

## Supporting Information

# Oxygen-Bridged Boron Derivatives as Electron Transport and Thermally Activated Delayed Fluorescence Host Materials for High-Performance Phosphorescent Organic Light-Emitting Diodes

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## Experimental

### General information

All reagents, except 9H-carbazole, were used for synthesis without further purification, and commercially available materials were utilized for the experiments. 9H-carbazole underwent purification through toluene recrystallization. Sigma-Aldrich provided 9H-carbazole, boron tribromide, sodium tert-butoxide, m-xylene, and n-BuLi. TCI supplied 1-bromo-3-methoxybenzene, 1-bromo-4-methoxybenzene, 2-bromo-1,3-difluorobenzene, and N,N-diisopropylethylamine. J&H Chem provided tris(dibenzylideneacetone)dipalladium(0), and P&H Tech supplied tri-tert-butylphosphine. Daejung Chemical & Metal Co. provided potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), while Duksan Chemical Industry Co. supplied toluene, tetrahydrofuran (THF), n-hexane (HEX), dichloromethane (MC), and N-methyl-2-pyrrolidone (NMP). All purifications involved column chromatography using a mixture of MC and HEX

on a silica gel column. Prior to device testing, vacuum sublimation was performed. Mass spectra were obtained using an Advion ExpressionL CMS spectrometer in APCI/FAB mode for mass spectrometry (MS). After purification,  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) analysis was carried out in deuteriochloroform ( $\text{CDCl}_3$ ) using a Unity Inova (Varian, 500 MHz) spectrometer. Cyclic voltammetry (CV) using an Ivium Tech, Iviumstat system was conducted to determine the HOMO and LUMO levels. The electrodes used were a carbon electrode, Ag/AgCl electrode, and Pt electrode. Ferrocene and 0.1 M tetrabutylammonium perchlorate in acetonitrile (ACN) served as the reference material and electrolyte, respectively. UV-vis spectra were recorded using a JASCO V-730 UV-vis spectrophotometer, while PL spectra were observed using a PerkinElmer LS-55 fluorescence spectrophotometer. Both UV-vis spectra and PL spectra measurements were conducted using solution samples. The analysis of triplet energy was performed at 77 K under a liquid nitrogen state. The photoluminescence quantum yield (PLQY) was measured using the Hamamatsu Quantaurus-QY system (C11347-11). Density functional computations were conducted using the Gaussian 09 program with the B3LYP/6-31G\* basis set. The vacuum evaporation process was utilized for device fabrication under a pressure of  $3.0 \times 10^{-7}$  Torr. The devices were stored in a glove box with a nitrogen-filled glass lid to protect them from oxygen. All device performances were measured outside the glove box using a Keithley 2400 source meter, and optical characterization was performed using a CS 2000 spectroradiometer.

## **Synthesis**

### **Synthesis of 9-(3-methoxyphenyl)-9H-carbazole (1)**

A 250 mL round-bottom flask was charged with 1-bromo-3-methoxybenzene (10.0 g, 53.46 mmol), 9H-carbazole (10.72 g, 64.15 mmol), tri-tert-butylphosphine (2.70 g, 13.36 mmol),

sodium tert-butoxide (20.55 g, 213.84 mmol), and tris(dibenzylideneacetone)dipalladium(0) (2.44 g, 2.67 mmol) in 100 mL of toluene. The reaction mixture was refluxed under a nitrogen atmosphere overnight. After completion, the mixture was cooled to room temperature, filtered through a celite/silica filter, and concentrated using a rotary evaporator. Further purification was achieved by performing silica gel column chromatography with n-hexane as the eluent, yielding 11 g of product (75% yield).

MS (APCI) m/z: Found 274.67 [M + H]<sup>+</sup>. Calculated For C<sub>19</sub>H<sub>15</sub>NO: 273.12.

### **Synthesis of 3-(9H-carbazol-9-yl)phenol (2)**

To a solution of 9-(3-methoxyphenyl)-9H-carbazole (11 g, 40.24 mmol) in dichloromethane (MC, 200 mL), cooled to -78 °C using dry ice, in a two-necked flask under a nitrogen atmosphere, stirring was carried out for 30 minutes to reach the desired temperature. Subsequently, BBr<sub>3</sub> (20 g, 80.48 mmol) was slowly added dropwise under nitrogen, and the reaction mixture was stirred at -78 °C for 1 hour. The temperature gradually increased to room temperature during continuous stirring after 1 hour. Following overnight stirring, the mixture was extracted with MC and distilled water. The resulting product was evaporated using a rotary evaporator. For purification, silica gel column chromatography was conducted using a solvent mixture of MC and n-hexane (HEX) in a 1:4 ratio. The final product was obtained with a yield of 8.2 g (78% yield).

MS (APCI) m/z : Found 260.32 [M + H]<sup>+</sup>. Calculated For C<sub>18</sub>H<sub>13</sub>NO : 259.10.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ/ppm): δ 8.13 (d, J = 7.8 Hz, 2H), 7.48 – 7.37 (m, 5H), 7.30 – 7.24 (m, 2H), 7.14 (ddd, J = 7.9, 1.9, 0.8 Hz, 1H), 7.04 (t, J = 2.2 Hz, 1H), 6.92 (ddd, J = 8.3, 2.5, 0.8 Hz, 1H), 4.97 (d, J = 3.7 Hz, 1H).

**Synthesis of 9,9'-(((2-bromo-1,3-phenylene)bis(oxy))bis(3,1-phenylene))bis(9H-carbazole)  
(3)**

Into a 100 mL two-necked flask, 3-(9H-carbazol-9-yl)phenol (8.2 g, 31.62 mmol), 2-bromo-1,3-difluorobenzene (3.05 g, 15.81 mmol), potassium carbonate (6.55 g, 47.43 mmol), and 30 mL of N-methyl-2-pyrrolidone (NMP) were combined. The reaction mixture was stirred and heated at 180 °C for 10 hours. Upon completion, the mixture was cooled to room temperature and extracted with dichloromethane (MC) and distilled water. The extracted product was evaporated using a rotary evaporator. Silica gel column chromatography using a solvent mixture of MC and n-hexane (HEX) in a 1:4 ratio was performed for purification. The final product was obtained with a yield of 8.58 g (80% yield).

MS (APCI) m/z : Found 670.98 [M + H]<sup>+</sup>. Calculated For C<sub>42</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>2</sub> : 670.13.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ/ppm): δ 8.12 (dt, J = 7.8, 3.9 Hz, 4H), 7.54 (td, J = 8.1, 4.2 Hz, 2H), 7.47 – 7.32 (m, 10H), 7.31 – 7.19 (m, 9H), 6.91 (d, J = 8.2 Hz, 2H).

