

Supplementary Information

Spatial separation of TADF sensitizer and fluorescent emitter with core-dendron system to block energy loss in deep blue organic light-emitting diodes

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Supporting Information

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 ^{13}C NMR spectra were obtained on a BRUKER AMX 600-MHz instrument. Elemental analysis was determined by an Elementar Vario EL CHN elemental analyzer. Molecular masses were measured by BRUKER DALTONICS Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The UV-Vis absorption spectra of the compounds were acquired by a SHIMADZU UV-2450. The photoluminescence emission spectra were obtained on a HORIBA FLUOROMAX-4 and the phosphorescence emission spectra were measured on Edinburgh FLS920 by setting delay time and liquid nitrogen was placed into the optical Dewar flask for low temperature (77 K). The film PL quantum efficiency was measured with an integrating sphere under optimal excitation wavelength. The integrating sphere was purged with flowing nitrogen during the entire measuring process. The films were prepared as follows: in a general procedure, the quartz plate substrates were pre-cleaned carefully and treated by UV ozone for 4 min. The solutions with the concentration of 10 mg/mL were spin coated onto the quartz plate substrates and dried in vacuum. 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 $10\text{ }^\circ\text{C min}^{-1}$. Cyclic voltammetry measurements were performed on a CHI750C voltammetric analyzer in CH_2Cl_2 solutions (10^{-3} M) (oxidation process) at a scan rate of 100 mV s^{-1} with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard.

Devices measurements and characterization

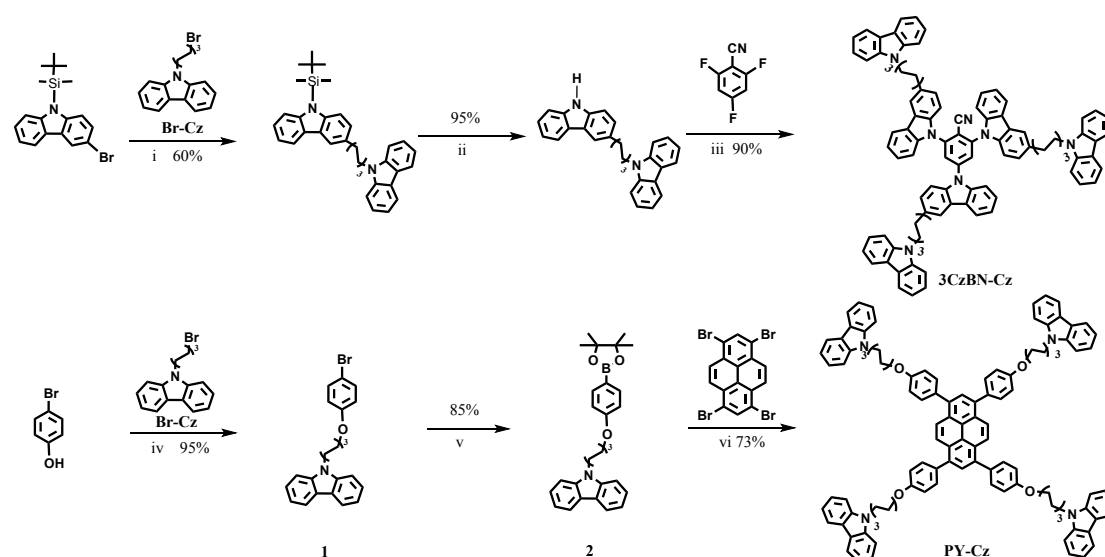
To fabricate the solution-processed OLEDs, a 40 nm thick poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) film was first deposited on the pre-cleaned ITO glass substrates and baked at $150\text{ }^\circ\text{C}$ for 10 min. Then EML with a thickness of about 60 nm was spin-coated from a 1, 2-dichloroethane solution onto the PEDOT: PSS layer and annealed at $100\text{ }^\circ\text{C}$ for 30 min to remove the residual solvent under N_2 atmosphere. Subsequently, a 40 nm thick TPBi layer was evaporated as the electron transporting layer. Finally, 2 nm thick Cs_2CO_3 and 100 nm thick Al layers were evaporated as the cathode. The EL spectra and CIE coordinates were measured using a PR655 spectra colorimeter. The current density-voltage and brightness-voltage curves of the devices were plotted using a Keithley 2400 source meter calibrated by a silicon photodiode. All the measurements were carried out at room

temperature with no protective encapsulation. The EQE was calculated from the brightness, current density and EL spectrum assuming a Lambertian distribution.

