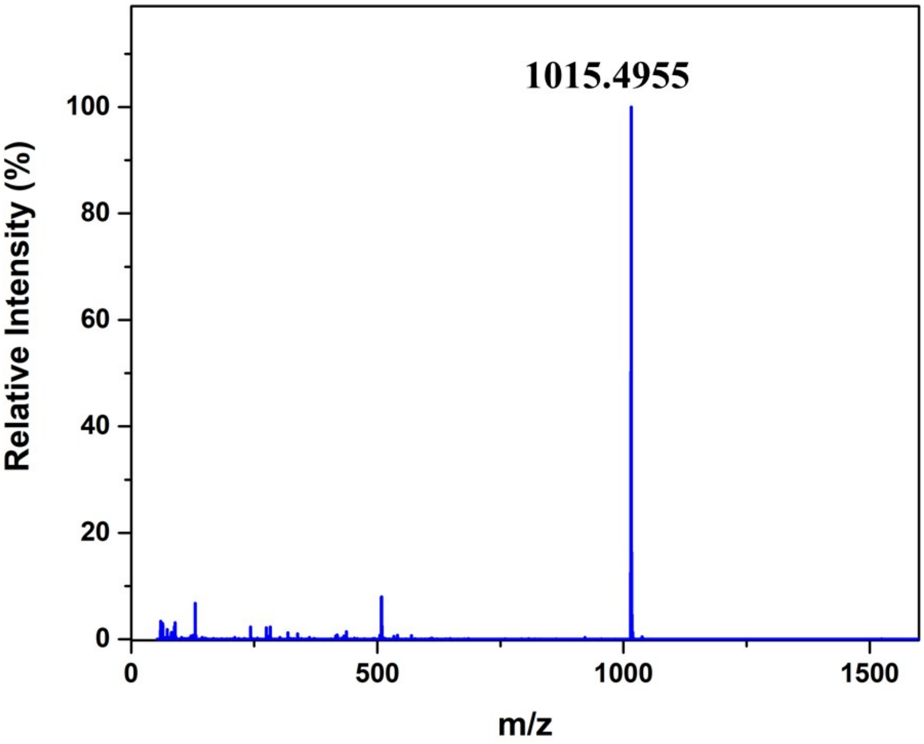


^{1}H-NMR of **Compound 4:**



12. Mass spectra

Mass spectra of switch **1**



References:

(1) Y. R. He, S. Zhang, H. K. Bisoyi, J. H. Qiao, H. Chen, J. J. Gao, J. B. Guo and Q. Li, Irradiation-Wavelength Directing Circularly Polarized Luminescence in Self-Organized Helical Superstructures Enabled by Hydrogen-Bonded Chiral Fluorescent Molecular Switches, *Angew. Chem., Int. Ed.*, 2021, **60**, 27158-27163.

(2) R. Cano, Interprétation des discontinuités de grandjean, *Bulletin de Minéralogie*, 1968, **91**, 20-27.