

Electronic Supplementary Information (ESI)

Design of encapsulated dendrimers for highly efficient blue and green thermally activated delayed fluorescence OLEDs based on solution-process

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General information

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. The manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere. ¹H and ¹³C HMR spectra were recorded on a BRUKER AMX instrument. Elemental analysis was determined by an Elementar Vario EL CHN elemental analyzer. Molecular masses were measured by a BRUKER DALTONICS Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The UV-Vis absorption spectra of the compounds were measured by SHIMADZU UV-2450. The photoluminescence emission spectra were recorded on HORIBA FLUOROMAX-4. The PL quantum efficiency was measured with an integrating sphere under an excitation wavelength of 350 nm. As for the investigation of oxygen quenching effect, the integrating sphere was purged with flowing nitrogen during the whole measuring process. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) curves were recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) and DSC 2910 modulated calorimeter under a dry nitrogen gas flow at a heating rate of 10 °C min⁻¹. Cyclic voltammetry (CV) was performed on a CHI750C voltammetric analyzer in a typical three-electrode cell with a platinum plate working electrode, a platinum wire counter electrode and a silver wire reference electrode.

Computational method

All the calculations were performed with the Gaussian 09 program package. The geometry optimization of ground states for the dendrimers was simulated with density functional theory (DFT) at the B3LYP/6-31g(d) levels. The calculated lowest optical transitions were performed with the time-dependent density functional theory (TD-DFT) method.

Device Fabrication and Measurements

ITO-coated glass substrates were rinsed in deionized water and then ultrasonicated sequentially in acetone and ethanol. Before device fabrication, the ITO substrate was treated in a UV-ozone oven for 20 min. Then 40 nm PEDOT:PSS was spin-coated onto the ITO substrate and dried at 200 °C for 10 min. The substrates were then taken into a nitrogen glove box, where the 60 nm emission layer was spin coated onto the PEDOT:PSS layer from chlorobenzene and annealed at 100 °C for 30 min. After that, 40 nm TPBI was vacuum-deposited as the electron transporting layer. Finally, Cs₂CO₃ (2 nm) and Al (100 nm) were deposited as the cathode for the three devices. The EL spectra, device luminance, and current density-voltage characteristics were recorded using a combination of a Photo-Research PR-655 SpectraScan and a Keithley 2400 Sourcemeter. The device was tested in the condition of the atmosphere with no protective encapsulation.

Materials

Unless otherwise indicated, all materials and solvents were obtained from commercial suppliers and used without further purification. 2,4,6-trifluorobenzonitrile and 2,3,5,6-tetrafluorobenzonitrile were purchased from Energy Chemical. 4-(6-(9H-carbazol-9-yl)hexyloxy)-9H-carbazole (Cz-Cz) were prepared according to the literature.

(2R)-2,4,6-tris(4-(6-(9H-carbazol-9-yl)hexyloxy)-9H-carbazol-9-yl)benzonitrile (Cz-3CzCN)

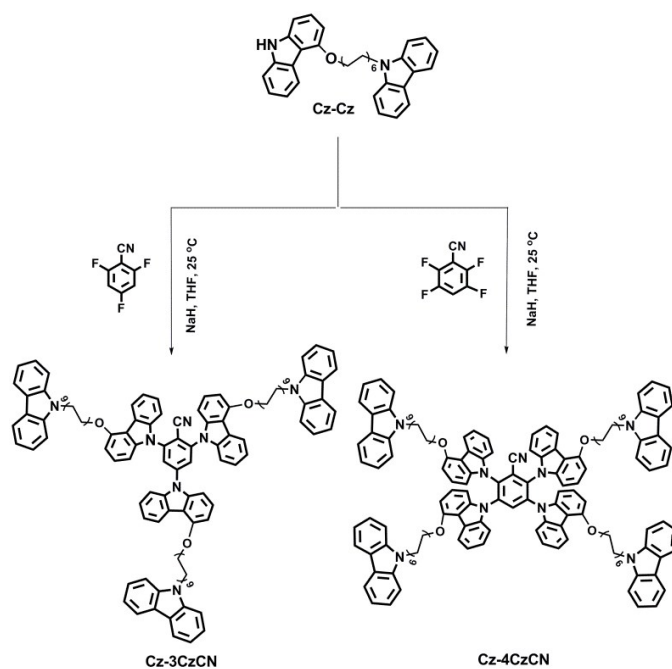
Under nitrogen atmosphere, Cz-Cz (1.8 g, 4 mmol) in anhydrous THF (40 ml) was added dropwise into an anhydrous THF (20 ml) solution containing NaH (0.60 g, 5 mmol) for 15 min and stirred for 3 h. Then, 2,4,6-trifluorobenzonitrile (0.16 g, 1 mmol) in anhydrous THF (20 ml) was added dropwise for 15 min. The solution was stirred for 24h at room temperature. After that, 250 mL water was added into the solution and the mixture was extracted with CH₂Cl₂ for three times. The combine organic layer was dried with anhydrous MgSO₄ and the solvent was removed

