Supporting information

Extremely Superb Efficiency and Lifetime of Deep Blue Phosphorescent OLEDs by Introducing Hypsochromic-shift Intermolecular Complex with Negligibly Small ΔE_{ST} and Fast Reverse Intersystem Crossing Rate

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EXPERIMENTAL SECTION

General Procedures

All reactions were carried out under a nitrogen atmosphere. Reagents were purchased from Aldrich chemical company and used without further purification. Thin-layer and flash chromatography were performed on silica gel. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometers. Deuterated solvents were purchased from Cambridge Isotopes. The UV-vis spectra were measured by UV-vis spectrophotometer (JASCO, V-730) and the PL spectra were obtained by fluorescence spectrophotometer (PerkinElmer, LS-55). The triplet energies of the materials were measured in THF solution at 77 K under liquid nitrogen. The instrument to measure mass spectra was an Advion, ExpresionL CMS spectrometer in APCI mode.

Synthesis of CzTrz : Carbazole (10.0 g, 60 mmol) was dissolved in 80 ml dry degassed THF in a 500 mL three-necked flask. The solution was cooled to 0°C in an ice bath, then *n*-BuLi (37.5 ml, 1.60 M in hexanes, 60 mmol) was added dropwise by dropping funnel over 30 minutes. After the mixture was stirred for 1 hr at room temperature to prepare a lithiated carbazole, 80 ml of THF solution of 2,4,6-trichloro-1,3,5-triazine (10.5 g, 57 mmol) was added dropwise. The resulting mixture stirred for one more hour at room temperature and 150 ml of water was added to the mixture to precipitate a white solid. The solid residue was collected by filtration and purified by recrystallization with methanol and toluene. The yield was 10.8 g and 60% based on **CzTrz.**

Synthesis of DSiCzTrz: **CzTrz** (10.0 g, 32 mmol), triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (30.8 g, 67 mmol), $Pd(PPh_3)_4$ (1.11 g, 0.96 mmol), K_2CO_3 (17.7 g, 0.128 mol) were mixed in 200 l of THF and 80 ml of water under N_2 atmosphere. The reaction mixture was heated to 90 ^{o}C for 6 h. After completion of the reaction, the results were cool to room temperature. The solvent was reduced *in vacuo* and the residue was partitioned between CH_2Cl_2 and water. The water layer was extracted twice with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$,

filtered, and purified on silica gel to afford 27.2 g of **DSiCzTrz** as a white solid (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.02 (s, 2H), 8.90 (d, J = 4.3 Hz, 2H), 8.67 (dt, J = 4.0 Hz, J = 1.5 Hz, 2H), 7.98 (d, J = 3.5 Hz, 2H), 7.84 (dd, J = 4.0 Hz, J = 0.5 Hz, 2H), 7.67 – 7.65 (m, 12H), 7.61 (t, J = 7.5 Hz, 2H), 7.46 – 7.45 (m, 6H), 7.44 – 7.38 (m, 12H), 7.31 (t, J = 7.5 Hz, 2H), 7.16 (td, J = 8.0 Hz, J = 0.5 Hz, 2H) ppm. ^{13}C {^{1}H}NMR (126 MHz, $CDCl_3$, δ): 172.6, 165.4, 140.8, 139.2, 137.1, 136.7, 135.9, 135.4, 134.1, 130.7, 130.0, 128.6, 128.3, 127.3, 126.7, 123.3, 119.6, 118.0 ppm. HRMS (EI, *m/z*): calcd for $C_{63}H_{46}N_4Si_2$ [M^+] 915.2590, found 915.3343. Anal. Calcd for $C_{63}H_{46}N_4Si$: C, 82.68; H, 5.07; N, 6.12. Found: C, 82.42; H, 5.13;N, 5.89.

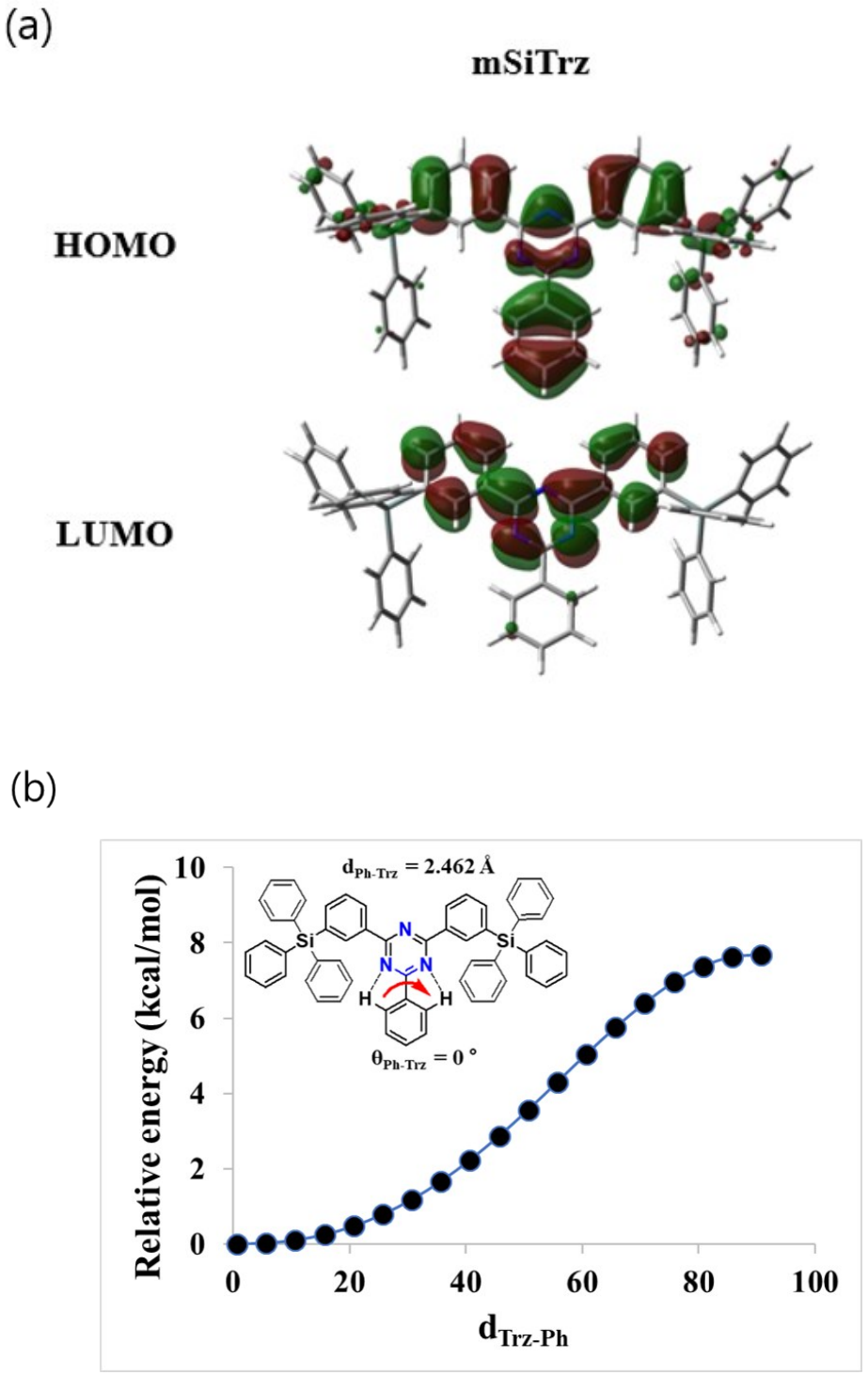
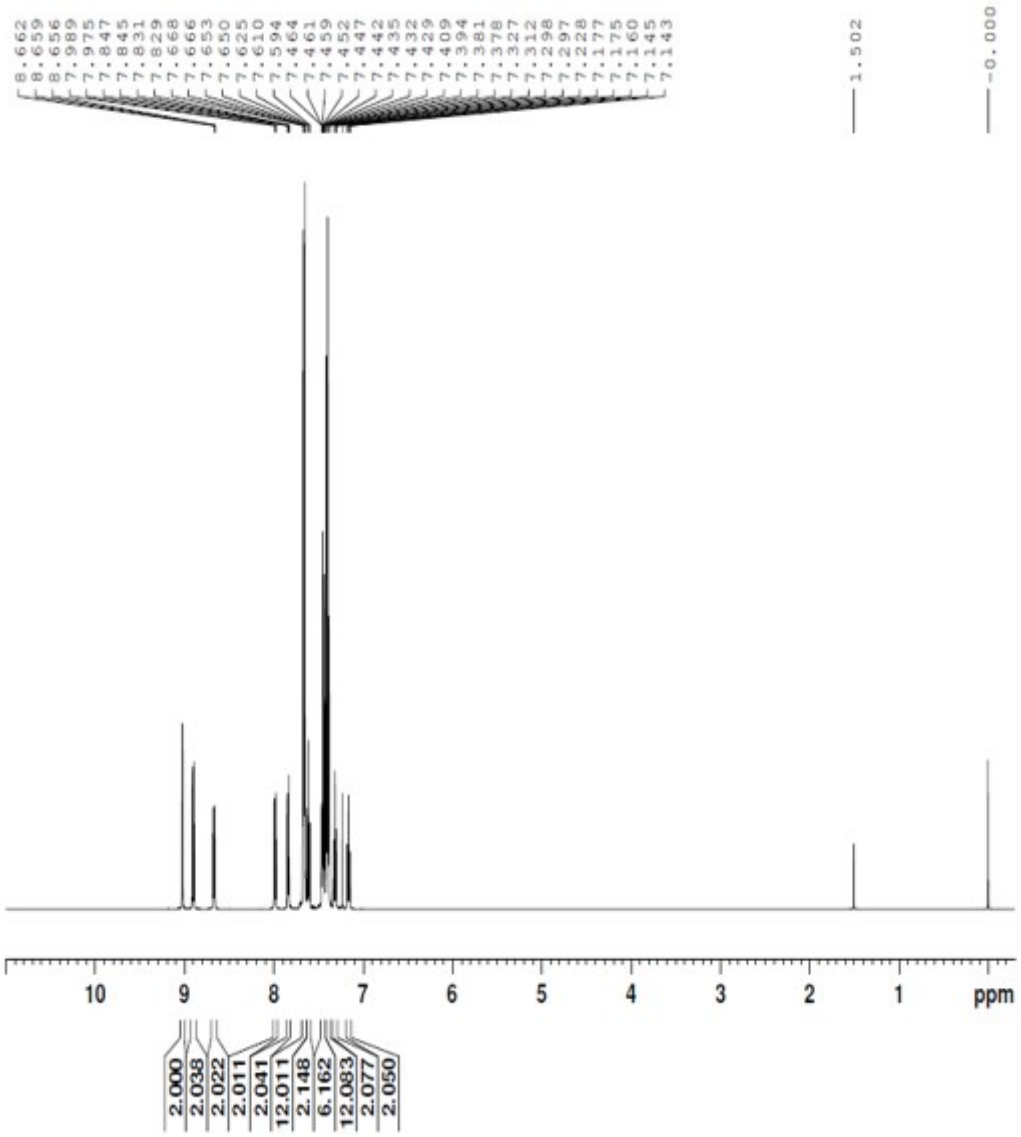


