New Bipolar Host Materials for Realizing Blue Phosphorescent Organic Light-Emitting Diodes with High Efficiency at 1000 cd/m²

Min Ju Cho,[†,ǁ] Sun Jae Kim,[†,ǁ] Seung Hee Yoon,[†,ǁ] Jicheol Shin,[†] Tae Ryang Hong,[†] Hyung Jong Kim,[†] Young Hoon Son,[‡] Ju Sik Kang,[†] Hyun Ah Um,[†] Tae Wan Lee,[†] Jong-Kwan Bin,[§] Bang Sook Lee,[§] Joong Hwan Yang,[§] Gee Sung Chae,[§] Jang Hyuk Kwon,*[‡] and Dong Hoon Choi*[†]

[†]Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-Gu, Seoul 136-701, Republic of Korea

[‡]Department of Information Display, Kyung Hee University, Dongdaemoon-gu, Seoul 130-701, Republic of Korea

[§]LG Display, Co., LTD., 1007 Deogeon-ri, Wollong-myeon, Paju-si, Gyeonggi-do 413-811, Republic of Korea

S *Supporting Information*

ABSTRACT: New host molecules such as 9-(6-(9H-carbazol-9-yl)pyridin-3-yl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]-indole (pPCB2CZ) and 9-(6-(9H-carbazol-9-yl)pyridin-2-yl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (mPCB2CZ) were designed and synthesized for blue phosphorescent organic light-emitting diodes (PhOLEDs). The glass transition temperatures of two host molecules were measured higher than 120 °C, and the identical triplet energies were determined to be 2.92 eV for both molecules. The bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic)-doped mPCB2CZ-based PhOLED exhibited practically useful driving voltage of 4.8 V in a simple organic three layer device configuration which has a smaller number of interfaces in conventional multilayer PhOLEDs. Also, the high quantum efficiency of 23.7% is reported at the practically useful brightness value of 1000 cd/m².

KEYWORDS: *organic light emitting diode, phosphorescence, bipolar host, carboline, quantum efficiency*
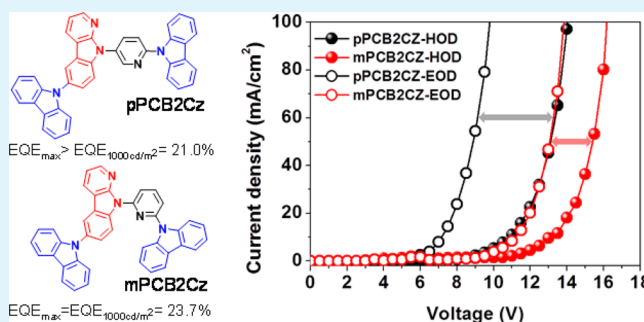
INTRODUCTION

Phosphorescent organic light-emitting diodes (PhOLEDs) exhibit desirable properties such as high external quantum efficiency (EQE) and low power consumption in device operation for future flat-panel and flexible displays.[1−4] The high performance of PhOLEDs has been aided by the development of new dopants, host materials, and auxiliary charge transport materials. However, blue PhOLEDs still show inferior quantum efficiencies, color coordinates of emission, and significantly poor lifetimes, which need to be greatly improved for use in practical applications. In multilayered PhOLEDs, one of the most important issues for achieving higher performance is the development of highly functional host materials with higher triplet energy (E_T) than the dopant. This higher E_T allows effective confinement of triplet excitons on the dopant with the lower E_T without reverse energy transfer from the dopant to the host material.[5,6]

Among the many design concepts for host materials, bipolar host materials have been the subject of interest because these materials have well-balanced charge transport properties that could extend the emitting zone in an emitting layer.[7,8] Along with well-optimized electronic properties and charge balance in the emitting layer of blue PhOLEDs, the thermal properties of the host materials are considered to be another important issue, because long-term operational stability of the device is believed to depend on the glass transition temperatures (T_g) of the host materials.

Various host materials have been synthesized for achieving efficient blue PhOLEDs. In many examples of blue host materials, carbazole, which has a rigid molecular frame, a sufficiently high E_T, and good hole transporting properties, has often been employed for organizing the structure of the desired host materials.[9,10] In addition, the carbazole unit has many reaction sites that allow for facile substitution with various electron-withdrawing moieties such as cyano group,[11] pyridine,[12,13] oxazole,[14,15] triazole,[16−18] and diphenylphosphine oxide,[19−21] which can alter the intrinsic characteristics of a bipolar host.

Compared with the above-mentioned electron-affine moieties, pyrido[2,3-b]indole (i.e., α-carboline) consists of a pyridine-containing heteroaromatic ring as an electron-accepting character. Recently, new α-carboline-based host materials comprising carbazole and a benzene ring have shown highly efficient bipolar characteristics with high E_T; the corresponding

blue PhOLED exhibited significantly improved device efficiency.[22−25] For example, Lee et al. reported a new bipolar host molecule, 3,3′-bis(9H-pyrido[2,3-b]indol-9-yl)-1,1′-biphenyl (CbBPCb, E_T = 2.77 eV), containing a carboline unit that displays the highest quantum efficiency (30.1% as maximum) obtained in sky-blue PhOLEDs with bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic).[24]

In our previous work, a bipolar host material, 9-(4-(9H-pyrido[2,3-b]indol-9-yl)phenyl)-9H-3,9′-bicarbazole (pBCb2Cz), also bearing carbazole and carboline moieties, was successfully synthesized and was reported to exhibit a very high E_T of 2.93 eV. FIrpic-doped blue PhOLEDs with this host material exhibited an almost ideal quantum efficiency higher than 20%.[25]

However, these limited studies showed that the structural combination of carbazole and carboline moieties was probably responsible for improved device efficiency in blue PhOLEDs. Therefore, it is worthwhile to study how varying the position of the carbazole and carboline moieties with a specific linking group can affect the device performance without deteriorating the physical properties such as T_g and E_T.

