

Supporting information

**Effect of frontier orbital distribution of the core structure on the
photophysics and device performances of thermally activated delayed
fluorescent emitters**

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Experimental

General information

1,4-Dibromo-2,5-difluorobenzene (Tokyo Chemical Industry Co., LTD.), 1-bromo-2,4-difluorobenzene and 2-methoxybenzeneboronic acid (Alfa Aesar Co., Inc.), tetrakis(triphenylphosphine)palladium(0) (P&H tech Co.), potassium carbonate, cesium carbonate, and N,N-dimethylformamide (Duksan Sci. Co.) were used without further purification. Tetrahydrofuran (THF, Samchun pure chemical Co. Ltd) was distilled over sodium and calcium hydride. Solvent for the NMR analysis was deuterated chloroform (CDCl₃). The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Avance-500 (Bruker, 500 MHz) spectrometer. The ultraviolet-visible (UV-vis) spectra were obtained using UV-vis spectrophotometer (JASCO, V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, LS-55). UV-vis and PL measurements were carried out using a diluted THF solution, and singlet, triplet energy were measured under liquid nitrogen condition using a frozen Toluene solution. The HOMO and LUMO levels were estimated using a cyclic voltammetry (Ivium Tech., Iviumstat). The mass spectra were recorded using a Advion, ExpressionL CMS spectrometer in APCI mode.

Synthesis

4-Bromo-2,5-difluoro-2'-methoxy-1,1'-biphenyl (P1-5)

1,4-Dibromo-2,5-difluorobenzene (20.00 g, 7.36 mmol), 2-methoxybenzeneboronic acid (5.56 g, 3.66 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.31 g, 0.11 mmol) were dissolved in tetrahydrofuran, and potassium carbonate (15.59 g, 0.11 mol) aq. solution was poured into the reaction mixture. The mixture was refluxed for 12 h under nitrogen and cooled to room temperature. The reaction mixture was extracted using dichloromethane and distilled water and the organic layer was dehydrated using MgSO₄. The mixture was purified using column chromatography using dichloromethane:n-hexane (1:10) eluent. A white powder was obtained as a product (7.69 g, yield 70.29%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 7.54 (t, J = 7.70 Hz, 1H), 7.39 (ddd, J = 8.30, 7.60, 1.70 Hz, 1H),

7.22 (dd, $J = 7.50, 1.20$ Hz, 1H), 7.02 (td, $J = 7.50, 1.00$ Hz, 1H), 7.00 – 6.93 (m, 2H), 3.81 (s, 3H). MS (APCI) m/z 299.07[(M+H)⁺].

4'-Bromo-2',5'-difluoro-[1,1'-biphenyl]-2-ol (P1-4)

Dissolution of 4-bromo-2,5-difluoro-2'-methoxy-1,1'-biphenyl (3.52 g, 11.77 mmol) in dichloromethane under a nitrogen atmosphere was followed by stirring at 77 K, and then boron tribromide (5.90 g, 23.54 mmol) was added slowly at 77 K. The reaction mixture was then allowed to be warmed to room temperature. Distilled water and NaOH (1 M) aqueous solution were added slowly into the reaction mixture. The reaction mixture was extracted using ethylacetate/distilled water and the organic layer was dehydrated using MgSO₄. The organic layer was evaporated to remove solvent. A white solid was obtained (3.15 g, yield 93.88%).

¹H NMR (500 MHz, CDCl₃): δ , ppm 7.59 (t, $J = 7.70$ Hz, 1H), 7.32 – 7.26 (m, 1H), 7.20 (d, $J = 7.60$ Hz, 1H), 7.02 – 6.98 (m, 2H), 6.96 (dd, $J = 8.10, 0.90$ Hz, 1H). MS (APCI) m/z 283.94[(M+H)⁺].

