

Electronic Supplementary Information

Nonplanar structure accelerates reverse intersystem crossing of TADF emitters: nearly 40% EQE and relieved efficiency roll off

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Experimental Section

General

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 500 MHz ^1H and 125 MHz ^{13}C NMR spectra were recorded on a Bruker Ascend 500 spectrometer using CDCl_3 and DMSO-d_6 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 with 25 ms delay from excitation. 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 $25\text{ }^\circ\text{C}$ 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 TA Q200. 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 $300\text{ }^\circ\text{C}$. Cyclic voltammetry (CV) was carried out in nitrogen-purged 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 pseudo-reference electrode with ferroceniumferrocene (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 solid-state absolute photoluminescence quantum yields (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%). The PPF (10 wt%) films were spin-coated from chlorobenzene solutions. During the PLQY measurements, the integrating sphere was purged with pure and dry nitrogen to maintain an inert environment.

Computational Methods

All the density functional theory (DFT) calculations were carried out using Gaussian 09 package^[1] on a PowerLeader cluster. The ground-state geometry was fully optimized using DFT with PBE0 hybrid functional at the basis set level of def2svp. The excited-state properties were obtained by time-dependent density functional theory (TD-DFT) at the basis set level of PBE0/def2svp. In addition, the overlaps between the hole and electron density distributions in the S_1 and T_1 states were extracted by the Multiwfn code^[2-4] and visualized using VMD.

Device Fabrication and Measurement

Glass substrates pre-coated with a 95-nm-thin layer of indium tin oxide (ITO) with a sheet resistance of $20\ \Omega$ per square were thoroughly cleaned for 10 minutes in ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol. Then, the substrates were totally dried in a $75\text{ }^\circ\text{C}$ oven. After that, in order to improving the hole injection ability of ITO, the substrates were treated by O_2 plasma for 10 minutes. Multilayer OLEDs were fabricated by the vacuum-deposition method. Organic layers were deposited by high-vacuum ($\sim 5 \times 10^{-4}\text{ Pa}$) thermal evaporation onto a glass substrate pre-coated with an ITO layer. All organic layers were deposited sequentially. The thermal deposition rates for the organic materials, LiF and Al were $1.0\sim 1.5$, 0.1 and $3\sim 5\ \text{\AA s}^{-1}$, respectively. The active area of each device was 9 mm^2 . The electroluminescence spectra, the current density-voltage characteristics and the current density-voltage-luminance curves characterizations of the OLEDs were carried out with a Photo Research SpectraScan PR-745 Spectroradiometer and a Keithley 2450 Source Meter and they are recorded simultaneously. All measurements were done at room temperature under ambient conditions.

Analysis of rate constants

Time-resolved transient photoluminescence decay measurements were utilized to research the delayed fluorescence phenomenon of the molecule in doped films (10 wt% in PPF), Rate constants of different kinetic processes were calculated following the equations (S1) - (S6) below:

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

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

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

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

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

Where $k_{r,s}$, k_{nr} , k_{ISC} , k_{RISC} represent the rate constant of singlet radiative decay, non-radiative decay, intersystem crossing and reverse intersystem crossing, respectively; Φ , Φ_p , Φ_d , τ_p and τ_d represent total PLQY, quantum yield of the prompt component, quantum yield of the delayed component, lifetimes of the prompt and delayed components, respectively.

In this study, Φ_p and 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 (rp) and delayed (rd) components were determined using two fluorescent lifetimes (τ_p , τ_d) and fitting parameter (A_p , A_d) as follow.

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

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

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

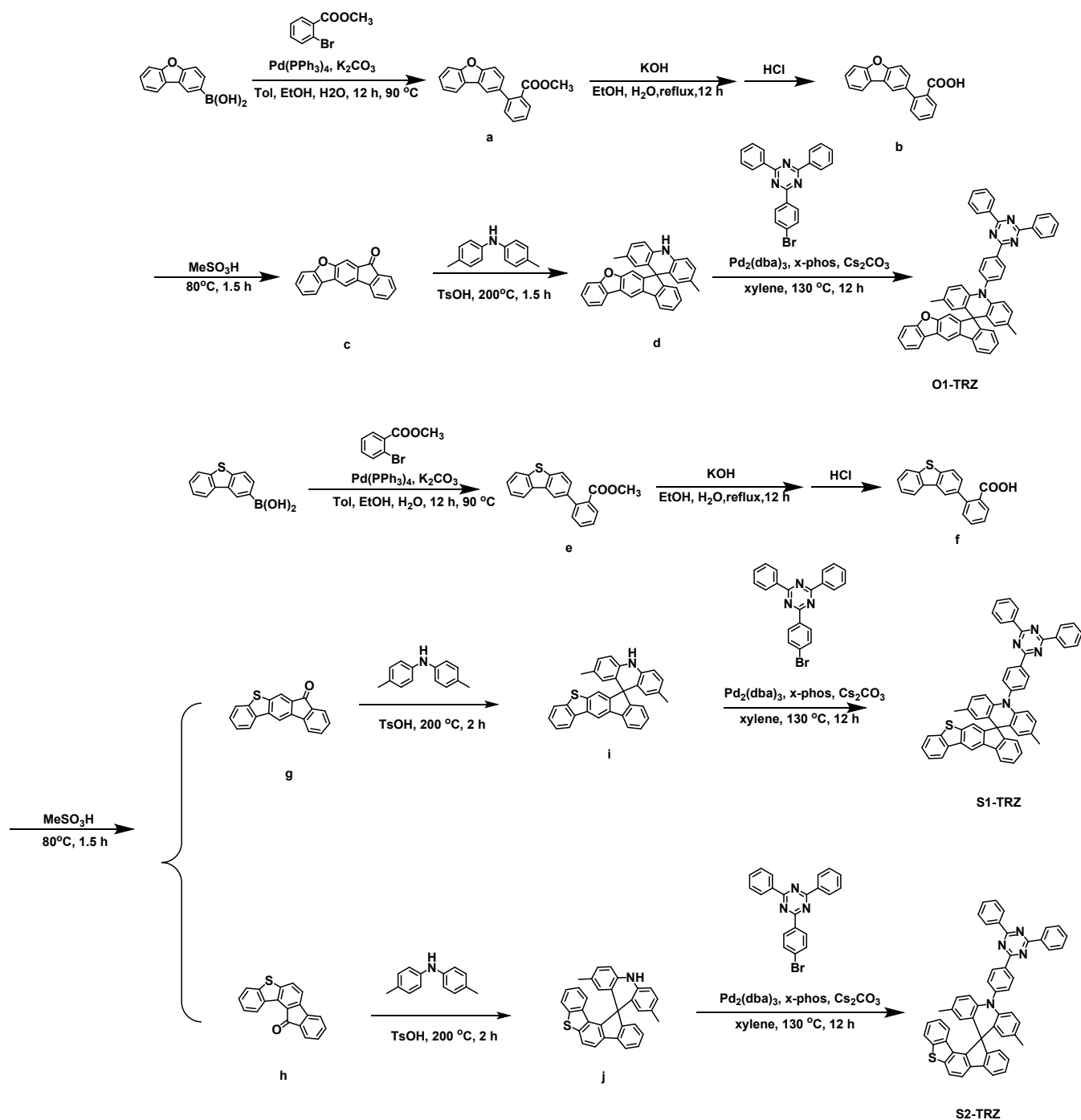
Then, the prompt PLQY (Φ_p) and delayed PLQY (Φ_d) were determined using intensity ratio (r_p , r_d) and total PLQY.

$$\Phi = \Phi_p + \Phi_d \quad (9)$$

$$\Phi_p = r_p \Phi \quad (10)$$

$$\Phi_d = r_d \Phi \quad (11)$$

Synthesis and Characterization



Scheme S1. Synthetic route of TRZ-QAc

Synthesis of 2-(dibenzo[b,d]furan-2-yl) methoxyacetate (a)

Under a nitrogen atmosphere, dibenzo[b,d]furan-2-boronic acid (5 g, 23.5 mmol), 2-bromomethylbenzoate (12.17 g, 56.6 mmol), and a mixed solution of toluene, ethanol, and water in a ratio of 4:2:1 (50 mL) are added to a 200 mL flask. After degassing the mixture for 10 minutes, tetrakis(triphenylphosphine)palladium (200 mg, 0.89 mmol) and potassium carbonate (9.8 g, 71 mmol) are added. The mixture is then heated to 90 °C and stirred overnight under a nitrogen atmosphere. After cooling, the mixture is vacuum filtered, and the filtrate is removed by vacuum evaporation. The crude product is purified by column chromatography (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) to obtain a white solid (6 g, yield: 86%), which is directly used for the next step.

Synthesis of 2-(dibenzo[b,d]furan-2-yl)benzoic acid (b)

Under atmospheric conditions, intermediate a (6 g, 28.3 mmol) is added to a 250 mL round-bottom flask containing a mixture of potassium hydroxide, ethanol, and water in a 1:1 ratio (50 mL). The mixture is refluxed with condensation and stirred overnight. After the reaction is complete, the ethanol is removed under reduced pressure. Sulfuric acid is then titrated into the reaction mixture until the pH is neutral. A white solid precipitates, which is collected by suction filtration to obtain the white solid (5 g, yield: 82%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.18 (d, J = 7.5 Hz, 1H), 8.12 (d, J = 1.9 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.73 (dd, J = 8.5, 2.4 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.57 - 7.39 (m, 5H).

Synthesis of 7-fluorenyl[2,3-b]benzofuran-7-one (c)

Intermediate b (5 g, 17.3 mmol) and methanesulfonic acid (30 mL) are added to a 100 mL single-neck round-bottom flask. Under atmospheric conditions, the mixture is heated to 80°C and stirred for 1.5 hours. After cooling, the mixture is vacuum filtered, and the filtrate is removed by vacuum evaporation. The crude product is purified by column chromatography (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) to obtain a white solid (2.3 g, yield: 48%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, J = 13.0 Hz, 2H), 7.86 (s, 1H), 7.70 (d, J = 7.3 Hz, 1H), 7.62 (t, J = 7.5 Hz, 2H), 7.58 - 7.51 (m, 2H), 7.45 - 7.39 (m, 1H), 7.31 (dd, J = 7.5, 1.0 Hz, 1H).