In this study, we synthesized two different host molecules bearing carbazole and carboline moieties in one molecular structure (i.e., 9-(6-(9H-carbazol-9-yl)pyridin-3-yl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (pPCB2CZ) and 9-(6-(9H-carbazol-9-yl)pyridin-2-yl)-6-(9H-carbazol-9-yl)-9H-pyrido-[2,3-b]indole (mPCB2CZ). For designing the host molecules, we employed two carbazole units and one carboline unit with an electron-affine pyridine linking moiety. Compared to the structure of pBCb2Cz,[25] the positions of carbazole and carboline unit were switched in the two host materials and pyridine linking unit was employed instead of benzene ring as shown in Figure 1. The objective of this study is to design and
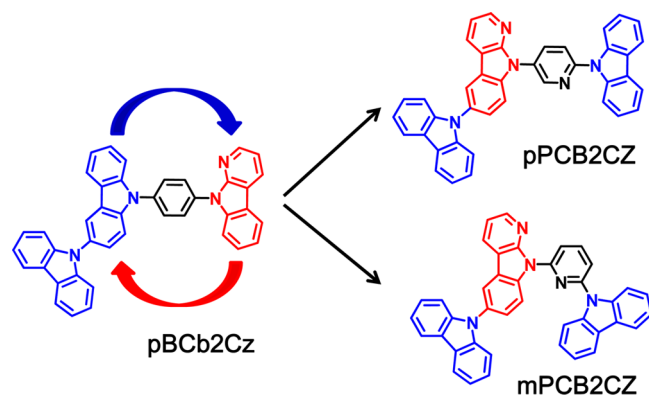

Figure 1. Molecular structures of **pBCb2Cz**,[25] **pPCB2CZ**, and **mPCB2CZ**.

synthesize new host molecules bearing carbazole, carboline, and pyridine core for enhancing bipolar characters. The two host molecules were observed to have high T_g values in the range 128−144 °C and the same E_T of 2.92 eV. The characterization of the FIrpic-doped blue PhOLED showed that the mPCB2CZ-based device exhibited markedly low roll-off behavior and practically useful driving voltage of 4.8 V in a simple organic three layer device configuration. Also, a high quantum efficiency of 23.7% is reported at the practically useful brightness value of 1000 cd/m², which is higher than the value we reported previously.[25]

■ EXPERIMENTAL SECTION

Materials. All reagents were purchased from Acros, TCI, and Sigma-Aldrich Co. and used without further purification unless stated otherwise. The reagent-grade solvents used in this study were freshly dried using standard distillation methods. Sublimated grade di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) and 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) were purchased from Jilin OLED Material Tech Co., Ltd. and were used as the HTL and host material, respectively. Twice sublimated 3,3′-[5′-[3-(3-pyridinyl)-phenyl][1,1′:3′,1″-terphenyl]-3,3″-diyl]bispyridine (TmPyPB) from Daejoo Electronic Materials was used as the ETL. FIrpic from Luminescence Technology was used as the sky-blue phosphorescent dopant material.

3-Iodo-9-tosyl-9H-carbazole (2). Under an argon atmosphere, compound **1** (7.9 g, 26.8 mmol) was first dissolved in 150 mL of anhydrous DMF, then NaH (0.71 g, 29.5 mmol) was added into the mixture, and the mixture was allowed to stir at room temperature for 1 h. To this solution was added tosyl chloride (6.14 g, 32.2 mmol), and the mixture was stirred at room temperature for 3 h. After completion of the reaction, the crude product was precipitated in distilled water. The product was purified by recrystallization from methanol (MeOH) and CHCl₃ to afford **2** in 83% yield (10 g). ¹H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.66 (d, J = 1.50 Hz, 1H) 8.62 (dd, J = 1.56 Hz, 7.84 Hz, 1H), 8.56 (dd, J = 1.56 Hz, 5.08 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.96 (dd, J = 1.60 Hz, 8.64 Hz,1H), 7.92 (d, J = 8.6 Hz, 2H), 7.48 (dd, J = 7.44 Hz, 7.84 Hz, 1H), 7.35 (d, J = 8.24 Hz, 2H), 2.28 (s, 3H). ¹³C NMR (100 MHz, DMSO-d_6): δ (ppm) 149.97, 147.83, 145.81, 136.85, 136.27, 134.72, 130.26, 130.21, 130.08, 127.10,124.95, 120.17, 116.91, 116.62, 88.73, 21.12.

General Procedure of Ullmann Coupling Amination. Under an argon atmosphere, the amine (10.0 mmol), aryl halide (10.0 mmol), potassium phosphate tribasic (K₃PO₄, 50.0 mmol), CuI (2.0 mmol), and trans-1,2-diaminocyclohexane (5.0 mmol) were added in dry toluene (30 mL), and the mixture was allowed to stir at 110 °C for 12 h. After completion of the reaction, the reaction mixture was filtered by Celite and washed with CH₂Cl₂. The crude product was purified either by column chromatography or by collection of the insoluble precipitates by filtration.

6-(9H-Carbazol-9-yl)-9-tosyl-9H-pyrido[2,3-b]indole (3). Following the general procedure for Ullmann coupling amination, compound **2** (10 g, 22.3 mmol) and carbazole (3.73 g, 22.3 mmol) were used for the preparation of compound **3**. The crude product was purified by silica-gel column chromatography (CH₂Cl₂: hexane = 2:1 v/v) to afford **3** in 94% yield (10.1 g). ¹H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.67 (dd, J = 1.56, 7.84 Hz, 1H), 8.64 (d, J = 9.0 Hz, 1H), 8.60 (dd, J = 1.56, 4.72 Hz, 1H), 8.58 (d, J = 1.96 Hz, 1H), 8.27 (d, J = 7.84 Hz, 2H), 8.07 (d, J = 8.6 Hz, 2H), 7.89 (dd, J = 2.36 Hz, 9.0 Hz, 1H), 7.48 (dd, J = 7.84 Hz, 7.84 Hz, 1H), 7.42−7.37 (m, 6H), 7.31−7.27 (m, 2H), 2.29 (s, 3H). ¹³C NMR (100 MHz, DMSO-d_6): δ (ppm) 150.49, 147.71, 145.74, 140.53, 135.66, 134.96, 133.00, 130.35, 130.06, 127.40, 127.24, 126.31, 124.00, 122.68, 120.55, 120.42, 120.12, 119.95, 117.73, 115.89, 109.74, 21.10.

6-(9H-Carbazol-9-yl)-9H-pyrido[2,3-b]indole (4). Compound **3** (8 g, 16.4 mmol) was dissolved in distilled THF. To this solution a mixture of NaOH (6.56 g, 164 mmol) and MeOH was added, and then the reaction mixture was heated to 50 °C for 8 h. The reaction mixture was poured into water, and the resulting precipitates were collected by filtration, washed with MeOH, and dried in vacuo. The crude product was purified by recrystallization from THF and MeOH to afford **4** in 73% yield (4 g). ¹H NMR (400 MHz, DMSO-d_6): δ (ppm) 12.12 (s, 1H), 8.60 (d, J = 7.8 Hz, 1H), 8.49 (dd, J = 1.56, 4.68 Hz, 1H), 8.45 (d, J = 1.92 Hz, 1H), 8.27 (d, J = 7.44 Hz, 2H), 7.78 (d, J = 8.24 Hz, 1H), 7.64 (dd, J = 2.36 Hz, 8.64 Hz, 1H), 7.43−7.40 (m, 2H), 7.34 (d, J = 7.84 Hz, 2H), 7.29−7.26 (m, 2H), 7.24 (dd, J = 7.80 Hz, 7.84 Hz, 1H). ¹³C NMR (100 MHz, DMSO-d_6): δ (ppm) 152.52, 146.86, 141.51, 137.99, 129.29, 128.61, 126.17, 125.80, 122.42, 121.51, 120.48, 120.28, 119.70, 115.33, 115.11, 112.63, 109.68.

