Oligofluorene with Multiple Spiro Connections: Its and Their Use in Blue and White OLEDs

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Materials and Methods

For the ^{1}H- and ^{13}C-NMR experiments,a 5 mm BBFO ^{1}H/X probe equipped with a z-gradient on the 500 MHz Bruker AVANCE III system was used. The temperature was kept at 393 K and calibrated by a standard ^{1}H ethylenglycol NMR sample using the topspin 3.1 software (Bruker). The control of the temperature was realized with a VTU (variable temperature unit) and an accuracy of +/- 0.1K. For the 2D H-H NOESY experiments,a spectroscopic width of 7500 Hz (15ppm) in both dimension (f1 and f2) was used and the relaxation delay of 1.5 s. The mixing time used in the 2D H-H NOESY was kept at 300 ms. The spectroscopic widths of the homo-nuclear 2D H-H COSY and H-H TOCSY experiments were typically 7500 Hz in both dimension (f1 and f2). The TOCSY measurement used a TOCSY mixing time of 80 ms and a relaxation delay of 1.5 s. The spectra were typically calibrated with the remaining C_2HDCl_4 solvent signal in the ^{1}H-NMR spectra at 5.93 ppm and the ^{13}C-NMR with the $C_2D_2Cl_4$ at 73.80 ppm.The mass spectrum was collected using Solarix ESI-/MALDI-ICR (9.4 T) system (Bruker Daltonics, Germany). UV-Vis and photoluminescence spectra were taken with a Perkin Elmer Lambda 15 and a SPEX-Fluorolog II (212) spectrometer, respectively. The fluorescence quantum yield in solution was measured using 9,10-diphenyl anthracene as a reference. Thermogravimetric analysis (TGA) was performed on a Mettler 500 at a heating rate of 10 ºC /min under nitrogen flow. Cyclic voltammetry (CV) studies were conducted with a computer-controlled GSTAT12 in a three-electrode cell in anhydrous solution of tetrabutylammonium hexafluorophosphate (0.1 M) with a scan rate of 100 mV/s, using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode.

OLEDs were fabricated by vacuum deposition with a bi-EML configuration of ITO|MoO_3 (6 nm)|NPB (70 nm)|mCP (5 nm)| **Spiro-F**:4CzPNPh (20 nm, 0.5 wt%)| Spiro-F (5 nm)|TPBI (30 nm)|LiF (1 nm)| Al, in which NPB was the hole-transporting layer, TPBI was the electron-transporting/hole-blocking layer. LiF was deposited to improve electron injection, and ITO and Al were used as the anode and cathode, respectively. Before loading into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 ^{o}Cfor 4 h, and treated with UV/ozone for 25 min. Devices were fabricated by evaporating organic layers at a rate of 0.1–0.3 nms^{-6} at a pressure below 1×10^{-6} mbar. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current–density–voltage and brightness–voltage curves of the devices were measured using a Keithley 4200 source meter and a calibrated silicon photo-diode. All the measurements were carried out at room temperature under ambient conditions.

Geometrical optimization for the ground state was carried out at the B3LYP/6-31G(d) level. The TDDFT B3LYP/6-31G(d) calculations of the excitation energies were then performed at the optimized geometries. All the quantum-chemical calculations were performed using the Gaussian09 suite of programs.

2D-NMR spectra

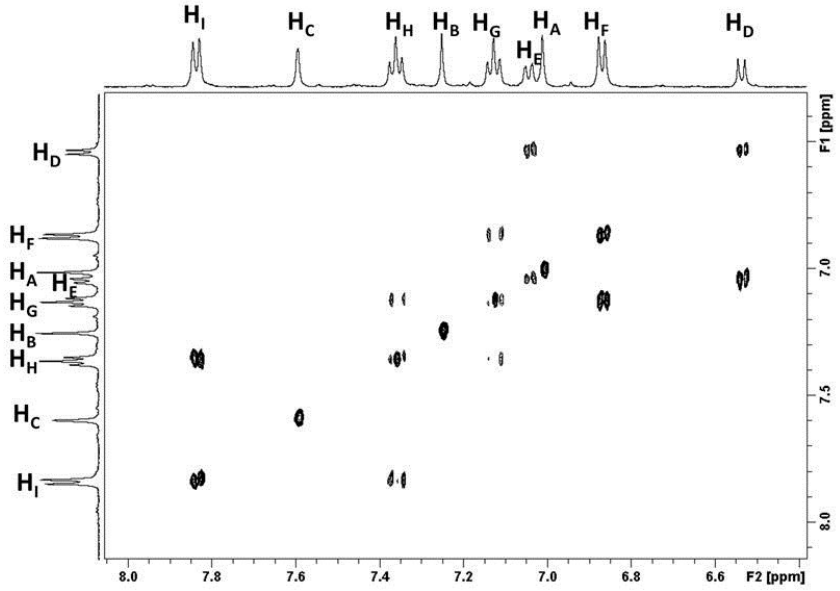


Figure S1. Aromatic region of H-HCOSY spectrum of **Spiro-F**: ($C_2D_2Cl_4$, 500 MHz, 393 K).