Experimental Section

Synthesis of PY, PY-Cz, 3CzBN and 3CzBN-Cz

They were prepared using various organic reactions such as Suzuki coupling reaction, lithium-halogen exchange and so on. The synthetic procedures were illustrated in Scheme 1. All reagents were used as purchased without further purification. The final product PY and 3CzBN were prepared according to literature procedure. And the bromohexane terminated carbazole dendron (Br-Cz), 3-bromo-9-(tert-butyl dimethylsilyl)-9H-carbazole and 3,6-dibromo-9-(tert-butyl dimethylsilyl)-9H-carbazole were prepared according to literature procedure.



Scheme S1 Synthesis of PY-Cz and 3CzBN-Cz. Reagents and conditions: (i) n-BuLi, THF, -78°C, 30 min; (ii) tetrabutylammonium fluoride (TBAF), THF, rt, 1h; (iii) NaH, DMF, 25°C, 24h; (iv) K₂CO₃, DMF, rt, 12h; (v) bis(pinacolato)diboron, PdCl₂(dppf), AcOK, 1,4-dioxane, 80°C, 24 h; (vi) Pd(PPh₃)₄, AcOK, 1,4-dioxane, 100°C, 48 h.

2,4,6-tris(3-(6-(9H-carbazol-9-yl) hexyl)-9H-carbazol-9-yl)benzonitrile (3CzBN-Cz)

Under nitrogen atmosphere, 3-(6-(9H-carbazol-9-yl) hexyl)-9H-carbazole (Cz-Cz) (1.0g, 2.5mmol) in anhydrous DMF (20 mL) was added dropwise into anhydrous DMF (10 mL) solution containing NaH (0.336g, 3 mmol) for 15 min and stirred for 3 h. Then, 2,4,6-trifluorobenzonitrile (0.078 g, 0.5 mmol) in anhydrous DMF (10 mL) was added dropwise for 15 min. Then the solution was stirred for 24 h at 25 °C. After that, 250 mL of water was added into the solution and the mixture was extracted with CH₂Cl₂ three times. The combined 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 white product (0.6 g, 90 %). ¹H NMR (600MHz, CDCl₃, δ) 8.13 (d, 7.8 Hz, 2H), 8.08 (m, 6H), 7.98 (s, 2H), 7.91(s, 2H), 7.84(s, 1H), 7.60 (d, 8.4Hz,

1H), 7.52 (d, 8.4Hz, 5H), 7.43-7.41 (m, 8H), 7.40-7.38 (m, 8H), 7.37 (d, 10.2Hz, 5H), 7.20 (m, 7H), 4.29 (m, 6H), 2.77 (m, 6H), 1.88 (m, 6H), 1.70 (m, 6H), 1.44 (m, 12H). ¹³C NMR (75 MHz, CDCl₃, δ): 140.40, 125.56, 125.53, 122.78, 118.67, 108.65, 108.59, 43.03, 35.84, 31.94, 29.03, 28.92, 27.22. MS (MALDI-TOF) [m/z]: calcd for C₉₇H₈₃N₇, 1346.67; found, 1346.56. Anal. Calcd for C₉₇H₈₃N₇: C, 86.51; H, 6.21; N, 7.28. Found: C, 86.52; H, 6.20; N, 7.28.

9-(6-(4-bromophenoxy) hexyl)-9H-carbazole (1)

Under nitrogen atmosphere, into a 250 mL round bottom flask equipped with a magnetic stirring bar and a dropping funnel were placed 9-(6-bromohexyl)-9H-carbazole (3.78 g, 11.35 mmol), 4-bromophenol (1.95 g, 11.35 mmol), K₂CO₃ (1.57 g, 11.96 mmol) and DMF (50 mL). After stirring at room temperature for 12 h, the reaction mixture was poured into water (50 mL) and extracted with dichloromethane (100 mL). The organic layer was separated and washed with water, brine solution and again with water. The organic layer was dried over anhydrous sodium sulfate and filtered. Removal of solvent on a rotary evaporator yielded a crude product which was purified by column chromatography on silica gel to give compound 1 as white powder (3.94 g, 95%). ¹H NMR (600 MHz, CDCl₃, δ) 8.14 (d, J = 7.78 Hz, 2H), 7.58–7.45 (m, 4H), 7.44–7.36 (m, 2H), 7.27 (t, J = 7.33 Hz, 2H), 6.67–6.55 (m, 2H), 4.33 (t, J = 7.10 Hz, 2H), 3.84 (t, J = 6.18 Hz, 2H), 2.02–1.88 (m, 2H), 1.84–1.72 (m, 2H), 1.59–1.47 (m, 4H). MS (MALDI-TOF) [m/z]: calcd for C₂₄H₂₄BrNO, 421.10; found, 421.15. Anal. Calcd for C₂₄H₂₄BrNO: C, 68.25; H, 5.73; Br, 18.92; N, 3.32; O, 3.79. Found: C, 68.30; H, 5.77; N, 3.30.

