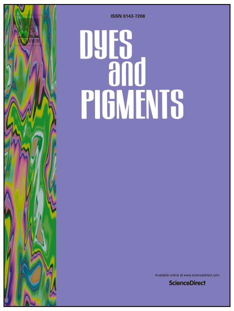

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Molecular design of modifying 4- position of dibenzofuran for high temperature stability and high efficiency

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Abstract

A molecular design modifying 4- position of dibenzofuran with a pyridoindole moiety for high temperature stability and high efficiency was examined as an approach to develop host materials for blue phosphorescent organic light-emitting diodes. The simple pyridoindole modification of 4- position of carbazole substituted dibenzofuran lead to high glass transition temperature above 130 ^{o}C in addition to high quantum efficiency in the blue phosphorescent device.

Key words : dibenzofuran, thermal stability, pyridoindole, blue device

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Introduction

The development of blue phosphorescent organic light-emitting diodes (PHOLEDs) is a critical issue in the field of organic light-emitting diodes (OLEDs) because blue PHOLEDs can solve the problem of high power consumption of OLED panels[1-3]. It was proven that the blue PHOLEDs would increase the current efficiency of blue device experimentally by more than three times, which motivated researchers to search and develop better blue PHOLEDs by material and device design[4-8].

Although it is essential to find and apply an optimized device structure, optimized host and dopant materials are even more important to reach the device performance level satisfying the specification of blue PHOLEDs. One of key parameters to be considered is thermal stability of the devices which is related with glass transition temperature (T_g) of host materials. High T_g above 120 ^oC is needed to satisfy the high temperature criteria of the OLED devices. Therefore, thermally stable host materials should be employed in the emitting layer of blue PHOLEDs[8-11]. Other than the temperature stability, the host material should have a design to reach high efficiency by balancing carriers[12-15].

In this work, a molecular design to increase the T_g of the host materials was approached by modification of 4- position of dibenzofuran with a pyridoindole moiety.

The 4- position modification approach using the pyridoindole moiety increased the T_g of the carbazole substituted dibenzofuran host materials above 130 ^oC and allowed bipolar charge transport characteristics. Moreover, the quantum efficiency (QE) values of the blue PHOLEDs having the high T_g host material were as high as 19.1% and 22.7% by doping phenylpyridine type and phenylimidazole type blue triplet emitters.

Experimental Section

General information

General analysis method of the synthesized compounds is described in previous work[16,17]. 9*H*-Carbazole (Cz), periodic acid, copper iodide (CuI), trans-1,2-diaminocyclohexane (1,2-TCH), and n-butyl lithium (n-BuLi) (Aldrich Chem. Co.), dibenzofuran and diiodoethane (TCI. Co.), 9*H*-pyrido[*2*,*3*-*b*]indole (α-carboline, α-Cb) (P&H tech Co.), sulfuric acid (H_2SO_4), acetic acid, potassium phosphate (K_3PO_4), and 1,4-dioxane (Duksan Sci. Co.), iodine (I_2) (Samchun Chem. Co.) were also used as received.

Synthesis

2-Iododibenzofuran (**1**), 9-(dibenzofuran-2-yl)-9*H*-carbazole (**2**), 9-(4-iododibenzofuran-2-yl)-9*H*-carbazole (**3**), 2,8-diiododibenzo[*b,d*]furan (**4**), 2,8-di(9*H*-carbazol-9-yl)dibenzo[*b,d*]furan (**5**), 9-(2-(9*H*-carbazol-9-yl)dibenzo[*b,d*]furan-4-yl)-9*H*-pyrido[*2,3-b*]indole (**CzDBFCb**), 9,9'-(4-iododibenzo[*b,d*]furan-2,8-diyl)bis(9*H*-carbazole) (**6**), and 9-(2,8-di(9*H*-carbazol-9-yl)dibenzo[*b,d*]furan-4-yl)-*9H*-pyrido[*2,3-b*]indole (**BCzDBFCb**) are synthesized according to previous literature[16,17].

