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Supporting Information

Simultaneous Optical Tuning of Reflection and Fluorescence in a Self-Organized Simple 3D Cubic Structure by *α*-cyanodiarylethene-based Chiral Fluorescence Photoswitches

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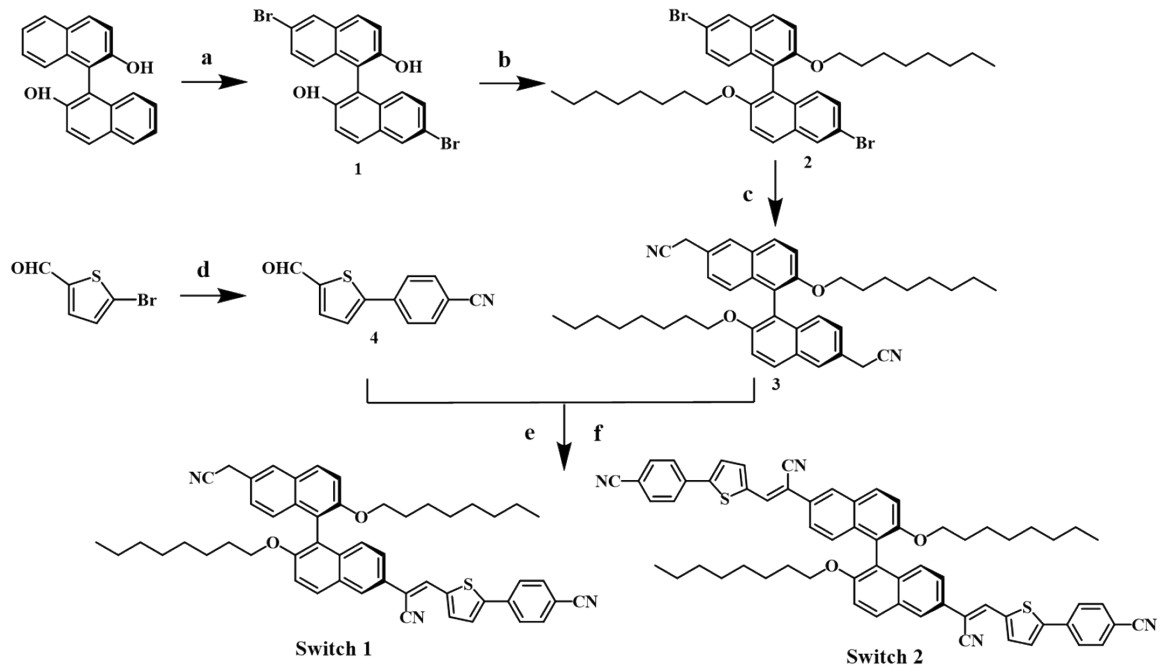
1. General information

In this study, all the reagents and solvents were acquired from commercial sources and used without further purification unless otherwise mentioned. Super dry tetrahydrofuran (THF) was dried with 3Å molecular sieves for more than 48 hours before use. Column chromatography (TLC) was carried out on silica gel (200~300 mesh). And commercially coated 60 mesh GF254 glass plates were performed as analytical thin-layer chromatography (TLC).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III (400 MHz ^{1}H; 100 MHz ^{13}C) spectrometer using DMSO-d_6 or $CDCl_3$ as the solvent. Chemical shifts are reported as δ in a unit part 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 designed as followed: s (singlet); d(doublet); and m (multiplet). Mass spectra data were acquired by high resolution mass spectrometry (Bruker SolanX 70 FT-MS) in positive ion mode.

2. Synthesis of chiral fluorescence photoswitches



Reaction conditions: (a)z Br_2, CH_2Cl_2, 0 ℃ to RT; (b) 1-bromootance, acetonitrile, K_2CO_3, 80 ℃; (c) Sodium 2-cyanoacetate, $Pd_2Cl_2(allyl)_2$, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthine, xylene, 140 ℃; (d) $C_{11}H_{16}BNO_2$, $Pd[P(Ph)_3]_4$, toluene, 90 ℃; (e) and (f) *t*-BuOK, THF, 60 ℃.

Scheme S1. Detailed synthetic routes of chiral fluorescence photoswitches.

Compound 1. We choose (S)-[1,1'-binaphthalene]-2,2'-diol as the raw material. And the product was synthesized according to our previously reported procedures.[1]

Compound 2. Compound 1 (4.51 g, 10.2 mmol) and anhydrous K_2CO_3 (8.0 eq) were dissolved in 100 ml dry acetonitrile solution. And then 1-bromooctane (13.49 g, 60.98 mmol) was added dropwise into it. Then the mixture was heated to 80 ℃ and stirred for about 24 h. The mixture was extracted with DCM and deionized water for three times. Then the combined organic layers were dried over Na_2SO_4 and concentrated. The coarse product was purified by column chromatography (DCM: PE=1: 6) to get yellow oily liquid (3.5 g, yield 52%). ^{1}H-NMR (400 MHz, Acetone-d6) δ 8.12 (s, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.03 (d, J = 9.1 Hz, 1H), 4.09 - 3.96 (m, 2H).

Compound 3. Compound 2 (1.5 g, 2.07 mmol) and the prepared sodium 2-cyanoacetate (0.89 g, 8.28 mmol) were dissolved in 80 ml anhydrous xylene. Adding allylpalladium chloride dimer (0.015 g, 0.02 eq) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (0.07 g, 0.06 eq) into the solution and refluxing for 8 h at 140 ℃ under nitrogen. After the reaction, the mixture was cooled down to room temperature and then concentrated by the vacuum rotary evaporator. The crude product was purified by column chromatography (pure DCM) to get yellow oily liquid (1.0 g, yield 75.6%).^{1}H-NMR (400 MHz, Chloroform-d) δ 7.92 (d, J = 9.0 Hz, 1H), 7.83 (s, 1H), 7.43 (d, J = 9.0 Hz, 1H), 7.10 (t, J = 7.9 Hz, 2H), 3.98 - 3.88 (m, 2H), 3.85 (s, 2H), 1.44 - 1.36 (m, 2H), 1.21 (t, J = 7.7 Hz, 2H), 1.12 - 0.98 (m, 6H), 0.92 (d, J = 7.0 Hz, 2H), 0.85 (t, J = 7.3 Hz, 3H).

