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Electronic Supplementary Information

Efficient triplet harvesting in fluorescence-TADF hybrid warm-white organic light-emitting diodes with a fully non-doped device configuration

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1. Experimental Section

1.1 General Methods

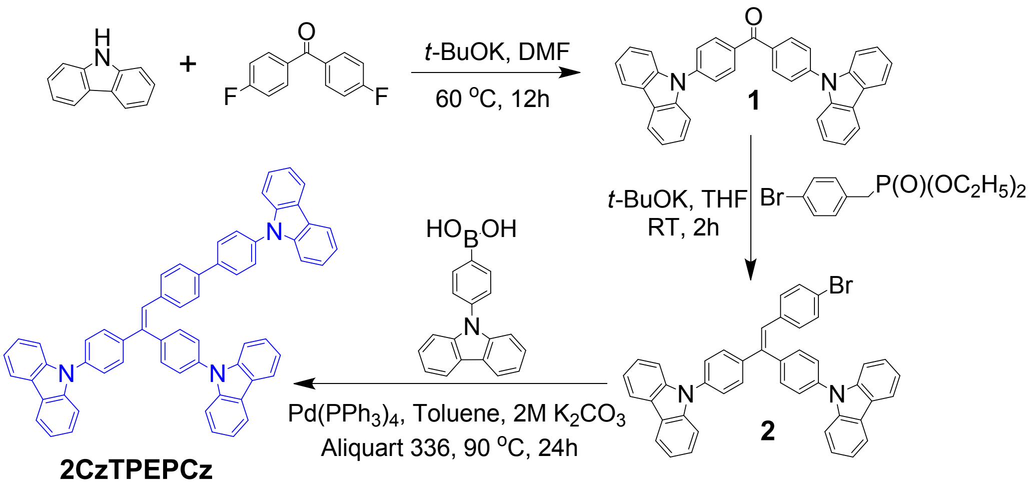
Hydrogen (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured using a Bruker AvanceIII 500HD spectrometer, with deuterated dimethylsulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as an internal reference. Electron impact-mass spectra (EI-MS) and high resolution mass spectra (HRMS) were collected from Thermo DSQ spectrometer and Thermo MAT95XP spectrometer, respectively. Differential scanning calorimetry (DSC) was performed using a NETZSCH DSC 204 F1 thermal analyzer. Ultraviolet photoelectron spectroscopy (UPS) measurements of the compounds in solid-state films were carried out by ThermoFisher Scientific Inc. ESCALAB 250Xi to determine the highest occupied molecular orbital (HOMO) energy levels. The time-resolved phosphorescence spectra of the films were performed using a Horiba PL spectrometer (Fluorolog-3). Photoluminescence (PL) spectra and UV-vis absorption spectra were measured using a Shimadzu RF-5301PC spectrometer and a Hitachi U-3900 spectrophotometer, respectively. Transient PL decay characteristics were recorded on a Quantaurus-Tau system equipped with Oxford Optistat DN.

1.2 Devices Fabrication and Characterization

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 8 Ω sq^{-1} were used as the anode and ultrasonically cleaned prior to device fabrication. Subsequently, PEDOT:PSS was spin-coated on the cleaned ITO at a speed of 2000 rpm for 60 seconds, and thermally annealed for 15 minutes at 200 °C under atmospheric environment. Then, the PEDOT:PSS coated ITO substrates were transferred to a thermal evaporation chamber. Finally, the organic layers and alloy metals were sequentially deposited under vacuum pressure of 4×10^{-4} Pa, resulting in an active area of 20 mm^2. The current density−voltage−luminance characteristics and EL spectra of the OLEDs were measured using a Keithley 2400 source combined with a Photo Research PR705 spectrometer under room temperature, while the EQEs were calculated using a computer program based on previously reported theory.[1]

1.3 Materials

Carbazole and [4-(9H-carbazol-9-yl)phenyl]boronic acid were purchased from Sukailu company. Potassium *tert*-butoxide (*t*-BuOK) was purchased from Alfa Aesar. Diethyl-4-bromobenzylphosphonate was purchased from J&K Chemical. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), 4,4'-bis(9H-carbazol-9-yl)biphenyl (CBP) and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) were used as purchased from Xi'an Polymer Light Technology Co. Ltd. The other reagents and all solvents were purchased from Aladdin or Guangzhou Chemical Reagent Factory. All chemicals and solvents were used as received without any purification. The yellow TADF material **OPDPO** was reported in our previous work.[2] Scheme S1 shows the synthetic route for **2CzTPEPCz**, wherein compound **1** and compound **2** were synthesized according to our previous procedures.[3]



Scheme S1. Synthetic route for 2CzTPEPCz.