9-(2-(9*H*-carbazol-9-yl)dibenzo[*b,d*]furan-4-yl)-9*H*-pyrido[*2,3-b*]indole (CzDBFCb)

Compound **3** (0.72g, 1.57mmol), α-carboline (0.37 g, 2.19 mmol), K_3PO_4 (0.83 g, 3.91 mmol) and CuI (0.21 g, 1.09 mmol) were dissolved in 1,4-dioxane. After nitrogen bubbling, 1,2-TCH (0.13 ml, 1.09 mmol) was added to the solution. The mixture was refluxed overnight under nitrogen atmosphere and then cooled down to room temperature. The mixture was filtered and the solution was extracted with methylene chloride and distilled water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated using a rotary evaporator. The product was purified by column chromatography using methylene chloride/n-hexane as an eluent. A white powder was obtained by vacuum train sublimation (0.28 g, yield: 36%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, 1H, J = 6.4 Hz), 8.46 (d, 1H, J = 9.2 Hz), 8.31 (d, 1H, J = 2.0 Hz), 8.21-8.18 (m, 3H), 8.04 (d, 1H, J = 8.0 Hz), 8.00 (d, 1H, J = 2.0 Hz), 7.70 (s, 2H), 7.55-7.29 (m, 11H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.08, 152.17, 150.42, 146.77, 141.35, 139.99, 133.39, 128.62, 128.49, 127.89, 127.30, 126.26, 126.14, 126.63, 124.00, 123.63, 123.59, 121.89, 121.44, 121.33, 121.23, 120.52, 120.29, 119.05, 116.98, 116.79, 112.48, 111.08, 110.05. MS (FAB) m/z 500 [$(M+H)^+$]. Elemental Analysis (calculated for $C_{35}H_{21}N_3O$) : C, 84.15; H, 4.24; N, 8.41; O, 3.20. Found : C, 84.22; H, 4.24; N, 8.46; O, 3.27.

9-(2,8-di(9*H*-carbazol-9-yl)dibenzo[*b*,*d*]furan-4-yl)-9*H*-pyrido[2,3-*b*]indole (BCzDBFCb)

Compound **6** (1g, 1.60 mmol), α-carboline (0.32 g, 1.92 mmol), K_3PO_4 (0.68 g, 3.20 mmol) and CuI (0.15 g, 0.80 mmol) were dissolved in 1,4-dioxane. After nitrogen bubbling, 1,2-TCH (0.10 ml, 0.80 mmol) was added to the solution. The mixture was refluxed overnight under nitrogen atmosphere and then cooled down to room temperature. The mixture was filtered, diluted with methylene chloride, and washed whith distilled water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated using a rotary evaporator. The product was purified by column chromatography using methylene chloride/n-hexane as an eluent. A white powder was obtained by vacuum train sublimation (0.31 g, yield: 29%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.54 (d, 1H, J = 6.4 Hz), 8.48 (d, 1H, J = 9.2 Hz), 8.30 (d, 1H, J = 2.4 Hz), 8.23-8.15 (m, 7H), 8.07 (d, 1H, J = 2.0 Hz), 7.70 (m, 4H), 7.56 (t, 1H, J = 7.8 Hz), 7.50-7.29 (m, 12H) ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.84, 152.10, 151.11, 146.78, 141.55, 141.20, 139.87, 133.82, 133.56, 128.69, 127.93, 127.37, 126.79, 126.30, 126.20, 125.52, 123.62, 123.45, 121.46, 121.32, 120.52, 120.39, 120.30, 120.17, 119.19, 116.99, 116.91, 113.75, 110.94, 109.90, 109.64. MS (FAB) m/z 665 [(M+H)$^+$]. Elemental Analysis (calculated for $C_{47}H_{28}N_4O$) : C, 84.92; H, 4.25; N, 8.43; O, 2.41. Found : C, 84.93; H, 4.24; N, 8.43; O, 2.42.

Device fabrication and measurements

The device structure of blue PHOLEDs was indium tin oxide (ITO, 50 nm)/polyethylene-3,4-dioxythiophene:poly-styrenesulfonate (PEDOT:PSS) (60 nm)/1, 1′-bis(di-4-tolylaminophenyl)cyclohexane (TAPC) (20 nm)/N,N-dicarbazolyl-3,5-benzene (mCP) (10 nm)/ **CzDBFCb** or **BCzDBFCb** : iridium (III) bis[2-(4,6-difluorophenyl)-pyridinato-N,C2]picolinate (FIrpic) (25 nm, 5%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSP01) (35 nm)/LiF (1 nm)/Al (100 nm). Single carrier device fabrication and device characterization were performed according to the method reported in the literature[18].

