

## Supporting Information

### Reverse Intersystem Crossing Managing Assistant Dopant for High External Quantum Efficiency Red Organic Light-Emitting Diode

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### Experimental

2,3,5,6-Tetrafluoroterephthalonitrile was supplied by Sigma-aldrich. Intermediates and final compounds were dissolved in deuterated  $\text{CDCl}_3$  and identified by  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra using Unity Inova (Varian, 500 MHz) spectrometer. The molecular weight of final compounds was measured by Advion, ExpressionL CMS spectrometer in APCI mode. The compounds were dissolved in  $1.0 \times 10^{-5}$  M toluene solution and PL spectra were obtained using a fluorescence spectrophotometer (PerkinElmer, LS-55). The triplet energies of compounds were measured by low temperature PL spectra at 77 K with delay time of 1ms. The UV-vis absorptions spectra were observed using UV-vis spectrophotometer (JASCO, V-730) and a sample dissolved in  $1.0 \times 10^{-5}$  M THF solution. The CV measurements of the compounds were carried out by IVIUM STAT. The standard material was Ferrocene, working electrode was carbon electrode, reference electrode was Ag, and counter electrode was Pt. PL quantum yield and transient PL decay data were recorded

using Quantaurus QY Absolute system (Hamamatsu, C11347-11) and Hamamatsu Quantaurus-Tau system (Hamamatsu, C11367-31).

## Synthesis

### **2,5-Di(9H-carbazol-9-yl)-3,6-difluoroterephthalonitrile (2Cz2FTPN)**

2,3,5,6-Tetrafluoroterephthalonitrile (4FTPN) (3.00 g, 14.99 mmol) and cesium carbonate (9.77 g, 29.98 mmol) were poured into a 100 ml two-neck round bottomed (RB) flask with 30 ml dimethyl formamide (DMF) solvent. 9H-carbazole (Cz) (4.76 g, 28.48 mmol) was dissolved in 28.5 ml DMF solvent and slowly added to previously prepared two-neck RB flask with stirring. The mixture was reacted at room temperature for 9 hours. To end-up the reaction, cesium carbonate was further quenched by distilled water (DW) and filtered directly. The residue solid organic material was purified with column chromatography using an eluent of dichloromethane (MC) : hexane (1 : 4) and sublimation. (3.12 g, yield : 41.83%)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.19 (d, 4H), 7.55 (dd, 4H), 7.45 (t, 4H), 7.28 (d, 4H).

HRMS (FAB+) m/z 494.1348 [(M+H)+]; Calcd. For C<sub>32</sub>H<sub>16</sub>F<sub>2</sub>N<sub>4</sub>, 494.1348.

### **2,3,5-Tri(9H-carbazol-9-yl)-6-fluoroterephthalonitrile (3CzFTPN)**

4FTPN (3 g, 14.99 mmol) and cesium carbonate (12.21 g, 37.48 mmol) were poured into a 100 ml two-neck RB flask with 30 ml DMF solvent. Cz (6.26 g, 37.48 mmol) was dissolved in DMF (38.5 ml) solvent and added slowly according to the synthetic procedure of 2F2CzTPN. The mixture was reacted at room temperature for 9 hours, further quenched and purified according to the method for the synthesis of 2F2CzTPN. (1.42 g, yield : 14.72%)

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.21 (d, J = 7.8 Hz, 2H), 7.70 (dd, J = 10.5, 4.4 Hz, 4H), 7.62 (t, J = 7.7 Hz, 2H), 7.45 (dd, J = 15.8, 8.3 Hz, 4H), 7.26 (d, J = 0.4 Hz, 2H), 7.16 – 6.96 (m, 10H).

**HRMS** (FAB+) m/z 641.2020 [(M+H)+]; Calcd. For C<sub>44</sub>H<sub>24</sub>FN<sub>5</sub>, 641.2020

**2,5-Bis(5H-benzo[4,5]thieno[3,2-c]carbazol-5-yl)-3,6-di(9H-carbazol-9-yl)terephthalonitrile (2BTCz2CzTPN)**

2F2CzTPN (0.5 g, 1.01 mmol), cesium carbonate (0.99 g, 3.03 mmol) and 5H-benzo[4,5]thieno[3,2-c]carbazole (BTCz) (0.83g, 3.03 mmol) were added in a pressure tube with DMF (5 ml) as solvent. The compound was stirred at 60 °C for 3 hours and purified according to the procedure for the synthesis of 2F2CzTPN. (0.91 g, yield : 90.3%)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.18 (d, J = 7.9 Hz, 2H), 8.00 (dd, J = 8.5, 6.5 Hz, 2H), 7.94 (t, J = 6.6 Hz, 4H), 7.71 – 7.66 (m, 4H), 7.53 – 7.42 (m, 6H), 7.36 – 7.29 (m, 8H), 7.23 – 7.04 (m, 10H).

