Supporting Information

Recyclable CPL Switch Regulated by Using the Applied DC Electric Field from Chiral Nematic Liquid Crystals (N*-LCs)

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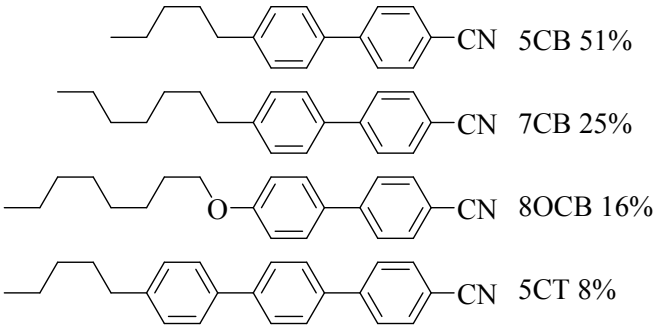
1. Instrumentation and Materials.

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*-1500 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 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_o = 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.

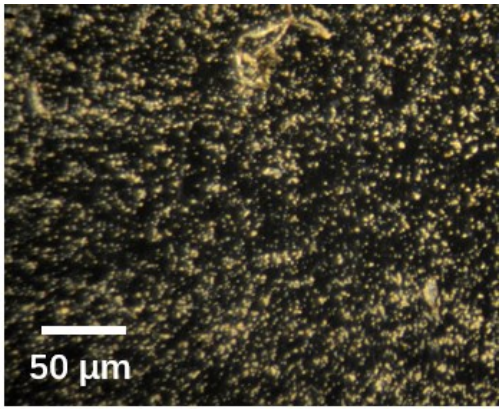


Fig. S1 POM images of E7 in a flat LC cell at 25℃.

2. 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 (tanθ = 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.

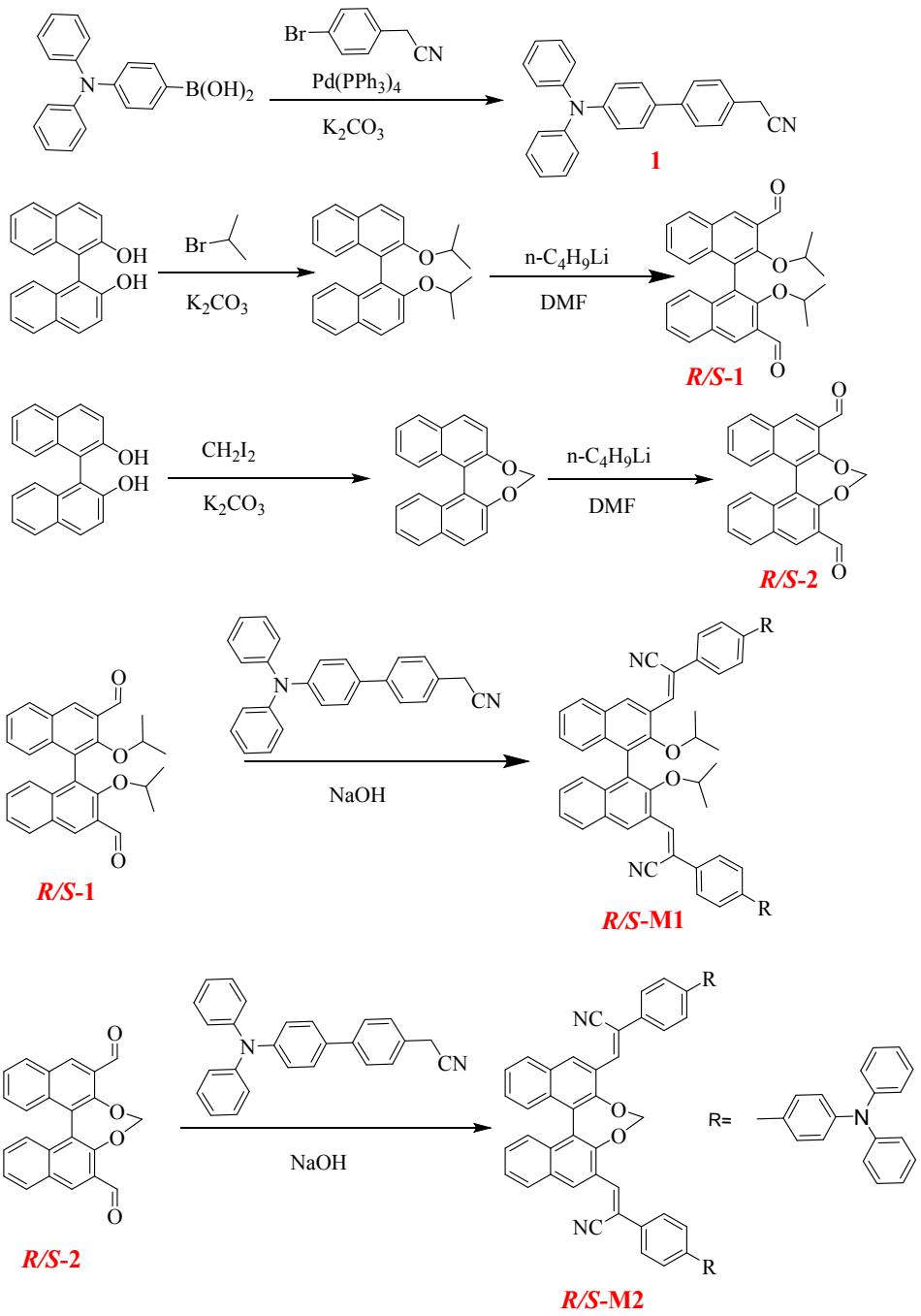
The influence of the isomerization on helical structure can be qualified by helical twisting power (HTP, β),

$$\beta = \frac{1}{P * C\% * ee}$$

where P, C% and ee are pitch of N*-LCs, the concentration and conformational change of the chiral dopant switch, respectively.[2]

3. Syntheses of compounds

Intermediate *R-/S*-BINOL-CHO were prepared as previously described[3]. ^{1}H NMR spectra are in accordance with literature values.



Scheme S2. The synthesis procedures of *R*/*S*-M1, M2 enantiomers.

Synthesis of Compound 1

(4-(diphenylamino) phenyl) boronic acid (0.90 g, 3.11 mmol), 2-(4-bromophenyl) acetonitrile (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 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 colum chromatography (eluent: petroleum ether/ethyl acetate, v/v, 5:1) to give 1.05 g of 1 (yellow solid in 82% yeild) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.49-7.42 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31-7.24 (m, 4H), 7.17-7.10 (m, 6H), 7.07-7.01 (m, 2H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.59, 140.59, 133.89, 129.33, 128.35, 128.24, 127.70, 127.29, 124.56, 123.72, 123.11, 117.86, 23.33.

Synthesis of *R-/S*-M1

n-BuLi (2.5 M in hexane,8.98mL, 22.2 mmol) was added to a solution of 2,2'-diisopropoxy-1,1'-binaphthalene (2.00 g, 5.4 mmol) in anhydrous THF (30 mL) at 0°C under N_2 atmosphere. Then the mixture was allowed to warm up to room temperature and stirred for 2 h. Re-cooled the mixture to 0°C, and DMF (1.44 mL, 21.6 mmol) was added. The reaction was allowed to warm up to room temperature and stirred for another 4 h. After the reaction complete, quenched by saturated NH_4Cl (30 mL). The aqueous layer was extracted with ethyl acetate (2×30 mL). Combined organic phase and dried over anhydrous Na_2SO_4. Then remove the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum ether/ethyl acetate (12:1) to afford the title compound *R*/*S*-1 in 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 2H), 8.61 (s, 2H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.49 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 2H), 7.41 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.28 – 7.25 (m, 3H), 3.60 (hept, *J* = 6.1 Hz, 2H), 0.95 (d, *J* = 6.1 Hz, 6H), 0.67 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.37, 155.66, 137.03, 130.63, 130.55, 130.01, 129.61, 129.42, 125.76, 125.69, 125.63, 77.73, 22.39, 21.82.