Results and discussion

A dibenzofuran core has been known to be activated at 2- position by halogenation and 4- position by lithiation[19-22]. The 2- position or 4- position activation followed by substitution with hole or electron transport moieties produced hole or electron or bipolar type compounds. Hole transport type substituent was mostly carbazole and electron transport type substituent was typically diphenylphosphine oxide. However, the diphenylphosphine oxide derived host materials have an issue of poor stability because of low dissociation energy of C-P bond[23-24]. Therefore, a molecular design route to stabilize the molecular structure, to obtain bipolar charge carrying property, and to secure high temperature stability is needed. The molecular stability and bipolar charge transport character requirements can be met by using a pyridoindole moiety and the high temperature stability can be satisfied by substituting the pyridoindole moiety at 4-position of dibenzofuran as reported in other articles[22,25-27]. Based on this concept, two compounds, **CzDBFCb** and **BCzDBFCb**, were designed, simulated, synthesized, characterized, and evaluated as the host materials of blue PHOLEDs.

Reaction scheme of **CzDBFCb** and **BCzDBFCb** is shown in **Scheme 1**. Carbazole substituted dibenzofuran intermediates were prepared and they were lithiated, iodinated, and coupled with a pyridoindole moiety via 9- position of pyridoindole. Wet and dry purification by column chromatography and sublimation provided highly pure **CzDBFCb** and **BCzDBFCb**.

In the case of the host materials, photophysical properties such as photoluminescence (PL) emission spectrum and triplet energy need to be characterized as they are directly related with light emission of dopant materials. Fluorescence and phosphorescence spectra of the host materials are presented in **Figure 1**. Fluorescent emission peaks of **CzDBFCb** and **BCzDBFCb** were positioned at 380 nm and 394 nm, and phosphorescent emission peaks were detected at 428 nm and 429 nm, respectively. The conversion of the emission wavelength into energy offered triplet energy of 2.89 eV in the two compounds. The triplet energy was similar in the two compounds because the degree of conjugation was not increased by the additional carbazole unit of **BCzDBFCb**. The long wavelength shift of the fluorescent emission peak in the **BCzDBFCb** host is caused by weak charge transfer character of the **BCzDBFCb** by two electron rich carbazole units and relatively electron poor dibenzofuran unit. Although there was long wavelength shift of the emission peak, the PL emission wavelength range of **CzDBFCb** and **BCzDBFCb** was well overlapped with absorption wavelength range of blue emitting FIrpic dopant. Ultraviolet-visible (UV-Vis) spectra were similar in the two host materials because the building units of the two host materials were carbazole, dibenzofuran, and pyridoindole except for the slight red-shift of absorption edge by two carbazole units.

Electrochemical characterization of the host materials was conducted using cyclic voltammetry (CV). **Figure 2** represents electrochemical oxidation and reduction behavior of **CzDBFCb** and **BCzDBFCb**. The oxidation behavior is dominated by electron rich group of the host materials and the reduction behavior is dictated by electron poor group of the host materials. The electron rich unit is carbazole and the electron poor unit is dibenzofuran both in the **CzDBFCb** and **BCzDBFCb** as presented in molecular orbital calculation results in **Figure 3**. Therefore, the oxidation and reduction of the **CzDBFCb** and **BCzDBFCb** were similar, which lead to similar ionization potential (IP) and electron affinity (EA) in the two host materials. The IP/EAs of **CzDBFCb** and **BCzDBFCb** were -5.78/-3.16 eV and -5.63/-3.27 eV, respectively. The HOMO was destabilized by the two carbazole units in the **BCzDBFCb** and the HOMO was stabilized by small UV-Vis gap. The IP-EA gaps of **CzDBFCb** and **BCzDBFCb** were 2.62 eV and 2.36 eV, respectively.

One of objectives of designing the **CzDBFCb** and **BCzDBFCb** host materials was to increase the T_g by substitution of pyridoindole at 4- position of dibenzofuran. The T_g

data obtained by differential scanning calorimeter scan of host materials are shown in **Figure 4**. The T_gs of **CzDBFCb** and **BCzDBFCb** determined from second heating scan of the host materials were 130 and 182 ^{o}C, respectively. The substitution of the pyridoindole moiety at 4- position of dibenzofuran played a crucial role of increasing the T_g of **CzDBFCb** and **BCzDBFCb** through restricted segmental motion of the pyridoindole moiety. In other works, the 4- position substitution of dibenzofuran increased the T_g and thermal stability of the host materials although the substituent was different[26,27]. The 4- position substitution was superior to 2- position substitution in terms of thermal stability. Similar results were observed in the CzDBFCb and BCzDBFCb.

