Electronic Supplementary Information for

(*R*)-Binaphthyl Derivatives as Chiral Dopants: Substituent Position Controlled Circularly Polarized Luminescence in Liquid Crystals

Xiaohui Gao,[ab] Xujin Qin,[b] Xuefeng Yang,[b] Yuangang Li,*[a] and Pengfei Duan*[b]

[a] College of Chemistry and Chemical Engineering，Xi'an University of Science and Technology，No.58，YanTa Road，Xi'an 710054，P. R. China.

[b] CAS Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, Division of Nanophotonics, National Center for Nanoscience and Technology (NCNST), No.11 ZhongGuanCun BeiYiTiao, Beijing 100190, P. R. China.

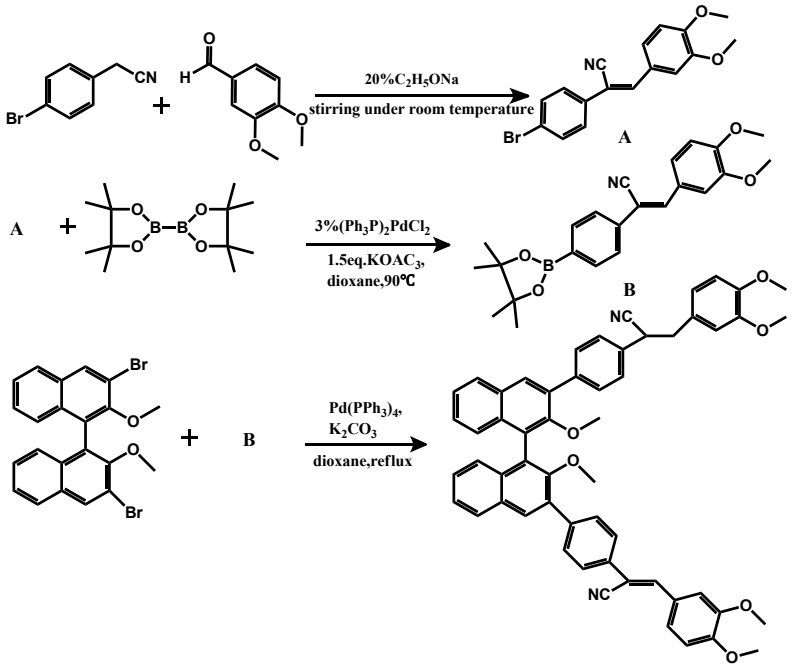
[c] Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, No. 2 ZhongGuanCun BeiYiJie, Beijing 100190, P. R. China

E-mail: liyuangang@xust.edu.cn; duanpf@nanoctr.cn; Tel: +86-10-82545510

S1. Synthetic procedures of binaphthyl derivatives

Materials: All reagents and solvents were used as received otherwise indicated. The molecules *R*-1, *R*-2 and *R*-3 are synthesized according to literatures.

Characterizations: The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker Fourier 300 (300MHz) spectrometer. High-resolution mass spectra (HR-MS) were obtained on a Finnigan MAT TSQ 7000 Mass Spectrometer System operated in a MALDI-TOF mode. UV-vis spectra were obtained by using Hitachi U-3900 spectrophotometer. Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer using a Xenon lamp as the excitation source. CD spectra and CPL spectra were measured on JASCO J-850 and JASCO CPL-200 spectrophotometers, respectively. Polarizing optical microscopy (POM) was recorded on the Olympus X83 using high-pressure mercury lamp as excitation source for fluorescent images. The desired AIE-gens *R/S*-1, *R/S*-2 and *R/S*-3 were synthesized by Suzuki coupling and Knoevenagel reactions and used as chiral dopants to prepare the N*-LCs samples.



Scheme S1 Synthesis of *R/S*-1

1. Synthesis of 2-(4-bromophenyl)-3-(3,4-dimethoxyphenyl)acrylonitrile(A)

A solution of the 4-Bromophenylacetonitrile (3.0 g, 15 mmol) and 3,4-dimethoxybenzaldehyde (3.0 g, 18 mmol) were added into a 100 mL round bottom flask with anhydrous EtOH (Chromatographically pure, 30 ml) and NaOMe (0.12 g, 2 mmol), stirred at room temperature for 30 h, then the mixture was filtered. The precipitate was washed with anhydrous EtOH to obtain blue powders (80 %, 4.8 g).

^{1}H NMR (300 MHz, Chloroform-d): 7.71 (s, 1H), 7.57-7.49 (m, 4H), 7.44 (s, 1H), 7.36 (d, J=8.4Hz, 1H), 6.96 (d, J=8.3Hz, 1H), 3.96 (s, J=5.7Hz, 6H).