9-(6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)hexyl)-9H-carbazole (2)

Under nitrogen atmosphere, 9-(6-(4-bromophenoxy) hexyl)-9H-carbazole (1) (1.22g, 3.3 mmol), bis(pinacolato)diboron (0.85g, 3.3 mmol), potassium acetate (AcOK) (0.33 g, 3.3mmol) was dissolved in 1,4-dioxane (15 mL) and stirred for 30 min. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.24 g, 0.33mmol) was added slowly and the solution was stirred for 24 h at 80°C. The reaction was quenched by addition of ice-cold water (100 mL) and extracted with dichloromethane (200 mL). The combined organic layers were washed with water, brine solution and again with water. The organic layer was dried over anhydrous sodium sulfate and filtered. Removal of the solvent on a rotary evaporator yielded a crude product, which was chromatographed on neutral alumina using 2% ethyl acetate in petroleum ether as an eluent to give compound 4 as a white solid (1.17 g, 85%). ¹H NMR (600 MHz, DMSO-d₆, δ) 8.14 (d, 7.2 Hz, 2H), 7.59–7.57 (d, 8.4 Hz, 4H), 7.45–7.42 (t, 7.8 Hz, 2H), 7.20-7.17 (t, 7.8 Hz, 2H), 6.86 (d, 8.4 Hz, 2H), 4.39-4.37 (t, 7.2 Hz, 2H), 3.92-3.89 (t, 6.6 Hz, 2H), 1.79-1.77 (m, 2H), 1.65-1.62 (m, 2H), 1.43-1.39 (m, 2H), 1.38-1.32 (m, 2H), 1.27 (s, 12H). MS (MALDI-TOF) [m/z]: calcd for C₃₀H₃₆BNO₃, 469.28; found, 469.29. Anal. Calcd for C₃₀H₃₆BNO₃: C, 76.76; H, 7.73; B, 2.30; N, 2.98; O, 10.22. Found: C, 76.57; H, 7.79; N, 2.96.

1,3,6,8-tetrakis(4-((6-(9H-carbazol-9-yl)hexyl)oxy)phenyl)pyrene (PY-Cz)

Under nitrogen atmosphere, 9-(6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)hexyl)-9H-carbazole (2) (1 g, 2.1 mmol), 1,3,6,8-tetrabromopyrene (0.18g, 0.36 mmol), potassium acetate (AcOK) (0.21 g, 2.1mmol) was dissolved in 1,4-dioxane (10 mL) and stirred for 30 min. Tetrakis(triphenylphosphine)palladium(0) (0.24 g, 0.21 mmol) was added and stirred at 100°C for 48 h. After that, 250 mL of water was added into the solution and the mixture was extracted with CH₂Cl₂ three times. The combined 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 faint yellow product (0.4 g, 73 %). ¹H NMR (600 MHz, CDCl₃, δ) 8.14 (s, 4H), 8.11 (d, 7.8 Hz, 8H), 7.94 (s, 2H), 7.57-7.55 (d, 8.4 Hz, 8H), 7.48-7.42 (m, 16H), 7.24-7.21 (t, 7.8Hz, 8H), 7.03-7.01 (d, 8H). 4.36-4.34 (d, 7.2Hz, 8H), 4.03-4.00 (t, 6.6 Hz, 8H), 1.97-1.94 (m, 8H), 1.83-1.80 (m, 8H), 1.51-1.49 (m, 8H), 1.26-1.24 (m, 8H). ¹³C NMR (600 MHz, CDCl₃, δ) 158.42, 140.41, 131.68, 122.82, 118.74, 114.35, 108.63, 67.83, 42.95, 29.17, 28.96, 27.10, 25.99. MS (MALDI-TOF) [m/z]: calcd for C₁₁₂H₁₀₂N₄O₄, 1567.79; found, 1567.82. Anal. Calcd for C₁₁₂H₁₀₂N₄O₄: C, 85.79; H, 6.56; N, 3.57; O, 4.08, Found: C, 85.78; H, 6.58; N, 3.55.

