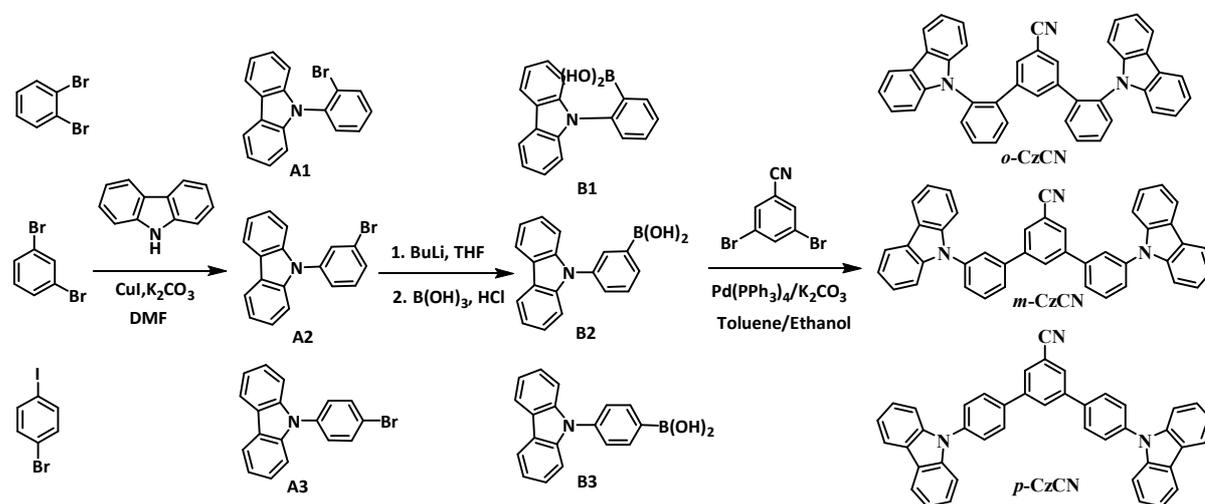## Supporting information

(1) Compound syntheses and characterization

The starting material, *3,5-dibromobenzonitrile* was purchased from J&K chemical and was used without further purification. All the arylboronic acid including (2-(9*H*-carbazol-9-yl)phenyl)boronic acid (B1), (3-(9*H*-carbazol-9-yl)phenyl)boronic acid (B2), and (3-(9*H*-carbazol-9-yl)phenyl)boronic acid (B3), and the brominated intermediates, namely 9-(2-bromophenyl)-9*H*-carbazole (A1), 9-(4-bromophenyl)-9*H*-carbazole 9-(3-bromophenyl)-9*H*-carbazole (A2) and 9-(4-bromophenyl)-9*H*-carbazole (A3) were synthesized according to the literature method.[1]

General procedure for the synthesis of target compounds o-CzCN, m-CzCN, and p-CzCN:[2] To a deoxygenated solution containing 3,5-dibromobenzonitrile (261 mg, 1 mmol), the corresponding boronic acid B1, B2, or B3 (631 mg, 2.2mmol), toluene (10 mL), ethanol (2 mL), and aqueous sodium carbonate (2 M, 2.5 mL, 5 mmol) was

added tetrakis(triphenylphosphino)palladium(0) (68 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was refluxed overnight. Upon being cooled to room temperature and diluted by water (20 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous magnesium sulfate and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography over silica using a petroleum ether/dichloromethane (2:1) as eluent, followed by recrystallization in methanol/chloroform to give a white solid of the target compound.

3,5-bis(2-(9H-carbazol-9-yl)phenyl)-1-benzonitrile (o-CzCN): Yield 45%. ^{1}H NMR (500 MHz, CDCl$_3$, δ): 8.07 (m, 4H), 7.52 (t, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.40 (t, *J* = 8.9 Hz, 2H), 7.26-7.18 (m, 8H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.78 (s, 1H), 6.69 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 141.10, 139.52, 138.60, 134.77, 132.21, 131.16, 130.06, 129.92, 129.26, 126.18, 123.22, 120.46, 120.40, 120.12, 118.03, 111.95, 109.80. TOF-EI-MS (*m/z*): 585.2215 [M]$^+$. IR ([cm^{-1}], KBr): 2234.00 ($v_{C≡N}$). Anal. calcd for C$_{43}$H$_{27}$N$_3$: C, 88.18; H, 4.65; N, 7.17; Found: C, 88.22; H, 4.60; N, 7.18.