9-(6-Bromopyridin-3-yl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (5). Following the general procedure for Ullmann coupling

amination, compound **4** (1.8 g, 5.4 mmol) and 2-bromo-5-iodopyridine (1.99 g, 7.0 mmol) were used for the preparation of compound **5**. The crude product was purified by silica-gel column chromatography (eluent: CH$_2$Cl$_2$). The resultant product was purified by recrystallization from CH$_2$Cl$_2$ and MeOH to afford **5** in 57% yield (1.5 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.94 (d, J = 2.36 Hz, 2H), 8.78 (dd, J = 4.56 Hz, 7.80 Hz, 1H), 8.62 (d, J = 1.96 Hz, 1H), 8.59 (dd, J = 1.56 Hz, 5.04 Hz, 1H), 8.54 (d, J = 9.00 Hz, H), 8.50 (dd, J = 2.32, 8.60 Hz, 1H), 8.30−8.27 (m, 3H), 7.76 (dd, J = 2.32, 9.00 Hz, 1H), 7.48−7.38 (m, 5H), 7.32−7.29 (m, 2H).

9-(6-(9H-Carbazol-9-yl)pyridin-3-yl)-6-(9H-carbazol-9-yl)-9H-pyrido-[2,3-b]indole (pPCB2Cz, 6). Following the general procedure for Ullmann coupling amination, compound **5** (1.3 g, 2.6 mmol) and carbazole (0.61 g, 3.6 mmol) were used for the preparation of **pPCB2CZ** (**6**). The crude product was purified by silica-gel column chromatography (eluent: toluene). The resultant product was purified by recrystallization from CH$_2$Cl$_2$ and MeOH to afford **6** in 87% yield (1.3 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.97 (d, J = 2.36 Hz, 1H), 8.77−8.73 (m, 2H), 8.64 (dd, J = 1.56 Hz, 5.08 Hz, 1H), 8.42 (dd, J = 1.56 Hz, 7.84 Hz, 1H), 8.29 (d, J = 1.96 Hz, 1H), 8.24 (dd, J = 2.36 Hz, 8.04 Hz, 2H), 8.21 (d, J = 7.84 Hz, 2H), 7.78 (dd, J = 1.96 Hz, 8.64 Hz, 1H), 7.55 (d, J = 7.84 Hz, 1H), 7.50−7.46 (m, 3H), 7.44 (d, J = 3.92 Hz, 3H), 7.40−7.30 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 151.52, 149.50, 146.88, 146.74, 141.56, 140.73, 137.74, 136.68, 131.98, 131.85, 128.88, 127.04, 126.33, 125.95, 123.70, 123.21, 122.89, 120.62, 120.56, 120.36, 117.81, 119.58, 117.72, 117.50, 115.43, 109.68, 109.44. Anal. Calcd for C$_{40}$H$_{25}$N$_5$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.55; H, 4.25; N, 12.19.

9-(6-Bromopyridin-2-yl)-6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole (7). Following the general procedure for Ullmann coupling amination, compound **4** (1.8 g, 5.4 mmol) and 2-bromo-6-iodopyridine (1.99 g, 7.0 mmol) were used for the preparation of compound **7**. The crude product was purified by silica-gel column chromatography (eluent: CH$_2$Cl$_2$). The resultant product was purified by recrystallization from CH$_2$Cl$_2$ and MeOH to afford **7** in 72% yield (1.9 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.79 (dd, J = 1.56 Hz, 7.44 Hz, 1H), 8.63 (d, J = 1.96 Hz, 1H), 8.61 (dd, J = 1.56 Hz, 5.09 Hz, 1H), 8.55 (dd, J = 9.0 Hz, 7.4 Hz, 2H), 8.29 (d, J = 7.44 Hz, 1H), 8.12−8.08 (m, 1H), 7.83 (dd, J = 1.96 Hz, 8.6 Hz, 1H), 7.75 (d, J = 7.84 Hz, 1H), 7.50 (dd, J = 7.84 Hz, 7.44 Hz, 1H), 7.44−7.40 (m, 4H), 7.32−7.29 (m, 2H).

9-(6-(9H-Carbazol-9-yl)pyridin-2-yl)-6-(9H-carbazol-9-yl)-9H-pyrido-[2,3-b]indole (mPCB2Cz, 8). Following the general procedure for Ullmann coupling amination, compounds **7** (2.2 g, 4.5 mmol) and carbazole (1.05 g, 6.3 mmol) were used for the preparation of **mPCB2CZ** (**8**). The crude product was purified by silica-gel column chromatography (CH$_2$Cl$_2$: hexane = 2:1 v/v). The resultant product was purified by recrystallization from ethyl acetate and hexane to afford **8** in 97% yield (2.5 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.75 (d, J = 8.6 Hz, 1H), 8.65 (dd, J = 1.56 Hz, 4.68 Hz, 1H) 8.59 (d, J = 8.2 Hz, 1H), 8.38 (dd, J = 1.60 Hz, 5.44 Hz, 1H), 8.23 (d, J = 2.32 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.16−8.13 (m, 3H), 8.01 (d, J = 8.24 Hz, 2H), 7.66 (d, J = 7.8 Hz, 1H), 7.55 (dd, J = 2.32, 9.00 Hz, 1H), 7.45−7.42 (m, 2H), 7.38−7.24 (m, 10H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 151.74, 150.77, 150.39, 146.64, 141.45, 140.39, 139.54, 137.79, 131.76, 128.69, 126.91, 126.27, 125.88, 124.37, 123.16, 121.09, 120.27, 120.20, 119.75, 119.37, 119.19, 117.62, 117.45, 116.21, 116.13, 115.71, 111.57, 109.66; Anal. Calcd for C$_{40}$H$_{25}$N$_5$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.36; H, 4.21; N, 12.17.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using CDCl$_3$ and DMSO-d_6 purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed by the Center for Organic Reactions using an EA1112 elemental analyzer (Thermo Electron Corporation). Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system using a heating rate of 10 °C/min. The redox properties of the thin films of the host materials were examined by CV using a potentiostat (EA161, eDAQ). A 0.10 M tetrabutylammonium hexafluorophosphate

(Bu$_4$NPF$_6$) solution in freshly dried acetonitrile was employed as the electrolyte. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was 50 mV s^{-1}. Absorption spectra of the film samples were obtained using a UV−vis spectrophotometer (HP 8453, PDA type) in the wavelength range 190−1100 nm. Photoluminescence (PL) spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer at room temperature and a Thermo FA-357 fluorescence spectrophotometer at 77 K. The triplet energy of the polymers was determined by the highest energy vibronic sub-band of the phosphorescence spectrum at 77 K.

