

Supplementary Information

Simultaneous improvement of emission color, singlet-triplet energy gap, and quantum efficiency of blue thermally activated delayed fluorescent emitters using 1-carbazolylcarbazole based donor

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Experimental

Synthesis

1-Bromo-2-nitrobenzene, potassium carbonate, tetrahydrofuran, and 1,4-dioxane were purchased from Duksan Sci. Co. Tetrakis(triphenylphosphine)palladium(0) was purchased from P&H Co. 2-Chloro-4,6-diphenyl-1,3,5-triazine, and 9H-3,9'-bicarbazole were obtained from Sun fine global Co. Copper iodide, triphenyl phosphine, 1,2-dichlorobenzene, sodium hydride, N, N-dimethylformamide, (±)-trans-1,2-diaminocyclohexane, and 9H-carbazole were obtained from Aldrich. Co.

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

Sodium hydride of 60% oil dispersion (0.14g, 5.69 mmol) was added in 100ml 2 neck round-bottom (RB) flask and washed with hexane 2times. After remove all hexane, N, N-dimethylformamide (30ml) was added in RB. After 10min, 1-bromo-9H-carbazole (0.70g, 2.84 mmol) powder was added. After 20min, 2-chloro-4,6-diphenyl-1,3,5-triazine (0.91g, 3.41 mmol) was added in the mixture. The mixture was heated 60 °C, 12h and poured into water and filtered residual product. The white powder was obtained to 1.1g (yield 80%). ¹H NMR (400

MHz, DMSO): δ 8.72 (d, 4H, $J=6.8\text{Hz}$), 8.48-8.29 (m, 3H), 7.85 (d, 1H, $J=7.2\text{Hz}$), 7.77-7.42 (m, 9H). MS (FAB) m/z 477.0 [(M+H)⁺].

9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-1,9'-bicarbazole (1CzCzTrz)

1-bromo-9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazole (0.70g, 1.47 mmol), 9H-Carbazole (0.32g, 1.91 mmol), copper iodide (0.16g, 0.88 mmol), and potassium phosphate (1.87g, 8.80 mmol) were added in 100ml 2 neck RB. After vacuum 2h, 1,4-dioxane (40ml) was added in RB. After 10min, (\pm)-trans-1,2-diaminocyclohexane (0.10g, 0.88mmol) were added in RB. And the mixture was reflux 24h and cooled room temperature and extracted with ethyl acetate and water. The organic layer was dried over MgSO_4 and concentrated. The mixture was purified by column chromatography (ethyl acetate : hexane = 1:16) and again by sublimation. The white powder was obtained to 0.2 g (yield 24%). ¹H NMR (400 MHz, CDCl_3): δ 8.28 (d, 1H, $J=8.0\text{Hz}$), 8.22 (d, 1H, $J=6.8\text{Hz}$), 8.10 (d, 1H, $J=8.0\text{Hz}$), 8.04 (d, 4H, $J=8.4\text{Hz}$), 7.80 (d, 1H, $J=8.0\text{Hz}$), 7.62 (t, 1H, $J=15.6\text{Hz}$), 7.55 (d, 2H, $J=7.6\text{Hz}$), 7.51-7.42 (m, 4H), 7.34-7.29 (m, 6H), 7.13 (t, 2H, $J=14\text{Hz}$), 6.75 (t, 2H, $J=15.2\text{Hz}$). ¹³C NMR (100MHz, CDCl_3): δ 171.6, 140.5, 139.5, 135.1, 132.1, 129.0, 128.7, 128.3, 127.5, 126.9, 125.8, 125.1, 123.9, 123.2, 122.9, 122.7, 120.3, 120.2, 119.8, 119.6, 113.0, 110.4. MS (FAB) m/z 564.3[(M+H)⁺].