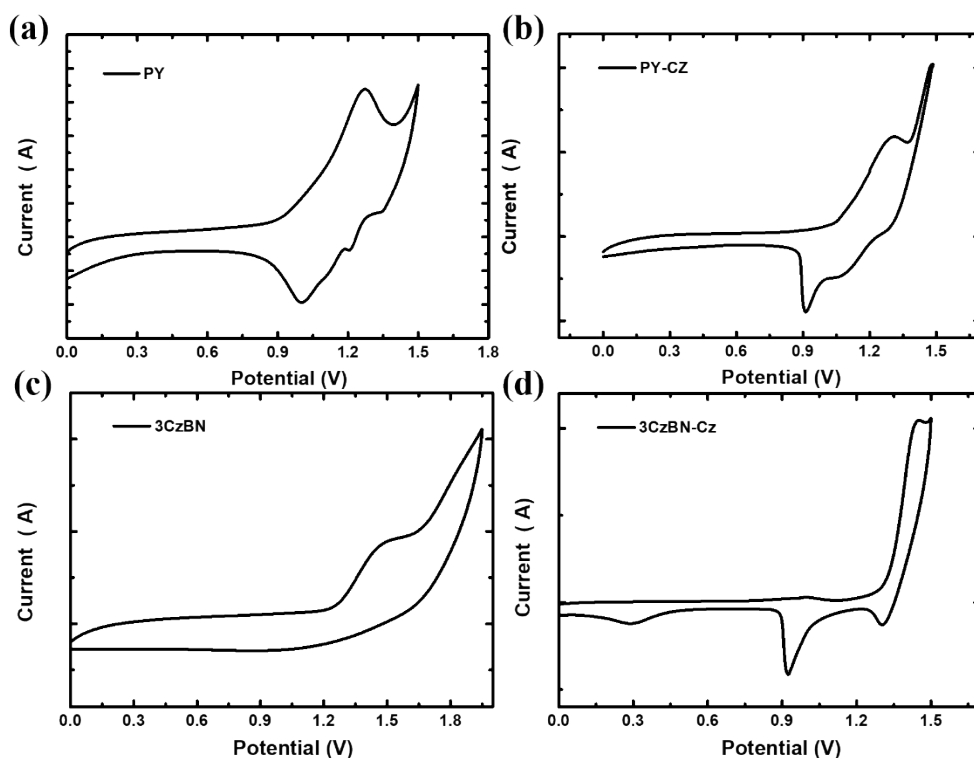


Figure S1. Cyclic voltammograms of PY (a), PY-Cz (b), 3CzBN (c) and 3CzBN-Cz (d) with a concentration of 10⁻³ in CH₂Cl₂ solution.

