

Supporting Information

Liquid Crystal Circularly Polarised TADF Emitters for High Efficiency, Solution-Processable Organic Light-Emitting Diodes

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General information

Unless other noted, all reagents used in the experiments were purchased from commercial sources without further purification. For column chromatography, silica gel with 200 ~ 300 mesh was used.

In order to determine the structure of the compound, ^1H NMR was acquired using a Bruker Dex-300/400/500 NMR instrument using CD_2Cl_2 as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using benzhydrol as a matrix. Thermogravimetric analysis (TGA) was detected with a NETZSCH STA449 at a $20^\circ\text{C}/\text{min}$ heating rate under N_2 atmosphere. UV-vis absorption spectra were recorded on a Shimadzu UV-1650PC. Steady-state fluorescence/phosphorescence spectra PL spectra were carried out by using Edinburgh FLS1000 fluorescence spectrophotometer. The CPL and CD spectra of the compound were measured in the film state, and the films for chiroptical property were prepared by drip film method. The preparation process for the films is as follows: the compound was dissolved in dichloromethane and slowly added to the quartz glass substrate, and the pure film was obtained after drying. CD and CPL spectra were measured on JASCO J-1500 and JASCO CPL-200 spectrophotometers, respectively. The film thickness was measured by Dektak-XT probe surface profiler, and the film thickness is about 30 nm. In this paper, the circular polarisation spectrum of the compound in the film state was tested. The films for chiroptical property were fabricated as regular neat films in a drop film manner. The sample preparation process was as follows: the compound was dissolved in dichloromethane and slowly added to the quartz glass substrate, and the pure film

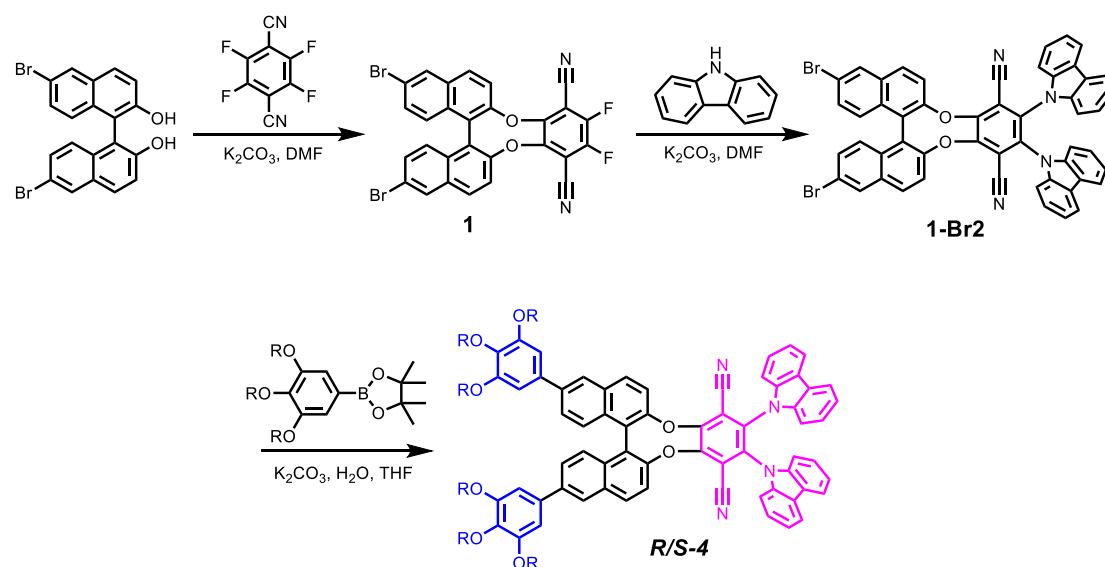
was obtained after drying. Polarised optical microscopy (POM) was carried out using an Olympus BX50 Optical Microscope equipped with a Linkam Scientific LTS350 heating stage, Linkam LNP2 cooling pump, and Linkam TMS92 controller. Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a bespoke temperature-controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was CuK_a ($\lambda = 0.154056$ nm) from a 1 μ s microfocus source. Diffraction patterns were recorded on a 2048 x 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.

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, PEDOT: PSS was used as hole injection material. TmPyPB and LiF were used as electron transport and injection materials, respectively. ITO (indium tin oxide) and Al (aluminium) were used as anode and cathode materials, respectively. 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 cm^2 . The thermally evaporated deposition rates were $0.6\text{-}1 \text{ \AA s}^{-1}$ for the TmPyPB, 0.1 \AA s^{-1} for LiF and $1.5\text{-}1.8 \text{ \AA s}^{-1}$ 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 SourceMeter unit under ambient atmosphere at room temperature.

Synthetic procedures and characterisation data

Synthetic procedures



Scheme S1. *R/S*-4 synthesis route.

Synthesis of Compound 1: *R/S* 6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol (0.5 g, 1.1 mmol), 2,3,5,6-tetrafluorophenyl dimethyl nitrile (0.2 g, 1.1 mmol), potassium carbonate (0.3 g, 0.3 g) were added to a 50 mL single-mouth bottle. 2.3 mmol), 8 mL anhydrous *N,N*-dimethylformamide, the reaction system was replaced with nitrogen for three times and reacted at room temperature for 12 hours. The monitoring reaction was complete. Carbazole (0.5 g, 2.8 mmol) and potassium carbonate (0.8 g, 5.7 mmol) were added again, and nitrogen was replaced again and the reaction was continued at room temperature for 12 hours. After the reaction, water was added and extracted with CH_2Cl_2 (3×15 mL), washed with water (3×30 mL), dried with anhydrous magnesium sulfate, filtered and collected the filtrate, and the solvent was removed with a rotary evaporator. Using PE and CH_2Cl_2 (volume ratio 1:1) as eluent, 0.56 g of white solid was obtained by column chromatography, and the yield was 55%. 1H NMR (400 MHz,

CD₂Cl₂) δ (ppm) 8.19 (d, J = 1.9 Hz, 2H), 8.05 (d, J = 8.9 Hz, 2H), 7.76-7.68 (m, 4H), 7.63 (d, J = 7.7 Hz, 2H), 7.49 (dd, J = 9.0, 2.0 Hz, 2H), 7.31 (d, J = 9.0 Hz, 2H), 7.22-7.17 (m, 2H), 7.15-7.09 (m, 4H), 6.93 (td, J = 7.5, 1.2 Hz, 2H), 6.77 (ddd, J = 14.8, 11.0, 4.5 Hz, 4H).

Synthesis of compound **R/S-4**: Add 2, 3-difluoro-4-ethoxyphenylboronic acid (10.0 g, 50.0 mmol), 1-iodo-4-(4-pentyl cyclohexyl) benzene (18.0 g, 50.0 mmol), tetra triphenylphosphine (0.5 g, 0.5 g) to a 250 mL single-mouth bottle. 0.5 mmol, 2.0 mol/L potassium carbonate aqueous solution (30 mL), 40 mL ethanol and 180 mL toluene, and the reaction system was reflowed at 80 °C for 24 h after replacing nitrogen gas (3 times). After cooling, the solvent was removed with a rotary evaporator, and after adding water, the solvent was extracted with dichloromethane (CH₂Cl₂) (3×60 mL), washed with water (3×80 mL), dried with anhydrous magnesium sulfate, filtered and collected for solvent removal. Using PE and CH₂Cl₂ (volume ratio 1:2) as eluent, white solid was obtained by column chromatography, **R-4** was 0.22 g, **S-4** was 0.26 g, and the yield was 55% and 61%, respectively. **R-4**: ¹H NMR (400 MHz, CD₂Cl₂) δ (ppm) 8.18 (d, J = 9.0 Hz, 4H), 7.69 (ddd, J = 17.1, 13.0, 7.8 Hz, 8H), 7.56 (d, J = 8.9 Hz, 2H), 7.29 (dd, J = 8.1, 1.6 Hz, 12H), 7.24-7.09 (m, 18H), 7.01-6.91 (m, 8H), 6.88 (s, 4H), 6.82-6.65 (m, 10H), 4.07-3.91 (m, 24H), 2.40 (ddd, J = 12.1, 7.4, 2.8 Hz, 6H), 1.86-1.69 (m, 48H), 1.59-1.48 (m, 22H), 1.37 (dd, J = 17.4, 7.7 Hz, 12H), 1.30-1.09 (m, 58H), 1.03-0.92 (m, 12H), 0.81 (t, J = 7.0 Hz, 18H). TOF-MS (ESI) m/z calcd for C₂₃₉H₂₆₈F₁₂N₄O₁₄: 3648.77; [M+H]⁺ found: 3649.222. **S-4**: ¹H NMR (400 MHz, CD₂Cl₂) δ (ppm) 8.18 (d, J = 8.9 Hz, 4H), 7.77-7.62 (m, 8H), 7.56 (d, J = 8.8 Hz, 2H),

7.29 (d, $J = 6.8$ Hz, 12H), 7.24-7.10 (m, 18H), 7.01-6.91 (m, 8H), 6.88 (s, 4H), 6.83-6.65 (m, 10H), 3.99 (ddt, $J = 19.7, 13.2, 6.4$ Hz, 24H), 2.40 (t, $J = 11.1$ Hz, 6H), 1.87-1.69 (m, 48H), 1.57-1.47 (m, 22H), 1.43-1.33 (m, 12H), 1.29-1.11 (m, 58H), 1.03-0.92 (m, 12H), 0.81 (t, $J = 7.0$ Hz, 18H). TOF-MS (ESI) m/z calcd for $C_{239}H_{268}F_{12}N_4O_{14}$: 3648.77; $[M+H]^+$ found: 3649.235.

