

Supporting Information

Electric-field, Temperature and Light Triggered Triple Dynamic Circularly Polarized Luminescence Switching in Luminescent Cholesteric Liquid Crystals with Large Dissymmetry Factor

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Materials

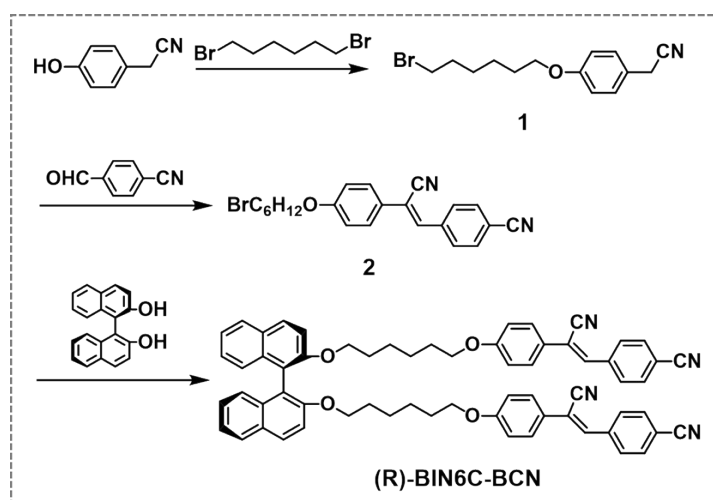
4-Hydroxyphenylacetonitrile (98%), 4-formylbenzonitrile (98%), 1, 6-dibromohexane (98%), potassium tert-butanolate, (R)-(+)-1,1'-Bi(2-naphthol) (98%), sodium methylate and 4-cyano-4'-pentylbiphenyl (98%) were purchased from Energy Chemical. Potassium iodide (AR), anhydrous potassium carbonate (AR), anhydrous magnesium sulfate (AR), dichloromethane (AR), acetone (AR), n-hexane (AR), anhydrous ethanol (AR), anhydrous ether (AR), and hydrochloric acid (AR) were obtained from Xilong Scientific Co., Ltd. No additional purification was carried out for all materials before use.

Measurements and characterizations.

^1H NMR and ^{13}C NMR spectra of all compounds were recorded on a Bruker ARX 400 MHz spectrometer, and CDCl_3 was used as solvent. Mass spectra (MALDI-TOF-MS) of all compounds were determined on a Bruker Biflex III MALDI-TOF spectrometer using α -cyano-4-hydroxycinnamic acid (CCA) as matrix. A Leica DMLM-P microscope equipped with a temperature control device was applied to observe the phase textures and measure the helical pitch of cholesteric liquid crystals. The UV-vis absorption spectra and emission spectra of (R)-BIN6C-BCN and cholesteric liquid crystals were measured by Carry-100 UV-vis spectrophotometer and PTI Qm 40 spectrometer, respectively. The solid photoluminescence quantum yield of (R)-BIN6C-BCN was measured by FLS980. The specific rotation $[\alpha]$ was measured by Rudolph Autopol IV-T. The circular dichroism (CD) spectra of cholesteric liquid crystals were recorded on a JASCO J-810 spectrometer. The circularly polarized luminescence (CPL) of cholesteric liquid crystals were measured by a JASCO CPL-200 spectrometer fluorescence spectrometer equipped with a temperature control device.

Preparation of (R)-BIN6C-BCN.

The synthetic method of (R)-BIN6C-BCN is elaborated in Scheme S1, and the detailed process is elucidated as follows:



Scheme S1 Synthetic route of (R)-BIN6C-BCN.

Preparation of compound 1.

The compound 1 were synthesized according to the reported procedures.¹

4-Hydroxyphenylacetonitrile (20.0 g, 150.2 mmol), K₂CO₃ (62.3 g, 450.6 mmol), catalyst amount of KI and 100 mL acetone were added into a 500 mL round-bottomed flask and stirred at 60°C. Then, 30 mL of acetone solution in which 1, 6-dibromohexane (91.6 g, 375.5 mmol) was dissolved was added dropwise and continuously stirred at 75°C for 6 h. When the reaction was completed, the filtrate was filtered by suction to remove insolubles, and the filtrate was collected and further purified by column chromatography using petroleum ether and dichloromethane mixed solvent (V_{PE}: V_{DCM} = 2 : 1) as eluent. Compound 1 was then obtained as a pale yellow solid (40.1 g, 90 % yield).

¹H NMR (400 MHz, CDCl₃, δ): 7.23 (d, *J* = 8.8 Hz, 2H); 6.90 (d, *J* = 8.4 Hz, 2H); 3.97 (t, *J* = 6.4 Hz, 2H); 3.69 (s, 2H); 3.44 (t, *J* = 6.8 Hz, 2H); 1.95-1.78 (m, 4H); 1.54-1.51 (m, 4H). MS: MALDI-MS: (m/z) [M]⁺ Calcd for C₁₄H₁₈BrNO, 295.06; found, 295.18. ¹³C NMR (100 MHz, CDCl₃) δ 158.75, 129.13, 121.81, 118.49, 115.01, 67.83, 34.14, 32.71, 29.06, 27.94, 25.29, 22.77.

