

Spiro-Type Host Materials with Rigidified Skeleton for RGB Phosphorescent OLEDs

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1. Chemicals and instruments

All chemicals and reagents were used as received from commercial resources without further purification. Tetrahydrofuran (THF), and 1,4-dioxane used in synthetic routes were purified by PURE SOLV (Innovative Technology) purification system. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker 400 and 600 spectrometers at room temperature. Mass spectra and time of Flight MS-MALDI (MALDI-TOF) were performed on a Thermo ISQ mass spectrometer using a direct exposure probe and Bruker Auto flex II/Compass 1.0, respectively. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. Photoluminescence (PL) spectra and phosphorescent spectra were performed on Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C/min under nitrogen. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on TA SDT 2960 instrument at a heating rate of 10 °C/min under nitrogen, the temperature at 5% weight loss was used as the decomposition temperature (T_d). The electrochemical measurement was made using a CHI600 voltammetric analyzer. A conventional three-electrode configuration consisting of a platinum working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode were used. The solvent in the measurement was CH_2Cl_2 , and the supporting electrolyte was 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$. Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium (Fc/Fc^+) couple at a scan rate of 100 mV/s. Theoretical calculations based on density functional theory (DFT) approach at the B3LYP/6-31G (d) level were performed with the use of the Gaussian 09 program.

2. OLED fabrication and measurements

All the material except two novel synthesized hosts were acquired from commercial source without further purification. OLEDs were all fabricated under a base vacuum of 4×10^{-6} Torr and on ITO glass substrates (160 nm, 15 Ω /sq). Before the evaporation, ITO glass substrates were ultrasonically cleaned sequentially with deionized water, acetone, ethanol, and deionized water, and dried in an oven at 110 °C for 6 h. After that, they were put in ultraviolet ozone for 15 mins. The charge injecting layers deposited rates were 0.2~0.4 Å/s, the charge transporting layers deposited rates were 2~3 Å/s and Al's is 6-8 Å/s. Quartz crystals would monitor all materials deposition rates and thicknesses.

The EL information such as current efficiency (CE), EL spectra, power efficiency (PE), CIE coordinate, values of driving voltages, J - V curves and luminance were all recorded via KEITHLEY 2400 source meter and programmable spectra scan photometer (PHOTO RESEARCH, PR 655). All the measurements were conducted in ambient air at a room temperature, and the external quantum efficiency was calculated assuming Lambertian distribution of light emission.

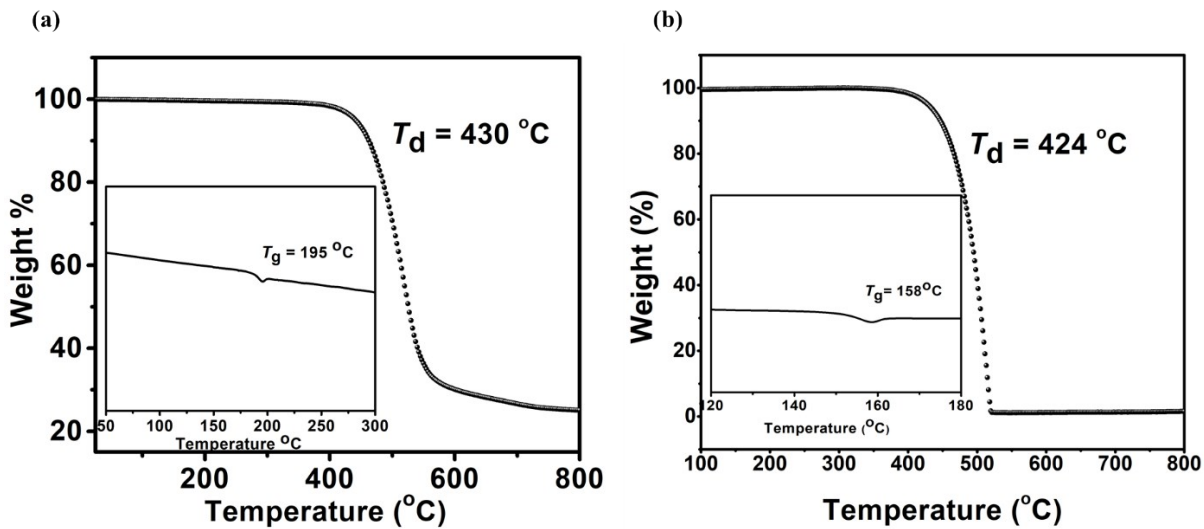


Fig. S1 The TGA and DSC (inset figure) plots of (a) QAF-TRZ and (b) STF-TRZ.

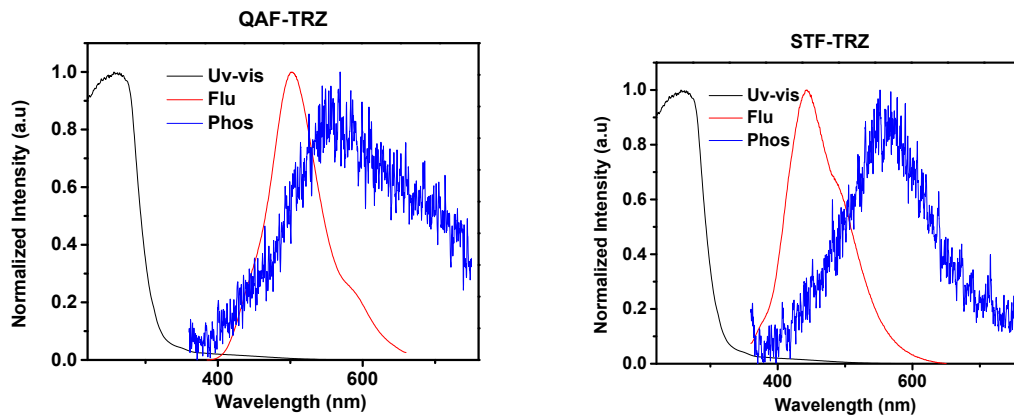


Fig. S2 Photophysical properties of QAF-TRZ and STF-TRZ in neat film.