Fundamentally, the **CzDBFCb** and **BCzDBFCb** host materials showed high triplet energy of 2.89 eV, high T_g above 130 ^{o}C, and fluorescence emission between 350 nm and 450 nm for energy transfer to blue emitting FIrpic, which satisfied basic requirements of host materials of blue PHOLEDs. Before device development, single carrier device performances of **CzDBFCb** and **BCzDBFCb** were tested using hole only and electron only devices. Hole and electron current densities of the **CzDBFCb** and **BCzDBFCb** devices are displayed in **Figure 5**. Although the hole current density of **CzDBFCb** was slightly higher than that of **BCzDBFCb**, both **CzDBFCb** and

BCzDBFCb exhibited similar hole and electron current densities in the single carrier devices, which demonstrates that they have similar hole and electron carrying capability. The carbazole was a main hole carrying moiety and dibenzofuran assisted by pyridoindole was a main electron carrying moiety in the **CzDBFCb** and **BCzDBFCb**.

Blue PHOLEDs were grown using the **CzDBFCb**:FIrpic and **BCzDBFCb**:FIrpic emitting layers and device data of the blue PHOLEDs were plotted in **Figure 6**. The **CzDBFCb** and **BCzDBFCb** devices behaved similarly in terms of current density (J), luminance (L) and voltage (V) of the devices. As demonstrated in the single carrier device data, the similarity of the hole and electron current densities of the **CzDBFCb** and **BCzDBFCb** devices lead to the similar J, V and L performances. However, the QEs of the **CzDBFCb** and **BCzDBFCb** blue PHOLEDs were quite different (**Figure 7**). The **CzDBFCb** blue PHOLEDs performed much better than the **BCzDBFCb** and achieved high QE of 19.1% relative to 12.4% of the **BCzDBFCb** device. In addition to the high QE, the **CzDBFCb** host also stabilized the high QE even at high luminance, resulting in high QE of 17.4% at 1,000 cd/m^2. The higher QE of the **CzDBFCb** device than that of the **BCzDBFCb** device is due to improved carrier balance associated with slightly higher hole current density and lower electron current density of **CzDBFCb** than those of **BCzDBFCb**.

Emission spectra of the **CzDBFCb** and **BCzDBFCb** devices in **Figure 8** were quite similar and the color coordinates of (0.15,0.30) and (0.15,0.31) were observed. Effective energy transfer and charge confinement produced the typical FIrpic emission spectra from the **CzDBFCb** and **BCzDBFCb** devices.

The two host materials were further doped with tris[1-(2,4-diisopropyldibenzo[b,d]furan-3-yl)-2-phenylimidazole] ($Ir(dbi)_3$) phosphorescent emitter and QE-L data are presented in **Figure 9**. QEs of the **CzDBFCb**:$Ir(dbi)_3$ and **BCzDBFCb**:$Ir(dbi)_3$ devices were 22.7% and 19.2%, respectively. The **CzDBFCb** host still performed better than the **BCzDBFCb** host in the $Ir(dbi)_3$ doped blue devices, but the QE gap between the two host materials was not as large as that of the FIrpic doped devices by hole trapping effect of $Ir(dbi)_3$.

Conclusions

Development of two pyridoindole modified dibenzofuran derivatives at 4-position, **CzDBFCb** and **BCzDBFCb**, as thermally stable host materials for blue PHOLEDs proposed that **CzDBFCb** would be suitable as the host materials of blue PHOLEDs by providing high QE of 19.1% in the FIrpic device, 22.7% in the $Ir(dbi)_3$ device, and high T_g of 130 ^oC. Therefore, the approach of developing blue host materials by modifying 4-

position of dibenzofuran was confirmed to be successful to guarantee good thermal stability and high QE.

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Scheme 1. Synthetic scheme of CzDBFCb and BCzDBFCb.

Figure 1. UV-vis absorption, solution PL and low temperature PL spectra of CzDBFCb and BCzDBFCb.

Figure 2. Oxidation and reduction curves of CzDBFCb and BCzDBFCb.

Figure 3. HOMO and LUMO distributions of CzDBFCb and BCzDBFCb.

Figure 4. DSC curves CzDBFCb and BCzDBFCb.