3,5-bis(3-(9H-carbazol-9-yl)phenyl)-1-benzonitrile (m-CzCN): Yield 65%. ^{1}H NMR (500 MHz, CDCl$_3$) 8.10-8.06 (m, 4H), 7.55 (t, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.42 (t, *J* = 8.9 Hz, 2H), 7.24 (m, 8H), 6.90 (s, 3H), 6.88 (s, 2H), 6.81 (d, *J* = 8.9 Hz, 2H). 6.71 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 142.43, 140.92, 140.84, 138.91, 130.98, 130.56, 130.06, 129.98, 127.43, 126.26, 126.01, 123.66,

120.61, 120.37, 118.58, 114.13, 109.74. TOF-EI-MS (m/z): 585.2212 [M]$^{+}$. IR ([cm^{-1}], KBr): 2233.70 ($\nu_{C \equiv N}$). Anal. calcd for $C_{43}H_{27}N_3$: C, 88.18; H, 4.65; N, 7.17; Found: C, 88.15; H, 4.69; N, 7.16.

3,5-bis(4-(9H-carbazol-9-yl)phenyl)-1-benzonitrile (*p*-CzCN): Yield 66%. ^{1}H NMR (500 MHz, CDCl$_3$, δ) 8.20 (s, 1H), 8.18 (d, J = 8.1 Hz, 4H), 8.00 (s, 2H), 7.90 (d, J = 8.4 Hz, 4H), 7.75 (d, J = 8.4 Hz, 4H), 7.50 (d, J = 8.1 Hz, 4H), 7.45 (t, J = 7.4 Hz, 4H), 7.33 (t, J = 7.4 Hz, 4H). ^{13}C NMR (125 MHz, CDCl$_3$, δ) 141.20, 139.96, 137.17, 137.03, 133.33, 129.03, 127.14, 126.35, 122.87, 120.64, 120.23, 113.11, 109.67, 105.22, 101.45, 100.56, 88.84. TOF-EI-MS (m/z): 585.2211 [M]$^{+}$. IR ([cm^{-1}], KBr): 2233.07 ($\nu_{C \equiv N}$). Anal. calcd for $C_{43}H_{27}N_3$: C, 88.18; H, 4.65; N, 7.17; Found: C, 88.25; H, 4.77; N, 6.98.

References

[1] C. H. Chen, W. S. Huang, M. Y. Lai, W. C. Tsao, J. T. Lin, Y. H. Wu, T. H. Ke, L. Y. Chen, C. C. Wu, *Adv. Funct. Mater.*, **2009**, *19*, 2661.

[2] A. Suzuki, *Chem. Commun.,* **2005**, 4759.
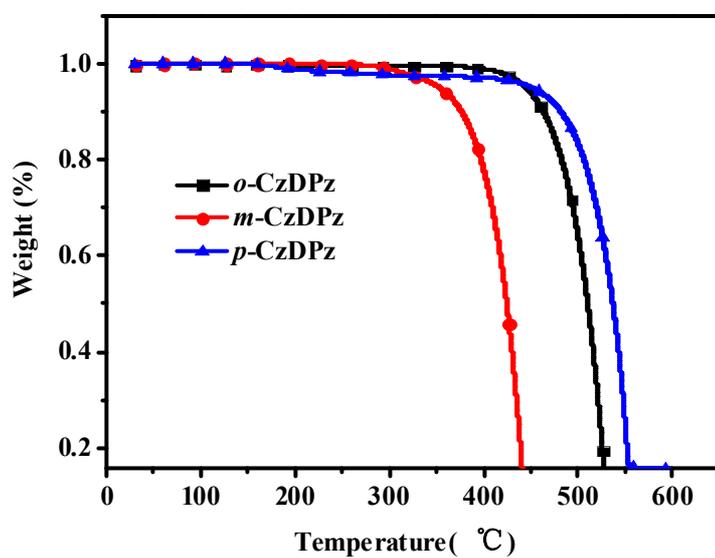
(2) Supplementary figures

