

Liquid Crystalline Circularly Polarized Fluorescent Emitter with High Luminescence Dissymmetry Factors

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Experimental part

All synthetic materials were commercial from Energy Chemical Company Ltd and Daicel Chiral Technologies (CHINA) Company Ltd and were used in the reaction directly. All reactions were carried out under N₂ atmosphere. To determine the structure of the compound, ¹H NMR spectra were obtained using either a Bruker Dex-300 or 400 NMR instrument with CD₂Cl₂ or CDCl₃ as solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix.

Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA449 from 25 to 600 °C at a heating rate of 20 °C min⁻¹ under a N₂ atmosphere. Differential scanning calorimetry (DSC) was measured at a heating rate of 10 °C min⁻¹ for both heating and cooling.

UV-Vis absorption spectra and steady-state photoluminescence (PL) spectra of the target compounds were obtained at room temperature using a Shimadzu UV-1650PC and a PTI QuantaMaster 40 steady-state fluorescence spectrometer. Low-temperature (77 K) fluorescence and phosphorescence spectra were measured in toluene solution (10⁻⁵ M) using an Edinburgh Instruments FLS1000 transient fluorescence spectrophotometer.

Electrochemical performance was evaluated by cyclic voltammetry using a 273A (Princeton Applied Research) in degassed CH₂Cl₂ solution at a rate of 100 mV/s. The CV system uses [Bu₄N][PF₆] as the electrolyte at a concentration of 0.1 mol dm⁻³. The experiment used a platinum disk working electrode, a platinum wire counter

electrode and a silver wire is the reference electrode. Ferrocene was used as the external standard compound. Each oxidation potential was calibrated using ferrocene as a reference.

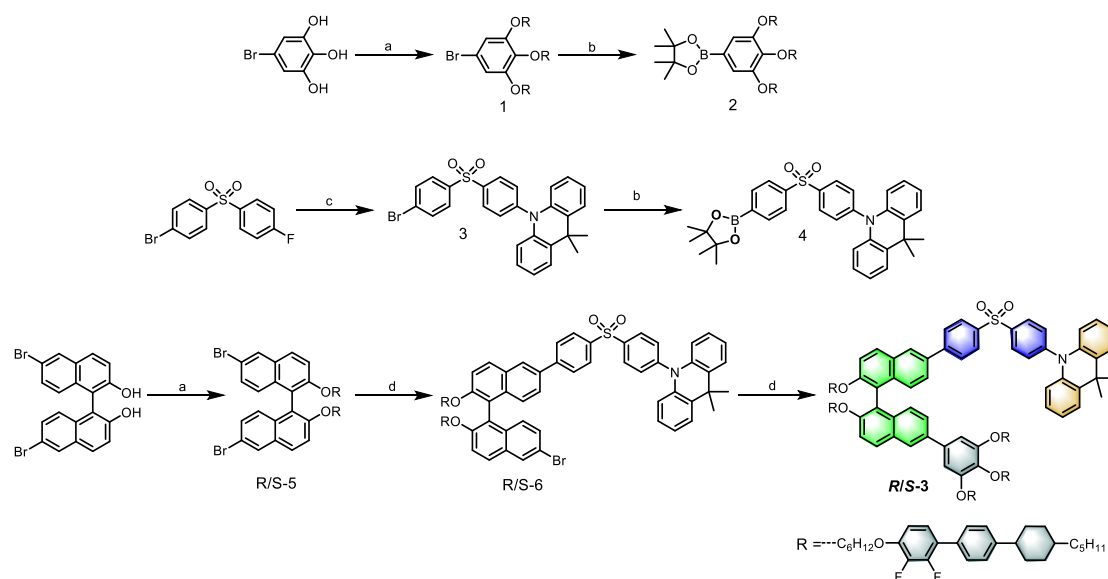
Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a bespoke temperature-controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was $\text{CuK}\alpha$ ($\lambda = 0.154056 \text{ nm}$) from a $1 \mu\text{s}$ microfocus source. Diffraction patterns were recorded on a 2048×2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample. Samples were filled into 0.9 mm capillary tubes.

The test film for chiroptical property is prepared by adding the ***R/S-3*** to dichloromethane into 10 mg/ml solution, and then it is obtained by drop-casting 70 μl volume sample solution to the quartz sheet by natural drying or annealing at $160 \text{ }^\circ\text{C}$ for 30 min. Circular dichroism spectrometer: Model JASCO J-1500, this paper tests the circular polarization spectrum of the compound in the state of pure film. The sample preparation process is as follows: The compound is dissolved in methylene chloride and slowly added to the quartz glass substrate, natural drying to form a pure film or annealing at $160 \text{ }^\circ\text{C}$ for 30min to obtain a pure film. The apparatus spectrophotometer with “Standard” sensitivity at 200 nm/min scan speed and respond time of 2.0 s employing “band” mode. Circular polarization spectrometer: Model JASCO CPL-200, test conditions and sample preparation method consistent with the circular dichroism spectrometer test.

Solution-processed device: Poly(styrene sulfonate) (PEDOT: PSS) was purchased from Xi'an Polymer Light Technology Corp. (1,3,5-tris(m-pyrid-3-ylphenyl)benzene) (TmPyPB), and LiF were purchased from Lumtec. All commercially available reagents were used without further purification. In devices, ITO (indium tin oxide) serves as the anode, PEDOT (poly(3,4-ethylenedioxythiophene):PSS(poly(styrenesulfonate) acts as the hole-injection layer, mCPCN is the host, TmPyPB (1,3,5-tris(3-pyridyl-3-phenyl)benzene) acts both as an electron-transporting layer and a hole-blocking layer, and LiF (lithium fluoride) acts as an electron-injection layer by modifying the work function of aluminum (Al) cathode. The substrates were successively cleaned with isopropyl alcohol, acetone, detergent, deionised water, and isopropyl alcohol in an ultrasonic bath and then dried overnight in the oven. The substrates pre-treated by oxygen plasma to increase the work function of the ITO film. Then, 40 nm-thick PEDOT: PSS was spin-coated onto the ITO substrates at 3200 rpm for 30 s and annealed at 150 °C for 15 minutes. And then emissive layer was spin-coated and annealed at 60 °C for 30 minutes using a precursor containing different materials co-dissolved in chlorobenzene or toluene. The films of TmPyPB, LiF and aluminium were prepared by thermal evaporation under a vacuum of 1×10^{-4} Pa. Each sample has an active area of 0.04 cm². The thermally evaporated deposition rates were 0.6-1 Å s⁻¹ for the TmPyPB, 0.1 Å s⁻¹ for LiF and 1.5-1.8 Å s⁻¹ for the Al electrode, respectively. The current-voltage-luminance (J-V-L) characteristics and the electroluminescence spectra of the devices were obtained simultaneously by using a

spectroradiometer (PR735) and a Keithley 2400 Source Meter unit under ambient atmosphere at room temperature.

Synthesis



Scheme 1. Synthetic route to **R/S-3**. a) K_2CO_3 , acetone, 80 °C; b) bis(pinacolato)diboron, $[\text{PdCl}_2(\text{dppf})]$, KOAc, toluene, 80 °C; c) NaH, dried THF, 70 °C; d) $[\text{Pd}(\text{PPh}_3)_4]$, K_2CO_3 , THF/water, 80 °C. (Taking **R-3** as an example in the synthesis part)

Synthesis of compound 1: A mixture of 1,2,3-trihydroxy-5-bromobenzene (0.7 g, 3.41 mmol), the liquid crystal unit (6.4 g, 12.08 mmol), K_2CO_3 (2.4 g, 17.30 mmol) in acetone (100 mL) was heated to 80 °C under reflux for 24 h. After the reaction stopped, acetone was removed by vacuum distillation and the remaining mixture was extracted with dichloromethane (3×40 mL), washed with water and dried over anhydrous MgSO_4 . The product was purified by column chromatography on silica (petrol ether (PE)/DCM, 3:2, v/v) to give a colorless liquid. (4.74 g, yield 91%). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, $J = 7.5$ Hz, 6H), 7.24 (d, $J = 6.3$ Hz, 6H), 7.09-6.98 (qt, 3H), 6.74 (dd, $J = 17.7, 8.7$ Hz, 3H), 6.69 (s, 2H), 4.08-4.01 (dt, 6H),

3.99-3.91 (dt 6H), 2.49 (t, $J = 12.2$ Hz, 3H), 1.97-1.70 (m, 25H), 1.58-1.44 (m, 30H), 1.37-1.19 (m, 29H), 1.06 (dd, $J = 23.1, 11.2$ Hz, 6H), 0.90 (t, $J = 6.9$ Hz, 9H). (**Figure S1**).