Compound 1 (0.192 g, 536.67 μmol) and *R*/*S*-1 (109 mg, 255.6 μmol) was dissolved in 10 mL ethanol and NaOH (40.89 mg,1.02 mmol) were added, then stirred at room temperature for 2.5 h. After reaction completed, the product was purified by recrystallization from ethanol to give compound *R*/*S*-M1 as a light-yellow solid in 60% yield. ^{1}H NMR (400 MHz, DMSO) δ 8.72 (s, 2H), 8.29 (s, 2H), 8.13 (d, *J* = 8.1 Hz,

2H), 7.86 (dd, *J* = 20.1, 8.5 Hz, 8H), 7.69 (d, *J* = 8.5 Hz, 4H), 7.49 (dt, *J* = 15.3, 7.1 Hz, 4H), 7.34 (t, *J* = 7.8 Hz, 8H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.14 – 7.01 (m, 16H), 3.67 (dt, *J* = 12.2, 6.1 Hz, 2H), 0.87 (d, *J* = 6.1 Hz, 6H), 0.62 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 153.30, 147.76, 147.36, 141.01, 139.67, 134.78, 132.91, 132.30, 130.13, 129.93, 129.52, 128.14, 127.40, 126.82, 125.06, 124.88, 123.96, 123.36, 118.04, 113.17, 77.02, 22.60.

Synthesis of *R-/S*-M2

n-BuLi (2.5 M in hexane,9.38mL, 23.45 mmol) was added to a solution of dinaphtho [2,1-d:1',2'-f] [1,3] dioxepin (2.0 g, 6.7 mmol) in anhydrous THF (50 mL) at 0°C under N_2 atmosphere. Then the mixture was allowed to warm up to room temperature and stirred for 2 h. Re-cooled the mixture to 0°C, and DMF (2.06 mL, 26.8 mmol) was added. The reaction was allowed to warm up to room temperature and stirred for another 4 h. After the reaction complete, quenched by saturated NH_4Cl (30 mL). The aqueous layer was extracted with ethyl acetate (2×30 mL). Combined organic phase and dried over anhydrous Na_2SO_4. Then remove the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum ether/ethyl acetate (10:1) to afford the title compound *R*/*S*-2 in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 2H), 8.63 (s, 2H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.59–7.51 (m, 2H), 7.48–7.40 (m, 4H), 5.91 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.39, 151.06, 134.87, 132.23, 130.83, 130.71, 129.20, 127.36, 126.77, 126.65, 126.41, 104.01.

Compound 1 (0.533 g, 1.480 mmol) and *R*/*S*-2 (250 mg, 705 μmmol) was dissolved in 10 mL ethanol and NaOH (67.72 mg,1.69 mmol) were added, then stirred at room temperature for 2.5 h. After reaction completed, the product was purified by recrystallization from ethanol to give compound *R*/*S*-M2 as a light-yellow solid in 58% yield. ^{1}H NMR (400 MHz, DMSO) δ 8.83 (s, 2H), 8.34 (s, 2H), 8.20 (d, *J* = 8.2 Hz, 2H), 7.87 (dd, *J* = 29.4, 8.5 Hz, 8H), 7.69 (d, *J* = 8.6 Hz, 4H), 7.55 (dt, *J* = 15.5, 7.4 Hz, 4H), 7.34 (t, *J* = 7.9 Hz, 10H), 7.08 (q, *J* = 8.4 Hz, 16H), 5.94 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 149.33, 147.77, 147.37, 141.18, 137.23, 132.96, 132.47, 132.37,

131.06, 130.23, 130.12, 129.92, 128.46, 128.17, 127.28, 127.15, 126.69, 126.35, 126.02, 124.85, 123.95, 123.41, 118.08, 113.98.

4. Optimized molecular structures of M1 and M2

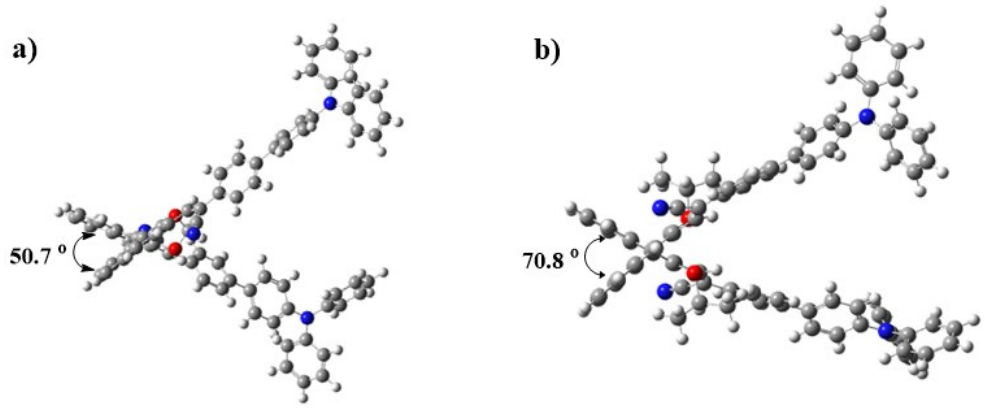


Fig. S2 Optimized structures and calculated spatial distributions of **M1** and **M2** at the M06-2X/6-31+G** level.

5. Preparation of *R*/*S*-M1, M2 in the spin-coated film state

Chiral dopant *R*/*S*-M1, M2 were mixed with 10mg/ml in DCM, spin-coated film rotation speed 1000r/min; rotation time in 10s.

6. Preparation of N*-LC with N*-LCs-1/2 for circular photoluminescence test

The samples used to investigate the UV-*vis*, fluorescence, CD and CPL spectra were obtained in the following method.

N*-LCs-1/2: The *R*/*S*-M1, M2 and nematic liquid crystal E7 were co-dissolved in the solvent CH_2Cl_2 at a mole ratio of 1:100. Then the solution was gently heated and stirred overnight 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 tanθ = 0.0183. Other N*-LCs were prepared in the similar method at different mole ratio.

7. Preparation of N*-LC with N*-LCs-1/2 for application of DC electric filed

The sample was put into the cell with a spacer (15 μm) between two pieces of ITO glass. Three-electrode liquid crystal cell with protective electrode, the ITO glass were evaporated as anode; Soda-lime glass was evaporated as cathode; homeotropic alignment layer cell gap 15um cell active area 100 (10 ×10 mm). When the voltage is rapidly removed, the liquid crystal and dye molecules relax to the planar state. The POM images of the two types of LC systems were measured under the application of the direct current (DC) bias of 5V, 10V, et.al. POM measurement was achieved by applying a DC between the piesces of ITO glass in the cell up to the elapsed time of 5min.

