

Supporting information

A novel electroplex host with dual triplet exciton up-converting channels suppressing triplet exciton induced degradation mechanisms in blue organic light-emitting diodes

**Ju Hui Yun^{1†}, Jae-Min Kim^{1†}, Won Jae Chung¹, Junseop Lim¹ and Jun Yeob Lee^{1*}
Yoonkyoo Lee², Changwoong Choo²**

¹School of Chemical Engineering, Sungkyunkwan University
2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Korea

²Display Research Center, Samsung Display Co.

1 Samsung-ro, Giheung-gu, Yongin, Gyeonggi-do, Korea

E-mail: leej17@skku.edu

* To whom correspondence should be addressed

†This work was equally contributed by J. H. Yun and J.-M. Kim

Experimental

General information

3-Bromobenzonitrile was purchased from Thermo Fisher Scientific Inc. and 9H-carbazole, n-butyllithium, cyanuric chloride were supplied from Sigma Aldrich Co.. 2,4-Dichloro-6-phenyl-1,3,5-triazine was received from Sunfine Global Co., Ltd. and bis(pinacolato)diboron, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($\text{PdCl}_2(\text{dppf})$), tetrakis(triphenylphosphine)palladium (0) ($\text{Pd}(\text{PPh}_3)_4$) were provided from GOM technology Co., LTD.. Potassium acetate, potassium carbonate, celite, magnesium sulfate, 1,4-dioxane from Daejung Chemicals & Metals Co. LTD. and tetrahydrofuran (THF), methylene chloride (MC), toluene, n-hexane from Samchun Pure Chemical Co. were used without further purification. 9H-carbazole was used after recrystallization with toluene and THF was distilled with calcium hydride and sodium.

Synthesis

Synthesis of (3-bromophenyl)triphenylsilane, triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane were described in our previous work.^[1]

9-(4,6-Dichloro-1,3,5-triazin-2-yl)-9H-carbazole

9H-carbazole (2.0 g, 12.0 mmol) was dissolved in dried THF (20 ml) under N_2 atmosphere and the solution was cooled down to 0 °C. n-Butyllithium (5.26 ml, 13.2 mmol) was added dropwisely and stirred for 30 min. The reagent was dropwised in cyanuric chloride (2.17 g, 12.0 mmol) dissolved in dehydrated THF (30 ml). After 10 min, distilled water was poured into the reaction and extracted with MC. The crude was purified by column chromatography and obtained as a white powder (2.21 g, yield 63.7%). ^1H NMR (300 MHz, CDCl_3): δ 8.847 (d, 2H, $J=8.4$ Hz), 7.987 (d, 2H, $J=7.5$ Hz), 7.533 (t, 2H, $J=7.2$ Hz), 7.451 (t, 2H, $J=7.5$ Hz).

LC/MS (m/z): found, 315.01 ($[M + H]^+$); Calcd. for $C_{15}H_8Cl_2N_4$, 315.16.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile was synthesized by following same synthetic route of 9-(4-(Diphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silyl)phenyl)-9H-carbazole. 3-Bromobenzotrile (5.0 g, 27.5 mmol) was used as a reactant instead of 9-(4-((4-bromophenyl)diphenylsilyl)phenyl)-9H-carbazole (5.70 g, yield 90.6%). 1H NMR (300 MHz, $CDCl_3$): δ 8.088 (s, 1H), 8.000 (d, 1H, $J=7.5$ Hz), 7.718 (d, 1H, $J=7.8$ Hz), 7.465 (t, 1H, $J=7.65$ Hz), 1.347 (s, 12H). LC/MS (m/z): found, 229.18 ($[M + H]^+$); Calcd. for $C_{13}H_{16}BNO_2$, 229.08.