Synthesis of 2,7-dimethyl-10H-spiro[acridine-9,7'-fluoreno[2,3-b]benzofuran] (d)

Under a nitrogen atmosphere, 4,4'-dimethyldiphenylamine (5 g, 25.5 mmol) and p-toluenesulfonic acid monohydrate (323 mg, 1.7 mmol) are added to a double-neck round-bottom flask. The mixture is heated to 120°C and stirred for 30 minutes. Intermediate c (2.3 g, 8.5 mmol) is then quickly added to the flask, and the temperature is raised to 200°C and maintained for 1.5 hours. After cooling, the crude product is dissolved in 30 mL of dichloromethane and the solvent is removed under reduced pressure. The crude product is purified by column chromatography using a solvent system of petroleum ether/dichloromethane (3:1 v/v). The product is obtained as a white solid (2 g, yield: 52%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.07 (s, 1H), 8.70 (d, J = 0.9 Hz, 1H), 8.22 - 8.19 (m, 1H), 8.03 - 7.99 (m, 1H), 7.70 - 7.64 (m, 1H), 7.52 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H), 7.48 - 7.38 (m, 3H), 7.26 - 7.15 (m, 2H), 7.05 - 6.94 (m, 1H), 6.93 - 6.85 (m, 4H), 5.97 - 5.93 (m, 2H), 1.87 (s, 5H).

Synthesis of 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,7-dimethyl-10H-spiro[acridine-9,7'-indeno[2,3-b]benzofuran (O1-TRZ)

Under a nitrogen atmosphere, d (500 mg, 1.1 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (600 mg, 1.5 mmol), and xylene (20 mL) are added to a 100 mL round-bottom flask. The mixture is degassed for 10 minutes, after which tris(dibenzylideneacetone)dipalladium (50 mg, 0.05 mmol), cesium carbonate (975 mg, 3 mmol), and X-phos (60 mg, 0.12 mmol) are added under a nitrogen atmosphere. The mixture is then heated to 110°C and stirred overnight. After cooling, the mixture is filtered, and the filtrate is removed by vacuum evaporation. The crude product is purified by column chromatography (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) to obtain a yellow solid (670 g, yield: 81%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.14 - 9.11 (m, 1H), 8.90 - 8.86 (m, 2H), 8.07 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.79 - 7.75 (m, 1H), 7.71 - 7.63 (m, 4H), 7.57 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.47 (td, J = 7.6, 1.8 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.33 (td, J = 7.3, 1.1 Hz, 1H), 6.79 (dd, J = 8.5, 2.0 Hz, 1H), 6.43 (d, J = 8.5 Hz, 1H), 6.29 (d, J = 2.0 Hz, 1H), 1.98 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 171.91, 171.11, 156.92, 139.13, 136.26, 136.12, 134.71, 132.74, 131.76, 129.08, 128.77, 128.04, 127.72, 126.99, 125.95, 124.39, 124.16, 122.77, 120.53, 119.57, 111.71, 111.40, 109.53, 20.40. MALDI-TOF-MS(M): m/z 755.65 [M-H]⁻. Anal. calcd for C₅₄H₃₆N₄O(%): C 85.69 H 4.79 N 7.40; found: C 85.32, H 4.73, N 7.38.

Synthesis of 2-(dibenzo[b,d]thiophen-2-yl)methoxyacetate (e)

Under a nitrogen atmosphere, dibenzo[b,d]thiophen-2-boronic acid (5 g, 21.9 mmol), 2-bromomethyl benzoate (11.3 g, 52.6 mmol), and a mixed solution of toluene, ethanol, and water in a ratio of 4:2:1 (50 mL) are added to a 200 mL round-bottom flask. The mixture is degassed for 10 minutes, after which tetrakis-(triphenylphosphine)palladium (200 mg, 0.89 mmol), potassium carbonate (9.8 g, 71 mmol), and Xantphos (an appropriate amount) are added. The mixture is then heated to 90°C and stirred overnight under a nitrogen atmosphere. After cooling, the mixture is vacuum filtered, and the filtrate is removed by vacuum evaporation. The crude product is purified by column chromatography (300-400 mesh, petroleum

ether/dichloromethane = 3:1 v/v) to obtain a white solid (6 g, yield: 82%). ¹H NMR (400 MHz, Chloroform-d) δ 8.20 - 8.15 (m, 1H), 8.14 (d, J = 1.8 Hz, 1H), 7.94 - 7.87 (m, 3H), 7.64 - 7.57 (m, 1H), 7.54 - 7.41 (m, 5H).

Synthesis of 2-(dibenzo[b,d]thiophen-2-yl)benzoic acid (f)

Under atmospheric conditions, intermediate e (6 g, 18.9 mmol) is added to a 250 mL round-bottom flask containing a mixture of potassium hydroxide, ethanol, and water in a 1:1 ratio (50 mL). The mixture is refluxed with condensation and stirred overnight. After the reaction is complete, the ethanol is removed under reduced pressure. Sulfuric acid is then titrated into the reaction mixture until the pH is neutral. A white solid precipitates, which is collected by suction filtration to obtain the white solid (4.6 g, yield: 80%). This solid is used directly in the next step.

Synthesis of 7-fluorenyl[2,3-b]benzothiophen-7-one (g) and 12-phenyl[b]fluoren-[1,2-d]thiophen-12-one (h)

Intermediate f (4.6 g, 15 mmol) and methanesulfonic acid (30 mL) are added to a 100 mL single-neck round-bottom flask. Under atmospheric conditions, the mixture is heated to 80°C and stirred for 1.5 hours. After cooling, the mixture is vacuum filtered, and the filtrate is removed by vacuum evaporation. The crude product is purified by column chromatography (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v), which can separate the isomers. The yellow solid g (1.3 g, yield: 30%) is obtained as one of the products. ¹H NMR (500 MHz, Chloroform-d) δ 8.56 (s, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.77 (s, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.46 (q, J = 7.0 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H), 7.30 (s, 1H), red solid h (2.8 g, yield: 65 %). ¹H NMR (500 MHz, Chloroform-d) δ 9.86 (dt, J = 6.1, 2.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.84 (dt, J = 7.4, 3.2 Hz, 1H), 7.68 (d, J = 7.3 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.58 - 7.53 (m, 2H), 7.54 - 7.46 (m, 2H), 7.34 - 7.29 (m, 1H).

Synthesis of 2,7-dimethyl-10H-spiro[acridine-9,7'-benzo[b]fluoren[3,2-d]thiophene] (i)

Under a nitrogen atmosphere, 4,4'-dimethyldiphenylamine (2.7 g, 13.5 mmol) and p-toluenesulfonic acid monohydrate (171 mg, 0.9 mmol) are added to a double-neck round-bottom flask. The mixture is heated to 120°C and stirred for 30 minutes. Intermediate g (1.3 g, 4.5 mmol) is then quickly added to the flask, and the temperature is raised to 200°C and maintained for 1.5 hours. After cooling, the crude product is dissolved in 30 mL of dichloromethane and the solvent is removed under reduced pressure. The crude product is purified by column chromatography using a solvent system of petroleum ether/dichloromethane (3:1 v/v). The product is obtained as a white solid (1.1 g, yield: 54%). ¹H NMR (400 MHz, DMSO-d₆) δ 9.07 (s, 1H), 8.95 (s, 1H), 8.49 (d, J = 7.7 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.65 - 7.40 (m, 3H), 7.23 (dd, J = 33.1, 7.5 Hz, 2H), 6.88 (q, J = 8.3 Hz, 4H), 5.95 (s, 2H), 1.87 (s, 6H).

Synthesis of 2,7-dimethyl-10H-spiro[acridine-9,12'-benzo[b]fluoren[1,2-d]thiophene] (j)

Under a nitrogen atmosphere, 4,4'-dimethyldiphenylamine (5.8 g, 29.4 mmol) and p-toluenesulfonic acid monohydrate (372 mg, 1.96 mmol) are added to a double-neck round-bottom flask. The mixture is heated to 120°C and stirred for 30 minutes. Intermediate h (2.8 g, 9.8 mmol) is then quickly added to the flask, and the temperature is raised to 200°C and maintained for 1.5 hours. After cooling, the crude product is dissolved in 30 mL of dichloromethane and the solvent is removed under reduced pressure. The crude product is purified by column chromatography using a solvent system of petroleum ether/dichloromethane (3:1 v/v). The product is obtained as a white solid (2.4 g, yield: 52%). ¹H NMR (400 MHz, DMSO-d₆) δ 9.27 (s, 1H), 8.25 (t, J = 1.8 Hz, 2H), 7.93 (t, J = 7.0 Hz, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.28 (m, 2H), 7.21 (d, J = 7.5 Hz, 1H), 7.14 - 7.09 (m, 1H), 6.94 (m, 3H), 6.82 (d, J = 8.2 Hz, 2H), 5.87 (d, J = 1.9 Hz, 2H), 1.71 (d, J = 2.3 Hz, 6H).

Synthesis of 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,7-dimethyl-10H-spiro[acridine-9,7'-benzo[b]indeno[3,2-d]thiophene] (S1-TRZ)

Under a nitrogen atmosphere, intermediate i (550 mg, 1.2 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (650 mg, 1.9 mmol), and xylene (20 mL) are added to a 100 mL round-bottom flask. The mixture is degassed for 10 minutes, after which tris(dibenzylideneacetone)dipalladium (50 mg, 0.5 mmol), cesium carbonate (780 mg, 2.4 mmol), and X-phos (240 mg, 0.5 mmol) are added under a nitrogen atmosphere. The mixture is then heated to 130°C and stirred overnight. After cooling, the mixture is filtered, and the filtrate is removed by vacuum evaporation. The crude product

is purified by column chromatography (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) to obtain a yellow solid (700 mg, yield: 73%).¹H NMR (500 MHz, Chloroform-d) δ 9.15 (dd, J = 8.1, 6.0 Hz, 2H), 8.90 - 8.86 (m, 4H), 8.60 (d, J = 3.2 Hz, 1H), 8.33 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.90 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.67 (dq, J = 14.0, 6.8 Hz, 6H), 7.53 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.2 Hz, 3H), 7.35 (t, J = 7.4 Hz, 1H), 6.78 (dd, J = 8.5, 2.1 Hz, 2H), 6.41 (d, J = 8.4 Hz, 2H), 6.27 (d, J = 2.0 Hz, 2H), 1.97 (s, 6H). ¹³C NMR (126 MHz, Chloroform-d) δ 171.91, 171.10, 156.77, 156.47, 145.59, 139.90, 139.76, 138.90, 138.82, 136.99, 136.30, 136.12, 135.48, 135.23, 132.75, 131.85, 131.79, 131.71, 129.83, 129.09, 128.77, 128.66, 128.48, 128.23, 127.72, 126.61, 126.10, 124.67, 124.47, 122.94, 121.54, 120.37, 119.81, 114.80, 114.62, 112.49, 56.62, 20.41. MALDI-TOF-MS(M): m/z 771.56 [M-H]. Anal. calcd for C₅₄H₃₆N₄S(%): C 83.91 H 4.69 N 7.25; found: C 83.73, H 4.54, N 7.33.