3-Bromo-2-fluorodibenzo[*b,d*]furan (P1-3)

4'-Bromo-2',5'-difluoro-[1,1'-biphenyl]-2-ol (4.64 g, 18.0 mmol) was dissolved in dichloromethane. K₂CO₃ (4.84 g, 35.00 mmol) was put into this reaction mixture, and the mixture was refluxed for 8 h and cooled to room temperature. The extracted solid was filtered, and white powder was obtained as a product (2.93 g, yield 61.39%).

¹H NMR (500 MHz, CDCl₃): δ , ppm 7.92 – 7.87 (m, 1H), 7.77 (d, $J = 5.40$ Hz, 1H), 7.67 (d, $J = 7.90$ Hz, 1H), 7.57 (d, $J = 8.30$ Hz, 1H), 7.51 (ddd, $J = 8.40, 7.20, 1.30$ Hz, 1H), 7.40 – 7.33 (m, 1H). MS (APCI) m/z 263.82[(M+H)⁺].

2-(2-Fluorodibenzo[*b,d*]furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (P1-2)

Under nitrogen, 3-bromo-2-fluorodibenzo[*b,d*]furan (4.00 g, 15.09 mol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi-1,3,2-dioxaborolane (5.75 g, 22.64 mmol), Pd(dppf)Cl₂ (0.33 g, 0.45 mmol), and potassium acetate (KOAc) (4.44 g, 45.27 mol) were dissolved in a round-bottomed flask filled with 1,4-dioxane

(80 ml). The mixed reactants were stirred for 12 h under nitrogen at 140 °C. After the reaction was terminated, the mixture was extracted with dichloromethane three times. The organic layer was separated and the moisture was removed by drying over MgSO₄. After removing the solvent by evaporation, the crude product was purified by column chromatography with an ethyl acetate and n-hexane (1:10) eluent. A white powder was obtained as a product (2.29 g, yield 48.51%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 7.94 – 7.87 (m, 2H), 7.58 (dd, J = 8.4, 4.3 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.40 – 7.31 (m, 1H), 1.40 (s, 12H). MS (APCI) m/z 313.82 [(M+H)⁺].

2-(2-Fluorodibenzo[*b,d*]furan-3-yl)-4,6-diphenyl-1,3,5-triazine (P1-1)

2-(2-Fluorodibenzo[*b,d*]furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.00 g, 6.41 mmol) and 2-chloro-4,6-diphenyl-1,3,5-triazine (2.06 g, 7.69 mmol) were dissolved in tetrahydrofuran (90 ml).

Potassium carbonate (2.66 g, 19.23 mol) aqueous solution was poured into the reaction mixture. After N₂ bubbling, Pd(PPh₃)₄ (0.33 g, 0.29 mmol) was added into reaction mixture and then heated under reflux for 8 h. After cooled down to room temperature, the reaction mixture was filtered and the residue was washed with ethyl acetate and distilled water. As a result, the 6,6'-(2,5-difluoro-1,4-phenylene)bis(2,4-diphenyl-1,3,5-triazine) was obtained as a white powder (1.71 g, yield 63.81%)

¹H NMR (500 MHz, CDCl₃): δ, ppm 8.82 – 8.77 (m, 4H), 8.74 (d, J = 5.80 Hz, 1H), 8.01 (d, J = 7.60 Hz, 1H), 7.81 (d, J = 10.40 Hz, 1H), 7.68 – 7.54 (m, 8H), 7.44 – 7.38 (m, 1H). MS (APCI) m/z 417.95[(M+H)⁺].

9-(3-(4,6-Diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan-2-yl)-9'-phenyl-9H,9'H-3,3'-bicarbazole (2Cz3Trz)

Cs₂CO₃ (1.09 g, 3.35 mmol), 9-phenyl-9H,9'H-3,3'-bicarbazole (1.03 g, 2.52 mmol) and DMF (10 mL) were put into a pressure tube and it was heated for 30 min. Then, 2-(2-fluorodibenzo[*b,d*]furan-3-yl)-4,6-diphenyl-1,3,5-triazine (0.70 g, 1.68 mmol) was added to this mixture and allowed to stir at 130 °C for 12 h. The reaction mixture was monitored by thin film chromatography. After full consumption of the starting materials, the mixture was extracted with dichloromethane. The organic layer was separated

and the moisture was removed by drying over MgSO_4 . After removing the solvent by evaporation, the crude product was purified by column chromatography with an ethyl acetate and n-hexane (1:1) eluent. A yellow powder was obtained as a product (1.51 g, yield 78.30%).

