Electronic Supplementary Information

Exciplex-forming Co-host Systems Featuring Highly Twisted Bis-(*N*-carbazolyl)benzene-based Donors for High Efficiency Orange OLEDs

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Experimental section

General information

NMR spectra were recorded on a *Varian Mercury Plus-400* (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) using deuterium substituted solvent as an internal reference.

Thermogravimetric analysis (TGA) was conducted 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)

As for absorption measurement, the three organic compounds were dissolved in dry toluene (10^{-5} M), being measured with a UV-visible spectrometer (JASCO V-670 spectrophotometer). The photoluminescence (PL) spectrum was measured using a spectrofluorometer (FluoroMax-4, Horiba Jobin Yvon) with a Xenon arc lamp as the excitation light source. The excitation wavelength of PL measurement was set to 290 nm. The fluorescence spectrum of the sample was measured at room temperature, and the phosphorescence spectrum was measured at 77 K. For the phosphorescence spectrum, the tested sample was placed in a quartz tube and placed in a Dewar with liquid nitrogen. The transient photoluminescence (TrPL) was measured by monitoring the different target wavelengths using the time-correlated single-photon counting (TCSPC) technique with a nanosecond pulsed light-emitting diode (320 nm).

The electrochemical properties of three molecules were investigated by cyclic voltammetry (CV). The oxidation potentials were carried out in anhydrous dichloromethane (DCM) solution (1.0 mM) containing 0.1 M tetrabutylammonium hexafluorophosphate ($^{n}\mathrm{Bu}_4\mathrm{NPF}_6$) as a supporting electrolyte with argon before conducting the experiments. A glassy carbon electrode and a platinum wire were used as the working and counter electrodes, respectively. All potentials were recorded versus Ag/AgCl as a reference electrode and calibrated with the ferrocene/ferrocenium redox couple.

Theoretical calculations with density functional theory (DFT) were performed in the gaseous state respectively at B3LYP/6-31G(d) level through Taiwania 1, built by the National Applied Research Laboratories, Taiwan.

OLEDs device fabrication and characterization

For OLED fabrication, all the materials including 1,1-Bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), 4,4′-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine] (TAPC), 3′,3′′′,3′′′′′-(1,3,5-triazine-2,4,6-triyl)tris(([1,1′-biphenyl]-3-carbonitrile)) (CN-T2T), lithium fluoride (LiF), and aluminum (Al) were purchased from Shine Material Technology Co., Ltd. Before device fabrication, all the organic materials were sublimated with a homemade vacuum purification system under high vacuum conditions (*ca.* 2×10^{-6} torr). The Indium tin oxide (ITO) was prepared with a thickness of 70 nm on the glass substrate through the reported DC sputtering process. The glass and glass/ITO substrates follow a series of continuously cleaning processes such as using deionized (DI) water, acetone, and isopropyl alcohol in an ultrasonic bath for 10 minutes for each solution and dried with a nitrogen (N_2) blower. The organic and metal layers were deposited by vacuum evaporation under high vacuum condition (*ca.* 2×10^{-6} torr). The surface profiler (Dektak XT, Bruker) and ellipsometer (SE-950, Radiation Technology Co., LTD.) utilized to ensure each material's precise thickness and refractive index before starting the device fabrication process. All the organic materials were deposited under a stable deposition rate (0.5 Å s^{-1}), where the metal cathode (Al) deposition rate around 5 Å s^{-1}. The active area of the device was set to 4 mm^2, which defined by the overlapping area of the patterned ITO anode and cathode shadow mask. After the deposition process, the device was encapsulated using encapsulation glass inside the glovebox under with oxygen and moisture concentration below 0.1 ppm. For OLED device characterization, all the electroluminescence characteristics were measured by integrated spectrometer system (LQ-100R, Enlitech) with source meter (B2901A, Keysight). The lifetime of OLED devices was measured by the multi-channel testing system (Model-58131, Chroma) under constant current mode. The capacitance-voltage (C-V) measurement were operated under 1000 Hz with electrochemical impedance spectroscopy (EIS) system (Material Lab XM series, Solartron Analytical).

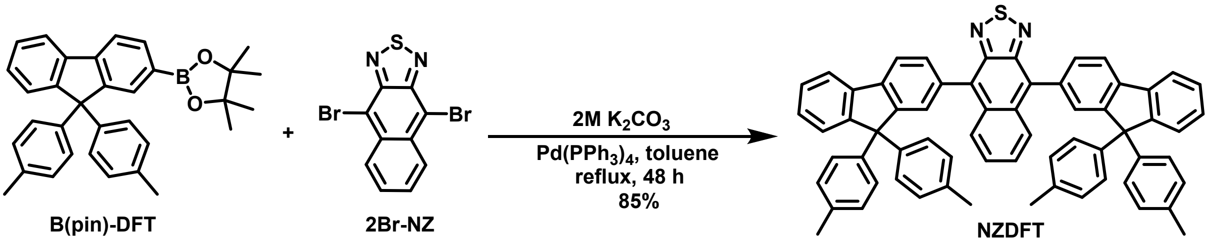
Synthesis and characterization

Synthesis of 9-(3-(9*H*-carbazol-9-yl)phenyl)-1-phenyl-9*H*-carbazole (Ph2Cz)

To a two-neck round-bottom flask was added a mixture of 1-phenyl-9*H*-carbazole (**PhCz**) (1.0 g, 4.1 mmol), 9-(3-bromophenyl)carbazole (1.6 g, 5.0 mmol), cesium carbonate (Cs_2CO_3) (4.0 g, 12 mmol), 18-crown-6 ether (0.44 g, 1.7 mmol), copper(I) iodide (CuI) (2.4 g, 12.3 mmol) and 40 mL of dry o-dichlorobenzene. The system was stirred at 180 °C under argon for 36 h. After cooling to room temperature, the mixture was pass through celite and washed with DCM and then purified by column chromatography with the eluent of 1/10 = DCM/*n*-hexane to obtain the white solid **Ph2Cz** (1.3 g, 2.6 mmol, 63%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ= 8.25 – 8.15 (m, 3H), 7.51 – 7.27 (m, 15H), 7.16 (m, 3H), 7.09 (m, 3H). HRMS (m/z, MALDI$^+$) Calcd for $C_{36}H_{24}N_2^+$: 484.1939, found: 484.1951; ^{13}C NMR (100 MHz, CD_2Cl_2) δ= 142.8, 140.9, 140.6, 139.5, 138.4, 138.2, 130.4, 123.0, 129.4, 128.0, 127.4, 127.1, 127.0, 126.7, 126.3, 126.2, 125.6, 125.4, 123.8, 120.9, 120.62, 120.59, 120.52, 120.50, 119.7, 110.5, 110.3.

Synthesis of 1,3-bis(1-phenyl-9*H*-carbazol-9-yl)benzene (2Ph2Cz)

To a two-neck round-bottom flask was added a mixture of **PhCz** (1.0 g, 4.1 mmol), 1,3-diiodobenzene (0.81 g, 2.5 mmol), Cs_2CO_3 (2.2 g, 6.2 mmol), 18-crown-6 ether (0.22 g, 0.82 mmol), CuI (1.2 g, 6.2 mmol) and 10 mL of dry *o*-dichlorobenzene. The system was stirred at 180 °C under argon for 19 h. After cooling to room temperature, the mixture was pass through celite and washed with DCM and then purified by column chromatography with the eluent of 1/10 = DCM/*n*-hexane to obtain the white solid **2Ph2Cz** (1.0 g, 1.8 mmol, 87%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ= 8.16 (t, J = 7.4 Hz, 4H), 7.48 (t, J = 7.7 Hz, 2H), 7.37 – 7.27 (m, 7H), 7.14 – 7.08 (m, 4H), 7.01 – 6.89 (m, 8H), 6.78 (s, 3H). HRMS (m/z, MALDI^{+}) Calcd for $C_{42}H_{28}N_2^{+}$: 560.2252, found: 520.2268; ^{13}C NMR (100 MHz, CD_2Cl_2) δ= 142.5, 139.4, 138.0, 129.5, 129.3, 128.9, 128.0, 127.0, 126.9, 126.5, 126.4, 125.8, 125.6, 123.7, 120.9, 120.6, 120.2, 119.6, 111.3.