3-(4-(9H-carbazol-9-yl)-6-chloro-1,3,5-triazin-2-yl)benzotrile

3-(4-(9H-carbazol-9-yl)-6-chloro-1,3,5-triazin-2-yl)benzotrile was synthesized with same procedure of 3-(4-(4-((4-(9H-carbazol-9-yl)phenyl)diphenylsilyl)phenyl)-6-phenyl-1,3,5-triazin-2-yl)benzotrile using 9-(4,6-dichloro-1,3,5-triazin-2-yl)-9H-carbazole (1.0 g, 3.17 mmol) and 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (0.73 g, 3.17 mmol) as reagents. The precipitate was filtered and grayish white powder was obtained without further purification (0.90 g, 74.4%). LC/MS (m/z): found, 382.09 ($[M + H]^+$); Calcd. for $C_{22}H_{12}ClN_5$, 381.82.

3-(4-(9H-carbazol-9-yl)-6-(3-(triphenylsilyl)phenyl)-1,3,5-triazin-2-yl)benzotrile (SiTCNCz)

3-(4-(9H-carbazol-9-yl)-6-chloro-1,3,5-triazin-2-yl)benzotrile (0.88 g, 2.30 mmol) and triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1.17 g, 2.54 mmol) were dissolved in 1,4-dioxane (20 ml). 2M aqueous potassium carbonate (10 ml) and $Ph(PPh_3)_4$

(0.08 g, 0.07 mmol) were added and refluxed overnight. The reaction solution was extracted with MC and purified by column chromatography with chloroform as an eluent. The product was recrystallized with toluene/methanol and sublimated under vacuum condition (0.81 g, yield 51.6 %). ^1H NMR (500 MHz, CDCl_3): δ 8.970 (s, 1H), 8.941 (d, 2H, $J=8.0$ Hz), 8.789 (s, 1H), 8.768 (d, 1H, $J=8.0$ Hz), 8.732 (d, 2H, $J=8.0$ Hz), 7.999 (d, 2H, $J=8.0$ Hz), 7.905 (d, 1H, $J=7.5$ Hz), 7.870 (d, 1H, $J=8.0$ Hz), 7.689-7.642 (m, 8H), 7.526-7.492 (m, 3H), 7.465-7.359 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3): δ 172.98, 170.39, 165.24, 141.14, 139.05, 137.62, 137.34, 136.66, 135.78, 135.30, 133.92, 133.14, 132.63, 130.51, 130.18, 129.80, 128.72, 128.31, 127.33, 126.91, 123.75, 119.88, 118.68, 117.85, 113.36. MS (m/z): found, 682.2427 ([FAB] $^+$); Calcd. for $\text{C}_{46}\text{H}_{31}\text{N}_5\text{Si}$, 682.2427.

List of figures

Figure S1. Molecular orbital distribution of SiTCNCz.

Figure S2. CV curve of SiTCNCz.

Figure S3. Current density-voltage characteristics of (a) electron only device and (b) hole only device of SiTrz and SiTCNCz.

Figure S4. (a) Differential scanning calorimetry and (b) thermogravimetric analysis curves of SiTCNCz.

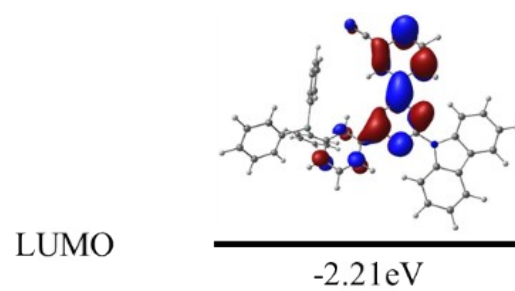
Figure S5. Modeling of transient EL decay curve of OLEDs with applying various values in one parameter from best fitting results. (a) k_{ISC} , (b) k_{RISC} , (c) k_T , (d) γ , and (e) N_{add} were varied.

Figure S6. Chemical structure of materials and device architecture of deep blue PhOLEDs.

Figure S7. (a) Current density (J)-Voltage (V)-Luminance (L), (b) external quantum efficiency (EQE)-Luminance (L), (c) EL spectrum, and (d) luminance decay during operation of mCBP single host based PhOLED. The condition of device lifetime was constant current aging corresponding to initial luminance of 100 cd/m².

Figure S8. Current-voltage characteristics of single n-type host based PhOLEDs.

Figure S9. Transient EL decay curve of SiTrz and SiTCNCz single host based PhOLEDs.