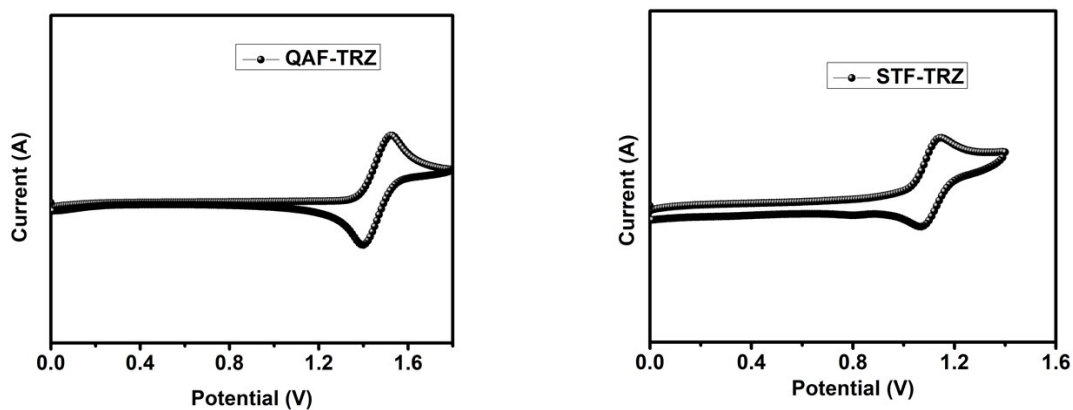


Fig. S3 Cyclic Voltammetry curves of **QAF-TRZ** and **STF-TRZ** in DCM solution at room temperature.

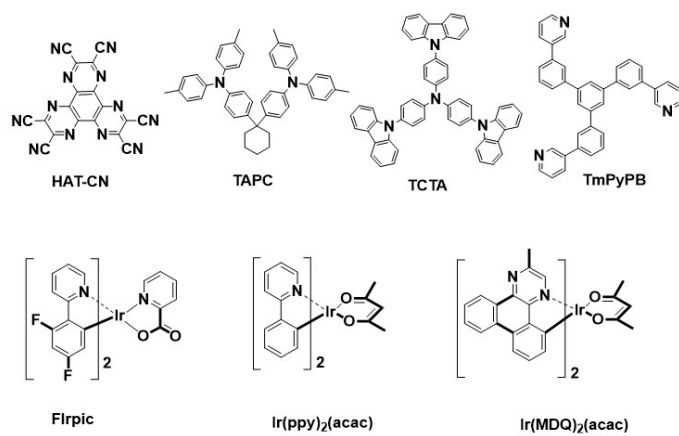


Fig. S4 Chemical structures of commercial materials applied in the PHOLEDs

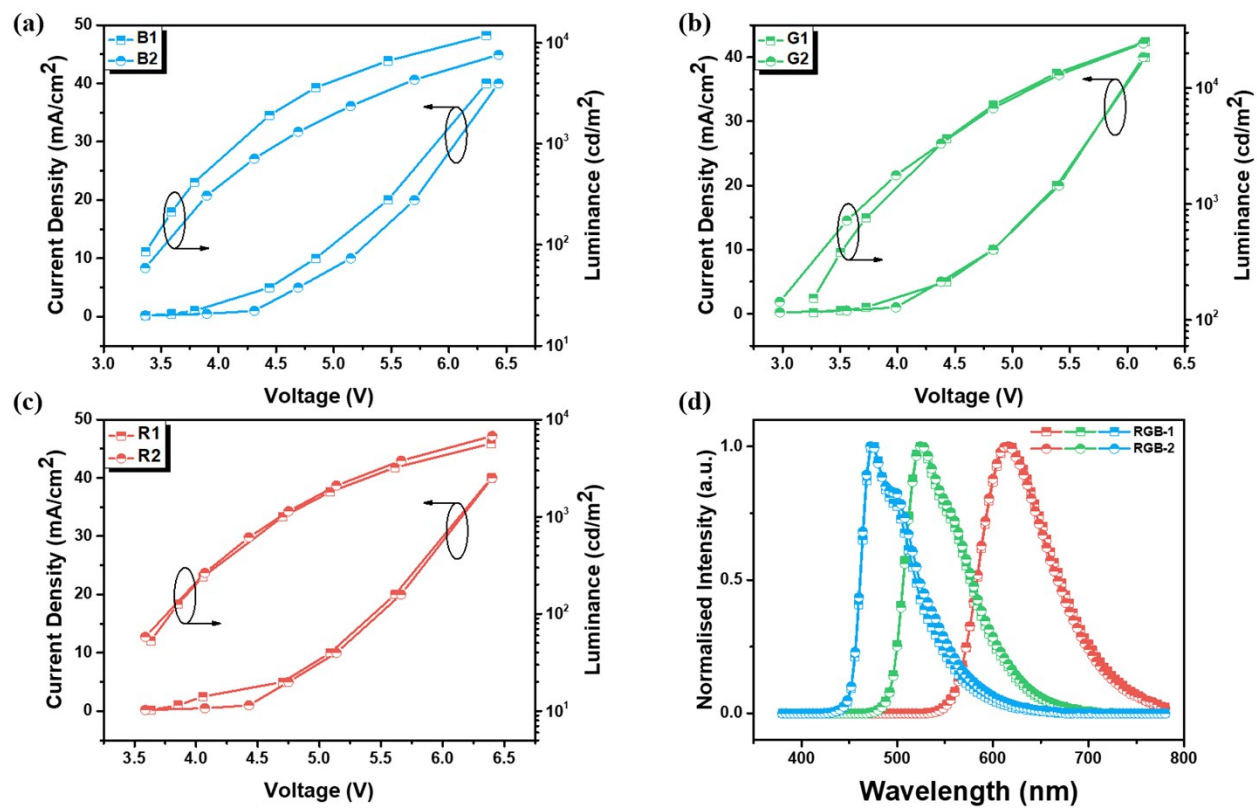


Fig. S5 (a) J–V–L characteristics of blue devices, (b) J–V–L characteristics of green devices, (c) J–V–L characteristics of red devices and (d) EL spectra of RGB three-color devices.

