

Electronic Supplementary Information (ESI)

Sterically shielded blue thermally activated delayed fluorescence emitters with improved efficiency and stability

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1. Experimental details

General Information: ¹H NMR spectra were measured on a JEOLAL-600 MHz spectrometer at ambient temperature with tetramethylsilane as the internal standard. Mass spectra were recorded on a Bruker Esquire iontrap mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a DSC 2910 modulated calorimeter at a heating rate of 10 °C min⁻¹ from 20 to 600 °C under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a STA 409PC thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min⁻¹ from 25 to 800 °C under nitrogen. Electrochemical measurement were performed with a Potentiostat/Galvanostat Model 283 (Princeton Applied Research) electrochemical workstation, using Pt as working electrode, platinum wire as auxiliary electrode, and a Ag wire as reference electrode standardized against ferrocene/ ferrocenium. The reduction/oxidation potentials were measured in

dichloromethane (CH_2Cl_2) solution containing 0.1 M $\text{n-Bu}_4\text{NPF}_6$ as supporting electrolyte at a scan rate of 100 mV s^{-1} . UV-vis absorption spectra were recorded by a Agilent 8453 spectrophotometer. The emission spectra, the PL quantum efficiency and the transient photoluminescence characteristics of the compounds were measured using a transient spectrometer (Edinburg FL920P). The time resolved spectra of the films were measured using Edinburgh Instruments LP920-KS with a pulse laser (Vibrant 355II). The geometrical and electronic properties of hosts were performed with the Gaussian 03 program package. The calculation was optimized by means of B3LYP (Becke three parameters hybrid functional with Lee–Yang–Perdew correlation functionals) with the 6-31G(d) atomic basis set.³² The triplet states DE ($\text{T}_1\text{-S}_0$) were calculated using time-dependent density functional theory (TD-DFT) calculations with B3LYP/6-311+g(d). The molecular orbitals were visualized using Gaussview.

Synthesis: Synthesis of 4CzBN: Under nitrogen atmosphere, 9H-carbazole (6.68 g, 40 mmol) in dehydrated N,N-dimethylformamide (20 ml) was added dropwise into a dehydrated N,N-dimethylformamide (20 ml) solution containing tBuOK (4.48 g, 40 mmol) for 15 min and stirred for 3 h. Then, 2,3,5,6-tetrafluorobenzonitrile (1.75 g, 10 mmol) in dehydrated N,N-dimethylformamide (10 ml) was added dropwise for 15 min. Then the solution was stirred for 10h at 80°C . After that, water (350 g) was added into the solution and the precipitate was filtered and dried in vacuum. The product was purified by column chromatography on silica gel, resulted in the product 4CzBN (6.94 g, 9.1 mmol, 91%).

^1H NMR (600 MHz, CDCl_3): δ = 8.42 (s, 1H), 7.80-7.76 (m, 8H), 7.35 (d, 4H), 7.31-7.30 (m, 4H), 7.18 (t, 4H), 7.14-7.09 (m, 12H). ESI-MS m/z : 764 $[\text{M}+\text{H}]^+$. Elemental analysis calcd for $\text{C}_{55}\text{H}_{33}\text{N}_5$: C 86.48, H 4.35, N 9.17; found: C 86.41, H 4.36, N 9.23.

Synthesis of 4TCzBN: Under nitrogen atmosphere, 3,6-di-tert-butyl-9H-carbazole (11.16 g, 40 mmol) in dehydrated N,N- dimethylformamide (20 ml) was added dropwise into a dehydrated N,N- dimethylformamide (20 ml) solution containing tBuOK (4.48 g, 40 mmol) for 15 min and stirred for 3 h. Then, 2,3,5,6-tetrafluorobenzonitrile (1.75 g, 10 mmol) in dehydrated N,N- dimethylformamide (10 ml) was added dropwise for 15 min. Then the solution was stirred for 10h at 80 °C. After that, water (350 g) was added into the solution and the precipitate was filtered and dried in vacuum. The product was purified by column chromatography on silica gel, resulted in the product 4TCzBN (11.14 g, 9.2 mmol, 92%).

^1H NMR (600 MHz, CDCl_3): δ = 8.42 (s, 1H), 7.60 (d, 8H), 7.06-6.98 (m, 16H), 1.366 (s, 72H). ESI-MS m/z : 1212 $[\text{M}+\text{H}]^+$. Elemental analysis calcd for $\text{C}_{87}\text{H}_{97}\text{N}_5$: C 86.16, H 8.06, N 5.77; found: C 86.10, H 8.10, N 5.79.