SiTCNCz

$E_S = 3.23 \text{ eV}$

$E_T = 3.05 \text{ eV}$

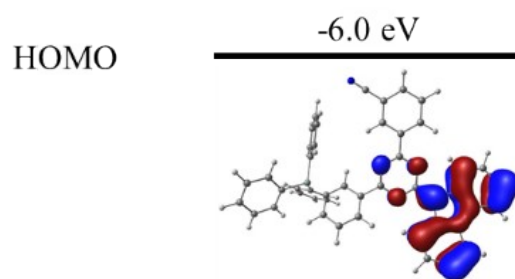


Figure S1. Molecular orbital distribution of SiTCNCz.

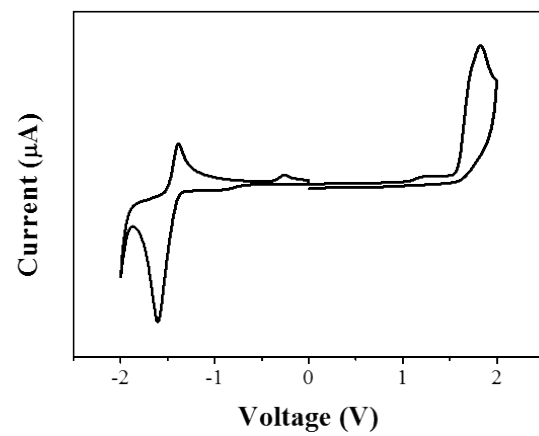


Figure S2. CV curve of SiTCNCz.

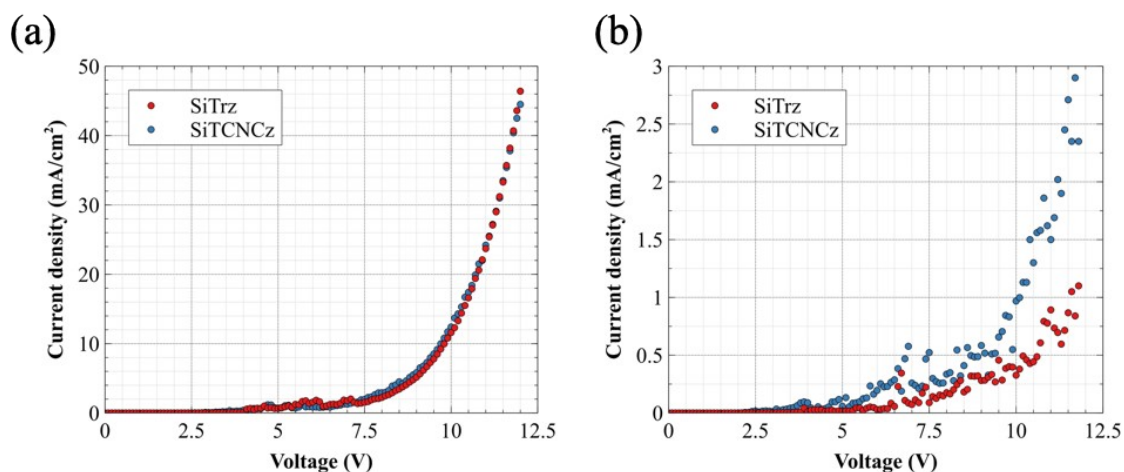


Figure S3. Current density-voltage characteristics of (a) electron only device and (b) hole only device of SiTrz and SiTCNCz. Device structures were ITO/DBFTrz (10 nm)/Material (50 nm)/DBFTrz(10 nm)/LiF/Al for EOD and ITO/BCFA:HATCN (30%, 10 nm)/BCFA(10 nm)/Material (50 nm)/BCFA(10 nm)/Al for HOD. (BCFA: N- 79 ([1,10-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine)