2. Synthesis of 3-(3,4-dimethoxyphenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)acrylonitrile(B)

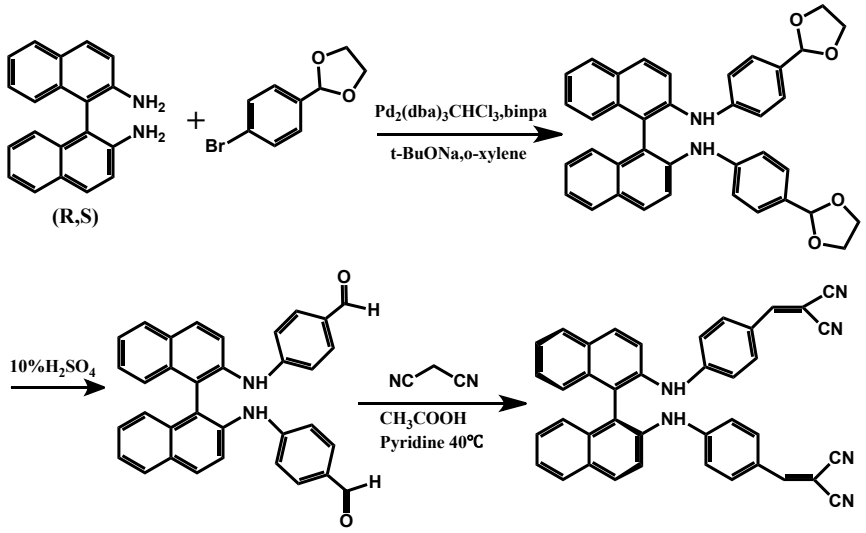
To a 100 mL round bottom flask with a magneton added with the A (3.0 g, 9 mmol), pinacol ester of diboron (5.0 g, 2.2 equiv) and $(Ph_3P)_2PdCl_2$ (0.19g, 3% equiv), then the flask was vacuum purged with nitrogen gas three times. 1,4-dioxane and the prepared KOAc (1.3 g, 1.5 equiv) were added in last and then was vacuum purged with nitrogen gas three times. The reaction mixture was stirred at 100 ℃ for 32h. After the solution was cooled to room temperature, the mixture was poured into ethyl acetate and washed with brine three times. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the product was purified by column chromatography using ethyl acetate/ hexane (1/20, v/v) as the eluent and the blue powder was obtained (75 % yield, 5.6g).

^{1}H NMR (300 MHz, DMSO-d): 7.86 (d, J=7.7Hz, 2H), 7.72 (s, 1H), 7.66 (d, J=7.7Hz, 2H), 7.52 (s, 1H), 7.39 (d, J=8.2Hz, 1H), 6.94 (d, J=8.4Hz, 1H), 3.96 (d, J=7.3Hz, 6H), 1.36 (s, 12H).

3. Synthesis of 2-(4-(3'-(4-(1-cyano-2-(3,4-dimethoxyphenyl)ethyl)phenyl)-2,2'-dimethoxy-[1,1'-binaphthalen]-3-yl)phenyl)-3-(3,4-dimethoxyphenyl)acrylonitrile(*R/S*-1)

(*R/S*)-3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (0.472 g, 1 mmol) and B (0.860 g, 2.2 mmol) were dissolved in 15 mL toluene in to a 50 mL two-neck round-bottom flask followed by addition of the prepared aqueous solution of potassium carbonate (5 mL, 2 mol/L). After that tetrakis(triphenylphosphine)-palladium (0) (5 mg, 8.7 μmol) was added. The flask was vacuum purged with nitrogen three times immediately and then reacted at 90℃ for 24 h. After the solution was cooled to room temperature, the mixture was poured into dichloromethane and washed three times with brine. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the product was purified by silica gel column chromatography by using dichloromethane/ hexane (1:30, v/v) was carried out to remove the impurities. The blue solid was obtained after dried (1.0 g, 80 % yield).

^{1}H NMR (300 MHz, Chloroform-d):7.95(s, 2H), 7.88(d, J=7.2Hz, 2H), 7.81(d, J=8.2Hz, 4H), 7.70(d, J=8.8Hz, 4H), 7.47(d, J=6.9Hz, 4H), 7.41-7.30(m, 4H), 6.91-6.80(m, 4H), 6.69(m, 2H) 3.93 (s, 12H), 3.80 (s, 6H). ^{13}C NMR (400 Hz, Chloroform-d): δ (ppm) 149.72, 149.05, 154.83, 154.83, 149.72, 149.05, 120.84, 120.84, 133.06, 133.06, 130.42, 130.42, 129.35, 129.35, 137.15, 137.15, 133.28, 133.28, 128.54, 128.54, 111.50, 111.77, 138.52, 138.52, 127.80, 127.80, 111.50, 126.94, 126.94, 122.51, 111.77, 127.84, 127.84, 127.12, 127.12, 128.08, 128.08, 122.55, 126.94, 126.94, 126.83, 126.83, 124.11, 124.11, 56.15, 56.15, 59.15, 59.15, 56.12, 56.12, 118.85, 118.85, 99.56, 99.56, 147.54, 147.54. HR-MS (MALDI, *m/z*): calcd: 842.9705, found: 842.9708 $[M]^+$.