Device Fabrication and Measurements. To fabricate devices, we used a clean glass substrate coated with a 150 nm-thick indium−tin-oxide (ITO) layer and a sheet resistance of 10 Ω/cm as the anode. The active pattern size of 2 × 2 mm^2 was formed using photolithography and wet etching processes. Ultrasonic cleaning of the glass substrate was carried out in an isopropyl alcohol, acetone, and methanol mixture. The substrate was then rinsed in deionized water, and finally treated in ultraviolet UV-ozone for 3 min. The ozone gas was generated using UV light to excite the oxygen in the air inside the chamber. Each organic layer was deposited under a pressure of ∼10^{-7} Torr with a total deposition rate of ∼0.5 Å/s. Subsequently, a 1.5 nm-thick layer of lithium fluoride (LiF) and a 100 nm-thick layer of aluminum (Al) were deposited in a vacuum chamber without breaking the vacuum and used as the cathode. Hole-only devices (HODs) and electron-only devices (EODs) were fabricated to compare the current density in the host materials. The device structure of HOD was ITO (150 nm)/TAPC (20 nm)/host material (50 nm)/TAPC (20 nm)/Al (100 nm). To enhance the hole injection and to suppress the electron injection, we inserted TAPC layer between both side electrodes and host material. The device configuration of EOD was ITO (150 nm)/TmPyPB (20 nm)/host material (50 nm)/TmPyPB (20 nm)/LiF (1.5 nm)/Al (100 nm). Pristine ITO substrates without UV-ozone treatment for EODs were used to suppress hole injection from ITO to organic layer. A 1.5 nm-thick LiF layer was used as electron injection layer. We used 50 nm thick host layer to measure the current density through the host layer dominantly.

The device structure of the blue PhOLED was ITO (150 nm)/TAPC (75 nm)/FIrpic 3 wt % doped host material (15 nm)/TmPyPB (40 nm)/LiF (1.5 nm)/Al (100 nm). The current density−voltage (J−V) and luminance−voltage (L−V) data of the blue PhOLEDs were measured employing a Keithley SMU 238 instrument and a Minolta CS-100A colorimeter. The electroluminescence (EL) spectra and Commission Internationale de I'Eclairage (CIE) color coordinates were obtained using Minolta CS-2000 spectroradiometer. All external quantum efficiency (EQE) values were measured by using integrating sphere instrument (Photal Labsphere).

■ RESULTS AND DISCUSSION

Design, Synthesis, and Characterization. The structural difference between the two newly synthesized host materials lies in the anchoring positions (i.e., 2,5- and 2,6-substitution) of the pyridine linker between the carbazole and carbazole-substituted carboline units (Figure 1). Density functional theory (DFT) calculations at the B3LYP level were utilized and provided the optimized molecular structures of the host materials, as well as the calculated energy levels for the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO).

The carbazole−carboline−pyridine−carbazole molecular arrangement in host molecules was more favorable for the delocalization of electron density between the HOMO and LUMO states than the carboline−carbazole−pyridine−carbazole molecular arrangement (Supporting Information Tables S1 and S2). The molecular orbital distribution in the HOMO and LUMO of **pPCB2CZ** and **mPCB2CZ** was well-separated into the carboline and carbazole units, respectively, in 6-(9H-
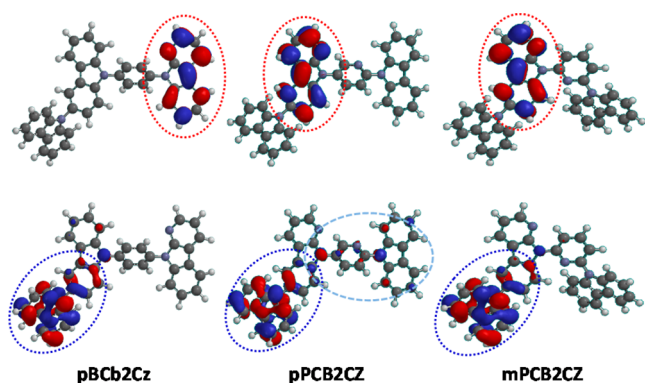
Figure 2. HOMO (bottom) and LUMO (top) distributions of **pBCb2Cz**,[25] **pPCB2CZ**, and **mPCB2CZ** according to DFT calculations.

carbazol-9-yl)-9H-pyrido[2,3-b]indole, as shown in Figure 2. The HOMOs of the two host molecules were localized on the carbazole unit as an electron-donating unit, and the LUMOs were distributed over the carboline unit owing to the electron-accepting property of the pyridinyl group. In particular, the **mPCB2CZ** host exhibited better delocalization of orbital distribution to the carbazole and carboline units in the HOMO and LUMO states, respectively, compared with the **pPCB2CZ** host. This means that the carbazole and carboline moieties may be involved in important hole and electron transport pathways, respectively, in the two host molecules, which shows that these hosts can show the characteristics of bipolar host materials.

The synthetic procedure for obtaining **pPCB2CZ** and **mPCB2CZ** is illustrated in Scheme 1, and detailed synthetic procedures and characterization data are described in the Experimental Section. First, 6-(9H-carbazol-9-yl)-9H-pyrido-[2,3-b]indole 4 was reacted with 2-bromo-5-iodopyridine and 2-bromo-6-iodopyridine via the Ullman coupling method to yield compounds 5 and 7, respectively. The synthetic yield of the coupling reaction was 65−70%. Finally, **pPCB2CZ**, 6, and **mPCB2CZ**, 8, were obtained through another Ullman coupling reaction of compounds 5 and 7, respectively, with a carbazole in which the 6-(9H-carbazol-9-yl)-9H-pyrido[2,3-b]indole and carbazole subunits were connected through a pyridine ring spacer; 2,5- and 2,6-disubstitution of compound 4 and carbazole on the spacer modulate molecular rigidity of the host material.

The thermal properties of the newly synthesized host materials were investigated using DSC and TGA under a nitrogen atmosphere. As shown in Figure 3a, the two host materials showed high T_g. In particular, **pPCB2CZ** exhibited a clear glass transition on heating at 144 °C, which is 16 °C higher than that observed for **mPCB2CZ**. The linear structure of **pPCB2CZ** should reduce the steric hindrance in the solid state compared with **mPCB2CZ**, resulting in the higher T_g for **pPCB2CZ**. In the TGA thermograms of the host materials, no significant weight loss was observed up to 400 °C. The onset temperatures of primary decomposition of **pPCB2CZ** and **mPCB2CZ** were 451 and 418 °C, respectively (Figure 3b). These results reveal that the two host materials are thermally stable, which might improve the operational stability of PhOLED devices.