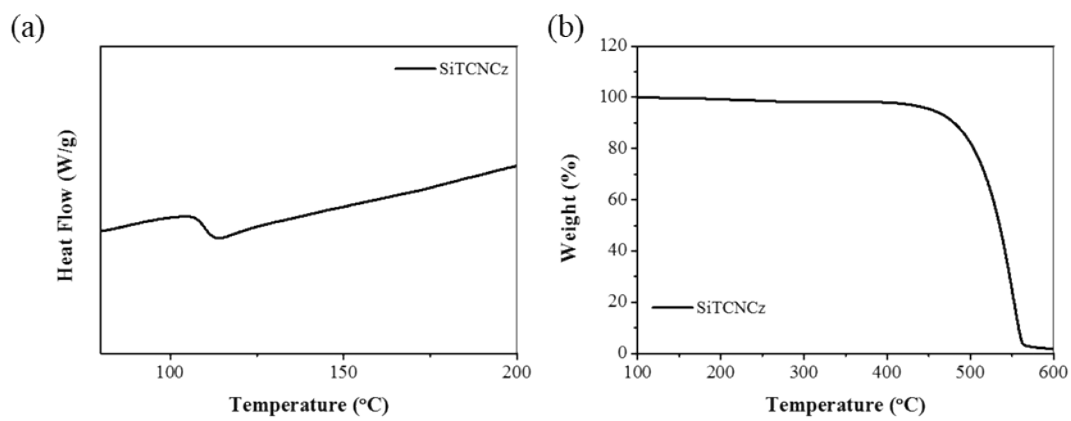


Figure S4. (a) Differential scanning calorimetry and (b) thermogravimetric analysis curves of SiTCNCz.

