

Supporting information

Novel molecular design employing a backbone freezing linker for improved efficiency, sharpened emission and long lifetime in thermally activated delayed fluorescent emitters

Ji Gwang Yu¹⁺, Si Hyun Han¹⁺, Ha Lim Lee¹⁺, Wan Pyo Hong^{2*}, Jun Yeob Lee^{1*}

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

² LG Chem, Ltd, LG Science Park, 30, Magokjungang 10-ro, Gangseo-gu, Seoul, 07796, Republic of Korea

* Corresponding author

E-mail: leej17@skku.edu, whongw@lgchem.com

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General information

A 2.5 M concentration of *n*-butyl lithium solution in *n*-hexane and triethyl borate were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) was purchased from Samchun Chem. Co. Ltd. Potassium carbonate (K₂CO₃) was purchased from Duksan Sci. 2-Chloro-4,6-diphenyl-1,3,5-triazine and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were products of P&H tech. 9-Phenyl-9H,9'H-3,3'-bicarbazole, 9,9'-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole and 5-phenyl-5,12-dihydroindolo[3,2-*a*]carbazole were obtained from LG Chem.

Synthesis

Synthesis of 2-(3-fluorodibenzo[*b,d*]furan-4-yl)-4,6-diphenyl-1,3,5-triazine

3-Fluorodibenzo[*b,d*]furan (2.86 g, 15.36 mmol) was put into a two-neck round-bottomed flask filled with distilled tetrahydrofuran (10 ml) under an inert gas condition (N₂) and stirred at room temperature for 10 min. Shortly thereafter, the solution was cooled to -78 °C and maintained at this temperature for 30 min. After 30 min, 2.5 M *n*-butyl lithium solution in *n*-hexane (7.37 mL, 18.43 mmol) was added very carefully and stirred at -78 °C for 1 h. Then, triethyl borate (3.15 ml, 18.43 mmol) was injected into the solution, which was then stirred for 6 h. The reaction was quenched using a 2 M HCl solution with deionized water, maintained for 30 min and extracted with methylene chloride and deionized water. The methylene chloride layer was separated and the solvent was evaporated. An oily intermediate (2.12 g, 9.22 mmol) was obtained and it was put into a two-neck round-bottomed flask filled with tetrahydrofuran (100 mL) and deionized water (50 mL) under an inert condition (N₂). 2-Chloro-4,6-diphenyl-1,3,5-triazine (2.96 g, 11.06 mmol), potassium carbonate (3.82 g, 27.66 mmol) and Pd(PPh₃)₄ (0.53 g, 0.46 mmol) were charged into the flask and were stirred at 260 °C overnight. Then, the flask was cooled and the reaction mixture was extracted using a separatory funnel with

methylene chloride and deionized water. The organic layer was separated and the methylene chloride was evaporated. Purification by column chromatography (methylene chloride: n-hexane=1:4) and drying afforded a white powder as a product (3.0 g, 78% yield).

¹H NMR (500 MHz, dimethylsulfoxide-d₆): δ=8.72-8.71 (d, J=8.5 Hz, 4H), 8.50-8.47 (t, J=7.0 Hz, 1H), 8.29-8.27 (d, J=8.0 Hz, 1H), 7.80-7.74 ppm (m, 3H), 7.71-7.68 (d, J=7.5 Hz, 4H), 7.60-7.56 (d, J=9.75 Hz, 2H), 7.52-7.49 (t, J=8.0 Hz, 1H); MS (API-) m/z: 418.3 [(M + H)-].

Synthesis of 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan-3-yl)-9'phenyl-9H,9'H-3,3'-bicarbazole (BCzTrzDBF)

2-(3-Fluorodibenzo[*b,d*]furan-4-yl)-4,6-diphenyl-1,3,5-triazine (0.37 g, 0.88 mmol), 9-phenyl-9*H*,9'*H*-3,3'-bicarbazole (0.43 g, 1.06 mmol) and cesium carbonate (0.34 g, 1.06 mmol) were stirred in a pressure tube filled with dimethylformamide (20 ml) at 250 °C using an oil bath. After 3 h, the pressure tube was cooled to room temperature and the reaction mixture was quenched using deionized water. The extraction of the reaction mixture using methylene chloride and deionized water, subsequent separation of the methylene chloride layer using a separatory funnel, and the final evaporation of the solvent provided a crude product. The product was purified using column chromatography (methylene chloride:n-hexane=1:4), followed by vacuum train sublimation, which afforded a pure yellow powder as a final product (0.6 g, 85% yield).