9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-3,9'-bicarbazole (3CzCzTrz)

3CzCzTrz was synthesized by the same procedure of 1-bromo-9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazole. 9H-3,9'-bicarbazole (0.70g, 2.11 mmol) was used instead of 1-bromo-9H-carbazole. The mixture was washed with hexane and dichloromethane followed by purification again by sublimation. The greenish powder was obtained to 0.9g (yield 76%). ¹H NMR (400 MHz, CDCl_3): δ 9.37 (d, 1H, $J=9.2\text{Hz}$), 9.21 (d, 1H, $J=8.8\text{Hz}$), 8.76 (d, 4H, $J=8.0\text{Hz}$), 8.22 (t, 3H, $J=15.6\text{Hz}$), 8.04 (d, 1H, $J=8.0\text{Hz}$), 7.77 (d, 1H, $J=8.8\text{Hz}$), 7.68-7.61 (m, 7H), 7.52-7.43 (m,

5H), 7.33 (t, 2H, J=16.0Hz). ¹³C NMR (100MHz, CDCl₃): δ 172.7, 165.3, 141.6, 139.9, 138.2, 136.3, 133.1, 133.0, 129.3, 129.0, 128.2, 127.9, 126.2, 126.1, 123.7, 123.5, 120.5, 120.1, 120.0, 119.2, 118.5, 118.1, 110.0. MS (FAB) m/z 564.4[(M+H)⁺].

9,9'-(2'-nitro-[1,1'-biphenyl]-3,5-diyl)bis(9H-carbazole)

1-Bromo-2-nitrobenzene (1.15g, 5.69 mmol) and 9,9'-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-phenylene)bis(9H-carbazole) (3.65g, 6.83 mmol) were added in 100ml 2 neck RB and added tetrahydrofuran (50 ml). 2M of potassium carbonate solution (25 ml) and tetrakis(triphenylphosphine)palladium(0) (0.19 g, 0.17 mmol) were added to the solution, and the solution was refluxed and stirred for 12h. The mixture was evaporated to remove residual solvent and extracted with methylene chloride and water. The combined organic layer was dried over MgSO₄ and concentrated. Purification by column chromatography using methylene chloride and hexane (from 1:9 to 1:4, gradually). The greenish yellow powder was obtained to 2.6 g (yield 85%). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, 4H, J=7.6Hz), 8.01 (d, 1H, J=8.4Hz), 7.87 (s, 1H), 7.72-7.55 (m, 9H), 7.46 (t, 4H, J=14.8Hz), 7.31 (t, 4H, J=15.2Hz).

9'H-9,1':3',9''-tercarbazole

9,9'-(2'-nitro-[1,1'-biphenyl]-3,5-diyl)bis(9H-carbazole) (2.55g, 4.82 mmol) and triphenyl phosphine (3.16g, 12.04 mmol) were added in 100ml 2 neck RB and added 1,2-dichlorobenzene (60ml). The mixture was refluxed for 24h and cooled to room temperature. The solvent was removed using oil bath with vacuum and washed hexane. The mixture was extracted with ethyl acetate and water. The organic layer was dried over MgSO₄ and concentrated. Purification by column chromatography using ethyl acetate and hexane (1:9). The white powder was obtained to 1.8g (yield 76%). ¹H NMR (400 MHz, CDCl₃): δ 8.40 (s,

1H), 8.23 (d, 2H, J=8.0Hz), 8.19 (d, 2H, J=7.6Hz), 8.15 (d, 1H, J=7.6Hz), 7.98 (s, 1H), 7.82 (s, 1H), 7.53-7.30 (m, 15H).

9'-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'H-9,1':3',9''-tercarbazole (13CzCzTrz)

13CzCzTrz was synthesized by the same procedure of 1-bromo-9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazole. 9'H-9,1':3',9''-tercarbazole (0.70g, 2.11 mmol) was used instead of 1-bromo-9H-carbazole. The mixture was washed with hexane and dichloromethane followed by purification and again by sublimation. The greenish powder was obtained to 0.2g (yield 45%). ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 8.20 (d, 4H, J=8.0Hz), 8.08 (d, 4H, J=8.0Hz), 8.01 (s, 1H), 7.62 (d, 2H, J=8.0Hz), 7.54 (d, 3H, J=8.4Hz), 7.46 (d, 4H, J=7.6Hz), 7.39 (s, 1H), 7.37-7.32 (m, 8H), 7.15 (t, 2H, J=15.2Hz), 6.76 (t, 2H, J=14Hz). ¹³C NMR (100MHz, CDCl₃): δ 171.7, 164.3, 141.5, 141.1, 139.3, 135.0, 133.0, 132.8, 132.3, 130.1, 128.8, 128.4, 128.3, 126.3, 126.0, 125.5, 124.9, 124.6, 123.6, 123.3, 123.1, 120.6, 120.23, 119.9, 118.4, 113.4, 110.3, 109.9. MS (FAB) m/z 729.8[(M+H)⁺].