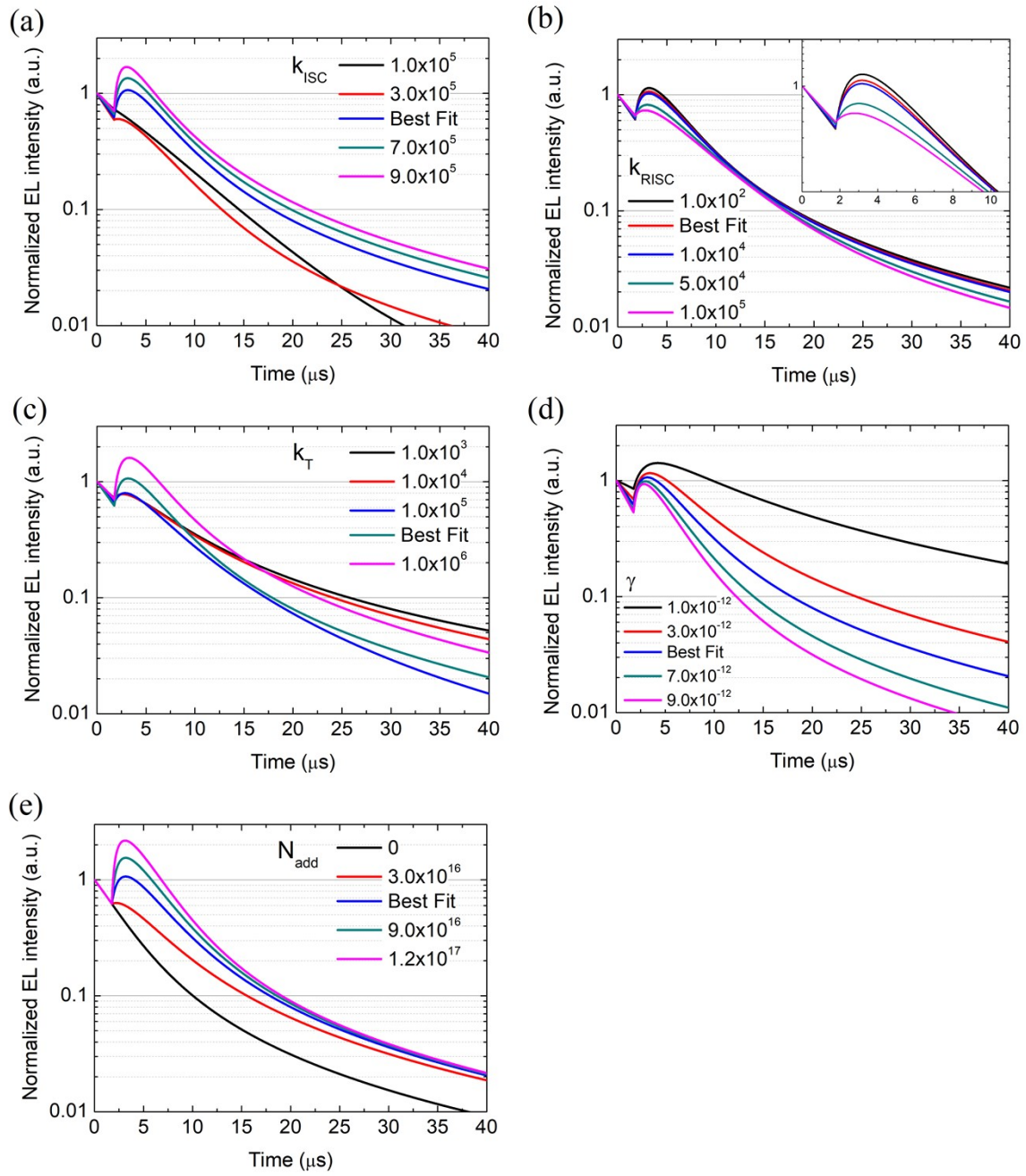


Figure S5. Modeling of transient EL decay curve of OLEDs with applying various values in one parameter from best fitting results. (a) k_{ISC} , (b) k_{RISC} , (c) k_T , (d) γ , and (e) N_{add} were varied.