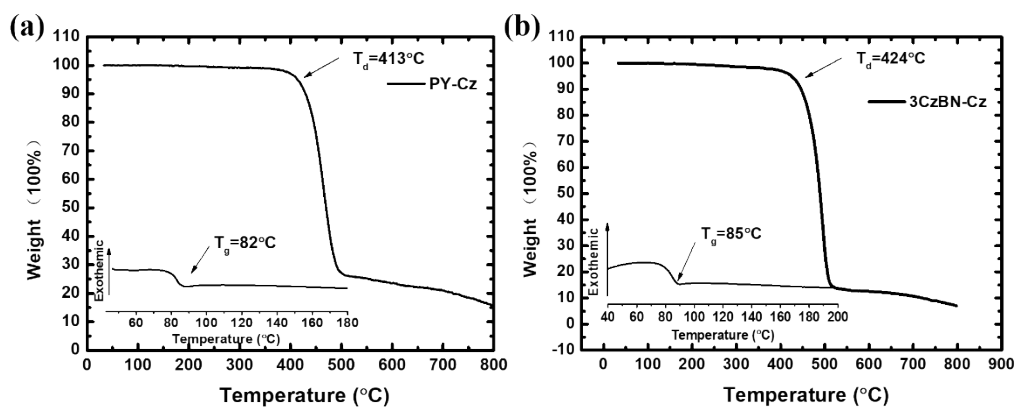
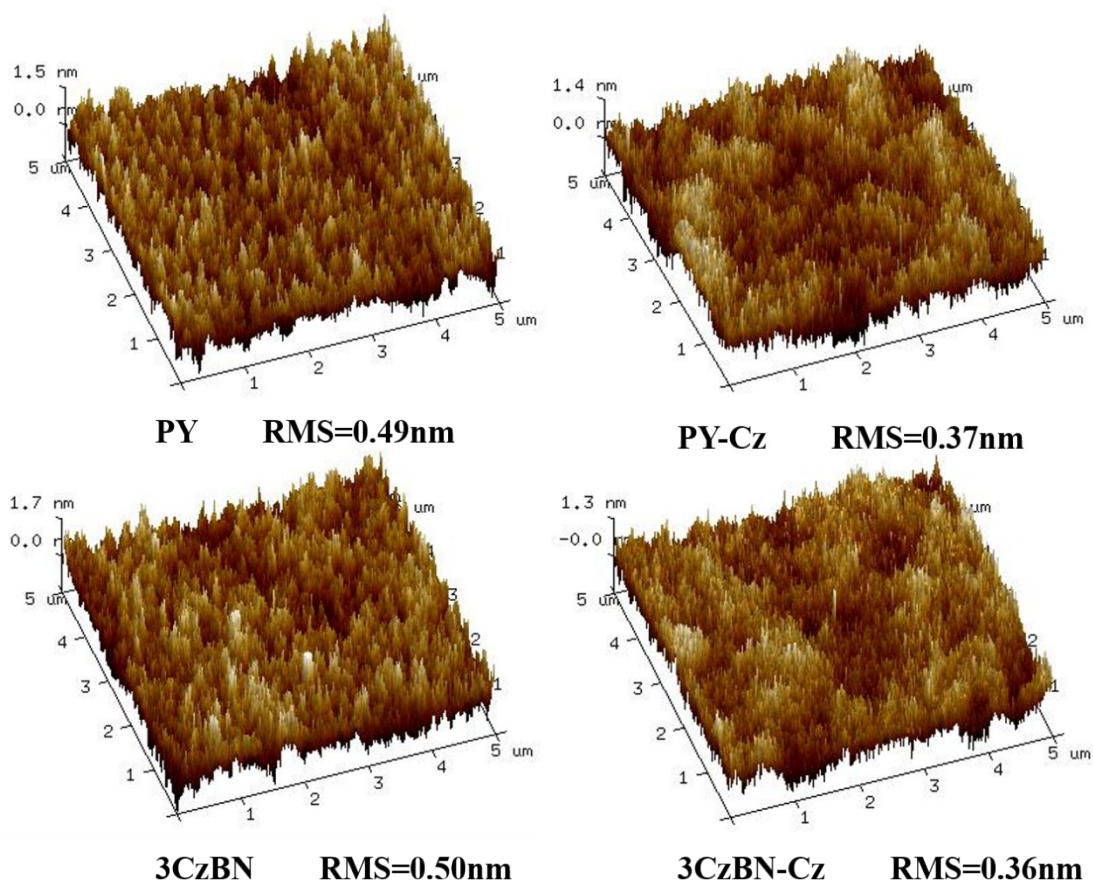
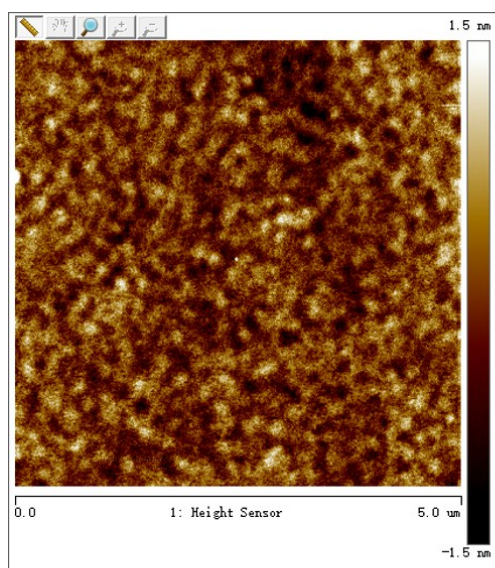
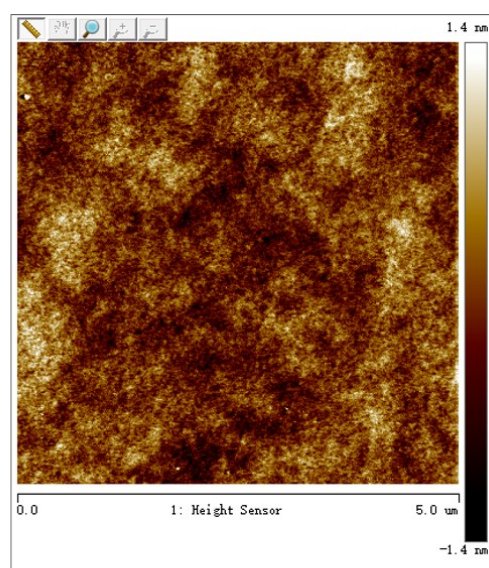


Figure S2. TGA curve of PY-Cz(a) and 3CzBN-Cz(b) recorded at a heating rate of $10^\circ\text{C min}^{-1}$; Inset: DSC curve at a heating rate of $10^\circ\text{C min}^{-1}$.