Synthesis of 5CzBN: Under nitrogen atmosphere, 9H-carbazole (8.35 g, 50 mmol) in dehydrated N,N- dimethylformamide (20 ml) was added dropwise into a dehydrated N,N- dimethylformamide (20 ml) solution containing tBuOK (4.60 g, 50 mmol) for 15 min and stirred for 3 h. Then, 2,3,4,5,6-pentafluorobenzonitrile (1.93 g, 10 mmol) in dehydrated N,N-dimethylformamide (10 ml) was added dropwise for 15 min. Then the solution was stirred for 10h at 80 °C. After that, water (350 g) was added into the solution and the precipitate was filtered and dried in vacuum. The product was purified by column chromatography on silica gel, resulted in the product 5CzBN (8.81 g, 9.5 mmol, 95%).

^1H NMR (600 MHz, DMSO): δ = 8.03-7.99 (m, 8H), 7.89-7.82 (m, 6H), 7.41 (d, 4H), 7.35 (d, 2H), 7.12 (t, 4H), 7.04 (t, 4H), 6.64-6.49 (m, 10H), 6.43 (t, 2H). ESI-MS m/z : 929 $[\text{M}+\text{H}]^+$. Elemental analysis calcd for $\text{C}_{67}\text{H}_{40}\text{N}_6$: C 86.61, H 4.34, N 9.05; found: C 86.52, H 4.36, N 9.12.

Synthesis of 5TCzBN: Under nitrogen atmosphere, 3,6-di-tert-butyl-9H-carbazole (13.95 g, 50 mmol) in dehydrated N,N- dimethylformamide (20 ml) was added dropwise into a dehydrated N,N- dimethylformamide (20 ml) solution containing tBuOK (4.60 g, 50 mmol) for 15 min and stirred for 3 h. Then, 2,3,4,5,6-pentafluorobenzonitrile (1.93 g, 10 mmol) in dehydrated N,N- dimethylformamide (10 ml) was added dropwise for 15 min. Then the solution was stirred for 10h at 80 °C. After that, water (350 g) was added into the solution and the precipitate was filtered and dried in vacuum. The product was purified by column chromatography on silica gel, resulted in the product 5TCzBN (13.86 g, 9.3 mmol, 93%).

¹H NMR (600 MHz, CDCl₃): δ =7.57 (s, 4H), 7.19 (m, 6H), 7.02 (d, 2H), 6.94 (s, 8H), 6.65 (d, 4H), 6.56 (d, 2H), 6.51 (d, 4H), 1.21 (t, 90H). ESI-MS m/z: 1489 [M+H]⁺. Elemental analysis calcd for C₁₀₇H₁₂₀N₆: C 86.24, H 8.12, N 5.64; found: C 86.16, H 8.16, N 5.68.

Device fabrication and characterization: All commercially available reagents were used as received unless otherwise stated. Before device fabrication, the ITO glass substrates were pre-cleaned carefully. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 2×10^{-4} Torr. The hole-injection material HATCN, hole-transporting material NPB, exciton blocking material TCTA and electron-transporting material DpyPA:Liq (1:1) were thermally evaporated at a rate of 1.0 \AA s^{-1} . After the organic film deposition, 0.5 nm of LiF and 150 nm of aluminum were thermally evaporated onto the organic surface. All of the organic materials used were purified by a vacuum sublimation approach. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The electroluminescence spectra and luminance of the devices were obtained on a PR650 spectrometer. All the device fabrication and characterization steps were carried out at room temperature under

ambient laboratory conditions. Lifetime analysis of the TADF devices was done at a constant current mode at an initial luminance of 500 cd/m².

