Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

Exciplex-forming Cohost Systems with Highly Twisted Hexaphenylbenzene-cored Donors for Highly Efficient Orange and Red OLEDs

Yi-Sheng Chen[1], Wei-Chih Wei[1], Hao Chen[1], Tsung-Lin Tsai[2], Yu-Cheng Kung[2], Wen-Yi Hung[2,], Ken-Tsung Wong[1,3]**

[1]Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan
[2] Department of Optoelectronics and Materials Technology, National Taiwan Ocean University, Keelung 202, Taiwan
[3]Institute of Atomic and Molecular Science Academia Sinica, Taipei 10617, Taiwan.
E-mail: kenwong@ntu.edu.tw (Ken-Tsung Wong); wenhung@mail.ntou.edu.tw (Wen-Yi Hung)

General Method

Material Characterization

All the chemicals and reagents were empoly from commercial sources. Solvents for chemical analysis and reaction were purified by distillation before use. NMR spectra were recored on a Varian Mercury Plus-400 for ^{1}H NMR (400 MHz) and ^{13}C (100 MHz) using deuterium substituted solvent as an internal reference.

Physical properties measurement

Optical absorption experiments were conducted in solution state by JASCO V-670 spectrophotometer. Photoluminescence spectra were measured using a spectrophotometer (HITACHI F-4500 fluorometer) equipped with a liquid nitrogen attachment at room temperature and 77K.

Electricchemical properties measurement

Electrochemical measurements were investigated by an electrochemical analyser (CHI619B, CH Instruments) employing Ag/Ag$^+$ (Ag/0.01 M AgNO$_3$) as the reference electrode, a Pt wire as the counter-electrode, a glassy carbon electrode as the working electrode and an internal ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. Molecules for oxidation potential were carried out in CH$_2$Cl$_2$ (1.0 mM) congaing 0.1M tertabutylalumm butylammonium hexafluorophosphate (nBu$_4$NPF$_6$) as a supporting electrolyte. Molecules for reduction potentials were prepared in THF (1.0 mM) containing 0.1 M TBAP as a supporting electrolyte with argon before conducting the experiments.

Thermal properties measurement

Thermogravimetric analysis (TGA) was measurement under a nitrogen atmosphere at a heating rate of 10 °C/min on a platinum pan via a TA Instruments Q500 TGA (V20.13 Build 39)

Method for Theoretical Calculation

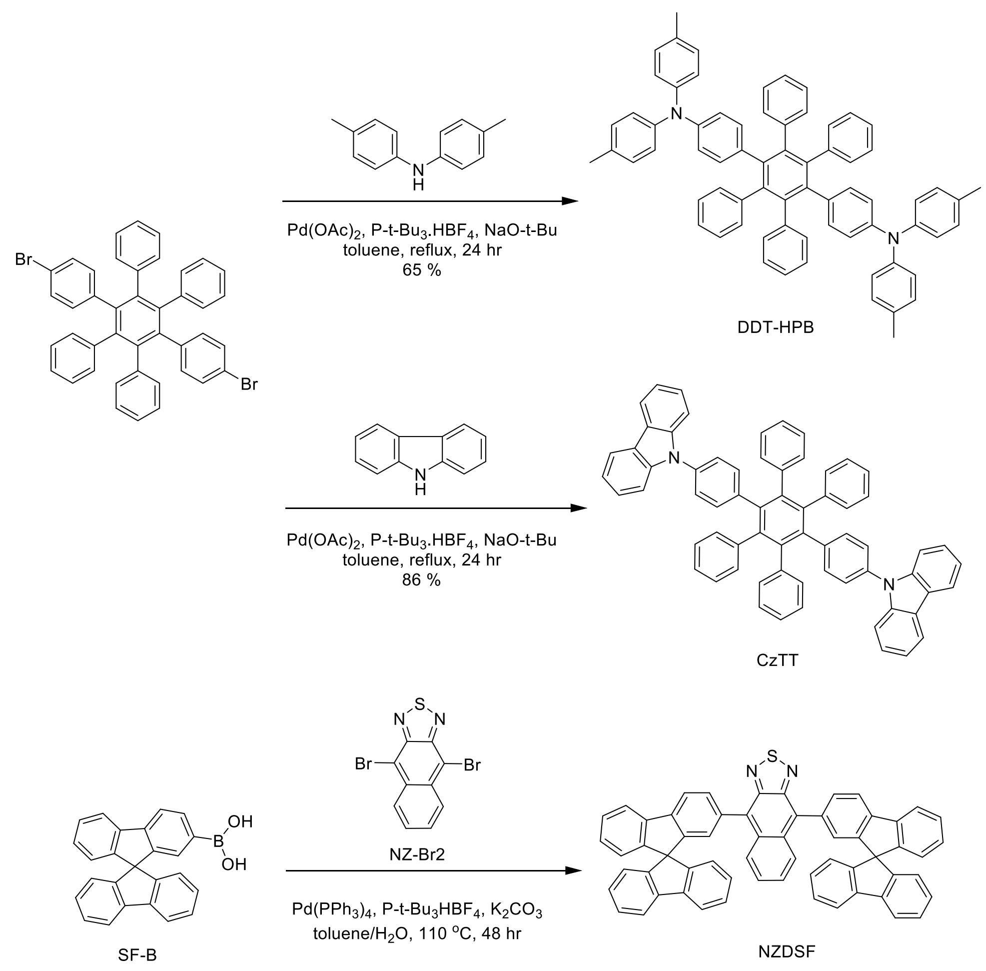
Density function theory (DFT) calculations were performed in gaseous state B3LYP/6-31+G(d) level by using a Gaussian 9 program package through Taiwania 1, built by the National Applied Research Laboratories, Taiwan.

PLQY, HOMO and TRPL lifetime measurements.

PLQYs of thin films were determined using quantum yield spectrometer (Hamamatsu C9920-02). During the PLQY measurements, the integrating sphere was purged with pure and dry nitrogen to keep the environment inert. The experimental values of HOMO levels in solid state were determined with a Riken AC-2 photoemission spectrometer (PES). The time-resolved studies were performed using a time-correlated single photon counting (TCSPC) system (TimeHarp 260, PicoQuant) with the pulse LED at 285 nm (PLS280, PicoQuant) as the photoexcitation light source.

OLED fabrications

All chemicals were purified through vacuum sublimation prior to use. The OLED were fabricated through vacuum deposition of the materials at 10^{-6} torr onto the ITO-coated glass substrates having a sheet resistance of 15 Ω sq^{-1}. Prior to use the ITO surface was cleaned ultrasonically; i.e. with acetone, methanol, and deionized water in sequence and finally with N_2 plasma. The deposition rate of each organic material was ca. 1 - 2 $Å \cdot s^{-1}$. The J–V–L characteristics of the devices were measured simultaneously in a glove-box. A programmable source measurement unit (2614B, Keithley) was used as a driving source of the device while the light intensity was measured by a calibrated silicon detector. EL spectra were measured using a photodiode array (Ocean Optics USB2000+).



