Supporting Information

Experimental

General information

5-phenyl-5,12-dihydroindolo[3,2-a]carbazole was supplied from LG Chem. The ¹H and ¹³C NMR spectra of synthesized compounds in deuterated CDCl₃ were recorded using Unity Inova (Varian, 500 MHz) spectrometer to identify the chemical structure of the compounds. Also, the instrument to measure the molecular weight was Advion, Expression^L CMS spectrometer in APCI mode. The PL spectra of the compounds dissolved in 1.0×10^{-5} M tretrahydrofuran (THF) solution were obtained using a fluorescence spectrophotometer (PerkinElmer, LS-55) and low temperature PL spectra was carried out at 77 K to measure triplet energy of compounds. The UV-vis absorptions spectra were observed using UV-vis spectrophotometer (JASCO, V-730 dissolved in 1.0×10^{-5} M THF solution. The CV measurement of the compounds was carried out by IVIUM STAT. The standard material was Ferrocene and working electrode was carbon electrode. Ag and Pt electrodes were used as reference and counter electrodes, respectively. PL quantum yield and Transient PL decay data were recorded using Quantaurus-QY Absolute system (Hamamatsu, C11347-11) and Hamamatsu Quantaurus-Tau system (Hamamatsu, C11367-31) at 10 wt% doped in the DPEPO host.

Synthesis

2-Fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

5-Bromo-2-fluoropyridine (5.00 g, 28.41 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane)(10.82 g, 42.62 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.62 g, 0.852 mmol), and potassium acetate (8.37 g, 85.23 mmol) were dissolved in 1,4-dioxane (50 ml) and stirred using a stir bar under a nitrogen atmosphere. The mixture was heated to reflux for 6 h and filtered to separate the base and catalyst. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane (0/1 \rightarrow 1/1) as an eluent. The product was obtained as a beige powder. (3.50 g, 55% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.597 (s, 1H), 8.18 (tt, *J*=10.1, 1.79 Hz, 1H), 6.95 – 6.90 (m, 1H), 1.36 (d, *J* = 2.3 Hz, 12H).

2-Chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nicotinonitrile

5-Bromo-2-chloronicotinonitrile (10.00 g, 45.99 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (20.00 g, 78.76 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1.00 g, 2.76 mmol), and potassium acetate (12.00 g, 137.97 mmol) were dissolved in 1,4-dioxane (100 ml) and stirred using a stir bar under a nitrogen atmosphere. The mixture was heated to reflux for 5 h and filtered to separate the base and catalyst. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane ($0/1 \rightarrow 1/1$) as an eluent. The product was obtained as a beige powder. (4.00 g, 33% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.87 (s, 1H), 8.34 (s, 1H), 1.36 (s, 14H).

2-Chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)pyridine

5-bromo-2-chloro-3-(trifluoromethyl)pyridine (5.00 g, 19.20 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane)

(7.30 g, 28.80 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.40 g, 0.57 mmol), and potassium acetate (5.65 g, 57.60 mmol) were dissolved in 1,4-dioxane (50 ml) and stirred using a stir bar under a nitrogen atmosphere. The mixture was heated to reflux for 4 h and filtered to separate the base and catalysis. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane ($0/1 \rightarrow 1/1$) as an eluent. The product was obtained as a white powder. (3.66 g, 62% yield). ¹H NMR (500 MH_Z, CDCl₃): δ 8.85 (s, 1H), 8.36 (s, 1H), 1.36 (s, 13H).

2-Fluoro-3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine

5-Bromo-2-fluoro-3-methylpyridine (10.00 g, 52.63 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (20.00 g, 78.76 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1.10 g, 1.50 mmol), and potassium acetate (15.50 g, 157.8 mmol) were dissolved in 1,4-dioxane (100 ml) and stirred using a stir bar under a nitrogen atmosphere. The mixture was heated to reflux for 7 h and filtered to separate the base and catalysis. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane ($0/1 \rightarrow 1/1$) as an eluent. The product was obtained as a white powder. (6.90 g, 55% yield). ¹H NMR (500 MH_Z, CDCl₃): δ 8.40 (s, 1H), 2.28 (s, 3H), 1.35 (s, 13H).