Scheme S1. Synthesis route of NZDFT

Synthesis of 4,9-bis(9,9-di-p-tolyl-9*H*-fluoren-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (NZDFT)

The **B(pin)-DFT** and **2Br-NZ** compound were prepared based on our previous work.[1,2] To a two-neck round-bottom flask was added a mixture of **B(pin)-DFT** (1.2 g, 2.5 mmol), **2Br-NZ** (0.34 g, 1.0 mmol), 2.0 M potassium carbonate (K_2CO_3) (0.83 g, 6.0 mmol), palladium(0)tetrakis(triphenylphosphine) ($Pd(PPh_3)_4$) (0.25 g, 0.2 mmol) and 20 mL of toluene. The system was refluxed under argon for 48 h. After cooling to room temperature, the mixture was extracted with DCM and water. Purified by column chromatography with the eluent of 1/10 = DCM/*n*-hexane to obtain the deep-red solid **NZDFT** (0.74 g, 0.85 mmol, 85%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ= 8.01 – 7.95 (m, 4H), 7.88 (d, J = 7.4 Hz, 2H), 7.65 (m, 4H), 7.44 – 7.40 (m, 4H), 7.36 – 7.24 (m, 4H), 7.14 (d, J = 7.9 Hz, 8H), 7.03 (m, 8H), 2.24 (s, 12H). HRMS (m/z, MALDI^{+}) Calcd for $C_{64}H_{46}N_2S^{+}$: 874.3376, found: 874.330; ^{13}C NMR (100 MHz, CD_2Cl_2) δ= 152.2, 151.9, 151.8, 143.0, 142.9, 140.4, 140.2, 136.9, 136.2, 132.2, 131.4, 130.6, 129.9, 129.3, 128.4, 128.3, 128.0, 127.4, 126.6, 126.6, 120.9, 120.4, 65.4, 21.0.

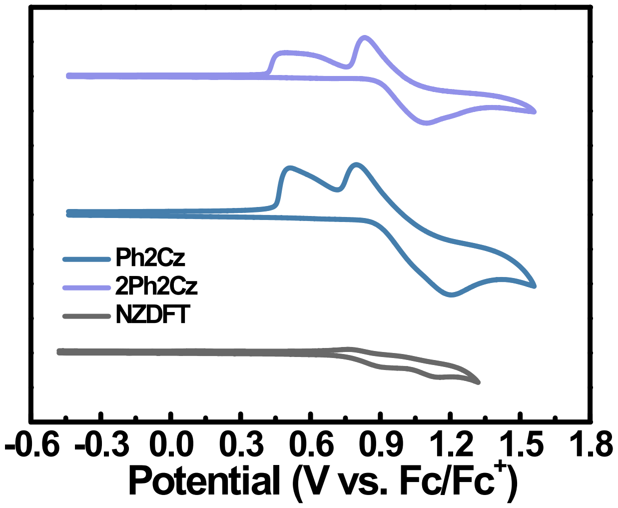


Figure S1. Cyclic voltammogram of **Ph2Cz**, **2Ph2Cz** and **NZDFT** in DCM containing 0.1 M TBAPF$_6$ as electrolyte.

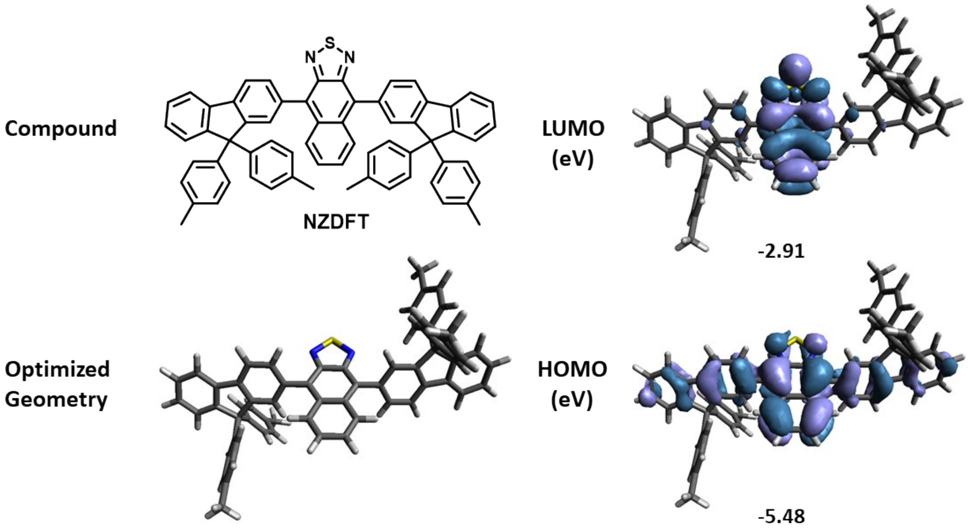


Figure S2. Chemical and optimized ground state structures with corresponding HOMO and LUMO orbitals of **NZDFT**.

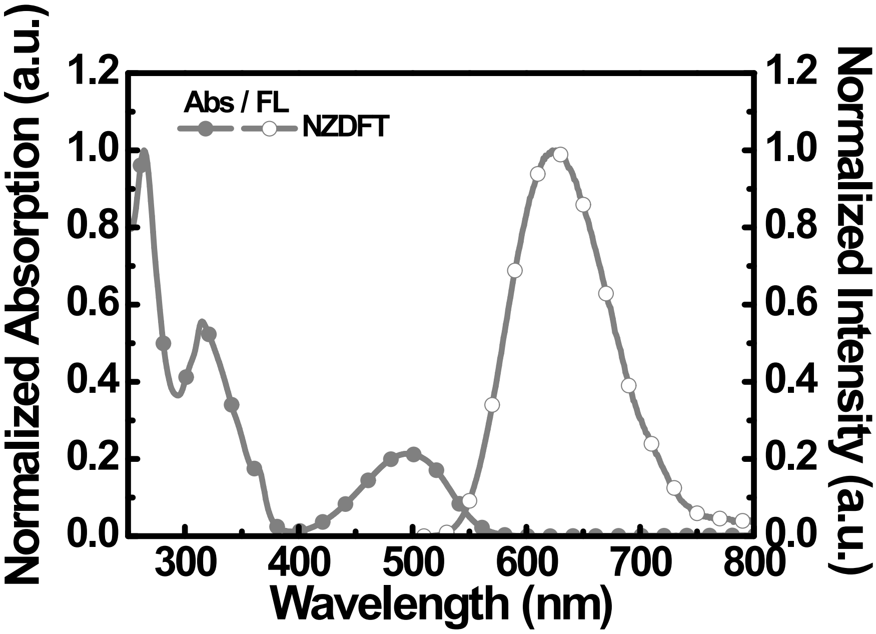


Figure S3. Room temperature UV-Vis absorption (Abs) and fluorescence (FL) spectra of **NZDFT** in toluene solution.

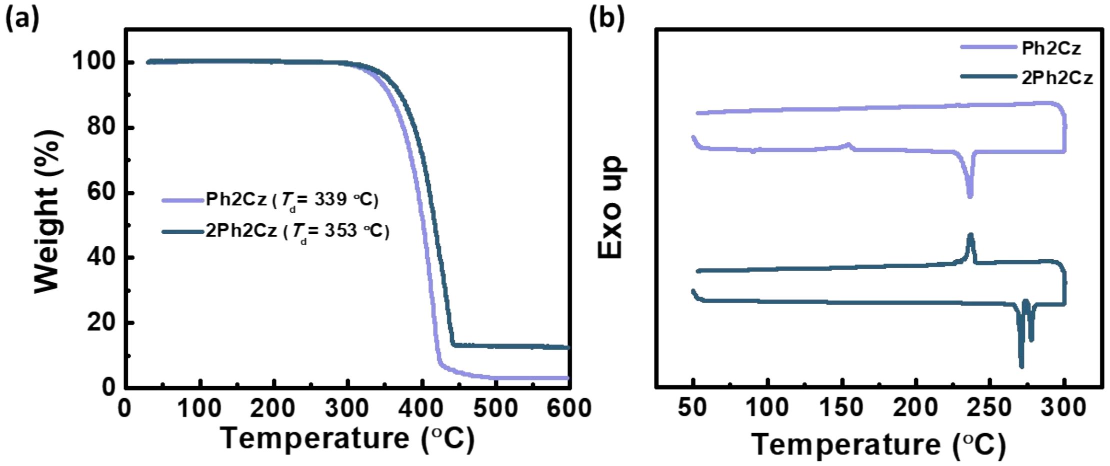


Figure S4. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) graphs of **Ph2Cz** and **2Ph2Cz**.

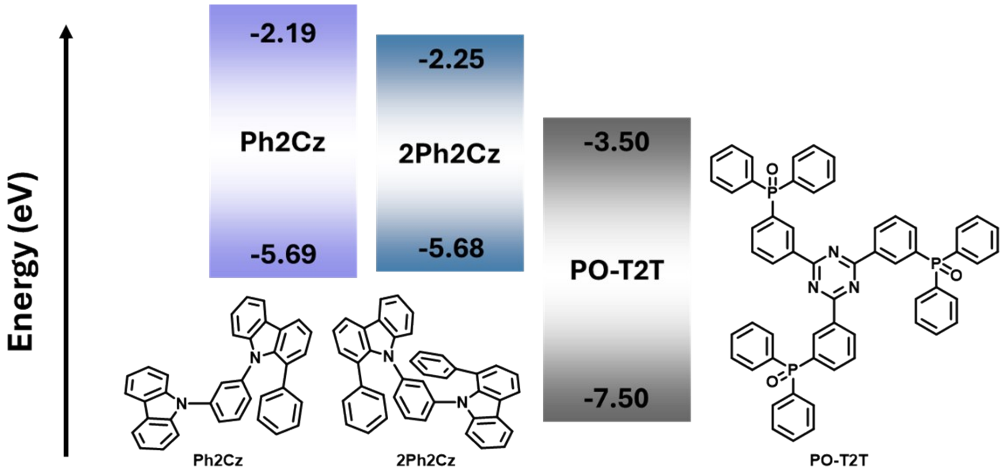


Figure S5. The structure and energy alignment of the donors (**Ph2Cz**, **2Ph2Cz**) and acceptor (PO-T2T).

