

Structure—Property Relationship of Pyridoindole-Type Host Materials for High-Efficiency Blue Phosphorescent Organic Light-Emitting Diodes

Chil Won Lee and Jun Yeob Lee*

Department of Polymer Science and Engineering, Dankook University, 126, Jukjeon-dong, Suji-gu, Yongin, Gyeonggi 448-701, Korea

ABSTRACT: The structure-property relationship of pyridoindole-type host materials for blue phosphorescent organic light-emitting diodes (PHOLEDs) was investigated by synthesizing three pyridoindole derivatives modified with dibenzofuran, dibenzothiophene, and 9-phenyl-carbazole. The 9-phenylcarbazole moiety was better than dibenzofuran or dibenzothiophene to manage the energy levels and charge-transport properties of the pyridoindole-derived host materials. The PCb-PCz host with the 9-phenylcarbazole moiety showed balanced charge density in the emitting layer and exhibited a high external quantum efficiency of 29.7% in blue PHOLEDs.



Article

■ INTRODUCTION

Quantum efficiency is one of the most important device performance characteristics of phosphorescent organic lightemitting diodes (PHOLEDs), and host materials play a key role in improving the quantum efficiency of PHOLEDs through charge balance and energy transfer. In particular, the host materials are critical to the quantum efficiency of blue PHOLEDs because high triplet energy is required for the host materials of blue PHOLEDs.

Many high-triplet-energy host materials have been developed to enhance the quantum efficiency of blue PHOLEDs, and most host materials were derived from high-triplet-energy moieties. Carbazole has been the most popular building block to obtain high triplet energy and high quantum efficiency in blue PHOLEDs.¹⁻¹⁰ However, the carbazole moiety showed poor electron-accepting properties in spite of its good electrondonating properties for stable cation radical formation. Therefore, pyridoindole was developed as a building block to improve the poor electron-accepting properties of the carbazole moiety.¹¹⁻¹⁵ The pyridoindole unit exhibited high triplet energy and better electron-accepting properties than carbazole. Several pyridoindole derivatives have been developed as the host materials for blue PHOLEDs and were effective at enhancing the quantum efficiency of blue PHOLEDs. Kido et al. reported a pyridoindole derivative as a host material for blue PHOLEDs that had a high quantum efficiency using iridium-(III) bis[(4,6-difluorophenyl)-pyridinato-N,C²]picolinate (FIrpic) as a blue triplet emitter.¹¹ A high-triplet-energy host material derived from an adamantane core and pyridoindole was reported by Tokito et al.,¹² and the effect of nitrogen orientation on the photophysical properties and device performance of pyridoindole-modified triplet host materials was studied by our group.¹³ Recently, bipolar-type pyridoindole

derivatives were developed and showed high quantum efficiency in blue PHOLEDs and white tandem PHOLEDs.¹⁴ Although several studies proved that the pyridoindole moiety would be effective as the building block of high-triplet-energy host materials for blue PHOLEDs, further systematic study is required to develop pyridoindole derivatives as the host materials for blue PHOLEDs.

In this work, three pyridoindole derivatives, 9-(3-(dibenzo-[b,d]furan-2-yl)phenyl)- α -carboline (PCb-DBF), 9-(3-(dibenzothiophen-2-yl)phenyl)- α -carboline (PCb-DBT), and 9-(3-(9phenylcarbazol-3-yl)phenyl)- α -carboline (PCb-PCz), were synthesized as the triplet host materials for blue PHOLEDs, and the effect of dibenzofuran, dibenzothiophene and 9-phenylcarbazole on the photophysical properties and device performance of the pyridoindole derivatives was systematically studied. It was demonstrated that the 9-phenylcarbazole moiety is better than other substituents for improving the device performance of the pyridoindole derivatives. A high quantum efficiency of 29.7% was achieved in FIrpic-doped blue PHOLEDs using PCb-PCz as the host material, which is one of the best efficiencies reported for blue PHOLEDs.

