A New Class of Non-Conjugated Bipolar Hybrid Hosts for Phosphorescent Organic Light-Emitting Diodes

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Materials Synthesis

All chemicals, reagents, solvents, and poly(N-vinylcarbazole) with a weight-average molecular weight of $1.1 \times 10^6$ g/mole were used as received from commercial sources without further purification except toluene and tetrahydrofuran (THF) that had been distilled over sodium and benzophenone, respectively. Intermediates 9-(2-methylpropyl)carbazole (1), $^1$ 2-chloro-4,6-biphenyl-1,3,5-triazine (9), $^2$ 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (10), $^3$ and 1,3-bis(5-(4-bromophenyl)-1,3,4-oxadiazole-2-yl)benzene (11) $^4$ were synthesized according to the literature procedures. All reactions were carried out under argon and anhydrous conditions unless noted otherwise.

3,6-Dibromo-9-(2-methylpropyl)carbazole, 2. Into a suspension of 1 (10.0 g, 44.8 mmol) and silica gel (230-400 mesh, 100 g) in methylene chloride (400 ml) was added NBS powder (15.9 g, 89.6 mmol) at room temperature. The reaction mixture was stirred in the dark for 3 h before silica gel was removed by filtration. The filtrate was washed with water and dried over MgSO$_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography with hexane as the eluent to yield 2 (16.9 g, 99 %) as white crystals. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.14-8.13 (d, $J$=4.0 Hz 2H), 7.55-7.53 (m, 2H), 7.27-7.25 (m, 2H), 4.04-4.02 (d, $J$=7.6 Hz 2H), 2.32-2.30 (m, 1H), 0.97-0.94 (m, 6H).

3-Bromo-9-(2-methylpropyl)carbazole, 3. The procedure for the synthesis of 2 was followed with 1 eq. NBS to prepare 3 from 1 as white crystals in an 84% yield. $^1$H NMR (400 MHz,
CDCl₃): $\delta$ (ppm) 8.20-8.19 (d, $J$=1.6 Hz 1H), 8.05-8.03 (d, $J$=8.0 Hz 1H), 7.53-7.38 (m, 3H), 7.28-7.21 (m, 2H), 4.04-4.02 (m, 2H), 2.32-2.30 (m, 1H), 0.97-0.94 (m, 6H).

2-(9-(2-Methylpropyl)carbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, 4. BuLi (2.5 M in hexane, 6.95 ml, 17.4 mmol) was added dropwise into a solution of 3 (4.2 g, 13.9 mmol) in THF (80 ml) at –78 °C, where the mixture was stirred for 3 h before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (4.05 g, 21.75 mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a period of 12 h, quenched with water, and then extracted with ether. The organic extracts were combined, washed with brine and water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/methylene chloride 3:1 (v/v) as the eluent to yield 4 (3.95 g, 81 %) as a white powder. $^1$H NMR (400 MHz, CDCl₃): $\delta$ (ppm) 8.60 (s, 1H), 8.15-8.10 (d, $J$=2.0 Hz 1H), 7.90-7.85 (d, $J$=2.0 Hz 1H), 7.45-7.35 (m, 3H), 7.25-7.15 (m, 1H), 4.10-4.09 (d, $J$=4.0 Hz 2H), 2.42-2.30 (m, 1H), 1.39(s, 12H), 0.97-0.95 (d, $J$=8.0 Hz 6H).

3-Bromo-6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazole, 5. Toluene (30 ml) and H₂O (10 ml) were added into a mixture of 4 (1.2 g, 3.43 mmol), 2 (3.27 g, 8.59 mmol), Pd(PPh₃)₄ (0.22 g, 0.17 mmol), and Na₂CO₃ (3.43 g, 34 mmol). The reaction mixture was stirred at 90 °C for 12 h, cooled to room temperature, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/methylene chloride 9:1 to 3:1 (v/v) to yield 5 (0.62 g, 34%) as a white powder. $^1$H NMR (400 MHz, CDCl₃): $\delta$ (ppm) 8.38-8.34 (m, 2H), 8.29-8.28 (d, $J$=1.6 Hz 1H), 8.19-8.17 (d, $J$=7.6 Hz 1H), 7.85-7.78 (m, 2H), 7.55-7.42 (m, 5H), 7.30-7.23 (m, 2H), 4.15-4.10 (m, 4H), 2.45-2.38 (m, 2H), 1.13-1.10 (m, 12H).