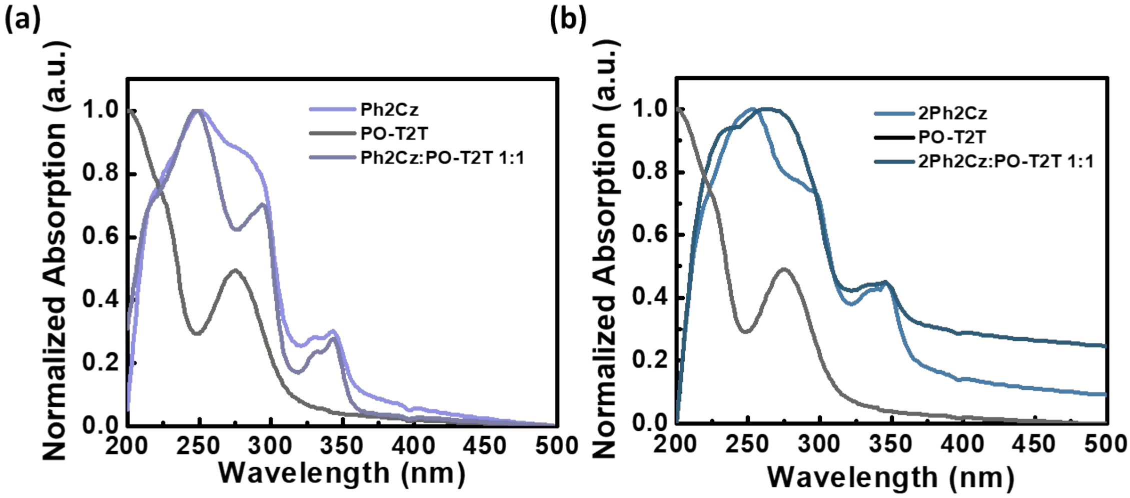


Figure S6. (a) Abs of **Ph2Cz**, PO-T2T and **Ph2Cz**:PO-T2T (1:1); (b) Abs of **2Ph2Cz**, PO-T2T and **2Ph2Cz**:PO-T2T (1:1).

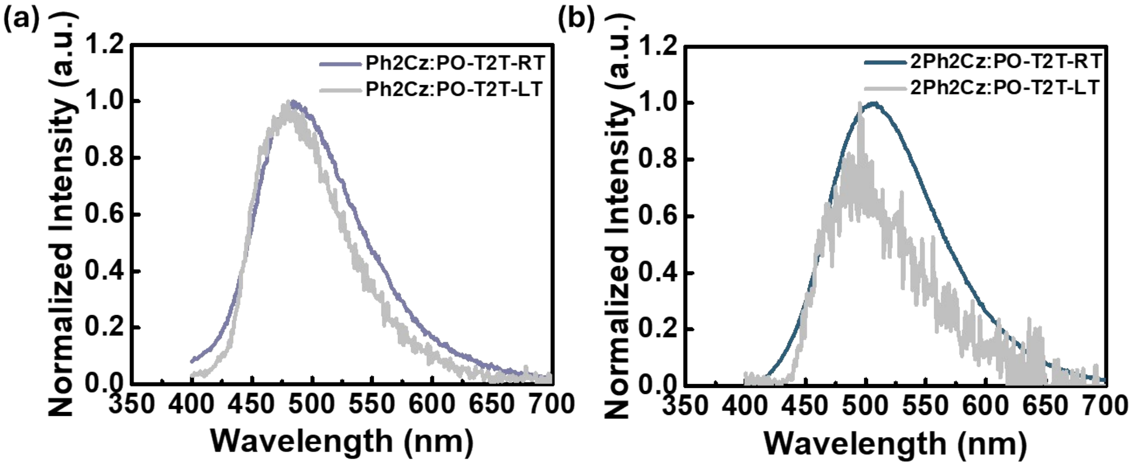


Figure S7. The PL spectra of (a) **Ph2Cz**:PO-T2T (1:1) (b) **2Ph2Cz**:PO-T2T (1:1) show the prompt fluorescence (delay = 0) at room temperature and delay fluorescence (delay 1 ms) at 77 K.

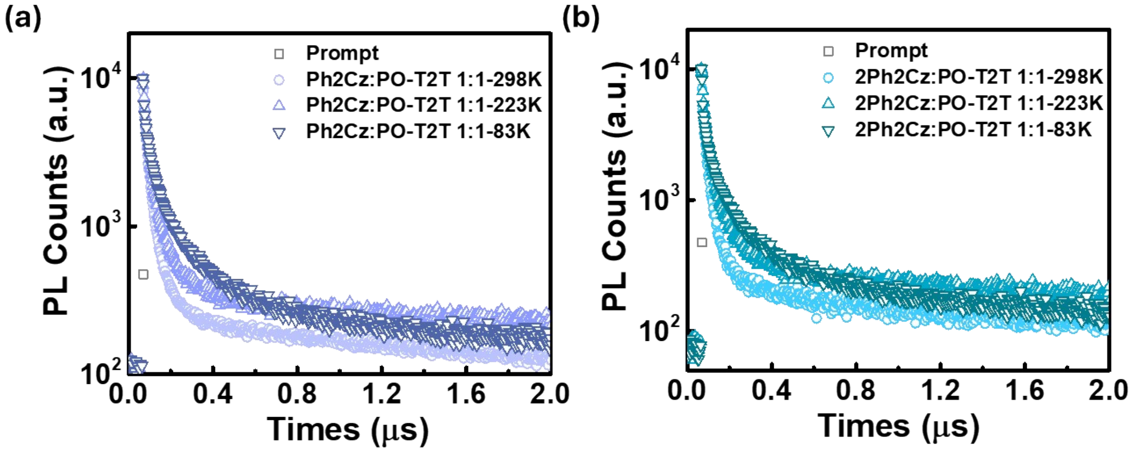


Figure S8. The temperature-dependent TrPL of (a)**Ph2Cz**:PO-T2T (1:1) (b) **2Ph2Cz**:PO-T2T (1:1).