Scheme S1 Synthesis route of **CzTT DDT-HPB** and **NZDSF**

Synthesis of **CzTT**

To a two-neck round-bottom flask was added dibormohexaphenylbenzene (2.00g, 3.00 mmol), carbazole (1.10 g, 6.6 mmol), palladium acetate (0.06 g, 0.30 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.34g, 1.20 mmol), sodium tert-butoxide (1.70 g, 18.0 mmol). The flask was evacuated and purged with argon gas, then toluene (30.0 mL) was added. The reaction mixture was refluxed overnight. After cooling temperature, the mixture was extracted with ether and washed with brine. The organic solution was dried over $MgSO_4$ and concentrated to give the crude product as brown liquid. The crude product was purified by the column chromatography on silica gel (hexane/DCM = 1/1) and reprecipitation from DCM/MeOH to afford the title compound as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.09 (d, J = 7.6 Hz, 4H), 7.36 (t, J = 6.8 Hz, 4H), 7.23 (d, J = 7.8 Hz, 4H), 7.11 (d, J = 2 Hz, 4H) 7.05-7.01 (m, 30H) ^{13}C NMR (100 MHz, CD_2Cl_2) δ 140.9, 140.5, 140.3, 140.1, 140.0, 134.5, 132.8, 131.5, 126.9, 125.7, 125.6, 125.5, 123.1, 120.1, 119.6, 109.6 MS (m/z, MALDI-TOF/TOF) Calcd for $C_{63}H_{46}N_2$ 864.3499, found 864.3533.

Synthesis of **DDT-HPB**

To a two-neck round-bottom flask was added dibormohexaphenylbenzene (4.15g, 6.00 mmol), Di-p-tolylamine (2.37 g, 12.03 mmol), palladium acetate (0.13g, 0.60 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.70g, 2.40 mmol), sodium tert-butoxide (3.46g, 36.00 mmol) The flask was evacuated and purged with argon gas, then toluene (60.0 mL) was added. The reaction mixture was refluxed overnight. After cooling temperature, the mixture was extracted with ether and washed with brine. The organic solution was dried over $MgSO_4$ an concertation to give the crude product as brown liquid. The crude product was purified by the column chromatography on silica gel (hexane/DCM = 3/1) and reprecipitation from DCM/MeOH to afford the title compound as a white solid (4.16 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.94 (s, 4H), 6.92-6.90 (m, 16H), 6.86-6.84 (m, 8H), 6.71 (d, *J*= 8.8 Hz 8H), 6.62 (d, *J* = 8.4 Hz, 4H), 6.53 (d, *J* = 8.8 Hz, 4H), 2.24 (s, 12H) ^{13}C NMR (100 MHz, CD_2Cl_2) δ 145.5, 145.1, 140.8, 140.3, 140.2, 135.2, 132.2, 131.6, 131.4, 129.5, 126.6, 125.1, 123.5, 122.7, 20.7 MS (m/z, MALDI-TOF/TOF) Calcd for $C_{70}H_{56}N_2$ 924.4443, found 924.4467.

Synthesis of **NZDSF**

To a two-neck round-bottom flask was added compound SF-B (3.30 g, 9.20 mmol), NZ-Br2 (1.00 g, 2.90 mmol), tetrakis(triphenylphosphine)palladium (0) (0.70 g, 0.60 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.35g, 1.20 mmol), potassium carbonate (2.50 g,18 mmol). The flask was evacuated and purged with argon gas, then toluene (50 mL) and water (9 mL) were added. The reaction mixture was refluxed for 48 h. After cooling to room temperature, the mixture was extracted with ethyl acetate and washed with brine. The organic solution was dried over MgSO4 and concentrated to give the crude product as brown solid. The crude product was purified by the column chromatography on silica gel (hexane/ THF = 1/1) and reprecipitation from THF/MeOH to afford the title compound as a red solid. (2.00 g, 84%). H^1 NMR (400 MHz, $CDCl_3$) *δ* 8.08 (d, *J* = 8 Hz, 2H) 7.98 (d, *J* = 7.6 Hz, 2H) 7.80-7.79 (m, 4H), 7.68-7.60 (m,4H), 7.46-7.32 (m, 6H), 7.20-7.06 (m, 8H), 6.85-6.78 (m, 6H), 6.74 (d, *J* = 8 Hz, 2H) ^{13}C NMR (100 MHz, CD_2Cl_2) *δ* 151.7, 149.8, 149.5, 149.2, 149.0, 148.7, 142.4, 142.3, 142.0, 136.6, 128.7, 128.4, 127.5, 126.5, 124.4, 124.1, 121.2, 121.1, 121.0, 120.8, 120.7, 120.7, 66.6 HRMS (m/z, MALDI-TOF/TOF) Calcd for $C_{60}H_{34}N_2$ 814.2437, found 814.2394.

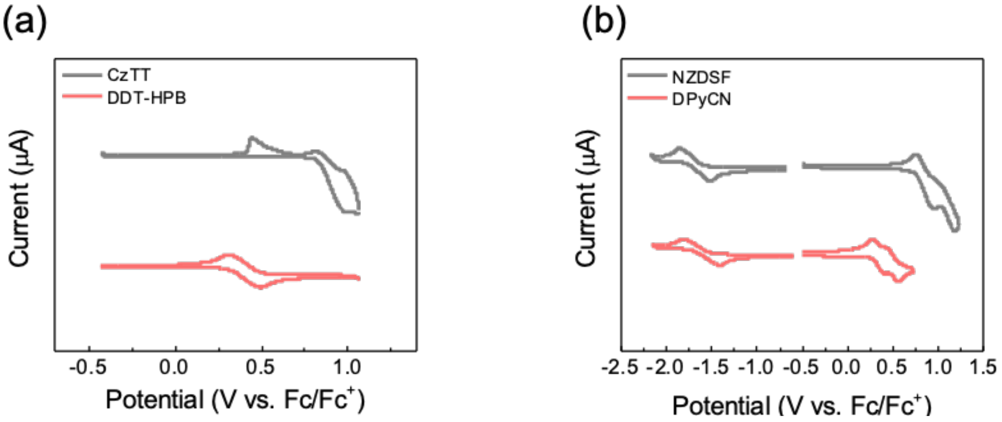


Figure S1 Cyclic voltammogram of (a) **CzTT** and **DDT-HPB** in DCM containing 0.1 M TBAPF$_6$ (b) **NZDSF** and **DPyCN** in DCM containing 0.1 M TBAPF$_6$ and in THF containing 0.1 M TBAP

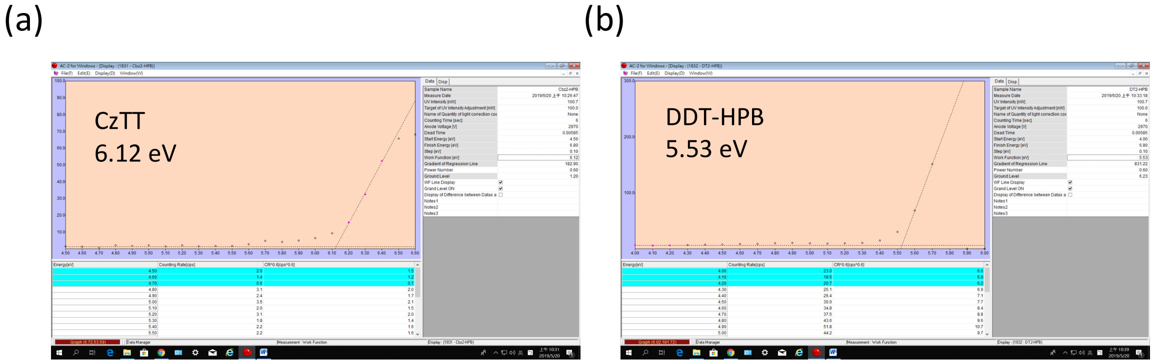


Figure S2 AC-2 measurement for (a) CzTT and (b) DDT-HPB

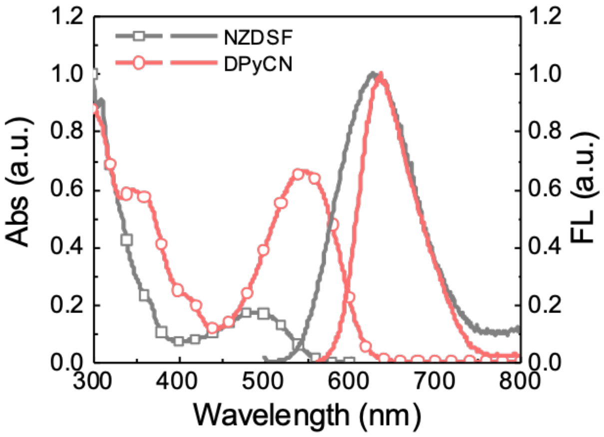


Figure S3 The UV-Vis absorption and photoluminescence of (a) **NZDSF** and (b) **DPyCN** in toluene