^1H NMR (500 MHz, CDCl_3): δ , ppm 8.82 (s, 1H), 8.44 (d, $J = 1.5$ Hz, 1H), 8.39 (d, $J = 1.5$ Hz, 1H), 8.29 (s, 1H), 8.23 (d, $J = 7.7$ Hz, 1H), 8.13 (d, $J = 7.7$ Hz, 1H), 8.09 – 8.01 (m, 5H), 7.80 – 7.72 (m, 3H), 7.67 – 7.60 (m, 4H), 7.53 – 7.40 (m, 8H), 7.37 (d, $J = 8.4$ Hz, 1H), 7.35 – 7.29 (m, 6H), 7.22 (dd, $J = 11.8, 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ , ppm 172.21, 171.62, 158.09, 155.87, 142.99, 141.96, 140.17, 135.71, 135.46, 134.74, 134.08, 132.59, 132.04, 130.12, 129.11, 129.03, 128.57, 128.27, 127.64, 127.29, 126.32, 126.22, 126.10, 126.03, 124.23, 124.20, 123.74, 123.32, 121.80, 120.17, 119.75, 119.16, 119.05, 116.05, 112.47, 110.23, 110.19, 110.09, 109.84. MS (APCI) m/z 806.18[(M+H) $^+$].

1,5-Dibromo-2,4-difluorobenzene (P2-6)

A solution of bromine (22.60 g, 141 mmol) was added slowly to a mixture of 1-bromo-2,4-difluorobenzene (24.80 g, 128 mmol), electrolytic grade iron powder (2 g) and dichloromethane (30 mL) at 50 °C over a 1.5 h. The mixture was stirred at 50 °C for 8 h and poured into a 1 M solution of $\text{Na}_2\text{S}_2\text{O}_2$ (150 mL). Organic products were extracted with dichloromethane, the extracts were dried (Na_2SO_4), and the solvent was removed. After removing the solvent by evaporation, the product was purified by column chromatography with a toluene eluent. A white powder was obtained as a product (28.00 g, 80% yield).

^1H NMR (500 MHz, CDCl_3): δ , ppm 7.76 (t, $J = 7.20$ Hz, 1H), 6.98 (t, $J = 8.10$ Hz, 1H). MS (APCI) m/z 271.68[(M+H) $^+$].

5-Bromo-2,4-difluoro-2'-methoxy-1,1'-biphenyl (P2-5)

5-Bromo-2,4-difluoro-2'-methoxy-1,1'-biphenyl was synthesized using same synthetic method of 4-bromo-2,5-difluoro-2'-methoxy-1,1'-biphenyl (P1-5). 1,5-Dibromo-2,4-difluorobenzene (20 g, 7.36 mmol) was used instead of 1,4-dibromo-2,5-difluorobenzene. A white powder was obtained as a

product (5.19 g, yield 47.43%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 7.54 (dd, J = 9.70, 5.60 Hz, 1H), 7.39 (ddd, J = 8.30, 7.60, 1.70 Hz, 1H), 7.22 (dd, J = 7.50, 1.20 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.96 (dd, J = 14.30, 5.10 Hz, 2H), 3.81 (s, 3H). MS (APCI) m/z 299.08[(M+H)⁺].

