

## Supporting Information

### **Carbazole-benzonitrile derivatives as universal hosts for triplet-harvesting blue organic light-emitting diodes**

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### **Experimental**

#### **General information**

All materials used for the experiments were commercially available, and all reagents, except 9H-carbazole, were used for synthesis without further purification. 9H-carbazole was purified through toluene recrystallization. The 9H-carbazole and boron tribromide, sodium tert-butoxide were purchased from Sigma-Aldrich. 1-Bromo-3-methoxybenzene, 1-bromo-4-methoxybenzene, and 2-bromo-1,3-difluorobenzene, bis(diphenylphosphino)ferrocene[1,1'-], were purchased from TCI. Copper(I) cyanide was purchased from Alfa Aesar. Tris(dibenzylideneacetone)dipalladium(0) was a product of J&H Chem. Tri-tert-butylphosphine was purchased from P&H Tech. Potassium carbonate ( $K_2CO_3$ ) was purchased from Daejung Chemical & Metal Co. Toluene, tetrahydrofuran (THF), n-hexane (HEX), dichloromethane (MC), N-methyl-2-pyrrolidone (NMP) and 1,4-dioxane were purchased from Duksan Chemical Industry Co.. All purifications were carried out through column chromatography and vacuum sublimation. The column chromatography was performed using a mixture of MC and HEX on a silica gel column. Vacuum sublimation was conducted prior to device testing. Mass spectra of all materials 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 using a Unity Inova (Varian, 500 MHz) spectrometer to identify the materials in deuteriochloroform ( $\text{CDCl}_3$ ). The properties of all materials were measured using cyclic voltammetry (CV) (Ivium Tech, Iviumstat) to calculate the HOMO and LUMO levels. Carbon electrode, Ag/AgCl electrode, and Pt electrode were used as the electrodes. Ferrocene and 0.1M tetrabutylammonium perchlorate in acetonitrile (ACN) were used as the reference material and electrolyte, respectively. UV-vis spectra were recorded using a UV-vis spectrophotometer (JASCO, V-730), and PL spectra were observed using a fluorescence spectrophotometer (PerkinElmer, LS-55). Both UV-vis spectra and PL spectra measurements were conducted using solution samples. When measuring the triplet energy of the materials, the analysis was performed at 77 K under a liquid nitrogen state. The photoluminescence quantum yield (PLQY) was measured using the Quantaury-QY system (Hamamatsu, C11347-11). Density functional computations were performed using the Gaussian 09 program with the B3LYP/6-31G\* basis set. The vacuum evaporation process was utilized under a pressure of  $3.0 \times 10^{-7}$  Torr for the fabrication of the devices. The devices were equipped with a glass lid filled with nitrogen and stored in a glove box to protect them from oxygen. All device performances were measured outside the glove box. The characterization of the devices was conducted 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)

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), tris(dibenzylideneacetone)dipalladium(0) (2.44 g, 2.67 mmol), and 100 mL of toluene were added to a 250 mL round-bottom flask. The reaction mixture was refluxed overnight under nitrogen conditions. After the completion of the reaction, the mixture was cooled to room temperature. It was then filtered using a celite/silica filter and concentrated using a rotary evaporator. For further purification, silica gel column chromatography was performed using n-hexane as the eluent (11 g, Yield = 75%).

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)

A solution of 9-(3-methoxyphenyl)-9H-carbazole (11 g, 40.24 mmol) dissolved in MC (200 mL) was stirred in a two-necked flask under a nitrogen atmosphere for 30 minutes to cool to -78 °C using dry ice. After cooling, BBr<sub>3</sub> (20 g, 80.48 mmol) was slowly injected under a nitrogen condition and stirred at -78 °C for 1 hour under a nitrogen atmosphere. After 1 hour, the reaction mixture gradually warmed up to room temperature with continuous stirring. After overnight, the mixture was then extracted with MC and distilled water. The extracted product was evaporated using a rotary evaporator. Silica gel column chromatography was performed using MC:HEX (1:4) as the solvent for purification. The final product was obtained (8.2 g, Yield = 78%).

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

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

(3)

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 NMP were added into a 100 mL two-necked flask. The reaction mixture was stirred and heated at 180 °C for 10 h. After completion, the reaction mixture was cooled to room temperature. The mixture was then extracted with MC and distilled water. The extracted product was evaporated using a rotary evaporator. Silica gel column chromatography was performed using MC:HEX (1:4) as the solvent for purification. The final product was obtained (8.58 g, Yield = 80%).

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.

### **Synthesis of 2,6-bis(3-(9H-carbazol-9-yl)phenoxy)benzotrile (3-CzPB)**

A solution of 9,9'-(((2-bromo-1,3-phenylene)bis(oxy))bis(3,1-phenylene))bis(9H-carbazole) (2 g, 2.97 mmol), copper(I) cyanide (1.06 g, 11.91 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.175 g, 0.19 mmol), and bis(diphenylphosphino)ferrocene[1,1'-] (0.264 g, 0.47 mmol) in 1,4-dioxane (15 mL) were refluxed in a two-necked flask overnight at 200 °C with stirring under a nitrogen atmosphere. The reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then purified through silica gel column chromatography using MC:HEX (1:1) as the eluent. A white powdery product was obtained (0.85 g, Yield = 46%).

MS (APCI) m/z: Found 618.56 [M + H]<sup>+</sup>. Calculated For C<sub>43</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>: 617.21.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ/ppm): δ 8.13 (d, J = 7.8 Hz, 4H), 7.64 (t, J = 8.1 Hz, 2H), 7.49 – 7.45 (m, 6H), 7.44 – 7.39 (m, 5H), 7.35 (t, J = 1.8 Hz, 2H), 7.29 (t, J = 7.3 Hz, 4H), 7.23 (dd, J = 8.3, 2.3 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz) : 161.07, 154.02, 140.99, 134.79, 134.65, 129.04, 126.16, 123.51, 121.54, 120.50, 120.23, 112.82, 111.22, 109.68, 96.47.

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

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), tris(dibenzylideneacetone)dipalladium(0) (2.44 g, 2.67 mmol), and 100 mL of toluene were added to a 250 mL round-bottom flask. The reaction mixture was refluxed overnight under nitrogen conditions. After the completion of the reaction, the mixture was cooled to room temperature. It was then filtered using a celite/silica filter and concentrated using a rotary evaporator. For further purification, silica gel column chromatography was performed using n-hexane as the eluent (13 g, Yield = 89%).