Figure S1. (a) HOMO, LUMO and (b) potential energy surface (PES) simulation of mSiTrz.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7.464
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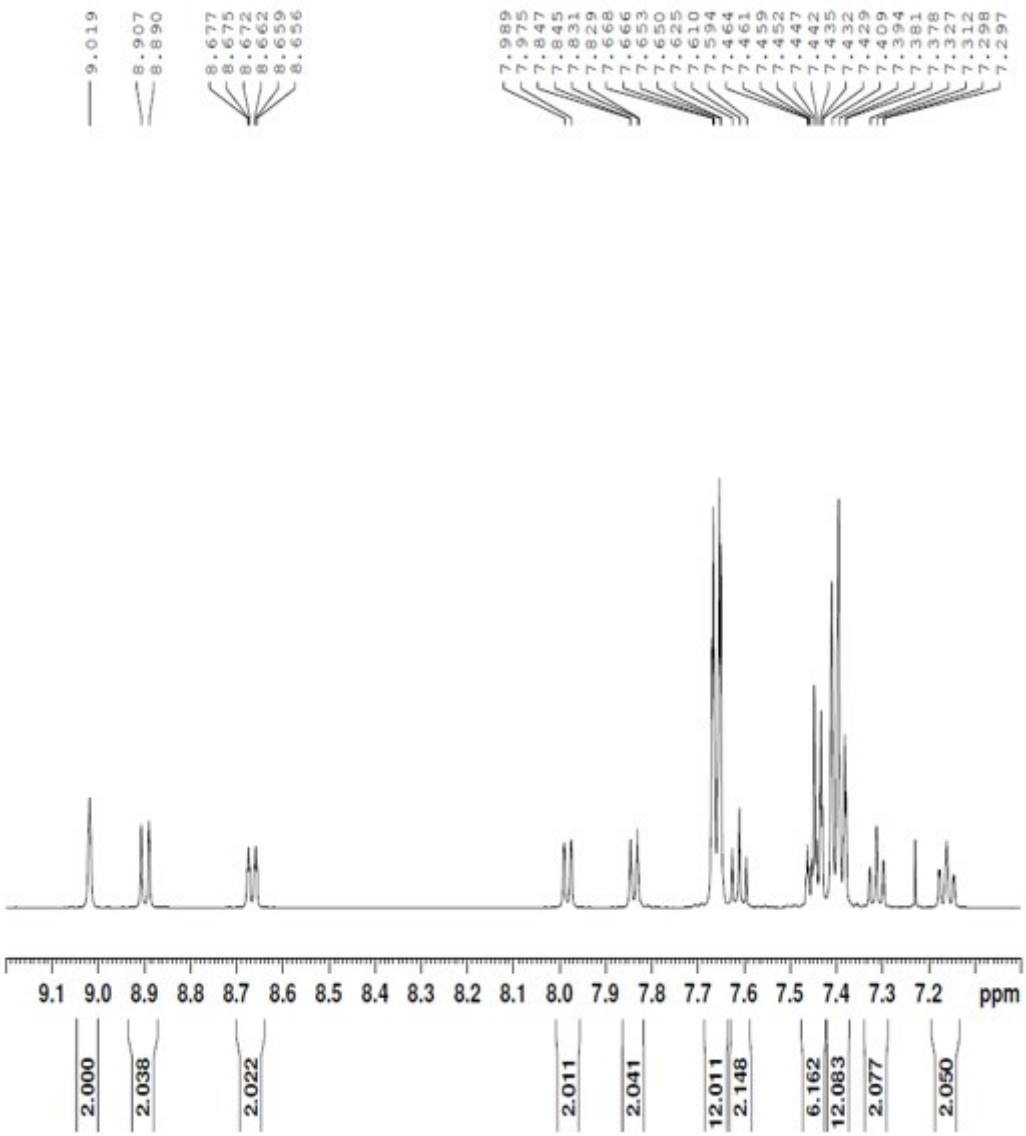
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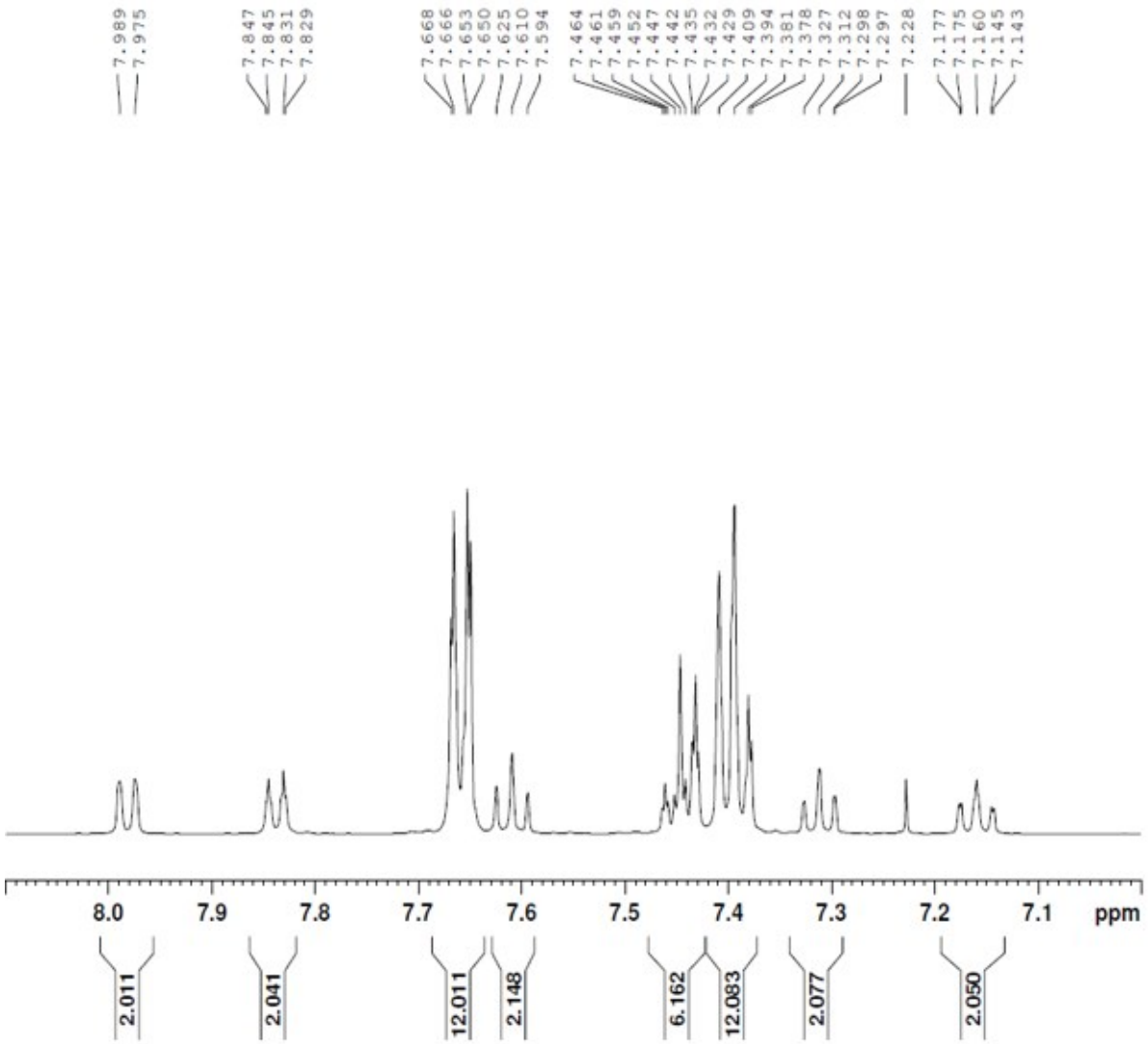
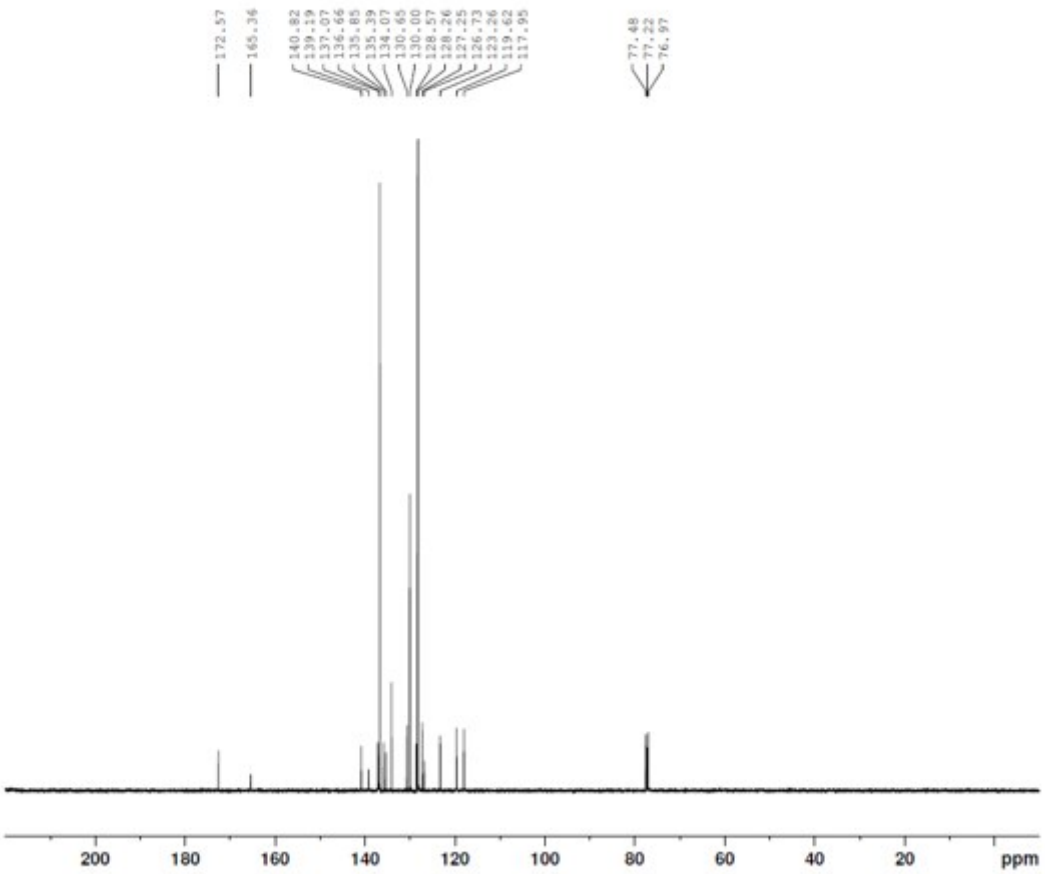