**<sup>13</sup>C NMR** : not detected due to the low solubility

**HRMS** (FAB+) m/z 1001.2519 [(M+H)+]; Calcd. For C<sub>68</sub>H<sub>36</sub>N<sub>6</sub>S<sub>2</sub>, 1001.2519.

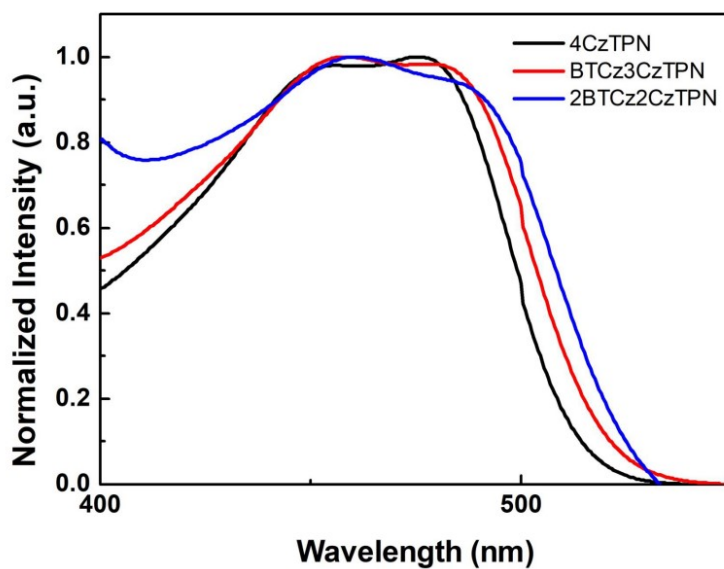
**2-(5H-benzo[4,5]thieno[3,2-c]carbazol-5-yl)-3,5,6-tri(9H-carbazol-9-yl)terephthalonitrile (BTCz3CzTPN)**

F3CzTPN (0.5 g, 0.78 mmol), cesium carbonate (0.38 g, 1.17 mmol) and 5H-benzo[4,5]thieno[3,2-c]carbazole (BTCz) (0.38 g, 1.17 mmol) were used and the synthetic procedures are the same as those of 2BTCz2CzTPN. (0.61 g, yield : 87.2%)

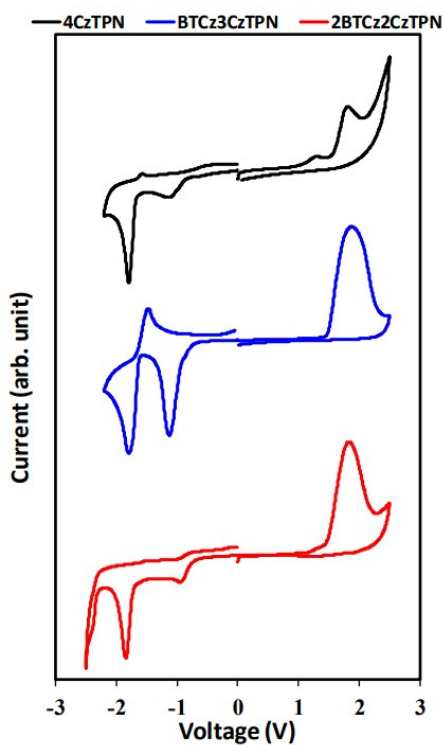
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.20 – 8.15 (m, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.95 – 7.90 (m, 3H), 7.78 – 7.72 (m, 2H), 7.70 – 7.64 (m, 4H), 7.52 (td, J = 7.5, 1.2 Hz, 2H), 7.47 (td, J = 7.5, 1.3 Hz, 2H), 7.41 (d, J = 8.6 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.25 – 7.22 (m, 1H), 7.22 – 7.11 (m, 10H), 7.09 – 7.04 (m, 2H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) 138.6, 138.5, 125.9, 125.7, 124.8, 124.6, 122.4, 121.9, 121.3, 120.7, 120.5, 109.7, 107.3.

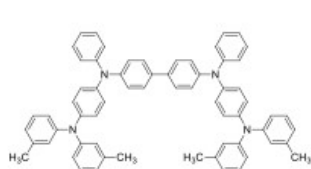
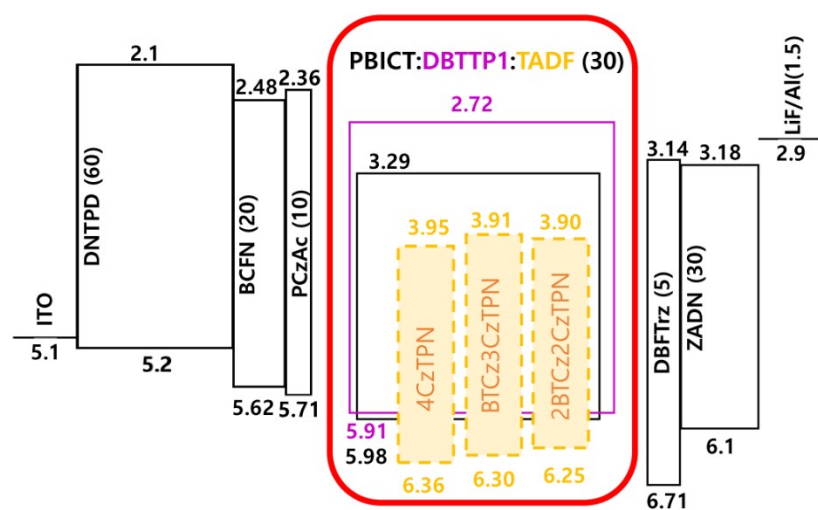
**HRMS** (FAB+) m/z 895.2645 [(M+H)+]; Calcd. For C<sub>62</sub>H<sub>34</sub>N<sub>6</sub>S, 895.2645.