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

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

A solution of 9-(4-methoxyphenyl)-9H-carbazole (13 g, 47.56 mmol) dissolved in MC (200 mL) was stirred in a two-necked flask under a nitrogen atmosphere for 30 minutes to cool to -78 °C using dry ice. After cooling,  $\text{BBr}_3$  (23.8 g, 95.12 mmol) was slowly injected under a nitrogen condition and stirred at -78 °C for 1 hour under a nitrogen atmosphere. After 1 hour, the resulting mixture was stirred overnight at room temperature. After overnight, the mixture was then extracted with MC and distilled water. The extracted product was evaporated using a rotary evaporator. Silica gel column chromatography was performed using MC:HEX (1:4) as the solvent for purification. The final product was obtained (9.3 g, Yield = 75%).

MS (APCI) m/z : Found 260.32 [M + H]<sup>+</sup>. Calculated For  $\text{C}_{18}\text{H}_{13}\text{NO}$  : 259.10.

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

(6)

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 NMP were added into a 100 mL two-necked flask. The reaction mixture was stirred and heated at 180 °C for 10 h. After completion, the reaction mixture was cooled to room temperature. The mixture was then extracted with MC and distilled water. The extracted product was evaporated using a rotary evaporator. Silica gel column chromatography was performed using MC:HEX (1:4) as the solvent for purification. The final product was obtained (1.19 g, Yield = 40%).

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.

#### **Synthesis of 2,6-bis(4-(9H-carbazol-9-yl)phenoxy)benzotrile (4-CzPB)**

A solution of 9,9'-(((2-bromo-1,3-phenylene)bis(oxy))bis(4,1-phenylene))bis(9H-carbazole) (2 g, 2.97 mmol), copper(I) cyanide (1.06 g, 11.91 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.175 g, 0.19 mmol), and bis(diphenylphosphino)ferrocene[1,1'-] (0.264 g, 0.47 mmol) in 1,4-dioxane (15 mL) were refluxed in a two-necked flask overnight at 200 °C with stirring under a nitrogen atmosphere. The reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then purified through silica gel column chromatography using MC:HEX (1:1) as the eluent. A white powdery product was obtained (1.05 g, Yield = 57%).

MS (APCI) m/z : Found 618.56 [M + H]<sup>+</sup>. Calculated For C<sub>43</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub> : 617.21.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ/ppm): δ 8.16 (d, J = 7.7 Hz, 4H), 7.71 – 7.57 (m, 4H), 7.52 – 7.37 (m, 13H), 7.31 (td, J = 7.1, 0.9 Hz, 4H), 6.78 (d, J = 8.4 Hz, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz) : 160.83, 156.27, 140.57, 139.60,

## Device preparation and measurements

To characterize the charge transport characteristics, hole-only devices (HODs) and electron-only devices (EODs) were fabricated. In the HODs, N1,N1'-(Biphenyl-4,4'-diyl)bis(N1-phenyl-N4,N4-di-m-tolylbenzene-1,4-diamine (DNTPD) was used to block electron injection. In the EODs, 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan (DBFTrz) was used to block hole injection. The device configurations for the HODs are as follows: ITO/PEDOT:PSS (60 nm)/3-CzPB or 4-CzPB (50 nm)/DNTPD (10 nm)/Al (200 nm). The device configuration for the EODs is as follows: ITO/PEDOT:PSS (60 nm)/DBFTrz (10 nm)/3-CzPB or 4-CzPB (50 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. The materials used in the blue phosphorescent OLED devices were as follows: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) worked as the hole injection layer, TAPC, 4,4',4''-Tris(carbazol-9-yl)triphenylamine (TCTA), which acted as the hole transport layer; 1,3-di(9H-carbazol-9-yl)benzene (mCP) and diphenyl(4-(triphenylsilyl)phenyl)phosphine oxide (TSPO1) served as the carrier and exciton blocking layer, 1,3,5-tris(1-phenyl-1H-benzo[d]imidazole-2-yl)benzene (TPBi) acted as the electron transport layer, and LiF/Al, which served as the electron injection layer and cathode.

The device structure of blue PhOLEDs was indium tin oxide (ITO, 50 nm)/PEDOT : PSS (40 nm)/TAPC (40 nm)/mCP (10 nm)/EML (25 nm)/TSPO1 (5 nm)/TPBi (10 nm)/LiF(1.5 nm)/Al(200 nm). The EMLs were 3-CzPB:CN-Im, 4-CzPB:CN-Im, 3-CzPB:Ir(cb)<sub>3</sub> and 4-CzPB:Ir(cb)<sub>3</sub>. The CN-Im was doped in each EML at a concentration of 15 wt% and that of Ir(cb)<sub>3</sub> was 20 wt%. The device structure of blue TADF OLEDs was indium tin oxide (ITO, 50 nm)/PEDOT : PSS (40 nm)/TAPC (5 nm)/mCP (10 nm)/EML (25 nm)/TSPO1 (25 nm)/LiF(1.5 nm)/Al(200 nm). The EMLs were 3-CzPB:p4TCzPhBN and 4-CzPB:p4TCzPhBN. The p4TCzPhBN was doped in each EML at a concentration of 20 wt%.

The device structure of blue MR TADF OLEDs was indium tin oxide (ITO, 50 nm)/PEDOT : PSS (40 nm)/TAPC (10 nm)/TCTA (5 nm)/mCP (5 nm)/EML (25 nm)/TSPO1 (25 nm)/LiF(1.5 nm)/Al(200 nm). The EMLs were 3-CzPB:t-DABNA and 4-CzPB:t-DABNA. The t-DABNA was doped in each EML at a concentration of 1, 3, 5 wt%.



## List of tables

**Table S1.** Summarized Device performances of the 3-CzPB and 4-CzPB hosted blue MR TADF OLEDs according to doping concentration of t-DABNA.

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**Figure S1.** The thermal decomposition temperature test curves of (a) 3-CzPB, (b) 4-CzPB.

**Figure S2.** The glass transition temperature test curves of (a) 3-CzPB, (b) 4-CzPB.

**Figure S3.** CV curves for the oxidation of (a) 3-CzPB, (b) 4-CzPB.

**Figure S4.** (a) Device structure and energy level diagram of Device 1, 2, 3 and 4 and (b) molecular structures used in blue PhOLEDs.

**Figure S5.** Device structure and energy level diagram of Device 5, 6 and molecular structure of blue TADF emitter.

**Figure S6.** (a) The HOMO and LUMO levels diagram and (b) chemical structures of materials used in the device.

**Figure S7.** The device data of 3-CzPB, 4-CzPB; (a) Current density–voltage–luminance curves, (b) Quantum efficiency–luminance curves, (c) Electroluminescence (EL) spectra of the blue MR TADF OLEDs 1, 3, 5 wt % doped with t-DABNA emitter at an initial luminance of  $100 \text{ cd m}^{-2}$ .