**Synthesis of 3,11-di(9H-carbazol-9-yl)-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene  
(p-BO-2Cz)**

Under a nitrogen atmosphere, a solution of 9,9'-(((2-bromo-1,3-phenylene)bis(oxy))bis(3,1-phenylene))bis(9H-carbazole) (4.5 g, 6.7 mmol) in anhydrous m-xylene (45 mL) was cooled to 0 °C. Slowly and carefully, a solution of butyllithium in hexane (3.4 mL, 2.5 M, 8.7 mmol) was added to the reaction mixture. After 20 minutes, the mixture was allowed to stir at room temperature for 1 hour. Then, boron tribromide (0.8 mL, 8.7 mmol) was gradually added at 0 °C. Following an additional 20 minutes, the reaction mixture was stirred at room temperature for 30 minutes, and then heated to 45 °C for 50 minutes. Subsequently, N,N-diisopropylethylamine (1.7 mL, 13.4 mmol) was added at 0 °C. The reaction mixture was

stirred at room temperature for 30 minutes, then heated to 120 °C for 20 hours, and finally cooled to room temperature. Filtration of the reaction mixture was performed using toluene as the eluent. The solvent was then removed under vacuum, and the resulting crude product was purified by column chromatography using hexane as the solvent. The desired compound (1.0 g, 15%) was obtained as a white solid.

HRMS (FAB) ( $m/z$ ): [(M+H)<sup>+</sup>] calculated for C<sub>42</sub>H<sub>25</sub>BN<sub>2</sub>O<sub>2</sub>: 600.47 ; found 600.20.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ /ppm):  $\delta$  8.95 (d,  $J$  = 8.2 Hz, 2H), 8.18 (d,  $J$  = 7.8 Hz, 4H), 7.86 (dd,  $J$  = 10.9, 5.0 Hz, 3H), 7.69 (dd,  $J$  = 11.0, 5.0 Hz, 6H), 7.47 (dd,  $J$  = 12.9, 5.7 Hz, 4H), 7.38 – 7.29 (m, 6H).

Elemental Analysis: Calculated for C: 84.01, H: 4.20, B: 1.80, N: 4.67, O: 5.33; found C: 84.09, H: 4.09, N: 4.59, O: 4.12.

#### **Synthesis of 9-(4-methoxyphenyl)-9H-carbazole (4)**

In a 250 mL round-bottom flask, 1-bromo-4-methoxybenzene (10.0 g, 53.46 mmol), 9H-carbazole (10.72 g, 64.15 mmol), tri-tert-butylphosphine (2.70 g, 13.36 mmol), sodium tert-butoxide (20.55 g, 213.84 mmol), and tris(dibenzylideneacetone)dipalladium(0) (2.44 g, 2.67 mmol) were combined with 100 mL of toluene. The reaction mixture was refluxed overnight under a nitrogen atmosphere. After the reaction was complete, the mixture was cooled to room temperature and filtered using a celite/silica filter. The filtrate was then concentrated using a rotary evaporator. To further purify the product, silica gel column chromatography was performed with n-hexane as the eluent. The resulting yield of the purified product was 13 g (89% yield).

MS (APCI)  $m/z$  : Found 274.67 [M + H]<sup>+</sup>. Calculated For C<sub>19</sub>H<sub>15</sub>NO : 273.12.

### **Synthesis of 4-(9H-carbazol-9-yl)phenol (5)**

In a two-necked flask, a solution of 9-(4-methoxyphenyl)-9H-carbazole (13 g, 47.56 mmol) in dichloromethane (MC) (200 mL) was stirred under a nitrogen atmosphere for 30 minutes to reach a temperature of -78 °C using dry ice. Once cooled, BBr<sub>3</sub> (23.8 g, 95.12 mmol) was gradually added under nitrogen conditions and stirred at -78 °C for 1 hour in a nitrogen atmosphere. Subsequently, the mixture was stirred overnight at room temperature. After the reaction, the mixture was extracted with MC and distilled water. The resulting product was then evaporated using a rotary evaporator. Silica gel column chromatography was performed using a solvent mixture of MC and n-hexane (HEX) in a 1:4 ratio for purification. The final product was obtained with a yield of 9.3 g (75% yield).

MS (APCI) m/z : Found 260.32 [M + H]<sup>+</sup>. Calculated For C<sub>18</sub>H<sub>13</sub>NO : 259.10.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ/ppm): δ 8.18 – 8.10 (m, 2H), 7.44 – 7.35 (m, 4H), 7.35 – 7.22 (m, 4H), 7.08 – 6.98 (m, 2H), 5.00 (s, 1H).

### **Synthesis of 9,9'-(((2-bromo-1,3-phenylene)bis(oxy))bis(4,1-phenylene))bis(9H-carbazole) (6)**

Into a two-necked flask with a capacity of 100 mL, a mixture of 4-(9H-carbazol-9-yl)phenol (4 g, 15.42 mmol), 2-bromo-1,3-difluorobenzene (0.86 g, 7.71 mmol), potassium carbonate (3.2 g, 23.13 mmol), and 20 mL of N-methyl-2-pyrrolidone (NMP) was added. The reaction mixture was then stirred and heated at 180 °C for 10 hours. Upon completion of the reaction, the mixture was cooled to room temperature and subsequently extracted with dichloromethane (MC) and distilled water. The extracted product was evaporated using a rotary evaporator, and further purification was performed using silica gel column chromatography with a solvent mixture of MC and n-hexane (HEX) in a 1:4 ratio. The final product was obtained with a yield

of 4.1 g (40% yield).

MS (APCI)  $m/z$  : Found 670.98  $[M + H]^+$ . Calculated For  $C_{42}H_{27}BrN_2O_2$  : 670.13.

$^1H$  NMR ( $CDCl_3$ , 500 MHz,  $\delta/ppm$ ):  $\delta$  8.17 – 8.11 (m, 4H), 7.58 – 7.52 (m, 2H), 7.44 – 7.34 (m, 8H), 7.31 – 7.24 (m, 11H), 6.97 (d,  $J = 8.2$  Hz, 2H).

### **Synthesis of 2,12-di(9H-carbazol-9-yl)-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (m-BO-2Cz)**

Under a nitrogen atmosphere, a solution of 9,9'-(((2-bromo-1,3-phenylene)bis(oxy))bis(4,1-phenylene))bis(9H-carbazole) (1.5 g, 2.1 mmol) in anhydrous *m*-xylene (15 mL) was cooled to 0 °C. Slowly and carefully, a solution of butyllithium in hexane (1.1 mL, 2.5 M, 2.7 mmol) was added to the reaction mixture. After 20 minutes, the mixture was allowed to stir at room temperature for 1 hour. Then, boron tribromide (0.3 mL, 2.7 mmol) was gradually added at 0 °C. Following an additional 20 minutes, the reaction mixture was stirred at room temperature for 30 minutes, and then heated to 45 °C for 50 minutes. Subsequently, *N,N*-diisopropylethylamine (0.5 mL, 4.2 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 30 minutes, then heated to 120 °C for 20 hours, and finally cooled to room temperature. Filtration of the reaction mixture was performed using toluene as the eluent. The solvent was then removed under vacuum, and the resulting crude product was purified by column chromatography using hexane as the solvent. The desired compound (0.3 g, 15%) was obtained as a yellow solid.