Scheme S2 Synthesis of *R/S*-2

4. Preparation of (R/S)-(+)- 4,4'-([1,1'-binaphthalene]-2,2'-diylbis(azanediyl))dibenzaldehyde

To a 100 mL round-bottom flask with a magneton were added the (*R/S*)-(+)-1,1′-binaphthyl-2, 2′-diamine (0.114 g, 0.4 mmol, 1.0 equiv.), 2-(4-Bromo-phenyl)-[1,3]dioxolane (0.201 g, 0.88 mmol, 2.2 equiv.), tri(dibenzylideneacetone)-dipalladium Dipalladium(0)•$CHCl_3$ (0.02 g, 0.02 mmol, 0.05 equiv.), 2,2′-bis (diphenylphosphino)-1,1′-binaphathalene (0.015 g, 0.024 mmol, 0.06 equiv.) , sodium t-butoxide (0.150g, 2.04 mmol, 3.9 equiv.) and o-xylene (30 mL). Then mixture was heated to 150℃ with stirring for 12h in N_2. After cooling, deionized water was added and the aqueous layer was filtrated. Then the rude product, acetone and 10% H_2SO_4 were added into round-bottom flask with stirring for one day. After that added $NaHCO_3$ into the mixture and repeated above extraction process. The product was purified by column chromatography using dichloromethane / petroleum (1/20, v/v) as the eluent, the powder was obtained (70 %, 0.220 g).

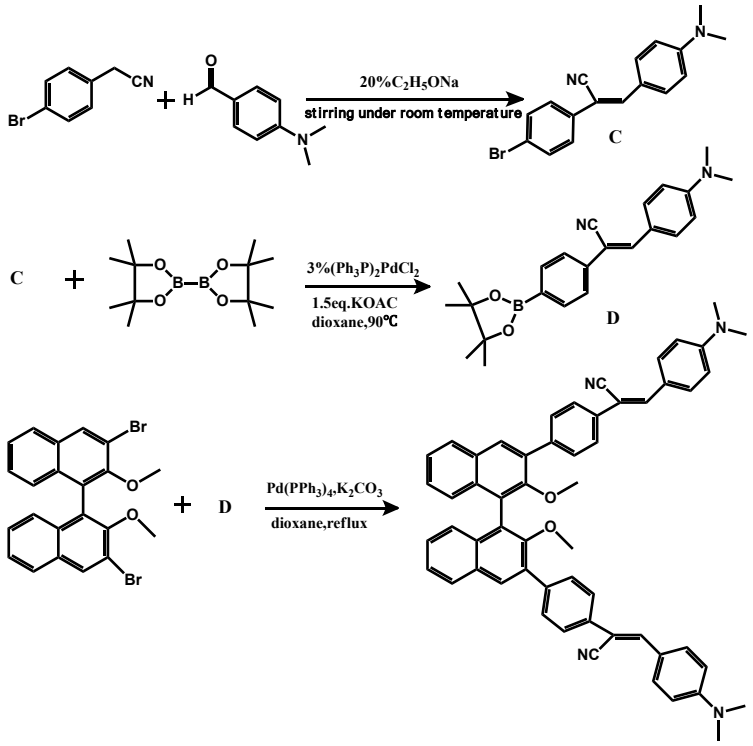
^{1}H NMR (300 MHz, CDCl3-d): 9.50 (s, 2H), 8.02 (s, 2H), 7.97 (d, J=7.9Hz, 2H), 7.91 (s, 2H), 7.63 (d, J=8.8Hz, 2H), 7.41 (d, J=7.0Hz, 4H), 7.35 (d, J=8.6Hz, 2H), 7.24 (d, J=8.5Hz, 2H), 6.99 (d, J=8.7Hz, 2H), 6.79 (d, J=8.6Hz, 4H).

5. Preparation of (S)-2,2'-((([1,1'-binaphthalene]-2,2'-diylbis(azanediyl))bis(4,1-phenylene)) bis(methanylylidene))dimalononitrile (*R/S*-2)

(*R/S*)- (+)-4,4'-([1,1'-binaphthalene]-2,2'-diylbis(azanediyl))dibenzaldehyde (0.200 g, 0.40 mmol) was dissolved in 30 mL pyridine and added into a 250 mL single-neck round-bottom flask. Subsequently, malononitrile (0.025 mL, 0.39 mmol) was added to the flask. Then acetic acid (0.11 ml, 0.62 mmol) was added and the flask was vacuum purged with nitrogen gas three times. The reaction mixture was stirred at 40 °C for 24h. The reaction mixture was poured into water and the aqueous layer was extracted with ethyl acetate three times. The organic layers were collected, dried over magnesium sulfate and filtration. The collected organic layers were removed under reduced pressure. The product was purified by column chromatography using ethyl acetate / petroleum (1/20, v/v) as the eluent, the red powder was obtained (60 %, 0.120 g).

^{1}H NMR (300 MHz, DMSO-d): 8.60 (s, 2H), 8.07 (m, 4H), 7.85 (s, 2H), 7.61 (d, J=8.9Hz, 2H), 7.47 (t, J=7.1Hz, 2H), 7.37 (d, J=9.0Hz, 2H), 7.30 (t, J=8.0Hz, 2H), 6.95 (d, J=8.5Hz, 2H), 6.61 (d, J=8.8Hz, 2H). ^{13}C NMR (400 Hz, Chloroform-d): δ (ppm) 141.50, 141.50, 141.65, 141.65, 115.54, 115.54, 133.06, 133.06, 127.25, 127.25, 120.96, 120.96, 117.48, 114.06, 114.06, 124.85, 127.12, 126.75, 129.74, 129.74, 117.44, 114.02, 114.02, 127.06, 124.85, 126.75, 129.74, 129.74, 125.48,

125.48, 121.55, 121.55, 113.64, 113.64, 113.64, 113.64, 161.55, 161.55, 81.40, 81.40. HR-MS (MALDI, *m/z*): calcd: 588.0955, found: 588.0952 $[M]^+$.