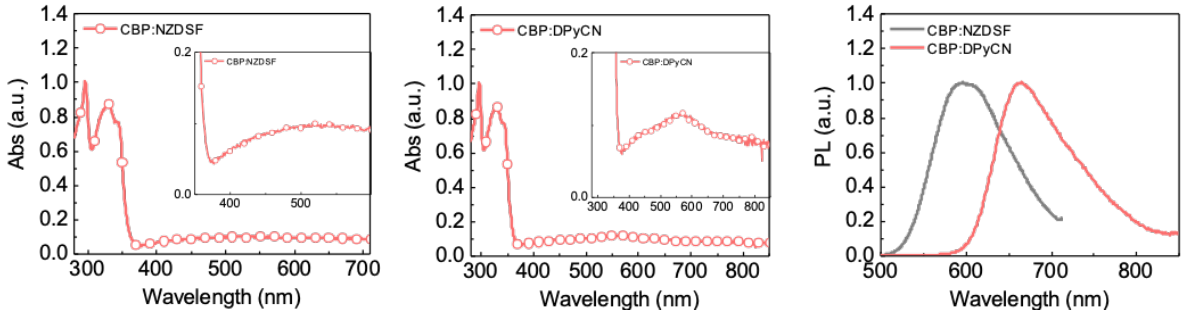


Figure S4 The film absorption of the (a) CBP:3 wt.% NZDSF and (b) CBP:3 wt.% DpyCN, (c) the film PL of the CBP:3 wt.% NZDSF and CBP:3 wt.% DPyCN

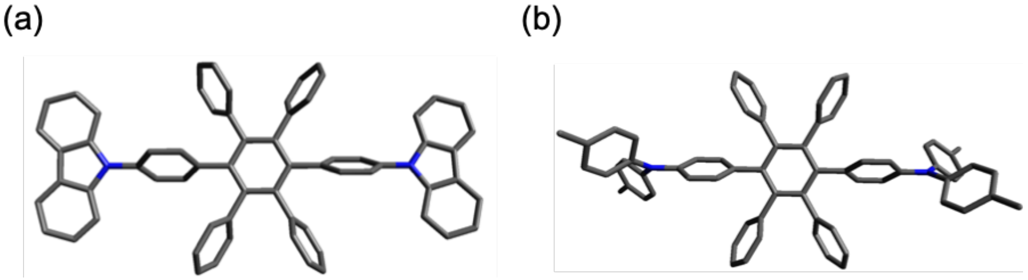


Figure S5 The optimized ground state conformation of (a) **CzTT** (b) **DDT-HPB**

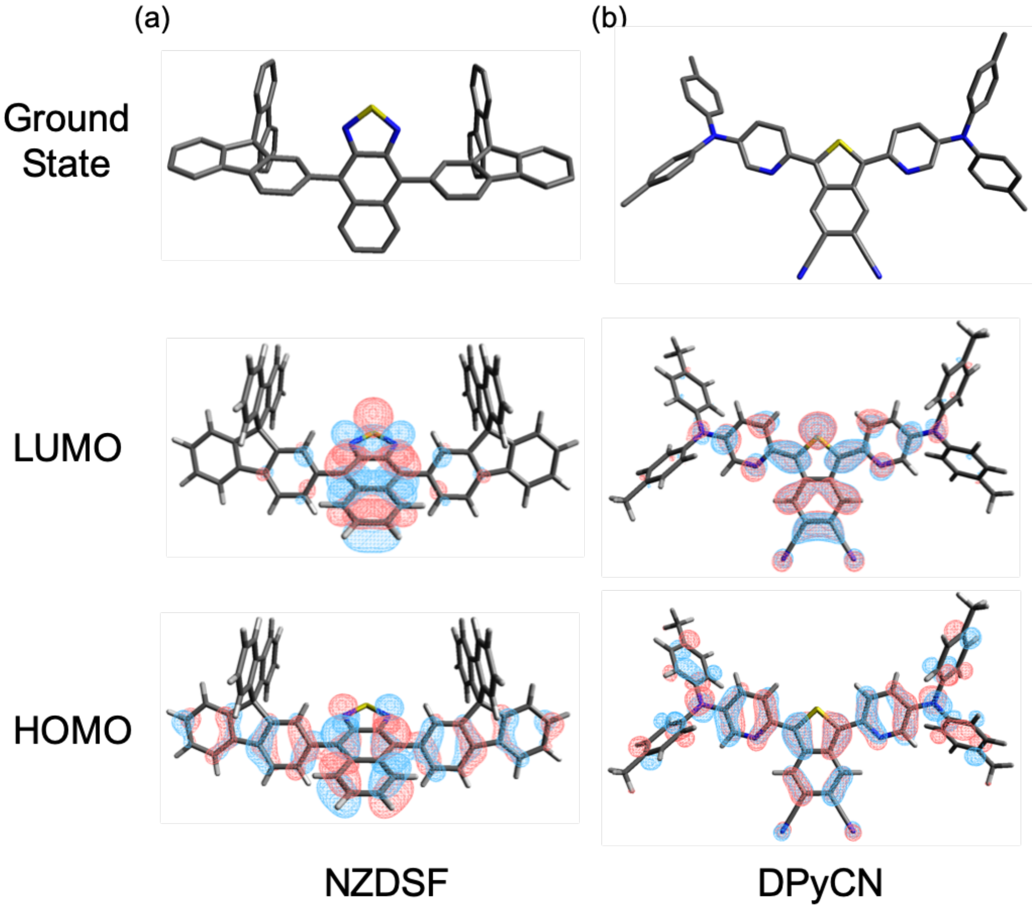


Figure S6 The optimized ground state conformation and the corresponding HOMO, LUMO of (a) **NZDSF** (b) **DPyCN**

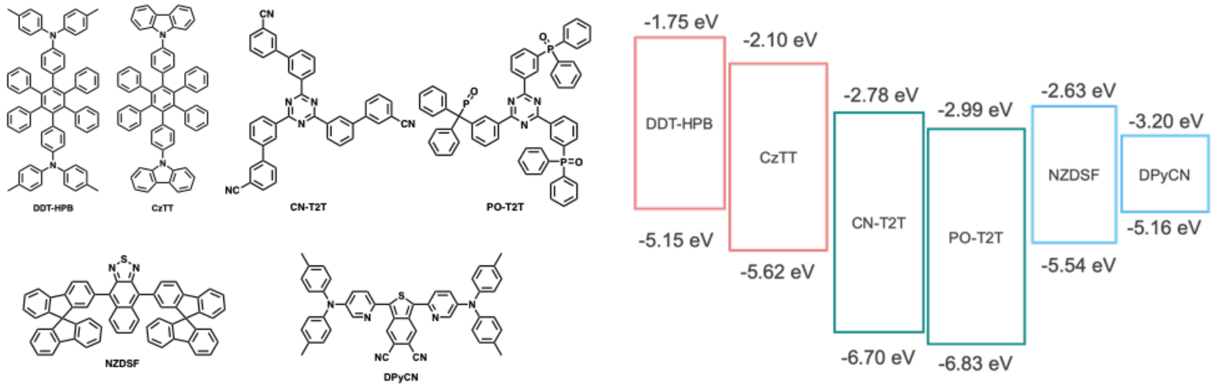


Figure S7 The chemical structures and energy levels of the donors, acceptors, and emitters.