5'-Bromo-2',4'-difluoro-[1,1'-biphenyl]-2-ol (P2-4)

5'-Bromo-2',4'-difluoro-[1,1'-biphenyl]-2-ol was synthesized using same synthetic method of 4'-bromo-2',5'-difluoro-[1,1'-biphenyl]-2-ol (P1-4). 5-Bromo-2,4-difluoro-2'-methoxy-1,1'-biphenyl (5.19 g, 17.35 mmol) was used instead of 4-bromo-2,5-difluoro-2'-methoxy-1,1'-biphenyl. A white solid was obtained as a product (4.95 g, yield 98.39%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 7.63 – 7.56 (m, 1H), 7.33 – 7.27 (m, 1H), 7.20 (d, J = 7.60 Hz, 1H), 7.04 – 6.93 (m, 3H), 5.45 – 4.90 (m, 1H). MS (APCI) m/z 283.93[(M+H)⁺].

2-Bromo-3-fluorodibenzo[*b,d*]furan (P2-3)

2-Bromo-3-fluorodibenzo[*b,d*]furan was synthesized using same synthetic method of 3-bromo-2-fluorodibenzo[*b,d*]furan (P1-3). 5'-Bromo-2',4'-difluoro-[1,1'-biphenyl]-2-ol (4.00 g, 11.9 mmol) was used instead of 4'-bromo-2',5'-difluoro-[1,1'-biphenyl]-2-ol. A white solid was obtained as a product (2.29 g, yield 72.94%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 8.11 (d, J = 6.80 Hz, 1H), 7.88 (dd, J = 7.70, 0.50 Hz, 1H), 7.56 (d, J = 8.30 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.39 – 7.35 (m, 2H). MS (APCI) m/z 263.87[(M+H)⁺].

2-(3-Fluorodibenzo[*b,d*]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (P2-2)

2-(3-Fluorodibenzo[*b,d*]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized using same synthetic method of 2-(2-fluorodibenzo[*b,d*]furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 2-Bromo-3-fluorodibenzo[*b,d*]furan was used instead of 3-bromo-2-fluorodibenzo[*b,d*]furan. The synthesized product was used in the next reaction without further purification (2.30 g, yield 8.55%). MS (APCI) m/z 313.82[(M+H)⁺].

2-(3-Fluorodibenzo[*b,d*]furan-2-yl)-4,6-diphenyl-1,3,5-triazine (P2-1)

2-(3-Fluorodibenzo[*b,d*]furan-2-yl)-4,6-diphenyl-1,3,5-triazine was synthesized using same synthetic method of 2-(2-fluorodibenzo[*b,d*]furan-3-yl)-4,6-diphenyl-1,3,5-triazine (P1-1). 2-(3-Fluorodibenzo[*b,d*]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used instead of 2-(2-fluorodibenzo[*b,d*]furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. A white solid was obtained as a product (1.60 g, yield 59.7%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 9.08 (d, J = 7.30 Hz, 1H), 8.84 – 8.78 (m, 4H), 8.09 (d, J = 7.60 Hz, 1H), 7.67 – 7.57 (m, 7H), 7.53 – 7.49 (m, 1H), 7.47 (d, J = 10.90 Hz, 1H), 7.43 (t, J = 7.40 Hz, 1H). MS (APCI) m/z 417.94[(M+H)⁺].

9-(2-(4,6-Diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan-3-yl)-9'-phenyl-9H,9'H-3,3'-bicarbazole (3Cz2Trz)

9-(2-(4,6-Diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan-3-yl)-9'-phenyl-9H,9'H-3,3'-bicarbazole was synthesized using same synthetic method of 9-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan-2-yl)-9'-phenyl-9H,9'H-3,3'-bicarbazole (2Cz3Trz). 2-(3-Fluorodibenzo[*b,d*]furan-2-yl)-4,6-diphenyl-1,3,5-triazine was used instead of 2-(2-fluorodibenzo[*b,d*]furan-3-yl)-4,6-diphenyl-1,3,5-triazine. A greenish-yellow powder was obtained as a product (1.59 g, yield 82.45%).