Scheme S3 Synthesis of *R/S*-3

6. Preparation of 2-(4-bromophenyl)-3-(4-(dimethylamino)phenyl)acrylonitrile(C)

A solution of the 4-Bromophenylacetonitrile (3 g, 15 mmol) and 4-(dimethylamino)benzaldehyde (3.0 g, 20 mmol) were added into a 100 mL round bottom flask with anhydrous EtOH (Chromatographically pure, 30 ml) and NaOMe (0.12 g, 2 mmol), stirred at room temperature for 30 h and the mixture was filtered. The precipitate was washed with EtOH to obtain green powders (78%, 4.7 g).

^{1}H NMR (300 MHz, DMSO-d):7.88 (d, J=9.2Hz, 3H), 7.64(m, 4H), 6.83 (s, 2H), 3.03 (s, 6H).

7. Preparation of 3-(4-(dimethylamino)phenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2- Dioxaborolan -2-yl)phenyl)acrylonitrile(D)

To a 100 mL round-bottom flask with a magneton added by the C (3.0 g, 9 mmol) and pinacol ester of diboron (4.5 g, 2.2 equiv), $(Ph_3P)_2PdCl_2$ (0.19g, 3% equiv), the flask was vacuum purged with nitrogen gas three times. 1, 4-dioxane and the prepared KOAc (1.3g, 1.5 equiv) were added in last and then was vacuum purged with nitrogen gas three times. The reaction mixture was stirred at 100 °C for 32h. The reaction mixture was pour into ethyl acetate and the solvent was removed under reduced pressure. The product was purified by column chromatography using ethyl acetate/ hexane (1/20, v/v) as the eluent, the green powder was obtained (80% yield, 7.6g).

^{1}H NMR (300 MHz, DMSO-d): 7. 92 (s, 1H), 7.90 (m, 2H), 7.75 (m, 4H), 6.82(d, J=8.7Hz, 2H), 3.42 (s, 6H), 1.30 (s, 12H).

8. Preparation of 2,2'-((2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(4,1-phenylene))bis (3-(4-(dimethylamino)phenyl)acrylonitrile) (*R/S*-3)

3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (0.9 mg, 1 mmol) and D(0.9 g, 2.2 mmol) were dissolved in 15 mL toluene in a 50 mL two-neck round-bottom flask followed by addition of the prepared aqueous solution of potassium carbonate (4 mL, 2 mol/L). After that

tetrakis(triphenylphosphine)-palladium (0) (5 mg, 8.7 μmol) was added. The flask was vacuum purged with nitrogen three times immediately and reacted at 90℃ for 24 h. After the mixture was cooled to room temperature, poured into dichloromethane and washed with brine three times. The organic layer was dried over anhydrous sodium sulfate and filtered. After removing the solvent under reduced pressure, the product was purified by silica gel column chromatography by using dichloromethane/ hexane (1:30, v/v) to remove the impurities. The green solid was obtained after dried (1.5 g, 85% yield).

^{1}H NMR (300 MHz, Chloroform-d): 8.03 (d, J=7.7Hz, 2H), 7.93(t, J=9.6Hz, 6H), 7.84 (t, J=6.7Hz, 4H), 7.76 (t, J=8.8Hz, 4H), 7.54(d, J=9.3Hz, 2H)，7.43(d, J=7.5Hz, 2H)，7.17(d, J=8.5Hz, 2H)，6.85(d, J=8.5Hz, 2H), 6.6(s, 2H), 3.10(s, 6H), 1.25(s, 12H). ^{13}C NMR (400 Hz, Chloroform-d): δ (ppm) 154.84, 154.84, 150.35, 150.35, 120.82, 120.82, 133.06, 133.06, 130.45, 130.45, 129.36, 129.36, 137.14, 137.14, 133.25, 133.25, 124.73, 124.73, 111.75, 111.75, 138.58, 138.58, 127.82, 127.82, 126.96, 126.96, 129.74, 129.74, 111.75, 111.75, 127.83, 127.83, 127.15, 127.15, 128.04, 128.04, 129.72, 129.72, 126.95, 126.95, 126.84, 126.84, 124.12, 124.12, 59.15, 59.15, 118.84, 118.84, 41.35, 41.35, 41.35, 41.35, 99.54, 99.54, 147.55, 147.55. HR-MS (MALDI, *m/z*): calcd: 806.3612, found: 805.3610 $[M]^{+}$.

9. **Preparation of N*-LCs including *R/S*-1, *R/S*-2 and *R/S*-3 for tests**.

The 0.5 wt% chiral dopant and achiral nematic liquid crystal 5CB were co-dissolved in the CH_2Cl_2 solvent. Then the mixture was slightly heated for half an hour to evaporate CH_2Cl_2. The N*-LCs samples were injected into flat liquid crystal cell after the solvent was completely evaporated.