2. Additional data

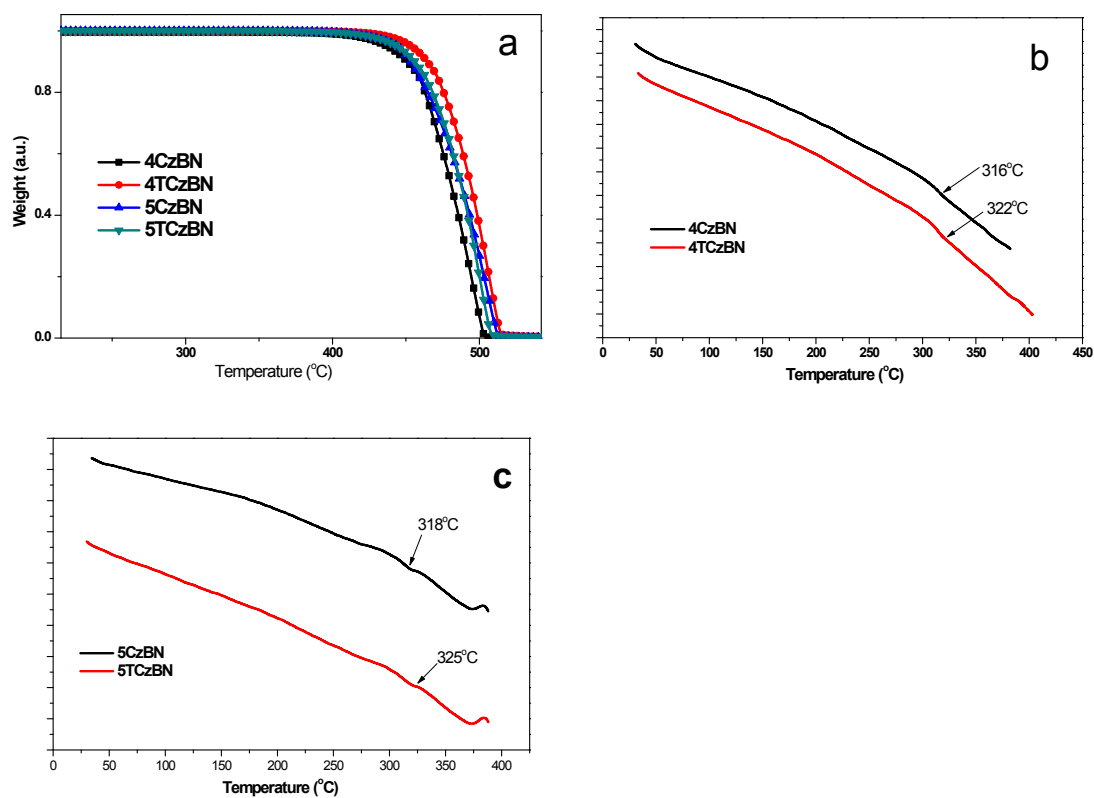
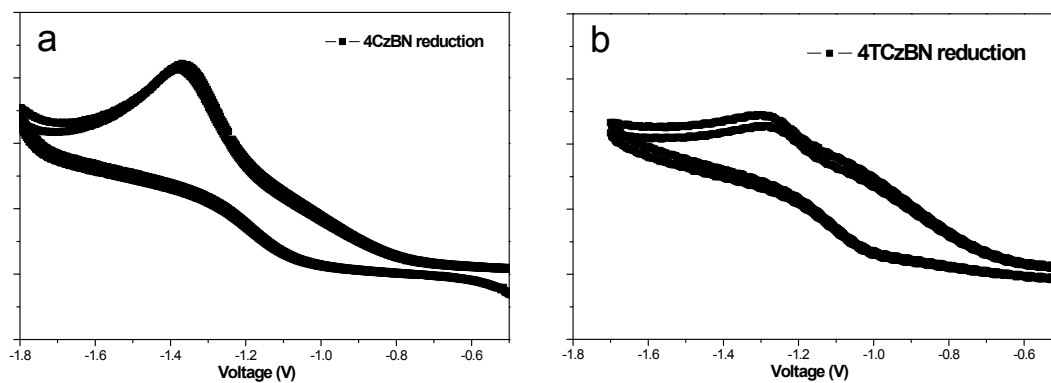


Figure S1. (a) The DSC thermograms of the four compounds. (b) The TGA thermograms of 4CzBN and 4TCzBN. (c) The TGA thermograms of 5CzBN and 5TCzBN.



