

Electronic supplementary information

Multi-spiro Junctions Enables Efficient Thermally Activated Delayed Fluorescent Emitter

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General information

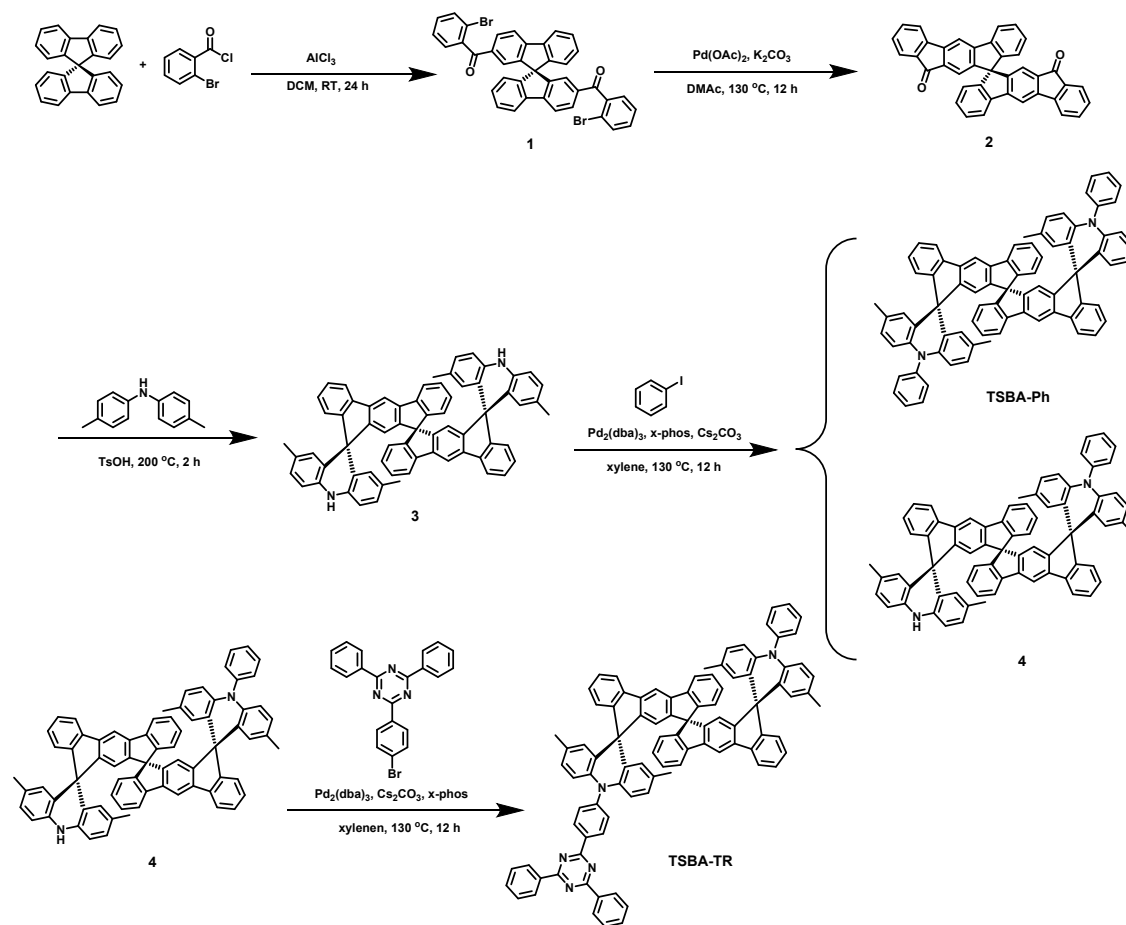
All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere. All the chemicals were purchased from commercial sources and used as received unless stated otherwise. Toluene was refluxed over Na and distilled under dry argon. Synthesized compounds were subject to purification by temperature gradient sublimation in high vacuum before used in subsequent studies. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Ascend spectrometer using CDCl_3 as solvent and tetramethylsilane (TMS) as an internal reference. Mass analyses were recorded by Bruker autoflex MALDI-TOF mass spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2700 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Phosphorescence spectra of thin films were conducted at 77 K. Thermogravimetric analysis (TGA) was recorded on a TA Q50 instrument under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from 25 to $800\text{ }^\circ\text{C}$. The temperature of degradation (T_d) was correlated to a 5% weight loss. Differential scanning calorimetry were carried out on a TGA 55. The glass transition temperature (T_g) was determined from the second heating scan at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $400\text{ }^\circ\text{C}$. Cyclic voltammetry (CV) was carried out in nitrogen-purged tetrahydrofuran or acetonitrile (reduction scan) or dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode and an Ag wire pseudoreference electrode with ferrocenium/ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV/s . Formal potentials were calculated as the average of cyclic voltammetric anodic and cathodic peaks. The HOMO energy levels of the compounds were calculated according to the formula: $-[4.8 + (E_{1/2(\text{ox/red})} - E_{1/2(\text{Fc}/\text{Fc}^+)})]$ eV. The onset potential was determined from the intersection of two tangents drawn at

the rising and background current of the cyclic voltammogram. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV- LASTER (LASTER377) as the excitation source. The solid state absolute PLQYs were measured on a Hamamatsu UV-NIR absolute PL quantum yield spectrometer (C13534, Hamamatsu Photonics) equipped with a calibrated integrating sphere in the host of PPF (10 wt%) under excitation of 320 nm. During the PLQY measurements, the integrating sphere was purged with pure and dry argon to maintain an inert environment. The ground state molecular structures were optimized at the PBE0/def2-SVP level of theory; the S1 and T1 geometries were optimized via time dependent DFT (TDDFT) at PBE0/def2-SVP level of theory. In addition, the overlaps between the hole and electron density distributions in the S1 and T1 states were estimated by the Multiwfn code.

Device Fabrication and Measurement

The ITO coated glass substrates with a sheet resistance of $15 \Omega \text{ square}^{-1}$ were consecutively ultrasonicated with acetone/ethanol and dried with nitrogen gas flow, followed by 20 min ultraviolet light-ozone (UVO) treatment in a UV-ozone surface processor (PL16 series, Sen Lights Corporation). Then the sample was transferred to the deposition system. Both 8-hydroxyquinolinolato-lithium (Liq) as electron injection layer and aluminum (Al) as cathode layer were deposited by thermal evaporation at $5 \times 10^{-5} \text{ Pa}$. Additionally, the organic layers were deposited at the rates of 0.2-3 $\text{\AA}/\text{s}$. After the organic film deposition, Liq and Al layer were deposited with rates of 0.1 and 3 $\text{\AA}/\text{s}$, respectively. The emitting area of the device is about 0.09 cm^2 . The current density-voltage-luminance (J-V-L), L-EQE curves and electroluminescence spectra were measured using a Keithley 2400 source meter and an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan).

Synthesis



Scheme S1. The synthetic route of TSBA-Ph and TSBA-TR.

Synthesis of 9,9'-spirobi[fluorene]-2,2'-diylbis((2-bromophenyl)methanone) (**1**)

Add 9,9'-spirobi[fluorene] (5 g, 15.8 mmol) in a side-necked flask and dissolve with 10 ml of dichloromethane. Add 2-bromobenzoyl chloride (10.4 g, 47.5 mmol) and AlCl_3 (6.3 g, 47.5 mmol) into a double-necked flask, dissolve with 30 ml of dichloromethane and stir at 0 °C for 30 minutes, drop 9,9'-spirobi[fluorene] solution into the double-necked flask. Then the mixture was stirred at room temperature for over-night. Extraction was carried out with an aqueous solution of concentrated hydrochloric acid and vacuum filtration, the filtrate was evaporated under reduced pressure. Purification via column chromatography on silica gel (300-400 mesh, petroleum ether/dichloromethane = 10:1) afford transparent oily product (7 g, Yield: 65%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, J = 7.7 Hz, 2H, Ar-H), 7.86 (d, J

= 8.0 Hz, 2H, Ar-H), 7.64 (dd, $J = 8.0, 1.6$ Hz, 2H, Ar-H), 7.60 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.47 – 7.39 (m, 4H, Ar-H), 7.39 – 7.34 (m, 2H, Ar-H), 7.33 – 7.27 (m, 4H, Ar-H), 7.21 (t, $J = 8.1$ Hz, 2H, Ar-H), 6.77 (d, $J = 7.6$ Hz, 2H, Ar-H), 5.30 (s, 1H, Ar-H).