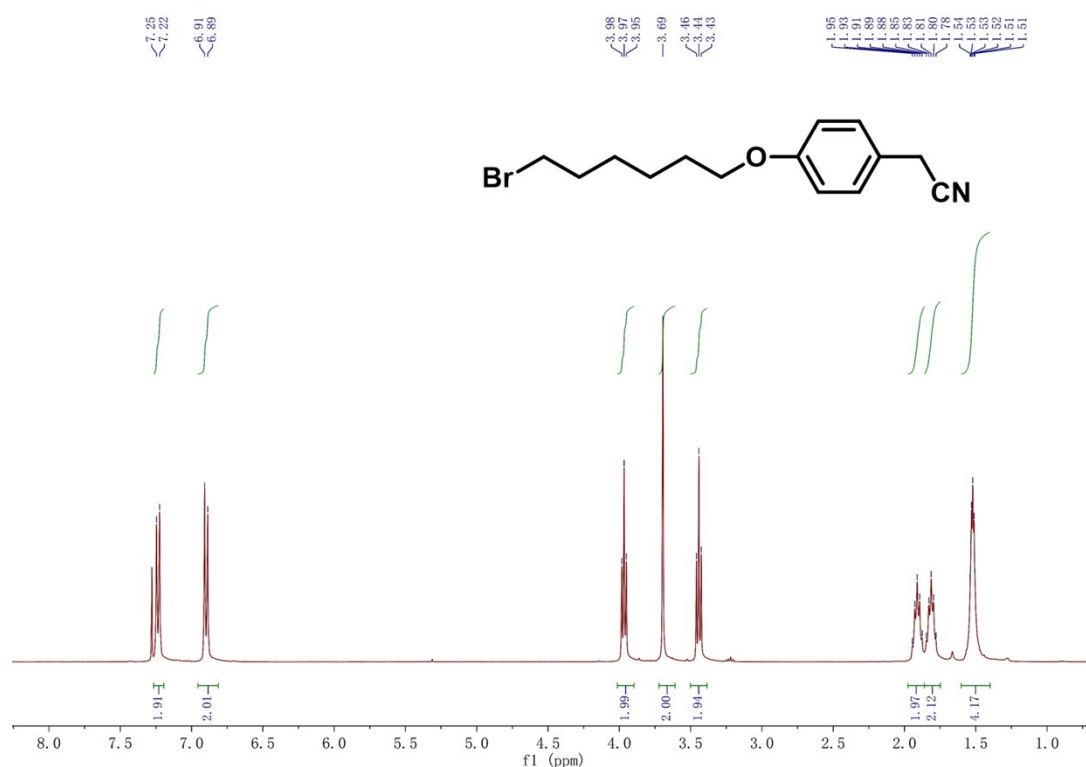


Fig. S1 ¹H NMR of compound 1 in CDCl₃.

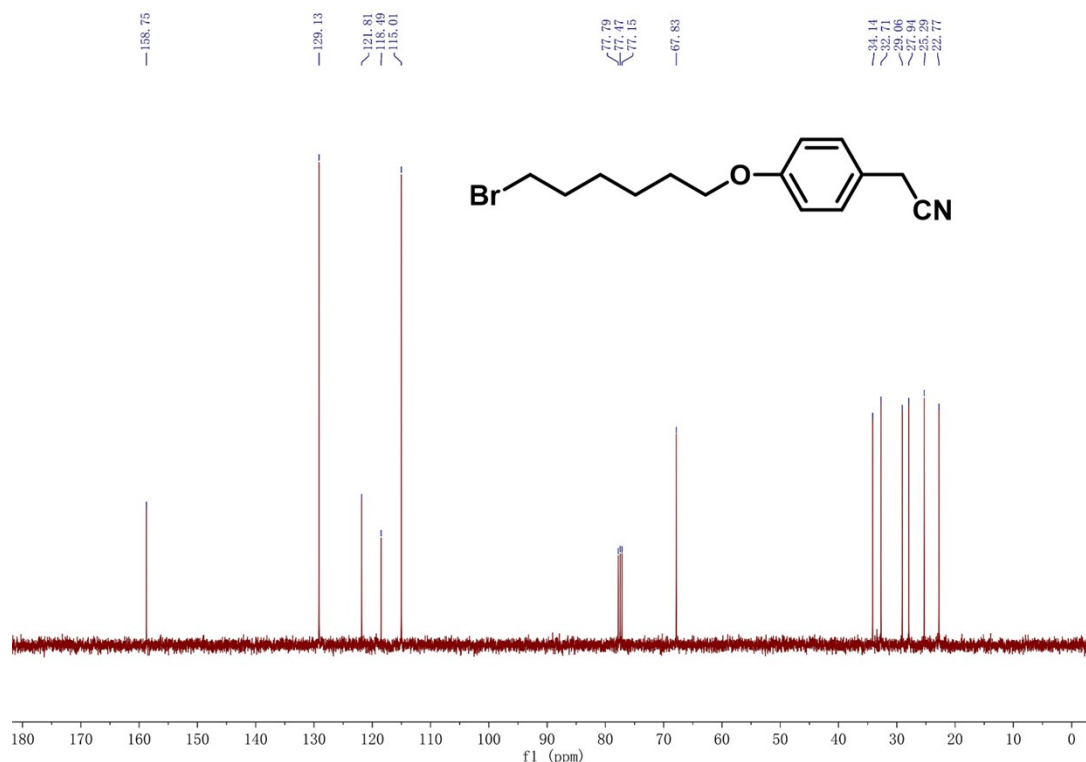


Fig. S2 ^{13}C NMR of compound 1 in CDCl_3 .

Preparation of compound 2.