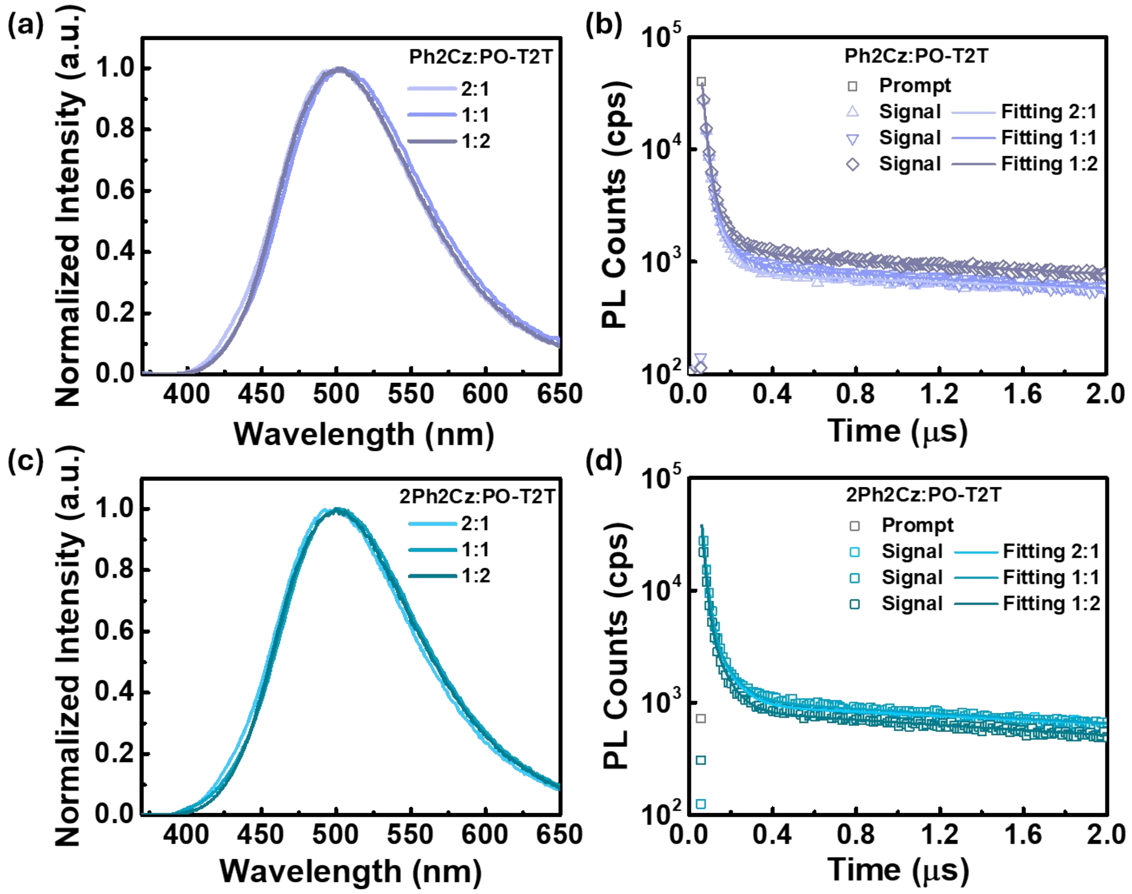


Figure S9. The PL spectra of (a) **Ph2Cz**:PO-T2T (2:1/1:1/1:2) and (c) **2Ph2Cz**:PO-T2T (2:1/1:1/1:2); The TrPL spectra of (b) **Ph2Cz**:PO-T2T (2:1/1:1/1:2) and (d) **2Ph2Cz**:PO-T2T (2:1/1:1/1:2).

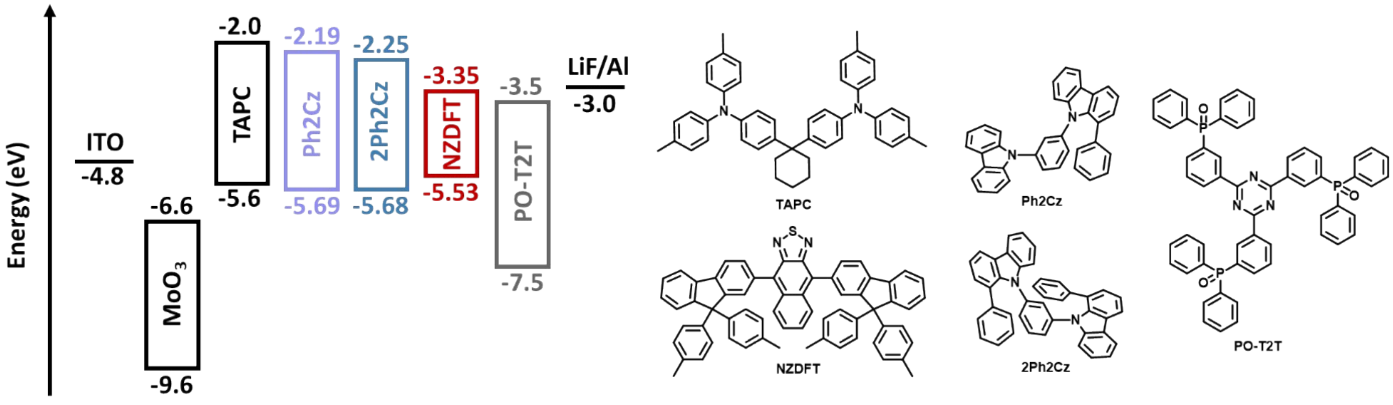


Figure S10. Energy level diagram of OLED device with exciplex-based EML structure and the molecular structures of the organic materials used in the device.

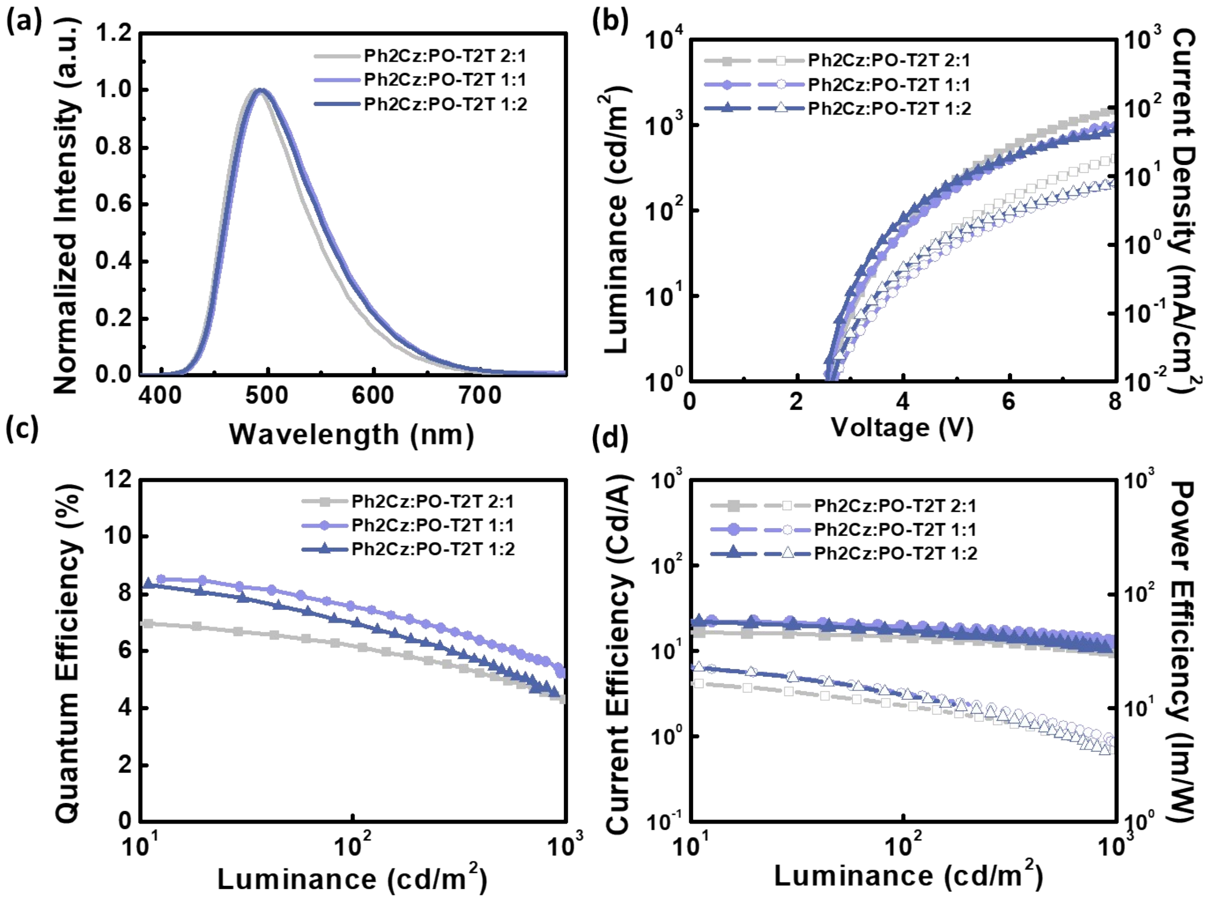


Figure S11. EL characteristic of different ratio for **Ph2Cz**:PO-T2T exciplex-OLED device.