Figure S1 TGA thermograms of *o*-CzCN, *m*-CzCN and *p*-CzCN, recorded at a
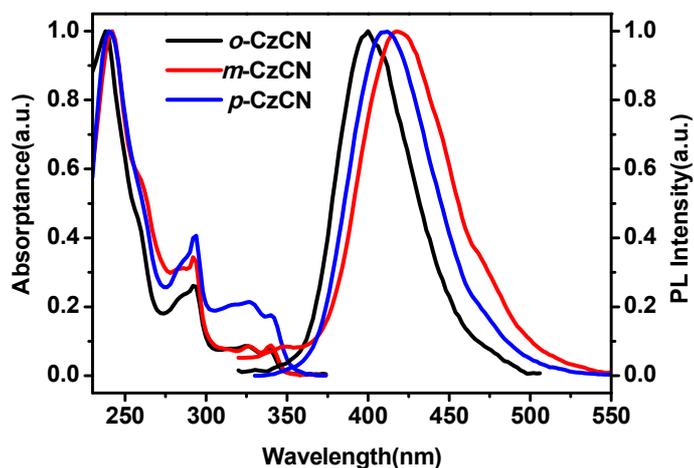
heating rate of 10 ℃ min^{-1}.

Figure S2. The UV-vis absorption and fluorescence spectra of *o*-CzCN, *m*-CzCN and

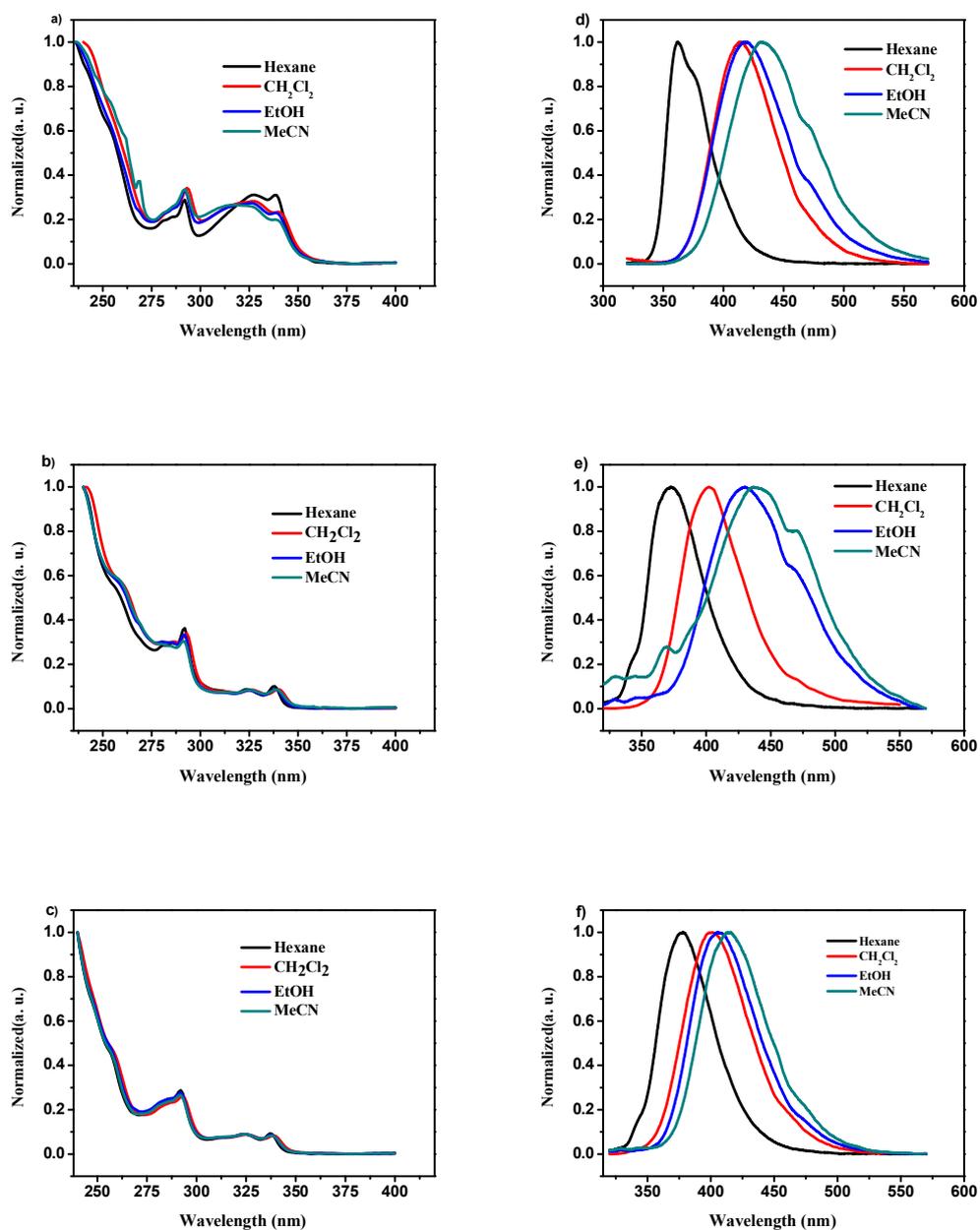*p*-CzCN in dilute CH_2Cl_2 solutions at room temperature.