The compound 2 were synthesized according to the reported procedures.¹

Adding compound 1 (20.0 g, 67.5 mmol), 4-formylbenzonitrile (9.7 g, 74.2 mmol), potassium t-butoxide (8.4 g, 33.8 mmol), anhydrous ethanol (120 mL) into a 500 mL round-bottomed flask, and the resulting solution was stirred and reacted at 30°C for 20 minutes. After that, the reaction mixtures were filtered by suction and the filter cake was washed twice with ethanol to obtain compound 2 as a pale yellow powder (23.5 g, 85.1% yield).

^1H NMR (400 MHz, CDCl_3 , δ): 7.95 (d, $J = 8.4$ Hz, 2H); 7.75 (d, $J = 8.4$ Hz, 2H); 7.64 (d, $J = 8.8$ Hz, 2H); 7.43 (s, 1H); 6.98 (d, $J = 8.8$ Hz, 2H); 4.03 (t, $J = 6.4$ Hz, 2H); 3.45 (t, $J = 6.8$ Hz, 2H); 1.96-1.82 (m, 4H); 1.56-1.52 (m, 4H). **MS:** MALDI-MS: (m/z) $[\text{M}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{BrN}_2\text{O}$, 408.08; found, 408.18. ^{13}C NMR (100 MHz, CDCl_3) δ 160.63, 138.19, 136.91, 132.59, 129.40, 127.64, 125.77, 118.43, 117.41, 115.10, 114.78, 112.93, 68.02, 33.96, 32.65, 28.99, 27.92, 25.28.

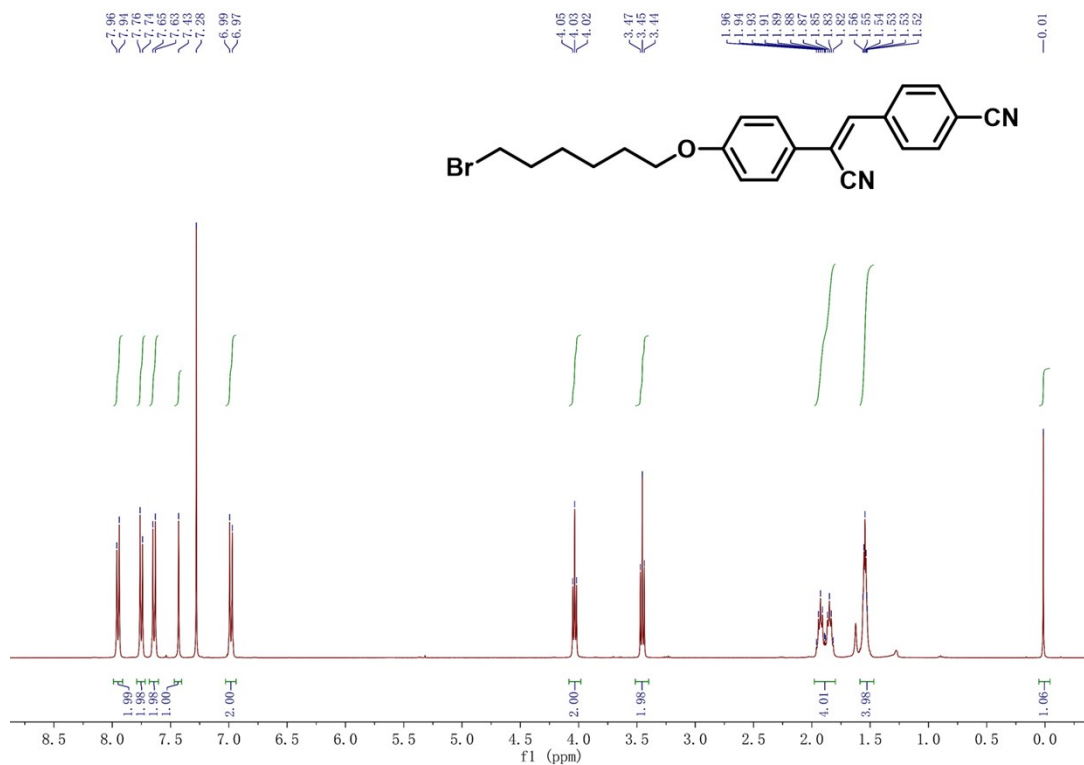


Fig. S3 ¹H NMR of compound 2 in CDCl₃.

