SUPPORTING INFORMATION

Strong CPL of Achiral AIE-active Dyes Induced by Supramolecular Self-assemble of Chiral Nematic Liquid Crystals (AIE-N*-LCs)

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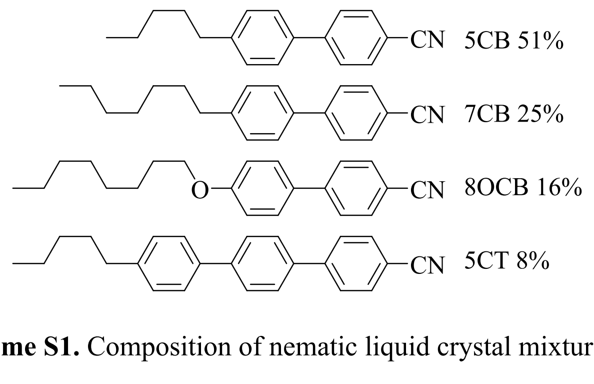
1. Instrumentation and Materials

1.1 Materials and Measurements

NMR spectra were obtained by using Bruker AVANCE III-400 spectrometer with 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR by using $CDCl_3$ or DMSO as solvent and the chemical shifts are reported as parts per million (ppm) relative to tetramethylsilane (TMS; δ=0) as the internal reference. UV-visible (UV-*vis*) absorption spectra were measured on a Hitachi U-3900 spectrophotometer. Fluorescence (FL) spectra were recorded on a HORIBA Scientific Fluoromax-4 Spectrofluorometer. Circular dichroism (CD) spectra were recorded on a JASCO *J*-810 spectropolarimeter, and the length of the sample cell was 1 cm. Circularly polarized luminescence (CPL) spectra were recorded with a JASCO CPL-300 spectrofluoropolarimeter. In the CPL measurements, the excitation wavelength was 360 nm, scan speed was 200 nm/min, number of scans was 1, and slit width was 3000 μm. The CPL spectra from the blended thin film were obtained by using a circularly polarizer on Jasco CPL-300 spectrophotometer at a scan rate of 500 nm min^{-1} and 1 nm resolution at room temperature. The magnitude of circular polarization in the excited state is defined as $g_{em} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R indicate the output signals for left and right circularly polarized light, respectively. ΔI is the difference in the intensities of left and right circularly polarized emissions from a chiral chromophore and provides their optical chiralities in the excited state, and I is the total emission intensity of the optical chiralities in the excited state. Experimentally, the value of g_{em} dissymmetry factor is defined as $\Delta I/I$ = 2[ellipticity/ (32980/ln 10)]/ (total fluorescence intensity at the CPL extremum). [1]All starting materials were purchased from Acros, Alfa Aesar, Energy and used directly. Nematic liquid crystal E7 ($n_e = 1.741$, $n_0 = 1.517$, at 589 nm; T_m = -40°C, T_i = 59 °C) was purchased from Suzhou King Optonics Co. Ltd. E7 is a eutectic mixture of LC components commercially designed and extensively employed for display application.

1.2 Materials of nematic liquid crystal



Scheme S1. Composition of nematic liquid crystal mixture E7.

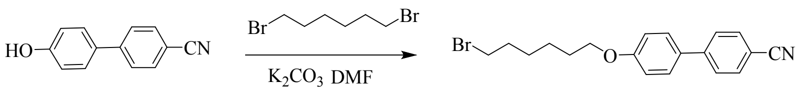
1.3 Measurements of Nematic liquid crystal.

The liquid crystalline textures were investigated and photographed using liquid crystal cells and wedge cells with a polarized optical microscope (POM) equipped with a Leitz-350 heating stage and an associated Nikon (D3100) digital camera. Liquid crystal cells and wedge cells ($\tan\theta = 0.0183$) were made in Prof. LU Yanqing and Prof. HU Wei's laboratory in Nanjing University. The helical pitch (P) of N*-LCs can be meatured by the traditional Grandjean-Cano methods,

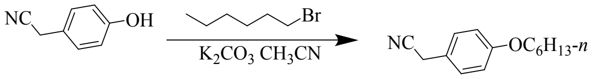
$$P/2 = R * tan\Theta$$

where R and Θ are width of Grandjean-Cano line and the angle of wedge cell, respectively.[2]

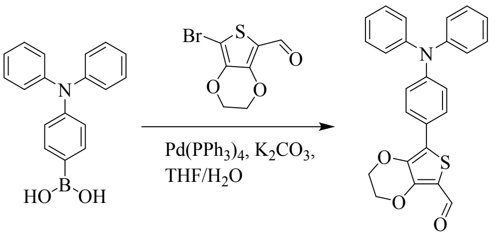
2. Syntheses of Guest-1 and Guest 2-1, 2, 3, 4



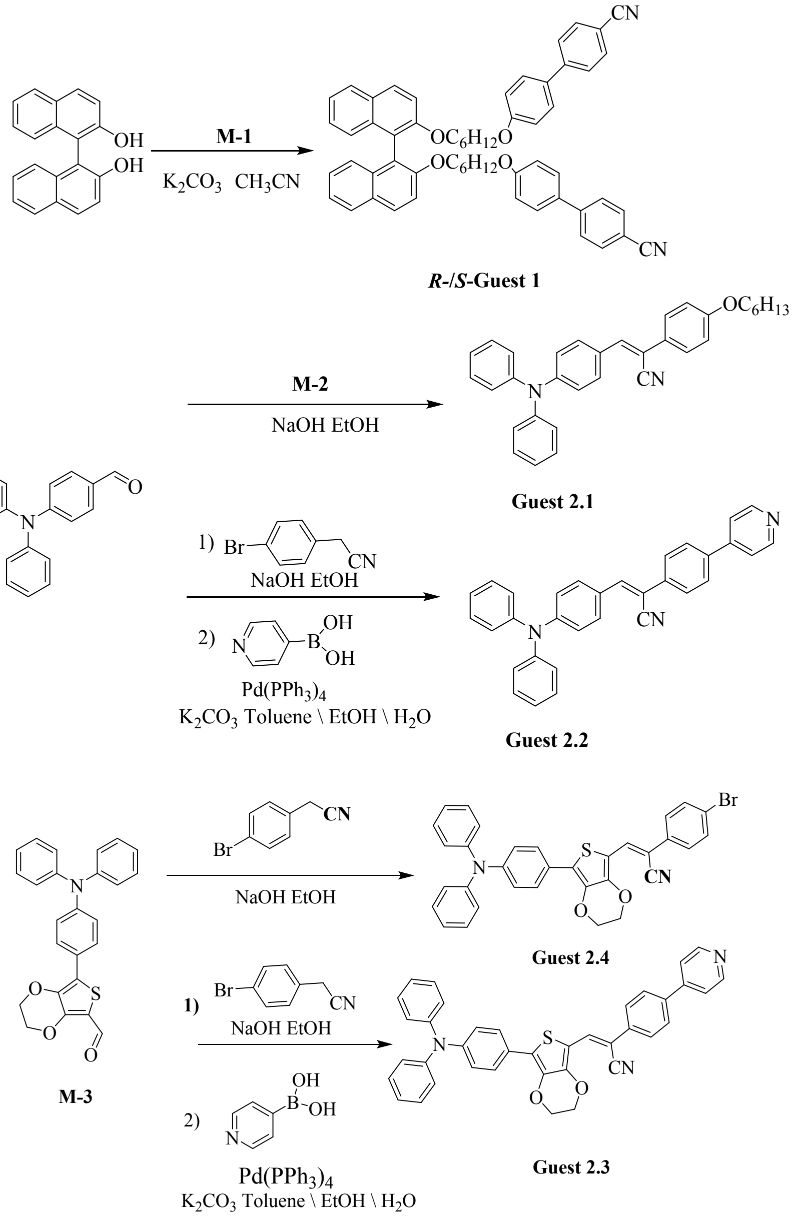
M-1



M-2



M-3



Scheme S2. The synthesis procedures of *R*-/*S*-Guest **1**, AIE-active Dyes Guest **2**.