Compound 4. 5-bromothiophene-2-carbaldehyde (4.0 g, 20.94 mmol) and 4-pyridineboronic acid pinacol eater (4.8 g, 20.94 mmol) were dissolved in 80 ml toluene. Then Tetrakis (triphenylphosphine) palladium (0) (1.3 g, 0.05 eq), 30 ml saturated Na_2CO_3 solution (2 M) and 20 ml n-propyl alcohol were added into the mixture in sequence. Afterwards, the mixture was stirred and refluxed at 90 ℃ for 18 h under nitrogen. After the reaction, the mixture was extracted with DCM and saturated NaCl solution for three times. The crude product was purified by column chromatography (chloroform) to get white solid (2.91 g, yield 65%). ^{1}H-NMR (400 MHz, Chloroform-d) δ 9.94 (s, 1H), 7.78 (d, J = 3.9 Hz, 3H), 7.73 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 4.0 Hz, 1H).

Switch 1. Compound 3 (1.0 g, 1.7 mmol) and compound 4 (0.36 g, 1.7 mmol) were dissolved in 50 ml dry THF. And t-BuOK (0.19 g, 1.7 mmol) was added into the mixture slowly in stirring. Then the mixture was stirred and refluxed at 55 ℃ for 6 h under nitrogen. After that, several diluted HCl solution was added into it to quench the reaction and adjust PH value to be neutral. Then the mixture was extracted with chloroform and deionized water for three times. The crude

product was purified by column chromatography (EtOAc and chloroform) to orange solid (0.59 g, yield 59%). ^{1}H-NMR (400 MHz, Chloroform-d) δ 8.19 (d, J = 1.8 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.88 (s, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 9.6 Hz, 3H), 7.60 (d, J = 4.0 Hz, 1H), 7.50 - 7.44 (m, 4H), 7.20 - 7.11 (m, 3H), 3.99 (dd, J = 10.3, 5.5 Hz, 4H), 3.88 (s, 2H), 1.44 (d, J = 4.3 Hz, 4H), 1.25 (dd, J = 14.8, 9.4 Hz, 4H), 1.14 - 0.96 (m, 16H), 0.90 - 0.83 (m, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 155.75, 155.05, 144.87, 139.47, 138.24, 134.26, 133.47, 131.78, 126.33, 125.49, 124.64, 120.12, 117.68, 116.26, 111.54, 110.42, 70.64, 31.68, 30.17, 25.64, 23.60, 21.64, 12.49. HRMS (ESI) calcd for $C_{52}H_{53}N_3O_2S$ (M+Na)+ : 783.39; found: 806.376.

Switch 2. We chose the same method as switch **1** to synthesize switch **2** with a higher yield (1,01 g, yield 75%). ^{1}H-NMR (400 MHz, Chloroform-d) δ 8.21 (d, J = 2.0 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.72 - 7.67 (m, 3H), 7.61 (d, J = 4.0 Hz, 1H), 7.51 - 7.45 (m, 3H), 7.21 (d, J = 8.9 Hz, 1H), 4.06 - 3.97 (m, 2H), 1.46 (d, J = 7.6 Hz, 2H), 1.22 (t, J = 7.3 Hz, 2H), 1.12 - 0.97 (m, 8H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (101 MHz, Chloroform-d) δ 133.65, 132.84, 132.18, 130.11, 128.84, 128.40, 126.46, 118.09, 116.20, 25.71. HRMS (ESI) calcd for $C_{64}H_{58}N_4O_2S_2$ (M+H)+ : 978.40; found: 978.491.

3. Photophysics characterizations of chiral fluorescence photoswitches

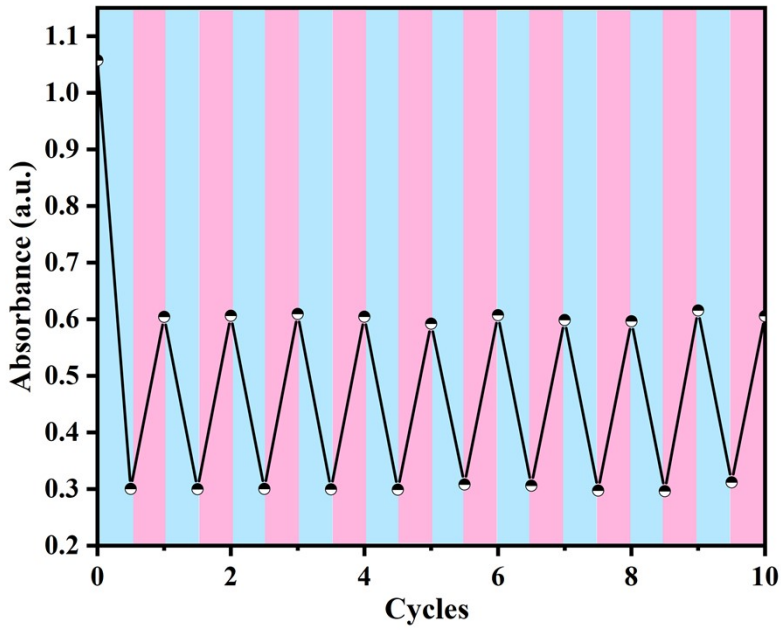
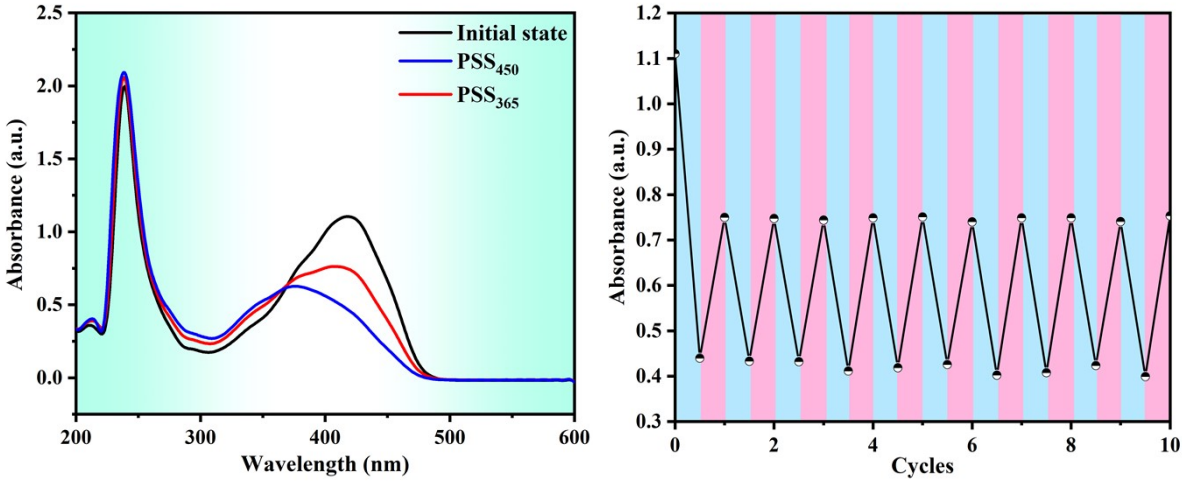
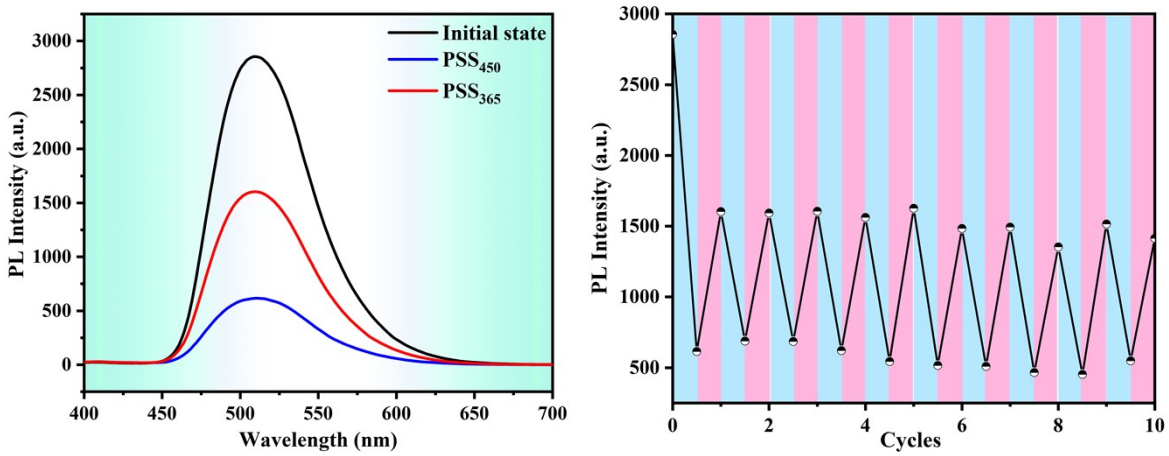