¹H NMR (500 MHz, CDCl₃): δ, ppm 9.13 (s, 1H), 8.43 (d, J = 1.60 Hz, 1H), 8.36 (d, J = 1.60 Hz, 1H), 8.22 (dd, J = 7.70, 1.00 Hz, 2H), 8.15 – 8.03 (m, 5H), 7.78 – 7.68 (m, 3H), 7.67 – 7.57 (m, 5H), 7.46 (dddd, J = 9.30, 8.30, 6.80, 3.70 Hz, 7H), 7.34 – 7.21 (m, 10H). ¹³C NMR (125 MHz, CDCl₃): δ, ppm 171.56, 171.56, 158.26, 157.65, 142.56, 141.54, 141.52, 140.19, 138.01, 136.10, 135.75, 134.67, 134.28, 132.56, 131.71, 130.12, 129.01, 128.57, 128.48, 127.65, 127.29, 126.38, 126.23, 126.02, 125.39, 125.21, 124.37, 124.19, 123.86, 123.84, 123.79, 121.58, 120.62, 120.17, 119.95, 119.15, 119.06, 114.10, 112.34, 110.23, 110.11, 110.09, 109.78. MS (APCI) m/z 806.10[(M+H)⁺].

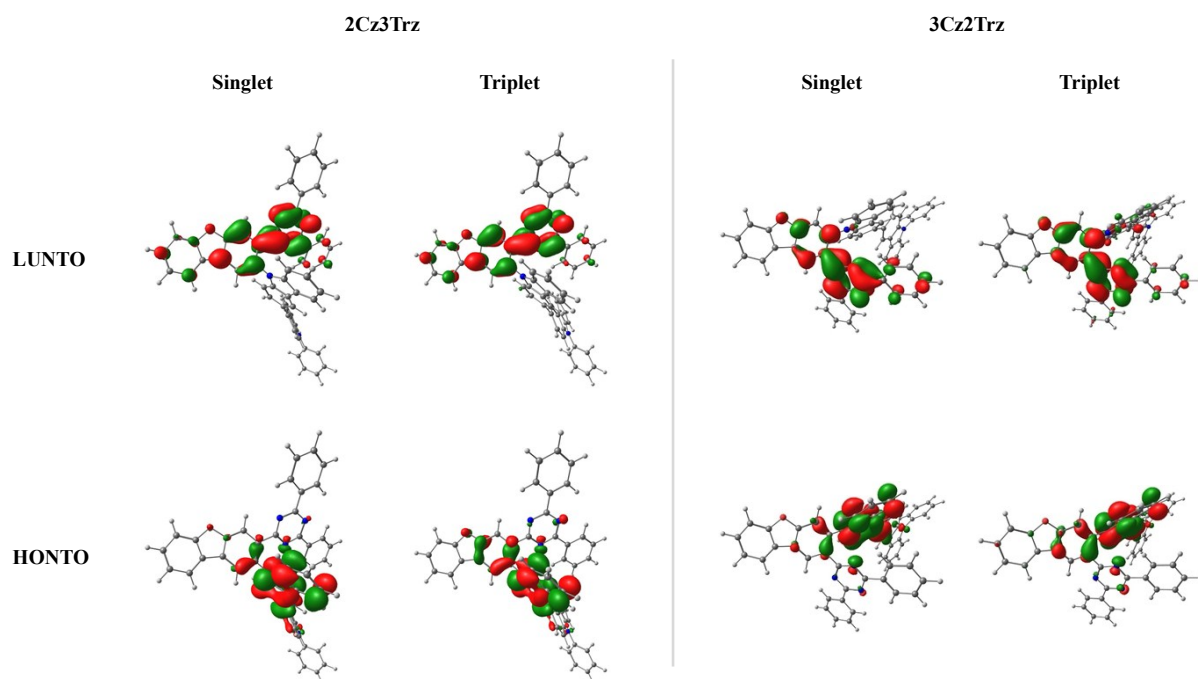


Figure S1. TDDFT simulations of singlet and triplet excited states for (a) 2Cz3Trz and (B) 3Cz2Trz.

