Supporting Information

Donor and Acceptor Interlock by a Planar Indolo[3,2,1-*jk*]carbazole for Suppressed Non-radiative Mechanism in Thermally Activated Delayed Fluorescent Emitters

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Experimental section

All the reagents and solvents were procured from the commercial sources and used without further purification. The chromatographic separations were performed using silica gel (200-300 nm). The final products were purified by column chromatography and then further purified by temperature gradient vacuum sublimation process. The final products were confirmed by ^{1}H, ^{13}C NMR and HRMS spectrometry. The ^{1}H and ^{13}C NMR data of the final products were recorded on JEOL 500 MHz spectrometer by using deuterated chloroform ($CDCl_3$) as a solvent and chemical shift are expressed in parts per million (ppm), with tetramethylsilane (TMS) as an internal standard. The details of instrumental tools used are Fourier transform-nuclear magnetic resonance 500 MHz (Unity Inova), Fourier transform-nuclear magnetic resonance 300 MHz (Oxford 300 NMR), cyclic-voltammetry (CV) (Ivium Tech., Iviumstat), UV-Visible absorption spectroscopy (JASCO, V-730), fluorescence spectroscopy (PerkinElmer, LS-55), mass spectroscopy (Advion, Expression LCMS spectrometer in APCI mode), and thermogravimetric analyzer (TGA) [Seiko Exstar 6000 (TG/DTA6100)].

Synthesis

Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolo[3,2,1-*jk*]carbazole (I-1)

To the 250 mL three-neck round-bottomed flask, 2-bromoindolo[3,2,1-*jk*]carbazole (6.0 g, 18.74 mmol, 1 equiv.), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (9.52 g, 37.48 mmol, 2 equiv.), 1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) [Pd(dppf)Cl_2] (0.69 g, 0.94 mmol, 0.05 equiv.), potassium acetate (K_2CO_3) (5.52 g, 56.22 mmol, 3 equiv.) and 1,-4-dioxane (220 mL) were added and reflux for 12 h under nitrogen atmosphere. The progress of the reaction was monitored on thin layer chromatography (TLC). After completion of reaction, the reaction mass cooled to room temperature and poured in water (500 mL) and extracted in dichloromethane (DCM) multiple time. The organic layer was dried using anhydrous magnesium sulphate ($MgSO_4$) and solvent evaporated under vacuum to give crude product. The crude product was purified by column chromatography using hexane: DCM (80:20) to give **I-1** as white solid. Yield: 6.88 g (61%). ^{1}H NMR (300 MHz, cdcl$_3$) δ 8.60 – 8.54 (m, 2H), 8.14 (ddd, J = 7.8, 1.1, 0.6 Hz, 2H), 7.94 – 7.87 (m, 2H), 7.55 (ddd, J = 8.1, 7.6, 1.2 Hz, 2H), 7.36 (td, J = 7.6, 1.0 Hz, 2H), 1.45 (s, 12H). MS (APCI) m/z: found 368.33 [$(M+H)^+$]. Calculated for $C_{24}H_{22}BNO_2$: 367.25.

Synthesis of 2-(3-chloro-2-fluorophenyl)indolo[3,2,1-*jk*]carbazole (I-2)

To the oven dried 250 mL three-neck round-bottomed flask, **1a** (2.91 g, 7.94 mmol, 1 equiv.), 1-bromo-3-chloro-2-fluorobenzene (1.65 g, 7.94 mmol, 1 equiv.), tetrakis(triphenyl phosphine)palladium (0) [Pd(PPh_3)$_4$] (0.28 g, 0.24 mmol, 0.03 equiv.), K_2CO_3 (3.29 g, 23.83 mmol, 3 equiv.), and tetrahydrofuran-water (100: 33 mL) were added at room temperature. The reaction mass was refluxed under nitrogen atmosphere for 12 h. The reaction mass was extracted in water-DCM (100-50 mL) mixture. The aqueous layer was further extracted in DCM multiple time. The organic layer was dried over anhydrous $MgSO_4$. A crude product obtained after evaporating the solvent was purified by column chromatography using hexane: DCM (80:20) to offer **I-2** as white solid. Yield: 2.93 g (38%). MS (APCI) m/z: found 370.79 $[(M+H)^+]$. Calculated for $C_{24}H_{13}ClFN$: 369.82. ^1H NMR (300 MHz, cdcl$_3$) δ 8.19 – 8.10 (m, 4H), 7.95 – 7.88 (m, 2H), 7.60 – 7.34 (m, 6H), 7.24 – 7.17 (m, 1H).