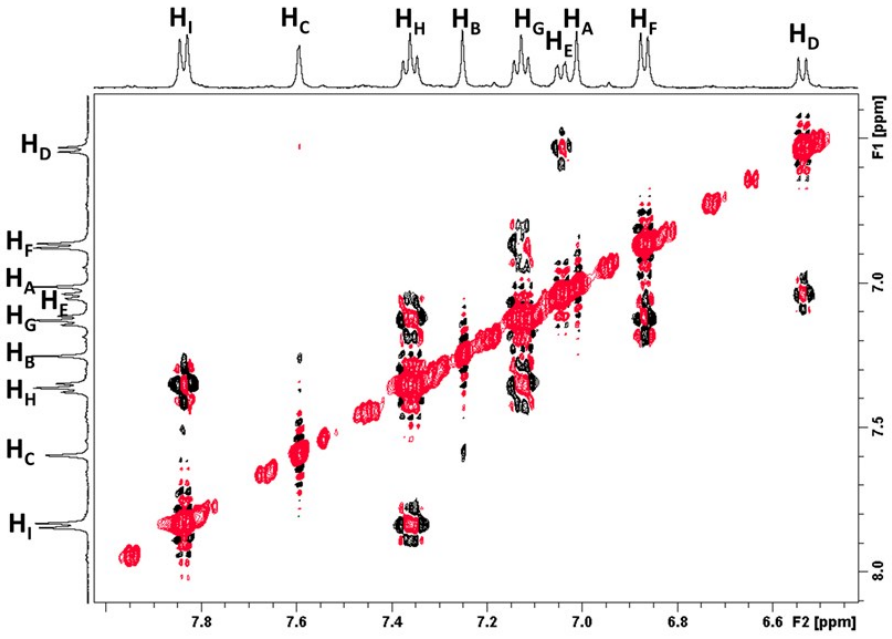


Figure S2. Aromatic region of H-H NOESY spectrum of **Spiro-F** ($C_2D_2Cl_4$, 500 MHz, 393 K).

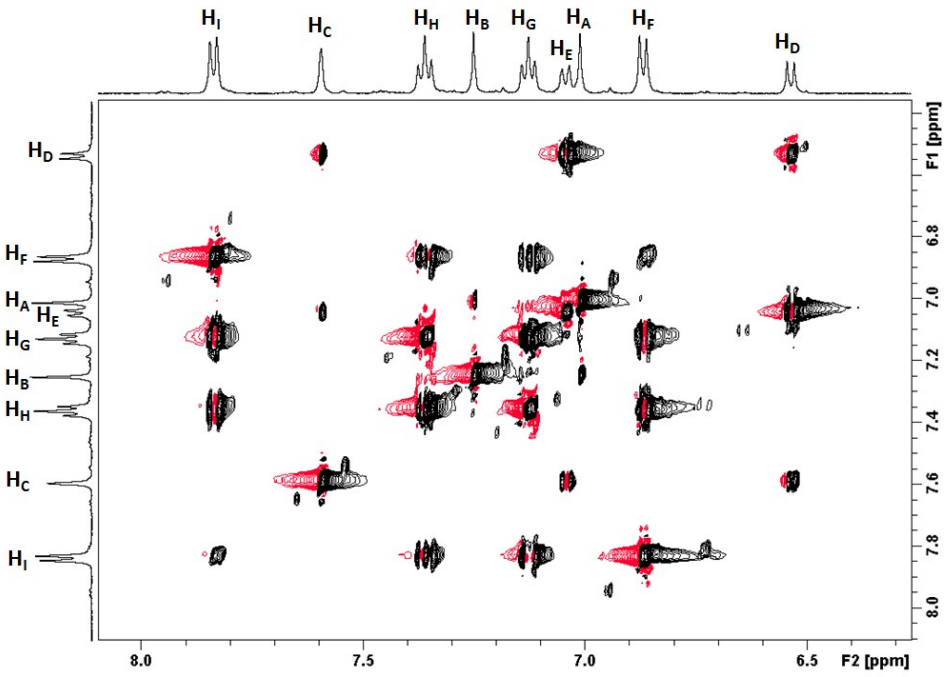


Figure S3. Aromatic region of H-H TOCSY spectrum of **Spiro-F** ($C_2D_2Cl_4$, 500 MHz, 393 K).

TGA curve

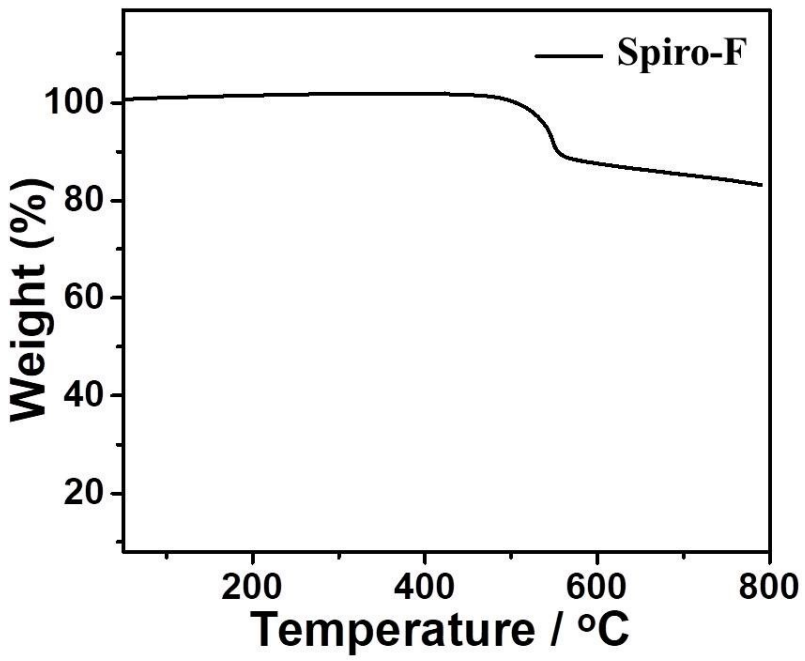


Figure S4. TGA curve for **Spiro-F** measured under a nitrogen atmosphere at a heating rate of 10 ºC/min.