Figure S2. ^{1}H-NMR data of DSiCzTrz.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139.19
137.07
136.66
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126.73
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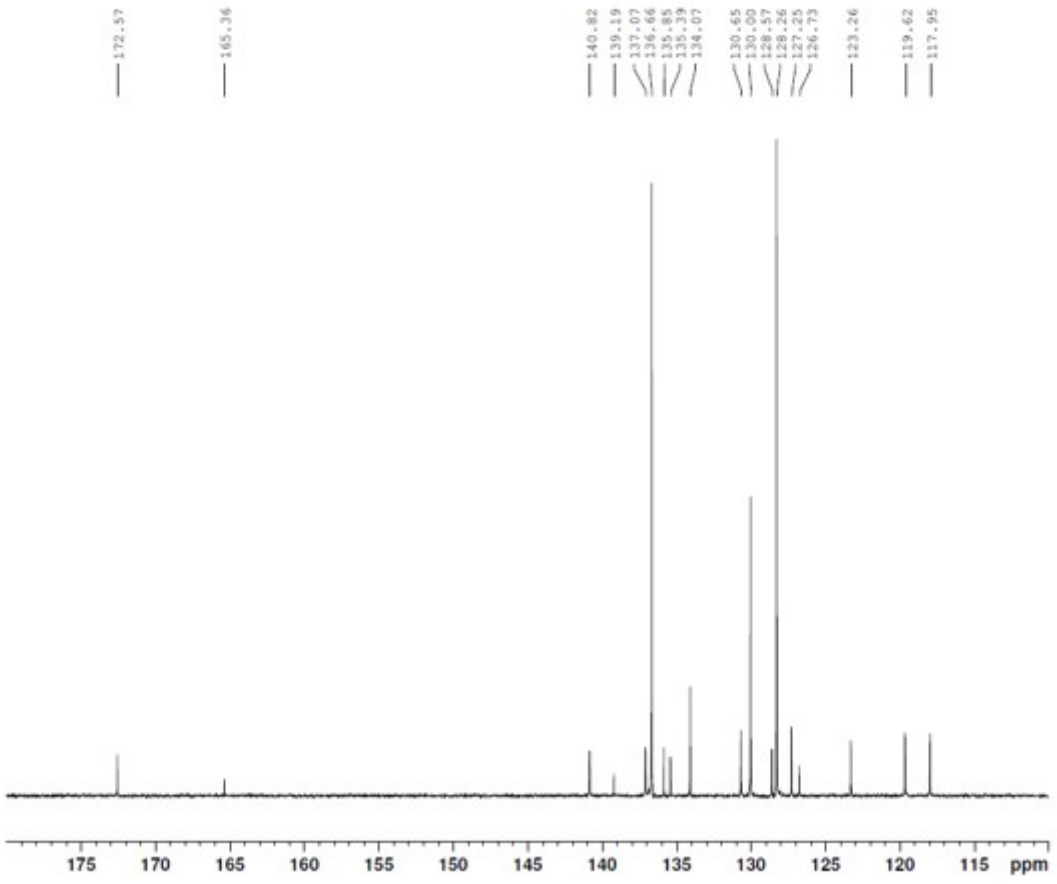
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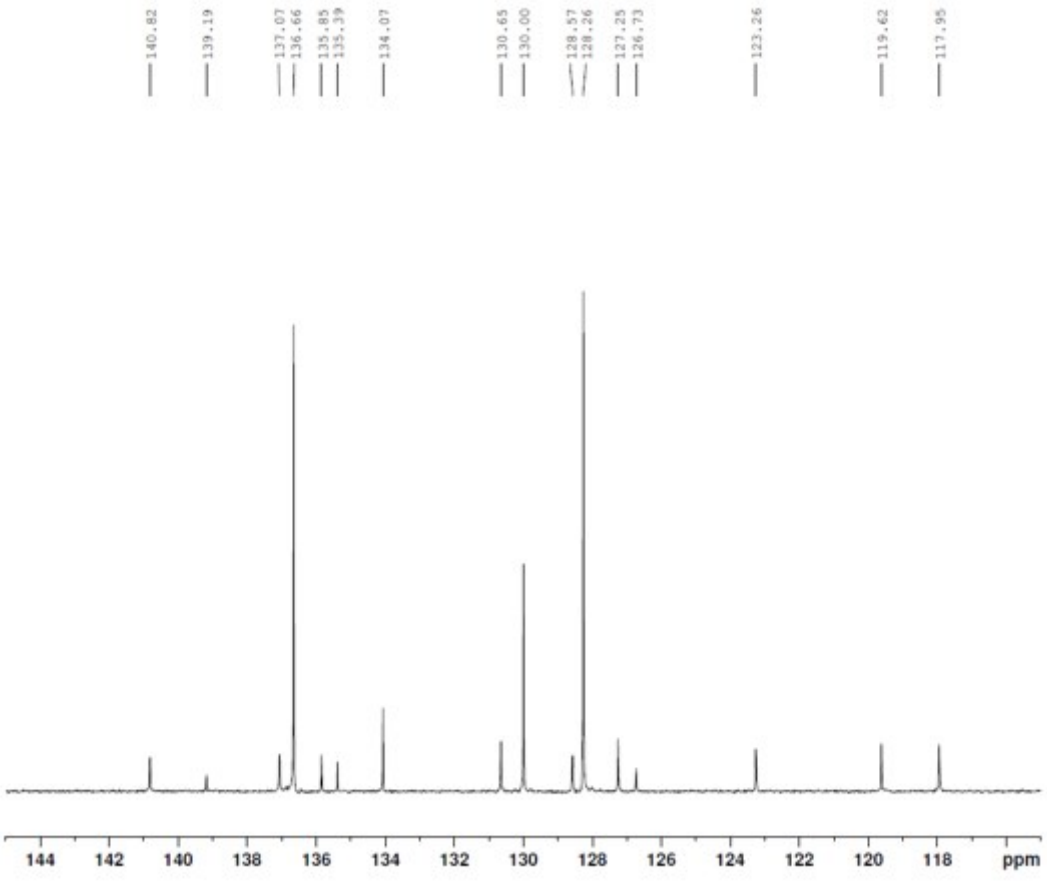
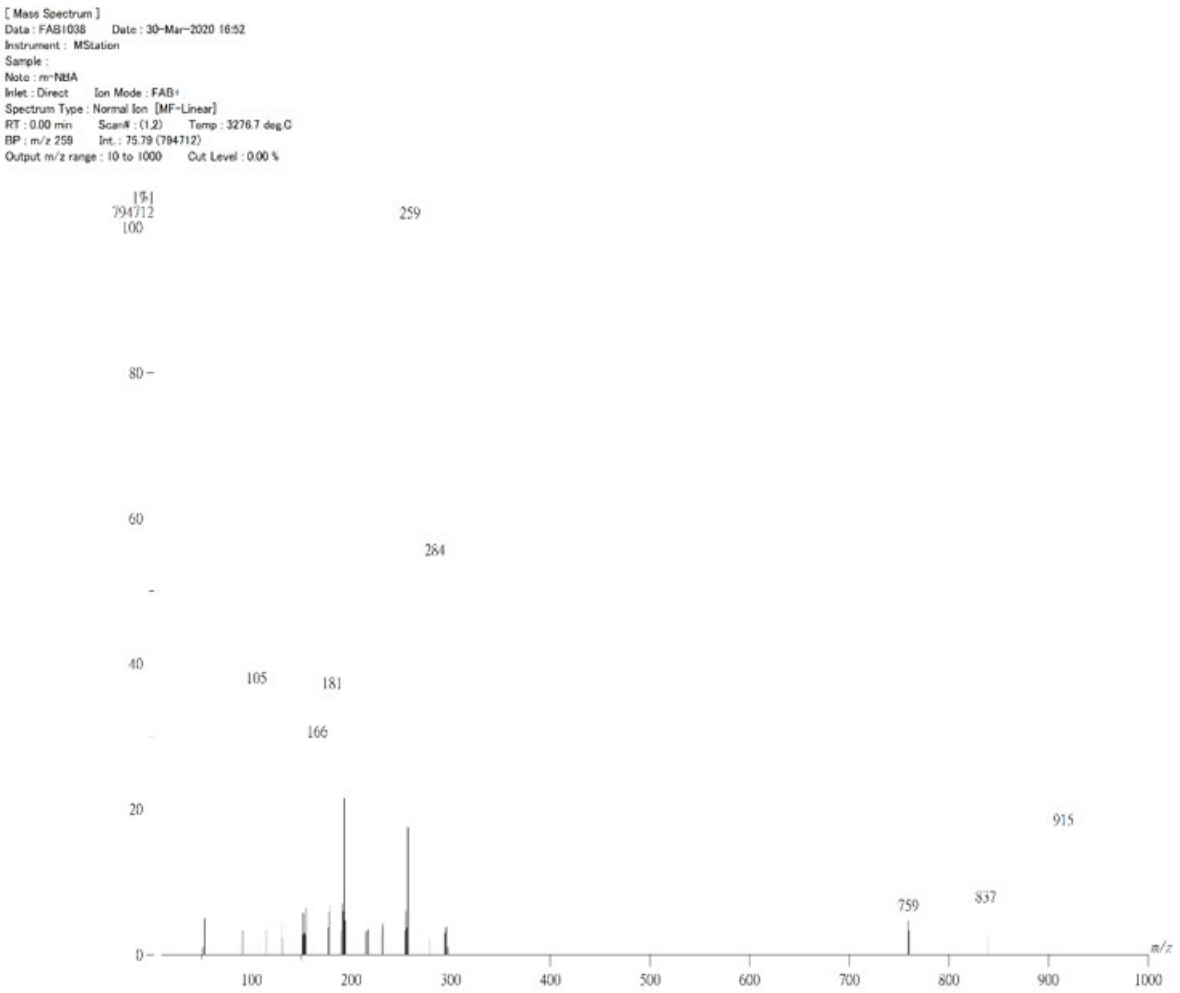