EXPERIMENTAL SECTION

General Information. All chemicals and reagents were used without further purification. 9-(3-Bromophenyl)- α -carboline was synthesized according to a method reported in the literature.¹⁶ The ¹H and ¹³C nuclear magnetic resonance (NMR) data were recorded on an Avance 500 (Bruker) NMR spectrometer, and the Fourier-transform infrared (FT-IR) spectra for all of the samples were

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obtained using a Nicolet 380 FT-IR spectrometer. The mass spectra were recorded using a JEOL JMS-600W spectrometer in fast-atombombardment mode. Elemental analysis of the materials was carried out using a Flash2000 (ThermoFisher). The differential scanning calorimetric (DSC) measurements were performed on a Mettler DSC822e under nitrogen at a heating rate of 10 °C/min. The PL and UV-vis spectra were obtained using a fluorescence spectrophotometer (HITACHI, F-7000) and a UV-vis spectrophotometer (Shimadzu, UV-2501PC), respectively. Low-temperature PL measurement for triplet-energy analysis was carried out using a PerkinElmer LS-55 in liquid nitrogen. The oxidation and reduction potentials of compounds were measured with a cyclic voltammetry. Cyclic voltammetry measurement of organic materials was carried out in an acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Ag was used as the reference electrode, and Pt was the counter electrode. The oxidation potential was converted to the highest occupied molecular orbital by a method reported previously.¹

Synthesis of 9-(3-(Dibenzo[b,d]furan-2-yl)phenyl)-a-carboline (PCb-DBF). 9-(3-Bromophenyl)- α -carboline (1.70 g, 5.21 mmol), dibenzofuran-2-ylboronic acid (1.45 g, 6.77 mmol), potassium carbonate (1.94 g, 14.1 mmol), THF (90 mL), and 30 mL of distilled water were placed in a two-necked 250 mL round-bottomed flask equipped with a magnetic stirrer bar, a reflux condenser, and a nitrogen inlet. The solution was stirred and bubbled with nitrogen gas for 30 min. Tetrakis(triphenylphosphine)palladium(0) (0.27 g, 0.23 mmol) was added to the above reaction mixture, and the resulting solution was refluxed for 24 h under nitrogen. The reaction mixture was cooled to room temperature and extracted with ethyl acetate and distilled water. The ethyl acetate phase was dried over magnesium sulfate, filtered, rotary-evaporated to remove solvent, and dried in a vacuum. The crude product was purified by column chromatography on silica gel using n-hexane/dichloromethane as eluent. Additional purification by vacuum train sublimation resulted in 1.5 g of PCb-DBF. 9-(3-(Dibenzothiophen-2-yl)phenyl)- α -carboline (PCb-DBT) and 9- $(3-(9-phenylcarbazol-3-yl)phenyl)-\alpha$ -carboline (PCb-PCz) were synthesized using a similar procedure as that for PCb-DBF.

PCb-DBF. Yield 70%. T_g 69 °C, T_m 150 °C. FT-IR: 3052, 1925, 1859, 1774, 1591, 1451, 1409, 1337, 1289, 1222, 1195, 1119, 1022, 964, 931, 873, 841, 807, 770, 736, 692 cm^{-1.} ¹H NMR (500 MHz, CDCl₃): δ 7.23 (t, 1H, J = 4.2 Hz), 7.30–7.35 (m, 2H), 7.42–7.49 (m, 2H), 7.55–7.56 (m, 2H), 7.59 (d, 1H, J = 4.3 Hz), 7.64 (d, 1H, J = 5.2 Hz), 7.68–7.76 (m, 3H), 7.93–7.94 (m, 2H), 8.12 (d, 1H, J = 3.8 Hz), 8.17 (s, 1H), 8.37 (d, 1H, J = 4.8 Hz), 8.50 (d, 1H, J = 3.0 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 110.4, 111.7, 111.8, 116.1, 116.4, 119.3, 120.7, 120.8, 120.9, 122.8, 124.1, 124.8, 126.0, 126.3, 126.6, 126.7, 127.0, 127.3, 128.3, 130.1, 135.5, 136.8, 140.1, 142.9, 146.5, 152.0, 155.9, 156.7. Mass (FAB) *m/z* 411 (M + H)⁺. Anal. Calcd for C₂₉H₁₈N₂O: C, 84.86; H, 4.42; N, 6.82; O, 3.90. Found: C, 84.83; H, 4.45; N, 6.91; O, 3.83.

