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Acceptor Modulation for Improving Spiro-Type Thermally Activated Delayed Fluorescence Emitter

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1. OLED fabrication and measurements

OLED devices were fabricated on ITO glass substrates (15 Ω per square). The emitting area of each device was 0.09 cm^2. The substrates were cleaned with ethanol, acetone and deionized water, and then dried in an oven before being exposed to UV ozone for 30 minutes. All of the organic materials and metal layers were deposited under a vacuum of ca. 10^{-6} Torr. The Electroluminescence spectra and current density-voltage (J-V-L) characteristics of the devices were measured using a constant current source (Keithley 2400 SourceMeter) combined with a photometer (Photo Research SpectraScan PR 655).

2. Experimental Section

All chemicals including 4-bromo-9H-fluoren-9-one (Suzhou ge'ao New Material Co. Ltd.) and reagents were used as received from commercial resources without further purification. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and N,N-Dimethylformamide (DMF) 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 spectrometer 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 Autoflex 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 ^oC/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 ^oC/min under nitrogen, the temperature at 5% weight loss was used as the decomposition temperature (T_d). The PLQY was measured using Hamamatsu C9920-02G.

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 [Bu4N]PF6. 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.

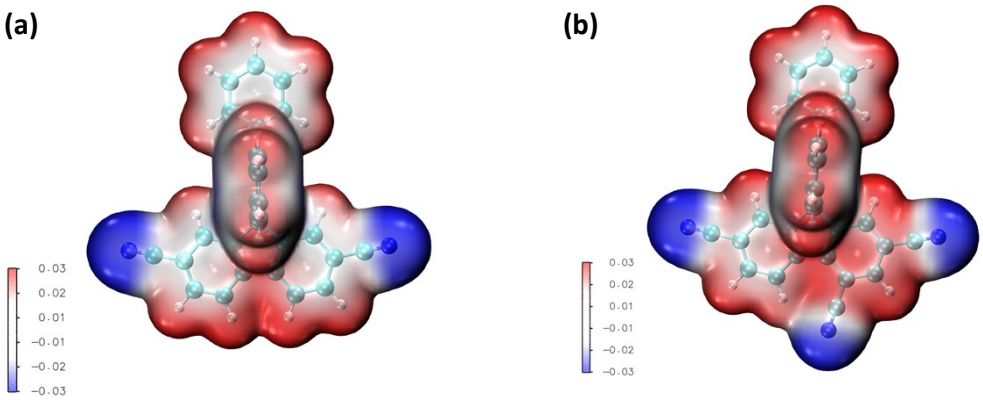


Figure S1. Electrostatic potential (ESP) mappings of **ACRFLCN** (a) and **SAF-3CN** (b).

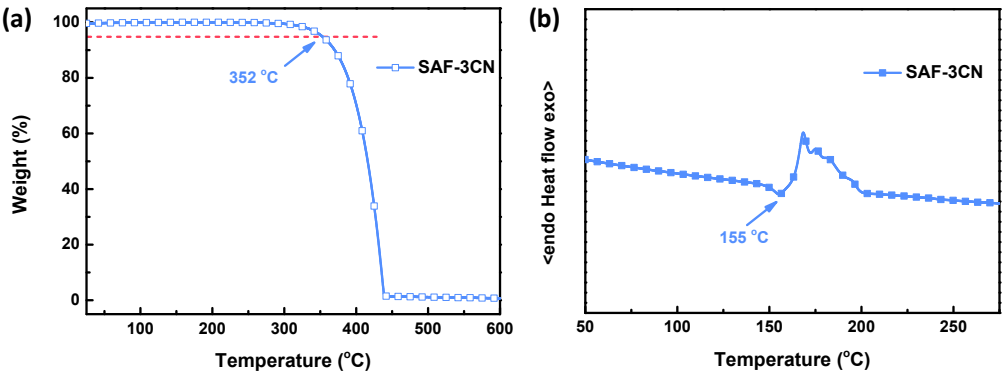


Figure S2. TGA and b) DSC curves of **SAF-3CN**.