Synthesis of 10-[4-[(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]]-2,7-dimethyl-10H-spiro[acridine-9,12'-benzo[b]indeno[1,2-d]thiophene] (S2-TRZ)

Under a nitrogen atmosphere, intermediate j (400 mg, 1.3 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (700 mg, 1.8 mmol), and xylene (20 mL) are added to a 100 mL round-bottom flask. The mixture is degassed for 10 minutes, after which tris(dibenzylideneacetone)dipalladium (50 mg, 0.05 mmol), cesium carbonate (800 g, 2.4 mmol), and X-phos (60 mg, 0.12 mmol) are added under a nitrogen atmosphere. The mixture is then heated to 130°C and stirred overnight. After cooling, the mixture is filtered, and the filtrate is removed by vacuum evaporation. The crude product is purified by column chromatography (300-400 mesh, petroleum ether/dichloromethane = 3:1 v/v) to obtain a yellow solid (650 mg, yield: 64%).¹H NMR (500 MHz, Chloroform-d) δ 9.19 (d, J = 8.1 Hz, 2H), 8.89 (dd, J = 7.9, 1.6 Hz, 4H), 8.16 - 8.08 (m, 3H), 7.84 (t, J = 8.5 Hz, 3H), 7.80 (d, J = 7.8 Hz, 1H), 7.67 (qd, J = 8.6, 7.6, 2.5 Hz, 6H), 7.52 (d, J = 7.5 Hz, 1H), 7.36 - 7.29 (m, 2H), 7.24 (td, J = 7.4, 1.1 Hz, 1H), 7.16 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 6.74 - 6.67 (m, 2H), 6.41 (d, J = 8.4 Hz, 2H), 6.19 (d, J = 2.2 Hz, 2H), 1.81 (s, 6H). ¹³C NMR (126 MHz, Chloroform-d) δ 171.96, 171.13, 158.67, 148.29, 145.82, 140.18, 140.07, 138.74, 136.38, 136.13, 135.44, 134.59, 132.78, 132.73, 131.93, 131.86, 130.09, 129.09, 128.79, 128.54, 128.32, 127.19, 126.78, 126.44, 125.99, 124.76, 123.65, 122.94, 122.54, 122.15, 119.58, 118.40, 114.60, 57.85, 20.40. MALDI-TOF-MS(M): m/z 771.46 [M-H]. Anal. calcd for C₅₄H₃₆N₄S(%): C 83.91 H 4.69 N 7.25; found: C 83.82, H 4.37, N 7.98.

Supplementary figures and tables

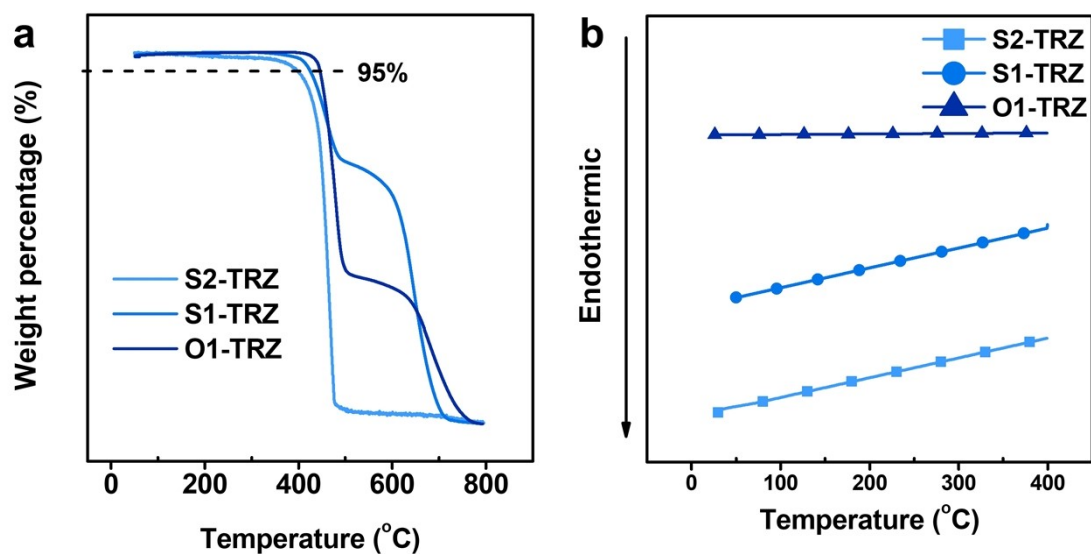


Figure S1. a) TGA and b) DSC profiles of O1-TRZ, S1-TRZ and S2-TRZ under a heating rate of 10 K/min.

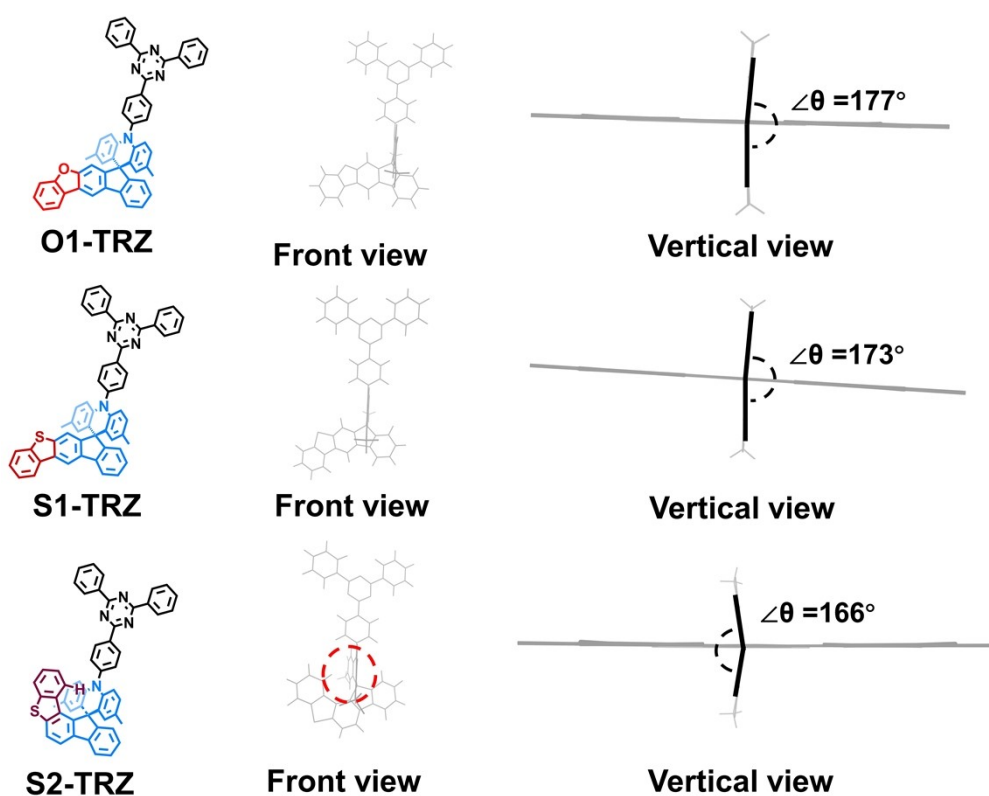


Figure S2. Optimized ground geometry of O1-TRZ, S1-TRZ and S2-TRZ.

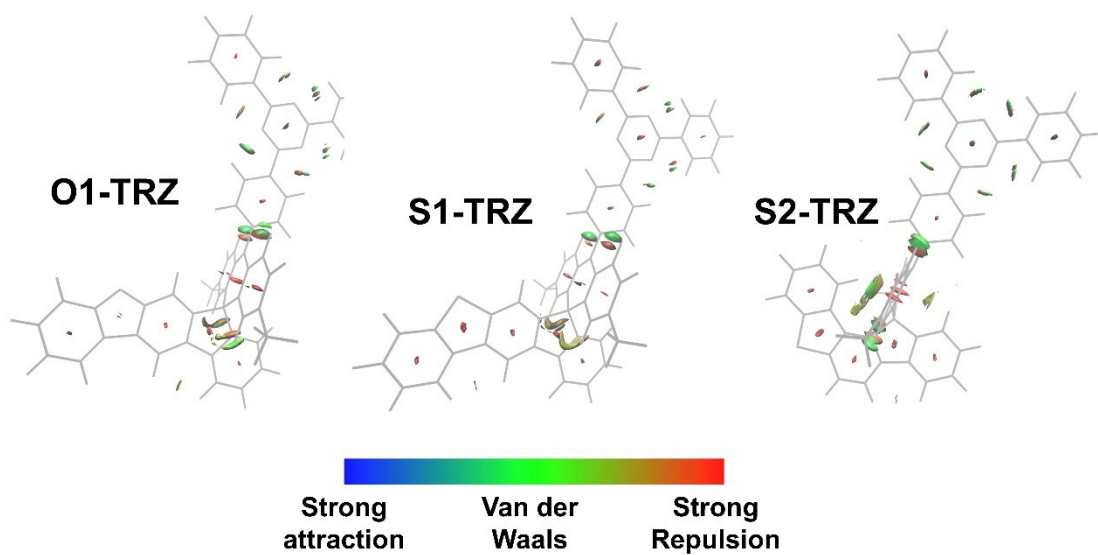


Figure S3. Reduced density gradient (RDG) isosurface maps with an isovalue of 0.5 of S2-TRZ.

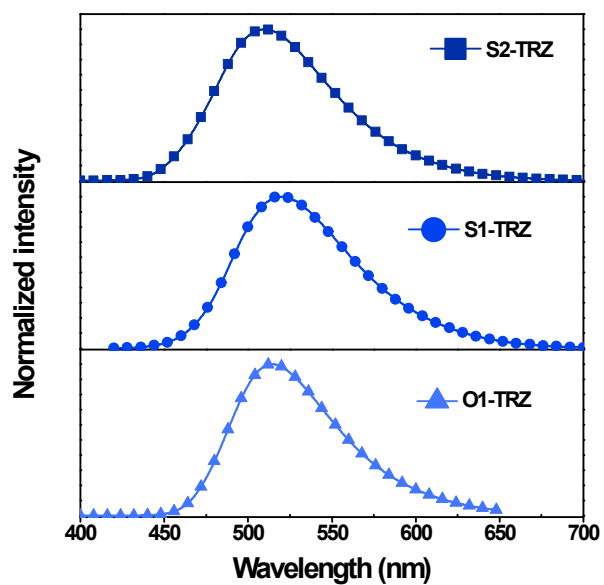


Figure S4. Fluorescent spectra of O1-TRZ, S1-TRZ and S2-TRZ in doped films (10 wt% in PPF) under room temperature.