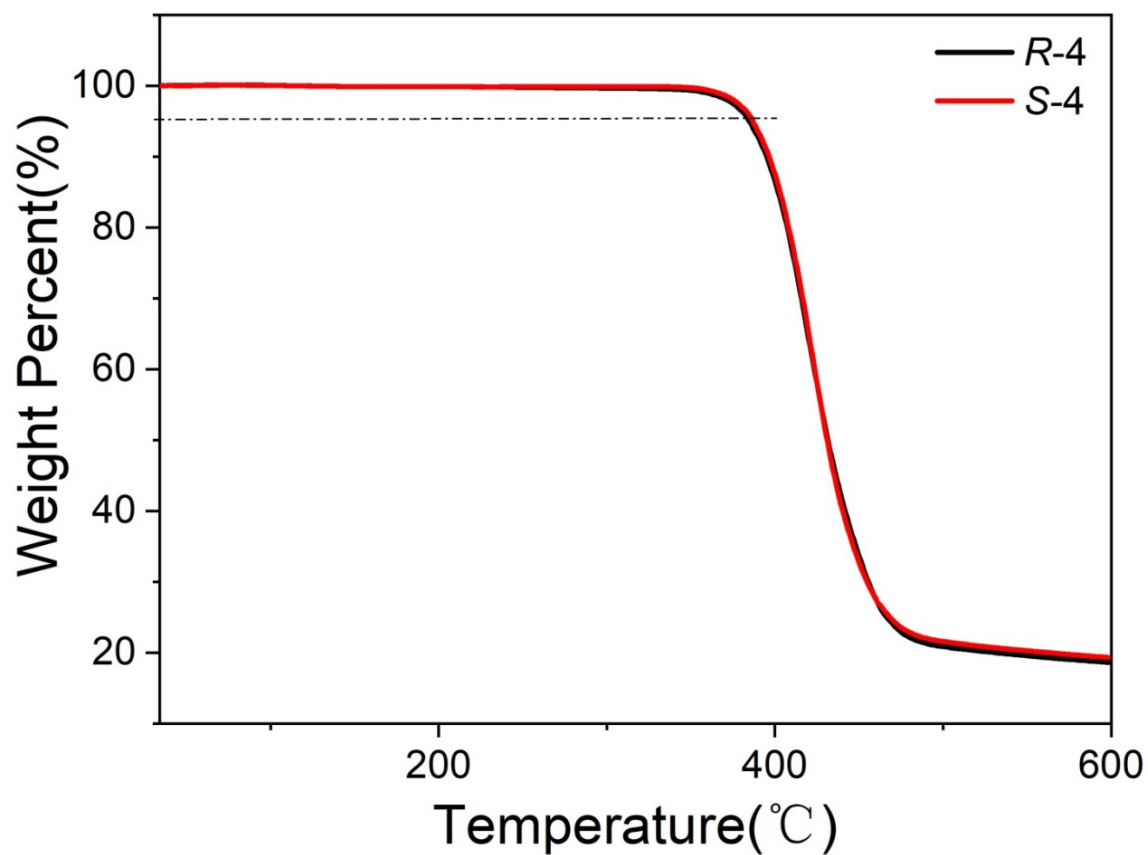


Figure S1. TGA curves of the emitters in N₂ with the heating rate of 20 °C min⁻¹.

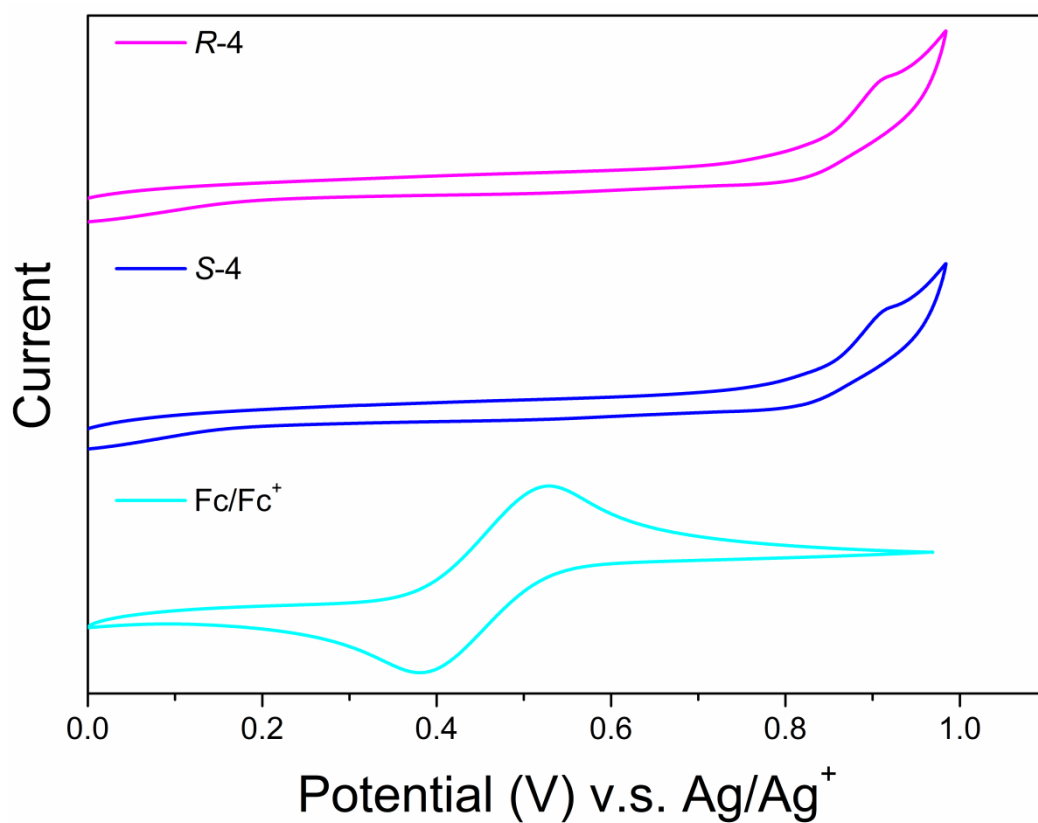


Figure S2. CV curves of target compounds *R/S-4* in CH₂Cl₂ solution.

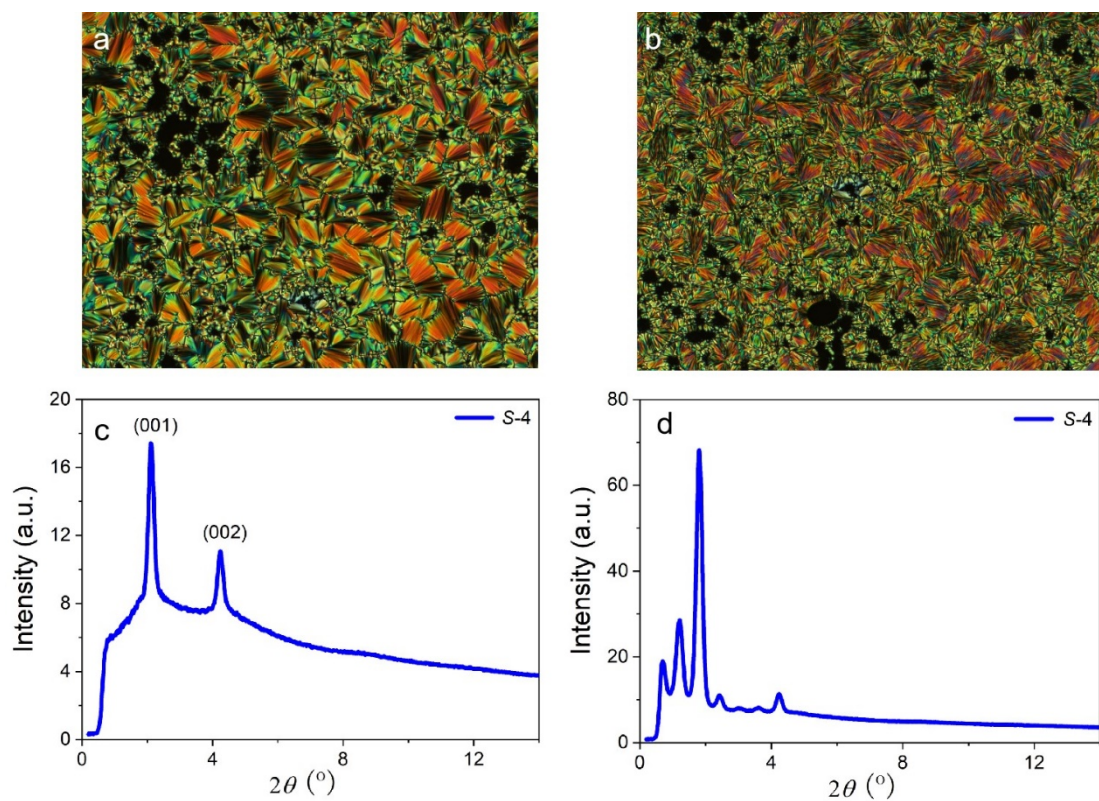


Figure S3. POM image of the SmA* phase of **S-4** on cooling at a) 182 °C and b) 155 °C. c) and d) SAXS pattern of **S-4** on cooling process at 173 °C.

