Electronic Supplementary Information (ESI)

Highly efficient blue thermally activated delayed fluorescent OLEDs with record-low driving voltages utilizing high triplet energy hosts with small singlet-triplet splittings

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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 N,N-Dimethylformamide (DMF) solution containing 0.1 M n-Bu₄NPF₆ as supporting electrolyte at a scan rate of 100 mV s⁻¹. UV-vis absorption spectra were recorded by a Agilent 8453 spectrophotometer. The emssion spectra, the PL quantum yield and the transient photoluminescence characteristics of the compounds were measured using a transient spectrometer (Edinburg FL920P). The geometrical and electronic properties of hosts were performed with the Gaussian 09 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. The triplet states DE (T₁-S₀) were calculated using time-dependent density functional theory (TD-DFT) calculations with B3LYP/ 6-31G (d). The excited energies of triplet and singlet were calculated based on the optimized excited states. The molecular orbitals were visualized using Gaussview.

Synthesis: We used the following general procedure for the synthesis of CzBNs. Under nitrogen atmosphere, 9H-carbazole (1.002 g, 6 mmol) in dehydrated N,N- dimethylformamide (20 ml) was added dropwise into a dehydrated N,N- dimethylformamide (20 ml) solution containing t-BuOK (0.672g, 6 mmol) for 15 min and stirred for 3 h. Then, 2,4-difluorobenzonitrile (0.278 g, 3 mmol), 2,4-difluorobenzonitrile (0.278 g, 3 mmol), 2,4-difluorobenzonitrile (0.278 g, 3 mmol) or 2,4,6-trifluorobenzonitrile (0.314 g, 2 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 white precipitate was filtered and dried in vacuum. The product was purified by column chromatography on silica gel, resulted in the product.

2,4-2CzBN (1.20 g, 2.76 mmol, yield: 92%).

¹H NMR (600 MHz, CDCl₃): δ =8.42 (s, 1H), 8.17-8.15 (q, 3H), 8.12 (d, 2H), 7.90 (d, 2H), 7.55 (d, 2H), 7.50-7.43 (m, 4H), 7.37-7.33 (m, 6H). ESI-MS m/z: 434 [M+H]⁺. Elemental analysis calcd for C₅₅H₃₃N₅: C 85.89, H 4.42, N 9.69; found: C 85.82, H 4.45, N 9.73.

2,6-2CzBN (1.21 g, 2.79 mmol, yield: 93%).

¹H NMR (600 MHz, CDCl₃): δ =8.44 (d, 4H), 8.260 (t, 1H), 7.96 (d, 2H), 7.62 (t, 4H), 7.45 (t, 8H). ESI-MS m/z: 434 [M+H]⁺. Elemental analysis calcd for C₅₅H₃₃N₅: C 85.89, H 4.42, N 9.69; found: C 85.80, H 4.46, N 9.74.

3,5-2CzBN (1.17 g, 2.70 mmol, yield: 90%).

¹H NMR (600 MHz, CDCl₃): δ =8.15 (d, 4H), 8.11 (t, 1H), 7.99 (d, 2H), 7.51 (d, 4H), 7.47 (t, 4H), 7.35 (t, 4H). ESI-MS m/z: 434 [M+H]⁺. Elemental analysis calcd for C₅₅H₃₃N₅: C 85.89, H 4.42, N 9.69; found: C 85.83, H 4.46, N 9.71.

3CzBN (1.10 g, 1.84 mmol, yield: 92%).

¹H NMR (600 MHz, CDCl₃): δ =8.17 (d, 4H), 8.11 (d, 2H), 8.06 (s, 2H), 7.66 (d, 2H), 7.57-7.53 (m, 8H), 7.45 (t, 2H), 7.39 (t, 4H), 7.34 (t, 2H). ESI-MS m/z: 599 [M+H]⁺. Elemental analysis calcd for C₅₅H₃₃N₅: C 86.26, H 4.38, N 9.36; found: C 86.22, H 4.39, N 9.39.

Device fabrication and characterization: All commercially available reagents were used as received unless otherwise stated. Before device fabrication, the ITO glass substrates were precleaned 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, holetransporting material NPB, exciton blocking material TCTA and electron-transporting material Bphen were thermally evaporated at a rate of 1.0 Å 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.

2. Additional data



Figure S1: The single-crystal structures of 2,4-2CzBN, 2,6-2CzBN and 3,5-2CzBN.





Figure S2. The DSC thermograms of the four compounds (a) and the TGA thermograms of 2,4-

2CzBN (b), 2,6-2CzBN (c), 3,5-2CzBN (d) and 3CzBN (e).



Figure S3. The PL spectra of 2,4-2CzBN (a), 2,6-2CzBN (b), 3,5-2CzBN (c) and 3CzBN (d) in toluene at room temperature (RT) and 77K.



Figure S4. The oxidation and reduction reaction CV curves of 2,4-2CzBN (a), 2,6-2CzBN (b), 3,5-

2CzBN (c) and 3CzBN (d).

	Emission (nm)	T ₁ (eV)	ΔE_{ST} (eV)	f	HOM O (eV)	LUM O (eV)	Τ _d (μs)	k _p (s ⁻¹)	φ _{PL} (prompt ^{a)/} total ^{b)})
4TCzBN	456	2.62	0.24	0.1087	5.48	2.73	3.9	2.07×10 ⁷	0.20/0.68

^{a)} Measured in toluene without degassing oxygen. ^{b)} Measured in toluene after bubbling nitrogen gas.



Figure S6: The current density-voltages curves of the devices.