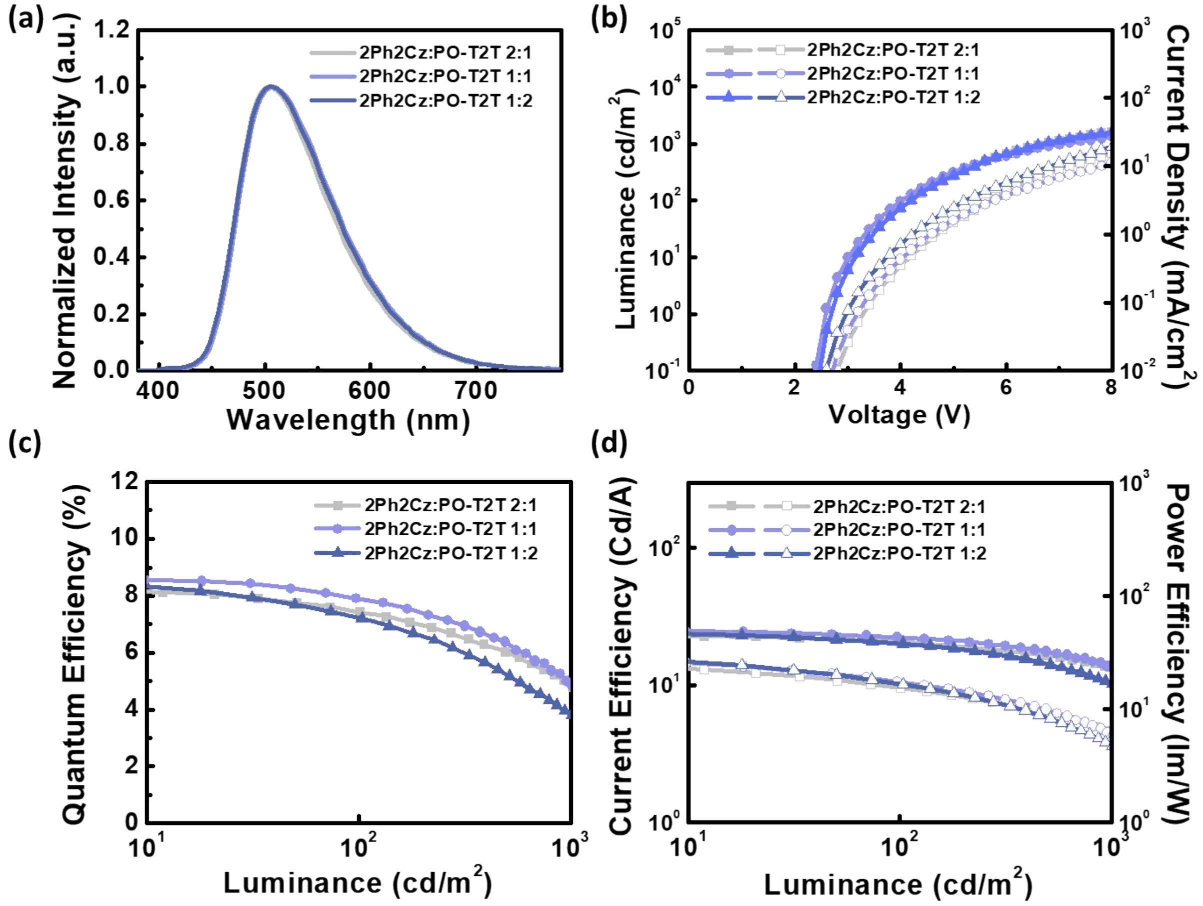


Figure S12. EL characteristic of different ratio for **2Ph2Cz**:PO-T2T exciplex-OLED device.

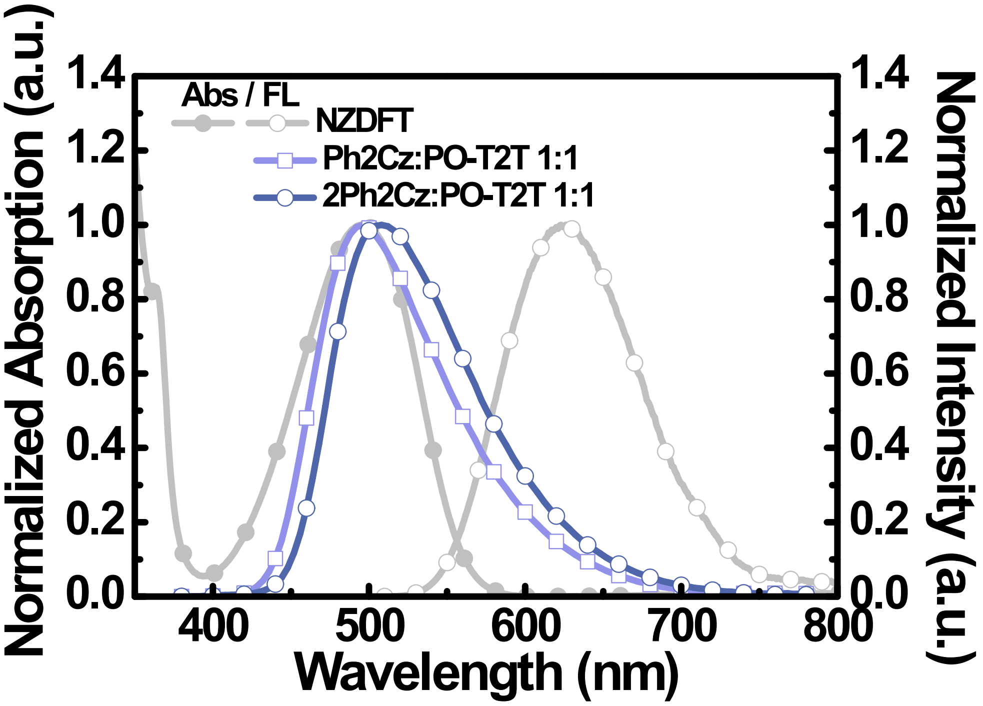


Figure S13. The overlap of UV-Vis absorption and electroluminescence spectra of **NZDFT**, **Ph2Cz**:PO-T2T (1:1) and **2Ph2Cz**:PO-T2T (1:1).

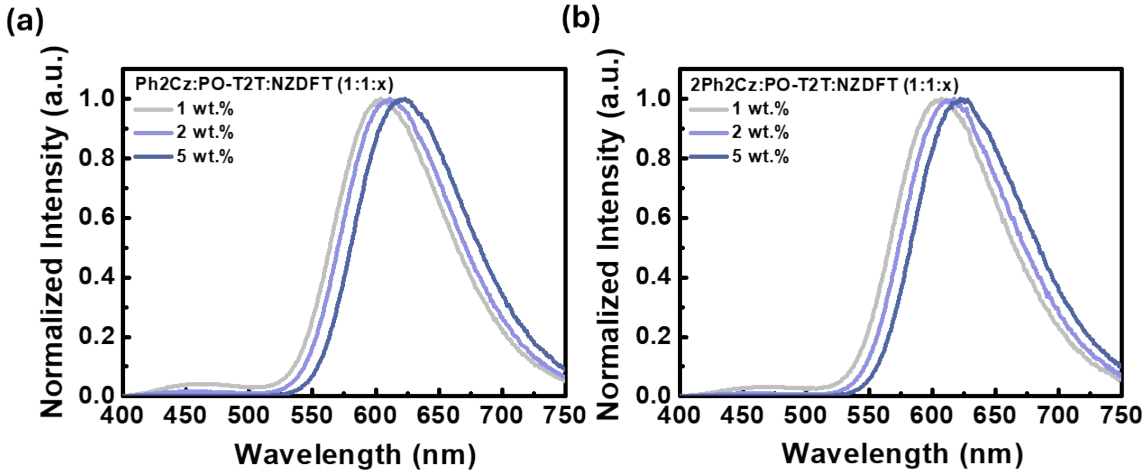


Figure S14. The EL spectra of 1, 2, 5 wt.% **NZDFT** doped in (a) **Ph2Cz**:PO-T2T (1:1) and (b) **2Ph2Cz**:PO-T2T (1:1).

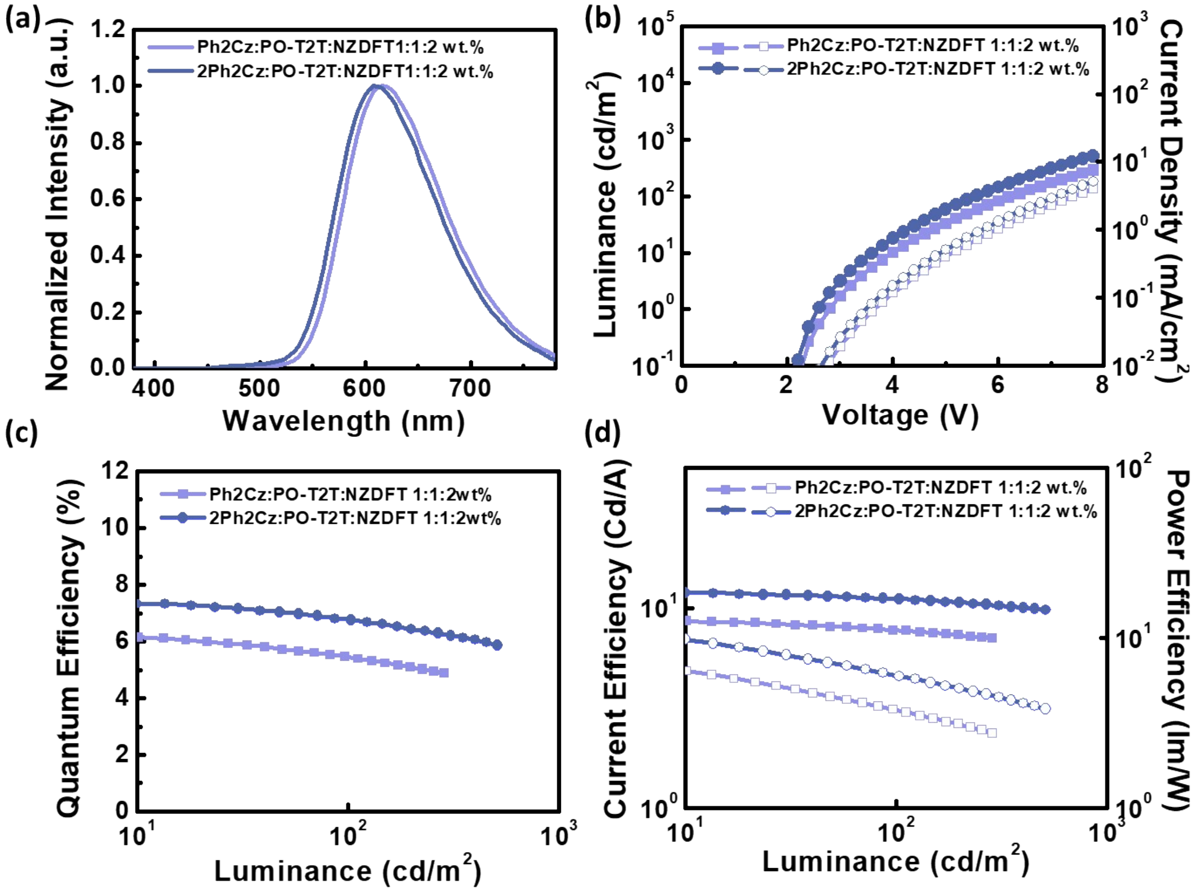


Figure S15. EL characteristic of 2 wt.% **NZDFT** doped into **Ph2Cz**:PO-T2T 1:1 and **2Ph2Cz**:PO-T2T 1:1 exciplex-OLED device.

