



# Molecular design of large-bandgap host materials and their application to blue phosphorescent organic light-emitting diodes



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## ABSTRACT

New large-bandgap host materials with carbazole and carboline moieties were designed and synthesized for high-performance blue phosphorescent organic light-emitting diodes (PhOLEDs). The two kinds of host materials, 9-(4-(9H-carbazol-9-yl)phenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (**pP2CZCB**) and 9-(3-(9H-carbazol-9-yl)phenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (**mP2CZCB**), displayed promisingly high triplet energies of ~2.92–2.93 eV for enhancing the exothermic energy transfer to bis[2-(4,6-difluorophenyl)pyridinato-C<sup>2</sup>,N](picolinato)iridium(III) (Flrpic) in PhOLED devices. It was found that the blue PhOLEDs bearing the new host materials and the Flrpic dopant exhibited markedly higher external quantum efficiencies (EQEs) than a device made with 1,3-bis(*N*-carbazolyl)benzene (mCP) as the host. In particular, the PhOLED device made with 3 wt% Flrpic as the dopant and **mP2CZCB** as the host material displayed a low driving voltage of 4.13 V and the high EQE of 25.3% at 1000 cd m<sup>-2</sup>.

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## 1. Introduction

Since 1999, phosphorescent organic light-emitting diodes (PhOLEDs) have been a focus of study due to their relatively high external quantum efficiencies (EQEs) compared to conventional fluorescent OLEDs; both singlet and triplet excitons are used to achieve a theoretical internal quantum efficiency of 100% [1–3]. Although green and red PhOLEDs have achieved desirably high EQEs for practical use as OLED displays [4–6], blue PhOLEDs still need further study on highly efficient host and dopant materials for improving the device performances [7].

To attain efficient blue PhOLEDs, the development of acceptable host materials has become essential; these materials must have high triplet energies ( $E_T$ ) and a specific electronic character with charge balance between their holes and electrons. High  $E_T$  values of the host materials can prevent endothermic energy transfers from the phosphorescent dopant to the host materials within a device, and host materials with well-balanced bipolar properties can form excitons throughout the entire emitting layer [8,9]. Additionally, well-controlled energy levels for the highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a host material can reduce the barrier for charge injection from an adjacent hole or electron transport auxiliary layer to the emitting layer.

Among the fused heterocycles available for use as effective bipolar hosts [10–13], carbazole and carboline moieties are particularly favorable, owing to their flexible attachments to specific aromatic core units. Although carboline is similar to carbazole in structure, it has a higher electron affinity because of its electron-deficient pyridine subunit. Some specific carbazole- and carboline-containing host materials have demonstrated well-balanced bipolar character, and have displayed EQEs of over 20% in blue PhOLEDs [14–15].

Concurrently, other researchers have suggested that the structural isomers of host materials bearing the same aromatic or heteroaromatic moieties can exhibit different device performances with the only change of a different anchoring position on the core units [16–19]. They accomplished the structural optimization of host materials for enhancing the EQEs of blue PhOLEDs on the bases of theoretical calculation and materials characterization, such as optical, photophysical, and electrochemical analyses.

In our previous work, we demonstrated a set of bipolar host materials bearing carbazole and carboline moieties [13]. It

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was found that the 9-(4-(9H-pyrido[2,3-b]indol-9-yl)phenyl)-9H-3,9'-bicarbazole (pBCb2Cz) host material showed a promising  $E_T$  (2.93 eV) for use in blue PhOLEDs, and that a Flrpic-based device exhibited a high EQE of over 20%. However, examining the structural variations of the host materials is needed for further improvement to the performance of blue PhOLEDs.

In this work, we synthesized two kinds of host materials bearing carbazole and carboline moieties with different substitution patterns on the benzene core: 9-(4-(9H-carbazol-9-yl)phenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (pP2CZCB) and 9-(3-(9H-carbazol-9-yl)phenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (mP2CZCB). To design potential host molecules for high-performance blue PhOLEDs, we varied the position of two carbazole units and one carboline unit, and compared the new materials' performances to that of previously reported pBCb2Cz-containing PhOLED [13]. pP2CZCB and mP2CZCB displayed  $E_T$  values of 2.92 eV and 2.93 eV, respectively, which are high enough to allow for energy transfer to Flrpic, the blue dopant. The PhOLEDs bearing the newly synthesized hosts and the Flrpic dopant were found to display significantly higher EQEs than the device made with 1,3-bis(*N*-carbazolyl)benzene (mCP). In particular, the mP2CZCB-based blue PhOLED exhibited a low operating voltage of 4.13 V and a markedly high EQE of 25.3% at 1000 cd m<sup>-2</sup>.