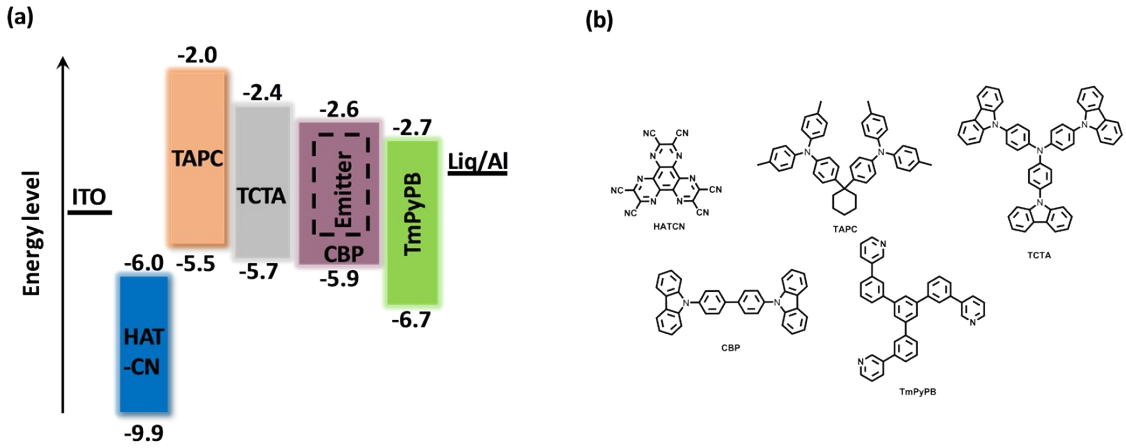


Figure S3. a) Energy level diagrams and b) chemical structures of the materials applied in the OLED devices.

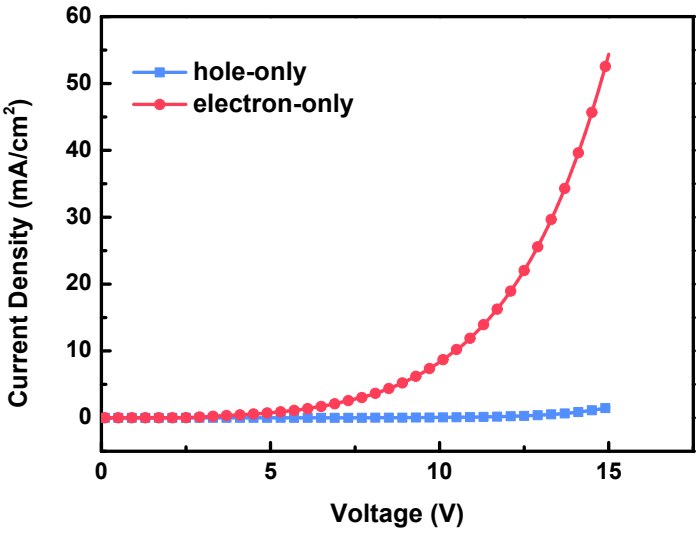


Figure S4. Current density versus voltage characteristic of the hole- and electron-only devices for **SAF-3CN**.

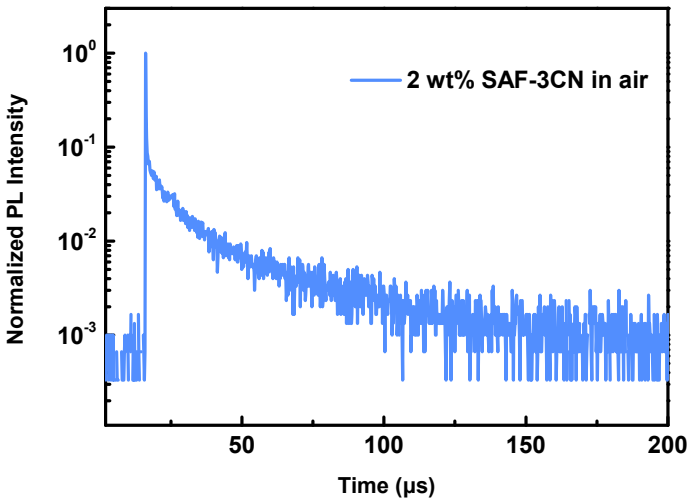


Figure S5. Transient PL spectrum of **SAF-3CN** in doped film at 300 K in air.