PCb-DBT. Yield 68%. T_g 79 °C, T_m 188 °C. FT-IR: 3051, 1862, 1783, 1727, 1673, 1591, 1451, 1408, 1335, 1290, 1223, 1167, 1120, 1086, 1020, 933, 883, 846, 766, 729, 691 cm^{-1.} ¹H NMR (500 MHz, CDCl₃): δ 7.24 (t, 1H, *J* = 4.0 Hz), 7.34 (t, 1H, *J* = 5.2 Hz), 7.42–7.44 (m, 2H), 7.48 (t, 1H, *J* = 5.3 Hz), 7.56 (d, 1H, *J* = 4.0 Hz), 7.66 (d, 1H, *J* = 4.0 Hz), 7.70–7.74 (m, 2H), 7.79 (d, 1H, *J* = 4.5 Hz), 7.83 (t, 1H, *J* = 3.0 Hz), 7.88 (d, 1H, *J* = 4.3 Hz), 7.98 (s, 1H), 8.13 (d, 1H, *J* = 3.8 Hz), 8.16 (t, 1H, *J* = 3.0 Hz), 8.37–8.39 (m, 2H), 8.51 (d, 1H, *J* = 3.2 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 110.4, 116.1, 116.4, 120.1, 120.8, 120.9, 121.0, 121.7, 122.9, 123.1, 124.4, 126.1, 126.3, 126.3, 126.6, 126.9, 127.0, 128.3, 130.1, 135.4, 136.1, 136.9, 137.0, 138.9, 139.9, 140.2, 142.8, 146.6, 152.0. Mass (FAB) *m/z* 427 (M + H)⁺. Anal. Calcd for C₂₉H₁₈N₂S: C, 81.66; H, 4.25; N, 6.57; S, 7.52;. Found: C, 81.65; H, 4.25; N, 6.59; S, 7.51.

PCb-PCz. Yield 75%. T_g 97 °C, T_m 215 °C. FT-IR: 3051, 1952, 1592, 1496, 1458, 1411, 1334, 1289, 1226, 1171, 1122, 997, 932, 891, 847, 760, 737, 695 cm^{-1.} ¹H NMR (500 MHz, CDCl₃): δ 7.21 (t, 1H, J = 4.2 Hz), 7.27(t, 1H, J = 4.2 Hz), 7.32 (t, 1H, J = 4.8 Hz), 7.39–7.39 (m, 2H), 7.43–7.48 (m, 3H), 7.53–7.61 (m, 6H), 7.67–7.70 (m, 2H), 7.80 (d, 1H, J = 4.0 Hz), 7.98 (s, 1H), 8.11 (d, 1H, J = 4.0 Hz), 8.15 (d, 1H, J = 3.8 Hz), 8.36 (d, 1H, J = 4.5 Hz), 8.40 (s, 1H), 8.50

(d, 1H, J = 3.2 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 109.9, 110.1, 110.5, 116.0, 116.3, 118.9, 120.1, 120.4, 120.7, 120.9, 120.9, 123.4, 123.9, 125.5, 126.2, 126.5, 126.9, 127.0, 127.5, 128.2, 129.9, 130.0, 132.5, 136.7, 137.6, 140.2, 140.6, 141.4, 143.6, 146.5, 152.1. Mass (FAB) m/z 486 (M + H)⁺. Anal. Calcd for C₃₅H₂₃N₃: C, 86.57; H, 4.77; N, 8.65. Found: C, 86.57; H, 4.71; N, 8.76.