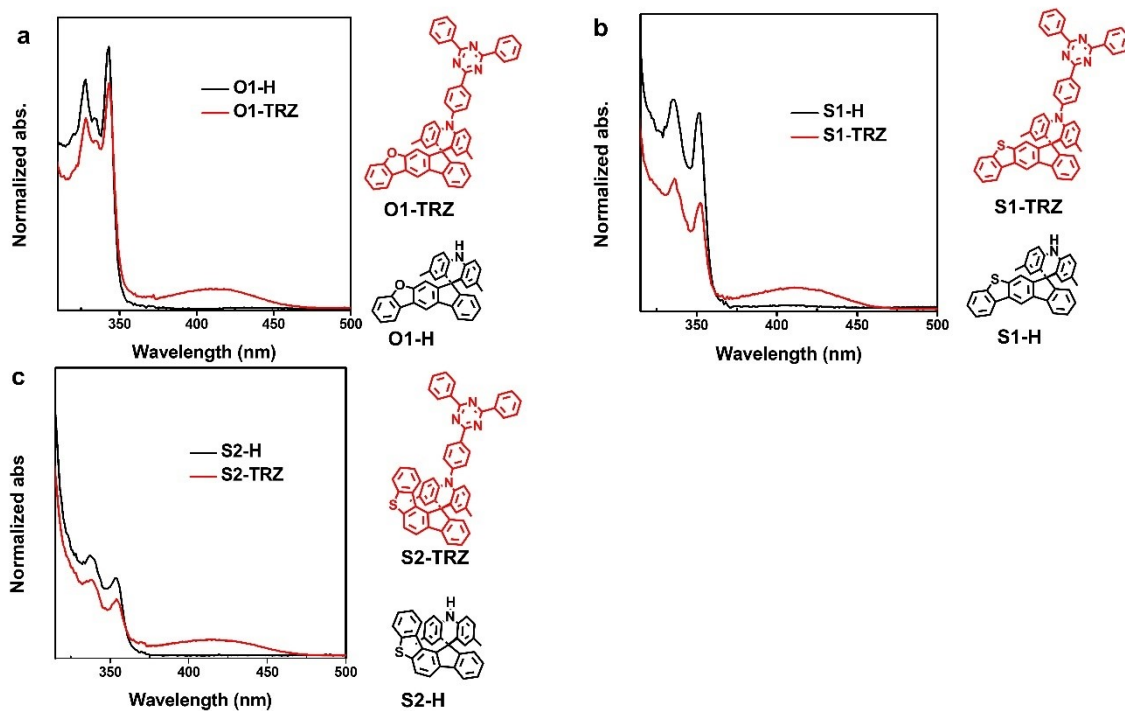


Figure S5. Comparison of the absorption spectrum of a) O1-TRZ, b) S1-TRZ and c) S2-TRZ with their donor units in dilute toluene.

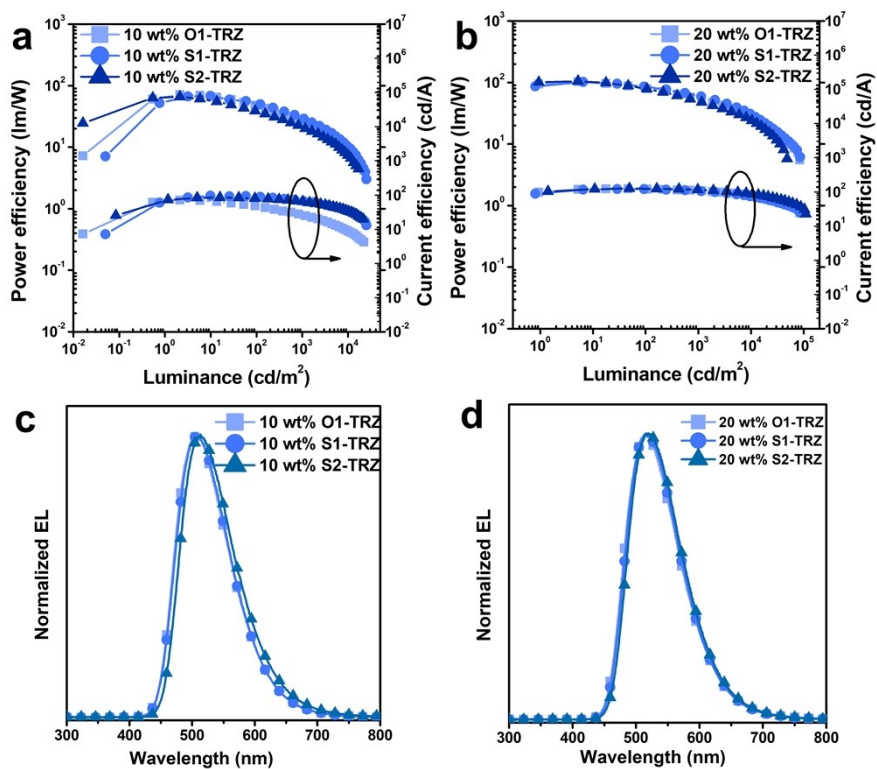


Figure S6. EL profiles of O1-TRZ, S1-TRZ and S2-TRZ with doping concentration of 10 and 20 wt%. a), b) J-V-L profiles, c), d) EL spectra.

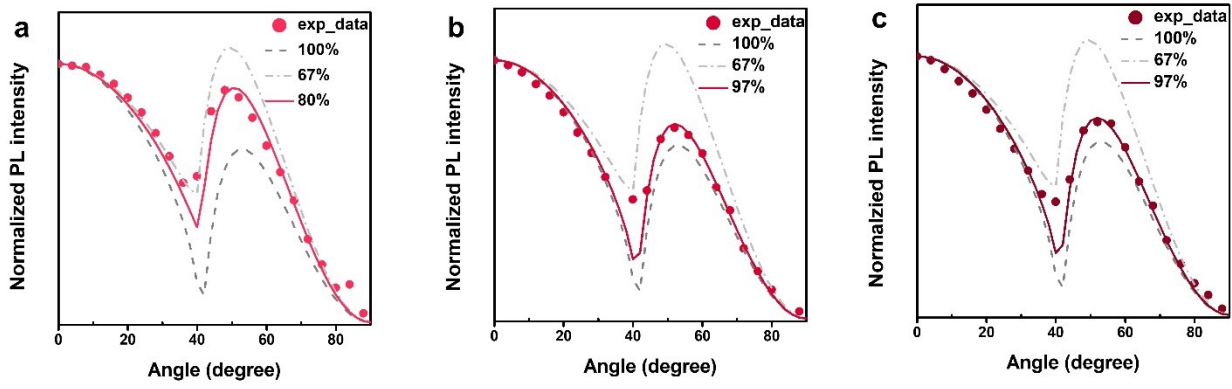


Figure S7. Measured p-polarized PL intensity (at PL peak wavelength) of a) O1-TRZ, b) S1-TRZ and c) S1-TRZ in doped films as a function of the emission angle.

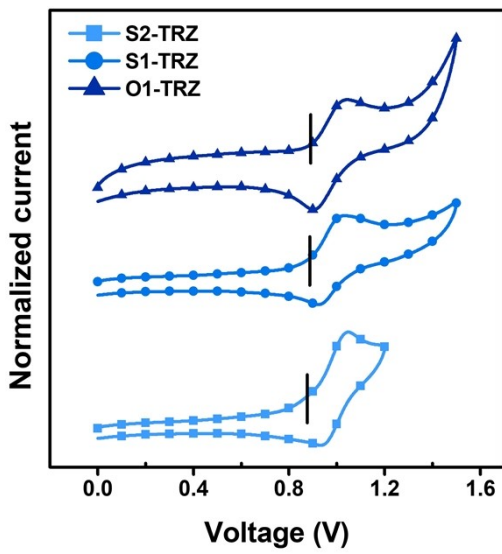
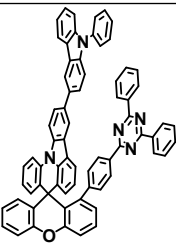
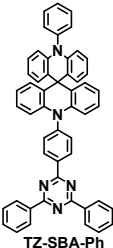
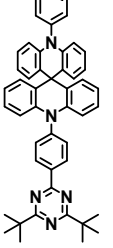
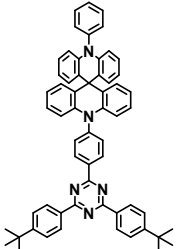
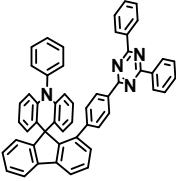
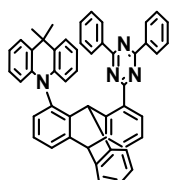
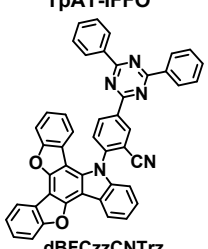
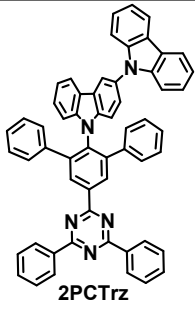
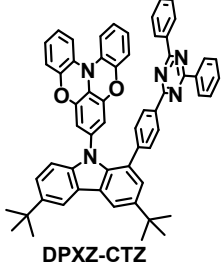
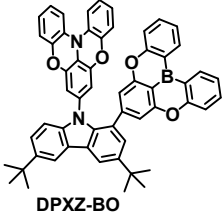
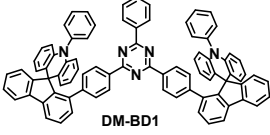
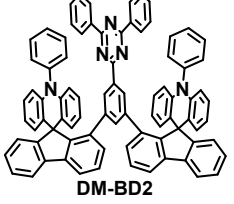
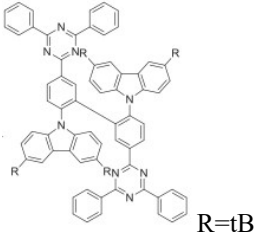
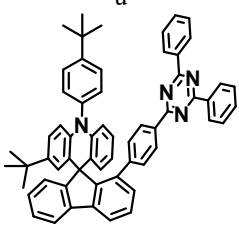
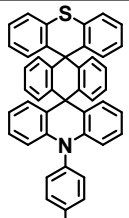
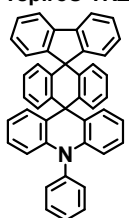
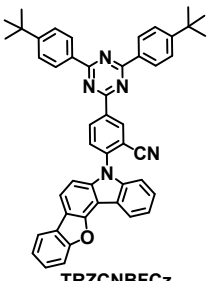
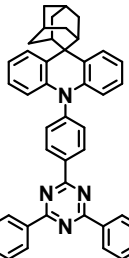
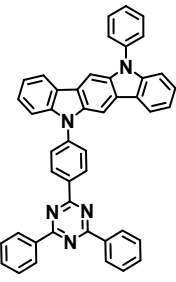
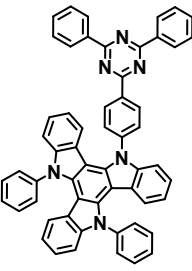


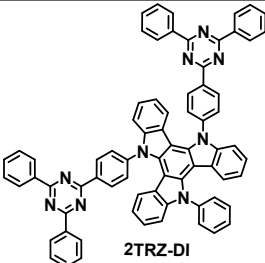
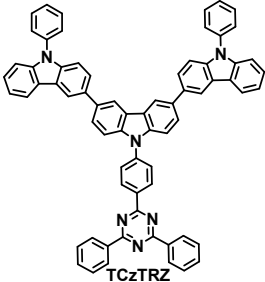
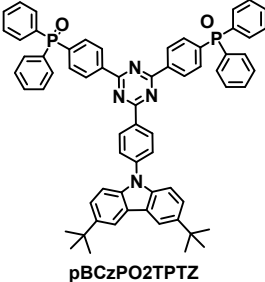
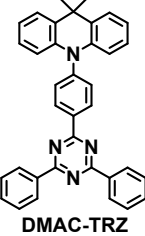
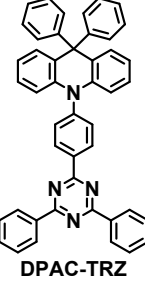
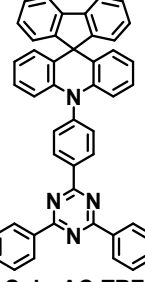
Figure S8. CV profiles of O1-TRZ, S1-TRZ and S2-TRZ.