**Figure S8.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR Spectrum of 3-CzPB.

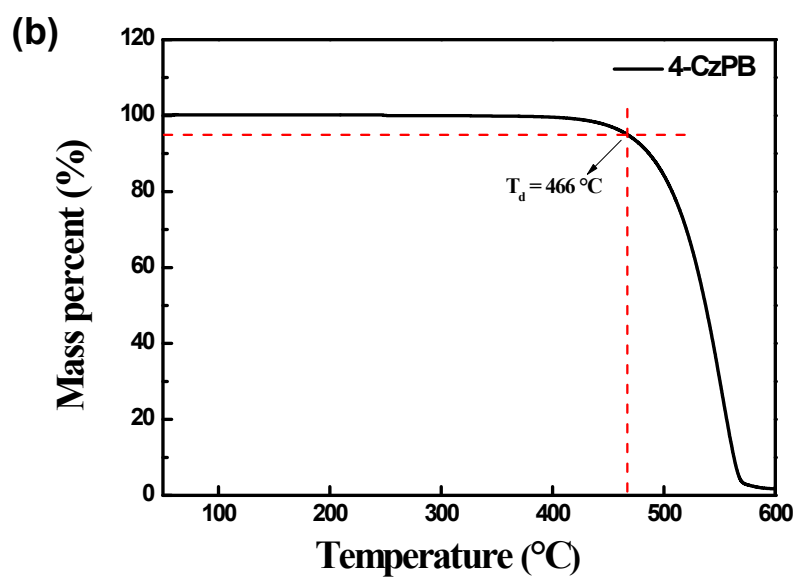
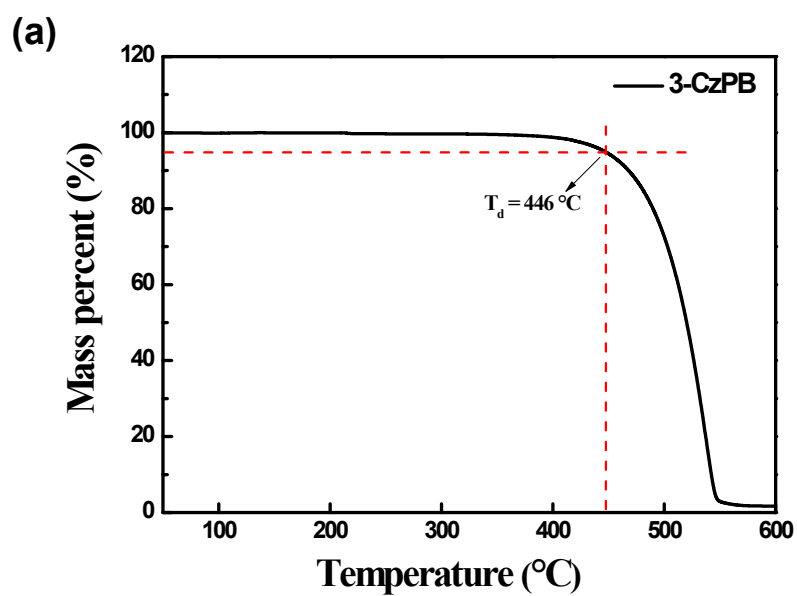
**Figure S9.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR Spectrum of 4-CzPB.

**Figure S10.** The repeated (10 cycle) CV data of the 3-CzPB(a) and 4-CzPB(b).

**Figure S11.** Changes in the PLQY of neat films of 3-CzPB and 4-CzPB in response to varying durations of UV irradiation.

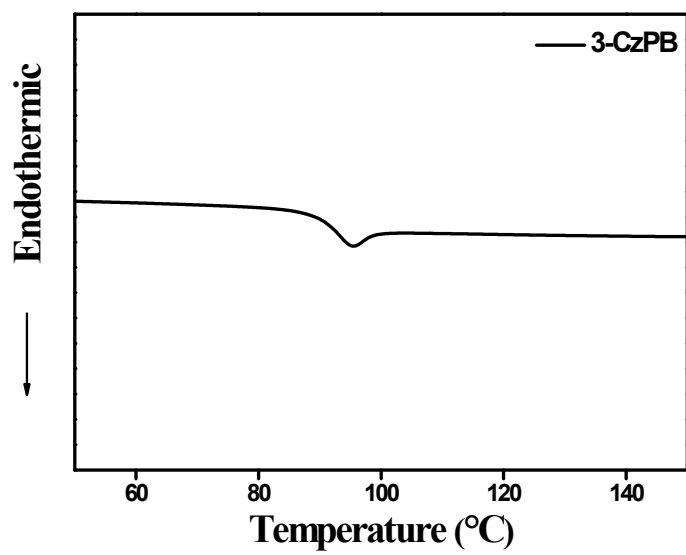
**Figure S12.** Luminance-lifetime curve of the 3-CzPB and 4-CzPB hosted OLEDs; (a)

PhOLEDs 15 wt% doped with CN-Im emitter at an initial luminance of  $1000 \text{ cd m}^{-2}$ , (b) PhOLEDs 20 wt% doped with Ir(cb)<sub>3</sub> emitter at an initial luminance of  $1000 \text{ cd m}^{-2}$ , (c) TADF OLEDs 20 wt % doped with p4tCzPhBN emitter at an initial luminance of  $1000 \text{ cd m}^{-2}$ , (d) MR TADF OLEDs 3 wt % doped with t-DABNA emitter at an initial luminance of  $100 \text{ cd m}^{-2}$ .

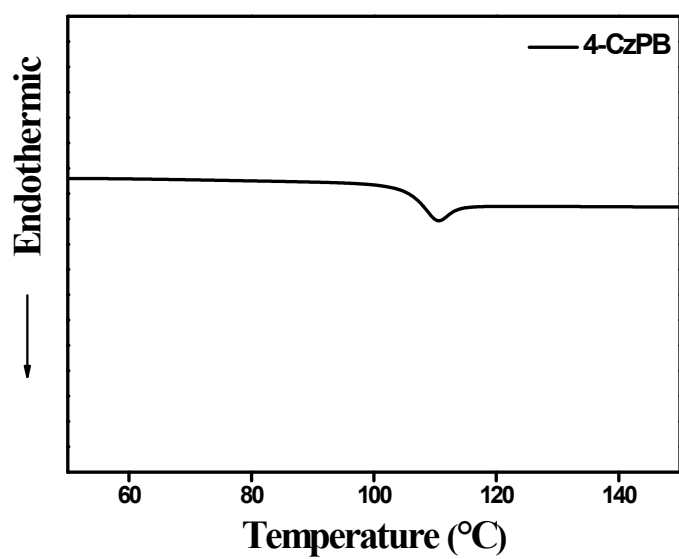


**Figure S1.** The thermal decomposition temperature test curves of (a) 3-CzPB, (b) 4-CzPB.

(a)