Synthesis of 2CzTPEPCz

A 2.0 M aqueous K_2CO_3 solution (3.0 mL) was added to a toluene solution (20 mL) containing compound **2** (1.33 g, 2.0 mmol) and [4-(9H-carbazol-9-yl)phenyl]boronic acid (0.58 g, 2.0 mmol) and stirred for 30 mins under an argon atmosphere. Then, $Pd(PPh_3)_4$ catalyst (0.05 g) was added to the reaction mixture and stirred at 90 °C for 24 h. After cooling down to room temperature, the product was extracted with dichloromethane/water. The organic layers were collected, dried over Na_2SO_4, concentrated using a rotary evaporator and purified by silica gel column chromatography (dichloromethane/n-hexane, gradient elution from 1:5 to 1:1 v/v) to yield 1.39 g white powder (84% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.26 (dd, J = 12.4, 5.1, 6H), 7.97 (d, J = 8.3, 2H), 7.78 (t, J = 7.3, 4H), 7.71 (dd, J = 16.5, 8.1, 6H), 7.62 (d, J = 8.1, 2H), 7.56 – 7.40 (m, 13H), 7.37 – 7.26 (m, 8H). ^{13}C NMR (125 MHz, deuterated chloroform ($CDCl_3$)) δ = 141.87, 141.38, 140.86, 140.79, 140.76, 139.51, 139.21, 138.89, 137.37, 137.29, 137.05, 136.56, 132.09, 130.36, 129.04, 128.97, 128.29, 127.45, 127.40, 126.89, 126.83, 126.06, 123.60, 123.56, 123.50, 120.50, 120.43, 120.40, 120.19, 120.15, 120.07, 110.04, 109.91, 109.86, 109.83. HRMS, *m/z*: $[M]^+$ 827.3291; calcd. for $C_{62}H_{41}N_3$, 827.3295. Anal. Calcd. for $C_{62}H_{41}N_3$: C 89.93%, H 4.99%, N 5.07%; found: C 89.90%, H 5.01%, N 5.03%.

References

[1] S. R. Forrest, D. D. C. Bradley, M. E. Thompson, *Adv. Mater*. **2003**, *15*, 1043.

[2] Z. G. Chi, Z. L. Xie, T. Yu, Q. Y. Huang, D. P. Ou, L. Y. Wang, Z. Mao, J. Q. Wang, Z. Y. Yang, Y. Zhang, S. W. Liu, J. R. Xu (Sun-Yat sen University), *CN201610914712.3*, **2016**.

[3] Z. Yang, Z. Chi, T. Yu, X. Zhang, M. Chen, B. Xu, S. Liu, Y. Zhang, J. Xu, *J. Mater. Chem*. **2009**, *19*, 5541.

2. Supplementary Tables and Figures

Table S1 Lifetime results of OPDPO fitted by a three-exponential decay model at different temperature.

Temperature [K]	τ_1 (A_1) [μs]$^{a)}$	τ_2 (A_2) [μs]$^{b)}$	τ_3 (A_3) [μs]$^{c)}$	τ [μs]$^{d)}$
77	0.15 (2.52%)	6.4 (27.85%)	52.2 (69.63%)	38.1
177	0.25 (6.64%)	3.8 (51.66%)	28.1 (41.71%)	13.7
300	0.13 (17.2%)	1.1 (70.54%)	18.4 (12.19%)	3.0

$^{a)}$prompt fluorescence lifetime component; $^{b)}$delayed fluorescence lifetime component; $^{c)}$phosphorescence lifetime component; $^{d)}$average lifetime. τ: lifetime; A: the proportion of lifetime component.

Table S2 Lifetime characteristics for the films.