Synthesis of **12H,12'H-10,10'-spirobi[indeno[2,1-b]fluorene]-12,12'-dione(2)**

1 (5 g, 7.3 mmol), palladium acetate (200 mg, 0.89 mmol) and potassium carbonate (5.8 g, 42 mmol) with 50 mL DMAc were added into a 200 mL double-neck flask under N₂ atmosphere. Then the mixture was stirred at 130 °C for 8 h. After cooling and vacuum filtrating, the filtrate was evaporated under reduced pressure. Purification via column chromatography on silica gel (300-400 mesh, petroleum ether/dichloromethane = 10:1 v/v) afford a white solid (2 g, Yield: 56%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 4H, Ar-H), 7.66 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.59 (d, $J = 7.3$ Hz, 2H, Ar-H), 7.53 (t, $J = 7.5$ Hz, 2H, Ar-H), 7.46 (t, $J = 8.0$ Hz, 2H, Ar-H), 7.31 – 7.27 (m, 2H, Ar-H), 7.22 (t, $J = 8.0$ Hz, 2H, Ar-H), 7.03 (s, 2H, Ar-H), 6.82 (d, $J = 7.6$ Hz, 2H, Ar-H).

Synthesis of **2,2''',7,7'''-tetramethyl-10H,10'''H-trispiro[acridine-9,10'-indeno[2,1-b]fluorene-12',10''-indeno[2,1-b]fluorene-12'',9'''-acridine](3)**

Di-*p*-tolylamine (5.7 g, 28.8 mmol) and *p*-Toluenesulfonic acid monohydrate (453 mg, 2.38 mmol) were added into a double neck flask in N₂ atmosphere. The mixture was heated to 120 °C and stirred for 20 minutes. Then **2** (5 g, 9.6 mmol) was added into the bottle quickly and heated to 200 °C for 2 h. After being cooling down, it was diluted with 30 mL of dichloromethane, then the solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica using petroleum ether/dichloromethane (3:1, v/v). the product is white solid. (3.5 g, Yield: 42%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.82 (s, 2H, Ar-H), 8.54 (s, 2H, Ar-H), 8.04 (d, $J = 7.7$ Hz, 2H, Ar-H), 7.97 (d, $J = 7.7$ Hz, 2H, Ar-H), 7.36 (dd, $J = 13.9, 7.5$ Hz, 4H, Ar-H), 7.13 (t, $J = 7.5$ Hz, 2H, Ar-H), 7.06 – 7.02 (m, 4H, Ar-H), 6.76 – 6.70 (m, 8H, Ar-H), 6.52 – 6.45 (m, 4H, Ar-H), 5.79 (d, $J = 10.8$ Hz, 4H, Ar-H), 1.81 (s, 6H, -CH₃), 1.60 (s, 6H, -CH₃).

Synthesis of **2,2''',7,7'''-tetramethyl-10,10'''-diphenyl-10H,10'''H-trispiro[acridine-9,10'-indeno[2,1-b]fluorene-12',10''-indeno[2,1-b]fluorene-12'',9'''-acridine](TSBA-Ph)**

3 (2.3g, 2.6 mmol), iodobenzene (1.6 g, 7.8 mmol) and xylene (30 mL) were added into a 100 mL branch bottle in N₂ atmosphere. After the mixture was degassed for 10 minutes, tris(dibenzylideneacetone)dipalladium (100 mg, 0.11 mmol), cesium carbonate (3.4 g, 10.4 mmol) and x-phos (410 mg, 3.8mmol) were added into the bottle under the N₂ atmosphere. The mixture was heated to 130 °C and stirred for overnight. After cooling and vacuum filtrating, the filtrate was evaporated under reduced pressure. Purification via column chromatography on silica gel (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) afford a yellow solid (2.1 g, Yield: 81%).¹H NMR (500 MHz, Chloroform-*d*) δ 8.26 (s, 2H, Ar-H), 7.91 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.84 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.63 – 7.59 (m, 4H, Ar-H), 7.50 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.37 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.34 – 7.27 (m, 8H, Ar-H), 7.13 (d, *J* = 3.0 Hz, 4H, Ar-H), 7.05 – 7.01 (m, 2H, Ar-H), 6.69 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.62 (d, *J* = 10.6 Hz, 2H, Ar-H), 6.50 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.16 – 6.04 (m, 8H, Ar-H), 1.86 (s, 6H, -CH₃), 1.47 (s, 6H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 171.88, 157.63, 150.42, 145.59, 138.60, 136.12, 132.72, 131.61, 131.46, 131.15, 130.84, 129.05, 128.75, 127.60, 124.63, 123.39, 122.86, 119.97, 110.95, 56.94, 20.23. HRMS (ESI): *m/z* Calcd for C₇₉H₅₄N₂ (M+H)⁺ 1031.315, found 1031.412.

Synthesis of **2,2''',7,7'''-tetramethyl-10,10'''-diphenyl-10H,10'''H-trispiro[acridine-9,10'-indeno[2,1-b]fluorene-12',10''-indeno[2,1-b]fluorene-12'',9'''-acridine](4)**

3 (1 g, 1.1 mmol), iodobenzene (0.23 g, 1.1 mmol) and xylene (20 mL) were added into a 100 mL branch bottle in N₂ atmosphere. After the mixture was degassed for 10 minutes, tris(dibenzylideneacetone)dipalladium (100 mg, 0.11 mmol), cesium carbonate (0.65 g, 2 mmol) and x-phos (248 mg, 0.52 mmol) were added into the bottle under the N₂ atmosphere. The mixture was heated to 130 °C and stirred for overnight. After cooling and vacuum filtrating, the filtrate was evaporated under reduced pressure. Purification via column chromatography on silica gel (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) afford a yellow solid (0.5 g, Yield:

48%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 5.8 Hz, 2H, Ar-H), 7.87 (s, 2H, Ar-H), 7.81 (d, *J* = 3.8 Hz, 2H, Ar-H), 7.61 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.49 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.37 – 7.27 (m, 7H, Ar-H), 7.22 (s, 1H, Ar-H), 7.13 – 7.08 (m, 2H, Ar-H), 7.07 – 6.99 (m, 4H, Ar-H), 6.96 (s, 1H, Ar-H), 6.77 (d, *J* = 9.3 Hz, 1H, Ar-H), 6.67 – 6.59 (m, 5H, Ar-H), 6.57 – 6.51 (m, 2H, Ar-H), 6.11 (d, *J* = 6.0 Hz, 4H, Ar-H), 6.03 (d, *J* = 9.5 Hz, 2H, Ar-H), 5.98 (s, 1H, Ar-H), 1.90 – 1.82 (m, 6H, -CH₃), 1.51 (d, *J* = 1.7 Hz, 6H, -CH₃).

Synthesis of **10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-2,2''',7,7'''-tetramethyl-10'''-phenyl-10H,10'''H-trispiro[acridine-9,10'-indeno[2,1-b]fluorene-12',10''-indeno[2,1-b]fluorene-12'',9'''-acridine](TSBA-TR)**

4 (0.4 g, 0.42 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (0.3 g, 0.84 mmol) and xylene (20 mL) were added into a 100 mL branch bottle in N₂ atmosphere. After the mixture was degassed for 10 minutes, tris(dibenzylideneacetone)dipalladium (50 mg, 0.05 mmol), cesium carbonate (0.3 g, 0.9 mmol) and x-phos (41 mg, 0.38 mmol) were added into the bottle under the N₂ atmosphere. The mixture was heated to 130 °C and stirred for overnight. After cooling and vacuum filtrating, the filtrate was evaporated under reduced pressure. Purification via column chromatography on silica gel (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) afford a yellow solid (0.46 g, Yield: 87%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.98 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.81 (d, *J* = 9.9 Hz, 4H, Ar-H), 8.67 (s, 1H, Ar-H), 8.61 (s, 1H, Ar-H), 8.12 (d, *J* = 7.7 Hz, 2H, Ar-H), 8.04 (dd, *J* = 16.8, 7.7 Hz, 2H, Ar-H), 7.71 (td, *J* = 16.9, 15.8, 8.1 Hz, 8H, Ar-H), 7.62 (d, *J* = 6.5 Hz, 3H, Ar-H), 7.45 – 7.35 (m, 4H, Ar-H), 7.29 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.24 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.09 (dd, *J* = 14.0, 7.1 Hz, 2H, Ar-H), 6.81 (s, 1H, Ar-H), 6.77 (s, 1H, Ar-H), 6.72 – 6.58 (m, 5H, Ar-H), 6.55 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.18 (t, *J* = 8.4 Hz, 2H, Ar-H), 6.04 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.00 – 5.95 (m, 3H, Ar-H), 1.84 (d, *J* = 7.7 Hz, 6H, -CH₃), 1.56 (d, *J* = 20.7 Hz, 6H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.64, 154.40, 150.42, 149.13, 142.30, 141.97, 141.44, 141.03, 139.70, 138.95, 136.50, 131.17, 130.85, 129.71, 129.21, 128.16 (d, *J* = 15.1 Hz), 127.75 (d, *J* = 6.7 Hz), 127.59 (d, *J* = 3.6 Hz), 127.25, 126.89, 124.89, 124.77, 124.63, 123.39, 122.87, 119.92 (d, *J* = 6.7 Hz),

114.03 (d, $J = 17.2$ Hz), 110.94, 66.28, 56.97, 20.23 (d, $J = 2.2$ Hz). HRMS (ESI): m/z Calcd for $C_{94}H_{63}N_5$ (M+H)⁺ 1261.508, found 1261.934. Anal. Calcd. for $C_{94}H_{63}N_5$: C, 89.42; H, 5.03; N, 5.55. found: C, 89.74; H, 6.58; N, 5.44.