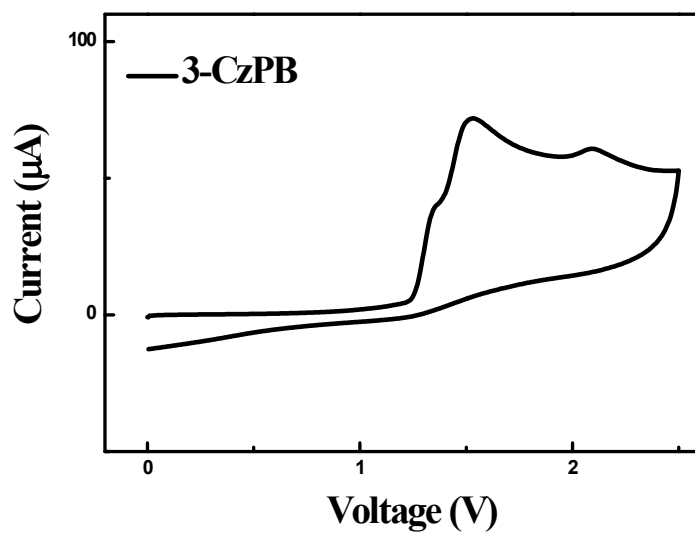


(b)

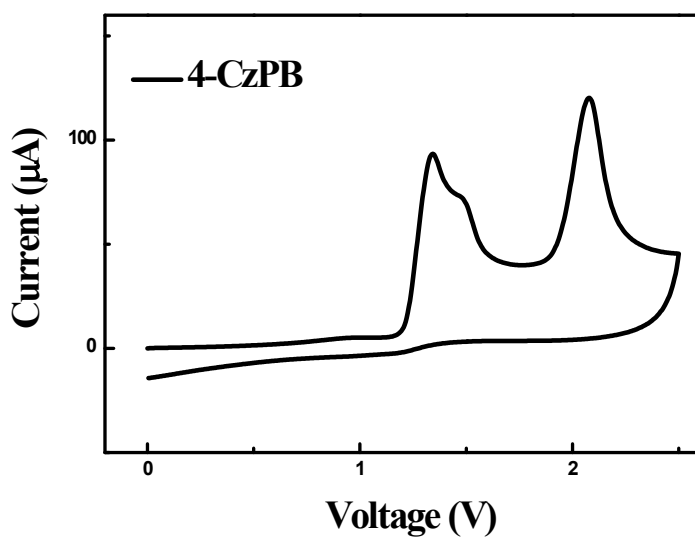


**Figure S2.** The glass transition temperature test curves of (a) 3-CzPB, (b) 4-CzPB.

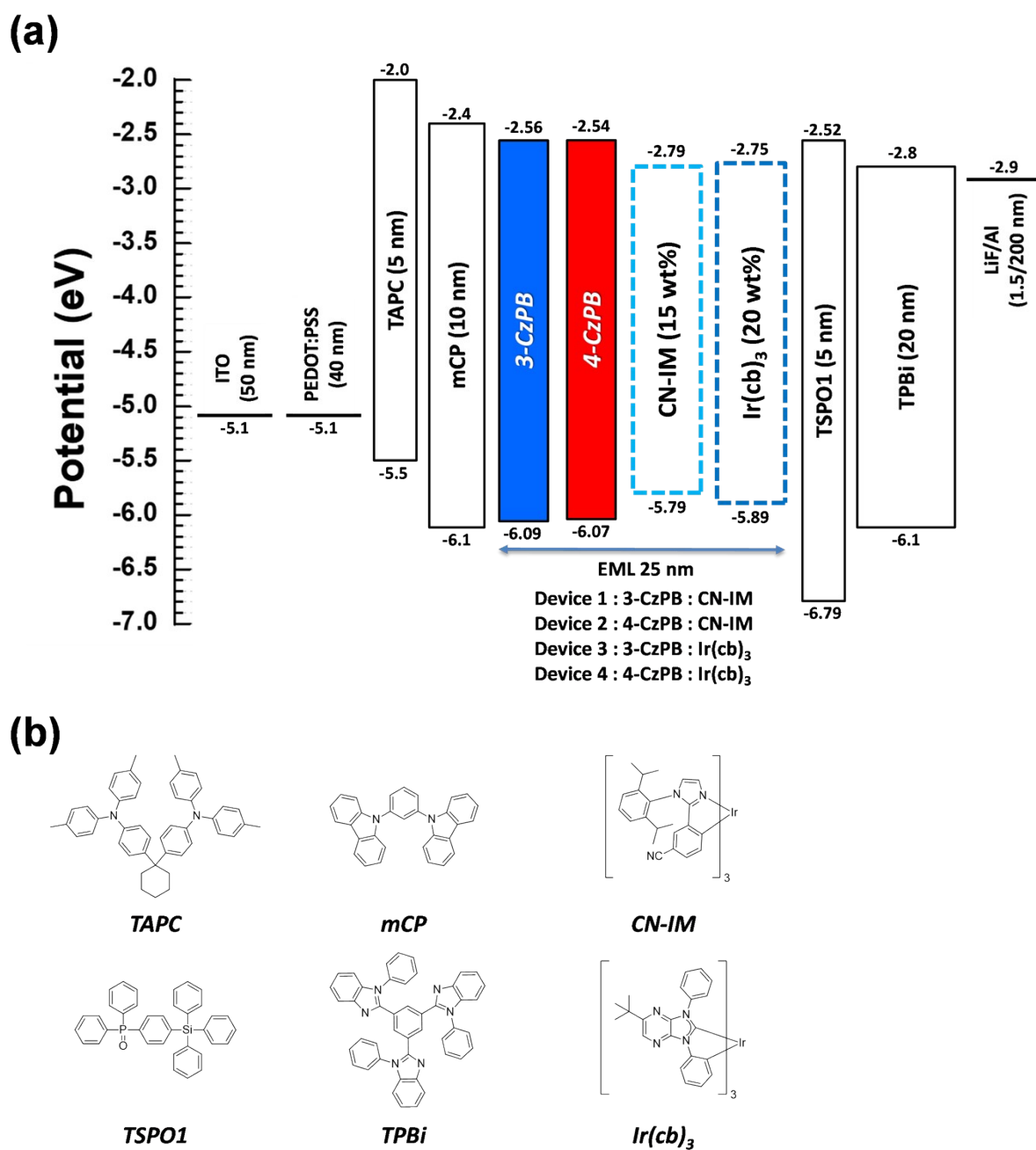
(a)