Lifetime	Film Y	Film B	Film Stack	
	(OPDPO)	(2CzTPEPCz)	OPDPO	2CzTPEPCz
τ_1 [ns]	6.5	1.8	17.7	2.0
τ_2 [μs]	11.3	\	24.6	\

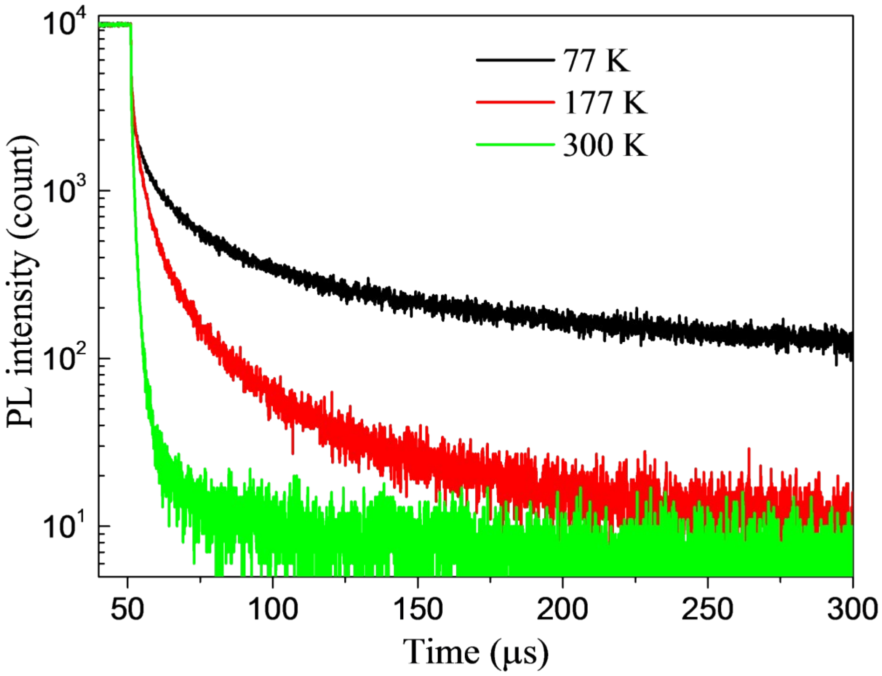


Fig. S1 Transient PL decay curves of OPDPO film carried out at 77, 177 and 300 K.

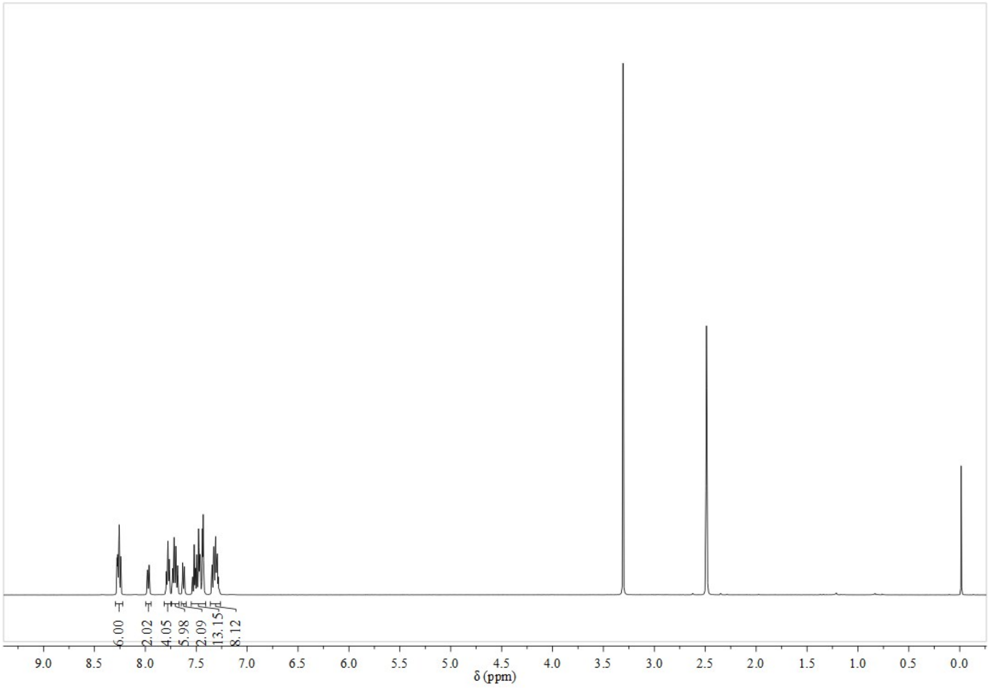


Fig. S2 ^{1}H NMR spectrum of 2CzTPEPCz.