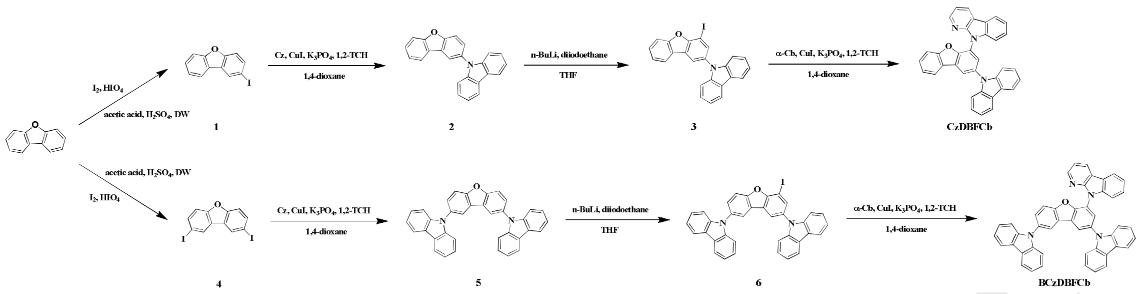
Figure 5. Current density-voltage curves of the hole only and electron only devices of CzDBFCb and BCzDBFCb.

Figure 6. Current density-voltage-luminance characteristics of CzDBFCb and BCzDBFCb devices doped with FIrpic.

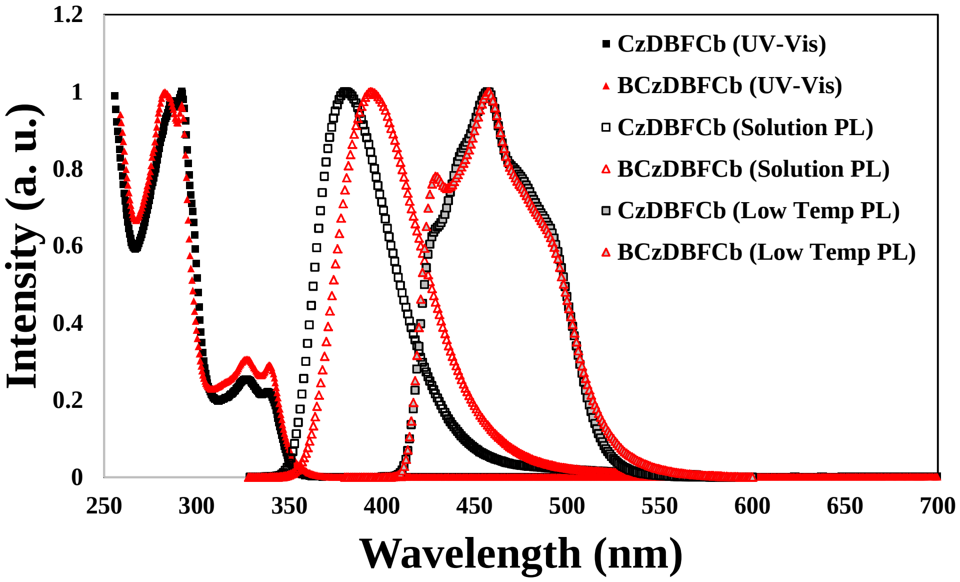
Figure 7. External quantum efficiency-luminance plots of CzDBFCb and BCzDBFCb devices doped with FIrpic.

Figure 8. Electroluminescence spectra of CzDBFCb and BCzDBFCb devices doped with FIrpic.

Figure 9. External quantum efficiency-luminance plots of CzDBFCb and BCzDBFCb devices doped with $Ir(dbi)_3$.


I$_2$, HIO$_4$
acetic acid, H$_2$SO$_4$, DW
1
Cz, CuI, K$_3$PO$_4$, 1,2-TCH
1,4-dioxane
2
n-BuLi, diiodoethane
THF
3
α-Cb, CuI, K$_3$PO$_4$, 1,2-TCH
1,4-dioxane
CzDBFCb
acetic acid, H$_2$SO$_4$, DW
I$_2$, HIO$_4$
4
Cz, CuI, K$_3$PO$_4$, 1,2-TCH
1,4-dioxane
5
n-BuLi, diiodoethane
THF
6
α-Cb, CuI, K$_3$PO$_4$, 1,2-TCH
1,4-dioxane
BCzDBFCb