Fig. S1 Absorbance fatigue resistance of switch **1** upon alternate irradiation with 450 nm and 365 nm light for ten cycles, respectively.



(a) (b)

Fig. S2 (a) UV-Vis of switch **2** (10^{-6} M in THF) at different PSS at room temperature and (b) fatigue resistance test of variation of UV-vis spectrum under alternate irradiation



(a) (b)

Fig. S3 (a) Fluorescence spectrum of switch **2** (10^{-6} M in THF) at different PSS at room temperature and (b) fatigue resistance test of variation of UV-vis spectrum under alternate irradiation

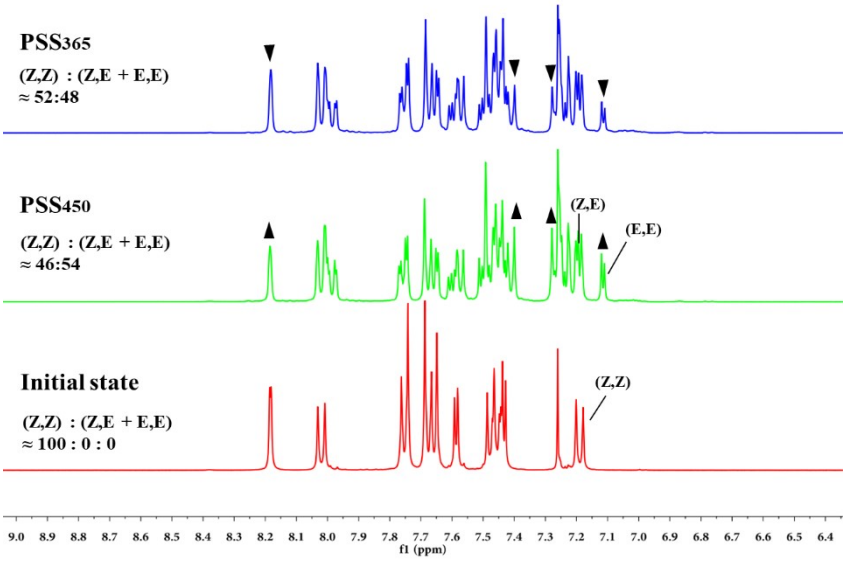


Fig. S4 ^{1}H-NMR spectra of switch **2** in $CDCl_3$ at different PSS after 25 min illumination of 450 nm and 365 nm light, respectively.

