



High-triplet-energy host materials derived from directly-coupled carbazole-pyridindole moieties



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ABSTRACT

Directly-coupled carbazole-pyridindole moieties containing host materials for green and blue phosphorescent organic light-emitting diodes were synthesized by linking the two moieties via two different positions on the carbazole-pyridindole core structure. The carbazole-pyridindole moieties were functionalized using benzonitrile and phenyl substituent groups to introduce controlled-charge transport properties. The host materials synthesized using the carbazole-pyridindole moieties showed a maximum quantum efficiency of 19.1% in green phosphorescent devices, and 18.2% in blue phosphorescent devices.

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1. Introduction

There have been tremendous efforts to obtain high efficiency in organic light-emitting diodes (OLEDs). Among these, phosphorescent organic light-emitting diodes (PHOLEDs) have emerged as a key technology in obtaining high efficiency [1–3]. PHOLEDs can approach approximately 100% internal maximum quantum efficiency (QE) through intersystem crossing, while fluorescent organic light-emitting diodes (FLOLEDs) can reach only 25% internal QE [4–5].

Although PHOLEDs are regarded as a promising technology in obtaining high efficiency, there are several challenges that need to be overcome. The long exciton lifetime of PHOLEDs in comparison with that of FLOLEDs may cause triplet-triplet annihilation (TTA) and result in a QE decrease at high doping concentrations [6]. Therefore, it is necessary for emitting materials to be dispersed throughout the host matrix in order to suppress the TTA process [7]. Further, especially for PHOLEDs, the triplet-energy of the host materials is significant since the phosphorescence emission originates from triplet excitons, and triplet exciton confinement can improve device performance [8–14].

The host materials for blue PHOLEDs are required to have higher triplet-energy than those for green PHOLEDs. Therefore, the molecular design of the host materials for blue PHOLEDs proceeded using high-triplet-energy moieties. Carbazole is a widely used hole-transporting moiety with a high-triplet-energy and good thermal stability. Despite the fact that the carbazole moiety has excellent expandability, the most common modification strategy is to use the 9-position via N-amination, and the 3-position via halogenation [12–18]. Our group recently reported the 4-position of carbazole-based host materials to increase the triplet-energy and dihedral angle in comparison with the 3-position [19].

Based on the results, we applied 2- and 4-position-modified carbazole in our work and developed carbazole-pyridindole derivatives [20]. The 2-position linking of the carbazole-pyridindole derivatives led to a relatively low triplet-energy of 2.63 eV compared with that of the 4-position connection of carbazole-pyridindole, and a maximum quantum efficiency of 19.1% in green PHOLEDs. The 4-position of carbazole-pyridindole-based host materials showed a high triplet-energy greater than 2.88 eV, and a maximum quantum efficiency of 18.2% in blue PHOLEDs. It was demonstrated that the carbazole-pyridindole moiety can be diversely applied as the core structure of triplet host materials for green and blue PHOLEDs by changing the linking position between carbazole and pyridindole.

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2. Experimental

2.1. General information

Potassium iodide, potassium iodate, copper iodide, (\pm)-*trans*-1,2-diaminocyclohexane, 3-bromobenzonitrile, triethylborate, *n*-butyllithium, and bromobenzene were purchased from Aldrich Chem. Co. Tetrakis(triphenylphosphane) palladium(0), 9H-pyrido[2,3-*b*]indole, and (9-phenyl-9H-carbazol-2-yl)boronic acid were provided by P&H tech Co. Acetic acid, sodium bicarbonate, potassium carbonate, and potassium phosphate tribasic from Duksan Sci. Co. were used without further purification. Tetrahydrofuran (THF, Duksan Sci. Co.) was distilled with calcium hydride and sodium. Chemical, electrochemical, and photophysical analysis were carried out using the instruments described in our previous work [19].

2.2. Synthesis

The synthetic schemes of the 2CzCbCN, 2CzCbPh, 4CzCbCN, and 4CzCbPh compounds are described in Scheme 1.

2.2.1. 6-iodo-9H-pyrido[2,3-*b*]indole (1)

The synthetic procedure of 6-iodo-9H-pyrido[2,3-*b*]indole was the same as that reported in the literature [20].

2.2.2. 4-bromo-9-Phenyl-9H-carbazole

The synthetic procedure of 4-bromo-9-phenyl-9H-carbazole was described in recent literature [21].