2-(6-Chloropyridin-3-yl)-4,6-diphenyl-1,3,5-triazine

2-Fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (3.00 g, 13.45 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (4.31 g, 16.09 mmol), potassium carbonate (5.60 g, 40.52 mmol) and tetrakis(triphenylphosphine)palladium (0) (0.46 g, 0.40 mmol) were dissolved in anhydrous THF (30 ml) and distilled water (15 ml). The reaction mixture was stirred and heated to reflux for overnight under a nitrogen atmosphere. The mixture was washed in distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using an anhydrous magnesium sulfate. The mixture was purified by column chromatography on silica gel using n-hexane/dichloromethane. A white powder was obtained as a product (2.00 g. 45% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.58 (d, *J* = 2.2 Hz, 1H), 9.09 (td, *J* = 8.1, 2.3 Hz, 1H), 8.77 – 8.69 (m, 4H), 7.68 (tt, *J*=26.3, 1.24 Hz, 6H), 7.12 (dd, *J* = 8.5, 2.9 Hz, 1H).

2-Chloro-5-(4,6-diphenyl-1,3,5-triazin-2-yl)nicotinonitrile

2-Chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nicotinonitrile (15.00 g, 56.71 mmol), 2-chloro-4,6-diphenyl-1,3,5triazine (18.20 g, 67.98 mmol), potassium carbonate (20.00 g, 144.71 mmol) and tetrakis(triphenylphosphine)palladium (0) (1.30 g, 1.50 mmol) were dissolved in anhydrous THF (100 ml) and distilled water (20 ml). The reaction mixture was stirred and heated to reflux for overnight under a nitrogen atmosphere. The mixture was washed in distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using an anhydrous magnesium sulfate. The mixture was purified by column chromatography on silica gel using n-hexane/dichloromethane. A white powder was obtained as a product (11.00 g. 55% yield). ¹H NMR (500 MHZ, CDCl₃): δ 9.86 (s, 1H), 9.28 (s, 1H), 8.75 (d, 4H, *J*=7), 7.69-7.66 (m, 2H), 7.63-7.60 (m, 4H).

2-(6-Chloro-5-(trifluoromethyl)pyridin-3-yl)-4,6-diphenyl-1,3,5-triazine

2-Chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)pyridine (1.00 g, 3.79 mmol), 2-chloro-4,6diphenyl-1,3,5-triazine (1.21 g, 4.54 mmol), potassium carbonate (1.57 g, 11.40 mmol) and tetrakis(triphenylphosphine)palladium (0) (0.13 g, 0.11 mmol) were dissolved in anhydrous THF (10 ml) and distilled water (2 ml). The reaction mixture was stirred and heated to reflux for 5 h under a nitrogen atmosphere. The mixture was washed in distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using anhydrous magnesium sulfate. The mixture was purified by column chromatography on silica gel using n-hexane/dichloromethane. A white powder was obtained as a product (0.90 g. 58% yield).

¹H NMR (500 MH_Z, CDCl₃): δ 9.83 (s, 1H), 9.26 (s, 1H), 8.74 (d, 4H, *J*=7), 7.68-7.65 (m, 2H), 7.62-7.59 (m, 4H).

2-(6-Fluoro-5-methylpyridin-3-yl)-4,6-diphenyl-1,3,5-triazine

2-Fluoro-3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (5.00 g, 21.09 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (6.20 g, 23.19 mmol), potassium carbonate (5.83 g, 42.17 mmol) and tetrakis(triphenylphosphine)palladium (0) (0.49 g, 0.42 mmol) were dissolved in anhydrous THF (50 ml) and distilled water (10 ml). The reaction mixture was stirred and heated to reflux for 4 h under a nitrogen atmosphere. The mixture was washed in distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using anhydrous magnesium sulfate. The mixture was purified by column chromatography on silica gel using n-hexane/dichloromethane. A yellow powder was obtained (5.10 g. 68% yield). ¹H NMR (500 MH_Z, CDCl₃): δ 9.39 (s, 1H), 8.88 (d, 1H, *J*=9.5), 8.75 (d, 4H, *J*=7.5), 7.65-7.57 (m, 6H), 2.456 (s, 3H).