Optical and Electrochemical Properties. UV−vis absorption and photoluminescence (PL) spectra of the two

Scheme 1. Synthetic Procedure for Host Materials[a]
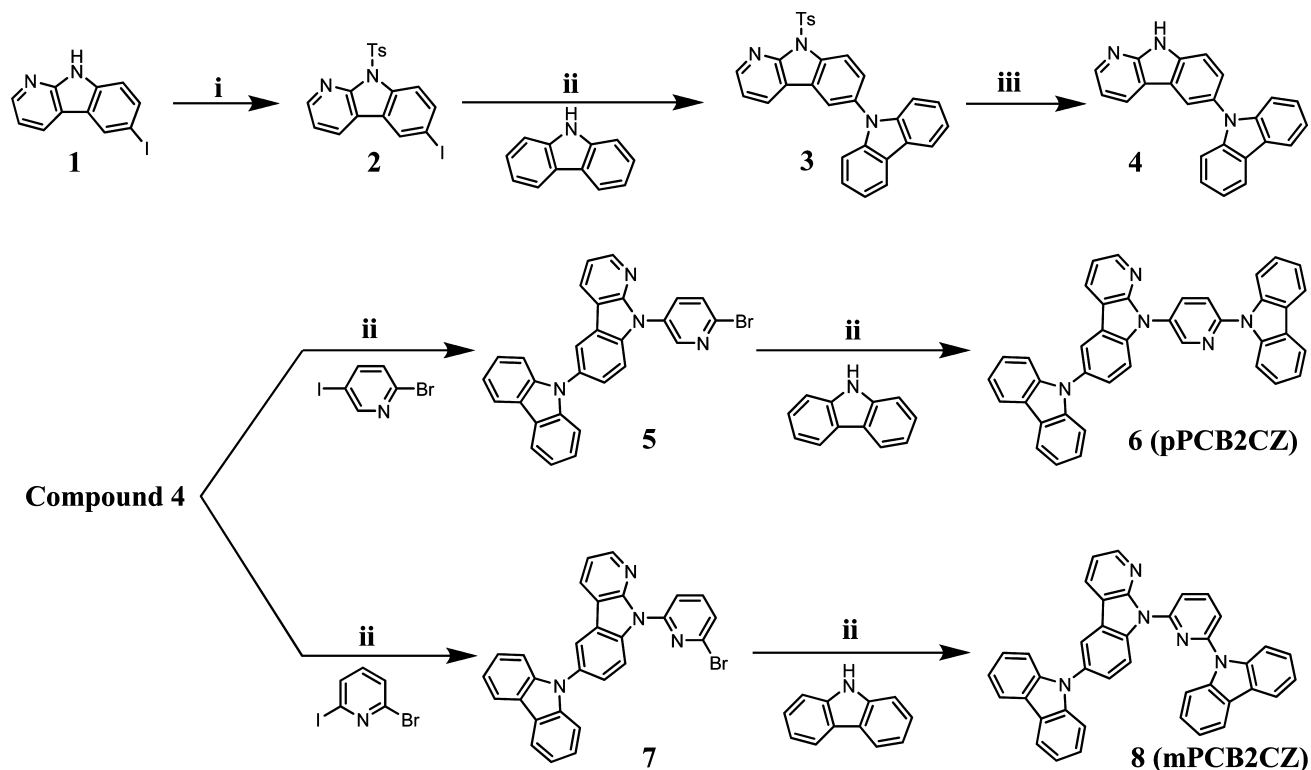
[a](i) NaH, tosyl chloride, DMF, rt. (ii) CuI, K₃PO₄, trans-1,2-diaminocyclohexane, toluene, 110 °C. (iii) NaOH, THF, MeOH, 50 °C.
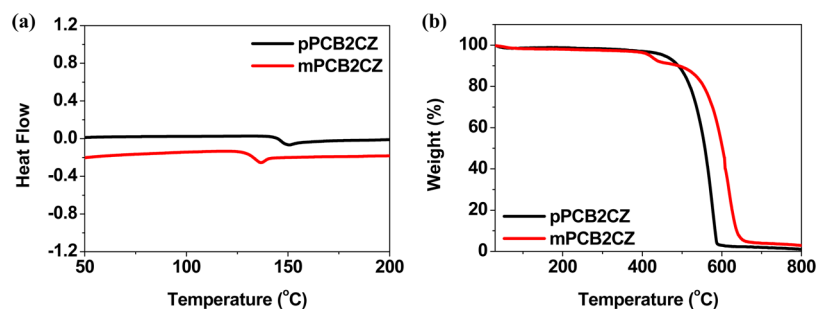
Figure 3. (a) Differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) curves of **pPCB2CZ** and **mPCB2CZ**.
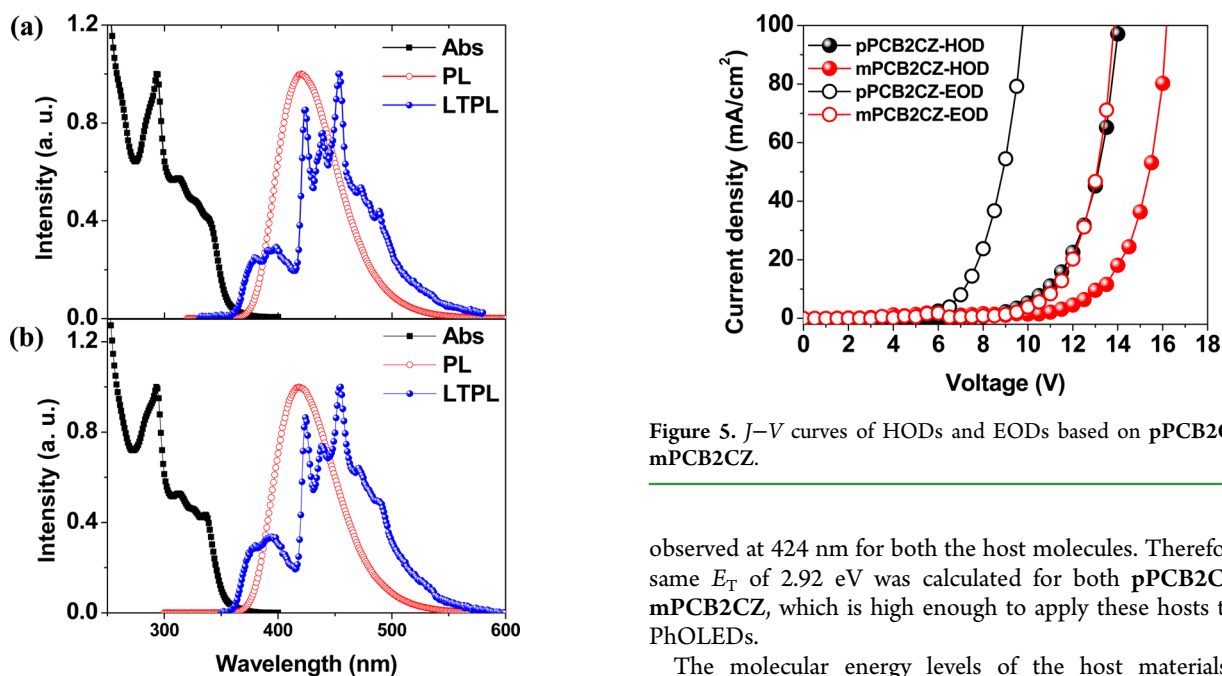

Figure 4. UV−vis absorption, photoluminescence (PL), and low-temperature PL (LTPL) spectra of **pPCB2CZ** (a) and **mPCB2CZ** (b).