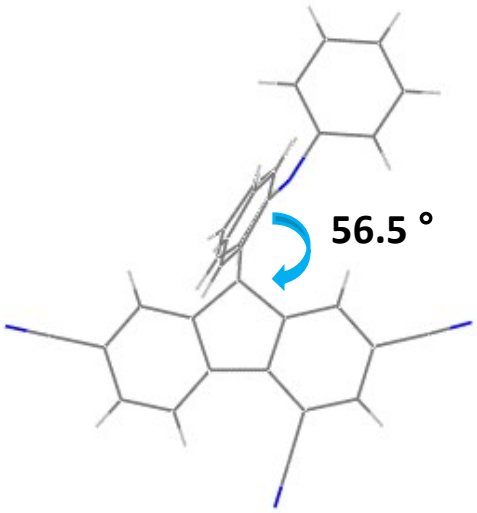


Figure S6. Single-crystal structures of **SAF-3CN**.

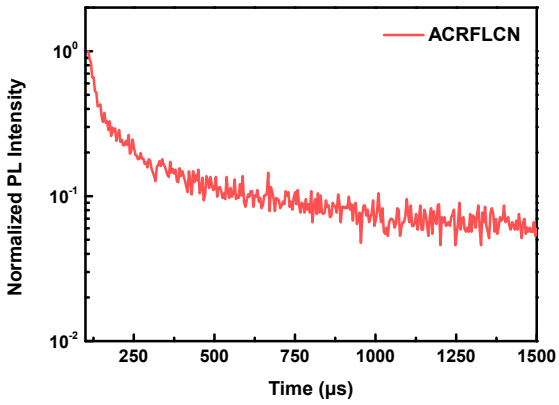
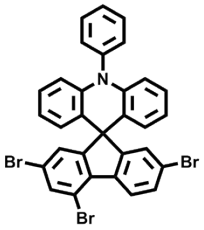
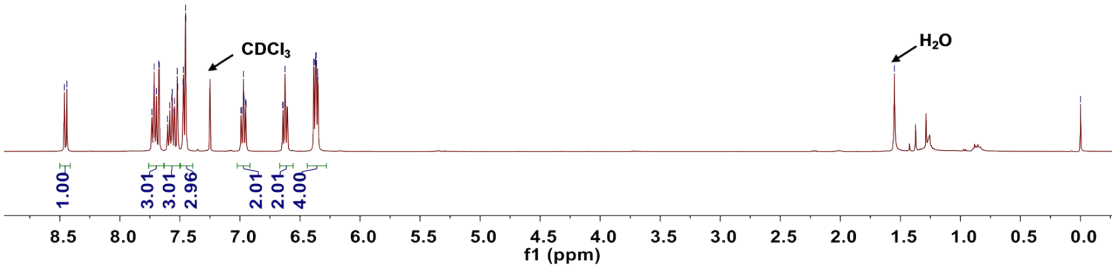
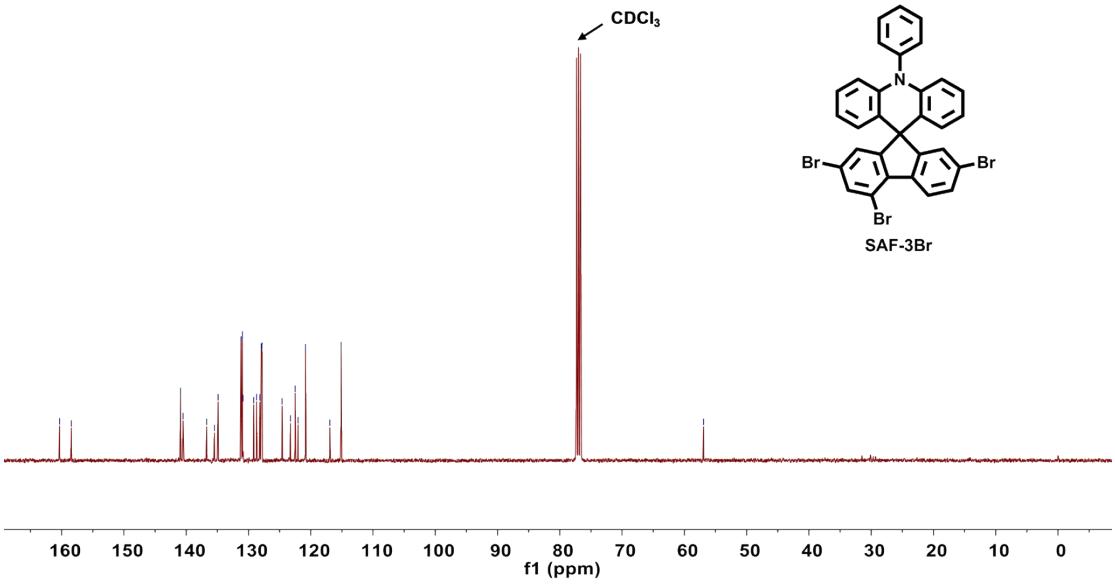


Figure S7. Transient PL spectrum of **ACRFLCN** in doped film at 300 K.