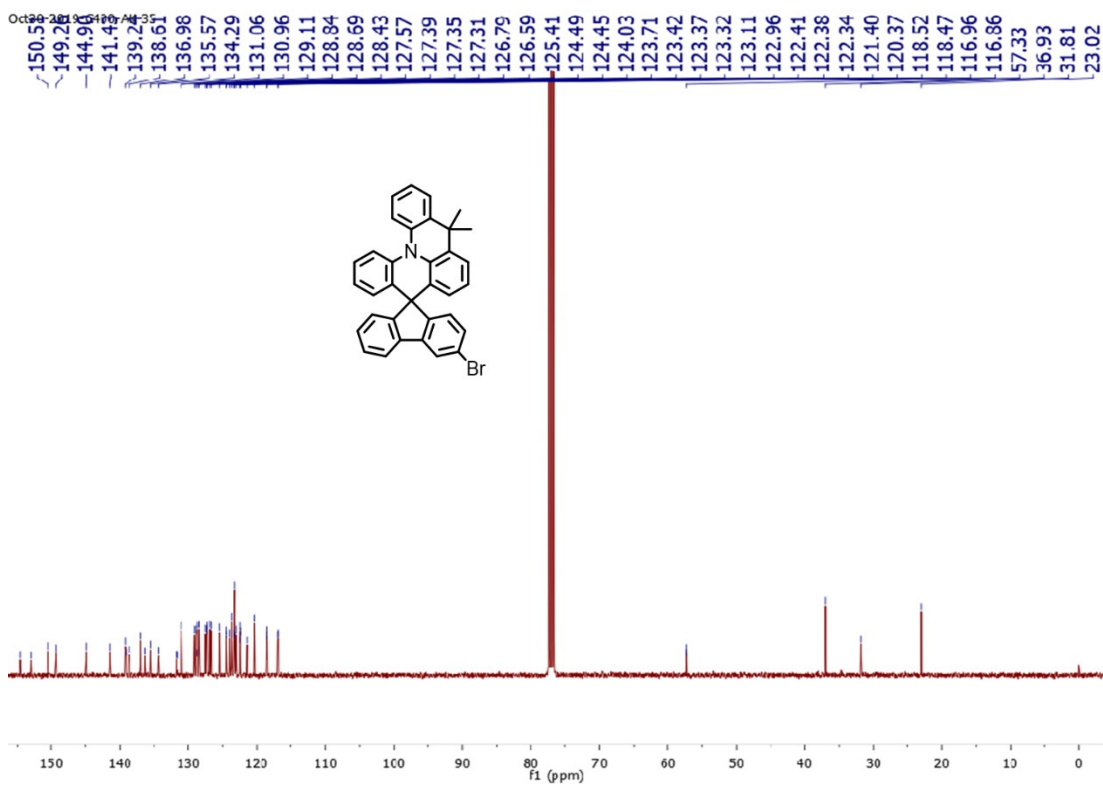
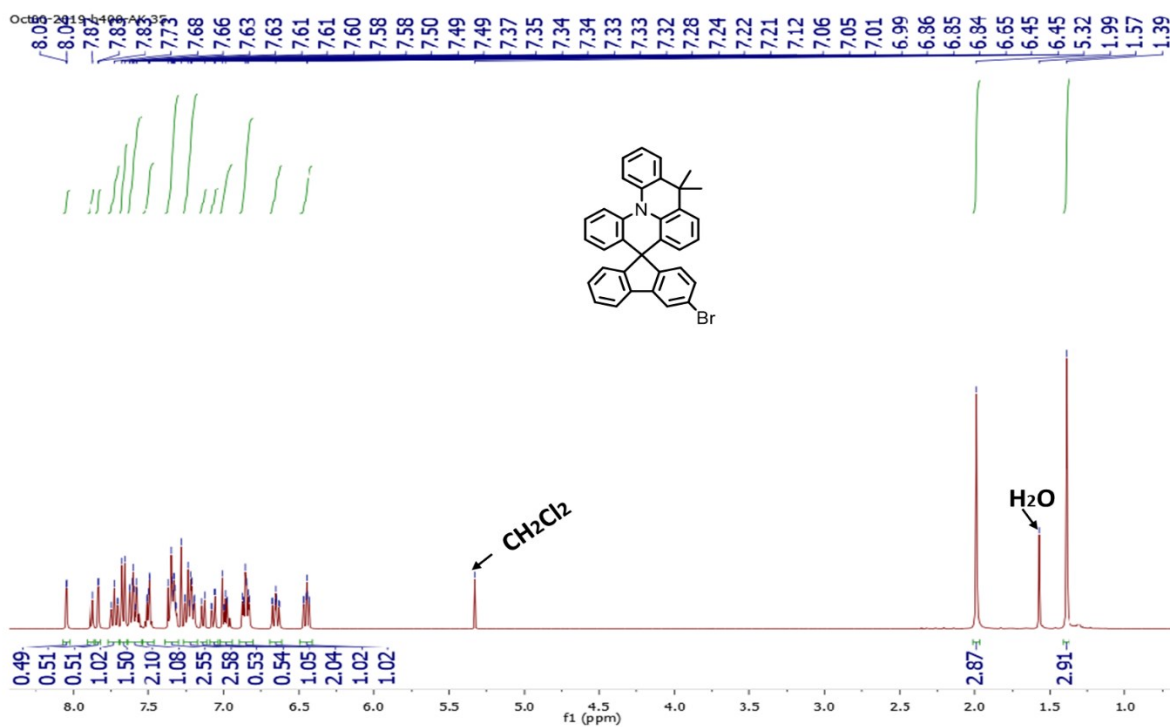


Fig. S6 ¹H NMR and ¹³C NMR spectra of **compound-3** in deuterated CDCl₃.