Chemical structures of Spiro-4S, Spiro-4SO2 and 4Ph

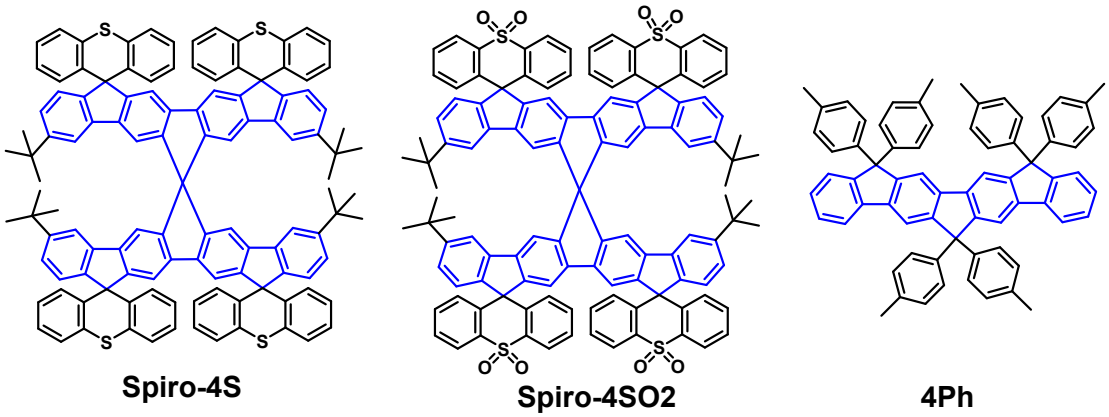


Figure S5. Chemical structures of **Spiro-4S**, **Spiro-4SO2** and **4Ph**.

Emission spectrum

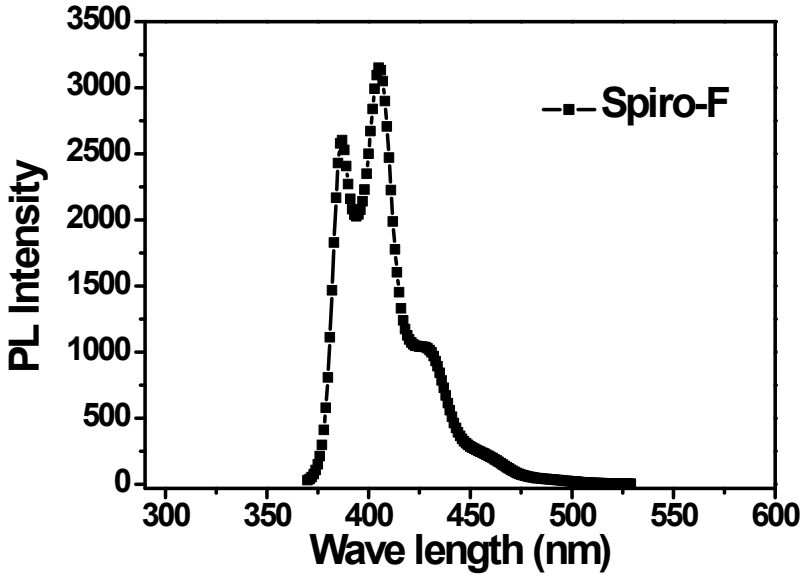


Figure S6. Photoluminance emission spectrum of **Spiro-F** in p-xylene (10^{-4} mol/L).

Cyclic voltammetric profile

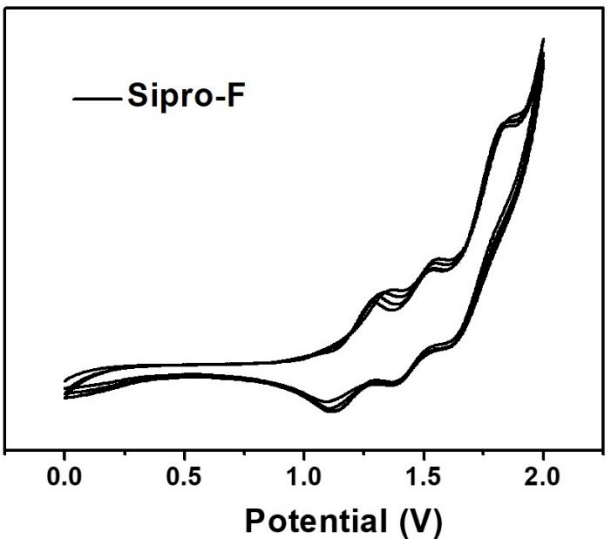


Figure S7. Cyclic voltammetric profile of **Spiro-F** in CH_2Cl_2 at a scan rate of 100 mV/s with 0.1 M Bu_4NPF_6 as supporting electrolyte.

TD-DFT calculations

Table S1. Calculated energy levels, oscillator strengths (f), and orbital transition analyses.

