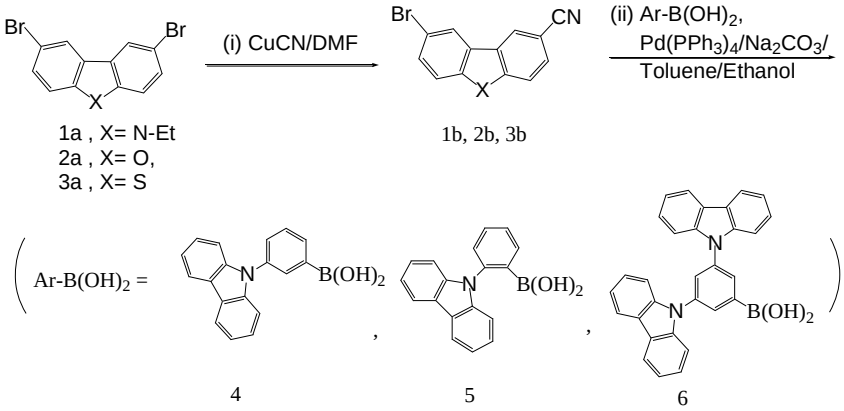
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting information

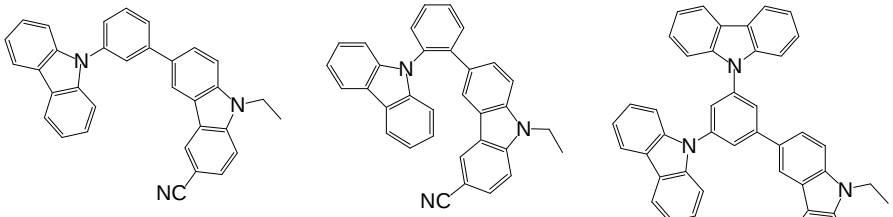
(1) Compound syntheses and characterization



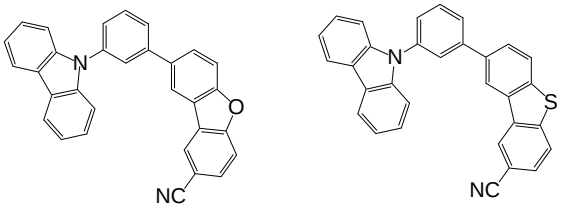
1a , X= N-Et
2a , X= O,
3a , X= S

1b, 2b, 3b

4 5 6



m-CzCzCN *o*-CzCzCN mCPCzCN



m-CzOCN *m*-CzSCN

All the arylboronic acid including (3-(9*H*-carbazol-9-yl)phenyl)boronic acid (4), (2-(9*H*-carbazol-9-yl)phenyl)boronic acid (5), and (3,5-di(9*H*-carbazol-9-yl)phenyl)boronic acid (6) were synthesized according to the literature method.[1] The bis-brominated intermediates, namely 3,6-dibromo-*N*-ethyl-carbazole (1a), 2,8-dibromodibenzo[*b*,*d*]furan (2a) and 2,8-dibromodibenzo[*b*,*d*]thiophene (3a), were also prepared according to the reported

procedure.[2] Then the cyanation products of these aromatic dibromide were obtained following the reported procedure.[3]

General procedure for the synthesis of 6-bromo-9-ethyl-9H-carbazole-3-carbonitrile (1b), *8-bromodibenzo[b,d]furan-2-carbonitrile* (2b), *and 8-bromodibenzo[b,d]thiophene-2-carbonitrile* (3b): A mixture of CuCN (1.08 g, 12 mmol) and equal molar of 3,6-dibromo-*N*-ethyl-carbazole (or 2,8-dibromodibenzo[*b*,*d*]furan or 2,8-dibromodibenzo[*b*,*d*]thiophene) in 20 mL of DMF was refluxed under a nitrogen atmosphere for 20 h. After removing the inorganic salts by filtration and the solvent by rotary evaporation, the residue was isolated by column chromatography on silica gel with petroleum ether/dichloromethane (1:3) as the eluent to give pure product.

6-bromo-9-ethyl-9H-carbazole-3-carbonitrile (1b): White solid, yield 46%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.31 (s, 1H), 8.19 (s, 1H), 7.72-7.70 (d, *J*= 8.0 Hz, 1H), 7.64-7.62 (d, *J*= 8.0 Hz, 1H), 7.45-7.42 (d, *J*= 9.0 Hz, 1H), 7.34-7.32 (d, *J*= 8.0 Hz, 1H), 4.39-4.33 (q, *J*= 8.0 Hz, 2H), 1.46-1.42 (t, *J*= 8.0 Hz, 3H). TOF-EI-MS (*m/z*): 298.0109 $[M]^+$.