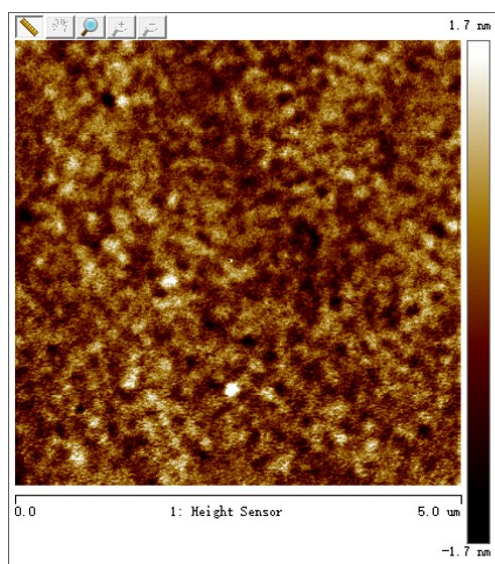




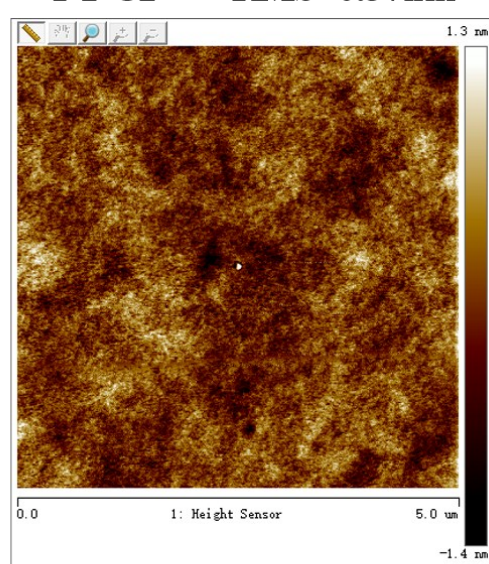
PY **RMS=0.49nm**



PY-Cz **RMS=0.37nm**



3CzBN **RMS=0.50nm**



3CzBN-Cz **RMS=0.36nm**

Figure S3. AFM topographic images of PY, PY-Cz, 3CzBN and 3CzBN-Cz.

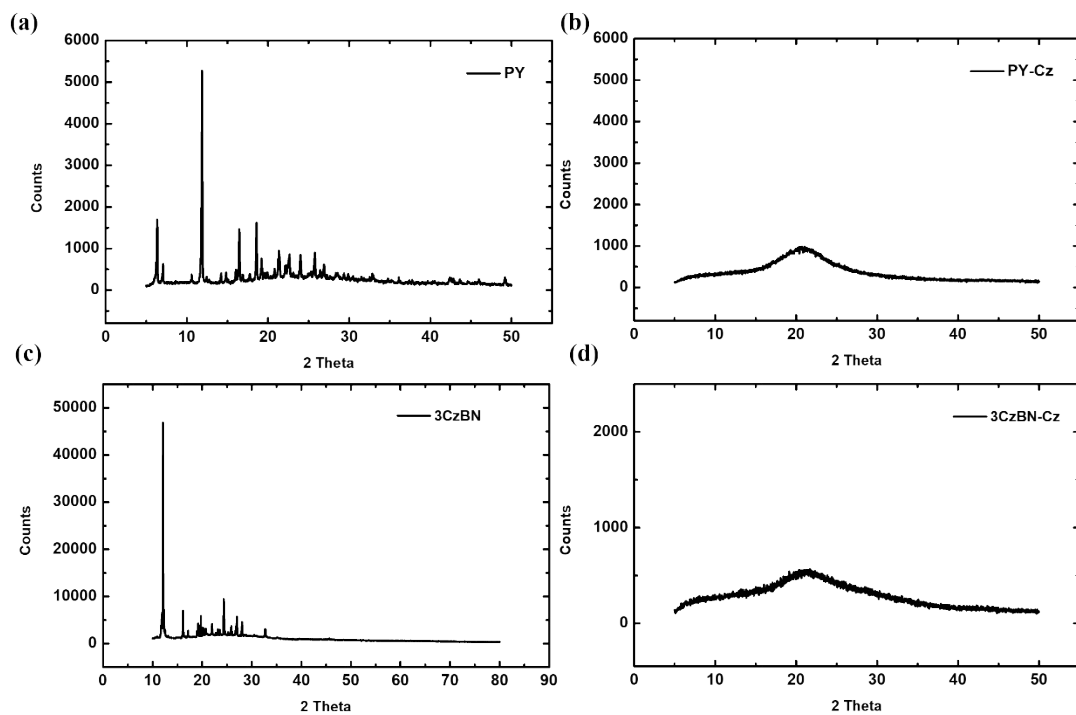


Figure S4. The XRD spectra of solid state PY (a), PY-Cz (b), 3CzBN (c) and 3CzBN-Cz (d).