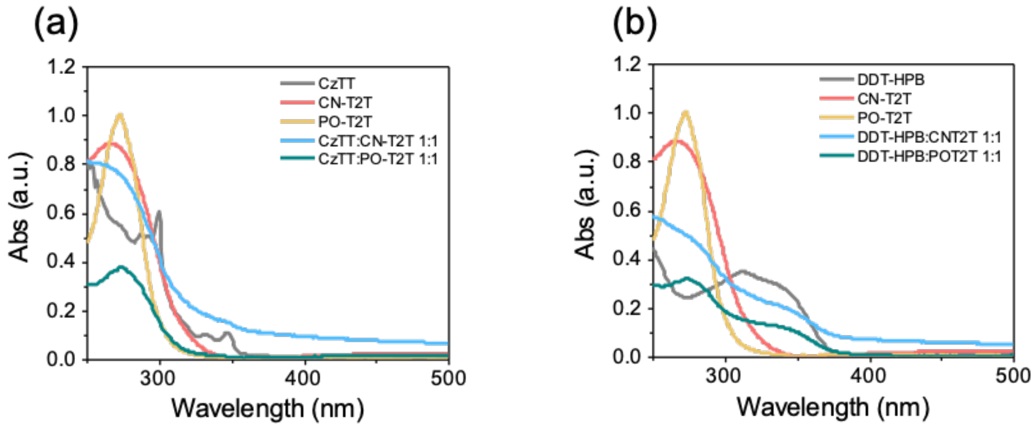


Figure S8 The film absorption of (a) **CzTT**, CN-T2T, PO-T2T, **CzTT**:CNT2T and **CzTT**:PO-T2T (b) **DDT-HPB**, CN-T2T, PO-T2T, **DDT-HPB**:CNT2T and **DDT-HPB**:PO-T2T

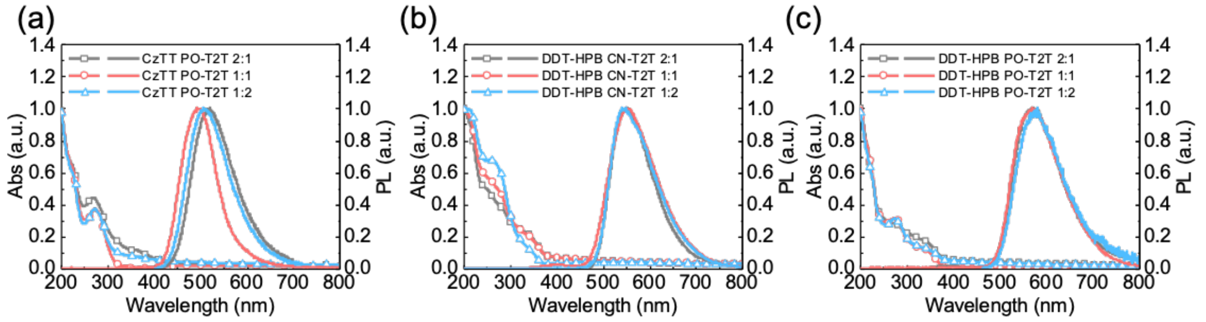


Figure S9 The photophysical properties of CzTT:PO-T2T, **DDT-HPB**:CN-T2T and **DDT-HPB**:PO-T2T blend films with different D:A ratios

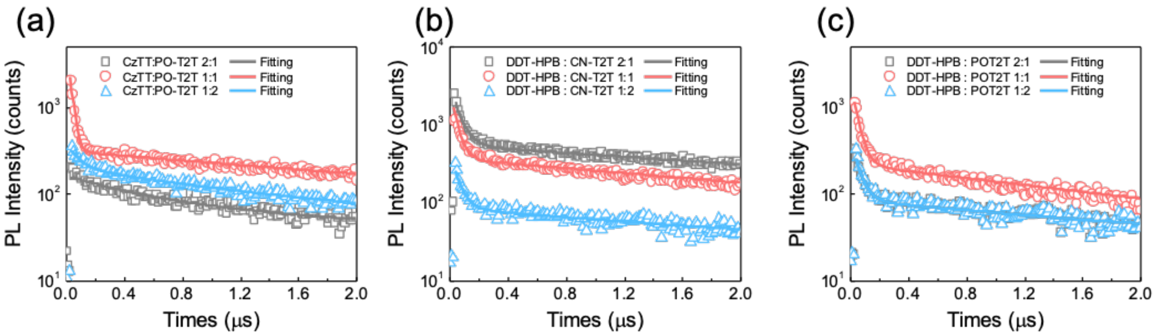


Figure S10 The TrPL of CzTT:PO-T2T, **DDT-HPB**:CN-T2T and **DDT-HPB**:PO-T2T blend films with different D:A ratio.