8-bromodibenzo[b,d]furan-2-carbonitrile (2b): White solid, yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23 (s, 1H), 8.10 (s, 1H), 7.78-7.76 (d, *J*= 8.0 Hz, 1H), 7.67-7.66 (t, 1H), 7.65-7.64 (t, 1H), 7.51-7.49 (d, *J*= 8.0 Hz, 1H). TOF-EI-MS (*m/z*): 270.9629 $[M]^+$.

8-bromodibenzo[b,d]thiophene-2-carbonitrile (3b): White solid, yield 43%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.39 (s, 1H), 8.31 (s, 1H), 7.96-7.94 (d, *J*= 8.0 Hz, 1H), 7.76-7.74 (d, *J*= 8.0 Hz, 1H), 7.72-7.70 (d, *J*= 8.0 Hz, 1H), 7.66-7.64 (d, *J*= 8.0 Hz, 1H). TOF-EI-MS (*m/z*): 286.9392 $[M]^+$.

General procedure for the Synthesis of 6-(3-(9H-carbazol-9-yl)phenyl)-9-ethyl-9H-carbazole-3-carbonitrile (m-CzCzCN) and other final products:[4] To a deoxygenated solution of 6-bromo-9-ethyl-9*H*-carbazole-3-carbonitrile (298 mg, 1 mmol), (3-(9*H*-carbazol-9-yl)phenyl)boronic acid (316 mg, 1.1mmol), toluene (10 mL), ethanol (2 mL), and aqueous sodium carbonate (2 M, 2.5 mL, 5 mmol) was added tetrakis(triphenylphosphino)palladium(0) (34 mg, 0.03 mmol) under nitrogen atmosphere. The reaction mixture was refluxed overnight. Upon 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 (1:1) as eluent, followed by recrystallization in methanol/chloroform to give a white solid (414 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.43 (s, 1H), 8.36 (s, 1H), 8.19-8.17 (d, *J*= 8.0 Hz, 2H), 7.90 (s, 1H), 7.84-7.79 (m, 2H), 7.74-7.70 (m, 2H), 7.57-7.55 (d, *J*= 8.0 Hz, 1H), 7.54-7.51 (m, 3H), 7.47-7.42 (m, 3H), 7.33-7.29 (t, *J*= 8.0 Hz, 2H), 4.44-4.39 (q, *J*= 8.0 Hz, 2H),

1.50-1.46 (t, *J*= 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 143.37, 142.08, 140.95, 140.24, 138.36, 132.84, 130.40, 129.28, 126.61, 126.26, 126.01, 125.88, 125.45, 123.45, 123.17, 122.69, 120.47, 120.39, 120.00, 119.38, 109.85, 109.58, 109.36, 101.90, 38.09, 13.84. TOF-EI-MS (*m/z*): 461.1903 $[M]^+$. IR ([cm^{-1}], KBr): 2220.84 (ν(C≡N)). Anal.calcd for $C_{33}H_{23}N_3$: C, 85.87; H, 5.02; N, 9.10; Found: C, 85.79; H, 5.12; N, 9.13.

6-(2-(9H-carbazol-9-yl)phenyl)-9-ethyl-9H-carbazole-3-carbonitrile (o-CzCzCN): Reaction of 6-bromo-9-ethyl-9*H*-carbazole-3-carbonitrile and (2-(9*H*-carbazol-9-yl)phenyl)boronic acid following the same procedure for *m-CzCzCN* produced pure *o-CzCzCN*. White solid. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.01 (d, *J*= 8.0 Hz, 2H), 7.98 (s, 1H), 7.84 (s, 1H), 7.78-7.76 (d, *J*= 8.0 Hz, 1H), 7.65-7.63 (t, *J*= 8.0 Hz, 1H), 7.57-7.55 (t, *J*= 8.0 Hz, 1H), 7.53-7.51 (d, *J*= 8.0 Hz, 2H), 7.29-7.27 (t, *J*= 8.0 Hz, 2H), 7.18-7.12 (m, 6H), 6.93-6.91 (d, *J*= 8.0 Hz, 1H), 4.09-4.04 (q, *J*= 8.0 Hz, 2H), 1.26-1.22 (t, *J*= 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.64, 141.48, 141.42, 139.62, 134.93, 131.88, 131.02, 130.16, 129.07, 128.83, 128.59, 127.00, 125.79, 125.02, 123.05, 122.93, 121.83, 120.57, 120.07, 119.50, 109.96, 109.00, 108.70, 101.39, 37.74, 13.63. TOF-MS TOF-EI-MS (*m/z*): 461.1899 $[M]^+$. IR ([cm^{-1}], KBr): 2212.08 (ν(C≡N)). Anal.calcd for $C_{33}H_{23}N_3$: C, 85.87; H, 5.02; N, 9.10; Found: C, 85.83; H, 5.10; N, 9.13.