HRMS (FAB) ( $m/z$ ):  $[(M+H)^+]$  calculated for  $C_{42}H_{25}BN_2O_2$  : 600.47 ; found 600.20.

$^1H$  NMR ( $CDCl_3$ , 500 MHz,  $\delta/ppm$ ):  $\delta$  8.67 (d,  $J = 2.6$  Hz, 2H), 8.09 – 8.03 (m, 4H), 7.92 – 7.84 (m, 3H), 7.40 – 7.33 (m, 6H), 7.22 – 7.33 (m, 6H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz) : 159.25, 157.45, 140.99, 135.46, 132.75, 132.68, 132.09, 126.08, 123.45, 120.36, 120.04, 109.36, 109.03.

Elemental Analysis: Calculated for C: 84.01, H: 4.20, B: 1.80, N: 4.67, O: 5.33; found C: 84.16, H: 4.06, N: 4.42, O: 4.00.

## **Device preparation and measurements**

### **Hole only devices and electron only devices**

To characterize the charge transport characteristics, hole-only devices (HODs) and electron-only devices (EODs) were fabricated. In the HODs, 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) was introduced to facilitate hole injection. In the EODs, diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide (TSPO1) was used to block hole leakage. The device configurations for the HODs are as follows: ITO/PEDOT:PSS (60 nm)/p-BO-2Cz or m-BO-2Cz (50 nm)/TAPC (10 nm)/Al (200 nm). The device configuration for the EODs is as follows: ITO/PEDOT:PSS (60 nm)/TSPO1 (10 nm)/p-BO-2Cz or m-BO-2Cz (50 nm)/TSPO1 (20 nm)/LiF (1.5 nm)/Al (200 nm). The OLED devices were fabricated using a 50 nm thick indium tin oxide (ITO) anode on a transparent glass substrate.

### **TADF OLEDs**

The OLED devices were fabricated using a 50 nm thick indium tin oxide (ITO) anode on transparent glass substrate. The materials used in TADF OLED devices were poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) which worked as hole injection layer, TAPC which worked as hole transport layer, 4,4',4''-Tris(carbazol-9-yl)triphenylamine (TCTA), 1,3-di (9H-carbazol-9-yl)benzene (mCP) and diphenyl(4-(triphenylsilyl)phenyl)phosphine oxide (TSPO1) which worked as exciton blocking layer,



Bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) which worked as host in emissive layer, 1,3,5-tris(1-phenyl-1H-benzo [d]imidazole-2-yl)benzene (TPBi) which worked as electron transport layer and LiF/Al which worked as electron injection layer and cathode. TADF OLEDs were fabricated with the device architecture of ITO/PEDOT:PSS(40 nm)/TAPC (10 nm)/TCTA (5 nm)/mCP (5 nm)/x wt% emitter in DPEPO (25 nm)/TSPO1 (5 nm)/TPBi (20 nm)/LiF (1.5 nm)/Al (200 nm).

### **Blue PhOLEDs**

The sky-blue PhOLEDs structure consisted of the following layers: devices 1 and 2: indium tin oxide (ITO, 50 nm)/1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN, 30 wt%): N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)-phenyl)-9H-fluoren-2-amine (BCFN, 40 nm)/N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)-phenyl)-9H-fluoren-2-amine (BCFN, 10 nm)/3,3-di(9H-carbazol-9-yl)biphenyl (mCBP, 10 nm)/mCBP (30 nm): fac-tris(1-(2,6-diisopropylphenyl)-2-(3-cyanophenyl)-1H-imidazolyl)iridium(III) (CN-Im, 15 wt%): p-BO-2Cz or m-BO-2Cz (50 wt%)/2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan (DBFTrz, 5 nm)/2-[4-(9,10-Di-naphthalen-2-yl-anthracen-2-yl)-phenyl]-1-phenyl-1H-benzoimidazole (ZADN, 20 nm)/LiF (1.5 nm)/Al (200 nm).

### **Green PhOLEDs**

The green PhOLEDs were fabricated with the following structure: devices 3 and 4: PEDOT:PSS(60 nm)/TAPC(20 nm)/ 9,10-Dihydro-9,9-dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-acridine (PCzAc) (10 nm)/mCBP: Bis(2-phenylpyridine)(acetylacetonate)iridium(III) (Ir(ppy)<sub>2</sub>acac): p-BO-2Cz or m-BO-2Cz (25 nm:3 wt%:50%)/TSPO1(5 nm)/TPBi(40 nm)/LiF(1.5 nm)/Al(200 nm).

## Supporting Figures

**Figure S1.** The thermal decomposition temperature test curves of (a) p-BO-2Cz, (b) m-BO-2Cz.

**Figure S2.** The glass transition temperature test curves of (a) p-BO-2Cz, (b) m-BO-2Cz.

**Figure S3.** The oxidation curves of p-BO-2Cz and m-BO-2Cz obtained from cyclic voltammetry scanning.

**Figure S4.** Current density-voltage curves of hole only device of p-BO-2Cz (blue) and m-BO-2Cz (red).

**Figure S5.** The HOMO and LUMO levels diagram of materials used in the TADF device.

**Figure S6.** (a) Device structure and energy level diagram (b) molecular structures of materials used in blue PhOLEDs.

**Figure S7.** (a) Device structure and energy level diagram of Device 3, 4 and (b) molecular structures used in green PhOLEDs.

**Figure S8.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR Spectrum of m-BO-2Cz.

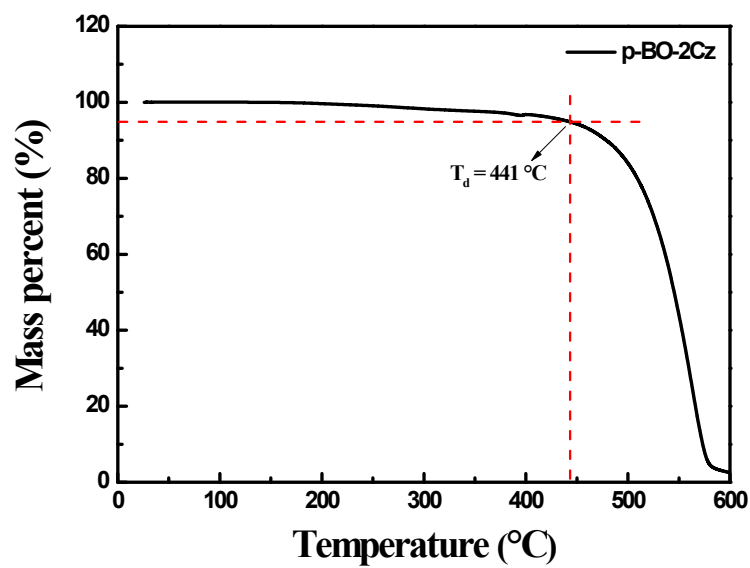
**Figure S9.** Device performance data of green PhOLEDs introducing only mCBP host: (a) Current density-voltage-luminance; (b) EQE-luminance curves.