Table S1. Calculated HOMO, LUMO, Bandgap, S_1 , T_1 , ΔE_{st} , f values of PY, PY-Cz, 3CzBN and 3CzBN-Cz from DFT and TD-DFT at B3LYP/6-31g(d) level.

Emitters	HOMO[eV]	LUMO[eV]	Bandgap	S_1 [eV]	T_1 [eV]	ΔE_{st}
PY	-4.74	-1.48	3.26	3.03	1.87	1.16
PY-Cz	-4.76	-1.52	3.24	3.00	1.86	1.14
3CzBN	-5.65	-1.92	3.73	3.09	2.78	0.31
3CzBN-Cz	-5.34	-1.98	3.36	3.02	2.81	0.21

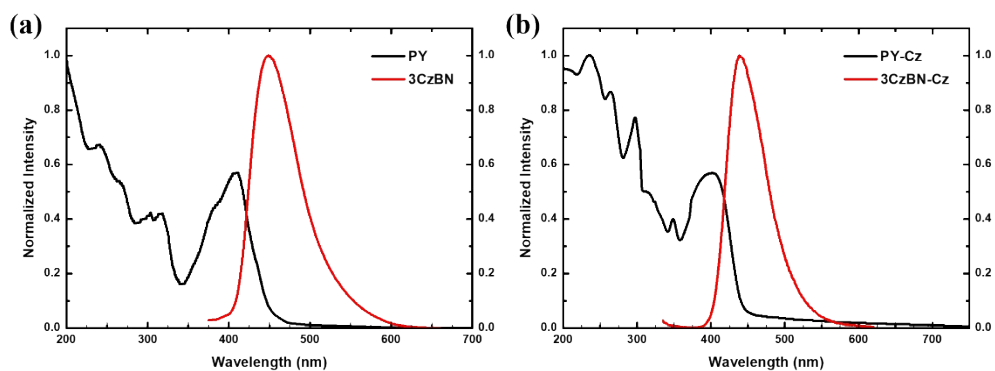


Figure S5. (a) The absorption spectra of solid state PY and the fluorescence spectra of 3CzBN. (b) The absorption spectra of solid state PY-Cz and the fluorescence spectra of 3CzBN-Cz.

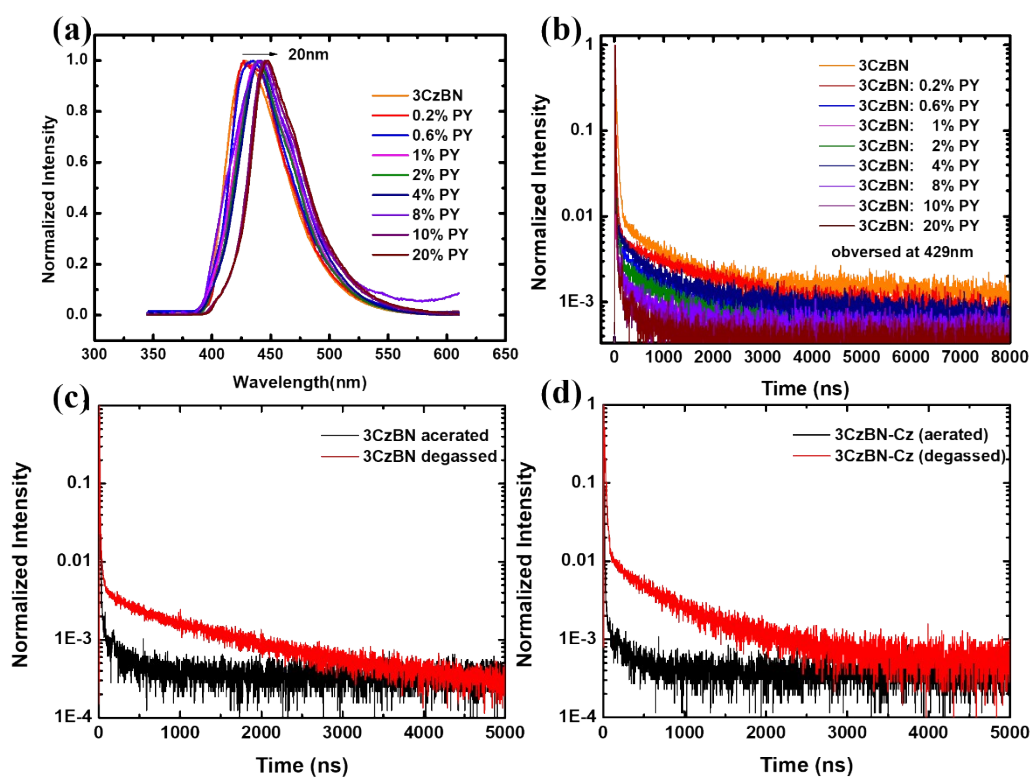


Figure S6. (a) The PL spectra of the 3CzBN:PY films. (b) The transient PL decay curves of the 3CzBN:PY films observed at 429 nm, (c) Transient PL characteristics of 3CzBN in toluene (10^{-5} M) under the aerated and degassed conditions at room temperature, and (d) Transient PL characteristics of 3CzBN-Cz under the aerated and degassed conditions.