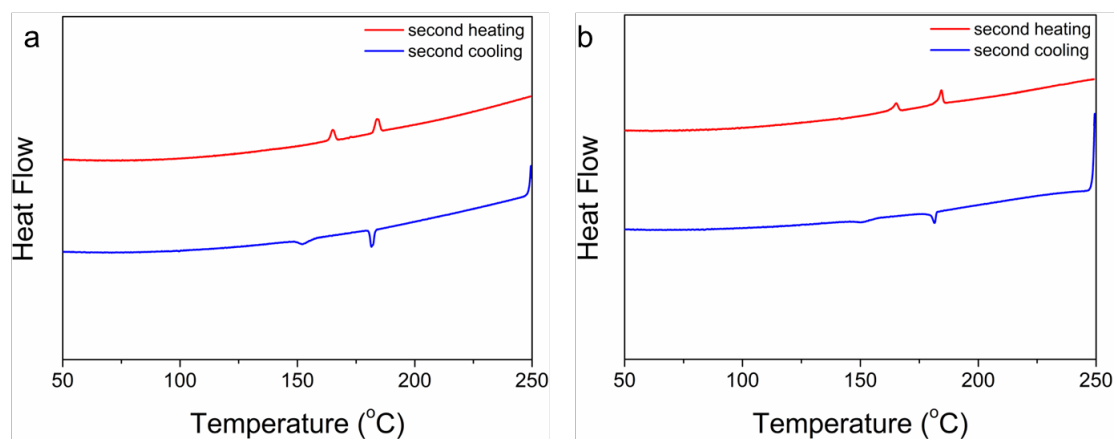


Figure S4. DSC curves of (a) **R-4** and (b) **S-4** with a heating/cooling rate of 10 °C min⁻¹. The data show a small hysteresis in the onset temperatures on cooling for the transition between the SmA* and the more ordered, lower-temperature mesophase, reflecting the more ordered nature of the latter.

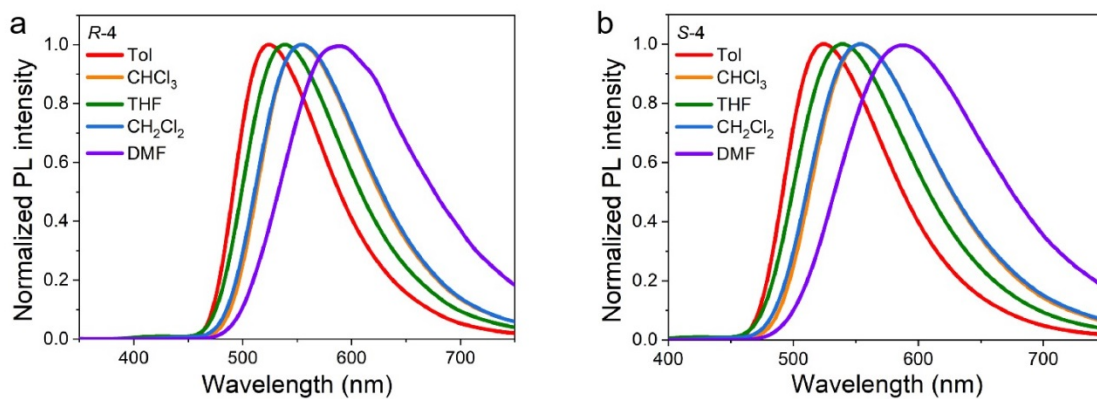


Figure S5. Emission spectra of a) *R-4* and b) *S-4* in different solvents (10^{-5} M).

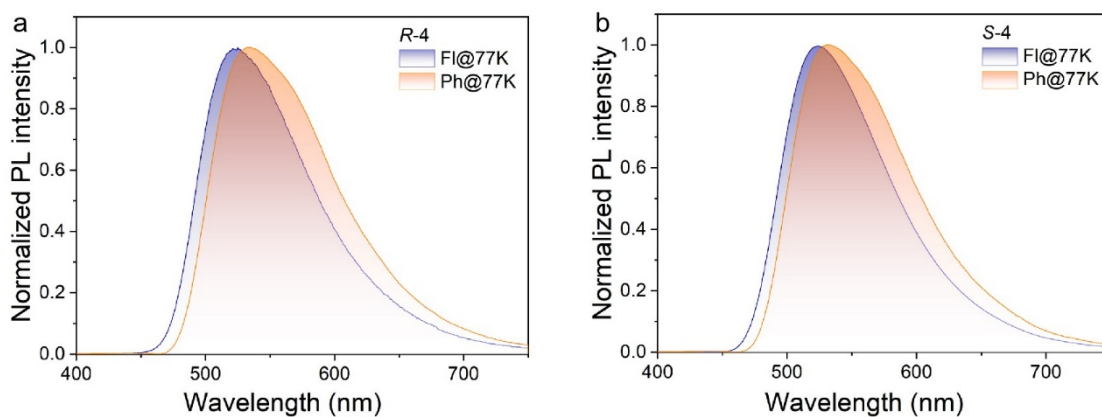


Figure S6. Low temperature fluorescence (FI) and phosphorescence (Ph) of a) *R-4* and b) *S-4* measured in toluene solution (10^{-5} M)

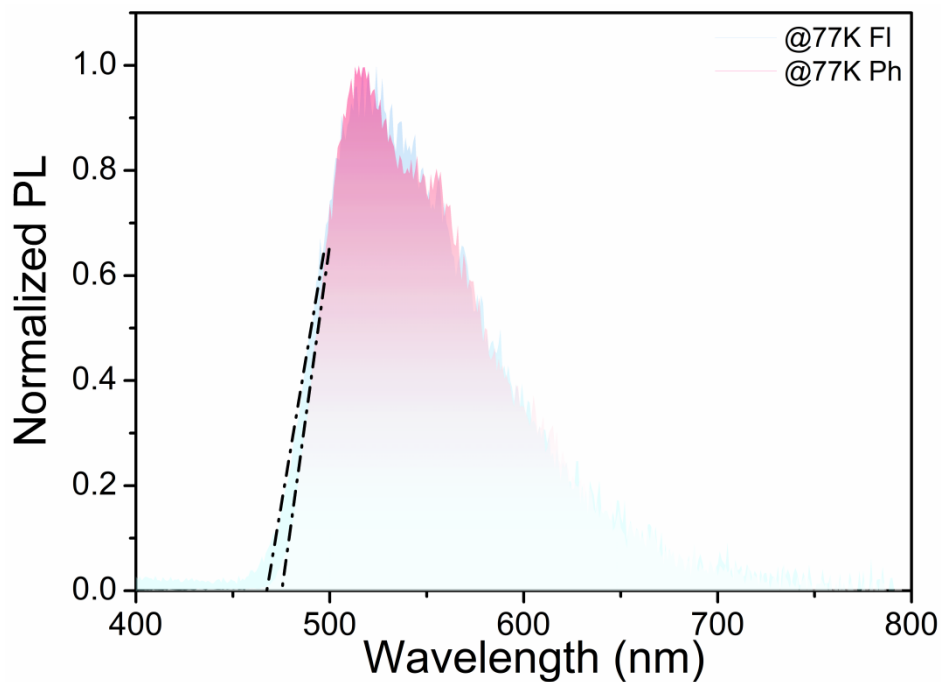


Figure S7. Low temperature fluorescence (FI) and phosphorescence (Ph) spectra of *S-4* doped in mCP film

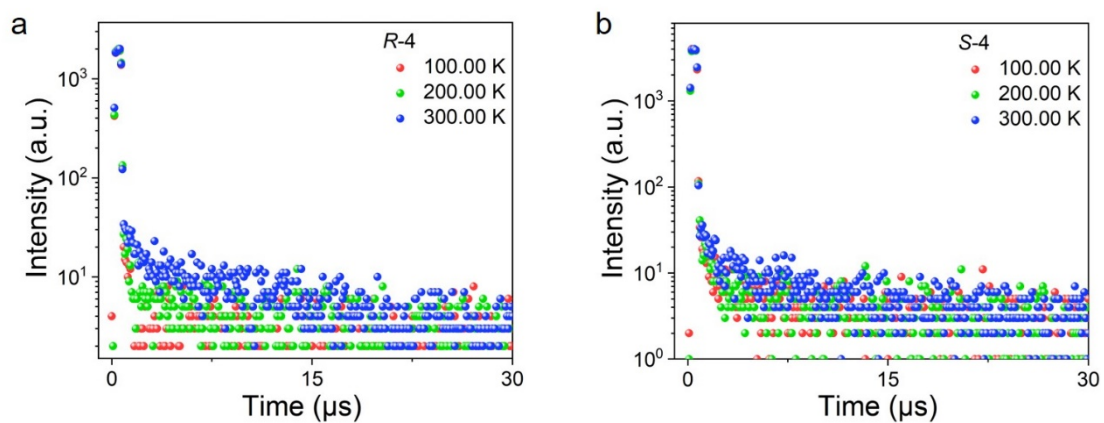


Figure S8. Transient PL decay curves of a) *R-4* and b) *S-4* in neat films with variable temperature.