Synthesis of compound 2: A mixture of compound **1** (2.3 g, 1.51 mmol), Bis(pinacolato)diboron (0.46 g, 1.81 mmol), [PdCl₂(dppf)] (60 mg, 0.075 mmol), KOAc (0.74 g, 7.53 mmol) in toluene (60 mL) was heated under reflux for 24 h. After the reaction stopped, the mixture was extracted with dichloromethane (3 × 30 mL), washed with water and dried over anhydrous MgSO₄. The product was purified by column chromatography on silica (PE/EA, 1:1, v/v) to give a colorless solid. (1.2 g, yield 50.6%). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (t, $J = 7.5$ Hz, 7H), 7.24 (d, $J = 8.0$ Hz, 5H), 7.05 (t, $J = 8.6$ Hz, 3H), 7.01 (s, 2H), 6.74 (q, $J = 9.0$ Hz, 3H), 4.03 (m, 12H), 2.49 (t, $J = 11.6$ Hz, 3H), 1.99 – 1.73 (m, 25H), 1.56 – 1.40 (m, 14H), 1.38 – 1.19 (m, 42H), 1.05 (dd, $J = 23.7, 10.4$ Hz, 6H), 0.90 (t, $J = 6.9$ Hz, 9H).

Synthesis of compound 3: A mixture of 1-bromo-4-((4-fluorophenyl)sulfonyl)benzene (2.2 g, 7 mmol), 9,9-dimethyl-9,10-dihydroacridine (1.33 g, 7 mmol), NaH (280 mg, 7 mmol) in dried THF (60 mL) was heated under reflux for 24 h. After the reaction stopped, the mixture was extracted with dichloromethane (3 × 30 mL), washed with water and dried over anhydrous MgSO₄. The product was purified by column chromatography on silica (PE/DCM, 3:1, v/v) to give a yellow solid. (1.6 g, yield 45.6%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, $J = 8.5$ Hz, 2H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.73 (d, $J = 8.6$ Hz, 2H), 7.53-7.44 (m, 4H), 7.03-6.95 (m, 4H), 6.30-6.23 (m, 2H), 1.65 (s, 6H).

Synthesis of compound 4: A mixture of compound **3** (0.95 g, 1.85 mmol), bis(pinacolato)diboron (0.57 g, 2.3 mmol), [PdCl₂(dppf)] (70 mg, 0.095 mmol), KOAc (0.9 g, 9.3 mmol) in dried toluene (25 mL) was heated under reflux for 24 h. After the reaction stopped, the mixture was extracted with dichloromethane (3 × 30 mL), washed with water and dried over anhydrous MgSO₄. The product was purified by column chromatography on silica (PE/DCM, 1:1, v/v) to give a yellow solid. (0.8 g, yield 53.9%). ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 2H), 8.02 (q, *J* = 8.3 Hz, 4H), 7.51-7.42 (m, 4H), 7.01-6.93 (m, 4H), 6.25-6.18 (m, 2H), 1.65 (s, 6H), 1.35 (s, 12H).

Synthesis of compound 5: A mixture of the liquid crystal unit (3 g, 5.75 mmol), *R/S*-6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol (1.27 g, 2.88 mmol), K₂CO₃ (1.99 g, 14.40 mmol) in acetone (50 mL) was heated under reflux for 24 h. After the reaction stopped, the mixture was extracted with dichloromethane (3 × 30 mL), washed with water and dried over anhydrous MgSO₄. The product was purified by column chromatography on silica (PE/DCM, 3:1, v/v) to give a colorless solid. (2.3 g, yield 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 1.8 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 6H), 7.28 (d, *J* = 3.5 Hz, 6H), 7.08 (td, *J* = 8.5, 2.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.72 (t, *J* = 8.6 Hz, 2H), 4.04 – 3.89 (m, 4H), 3.87 (t, *J* = 6.5 Hz, 4H) 2.50 (t, *J* = 12.1 Hz, 2H), 1.91 (t, *J* = 14.4 Hz, 8H), 1.54-1.38 (m, 12H), 1.34-1.03 (m, 26H), 0.98-0.87 (m, 10H).

Synthesis of compound 6: A mixture of compound **5** (1.1 g, 0.81 mmol), compound **4** (0.3 g, 0.55 mmol), [Pd(PPh₃)₄] (35 mg, 0.03 mmol), K₂CO₃ (828 mg, 6 mmol) in

THF/water (13 mL, 10:3 v/v) was under reflux for 24 h. After the reaction stopped, the mixture was extracted with dichloromethane (3 × 20 mL), washed with water and dried over anhydrous MgSO₄. The product was purified by column chromatography on silica (PE/DCM, 3:4, v/v) to give a colorless solid. (0.35 g, yield 40%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.12-7.92 (m, 7H), 7.80 (dd, *J* = 8.9, 2.6 Hz, 3H), 7.46-7.28 (m, 11H), 7.19 (dd, *J* = 8.1, 6.5 Hz, 5H), 7.12 (d, *J* = 8.9 Hz, 1H), 6.98 (ddd, *J* = 13.0, 12.0, 6.2 Hz, 3H), 6.89-6.80 (m, 4H), 6.64 (dt, *J* = 41.4, 8.1 Hz, 2H), 6.14 (dd, *J* = 6.1, 3.3 Hz, 2H), 4.02-3.70 (m, 8H), 2.49-2.36 (m, 2H), 1.80 (d, *J* = 9.7 Hz, 8H), 1.47 (s, 12H), 1.41 (d, *J* = 6.8 Hz, 8H), 1.28-1.13 (m, 20H), 1.03-0.90 (m, 8H), 0.82 (t, *J* = 7.0 Hz, 6H).

Synthesis of compound R-3: A mixture of compound 2 (0.23 g, 0.14 mmol), compound 6 (0.2 g, 0.12 mmol), [Pd(PPh₃)₄] (10 mg, 0.01 mmol), K₂CO₃ (300 mg, 2.2 mmol) in THF/water (13 mL, 10:3 v/v) was under reflux for 24 h. After the reaction stopped, the mixture was extracted with dichloromethane (3 × 20 mL), washed with water and dried over anhydrous MgSO₄. The product was purified by column chromatography on silica (PE/DCM, 3:4, v/v) to give a colorless solid. (0.31 g, yield 78.9 %). *R-3:* ¹H NMR (400 MHz, CD₂Cl₂) δ 8.07 (dd, *J* = 13.6, 4.8 Hz, 3H), 7.97 (dd, *J* = 17.5, 8.9 Hz, 5H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.37 (ddt, *J* = 18.0, 11.2, 5.0 Hz, 18H), 7.20-7.08 (m, 12H), 6.96 (tt, *J* = 8.4, 4.4 Hz, 5H), 6.82 (dd, *J* = 12.8, 8.3 Hz, 6H), 6.61 (ddd, *J* = 32.3, 16.0, 8.5 Hz, 5H), 6.16-6.11 (m, 2H), 4.03-3.86 (m, 16H), 3.78-3.67 (m, 4H), 2.47-2.35 (m, 5H), 1.85-1.66 (m, 33H), 1.55 (s, 6H), 1.46 (s, 16H), 1.42-1.32 (m, 14H), 1.18 (tdd, *J* = 22.0, 14.1, 7.5 Hz, 52H), 1.05-0.89 (m, 15H),

0.85-0.78 (m, 15H). TOF-MS (ESI) m/z calcd for $C_{198}H_{229}F_{10}NO_{12}S$: 3037.05;

$[M+H]^+$ found: 3037.896.