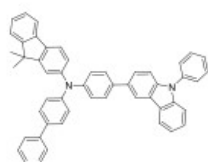
**Figure S1.** Enlarged UV-vis absorption spectra of 4CzTPN, BTCz3CzTPN and 2BTCz2CzTPN.



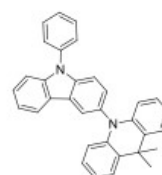
**Figure S2.** Scanned oxidation and reduction data of 4CzTPN, BTCz3CzTPN and 2BTCz2CzTPN.



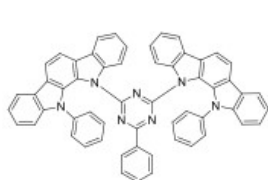
DNTPD



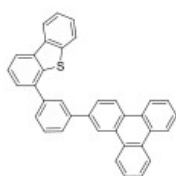
BCFN



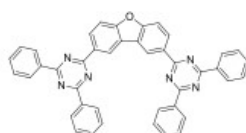
PCzAc



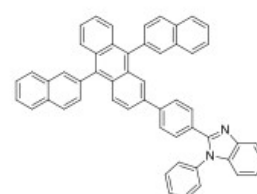
PBICT



DBTTP1

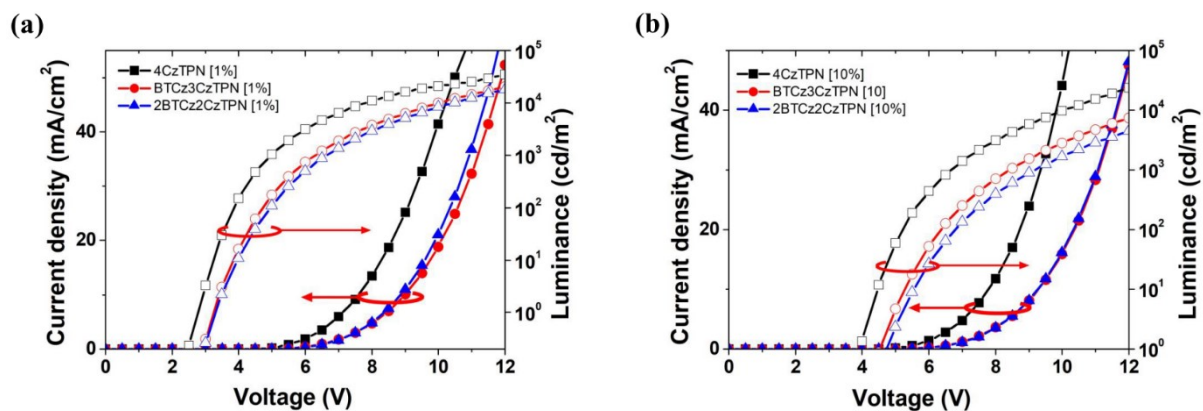


DBFTrz

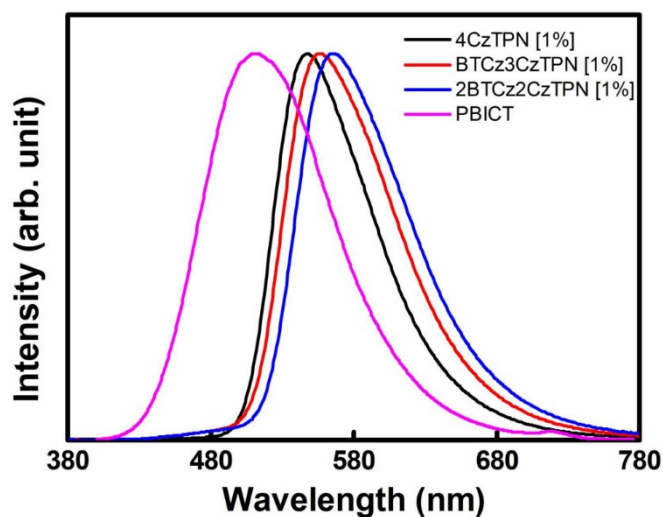


ZADN

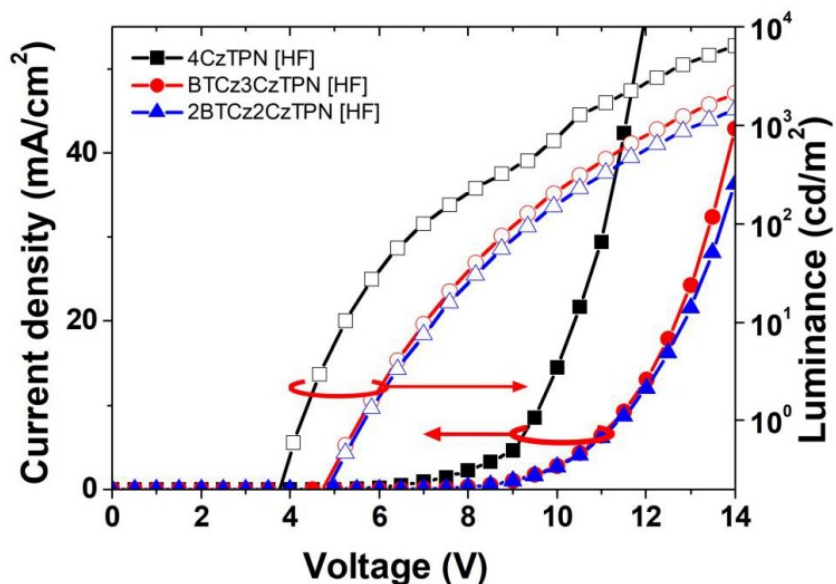
**Figure S3.** Device energy level diagram of the 4CzTPN, BTCz3CzTPN and 2BTCz2CzTPN devices and chemical structures of each layer.