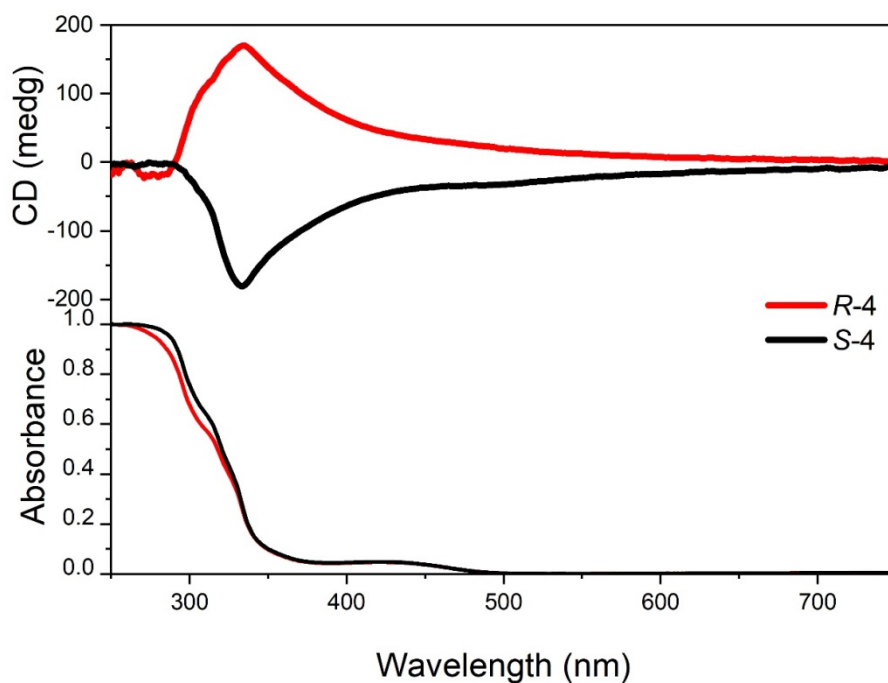


Figure S9. CD spectrum and absorption spectrum of *R/S-4* in neat films at room temperature.

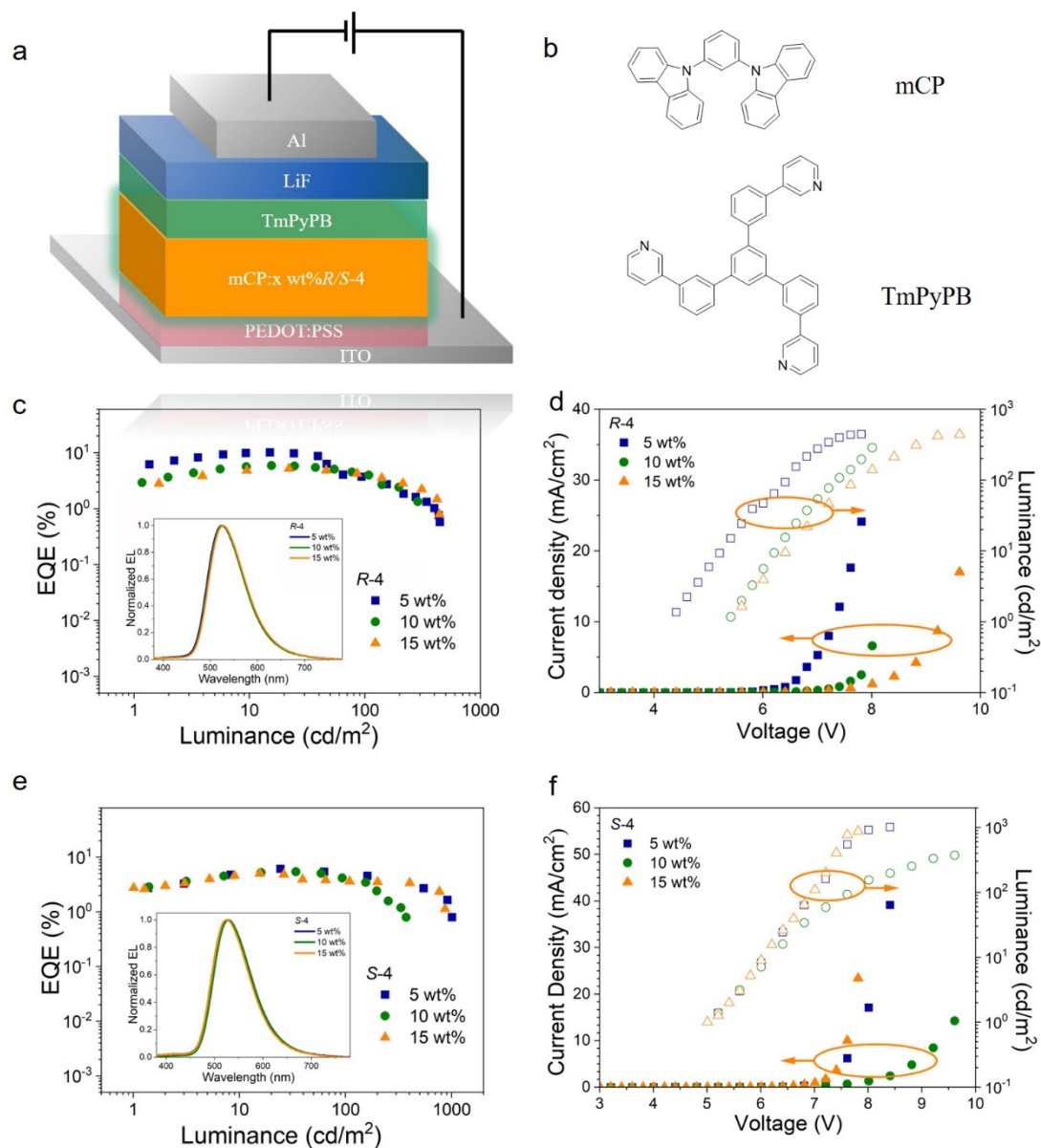


Figure S10. a) Device architecture and b) materials used in the devices; c) and e) EQE-current density (inset: EL spectra of the devices) of *R/S-4*; d) and f) Current density–voltage–luminance curves of *R/S-4*.

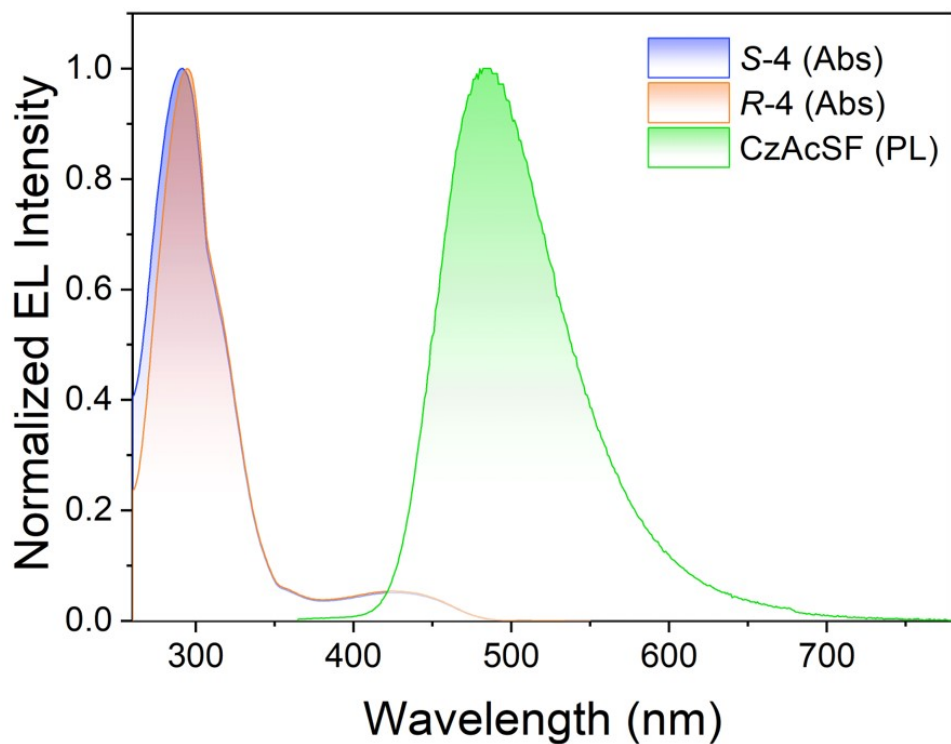


Figure S11. The photoluminescence (PL) and absorption (UV) spectra of CzAcSF and *R/S-4* in films.