Table S1. X-ray data and structure refinement parameters for **Ph2Cz** and **2Ph2Cz**.

Crystal data	**Ph2Cz** (CCDC 2347701)	**2Ph2Cz** (CCDC 2347702)
Empirical formula	$C_{36}H_{24}N_2$	$C_{42}H_{28}N_2$
Formula weight	484.57	560.66
Crystal system	Orthorhombic	Triclinic
Space group	Fdd2	P-1
Unit cell dimensions	a = 137.779(2) Å a= 90°	a = 11.8500(4)Å a= 101.0450(12)°
	b = 150.791(3) Å b= 90°	b = 14.5179(4) Å b= 97.0994(12)°
	c = 10.4737(8) Å g = 90°	c = 18.7751(6) Å g = 110.3670(11)°
Volume	20097(2) Å^3	2907.75(16) Å^3
Z	32	4
F(000)	8128	1176
Density (calculated)	1.281 Mg/m^3	1.281 Mg/m^3
Wavelength	0.71073 Å	1.54178 Å
Cell parameters reflections used	2693	9964
Theta range for Cell parameters	3.2210 to 22.6270°	3.36 to 78.06°
Absorption coefficient	0.075 mm^{-1}	0.570 mm^{-1}
Temperature	100(2) K	100(2) K
Crystal size	0.20 x 0.15 x 0.10 mm^3	0.20 x 0.15 x 0.10 mm^3
No. of measured reflections	32272	58062
No. of independent reflections	11527 [R(int) = 0.1123]	11848 [R(int) = 0.0406]
Final R indices [I>2sigma(I)]	R1 = 0.0877, wR2 = 0.1847	R1 = 0.0487, wR2 = 0.1273
R indices (all data)	R1 = 0.2400, wR2 = 0.2892	R1 = 0.0525, wR2 = 0.1312

Table S2. Summary of photophysical properties of exciplex films.

EML	ratio	λ_{PL} (nm)	PLQY (%)	Lifetime			
				A_1	t_1 (ns)	A_2	t_2 (μs)
Ph2Cz:PO-T2T	2:1	500	26	0.89	60.3	0.11	4.96
	1:1	503	32	0.85	65.8	0.15	3.58
	1:2	504	34	0.77	85.4	0.23	3.92
2Ph2Cz:PO-T2T	2:1	502	29	0.86	77.5	0.14	4.02
	1:1	502	35	0.83	81.1	0.17	3.38
	1:2	500	32	0.88	66.9	0.12	3.13

Table S3. EL characteristic of different ratio for exciplex-OLED device.

EML	EL_{max} (nm)	V_{on} [a] (V)	EQE_{max} (%)	CE_{max} (cd/A)	PE_{max} (lm/W)	at 10^2 nits (%)	Luminance at 8V (cd/m^2)
Ph2Cz:PO-T2T 2:1	484	3.2	6.95	16.63	16.32	6.17	1500
Ph2Cz:PO-T2T 1:1	492	3.2	8.51	22.27	19.15	7.56	988
Ph2Cz:PO-T2T 1:2	488	3.0	8.34	21.75	22.78	6.98	886
2Ph2Cz:PO-T2T 2:1	500	3.2	8.11	22.84	22.42	7.42	1595
2Ph2Cz:PO-T2T 1:1	504	3.2	8.51	24.43	23.98	7.89	1311
2Ph2Cz:PO-T2T 1:2	500	3.0	8.16	23.23	24.33	7.21	1503

a. Recorded at 10 cd/A.

Table S4. Summary of photophysical properties of fluorescent emitter with exciplex films.

EML	λ_{PL} (nm)	PLQY (%)	Lifetime			
			A_1	t_1 (ns)	A_2	t_2 (ns)
Ph2Cz:PO-T2T:**NZDFT** (1:1:2 wt.%)	610	76	99.6	12.9	0.4	370.4
2Ph2Cz:PO-T2T:**NZDFT** (1:1:2 wt.%)	610	65	99.7	12.7	0.3	347.6

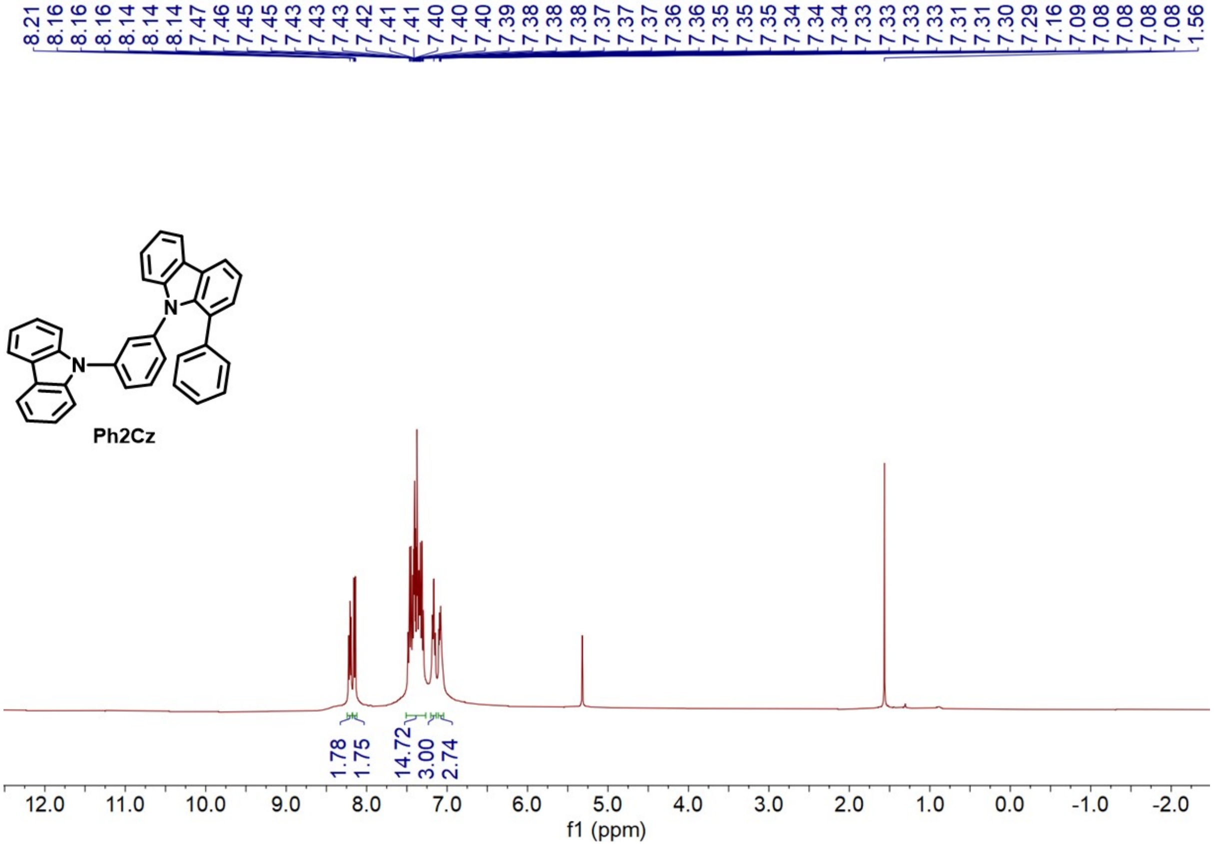


Figure S16. ^{1}H NMR (400 MHz, CD_2Cl_2) of **Ph2Cz**.