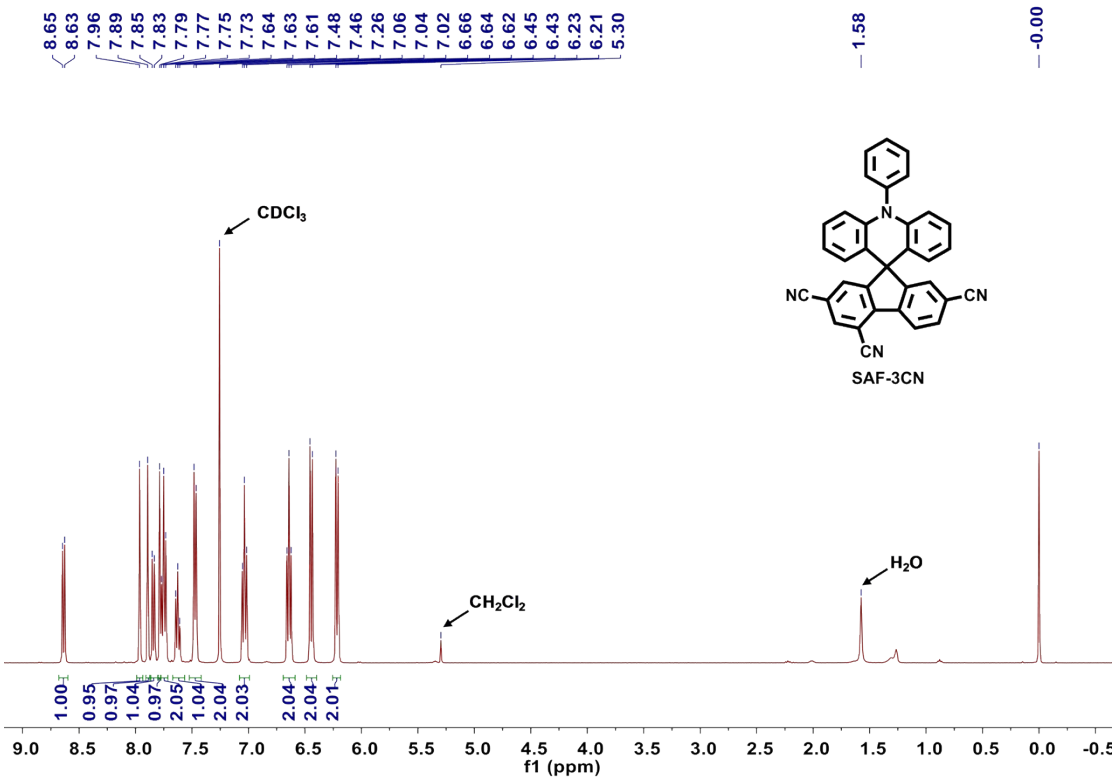


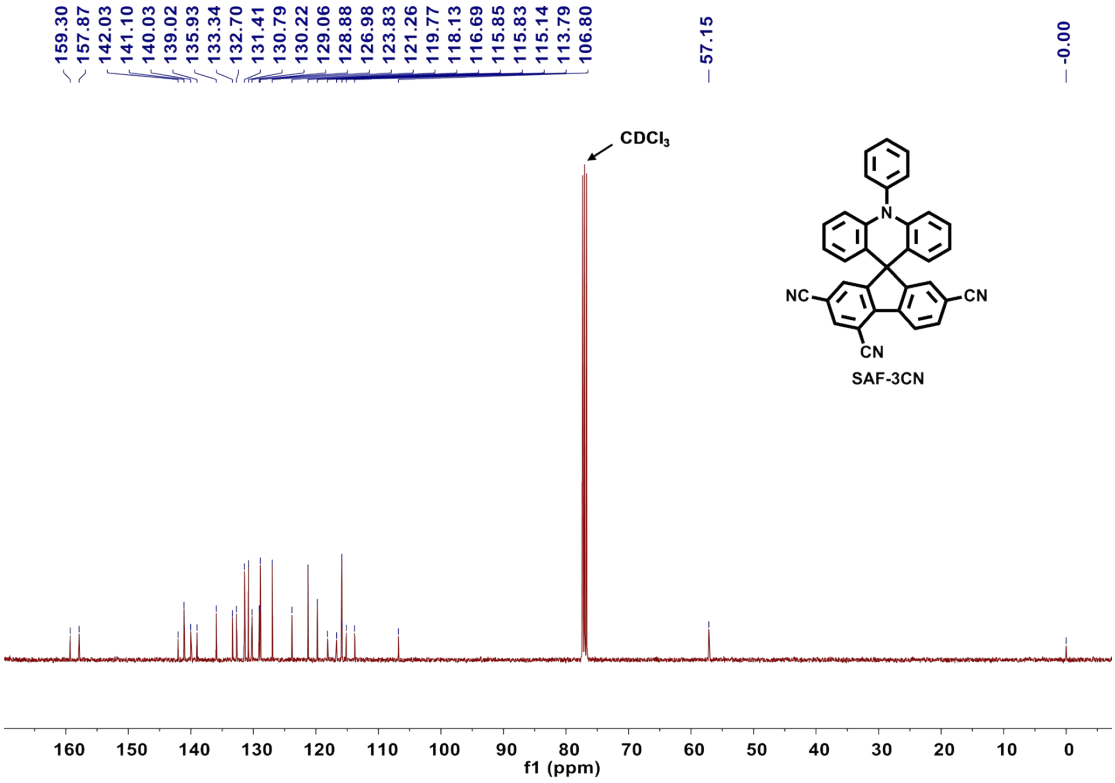
SAF-3Br





SAF-3Br


8.65
8.63
7.96
7.89
7.85
7.83
7.79
7.77
7.75
7.73
7.64
7.63
7.61
7.48
7.46
7.26
7.06
7.04
7.02
6.66
6.64
6.62
6.45
6.43
6.23
6.21
5.30
1.58
-0.00
CDCl3
CH2Cl2
H2O
NC
CN
CN
SAF-3CN
1.00
0.95
0.97
1.04
0.97
2.05
1.04
2.04
2.03
2.04
2.04
2.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


159.30
157.87
142.03
141.10
140.03
139.02
135.93
133.34
132.70
131.41
130.79
130.22
129.06
128.88
126.98
123.83
121.26
119.77
118.13
116.69
115.85
115.83
115.14
113.79
106.80
57.15
-0.00
CDCl3
NC
CN
CN
SAF-3CN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

X-Ray Crystal Structure Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1979497 (**SAF-3CN** (plate)). These data can beobtained free of charge from The Cambridge Crystallographic Data Centre *via*https://www.ccdc.cam.ac.uk/structures-beta/.

Datablock: 0613zxd4_0m_sq (SAF-3CN)

Bond precision: C-C = 0.0020 A Wavelength=0.71073
Cell: a=9.2430(3) b=11.5338(3) c=14.2060(4)
alpha=97.781(1) beta=99.094(1) gamma=90.970(1)
Temperature: 100 K

	Calculated	Reported
Volume	1480.52(7)	1480.52(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C34 H18 N4 [+ solvent]	C34 H18 N4
Sum formula	C34 H18 N4 [+ solvent]	C34 H18 N4
Mr	482.52	482.52
Dx,g cm-3	1.082	1.082
Z	2	2
Mu (mm-1)	0.065	0.065
F000	500.0	500.0
F000'	500.17	
h,k,lmax	11,14,17	11,14,17
Nref	5628	5564
Tmin,Tmax	0.996,0.998	0.681,0.745
Tmin'	0.995	

Correction method= # Reported T Limits: Tmin=0.681
Tmax=0.745 AbsCorr = MULTI-SCAN
Data completeness= 0.989 Theta(max)= 25.694
R(reflections)= 0.0392(4285) wR2(reflections)= 0.1010(5564)
S = 1.045 Npar= 343