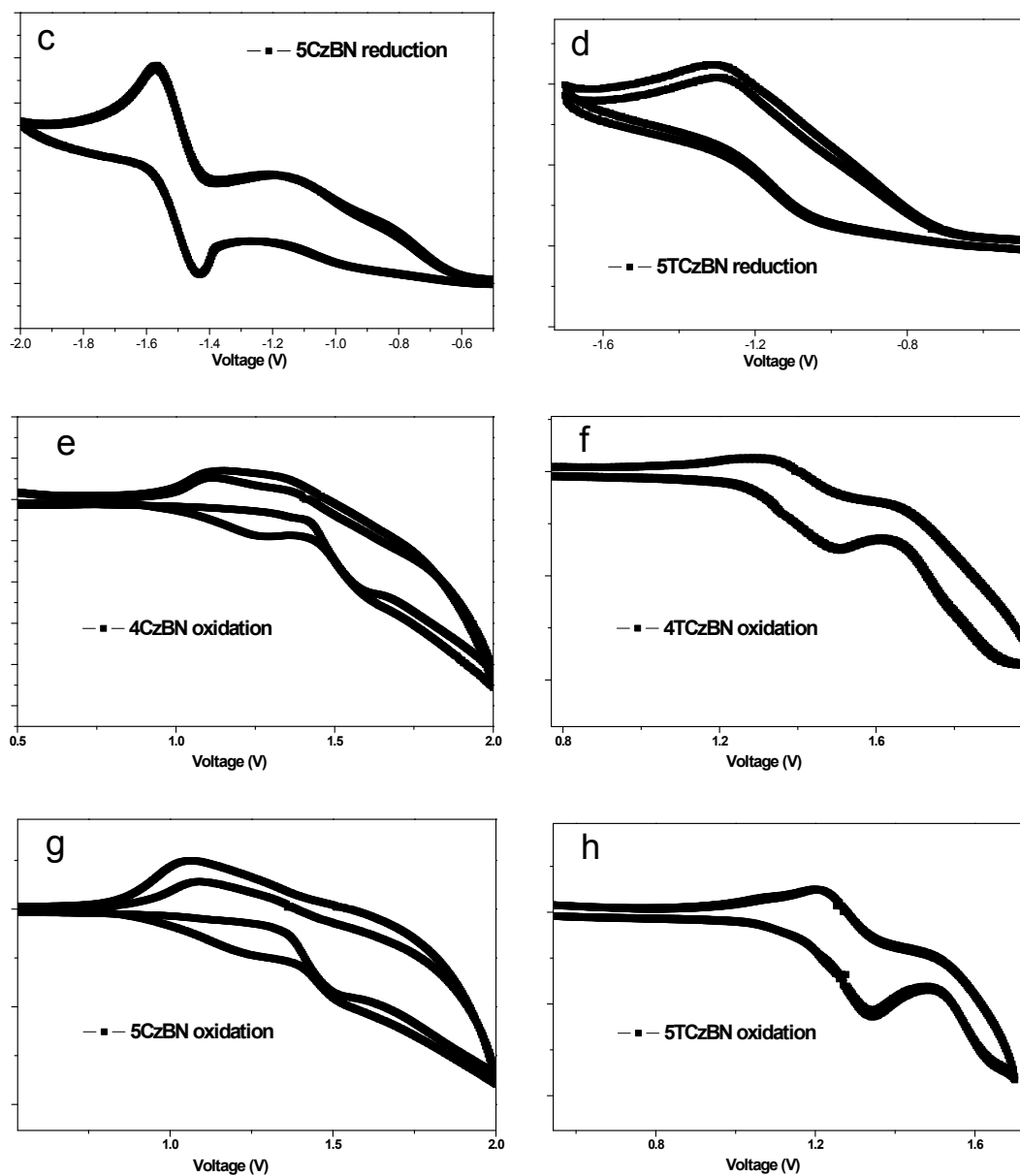


Figure S2. The oxidation reaction CV curves of 4CzBN (a), 4TCzBN (b), 5CzBN (c), 5TCzBN (d) and reduction reaction CV curves of 4CzBN (e), 4TCzBN (f), 5CzBN (g), 5TCzBN (h).