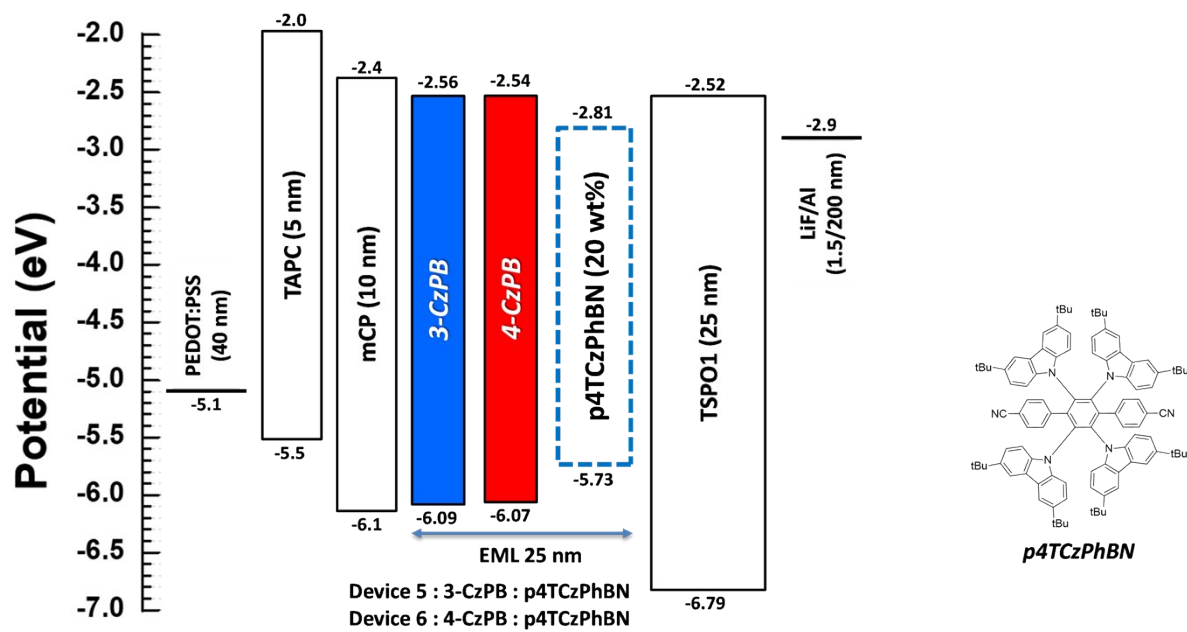
(b)



**Figure S3.** The oxidation curves of (a) 3-CzPB and (b) 4-CzPB obtained from cyclic voltammetry scanning.

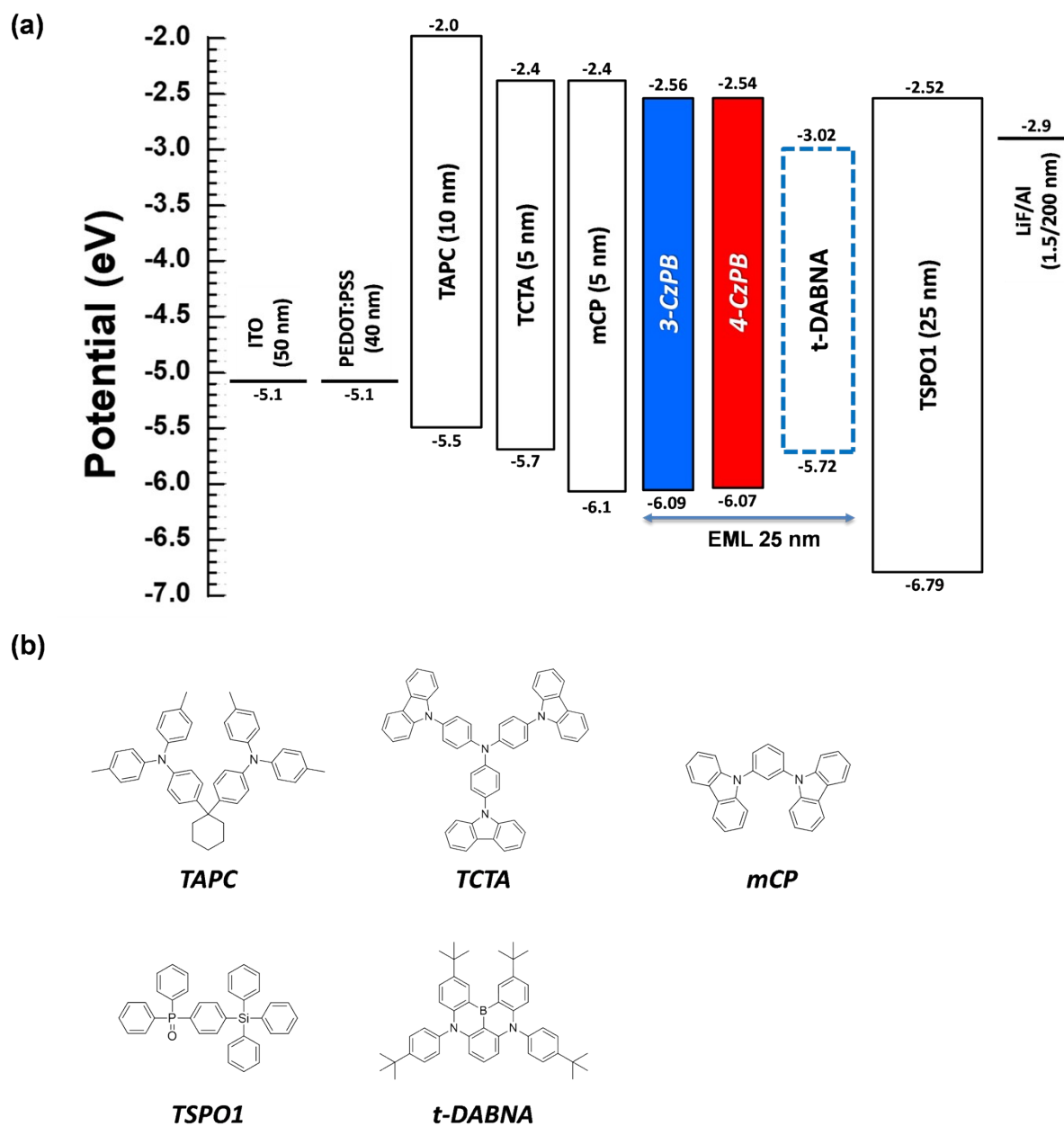


**Figure S4.** (a) Device structure and energy level diagram of Device 1, 2, 3 and 4 and (b) molecular structures used in blue PhOLEDs.