	E_g (eV)	E_g (nm)	f	transition	coefficient	transition	coefficient
S_1	3.3027	375.40	0.3171	HOMO-1 -> LUMO+1 HOMO -> LUMO+1	0.10392 -0.14652	HOMO -> LUMO	0.67683
S_2	3.3027	375.40	0.3170	HOMO-1 -> LUMO HOMO -> LUMO+1	0.10392 0.67683	HOMO -> LUMO	0.14652
S_3	3.4854	355.73	0.7486	HOMO-1 -> LUMO	0.69173		
S_4	3.4854	355.73	0.7486	HOMO-1 -> LUMO+1	0.69173		
S_5	3.8343	323.35	0.0083	HOMO-1 -> LUMO+2 HOMO -> LUMO+2	-0.19820 0.46279	HOMO-1 -> LUMO+3 HOMO -> LUMO+3	0.22650 -0.42182
S_6	3.8343	323.35	0.0083	HOMO-1 -> LUMO+2 HOMO -> LUMO+2	0.22644 0.42181	HOMO-1 -> LUMO+3 HOMO -> LUMO+3	0.19817 0.46278
S_7	3.8355	323.25	0	HOMO-1 -> LUMO+4	0.30494	HOMO -> LUMO+5	0.62706
S_8	3.8356	323.25	0	HOMO-1 -> LUMO+5	0.30471	HOMO -> LUMO+4	0.62721
S_9	3.8899	318.73	0.0002	HOMO-3 -> LUMO HOMO-2 -> LUMO	0.23337 0.42739	HOMO-3 -> LUMO+1 HOMO-2 -> LUMO+1	-0.42708 0.23348
S_{10}	3.8920	318.56	0	HOMO-3 -> LUMO HOMO-2 -> LUMO	-0.16714 0.45864	HOMO-3 -> LUMO+1 HOMO-2 -> LUMO+1	0.45892 0.16698
T_1	2.4375	508.65	0	HOMO-1 -> LUMO HOMO -> LUMO	-0.38770 0.44217	HOMO-1 -> LUMO+1 HOMO -> LUMO+1	-0.16974 0.20633
T_2	2.4375	508.65	0	HOMO-1 -> LUMO HOMO -> LUMO	-0.16974 -0.20633	HOMO-1 -> LUMO+1 HOMO -> LUMO+1	0.38771 0.44216

T_3	3.0440	407.31	0	HOMO-7 -> LUMO+4	-0.12116	HOMO-7 -> LUMO+5	-0.12286
				HOMO-5 -> LUMO+2	0.28163	HOMO-4 -> LUMO+3	0.27620
				HOMO-3 -> LUMO+4	-0.23751	HOMO-3 -> LUMO+5	-0.25705
				HOMO-2 -> LUMO+4	0.14557	HOMO-2 -> LUMO+5	-0.10797
T_4	3.0440	407.31	0	HOMO-6 -> LUMO+4	0.12115	HOMO-6 -> LUMO+5	-0.12246
				HOMO-5 -> LUMO+3	0.28132	HOMO-4 -> LUMO+2	0.27589
				HOMO-3 -> LUMO+4	-0.14563	HOMO-3 -> LUMO+5	-0.10851
				HOMO-2 -> LUMO+4	-0.23750	HOMO-2 -> LUMO+5	0.25626
T_5	3.0440	407.31	0	HOMO-7 -> LUMO+2	0.13608	HOMO-7 -> LUMO+3	0.13271
				HOMO-5 -> LUMO+4	-0.16427	HOMO-5 -> LUMO+5	-0.24502
				HOMO-4 -> LUMO+4	-0.24162	HOMO-4 -> LUMO+5	-0.16251
				HOMO-3 -> LUMO+2	0.27999	HOMO-3 -> LUMO+3	0.26630
				HOMO-3 -> LUMO+12	-0.10013		
T_6	3.0440	407.31	0	HOMO-6 -> LUMO+2	-0.13312	HOMO-6 -> LUMO+3	0.13519
				HOMO-5 -> LUMO+4	0.24434	HOMO-5 -> LUMO+5	-0.16336
				HOMO-4 -> LUMO+4	-0.16161	HOMO-4 -> LUMO+5	0.24095
				HOMO-2 -> LUMO+2	0.27404	HOMO-2 -> LUMO+3	-0.27142
T_7	3.0743	403.29	0	HOMO-12 -> LUMO+1	-0.11230	HOMO-11 -> LUMO	-0.11233
				HOMO-7 -> LUMO+1	-0.21217	HOMO-6 -> LUMO	-0.21232
				HOMO-3 -> LUMO+1	0.15453	HOMO-2 -> LUMO	-0.15464
				HOMO-1 -> LUMO+9	-0.29237	HOMO -> LUMO+8	0.32451
T_8	3.0819	402.29	0	HOMO-7 -> LUMO+1	0.21693	HOMO-6 -> LUMO	-0.21679
				HOMO-3 -> LUMO+1	-0.16804	HOMO-2 -> LUMO	-0.16794
				HOMO-1 -> LUMO+8	-0.29588	HOMO -> LUMO+9	0.30352
T_9	3.3436	370.81	0	HOMO-1 -> LUMO	0.19660	HOMO-1 -> LUMO+1	-0.45823
				HOMO -> LUMO	-0.20504	HOMO -> LUMO+1	0.43110
T_{10}	3.3436	370.81	0	HOMO-1 -> LUMO	0.45824	HOMO-1 -> LUMO+1	0.19661
				HOMO -> LUMO	0.43110	HOMO -> LUMO+1	0.20504