6-(3,5-di(9H-carbazol-9-yl)phenyl)-9-ethyl-9H-carbazole-3-carbonitrile (mCPCzCN): Reaction of 6-bromo-9-ethyl-9*H*-carbazole-3-carbonitrile and (3,5-di(9*H*-carbazol-9-yl)phenyl)boronic acid following the same procedure for

synthesis of *m-CzCzCN* produced the pure mCPCzCN. White solid. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.42 (s, 2H), 8.19-8.17 (d, *J*= 8.0 Hz, 4H), 8.03 (s, 2H), 7.89-7.87 (d, *J*= 8.0 Hz, 1H), 7.80 (s, 1H), 7.72-7.70 (d, *J*= 8.0 Hz, 1H), 7.66-7.64 (d, *J*= 8.0 Hz, 4H), 7.56-7.54 (d, *J*= 8.0 Hz, 1H), 7.49-7.44 (m, 5H), 7.35-7.31 (t, *J*= 8.0 Hz, 4H), 4.44-4.38 (q, *J*= 8.0 Hz, 2H), 1.50-1.46 (t, *J*= 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.98, 142.14, 140.68, 140.53, 139.89, 131.81, 129.44, 126.51, 126.26, 125.51, 124.49, 123.69, 123.41, 123.06, 122.81, 120.56, 120.43, 120.38, 119.48, 109.80, 109.45, 102.11, 38.14, 13.86. TOF-EI-MS (*m/z*): 626.2480 $[M]^+$. IR ($[cm^{-1}]$, KBr): 2218.40 (ν(C≡N)). Anal.calcd for $C_{45}H_{30}N_4$: C, 86.24; H, 4.82; N, 8.94; Found: C, 86.21; H, 4.86; N, 8.91.

8-(3-(9H-carbazol-9-yl)phenyl)dibenzo[b,d]furan-2-carbonitrile (m-CzOCN): Reaction of 8-bromodibenzo[b,d]furan-2-carbonitrile and (3-(9*H*-carbazol-9-yl)phenyl)boronic acid following the same procedure for synthesis of *m-CzCzCN* produced the pure *m-CzOCN*. White solid. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.30 (s, 1H), 8.21 (s, 1H), 8.18-8.16 (d, *J*= 8.0 Hz, 2H), 7.86 (s, 1H), 7.83-7.81 (d, *J*= 8.0 Hz, 1H), 7.77-7.75 (m, 3H), 7.70-7.66 (m, 2H), 7.62-7.60 (m, 1H), 7.51-7.49 (d, *J*= 8.0 Hz, 2H), 7.46-7.42 (t, *J*= 8.0 Hz, 2H), 7.31-7.29 (t, *J*= 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.47, 156.56, 142.57, 140.88, 138.47, 136.47, 131.21, 130.54, 128.20, 126.38, 126.07, 126.06, 126.03, 125.53, 125.16, 123.48, 123.32, 120.44, 120.10, 119.67, 119.10, 113.06, 112.50, 109.75, 106.86. TOF-EI-MS (*m/z*): 434.1422 $[M]^+$. IR ($[cm^{-1}]$, KBr): 2223.16 (ν(C≡N)). Anal.calcd for $C_{31}H_{18}N_2O$: C, 85.69; H, 4.18; N, 6.45; Found: C, 85.67; H, 4.21; N, 6.47.