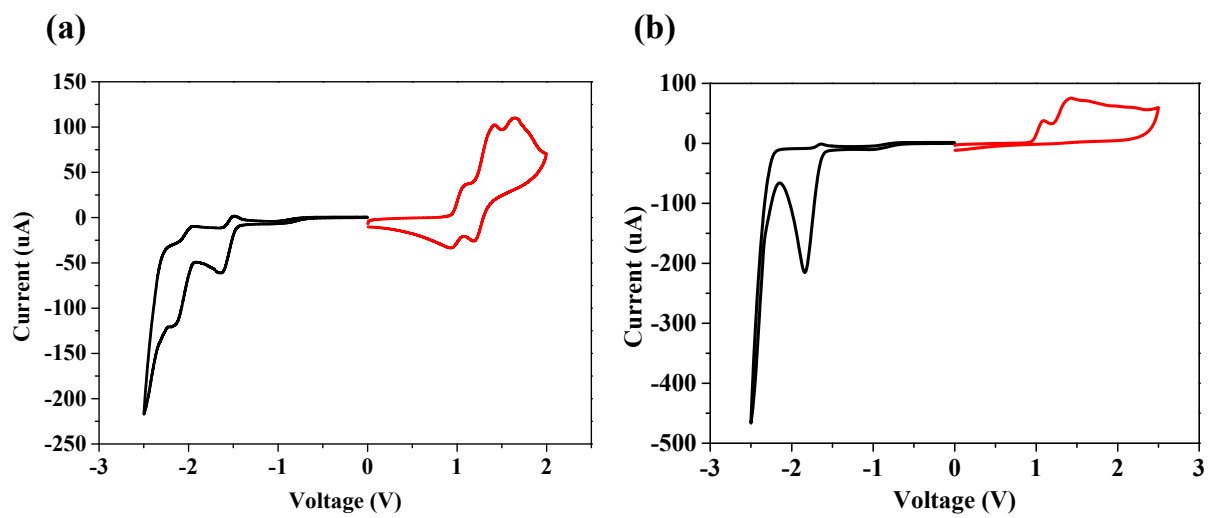


Figure S2. Cyclic voltammetry scan data of (a) 2Cz3Trz and (b) 3Cz2Trz emitters.