Exciton Lifetime and Rate Constant

The rate constants of ISC (k_{ISC}) and RISC (k_{RISC}) of three emitters based on the following equations:

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

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

$$k_{r,s} = \Phi_p k_p + \Phi_d k_d \quad (3)$$

$$k_{RISC} \approx \frac{k_p k_d \Phi}{k_{r,s}} \quad (4)$$

$$k_{ISC} \approx \frac{k_p k_d \Phi_d}{k_{RISC} \Phi_p} \quad (5)$$

In this study, the prompt PLQY (Φ_p) and delayed PLQY (Φ_d) were determined by using the total PLQY and the integrated intensity ratio between prompt and delayed components which was calculated from transient photoluminescence measurements. The intensity ratio between prompt (r_p) and delayed (r_d) components were determined using two fluorescent lifetimes (τ_p , τ_d) and fitting parameter (A_p , A_d) as follow.

$$I(t) = A_p e^{-\frac{t}{\tau_p}} + A_d e^{-\frac{t}{\tau_d}} \quad (6)$$

$$r_p = \frac{A_p \tau_p}{A_p \tau_p + A_d \tau_d} \quad (7)$$

$$r_d = \frac{A_d \tau_d}{A_p \tau_p + A_d \tau_d} \quad (8)$$

Then, the prompt PLQY (Φ_p) and delayed PLQY (Φ_d) were determined using intensity ratio (r_p , r_d) and total PLQY.

$$\Phi_{total} = \Phi_p + \Phi_d \quad (9)$$

$$\Phi_p = r_p \Phi_{total} \quad (10)$$

$$\Phi_d = r_d \Phi_{total} \quad (11)$$

Supplementary Figures

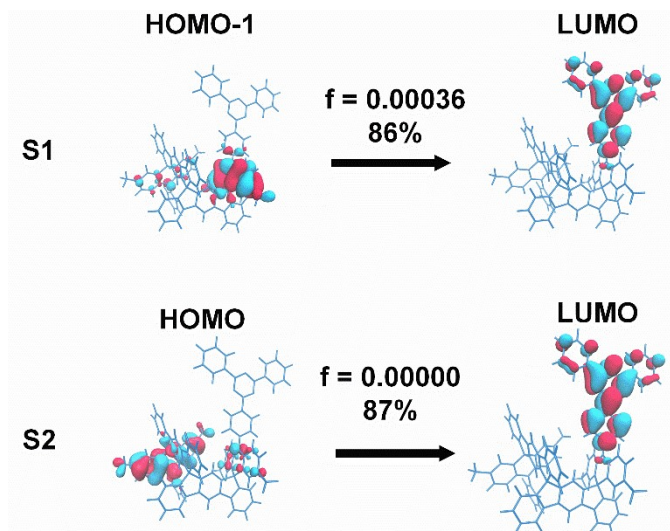


Fig. S1 The simulated transition patterns of S1 and S2 states.

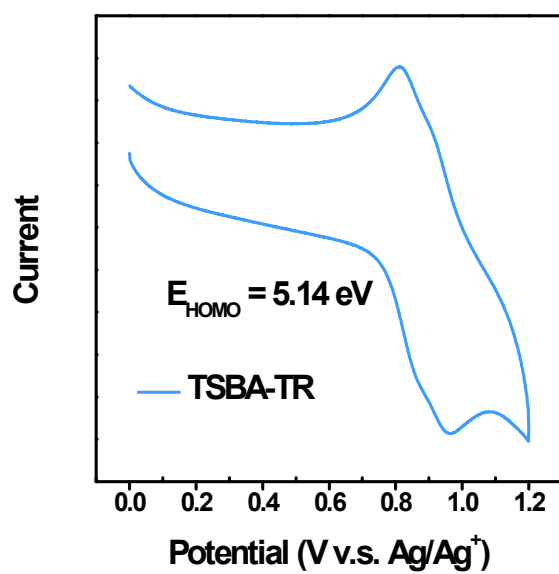


Fig. S2 Cyclic voltammetry profile of TSBA-TR.

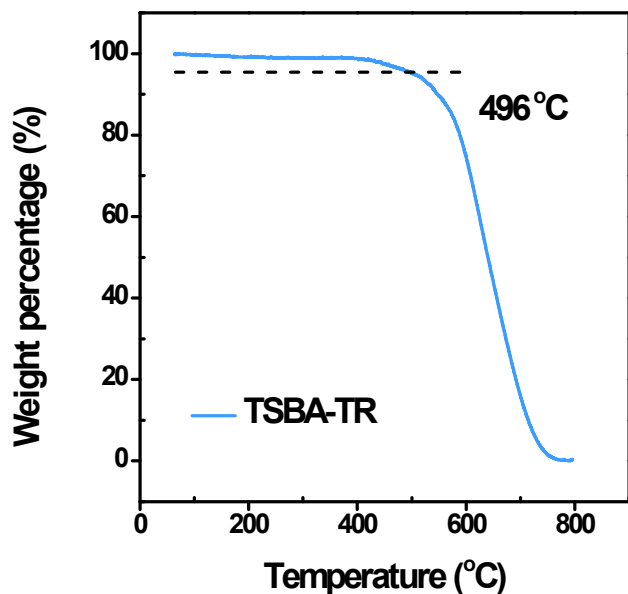


Fig. S3 Thermal gravity analysis profile in N_2 atmosphere under a heating rate of 10 K/min^{-1} .

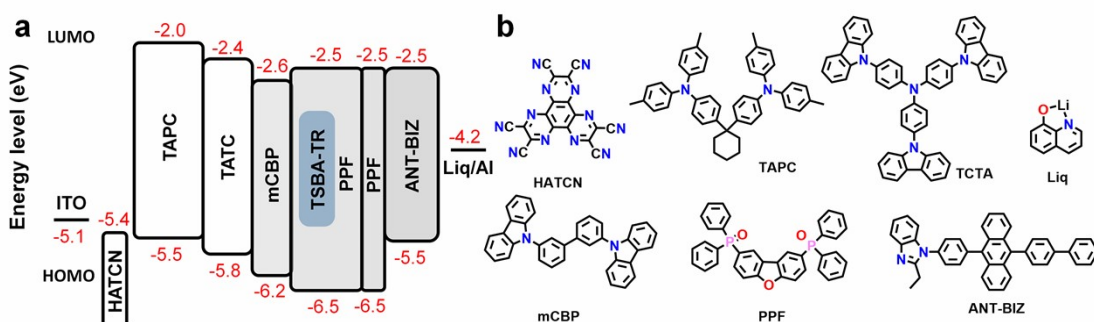


Fig. S4 ^a Energy diagram of doping devices, ^b chemical structures of the compounds used in devices.

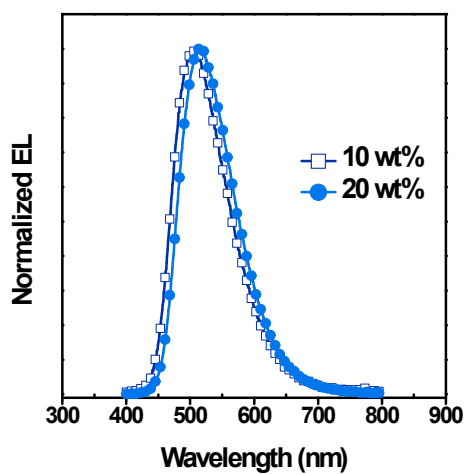


Fig. S5 Electroluminescent spectra of devices under doping level of 10 wt% and 20 wt%.

