Electronic Supplementary Information

Efficient Deep-Blue Emitters Comprised of Anthracene Core and Terminal Bifunctional Groups for Nondoped Electroluminescence

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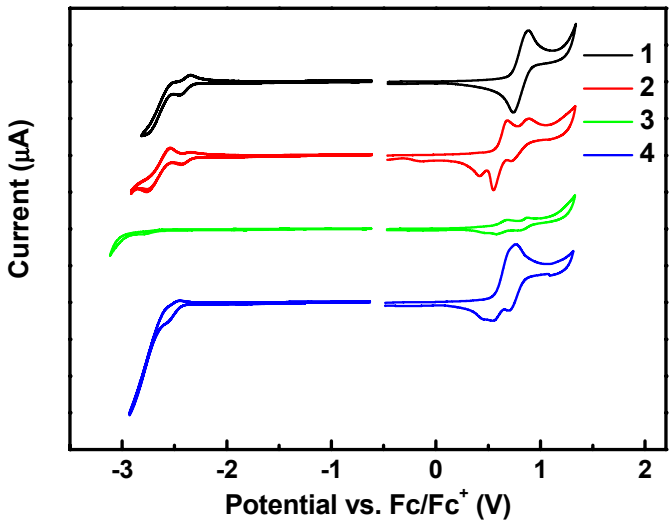
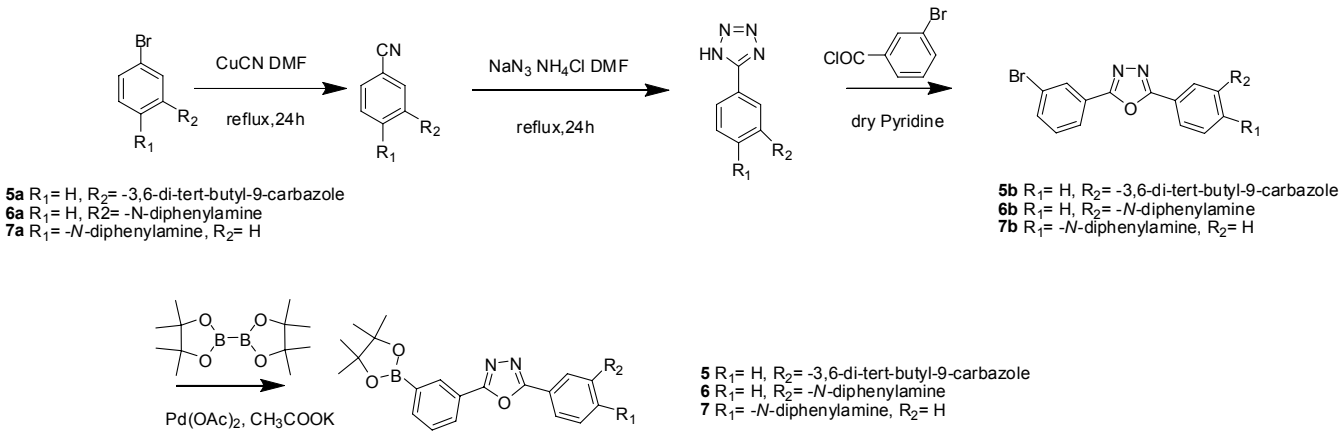


Figure S1. Cyclic voltammograms of **1**-**4** in CH_2Cl_2 for oxidation and THF for reduction.

Synthesis: 9-(3-bromophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (**5a**), 3-bromo-*N*,*N*-diphenylaniline (**6a**) and 4-bromo-*N*,*N*-diphenylaniline (**7a**) were prepared according to the literature procedure.[1-3] 3-bromobenzoyl chloride was freshly prepared by refluxing corresponding benzoyl acid with $SOCl_2$ and used immediately after distillation of excess $SOCl_2$.



Scheme S1. Synthetic routes of oxadiazole-containing arylboronic ester.

General procedure for the synthesis of oxadiazole-containing arylboronic ester.

A mixture of bromide end-capping groups (**5a**, **6a** or **7a**) (20 mmol) and 20 mmol CuCN in dry DMF (60 ml) was refluxed for 36 h. The cooled reaction mixture was added with a solution of HCl (10 ml),

$FeCl_3$ (21 g, 129.2 mmol), and water (150 ml). Then the mixture was heated at 70 °C for 0.5 h. After the reaction was complete, the mixture was extracted with CH_2Cl_2 three times. Recrystallization from $CHCl_3$ and methanol gave pure cyano substituted compounds.

The mixture containing 15 mmol of the above crude products and NaN_3 (15 mmol), and NH_4Cl (15 mmol) in 30 ml DMF was heated at 150 °C overnight. After cooling, the resulting mixture was poured into 400 ml water and acidified with 1 N HCl to pH ~ 2. The precipitated solid was collected by filtration, washed with water, and dried to give a white solid as the tetrazole intermediate.

Subsequently, a mixture of the above tetrazole derivatives (10 mmol) and 3-bromobenzoyl chloride (10 mmol) in dry pyridine was heated to reflux overnight. Then the mixture was quenched with dilute HCl (10 mL), extracted with CH_2Cl_2, and dried with anhydrous Na_2SO_4. Column chromatography of the crude mixture on silica gel (eluent: petroleum/EtOAc = 4:1) gave **5b**, **6b** or **7b** in moderate yields.