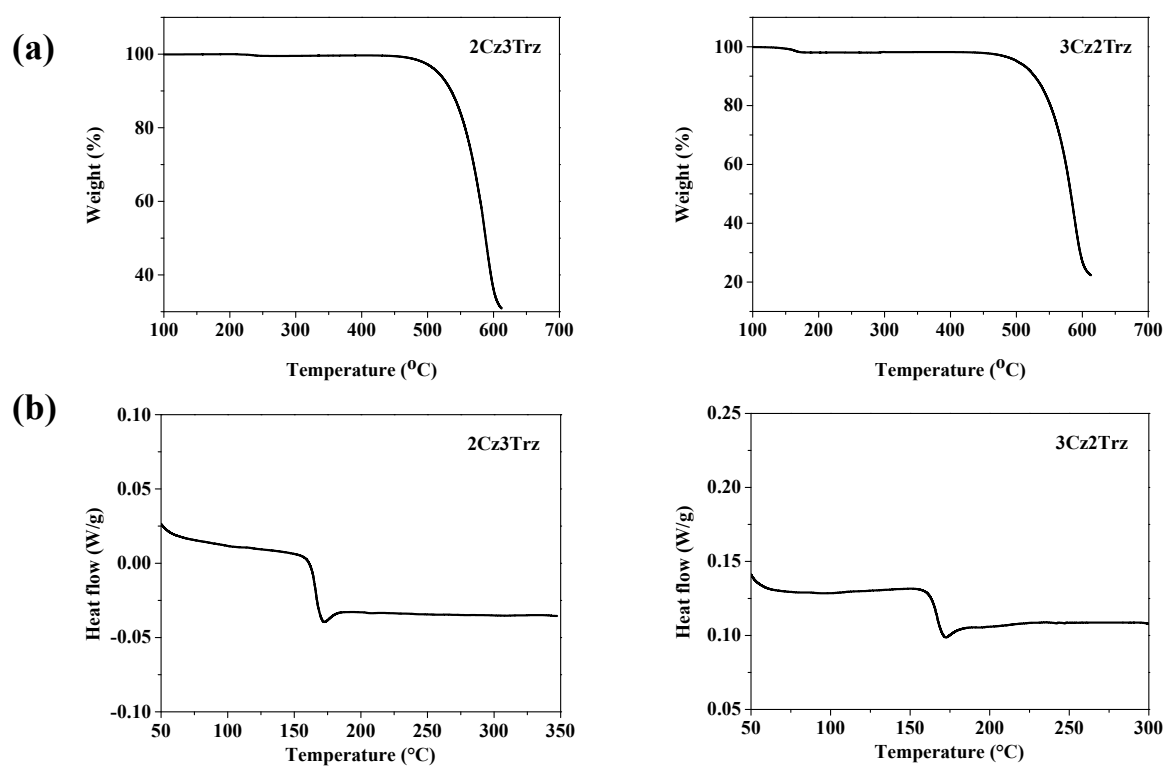
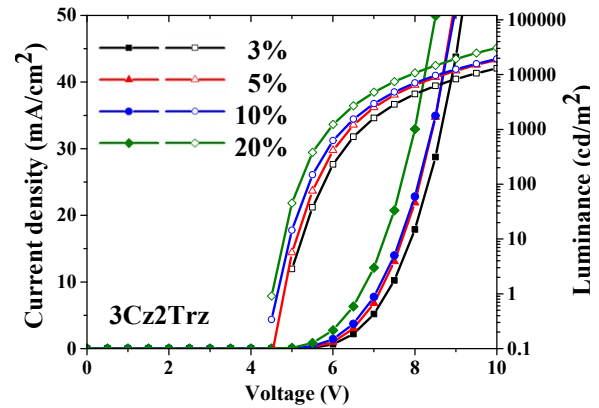
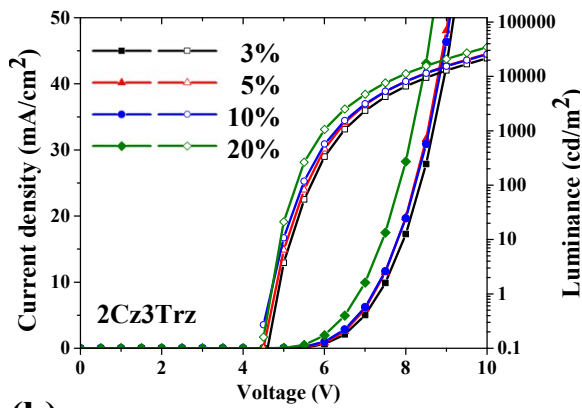


Figure S3. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) results of the 2Cz3Trz and 3Cz2Trz.

(a)



(b)

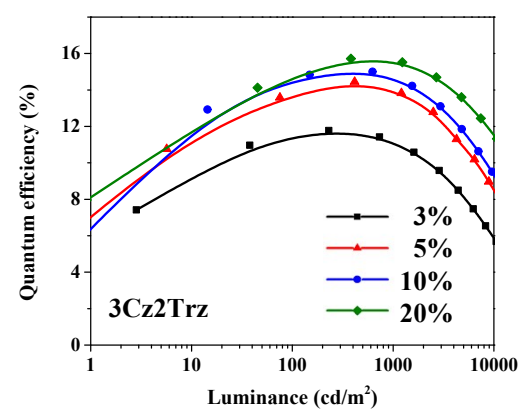
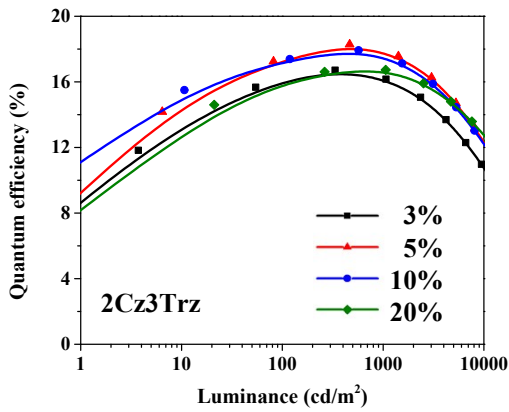