4. Simulated optimal configurations of chiral fluorescence photoswitches

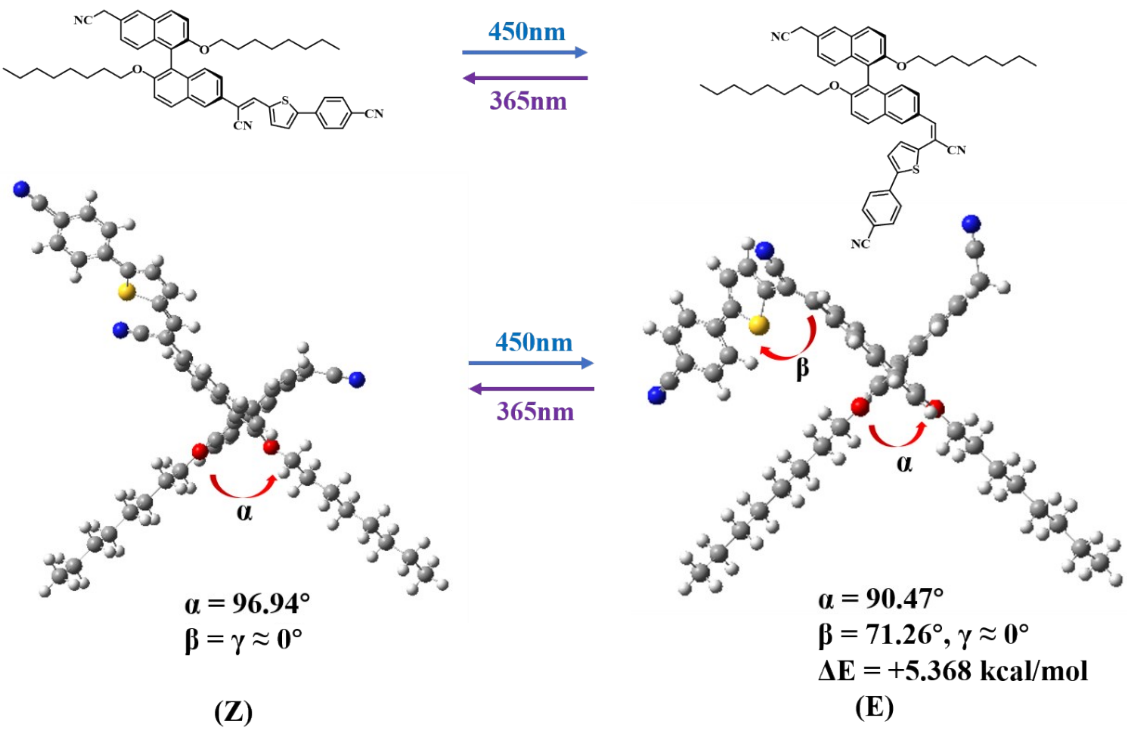


Fig. S5 Photoisomerization process of chiral fluorescence switch **1**. Optimized structures in different configuration forms obtained by Gaussian 09 calculations at B3LYP/6-31G(d) level. Thereinto, α is the dihedral angle between two naphthalenes. β and γ indicate the dihedral angle

between the thiophene ring and the naphthalene around C=C bond. ΔE is the energy level difference between different configurations.

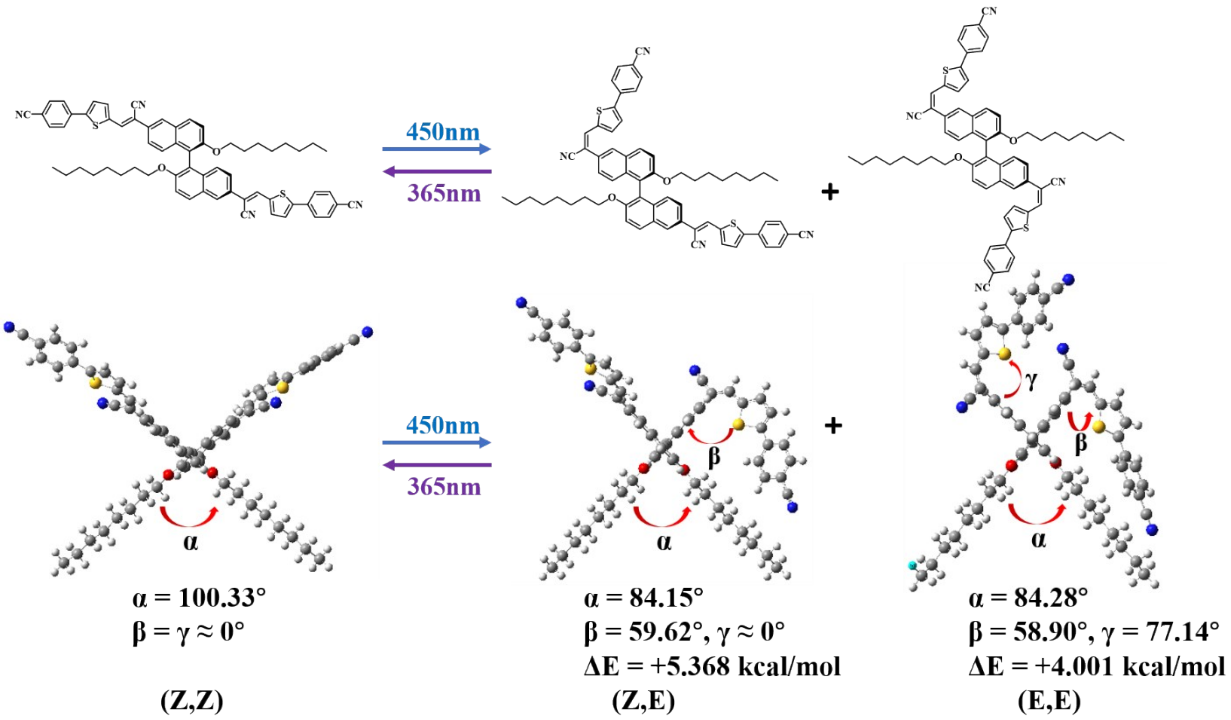


Fig. S6 Photoisomerization process of chiral fluorescence switch **2**. Optimized structures in different configuration forms obtained by Gaussian 09 calculations at B3LYP/6-31G(d) level.

Moreover, the differential absorption characteristics of different isomers are obtained by Gaussian calculations, leading to different photoisomerization yields. The data in Table S1 and Table S2 show singlet transitions, energy gaps, absorption wavelengths and oscillator strengths. For example, there are two isomers for switch **1**. For the *Z* isomer, there are two primary electronic transitions, HOMO→LUMO (S1), HOMO-2→LUMO (S3), HOMO→LUMO+3 (S9). The high oscillator strength (0.7793) of S1 leads to strong absorption bandgap at 482.67 nm. Therefore, lights in blue region can effectively trigger *Z* to *E* photoisomerization. However, the oscillator strength in ultraviolet region of *E* isomer is higher than that of *Z* isomer. So, the UV light can lead to reversible photoisomerization but not complete. Similarly, switch **2** has the analogical trend.

Table S1. Energy gaps of the singlet transitions, maximum absorption wavelengths and oscillator strengths of switch 1 calculated by TD-DFT

Switch 1	Excitation	E_{cal} (eV)	$\lambda_{max,\ abs}$ (nm)	Oscillator Strength (f)
Z	S1 HOMO→LUMO (98%)	2.5687	482.67	0.7793
	S3 HOMO-2→LUMO (90%)	3.1994	387.52	0.6851
	S9 HOMO→LUMO+3 (65%)	3.9144	316.74	0.0864
E	S1 HOMO→LUMO (98%)	2.8554	434.21	0.5435
	S3 HOMO-2→LUMO (81%)	3.3203	373.41	0.1706
	S12 HOMO-2→LUMO+1 (52%)	4.1042	302.09	0.2074

Table S2. Energy gaps of the singlet transitions, maximum absorption wavelengths and oscillator strengths of switch **2** calculated by TD-DFT

Switch 2	Excitation	E_{cal} (eV)	$\lambda_{max,\ abs}$ (nm)	Oscillator Strength (f)
Z,Z	S1 HOMO→LUMO (95%)	2.5310	489.87	0.8238
	S3 HOMO-1→LUMO+1 (95%)	2.6390	469.82	0.4961
	S5 HOMO-2→LUMO (68%)	3.1857	389.19	0.8926
Z,E	S1 HOMO→LUMO (98%)	2.5498	486.25	0.0006
	S3 HOMO-1→LUMO (56%)	2.5984	477.16	0.7231
	S12 HOMO-2→LUMO (69%)	3.1802	389.87	0.6592
E,E	S1 HOMO→LUMO (93%)	2.5035	495.25	0.0165
	S6 HOMO-3→LUMO (52%)	3.2582	380.53	0.4429
	S7 HOMO-2→LUMO+1 (50%)	3.2862	377.29	0.6453