8. UV-*vis* absorption and PL spectra of M1 and M2 in DCM solution

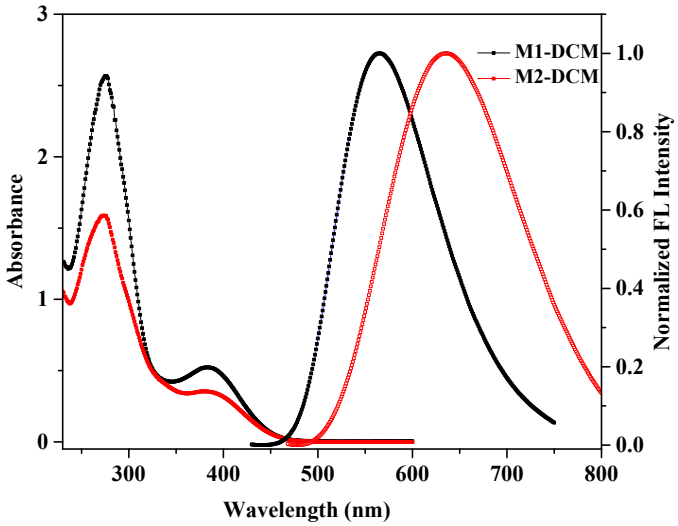


Fig. S3 UV-*vis* absorption and FL spectra of M1(black lines) and M2 (red lines) in DCM solution (1×10^{-5} mol·L^{-1}, λ_{ex} = 360 nm).

9. CD and CPL spectra of *R*/*S*-M1 and *R*/*S*-M2 in solution

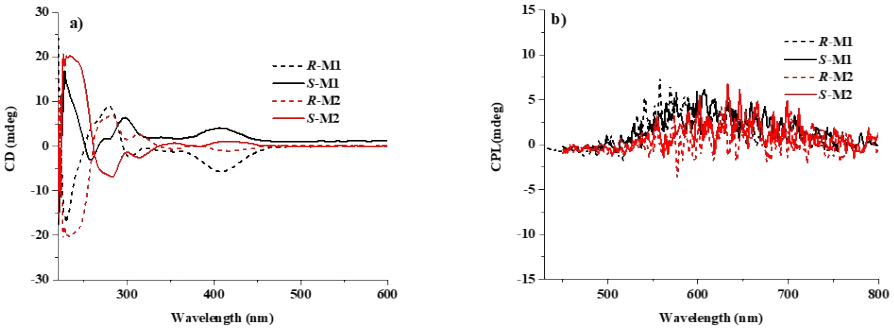


Fig. S4 a) CD spectra of *R*/*S*-M1, M2 in DCM solution (1.0×10^{-5} mol·L^{-1}); b) CPL spectra *R*/*S*-M1, M2 in DCM solution (1.0×10^{-5} mol·L^{-1}, λ_{ex} = 360 nm).

10. POM images of N*-LCs

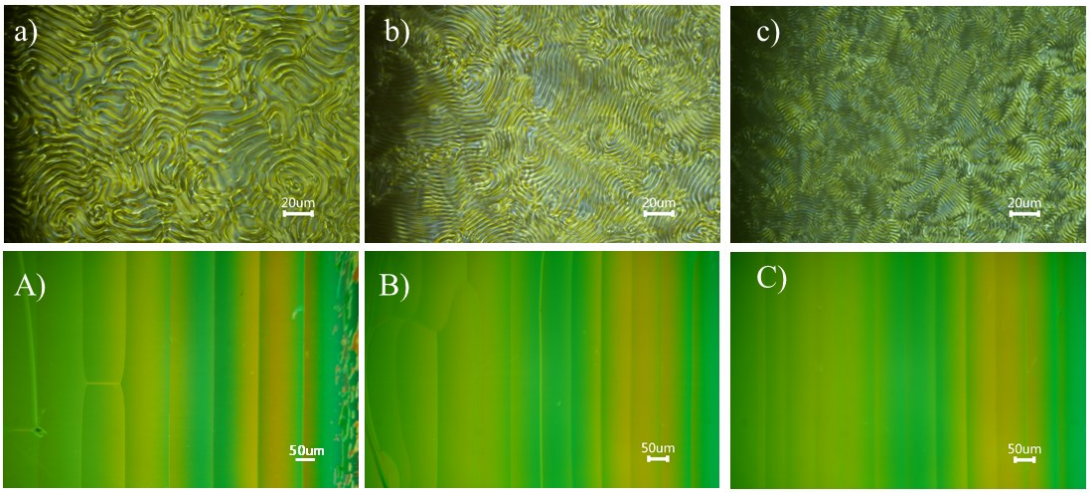


Fig. S5 POM images of a) N*-LCs of E7 doped with 1.0 wt%, b) 1.5 wt%, c) 2.0 wt% *R*-M1 in a flat LC cell at 25℃; N*-LCs of E7 doped with A),1.0 wt%, B), 1.5 wt%, C) 2.0 wt% *R*-M1 in wedge LC cells 25℃.

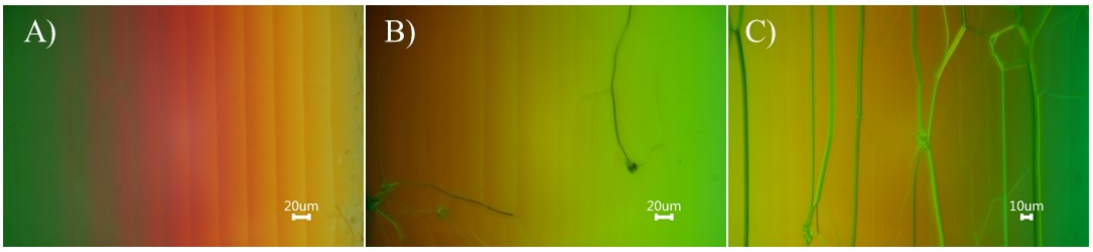


Fig. S6 POM images of A) N*-LC of E7 doped with 1.0 wt% *R*-M2, B) 1.5 wt% *R*-M2, C) 2.0 wt% *R*-M2 in wedge LC cells at 25℃.

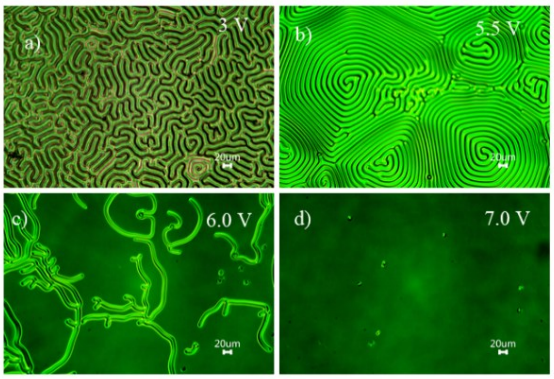


Fig. S7 POM images of N*-LCs-1 of E7 doped with 0.5 wt% *R*-M1 on DC electric filed a) 3 V, b) 3.5 V, c) 6 V, d) 7.0 V. (cells: homeotropic surface anchoring conditions).

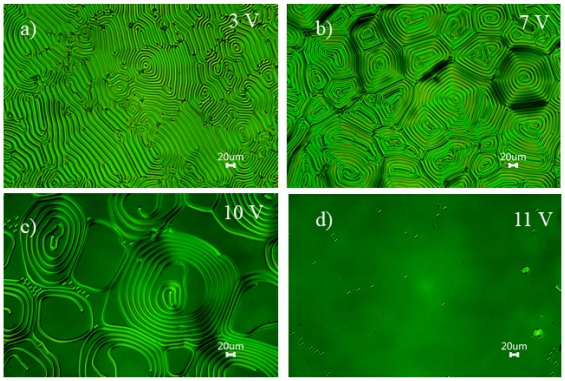


Fig. S8 POM images of N*-LCs-1 of E7 doped with 0.5 wt% *R*-M2 on DC electric filed a) 3 V, b) 7 V, c) 10 V, d) 11 V. (cells: homeotropic surface anchoring conditions).