Synthesis of M-1

1,6-dibromohexane (4.83g, 19.98 mmol) was added to a solution of 4'-Hydroxy-4-biphenylcarbonitrile (3.0 g, 15.37 mmol) and K_2CO_3 (8.48 g, 61.48 mmol) in DMF (60 ml). After stirring the solution at reflux for 6 h, the reaction mixture was poured into H_2O (100 ml) and extracted with CH_2Cl_2 (2×50 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was purified by recrystallization from hexane to give compound **M-1** as a white solid in 91% yield. ^{1}H NMR (400 MHz, DMSO) δ 7.91-7.80 (m, 3H), 7.74-7.66 (m, 2H), 7.08-7.03 (m, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.55 (t, *J* = 6.7 Hz, 2H), 1.91-1.68 (m, 4H), 1.45 (dt, *J* = 7.1, 3.6 Hz, 4H).

Synthesis of M-2

1-Bromohexane (4.43, 27.05 mmol) was added to a solution of 2-(4-hydroxyphenyl) acetonitrile (3.0 g, 22.54 mmol) and K_2CO_3 (12.43 g, 90.16 mmol) in acetonitrile (60 ml). After stirring the solution at reflux for 3 h, the reaction mixture was poured into H_2O (100 ml) and extracted with CH_2Cl_2 (2×50 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was purified by recrystallization from hexane to give compound **M-2** as a colorless liquid in 93% yield. ^1H NMR (400 MHz, DMSO) δ 7.48-7.06 (m, 2H), 7.07-6.73 (m, 2H), 4.22-3.73 (m, 4H), 1.78-1.60 (m, 2H), 1.46-1.35 (m, 2H), 1.35-1.25 (m,4H), 0.88 (dd, *J* = 8.7, 5.4 Hz, 3H).

Synthesis of *R*-/*S* -Guest 1

R-/*S*-1,1'-binaphthol (0.54g, 1.91 mmol) and **M-1** (1.5g, 4.20 mmol) were added in 50 ml acetone. After all the reagents were dissolved, K_2CO_3 (1.06 g, 7.64 mmol) were added and refluxed at 80 °C for 24h. The crude product was extracted with CH_2Cl_2 (2×50 ml). The organic layer was washed with saturated NaCl solution and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with silica gel column chromatography (eluent: petroleum ether/ethyl acetate, v/v, 30:1) to give 1.38 g of ***R*-/*S*-Guest 1** (79% yield) as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.71-7.66 (m, 4H), 7.65-7.60 (m, 4H), 7.55-7.48 (m,4H), 7.40 (d, J = 9.0 Hz,2H), 7.29 (ddd, J = 8.1, 6.4, 1.5 Hz, 2H), 7.23-7.12 (m, 4H), 4.00 (dt, J = 9.3, 6.0 Hz, 2H), 3.90 (dt, J = 9.3, 6.3 Hz, 2H), 3.78 (t, J = 6.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.77, 154.52, 145.26, 134.23, 132.60, 131.26, 129.33, 129.11, 128.32, 127.81, 127.08, 126.11, 125.54, 123.52, 120.84, 119.14, 115.96, 115.08, 110.08, 69.71, 67.91, 29.32, 28.97, 28.90, 25.43, 25.41.

Synthesis of Guest 2.1

4-(N, N-Diphenylamino) benzaldehyde (2.0 g, 7.32 mmol) was dissolved in 30 mL ethanol, **M-2** (1.91 g, 8.78 mmol) and NaOH (0.35 g, 8.78 mmol) were added, then stirred at room temperature for 2.5 h. After reaction completed, the mixture was filtered to afford the title compound (yellow solid) in 60% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.36 – 7.28 (m, 4H), 7.16 (d, *J* = 1.1 Hz, 5H), 7.13–7.07 (m, 2H), 7.07–7.01 (m, 2H), 6.97 – 6.89 (m, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.90 -1.70 (m, 2H), 1.52 – 1.41 (m, 6H), 1.35 (td, *J* = 7.0, 3.5 Hz, 2H), 0.95–0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.64, 149.55, 146.77, 139.62, 130.33, 129.54, 127.31, 126.99, 126.91, 125.57, 124.20, 121.22, 118.91, 114.92, 107.70, 68.23, 31.60, 29.19, 25.72, 22.62, 14.06.

Synthesis of Guest 2.2

4-(N, N-Diphenylamino) benzaldehyde (2.43g, 8.89mmol) was dissolved in 30 mL ethanol, **4-Bromophenylacetonitrile** (2.08 g, 10.67 mmol) and NaOH (0.43 g, 10.67 mmol) were added, then stirred at room temperature for 2.5 h. After reaction completed, the product was purified by recrystallization from EtOH to give compound **M-2** as a yellow solid, which used directly for the next step. The products above mentioned (1.00 g, 2.22 mmol), Pyridine-4-boronic acid (0.41g, 3.33 mmol), $Pd(PPh_3)_4$ (0.205 g, 0.18 mmol) and K_2CO_3 (1.2 g, 8.88 mmol) were added to a mixture solvent of 24 mL Toluene,12 mL EtOH and 6ml H_2O. The mixture was stirred at 100 °C under N2 atmosphere. After the reaction was finished, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was filtrated through a short silica gel column, then evaporated under reduced pressure. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with silica gel column chromatography (eluent: petroleum ether/ethyl acetate, v/v, 10:1) to give 0.5 g of **Guest 2.2** (orange solid, 50.2 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.84–7.75 (m, 4H), 7.74-7.68 (m, 2H), 7.56 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.50 (s, 1H), 7.33 (tt, *J* = 4.0, 2.0 Hz, 4H), 7.17 (dt, *J* = 8.8, 1.7 Hz, 6H), 7.15-7.09 (m, 5H), 7.08-7.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.30, 150.09, 147.55, 146.50, 142.24, 137.92, 135.99, 130.90, 129.63, 127.58, 126.37, 126.07, 125.85, 124.58, 121.48, 120.67, 118.59, 106.58.

Synthesis of M-3

4-(Diphenylamino) phenylboronic acid (0.90 g, 3.11 mmol), 7-bromo-2,3-dihydrothieno[3,4-b] [1,4] dioxine-5-carbaldehyde (0.78 g, 3.11 mmol), $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol) and K_2CO_3 (1.2 g, 6.53 mmol) were added to a mixture solvent of 24 mL Toluene,12 mL EtOH and 6ml H_2O. The mixture was stirred at 100 °C under N2 atmosphere. After the reaction was finished, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was filtrated through a short silica gel column, then evaporated under reduced pressure. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with silica gel column chromatography (eluent: petroleum ether/ethyl acetate, v/v, 5:1) to give 1.05 g of **M-3** (yellow solid in 82% yeild) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.29 (dd, *J* = 7.0, 1.4 Hz, 2H), 7.16 – 7.10 (m, 4H), 7.10 – 7.01 (m, 8H), 4.38 (m, *J* = 6.0, 3.7, 2.3 Hz, 4H).