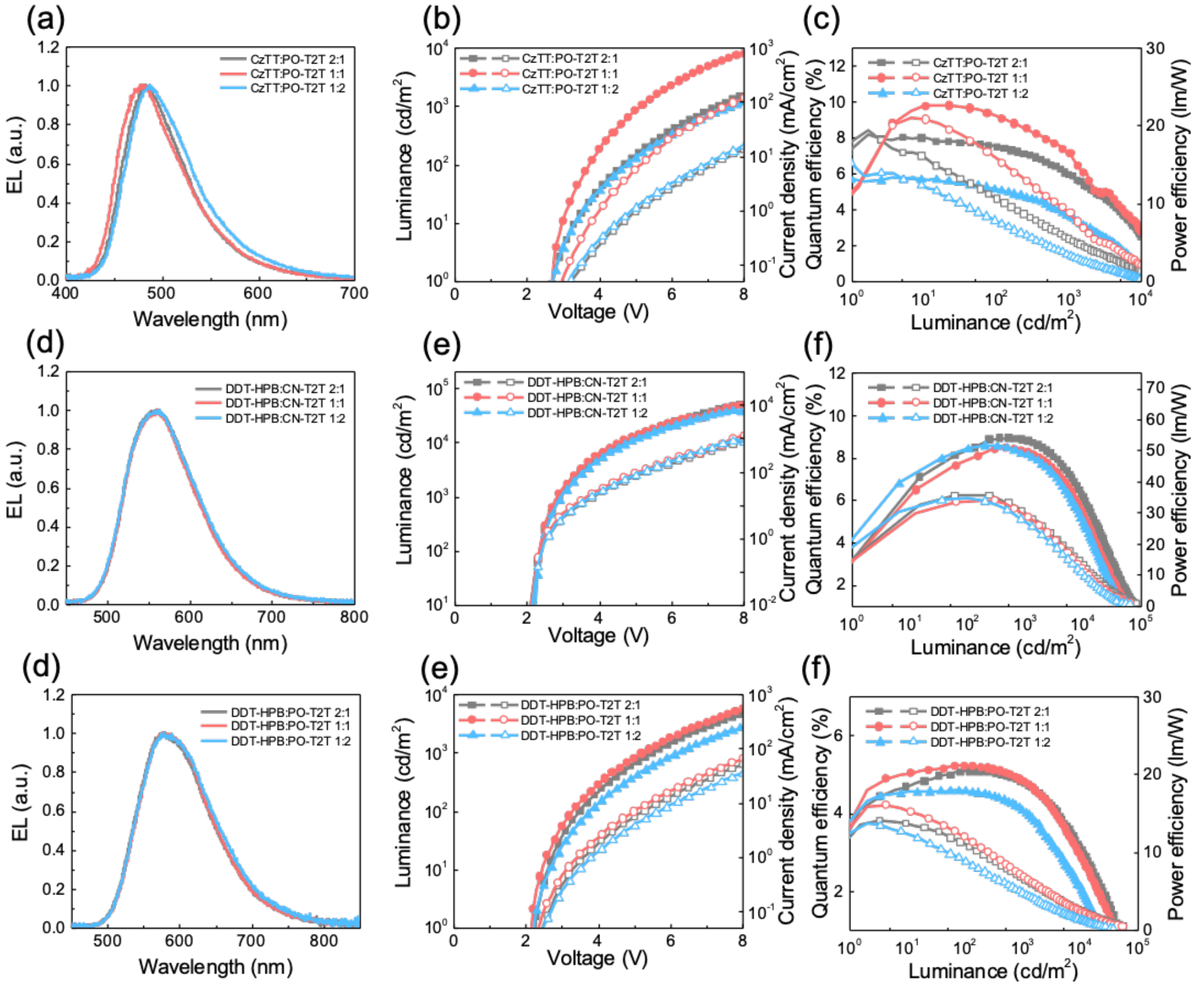


Figure S11 The different D:A ratio device characteristic of (a) – (c) **CzTT:**PO-T2T (d) – (f) **DDT-HPB**:CN-T2T (g) – (i) **DDT-HPB**:PO-T2T.

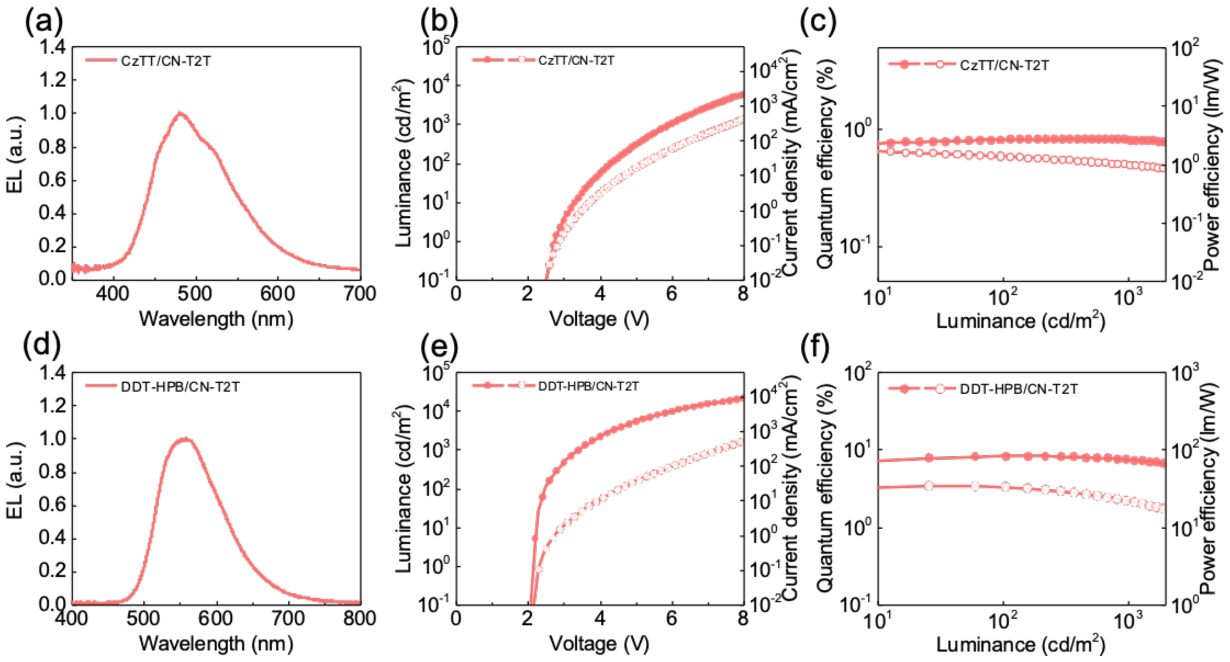


Figure S12 The characteristics of the bilayer CzTT/CN-T2T OLED and DDT-HPB/CN-T2T OLED devices

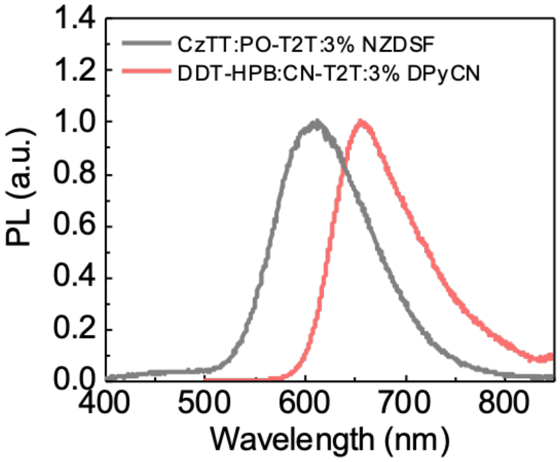


Figure S13 The PL of **CzTT**:PO-T2T:3% **NZDSF** (b) **DDT-HPB**:CN-T2T:3% DPyCN.

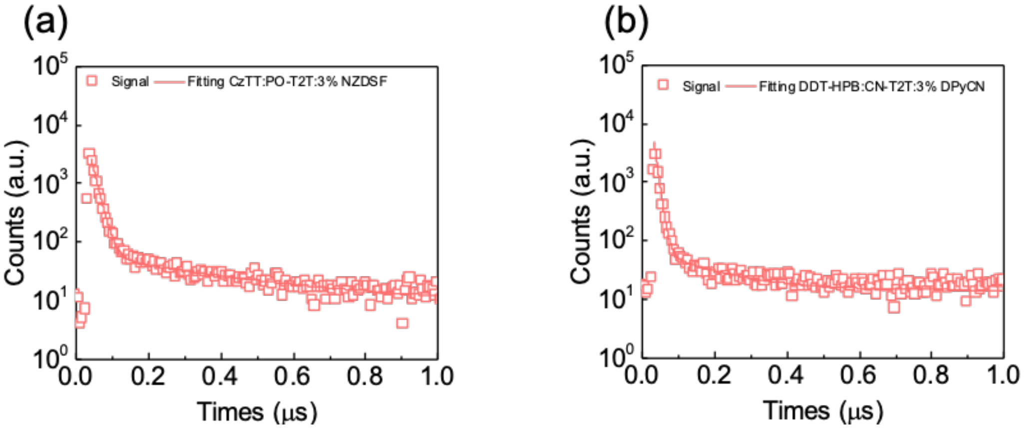


Figure S14 The TrPL of (a) **CzTT**:PO-T2T:3 wt.% **NZDSF** (b) **DDT-HPB**:CN-T2T:3 wt.% DPyCN.