3-Allyl-6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazole, 6. THF (20 ml) was added into a mixture of 5 (0.62 g, 1.18 mmol), allyltributyltin (0.78 g, 2.36 mmol), Pd(PPh₃)₄ (0.068 g, 0.06 mmol), and LiCl (0.092 g, 3.54 mmol). The reaction mixture was stirred at 90 °C for 24 h. After evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/methylene chloride 9:1 to 4:1 (v/v) as the eluent to yield 6 (0.35g, 61 %) as a white powder. $^1$H NMR (400 MHz, CDCl₃): $\delta$ (ppm) 8.40-8.38 (m, 2H), 8.19-8.17 (d, $J$=7.6 Hz 1H), 8.00 (s, 1H), 7.93-7.79 (m, 2H), 7.50-7.41 (m, 4H), 7.34-7.22
1-Bromo-4-(3-(6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)-benzene, 7. 9-BBN (0.5 M in THF, 6 ml, 3.0 mmol) was added dropwise into a solution of 6 (0.46 g, 0.95 mmol) in THF (3 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 18 h before transferring into a mixture of p-dibromobenzene (1.12 g, 4.7 mmol), Pd(PPh3)4 (0.055 g, 0.047 mmol), K2CO3 (0.98 g, 7.1 mmol), H2O (3 ml) and THF (5 ml). The reaction mixture was stirred at 85 °C for 40 h, cooled to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 4:1 (v/v) as the eluent to yield 7 (0.36 g, 59 %) as a white powder. 1H NMR (400 MHz, CDCl3): δ (ppm) 8.40-8.38 (m, 2H), 8.19-8.17 (d, J=7.6 Hz, 1H), 7.98-7.97 (d, J=0.8 Hz, 1H), 7.81-7.79 (m, 2H), 7.50-7.39 (m, 6), 7.33-7.23 (m, 3H), 7.10-7.08 (d, J=8.4 Hz, 2H), 4.15-4.11 (m, 4H), 2.86-2.83 (t, J=7.6 Hz, 2H), 2.69-2.65 (t, J=7.6 Hz, 2H), 2.44-2.42 (m, 2H), 2.09-2.03 (m, 2H), 1.04-1.01 (m, 12H).

2-(4-(3-(6-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, 8. The procedure for the synthesis of 4 was followed to prepare 8 from 7 as a white powder in an 88 % yield. 1H NMR (400 MHz, CDCl3): δ (ppm) 8.40-8.38 (m, 2H), 8.19-8.17 (d, J=7.6 Hz, 1H), 7.99 (s, 1H), 7.84-7.78 (m, 2H), 7.75-7.74 (d, J=8.8 Hz, 2), 7.50-7.43 (m, 4H), 7.32-7.23 (m, 3H), 4.15-4.10 (m, 4H), 2.86-2.83 (t, J=7.6 Hz, 2H), 2.69-2.65 (t, J=7.6 Hz, 2H), 2.44-2.42 (m, 2H), 2.09-2.03 (m, 2H), 1.34 (s, 12H), 1.04-1.01 (m, 12H).

3-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazole, Cz(MP)2. A solution of 1 (0.3 g, 1.34 mmol) in chloroform (16 ml) was slowly added into a mixture of Iron(III) chloride (0.92 g, 5.37 mmol) and chloroform(30 ml) under argon. The reaction mixture was stirred at room temperature for 4 h, quenched with 10 % sodium hydroxide aqueous solution (100 ml), and extracted with chloroform. The organic extracts were combined, washed with water and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 1:4 (v/v) as the eluent to yield Cz(MP)2 (0.23 g, 76 %) as a white powder (Found: C, 86.08; H, 7.22; N, 6.24. Calc. for C32H32N2: C, 86.45; H, 7.25; N, 6.30%). 1H NMR (400 MHz, CDCl3): δ (ppm) 8.40 (s, 2H), 8.19-8.18 (d,
2-(4-(3-(6-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)phenyl)-4,6-diphenyl-1,3,5-triazine, **TRZ-1Cz(MP)2**. Toluene (10 ml) and H2O (2 ml) were added into a mixture of 8 (0.34 g, 0.49 mmol), 9 (0.16 g, 0.62 mmol), Pd(PPh3)4 (0.056 g, 0.049 mmol), and Na2CO3 (0.39 g, 3.68 mmol). The reaction mixture was stirred at 95 °C for 40 h, cooled to room temperature, and then extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/methylene chloride 4:1 (v/v) to yield **TRZ-1Cz(MP)2** (0.28 g, 69 %) as a yellow powder (Found: C, 84.52; H, 6.39; N, 8.74. Calc. for C56H51N5: C, 84.71; H, 6.47; N, 8.82%); 1H NMR (400 MHz, CDCl3): δ (ppm) 8.79-8.76 (m, 4H), 8.71-8.69 (d, J=8.4 Hz, 2H), 8.41-8.39 (m, 2H), 8.19-8.17 (d, J=7.6 Hz, 1H), 8.02 (s, 1H), 7.81-7.79 (m, 2H), 7.60-7.55 (m, 6),7.49-7.42 (m, 6H), 7.35-7.33 (m, 2H), 7.25-7.20 (m, 1H), 4.14-4.11 (m, 4H), 2.93-2.82 (m, 4H), 2.44-2.40 (m, 2H), 2.20-2.10 (m, 2H), 1.03-1.01 (m, 12H). MALD/I TOF MS (DCTB) m/z ([M]+): 793.4.