Synthesis of 2-(2-fluoro-3-(3,3,4,4-tetramethylborolan-1-yl)phenyl)indolo[3,2,1-*jk*]carbazole (I-3)

To the 100 mL three-neck round-bottomed flask, **I-2** (2.5 g, 6.76 mmol, 1 equiv.), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (5.15 g, 20.28 mmol, 3 equiv.), tris(dibenzylideneacetone)dipalladium (0) $[Pd_2(dba)_3]$ (0.06 g, 0.07 mmol, 0.01 equiv.), K_2CO_3 (1.99 g, 20.18 mmol, 3 equiv.), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) (0.16 g, 0.34 mmol, 0.05 equiv.) and 1, 4-dioxane (80 mL) were reflux for 12 h under nitrogen atmosphere. After completion of reaction, the reaction mass poured in water (200 mL) and extracted in dichloromethane (DCM). The organic layer was dried using anhydrous $MgSO_4$ and the crude product obtained after evaporation of solvent was purified by column chromatography using hexane: DCM (80:20) as eluent. The intermediate **I-3** obtained as wheat colored solid. Yield: 1.50 g (48%). ^1H NMR (300 MHz, cdcl$_3$) δ 8.23 (d, *J* = 1.7 Hz, 2H), 8.13 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 2H), 7.95 – 7.90 (m, 2H), 7.81 – 7.69 (m, 2H), 7.60 – 7.53 (m, 2H), 7.39 – 7.27 (m, 3H), 1.41 (s, 12H). MS (APCI) m/z: found 462.27 $[(M+1)^+]$. Calculated for $C_{30}H_{25}BFNO_2$: 461.34.

Synthesis of 2-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorophenyl)indolo[3,2,1-*jk*]carbazole (I-4)

A mixture of **I-3** (1.03 g, 2.24 mmol, 1 equiv.), 2-chloro-4,6-diphenyl-1,3,5-triazine (0.6 g, 2.24 mmol, 1 equiv.), $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol, 0.03 equiv.), K_2CO_3 (0.93 g, 6.72 mmol, 3 equiv.), and tetrahydrofuran (THF): water (33: 11 mL) was refluxed under nitrogen atmosphere for 12 h. The reaction was cooled to room temperature and extracted in water-DCM mixture. The organic layer dried over anhydrous $MgSO_4$ and evaporated under vacuum to give the crude product. The pure **I-4** was obtained as white solid after column chromatography using hexane: DCM (70: 30). ^{1}H NMR (300 MHz, cdcl$_3$) δ 8.79 (dd, *J* = 8.0, 1.6 Hz, 4H), 8.53 – 8.47 (m, 1H), 8.30 (d, *J* = 1.5 Hz, 2H), 8.20 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.82 (dd, *J* = 10.7, 3.7 Hz, 1H), 7.65 – 7.54 (m, 8H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H). Yield: 0.6 g (47%). MS (APCI) m/z: found 568.33 [$(M+2)^+$]. Calculated for $C_{39}H_{23}FN_4$: 566.64.

Synthesis of 2-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-(9'-phenyl-9*H*,9'*H*-[3,3'-bicarbazol]-9-yl)phenyl)indolo[3,2,1-*jk*]carbazole (TrzCbzICz-1)

The intermediate **I-4** (0.8 g, 1.41 mmol, 1 equiv.), 9-phenyl-9*H*,9'*H*-3,3'-bicarbazole (0.71 g, 1.55 mmol, 1.1 equiv.) and cesium carbonate (Cs_2CO_3) (2.3 g, 7.06 mmol, 5 equiv.) were refluxed in *N*,*N*-dimethylformamide (DMF) (45 mL) for 6 h. The reaction mass was cooled to room temperature and extracted in DCM. The organic layer was dried over $MgSO_4$ and solvent was evaporated under vacuum to give crude product which was purified by column chromatography using hexane: DCM (80:20). The final product **TrzCbzICz-1** was obtained as yellow solid. Yield: 0.6 g (45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 5H), 7.92 (d, *J* = 7.6 Hz, 7H), 7.74 (dd, J = 14.5, 6.8 Hz, 11H), 7.60 (s, 4H), 7.48 (t, J = 7.5 Hz, 9H), 7.44 – 7.36 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.10 (s), 168.63 (s), 138.63 (s), 133.91 (s), 130.92 (s), 130.59 (d, J = 12.4 Hz), 129.30 (s), 119.67 (s), 118.95 (s), 118.16 (s), 115.90 (s), 113.64 (s), 111.39 (s). Elemental analysis (%): calculated for $C_{69}H_{42}N_6$; C, 86.77; N, 8.80; H, 4.43. Found: C, 86.71; N, 8.77; H, 4.43.

Synthesis of 2-(5-chloro-2-fluorophenyl)indolo[3,2,1-*jk*]carbazole (I-5)

Synthetic procedure same as **I-2**. The **1a** (3.00 g, 8.16 mmol, 1 equiv.), 2-bromo-4-chloro-1-fluorobenzene (1.71 g, 8.16 mmol, 1 equiv.), $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol, 0.03 equiv.), K_2CO_3 (3.39 g, 24.48 mmol, 3 equiv.), and THF-water (100: 33 mL). The **I-5** obtained as white solid. Yield: 1.0 g (33%). ^{1}H NMR (300 MHz, cdcl$_3$) δ 8.20 – 8.12 (m, 4H), 7.92 (d, J = 8.1 Hz, 2H), 7.65 – 7.53 (m, 3H), 7.43 – 7.28 (m, 3H), 7.17 (dd, J = 9.8, 8.7 Hz, 1H). MS (APCI) m/z: found 370.79 [$(M+H)^+$]. Calculated for $C_{24}H_{13}ClFN$: 369.82.