Synthesis of Guest 2.3 and 2.4

M-3 (0.50 g, 1.20 mmol) was dissolved in 20 mL ethanol, 4-Bromophenylacetonitrile (0.22 g, 1.2 mmol) and NaOH (0.14 g, 3.6 mmol) were added, then stirred at room temperature for 5 h. After reaction completed, the product was purified by recrystallization from EtOH to give compound Guest **2.4** as orange solid in 78% yield. And then, Guest **2.4** (0.50, 0.84 mmol), Pyridine-4-boronic acid (0.11 g, 0.84 mmol), $Pd(PPh_3)_4$ (0.048 g, 0.042 mmol) and K_2CO_3 (0.46 g, 3.36 mmol) were added to a mixture solvent of 24 mL Toluene,12 mL EtOH and 6ml H_2O. The mixture was stirred at 100 °C under N_2 atmosphere. After the reaction was finished, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was filtrated through a short silica gel column, then evaporated under reduced pressure. The precipitate was removed by filtration, and filtrate was evaporated under reduced pressure. The residue was purified with silica gel column chromatography (eluent: petroleum ether/ethyl acetate, v/v, 1:1) to give 0.5 g of **Guest 2.3** (red solid, 50.2 %). Guest **2.3** ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.8 Hz, 2H), 7.84 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 4H), 7.54 (d, *J* = 6.1 Hz, 2H), 7.31-7.26 (m, 3H), 7.16-7.10 (m, 4H), 7.07 (dd, *J* = 8.0, 6.6 Hz, 4H), 4.42-4.33 (m, 4H). Guest **2.4** ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.70-7.64 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.12 (d, *J* = 7.7 Hz, 4H), 7.05 (dd, *J* = 10.2, 3.6 Hz, 8H), 4.36 (d, *J* = 5.7 Hz, 4H).

3. Preparation of N*-LCs and AIE-N*-LCs

The sample used to investigate the UV-*vis* and fluorescence spectra, CD and CPL was fabricated by the following method.N*-LCs: The *R*-/*S*-Guest **1** and nematic liquid crystal E7 were co-dissolved in the solvent CH_2Cl_2 at a weight ratio of 1:100. Then the solution was gently heated and stirred for several hours to evaporate CH_2Cl_2. After completely removing the solvent, the mixture was injected into a flat liquid crystal cell consisting of two sandwiched quartz slides with a 15 μm spacer or a wedge cell of $\tan\theta = 0.0183$. AIE-N*-LCs: The *R*-/*S*-Guest **1** and nematic liquid crystal E7 were co-dissolved in the solvent CH_2Cl_2 at a weight ratio of 1:100. Then doping 1 mole ratio of four achiral Guest **2** in the solvent CH_2Cl_2 into the above N*-LCs, respectively. After completely removing the solvent, the mixture was injected into a flat liquid crystal cell consisting of two sandwiched quartz slides with a 15 μm spacer or a wedge cell of $\tan\theta = 0.0183$.

4. Fluorescence spectra and UV-*vis* spectra of *R*-Guest 1

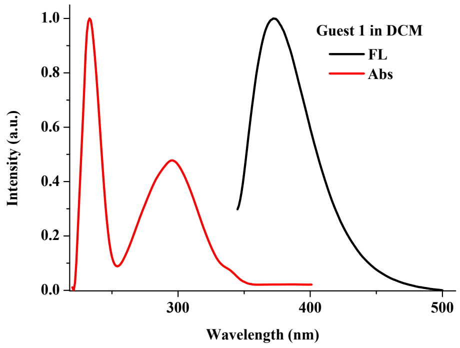


Fig. S1 The UV-*vis* absorption and fluorescence emission spectra of *R*-Guest **1** in the DCM solution (1.0×10^{-5} mol·L^{-1}, λ_{ex} = 310 nm).

5. CD and CPL spectra of *R*-/*S*-Guest 1

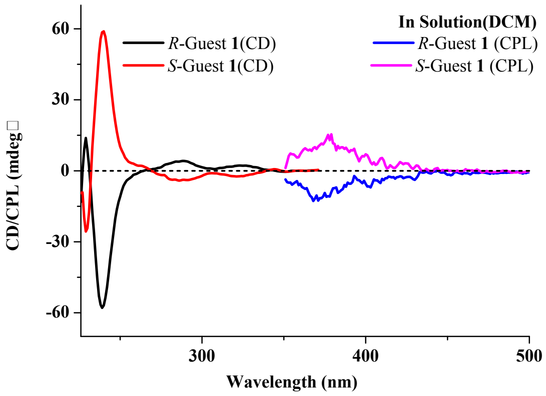


Fig. S2 CD/CPL spectra of *R*-/*S*- Guest **1** in the DCM solutions (1.0×10^{-5} mol·L^{-1}, λ_{ex} = 310 nm).

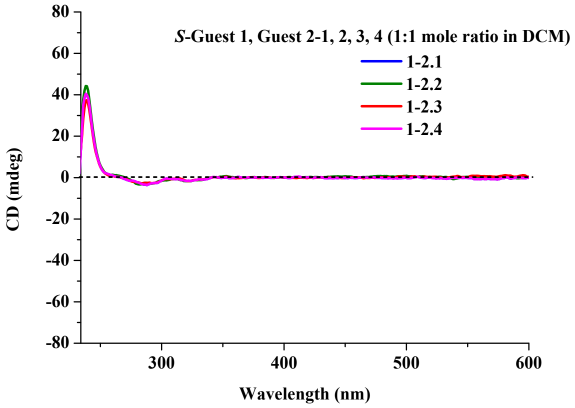


Fig. S3 CD spectra of Guest **1** and Guest **2** in DCM solution (1.0×10^{-5} mol·L^{-1}, 1:1 mole ratio).

6. Fluorescence spectra of Guest 2

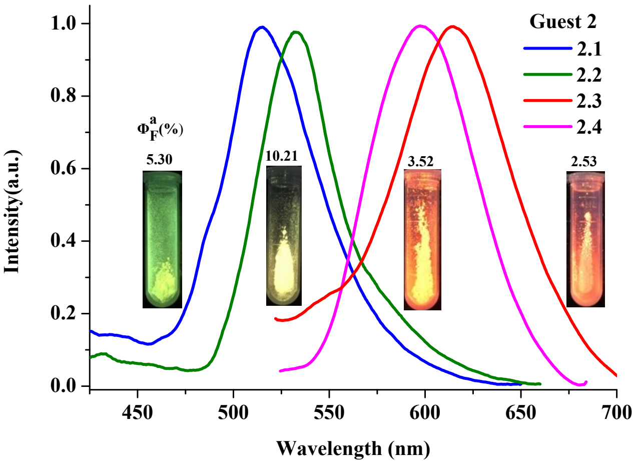


Fig. S4 The fluorescence spectra of four AIE-active dyes (Guest **2**) in solid state. (λ_{ex} = 360 nm) Inset: Images of AIE-active dyes (Guest **2**) taken by a 365 nm UV lamp. (^{a}Absolute quantum yield measured using integrating-sphere method).