Figure S3. The UV-vis absorption and fluorescence spectra of *o*-CzCN (a, b), *m*-CzCN (c, d) and *p*-CzCN (e, f) in dilute Hexane, CH₂Cl₂, EtOH and MeCN solutions at room temperature , respectively.
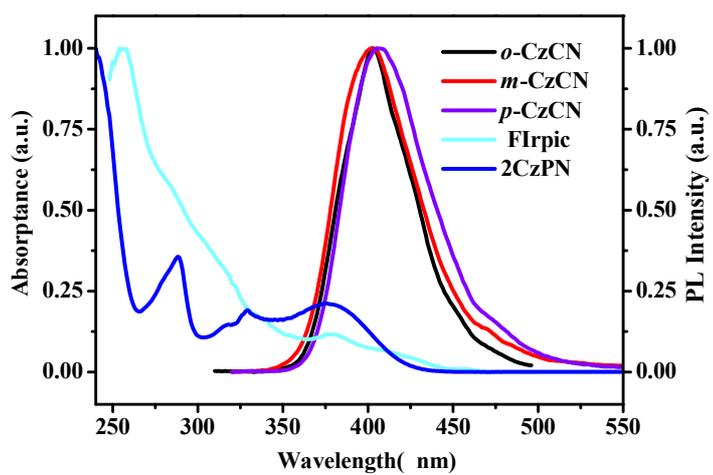
Figure S4. UV-Vis absorption spectra of 2CzPN and FIrpic and the PL spectra of *o*-CzCN, *m*-CzCN and *p*-CzCN thin films.