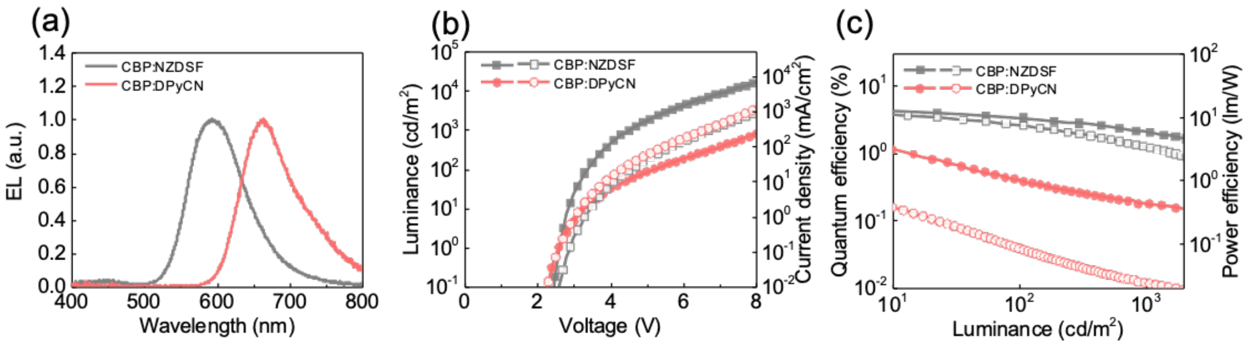


Figure S15 (a) EL spectra of the dopants **NZDSF** and DPyCN in CBP host. **(**b) J-V-L characteristics of the dopants **NZDSF** and DPyCN in CBP host. (c) EQE and PE of the dopants **NZDSF** and DPyCN **i**n CBP host as a function of luminance.

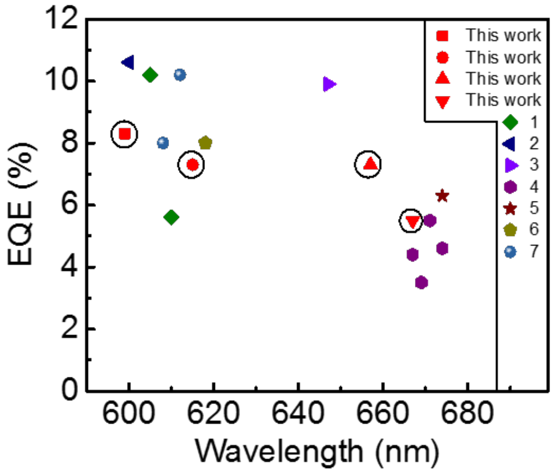


Figure S16 The EQE summary of orange-red OLEDs using fluorescent emitters doped in exciplex cohost system

Table S1 The PLQY summary of the blend films

Emitter	λ$_{max}$ (nm)	PLQY (%)
CzTT:CN-T2T 1:1	396	6
CzTT:PO-T2T 2:1	522	24
CzTT:PO-T2T 1:1	496	46
CzTT:PO-T2T 1:2	506	30
DDT-HPB:CN-T2T 2:1	553	37
DDT-HPB:CN-T2T 1:1	550	30
DDT-HPB:CN-T2T 1:2	545	33
DDT-HPB:PO-T2T 2:1	573	11
DDT-HPB:PO-T2T 1:1	570	15
DDT-HPB:PO-T2T 1:2	580	13
CzTT:PO-T2T:**NZDSF** 1:1:3%	610	68
DDT-HPB:CN-T2T:DPyCN 2:1 3%	656	36
CBP:3 wt % **NZDSF**	599	47
CBP:3 wt % DPyCN	666	52

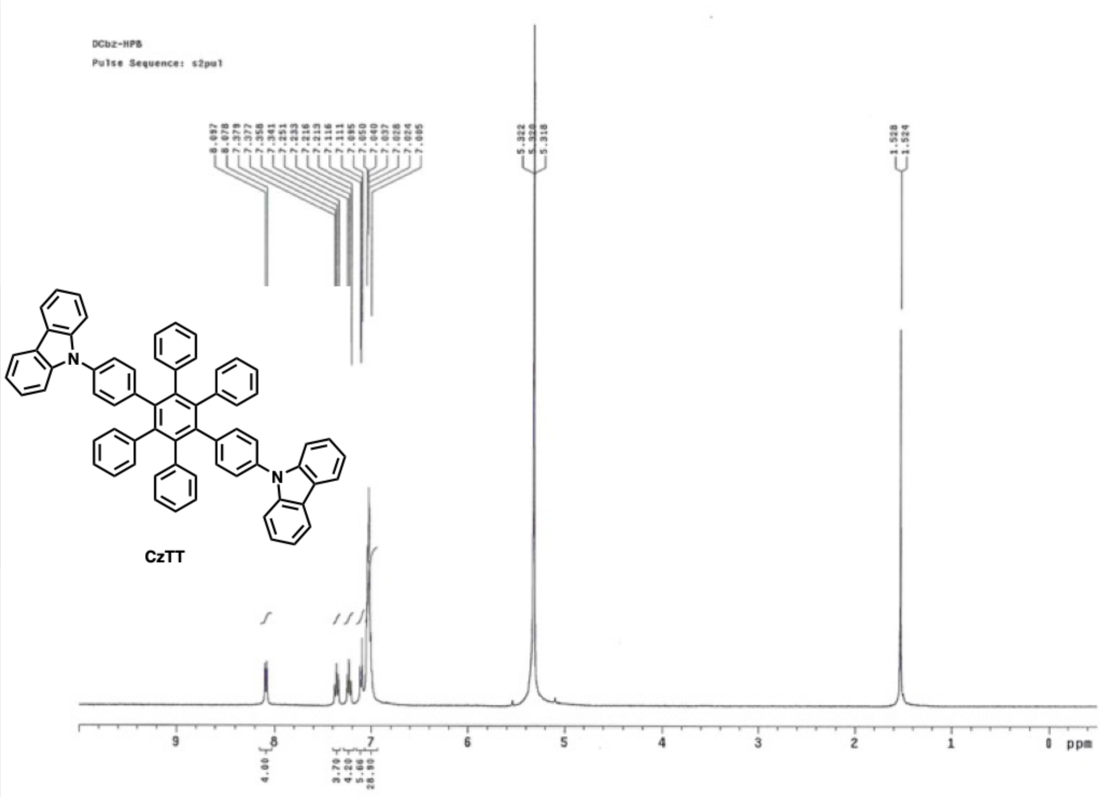
Table S2 The characteristics of devices using exciplex-based EML with different D:A ratios

Emitter	EL$_{max}$ (nm)	V$_{on}$^{a} (V)	EQE$_{max}$ (%)	CE$_{max}$ (cd A^{-1})	PE$_{max}$ (lm W$_{-1}$)	at 10^3 nits (%)	CIE$_{max}$ (x, y)
CzTT:PO-T2T 2:1	482	2.5	8.2	17.29	19.41	5.92	(0.18, 0.34)
CzTTPO-T2T 1:1	481	2.6	9.8	19.94	20.22	7.2	(0.18, 0.31)
CzTT:PO-T2T 1:2	487	2.5	5.8	13.15	13.78	3.61	(0.20, 0.38)
DDT-HPB:CN-T2T 2:1	560	2.1	8.9	28.42	34.36	8.8	(0.43, 0.54)
DDT-HPB:CN-T2T 1:1	560	2.1	8.5	27.07	32.73	8.3	(0.43, 0.54)
DDT-HPB:CN-T2T 1:2	560	2.1	8.6	26.86	33.77	8.2	(0.43, 0.54)
DDT-HPB:PO-T2T 2:1	580	2.2	5.1	12.28	10.15	4.8	(0.50,0.49)
DDT-HPB:PO-T2T 1:1	580	2.1	5.2	12.53	12.31	4.8	(0.51,0.48)
DDT-HPB:PO-T2T 1:2	580	2.1	4.6	10.65	9.56	4.1	(0.51,0.48)