S2. Supplementary Figures

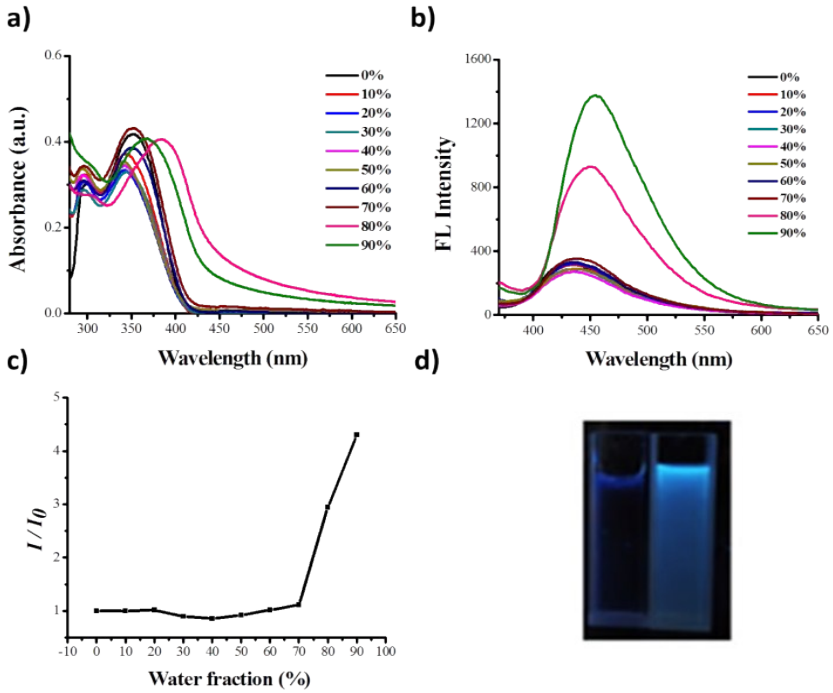
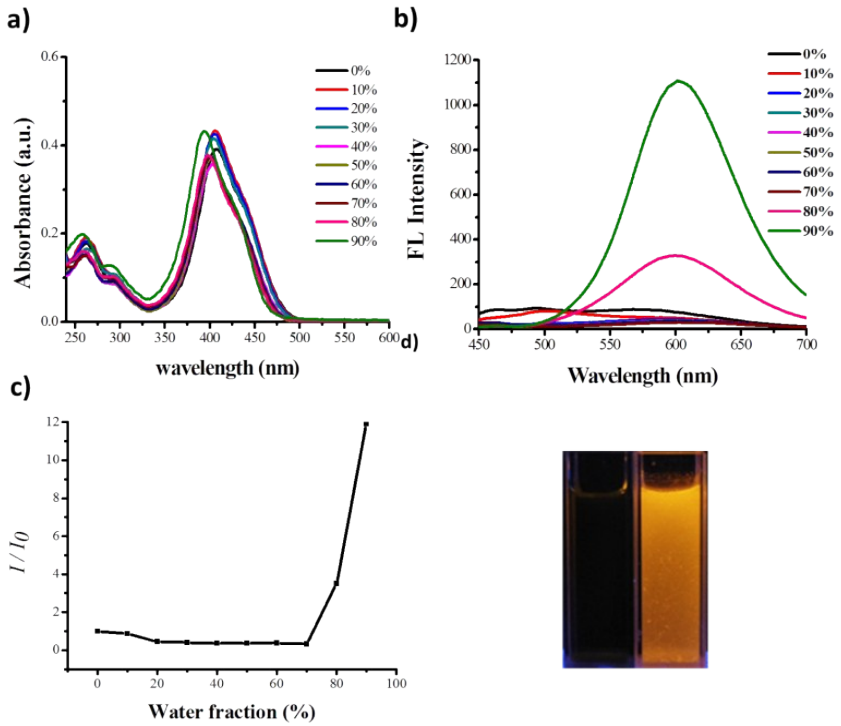


Figure S1 a) UV-vis absorption spectra of *R*-1 in THF/water mixtures with different water fraction (f_w); b) Fluorescent (FL) spectra of *R*-1 under the excitation wavelength at 340 nm; c) plot



of relatively fluorescent intensities of *R*-1 as a function of THF/water mixtures with different volume water fraction; d) Fluorescent images of *R*-1 in the THF solvent and THF/water mixture (f_w=90%).

Figure S2 a) UV-vis absorption spectra of *R*-2 in THF/water mixtures with different water fraction (f_w); b) Fluorescent (FL) spectra of *R*-2 under the excitation wavelength at 360 nm; c) plot of relatively fluorescent intensities of *R*-2 as a function of THF/water mixtures with different volume water fraction; d) Fluorescent images of *R*-2 in the THF solvent and THF/water mixture (f_w=90%).