5. Determination of HTP by using Grandjean-Cano method in POM

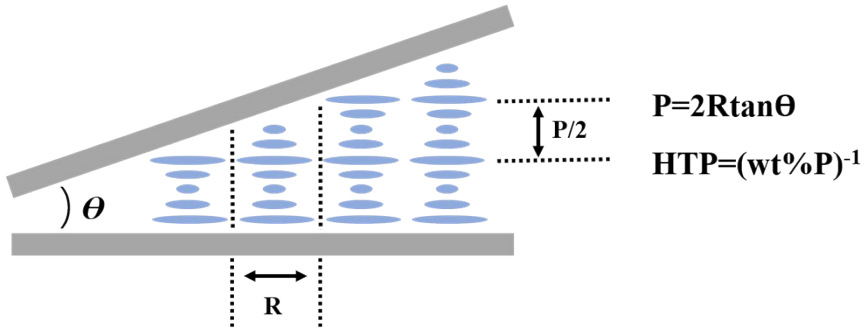


Fig. S7 Schematic diagram of the HTP value measurement by the Grandjean-Cano method. P is the helical pitch, c is the concentration of the chiral dopant, while R is the distance between two adjacent Cano lines.

Table S3. The HTP value (μm^{-1}) of cholesteric systems doping switch **1** or switch **2** at different photostationary state.

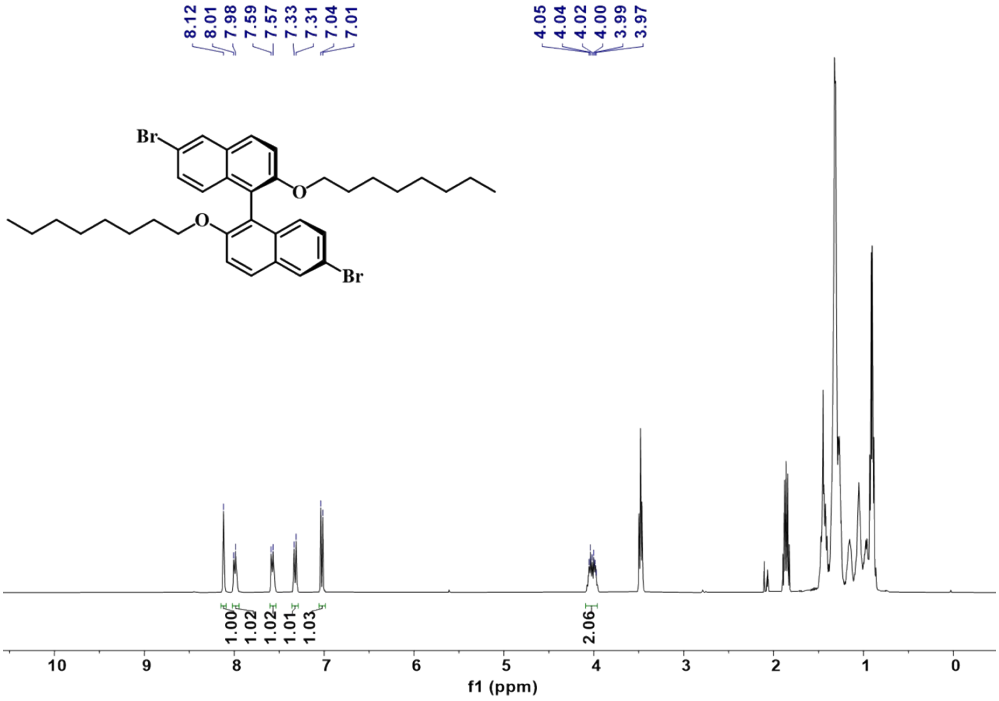
	Initial state	PSS_{450}	PSS_{365}
switch **1**	21.68	40.18	27.19
switch **2**	7.89	31.77	22.67

Table S4. The phase transitions and the blue phase temperature ranges of the BPLC systems

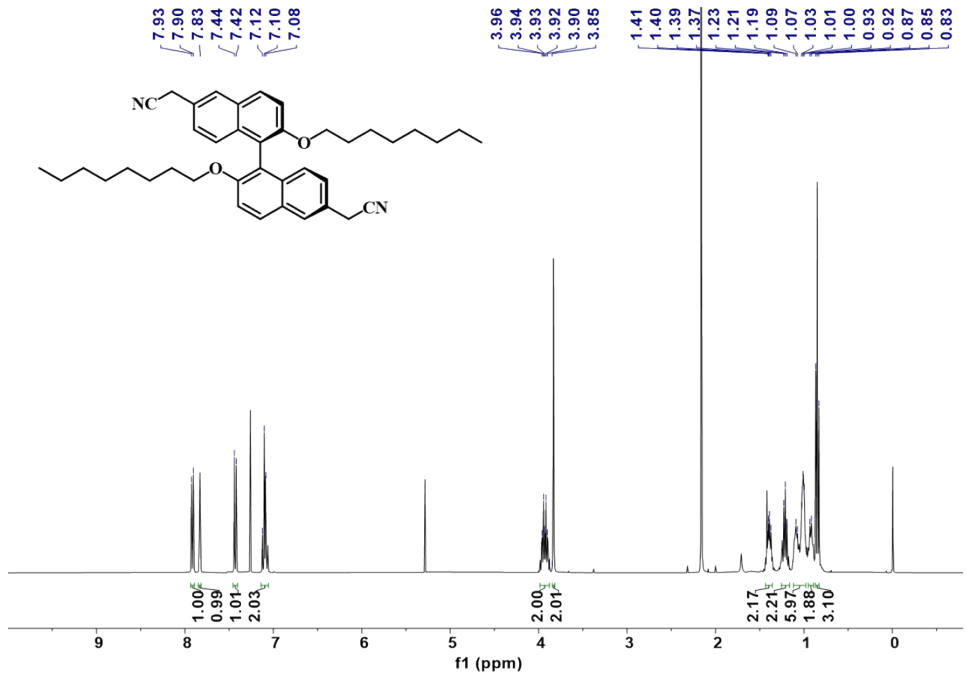
Sample	**Switch 1/2 (wt%)**	**T_{Iso-BP} (°C)**	**T_{BP-N^*} (°C)**	**Temperature range (°C)**
A0	0	50.4	45.7	4.7
A1	2.0 (switch **1**)	50.0	38.2	11.8
A2	3.0 (switch **1**)	47.6	37.3	10.3
B1	2.0 (switch **2**)	50.0	37.8	12.2
B2	3.0 (switch **2**)	48.1	36.5	11.6