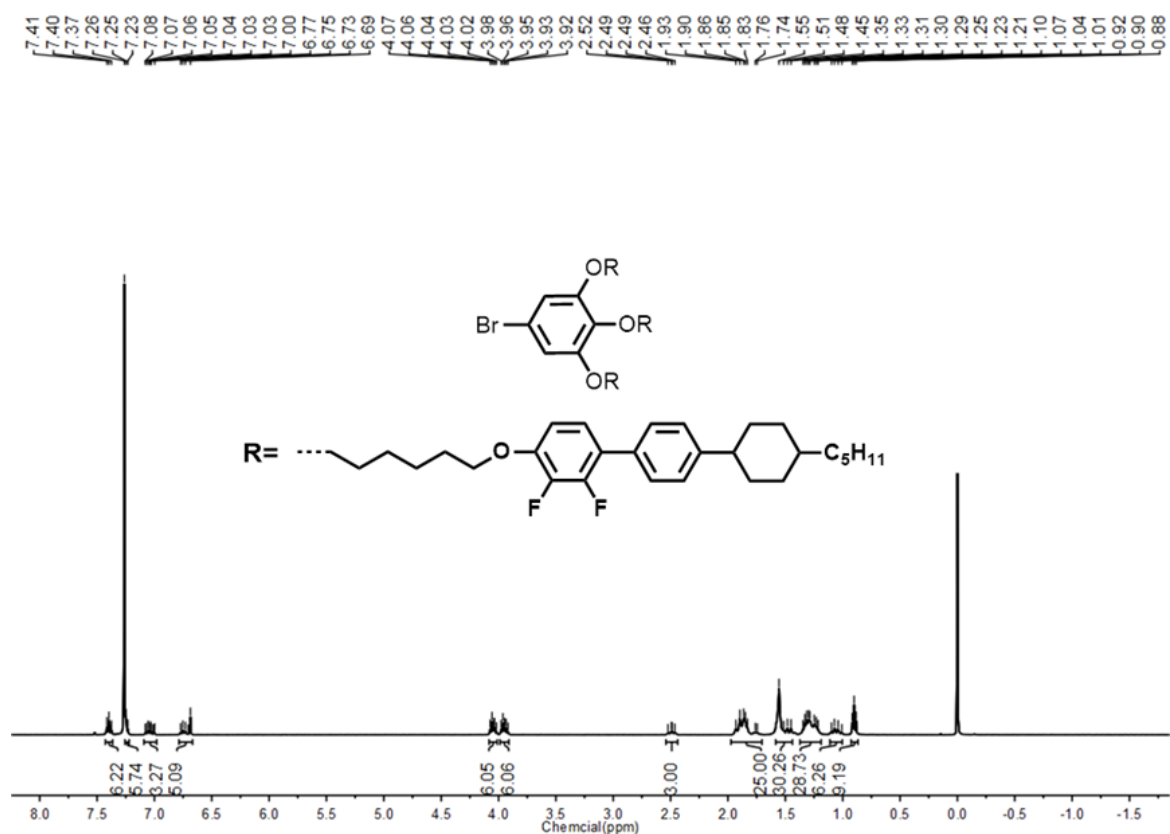


Figure S1. ^1H NMR spectrum of **1** in CDCl_3 .

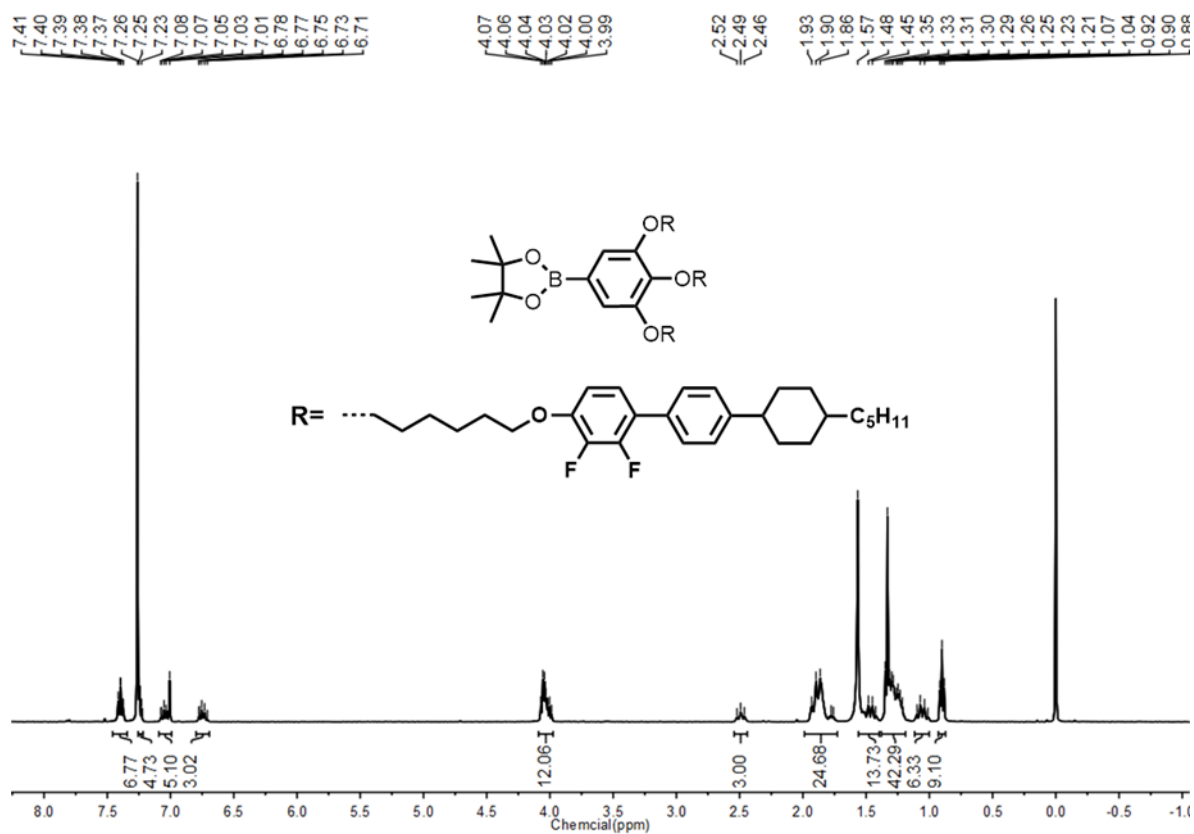


Figure S2. ^1H NMR spectrum of **2** in CDCl_3 .