Figure 5. J−V curves of HODs and EODs based on **pPCB2CZ** and **mPCB2CZ**.

host materials were measured in dilute chloroform solution (Figure 4). The spectroscopic parameters are tabulated in Table 1. Although the substitution position of carbazole on the pyridine linking unit is different, the two host molecules exhibited almost identical photophysical properties in solution. In the absorption spectra, a $\pi-\pi^*$ transition of the two host materials appeared below 300 nm, and $n-\pi^*$ transitions of carbazole and carboline were observed between 300 and 365 nm. The optical bandgap energies (E_g^{opt}) were determined from the absorption edges (λ_{cutoff}) as 3.49 and 3.52 eV for **pPCB2CZ** and **mPCB2CZ**, respectively. To investigate the excited E_T levels of the two host molecules, low-temperature PL was conducted at 77 K. The highest-energy PL peak was
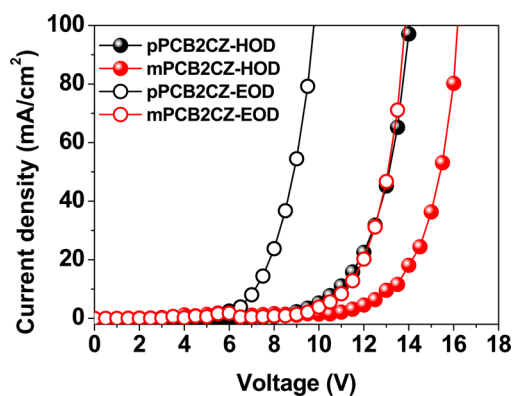
observed at 424 nm for both the host molecules. Therefore, the same E_T of 2.92 eV was calculated for both **pPCB2CZ** and **mPCB2CZ**, which is high enough to apply these hosts to blue PhOLEDs.

The molecular energy levels of the host materials in a PhOLED are critical to govern the efficacy of energy transfer and charge transport. The electrochemical properties of the synthesized host materials were examined by cyclic voltammetry in order to study the molecular energy levels. The oxidation potentials of **pPCB2CZ** and **mPCB2CZ** were found to be 0.80 and 0.93 V, respectively (Supporting Information Figure S1). The energy of the HOMO level of **pPCB2CZ** was −5.60 eV, which is higher by 0.13 eV compared with that of **mPCB2CZ** (−5.73 eV). The energies of the LUMO levels of **pPCB2CZ** and **mPCB2CZ** were −2.11 and −2.21 eV, respectively, calculated using the energy of the HOMO level and E_g^{opt}.

Blue PhOLED Properties. Before characterizing the performance of blue PhOLEDs, we investigated the charge balance properties of the two host molecules by fabricating hole- and electron-only devices (HOD and EOD). The well-known bipolar host material, **26DCzPPy**-based HOD, and EOD were also fabricated as control devices for comparison. Figure 5 and Supporting Information Figure S2 show the

**Table 1. Physical, Optical, and Electrochemical Properties of Host Materials pPCB2CZ and mPCB2CZ**

host material	T_g [°C]	T_d [°C]	absorption[a] [nm]	PL[a] [nm]	λ_{cutoff}[a,b] [nm]	$E_g^{opt \, a,b}$ [eV]	E_T^c [eV]	E_{ox}^d [V]	HOMO[d] [eV]	LUMO[e] [eV]
pPCB2CZ	144	451	292, 338	420	355	3.49	2.92	0.80	−5.60	−2.11
mPCB2CZ	128	418	293, 336	418	352	3.52	2.92	0.93	−5.73	−2.21

[a]Data were measured in chloroform solution. [b]The optical bandgap energies were calculated from the absorption edges (λ_{cutoff}), $E_g^{opt} = 1240/\lambda_{cutoff}$. [c]Triplet energy was measured at 77 K. [d]First oxidation and HOMO energies were measured by CV. [e]LUMO energy was calculated from the difference between the HOMO and optical bandgap energies.

Table 2. Performance of Blue PhOLED with Host Materials pPCB2CZ, mPCB2CZ, and 26DCzPPy

host material	turn-on [V]	operating voltage[a] [V]	luminance[b] [cd/m^2]	CE[b] [cd/A]	PE[b] [lm/W]	EQE[b] [%]	CIE[a] [x, y]
pPCB2CZ	3.1	4.1	21 300	40.5	32.6	22.6 (21.0)[a]	(0.15, 0.30)
mPCB2CZ	3.7	4.8	16 800	44.8	31.3	23.7 (23.7)[a]	(0.15, 0.29)
26DCzPPy	3.5	5.1	18 400	36.9	22.8	19.2 (19.0)[a]	(0.15, 0.31)

[a]At 1000 cd/m^2. [b]Maximum value.
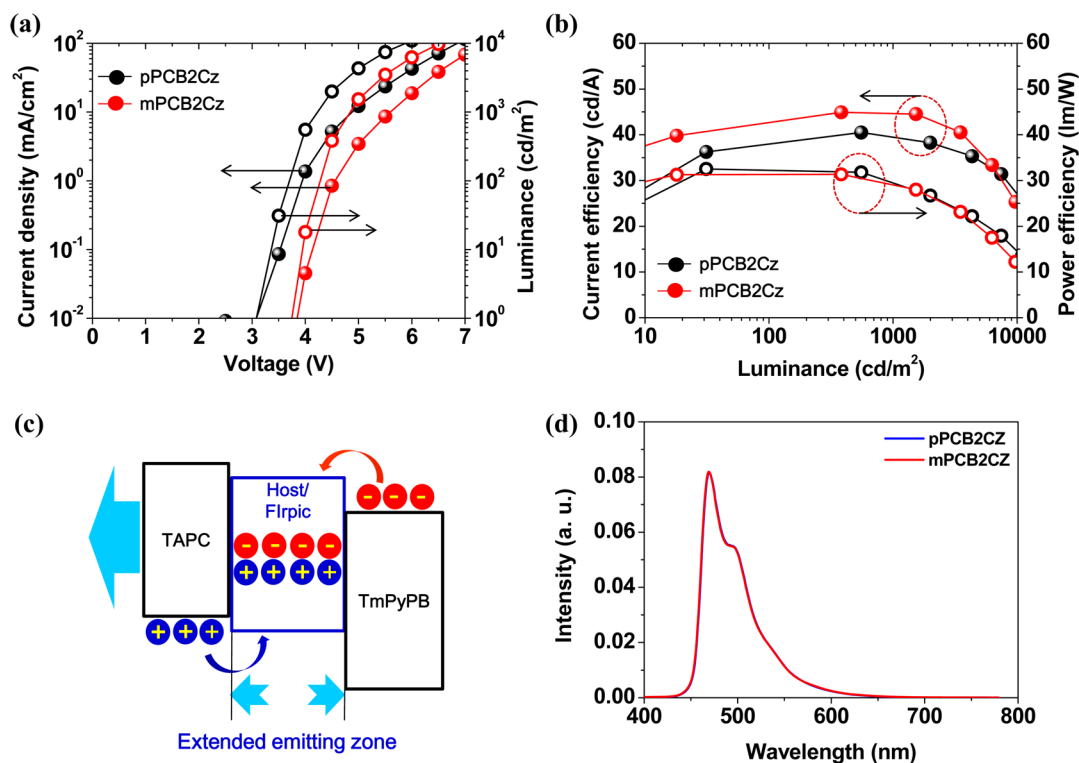
Figure 6. (a) J−V−L and (b) CE−V−PE curves of **pPCB2CZ**- and **mPCB2CZ**-based blue PhOLEDs. (c) Extended emitting zone through well-balanced charge recombination. (d) EL spectra of **pPCB2CZ**- and **mPCB2CZ**-based blue PhOLED: (*J) current density, (V) applied bias, (L) luminance, (CE) current efficiency, (PE) power efficiency.