Electroluminance spectra and curves

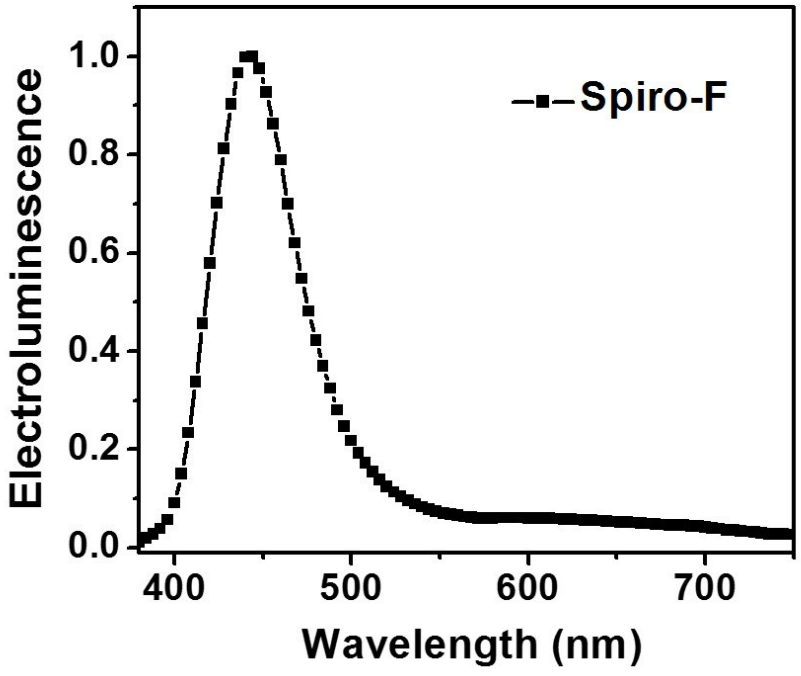


Figure S8. Electroluminance spectrum of **Spiro-F.**

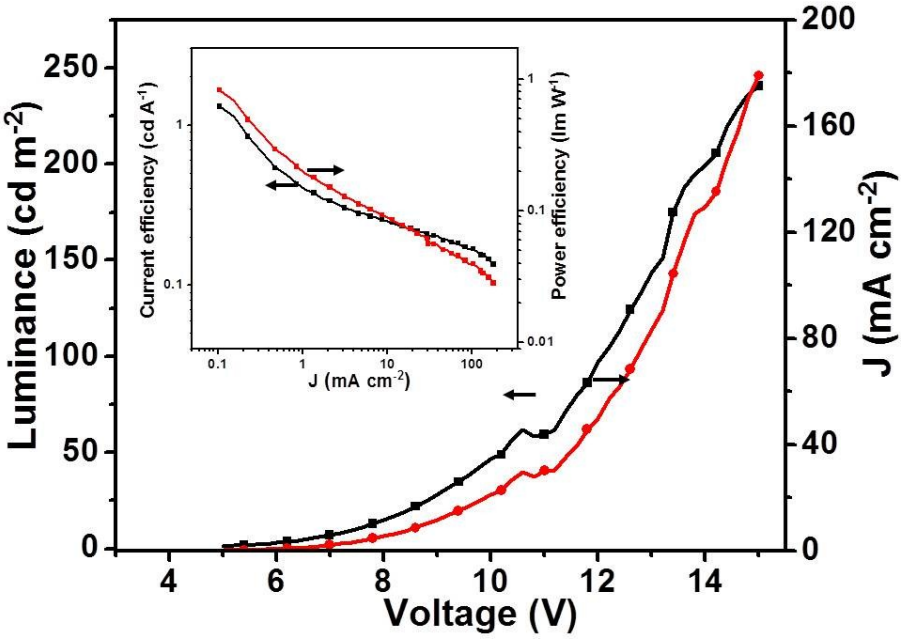


Figure S9. J-V-L curves of the blue OLED. (Inset: the currentefficiency-current density-power efficiency curves of the device.)