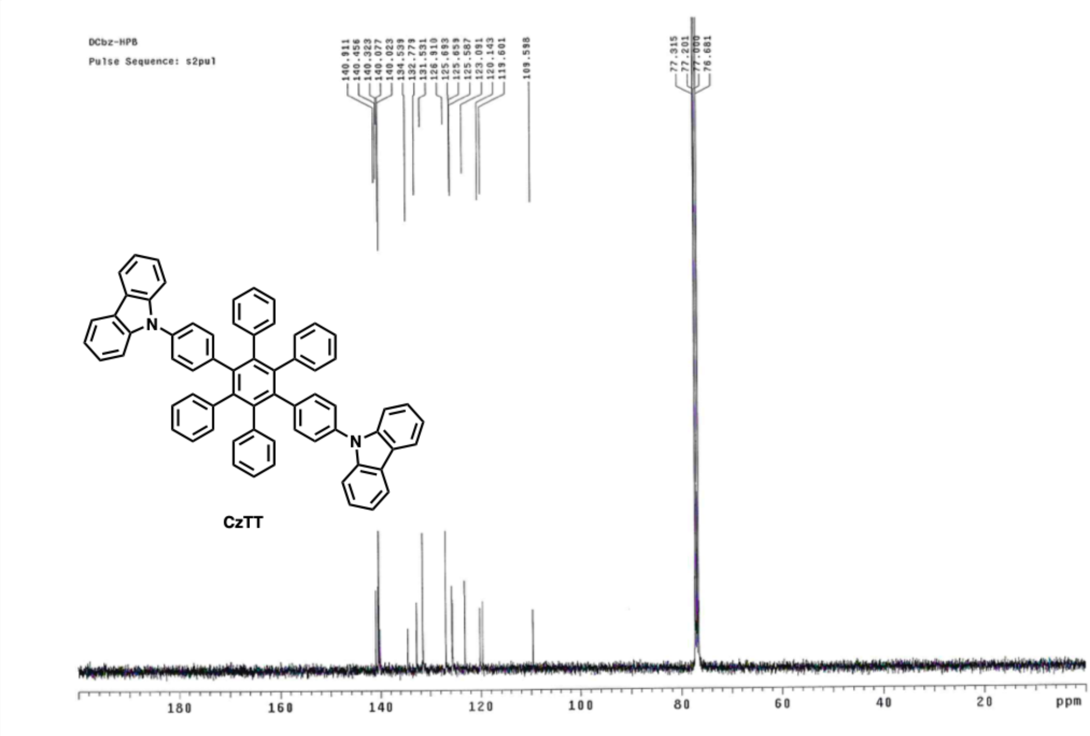
a. Recorded at 0.1 cd m^{-2}

Table S3 The summary of EL λ_{max} and EQE of reported organe and red OLEDs

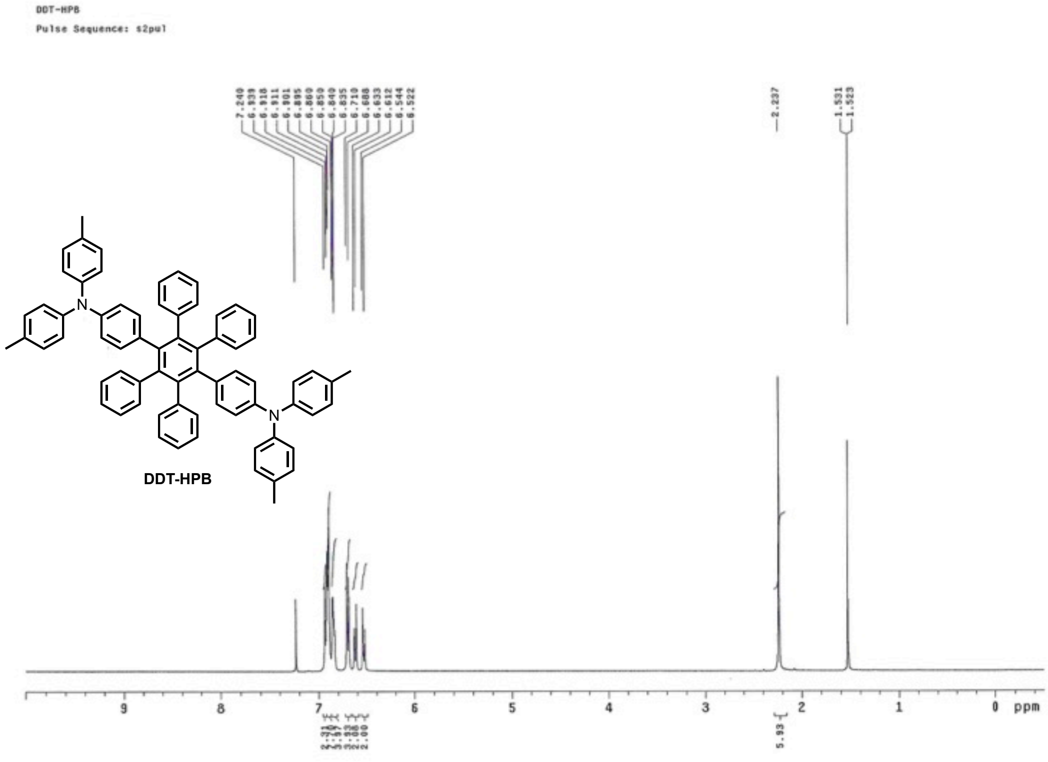
Legend	Doped Emitter	λ_{max} (nm)	EQE (%)	PLQY (%)	Reference
1	TCTA:3P-T2T:0.5 wt.% DCJTB	586	7.5	53	*Sci. Rep.* **2015**, *5*, 10967
1	TCTA:3P-T2T:1.0 wt.% DCJTB	605	10.2	69	*Sci. Rep.* **2015**, *5*, 10967
1	TCTA:3P-T2T:1.5 wt.% DCJTB	610	5.6	62	*Sci. Rep.* **2015**, *5*, 10967
2	TCTA:B4PYMPM:0.5% DCJTB	600	10.6	73	*Adv. Opt. Mater.* **2015**, *3*, 895–899
3	TCTA:3P-T2T 5 wt.% DTPNT	647	9.9	74	*ACS Appl. Mater. Interfaces.* **2019**, *11*, 23417–23427
4	Tr-Ph:3P-T2T:10 wt.% (DT)2BTh2CN	674	4.6	40	*Mater. Chem. Front.* **2020**, *4*, 2029–2039
4	Tr-Ph:3P-T2P:10 wt.% (DT)2BTh2CN	671	5.5	50	*Mater. Chem. Front.* **2020**, *4*, 2029–2039
4	Tr-Tol:3P-T2T:10 wt.% (DT)2BTh2CN	669	3.5	37	*Mater. Chem. Front.* **2020**, *4*, 2029–2039
4	Tr-Tol:3P-T2P:10 wt.% (DT)2BTh2CN	667	4.4	47	*Mater. Chem. Front.* **2020**, *4*, 2029–2039
5	Tr-iBu:PO-T2P:3 wt.% DPy2CN	674	6.3	44	*J. Chin. Chem. Soc.* **2022**, *1*, 1-10
6	PTCz-9’Cz:PO-T2T:10% iCzPNT	578	7.8	67	*Mater. Chem. Front.* **2021**, *5*, 5044–5054
6	PTCz-9’Cz:PO-T2T:10% iCzBTh2CN	618	8.0	64	*Mater. Chem. Front.* **2021**, *5*, 5044–5054
7	TCTA:3P-T2T 3 wt.% D-2-3	608	8.0	56	*J. Mater. Chem. C*, **2021**, *9*, 6834–6840
7	TCTA:3P-T2T 6 wt.% D-2-3	612	10.2	64	*J. Mater. Chem. C*, **2021**, *9*, 6834–6840