**Figure S5.** Device structure and energy level diagram of device 5 and 6, and molecular structure of blue TADF emitter.



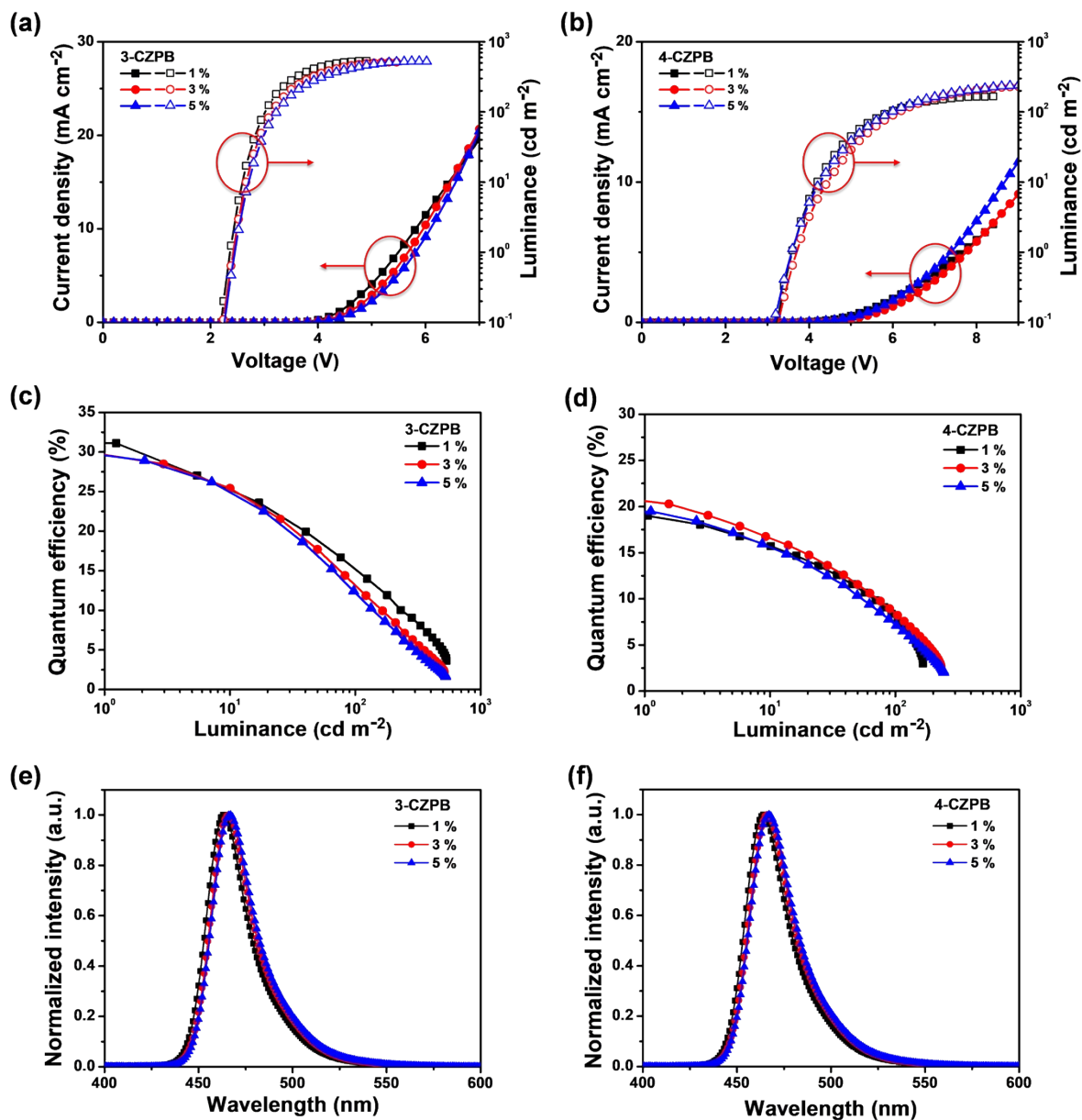


**Figure S6.** (a) The HOMO and LUMO levels diagram and (b) chemical structures of materials used in the device.

Device structure: PEDOT:PSS(40)/TAPC(10)/TCTA(5)/mCP(5)/X:t-DABNA(25:Y%)/TSPO1(25)/LiF(1.5)/Al(200)

X = 3-CzPB, 4-CZPB

Y = 1, 3, 5 wt%



**Figure S7.** The device data of 3-CzPB and 4-CzPB; (a), (b) Current density–voltage–luminance curves, (c), (d) Quantum efficiency–luminance curves, (e), (f) Electroluminescence (EL) spectra of the blue MR TADF OLEDs 1, 3, 5 wt % doped with t-DABNA emitter at an initial luminance of 100 cd m<sup>-2</sup>.

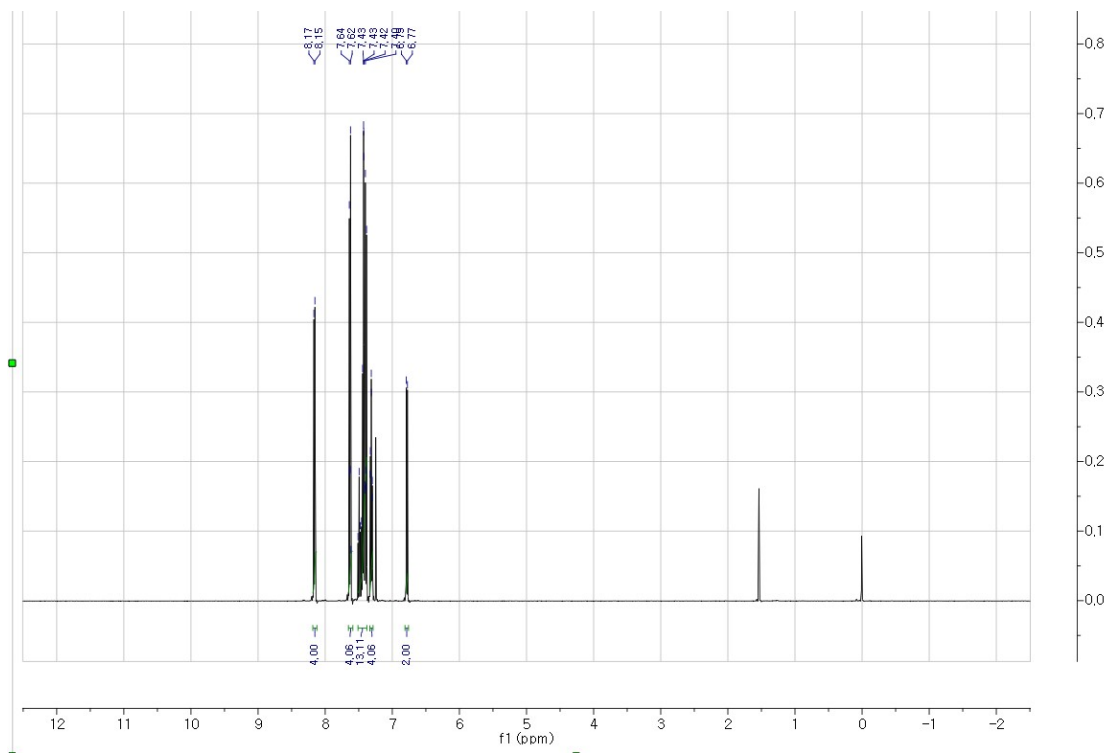
**Table S1.** Summarized Device performances of the 3-CzPB and 4-CzPB hosted blue MR TADF OLEDs according to doping concentration of t-DABNA.