Figure S3. ^{13}C-NMR data of DSiCzTrz



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Data : FAB1039 Date : 30-Mar-2020 16:58
Instrument : MStation
Sample :
Note : Glycerol
Inlet : Direct Ion Mode : FAB+
RT : 1.51 min Scan# : (62,70)
Elements : C 100/0, H 100/0, N 10/0, Si 3/0
Mass Tolerance : 1000ppm, 5mmu if m/z < 5, 10mmu if m/z > 10
Unsaturation (U.S.) : 30.0 – 60.0

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	915.3343	100.00	-2.1 / -1.9	50.0	C67 H41 N5
2			+2.4 / +2.2	49.0	C69 H45 N Si
3			-4.0 / -3.7	45.5	C61 H43 N8 Si
4			+9.7 / +8.9	46.0	C60 H41 N9 Si
5			+0.4 / +0.4	44.5	C63 H47 N4 Si2
6			+4.8 / +4.4	43.5	C65 H51 Si3
7			-1.6 / -1.4	40.0	C57 H49 N7 Si3

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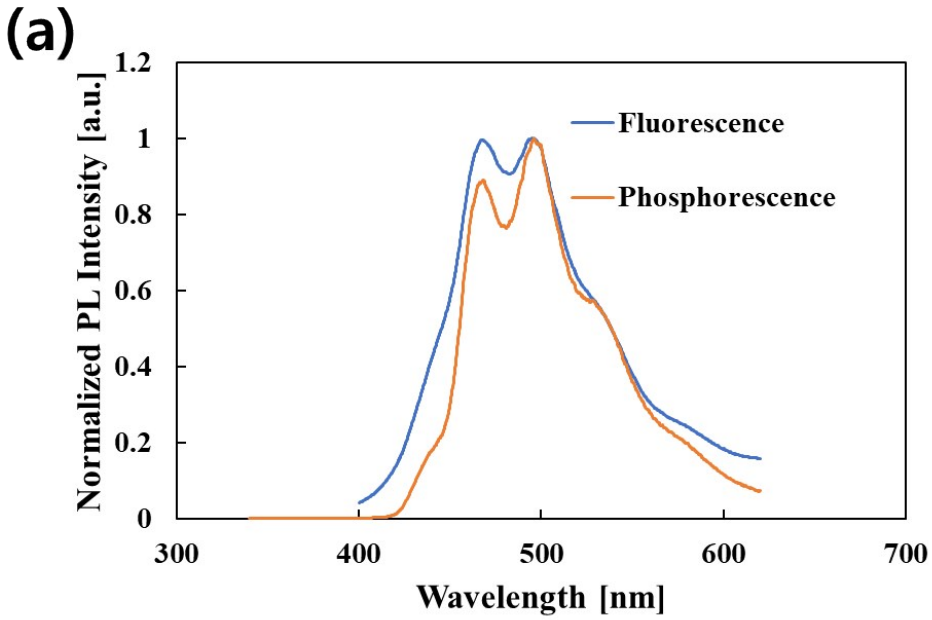
98 **Figure S4.** HR-MS data of DSiCzTrz.



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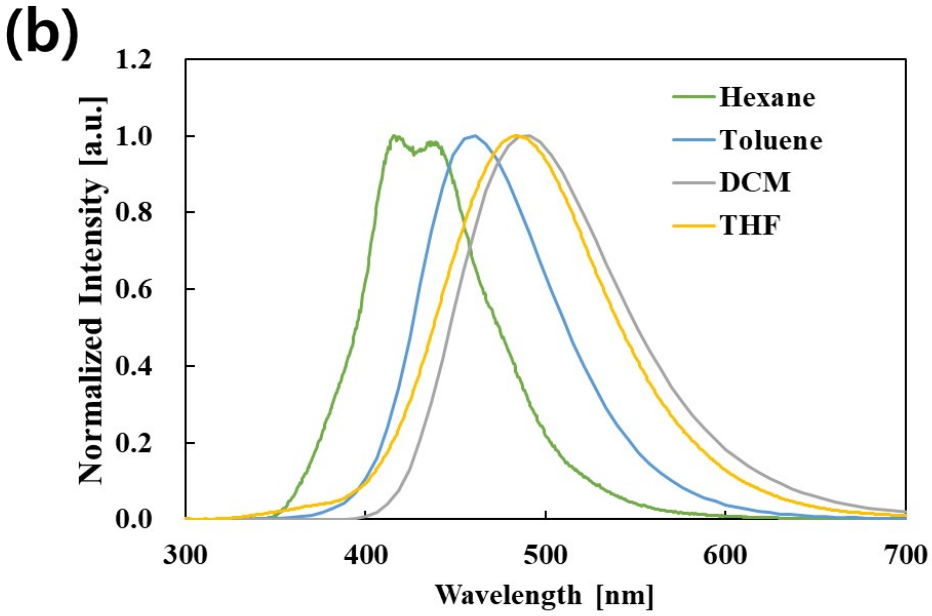

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101 **Figure S5.** (a) Fluorescence and phosphorescence spectra of DSiCzTrz in solid-state at 77 K and (b)

102 bathochromic shifts of DSiCzTrz in different solutions

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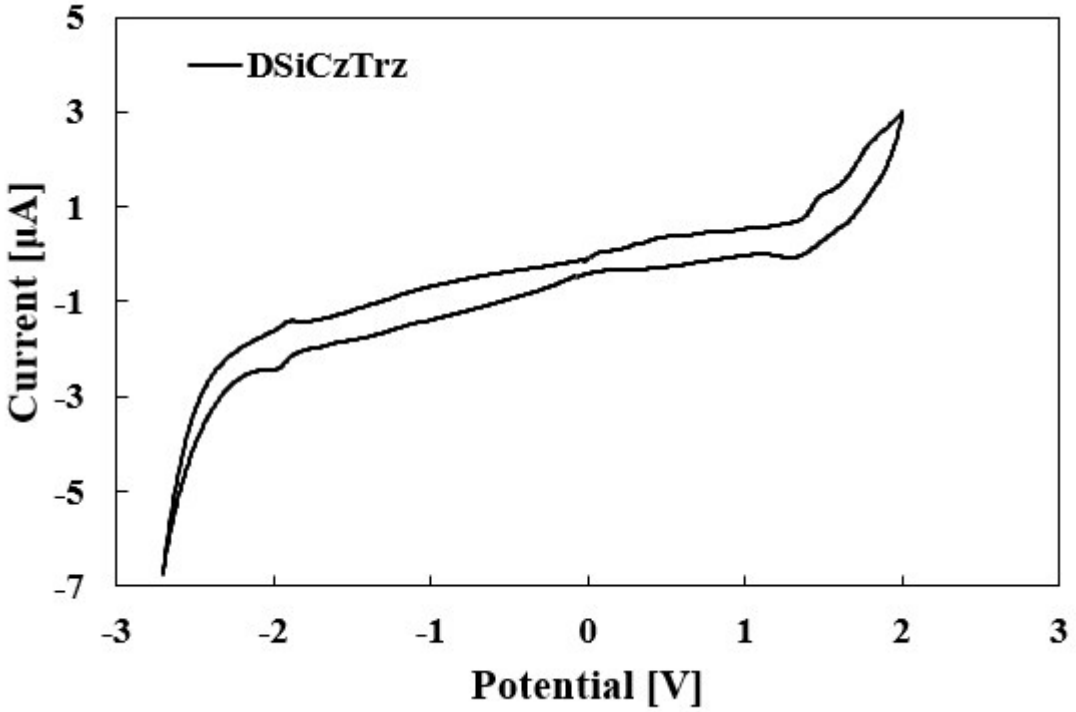

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107 **Figure S6.** The electrochemical measurement results of DSiCzTrz.

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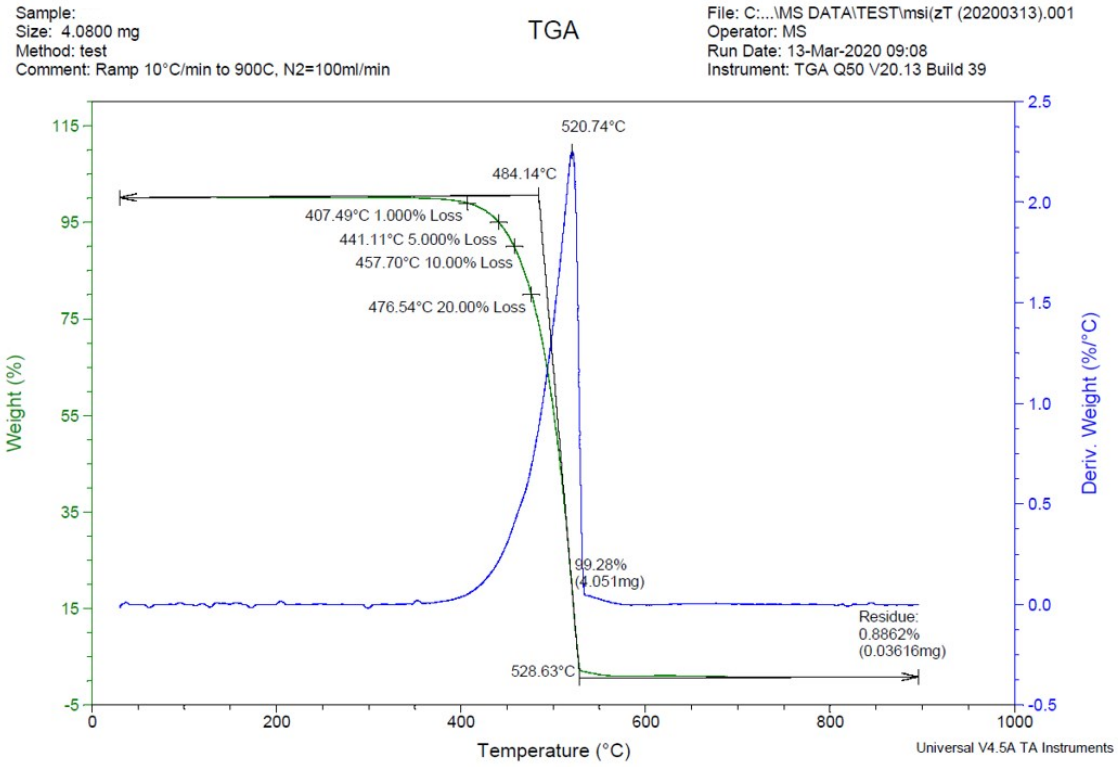