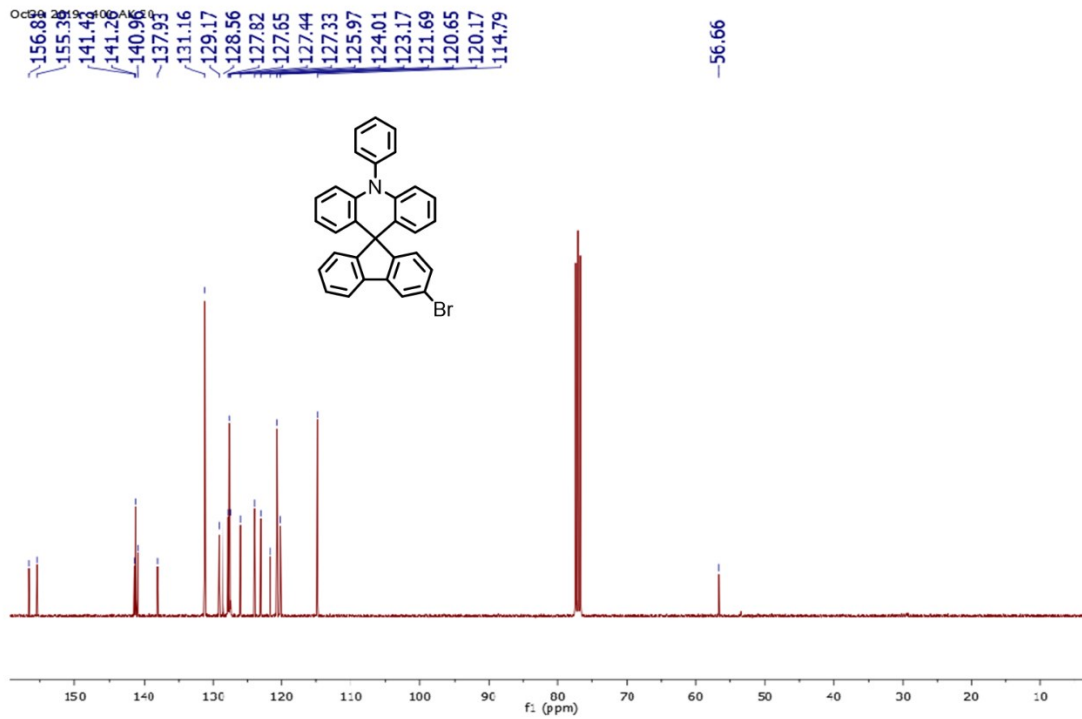
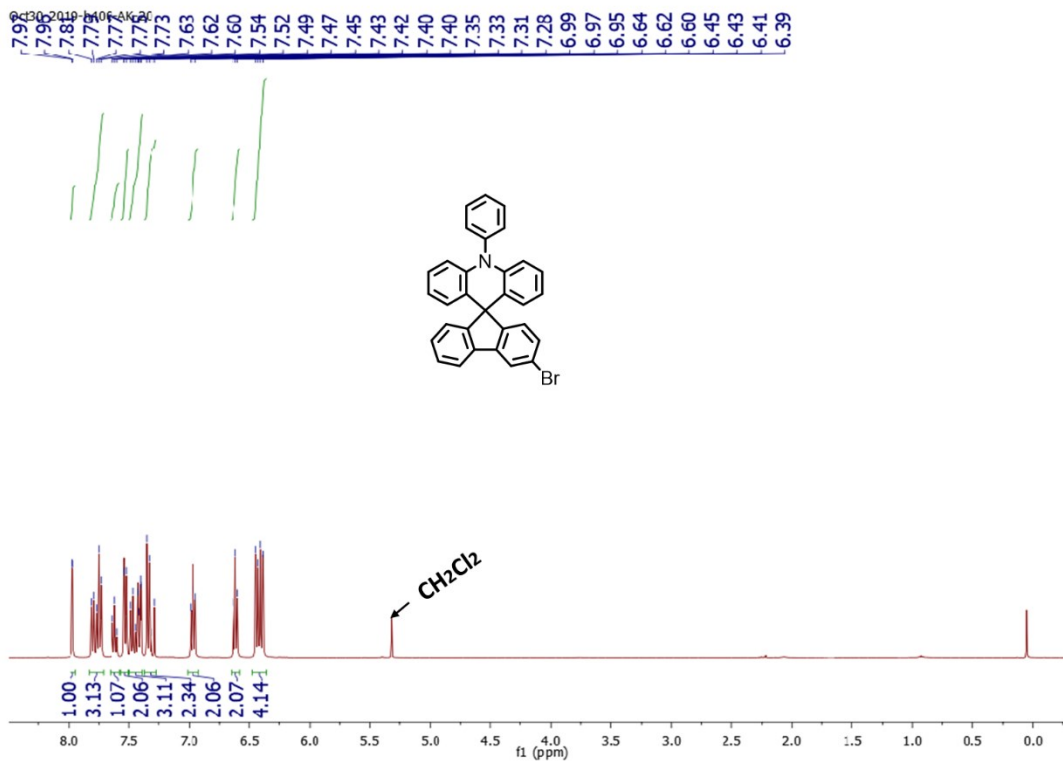


Fig. S7 ¹H NMR and ¹³C NMR spectra of **compound-3'** in deuterated CDCl₃.