2.2.3. (9-Phenyl-9H-carbazol-4-yl)boronic acid

4-bromo-9-phenyl-9H-carbazole (0.50 g, 0.16 mmol) was vacuum dried for 3 h, dissolved in THF under a nitrogen atmosphere, and stirred for 30 min at -30 °C. *n*-butyl lithium (0.12 g, 0.19 mmol) was slowly injected into the solution, which was subsequently stirred for 1 h. Triethylborate (0.27 g, 0.19 mmol) was added into the reaction mixture, and the solution was stirred for a further 12 h at room temperature. 2 M aqueous hydrochloric acid was poured into the solution, which was then stirred for 30 min. The solution was neutralized with potassium carbonate and extracted using methylene chloride and distilled water. The organic layer was dehydrated with magnesium sulfate and reprecipitated using *n*-hexane. The mixture was filtered, and the precipitate was obtained as a white solid.

Yield 90% (0.40 g), $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.55 (s, 2H), 8.50 (d, 1H, $J=8.0$ Hz), 7.70 (t, 2H, $J=7.8$ Hz), 7.57 (t, 3H, 7.0 Hz), 7.38 (d, 2H, $J=8.4$ Hz), 7.34–7.31 (m, 2H), 7.26–7.22 (m, 2H) MS (ESI) m/z 211.2 [(M + H) $^+$].

2.2.4. 6-(9-Phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indole

The synthetic procedure of 6-(9-phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indole was the same as the method listed in our previous work [20]. (9-Phenyl-9H-carbazol-2-yl)boronic acid was used instead of (9-phenyl-9H-carbazol-3-yl)boronic acid.

Yield 56%, $^1\text{H NMR}$ (400 MHz, DMSO): δ 11.81 (s, 1H), 8.58 (s, 1H, $J=7.6$ Hz), 8.47 (s, 1H), 8.39 (d, 1H, $J=6.4$ Hz), 8.31 (s, 1H, $J=7.6$ Hz), 8.24 (d, 1H, 7.2 Hz), 7.75 (d, 1H, $J=8.8$ Hz), 7.70–7.49 (m, 8H), 7.42–7.34 (m, 2H), 7.27 (t, 1H, $J=7.4$ Hz), 7.17 (t, 1H, $J=6.4$ Hz) MS (ESI) m/z 410.2 [(M + H) $^+$].

2.2.5. 6-(9-Phenyl-9H-carbazol-4-yl)-9H-pyrido[2,3-*b*]indole

The synthetic procedure of 6-(9-phenyl-9H-carbazol-4-yl)-9H-pyrido[2,3-*b*]indole was the same as the method listed in our previous work [20]. (9-phenyl-9H-carbazol-4-yl)boronic acid was used instead of (9-phenyl-9H-carbazol-3-yl)boronic acid.

Yield 80%, $^1\text{H NMR}$ (400 MHz, DMSO): δ 11.99 (s, 1H), 8.56 (d, 1H,

$J=8.0$ Hz), 8.47 (d, 1H, $J=6.4$ Hz), 8.41 (s, 1H), 7.75–7.65 (m, 6H), 7.59 (t, 1H, $J=8.0$ Hz), 7.51 (t, 1H, $J=7.8$ Hz), 7.42–7.31 (m, 4H), 7.24–7.17 (m, 2H), 6.99–6.94 (m, 1H) MS (ESI) m/z 410.2 [(M + H) $^+$].

2.2.6. 3-(6-(9-phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indol-9-yl)benzonitrile (2CzCbCN)

The synthetic procedure of 3-(6-(9-phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indol-9-yl)benzonitrile was the same as that described in previous work [20]. 6-(9-phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indole was used instead of 6-(9-phenyl-9H-carbazol-3-yl)-9H-pyrido[2,3-*b*]indole.

Yield 72%, T_g 121 °C, $^1\text{H NMR}$ (500 MHz, DMSO): δ 8.79 (d, 1H, $J=7.5$ Hz), 8.65 (s, 1H), 8.46 (d, 1H, $J=6.0$ Hz), 8.37 (s, 1H, $J=8.0$ Hz), 8.27 (t, 2H, $J=7.8$ Hz), 8.01 (d, 1H, $J=8.5$ Hz), 8.00 (d, 1H, $J=8.0$ Hz), 7.85 (t, 2H, $J=7.8$ Hz), 7.73–7.70 (m, 5H), 7.66–7.61 (m, 2H), 7.56 (t, 1H, $J=8.5$ Hz), 7.44 (t, 1H, $J=7.8$ Hz), 7.40–7.38 (m, 2H), 7.31 (t, 1H, 7.5 Hz) $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 151.3, 146.5, 140.8, 140.7, 139.0, 138.1, 136.8, 136.6, 134.6, 132.0, 131.1, 130.9, 130.5, 130.3, 129.6, 127.8, 126.8, 126.2, 122.5, 121.7, 121.3, 121.0, 120.6, 120.2, 120.1, 119.7, 118.2, 117.2, 116.1, 112.5, 110.7, 109.6, 107.6 MS (ESI) m/z 511.1 [(M + H) $^+$].