## 2. Experimental section

### 2.1. Materials

All reagents for synthesizing the two host materials were purchased from Sigma–Aldrich, TCI (SEJINCI), and Acros Organics, and used without additional purification. The solvents were distilled by using a Solvent Dispensing System (J.C. Meyer, Laguna Beach, CA, USA). The hole-injection material, dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN), was purchased from Luminescence Technology. Di-[4-(*N,N*-ditolyl-amino)-phenyl]cyclohexane (TAPC), for preparing the hole-transport layer, was purchased from Jilin OLED Material Tech Co., Ltd. Flrpic and 3,3'-[5'-[3-(3-pyridinyl)-phenyl]][1,1':3',1''-terphenyl]-3,3''-diyl]bis pyridine (TmPyPB) were purchased from Daejoo Electronic Materials. 6-(9H-Carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (1), used as an intermediate compound, was prepared by following reported procedures [16].

### 2.2. Synthesis

#### 2.2.1. 9-(4-Bromophenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (2)

A portion of (1) (1.50 g, 4.50 mmol), 1-bromo-4-iodobenzene (1.65 g, 5.85 mmol), potassium phosphate tribasic (K<sub>3</sub>PO<sub>4</sub>, 4.78 g, 22.5 mmol), CuI (0.17 g, 0.90 mmol), and *trans*-1,2-diaminocyclohexane (0.26 g, 2.25 mmol) were suspended in dry toluene (30 mL) under an argon atmosphere, and the mixture was stirred at 110 °C for 18 h. After finishing the reaction, the mixture was filtered through Celite and washed with methylene chloride (MC). The crude product was purified by silica-gel column chromatography using *n*-hexane/MC as eluents to give 85% yield (1.87 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.54 (d, *J* = 4.68 Hz, 1H), 8.35 (d, *J* = 7.44 Hz, 1H), 8.25 (s, 1H), 8.18 (d, *J* = 7.44 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.66 (m, 4H), 7.42 (m, 4H), 7.31 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 151.80, 146.88, 141.26, 138.32, 134.64, 132.62, 130.56, 128.52, 128.50, 126.28, 125.56, 122.80, 121.6, 121.20, 119.98, 119.82, 119.43, 116.40, 115.68, 111.05, 109.24; Anal. Calcd. for C<sub>29</sub>H<sub>18</sub>BrN<sub>3</sub>: C, 71.32; H, 3.71; Br, 16.36; N, 8.60, found, C, 70.46; H, 3.72; N, 8.46.

#### 2.2.2. 9-(4-(9H-Carbazol-9-yl)phenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (3, pP2CZCB)

9-(4-Bromophenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (2) (1.60 g, 3.28 mmol), and carbazole (0.60 g, 3.60 mmol) were suspended in a mixture of K<sub>3</sub>PO<sub>4</sub> (3.48 g, 16.4 mmol), CuI (0.12 g, 0.66 mmol), and *trans*-1,2-diaminocyclohexane (0.19 g, 1.64 mmol) in dry toluene (30 mL) under Ar. The reaction mixture was stirred at 110 °C for 18 h. Then, the mixture was filtered through Celite and washed with MC. The crude product was purified by silica-gel column chromatography using *n*-hexane/MC as an eluent to give 84% yield (1.58 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.62 (d, *J* = 4.72 Hz, 1H), 8.40 (d, *J* = 7.44 Hz, 1H), 8.31 (s, 1H), 8.20 (t, *J* = 7.80 Hz, 4H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.88 (t, *J* = 8.60 Hz, 3H), 7.69 (d, *J* = 8.60 Hz, 1H), 7.62 (d, *J* = 8.24 Hz, 2H), 7.48 (t, *J* = 8.20 Hz, 2H), 7.43 (m, 4H), 7.34 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 152.27, 147.26, 141.65, 140.65, 138.89, 137.06, 134.82, 131.00, 128.94, 128.59, 128.13, 126.68, 126.07, 125.94, 123.53, 123.19, 122.04, 120.38, 120.37, 120.23, 120.20, 119.81, 116.80, 116.19, 111.66, 109.86, 109.63; HR-MS (EI) *m/z* (M<sup>+</sup>): Calcd for C<sub>41</sub>H<sub>26</sub>N<sub>4</sub>, 574.22; found, 573.51. Anal. Calcd. for C<sub>41</sub>H<sub>26</sub>N<sub>4</sub>: C, 85.69; H, 4.56; N, 9.75, found, C, 84.99; H, 4.55; N, 9.64.