current density−voltage curves of HOD and EOD for the three host materials.

In this measurement, **pPBCB2CZ** and **mPBCB2CZ** showed smaller difference of current density between HODs and EODs than that of **26DCzPPy**-based devices. Our two hosts were found to exhibit a more balanced bipolar character compared with **26DCzPPy** in TAPC/TmPyPB-containing device structure. In particular, mPBCB2CZ-based device showed the smallest current density difference between the HOD and EOD.

Blue PhOLEDs containing the newly synthesized host materials with high E_T (2.92 eV) were fabricated (Supporting Information Figure S3). The **26DCzPPy**-based device was also prepared under the same conditions as a control device (E_T of **26DCzPPy** = 2.70 eV).

The device performance data are summarized in Table 2, and the current density−voltage−luminance (J−V−L) and the efficiency−luminance characteristics are shown in Figure 6a,b, respectively. The performances of 26DCzPPy-based PhOLED device are presented in Supporting Information Figure S4. The turn-on and driving voltages at 1000 cd/m^2 were 3.1 and 4.1 V, respectively, for the **pPCB2CZ**-based device and 3.7 and 4.8 V, respectively, for the **mPCB2CZ**-based device. These results indicate that the HOMO (−5.60 eV) of **pPCB2CZ** more favorably reduces the energy barrier between the TAPC-based hole transport layer and the host material compared with **mPCB2CZ**, which has a deeper HOMO level (−5.73 eV). Therefore, the operating voltage of a **pPCB2CZ**-based device could be lower than that for an **mPCB2CZ**-based device. Our host materials show low driving voltage characteristics as 4−5 V, which are suitable for operating practical blue emitting devices.

In Figure 6b, the maximum current efficiency and power efficiency are 40.5 cd/A and 32.6 lm/W, respectively, for **pPCB2CZ**, and 44.8 cd/A and 31.3 lm/W, respectively, for **mPCB2CZ**, which are much higher than those of the **26DCzPPy**-based PhOLED (36.9 cd/A and 22.8 lm/W), as shown in Supporting Information Figure S4.

The maximum external quantum efficiencies (EQEs) of **pPCB2CZ**- and **mPCB2CZ**-based blue PhOLEDs were 22.6% and 23.7%, respectively, which are much higher than the efficiency of 19.2% for the **26DCzPPy**-based device. Intriguingly, the EQE values at the practically useful luminance of 1000 cd/m^2 for the **pPCB2CZ**- and **mPCB2CZ**-based devices were 21.0% and 23.7%, respectively. The high EQE at high luminance for the two host material-based devices are presumably attributed to the balanced charge density and efficient exciton recombination in the broad area of the emitting zone (Figure 6c). These properties could result in the low roll-off behaviors of the device efficiencies. The efficiencies

of the devices were improved by our molecular design and synthetic strategy, by only changing the position of the substituents. In addition, the EQE values at 1000 cd/m^2 reported herein are impressive in blue PhOLEDs, which was obtained from typical device [e.g., ITO/HTL/EML/ETL/LiF/Al] without any exciton blocking layer and any interlayers for facilitating charge injection and blocking.

The electroluminescence (EL) spectra of **pPCB2CZ**- and **mPCB2CZ**-based blue PhOLEDs showed identical emission peaks at 470 nm, which are consistent with the EL spectrum of a general FIrpic-doped device (Figure 6d). This result means that the host materials undergo highly efficient exothermic energy transfer from the host to FIrpic in the emitting layer. Additionally, no other emission bands could be observed in the devices with the new host materials, which is due to the well-balanced charge density in the emission zone. Therefore, the balanced charge density in the emitting layer played a highly important role in increasing the quantum efficiency and maintaining color purity of the blue PhOLEDs.

CONCLUSION

New host materials, **pPCB2CZ** and **mPCB2CZ**, containing carbazole and carboline moieties were successfully synthesized. These host materials showed sufficiently high triplet energies, high T_g's, and balanced charge density in the emitting layer of blue PhOLEDs. Compared to the PhOLED with the host molecule that we reported previously, the devices bearing **mPCB2CZ** displayed a higher external quantum efficiency of ~24% at practically high luminance as 1000 cd/m^2. By changing only the positions of carbazole and carboline on the pyridine linking unit, the device efficiency could be promoted further; the building blocks of carbazole and carboline are great candidates for the future development of highly promising blue PhOLEDs.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational simulations, electrochemical properties, device performance of 26DCzPPy-based PhOLED, and electroluminescence spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: jhkwon@khu.ac.kr. Fax: +82-2-961-9154. Phone: +82-2-961-0948.
*E-mail: dhchoi8803@korea.ac.kr. Fax: +82-2-925-4284. Phone: +82-2-3290-3140.

Author Contributions
‖These authors contributed equally.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Ulbricht, C.; Beyer, B.; Friebe, C.; Winter, A.; Schubert, U. S. Recent Developments in the Application of Phosphorescent Iridium-(III) Complex Systems. *Adv. Mater.* **2009**, *21*, 4418−4441.

(2) Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y. Strategies to Design Bipolar Small Molecules for OLEDs: Donor-Acceptor Structure and Non-Donor-Acceptor Structure. *Adv. Mater.* **2011**, *23*, 1137−1144.

(3) Chaskar, A.; Chen, H.-F.; Wong, K.-T. Bipolar Host Materials: A Chemical Approach for Highly Efficient Electrophosphorescent Devices. *Adv. Mater.* **2011**, *23*, 3876−3895.