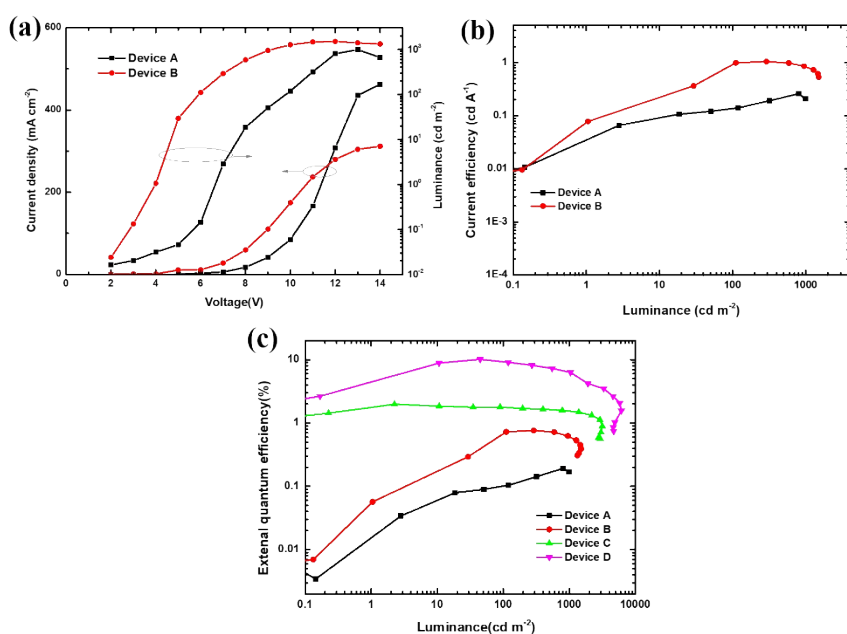


Figure S7. (a) Current density-voltage-luminance (J-V-L) characteristics; (d) Current efficiencies versus luminance plots; (c) The external quantum efficiencies versus luminance plots of Device A-D.

Table 2. Photophysical characteristic and kinetic parameters of 5CzBN derivatives.²³⁻

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Materials	$\phi_{\text{PL}}(\%)$		$\tau_{\text{p}}(\text{ns})$	$\tau_{\text{d}}(\mu\text{s})$	$k_{\text{r}}^{\text{b)}$	$k_{\text{nr}}^{\text{b)}$	$k_{\text{F}}^{\text{c)}$	$k_{\text{IC}}^{\text{c)}$	$k_{\text{ISC}}^{\text{c)}$	$k_{\text{RISC}}^{\text{c)}$
	Solv ^{a)}	Film	R_{p}	R_{d}	$[10^5 \text{ s}^{-1}]$	$[10^5 \text{ s}^{-1}]$	$[10^6 \text{ s}^{-1}]$	$[10^6 \text{ s}^{-1}]$	$[10^7 \text{ s}^{-1}]$	$[10^6 \text{ s}^{-1}]$
PY	20/73	32	6.9,	-			7.9	17.0		
PY-Cz	25/85	86	6.3,	-			14.1	2.3		
3CzBN	18/69	45	7.2, 28.7%	1.8,	2.6	2.9	18.7	21.1	9.9	1.9
				71.3%						
3CzBN-Cz	26/89	63	14.5, 11.5%	2.3,	2.7	1.6	5.0	2.9	6.1	3.8
				88.5%						

a) Measured in toluene at 300K and before (left) and after (right) N_2 bubbling. b) Calculated radiative decay rate k_{r} and nonradiative decay rate k_{nr} according to the equations: $\tau=1/(k_{\text{r}}+k_{\text{nr}})$, and $\phi_{\text{PL}}=k_{\text{r}}/(k_{\text{r}}+k_{\text{nr}})$. where τ is the total lifetimes of the transient and the delayed components, ϕ_{PL} is the PLQY of films. c) Calculated fluorescence decay rate k_{F} , internal conversion decay rate k_{IC} , intersystem crossing decay rate k_{ISC} from S_1 to S_0 and the rate constant of reverse intersystem crossing process k_{RISC} .