**Figure S10.** Device performance data of blue PhOLEDs introducing only mCBP host: (a) Current density-voltage-luminance; (b) EQE-luminance curves.

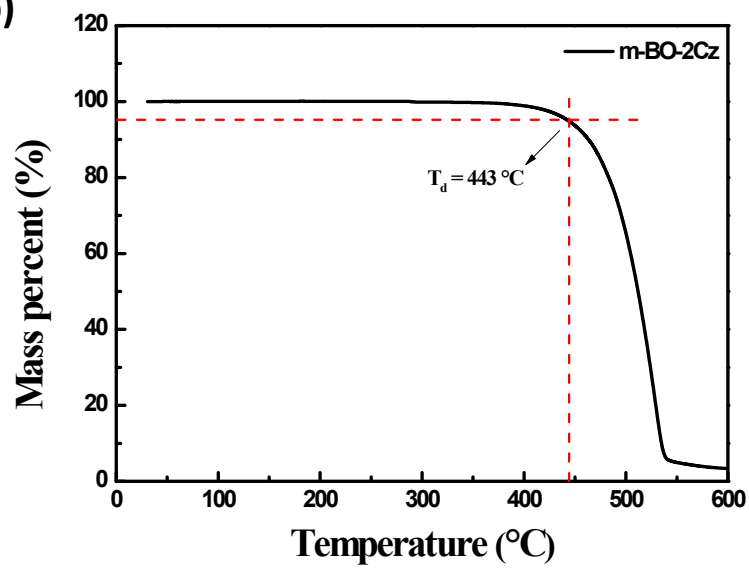
## List of tables

**Table S1.** Summarized device performances of the only mCBP host in green and blue PhOLEDs.

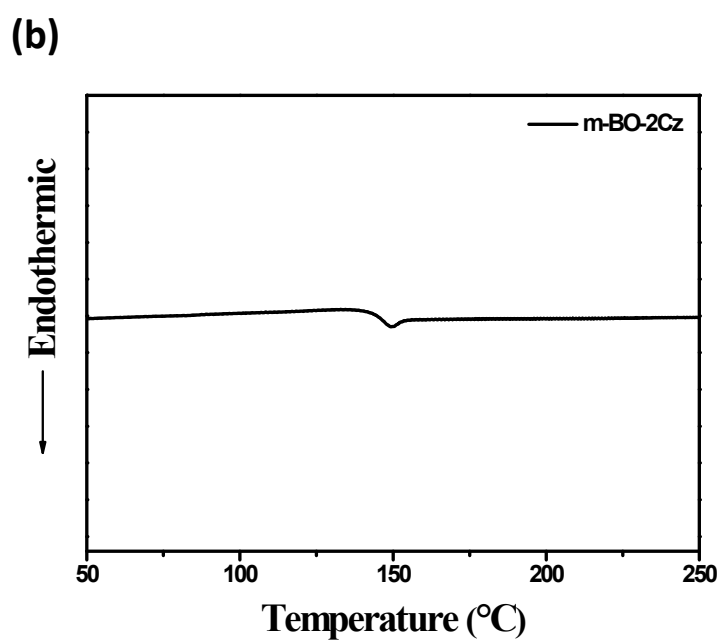
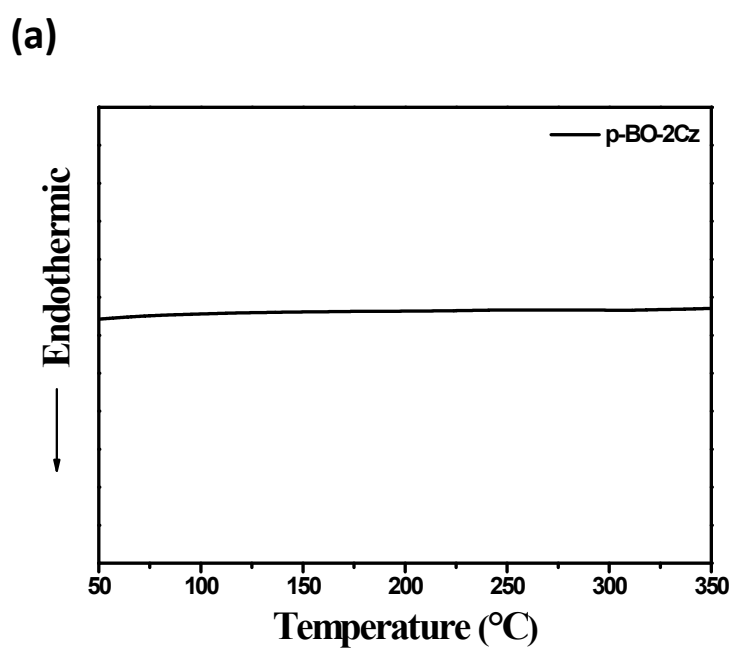
(a)