¹H NMR (500 MHz, dimethylsulfoxide-d₆): δ=8.73-8.71 (d, J= 8.0Hz, 1H), 8.59 (s, 1H), 8.48 (s, 1H), 8.41-8.39 (t, J=8.5Hz, 1H), 8.33-8.32 (d, J=7.5Hz, 1H), 8.14-8.13 (d, J=7.5 Hz, 1H), 8.01-7.99 (d, J=7.0Hz, 4H), 7.94-7.92 (d, J=8.0Hz, 1H), 7.83-7.79 (m, 3H), 7.71-7.62

(m, 5H), 7.57-7.52 (m, 4H), 7.45-7.42 (t, J=8.25Hz, 2H), 7.40-7.35 (m, 6H), 7.32-7.28 (t, J=9.25Hz, 2H), 7.23-7.21 (d, J=8.0Hz, 1H), 7.19-7.16 (t, J=7.75Hz, 1H). ¹³C NMR (125 MHz, dimethylsulfoxide-d₆): δ=170.72, 169.68, 156.54, 154.18, 141.78, 140.85, 140.55, 139.22, 139.20, 136.87, 134.48, 134.47, 133.21, 133.01, 133.00, 132.96, 132.94, 130.16, 128.87, 128.86, 128.84, 128.74, 128.72, 128.63, 128.59, 128.54, 128.48, 127.60, 126.58, 126.33, 125.98, 125.38, 125.25, 125.17, 124.91, 124.88, 124.46, 123.86, 123.43, 123.38, 122.93, 122.85, 122.72, 121.74, 121.38, 121.35, 120.72, 120.55, 120.53, 120.05, 119.77, 118.33, 112.03, 110.09, 109.94, 109.63, 109.58 ppm; MS (API-) m/z: 806.9 [(M + H)⁺].

Synthesis of 9'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan-3-yl)-9,9'-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (TCzTrzDBF)

TCzTrzDBF was synthesized according to the synthetic method of BCzTrzDBF using 9,9'-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (0.82 g, 1.26 mmol) instead of 9-phenyl-9H,9'H-3,3'-bicarbazole. A pure yellow powder was obtained as a final product (0.9 g, 82% yield).

¹H NMR (500 MHz, CDCl₃): δ=8.42-8.38 (t, J= 10.25Hz, 6H), 8.23-8.21 (d, J=8.0Hz, 2H), 8.13-8.11 (d, J=9.5Hz, 4H), 7.83-7.81 (d, J=8.0Hz, 1H), 7.76-7.72 (t, J=8.5Hz, 5H), 7.64-7.61 (t, J=7.65 Hz, 8H), 7.51-7.46 (m, 6H), 7.45-7.43 (d, J=8.0Hz, 8H), 7.34-7.31 (t, J=9.0Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ=145.20, 142.06, 142.03, 140.43, 139.19, 135.96, 135.54, 135.39, 130.46, 129.86, 127.63, 127.47, 127.14, 126.40, 126.26, 126.11, 125.97, 124.81, 124.24, 123.36, 123.30, 121.22, 121.11, 121.06, 120.99, 120.93, 120.53, 119.89, 119.83, 119.79, 119.15, 110.84, 110.10, 109.99, 108.79 ppm; MS (API-) m/z: 1048.3 [(M + H)⁺].

Synthesis of 12-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan-3-yl)-5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (IDCzTrzDBF)

The IDCzTrzDBF was synthesized according to the synthetic method of BCzTrzDBF, but using 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (0.45 g, 1.36 mmol) instead of 9-phenyl-9*H*,9'*H*-3,3'-bicarbazole. A greenish yellow powder was obtained as a final product (0.43 g, 52% yield).