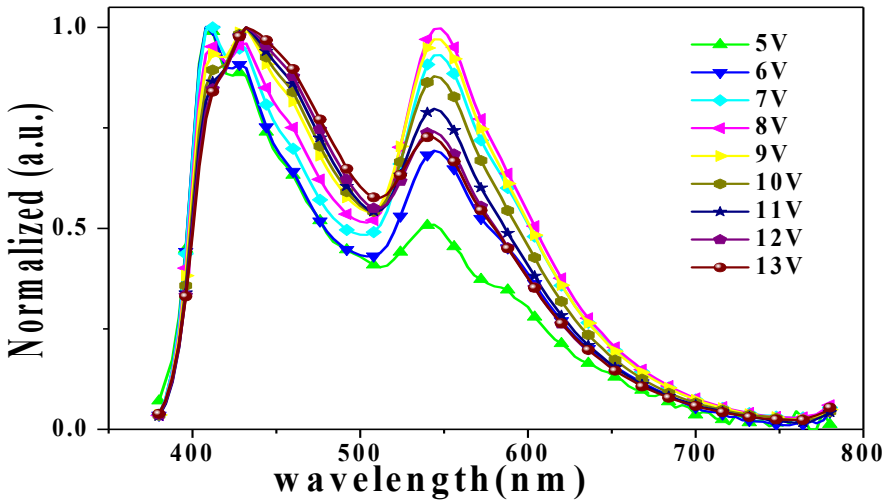


Figure S10. Electroluminance spectrawith 0.5% doping ratio of **Spiro-F.**

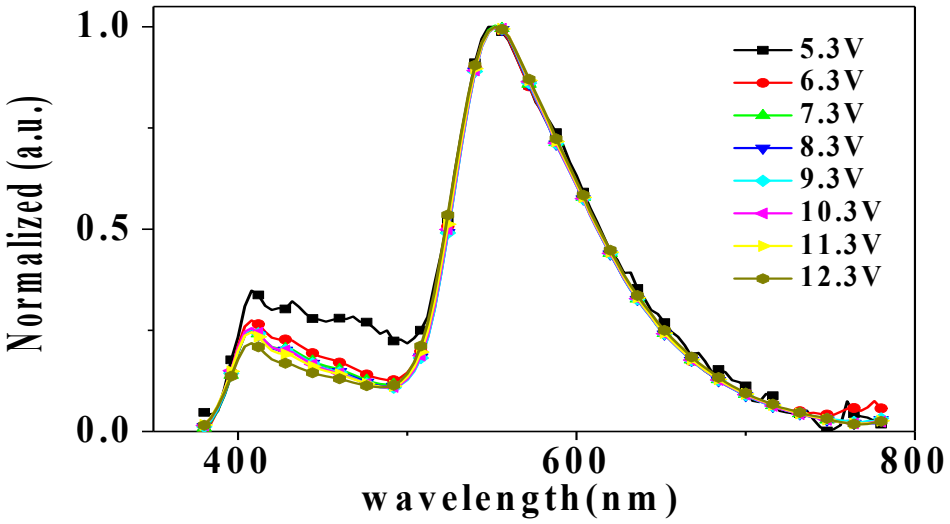


Figure S11.Electroluminance spectrawith 5% doping ratio of **Spiro-F.**

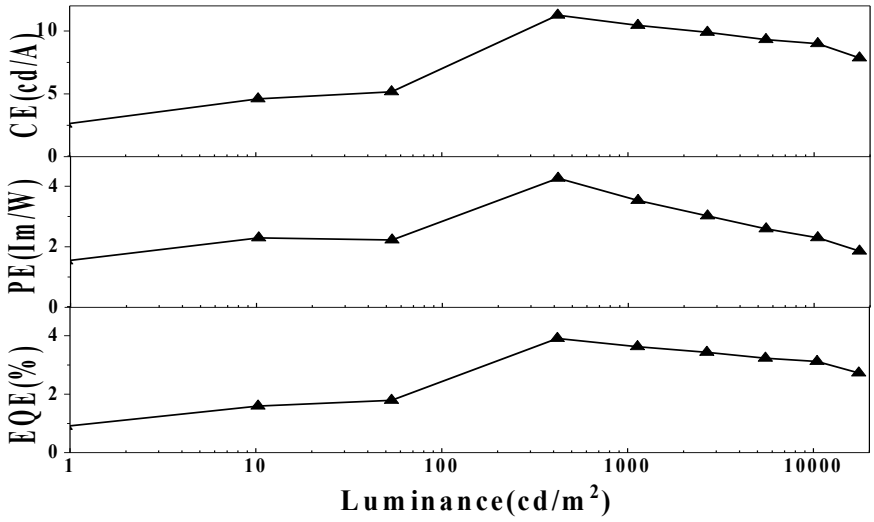


Figure S12. Luminance-current density and (J)-voltage characteristics (5% doping ratio of **Spiro-F**).