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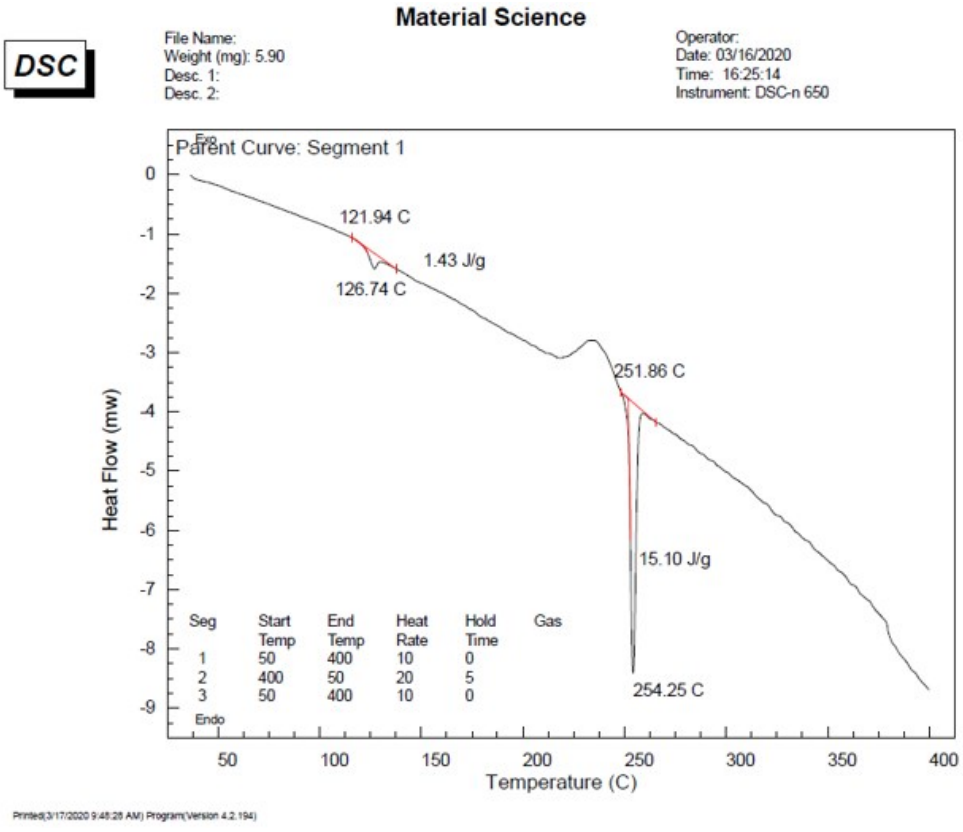

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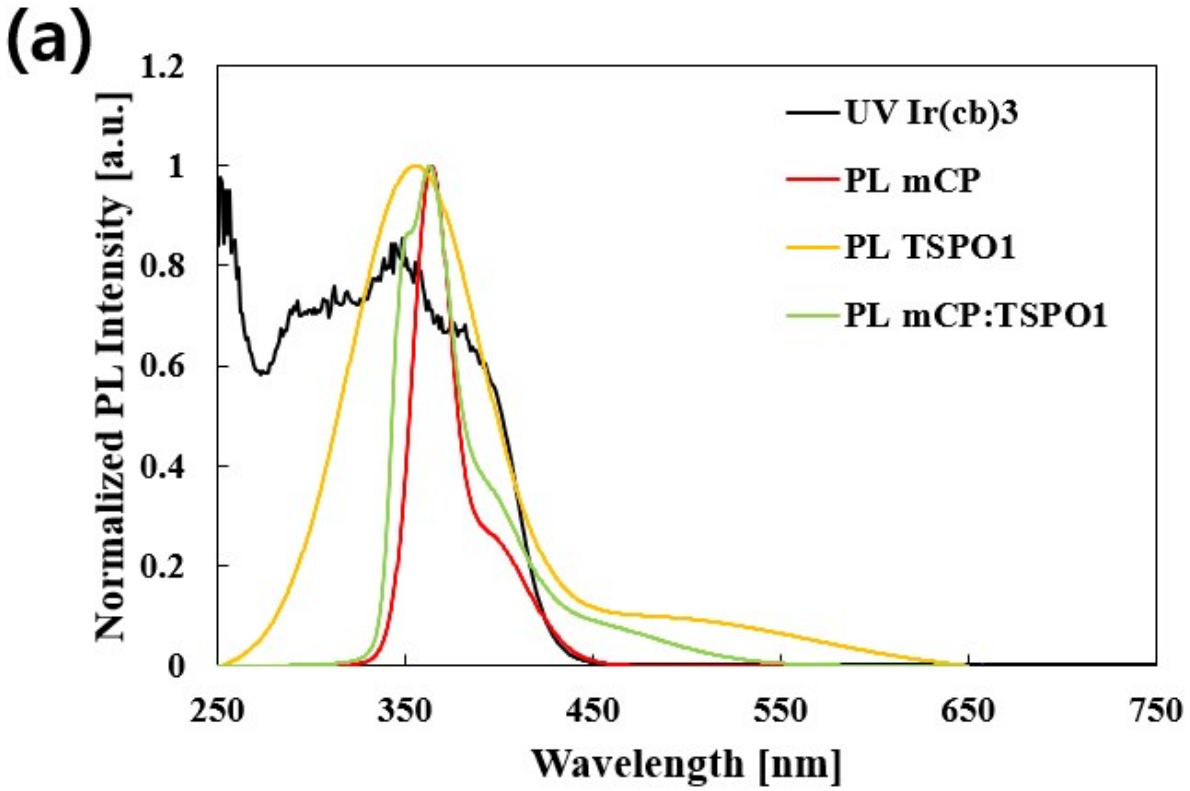
120 **Figure S7.** Thermal stability measurement (TGA and DSC) of DSiCzTrz.



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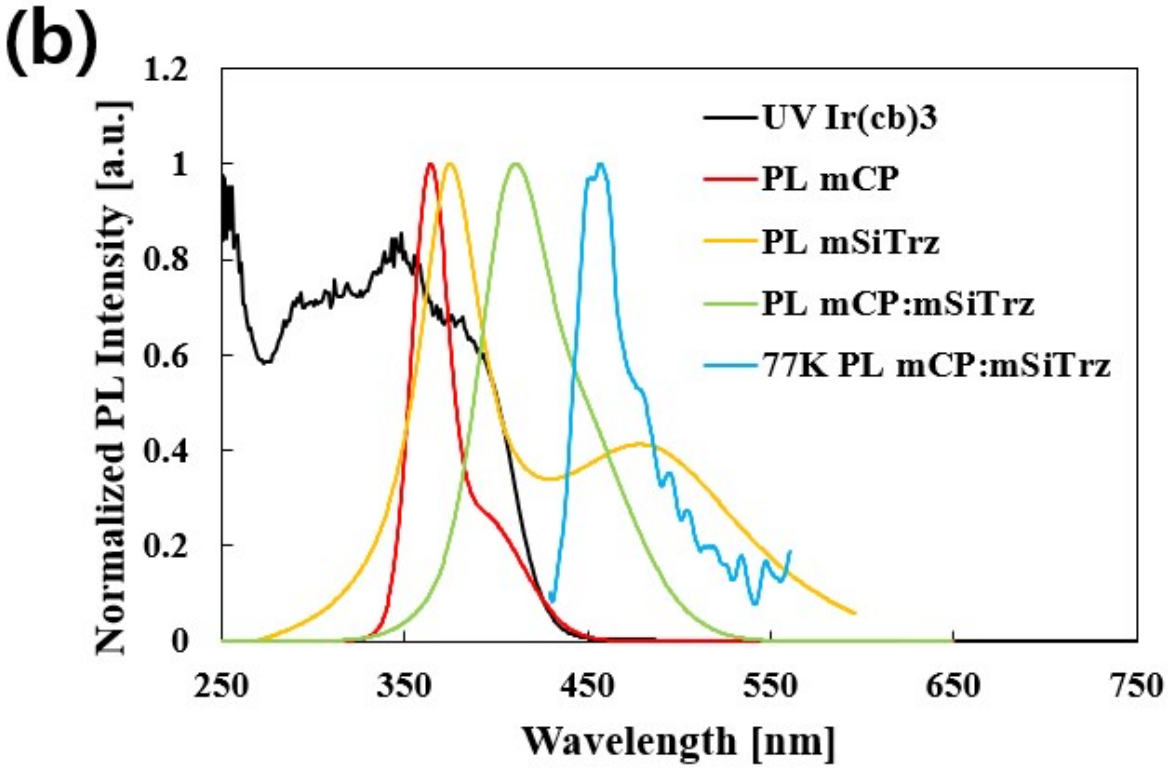

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124 **Figure S8.** PL spectra of (a) mCP:TSPO1 and (b) mCP:mSiTrz.

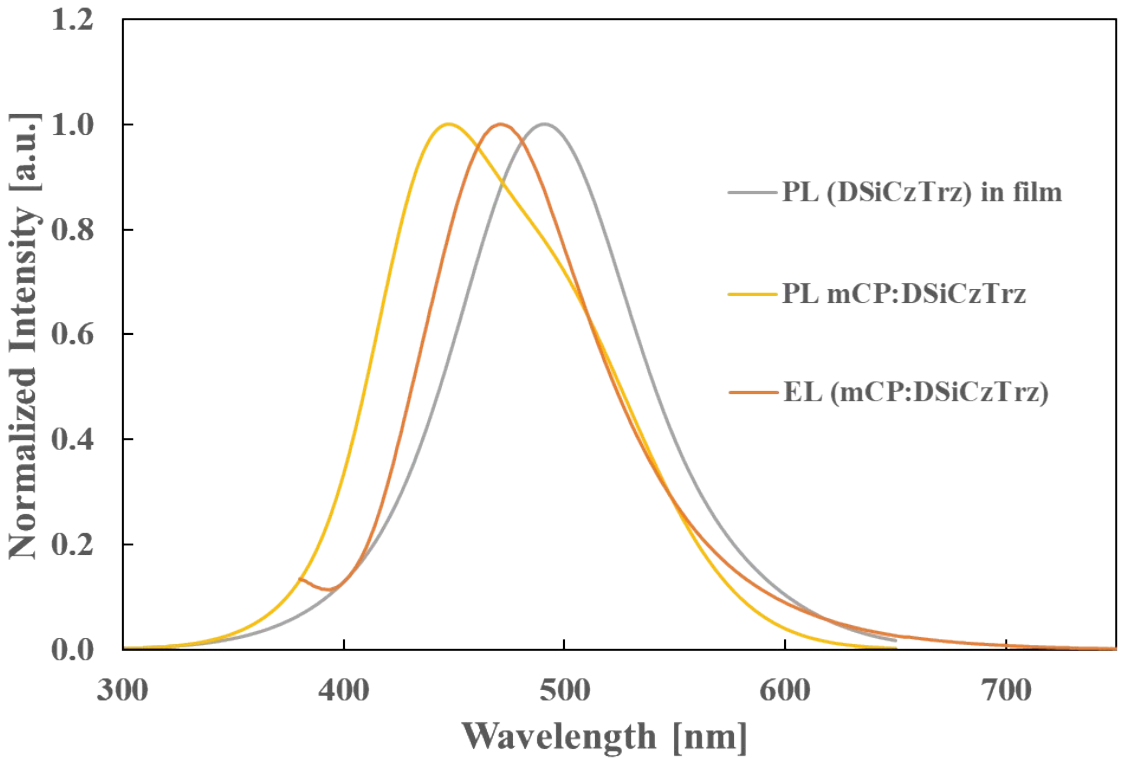


Figure. S9 Comparison of photoluminescence spectra of DSiCzTrz and mCP:DSiCzTrz mixed film and electroluminescent spectrum of mCP:DSiCzTrz.