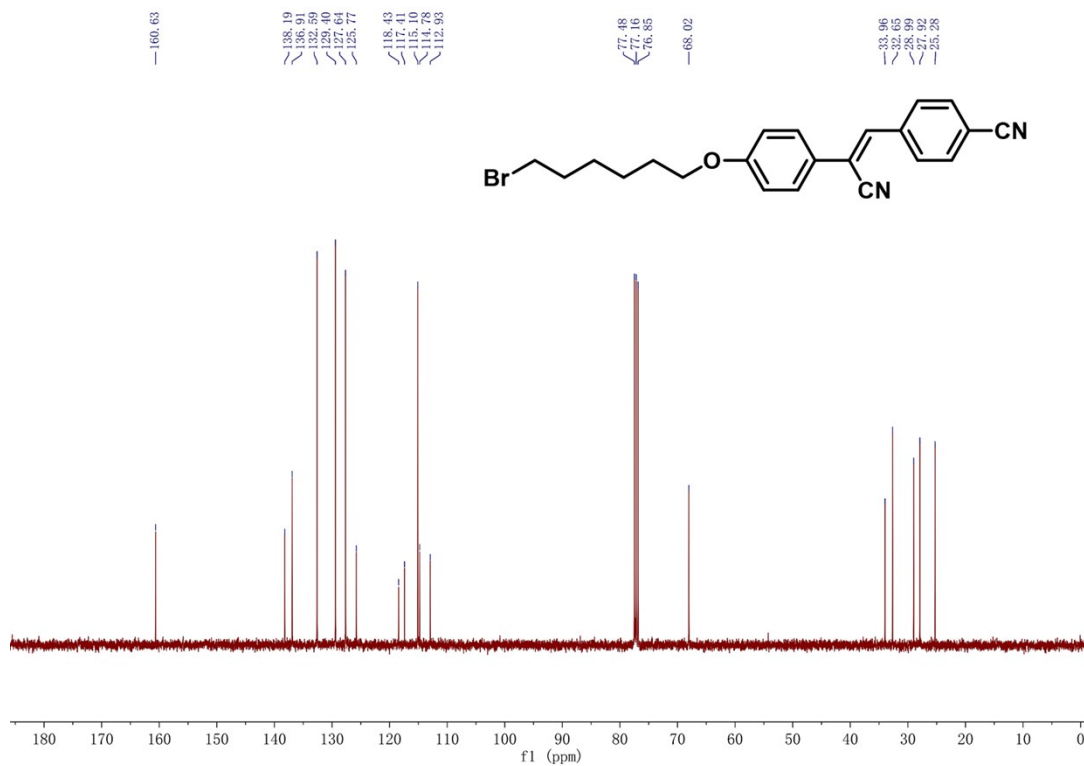


Fig. S4 ¹³C NMR of compound 2 in CDCl₃.

Preparation of (R)-BIN6C-BCN.

The (R)-BIN6C-BCN was synthesized according to the reported procedures.²

Adding compound 2 (20.0 g, 49.1 mmol), K₂CO₃ (20.3 g, 147.0 mmol), catalyst amount of KI and 150 mL acetone into a 250 mL round-bottomed flask. Then, (R)-(+)-1, 1'-Bi(2-naphthol) (7.0 g, 24.5 mmol) dissolved in 30 mL acetone were added into above flask and the mixtures were reacted at 60°C for 6 hours. When reaction was complete, the reaction mixtures were cooled down to room temperature. Suction filtration was carried out to remove insoluble matter. After filtration, the filtrate was concentrated by a rotary evaporator, and then was further purified by column chromatographic using petroleum ether, dichloromethane and ethyl acetate mixed solvent ($V_{PE} : V_{DCM} : V_{EA} = 1 : 1 : 0.05$) as eluents. The target product (R)-BIN6C-BCN was obtained as a pale yellow powder (14.9 g, 65.0% yield).

¹H NMR (400 MHz, CDCl₃, δ): 7.93 (d, $J = 8.4$ Hz, 4H); 7.91 (d, $J = 8.8$ Hz, 2H); 7.83 (d, $J = 8.0$ Hz, 2H); 7.73 (d, $J = 8.4$ Hz, 4H); 7.62 (d, $J = 8.8$ Hz, 4H); 7.41 (d, $J = 8.8$ Hz, 4H); 7.32-7.28 (m, 2H); 7.23-7.18 (m, 2H); 7.16 (d, $J = 8.0$ Hz, 2H); 6.91 (d, $J = 8.8$ Hz, 4H); 4.04-3.99 (m, 2H); 3.93-3.88 (m, 2H); 3.77 (t, $J = 6.8$ Hz, 4H); 1.52-1.37 (m, 8H); 1.16-1.08 (m, 4H); 0.98-0.84 (m, 4H). MS: MALDI-MS: (m/z) [M]⁺ Calcd for C₆₄H₅₄N₄O₄, 942.41; found 942.51. ¹³C NMR (100 MHz, CDCl₃) δ 160.72, 154.55, 138.21, 136.89, 134.25, 132.57, 129.43, 129.34, 129.23, 127.93, 127.64, 126.20, 125.68, 125.55, 123.60, 120.71, 118.49, 117.49, 115.87, 115.14, 114.70, 112.89, 69.62, 68.06, 29.34, 28.94, 25.50, 25.43.