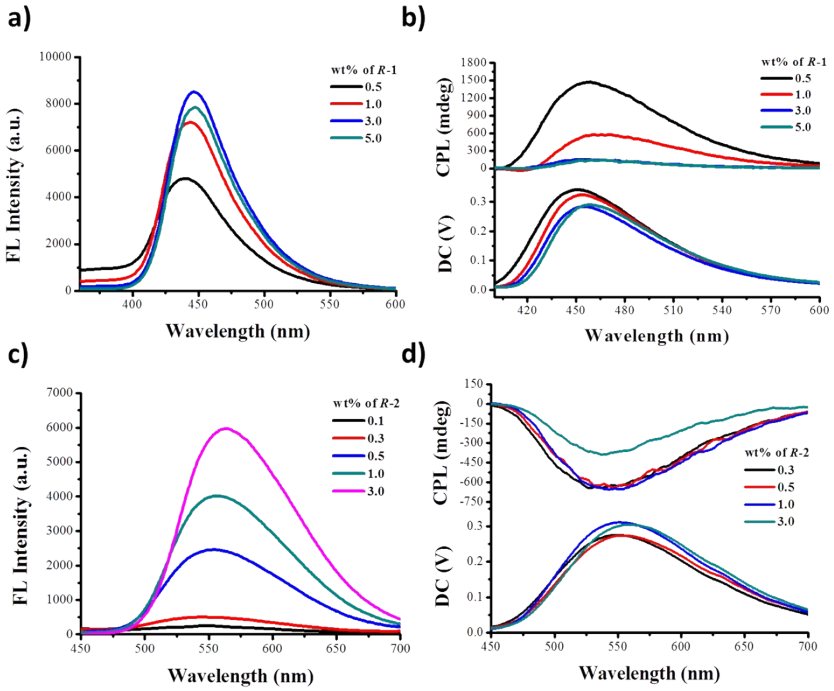


Figure S3 a) Fluorescent (FL) spectra of N*-LCs including different concentrations of *R*-1 under the excitation wavelength at 340 nm; b) CPL spectra of N*-LCs including different concentrations of *R*-1 under the excitation wavelength at 340 nm; c) Fluorescent (FL) spectra of N*-LCs including different concentrations of *R*-2 under the excitation wavelength at 360 nm; d) CPL spectra of N*-LCs including different concentrations of *R*-2 under the excitation wavelength at 360nm.

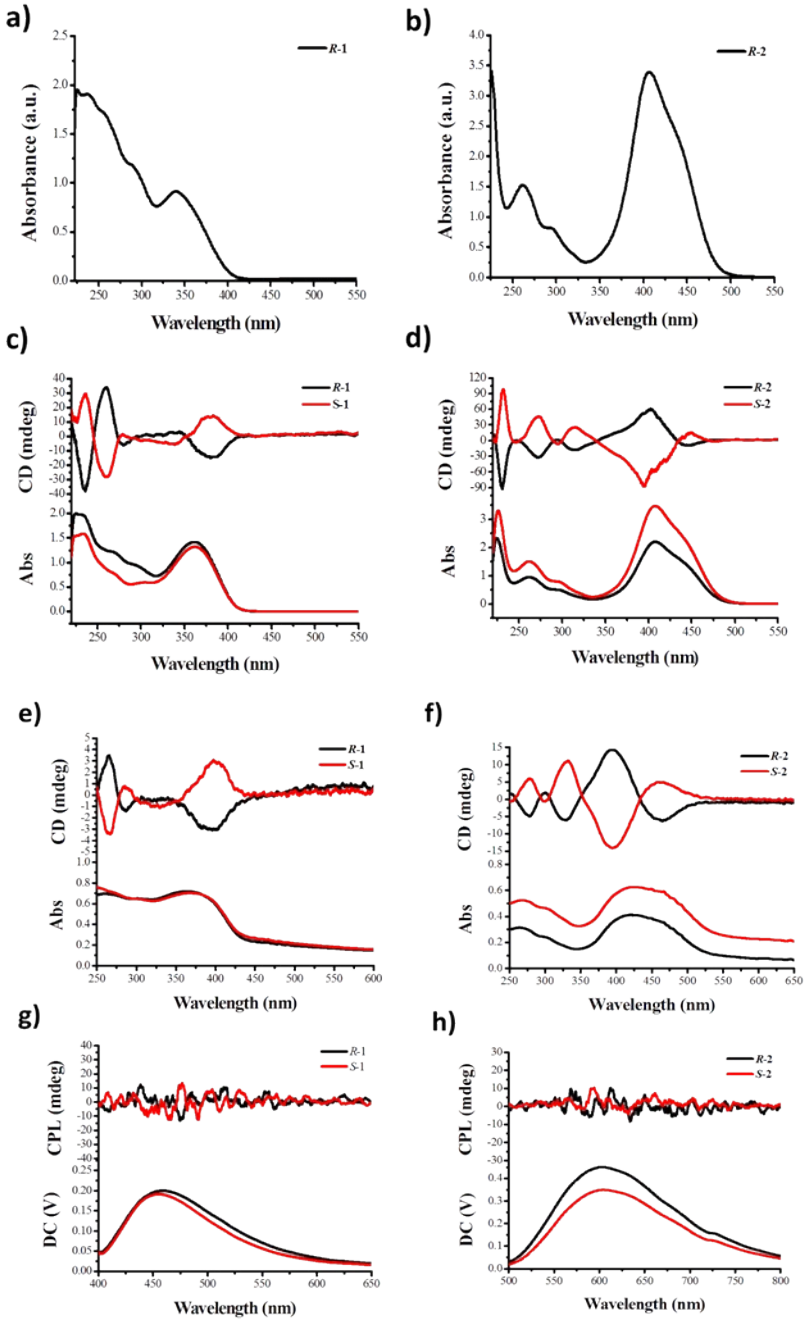


Figure S4 UV-vis absorption spectra of a) N*-LC including *R*-1 in dichloromethane (10^{-4} M); b) N*-LC including *R*-2 in dichloromethane (10^{-4} M); CD spectra of c) *R/S*-1 in dichloromethane (10^{-4} M)**;** d) *R/S*-2 in dichloromethane (10^{-4} M)**;** e) CD spectra of the thin films made by *R/S*-1 in the dichloromethane; f) CD spectra of the thin films made by *R/S*-2 in the dichloromethane; g) CPL spectra of the thin films made by *R/S*-1 in the dichloromethane solvent under the excitation wavelength at 340 nm; h) CPL spectra of the thin films made by *R/S*-2 in the dichloromethane under the excitation wavelength at 360 nm.