Device Fabrication and Measurements. The basic device structure of blue PHOLEDs was indium tin oxide (ITO, 50 nm)/ poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PE-DOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(N-carbazolyl)benzene (mCP, 10 nm)/PCb-DBF:Firpic or PCb-DBT:Firpic or PCb-PCz:FIrpic (25 nm)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 35 nm)/LiF (1 nm)/Al (200 nm). Device structures of hole and electron devices were ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/ mCP (10 nm)/PCb-PCz or PCb-DBT or PCb-DBF (25 nm)/TAPC (5 nm)/Al (100 nm) and ITO (50 nm)/Ca (10 nm)/PCb-PCz or PCb-DBT or PCb-DBF (25 nm)/LiF (1 nm)/Al (100 nm), respectively. All devices were fabricated by a vacuum thermalevaporation process. Only PEDOT:PSS was spin-coated on the ITO substrate. Current density-voltage-luminance characteristics of blue PHOLEDs were measured using a CS1000 spectroradiometer and a Keithley 2400 source measurement unit.

RESULTS AND DISCUSSION

The three host materials synthesized in this work were designed to study the effect of dibenzofuran, dibenzothiophene, and 9phenylcarbazole with different heteroatoms in the backbone structure on the photophysical properties and device performance of pyridoindole-based triplet host materials. The three moieties have a high triplet energy above 3.00 eV and are suitable as high-triplet-energy units for blue triplet host materials. In addition, the three moieties have different electron-donating character, and the comparison of the three host materials can be used to guide the design of host materials derived from pyridoindole to achieve high quantum efficiency in blue PHOLEDs.

The three host materials were synthesized by a simple Suzuki coupling reaction between 9-(3-bromophenyl)- α -carboline and the corresponding boronic acid of dibenzofuran, dibenzothiophene, and 9-phenylcarbazole. The boronic acid functional group was substituted at the para position of the heteroatom to obtain high triplet energy from the synthesized host materials. The synthetic process for the three host materials is shown in Scheme 1. All three host materials were purified by vacuum train sublimation after purification by column chromatography. Synthetic yields of PCb-DBF, PCb-DBT, and PCb-PCz were 70, 68, and 75%, respectively. Chemical structures of the host materials were confirmed by chemical analysis.

Molecular simulation of PCb-DBF, PCb-DBT, and PCb-PCz was carried out to investigate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the host materials. Gaussian 09 using the density functional of B3LYP with the 6-31G* basis set was used for the molecular simulation. Figure 1 shows the HOMO and LUMO distribution of the host materials. The LUMO distribution was similar among the host materials, but the HOMO distribution was different in the three host materials. The LUMO was localized on the pyridoindole unit of the host materials because of the electron-accepting pyridine unit of the pyridoindole moiety. The pyridine unit of pyridoindole strengthened the electron-accepting properties of the pyridoindole unit, resulting in the localization of the LUMO on the pyridoindole unit. The HOMO was dispersed over 9-phenylcarbazole in PCb-PCz because of the strong electron-donating character of the

Scheme 1. Synthetic Scheme of PCb-DBF, PCb-DBT, and PCb-PCz



Figure 1. Molecular orbital distribution of PCb-DBF, PCb-DBT, and PCb-PCz.

carbazole unit, whereas it was dispersed over 9-phenylpyridoindole in PCb-DBF and PCb-DBT. The dibenzofuran and disbenzothiophene possess very weak electron-donating character, which leads to the localization of the HOMO on the pyridoindole unit. The pyridineindole unit plays the role of the electron-accepting unit because of pyridine and the electrondonating unit because of indole. Therefore, it is presumed that the HOMO and LUMO levels of PCb-DBF and PCb-DBT would be similar, whereas the HOMO level of PCb-PCz would be destabilized compared to that of PCb-DBF and PCb-DBT.

Oxidation and reduction potentials of the three host materials were measured by cyclic voltammetry (CV). The oxidation and reduction curves of the host materials are shown in Figure 2. The oxidation potentials of PCb-DBF and PCb-DBT were 1.06 and 1.04 V, whereas the oxidation potential of PCb-PCz was 0.82 V. As the oxidation of PCb-PCz occurs in the electron-donating carbazole unit compared to carboline unit of PCb-DBF and PCb-DBT, the oxidation potential was low in PCb-PCz. The reduction potentials of PCb-DBF, PCb-DBT, and PCb-PCz were -2.62, -2.59, and -2.62 V, respectively, and there was little difference of the reduction



Figure 2. CV curves of PCb-DBF, PCb-DBT, and PCb-PCz.

potential. As explained in the molecular simulation result, pyridoindole is an electron-accepting moiety in the three host materials, which resulted in similar reduction potentials in the three host materials. Therefore, the difference between the oxidation and reduction potential was 3.44 V in the PCb-PCz host with electron donor-acceptor structure compared with 3.68 and 3.63 V for PCb-DBF and PCb-DBT, respectively.