6. ^{1}H-NMR and ^{13}C-NMR spectra:

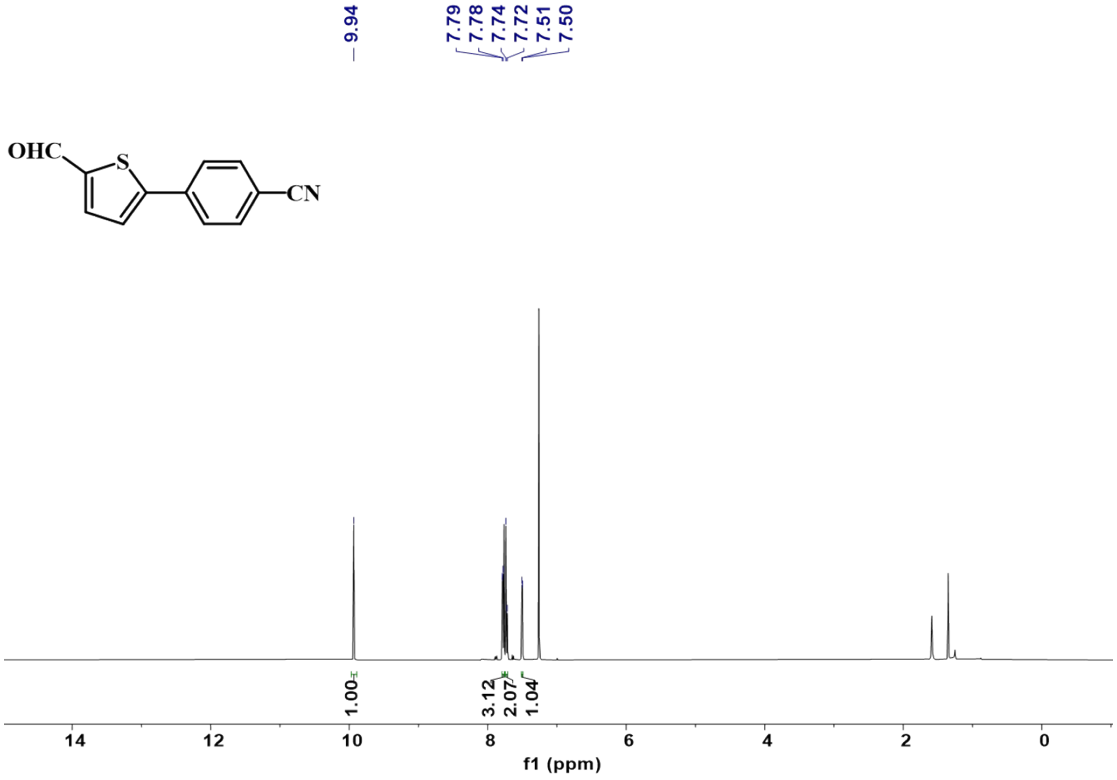
^{1}H-NMR of ***compound 2***:



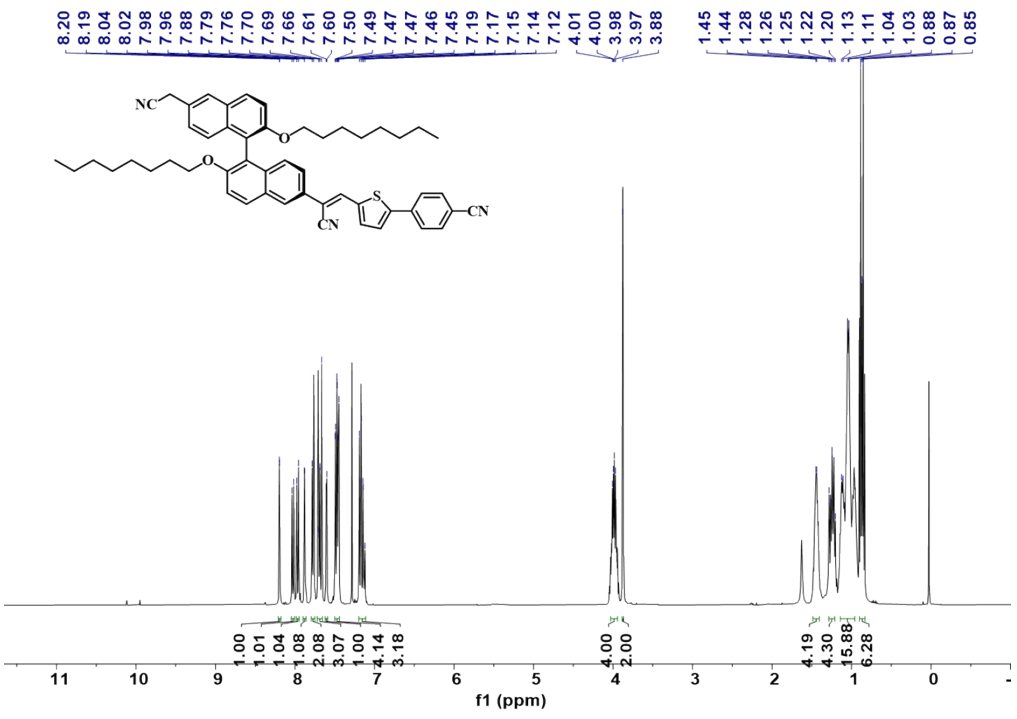
^{1}H-NMR of ***compound 3:***



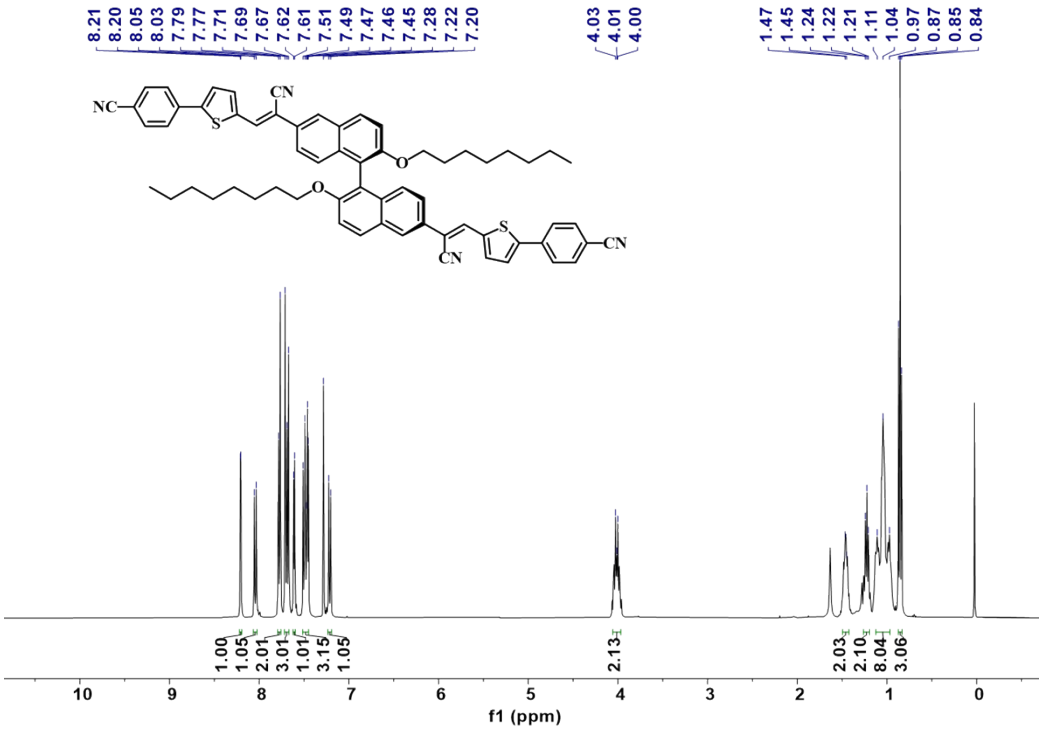
^{1}H-NMR of ***compound 4:***



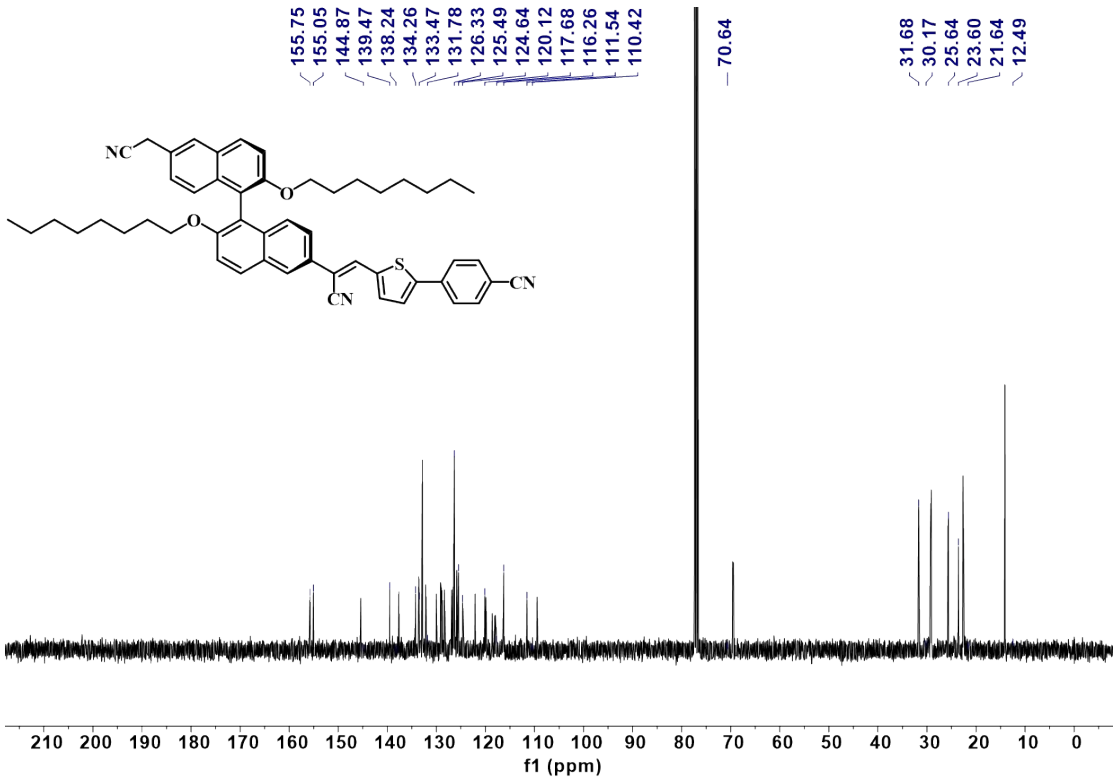
^{1}H-NMR of ***switch 1:***



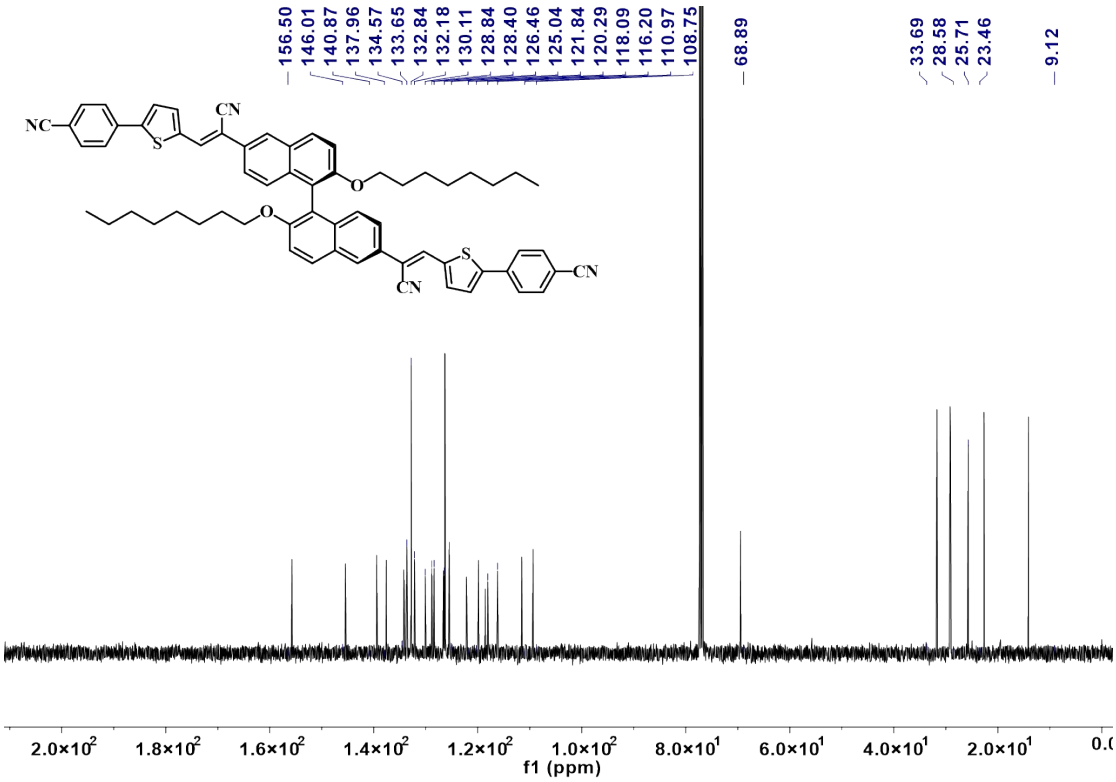
^{1}H-NMR of ***switch 2:***