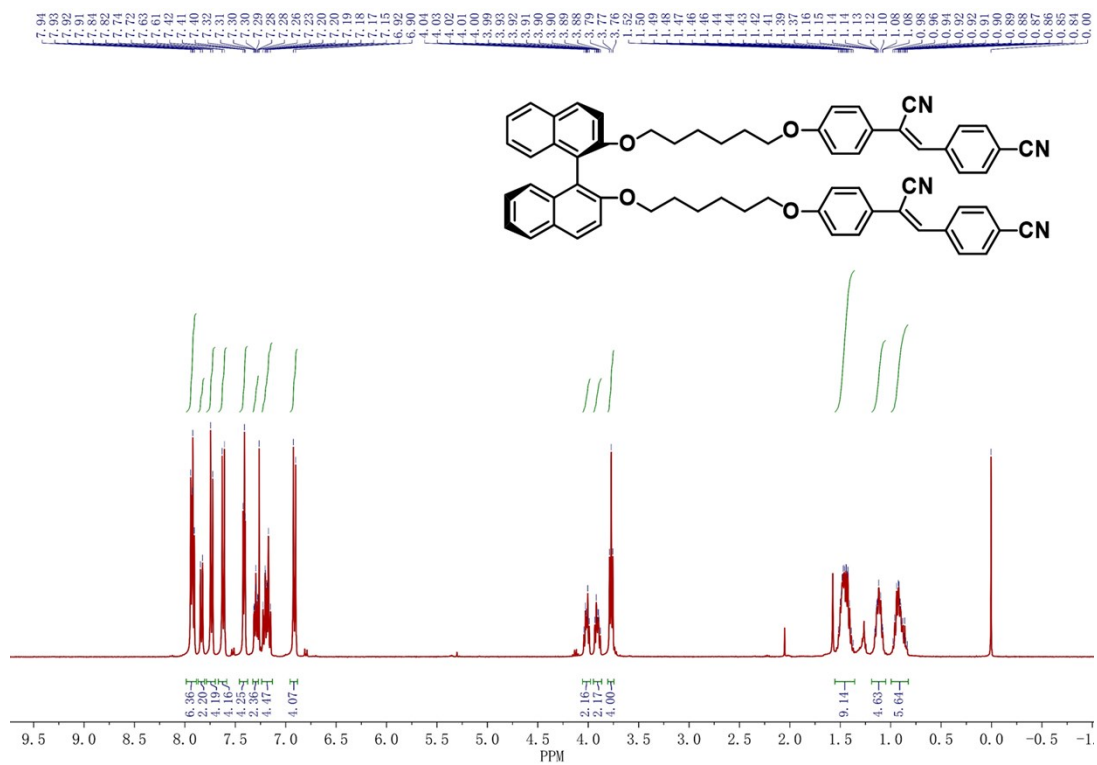


Fig. S5 $^1\text{H NMR}$ of (R)-BIN6C-BCN in CDCl₃.

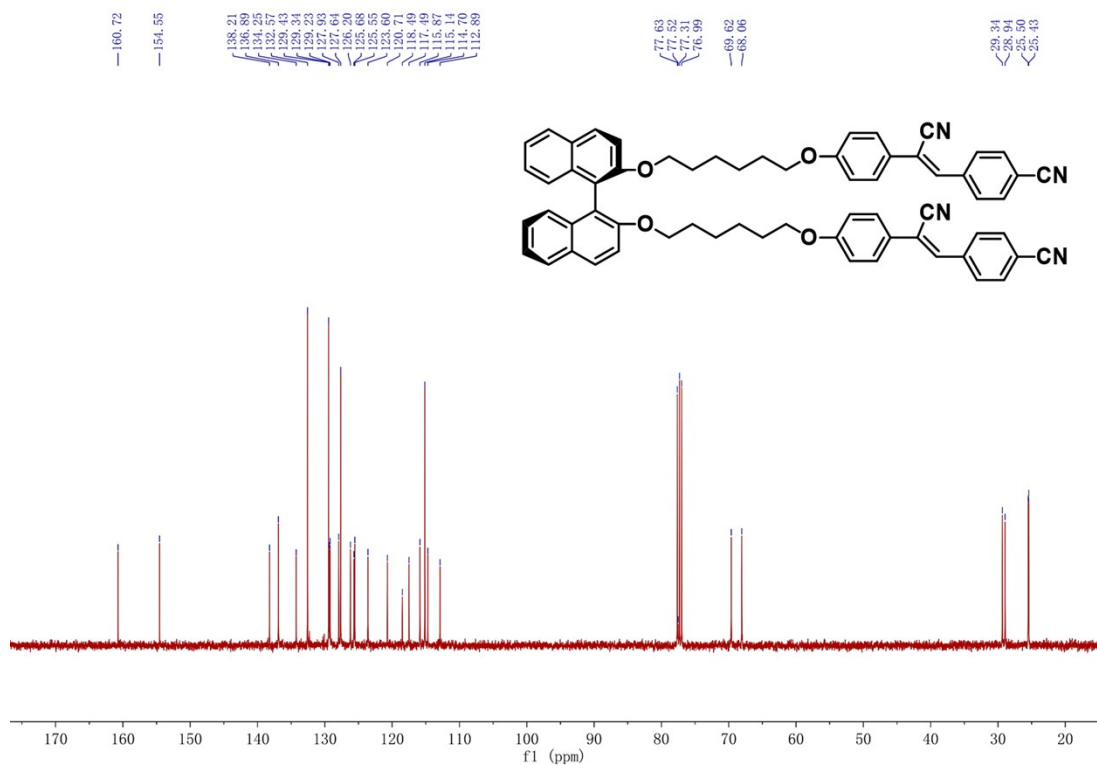


Fig. S6 $^{13}\text{C NMR}$ of (R)-BIN6C-BCN in CDCl₃.

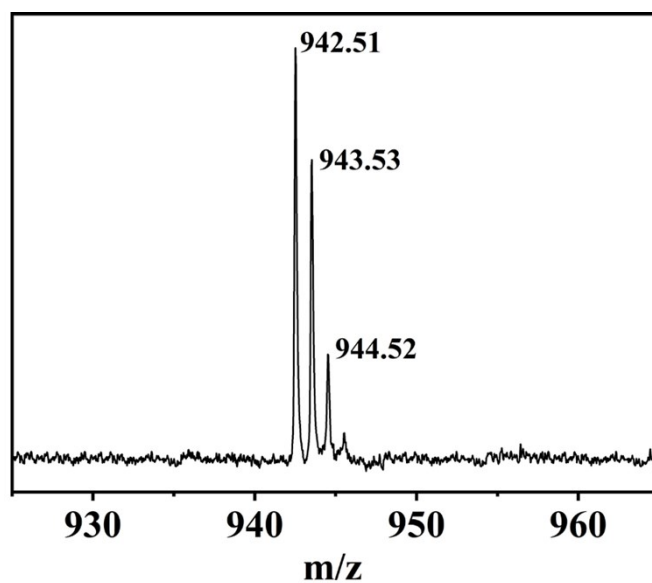


Fig. S7 Mass spectrum of (R)-BIN6C-BCN.