2.2.7. 9-phenyl-6-(9-phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indole (2CzCbPh)

The synthetic procedure of 2CzCbPh was the same as that described in previous work [20]. 6-(9-phenyl-9H-carbazol-2-yl)-9H-pyrido[2,3-*b*]indole was used instead of 6-(9-phenyl-9H-carbazol-3-yl)-9H-pyrido[2,3-*b*]indole.

Yield 81%, T_g 111 °C, $^1\text{H NMR}$ (500 MHz, DMSO): δ 8.77 (d, 1H, $J=7.5$ Hz), 8.65 (s, 1H), 8.45 (d, 1H, $J=6.5$ Hz), 8.37 (d, 1H, $J=8.5$ Hz), 8.29 (d, 1H, $J=7.5$ Hz), 7.84 (d, 1H, $J=8.5$ Hz), 7.74–7.65 (m, 10H), 7.59–7.51 (m, 3H), 7.45 (t, 1H, $J=7.5$ Hz), 7.40–7.31 (m, 3H) $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 151.6, 146.5, 140.8, 140.7, 139.2, 138.6, 136.8, 135.8, 134.1, 130.3, 129.5, 129.4, 127.8, 127.5, 127.1, 126.8, 126.7, 126.2, 122.6, 121.7, 121.0, 120.6, 120.2, 120.0, 119.7, 116.6, 115.8, 110.6, 109.6, 107.6 MS (ESI) m/z 485.7 [(M + H) $^+$].

2.2.8. 3-(6-(9-phenyl-9H-carbazol-4-yl)-9H-pyrido[2,3-*b*]indol-9-yl)benzonitrile (4CzCbCN)

The synthetic procedure of 4CzCbCN was the same as described in previous work [20]. 6-(9-phenyl-9H-carbazol-4-yl)-9H-pyrido[2,3-*b*]indole was used instead of 6-(9-phenyl-9H-carbazol-3-yl)-9H-pyrido[2,3-*b*]indole.

Yield 80%, T_g 119 °C, $^1\text{H NMR}$ (400 MHz, DMSO): δ 8.72 (d, 1H, $J=8.0$ Hz), 8.57 (s, 1H), 8.51 (d, 1H, $J=6.4$ Hz), 8.36 (s, 1H), 8.20 (d, 1H, $J=8.0$ Hz), 8.01 (d, 1H, $J=8.4$ Hz), 7.90 (t, 1H, $J=8.0$ Hz), 7.80–7.71 (m, 4H), 7.65 (d, 2H, $J=8.4$ Hz), 7.59 (t, 1H, $J=7.8$ Hz), 7.52 (t, 1H, $J=7.8$ Hz), 7.44–7.31 (m, 5H), 7.23 (d, 1H, $J=7.6$ Hz), 6.97 (t, 1H, $J=8.0$ Hz) $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 151.3, 146.6, 140.8, 140.6, 138.3, 137.3, 136.7, 136.7, 136.6, 133.8, 132.1, 131.0, 130.8, 130.6, 130.2, 129.3, 128.3, 127.9, 127.1, 125.9, 122.2, 121.9, 121.7, 121.6, 120.9, 120.1, 119.5, 118.1, 117.1, 116.0, 112.5, 110.2, 109.5, 108.5 MS (ESI) m/z 511.4 [(M + H) $^+$].

2.2.9. 9-phenyl-6-(9-phenyl-9H-carbazol-4-yl)-9H-pyrido[2,3-*b*]indole (4CzCbPh)

The synthetic procedure of 4CzCbPh was the same as that described in previous work [20]. 6-(9-phenyl-9H-carbazol-4-yl)-9H-pyrido[2,3-*b*]indole was used instead of 6-(9-phenyl-9H-carbazol-3-yl)-9H-pyrido[2,3-*b*]indole.

Yield 70%, T_g 106 °C, $^1\text{H NMR}$ (400 MHz, DMSO): δ 8.68 (d, 1H, $J=8.0$ Hz), 8.55 (s, 1H), 8.48 (d, 1H, $J=6.4$ Hz), 7.79–7.62 (m, 10H), 7.60–7.48 (m, 3H), 7.43 (d, 1H, $J=8.0$ Hz), 7.36–7.30 (m, 4H), 7.22 (d, 1H, $J=8.0$ Hz), 6.96 (t, 1H, $J=8.2$ Hz) $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 151.6, 146.5, 140.8, 140.6, 138.8, 137.4, 136.7, 135.8, 133.3, 130.1,

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