8-(3-(9H-carbazol-9-yl)phenyl)dibenzo[b,d]thiophene-2-carbonitrile (m-CzSCN): Reaction of *8-bromodibenzo[b,d]thiophene-2-carbonitrile* and (3-(9*H*-carbazol-9-yl)phenyl)boronic acid following the same procedure for synthesis of *m-CzCzCN* produced the pure *m-CzSCN*. White solid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.48 (s, 1H), 8.40 (s, 1H), 8.18-8.16 (d, *J*= 8.0 Hz, 2H), 7.97-7.94 (q, *J*= 9.0 Hz, 2H), 7.91-7.90 (s, 1H), 7.84-7.80 (m, 2H), 7.79-7.75 (t, *J*= 8.0 Hz, 1H), 7.70-7.68 (d, *J*= 8.0 Hz, 1H), 7.63-7.61 (d, *J*= 8.0 Hz, 1H), 7.51-7.49 (d, *J*= 8.0 Hz, 2H), 7.46-7.42 (t, *J*= 8.0 Hz, 2H), 7.34-7.30 (t, *J*= 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.67, 142.44, 140.90, 139.24, 138.55, 137.75, 135.76, 134.79, 130.60, 126.23, 127.39, 126.34, 126.32, 126.07, 126.00, 125.74, 123.84, 123.50, 123.45, 120.44, 120.39, 120.11, 119.13, 109.74, 108.28. TOF-MS TOF-EI-MS (*m/z*): 450.1196 $[M]^+$. IR ([cm^{-1}], KBr): 2225.78 (ν(C≡N)). Anal.calcd for $C_{31}H_{18}N_2S$: C, 82.64; H, 4.03; N, 6.22; Found: C, 82.61; H, 4.09; N, 6.20.

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 S. Zhang, R. Chen, J. Yin, F. Liu, H. Jiang, N. Shi, Z. An, C. Ma, B. Liu, W. Huang, *Org. Lett*., 2010, **12**, 3438.

3 G. P. Ellis, T. M. Romney-Alexander, *Chem. Rev*., 1987, **87**, 779.

4 A. Suzuki, *Chem. Commun*., 2005, 4759.

(2) Supplementary figures and tables

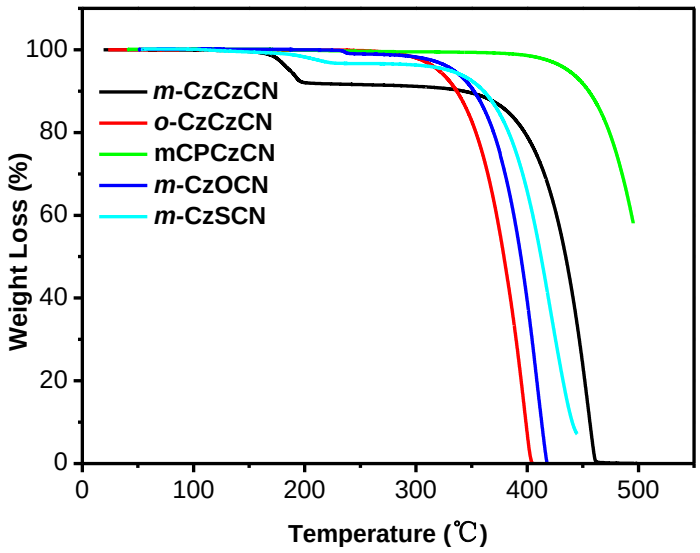
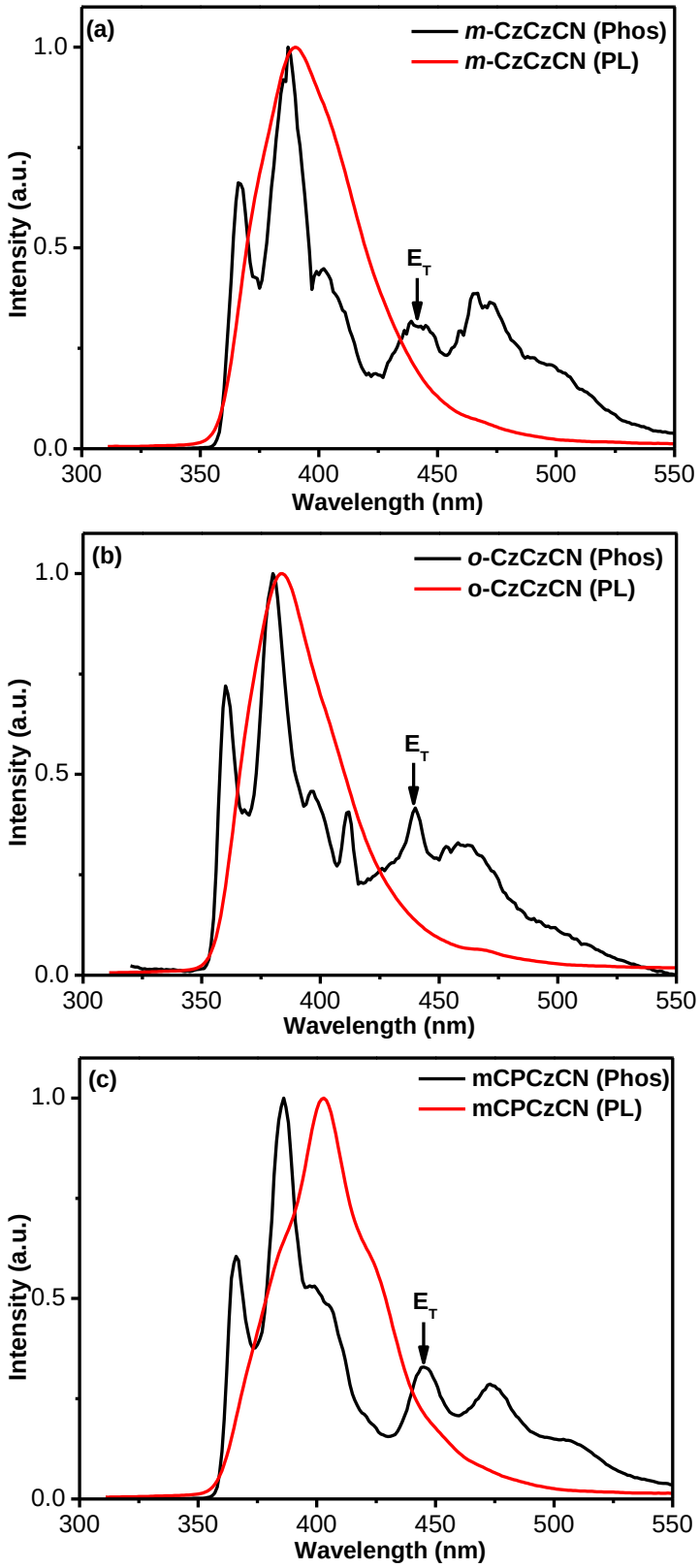