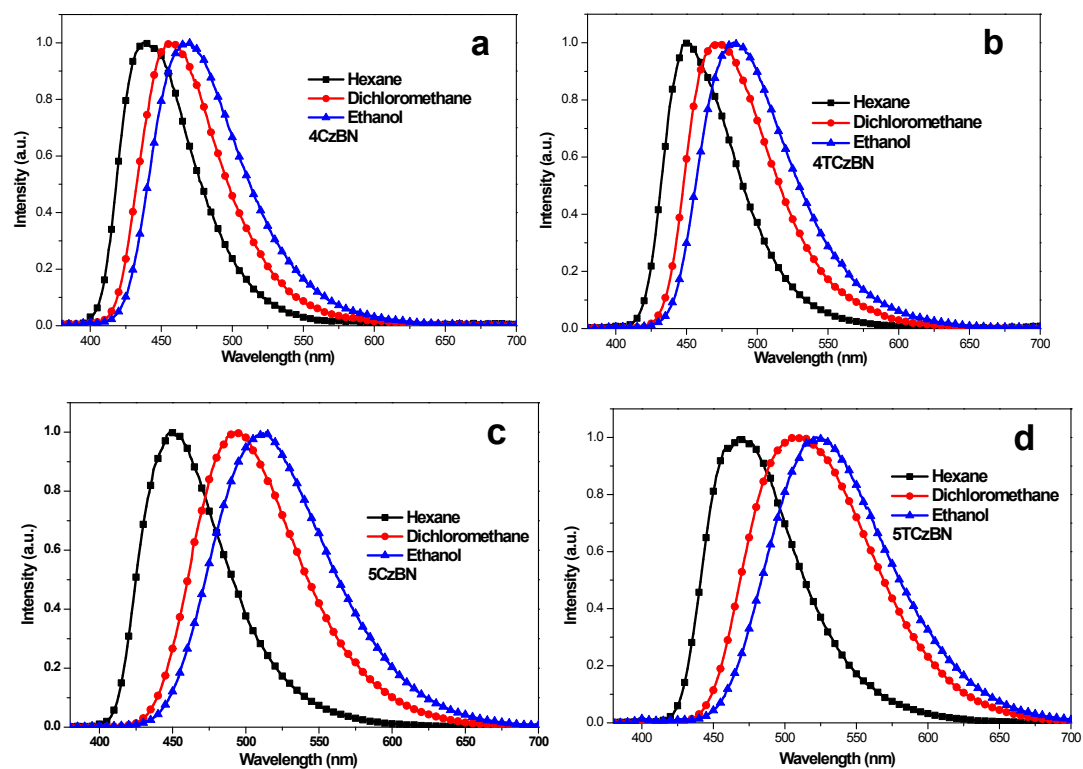


Figure S3. Solvent dependent PL spectra of 4CzBN (a), 4TCzBN (b), 5CzBN (c) and 5TCzBN

(d).

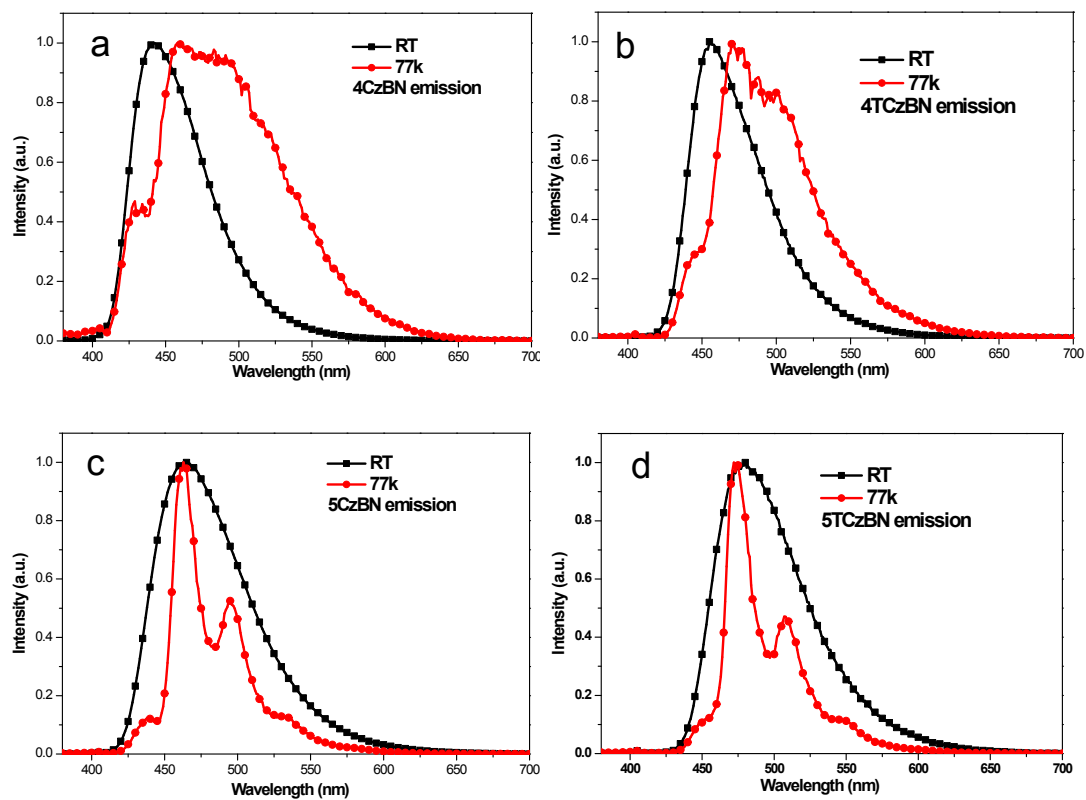


Figure S4. The PL spectra of 4CzBN (a), 4TCzBN (b), 5CzBN (c) and 5TCzBN (d) in toluene at

room temperature (RT) and 77K.