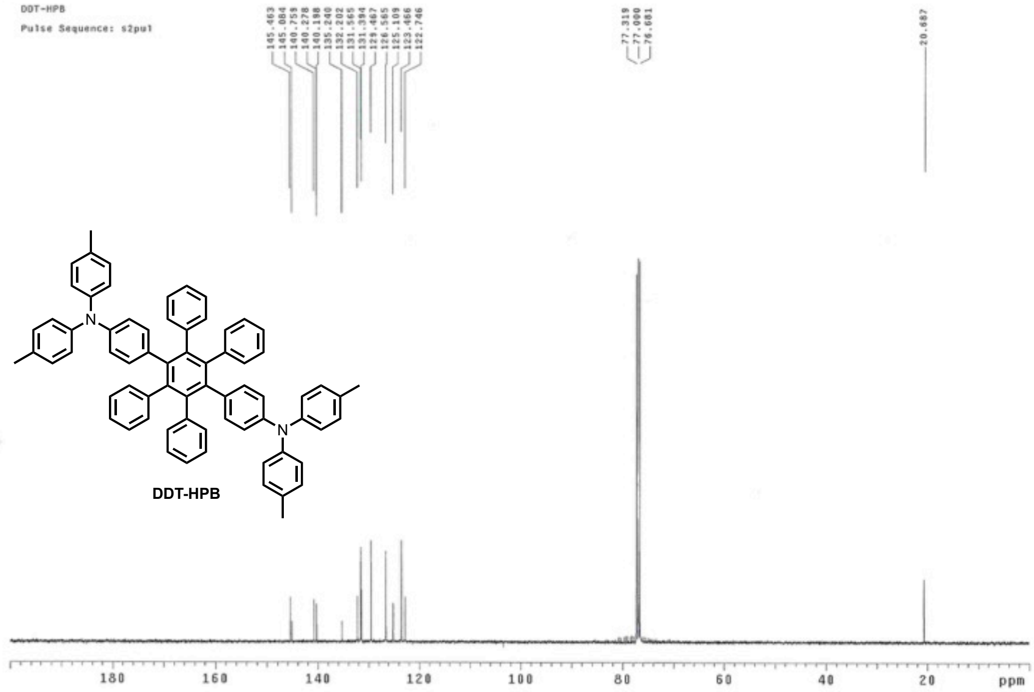
^{13}H-NMR spectra of **CzTT**



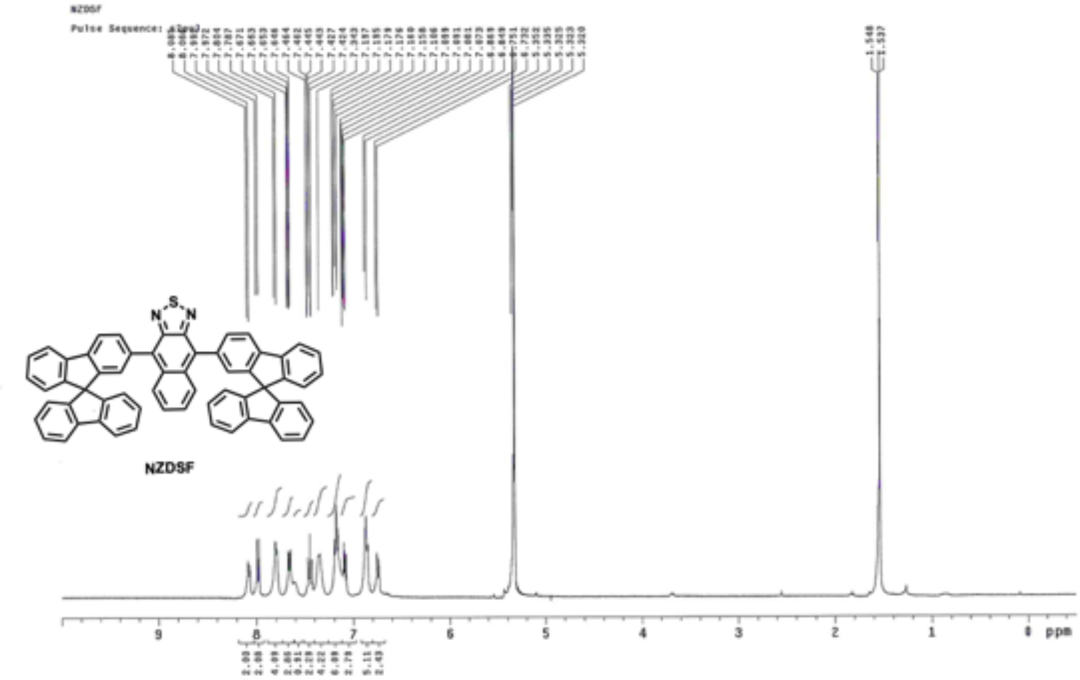
^{13}C-NMR spectra of **CzTT**



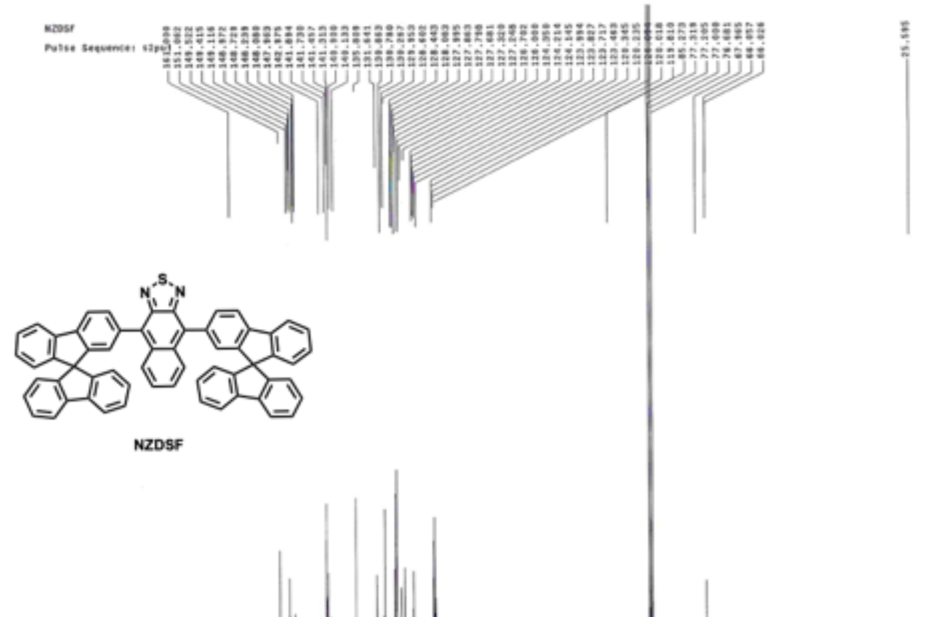
^{1}H-NMR spectrum of **DDT-HPB**



^{13}C-NMR spectrum of **DDT-HPB**



^{1}H-NMR spectrum of **NZDSF**



^{13}C-NMR spectrum of **NZDSF**