Synthesis of 2-(2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)indolo[3,2,1-*jk*]carbazole (I-6)

Synthetic procedure same as **I-3**. The **I-5** (2.5 g, 6.76 mmol, 1 equiv.), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (5.15 g, 20.28 mmol, 3 equiv.), $Pd_2(dba)_3$ (0.06 g, 0.07 mmol, 0.01 equiv.), K_2CO_3 (1.99 g, 20.18 mmol, 3 equiv.), Xantphos (0.16 g, 0.34 mmol, 0.05 equiv.) and 1, 4-dioxane (80 mL). The **I-6** obtained as wheat colored solid. Yield: 1.41 g (45%). ^{1}H NMR (300 MHz, cdcl$_3$) δ 8.22 (d, J = 1.5 Hz, 2H), 8.15 (d, J = 7.7 Hz, 2H), 8.08 (dd, J = 8.5, 1.6 Hz, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.83 (ddd, J = 8.0, 5.4, 1.7 Hz, 1H), 7.57 (td, J = 7.9, 1.2

Hz, 2H), 7.40 – 7.33 (m, 2H), 7.25 (dd, *J* = 6.8, 3.9 Hz, 1H), 1.38 (s, 12H). MS (APCI) m/z: found 462.11 [(M+H)$^+$]. Calculated for $C_{30}H_{25}BFNO_2$: 461.34.

Synthesis of 2-(5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorophenyl)indolo[3,2,1-*jk*]carbazole (I-7)

Synthetic procedure same as **I-4**. The **I-6** (1.03 g, 2.24 mmol, 1 equiv.), 2-chloro-4,6-diphenyl-1,3,5-triazine (0.6 g, 2.24 mmol, 1 equiv.), $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol, 0.03 equiv.), K_2CO_3 (0.93 g, 6.72 mmol, 3 equiv.), and THF-water (33: 11 mL). The **I-7** obtained as white solid. Yield: 0.60 g (47%). ^{1}H NMR (300 MHz, cdcl$_3$) δ 9.03 (dd, *J* = 7.7, 2.2 Hz, 1H), 8.82 – 8.76 (m, 2H), 8.65 – 8.59 (m, 2H), 8.33 – 8.12 (m, 5H), 7.96 (dd, *J* = 11.9, 8.1 Hz, 2H), 7.59 (ddd, *J* = 13.7, 10.3, 7.0 Hz, 7H), 7.46 – 7.32 (m, 4H). MS (APCI) m/z: found 568.36 [(M+2)$^+$]. Calculated for $C_{39}H_{23}FN_4$: 566.64.

Synthesis of 2-(5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-(9'-phenyl-9*H*,9'*H*-[3,3'-bicarbazol]-9-yl)phenyl)indolo[3,2,1-*jk*]carbazole (TrzCbzICz-2)

Synthetic procedure same as **TrzCbzICz-1**. The I-7 (0.8 g, 1.41 mmol, 1 equiv.), 9-phenyl-9*H*,9'*H*-3,3'-bicarbazole (0.71 g, 1.55 mmol, 1.1 equiv.) and cesium carbonate (Cs_2CO_3) (2.3 g, 7.06 mmol, 5 equiv.) were refluxed in *N*,*N*-dimethylformamide (DMF) (45 mL). The final product **TrzCbzICz-2** was obtained as yellow solid. Yield: 0.55 g (41%). ^{1}H NMR (500 MHz, Trifluoroacetic Acid-d: CDCl$_3$) δ 8.39 (d, *J* = 7.9 Hz, 8H), 8.18 (s, 6H), 7.81 (t, *J* = 7.3 Hz, 7H), 7.62 (dd, *J* = 27.7, 20.0 Hz, 13H), 7.32 (d, *J* = 21.5 Hz, 8H). ^{13}C NMR (126 MHz, Trifluoroacetic Acid-d: CDCl$_3$) δ 168.77 (s), 167.48 (s), 138.02 (s), 133.99 (s), 130.71 (s), 130.50 (s), 128.70 (s), 119.96 (s), 119.16 (s), 118.25 (s), 115.99 (s), 113.73 (s), 111.48 (s). Elemental analysis (%): calculated for $C_{69}H_{42}N_6$; C, 86.77; N, 8.80; H, 4.43. Found: C, 85.88; N, 8.95; H, 4.77.