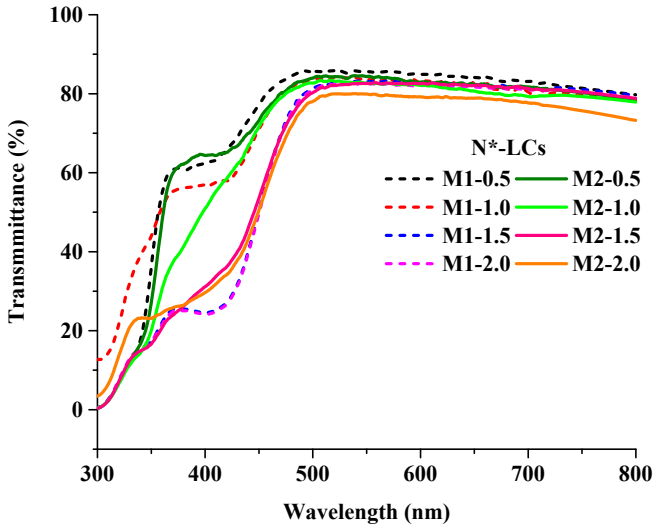


Fig. S9 Transmittance of N*-LCs-1 and N*-LCs-2.

11. g_{em} of N*-LCs

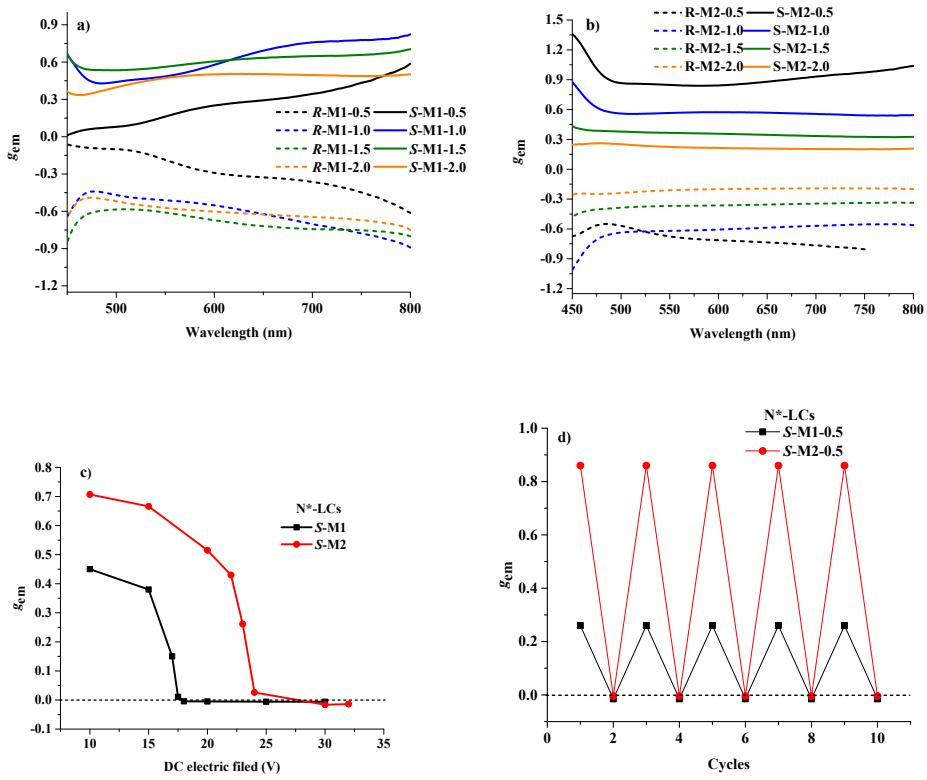


Fig. S10 g_{em} spectra of N*-LCs (λ_{ex} =360 nm). a) N*-LCs of E7 doped with 0.5, 1.0, 1.5 wt % *R*/*S*-M1 in flat LC cells at 25°C. b) N*-LCs of E7 doped with 0.5, 1.0, 1.5 wt

% *R*/*S*-M2 in flat LC cells at 25°C. c) g_{em} of N*-LCs of E7 doped with 1.0wt % *S*-M1, *S*-M2 at at various DC electric filed. d) g_{em} spectra of N*-LCs with 0.5 wt% *S*-M1, *S*-M2 on ITO glass LCDs (λ_{ex} = 360 nm, DC 10-32 V, 15s). (cells: homeotropic surface anchoring conditions)

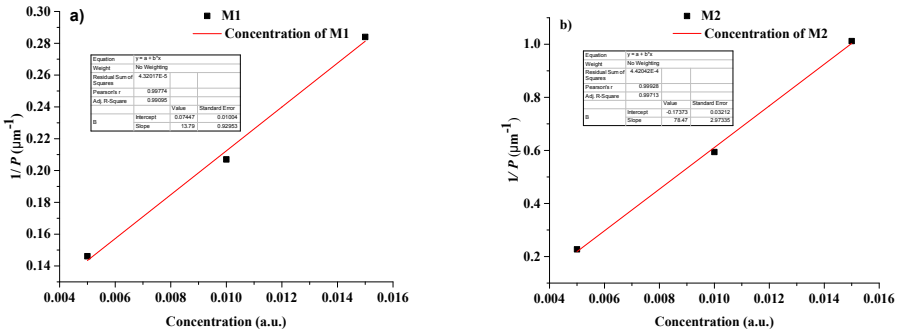


Fig. S11 Calculation of helical twisting power (β) a) M1, b) M2 by ploting 1/*P* against concentration.

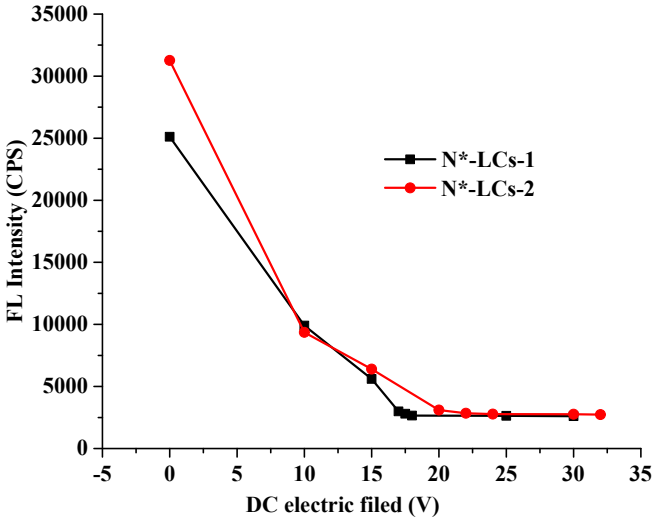


Fig. S12 PL Intensity-voltage curves of N*-LCs-1 (Guest, 1.0wt% M1) and N*-LCs-2 (Guest, 1.0wt% M2) on ITO glass LCDs (λ_{ex} = 360 nm, DC 10-32 V, 15s). (cells: homeotropic surface anchoring conditions).

Table S1. Summary of N*-LCs at various concentration.