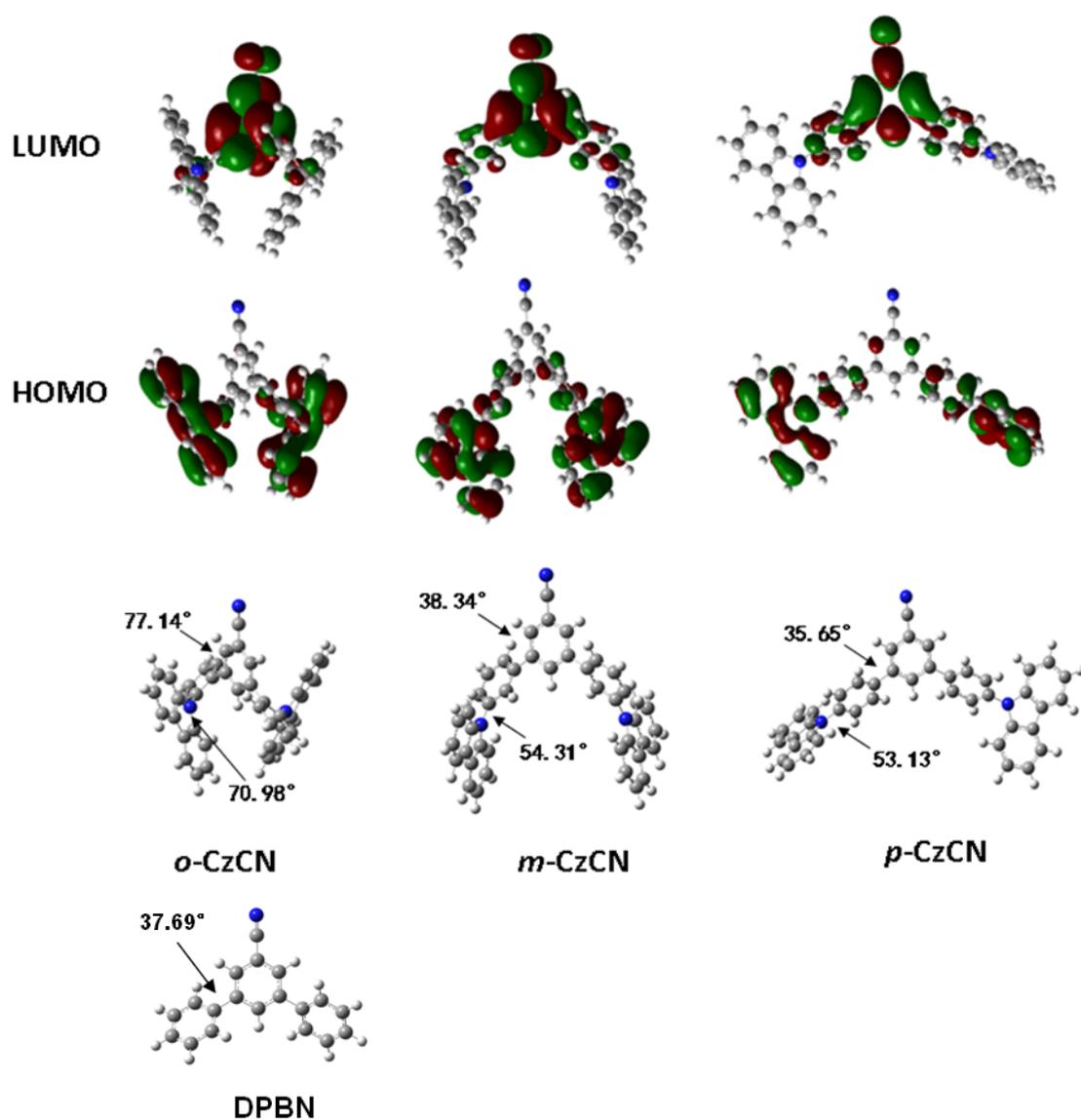
Figure S5. HOMO and LUMO distribution and optimized geometry of *o*-CzCN, *m*-CzCN and *p*-CzCN. The model compound m,m-diphenylbenzonitrile (DPBN) was also given for comparison.
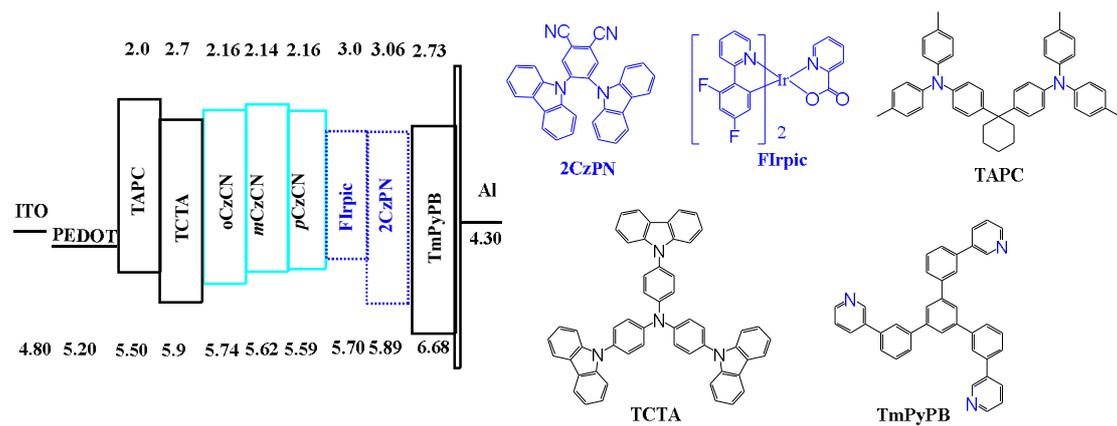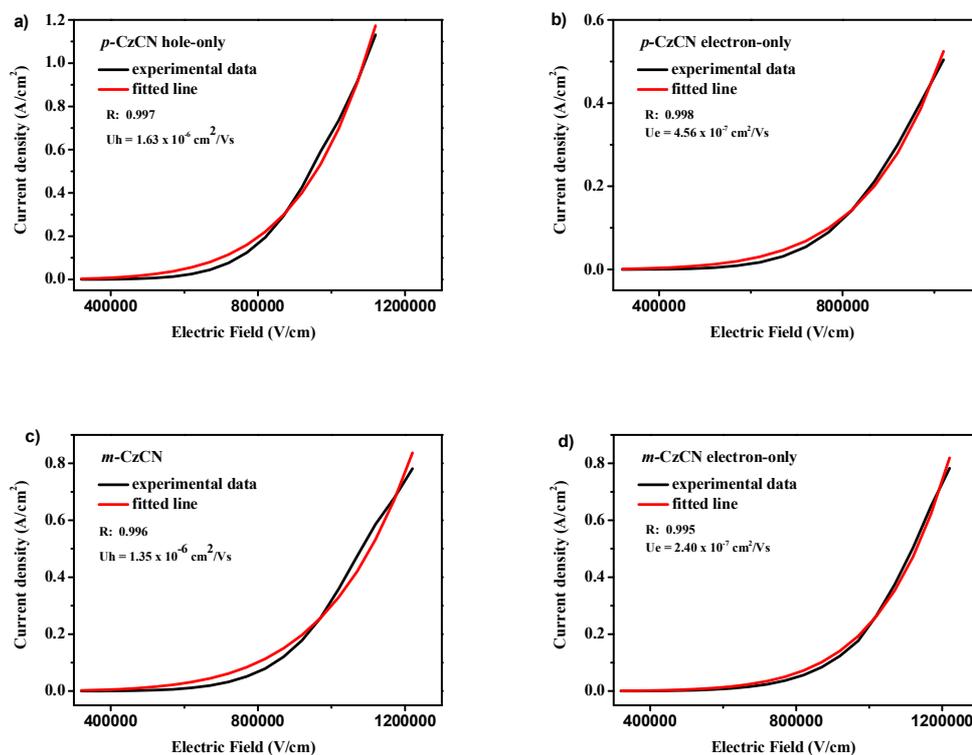