Then, oxadiazole-containing arylbromide (6 mmol), bis(pinacolato)diborane (1.828 g, 7.2 mmol), and KOAc (2.06 g, 21 mmol) were mixed together in a 100 ml flask. After degassing, dioxane (40 ml) was added to the mixture under flow of argon. Afterward, [Pd(dppf)Cl_2] (150 mg, dppf = 1,1'-bis(diphenylphosphanyl)ferrocene) was added. The reaction mixture was kept at 85 ^oC overnight and then cooled to room temperature. The solvent was concentrated and the inorganic salt was dissolved completely after addition of water. After extracted with CH_2Cl_2, the combined organic layer was washed with brine and then dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (eluent: petroleum/EtOAc = 4:1) and recrystallized from ethanol to afford **5, 6** or **7** in good yields.

2-(3-bromophenyl)-5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-1,3,4-oxadiazole (5b). White solid, 4.616 g, yield: 40% in three steps. ^1H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.20 (s, 1H), 8.15 (d, J = 9.3 Hz, 1H), 8.09 (s, 2H), 8.01 (d, J = 7.8 Hz, 1H), 7.70-7.69 (m, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 9.3 Hz, 1H), 7.33 (d, J = 9.3 Hz, 2H), 1.40 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.94, 158.24, 138.11, 133.98, 133.62, 129.51, 125.53, 125.39, 124.75, 124.47,

120.23, 120.06, 119.64, 118.61, 118.39, 117.86, 111.16, 103.77, 29.52, 26.79. Anal. calcd. for $C_{34}H_{32}BrN_3O$ (%): C 70.59, H 5.58, N 7.26; Found: C 70.54, H 5.78, N 7.14. MS (ESI): m/z 577 (M^+).

2-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole (5). White solid, 3.375 g, yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.36 (s, 1H), 8.26 (d, *J* = 6 Hz, 2H), 8.17 (s, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 4.2 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 1.47 (s, 18H), 1.36 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.49, 159.53, 138.82, 134.69, 134.48, 133.71, 128.64, 126.66, 125.36, 125.27, 124.03, 121.29, 120.95, 120.49, 119.43, 119.13, 118.72, 111.90, 104.64, 79.79, 30.31, 27.58, 20.43. Anal. calcd. for $C_{40}H_{44}BN_3O_3$ (%): C 76.79, H 7.09, N 6.72; Found: C 77.01, H 6.83, N 6.75. MS (ESI): m/z 625 (M^+).

3-(5-(3-bromophenyl)-1,3,4-oxadiazol-2-yl)-*N*,*N*-diphenylaniline (6b). Off white powder, 4.203 g, yield: 45% in three steps. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.80 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 2H), 7.31-7.22 (m, 5H), 7.14- 7.05 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.00, 158.47, 144.05, 142.46, 129.88, 125.92, 125.36, 124.86, 121.93, 120.95, 120.73, 119.95, 118.92, 118.36, 116.54, 115.90. Anal. calcd. for $C_{26}H_{18}BrN_3O$ (%): C 66.68, H 3.87, N 8.97; Found: C 67.02, H 4.22, N 8.98. MS (ESI): m/z 467 (M^+).

***N*,*N*-diphenyl-3-(5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)aniline (6).** White solid, 2.781 g, yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.21 (d, *J* = 6.9 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.87 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 8.7 Hz, 1H), 7.31-7.21 (m, 5H), 7.14-7.09 (m, 5H), 7.07 (d, *J* = 7.2 Hz, 1H), 1.37 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.14, 160.11, 144.22, 142.75, 133.48, 128.57, 125.49, 125.17, 125.02, 123.93, 122.05, 120.48, 120.12, 119.02, 118.83, 116.91, 116.23, 79.75, 20.42. Anal. calcd. for $C_{32}H_{30}BN_3O_3$ (%): C 74.57, H 5.87, N 8.15; Found: C 74.79, H 6.20, N 8.17. MS (ESI): m/z 515 (M^+).

4-(5-(3-bromophenyl)-1,3,4-oxadiazol-2-yl)-*N*,*N*-diphenylaniline (7b). Light green crystal, 3.756 g, yield: 40% in three steps: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.17 (d, *J* = 5.7 Hz, 1H), 7.87 (d,

J = 6.6 Hz, 2H), 7.59 (d, *J* = 5.4 Hz, 1H), 7.34 (t, *J* = 6.0 Hz, 1H), 7.27-7.19 (m, 5H), 7.10-7.06 (m, 5H), 7.04 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.50, 157.21, 145.72, 141.17, 128.98, 125.28, 124.33, 124.19, 122.76, 120.42, 119.92, 119.19, 117.72, 115.51, 110.21. Anal. calcd. for $C_{26}H_{18}BrN_3O$ (%): C 66.68, H 3.87, N 8.97; Found: C 67.00, H 4.20, N 9.14. MS (ESI): m/z 467 (M^+).

***N*,*N*-diphenyl-4-(5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)aniline (7).** Off white powder, 2.720 g, yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.35- 7.30 (m, 5H), 7.18-7.16 (m, 5H), 7.13 (d, *J* = 7.8 Hz, 3H), 1.37 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.12, 159.55, 146.39, 142.14, 133.28, 128.41, 125.13, 125.05, 123.94, 123.58, 121.17, 119.91, 119.09, 116.57, 111.54, 79.73, 20.43. Anal. calcd. for $C_{32}H_{30}BN_3O_3$ (%): C 74.57, H 5.87, N 8.15; Found: C 74.85, H 6.07, N 8.20. MS (ESI): m/z 515 (M^+).

References:

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