under vacuum. The precipitate was purified by column chromatography on silica gel, resulted in the bright green product (1.19 g, 88%). ¹H NMR (400 MHz, CDCl₃, δ): 8.39 (d, J = 7.7 Hz, 2H), 8.34 (d, J = 7.8 Hz, 1H), 8.13 – 8.05 (m, 6H), 8.01 (s, 2H), 7.59 (d, J = 8.2 Hz, 1H), 7.54 – 7.27 (m, 22H), 7.21 (dd, J = 12.0, 6.3 Hz, 8H), 7.09 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 6.73 (d, J = 8.1 Hz, 1H), 4.34 (dt, J = 10.5, 7.1 Hz, 6H), 4.21 (dt, J = 16.2, 6.3 Hz, 6H), 1.97 (tt, J = 9.5, 4.9 Hz, 12H), 1.75 – 1.61 (m, 6H), 1.60 – 1.53 (m, 6H). ¹³C NMR (125 MHz, CDCl₃, δ): 155.89, 155.84, 144.42, 144.27, 141.87, 140.73, 140.44, 140.41, 140.34, 139.76, 138.57, 127.58, 127.48, 127.46, 125.82, 125.72, 125.62, 125.60, 124.01, 123.80, 123.62, 122.84, 121.95, 121.54, 120.36, 120.34, 118.74, 113.71, 113.56, 112.98, 110.29, 109.06, 108.96, 108.65, 108.59, 103.57, 103.20, 102.33, 102.16, 68.01, 67.96, 42.97, 42.93, 29.31, 29.22, 29.01, 28.98, 27.11, 27.07, 26.16, 26.11. MS (MALDI-TOF) [m/z]: calcd for C₉₇H₈₃N₇O₃, 1393.6; found, 1393.6. Anal. Calcd. for C₉₇H₈₃N₇O₃: C, 83.53; H, 6.00; N, 7.03. Found: C, 83.50; H, 6.03; N, 6.69.

(2R,3R,5S,6S)-2,3,5,6-tetrakis(4-(6-(9H-carbazol-9-yl)hexyloxy)-9H-carbazol-9-yl)benzotrile (Cz-4CzCN)