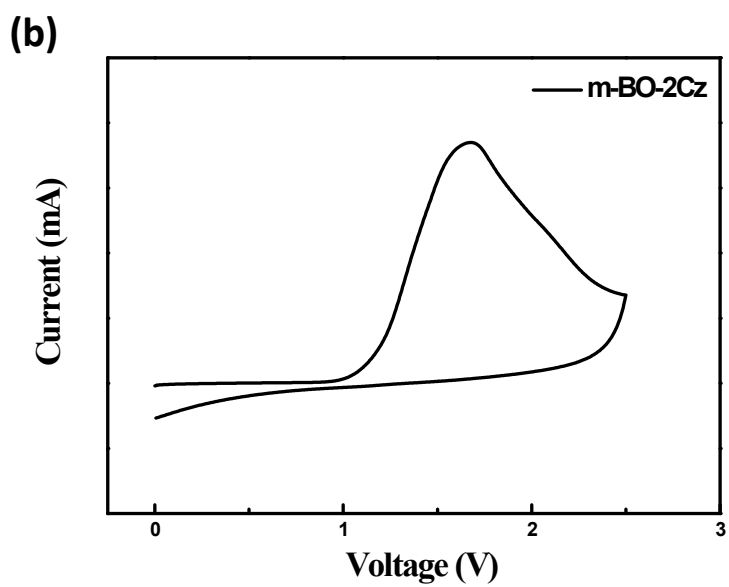
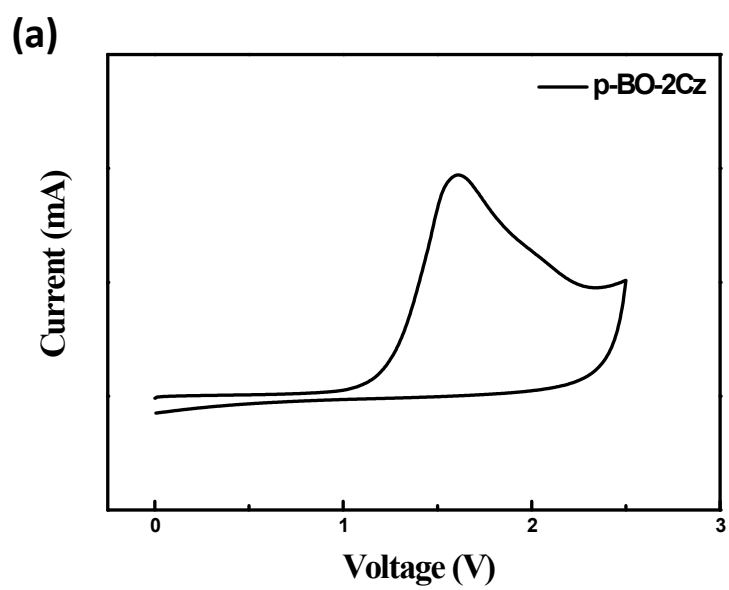
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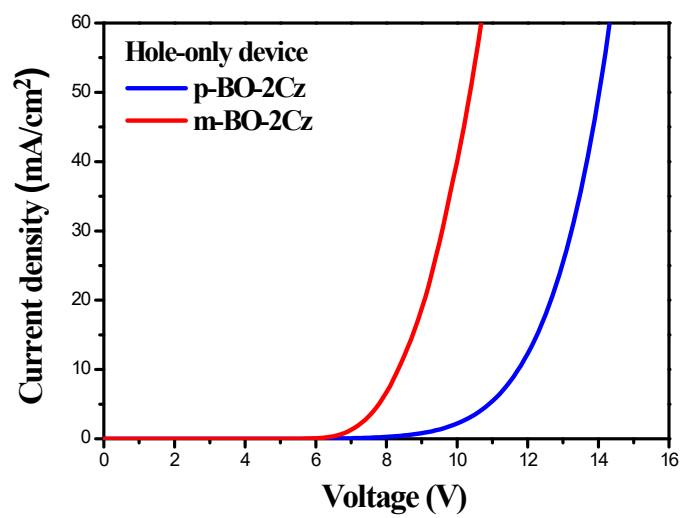
**Figure S1.** The thermal decomposition temperature test curves of (a) p-BO-2Cz, (b) m-BO-2Cz.



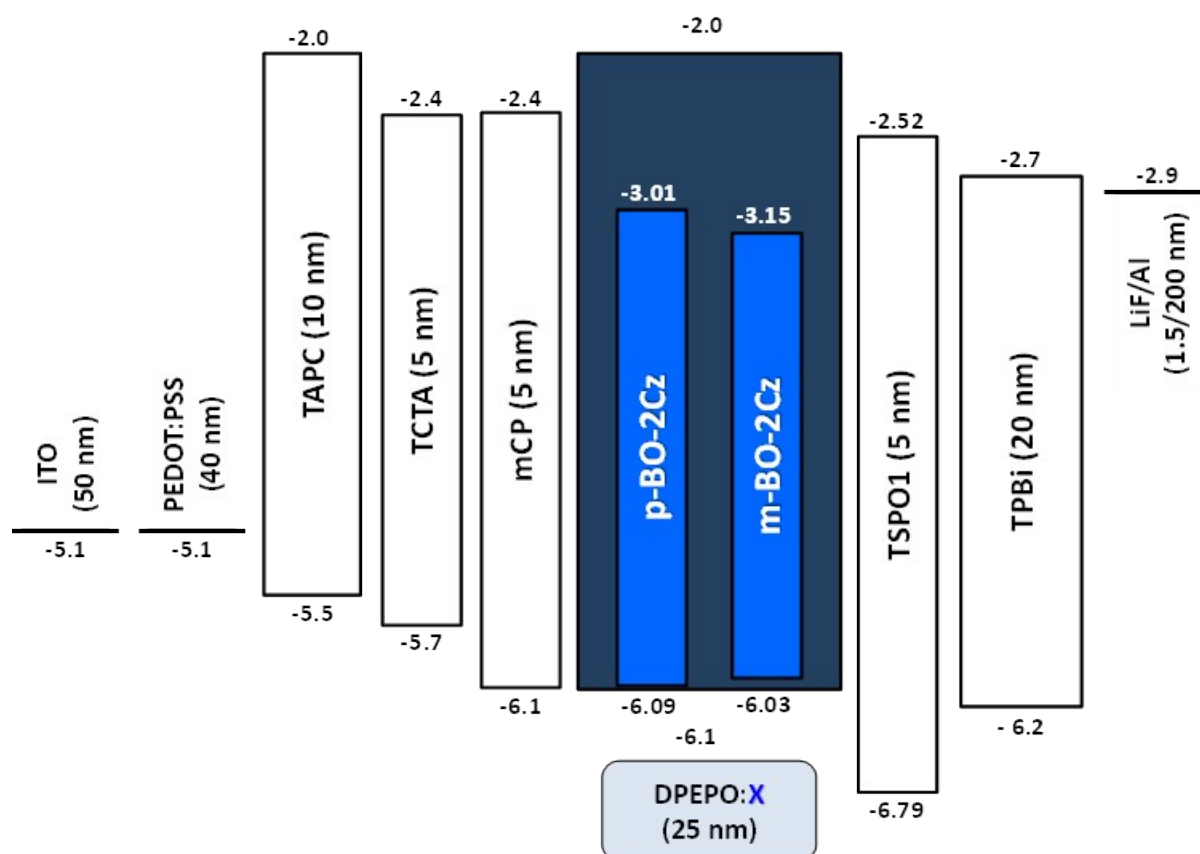
**Figure S2.** The glass transition temperature test curves of (a) p-BO-2Cz, (b) m-BO-2Cz.