Figure S6. Energy diagram and chemical structures of materials used for fabrication of single-carrier devices and blue PhOLEDs.
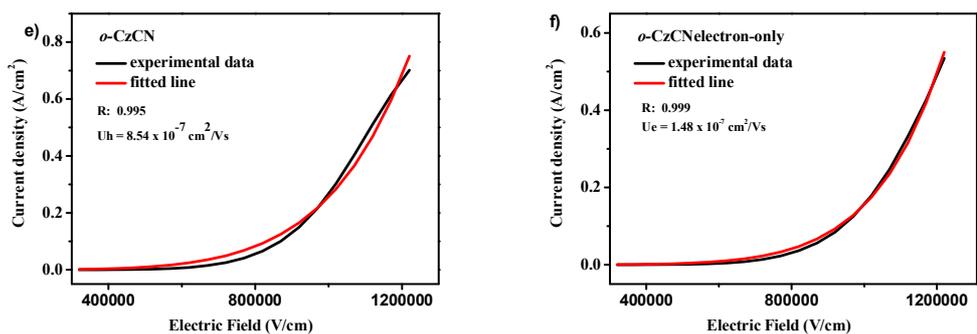
Figure S7. The measured current density-electrical field (*J-E*) characteristics for *o*-CzCN, *m*-CzCN and *p*-CzCN based hole-only (a) and electron-only (b) devices.
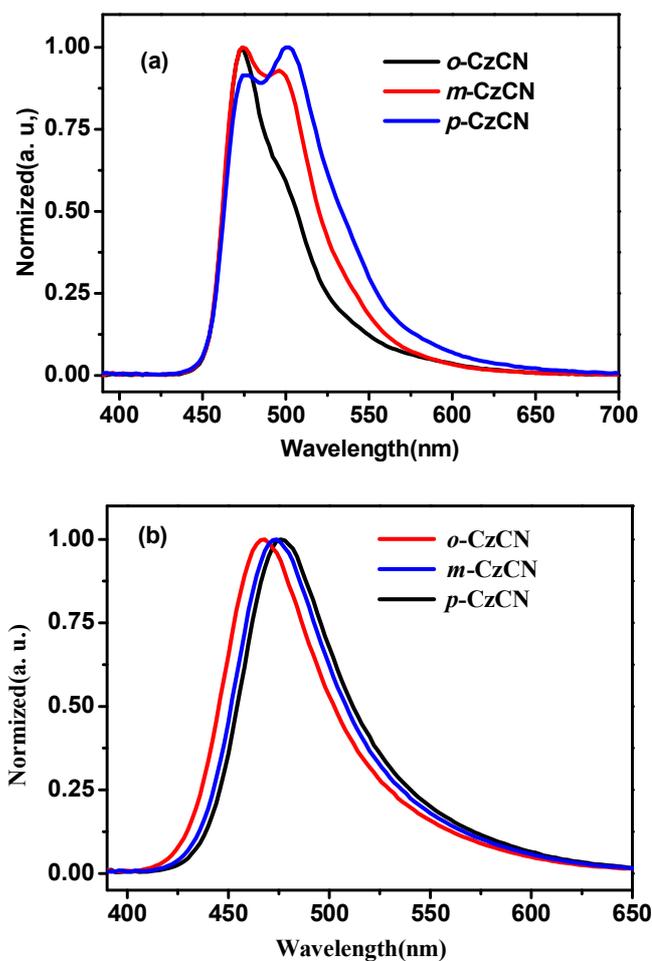