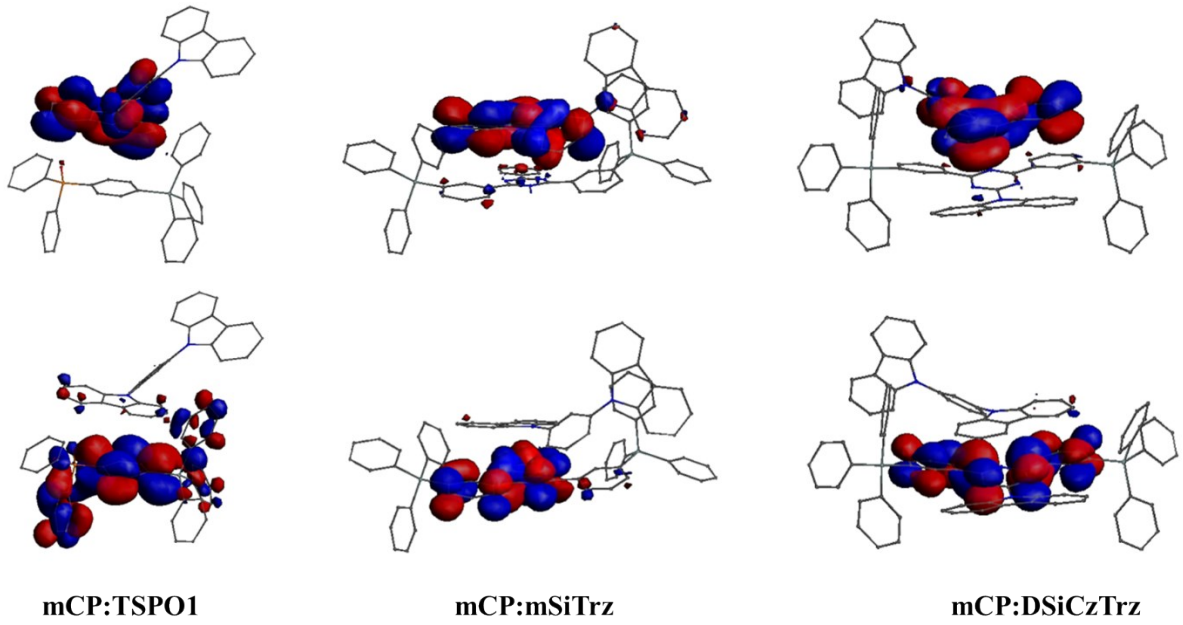


Figure. S10 The calulated configuration of HOMO (upper) and LUMO (lower) in mixed host systems.

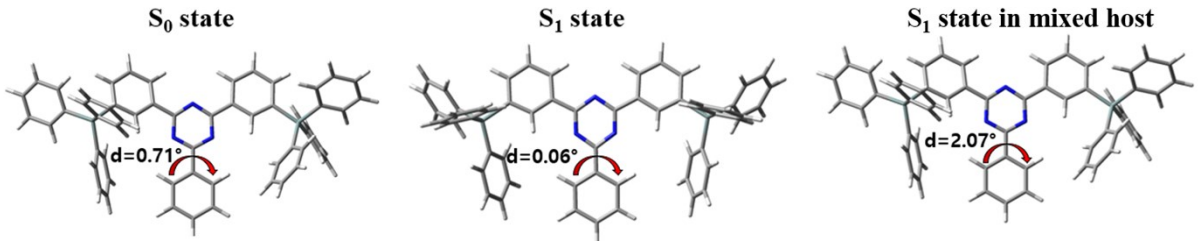


Figure. S11 The representative structural variation of dihedral angle of Trz-Ph in mSiTrz.

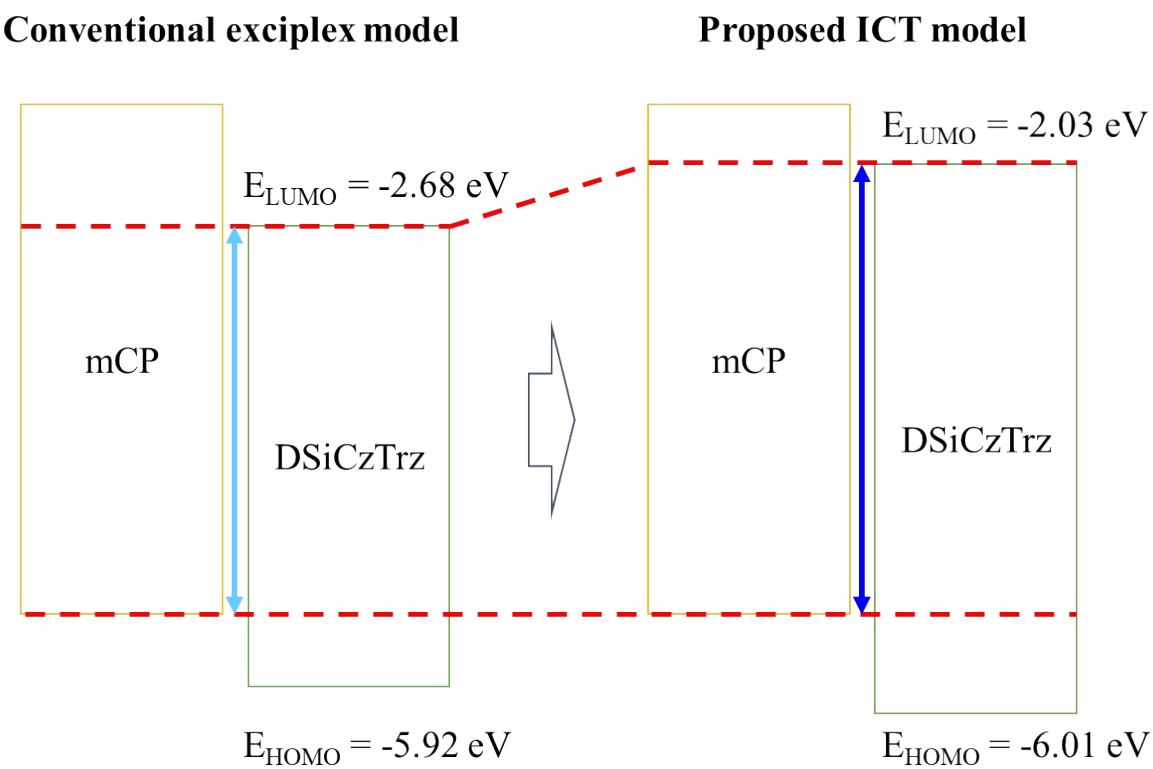


Figure. S12 The proposed mechanism of hypsochromic shift of emission wavelength in mCP-DSiCzTrz.

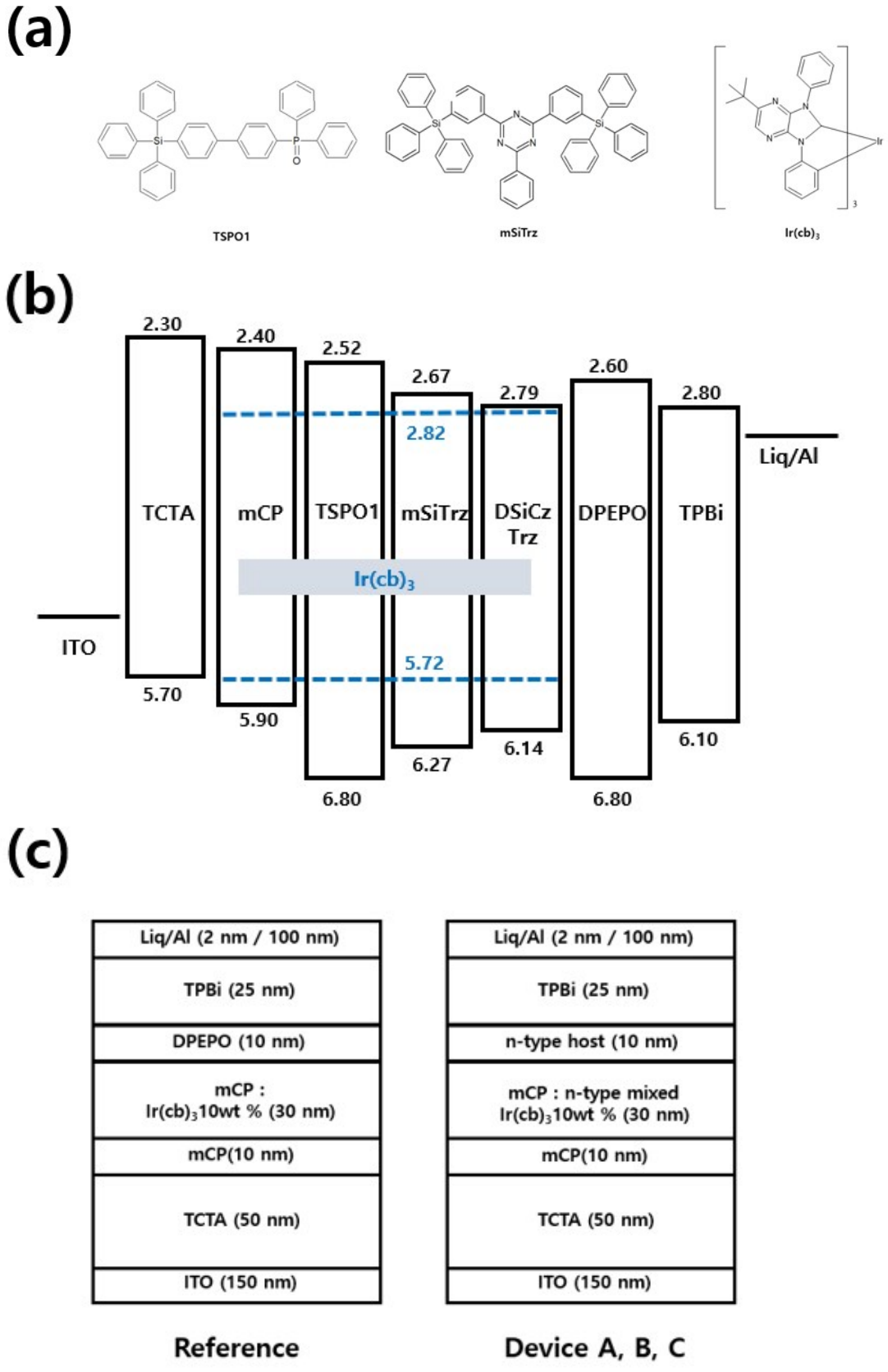
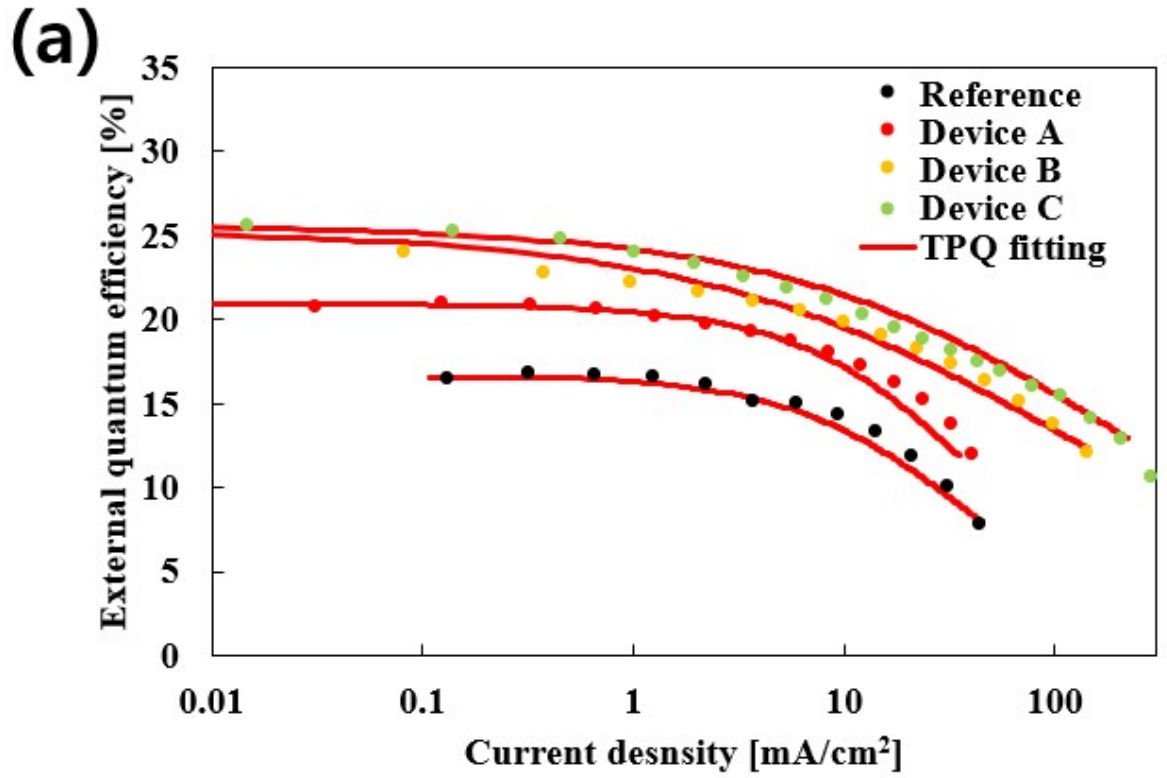