Measurements

Electrical characteristics of the fabricated devices were analyzed using Keithley 2400 source measurement unit and light emission characteristics were measured using CS 2000 spectroradiometer. The photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (HITACHI, F-7000) and the ultraviolet-visible (UV-vis) spectra were obtained using a UV-vis spectrophotometer (Shimadzu, UV-2501PC). The ¹H nuclear magnetic resonance (NMR) was recorded on a JEOL 400 (400 MHz) spectrometer. The ¹³C nuclear magnetic resonance (NMR) was recorded on a JEOL 400 (100 MHz) spectrometer.

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Figure S2. Cyclic voltametry curves of (a) 1CzCzTrz, (b) 3CzCzTrz, and (c) 13CzCzTrz.

Figure S3. Current density-voltage-luminance data of 1CzCzTrz, 3CzCzTrz, and 13CzCzTrz devices.

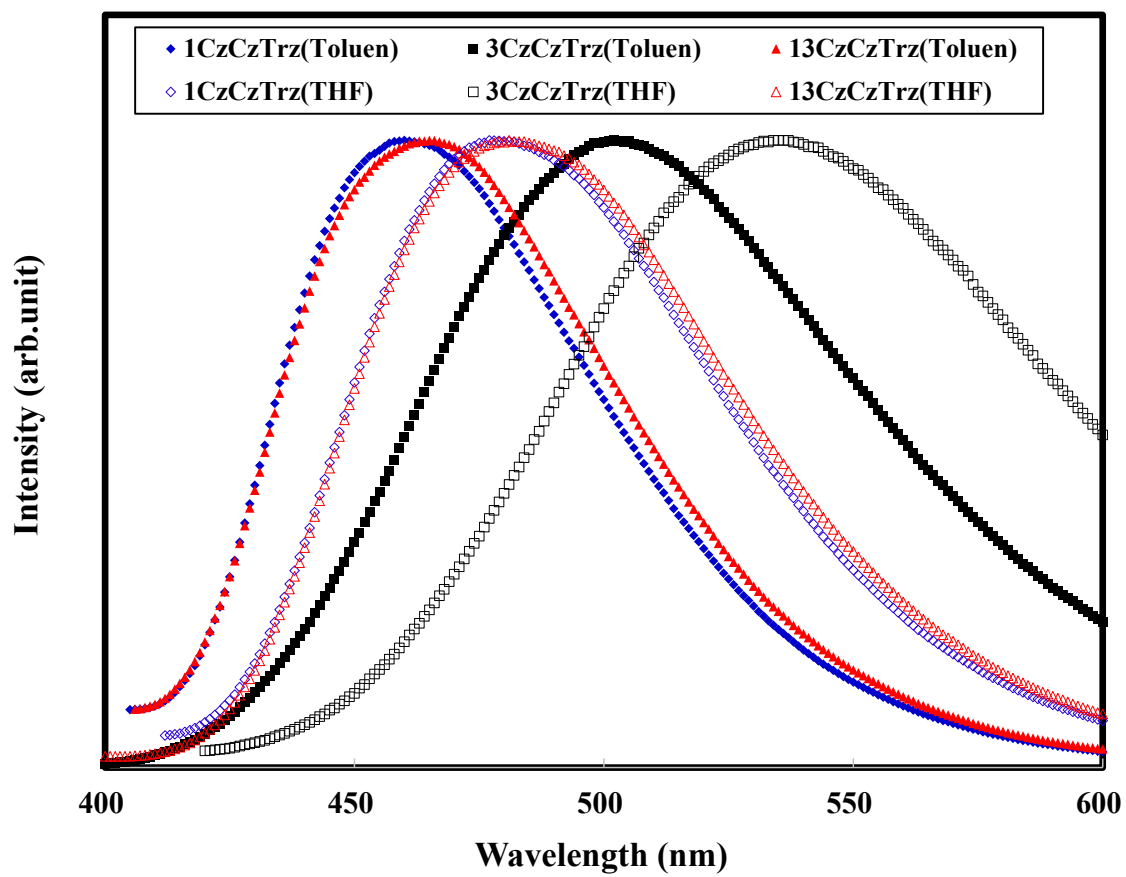


Figure S1

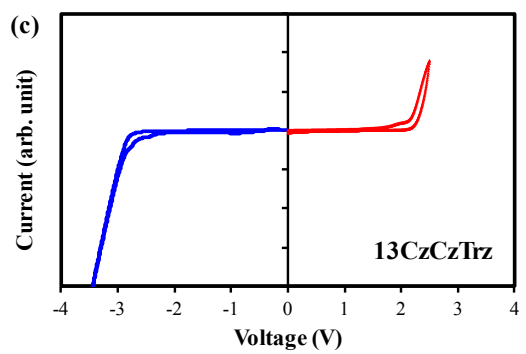
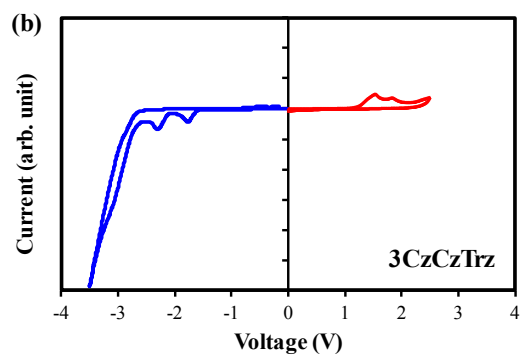
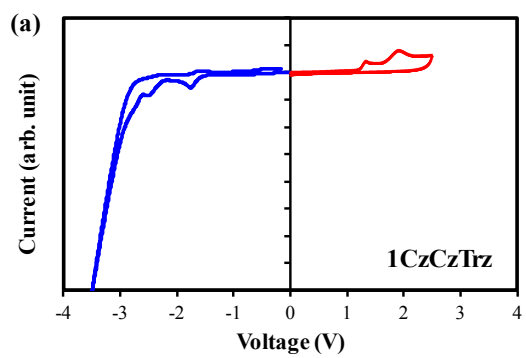


Figure S2

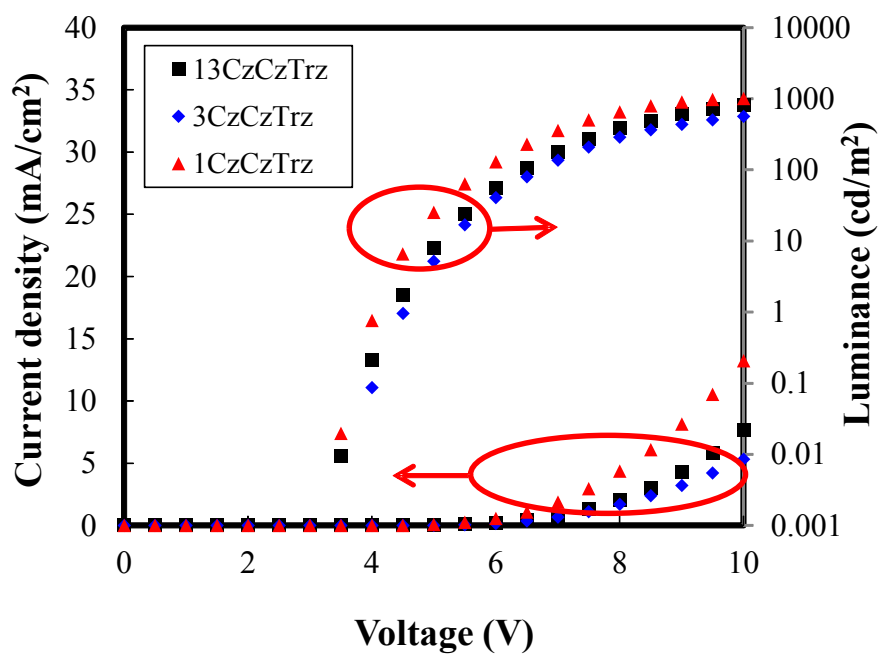


Figure S3