#### 2.2.3. 9-(3-Bromophenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (4)

A portion of (1) (1.50 g, 4.50 mmol), 1-bromo-3-iodobenzene (1.65 g, 5.85 mmol), K<sub>3</sub>PO<sub>4</sub> (4.78 g, 22.5 mmol), CuI (0.17 g, 0.90 mmol), and *trans*-1,2-diaminocyclohexane (0.17 g, 0.90 mmol) were mixed in dry toluene (30 mL) under Ar, and the mixture was stirred at 110 °C for 24 h. After completion of the reaction, the mixture was filtered through Celite and washed with MC. After concentrating the MC layer, the crude product was purified by silica-gel column chromatography using *n*-hexane/MC as an eluent to give 80% yield (1.75 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.55 (d, *J* = 4.68 Hz, 1H), 8.36 (d, *J* = 7.80 Hz, 1H), 8.26 (s, 1H), 8.19 (d, *J* = 7.40 Hz, 2H), 7.91 (s, 1H), 7.71 (m, 4H), 7.55 (t, *J* = 8.20 Hz, 1H), 7.43 (d, *J* = 7.84 Hz, 1H), 7.40 (m, 3H), 7.32 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 152.16, 147.28, 141.62, 138.71, 137.27, 131.03, 131.00, 130.41, 128.87, 126.69, 126.09, 125.93, 123.16, 123.12, 121.99, 120.35, 120.17, 119.79, 116.84, 116.05, 111.49, 109.62; Anal. Calcd. for C<sub>29</sub>H<sub>18</sub>BrN<sub>3</sub>: C, 71.32; H, 3.71; Br, 16.36; N, 8.60, found, C, 69.67; H, 3.65; N, 8.45.

#### 2.2.4. 9-(3-(9H-Carbazol-9-yl)phenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (5, mP2CZCB)

9-(3-Bromophenyl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-*b*]indole (4) (1.60 g, 3.28 mmol), carbazole (0.60 g, 3.60 mmol), K<sub>3</sub>PO<sub>4</sub> (3.48 g, 16.4 mmol), CuI (0.12 g, 0.66 mmol), and *trans*-1,2-diaminocyclohexane (0.19 g, 1.64 mmol) were suspended in dry toluene (30 mL) under Ar, and the mixture was stirred at 110 °C for 24 h. After completion of the reaction, the mixture was filtered through Celite and washed with MC. The MC portion was concentrated and the crude product purified by silica-gel column chromatography using an eluent of *n*-hexane/MC, to give 81% yield (1.45 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 8.59 (d, *J* = 5.08 Hz, 1H), 8.34 (d, *J* = 7.84 Hz, 1H), 8.26 (s, 1H), 8.18 (t, *J* = 8.20 Hz, 4H), 8.03 (s, 1H), 7.87 (d, *J* = 5.12 Hz, 2H), 7.84 (d, *J* = 8.60 Hz, 1H), 7.74 (m, 1H), 7.70 (d, *J* = 8.24 Hz, 2H), 7.64 (d, *J* = 7.04 Hz, 1H), 7.47 (t, *J* = 7.04 Hz, 2H), 7.40 (m, 4H), 7.32 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 151.53, 146.64, 140.99, 139.88, 138.36, 137.95, 136.84, 130.37, 130.32, 128.22, 126.05, 125.48, 125.29, 125.13, 124.93, 122.96, 122.53, 121.48, 119.74, 119.70, 119.65, 119.58, 119.16, 116.25, 115.48, 110.95, 109.31, 109.00; HR-MS (EI) *m/z* (M<sup>+</sup>): Calcd for C<sub>41</sub>H<sub>26</sub>N<sub>4</sub>, 574.22; found, 573.486. Anal. Calcd. for C<sub>41</sub>H<sub>26</sub>N<sub>4</sub>: C, 85.69; H, 4.56; N, 9.75, found, C, 83.50; H, 4.51; N, 9.50.

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