¹H NMR (500 MHz, dimethylsulfoxide-*d*₆): δ=8.48-8.47 (d, *J*=8.5Hz, 1H), 8.21-8.19 (d, *J*=8.5Hz, 1H), 8.08-8.06 (d, *J*=8.0Hz, 1H), 7.91-7.89 (d, *J*=7.0Hz, 1H), 7.77-7.71 (m, 5H), 7.60-7.48 (m, 6H), 7.43-7.40 (t, *J*=8.75Hz, 5H), 7.33-7.30 (t, *J*=8.0Hz, 1H), 7.26-7.21 (m, 5H), 7.19-1.16 (t, *J*=8.0Hz, 1H), 7.12-7.10 (d, *J*=8.0Hz, 1H), 6.99-6.97 (d, *J*=8.5Hz, 1H), 6.69-6.66 (t, *J*=8.0Hz, 1H). ¹³C NMR (125 MHz, dimethylsulfoxide-*d*₆): δ=170.84, 155.19, 154.19, 153.74, 143.17, 142.00, 141.91, 140.50, 139.61, 138.15, 137.79, 137.59, 135.55, 132.31, 129.84, 129.08, 128.36, 128.11, 124.79, 124.62, 124.39, 123.68, 123.59, 123.57, 122.98, 121.27, 120.49, 119.37, 118.34, 117.66, 116.52, 112.62, 109.59, 109.36, 108.13, 103.52 ppm; MS (API-) *m/z*: 730.7 [(*M* + *H*)⁺].

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Figure S5. Hole only and electron only device data of (a) TCzTrzDBF and (b) IDCzTrzDBF.

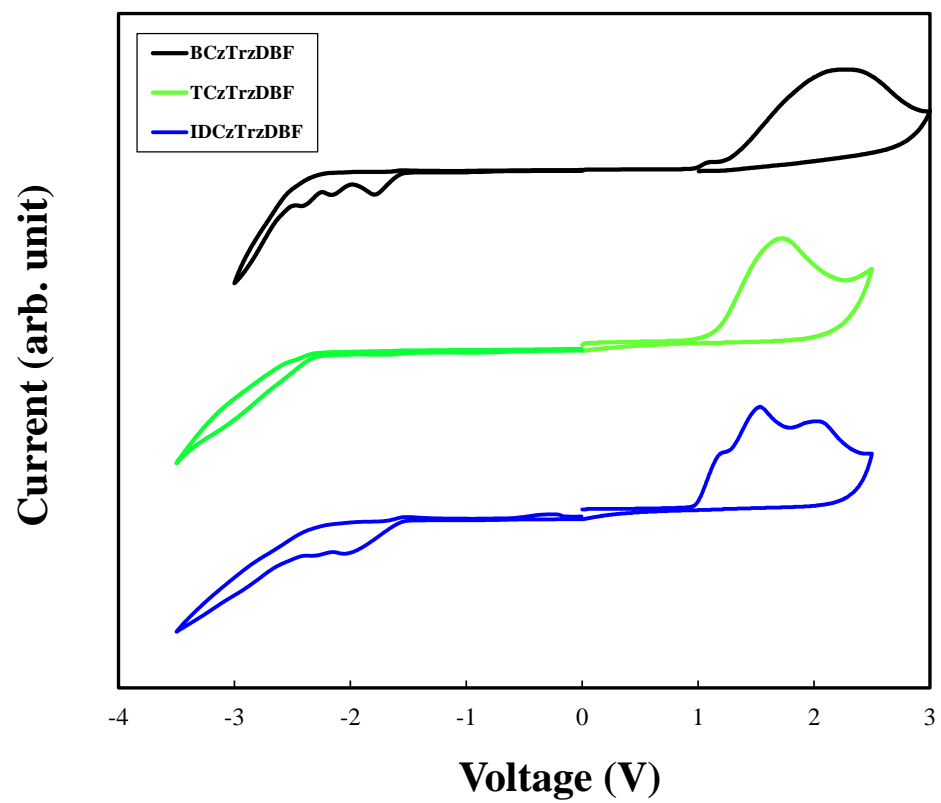


Figure S1.

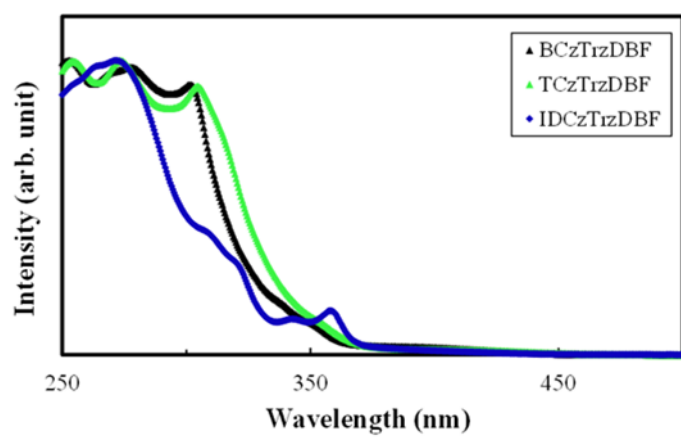


Figure S2.