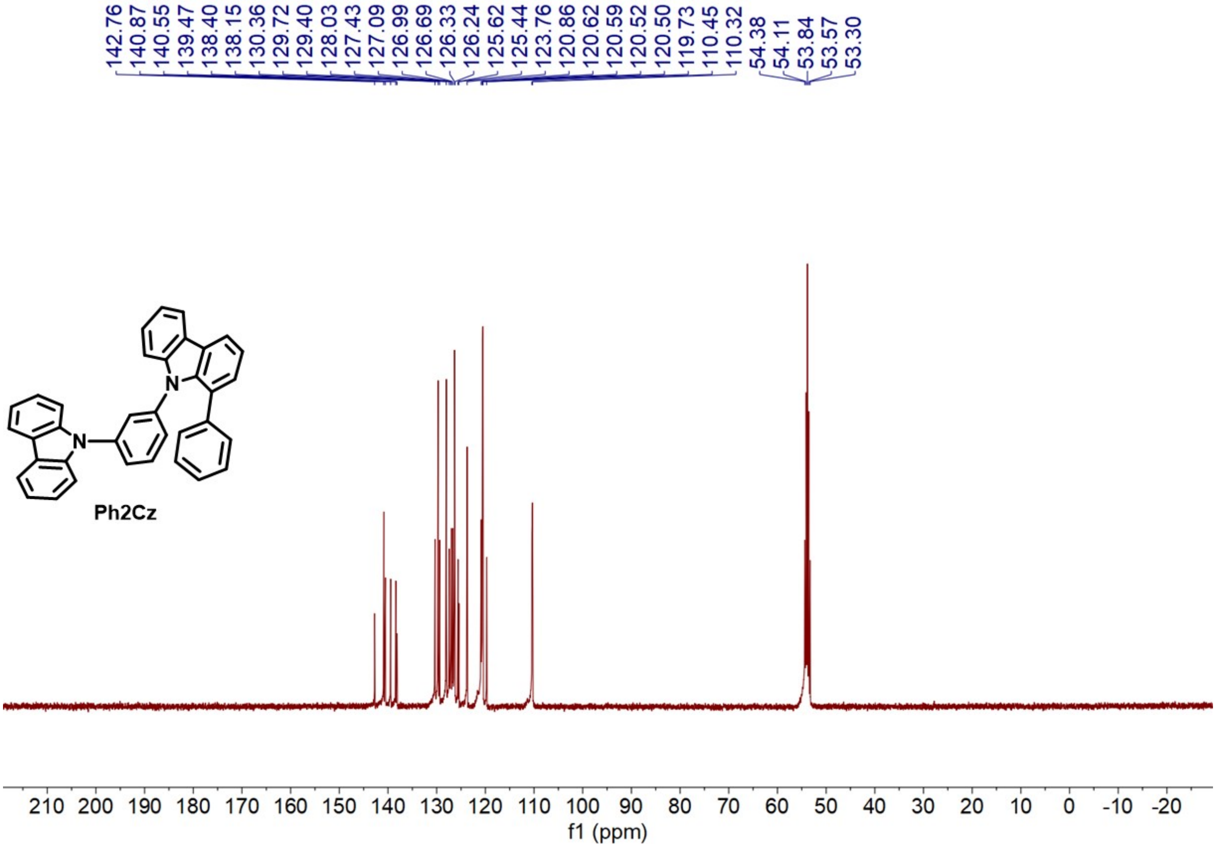


Figure S17. ^{13}C NMR (100 MHz, CD_2Cl_2) of **Ph2Cz**.

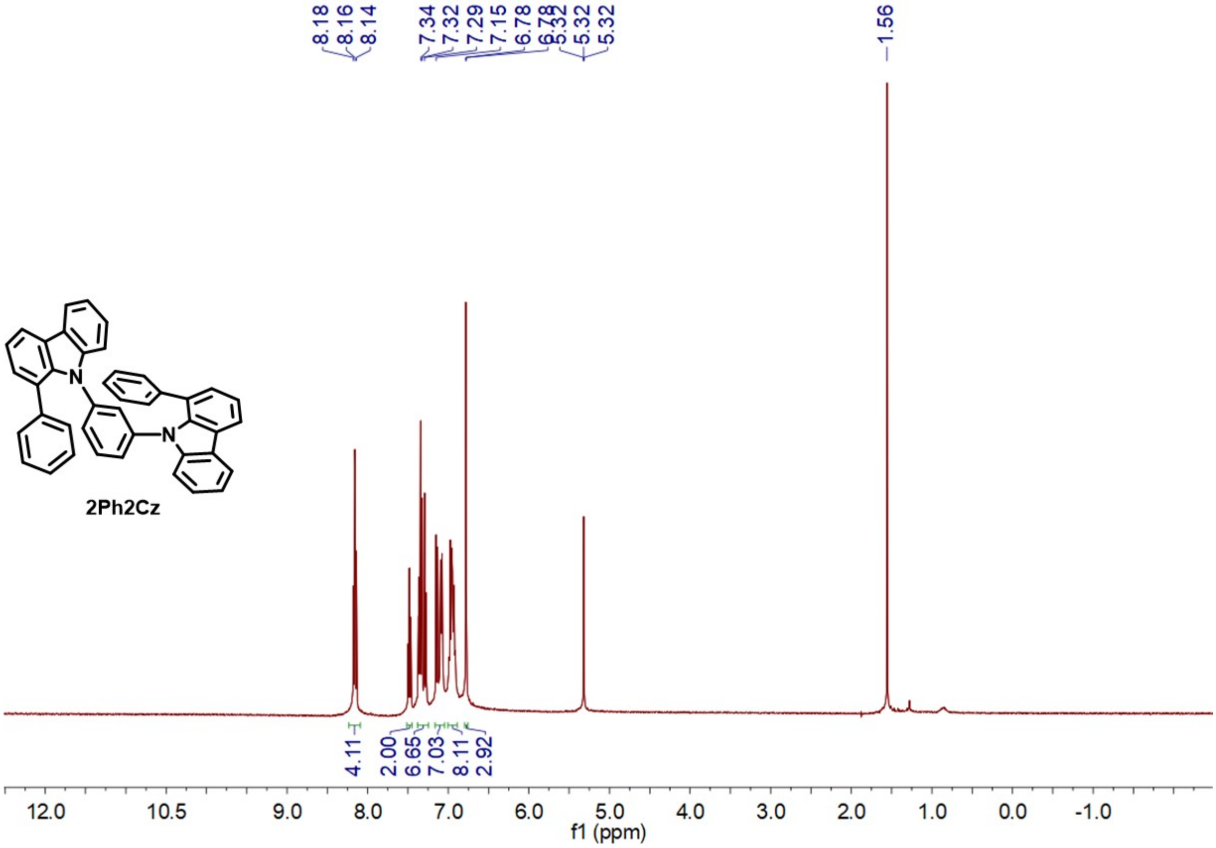


Figure S18. ^{1}H NMR (400 MHz, CD_2Cl_2) of **2Ph2Cz**.