Under nitrogen atmosphere, Cz-Cz (2.2 g, 5 mmol) in anhydrous THF (40 ml) was added dropwise into an anhydrous THF (20 ml) solution containing NaH (0.67 g, 6 mmol) for 15 min and stirred for 3 h. Then, 2,3,5,6-tetrafluorobenzotrile (0.18 g, 1 mmol) in anhydrous THF (20 ml) was added dropwise for 15 min. The solution was stirred for 24h at room temperature. After that, 250 mL water was added into the solution and the mixture was extracted with CH₂Cl₂ for three times. The combine organic layer was dried with anhydrous MgSO₄ and the solvent was removed under vacuum. The precipitate was purified by column chromatography on silica gel, resulted in the bright yellow product (1.55 g, 82%). ¹H NMR (600 MHz, CDCl₃, δ): 8.27 (s, 1H), 8.07 (t, J = 8.1 Hz, 8H), 8.05 – 7.98 (m, 4H), 7.44 – 7.27 (m, 20H), 7.21 – 7.17 (m, 10H), 7.16 – 6.90 (m, 14H), 6.51 (qd, J = 17.2, 8.8 Hz, 4H), 4.27 (t, J = 8.4 Hz, 8H), 4.04 – 3.95 (t, J = 7.2 Hz, 8H), 1.91 – 1.84 (m, 8H), 1.82 – 1.77 (m, 8H), 1.57 – 1.49 (m, 8H), 1.48 – 1.38 (m, 8H). ¹³C NMR (75 MHz, DMSO, δ): 155.89, 155.84, 144.42, 144.27, 141.87, 140.73, 140.44, 140.41, 139.76, 138.57, 137.45, 136.23, 135.78, 127.58, 127.46, 125.82, 125.72, 125.62, 125.60, 124.01, 123.79, 123.62, 122.84, 121.95, 121.54, 120.34, 118.74, 113.71, 113.56, 112.98, 110.29, 109.06, 108.96, 108.65, 108.59, 103.57, 103.20, 102.33, 102.16, 67.96, 67.73, 42.97, 42.93, 42.80, 29.31, 29.22,

29.01, 28.98, 27.11, 27.07, 26.16, 26.11, 25.93, 25.75. MS (MALDI-TOF) [m/z]: calcd for $C_{127}H_{109}N_9O_4$, 1823.8; found, 1823.8. Anal. Calcd. for $C_{127}H_{109}N_9O_4$: C, 83.57; H, 6.02; N, 6.91. Found: C, 83.55; H, 6.06; N, 6.87.



Scheme S1. Synthetic route of Cz-3CzCN and Cz-4CzCN.

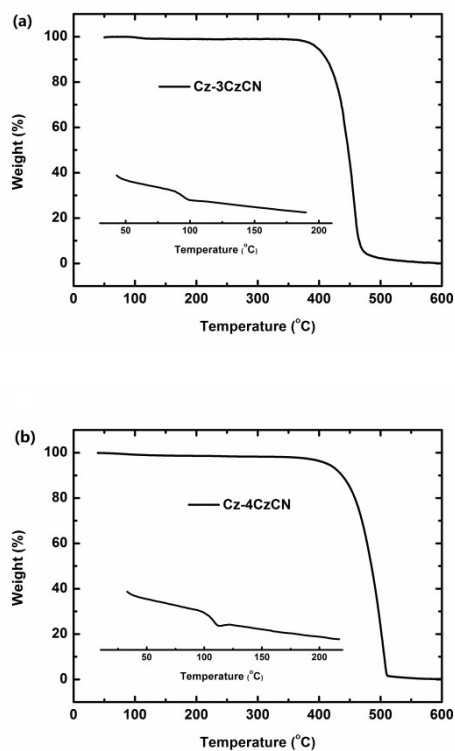


Fig. S1 TGA curve of (a) Cz-3CzCN and (b) Cz-4CzCN recorded at a heating rate of 10 °C min⁻¹; Inset: DSC trace recorded at a heating rate of 10 °C min⁻¹.

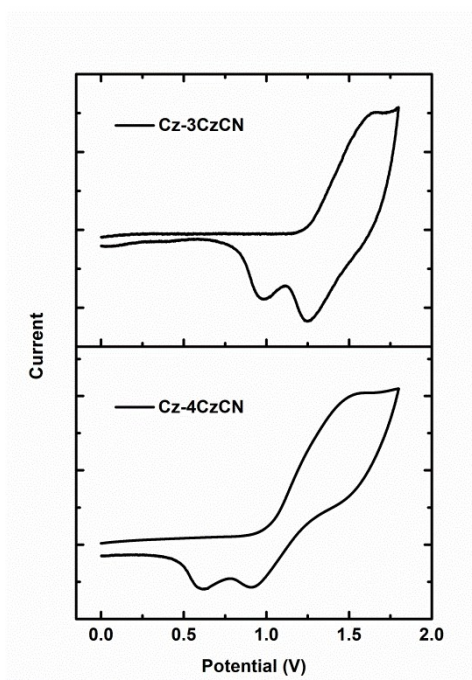


Fig. S2 Cyclic voltammogram of Cz-3CzCN and Cz-4CzCN in CH_2Cl_2 solution.