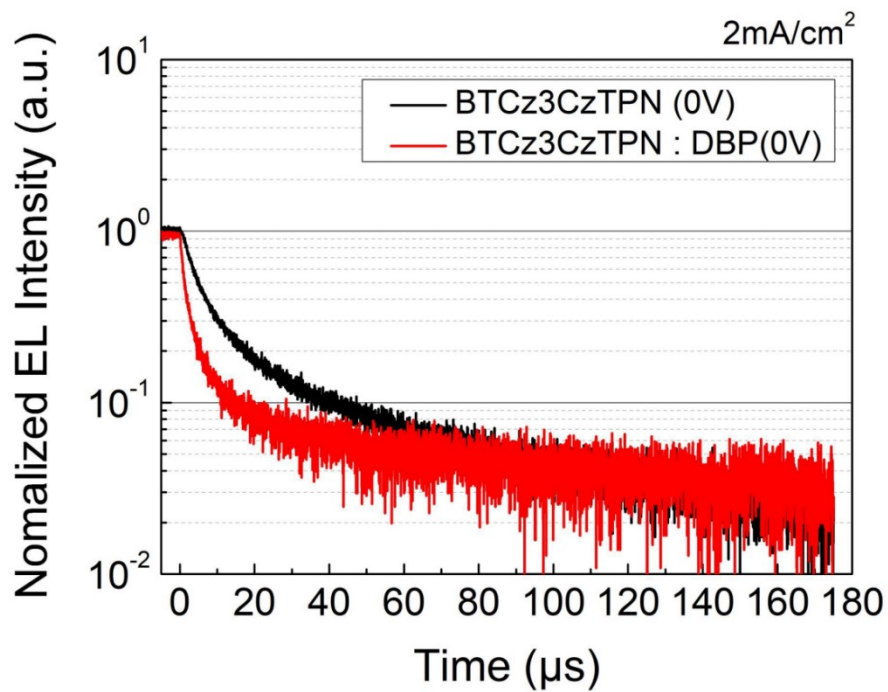
**Figure S4.** Current density, luminance and voltage plots of the TADF devices with doping concentrations of (a) 1 wt% and (b) 10 wt%.



**Figure S5.** PBICT matrix emission and TADF emission spectra at 1 wt% concentration.



**Figure S6.** Current density, luminance and voltage plots of the TADF assisted fluorescence device.



**Figure S7.** Time resolved electroluminescence of BTCz3CzTPN based TADF device and hyperfluorescence device.



**Table S1.** Rate constants of 4CzTPN, BTCz3CzTPN and 2BTCz2CzTPN calculated from PL decay curves measured using a 1 wt% emitter doped films.

	$\tau_p^{[a]}$ [ns]	$k_p$ [ $\times 10^7 \text{ s}^{-1}$ ]	$\tau_d^{[c]}$ [ $\mu\text{s}$ ]	$k_d$ [ $\times 10^5 \text{ s}^{-1}$ ]	PLQY <sup>[b] / [c]</sup> [%]	$k_{\text{ISC}}$ [ $\times 10^7 \text{ s}^{-1}$ ]	$k_{\text{RISC}}$ [ $\times 10^5 \text{ s}^{-1}$ ]	$k_r$ [ $\times 10^6 \text{ s}^{-1}$ ]	$k_{\text{nr}}$ [ $\times 10^5$ ]
4CzTPN	14.5	6.90	5.51	1.81	6.6 <sup>[a]</sup> / 27.5 <sup>[b]</sup>	6.44	8.03	4.59	1.28
BTCz3CzTPN	16.4	6.10	3.55	2.82	7.0 <sup>[a]</sup> / 20.9 <sup>[b]</sup>	5.67	9.08	4.25	2.18
2BTCz2CzTPN	17.6	5.68	2.47	4.05	7.6 <sup>[a]</sup> / 17.7 <sup>[b]</sup>	5.25	10.22	4.31	3.27

[a] Measured value at 1 wt% doped DPEPO film. under nitrogen.

[b] PLQY measured in 1 wt% doped DPEPO film. under air. [c] PLQY measured in 1 wt% doped DPEPO film. under nitrogen.

**Table S2.** Rate constants of 4CzTPN, BTCz3CzTPN and 2BTCz2CzTPN.

	$\tau_p^{[a]}$ [ns]	$k_p$ [ $\times 10^7 \text{ s}^{-1}$ ]	$\tau_d^{[a]}$ [ $\mu\text{s}$ ]	$k_d$ [ $\times 10^5 \text{ s}^{-1}$ ]	PLQY <sup>[b] / [c]</sup> [%]	$k_{\text{ISC}}$ [ $\times 10^7 \text{ s}^{-1}$ ]	$k_{\text{RISC}}$ [ $\times 10^5 \text{ s}^{-1}$ ]	$k_r$ [ $\times 10^6 \text{ s}^{-1}$ ]	$k_{\text{nr}}$ [ $\times 10^5$ ]
4CzTPN	14.4	6.96	2.93	3.41	14.3 <sup>[a]</sup> / 20.0 <sup>[b]</sup>	5.97	5.58	9.95	2.62
BTCz3CzTPN	12.7	7.87	2.10	4.76	10.4 <sup>[a]</sup> / 12.3 <sup>[b]</sup>	7.06	6.30	8.18	4.11
2BTCz2CzTPN	11.3	8.85	1.88	5.32	8.8 <sup>[a]</sup> / 10.1 <sup>[b]</sup>	8.07	6.75	7.75	4.73