Device <sup>[a]</sup>	V <sub>d</sub> <sup>[b]</sup> (V)	EQE <sup>[c]</sup> (%)		PE <sup>[d]</sup> (lm W <sup>-1</sup> )		CE <sup>[e]</sup> (cd/A <sup>-1</sup> )		CIE coordinate
		100 cd m <sup>-2</sup>	Max	100 cd m <sup>-2</sup>	Max	100 cd m <sup>-2</sup>	Max	
3-CzPB_1 %	4.5	15.4	31.1	8.8	24.4	11.9	24.9	(0.13, 0.09)
3-CzPB_3 %	4.5	13.3	30.1	8.0	25.6	11.4	26.3	(0.13, 0.10)
3-CzPB_5 %	4.6	12.2	30.3	7.5	25.4	11.0	27.5	(0.12, 0.11)
4-CzPB_1 %	6.1	8.0	19.2	3.5	14.7	6.5	15.9	(0.13, 0.09)
4-CzPB_3 %	6.1	8.4	20.9	3.8	17.1	7.5	18.8	(0.13, 0.10)
4-CzPB_5 %	6.0	7.2	19.5	3.5	17.3	6.6	18.1	(0.12, 0.11)

[a] MR TADF OLED with t-DABNA as emitter, [b] Driving voltage at 100 cd/m<sup>2</sup>, [c] External quantum efficiency, [d] Power efficiency, [e] Current efficiency.



(a)



(b)

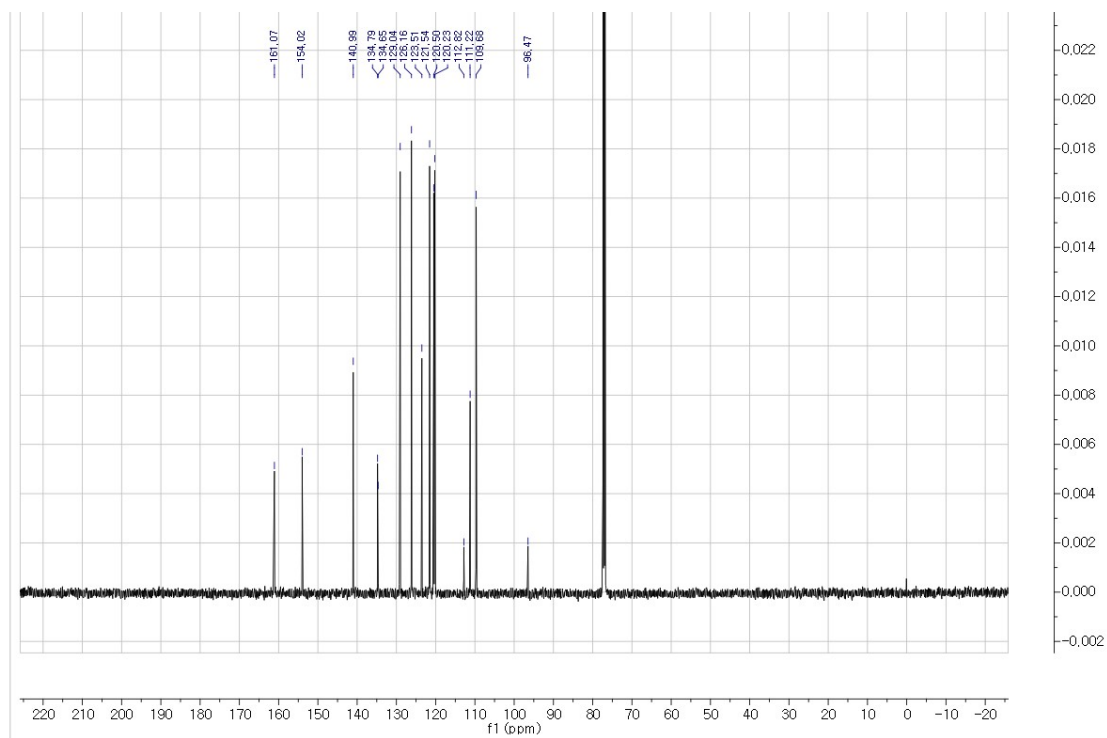


Figure S9. (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR Spectrum of 4-CzPB.