The specific rotation $[\alpha]$ of (R)-BIN6C-BCN. We measured the specific rotation $[\alpha]$ of (R)-BIN6C-BCN, and the value is $+10.6^\circ$ ($\alpha = +0.005^\circ$, $l = 0.5$ dm, $C = 9.4 \times 10^{-4}$ g mL $^{-1}$ (in THF), $T = 20^\circ\text{C}$).

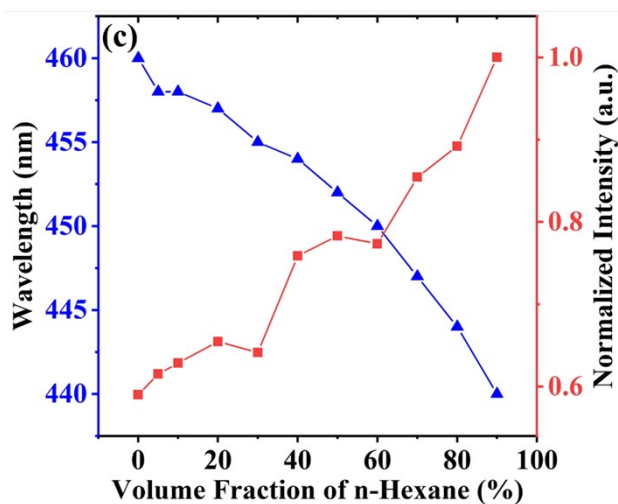
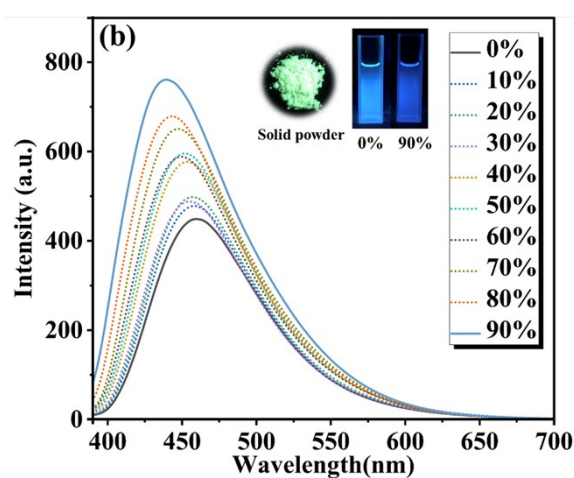
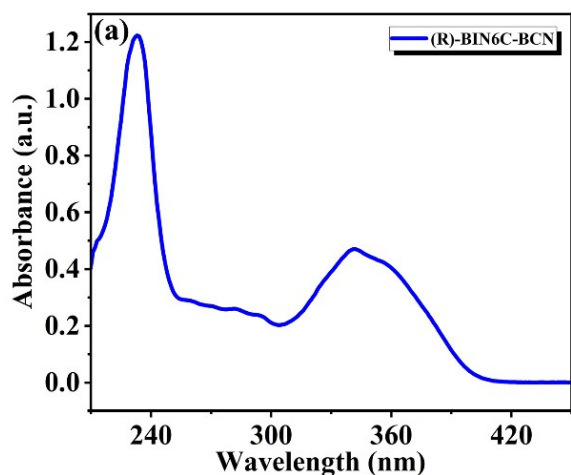


Fig. S8 (a) UV-vis absorption spectrum of (R)-BIN6C-BCN in dilute THF solution ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$); (b) Fluorescent emission spectra of (R)-BIN6C-BCN ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) in THF and n-hexane-THF mixtures with different n-hexane volume fractions ($\lambda_{\text{ex}} = 365 \text{ nm}$); (c) Relationship between maximum PL intensity and wavelength of (R)-BIN6C-BCN ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) in different ratio n-hexane / THF ($\lambda_{\text{ex}} = 365 \text{ nm}$).

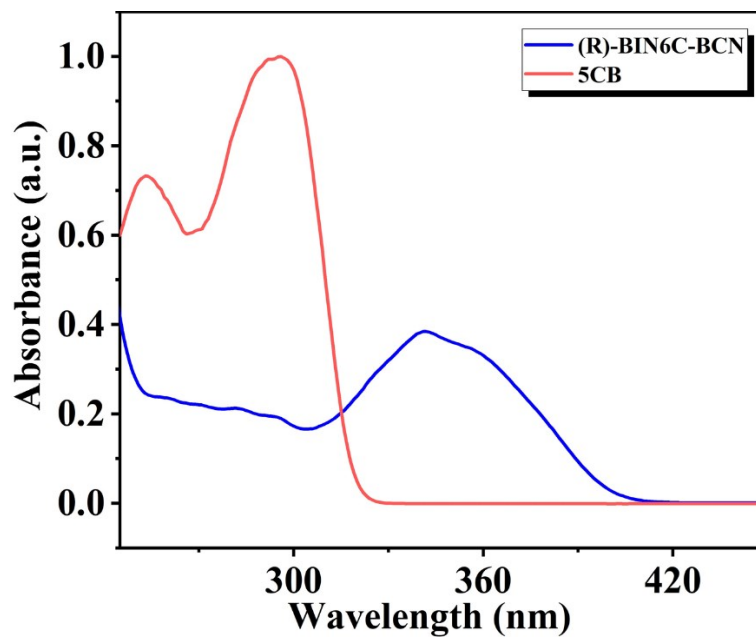


Fig. S9 UV-vis absorption spectra of (R)-BIN6C-BCN and 5CB in dilute THF solution ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$).