Device fabrication and measurement

To fabricate the OLED devices, transparent glass substrates with a 50 nm thick indium tin oxide (ITO) were used. The cleaning of the ITO glass substrates was carried out by ultrasonic treatment for 10 min using acetone and deionized water. The deposition of all the layers was performed by a vacuum thermal evaporation under a pressure of 3.0 x 10^{-7} torr. The deposition rates for the organic layers, LiF, and Al were controlled at 0.1, 0.01, and 0.5 nm/s, respectively. The green device structure was, ITO (50 nm)/ PEDOT: PSS (60 nm)/ TAPC (20 nm)/ *m*-CP (10 nm)/ DPEPO : **TrzCbzICz-1**: DPEPO : **TrzCbzICz-2** (25: X%)/ TSPO1 (5 nm)/ TPBi (20 nm)/ LiF (1.5 nm)/ Al (200 nm). To protect the devices from the oxygen, encapsulation on glass was done under a nitrogen atmosphere in the glove box. All the device measurements were performed at ambient temperature. The electrical and optical characterizations of the devices were carried out using Keithley 2400 Source Meter and CS 2000 spectroradiometer, respectively.

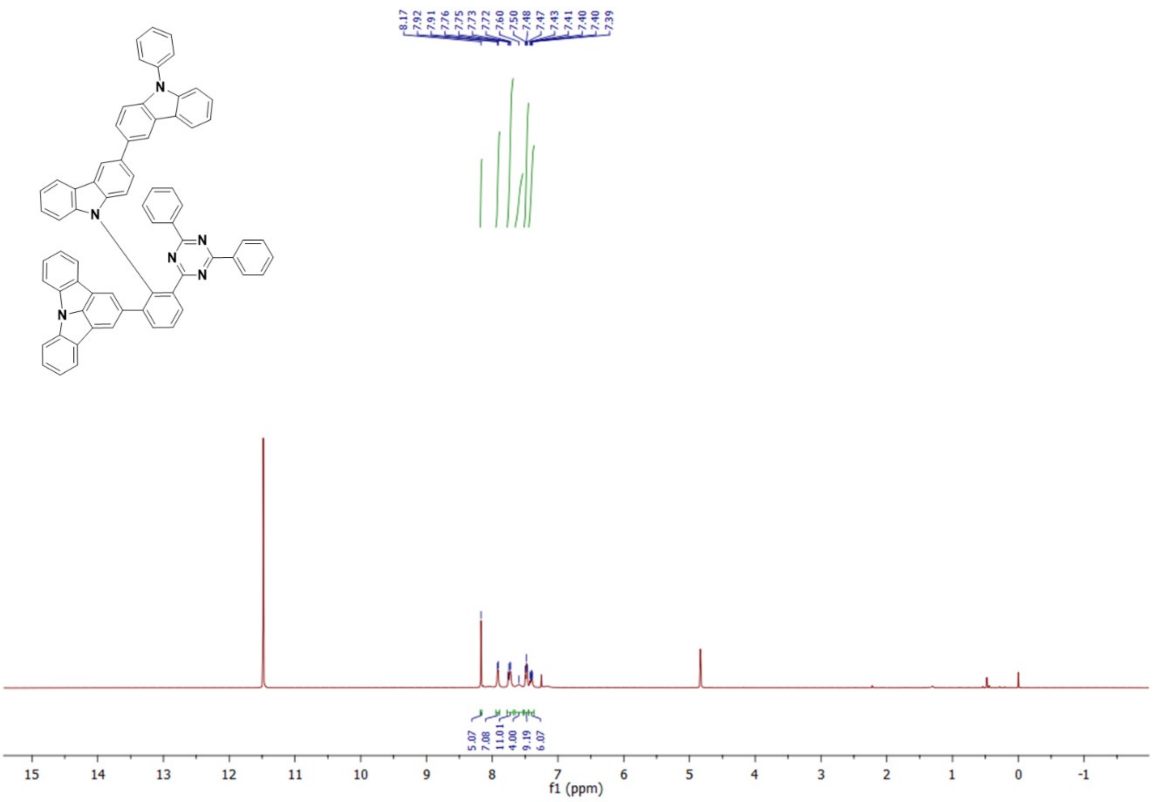

Figure S1. The ^{1}H-NMR spectrum of **TrzCbzICz-1**

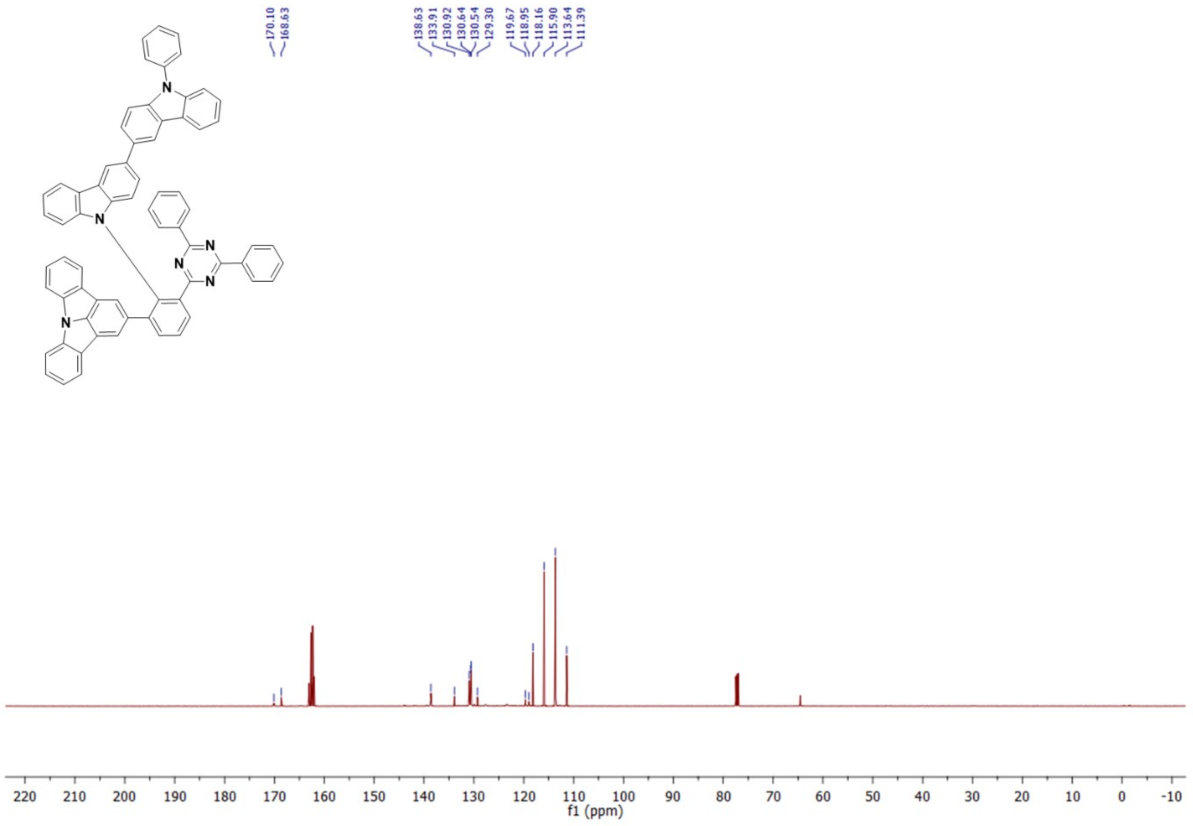

Figure S2. The ^{13}C-NMR spectrum of **TrzCbzICz-1**