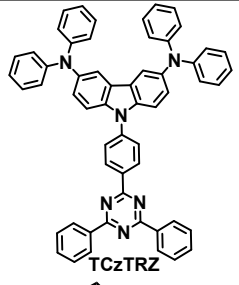
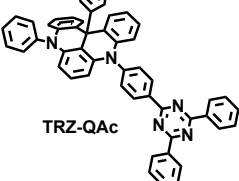
Table S1. Comparison of TADF emitters.

Compounds	τ_p (ns)	τ_d (μ s)	k_r (10^6 s $^{-1}$)	k_{RISC} (10^6 s $^{-1}$)	ΔE_{ST} (eV)	$EQE_{max/100/1000}$ (%)	Roll-off _{100/1000} (%)	Ref
 dCz-Xo-TRZ	40	7.5	8.74	0.33	0.24	27.8/27.4/23.9	1/14	5
 TZ-SBA-Ph	1.7	6.9		0.57	0.10	31.2/30.6/26.5	2/15	6
 tBuTZ-SBA-Ph	11.1	17.9		0.09	0.09	24.1/17.2/10.1	29/58	6
 tBuPhTZ-SBA-Ph	2.0	13.3		0.14	0.08	28.3/24.5/19.0	13/33	6
 DM-B	91	5.0	6.75	0.18	0.17	27.4/24.4/19.2	11/30	7
 TpAT-IFFO	15.3	4.1	1.1	12		19.2/19.1/18.1	1/6	8
 dBFCzzCNTrz	24.8	4.9		0.40	0.09	27.5/-/24.3	-/12	9

 <p>2PCTrz</p>	29.3	31.4		0.07	0.11	28.5/-/19.4	/32	10
 <p>DPXZ-CTZ</p>	117	3.38	0.84	2.31	-0.03	19.7/-/9.25	-/53	11
 <p>DPXZ-BO</p>	178	11.3	2.36	0.21	0.03	23.9/-/20.2	-/15	11
 <p>DM-BD1</p>	105	3.1	4.41	0.29	0	28/-/22.7	-/19	12
 <p>DM-BD2</p>	97	2.8	3.03	0.31	-0.07	26.6/-/22.4	-/16	12
 <p>R=tB</p>	11.4	15.0			0.06	26.6/26/18	2/32	13
 <p>2tDMG</p>	106	3.43	4.24	0.22	0.03	30.8/-/28.5	-/7	14

 TspiroS-TRZ	21.4	3.03	29	0.26	0.032	33.3/31.1/23.7	7/29	15
 TspiroF-TRZ	24	4.6	22	0.19	0.038	28.1/27.7/23.1	1/18	15
 TRZCNBFCz	13.8	9.4			0.13	26.6/22/16.8	17/37	16
 a-DMAc-TRZ	23	4.09	27	0.33	0.2	28.9/12.7/3.6	56/88	17
 IndCzpTr-2	11.09	34.31	75	0.02	0.11	30.0/15.3/-	49/-	18
 TRZ-DI	21	1/32	18	1.63	0.023	31.4/31/29	1/8	19

	20	1.47	16.4	1.59	0.026	26.2/25/22	5/16	19
		23.6		0.05	0.01	31.8/26/16	18/50	20
			11.4	0.05	0.01	28.9/26.1/16.4	10/43	21
	20	1.9	15.8	1.50	0.06	27.4/25.8/22.4	6/18	22
	15	2.9	8.28	2.28	0.13	25.8/24.1/18.3	7/29	22
	17	2.1	12.7	2.20	0.07	36.7/34.9/30.5	5/17	22

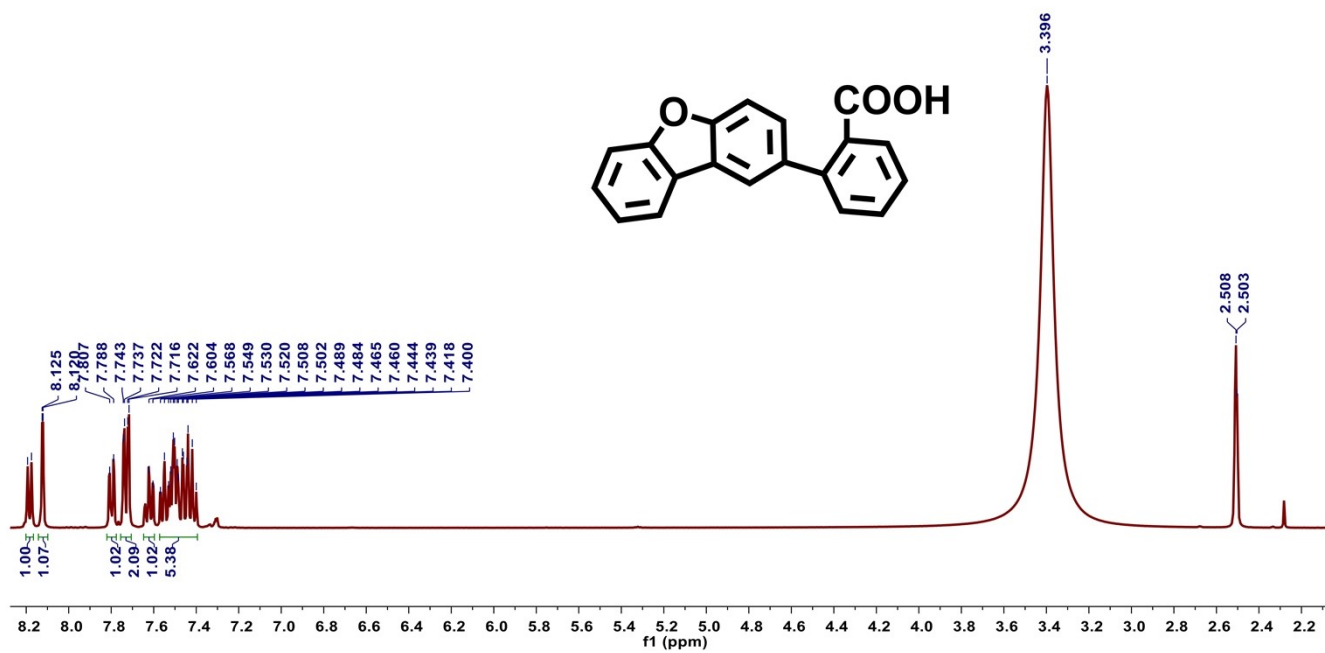
	8.7	16.2	106	0.006	0.009	29.6/26.5/20.0	10/32	23
	28	4.3	12.4	0.78	0.08	37.3/36.6/31.7	3/15	24

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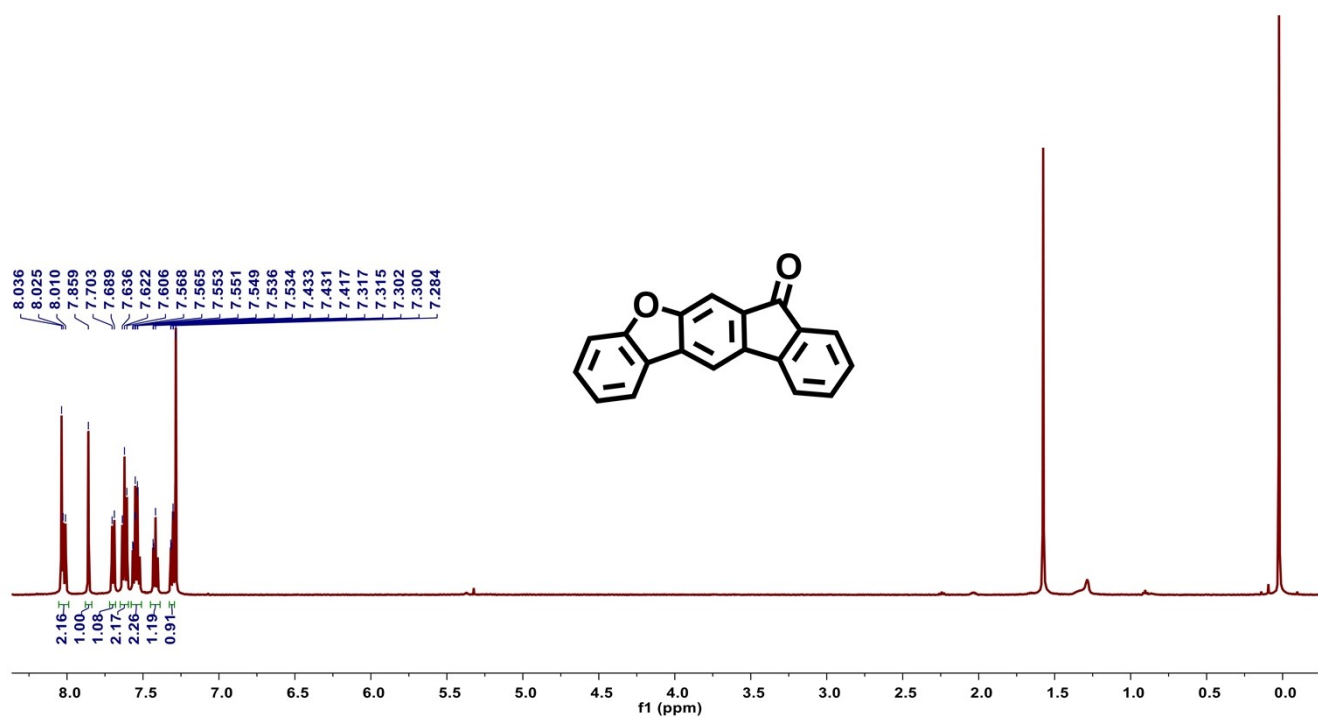
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NMR spectra