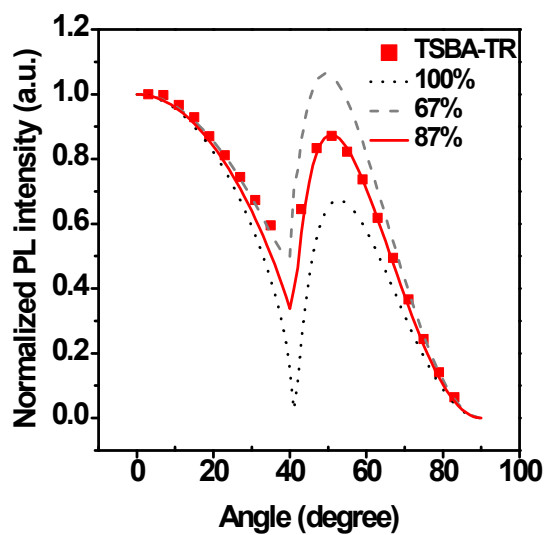
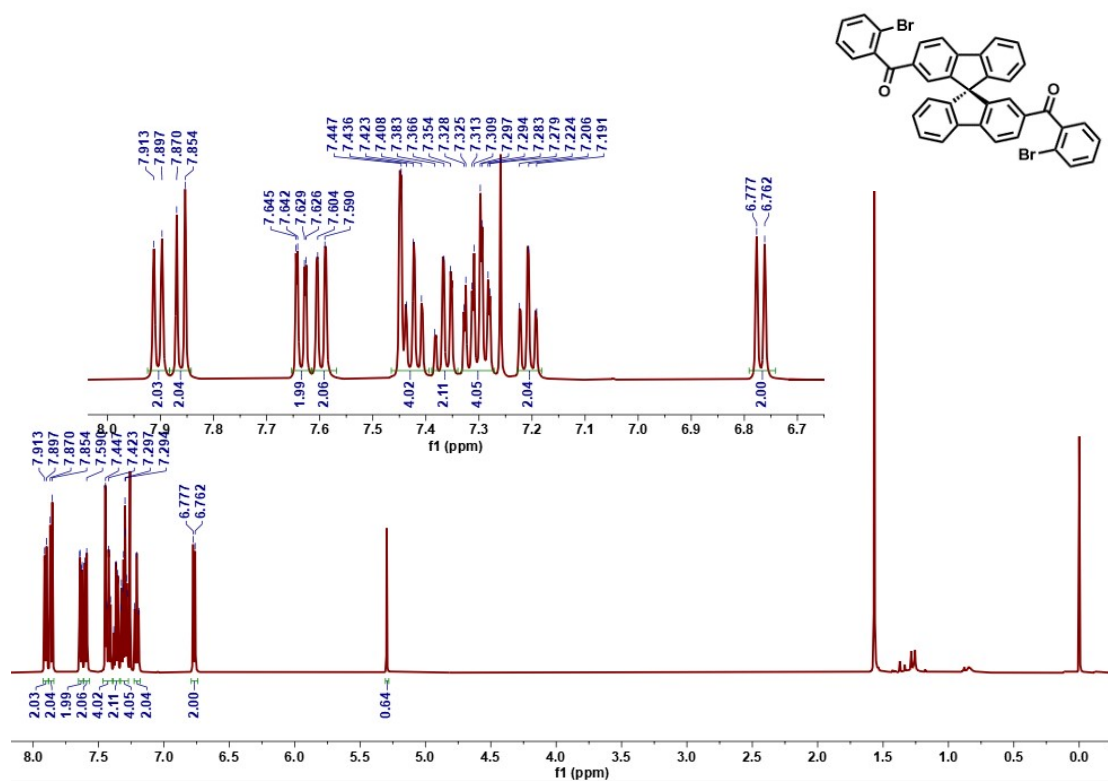


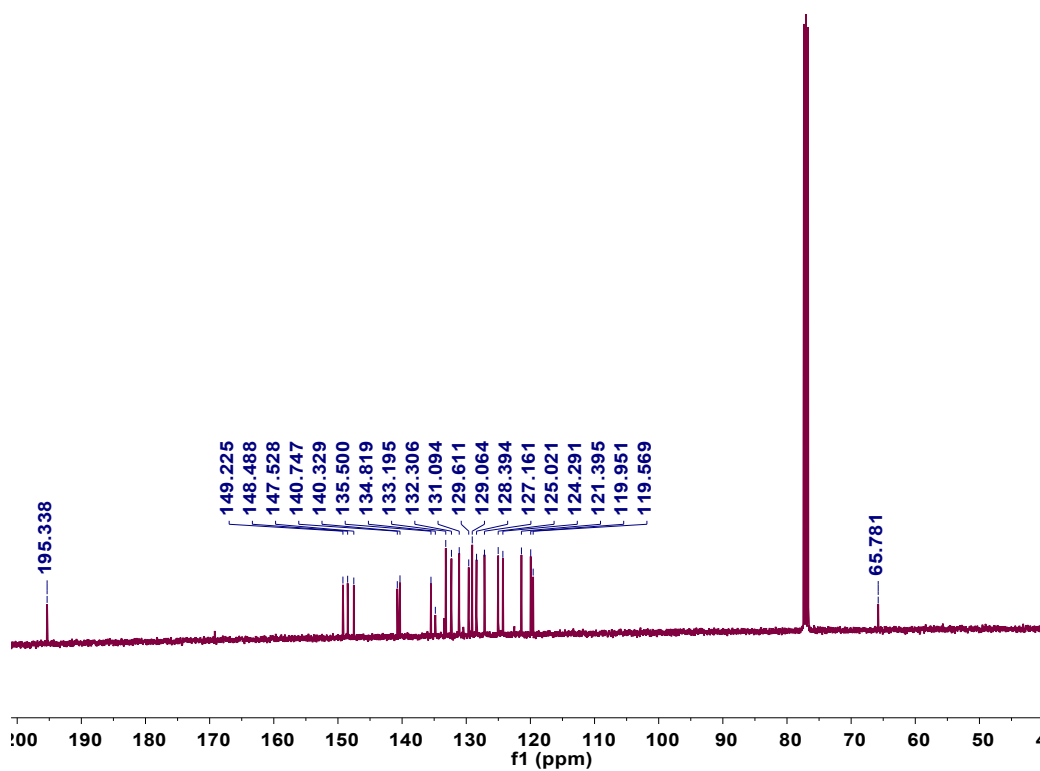
Fig. S6 Measured p-polarized PL intensity (at PL peak wavelength) of 10 wt% TSBA-TR doped in PPF as a function of the emission angle.

NMR spectra

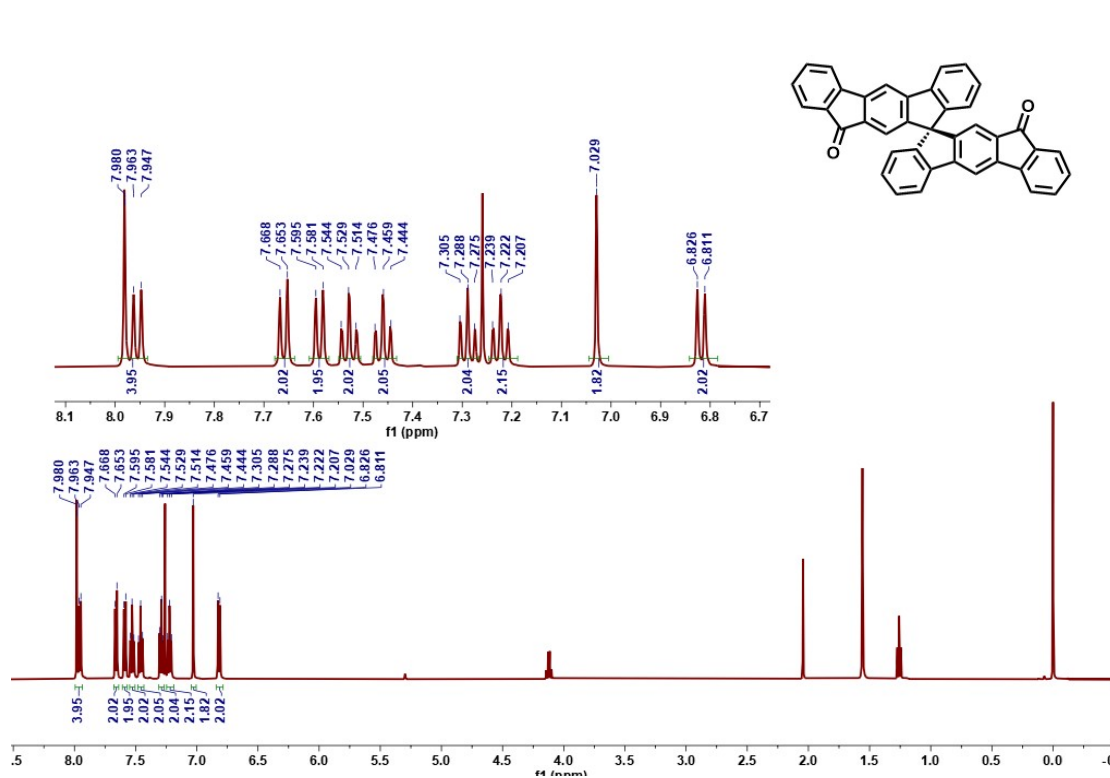
^1H NMR spectra of **1** (CDCl_3)