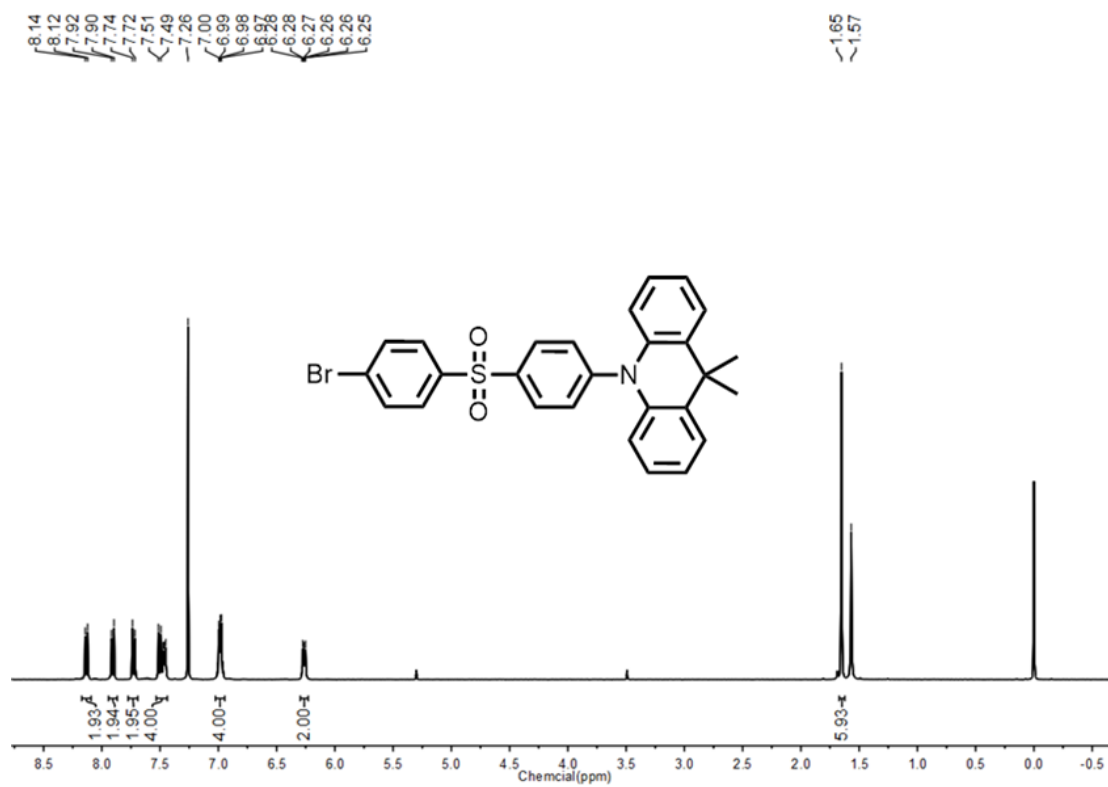


Figure S3. ^1H NMR spectrum of **3** in CDCl_3 .

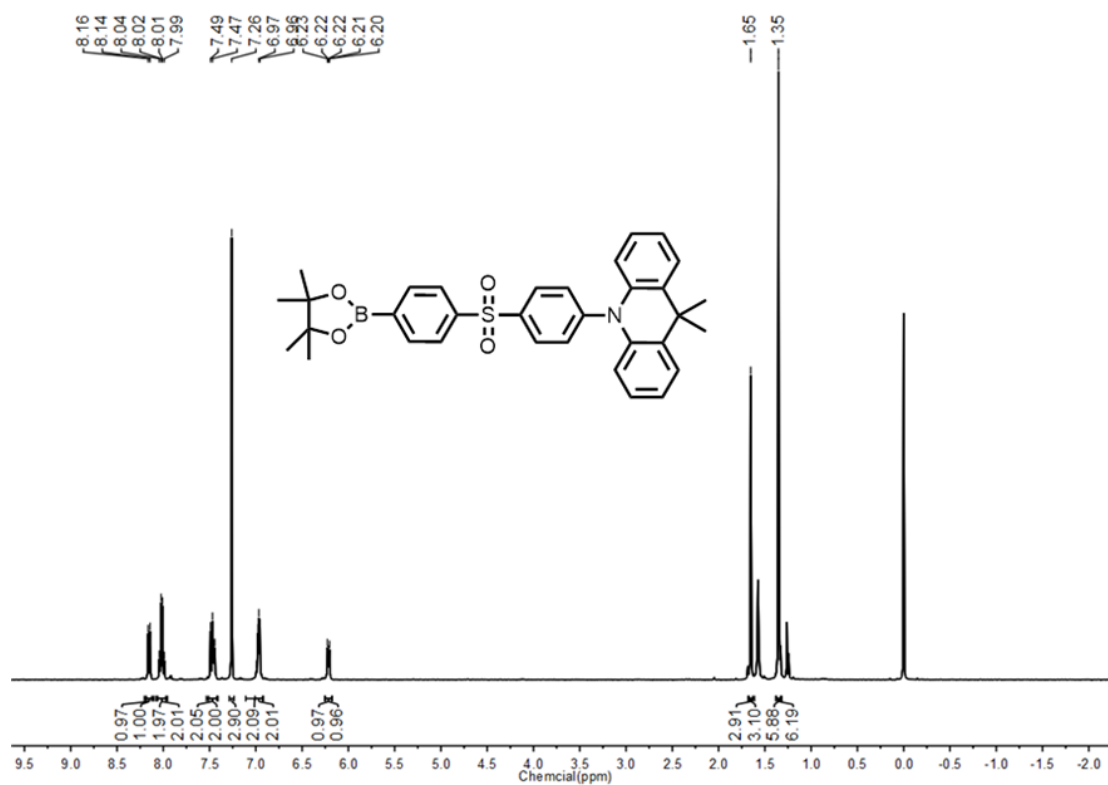
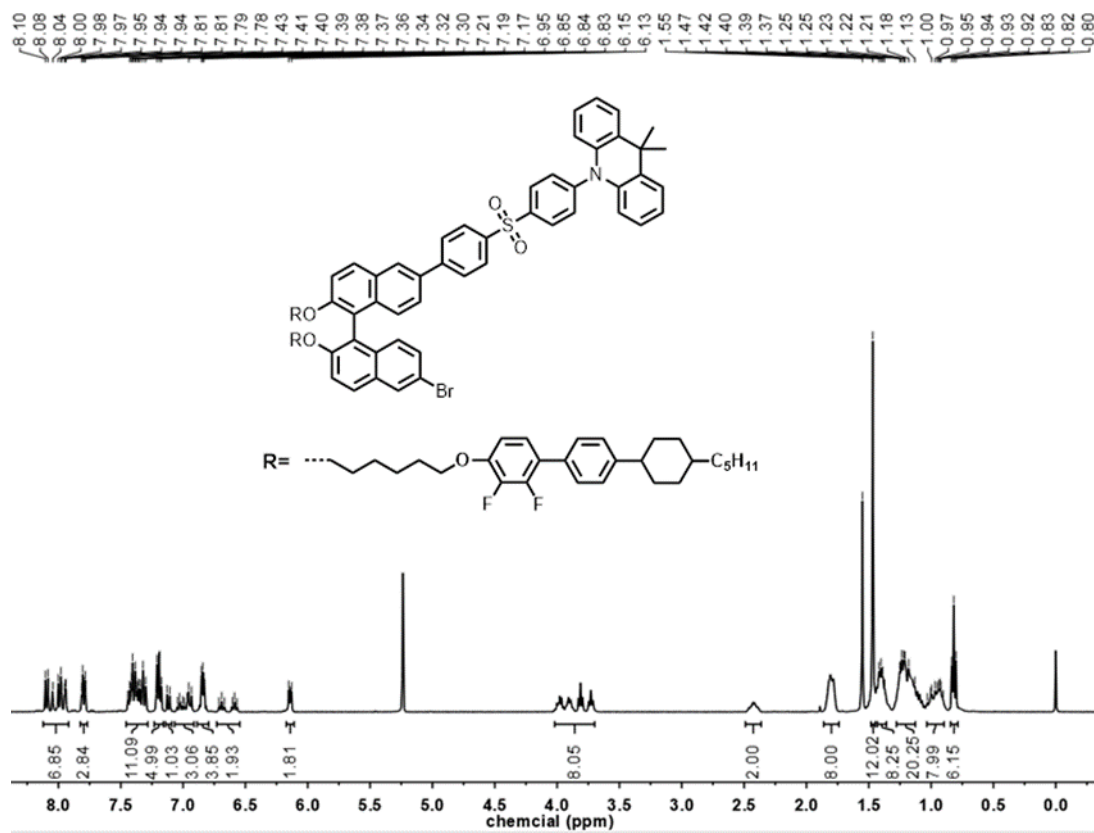
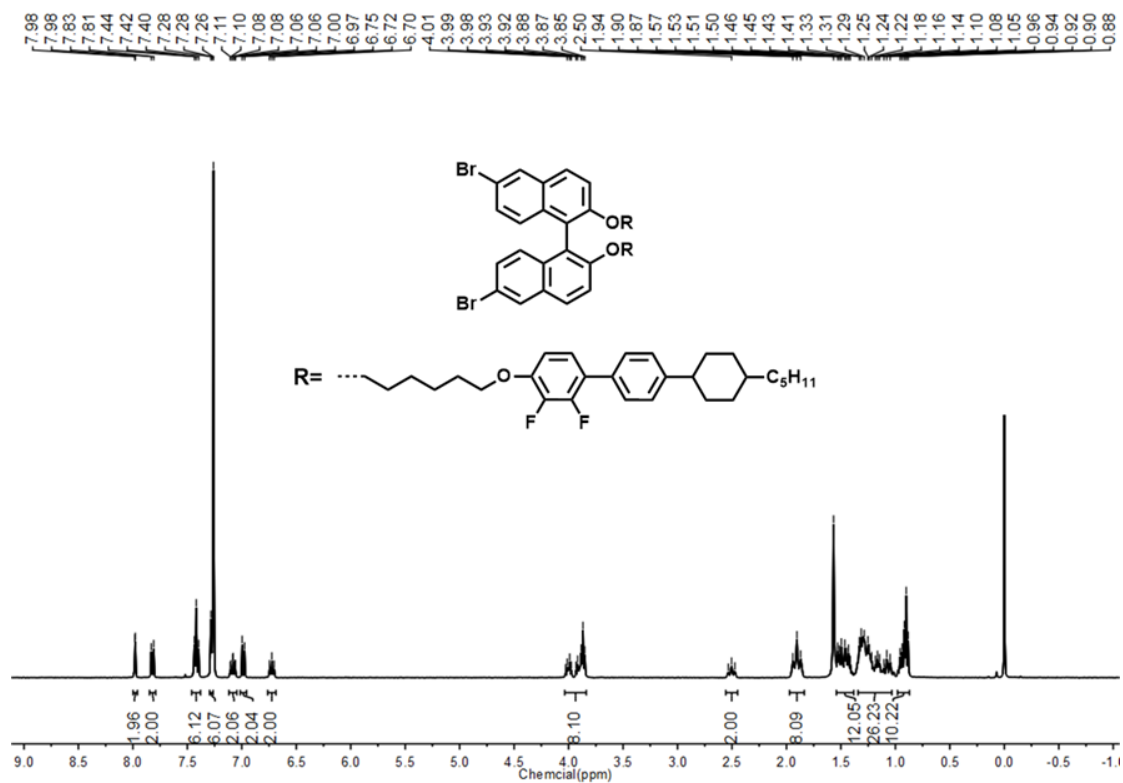