[a] Measured value using PBICT:DBTTP1:10 wt% TADF films under nitrogen. [b] PLQY measured using PBICT:DBTTP1:10 wt% TADF films under air. [c] PLQY measured using PBICT:DBTTP1:10 wt% TADF films under nitrogen.

Rate constants are calculated from PL decay curves measured in PBICT:DBTTP1:10 wt% TADF doped films.

**Table S3.** Rate constants of 4CzTPN, BTCz3CzTPN and 2BTCz2CzTPN in a DBP and TADF assistant dopant co-doped films. (Detected at 550 nm wavelength)

	$\tau_p^{[a]}$ [ns]	$k_p$ [ $\times 10^7 \text{ s}^{-1}$ ]	$\tau_d^{[a]}$ [ $\mu\text{s}$ ]	$k_d$ [ $\times 10^5 \text{ s}^{-1}$ ]	$k_{\text{ISC}}$ [ $\times 10^7 \text{ s}^{-1}$ ]	$k_{\text{RISC}}$ [ $\times 10^5 \text{ s}^{-1}$ ]	$k_r$ [ $\times 10^6 \text{ s}^{-1}$ ]	$k_{\text{nr}}$ [ $\times 10^5$ ]
4CzTPN	10.0	10.00	1.78	5.62	5.97	5.58	9.95	2.62
BTCz3CzTPN	11.1	9.09	1.66	6.02	7.06	6.30	8.18	4.11
2BTCz2CzTPN	10.7	9.35	1.63	1.63	8.07	6.75	7.75	4.73

[a] PLQY measured in PBICT:DBTTP1:10 wt% assistant dopant:0.5 wt% DBP doped films, under air.

Rate constants are calculated from PL decay curves measured in 550 nm region of PBICT:DBTTP1:10 wt% assistant dopant:0.5 wt% DBP doped films.

FRET radius ( $R_0$ ) can be calculated by equation S1.

$$R_0^6 = \phi_D k^2 \left( \frac{9000(\ln 10)}{128\pi^5 N_A n^4} \right) J \quad (\text{S1})$$

$k_{\text{FRET}}$  and  $k_{\text{DET}}$  are calculated by equation (S2) and (S3).

$$k_{\text{FRET}} = k_{p, 0.5 \text{ wt}\%} - k_{p, 0 \text{ wt}\%} \quad (\text{S2})$$

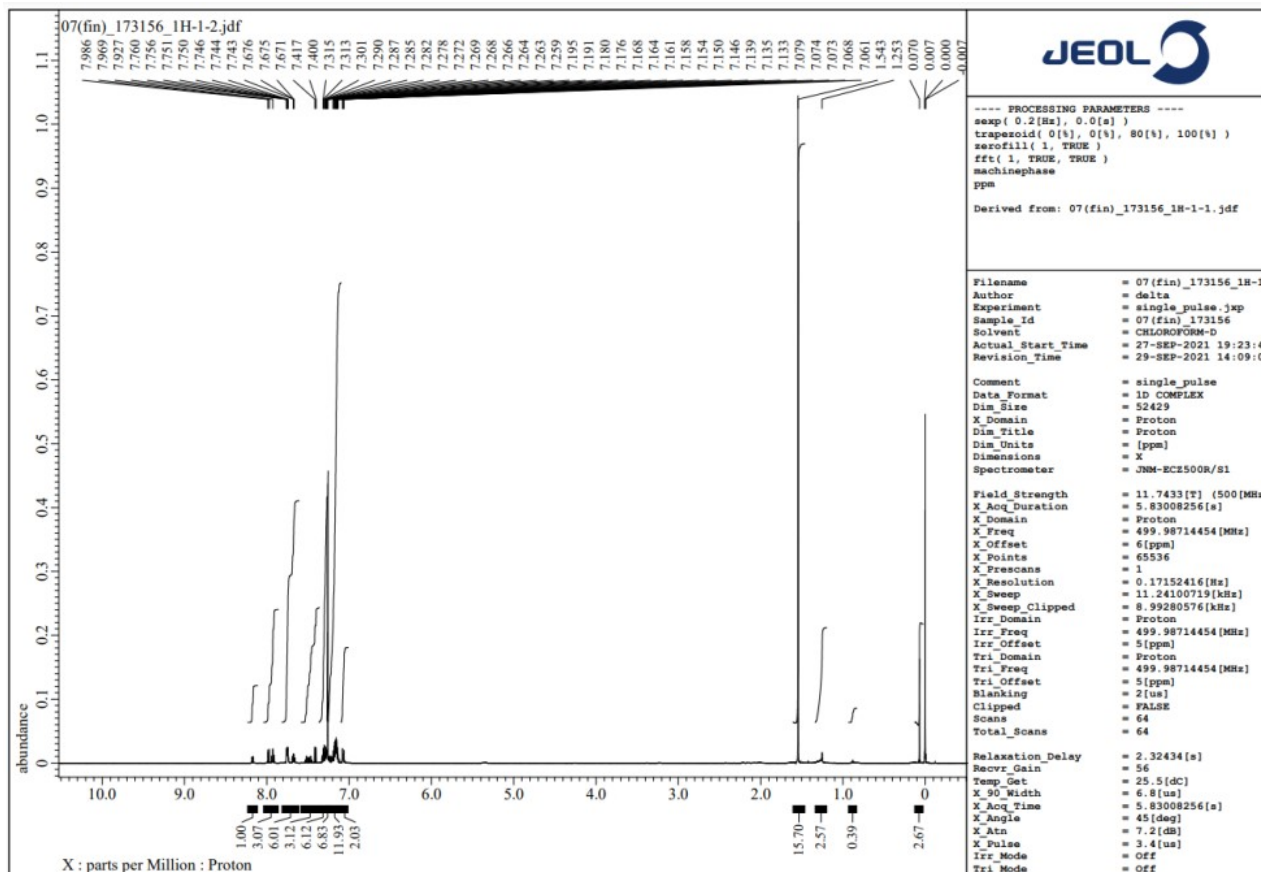
$$k_{\text{DET}} = k_{d, 0.5 \text{ wt}\%} - k_{d, 0 \text{ wt}\%} + k_{\text{RISC}} k_{\text{ISC}} * (k_{p, 0.5 \text{ wt}\%} - k_{p, 0 \text{ wt}\%}) \quad (\text{S3})$$