7. POM images of N*-LCs and AIE-N*-LCs

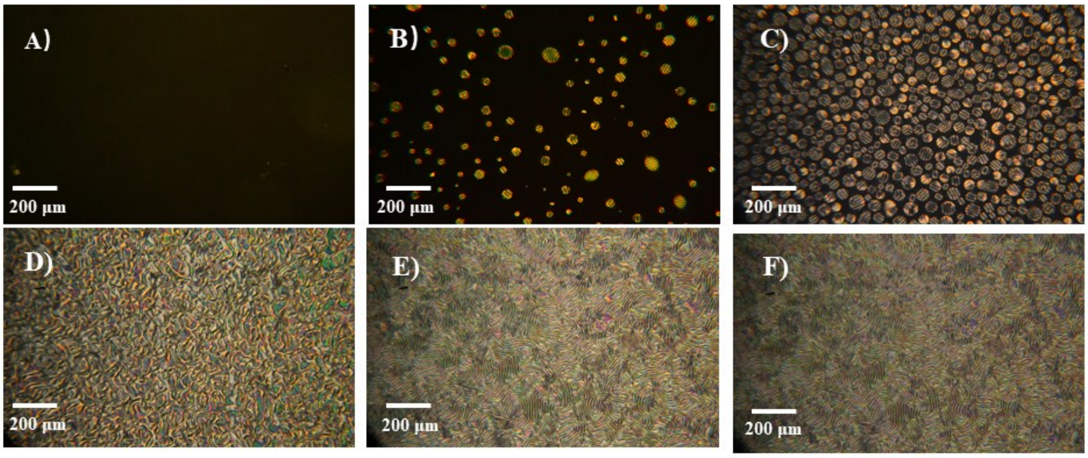


Fig. S5 POM images of the mixture E7 doped with 1 wt% *R*-Guest **1** and mole rato Guest 2-1, in a flat LC cell upon cooling down from the isotropic melting at a rate of 20 °C /min, with temperatures respectively at A) 65 °C, B) 52 °C, C) 50 °C, D) 40°C, E) 35°C and F) 25°C.

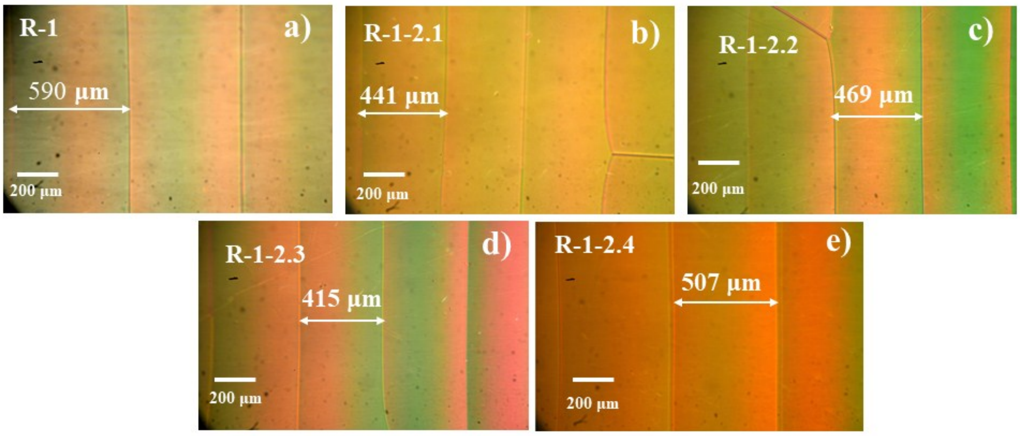


Fig. S6 a) POM images of N*-LC of E7 doped with 1 wt% *R*-Guest **1**; b, c, d, e) AIE-N*-LC of N*-LCs doped with 1 mole ratio of Guest **2-1**, **2**, **3**, **4** in a wedge cell at 25℃ at film state.

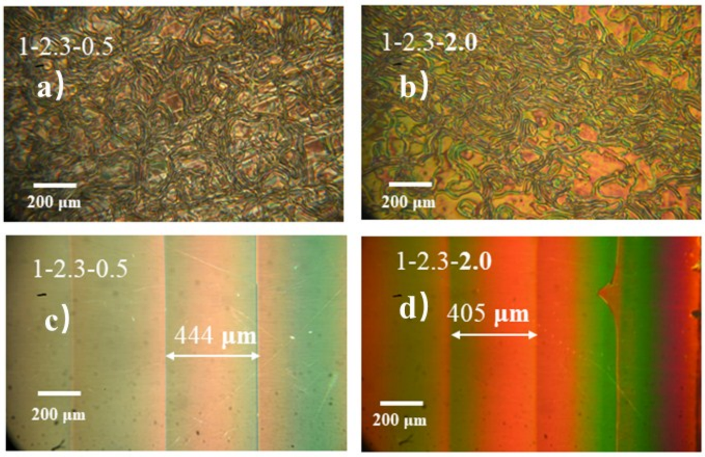


Fig. S7 POM images of a) AIE-N*-LCs of E7 doped with 1 wt% Guest **1** and Guest **2.3** of 0.5 molar ratio in a flat LC cell; b) AIE-N*-LCs of E7 doped with 1wt% Guest **1** and Guest **2.3** of 2 molar ratio in a flat LC cell; c) AIE-N*-LCs of E7 doped with 1 wt% Guest **1** and Guest **2.3** of 0.5 molar ratio in a wedge cell; d) AIE-N*-LCs of E7 doped with 1 wt% Guest **1** and Guest **2.3** of 2 molar ratio in a wedge cell at 25°C.

8. CPL spectra of AIE-N*-LCs (Guest 1, Guest 2.3)

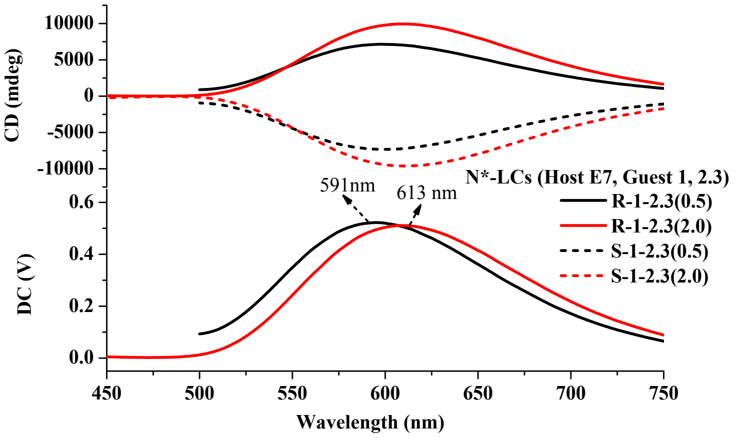


Fig. S8 CPL (upper panel) and fluorescence (FL, lower panel) spectra of AIE-N*-LCs of E7 doped with 1 wt% Guest **1** and Guest **2.3** of 0.5, 2.0 molar ratio. (λ_{ex} = 360 nm).

We doped the same Guest **1** (1 wt%) and Guest **2.3** with 0.5, 2.0, 3.0 molar ratios and to study the effect of doping ratio of Guest **2** on liquid crystal behavior, respectively. But when the concentration rises up to 3.0 molar ratio, E7 and N*-LCs structure partly destroyed by the undissolved chiral additives. The helical pitch for AIE-N*-LCs of E7 doped with 0.5 and 2 molar ratio of Guest **2.3** in wedge cells at 25°C were also calculated. The g_{em} of AIE-N*-LCs were shown in **Fig. S8**. The data of AIE-N*-LCs at various concentrations of Guest **2.3** are summarized in Table S**1**. The pitch of ternary AIE-N*-LCs varies with different concentrations of Guest **2.3**, which indicates the different forces of system assembly in Guest **2** and Host E7.

Table S**1.** Summary of AIE-N*-LCs at various concentrations of Guest 2.3.

concentrations	λ_{em}(nm)[a]	g_{em}[b]	R(μm)[c]	p(μm) [d]
0.5	591	+0.96/-0.97	444	16.28
2.0	613	+1.37/-1.33	405	14.87
3.0	-	-	-	

[a] λ_{em} of AIE-N*-LCs. [b] The luminescence dissymmetry factor. [c] The width of Grandjean-Cano line (R). [d] The helical pitches (*P*).

9. ^{1}H NMR and ^{13}C NMR spectra of compounds.