Figure S4. ^1H NMR spectrum of **4** in CDCl_3 .



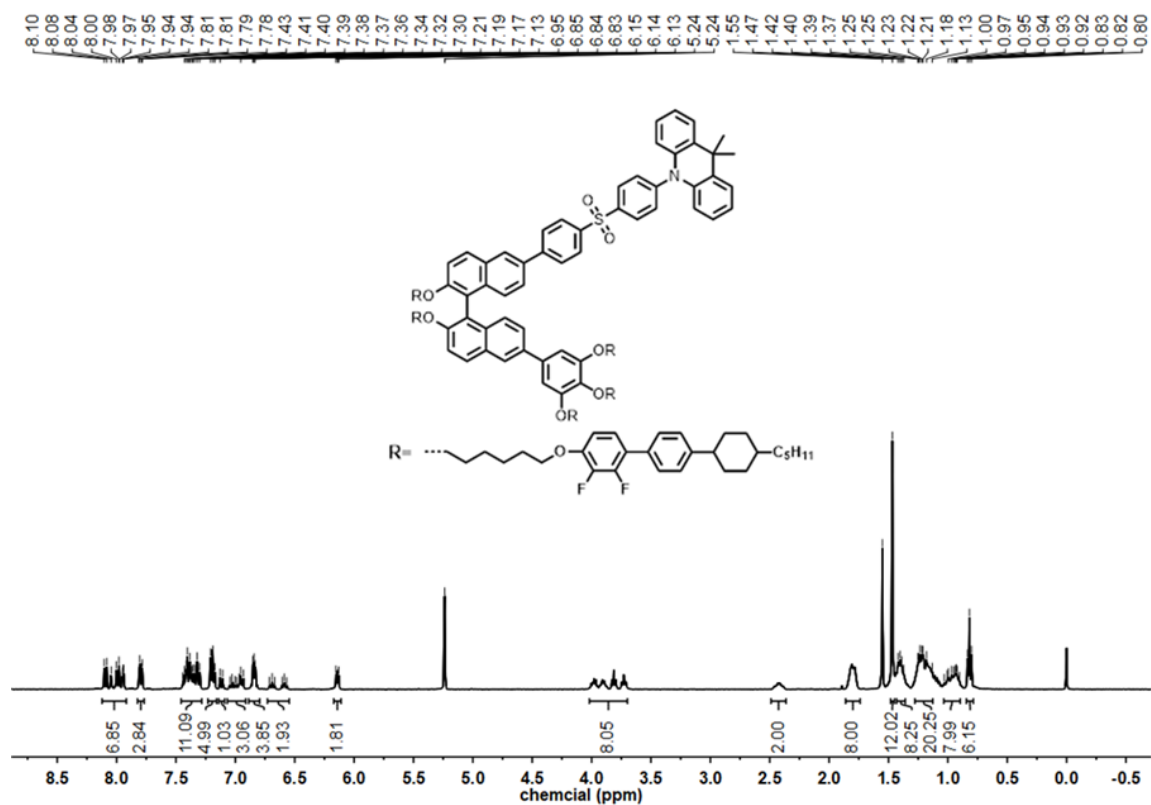


Figure S7. ^1H NMR spectrum of *R*-3 in CD_2Cl_2 .

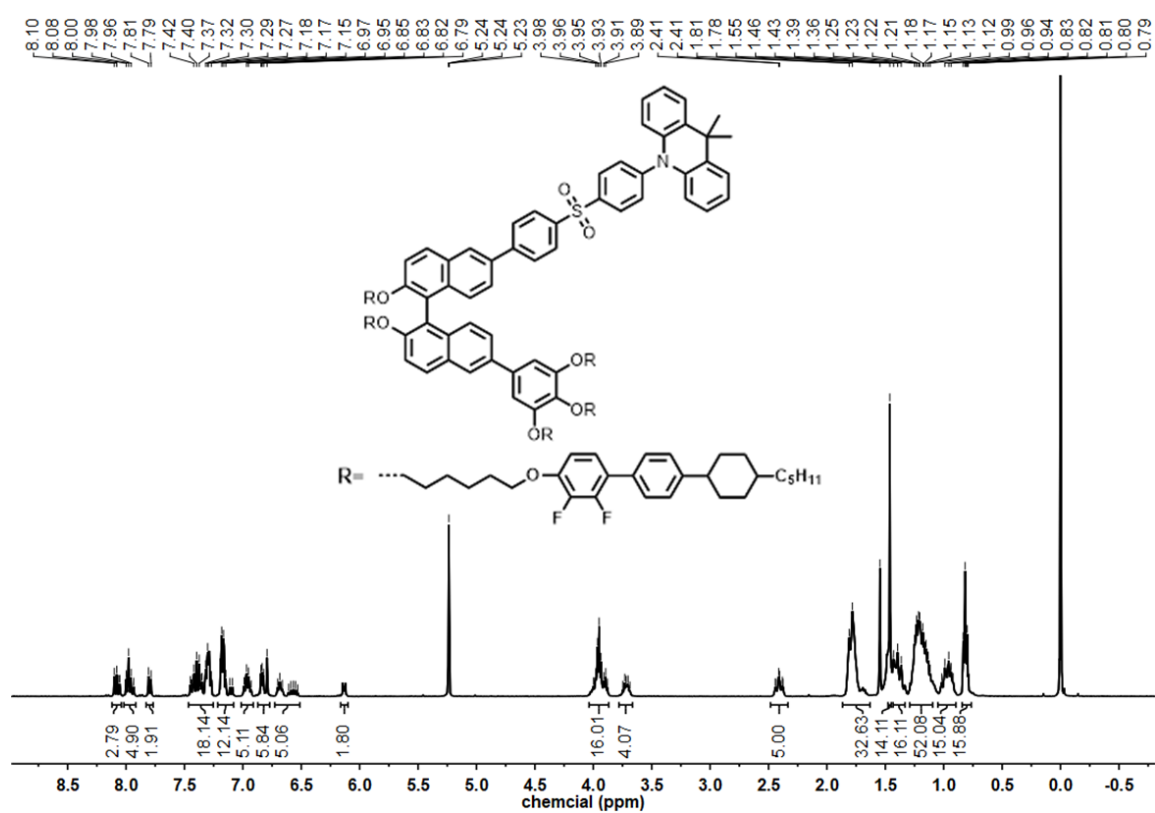


Figure S8. ^1H NMR spectrum of *S*-3 in CD_2Cl_2 .