Scheme 1



1.2
1
0.8
0.6
0.4
0.2
0
Intensity (a. u.)
250
300
350
400
450
500
550
600
650
700
Wavelength (nm)
■ CzDBFCb (UV-Vis)
▲ BCzDBFCb (UV-Vis)
□ CzDBFCb (Solution PL)
△ BCzDBFCb (Solution PL)
▣ CzDBFCb (Low Temp PL)
△ BCzDBFCb (Low Temp PL)

Figure 1

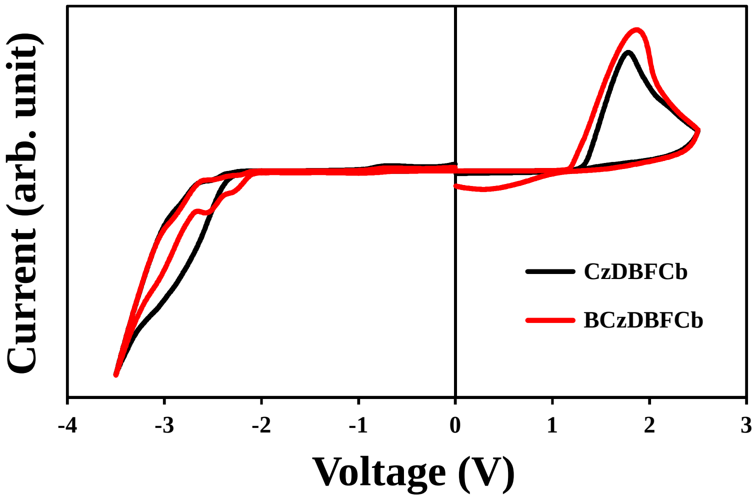


Figure 2

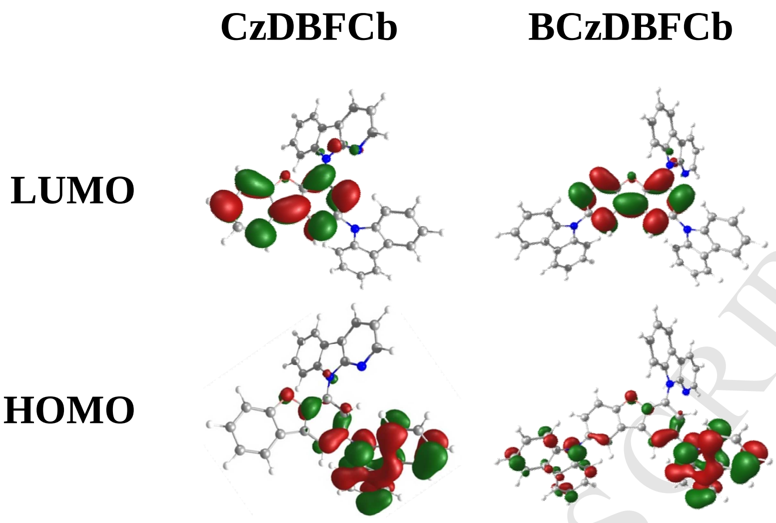


Figure 3

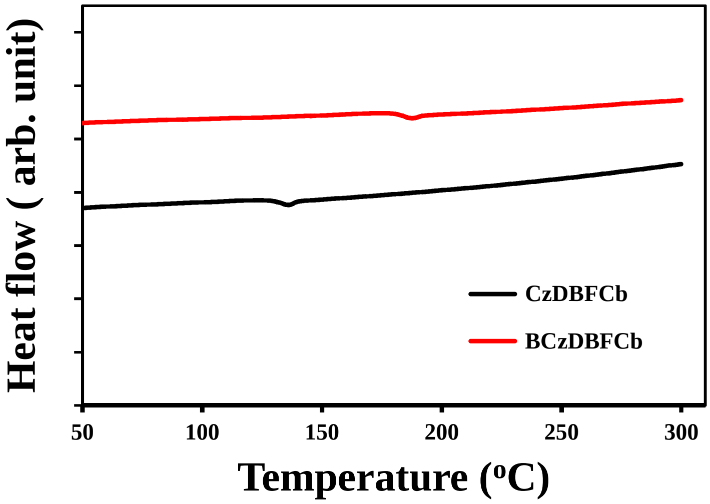

Heat flow (arb. unit)
Temperature (°C)
50
100
150