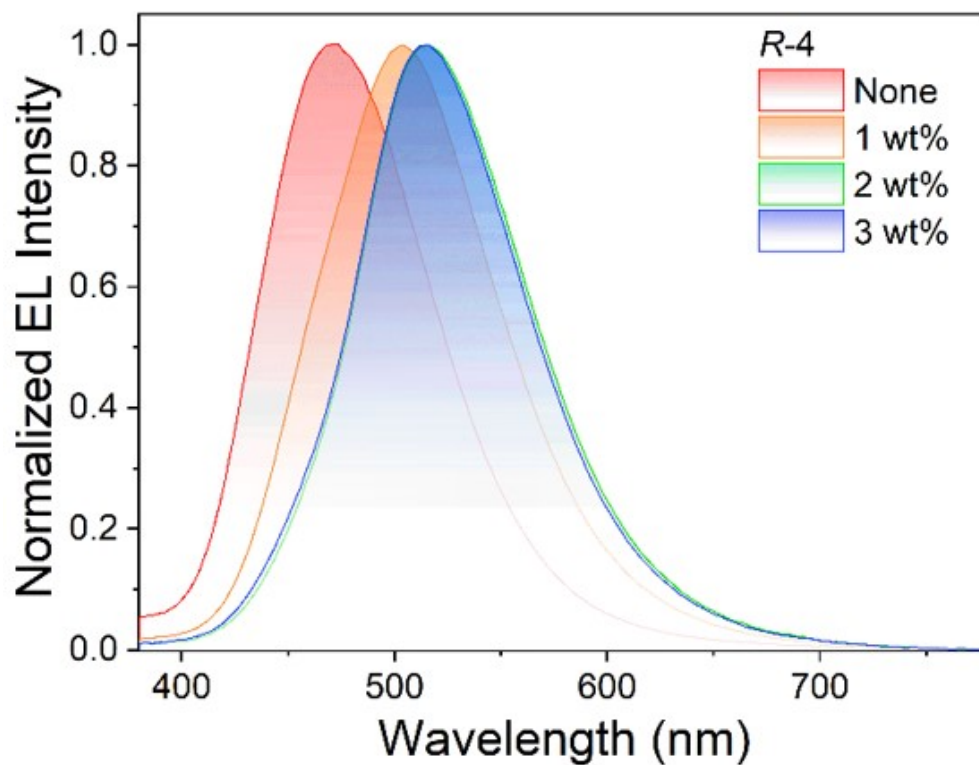


Figure S12. EL spectra of the change in the concentration of *R-4* when the sensitizer concentration was held at 30 wt%.

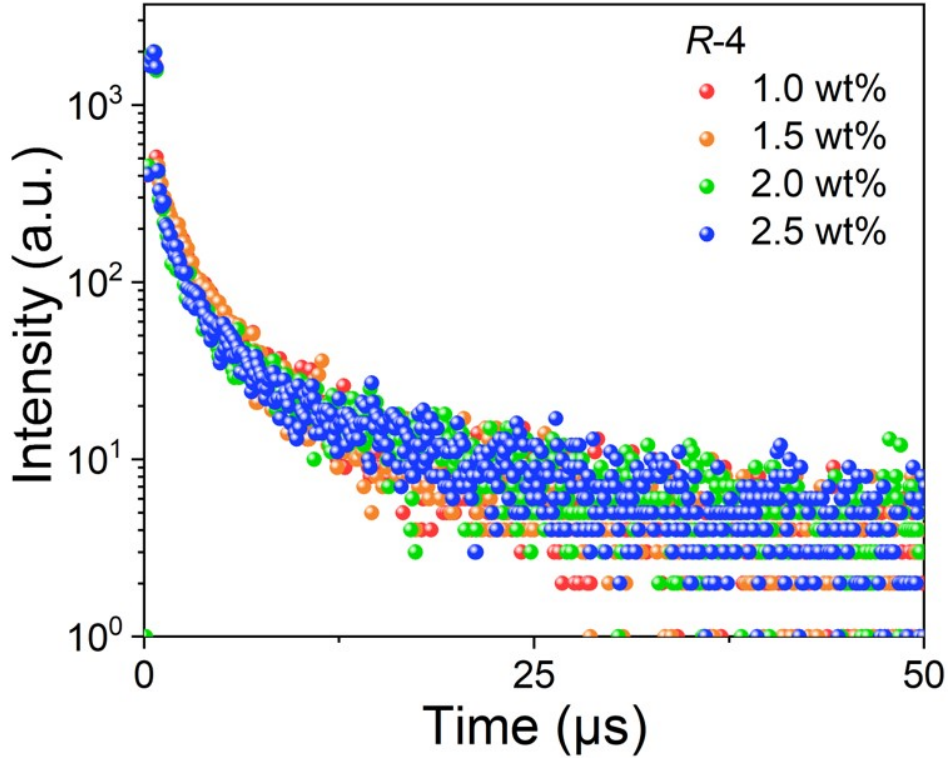


Figure S13. Transient PL decay curves of co-doped films of *R-4* doped with different concentrations.

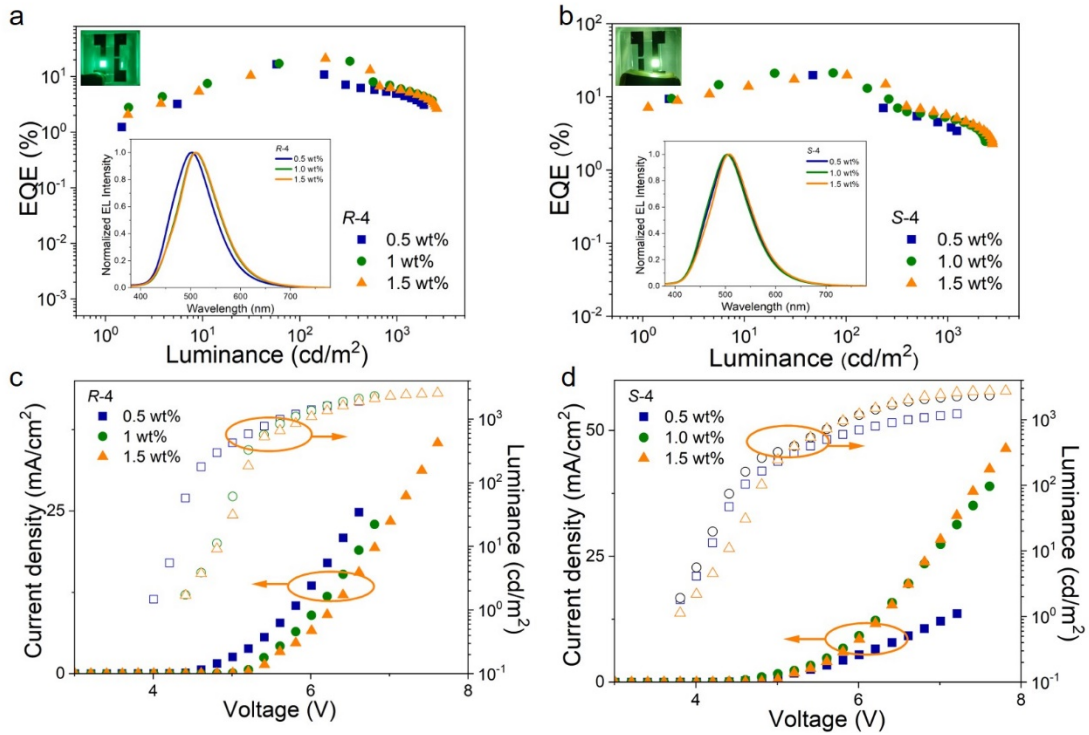


Figure S14. a) and b) EQE-current density (inset: EL spectra of the devices); c) and d) Current density–voltage–luminance curves of *R/S-4*.

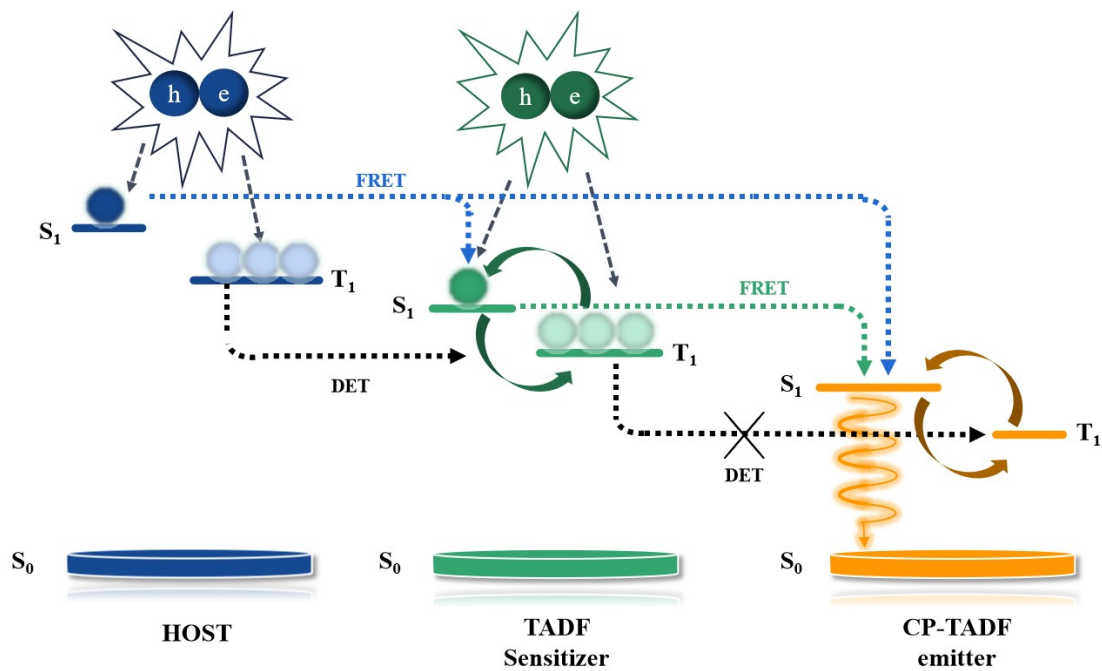


Figure S15. Mechanism of sensitisation.