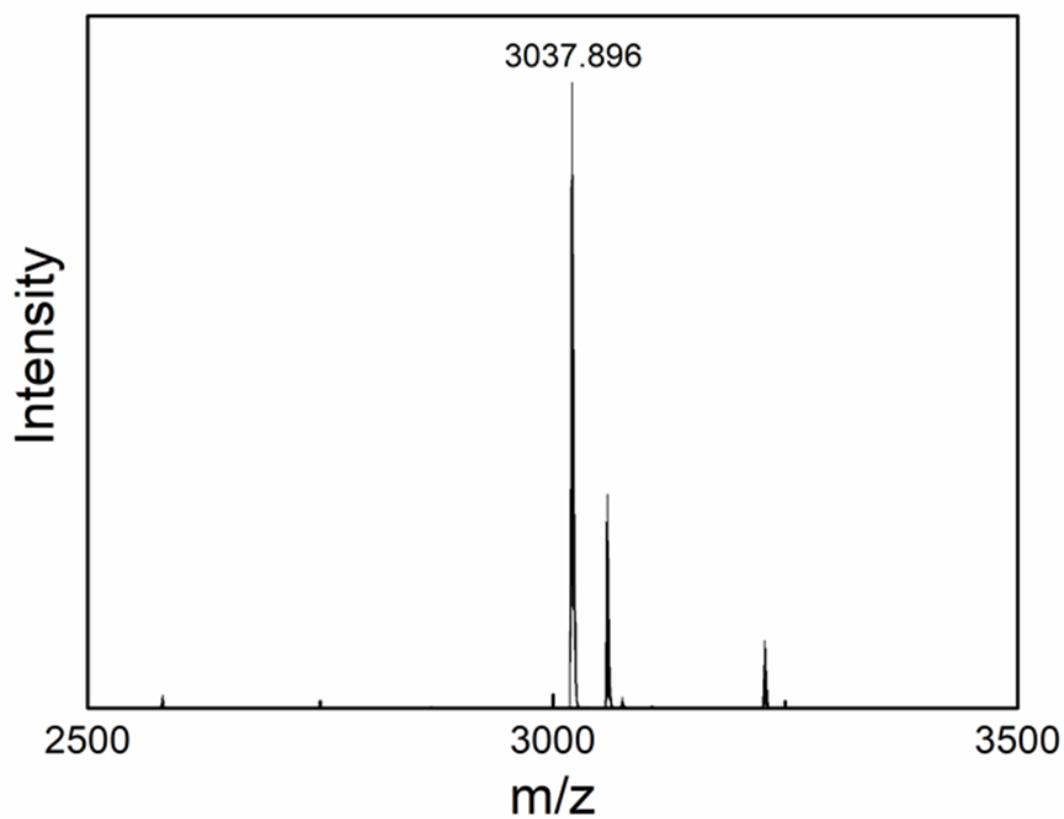


Figure S9. Mass spectrum of *R*-3.

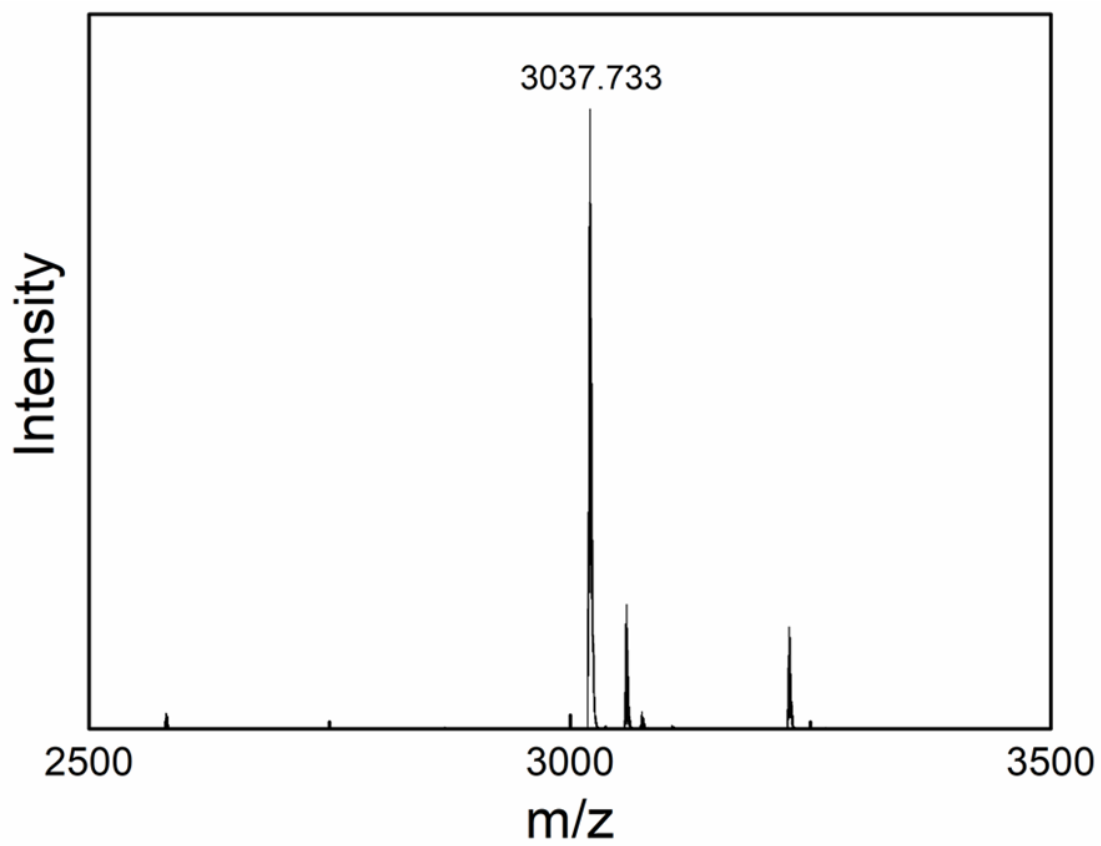


Figure S10. Mass spectrum of *S*-3.

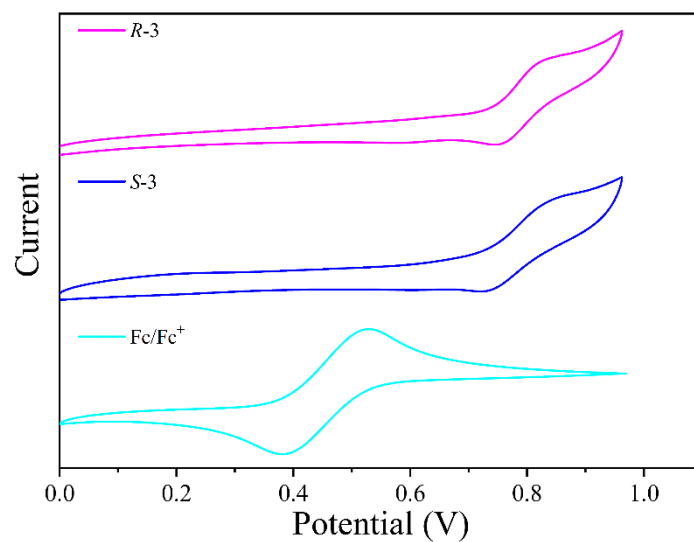


Figure S11. CV curves of *R/S*-3 in CH₃CN solution.