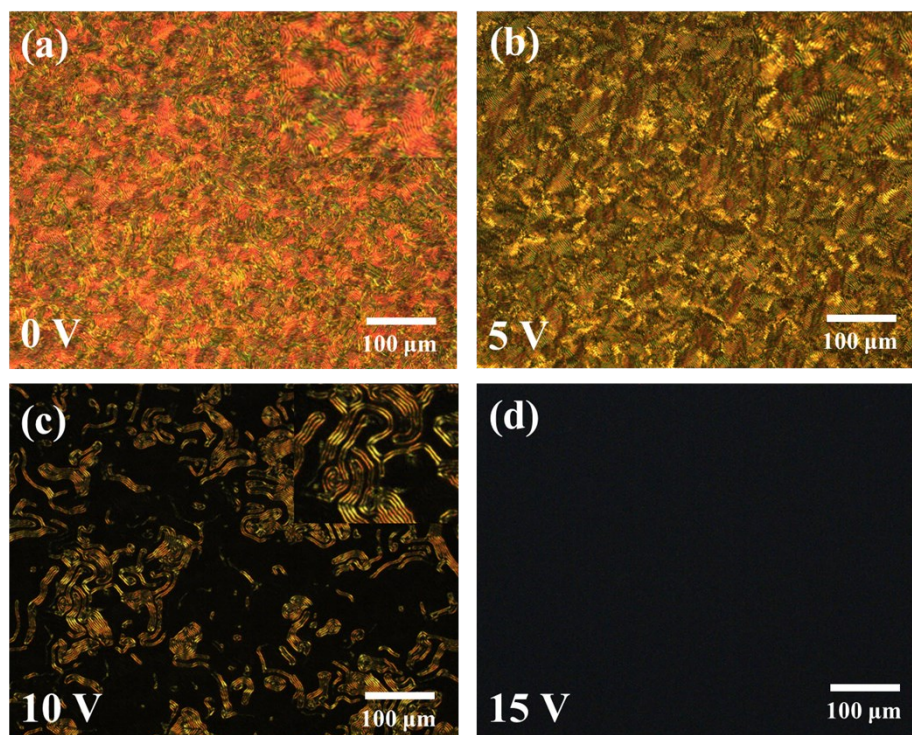


Fig. S10 POM images of cholesteric liquid crystal (doped with 2 wt % (R)-BIN6C-BCN) under different voltages; 0 V (a), 5 V (b), 10 V (c), and 15 V (d). All POM images were taken at 25°C.

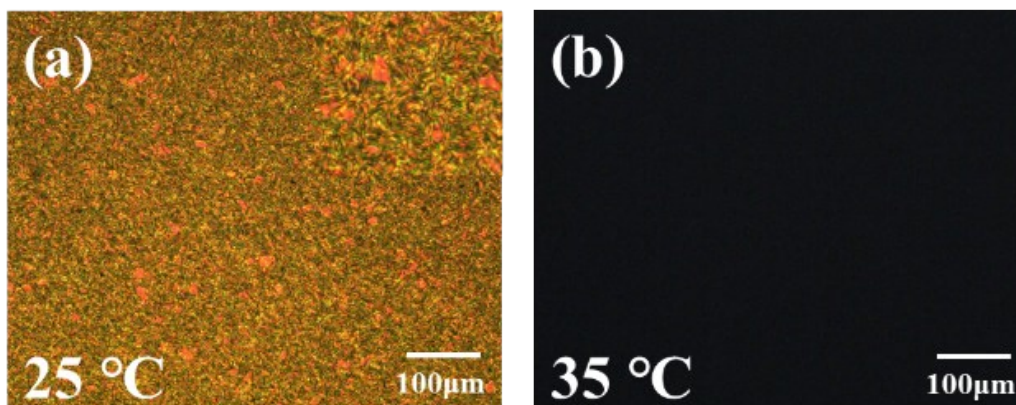


Fig. S11 POM images of cholesteric liquid crystal (doped with 2 wt % (R)-BIN6C-BCN) at different temperature; (a) at 25°C and (b) at 35°C.