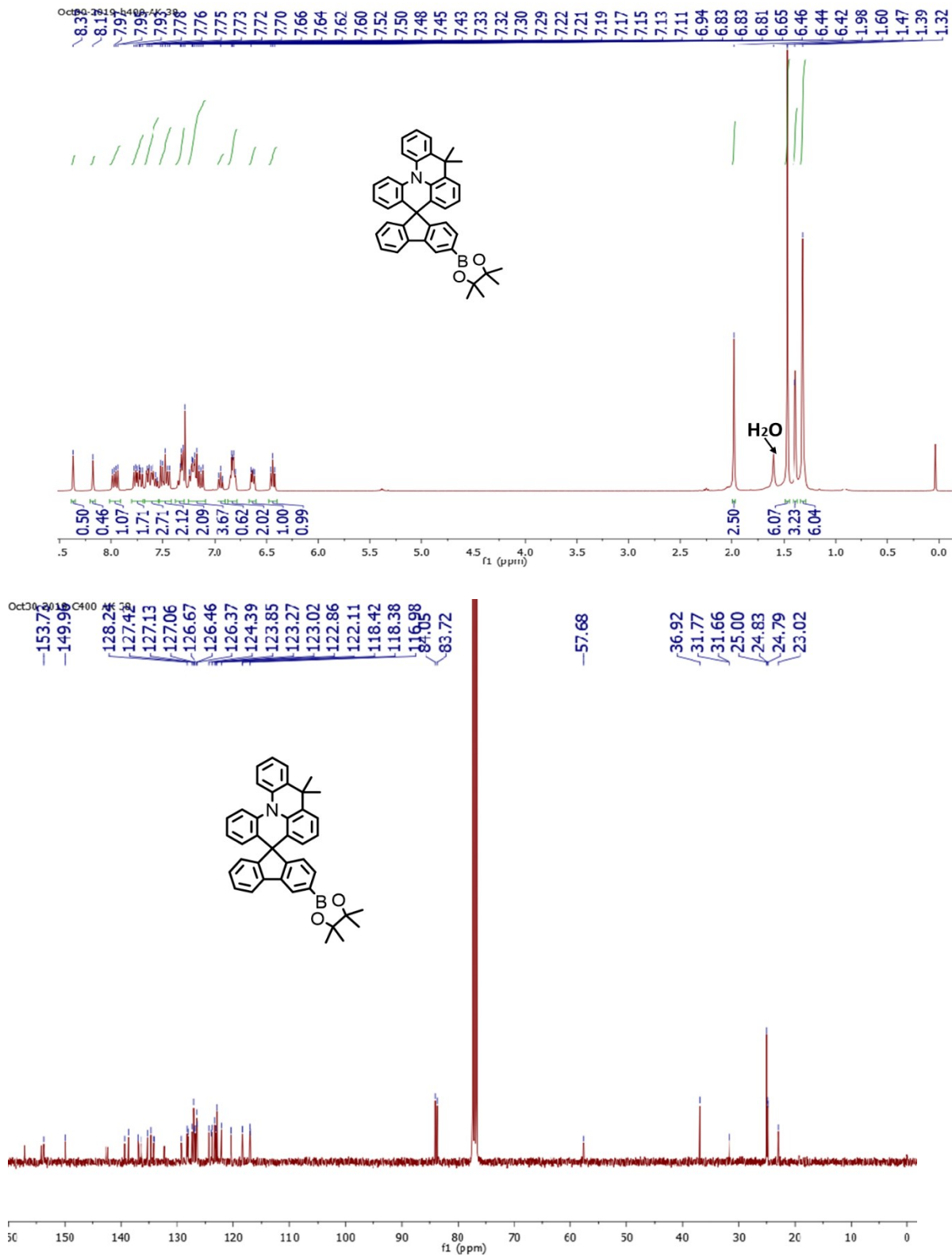


Fig. S8 ¹H NMR and ¹³C NMR spectra of **compound-4** in deuterated CDCl₃.