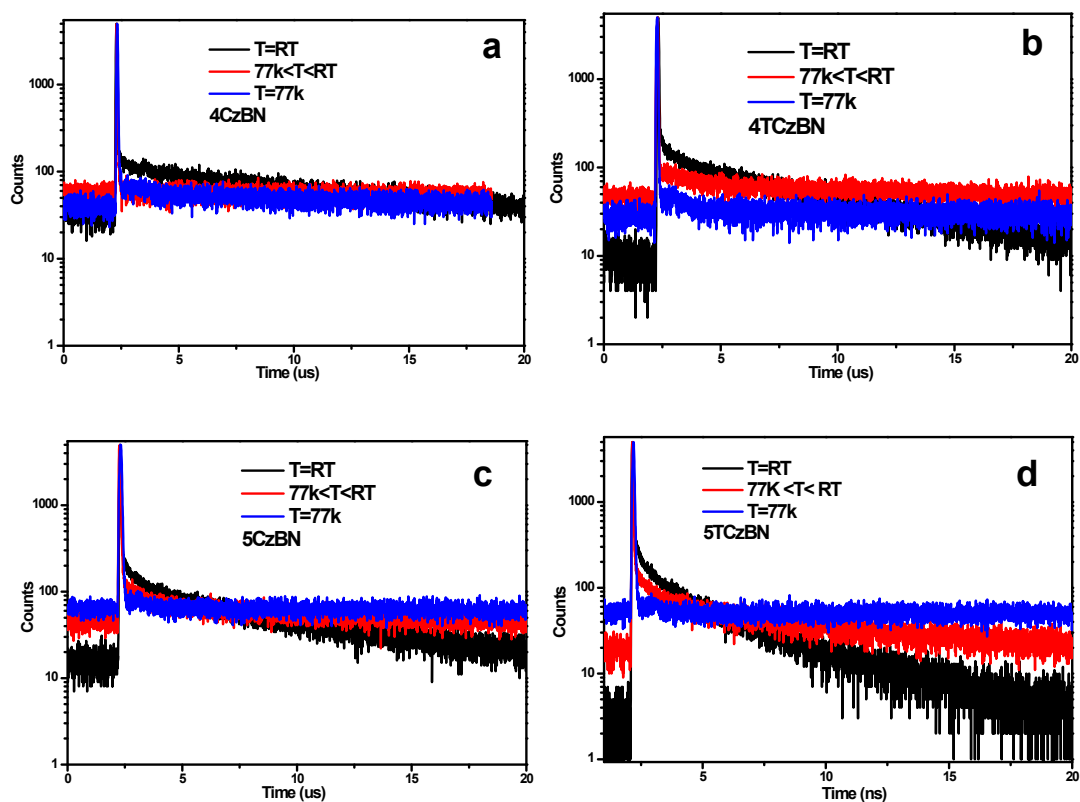


Figure S5: The PL decay curves of 4CzBN (a), 4TCzBN (b), 5CzBN (c) and 5TCzBN (d) at different temperature.

Table S1: The calculated rate constants of the transition processes of the emitters.

	τ_p	τ_d	Φ_p	Φ_d	k_p	k_d	k_{ISC}	k_{RISC}	Φ_{RISC}
	(ns)	(μ s)			($10^7 s^{-1}$)	($10^5 s^{-1}$)	($10^7 s^{-1}$)	($10^5 s^{-1}$)	
4CzBN	10.0	4.0	0.10	0.39	1.03	0.98	9.0	0.42	0.43
4TCzBN	10.0	3.9	0.20	0.48	2.07	1.23	8.0	0.74	0.60
5CzBN	14.0	3.7	0.08	0.62	0.57	1.68	6.6	1.13	0.68
5TCzBN	15.0	3.4	0.13	0.73	0.87	2.15	5.8	1.81	0.83

Note: τ_p , Φ_p and k_p is the lifetime, photoluminance quantum efficiency and the decay rate of the

prompt part, respectively. τ_p , Φ_p and k_p is the lifetime, photoluminance quantum efficiency and the decay rate of the prompt part, respectively. k_{ISC} stands for the rate of the ISC process while k_{RISC} is the rate of the RISC process. Φ_{RISC} is the efficiency of the RISC process. The calculated equations are shown below.