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

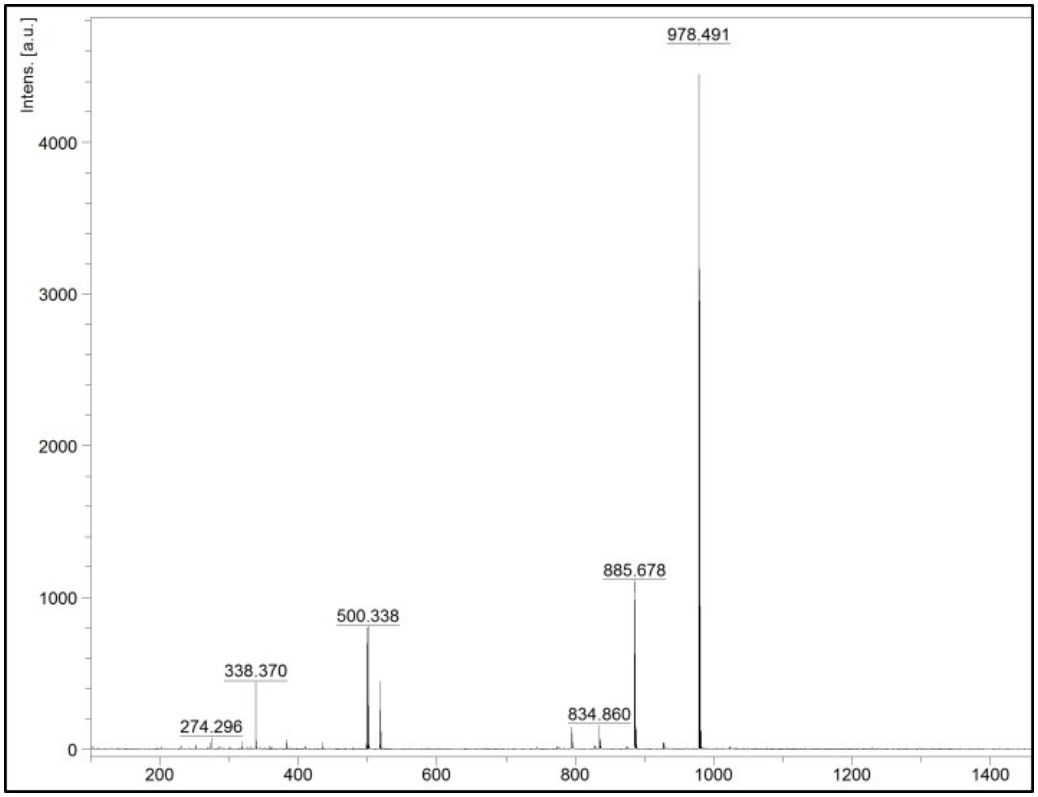


^{13}C-NMR of ***switch 2:***

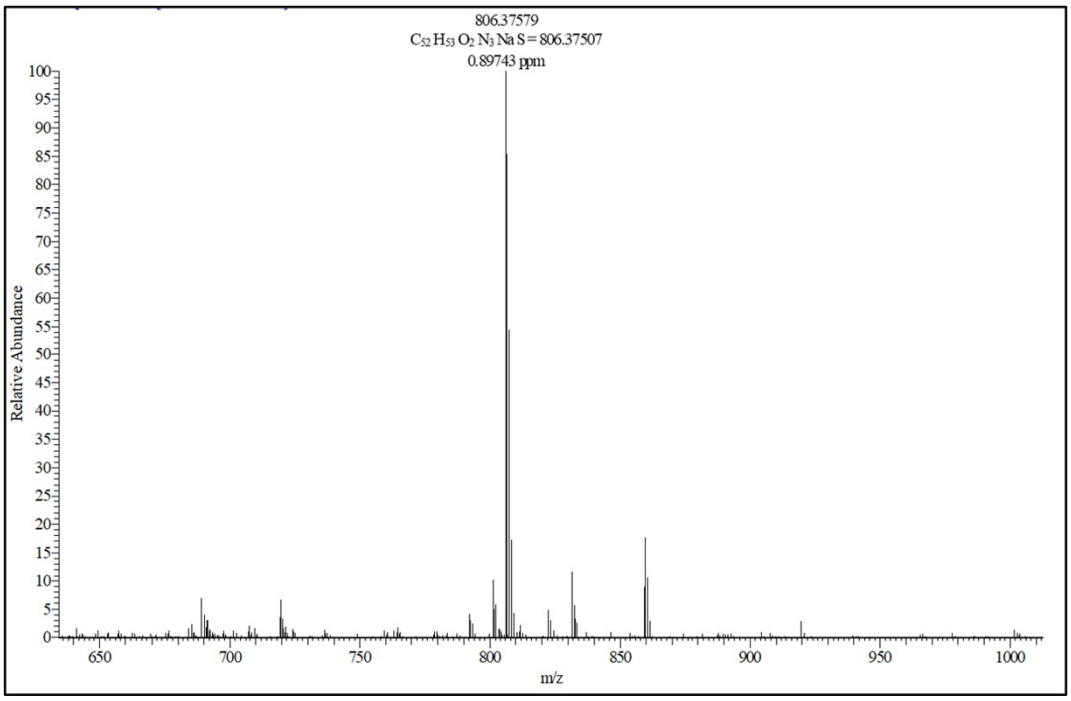


7. Mass spectra

switch 1:



switch 2:



Notes and references:

1 S. Lin, J. Li, H. Krishna Bisoyi, A. Juan, J. Guo and Q. Li, *ChemPhotoChem*, 2019, **3**, 480-486.