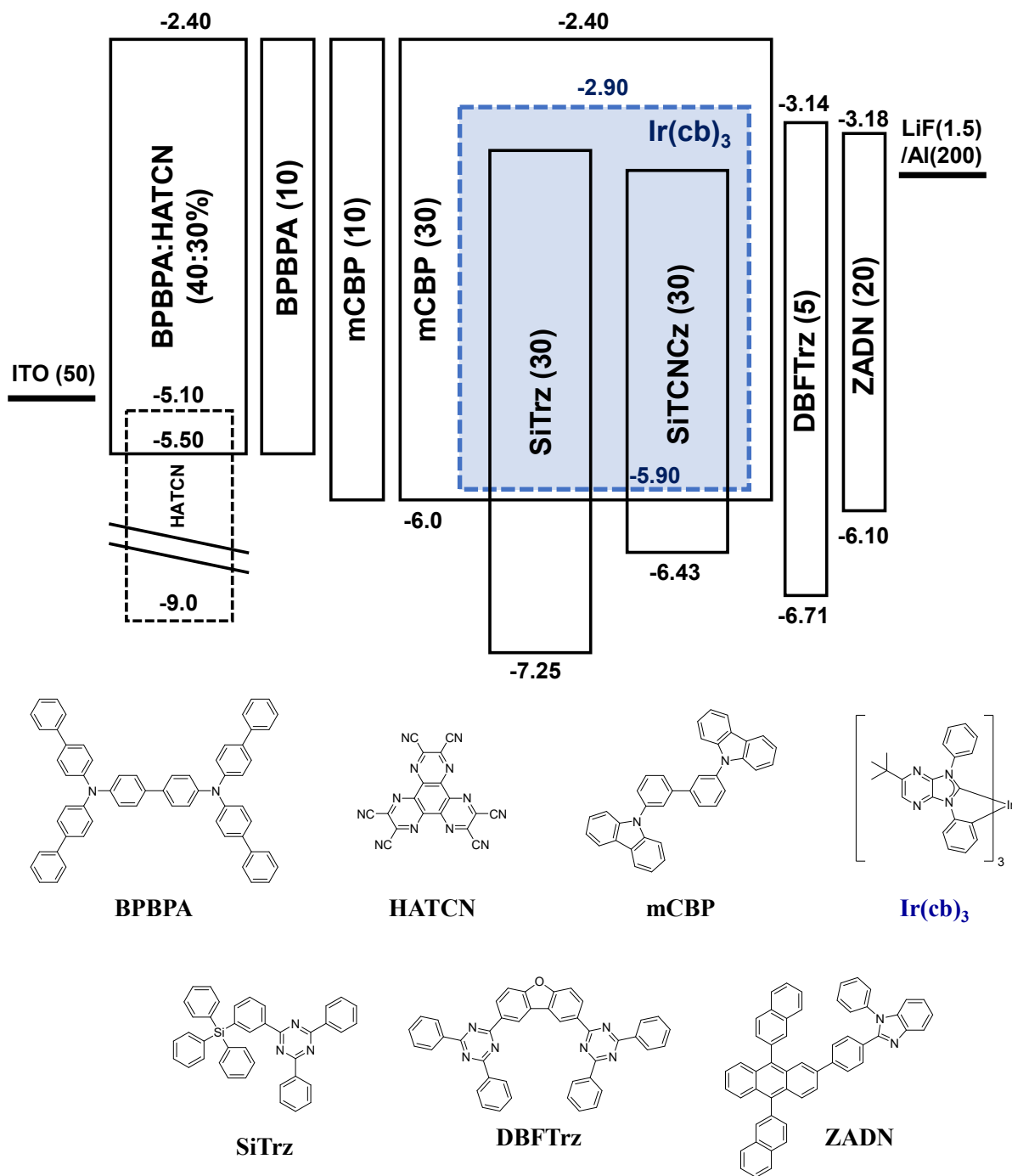


Figure S6. Chemical structure of materials and device architecture of deep blue PhOLEDs.