**Figure S3.** The oxidation curves of p-BO-2Cz and m-BO-2Cz obtained from cyclic voltammetry scanning.



**Figure S4.** Current density-voltage curves of hole only device of p-BO-2Cz (blue) and m-BO-2Cz (red).



**Figure S5.** The HOMO and LUMO levels diagram of materials used in the TADF device.

Device structure:

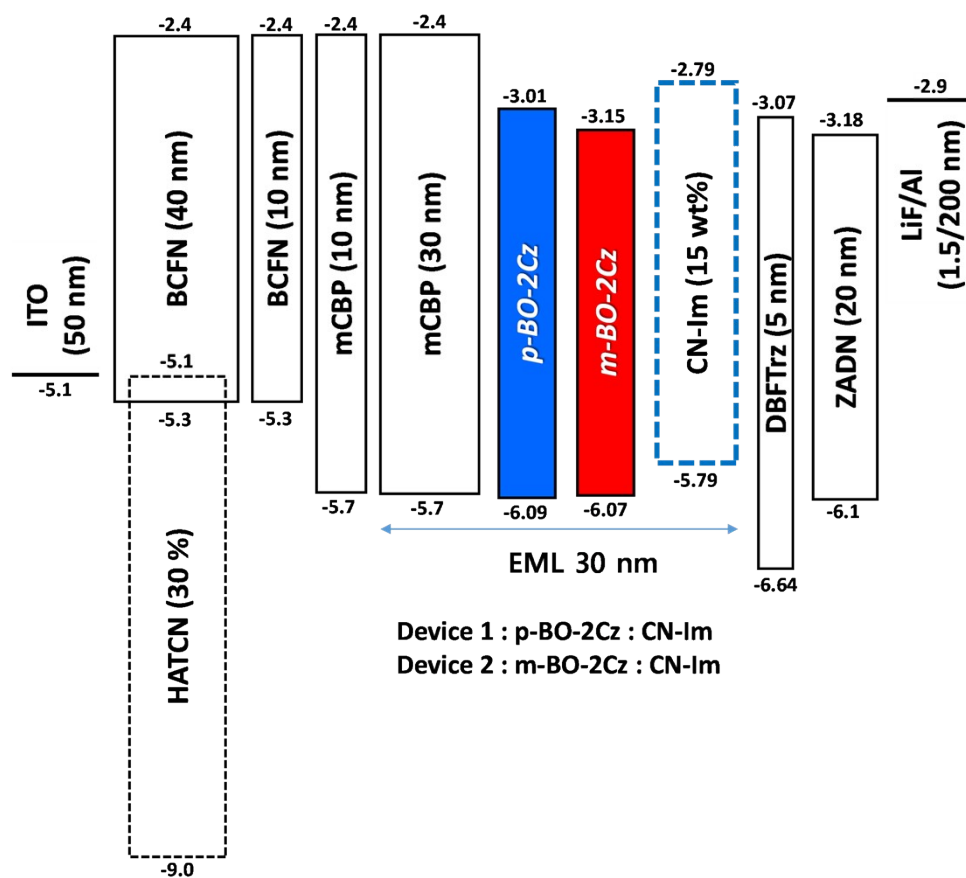
PEDOT:PSS(40)/TAPC(10)/TCTA(5)/mCP(5)/DPEPO:X(25:Y%)/TSPO1(5)/TPBi(20)/LiF(1.5)/Al(200)