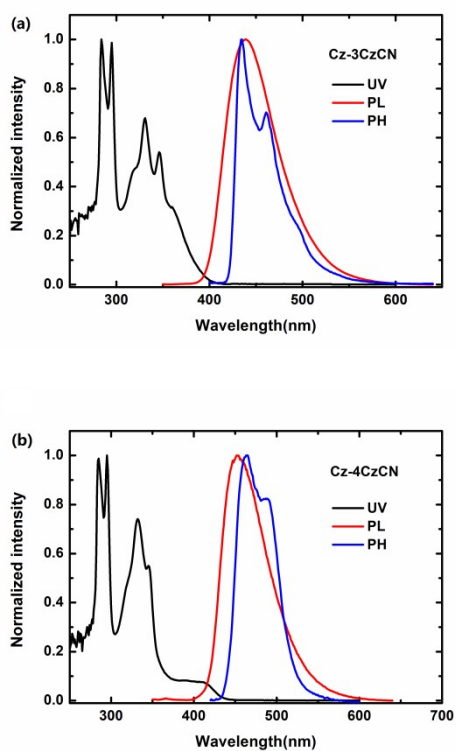


Fig. S3 UV-vis absorption, fluorescence and phosphorescence spectra of (a) Cz-3CzCN, (b) Cz-4CzCN in Toluene.

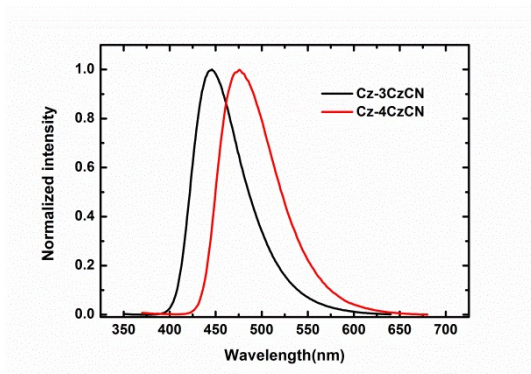


Fig. S4. Photoluminescence spectra of Cz-3CzCN and Cz-4CzCN films.

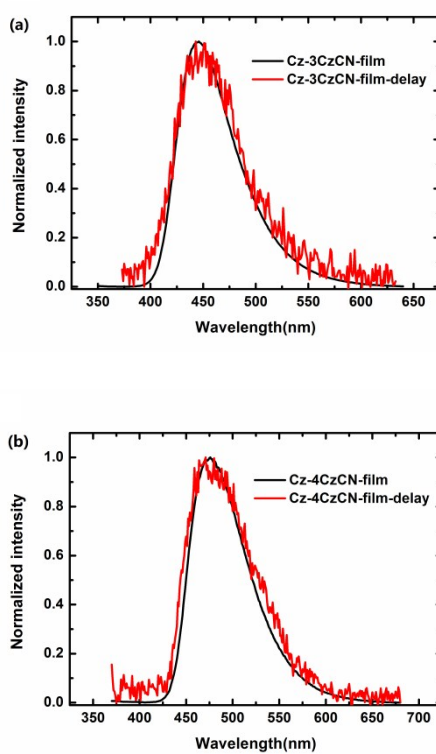
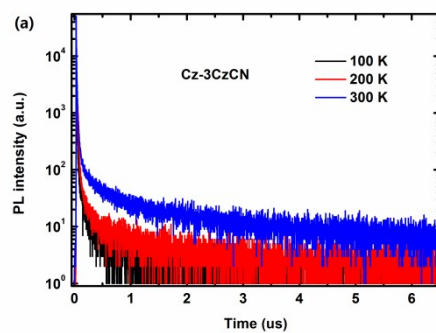


Fig. S5. PL spectra of Cz-3CzCN and Cz-4CzCN films before and after applying delay time.