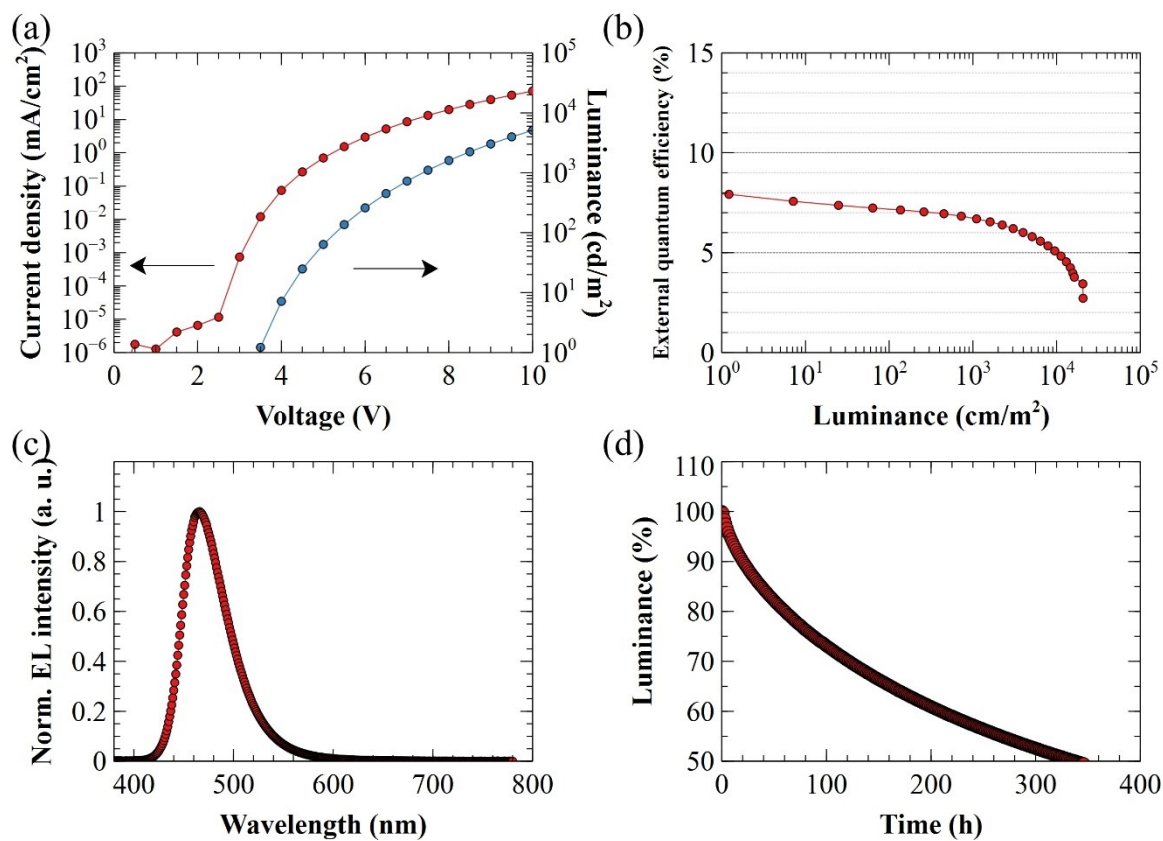


Figure S7. (a) Current density (J)-Voltage (V)-Luminance (L), (b) external quantum efficiency (EQE)-Luminance (L), (c) EL spectrum, and (d) luminance decay during operation of mCBP single host based PhOLED. The condition of device lifetime was constant current aging corresponding to initial luminance of 100 cd/m².

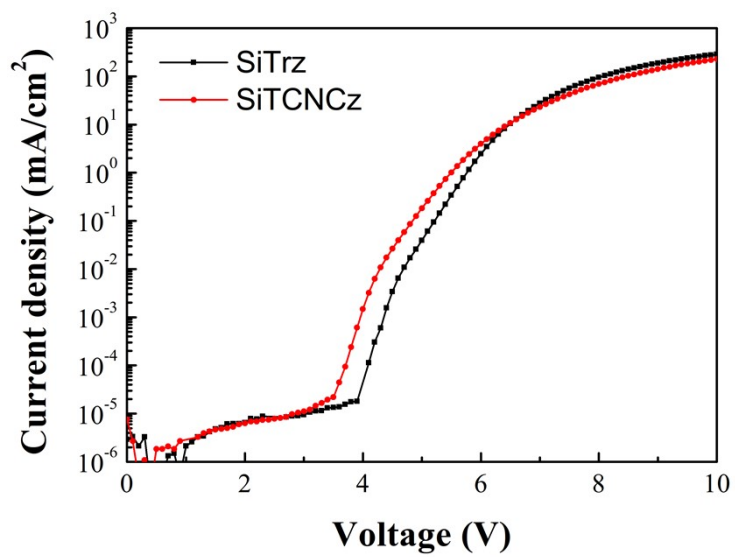


Figure S8. Current-voltage characteristics of single n-type host based PhOLEDs.

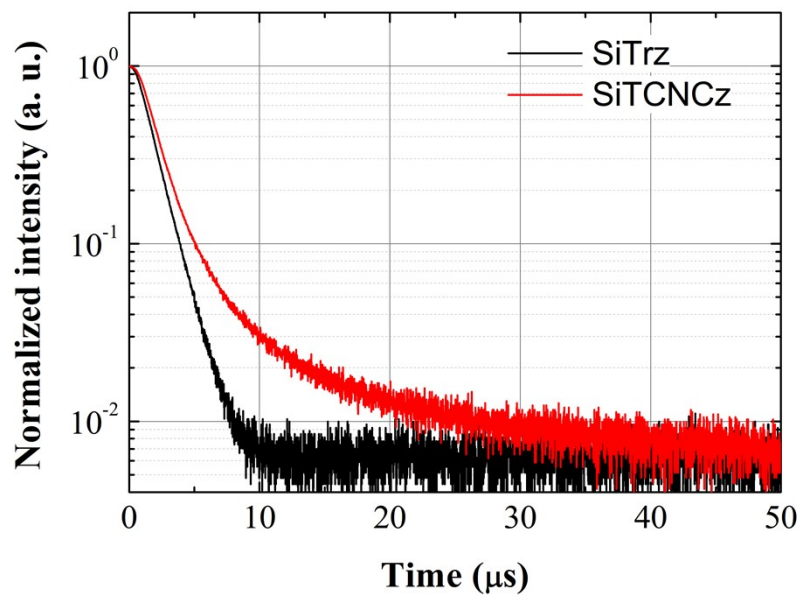


Figure S9. Transient EL decay curve of SiTrz and SiTCNCz single host based PhOLEDs.

References

- [1] K. H. Choi, K. H. Lee, J. Y. Lee, T. Kim, *Adv. Opt. Mater.* **2019**, 7, 1.