Guest	R(μm) [a]	*P*(μm) [b]	HTP(μm^{-1}) [c]	g_{em}[d]
M1-0.5	187	6.84	13.80	-0.20/+0.26
M1-1.0	132	4.83		-0.51/+0.50
M1-1.5	96	3.52		-0.63/+0.57
M1-2.0	-	-		-0.53/+0.49
M2-0.5	120	4.40		-0.83/+0.86
M2-1.0	46	1.69	78.47	-0.60/+0.57
M2-1.5	27	0.99		-0.37/+0.36
M2-2.0	-	-		-0.20/+0.22

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

12. ^{1}H NMR and ^{13}C NMR spectra of compounds

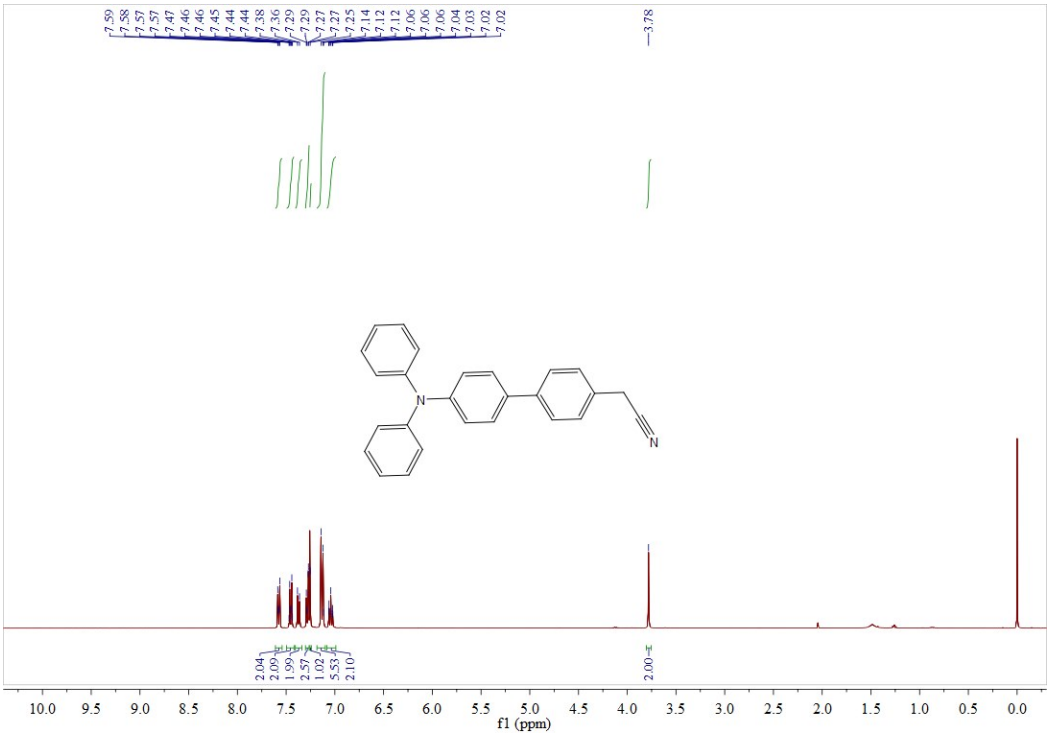


Fig. S13 ^{1}H NMR of *R-/S*-2 (400 MHz, $CDCl_3$).

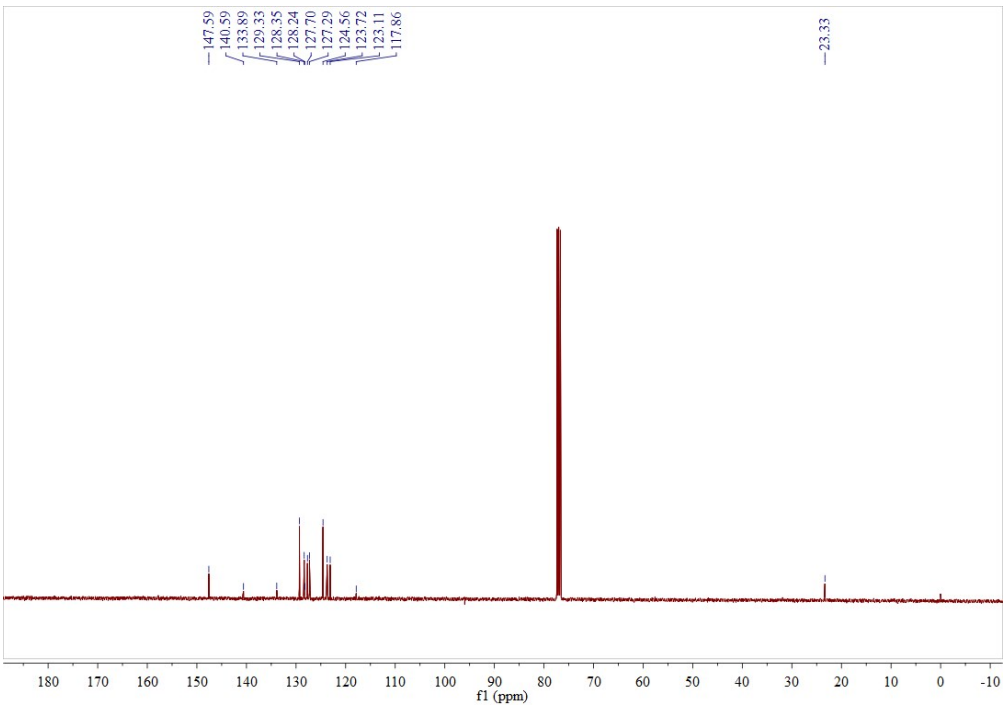


Fig. S14 ^{13}C NMR of 1 (100 MHz, $CDCl_3$).

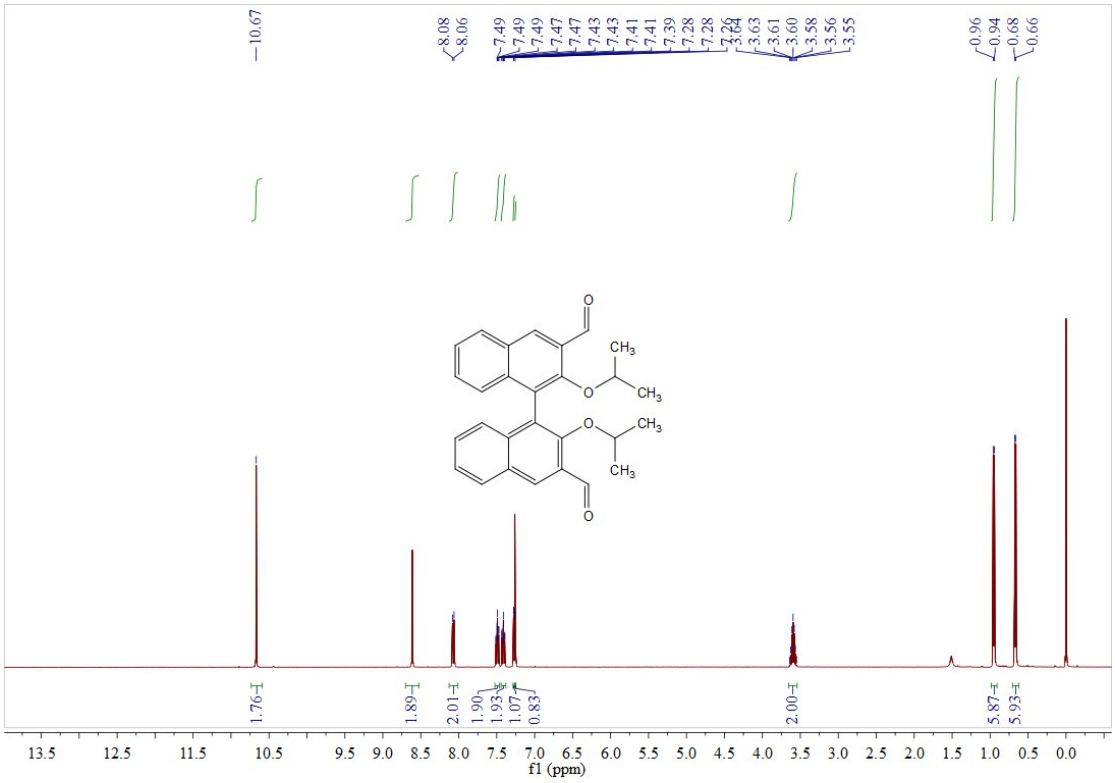


Fig. S15 ^{1}H NMR of *R/S*-2 (400 MHz, $CDCl_3$).