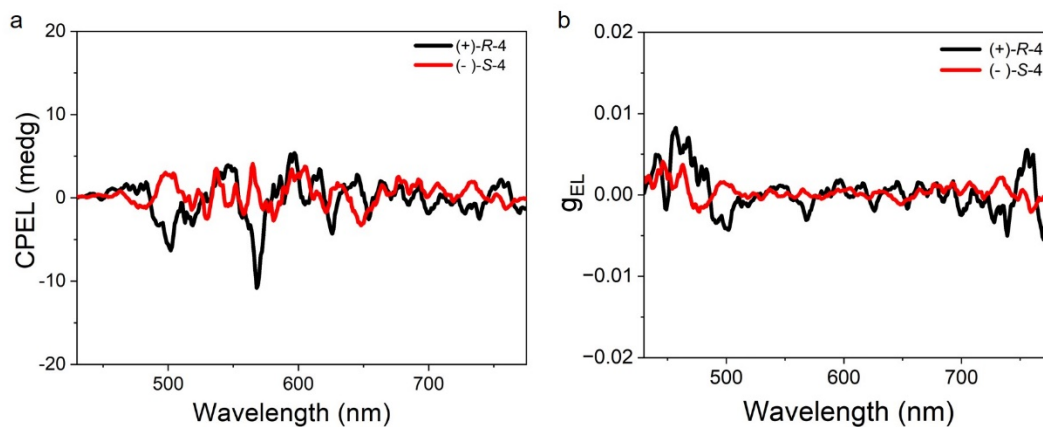


Figure S16. a) CPEL spectra and b) g_{EL} values of CPEL versus wavelength of (+)-*R*-4/ (-)-*S*-4 in device ($\lambda_{ex} = 340$ nm).

Table S1. Calculated the SOC constant of the molecules.

Compound	$\langle S_1 H_{soc} T_1 \rangle$	$\langle S_1 H_{soc} T_2 \rangle$	$\langle S_1 H_{soc} T_3 \rangle$
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
R-4	0.552 cm	0.255	0.181

Table S2. Thermal data of the emitters.

Compound	$T/^\circ\text{C}$	Transition	$\Delta H/\text{J g}^{-1}$
R-4	164.9	Cr-SmA*	2.0
	184.8	SmA*-Iso	3.2
S-4	165.1	Cr-SmA*	1.8
	184.3	SmA*-Iso	2.7

Transition temperature and enthalpy measured during the second heating process at 20 °C/min.

Table S3. Summary of photophysical parameters for 5 wt% **R/S-4** doped into mCP at various concentration

Compound	τ_p/Φ_p	τ_d/Φ_d	PLQY	k_p	k_d	k_{ISC}	k_{rISC}	k_r	k_{nr}
	(ns)/%	(μs)/%	(%)	(10 ⁷ s ⁻¹)	(10 ⁵ s ⁻¹)	(10 ⁷ s ⁻¹)	(10 ⁵ s ⁻¹)	(10 ⁷ s ⁻¹)	(10 ⁵ s ⁻¹)
R-4	13.69/44.72	4.4/6.58	51.3	7.31	2.27	4.04	0.60	3.27	2.00
S-4	13.60/39.78	4.7/13.92	53.7	7.35	2.13	4.43	1.24	2.93	1.64

Notes: Measured In 5 wt % doped in mCP films.

$$k_p = \frac{1}{\tau_p} \quad (1)$$

$$k_d = \frac{1}{\tau_d} \quad (2)$$

$$k_{ISC} = (1 - \Phi_p)k_p \quad (3) \quad k_{rISC} = \frac{k_p k_d \Phi_d}{k_{ISC} \Phi_p} \quad (4)$$

$$k_r = \frac{\Phi_p}{\tau_p} \quad (5) \quad k_{nr} = k_d - \Phi_p k_{rISC} \quad (6)$$

Herein, τ_p and τ_d are the lifetime of prompt and delayed components. Φ_p and Φ_d are the prompt and delayed luminescence quantum efficiency, respectively. The k_p and k_d are the rate constant of prompt and delayed fluorescence. k_{ISC} is the rate constant of intersystem crossing, while k_{rISC} is the rate constant of reverse intersystem crossing between the S_1 and T_1 . k_r and k_{nr} are the radiative and nonradiative decay rate constant from S_1 to S_0 , respectively.

Table S4. Unsensitized device data for *R/S-4*

	V_{on}	L_{max}	CE_{max}	EQE_{max}	Peak	FWHM	CIE	
Dopant	(V)	(cd/m ²)	(cd/A)		(nm)			
	5 wt%	4.4	444.9	32.5	10.1	524	90.2	(0.31,0.56)
R-4	10 wt%	5.4	286.9	19.6	5.9	524	88	(0.31,0.57)
	15 wt%	5.6	441.4	17.5	5.2	528	89.2	(0.32,0.57)
	5 wt%	5.2	1007	20.1	6.1	528	91.0	(0.31,0.56)
S-4	10 wt%	5.2	372.9	18.2	5.4	528	90.3	(0.33,0.57)
	15 wt%	5.0	866.3	15.8	5.0	528	90.0	(0.31,0.56)

(Device structure is ITO/ PEDOT:PSS/ mCP: *x* wt% *R/S-4* (50 nm)/ TmPyPB (45 nm)/ LiF (0.5 nm)/ Al (120 nm))

Table S5. Sensitized device for changing the concentration of *R-4*

	V_{on}	L_{max}	CE_{max}	EQE_{max}	Peak	FWHM	CIE
Dopant	(V)	(cd/m ²)	(cd/A)		(nm)		
10 wt%	4.0	1998	19.46	6.61	508	100.5	(0.22,0.40)
20 wt%	4.0	2097	42.26	15.18	504	100.4	(0.21,0.38)
30 wt%	3.8	2238	51.74	18.27	504	99.5	(0.21,0.40)

(Device structure is ITO/ PEDOT:PSS/ mCP:*x* wt% CzAcSF: 1 wt% *R-4* (50 nm)/ TmPyPB (45 nm)/ LiF (0.5 nm)/ Al (120 nm))

Table S6. Sensitized device data for *S-4*.

Device	V_{on}	L_{max}	CE_{max}	EQE_{max}	Peak	FWHM	CIE
	(V)	(cd/m ²)	(cd/A)		(nm)		
S4	3.8	2737	58.3	19.7	508	95	(0.23,0.43)
S5	3.8	1223	54.8	19.8	504	97.6	(0.22,0.41)
S6	3.8	2341	60.3	21.2	504	98	(0.21,0.40)

(Device structure is ITO/ PEDOT:PSS/ mCP:30 wt% CzAcSF: *x* wt% *S-4* (50 nm)/ TmPyPB (45 nm)/ LiF (0.5 nm)/ Al (120 nm) (where *x* wt%=0.5 wt%*S-4* (S4),1 wt% *S-4* (S5), and 1.5 wt%*S-4* (S6)).