12-(5-(4,6-Diphenyl-1,3,5-triazin-2-yl)pyridin-2-yl)-5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (HPy)

2-(6-Chloropyridin-3-yl)-4,6-diphenyl-1,3,5-triazine(1.00 g, 3.05 mmol), 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (0.92 g, 2.77 mmol) and cesium carbonate (1.35 g, 4.14 mmol) were added in the pressure tube and dissolved in N,N-dimethylformamide (10 ml). The mixture was stirred and heated at 150 °C. After 3 h, the mixture was washed with distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using anhydrous magnesium sulfate. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane ($1/9 \rightarrow 1/5 \rightarrow 1/1$). An orange powder product was purified by sublimation (0.70 g, 36% yield). ¹H NMR (500 MHz, CDCl₃) δ 10.19 (d, J = 2.1 Hz, 1H), 9.15 (dd, J = 8.3, 2.3 Hz, 1H), 8.86 – 8.77 (m, 3H), 8.22 – 8.11 (m, 2H), 8.09 (d, J = 7.7 Hz, 1H), 7.71 – 7.50 (m, 11H), 7.47 – 7.33 (m, 4H), 6.96 – 6.83 (m, 1H), ¹³C NMR (125 MH_Z, CDCl₃): δ 172.14, 169.99, 156.24, 150.99, 142.05, 141.46, 140.98, 139.03, 137.89, 136.06, 135.25, 133.10, 130.22, 130.18, 129.30, 128.99, 128.25, 128.23, 126.31, 125.22, 125.01, 123.78, 122.23, 121.37, 120.85, 119.68, 119.43, 119.32, 118.57, 112.02, 109.74, 109.25, 105.48, 77.48, 77.23, 76.98 HRMS (FAB+) m/z 641.2454 [(M+H)+]; Calcd. For C44H29N6, 641.2454.



Figure S1. ¹H NMR spectrum of HPy in CDCl₃ (500 MHz)



Figure S2. ¹³C NMR spectrum of HPy in CDCl₃ (125 MHz)

5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-2-(5-phenylindolo[3,2-a]carbazol-12(5H)-yl)nicotinonitrile (CNPy)

2-chloro-5-(4,6-diphenyl-1,3,5-triazin-2-yl)nicotinonitrile (2.00 g, 5.42 mmol), 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (1.98 g, 5.96 mmol) and cesium carbonate (2.65 g, 8.13 mmol) were added in the pressure tube and dissolved in N,N-dimethylformamide (20 ml). The mixture was stirred and heated at 150 °C. After 3 h, the mixture was washed with distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using anhydrous magnesium sulfate. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane ($1/9 \rightarrow 1/5 \rightarrow 1/1$). An orange powder product was purified by sublimation (0.75 g, 21% yield). ¹H NMR (500 MH_Z, CDCl₃): δ 10.17 (s, 1H), 9.65 (s, 1H), 8.80 (d, 4H, *J*=7.75), 8.19-8.16 (m, 2H), 7.69-7.61 (m, 12H), 7.53 (1H, *J*=7), 7.47-7.43 (m, 3H), 7.36 (d, 1H, *J*=8), 6.84 (t, 1H, *J*=7.5), 6.13 (d, 1H, *J*=8), ¹³C NMR (125 MH_Z, CDCl₃): δ 172.53, 157.32, 154.02, 143.65, 140.57, 137.81, 135.51, 133.54, 131.03, 130.21, 129.40, 129.13, 128.31, 128.27, 126.74, 125.27, 125.17, 122.81, 121.70, 119.90, 119.84, 118.71, 114.95, 111.18, 110.17, 109.17, 108.51, 106.27, 77.48, 77.22, 76.97, 68.19, 25.83. HRMS



Figure S3. ¹H NMR spectrum of CNPy in CDCl₃ (500 MHz)



Figure S4. ¹³C NMR spectrum of CNPy in CDCl₃ (125 MHz)

12-(5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-3-(trifluoromethyl)pyridin-2-yl)-5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (CF3Py)