Figure S1. TGA thermograms of *m*-CzCzCN, *o*-CzCzCN, mCPCzCN, *m*-CzOCN, *m*-CzSCN recorded at a heating rate of 10 ℃ min^{-1}.



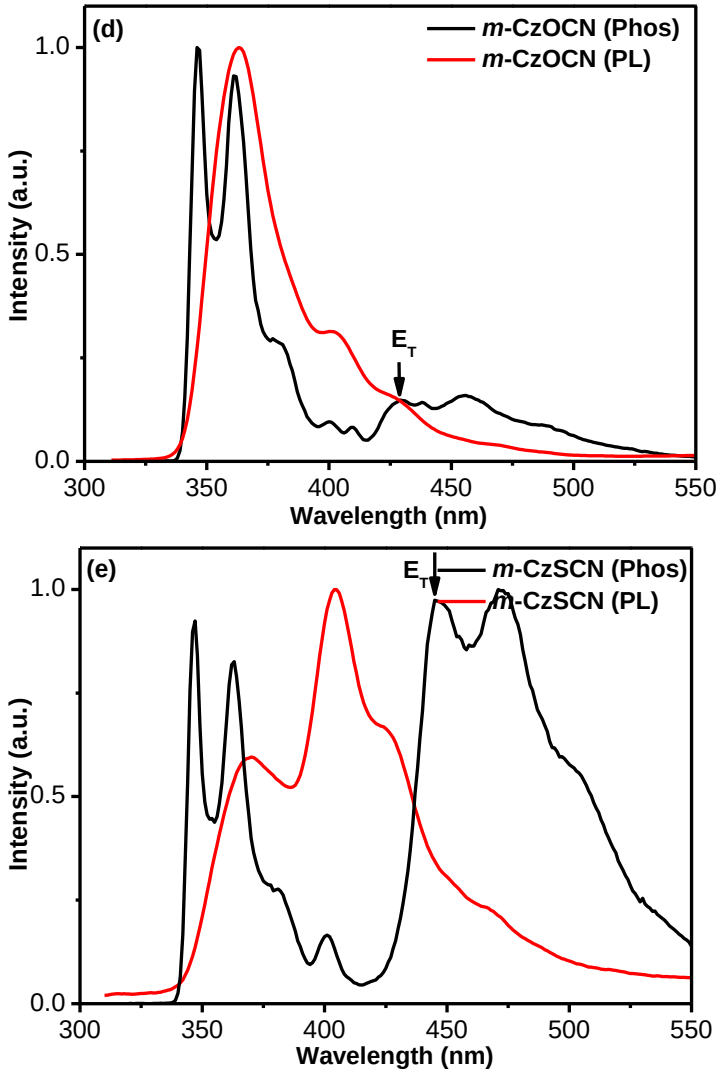


Figure S2. The phosphorescence spectra (black line, recorded in 2-MeTHF at 77K) and the PL spectra (red line, in CH_2Cl_2 at room temperature) of *m*-CzCzCN, *o*-CzCzCN, mCPCzCN, *m*-CzOCN and *m*-CzSCN.

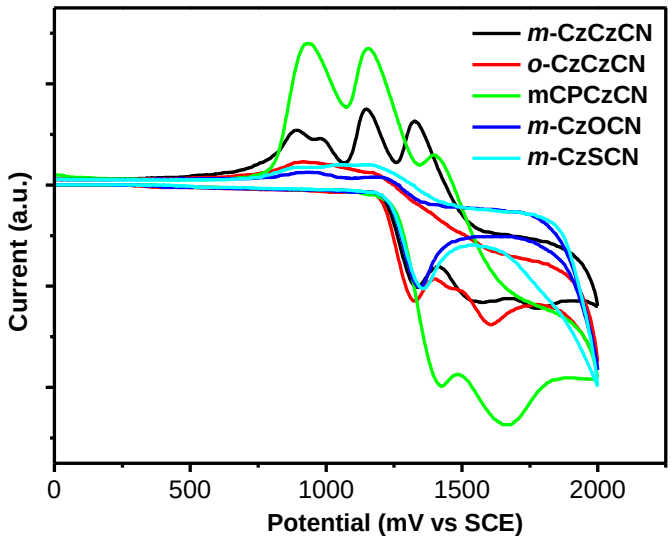


Figure S3. Cyclic voltammograms of *m*-CzCzCN, *o*-CzCzCN, mCPCzCN, *m*-CzOCN and *m*-CzSCN measured in CH_2Cl_2 at a scan rate of 100 mV s^{-1}.