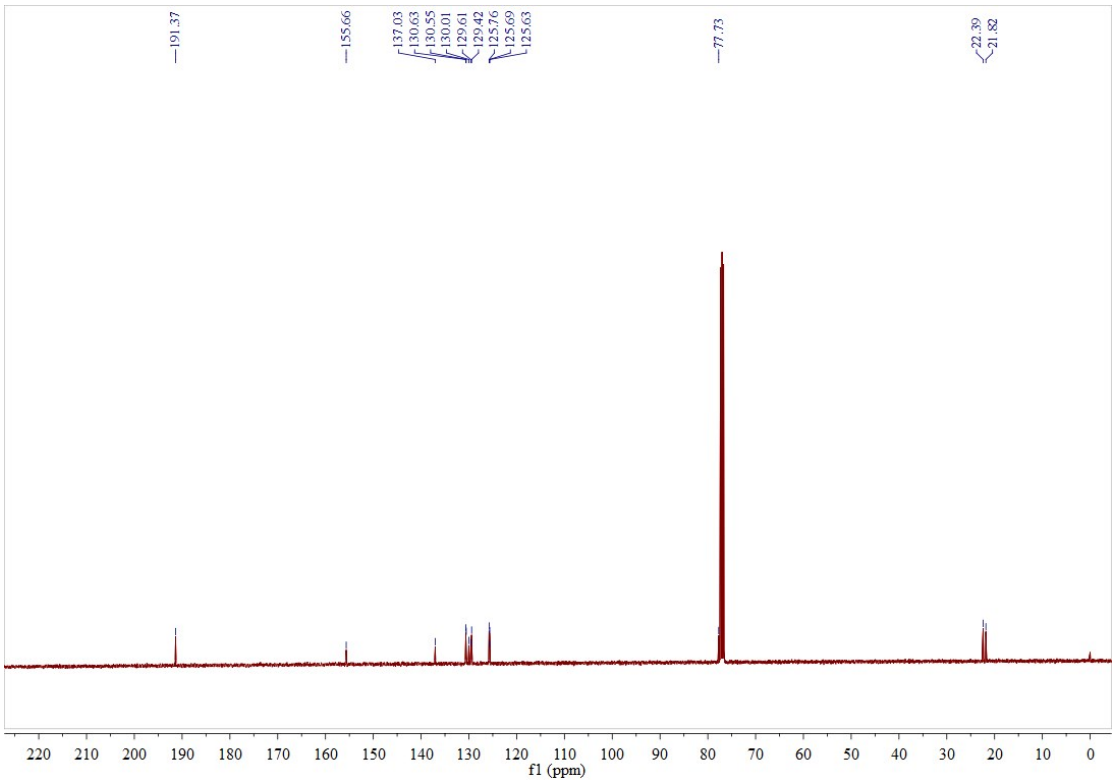


Fig. S16 ^{13}C NMR of *R/S*-2 (100 MHz, $CDCl_3$).

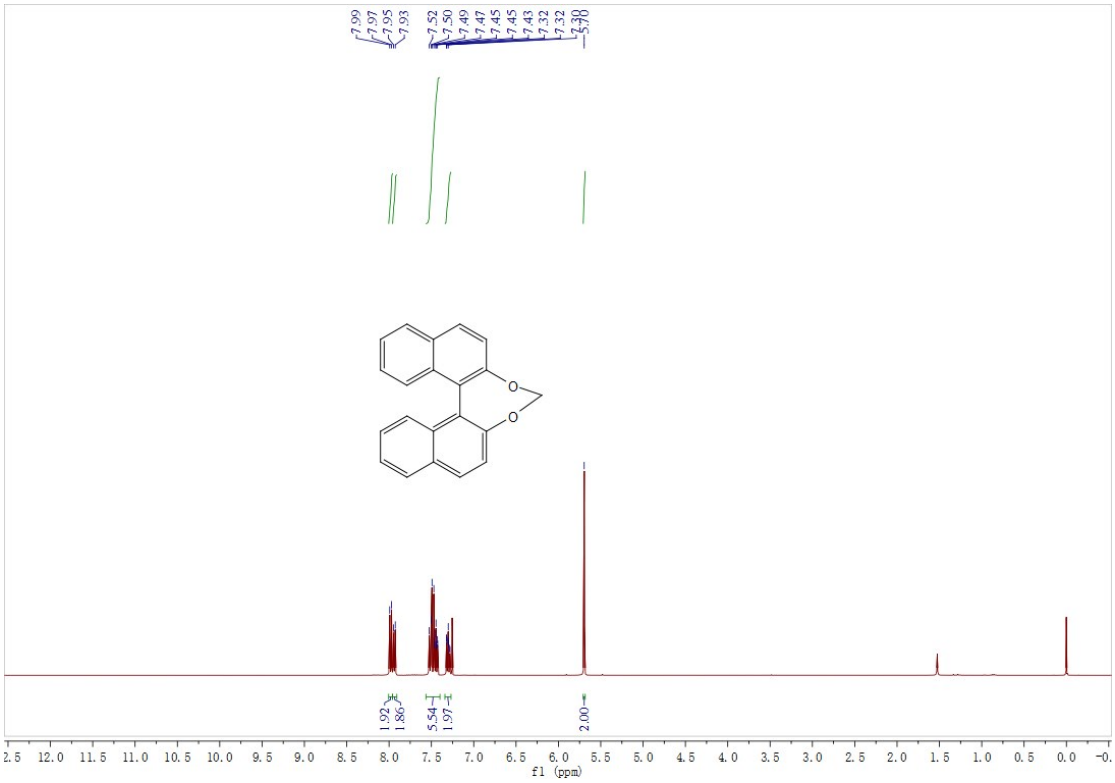


Fig. S17 ^{1}H NMR of *R-/S*-2 (400 MHz, $CDCl_3$).

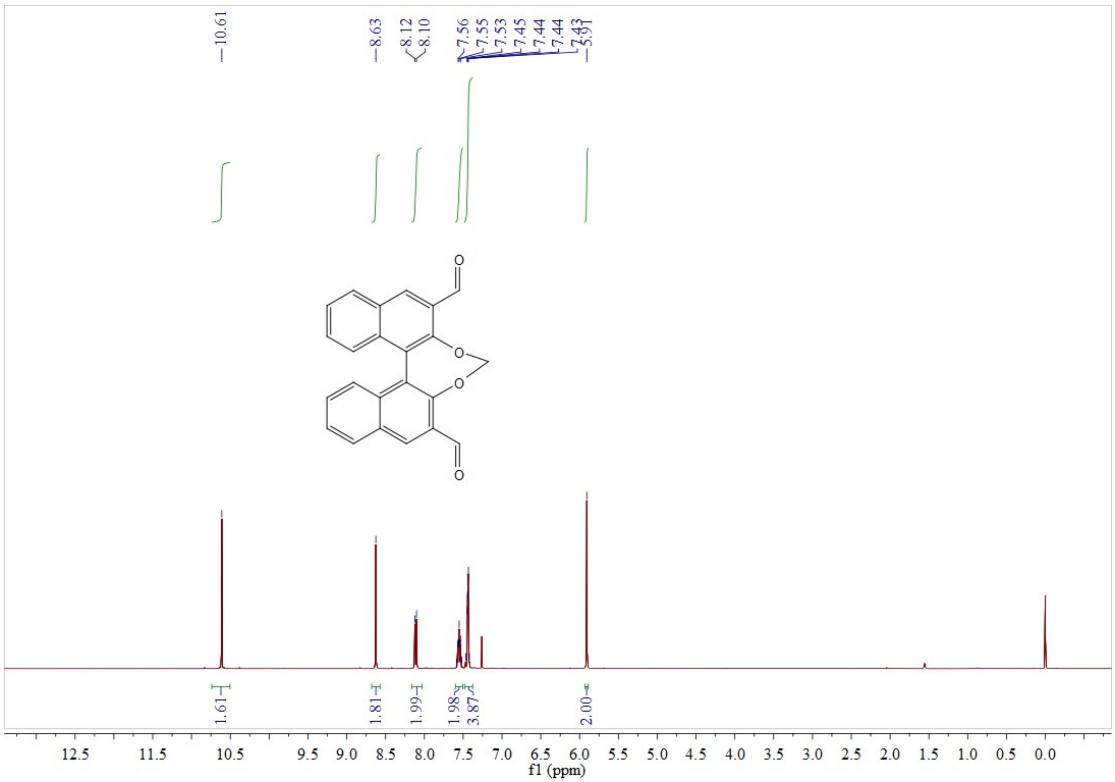


Fig. S18 ^{1}H NMR of *R/S*-2 (400 MHz, $CDCl_3$).