The ionization potentials (IPs) calculated from the oxidation potential of PCb-DBF, PCb-DBT, and PCb-PCz according to the conversion factor proposed by Forrest et al.¹⁷ were -6.08, -6.06, and -5.75 eV, respectively. As expected from the HOMO distribution, the IPs of PCb-DBF and PCb-DBT were stabilized compared with that of PCb-PCz because of the weak electron-donating property of pyridonindole that dominates the HOMO distribution of PCb-DBF and PCb-DBT. The strong electron-donating character of 9-phenylcarbazole shifted the IP of PCb-PCz to -5.75 eV. The electron affinities (EAs) of PCb-DBF, PCb-DBT, and PCb-PCz from the reduction potentials were -2.40, -2.43, and -2.31 eV, respectively. The EA was similar in the three host materials because of the LUMO localization on the pyridoindole unit.

Photophysical properties of the host materials were analyzed using ultraviolet-visible (UV-vis) and photoluminescence (PL) spectrometers. Figure 3 shows UV-vis absorption, solution PL, and low-temperature PL spectra of PCb-DBF, PCb-DBT, and PCb-PCz. Weak broad UV-vis absorption between 310 and 360 nm was observed in all three host materials because of the $n-\pi^*$ transition of pyridoindole. The $n-\pi^*$ transition of PCb-PCz was stronger than that of other host materials because of the additional $n-\pi^*$ transition of 9phenylcarbazole. Strong absorption peaks below 300 nm are assigned to the $\pi - \pi^*$ transition of the conjugated backbone structure of the host materials. Optical band gaps calculated from the absorption edge of the UV-vis absorption spectra were 3.45, 3.46, and 3.44 eV for PCb-DBF, PCb-DBT, and PCb-PCz, respectively. There was little difference in the band gap from the UV-vis absorption spectra because the absorption edge was dominated by the $n-\pi^*$ transition of the pyridoindole unit. Solution PL emission spectra were also similar, and the PL emission peak was observed at 382 nm in all three host materials. Phosphorescent emission spectra of the host materials were measured in liquid nitrogen with a delay time of 0.1 ms to remove fluorescent emission. Triplet energies of the host materials were determined from the first



Figure 3. UV-vis, solution PL, and low-temperature PL spectra of PCb-DBF (a), PCb-DBT (b), and PCb-PCz (c).

material	UV-vis $(nm)^a$	solution PL (nm) ^a	$_{(\mathrm{eV})^{b}}^{\mathrm{IP}}$	EA (eV) ^c	band gap $(eV)^d$	triplet energy (eV) ^e	$T_{\rm g}$ (°C)	$T_{\rm m}$ (°C)	hole mobility (cm²/V s) ^f	electron mobility (cm²/V s) ^f
PCb-DBF	243, 254, 291, 298, 320, 338	382	-6.08	-2.40	3.68	2.82	69	150	8.1×10^{-4}	4.2×10^{-5}
PCb-DBT	242, 251, 267, 287, 337	382	-6.06	-2.43	3.63	2.72	79	188	9.2×10^{-5}	4.3×10^{-5}
PCb-PCz	238, 254, 294, 339, 345	383	-5.75	-2.31	3.44	2.74	97	215	1.3×10^{-4}	4.1×10^{-5}