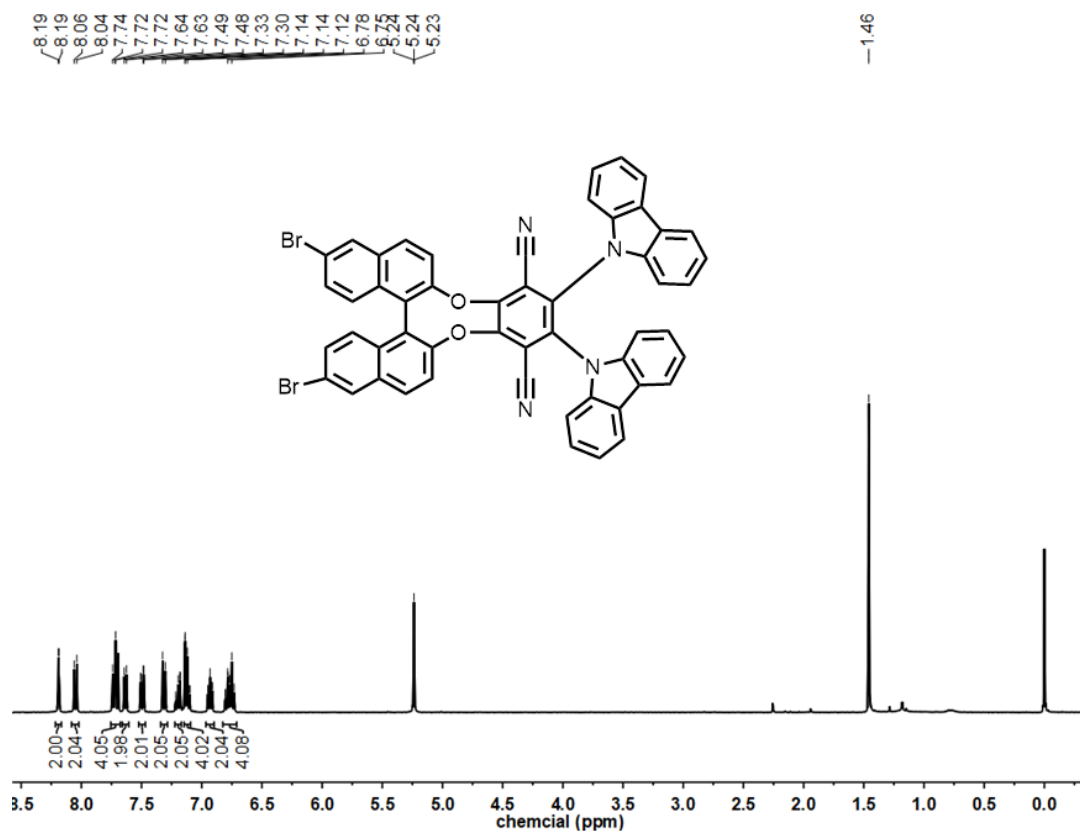


Figure S17. ¹H NMR spectrum of compound 1 in CD₂Cl₂

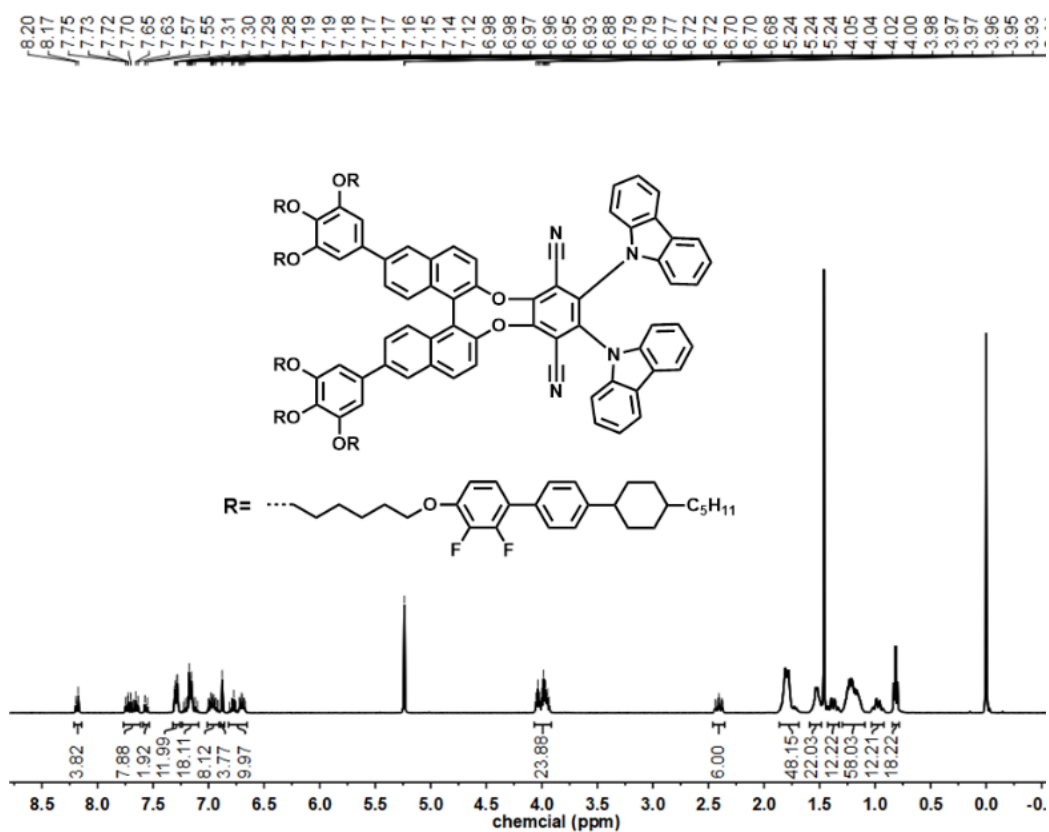


Figure S18. ¹H NMR spectrum of R-4 in CD₂Cl₂

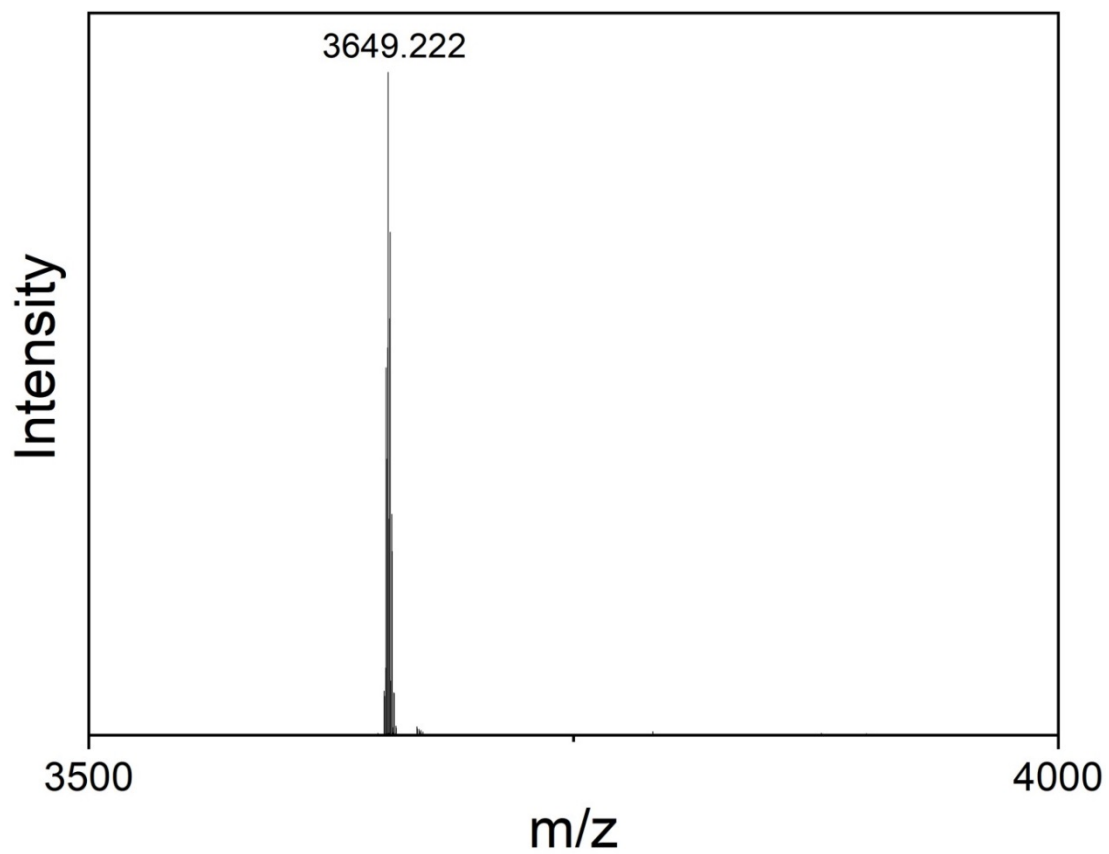
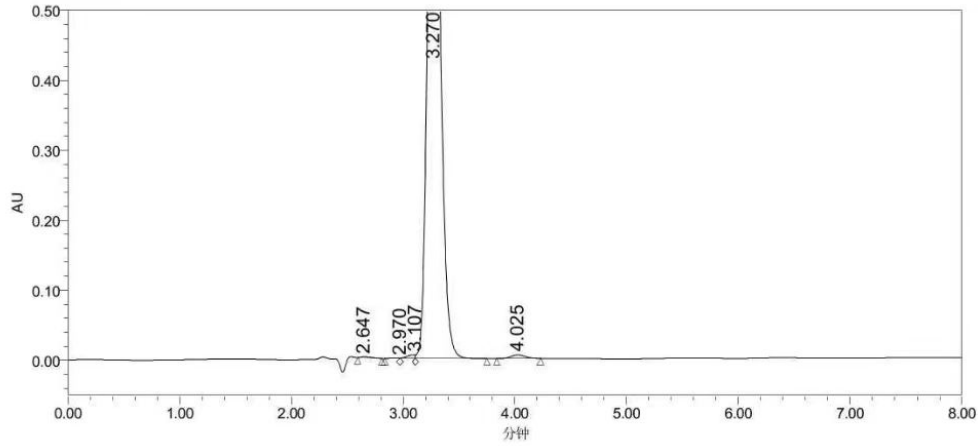