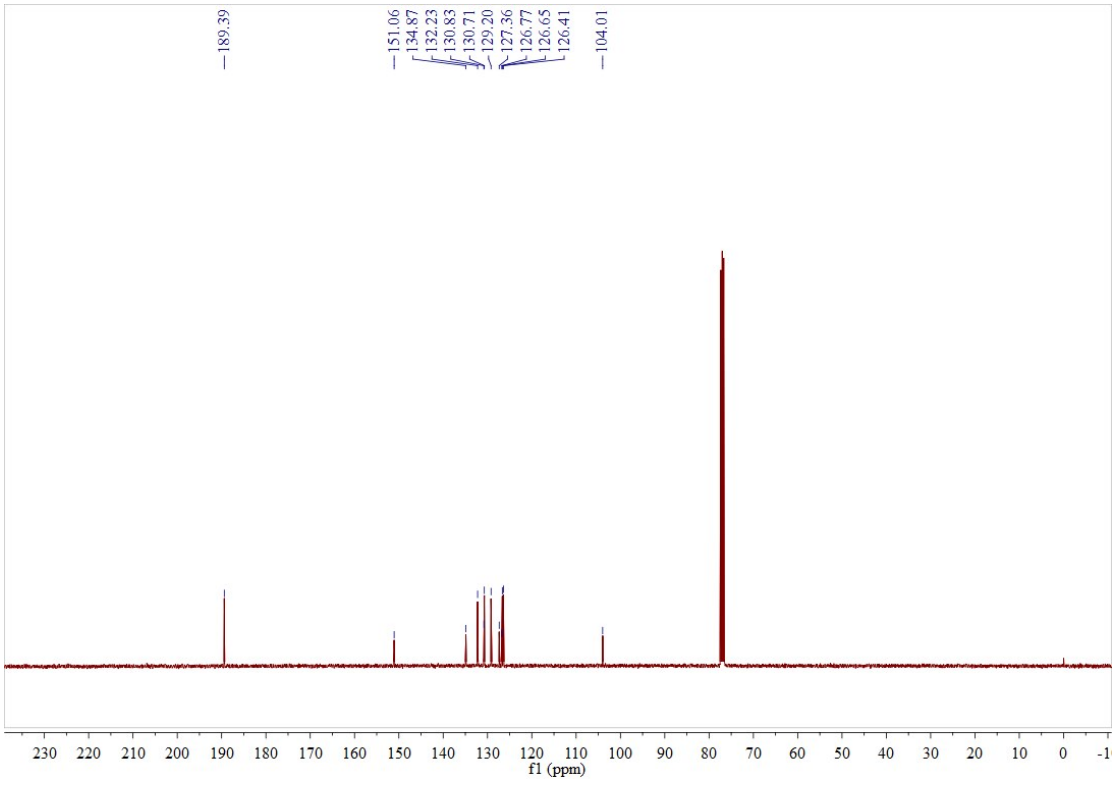


Fig. S19 ^{13}C NMR of *R/S*-2 (100 MHz, $CDCl_3$).

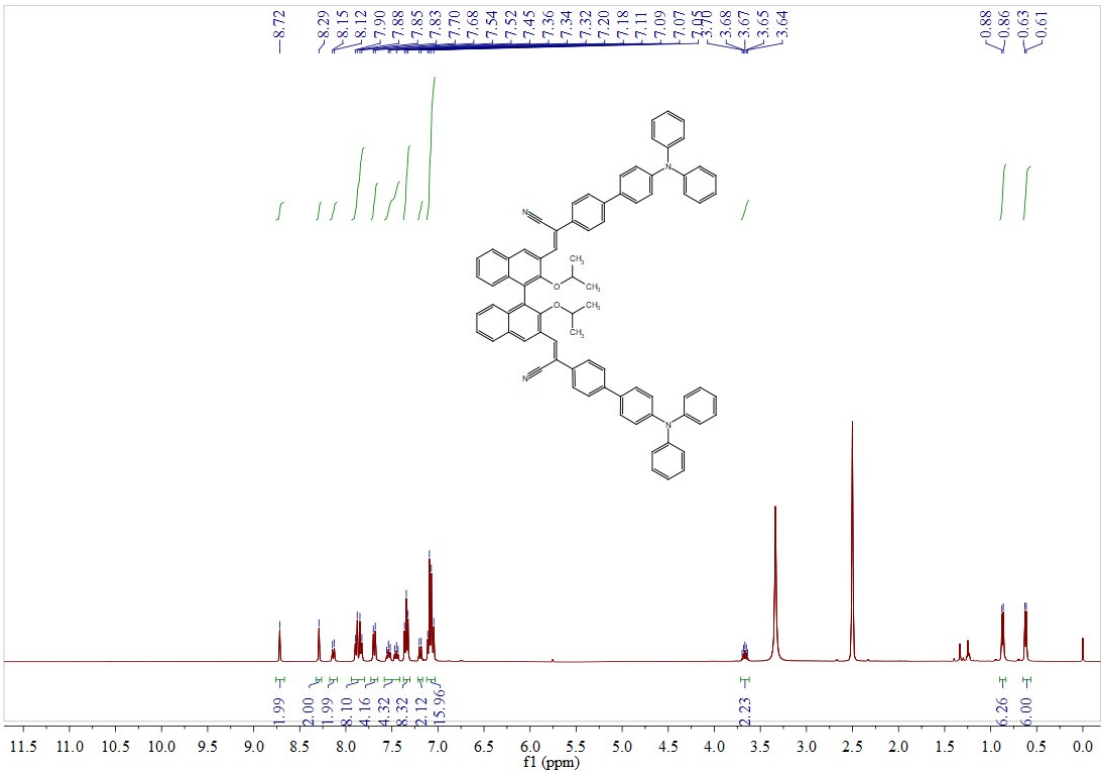


Fig. S20 ^{1}H NMR of *R/S*-M1 (400 MHz, DMSO-d6).