Table S1. Parameters of N*-LCs induced by 0.5 wt% *R*-1 and 0.5 wt% *R*-2, respectively.

Chiral dopants		**N*-LCs**	
Abbreviate	**Twisting powder (um^{-1})**	**Helical pitch (um)**	g_{lum}
R-1	**26.0**	**7.69**	***0.23***
R-2	**15.6**	**12.81**	**0.27**

The helical pitch (P) of N*-LCs were measured by the Cano's method by measuring the distance between Cano lines appeared on the surface of the wedge Cell ($\tan\theta = 0.0183$) and evaluated according to the following equation

$P = 2a\tan\theta$

where θ is the angle of the wedge cell. The helical twisting powers ($HTP,\ \beta_W$) of the chiral dopant, i.e., an ability to convert N-LC into N*-LC, was evaluated using the following equation

$$\beta_M = \frac{1}{p * c\% * r}$$

where p is the helical pitch and c is the concentration of the chiral dopant and r is the enantiomeric purity of the chiral dopant; here, r is assumed to be 1.

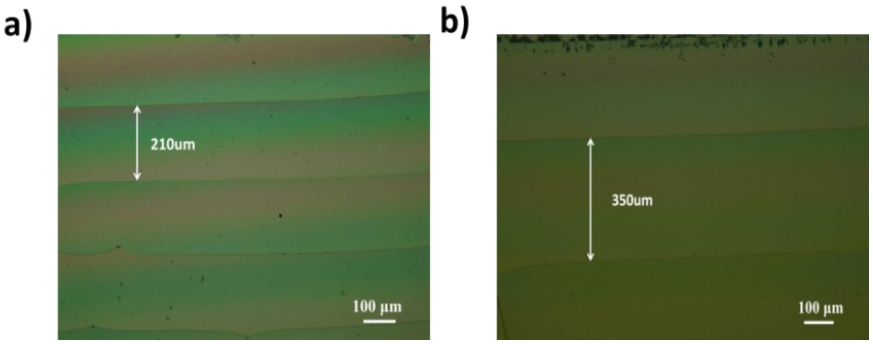


Figure S5 POM images of a) N*-LC including 0.5 wt% *R*-1; b) N*-LC including 0.5 wt% *R*-2 in wedge cells at room temperature.