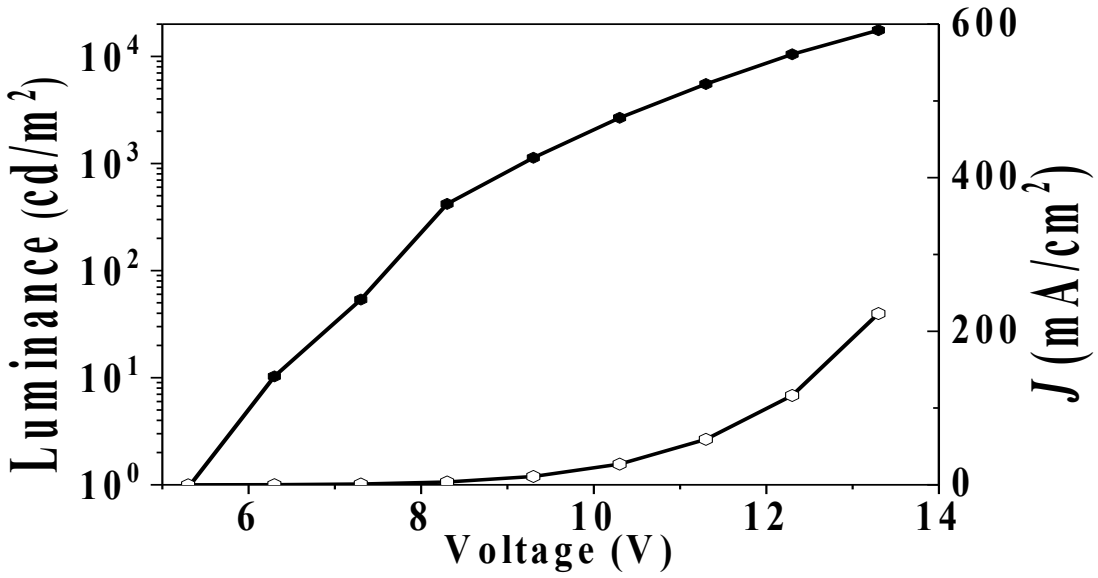
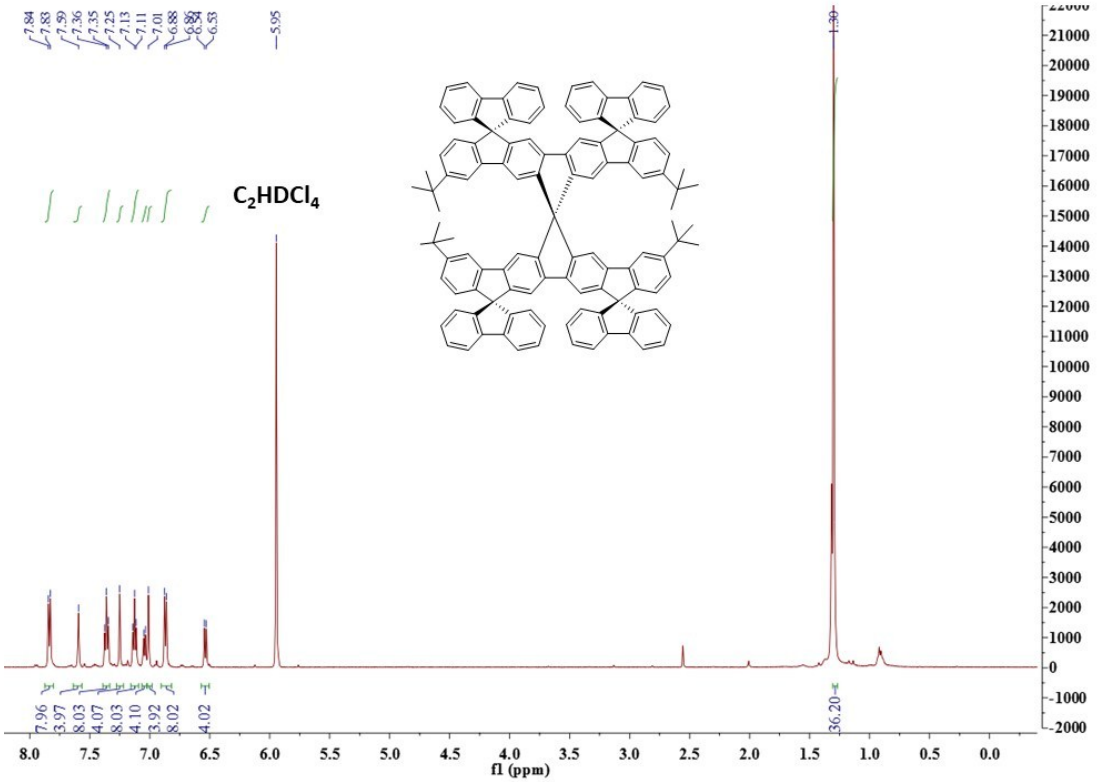
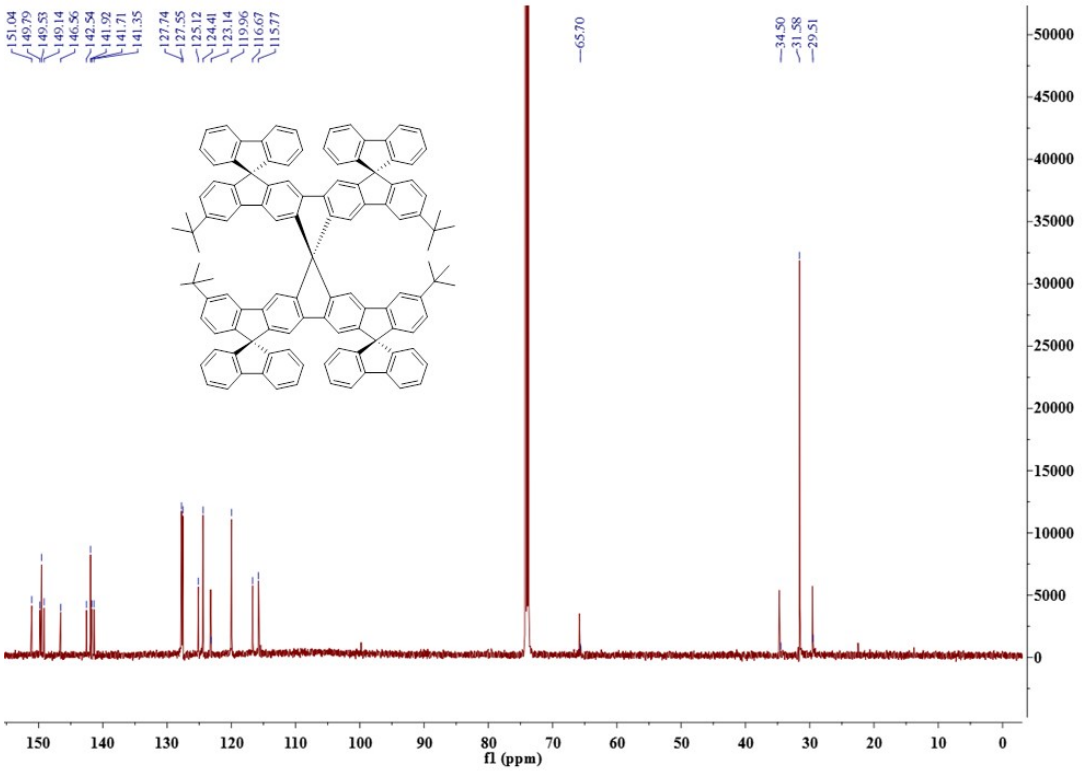


Figure S13. Efficiency-luminance correlations of devices (5% doping ratio of **Spiro-F**).