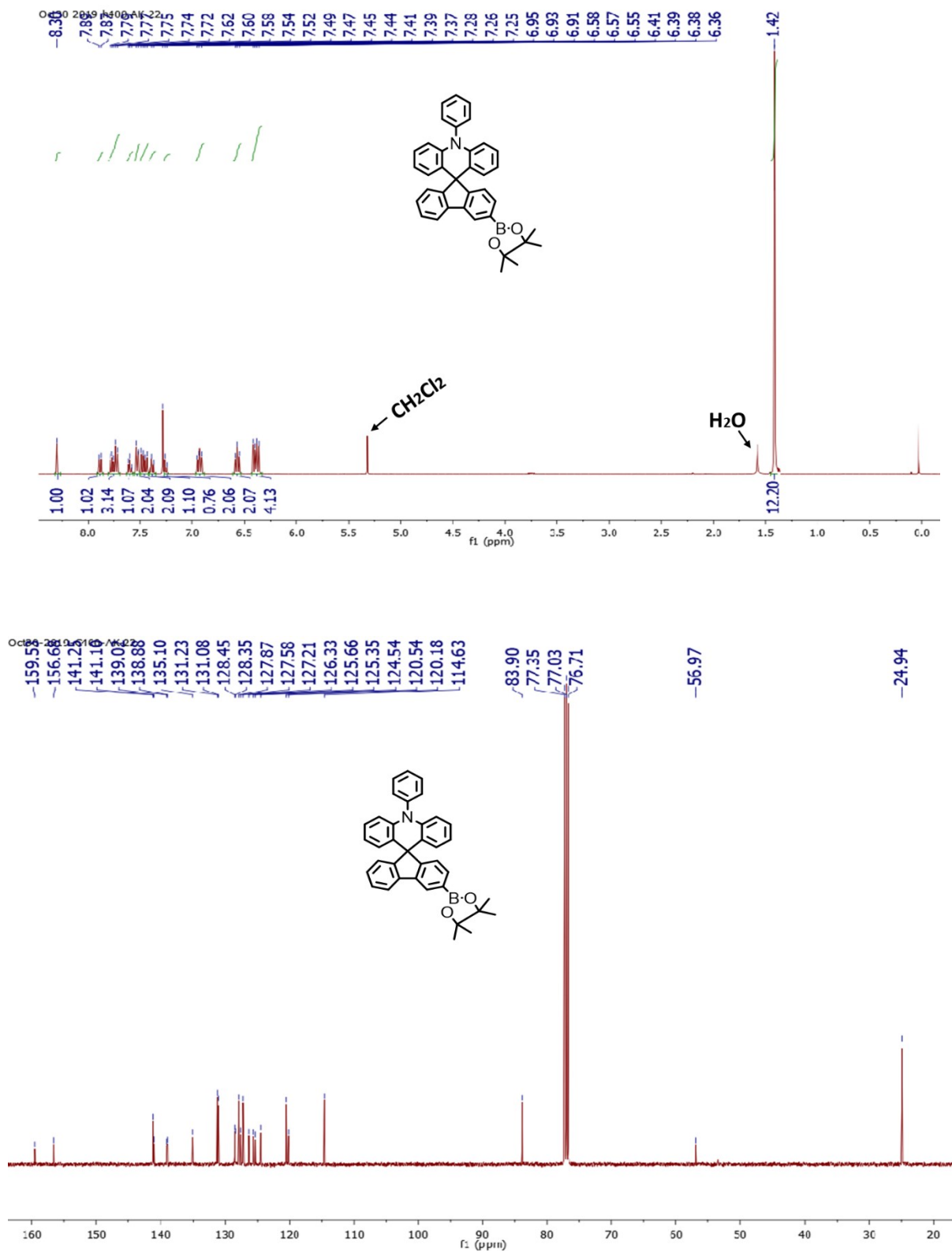


Fig. S9 ¹H NMR and ¹³C NMR spectra of **compound-4'** in deuterated CDCl₃.

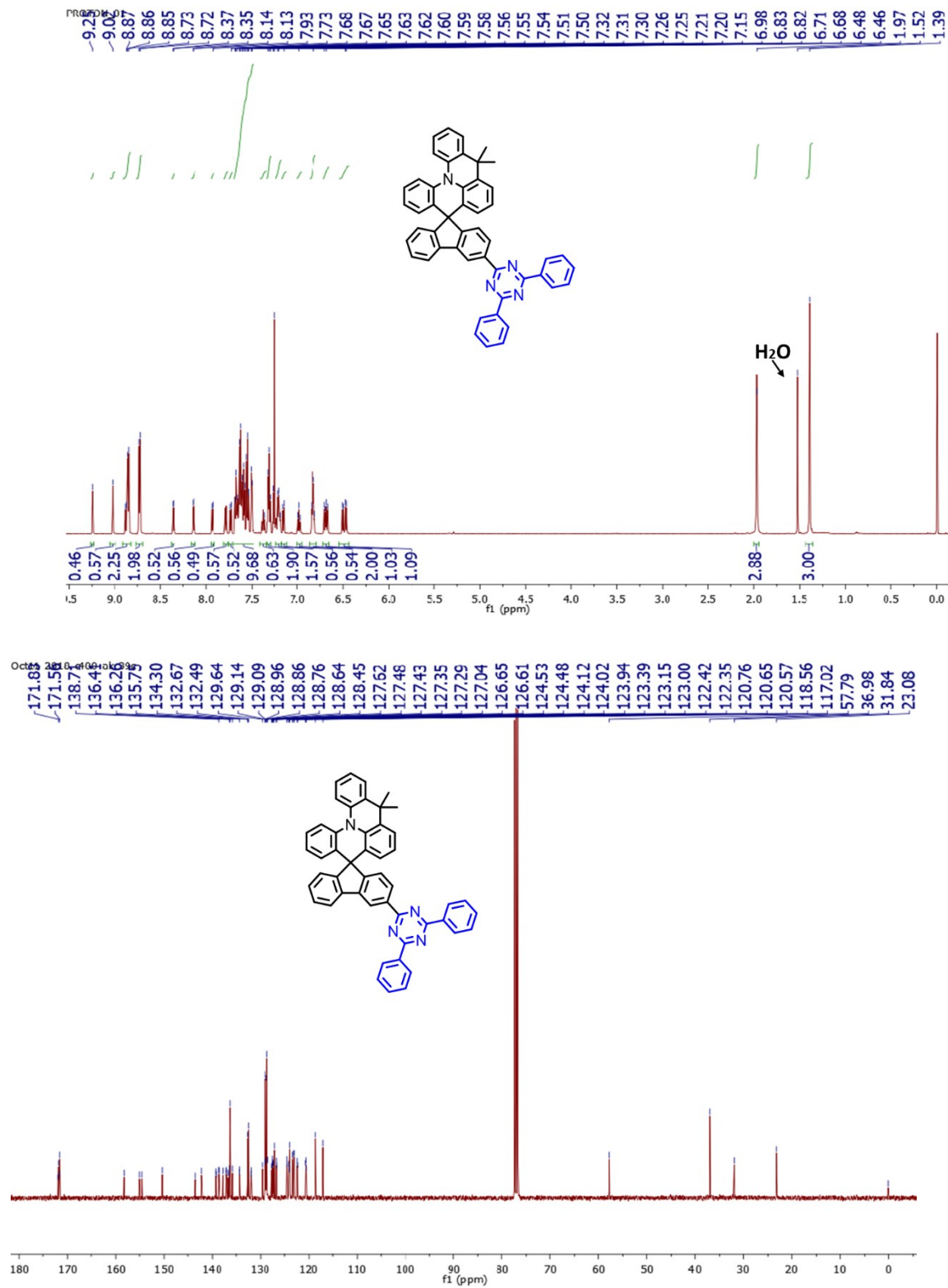


Fig. S10 ^1H NMR and ^{13}C NMR spectra of QAF-TRZ in deuterated CDCl_3 .