$$k_p = \frac{\phi_p}{\tau_p}$$

$$k_d = \frac{\phi_d}{\tau_d}$$

$$k_{RISC} = \frac{k_p k_d \phi_d}{k_{ISC} \phi_p}$$

$$\phi_{RISC} = \frac{\phi_d}{1 - \phi_p}$$

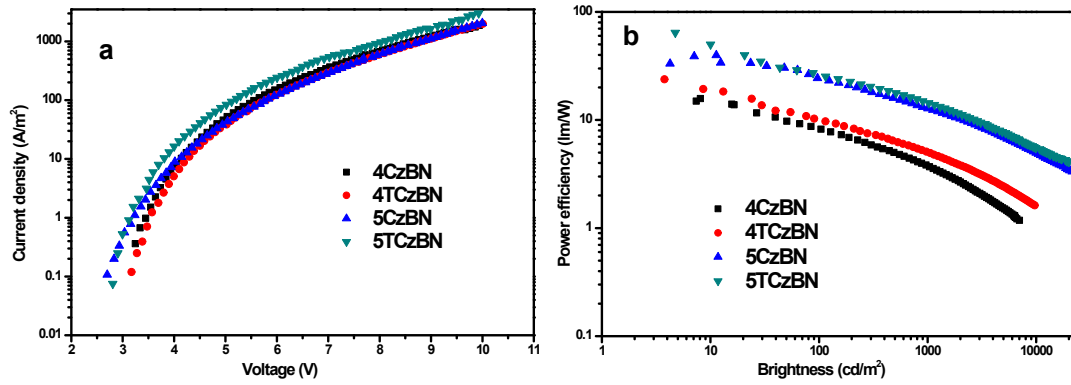


Figure S6: (a) The current density-voltages curves of the devices. (b) The power efficiency-brightness curves of the devices.