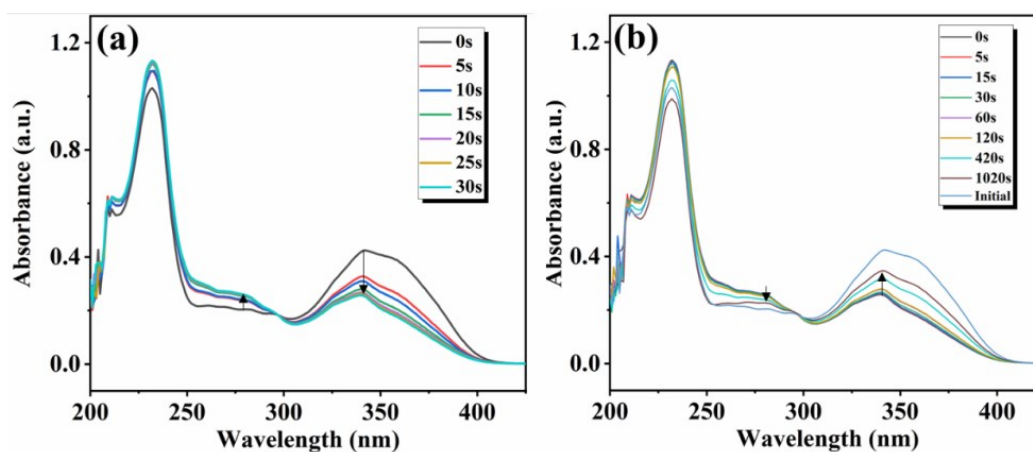
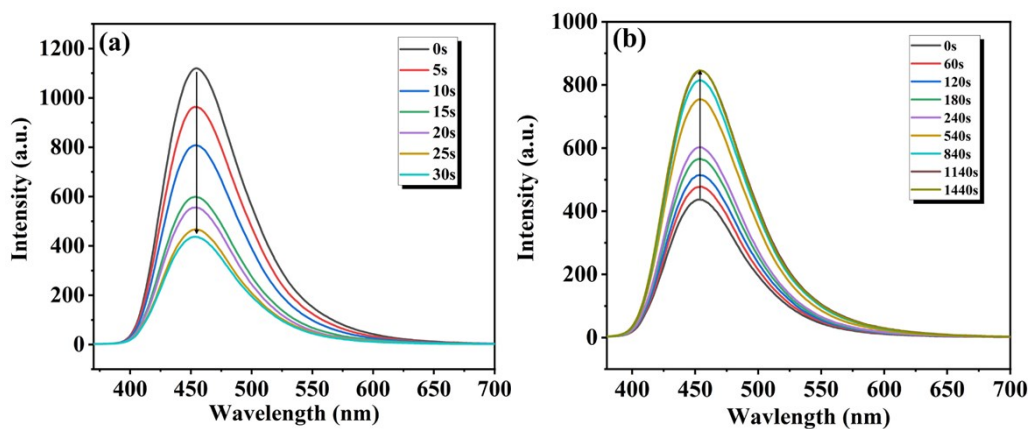


Fig. S12 (a) The photoresponse behavior of UV-vis absorption of (R)-BIN6C-BCN in THF solution ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) under different 365 nm UV irradiation time; (b) The absorption reversion under different 254 nm UV irradiation time.



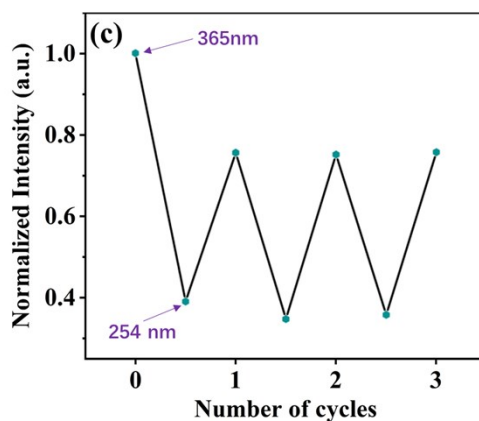


Fig. S13 (a) The photoresponse behavior of PL emission of (R)-BIN6C-BCN in THF solution ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) under different 365 nm UV irradiation time; (b) the PL reversion under different 254 nm UV irradiation time; (c) Fatigue resistance test of PL intensity variation upon alternate irradiations with 365 nm and 254 nm light.

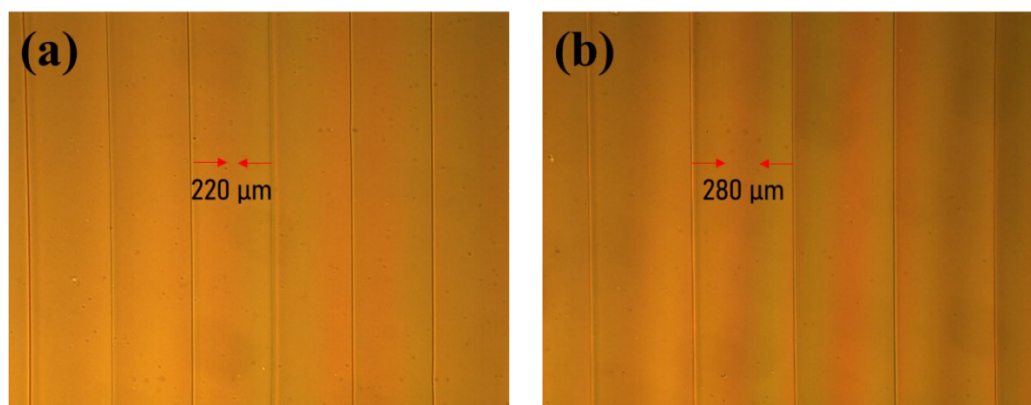


Fig. S14 The width variation of adjacent Grandjean-Cano thread of cholesteric liquid crystal (doped 2 wt% (R)-BIN6C-BCN) before 365 nm UV irradiation (a) and after 365 nm UV irradiation for 25 mins (b).

References

- 1 Y. Yuan, L. He, J. Li and H. Zhang, *Polym. Chem.*, 2019, **10**, 2706-2715.
- 2 K. Yao, Y. Shen, Y. Li, X. Li, Y. Quan, and Y. Cheng, *J. Phys. Chem. Lett.* 2021, **12**, 598-603.