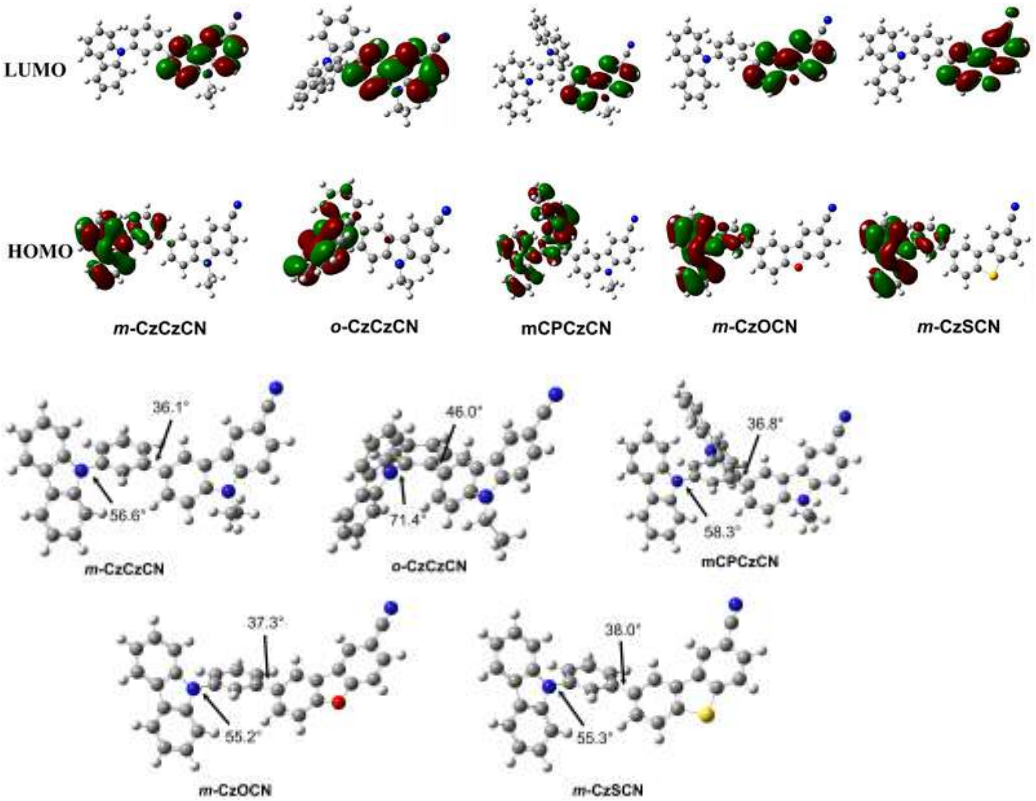


Fig. S4 HOMO and LUMO distributions and geometry optimized strucutres of *m*-CzCzCN, *o*-CzCzCN, mCPCzCN, *m*-CzOCN and *m*-CzSCN. The torsion angles are indicated in the figure.

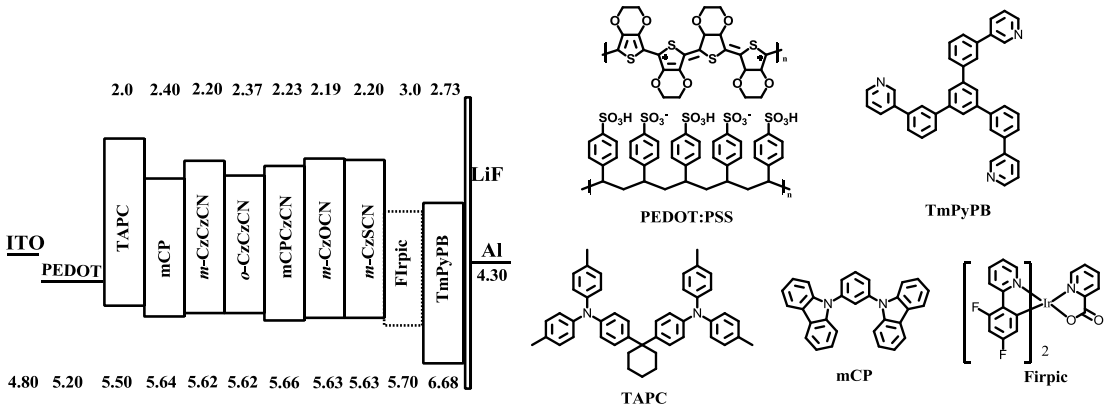


Fig. S5 Energy diagram and chemical structures of materials used for fabrication of single-carrier devices and blue PhOLEDs.

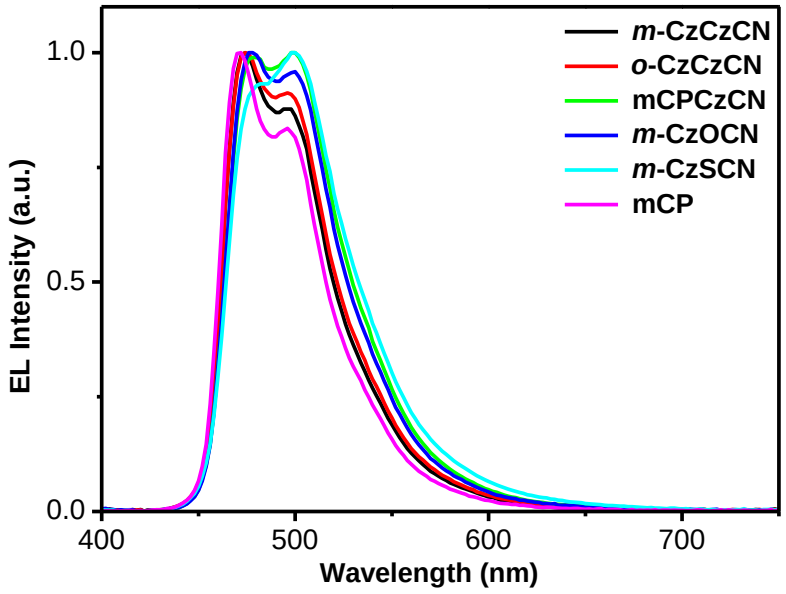


Fig. S6 EL spectra of the blue devices A-F.