X = p-BO-2Cz, m-BO-2Cz

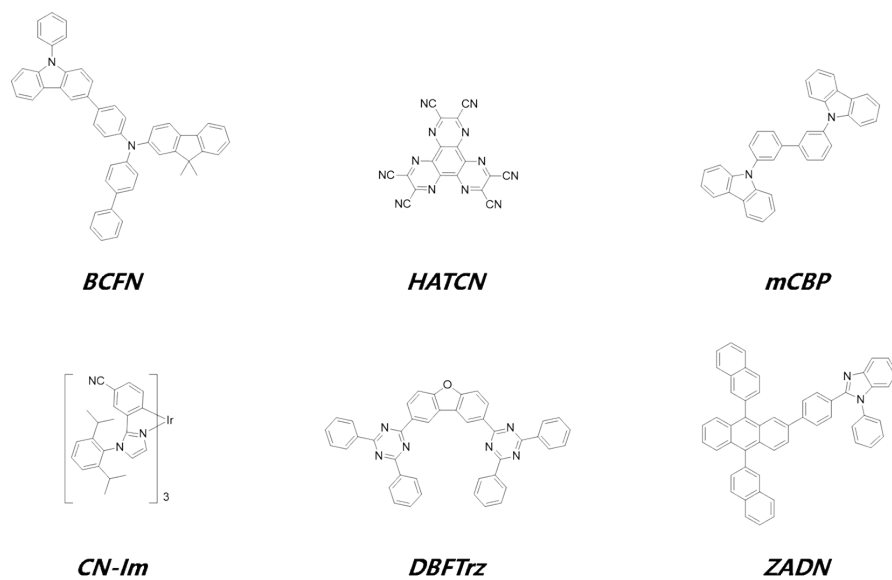
Y = 10, 20, 30 wt%



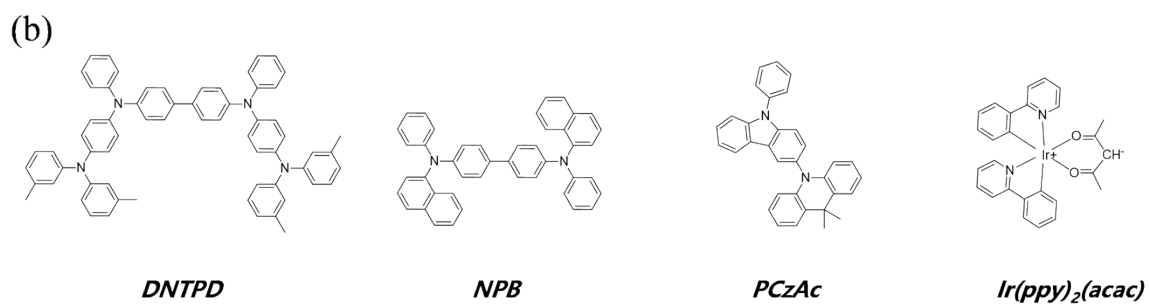
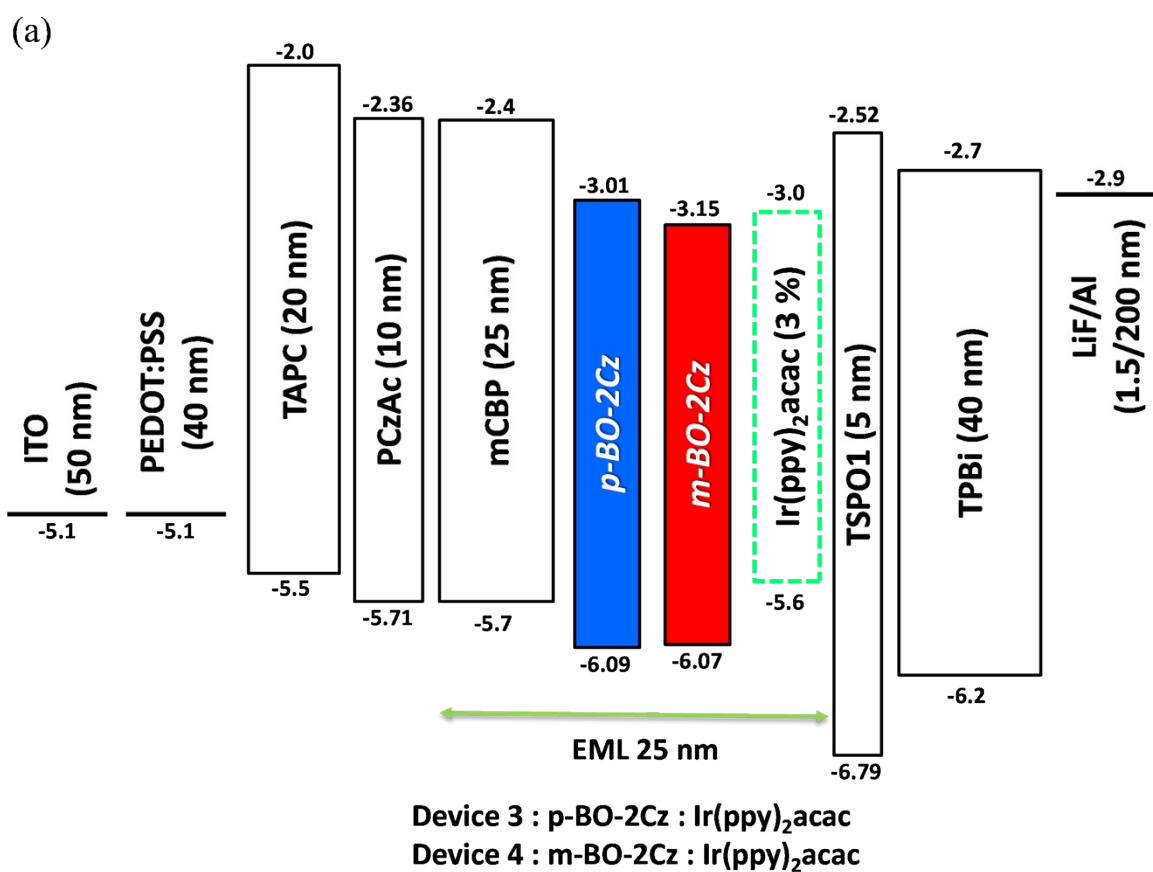
(a)



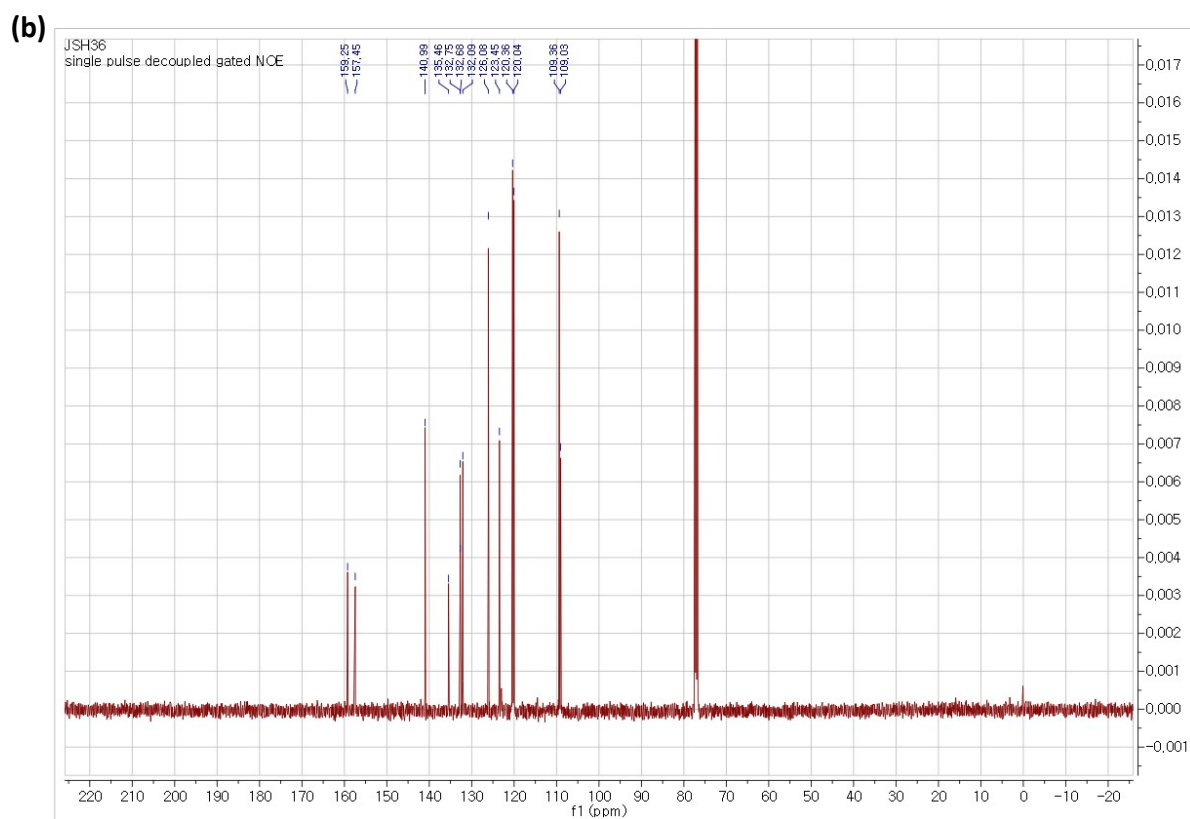
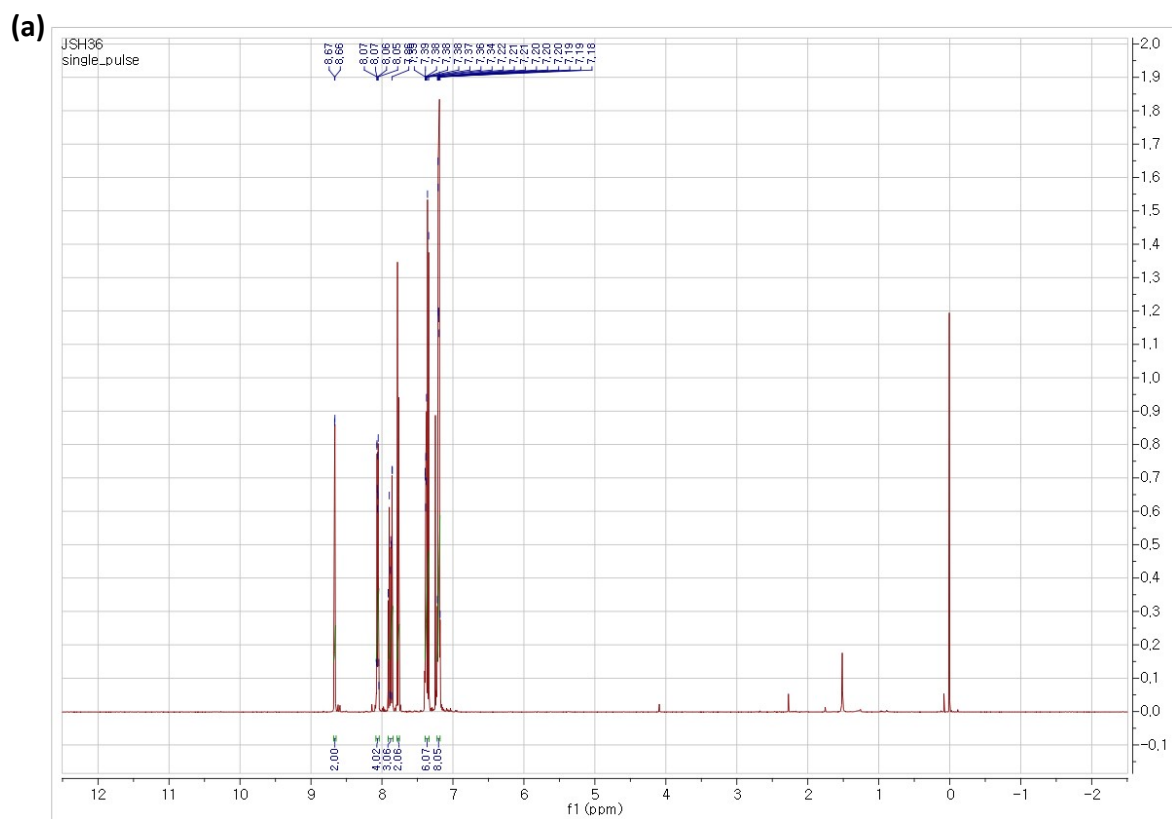
(b)