$k_{p/d, 0.5 \text{ wt}\%}$  : prompt / delayed rate constants at 0.5 wt% DBP fluorescent emitter doped films.

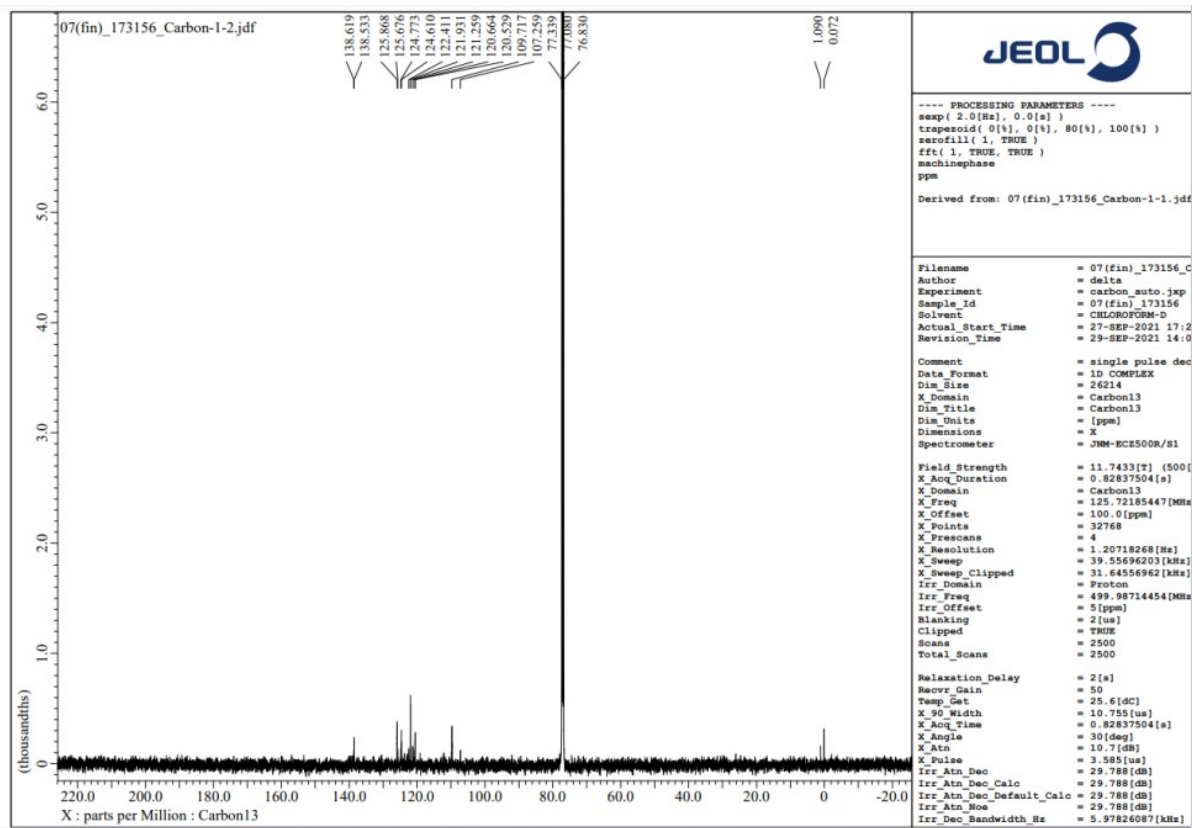
$k_{p/d}$  : prompt / delayed rate constants at pristine TADF doped films.