Figure S19. Mass spectrum of *R-4*

样品信息

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样品类型: 未知
瓶号: 14
进样次数: 1
进样体积: 1.00 ul
运行时间: 30.0 Minutes
样品组名称: 202308302

采集者: CZCS
采集时间: 2023/8/30 19:10:40 CST
采集方法组: THF_9 H2O_1 230nm 40°C
处理日期: 2023/8/31 8:54:57 CST
处理方法: 202209012
通道名称: UV Ch1 (230nm)
处理通道注释: UV Ch1 (230nm)



色谱峰结果

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1	2.647	0.10865	8244	1388			
2	2.970	0.03195	2425	429			
3	3.107	0.33530	25441	5134			
4	3.270	98.90310	7504316	1004114			
5	4.025	0.62099	47118	5241			

报告用户: CZCS
报告方法: 创索LC谱图报告
报告方法 ID: 2369 23694
页码: 1 (共计 1)

项目名称: CZCS OLED
打印日期:
2023/8/31
8:56:11 PRC

Figure S20. HPLC trace of R-4

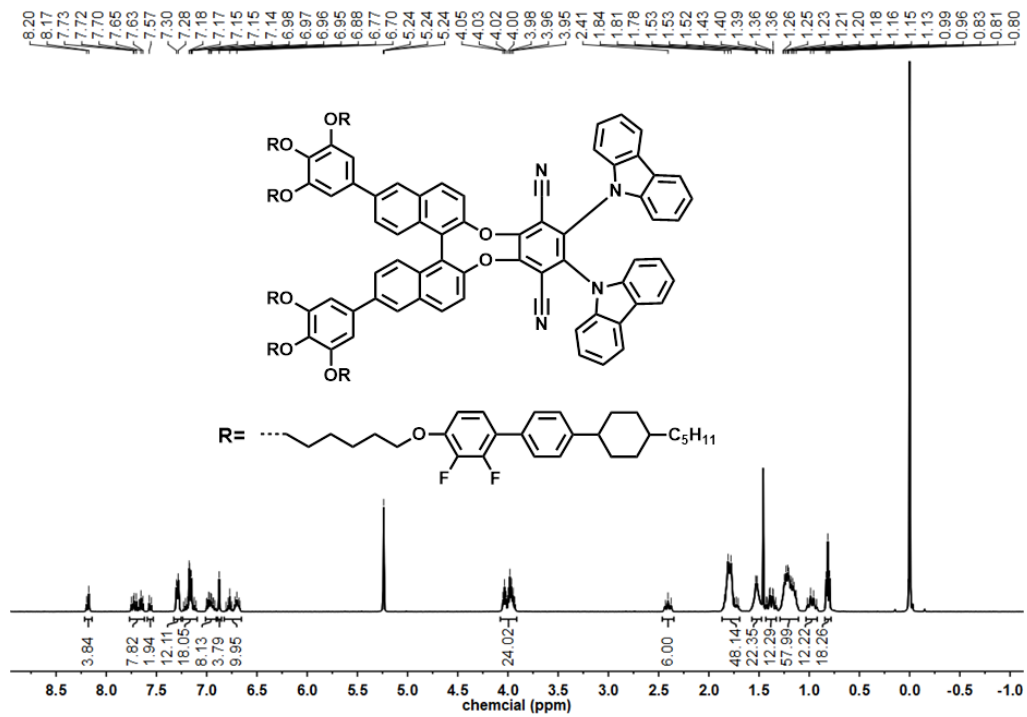


Figure S21. ^1H NMR spectrum of **S-4** in CD_2Cl_2

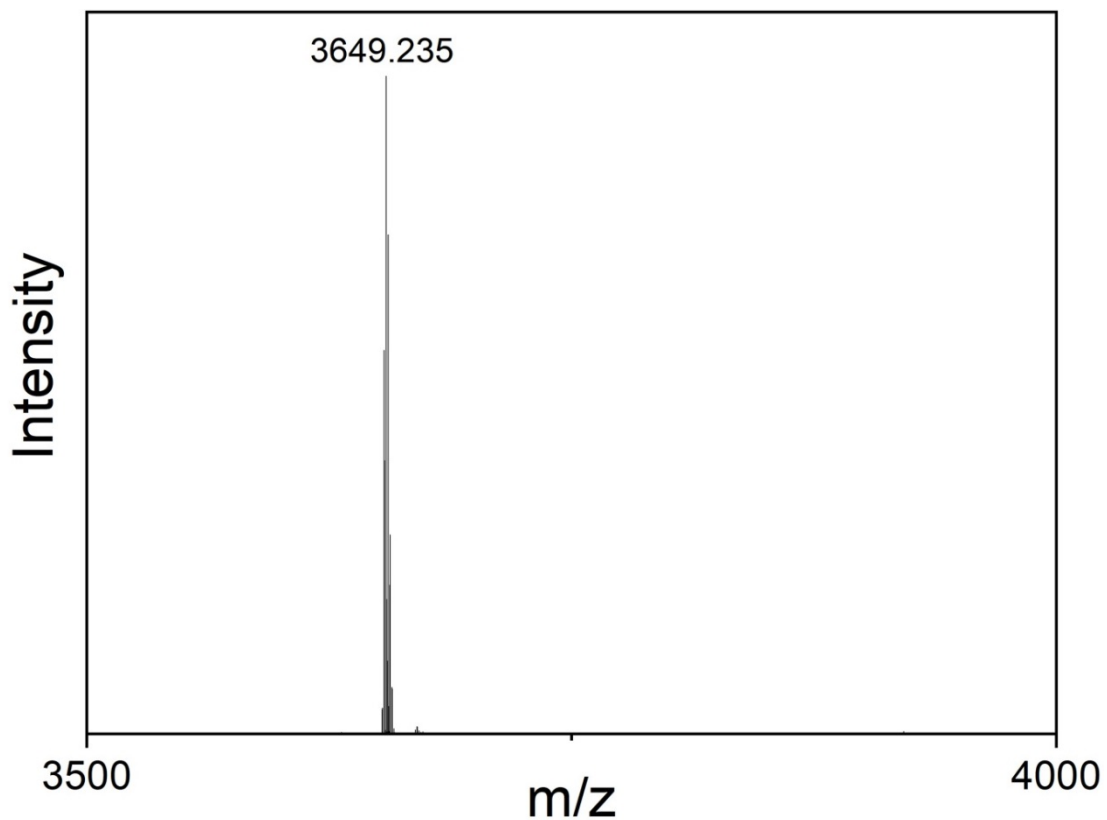
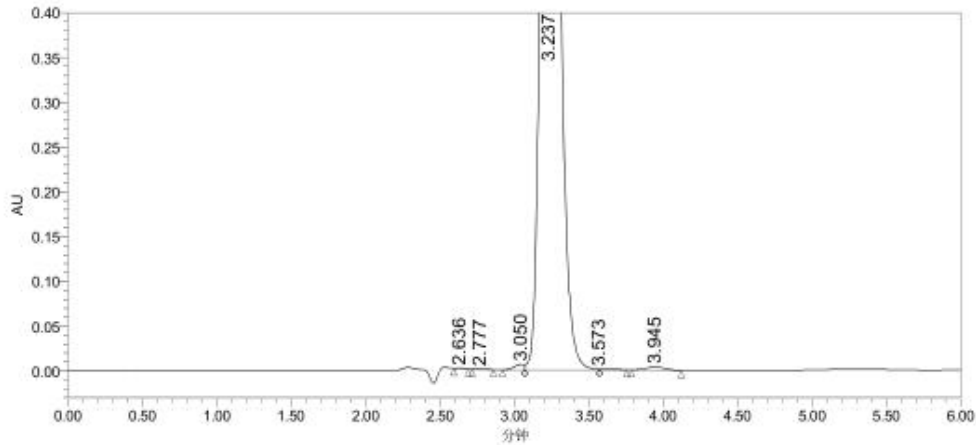


Figure S22. Mass spectrum of **S-4**

样品信息

样品名称:	S4	采集者:	CZCS
样品类型:	未知	采集时间:	2023/8/30 19:41:34 CST
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进样次数:	1	处理日期:	2023/8/31 8:56:41 CST
进样体积:	1.00 ul	处理方法:	2022090111
运行时间:	30.0 Minutes	通道名称:	UV Ch1 (230nm)
样品组名称:	202308302	处理通道注释:	UV Ch1 (230nm)



色谱峰结果

保留时间	% 面积	面积	峰高	含量	单位	名称
1	2.636	0.01687	1787	582		
2	2.777	0.01491	1412	328		
3	3.050	0.29603	28037	6175		
4	3.237	99.30424	9404801	1257272		
5	3.573	0.04028	3815	599		
6	3.945	0.32567	30843	3483		

报告用户: CZCS
报告方法: 创索LC谱图报告
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页码: 1 (共计 1)

项目名称: CZCS OLED
打印日期:
2023/8/31
8:57:26 PRC

Figure S23. HPLC trace of S-4