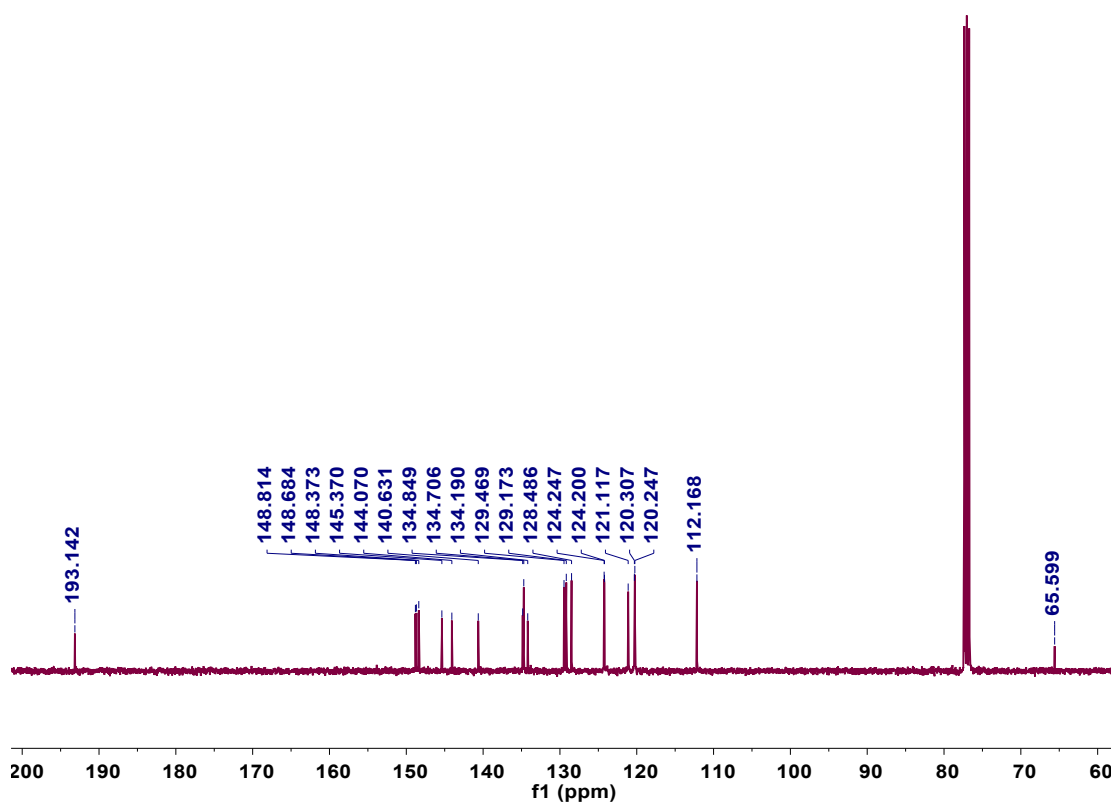
^{13}C NMR spectra of **1** (CDCl_3)



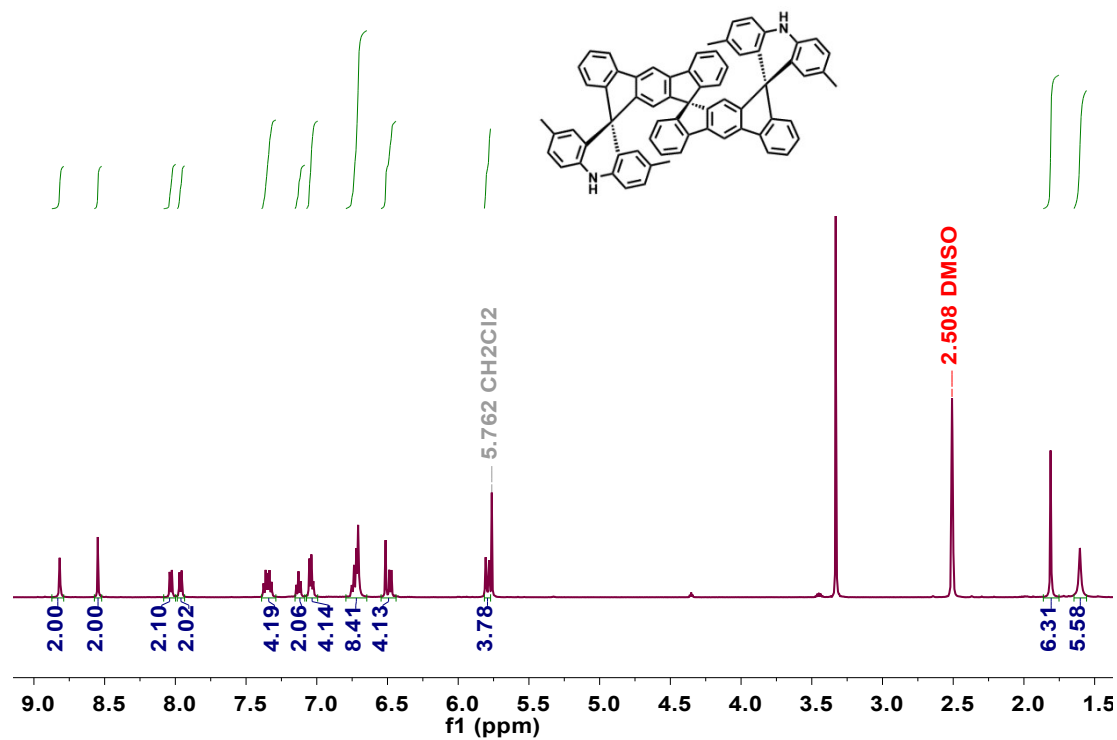
^1H NMR spectra of **2** (CDCl_3)



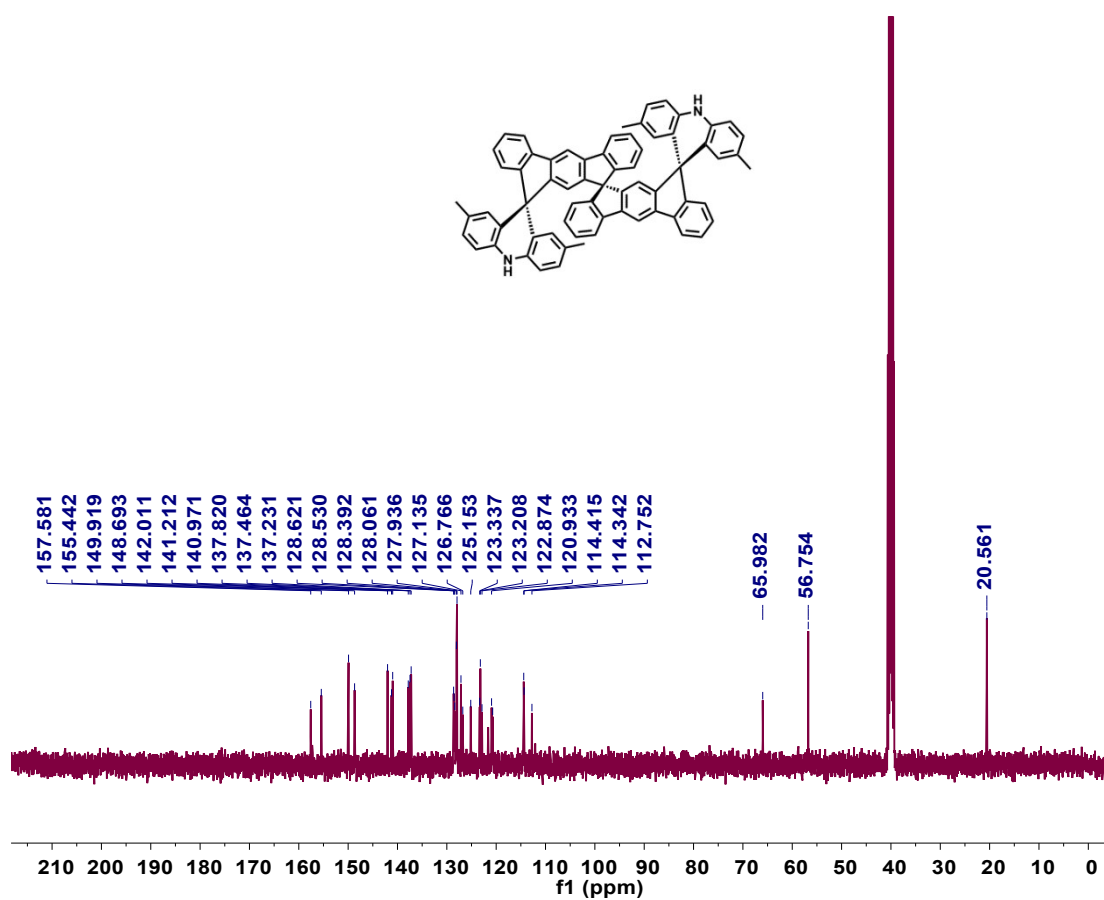
^{13}C NMR spectra of **2** (CDCl_3)