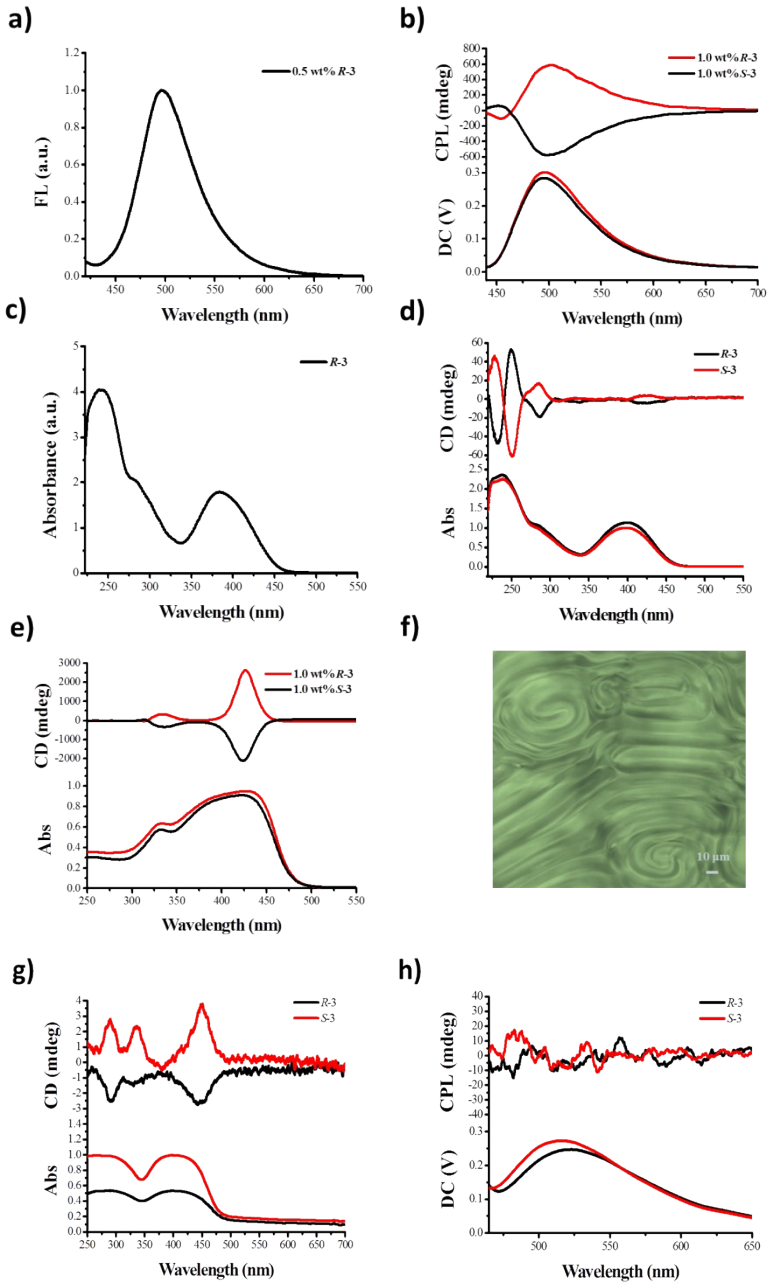


Figure S6 a) Fluorescent (FL) spectra of N*-LCs including 1.0 wt% *R*-3 under the excitation wavelength at 380nm; b) CPL spectra of N*-LC including 1.0 wt% *R/S*-3 under the excitation wavelength at 380nm; c) UV-vis absorption spectra of *R*-3 in the dichloromethane solvent (10^{-4} M); d) CD spectra of *R/S*-3 in the dichloromethane solvent (10^{-4} M); e) CD spectra of N*-LC including 1.0 wt% *R/S*-3； f) POM image of N*-LC films including 1.0 wt% *R*-3; g) CD spectra of the thin films made by *R/S*-3 in the dichloromethane solvent; h) CPL spectra of the thin films made by *R/S*-3 in the dichloromethane solvent under the excitation wavelength at 380nm.

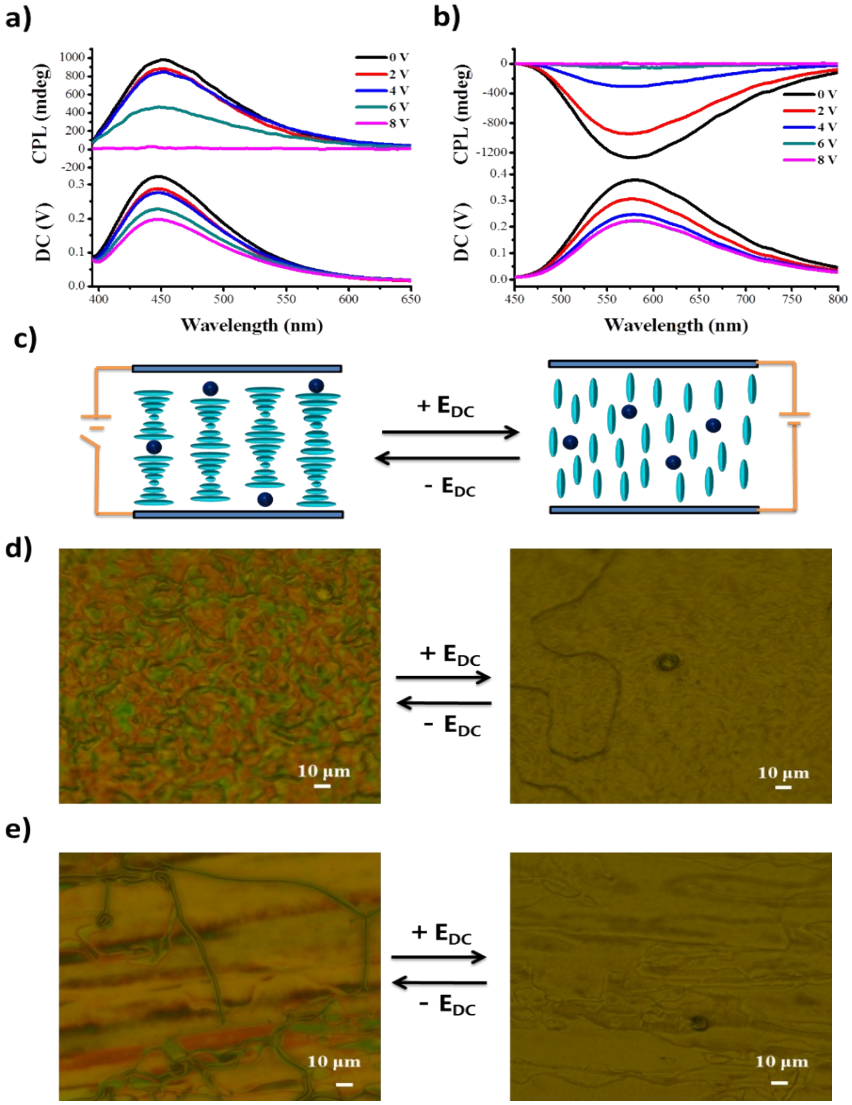


Figure S7 CPL spectra of a) N*-LCs including 0.5 wt% *R*-1; b) N*-LCs including 0.5 wt% *R*-2 under the electric field with different voltages; c) Schematic representation of the molecular arrangements of N*-LCs under the electric field "off " and "on", respectively; POM images of d) N*-LCs including 0.5 wt% *R*-1; e) N*-LCs including 0.5 wt% *R*-2 in liquid crystal cells under the electric field "off" and "on".