Table 1. Basic Material Properties of PCb-DBF, PCb-DBT, and PCb-PCz

^{*a*}Data were measured in tetrahydrofuran solution. ^{*b*}IP was calculated from oxidation potential by cyclic voltammetry. ^{*c*}EA was calculated from reduction potential by cyclic voltammetry. ^{*d*}Band gap was calculated from the IP and EA. ^{*e*}Triplet energy was calculated from the first emission peak of low-temperature PL spectra. ^{*f*}Mobility value at 600 (V/cm)^{1/2}.

phosphorescent emission peak of the low-temperature PL spectra, which were 2.82, 2.72, and 2.74 eV for PCb-DBF, PCb-DBT, and PCb-PCz, respectively. The extension of conjugation through cental phenyl linkage resulted in relatively low triplet energy compared to that of dibenzofuran, dibenzothiphene, and 9-phenylcarbazole. However, the triplet energy of the host materials was high enough for application as the host materials for Firpic (2.65 eV)-doped blue PHOLEDs. Basic material parameters are summarized in Table 1.

Single-carrier devices of the host materials were fabricated to compare hole and electron density in the emitting layer. Figure 4 shows current density–voltage curves of hole-only and electron-only devices of PCb-DBF, PCb-DBT, and PCb-PCz host materials. The order of hole current density was PCb-PCz > PCb-DBT > PCb-DBF, and PCb-PCz showed a high hole current density. The high hole current density of the PCb-PCz device is related to the HOMO distribution of the host materials. The HOMO of PCb-PCz is localized on the carbazole unit, which has stronger hole-transport character



Figure 4. Current density-voltage curves of hole-only and electrononly devices of PCb-DBF, PCb-DBT, and PCb-PCz.

than the carboline unit, resulting in high hole current density in the PCb-PCz device. There was little energy barrier for hole injection, as shown in the energy-level diagram in Figure 5. The electron current density was similar in the three host materials



Figure 5. Energy-level diagram of PCb-DBF, PCb-DBT, and PCb-PCz devices.

because the electron-transport properties are dominated by the pyridoindole unit, which is present in all three host materials. The hole current density and the electron current density were well-balanced in the PCb-PCz device compared to the PCb-DBF and PCb-DBT devices. Hole and electron mobilities of the host materials were further studied to correlate the molecular structure of the host materials with charge-transport properties, which are summarized in Table 1. The order of hole mobility of the host materials was similar to that of the hole current density of the host materials, and the electron mobility of the host materials was similar in all host materials.

Blue PHOLEDs were fabricated to compare the device performance of the three host materials. The device structure was ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/ mCP (10 nm)/PCb-DBF:Firpic or PCb-DBT:Firpic or PCb-PCz:FIrpic (25 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm). The doping concentration of FIrpic was 3% in all host materials. Current density–voltage–luminance curves of the blue PHOLEDs are shown in Figure 6. The current density and



Figure 6. Current density-voltage-luminance curves of PCb-DBF, PCb-DBT, and PCb-PCz devices.

luminance of the PCb-PCz device were higher than those of the PCb-DBF and PCb-DBT devices. The high current density of the PCb-PCz device is related to the high hole current density of the PCb-PCz hole-only device. Because the hole current density of the PCb-PCz hole-only device was higher than that of the PCb-DBF and PCb-DBT devices while maintaining a similar electron current density, a high current density was obtained in the PCb-PCz device. The turn-on voltage of the PCb-PCz device was also lower than that of the PCb-DBF and PCb-DBT devices.

External quantum efficiency-luminance curves of the blue PHOLEDs are shown in Figure 7. The PCb-PCz device



Figure 7. External quantum efficiency–luminance curves of PCb-DBF, PCb-DBT, and PCb-PCz devices.