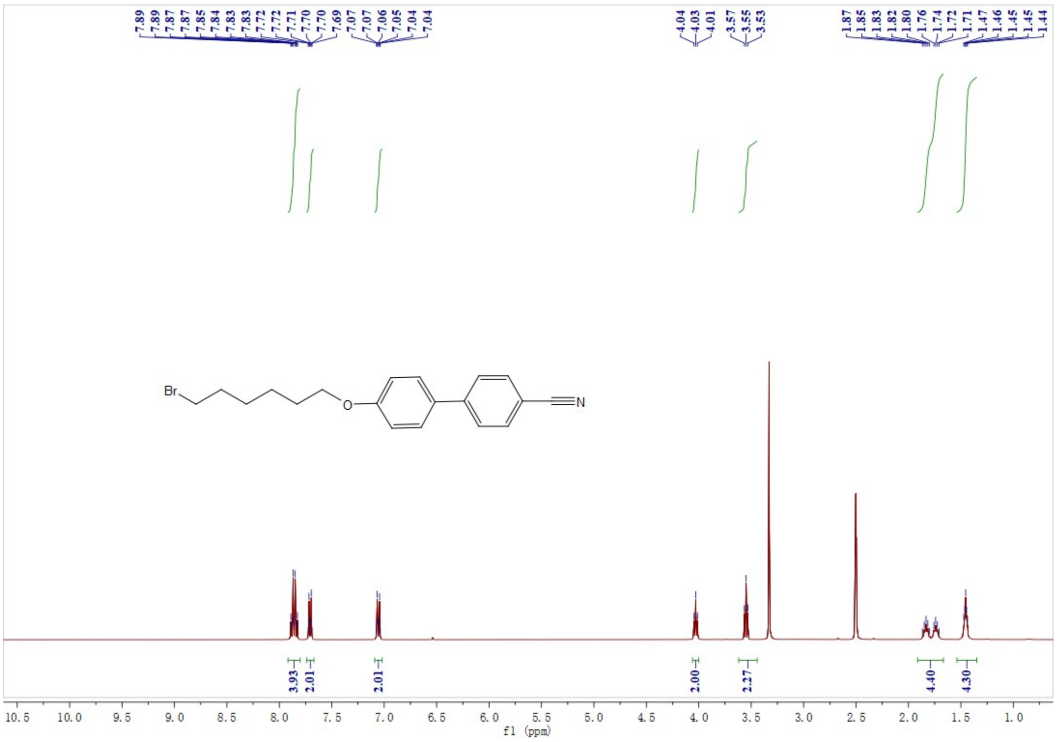


Fig. S9 ^{1}H NMR of M-1(400 MHz, DMSO-d6).

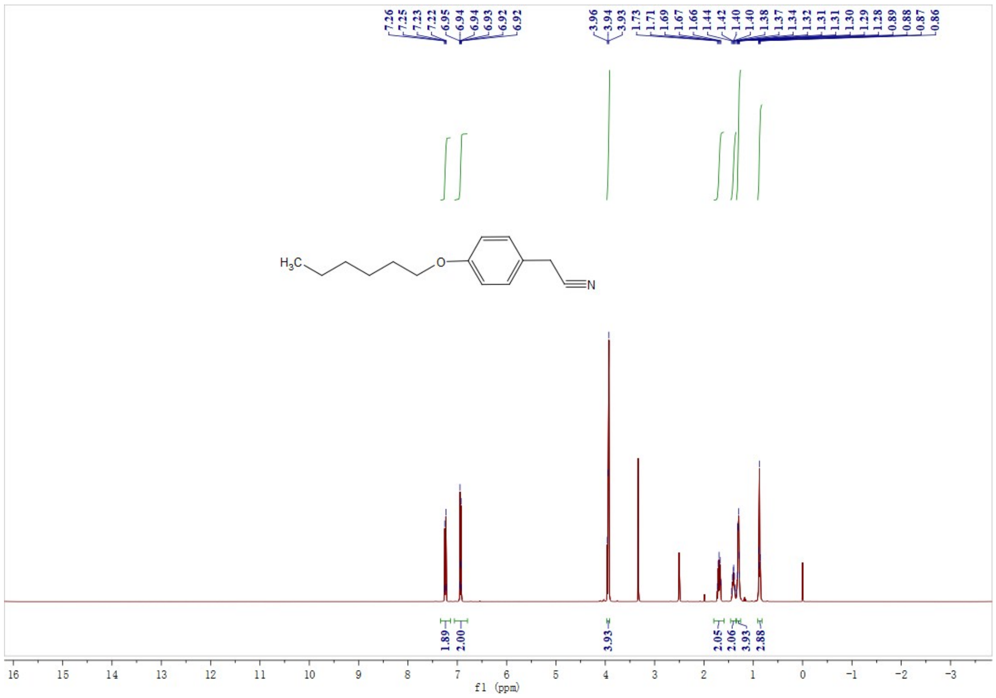


Fig. S10 ^{1}H NMR of M-2 (400 MHz, DMSO-d6).

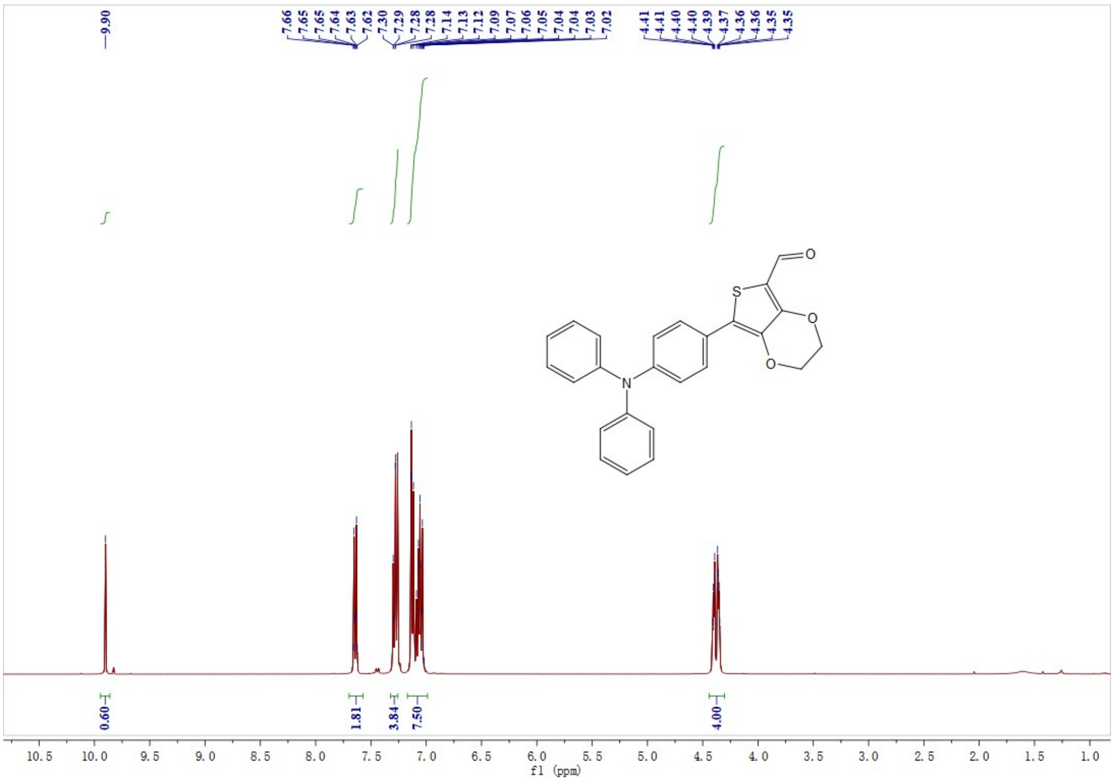


Fig. S11 ^{1}H NMR of M-3 (400 MHz, $CDCl_3$).