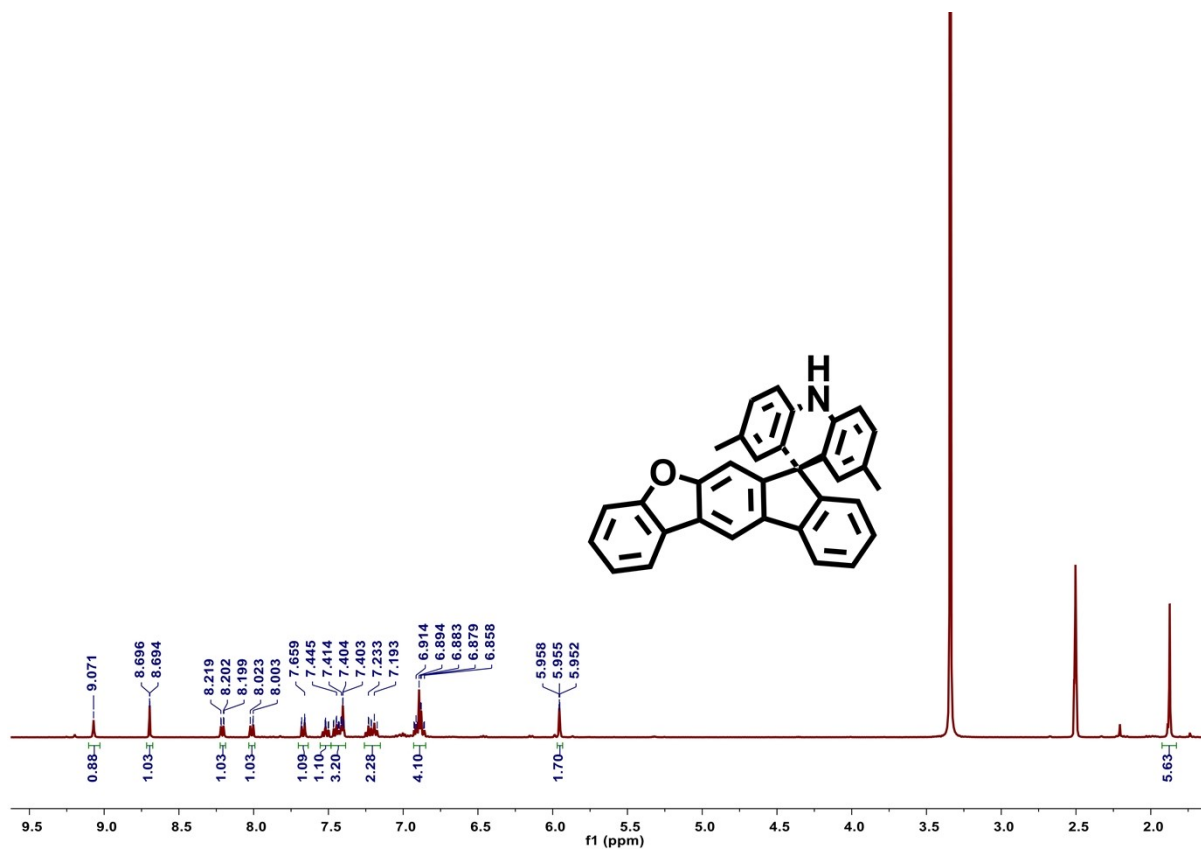
^1H NMR spectra of **b** ($\text{DMSO-}d_6$)



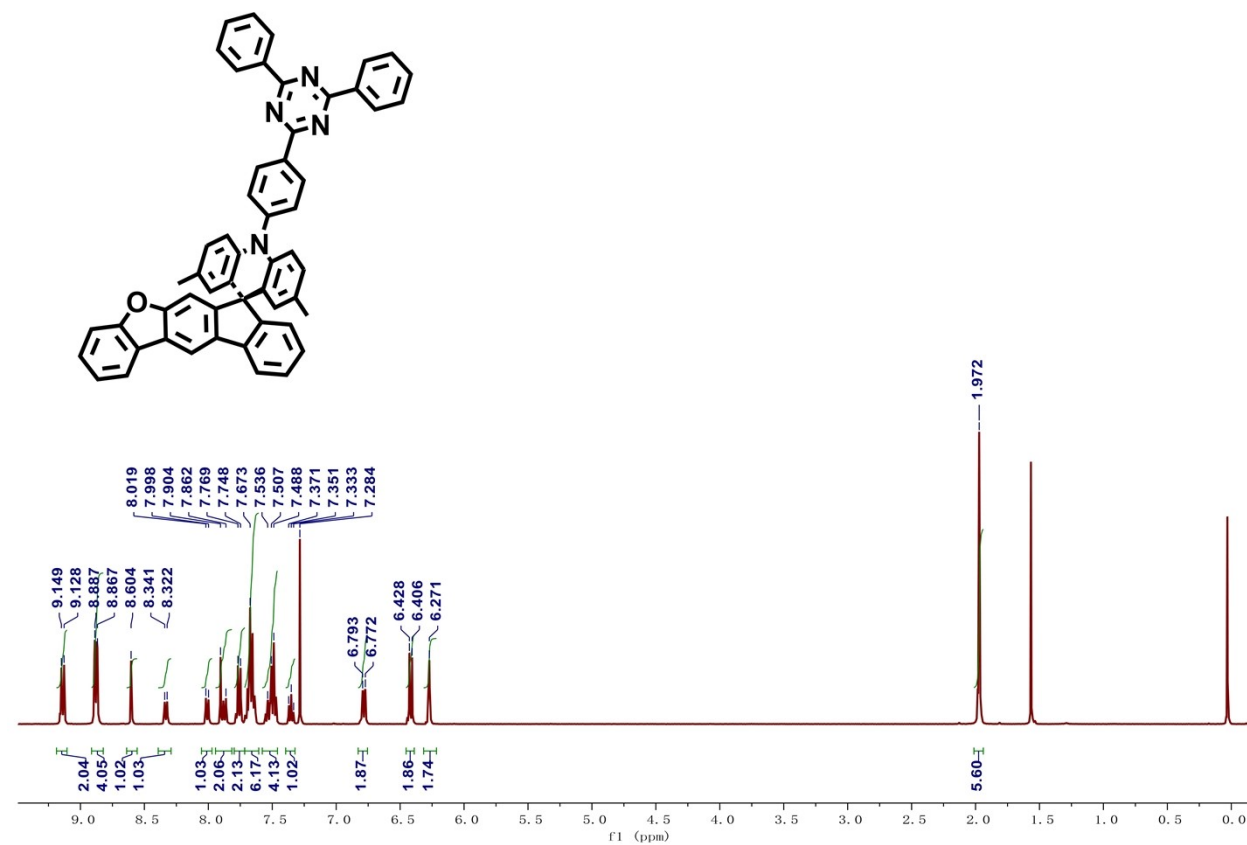
^1H NMR spectra of **c** (CDCl_3)



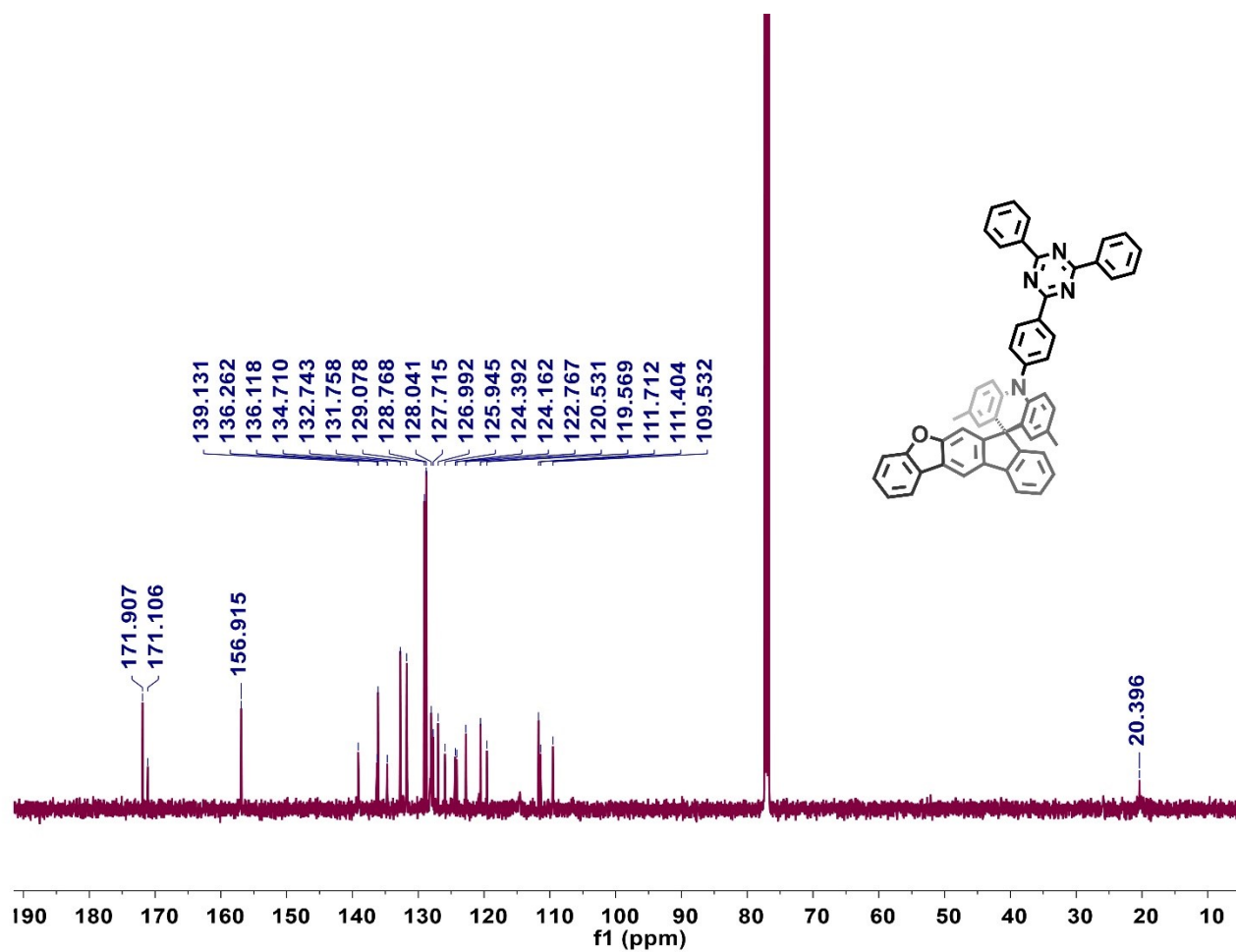
^1H NMR spectra of **d** (DMSO- d_6)