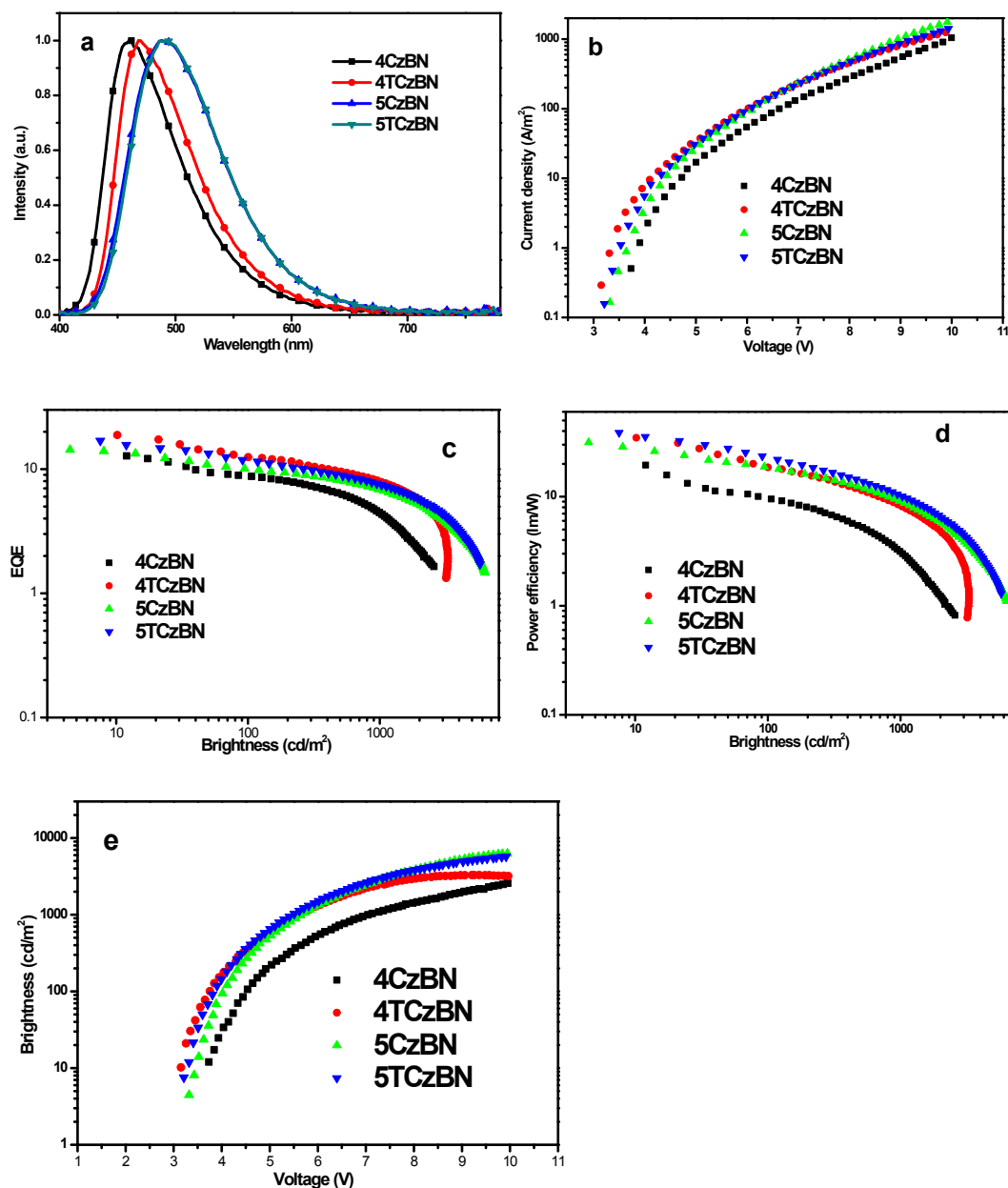


Figure S7: (a) The spectra of the devices. (b) The current density-voltages curves of the devices. (c) The EQE-brightness curves of the devices and (d) The power efficiency-brightness curves of the devices. (e) The brightness-voltage curves of the devices. The device structure is ITO/HATCN (5 nm)/ NPB (30 nm)/ TCTA (10 nm)/ mCP (10 nm)/ EML (30 nm)/ DPEPO (10 nm)/ Bphen (30 nm)/ LiF (0.5 nm)/ Al (150 nm). The dopant concentrations are optimized to be 40% for 4CzBN and 4TCzBN while 20% for 5CzBN and 5TCzBN, respectively.

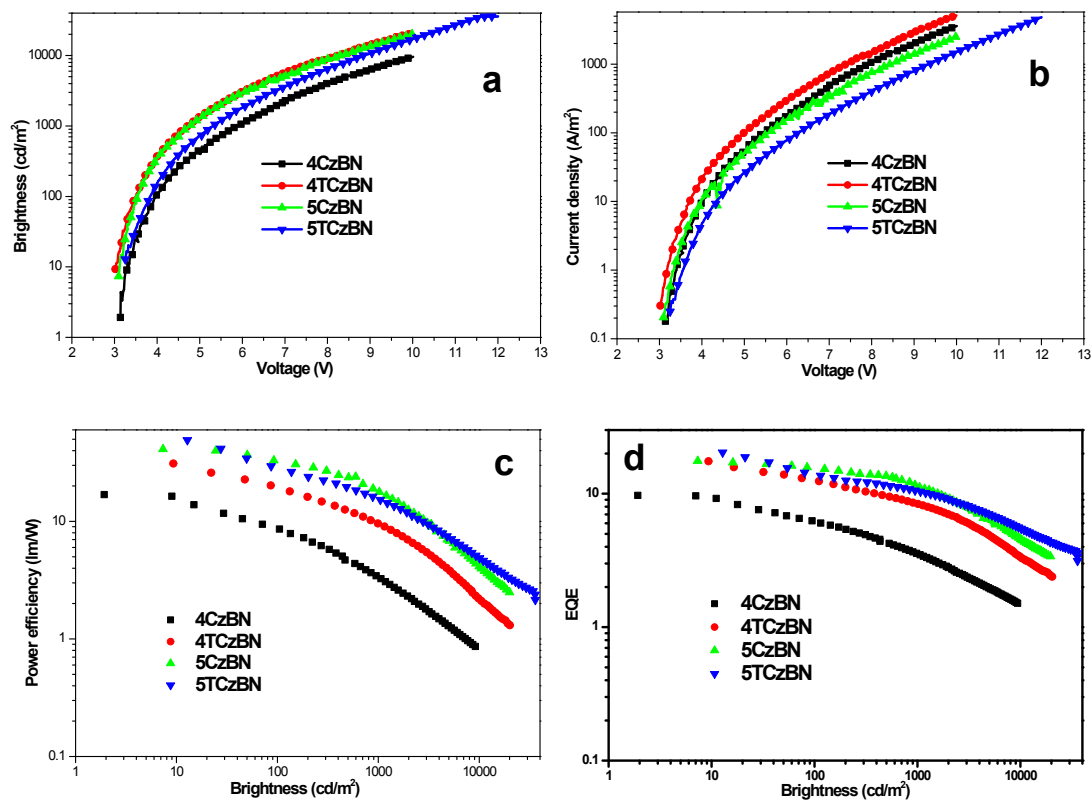


Figure S8: (a) The brightness-voltage curves of the devices with 26DCzPPy as the host. (b) The current density-voltage curves of the devices with 26DCzPPy as the host. (c) The power efficiency-brightness curves of the devices with 26DCzPPy as the host. (d) The EQE-brightness curves of the devices with 26DCzPPy as the host. The device structure is ITO/ HATCN (5 nm)/ NPB (30 nm)/ TCTA (10 nm)/ EML (30 nm)/ 26DCzPPy (10 nm)/ DPyPA (30 nm)/ LiF (0.5 nm)/ Al (150 nm). The dopant concentrations are optimized to be 40% for 4CzBN and 4TCzBN while 30% for 5CzBN and 5TCzBN, respectively.