200
250
300
CzDBFCb
BCzDBFCb

Figure 4

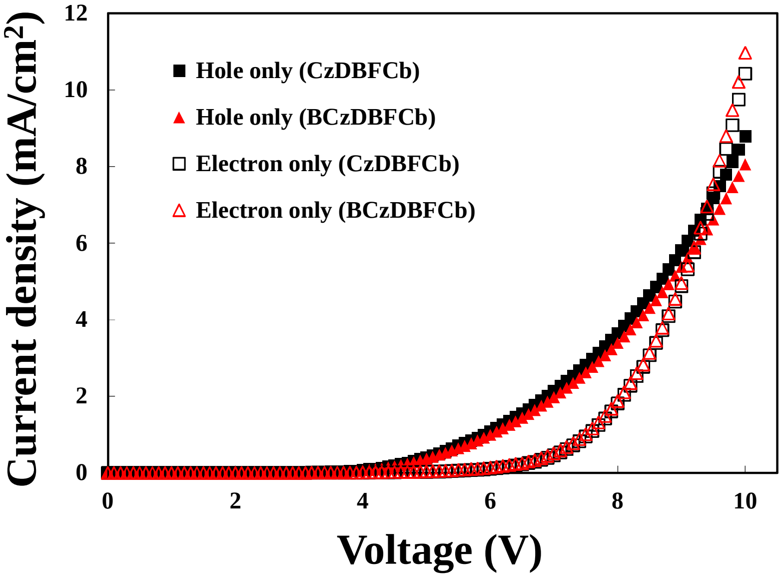

Current density (mA/cm^2)
Voltage (V)
0
2
4
6
8
10
12
0
2
4
6
8
10
■ Hole only (CzDBFCb)
▲ Hole only (BCzDBFCb)
□ Electron only (CzDBFCb)
△ Electron only (BCzDBFCb)

Figure 5

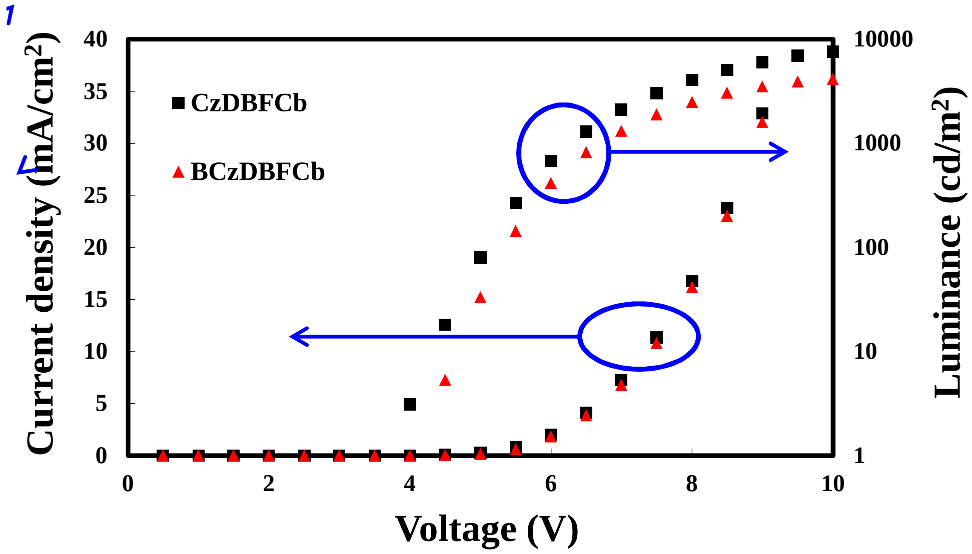

1
2
Current density (mA/cm^2)
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
Voltage (V)
■ CzDBFCb
▲ BCzDBFCb
10000
1000
100
10
1
Luminance (cd/m^2)