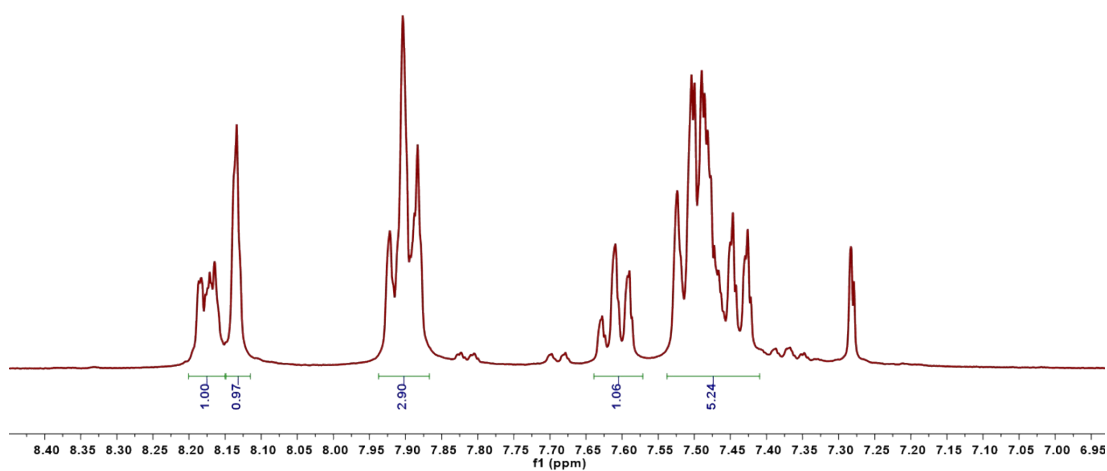
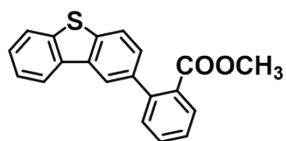
^1H NMR spectra of **O1-TRZ** (CDCl_3)



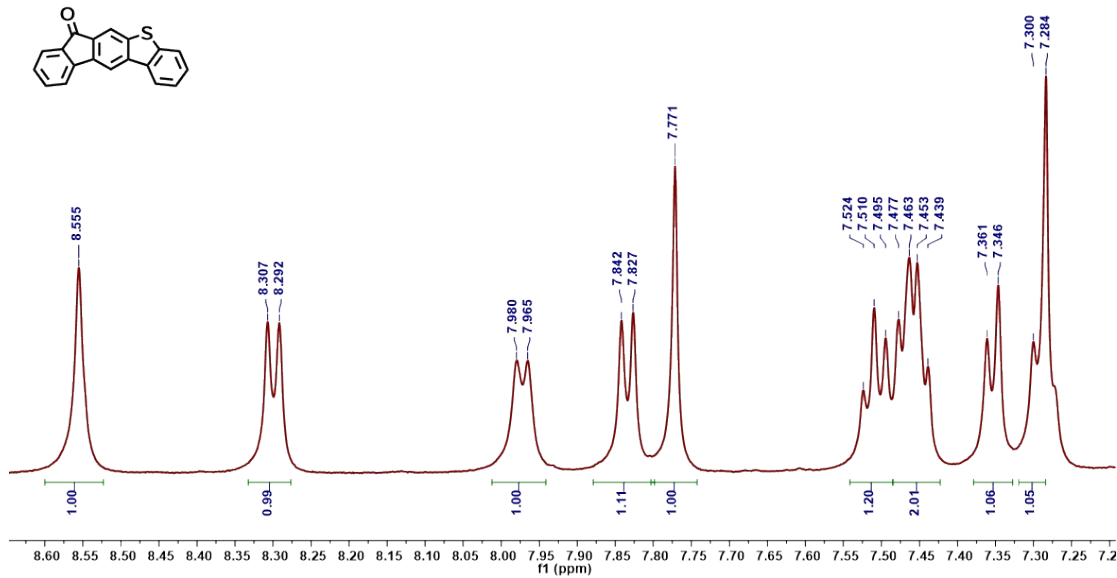
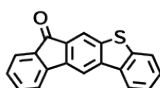
^{13}C NMR spectra of **O1-TRZ** (CDCl_3)



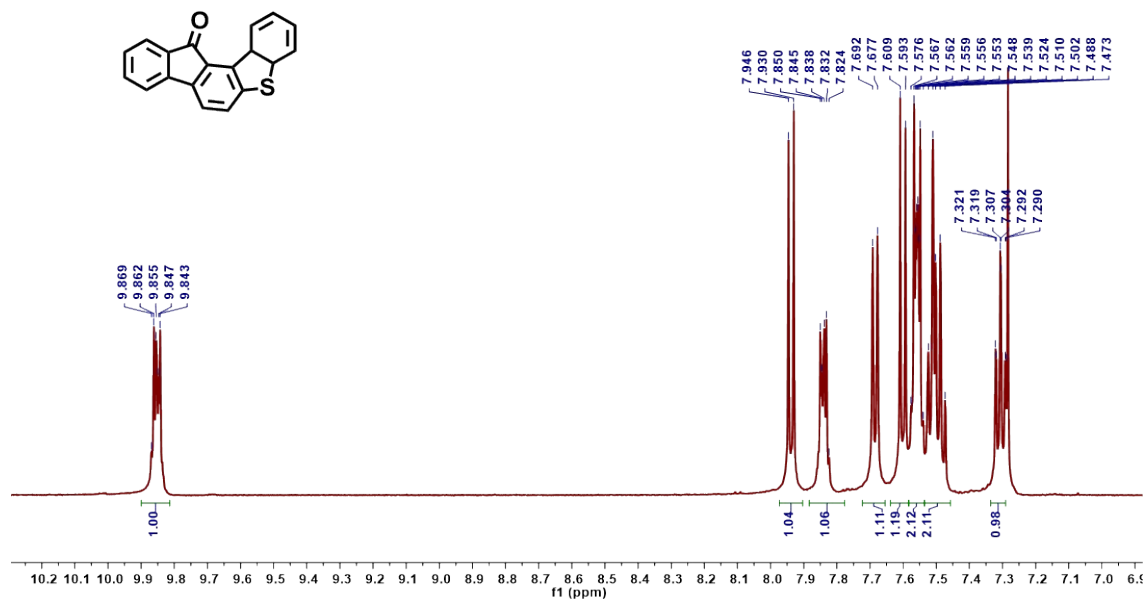
^1H NMR spectra of **a** (CDCl_3)



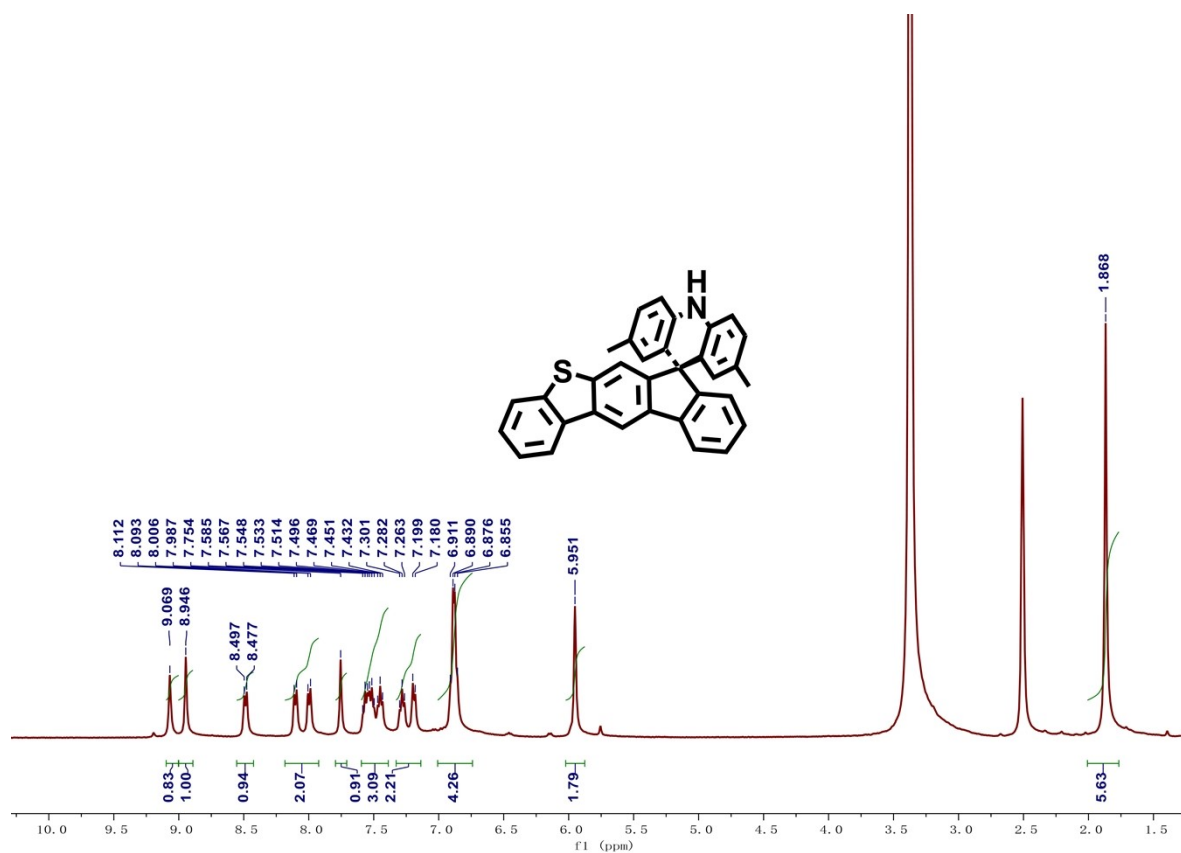
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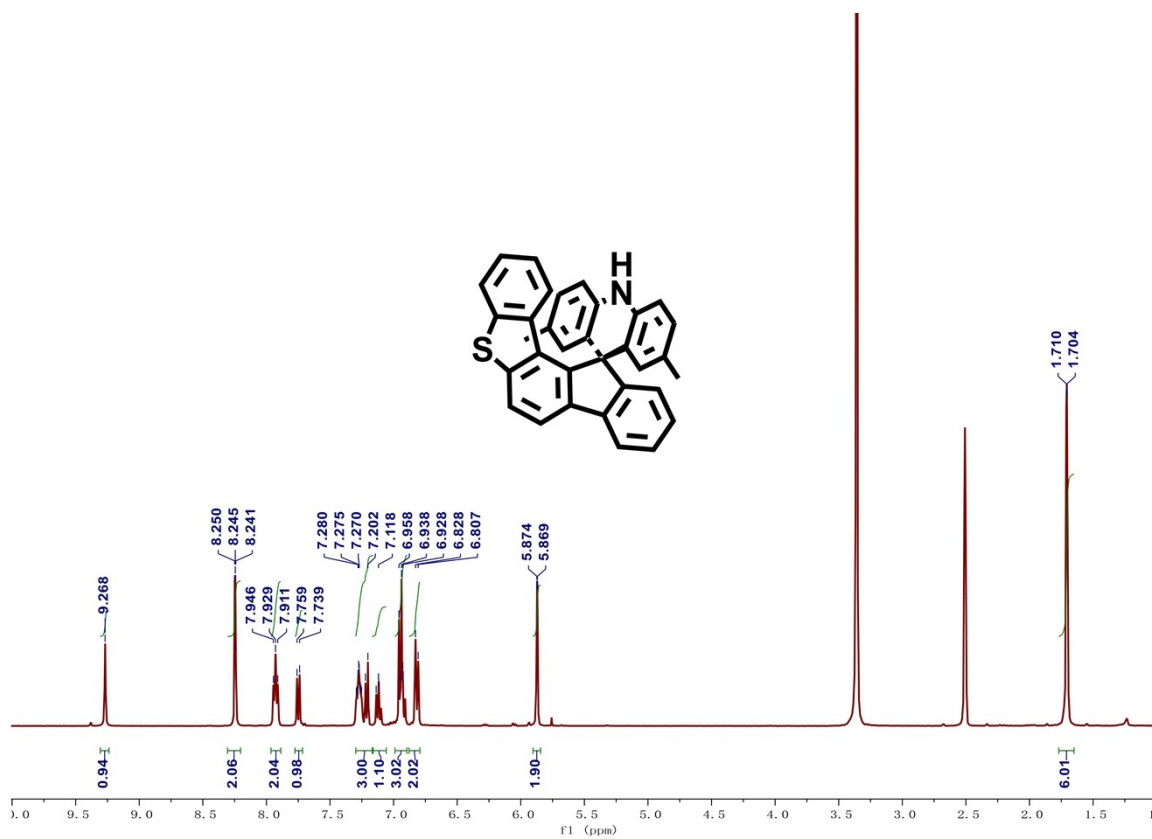
^1H NMR spectra of **h** (CDCl_3)