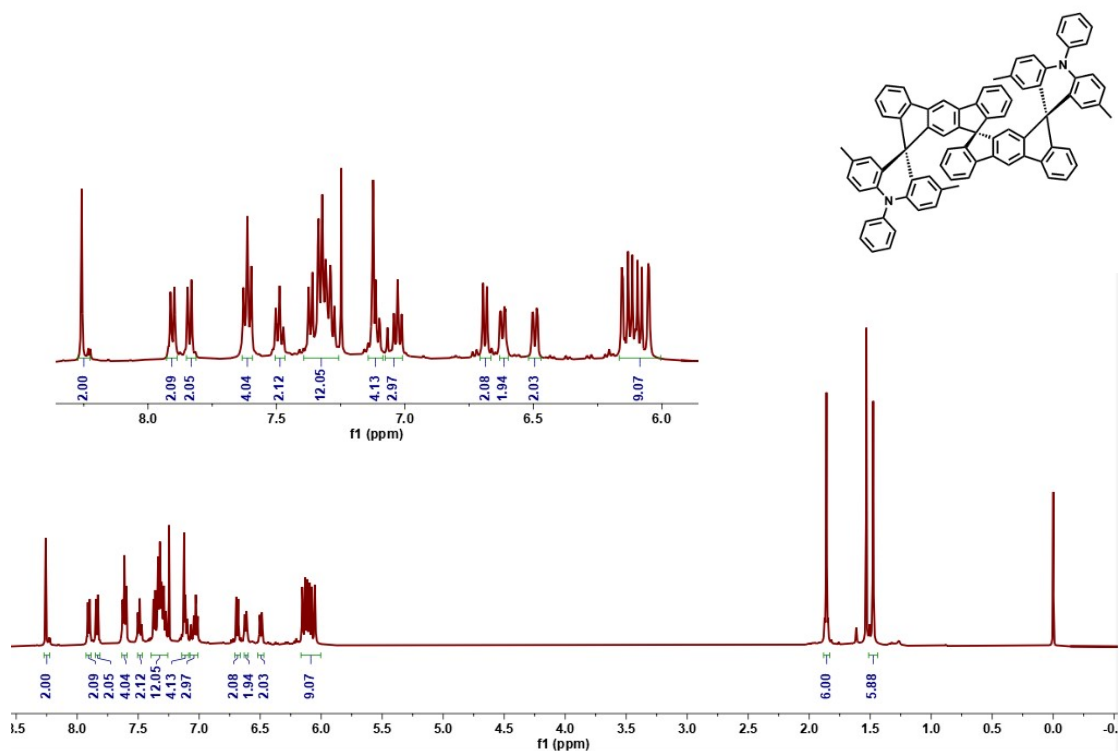
^1H NMR spectra of **3** ($\text{DMSO-}d_6$)



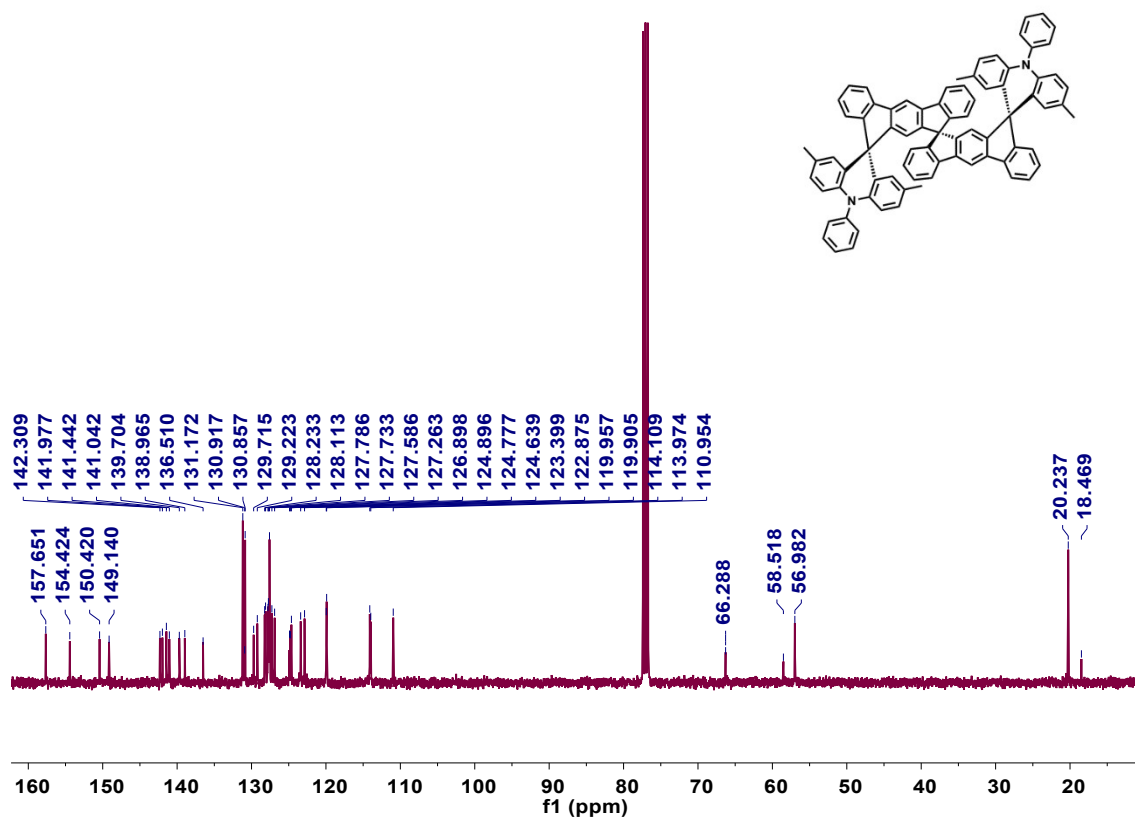
^{13}C NMR spectra of **3** (CDCl_3)



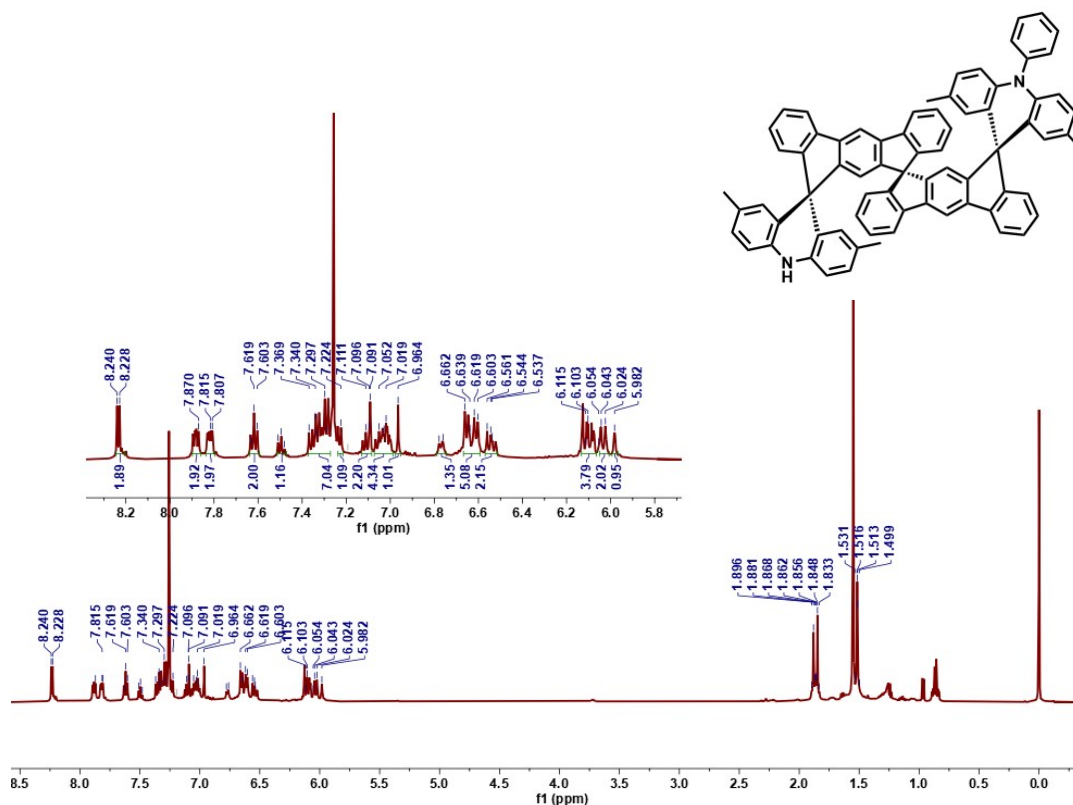
^1H NMR spectra of **TSBA-Ph** (CDCl_3)