Figure 6

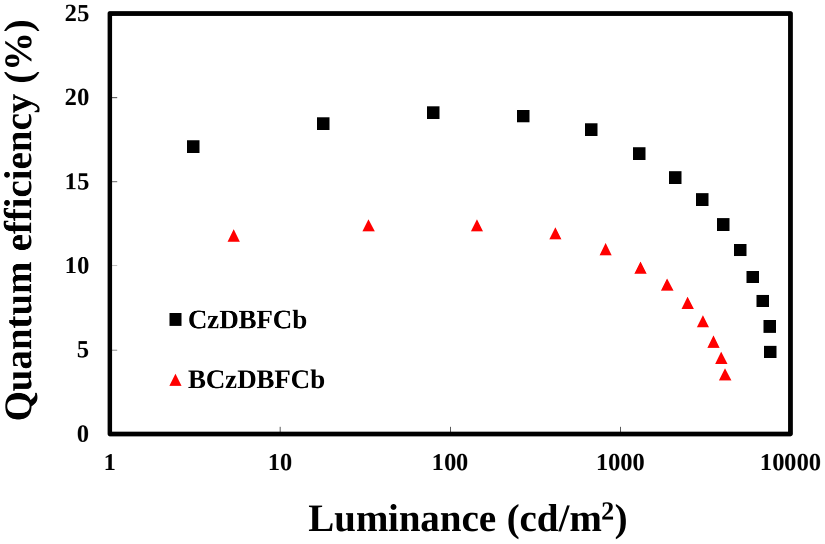

Quantum efficiency (%)
25
20
15
10
5
0
1
10
100
1000
10000
Luminance (cd/m²)
■ CzDBFCb
▲ BCzDBFCb

Figure 7

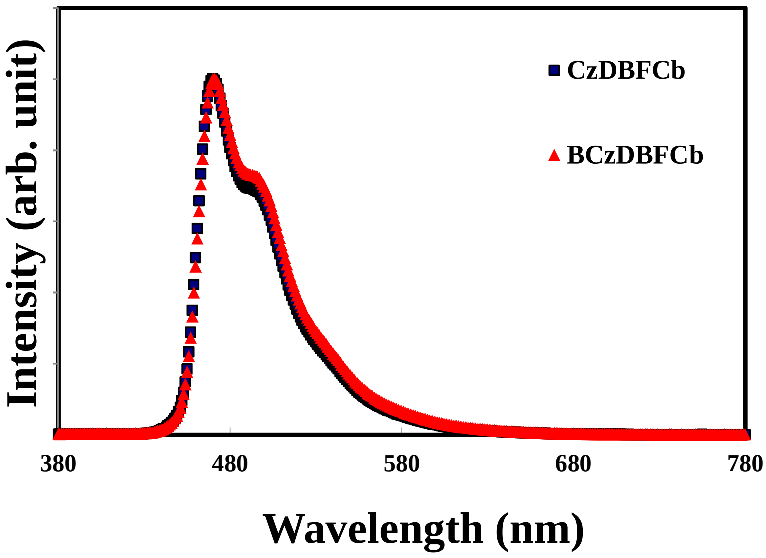

Intensity (arb. unit)
■ CzDBFCb
▲ BCzDBFCb
380
480
580
680
780
Wavelength (nm)

Figure 8

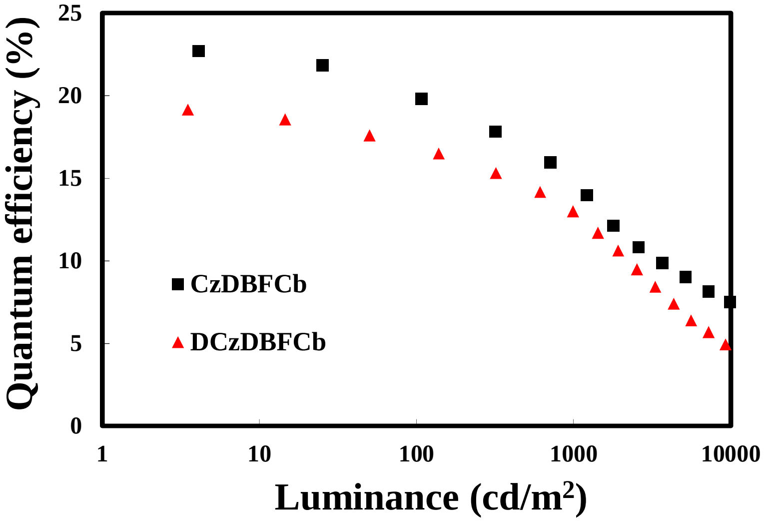

Quantum efficiency (%)
25
20
15
10
5
0
1
10
100
1000
10000
Luminance (cd/m2)
■ CzDBFCb
▲ DCzDBFCb

Figure 9

Host materials with a 4- position modified dibenzofuran as a core structure

Pyridoindole modification of dibenzofuran for high temperature stability

High efficiency in blue phosphorescent organic light-emitting diodes using dibenzofuran derived host materials