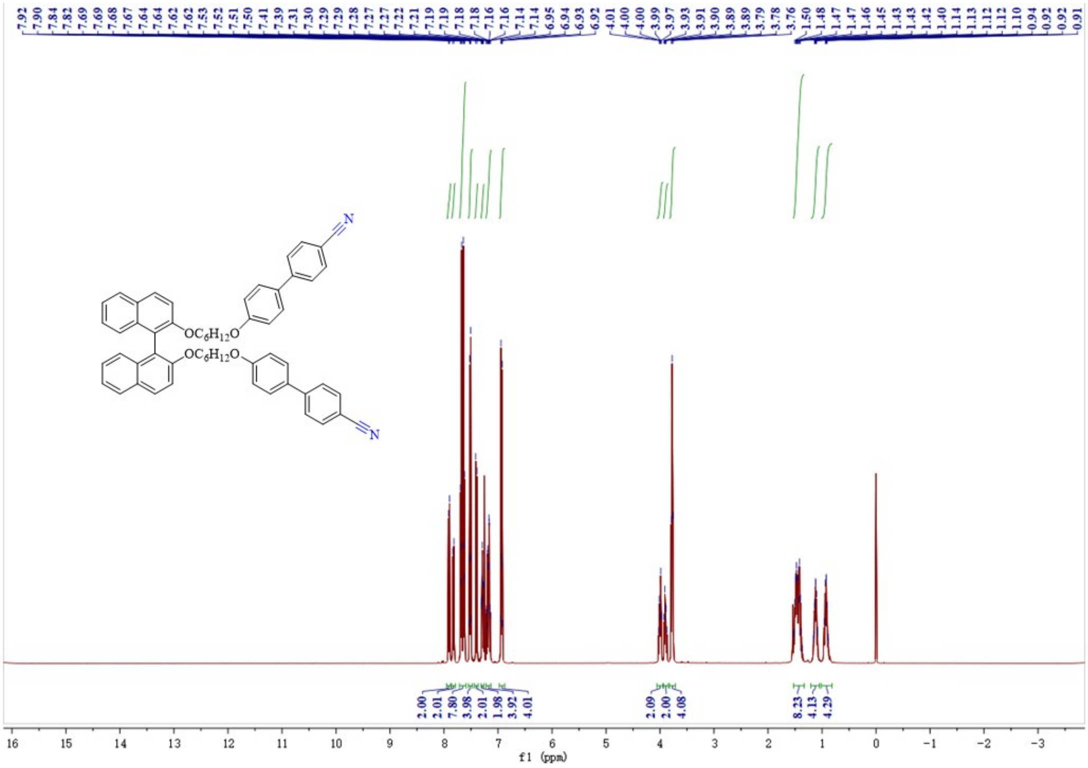


Fig. S12 ^{1}H NMR of *R*/*S*-Guest **1** (400 MHz, $CDCl_3$).

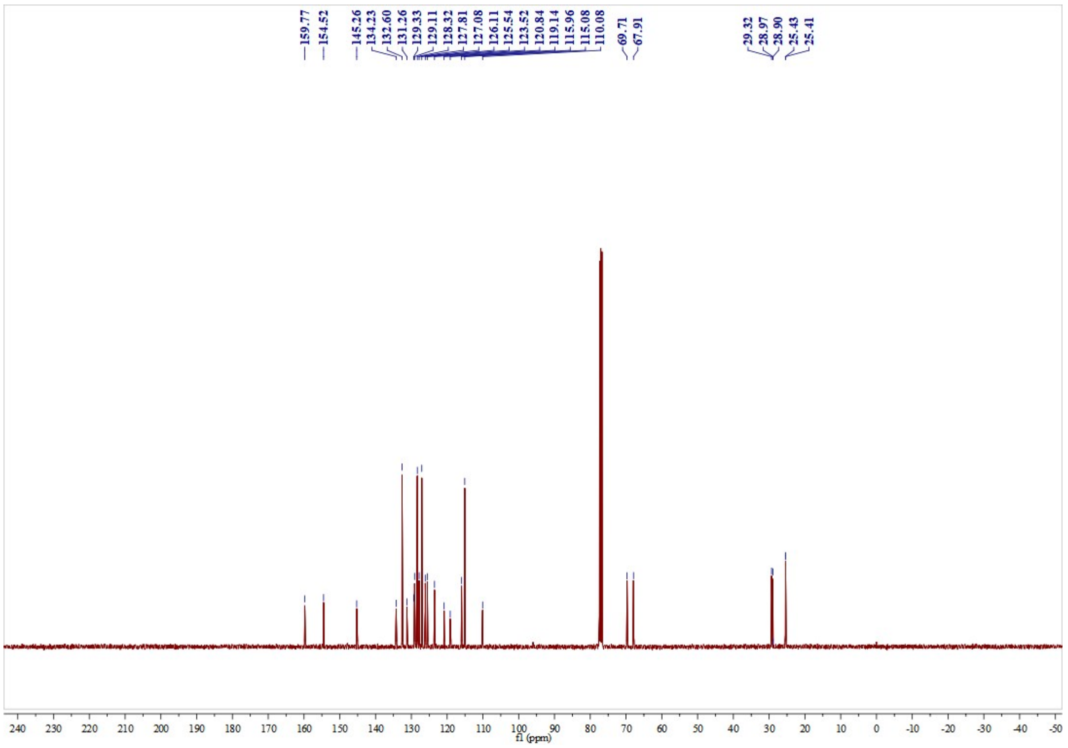


Fig. S13 ^{1}H NMR of *R*/*S*-Guest **1** (100 MHz, CDCl$_3$).

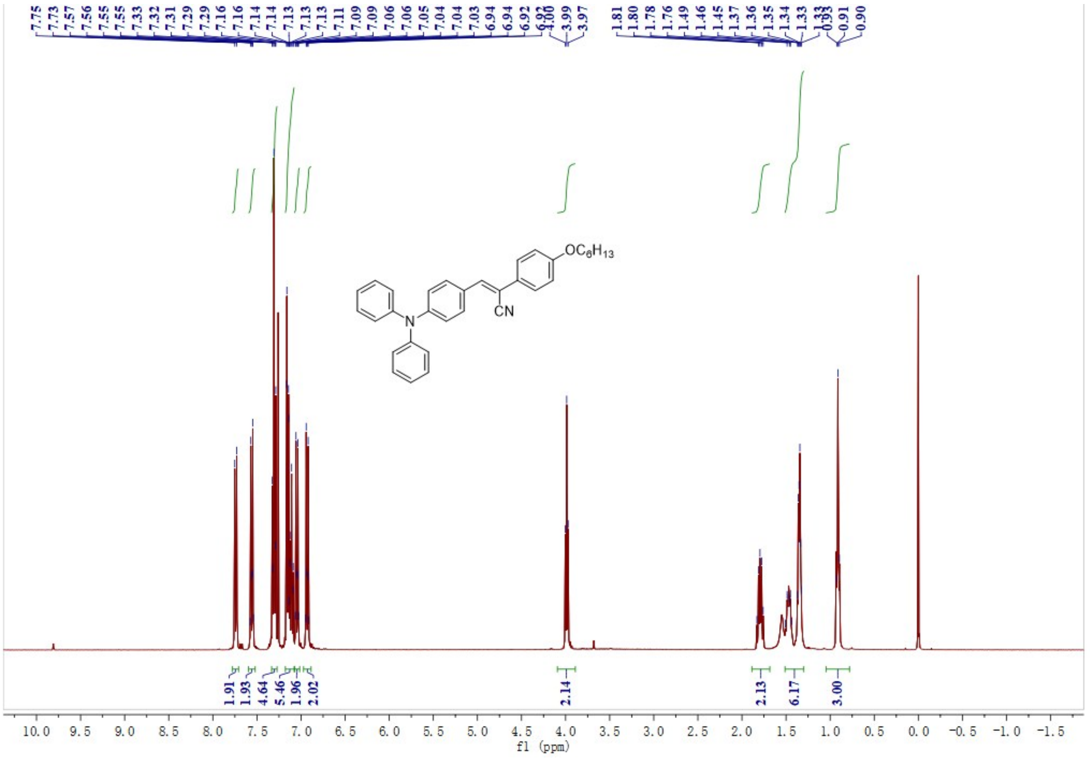


Fig. S14 ^{1}H NMR of Guest-**2.1** (400 MHz, CDCl$_3$).