^{1}H–NMR and ^{13}C–NMR spectra

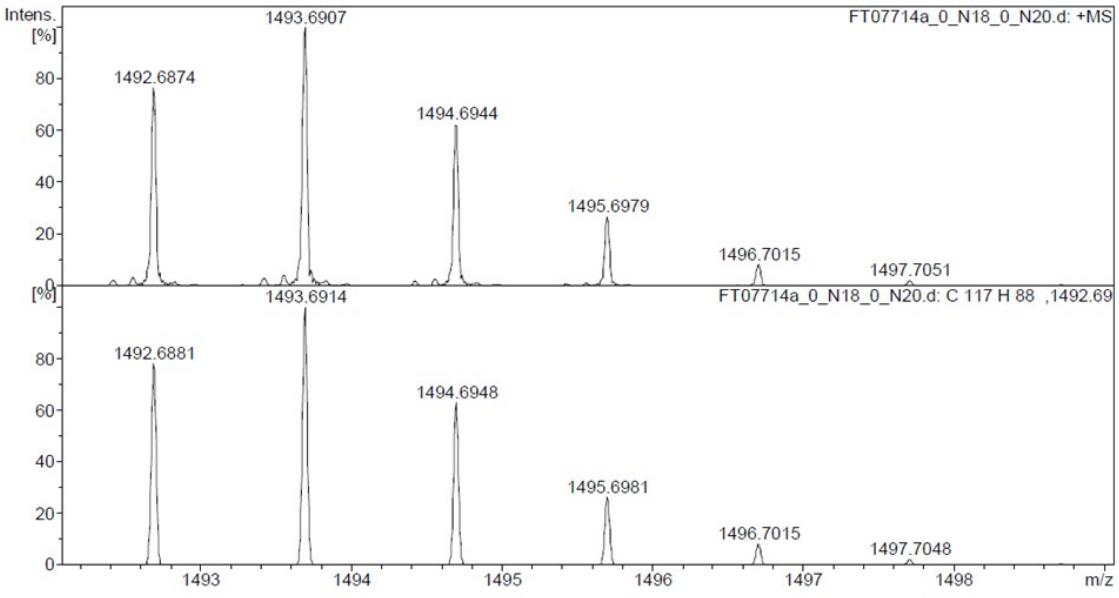


^{1}H NMR spectrum of **Spiro-F** ($C_2D_2Cl_4$, 500 MHz, 393 K).



^{13}C NMR spectrum of **Spiro-F** ($C_2D_2Cl_4$, 125 MHz, 393 K).

HRMS spectrum



Evaluation Spectra / Validation Formula:

#	Formula	m/z	Meas. m/z	z	mSigma	N-Rule	err [mDa]	err [ppm]
1	C 117 H 88	1492.6881	1492.6874	1+	7.0	ok	0.6	0.4

Single crystal structure

Cambridge Crystallographic Data Centre deposition number: CCDC 1408340

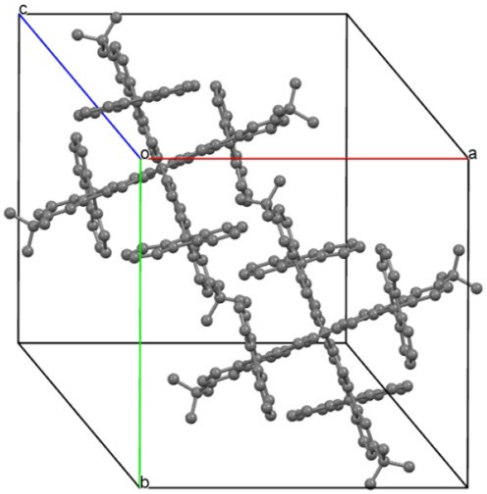


Table S2. Crystallographic table.

Compound	**Spiro-F**
Molecular formula	$C_{117}H_{88}$
Formula weight	1493.8 $gmol^{-1}$
Absorption coefficient	μ = 0.05 mm^{-1}
Crystal size	0.18 x 0.34 x 0.44 mm^3 colourless block
Space group	P-1(triclinic)
Lattice parameters	a = 18.8798(13) Å α = 114.305(5)°
	b = 18.9690(12) Å ß = 110.247(5)°
	c = 20.2269(15) Å γ = 90.152(5)°
Volume	6104.0(7) $Å^3$
Z value	2
F (000)	1580.0
Calculated density	d_{xray} = 0.813 gcm^{-3}
Temperature	-70 °C
Scan type	ω-scans
Theta range for data collection	2.1° <θ< 28.1°
Limiting indices	-24 ≤ h ≤ 24, -25 ≤ k ≤ 25, -26 ≤ l ≤ 26
Total number of reflections	61356

Unique number of reflections	29346 (R_{int} = 0.1327)
Observed number of reflections	8229 (|F|/σ(F) > 4.0)
Structure solution	SIR-97 (Direct methods)
R-values	wR2 = 0.3632 (R1 = 0.1122 for observed reflections, 0.2521 for all reflections)
Goodness of fit	S = 0.899
Max Shift / Error	0.001 * e.s.d
Largest diff. peak and hole	0.39 and -0.27 eÅ^{-3}