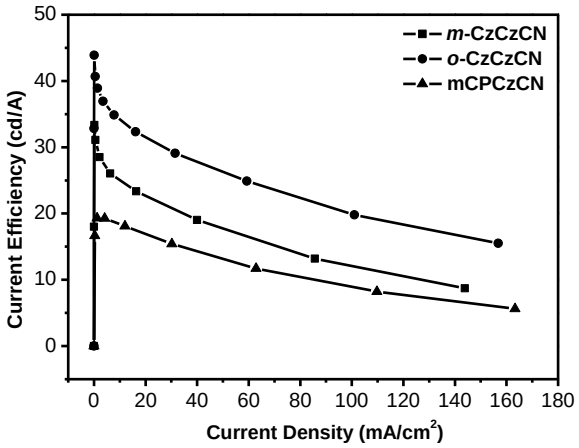


Fig. S7 Current efficiency-Current density characteristics for devices A (*m*-CzCzCN), B (*o*-CzCzCN), and C (mCPCzCN).

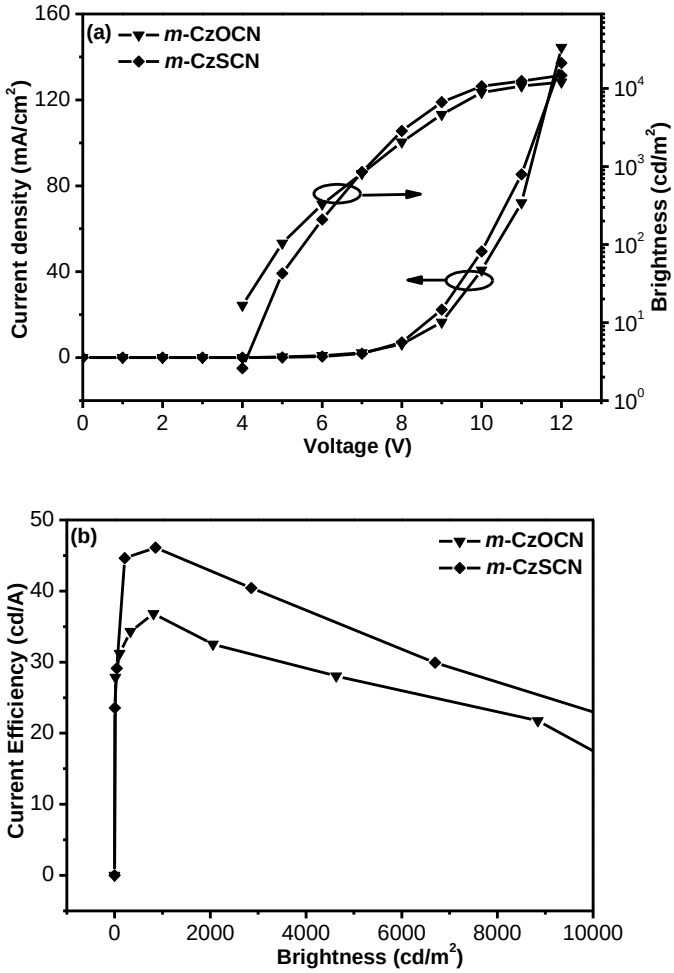


Fig. S8 a) Current density-voltage-Brightness and b) Current efficiency-Brightness characteristic for devices D (*m*-CzOCN) and E (*m*-CzSCN).

Table S1. Physical data of *m*-CzCzCN, *o*-CzCzCN, mCPCzCN, *m*-CzOCN and *m*-CzSCN.

Compound	λ_{abs} [a] [nm]	λ_{em} [a] [nm]	E_g [b] [eV]	E_T [c] [eV]	HOMO/LUMO [eV]	T_g [℃]	T_d [d] [℃]
m-CzCzCN	289, 340	390	3.42	2.82	-5.62/ -2.20	NA [e]	186
o-CzCzCN	286, 340	384	3.25	2.82	-5.62/ -2.37	104	320
mCPCzCN	292, 340	402	3.43	2.78	-5.66/ -2.23	167	437
m-CzOCN	293, 340	363	3.44	2.89	-5.63/ -2.19	98	334
m-CzSCN	290, 340	404	3.43	2.78	-5.63/ -2.20	111	330

[a] Measured in CH_2Cl_2; [b] The optical band gap, calculated by the absorption edge technique; [c] Measured in 2-MeTHF at 77K; [d] Decomposition temperature corresponds to a weight loss of 5%. [e] NA = not obtained.