# NMR and HRMS Information

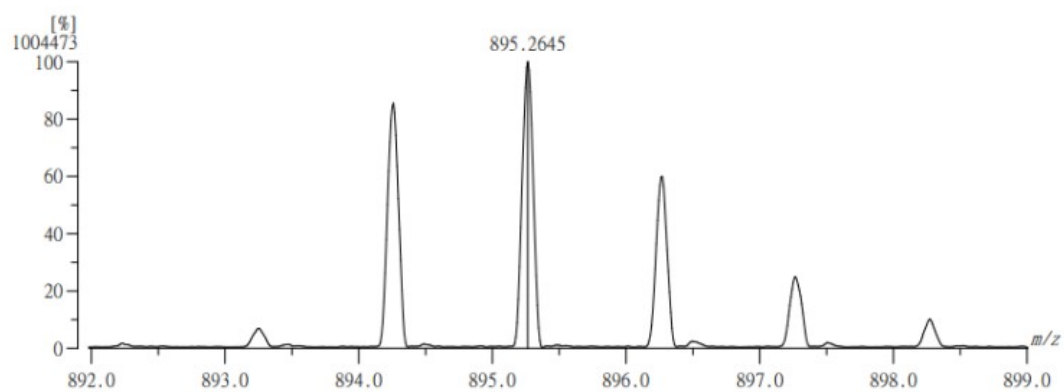
## BTCz3CzTPN



(a)



(b)



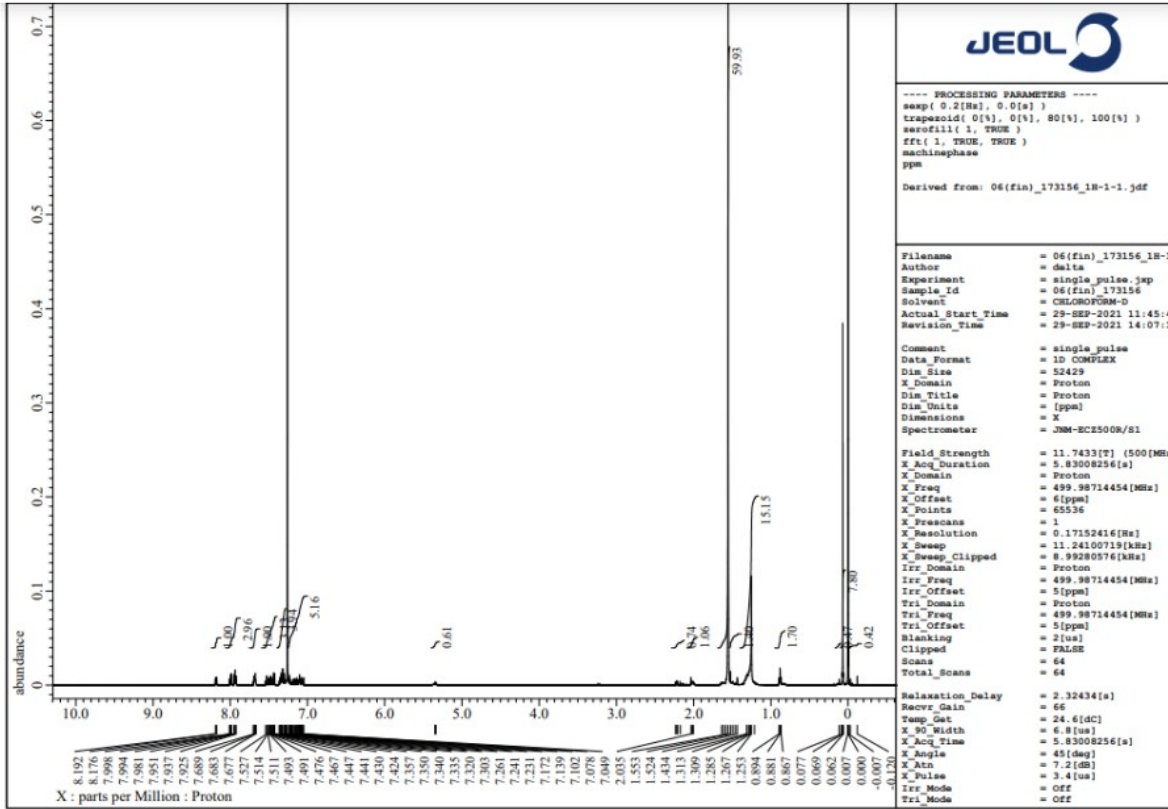
Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
1 895.2645	100.00	+3.9 / +3.5	53.5	C65 H31 N6
2		+0.1 / +0.1	49.5	C62 H35 N6 S
3		-3.6 / -3.3	45.5	C59 H39 N6 S2
4		-7.4 / -6.6	41.5	C56 H43 N6 S3
5		+6.6 / +5.9	42.0	C55 H41 N7 S3

(c)