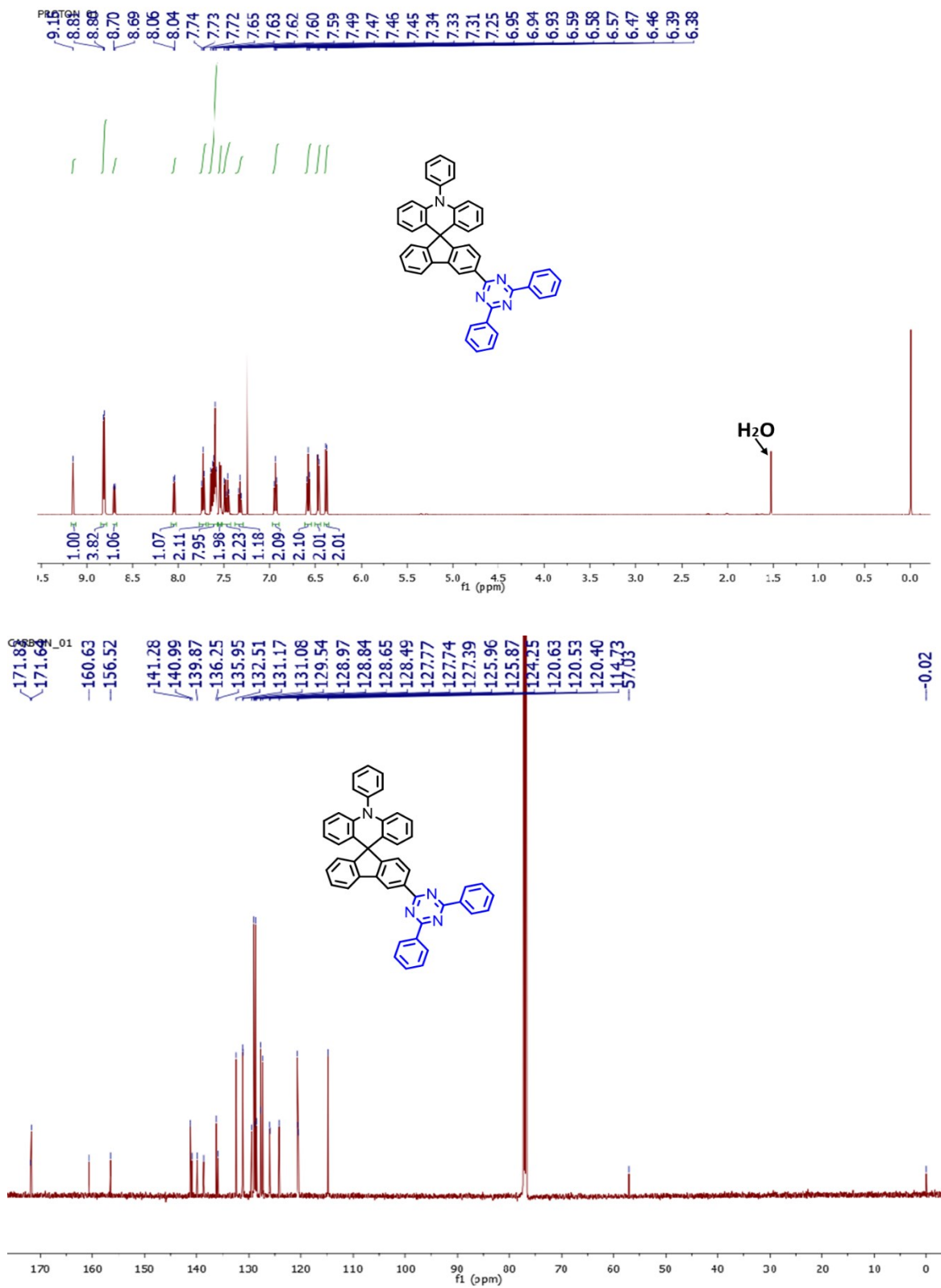


Fig. S11 ^1H NMR and ^{13}C NMR spectra of STF-TRZ in deuterated CDCl_3 .

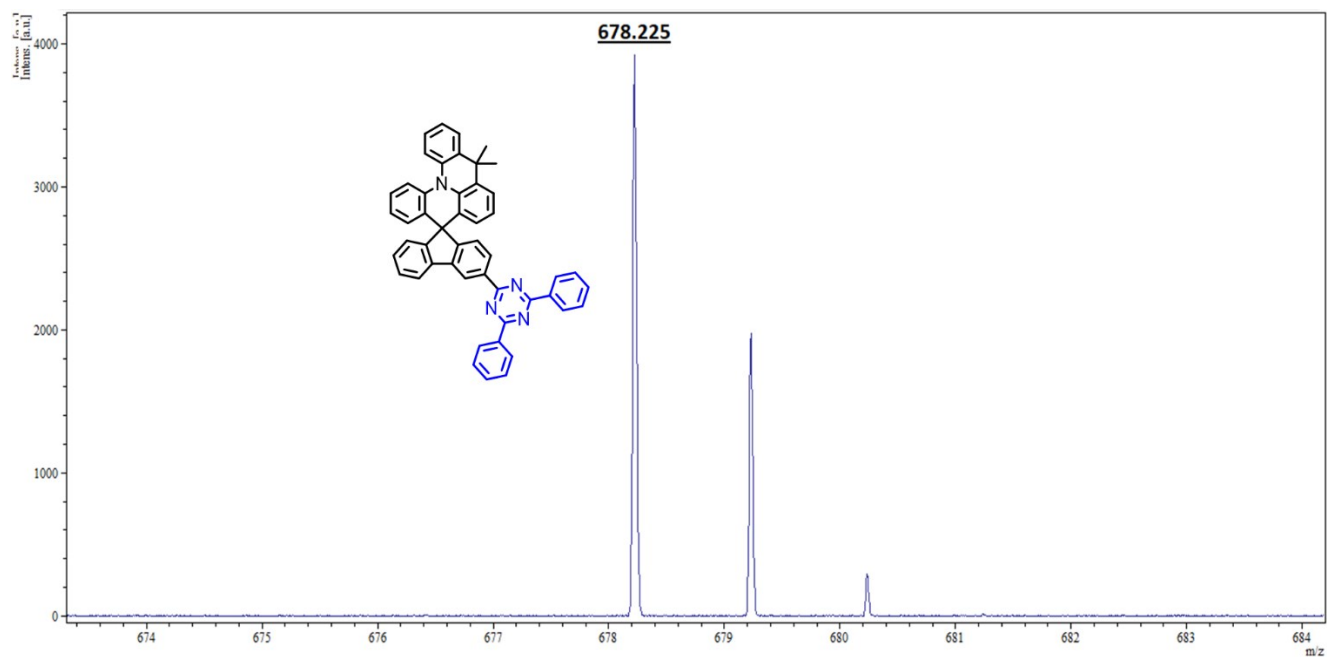


Fig. S12 MALDI TOF spectrum of **QAF-TRZ**.