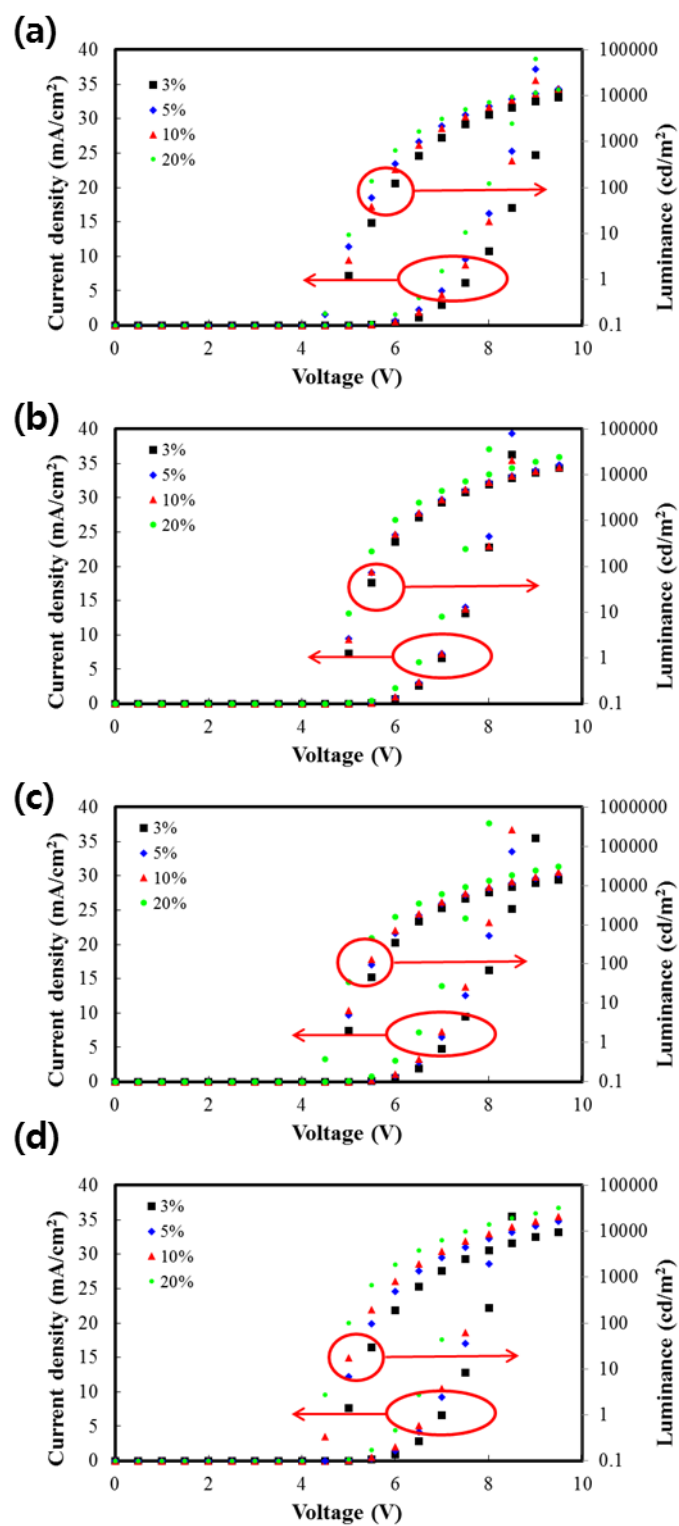


Figure S3.