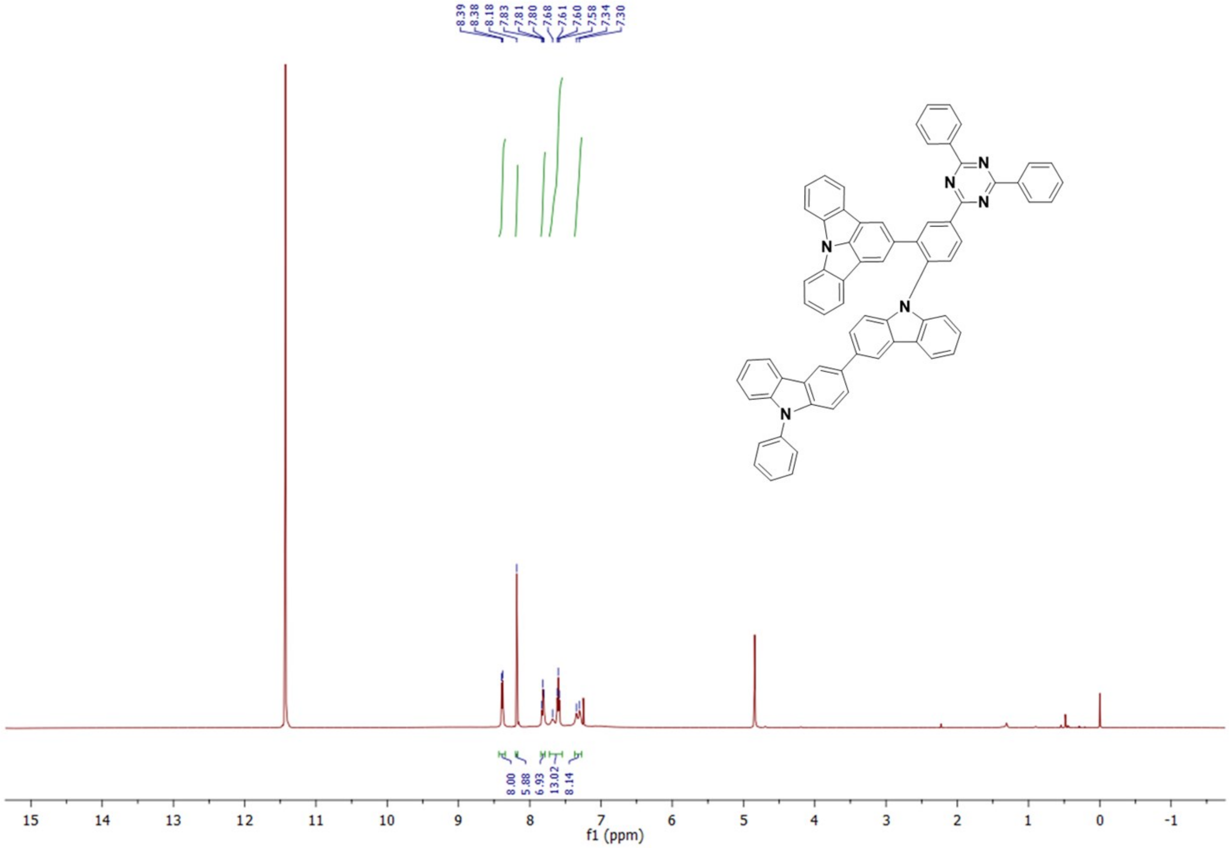

Figure S3. The ^{1}H-NMR spectrum of **TrzCbzICz-2**

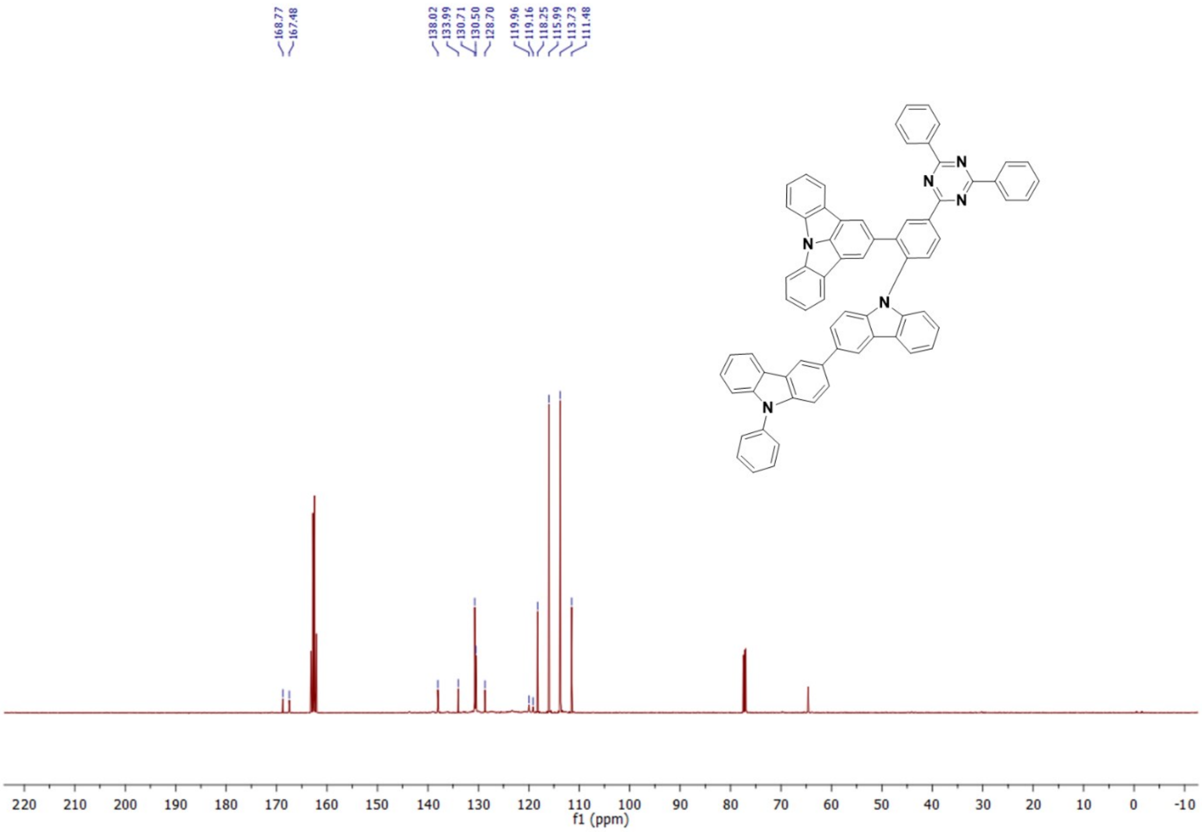

Figure S4. The ^{13}C-NMR spectrum of **TrzCbzICz-2**

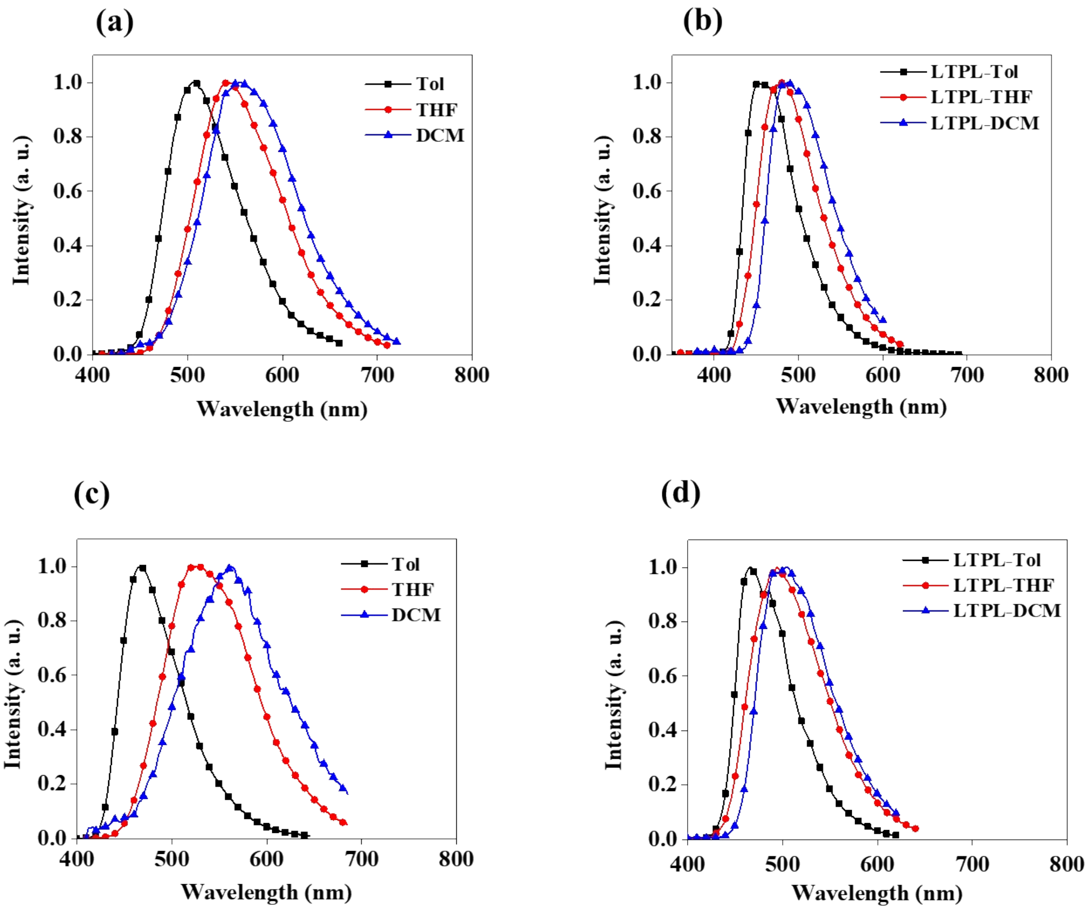

Figure S5. The **(a)** solution PL and **(b)** LTPL curves of **TrzCBzICz-1** and **(c)** solution PL and **(d)** LTPL curves of **TrzCBzICz-2** in solvents with different polarity