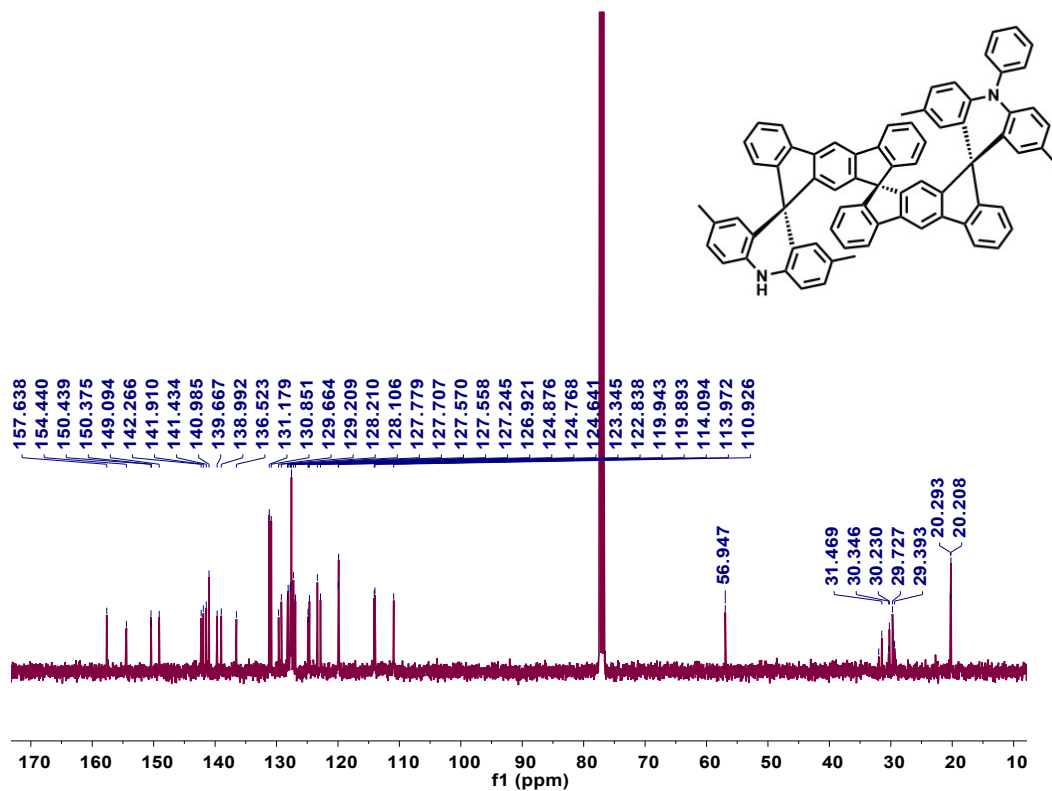
^{13}C NMR spectra of **TSBA-Ph** (CDCl_3)



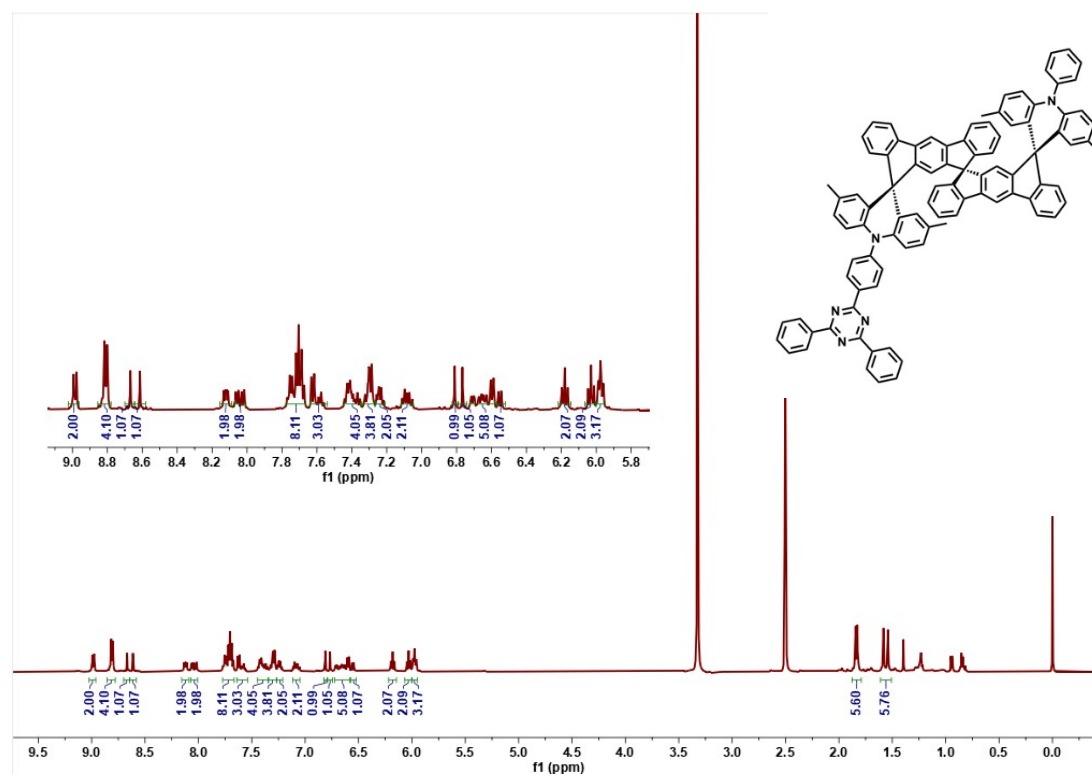
^1H NMR spectra of **4** (CDCl_3)



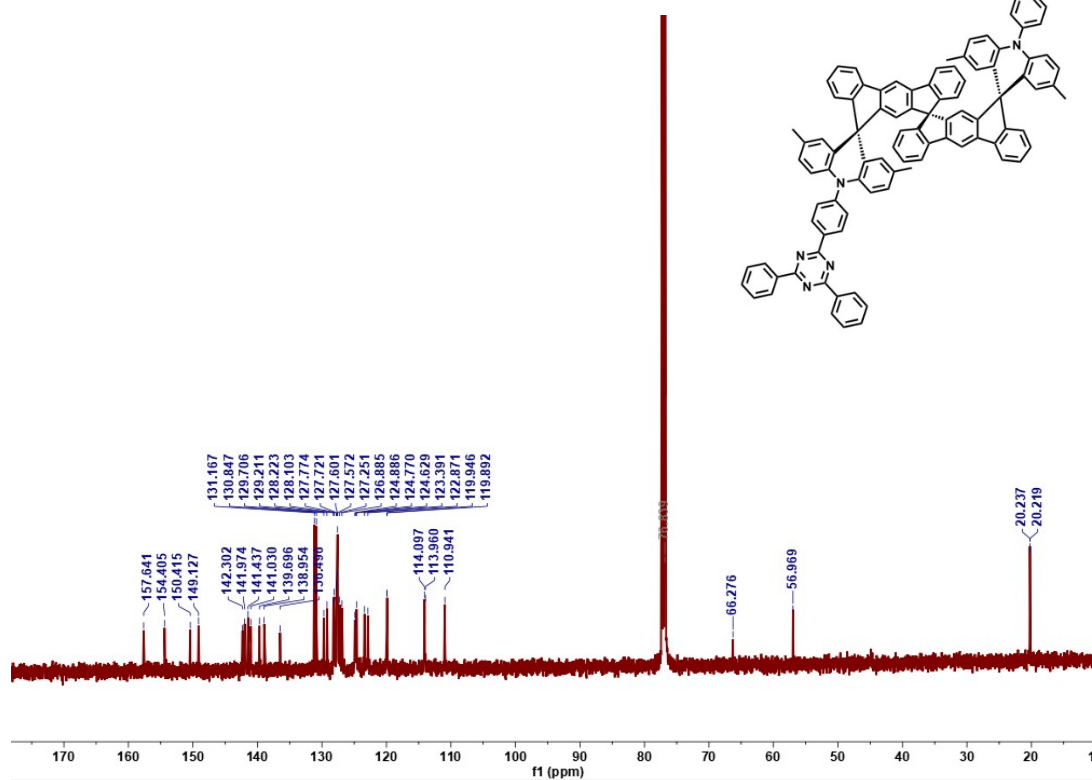
^{13}C NMR spectra of **4** (CDCl_3)