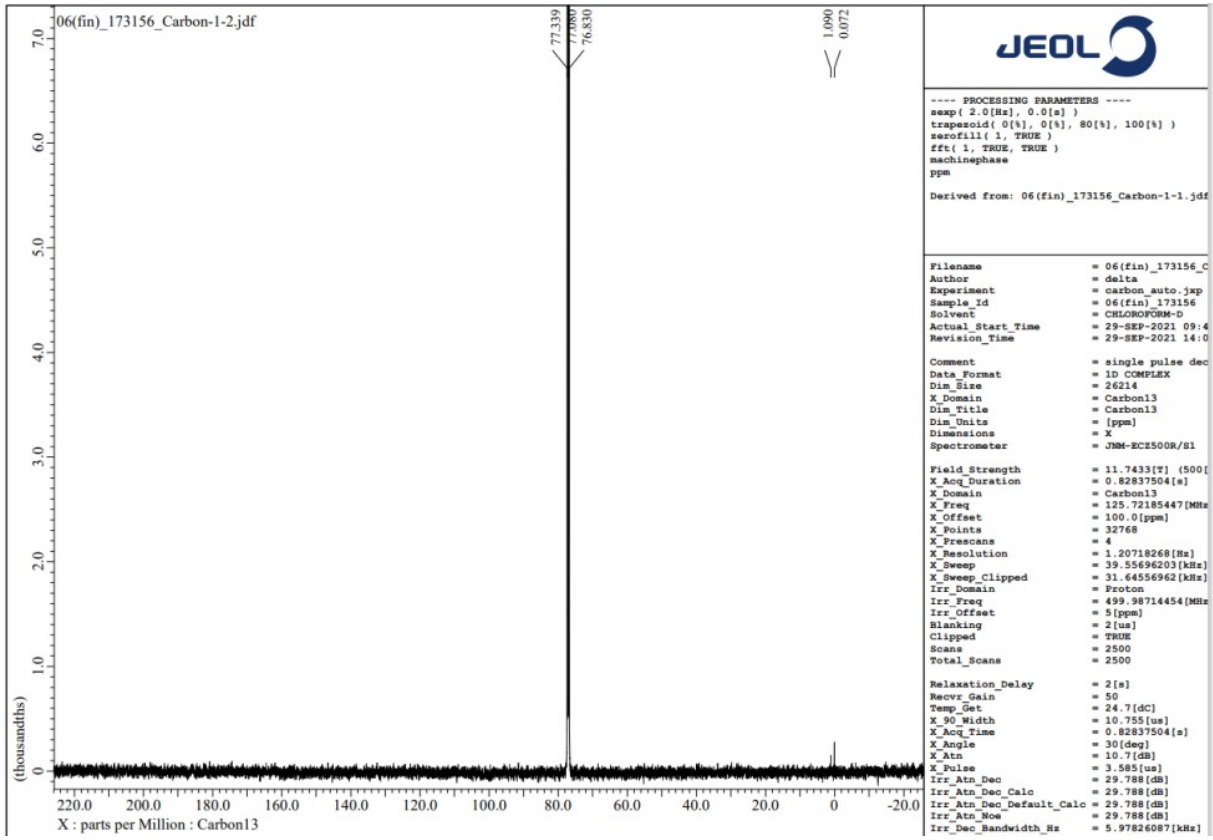
Figure S8. (a)  $^1\text{H}$  NMR spectrum of BTCz3CzTPN (500 MHz,  $\text{CDCl}_3$ ), (b)  $^{13}\text{C}$  NMR spectrum of BTCz3CzTPN (176 MHz,  $\text{CDCl}_3$ ), (c) HRMS spectrum of BTCz3CzTPN

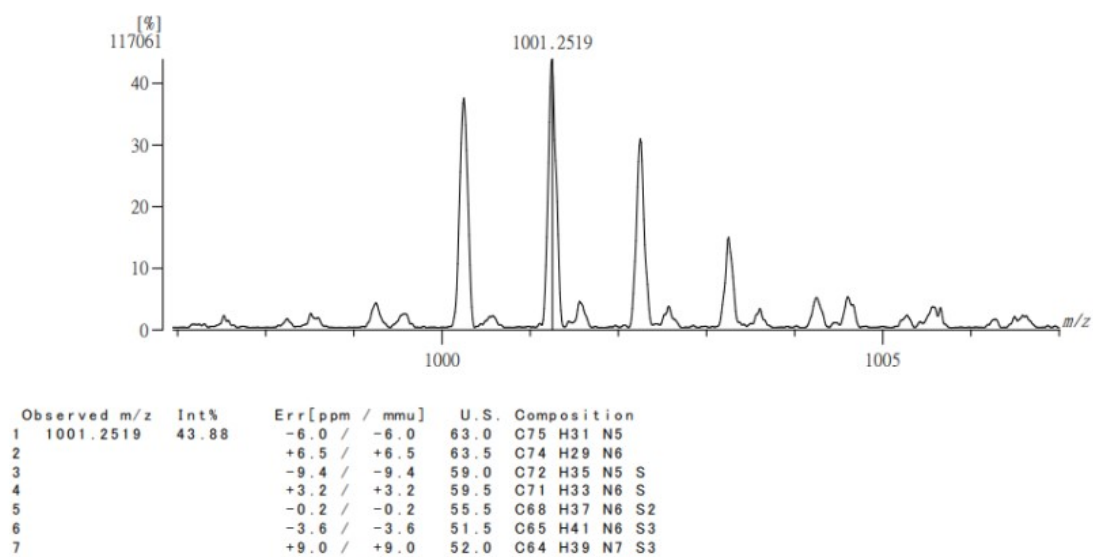
2BTCz2CzTPN

(a)



(b)





(c)

Figure S9. (a)  $^1\text{H}$  NMR spectrum of 2BTCz2CzTPN (500 MHz,  $\text{CDCl}_3$ ), (b)  $^{13}\text{C}$  NMR spectrum of 2BTCz2CzTPN (176 MHz,  $\text{CDCl}_3$ ), (c) HRMS spectrum of 2BTCz2CzTPN