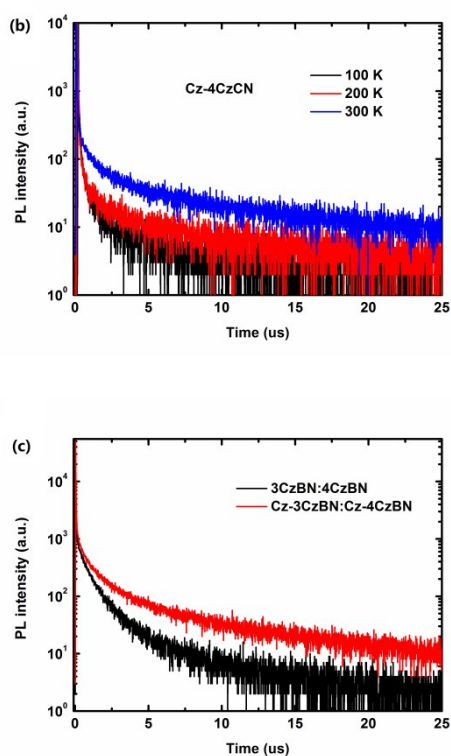


Fig. S6. (a) The temperature-dependent transient decay spectra of Cz-3CzCN in the neat film from 100 to 300 K. (b) The temperature-dependent transient decay spectra of Cz-4CzCN in the neat film. (c) Fluorescence decays of the doping films of 3CzBN:4CzBN and Cz-3CzCN:Cz-4CzCN.

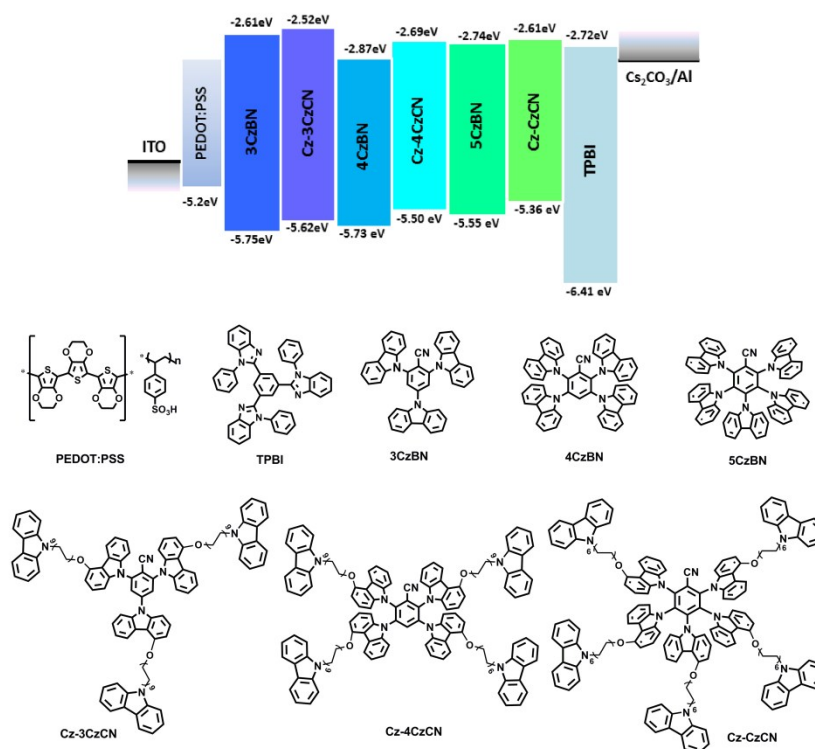


Fig. S7. The energy levels and molecular structures of the organic compounds used in the devices.