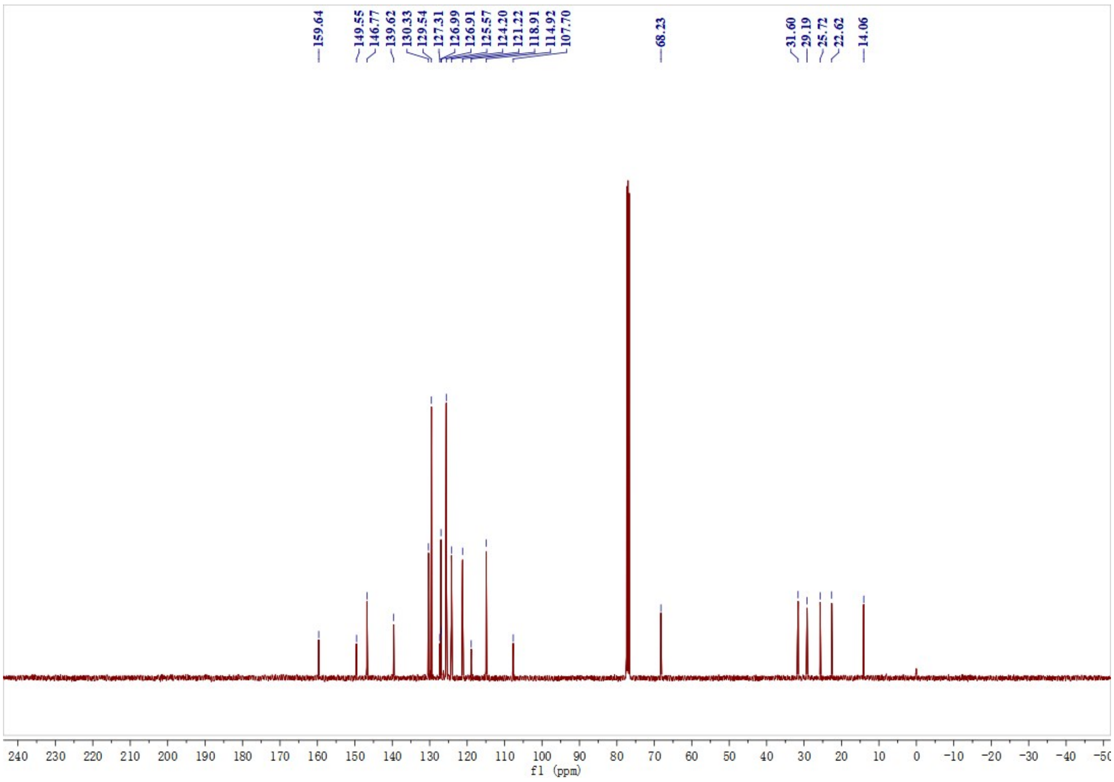


Fig. S15 ^{13}C NMR of Guest-**2.1** (100 MHz, CDCl$_3$).

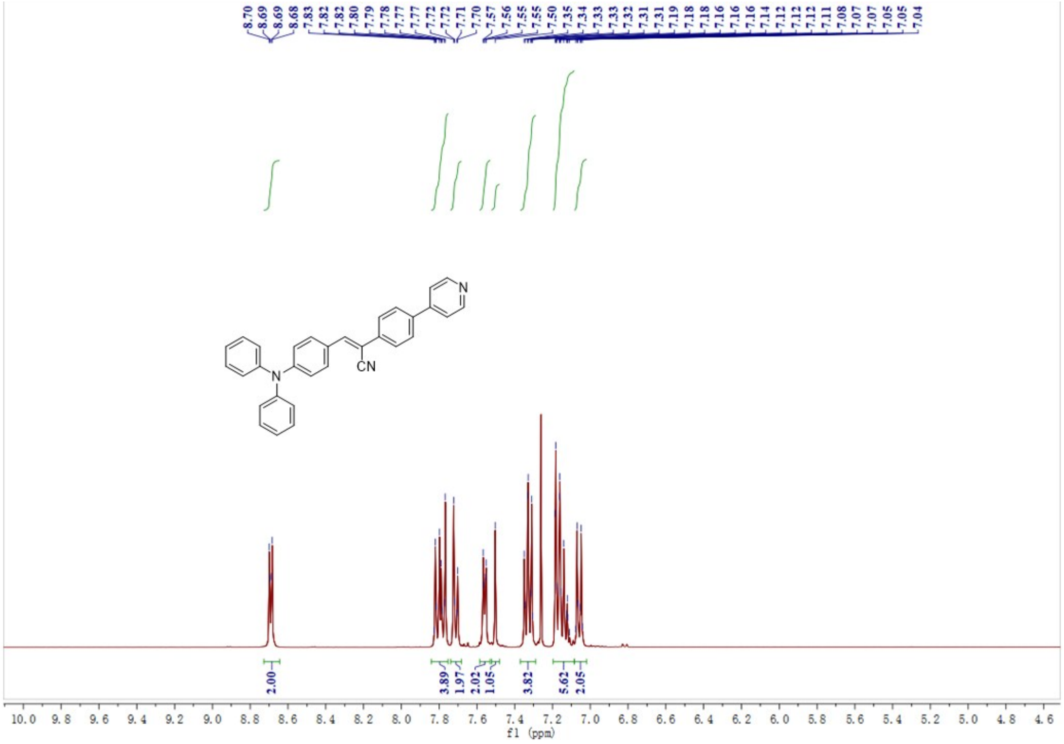


Fig. S16 ^{1}H NMR of Guest-**2.2** (400 MHz, CDCl$_3$).