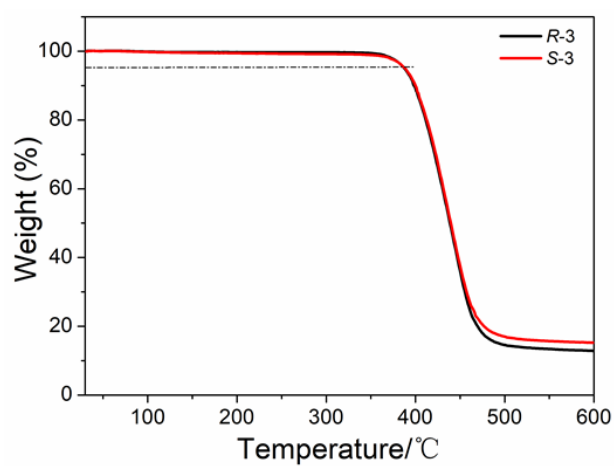


Figure S12. TGA curves of the *R/S*-3.

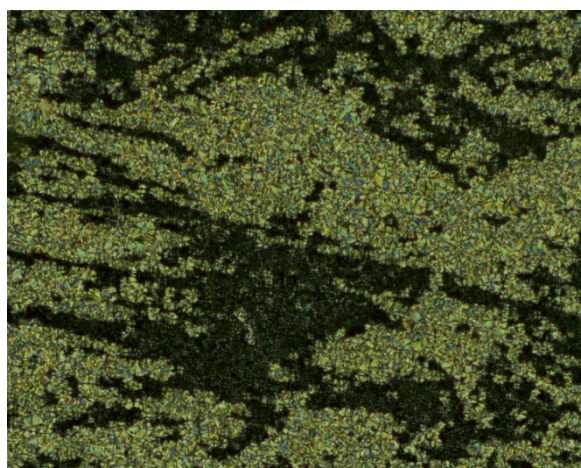


Figure S13. Optical texture of *R*-3 in the SmA₂* phase at 136 °C.

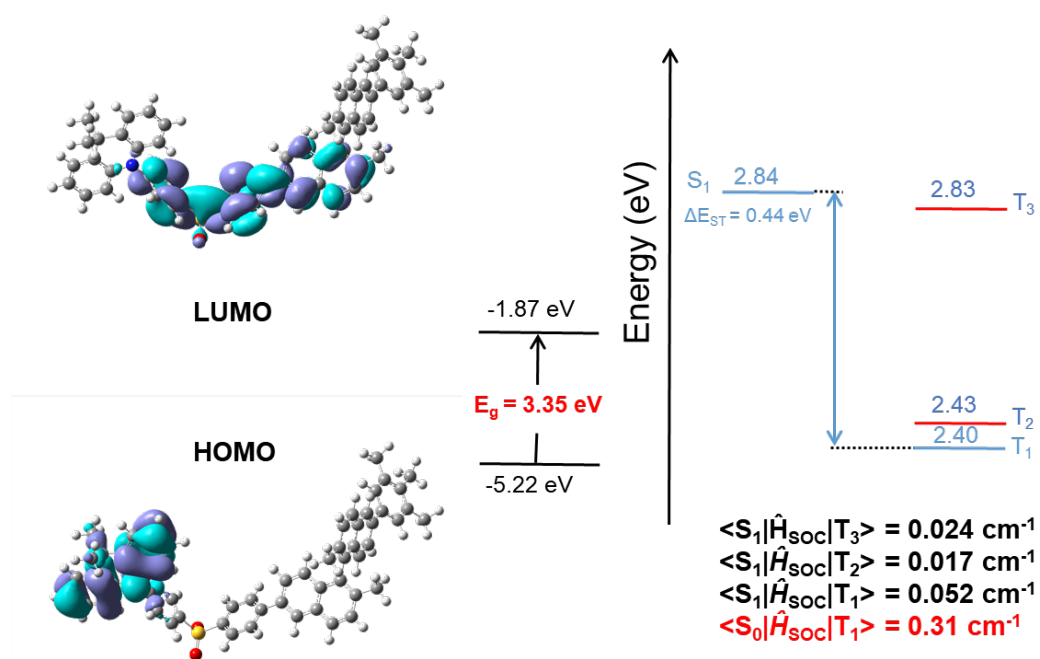


Figure S14. Theoretical calculation diagram of *R/S*-3

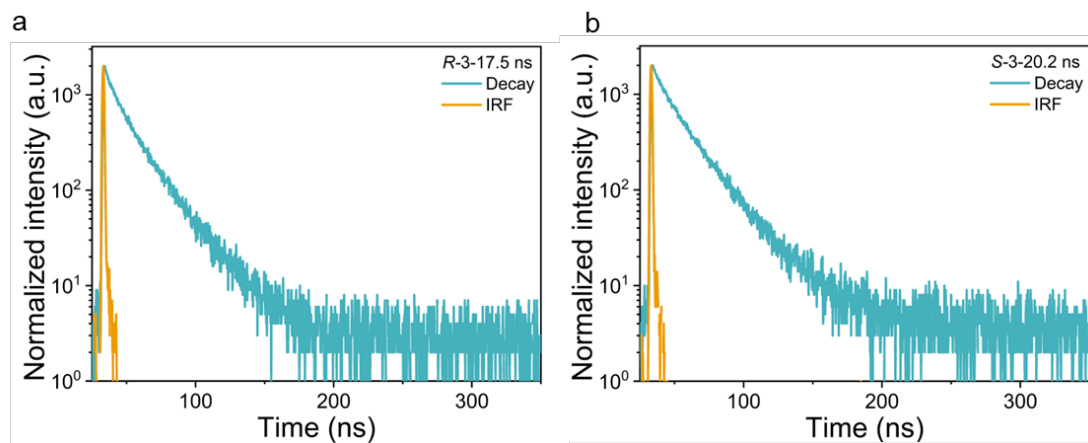


Figure S15. Time-resolved emission in doped PMMA films ($\lambda_{ex} = 350$ nm).