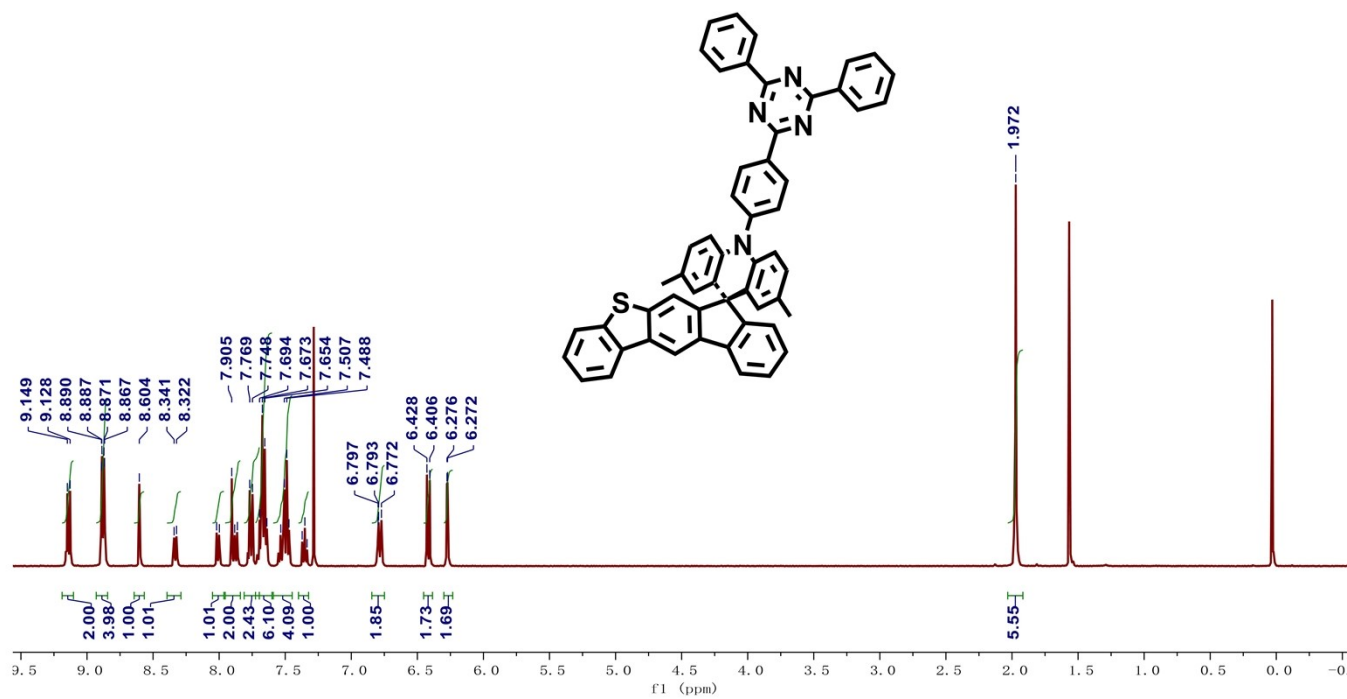
^1H NMR spectra of **i** ($\text{DMSO}-d_6$)



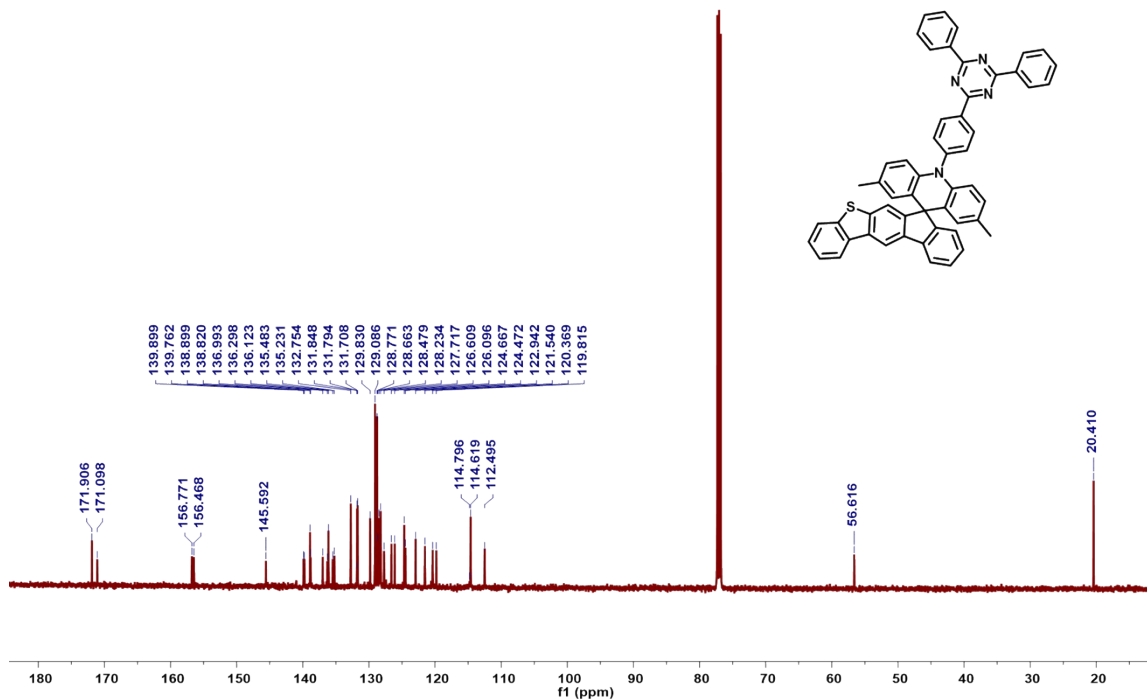
^1H NMR spectra of **j** ($\text{DMSO}-d_6$)



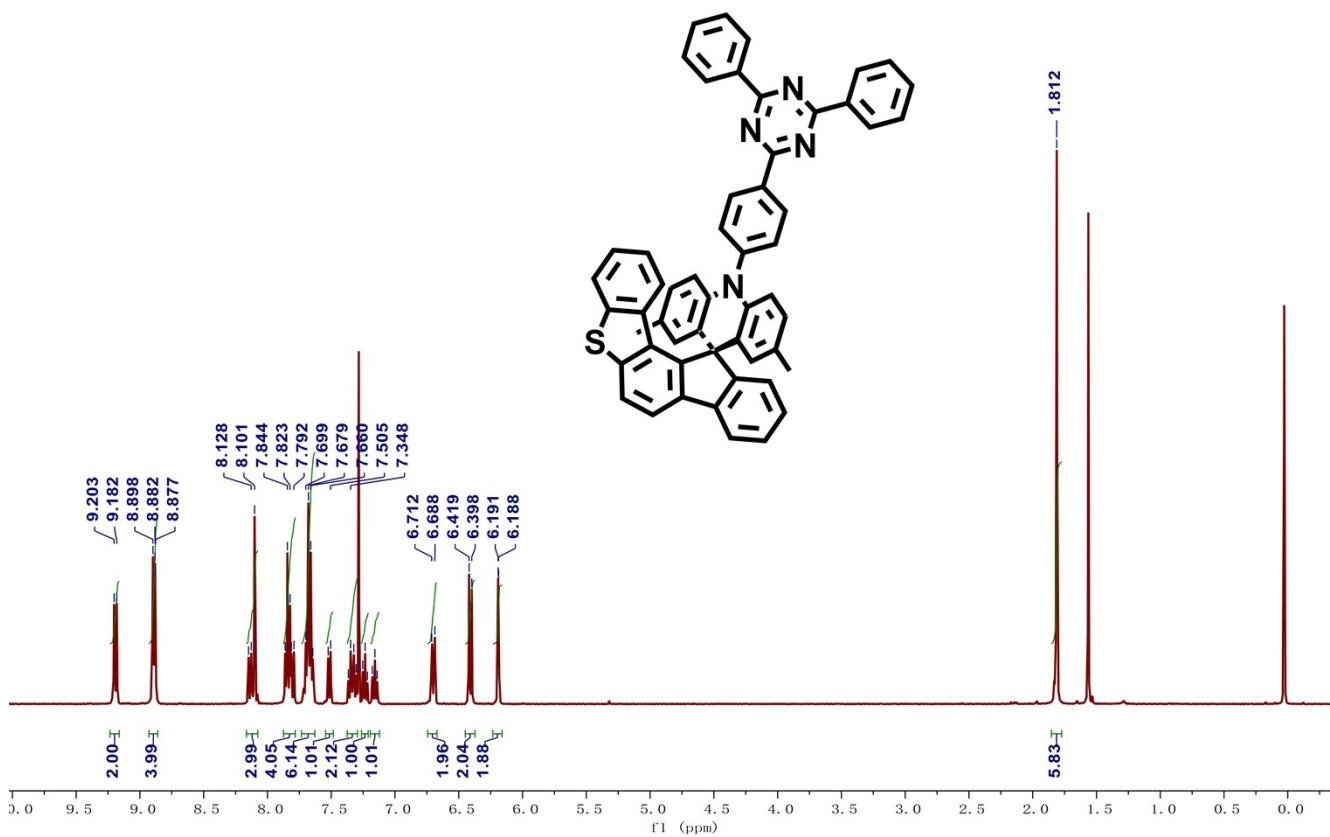
¹H NMR spectra of S1-TRZ (CDCl₃)



¹³C NMR spectra of **S1-TRZ** (CDCl₃)



¹H NMR spectra of **S2-TRZ** (CDCl₃)



¹³C NMR spectra of **S2-TRZ** (CDCl₃)