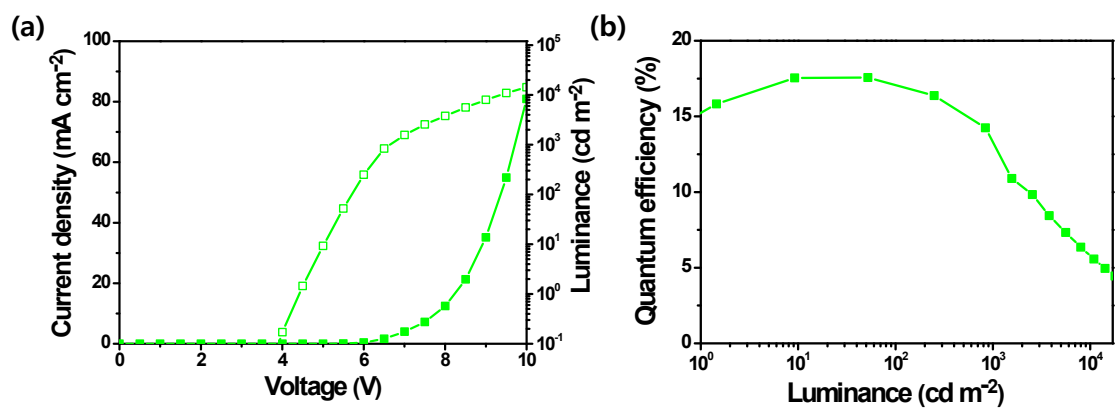


**Figure S6.** (a) Device structure and energy level diagram (b) molecular structures of materials used in blue PhOLEDs.

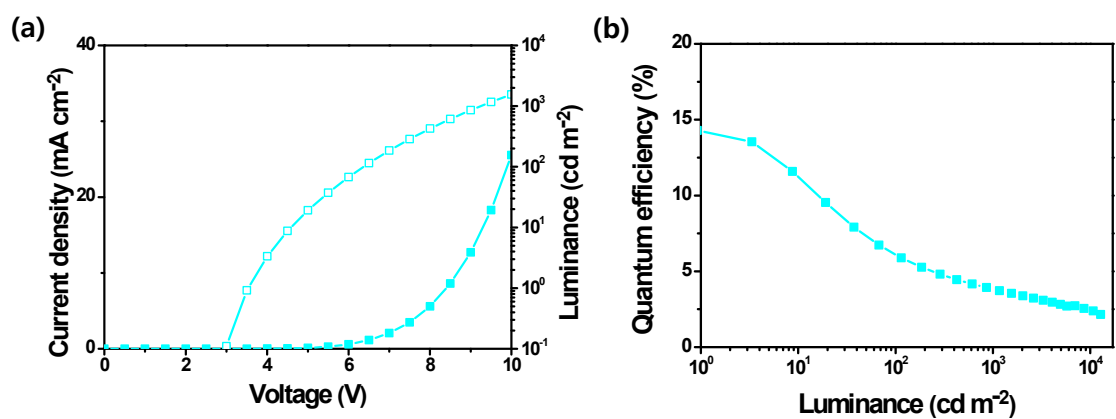


**Figure S7.** (a) Device structure and energy level diagram of Device 3, 4 and (b) molecular structures used in green PhOLEDs.





**Figure S9.** Device performance data of green PhOLEDs introducing only mCBP host: (a) Current density-voltage-luminance; (b) EQE-luminance curves.



**Figure S10.** Device performance data of blue PhOLEDs introducing only mCBP host: (a) Current density-voltage-luminance; (b) EQE-luminance curves.

**Table S1.** Summarized device performances of the only mCBP host in green and blue PhOLEDs.

Dopant	$V_d^{[a]}$ (V)	EQE <sup>[b]</sup> (%)		PE <sup>[c]</sup> (lm W <sup>-1</sup> )		CE <sup>[d]</sup> (cd/A <sup>-1</sup> )		CIE coordinate
		1000 cd m <sup>-2</sup>	Max	1000 cd m <sup>-2</sup>	Max	1000 cd m <sup>-2</sup>	Max	
<b>Ir(ppy)<sub>2</sub>(acac)</b>	7.7	9.1	17.5	4.7	16.6	14.3	26.6	(0.63, 0.36)
<b>CN-Im</b>	9.3	3.8	14.3	2.2	24.3	6.5	24.4	(0.15, 0.24)

[a] Driving voltage at 1,000 cd/m<sup>2</sup>, [b] External quantum efficiency, [c] Power efficiency, [d]

Current efficiency.