Figure S13. (a) Chemical structures of TSPO1, mSiTrz and $Ir(cb)_3$, (b) energy level diagram of materials used, and (c) schematic structures of the deep blue PhOLEDs.



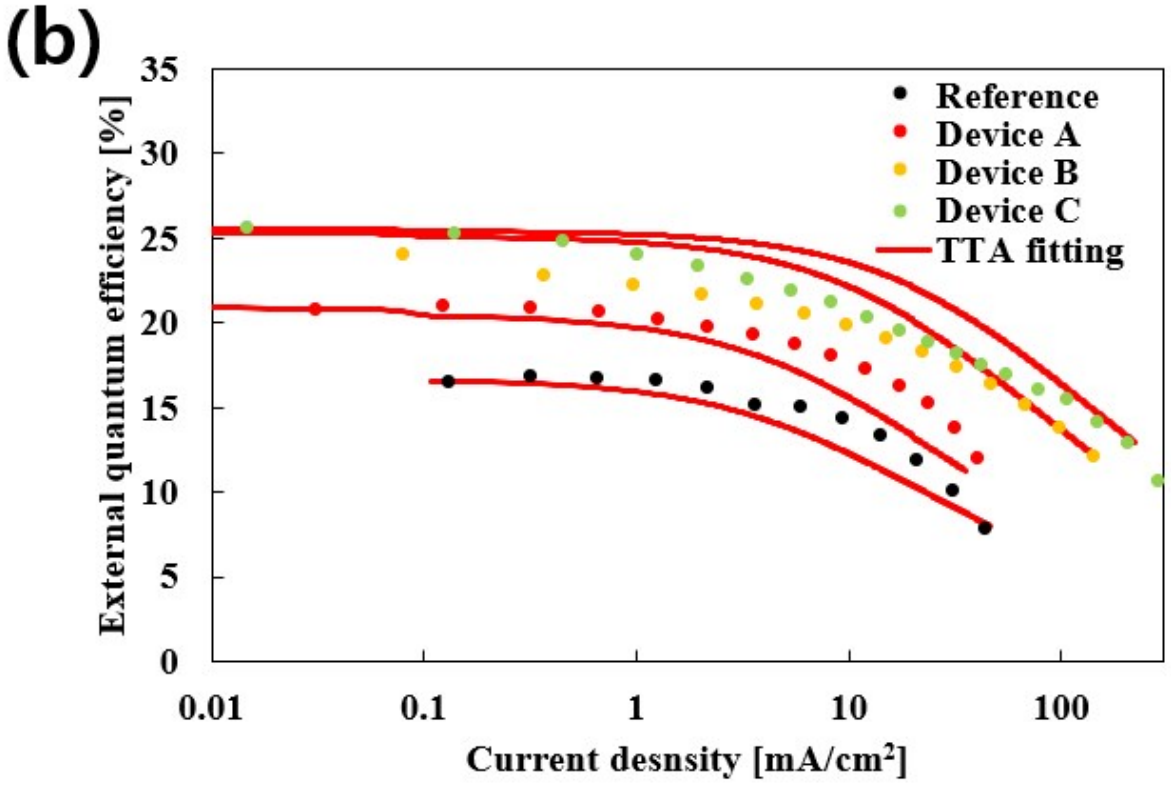
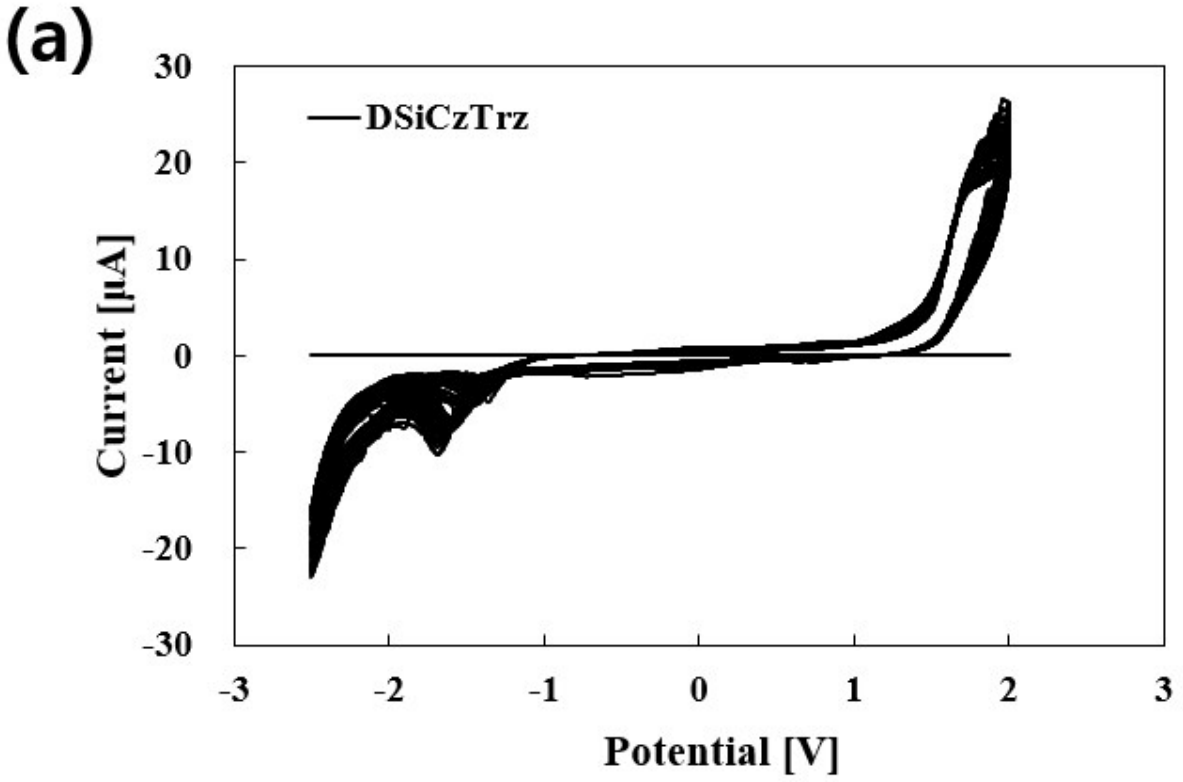