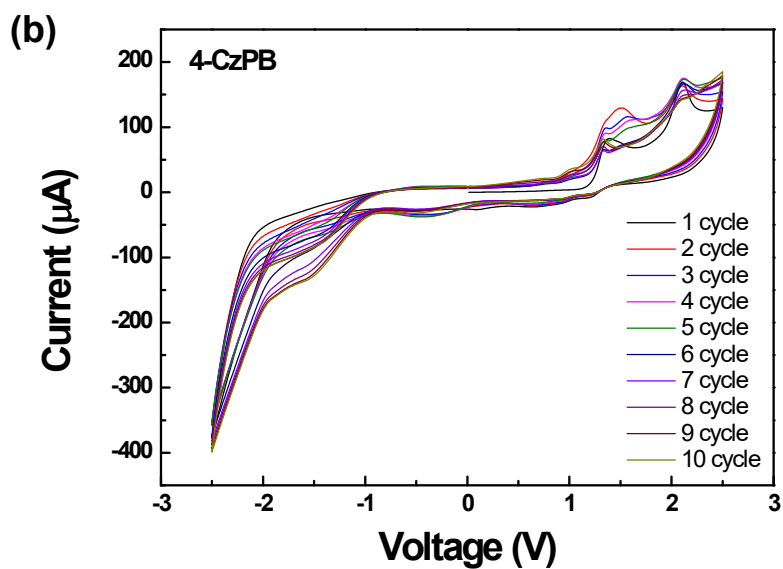
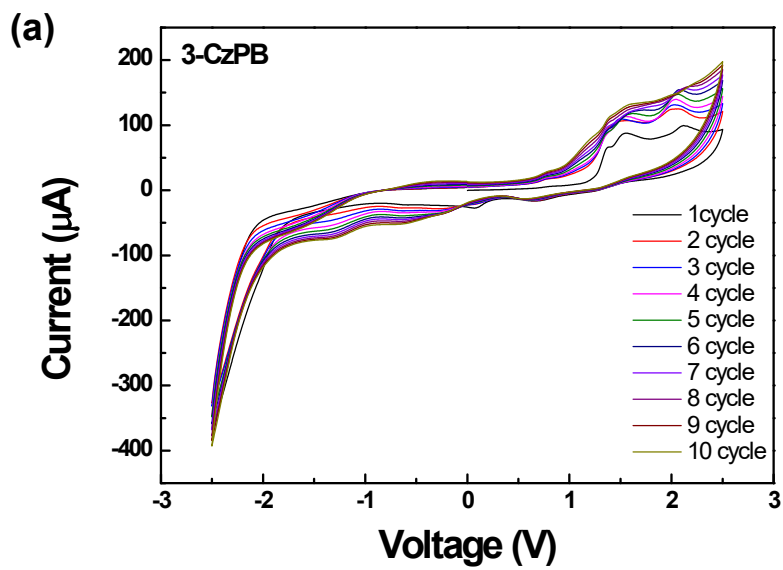


Figure S10. The repeated (10 cycle) CV data of the 3-CzPB(a) and 4-CzPB(b).

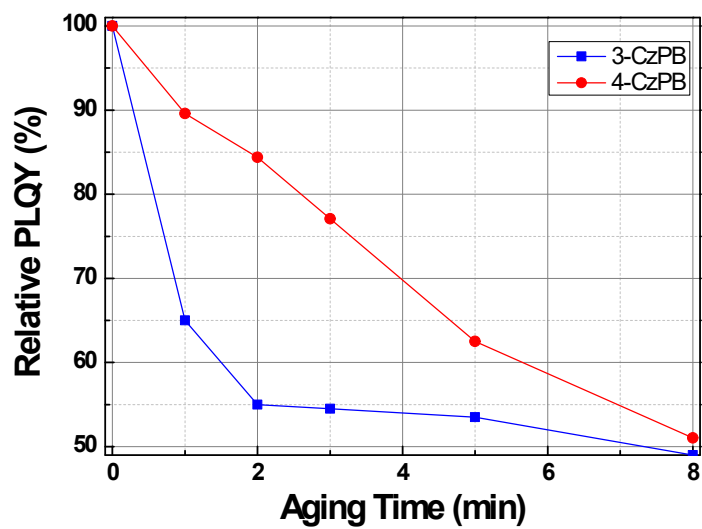
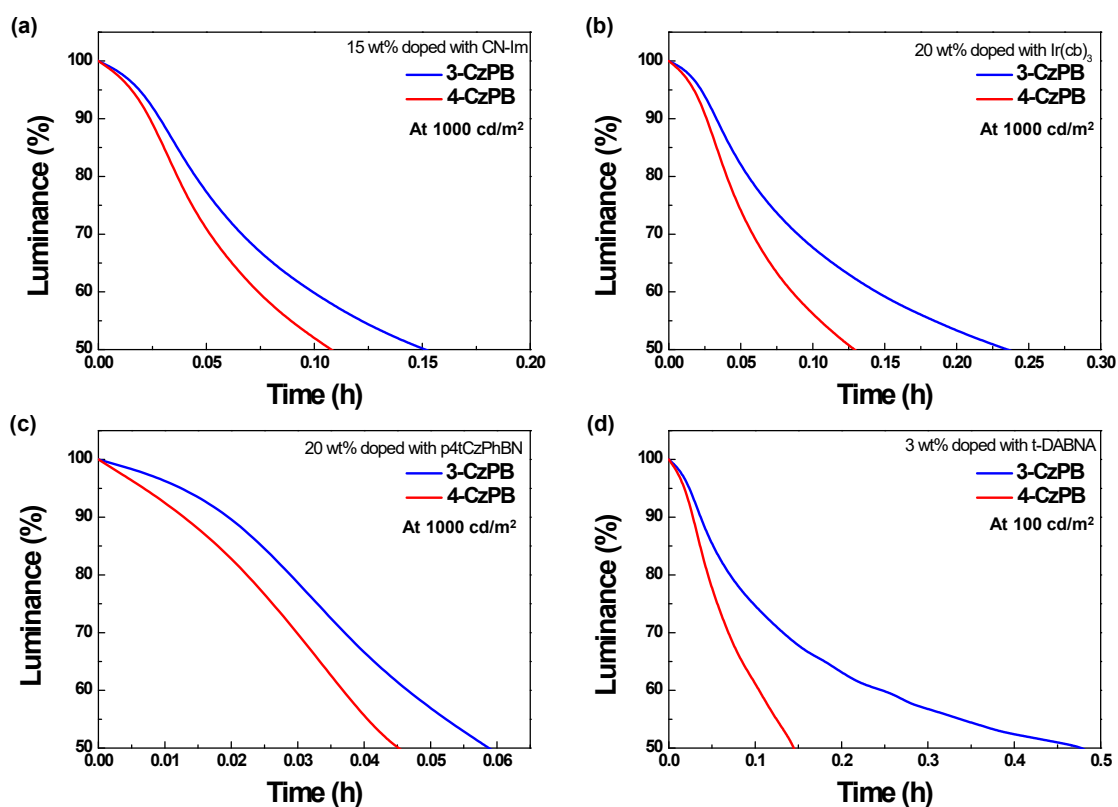


Figure S11. Changes in the PLQY of neat films of 3-CzPB and 4-CzPB according to UV irradiation time.



**Figure S12.** Luminance-lifetime curve of the 3-CzPB and 4-CzPB hosted OLEDs; (a) PhOLEDs doped with CN-Im emitter at an initial luminance of  $1000 \text{ cd m}^{-2}$ , (b) PhOLEDs doped with Ir(cb)<sub>3</sub> emitter at an initial luminance of  $1000 \text{ cd m}^{-2}$ , (c) TADF OLEDs doped with p4tCzPhBN emitter at an initial luminance of  $1000 \text{ cd m}^{-2}$ , (d) MR TADF OLEDs doped with t-DABNA emitter at an initial luminance of  $100 \text{ cd m}^{-2}$ .