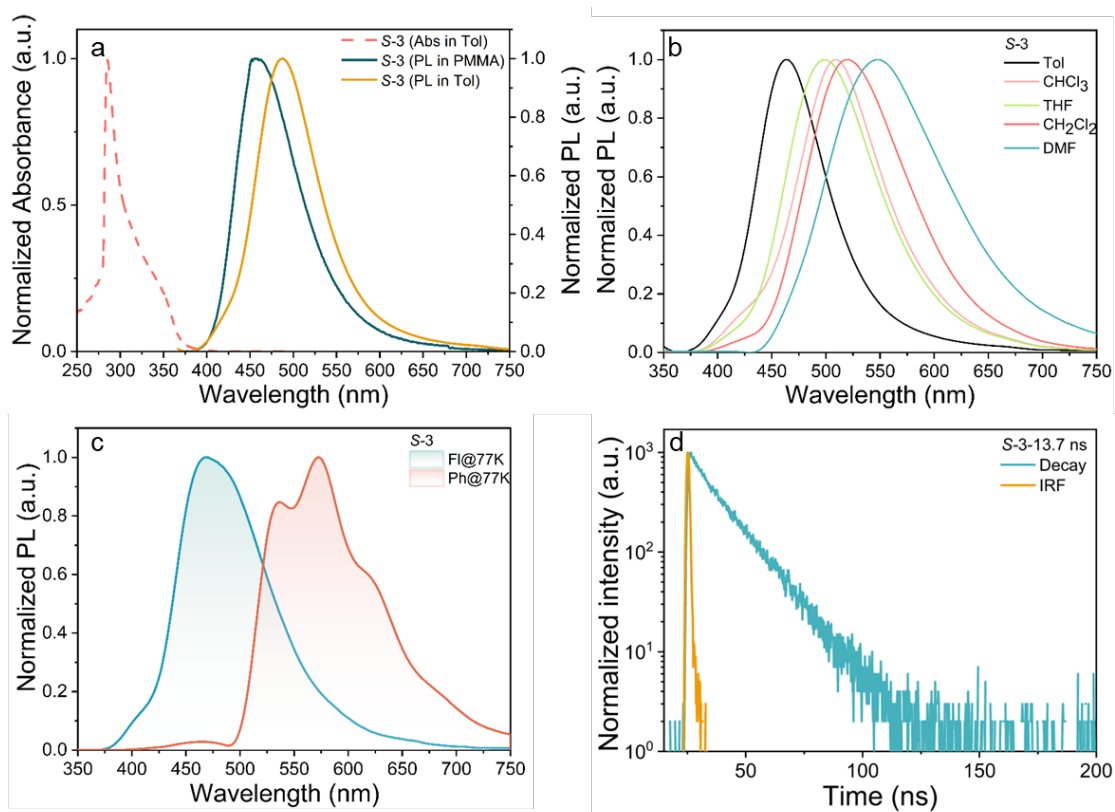


Figure S16. Photophysical properties of **S-3**. a) normalized UV absorption and PL spectra in toluene solution (10^{-5} mol dm $^{-3}$) and doped PMMA film; b) PL spectra in different solvents; c) low temperature fluorescence and phosphorescence spectra in toluene solution. d) time-resolved emission of time-resolved emission o in toluene solution (10^{-5} M) ($\lambda_{\text{ex}} = 350$ nm).

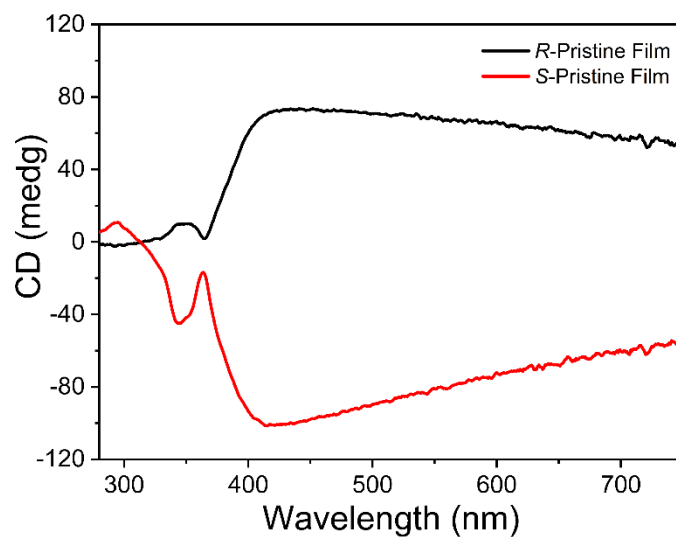


Figure S17. The CD spectra of *R/S*-3 in neat film by spin coating.

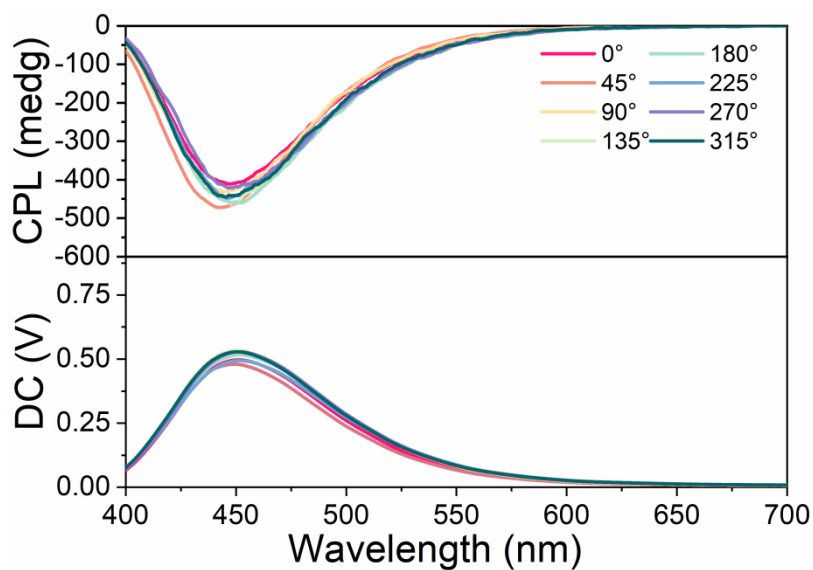


Figure S18. The CPL spectra of *S-3* in pristine film with different rotation angles at room temperature.

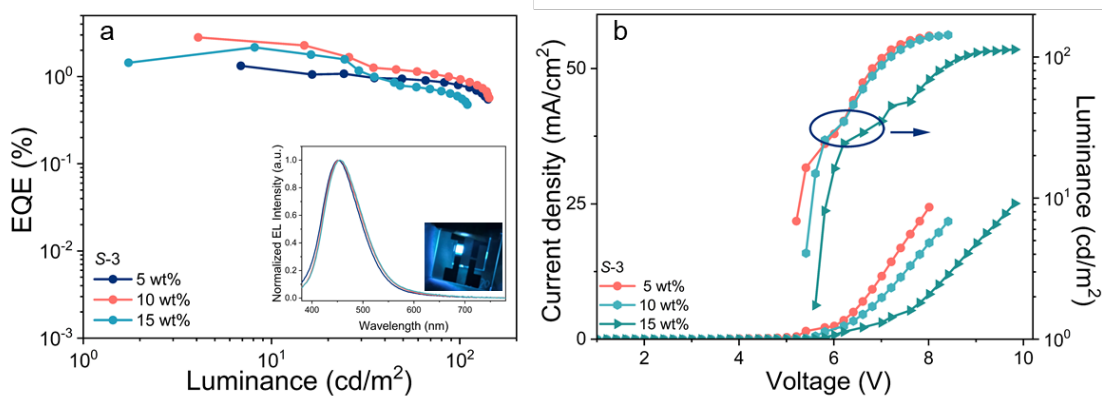


Figure S19. Device data for *S-3*. a) The EQE-value versus luminance. Inset: EL spectra and device photo; b) Current density -voltage-luminance (J-V-L).

Table S1. Physical data of *R/S-3*.

compound	$\lambda_{\text{abs}}^{\text{a}}$ (nm)	$\lambda_{\text{em}}^{\text{a}}$ (nm)	$\lambda_{\text{Fl}}^{\text{b}}$ (nm)	$\lambda_{\text{Ph}}^{\text{b}}$ (nm)	$\Delta E_{\text{ST}}^{\text{b}}$ (eV)	$\tau_{\text{PF}}^{\text{c}}$ (ns)	<i>PLQY</i> ^c (%)	g_{PL}^{d} (10 ⁻²)	g_{PL}^{e} (10 ⁻¹)	$E_{\text{g}}^{\text{opt}}$ (eV)
<i>R-3</i>	350	466	469	539,572	0.47	19.5	33.7	2.6	1.31	3.28
<i>S-3</i>	350	465	469	537,572	0.50	19.3	34.6	3.5	1.36	3.29

^aIn toluene solution (10⁻⁵ M) at room temperature; ^bin toluene solution (10⁻⁵ M) at 77K; ^c10 wt % in PMMA at room temperature; ^din neat film at room temperature; ^ein neat film after annealing process.

Table S2. EL data for the devices.

Material	Dopant /wt%	V_{ON} /V	L_{max} /cd m ⁻²	CE_{max} /cd A ⁻¹	EQE_{max} /%	CIE (x, y)	Peak /nm
<i>R-3</i>	5%	5.2	140.6	1.74	1.72	(0.16,0.14)	450
	10%	5.4	105.8	2.74	2.52	(0.15,0.14)	454
	15%	5.6	106.0	2.46	2.19	(0.15,0.15)	454
<i>S-3</i>	5%	5.2	141.1	1.12	1.08	(0.15,0.14)	450
	10%	5.4	143.1	1.87	1.66	(0.16,0.15)	456
	15%	5.6	112.9	2.43	2.16	(0.16,0.16)	456