Figure S14. EQE fitting with (a) TPQ and (b) TTA model vs Current density



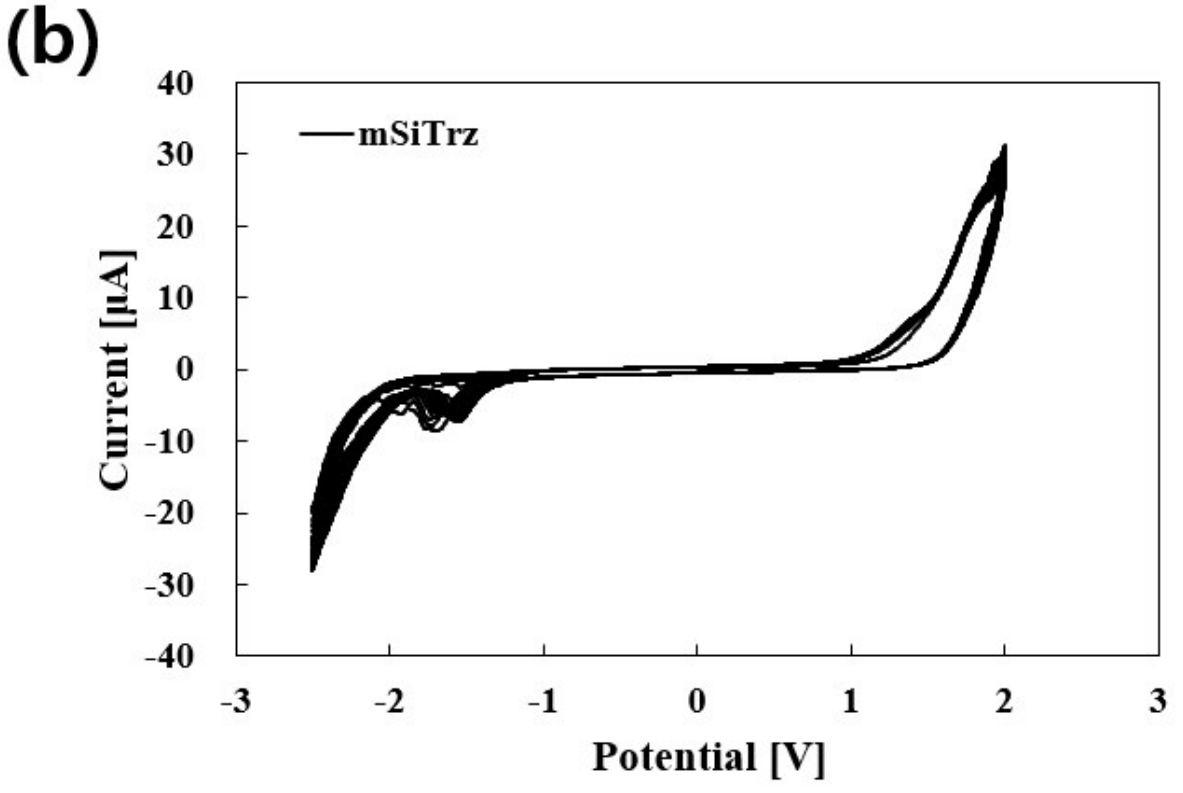
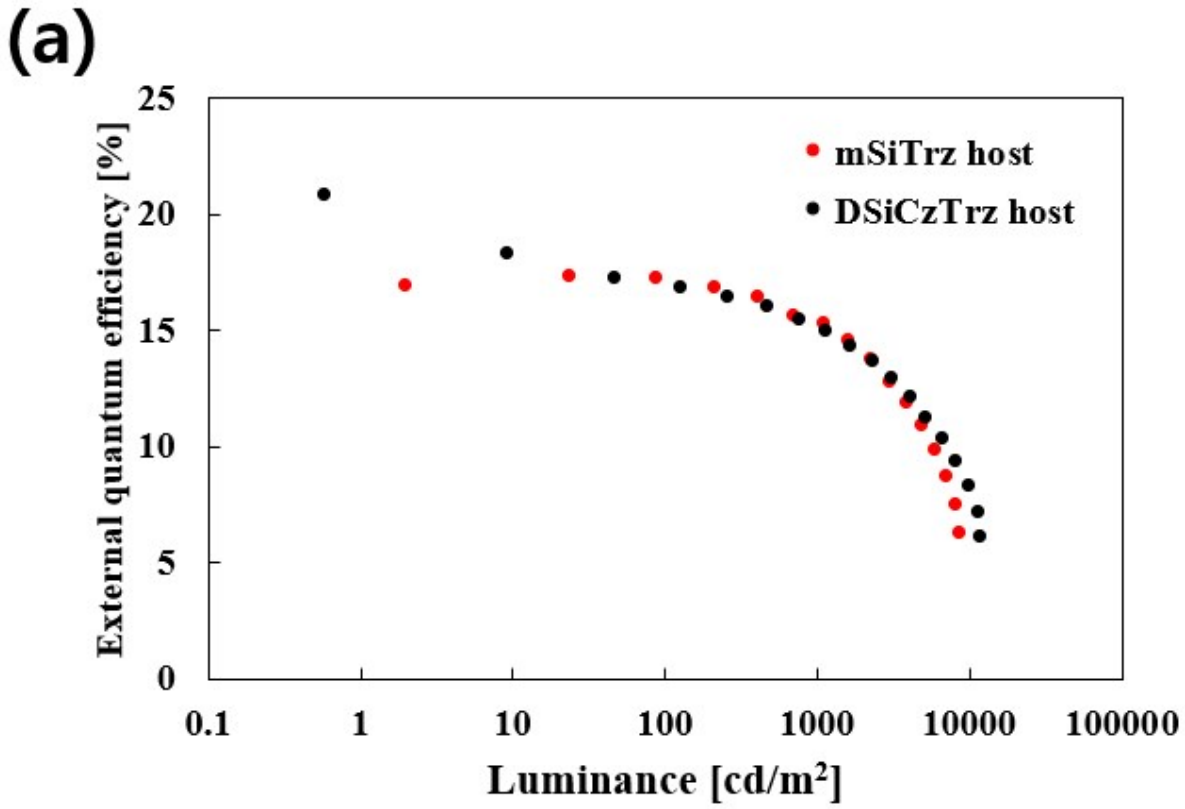


Figure S15. Cyclic voltammetry curves of (a) DsiCzTrz and (b) mSiTrz after 50 repeated cycles



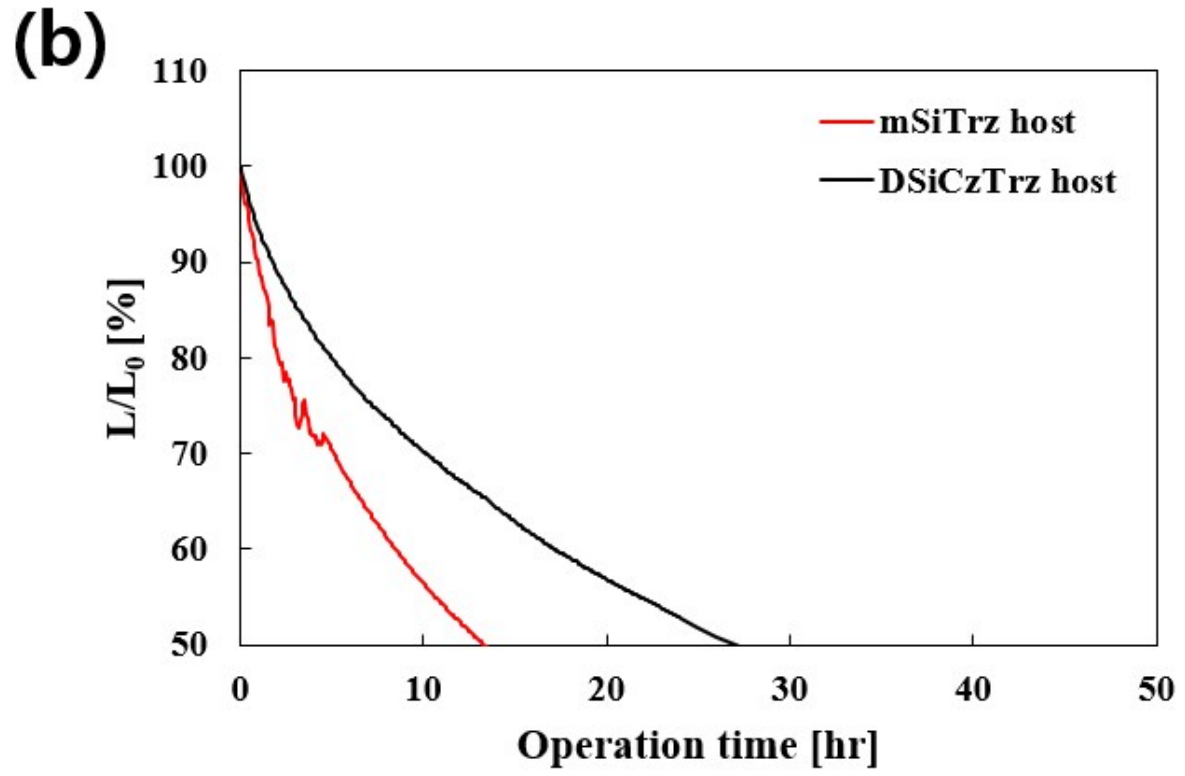


Figure S16. (a) EQE and (b) lifetime at initial luminance 500 cd/m^2 of single host deep blue

PhOLEDs

Compound	S_1 (eV)	T_1 (eV)	$\lambda_{emi\ max}$ (nm)	FWHM[c] (nm)	ΔE_{ST} (eV)
TSPO1	3.49[a]	3.4	355[b]	84	-
mSiTrz	3.63[a]	2.92[b] /3.07[a]	375[a] /370[b]	78	0.59[a]
DSiCzTrz	3.40[a]	2.81[b]/3.06[a]	491[a] /490[b]	96	0.34[a]
mCP:TSPO1	3.41[b]		363[b]	37	
mCP:mSiTrz	3.01[b]	2.75[b]	411[b]	63	0.26[b]
mCP:DSiCzTrz	2.79[b]	2.76[b]	447[b]	115	0.03[b]

Table S1. Photophysical properties for n-type hosts and their mixed systems with mCP. [a] in dilute solution, [b] in film, [c] Full width at half maximum (FWHM)

Device	V		L[a]		L.E[b] (cd/A)		EQE[d] (%)		λ_{EL}[e] (nm)	CIE[f]	LT_{50} (hr)
	V_{to}[g]	at 10 mA/cm^2	at 10 mA/cm^2	Max	at 10 mA/cm^2	Max	at 10 mA/cm^2	Max	7V	1000 cd/m^2	
Reference	3.53	7.42	1737	4330	16.3	19.7	14.2	16.7	464	0.14, 0.16	1.04
Device A	3.51	8.21	2032	5552	20.4	26.3	16.6	20.9	463	0.14, 0.14	1.06
Device B	3.47	7.00	2187	30583	21.9	28.2	17.8	25.3	462	0.14, 0.13	68.5
Device C	3.33	7.21	2366	37321	23.8	30	19.3	25.6	460	0.14, 0.14	114.7

Table S2. Device performances of deep blue PhOLEDs that use various kinds of n-type hosts.

[a] Maximum luminance, [b] Luminous efficiency, [c] Power efficiency, [d] External quantum efficiency, [e] EL emission peak, [f] Commission Internationale de I'Éclairage coordinates, [g] Turn-on voltage at 1 cd/m^2.

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Device	At 40 mA/cm^2			*Je* (mA/cm^2)
	max EQE	EQE	Roll-off (%)	
Reference	16.7	8.69	48.06	40.86
Device A	20.9	11.19	46.46	45.95
Device B	25.3	14.98	40.81	128.25
Device C	25.6	16.33	36.14	230.71

198 **Table S3.** EQE roll-off and critical current density (J_e) of deep blue PhOLEDs.