^1H NMR spectra of TSBA-TR (DMSO- d_6)

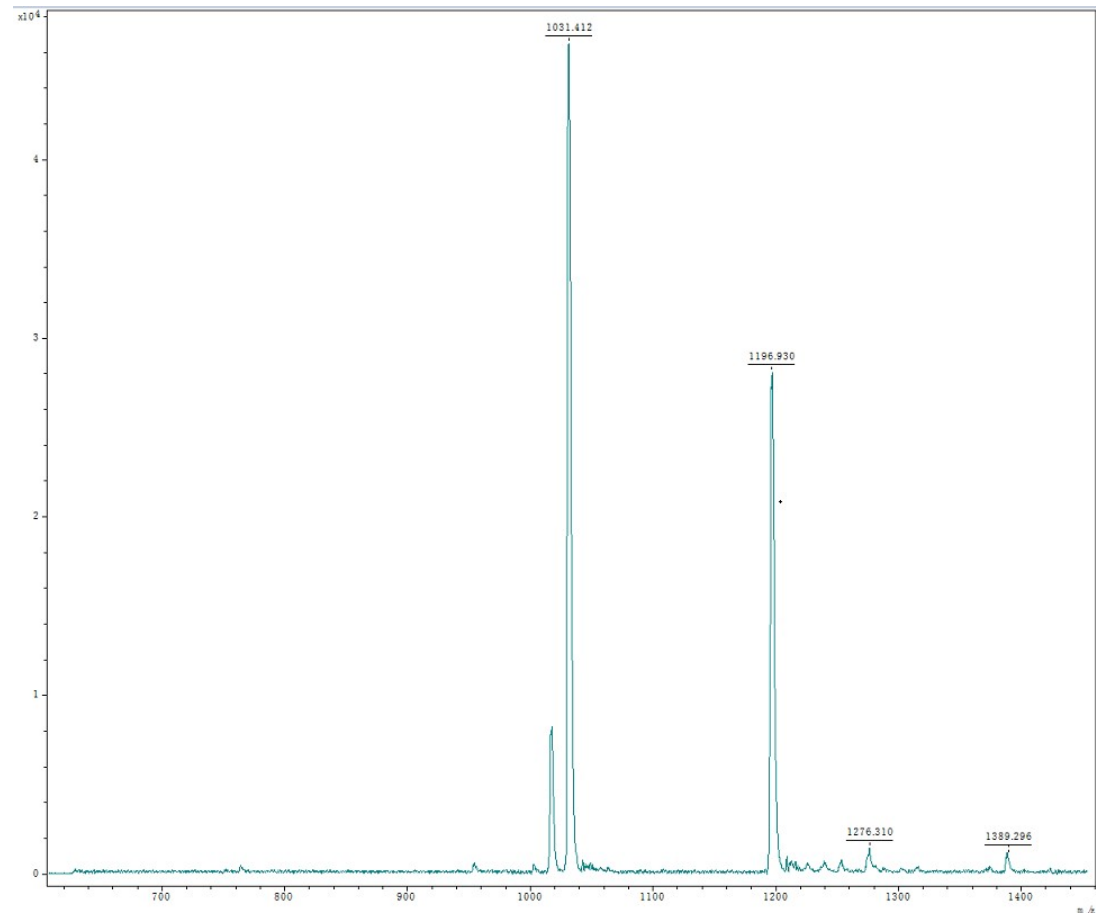


^{13}C NMR spectra of TSBA-TR (CDCl_3)

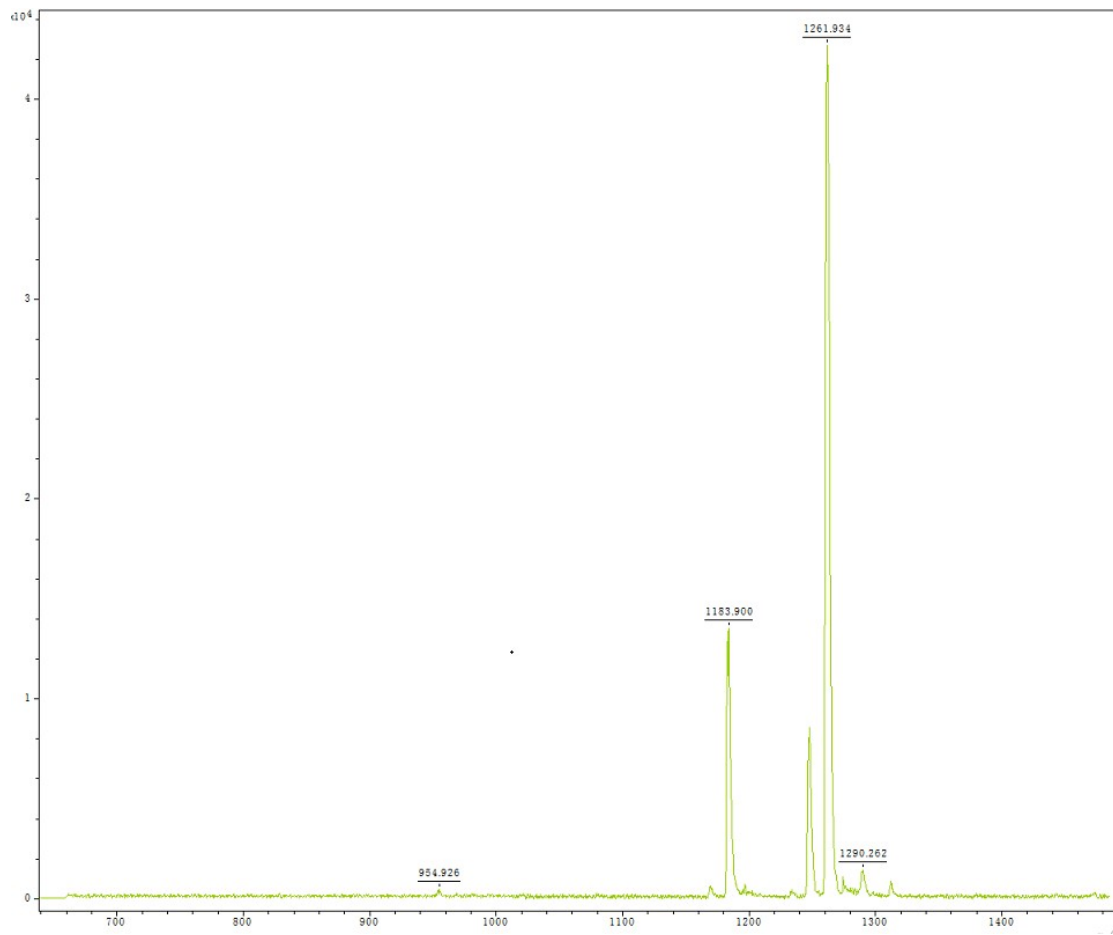


Mass spectrometry

TSBA-Ph



TSBA-TR



Crystal data and structure refinement for TSBA-Ph.

Identification code	TSBA-Ph
Empirical formula	C ₈₆ H ₆₂ N ₂
Formula weight	1123.37
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
a/Å	10.2159(5)
b/Å	13.4631(7)
c/Å	22.6351(10)
α/°	82.798(2)
β/°	83.730(2)
γ/°	85.690(2)
Volume/Å ³	3064.2(3)
Z	2
ρ _{calc} /g/cm ³	1.218
μ/mm ⁻¹	0.070
F(000)	1184.0
Crystal size/mm ³	0.39 × 0.12 × 0.07
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.242 to 54.34
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -29 ≤ l ≤ 27
Reflections collected	65055
Independent reflections	13557 [R _{int} = 0.0833, R _{sigma} = 0.0619]
Data/restraints/parameters	13557/0/798
Goodness-of-fit on F ²	1.018
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0574, wR ₂ = 0.1243
Final R indexes [all data]	R ₁ = 0.1039, wR ₂ = 0.1492
Largest diff. peak/hole / e Å ⁻³	0.22/-0.28