Figure S8 (a) EL spectra of the FIrpic doped devices; (b) EL spectra of the 2CzPN doped devices.
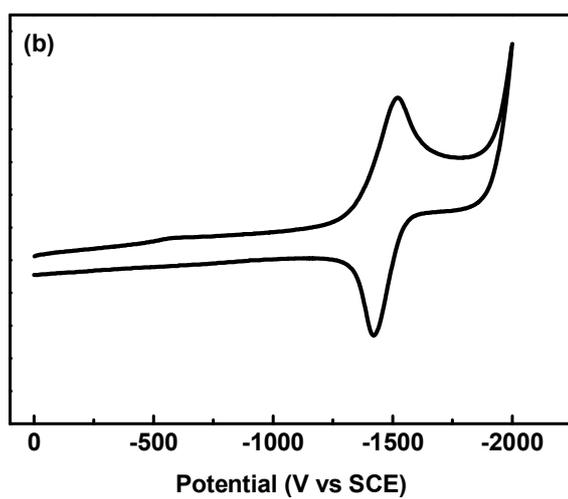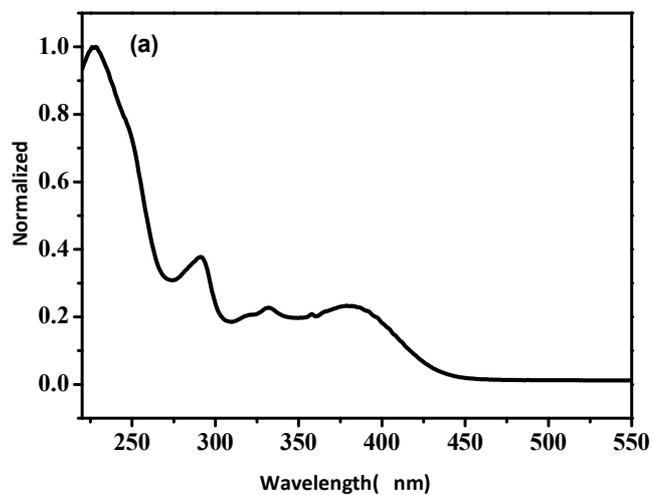
Figure S9. (a) The UV-vis absorption absorption of 2CzPN in thermally evaporated film (ca.30 nm); (b) Cyclic voltammograms of 2CzPN measured in CH_2Cl_2 at a scan rate of 100 mV s^{-1}.

Table S1 The PL quantum yields of the doped films and comparison of the calculated and experimentally obtained external quantum efficiency of the studied OLEDs.

Compound	2CzPN			FIrpic		
	Φ_{PL}[a] (%)	η_{ext}[b] (%)	η_{ext}[c] (%)	Φ_{PLQY}[a] (%)	η_{ext}[b] (%)	η_{ext}[c] (%)
o-CzCN	74.46	15.5~22.3	14.52	93.21	18.6~28.0	19.08
m-CzCN	73.7	14.7~22.1	14.98	91.83	18.4~27.5	23.14
p-CzCN	46.4	9.28~13.9	8.10	53.71	10.7~16.1	7.03

[a] Φ_{PL}: the PL quantum yield of the doped films measured by intergrating sphere under an oxygen-free condition. [b] The external quantum efficiency of the corresponding OLED calculated from the PL quantum yield using the equation of $\eta_{ext} = \eta_{int}\eta_{out} = \gamma\,\eta_r\,\Phi_{PL}\,\eta_{out}$, in which both the charge injection ratio γ and the excitation production ratio η_r are supposed as 1, the out-coupling constant η_{out} is taken as 20%~30. [c] The external quantum efficiency obtained experimentally in present study.