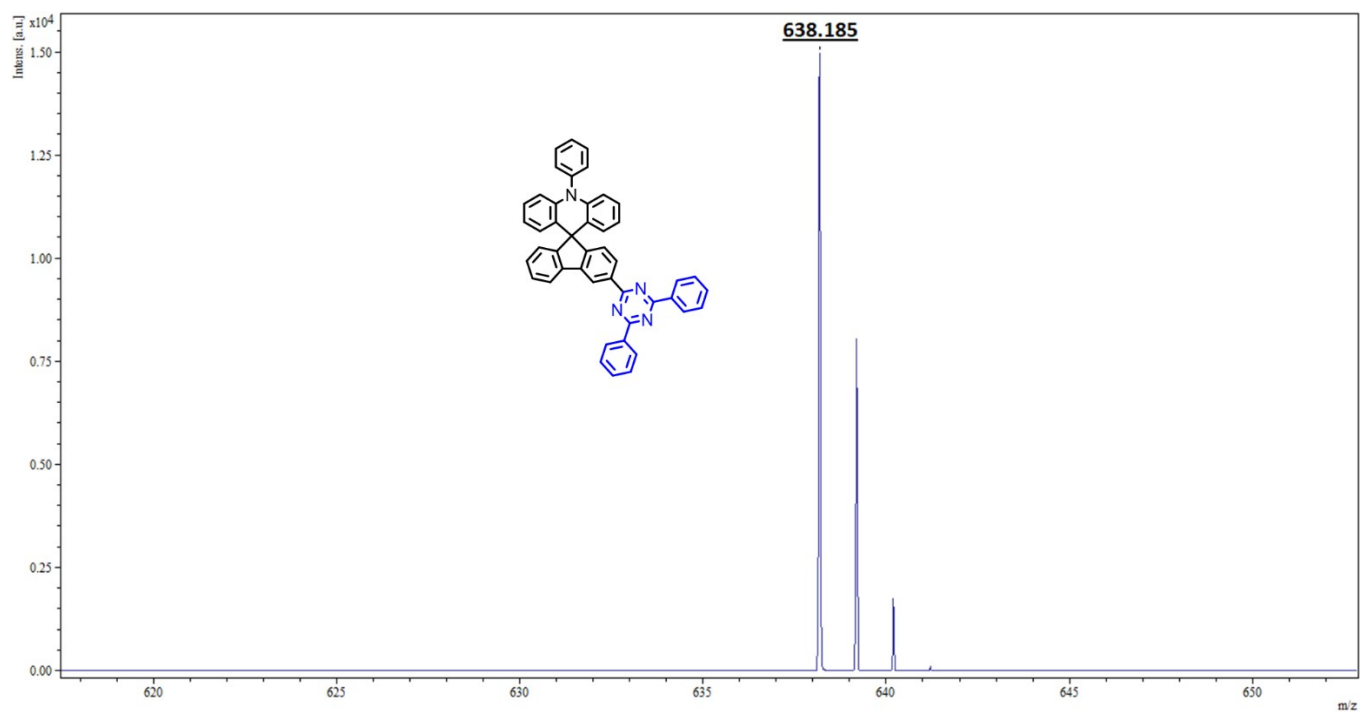


Fig. S13 MALDI TOF spectrum of **STF-TRZ**.

Table S1. Electroluminescence characteristics of the blue devices with different concentrations

Device	Ratio (%)	V^a (V)	CE^b (cd/A)	PE^b (lm/W)	EQE^c (%)	CIE^d (x,y)
B1	10	3.5	40.5	37.3	17.7/16.3/13.5	(0.16,0.35)
	12	3.5	42.0	38.7	18.2/16.7/14.0	(0.16,0.35)
	15	3.4	45.0	47.8	19.4/18.3/17.2	(0.16,0.35)
	20	3.4	42.5	39.5	18.2/17.2/14.7	(0.16,0.35)
B2	10	3.7	23.8	18.4	10.3/ 10.1/ 7.8	(0.16,0.34)
	12	3.7	27.6	19.4	12.2/ 11.6/ 8.4	(0.16,0.35)
	15	3.5	30.8	27.5	12.7/12.3/11.3	(0.17,0.37)
	20	3.5	29.4	20.9	12.6/ 12.1/ 8.6	(0.17,0.37)

^aDriving voltage at 100 cd/m²; ^bMaximum data of current efficiency and power efficiency; ^cEQEs of maximum data, 100 cd/m² and 1000 cd/m²; ^dCIE (Commission International de l'Eclairge); Measured at a driving current density at 5 mA/cm²

Table S2. Electroluminescence characteristics of the blue devices with different hosts

Device	V^a (V)	CE^b (cd/A)	PE^b (lm/W)	EQE^c (%)	CIE^d (x,y)
B1	3.4	45.0	47.8	19.4/18.3/17.2	(0.16,0.35)
B2	3.5	30.8	27.5	12.7/12.3/11.3	(0.17,0.37)
mCP	3.9	40.5	33.6	18.0/ 16.4/ 13.4	(0.16,0.33)
26DCzppy	3.3	34.0	35.5	15.1/ 14.0/ 9.9	(0.16,0.34)

^aDriving voltage at 100 cd/m²; ^bMaximum data of current efficiency and power efficiency; ^cEQEs of maximum data, 100 cd/m² and 1000 cd/m²; ^dCIE (Commission International de l'Eclairge); Measured at a driving current density at 5 mA/cm²