2-(6-Chloro-5-(trifluoromethyl)pyridin-3-yl)-4,6-diphenyl-1,3,5-triazine (0.50 g, 1.21 mmol), 5-phenyl-5,12dihydroindolo[3,2-a]carbazole (0.34 g, 1.33 mmol) and cesium carbonate (0.59 g, 1.85 mmol) were added in the pressure tube and dissolved in N,N-dimethylformamide (10 ml). The mixture was stirred and heated at 150 °C. After 3 h, the mixture was washed with distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using anhydrous magnesium sulfate. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane (0/1 \rightarrow 1/8 \rightarrow 1/4). A green powder product was purified by sublimation (0.31 g, 36% yield). ¹H NMR (500 MH_Z, CDCl₃): δ 10.16 (s, 1H), 9.77 (s, 1H), 8.82 (d, 4H, *J*=7.5), 8.19 (d, 1H, *J*=8.5), 8.16-8.14 (m, 1H), 7.65-7.52 (m, 11H), 7.39-7.29 (m, 3H), 7.26-7.17 (m, 1H), 7.10 (m, 1H, *J*=7), 6.78 (t, 1H, *J*=7.5), 5.93 (d, 1H, *J*=8.5), 25 MH_Z, ¹³C NMR (125 MH_Z, CDCl₃): δ 172.59, 168.64, 154.08, 142.40, 142.05, 140.88, 137.85, 137.75, 137.55, 133.53, 132.92, 130.18, 129.43, 129.14, 128.34, 128.26, 125.66, 124.75, 124.65, 121.57, 121.38, 121.13, 119.99, 118.79, 118.72, 110.87, 110.01, 108.57, 105.11, 77.48, 77.22, 76.97, 36.13, 29.92, 29.54, 27.43. HRMS (FAB+) m/z 709.2328 [(M+H)+]; Calcd. For C45H28F3N6, 709.2328.



Figure S5. ¹H NMR spectrum of CF3Py in CDCl₃ (500 MHz)



12-(5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-3-methylpyridin-2-yl)-5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (CH3Py)

2-(6-Fluoro-5-methylpyridin-3-yl)-4,6-diphenyl-1,3,5-triazine (1.00 g, 2.92 mmol), 5-phenyl-5,12-dihydroindolo[3,2a]carbazole (1.06 g, 3.21 mmol) and cesium carbonate (2.85 g, 8.76 mmol) were added in the pressure tube and dissolved in N,N-dimethylformamide (20 ml). The mixture was stirred and heated at 150 °C. After 4 h, the mixture was washed with distilled water three times and then extracted by dichloromethane. The separated dichloromethane layer was dried using anhydrous magnesium sulfate. The reaction product was purified by silica gel chromatography using a mixture of dichloromethane and n-hexane (0/1 \rightarrow 1/5 \rightarrow 1/2). A green powder product was purified by sublimation (0.30 g, 16% yield).

¹H NMR (500 MH_Z, CDCl₃): δ 9.96 (s, 1H), 9.22 (s, 1H), 8.83 (d, 4H, *J* =7), 8.21-8.17 (m, 2H),7.68-7.59 (m, 11H), 7.54 (t, 1H, *J* =7), 6.78 (t, 1H, *J* =7.5), 6.02 (d, *J* =8), 3.16 (s, 3H), ¹³C NMR (125 MH_Z, CDCl₃): δ 172.26, 170.01, 155.46, 148.84, 141.94, 140.80, 140.74, 137.95, 136.00, 133.18, 132.46, 130.16, 129.34, 129.04, 128.28, 128.18, 125.40, 124.71, 121.89, 121.16, 120.01, 119.44, 118.83, 118.02, 110.63, 109.75, 104.47, 77.48, 77.22, 76.97, 18.01. HRMS (FAB+) m/z 655.2610



Figure S7. ¹H NMR spectrum of CH3Py in CDCl₃ (500 MHz)



Figure S8. ¹³C NMR spectrum of CH3Py in CDCl₃ (125 MHz)



Figure S9. The cyclic voltammetry data of four TADF emitters.