(4) Tao, Y.; Yang, C.; Qin, J. Organic Host Materials for Phosphorescent Organic Light-Emitting Diodes. *Chem. Soc. Rev.* **2011**, *40*, 2943−2970.

(5) Adachi, C.; Kwong, R. C.; Djurovich, P.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. Endothermic Energy Transfer: A Mechanism for Generating Very Efficient High-Energy Phosphorescent Emission in Organic Materials. *Appl. Phys. Lett.* **2001**, *79*, 2082−2084.

(6) Holmes, R. J.; Forrest, S. R.; Tung, Y.-J.; Kwong, R. C.; Brown, J. J.; Garon, S.; Thompson, M. E. Blue Organic Electrophosphorescence Using Exothermic Host−Guest Energy Transfer. *Appl. Phys. Lett.* **2003**, *82*, 2422−2424.

(7) Yook, K. S.; Lee, J. Y. Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* **2012**, *24*, 3169−3190.

(8) Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y. Strategies to Design Bipolar Small Molecules for OLEDs: Donor-Acceptor Structure and Non-Donor-Acceptor Structure. Y. *Adv. Mater.* **2011**, *23*, 1137−1144.

(9) Tsai, M.-H.; Lin, H.-W.; Su, H.-C.; Ke, T.-H.; Wu, C.-C.; Fang, F.-C.; Liao, Y.-L.; Wong, K.-T.; Wu, C.-I. Highly Efficient Organic Blue Electrophosphorescent Devices Based on 3,6-Bis(triphenylsilyl)-carbazole as the Host Material. *Adv. Mater.* **2006**, *18*, 1216−1220.

(10) Li, J.; Liu, D.; Li, Y.; Lee, C.-S.; Kwong, H.-L.; Lee, S. A High Tg Carbazole-Based Hole-Transporting Material for Organic Light-Emitting Devices. *Chem. Mater.* **2005**, *17*, 1208−1212.

(11) Lin, M.-S.; Yang, S.-J.; Chang, H.-W.; Huang, Y.-H.; Tsai, Y.-T.; Wu, C.-C.; Chou, S.-H.; Mondal, E.; Wong, K.-T. Incorporation of a CN Group into mCP: a New Bipolar Host Material for Highly Efficient Blue and White Electrophosphorescent Devices. *J. Mater. Chem.* **2012**, *22*, 16114−16120.

(12) Williams, E. L.; Haavisto, K.; Li, J.; Jabbour, G. E. Excimer-Based White Phosphorescent Organic Light-Emitting Diodes with Nearly 100% Internal Quantum Efficiency. *Adv. Mater.* **2007**, *19*, 197−202.

(13) Su, S.-J.; Sasabe, H.; Takeda, T.; Kido, J. Pyridine-Containing Bipolar Host Materials for Highly Efficient Blue Phosphorescent OLEDs. *Chem. Mater.* **2008**, *20*, 1691−1693.

(14) Chien, C.-H.; Kung, L.-R.; Wu, C.-H.; Shu, C.-F.; Chang, S.-Y.; Chi, Y. A Solution-Processable Bipolar Molecular Glass as a Host Material for White Electrophosphorescent Devices. *J. Mater. Chem.* **2008**, *18*, 3461−3466.

(15) Zeng, L.; Lee, T. Y.-H.; Merkel, P. B.; Chen, S. H. A New Class of Non-Conjugated Bipolar Hybrid Hosts for Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem.* **2009**, *19*, 8772−8781.

(16) Li, W.; Liu, D.; Shen, F.; Ma, D.; Wang, Z.; Feng, T.; Xu, Y.; Yang, B.; Ma, Y. A Twisting Donor-Acceptor Molecule with an Intercrossed Excited State for Highly Efficient, Deep-Blue Electroluminescence. *Adv. Funct. Mater.* **2012**, *22*, 2797−2803.

(17) Wang, Q.; Wallace, J. U.; Lee, T. Y.-H.; Ou, J. J.; Tsai, Y.-T.; Huang, Y.-H.; Wu, C.-C.; Rothberg, L. J.; Chen, S. H. Evaluation of Propylene-, Meta-, and Para-Linked Triazine and tert-Butyltriphenyl-amine as Bipolar Hosts for Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2013**, *1*, 2224−2232.

(18) Chang, C.-H.; Kuo, M.-C.; Lin, W.-C.; Chen, Y.-T.; Wong, K.-T.; Chou, S.-H.; Mondal, E.; Kwong, R. C.; Xia, S.; Nakagawa, T.; Adachi, C. A Dicarbazole−Triazine Hybrid Bipolar Host Material for Highly Efficient Green Phosphorescent OLEDs. *J. Mater. Chem.* **2012**, *22*, 3832−3838.

(19) Liu, H.; Cheng, G.; Hu, D.; Shen, F.; Lv, Y.; Sun, G.; Yang, B.; Lu, P.; Ma, Y. A Highly Efficient, Blue-Phosphorescent Device Based on a Wide-Bandgap Host/FIrpic: Rational Design of the Carbazole and Phosphine Oxide Moieties on Tetraphenylsilane. *Adv. Funct. Mater.* **2012**, *22*, 2830−2836.

(20) Jeon, S. O.; Jang, S. E.; Son, H. S.; Lee, J. Y. External Quantum Efficiency Above 20% in Deep Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* **2011**, *23*, 1436−1441.

(21) Chou, H.; Cheng, C. A Highly Efficient Universal Bipolar Host for Blue, Green, and Red Phosphorescent OLEDs. *Adv. Mater.* **2010**, *22*, 2468−2471.

(22) Motoyama, T.; Sasabe, H.; Seino, Y.; Takamatsu, J.-I.; Kido, J. An α-Carboline-Containing Host Material for High-Efficiency Blue and Green Phosphorescent OLEDs. *Chem. Lett.* **2011**, *40*, 306−308.

(23) Lee, C. W.; Lee, J. Y. Structure−Property Relationship of Pyridoindole-Type Host Materials for High-Efficiency Blue Phosphorescent Organic Light-Emitting Diodes. *Chem. Mater.* **2014**, *26*, 1616−1621.

(24) Lee, C. W.; Lee, J. Y. Above 30% External Quantum Efficiency in Blue Phosphorescent Organic Light-Emitting Diodes Using Pyrido[2,3-*b*]indole Derivatives as Host Materials. *Adv. Mater.* **2013**, *25*, 5450−5454.

(25) Kim, S. J.; Kim, Y. J.; Son, Y. H.; Hur, J. A.; Um, H. A.; Shin, J.; Lee, T. W.; Cho, M. J.; Kim, J. K.; Joo, S.; Yang, J. H.; Chae, G. S.; Choi, K.; Kwon, J. H.; Choi, D. H. High-Efficiency Blue Phosphorescent Organic Light-Emitting Diodes Using a Carbazole and Carboline-Based Host Material. *Chem. Commun.* **2013**, *49*, 6788−6790.