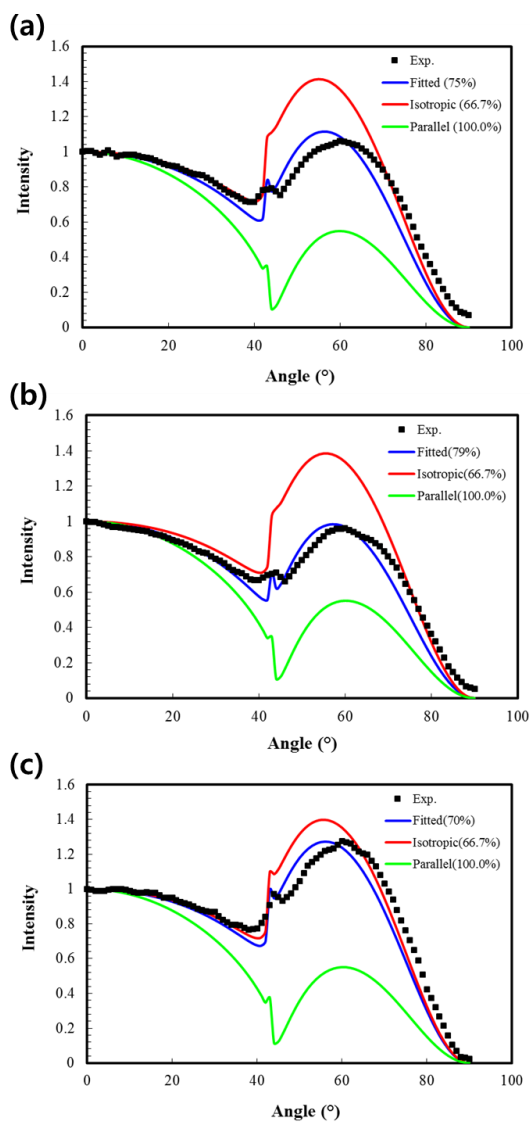


Figure S4.

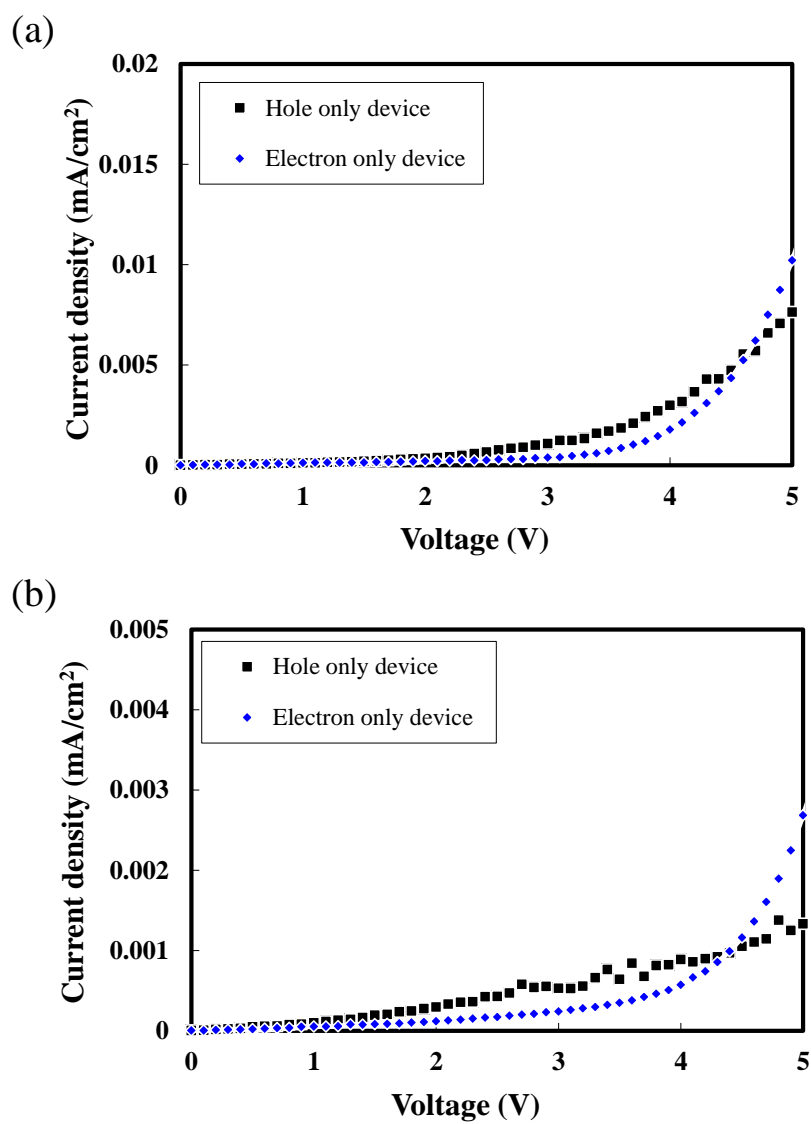


Figure S5