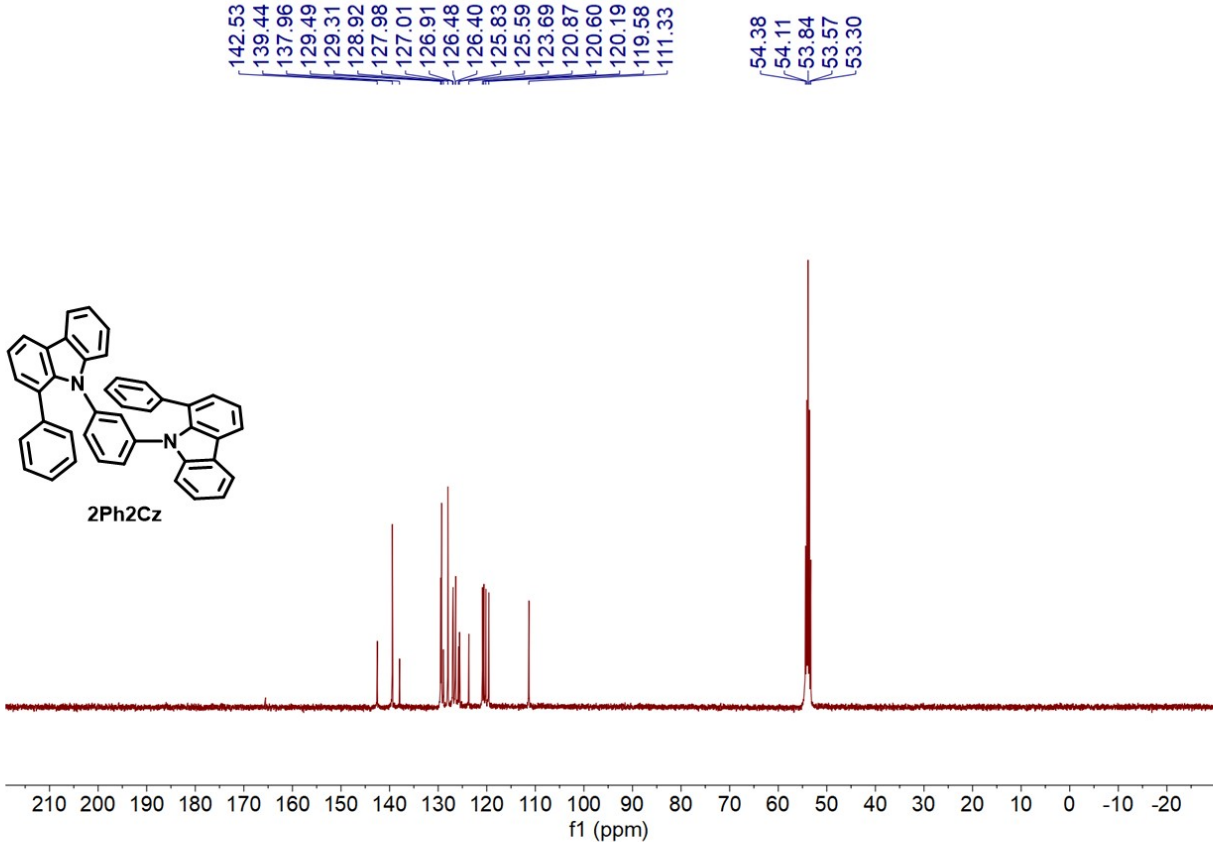


Figure S19. ^{13}C NMR (100 MHz, CD_2Cl_2) of **2Ph2Cz**.

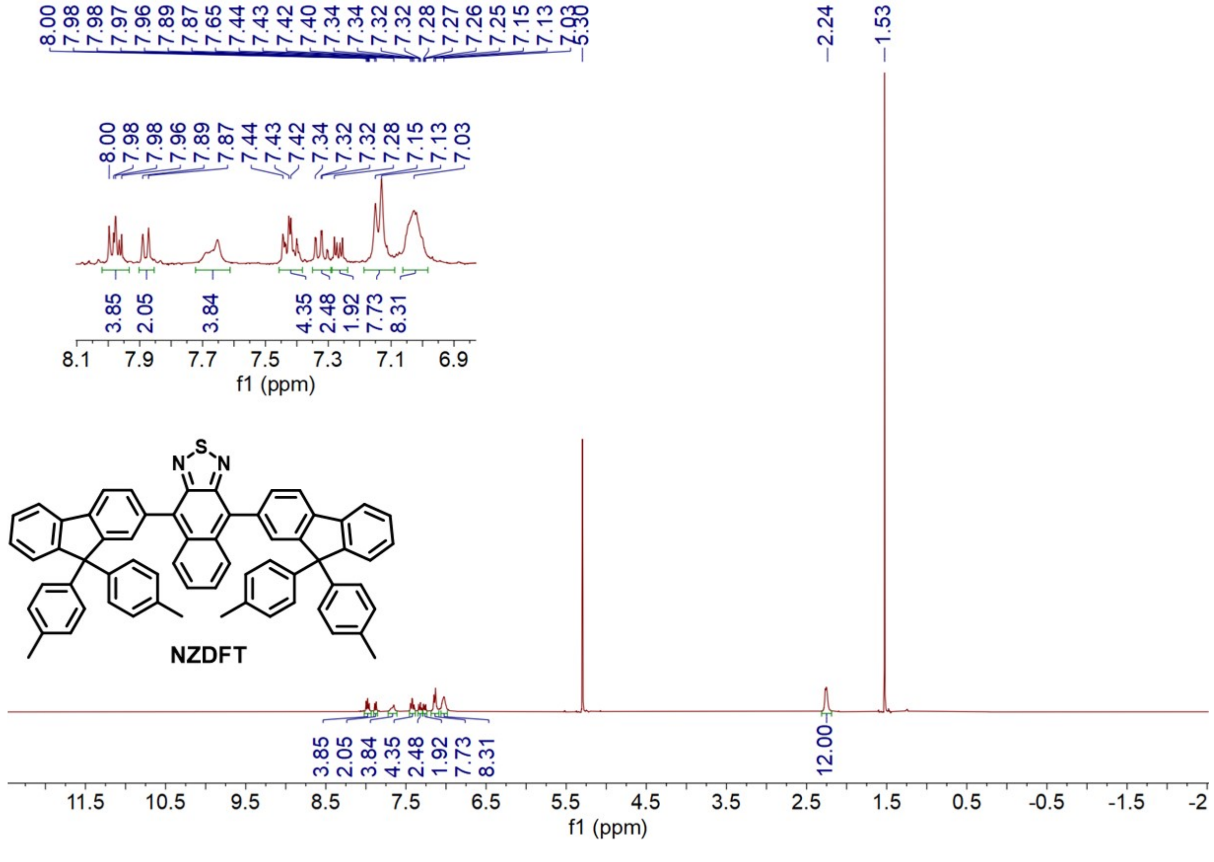


Figure S20. ^{1}H NMR (400 MHz, CD_2Cl_2) of **NZDFT**.

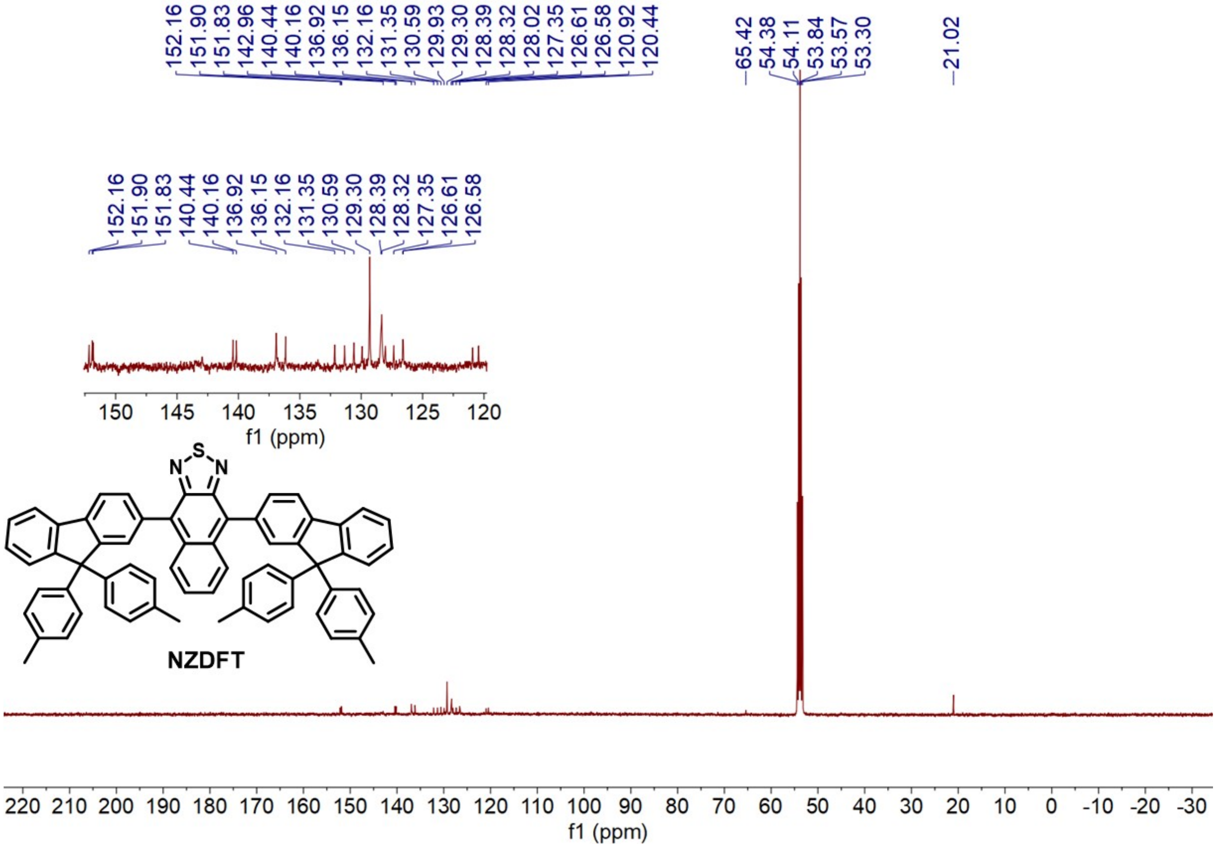


Figure S21. ^{13}C NMR (100 MHz, CD_2Cl_2) of **NZDFT**.

Reference

1. K.-P. Tseng, F.-C. Fang, J.-J. Shyue, K.-T. Wong, G. Raffy, A. Del Guerzo and D. M. Bassani, *Angew. Chem. Inter. Edit.*, 2011, **50**, 7032-7036.

2. C.-K. Wang, X. Che, Y.-C. Lo, Y.-Z. Li, Y.-H. Wang, S. R. Forrest, S.-W. Liu and K.-T. Wong, *Chem. Asian J.*, 2020, **15**, 2520-2531.