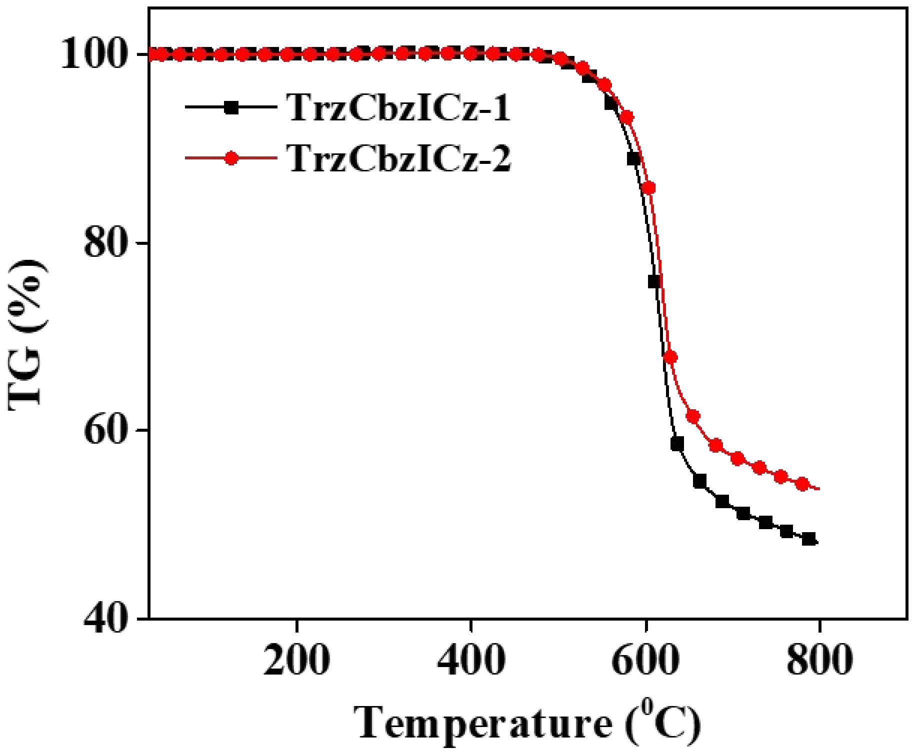

Figure S6. The TGA curves of **TrzCbzICz-1** and **TrzCbzICz-2**

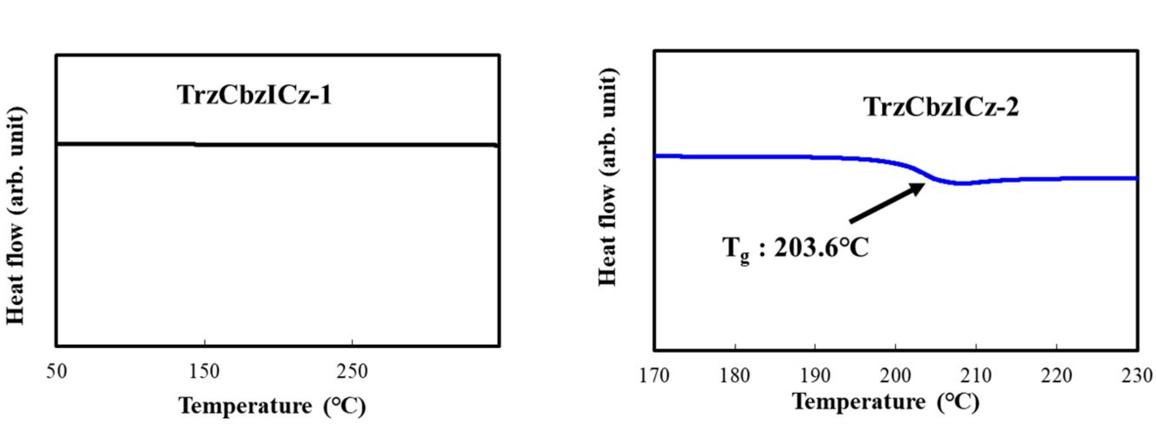

Figure S7. The DSC curves of **TrzCbzICz-1** and **TrzCbzICz-2**

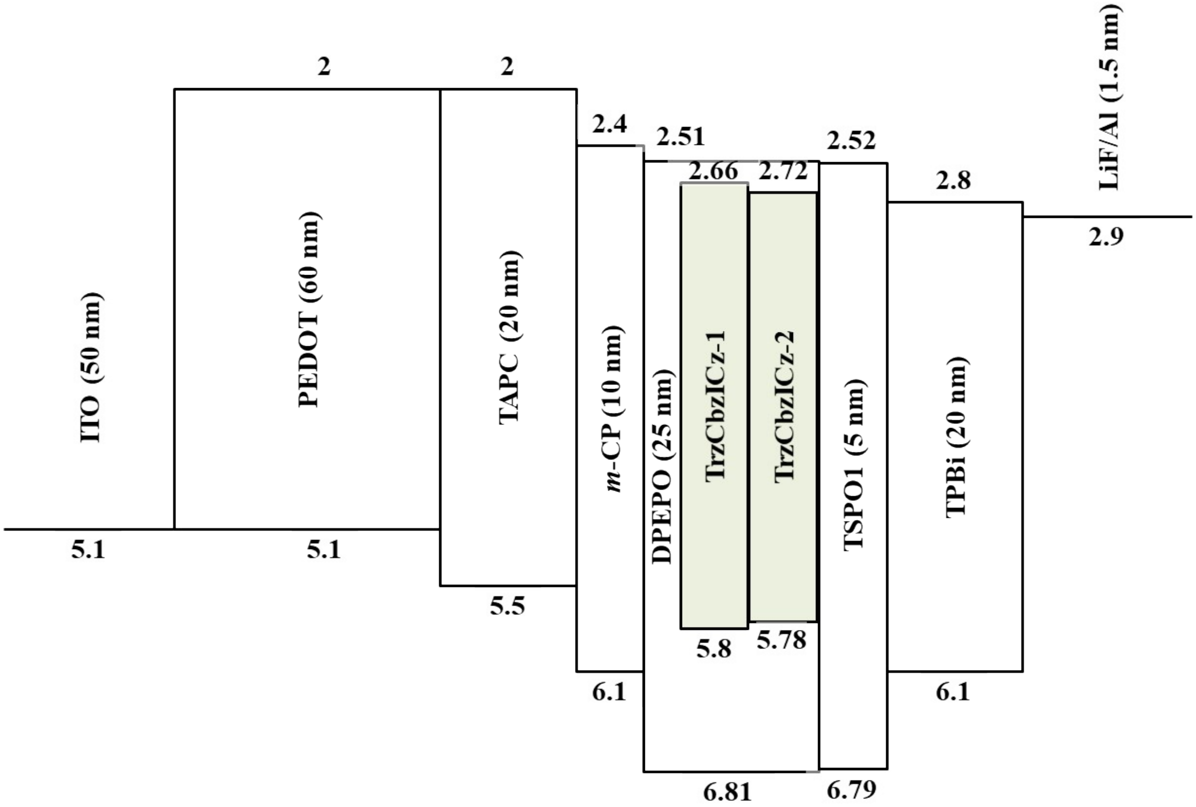

Figure S8. The optimized device diagram of **TrzCbzICz-1** and **TrzCbzICz-2** doped devices