Figure S4. (a) Current density and luminance data of the 2Cz3Trz and 3Cz2Trz devices according to voltage, (b) EQE of the 2Cz3Trz and 3Cz2Trz devices according to current density at 3, 5, 10, 20% doping concentrations.

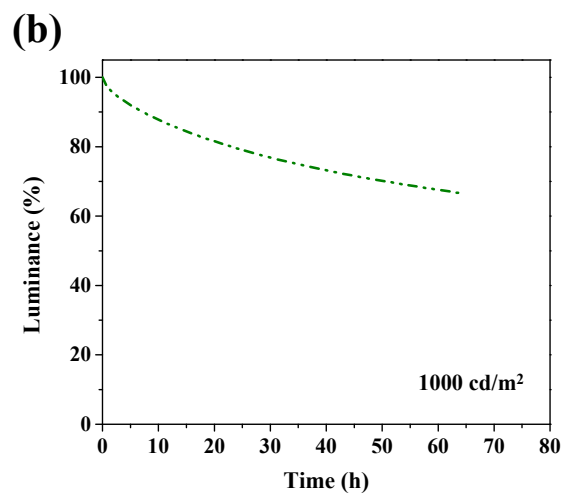
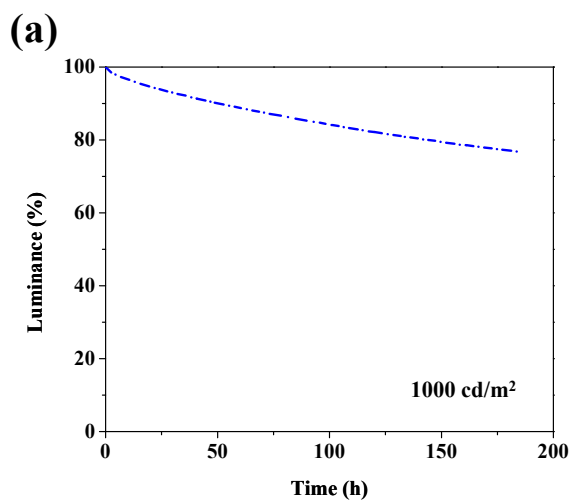


Figure S5. Device stability at 10% doping concentration of (a) 2Cz3Trz and (b) 3Cz2Trz devices.

Table S1. Device performance of 2Cz3Trz and 3Cz2Trz devices.

2Cz3Trz	V(V)	CIE (x, y)	QE(%)	LE(lm/W)	J(Cd/A)
			[Max]	[Max]	[Max]
3%	7.2	(0.30, 0.55)	16.7	28.0	52.3
5%	7.0	(0.30, 0.56)	18.3	31.0	57.5
10%	7.0	(0.31, 0.56)	17.9	31.6	57.0
20%	6.6	(0.31, 0.57)	16.7	30.5	53.8

3Cz2Trz	V(V)	CIE (x, y)	QE(%)	LE(lm/W)	J(Cd/A)
			[Max]	[Max]	[Max]
3%	7.5	(0.26, 0.50)	11.8	18.3	34.5
5%	7.1	(0.25, 0.50)	14.5	22.4	41.9
10%	7.0	(0.26, 0.50)	15.0	24.7	43.8
20%	6.6	(0.25, 0.50)	15.7	25.9	45.4