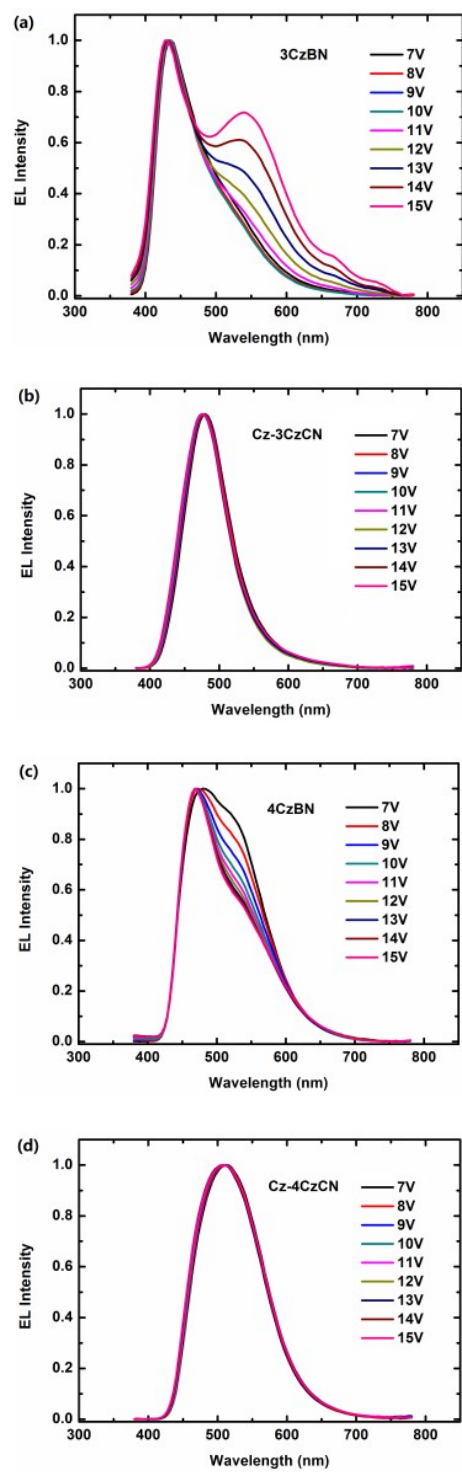


Fig. S8 The EL spectra of the pure films at different voltages.

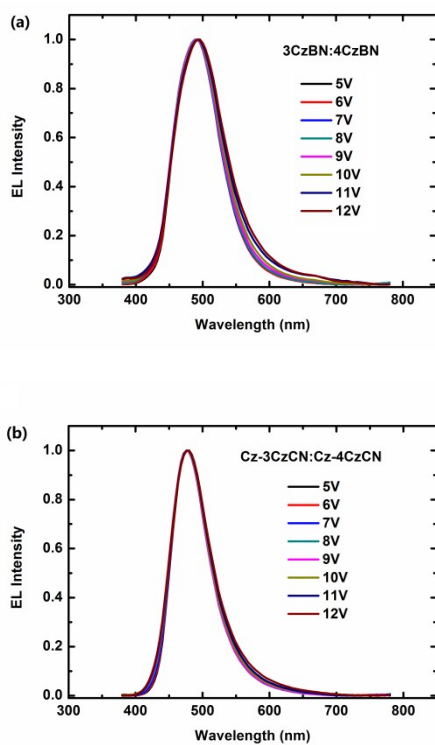


Fig. S9 The EL spectra of the devices at different voltages (a) 3CzBN:4CzBN, (b) Cz-3CzCN:Cz-4CzCN.

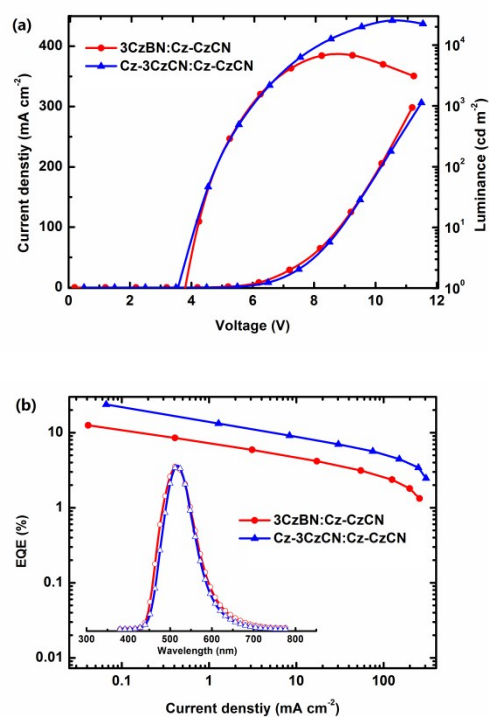


Fig. S10. (a) Current density-voltage-luminance (J-V-L) characteristics; (b) External quantum efficiencies versus current density plots of 3CzBN:Cz-CzCN and Cz-3CzCN:Cz-CzCN based devices, Inset: EL spectra of the solution-processed devices at the applied voltage of 6V.