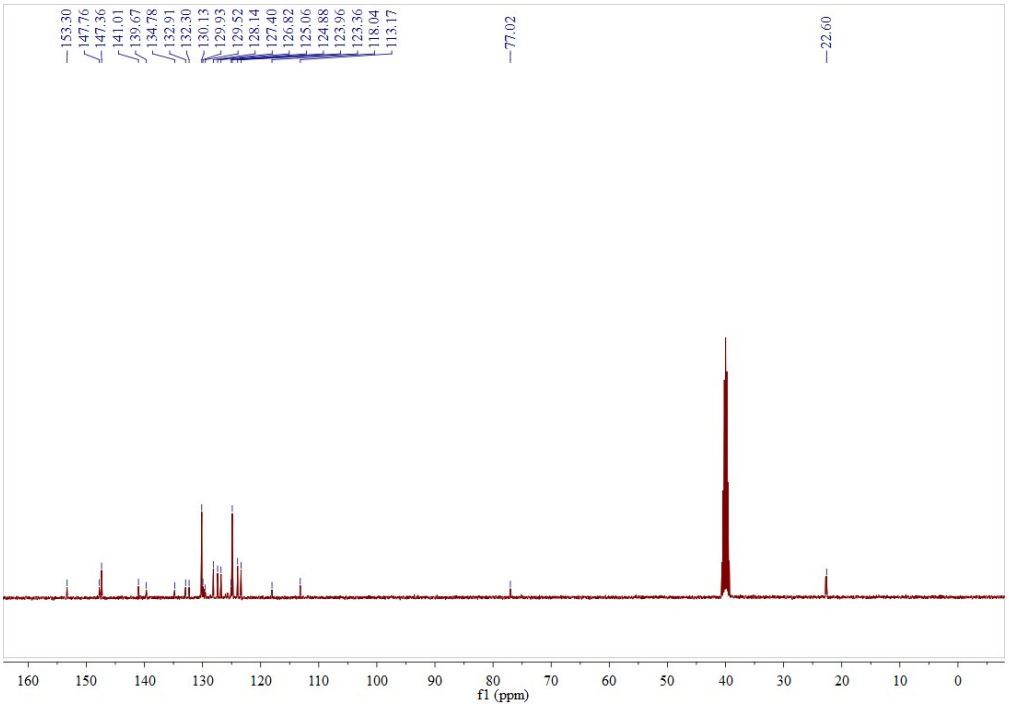


Fig. S21 ^{13}C NMR of *R/S*-M1 (100 MHz, DMSO-d6).

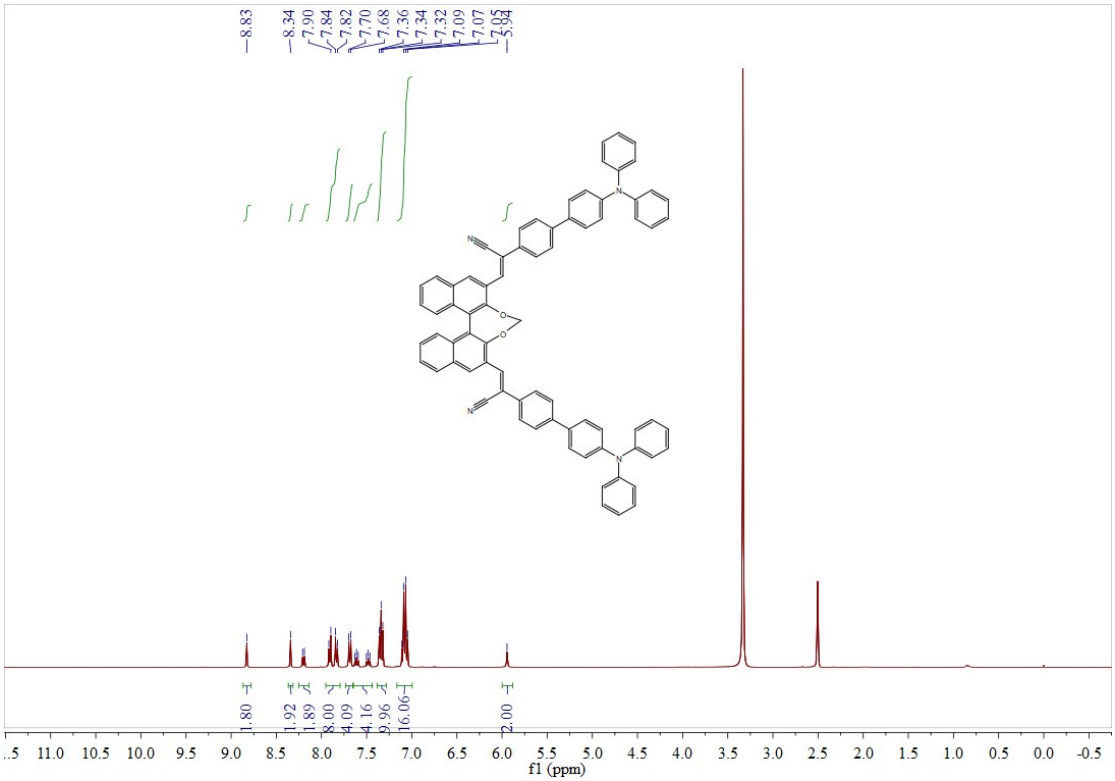


Fig. S22 [1]H NMR of *R/S*-M2 (400 MHz, DMSO-d6).

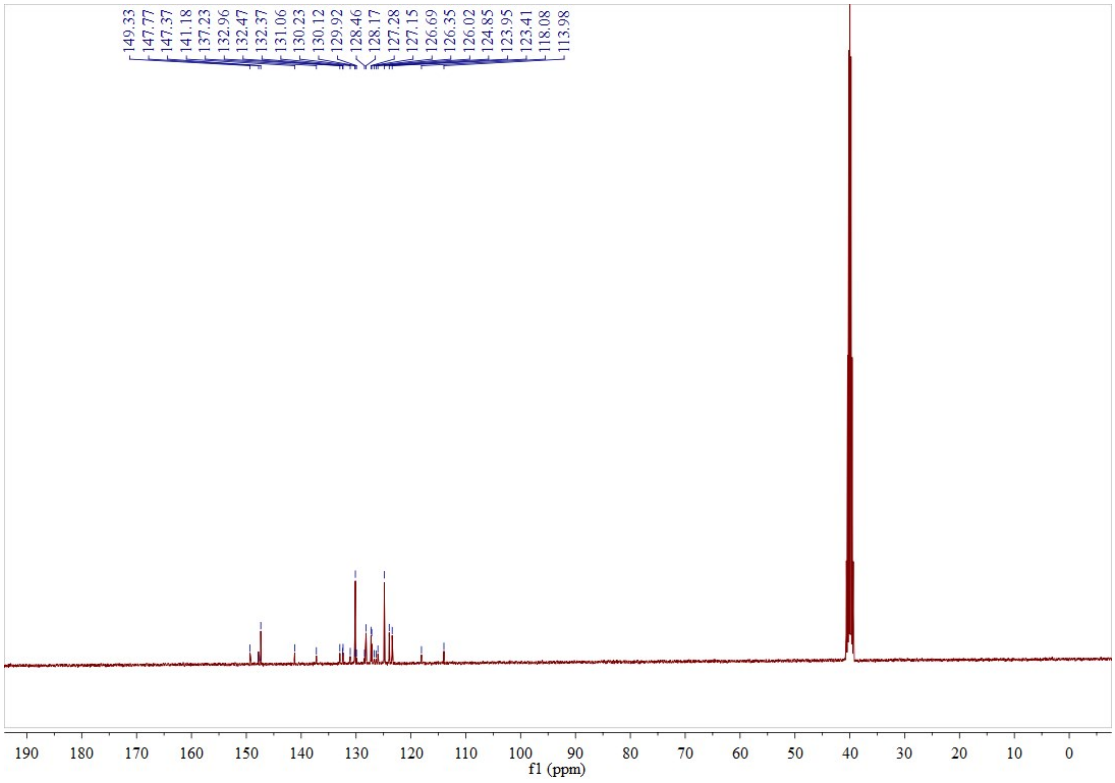


Fig. S23 [13]C NMR of *R/S*-M2 (100 MHz, DMSO-d6).

13. References

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