exhibited a higher quantum efficiency than the PCb-DBT and PCb-DBF devices, and the maximum external quantum efficiency of the PCb-PCz device was 29.6 \pm 0.1%. The high quantum efficiency of PCb-PCz was maintained at high luminance, and the quantum efficiency at 1000 cd/m² was $27.1 \pm 0.2\%$. There was less than a 10% decrease of the quantum efficiency from the maximum quantum efficiency. The maximum quantum efficiencies of the PCb-DBT and PCb-DBF devices were 25.9 \pm 0.1 and 24.0 \pm 0.1%, respectively. The high quantum efficiency of the PCb-PCz blue PHOLEDs is related to the charge balance in the emitting layer and the high PL quantum yield of PCb-PCz film. The hole and electron current densities of the single-carrier devices were well-balanced in the PCb-PCz devices compared to the PCb-DBT and PCb-DBF devices, which improved the quantum efficiency of the PCb-PCz blue PHOLEDs. The high PL quantum efficiency of PCb-PCz:Firpic also enhanced the quantum efficiency of the PCb-PCz blue PHOLEDs, as the PL quantum efficiencies of PCb-PCz:FIrpic, PCb-DBF:FIrpic, and PCb-DBT:FIrpic were 98, 82, and 85%, respectively. Other parameters, such as triplet energy, charge confinement, and optical outcoupling effect by thin ITO, were similar in the three host materials, and they enhanced the quantum efficiency of the blue PHOLEDs fabricated in this work. Outcoupling improvement by thin ITO (50 nm) used in this work was 2% compared to common ITO with a thickness of 150 nm. The quantum efficiency achieved in this work is close to the state-of-the-art efficiency data reported in the literature. The maximum power efficiencies of PCb-DBF, PCb-DBT, and PCb-PCz devices were 30.3 ± 0.4 , 36.2 ± 1.6 , 44.2 \pm 0.2 lm/W, respectively. All device performance characteristics are summarized in Table 2.

Electroluminescence (EL) spectra of the blue PHOLEDs are shown in Figure 8. All devices showed maximum emission peaks at 470 nm and a shoulder peak at 492 nm without any emission from mCP or TSPO1, indicating that there was little charge leakage in the device. The color coordinates of the PCb-DBF, PCb-DBT, and PCb-PCz devices were (0.14,0.29), (0.14,0.29), and (0.14,0.28), respectively. The rather strong shoulder peak in the PCb-DBF and PCb-DBT blue PHOLEDs is due to recombination zone shift compared to that of PCb-PCz blue PHOLED. The strong hole-transport properties of PCb-PCz shift the recombination zone from the hole-transport layer side to electron-transport layer side, which induces an optical effect in the device and changes the EL spectra.

Table	2.	Performance	of	PCb-DBF,	PCb-DBT,	and	PCb-	PCz	Devices
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host material	maximum quantum efficiency (%)	quantum efficiency at 1000 cd/m^2 (%)	maximum power efficiency (lm/W)	power efficiency at 1000 cd/m^2 $(lm/W)^c$	color coordinate
PCb-DBF	24.0 ± 0.1	20.4 ± 0.2	30.3 ± 0.4	18.0 ± 0.1	(0.14,0.29)
PCb-DBT	25.9 ± 0.1	21.7 ± 0.1	36.2 ± 1.6	19.0 ± 0.1	(0.14,0.29)
PCb-PCz	29.6 ± 0.1	27.1 ± 0.2	44.2 ± 0.2	25.1 ± 0.1	(0.14,0.28)



Figure 8. Electroluminescence spectra of PCb-DBF, PCb-DBT, and PCb-PCz devices.

CONCLUSIONS

Three host materials derived from a pyridoindole moiety, PCb-PCz, PCb-DBT, and PCb-DBF, were synthesized as high-triplet-energy host materials for blue PHOLEDs, and the molecular structure could be well-correlated with the photophysical properties and device performance of the host materials. The 9-phenylcarbazole moiety was better than dibenzofuran or dibenzothiophene to manage the energy levels and charge-transport properties of the pyridoindole-derived host materials. The PCb-PCz host with the 9-phenylcarbazole moiety showed balanced charge density in the emitting layer and exhibited a high external quantum efficiency of 29.6% \pm 0.1% in blue PHOLEDs. Therefore, the combination of pyridoindole and 9-phenylcarbazole is one effective way of developing high-triplet-energy host materials for blue PHOLEDs.

AUTHOR INFORMATION

Corresponding Author

*E-mail: leej17@dankook.ac.kr. Tel: 82-31-8005-3585. Fax: 82-31-8005-3585.

Notes

The authors declare no competing financial interest.

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