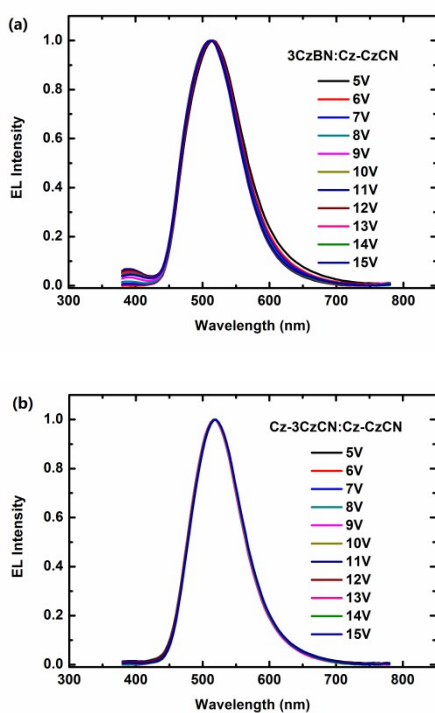


Fig. S11 The EL spectra of the devices at different voltages (a) 3CzBN:Cz-CzCN, (b) Cz-3CzCN:Cz-CzCN.

Table S1. Physical properties of Cz-3CzCN and Cz-4CzCN.

	T_d/T_g [°C]	λ_{abs} [nm] ^a	λ_{ems} [nm]	E_g [eV]	S_1/T_1 [eV]	ΔE_{ST} [eV]	HOMO [eV]	LUMO [eV]
Cz-3CzCN	398/97	284,295,	439 ^a	3.62 ^c	2.96/2.81 ^c	0.15 ^c	-5.38 ^c	-1.76 ^c
		330,346,363	445 ^b	3.10 ^d	3.10/2.86 ^e	0.24 ^e	-5.62 ^f	-2.52 ^g
Cz-4CzCN	416/110	285,295,	452 ^a	3.39 ^c	2.76/2.64 ^c	0.12 ^c	-5.32 ^c	-1.93 ^c
		332,345,412	475 ^b	2.81 ^d	2.90/2.68 ^e	0.22 ^e	-5.50 ^f	-2.69 ^g

^a Measured in toluene solution at 300 K. ^b Measured in deposited films at 300 K. ^c Obtained from Gauss simulation.

^d Estimated from the absorption edges in Toluene. ^e Estimated from fluorescent and phosphorescent spectra. ^f

Determined by the CV measurement. ^g Calculated from the energy gap and HOMO level.

Table S2. Device Performances of the solution-processed OLEDs.

EML	V _{on} ^a [V]	CE _{max} ^b [cd A ⁻¹]	PE _{max} ^c [lm W ⁻¹]	EQE _{max} ^d [%]	EQE ^e [%]	L _{max} ^f [cd m ⁻²]	CIE [x, y] ^g
3CzBN:4CzBN	4.2	12.1	8.5	5.9	3.1/1.9	3100	(0.16, 0.32)
Cz-3CzCN:Cz-4CzCN	3.5	48.6	35.2	23.5	15.5/7.8	7800	(0.15, 0.30)
3CzBN: Cz-CzCN	3.8	35.1	27.0	12.5	10.2/6.8	7400	(0.26, 0.49)
Cz-3CzCN:Cz-CzCN	3.5	69.5	48.3	23.8	21.1/12.6	28000	(0.25, 0.52)

^{a)} V_{on} = turn-on voltage at 1 cd m⁻², ^{b)} CE_{max} = maximum current efficiency, ^{c)} PE_{max} = maximum power efficiency,

^{d)} EQE_{max} = maximum external quantum efficiency, ^{e)} EQE at the luminescence of 100 and 1000 cd m⁻², ^{f)} L_{max} = maximum luminance, ^{g)} CIE = the Commission Internationale de L'Eclairage coordinates.