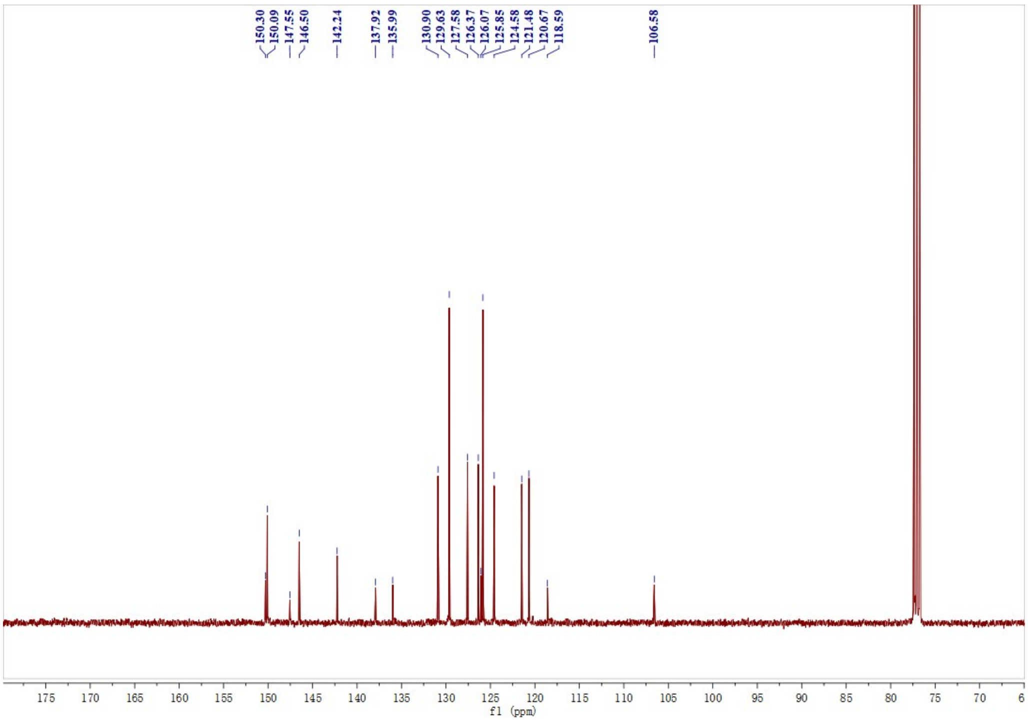


Fig. S17 ^{13}C NMR of Guest-**2.2** (100 MHz, $CDCl_3$).

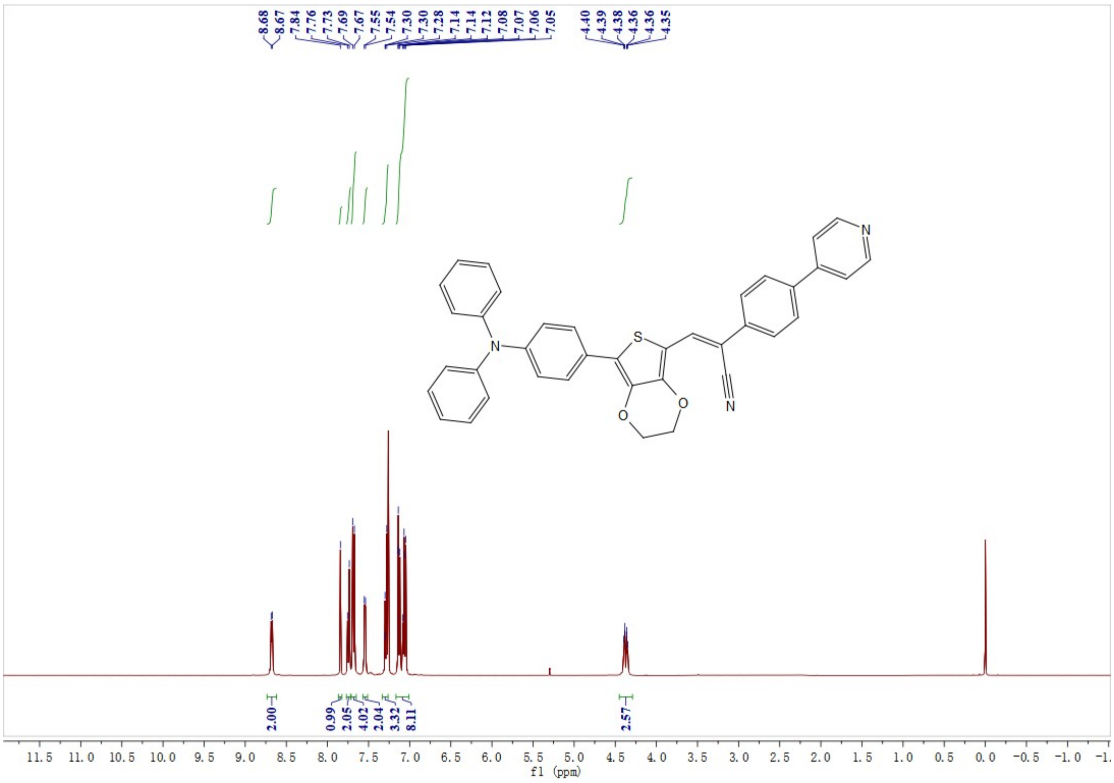


Fig. S18 ^{1}H NMR of Guest-**2.3** (400 MHz, $CDCl_3$).

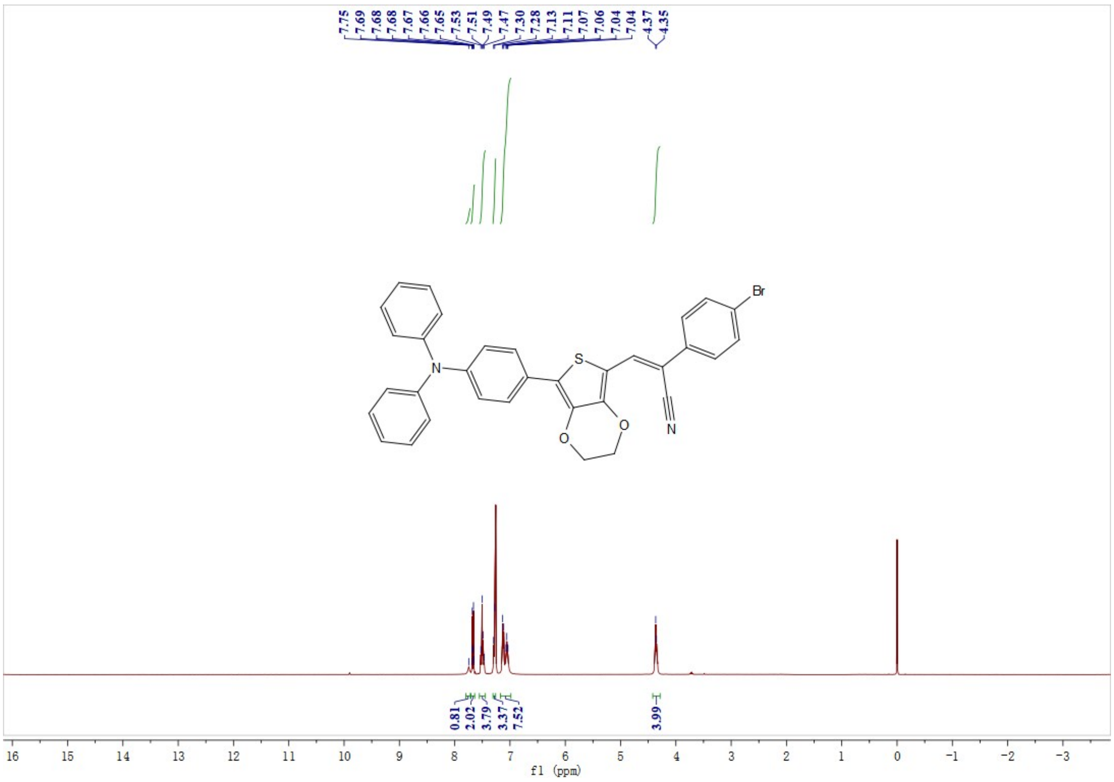


Fig. S19 ^{1}H NMR of Guest-**2.4** (400 MHz, $CDCl_3$).

References

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2 (*a*) Here we follow the convention used in chiroptical spectroscopy: right polarized light is defined as the point of the electric field vector E of the electromagnetic wave describing a right-handed screw; see L. D. Barron, Molecular Light Scattering and Optical Activity, Cambridge University Press, Cambridge, UK 2004; (*b*) I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003 R. (c) M. Eelkema, N. Pollard, J. Katsonis, D. J. Vicario, B. L. Feringa, *J. Am. Chem. Soc*., 2006, **128**, 14397.