2,4,6-Tris(4-(3-(6-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)phenyl)-1,3,5-triazine, **TRZ-3Cz(MP)2**. 9-BBN (0.5 M in THF, 3.30 ml, 1.65 mmol) was added dropwise into a solution of 6 (0.21 g, 0.42 mmol) in THF (2 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 18 h before transferring into a mixture of 10 (0.07 g, 0.13 mmol), Pd(PPh3)4 (0.030 g, 0.026 mmol), Na2CO3 (3.82 g, 36.0 mmol), H2O (18 ml) and toluene (30 ml). The reaction mixture was stirred at 85 °C for 40 h, cooled to room temperature, and then extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/methylene chloride 3:2 (v/v) to yield **TRZ-3Cz(MP)2** (0.147 g, 65 %) as a pale yellow powder (Found: C, 85.43; H, 7.01; N, 7.11. Calc. for C126H123N9: C, 85.82; H, 7.03; N, 7.15%). 1H NMR (400 MHz, CDCl3): δ (ppm) 8.69-8.67 (d, 6H), 8.40-8.39 (t, J=2.2Hz, 6H), 8.18-8.16 (d, J=3.8Hz, 3H), 8.01 (s, 3H), 7.82-7.78 (m, 6H), 7.47-7.30 (m, 27H), 4.12-4.09 (m, 12H), 2.92-2.82 (m, 12H), 2.48-2.35 (m, 6H), 2.19-2.11 (m, 6H), 1.03-0.99 (m, 36H). MALD/I TOF MS (DCTB) m/z ([M]+): 1762.1.

1,3-Bis(5-(4-(3-(6-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)phenyl)-1,3,4-oxadiazol-2-yl)benzene, **OXD-2Cz(MP)2**. 9-BBN (0.5 M in THF, 3.0 ml, 1.50
5 mmol) was added dropwise into a solution of 6 (0.20 g, 0.41 mmol) in THF (3 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 18 h before transferring into a mixture of 11 (0.11 g, 0.20 mmol), Pd(PPh3)4 (0.033 g, 0.029 mmol), Na2CO3 (0.60 g, 4.35 mmol), H2O (2 ml) and toluene (5 ml). The reaction mixture was stirred at 85 °C for 40 h, cooled to room temperature, and then extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with chloroform/ethyl acetate 50:1 (v/v) as the eluent to yield OXD-2Cz(MP)2 (0.12 g, 44 %) as a pale yellow powder (Found: C, 82.38; H, 6.42; N, 8.42. Calc. for C92H86N8O2: C, 82.73; H, 6.49; N, 8.39%). \(^1\)H NMR (400 MHz, CDCl3): \(\delta\) (ppm) 8.84 (s, 1H), 8.40-8.39 (m, 4H), 8.32-8.30 (m, 2H), 8.18-8.16 (d, \(J=7.6\) Hz, 2H), 8.11-8.08 (d, \(J=8.4\) Hz, 4H), 8.00 (s, 2H), 7.82-7.78 (m, 4H), 7.66-7.63 (t, \(J=8.4\) Hz, 1H), 7.49-7.32 (m, 16H), 7.25-7.21 (m, 2H), 4.13-4.11 (m, 8H), 2.90-2.88 (t, \(J=7.6\) Hz, 4H), 2.82-2.80 (t, \(J=7.6\) Hz, 2H), 2.46-2.40 (m, 4H), 2.20-2.10 (m, 4H), 1.03-1.01 (m, 24H). MALD/I TOF MS (DCTB) m/z ([M]+): 1334.8.

References:
Figure S1: Polarizing optical micrographs of spin-cast films of TRZ:1Cz(MP)2 mixture (a) and TRZ-1Cz(MP)2 hybrid after thermal annealing at 70 and 120 °C, respectively, for ½ h.