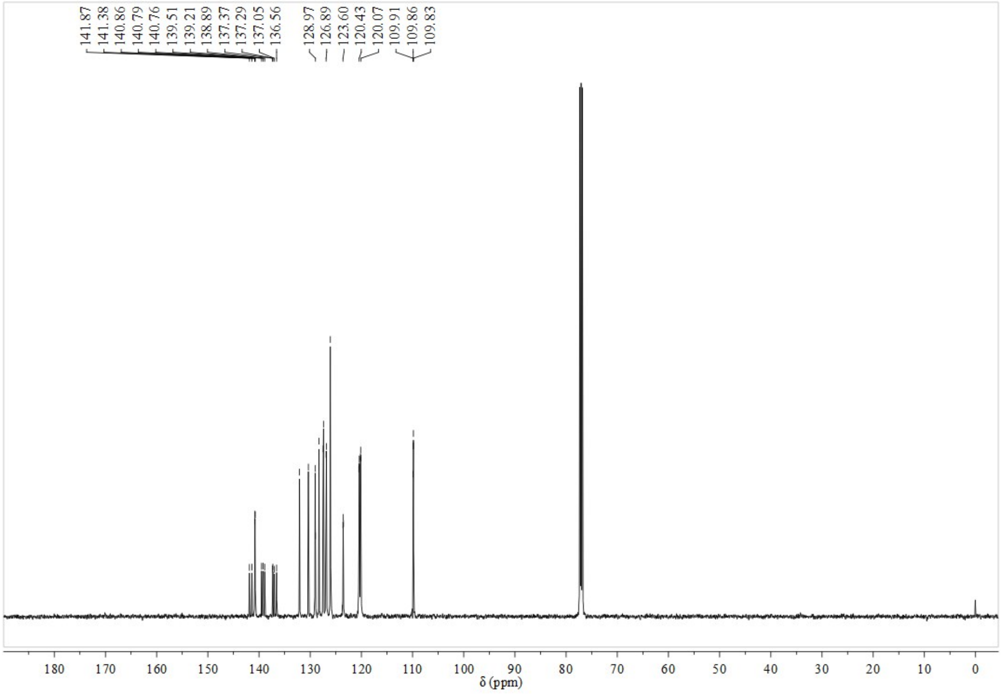


Fig. S3 ^{13}C NMR spectrum of 2CzTPEPCz.

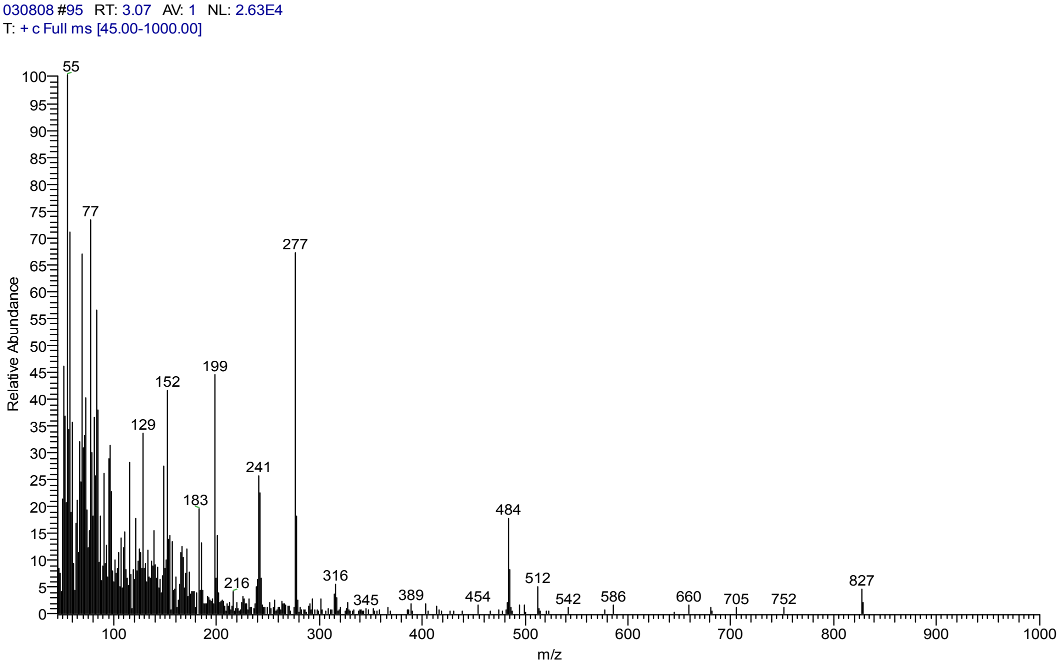
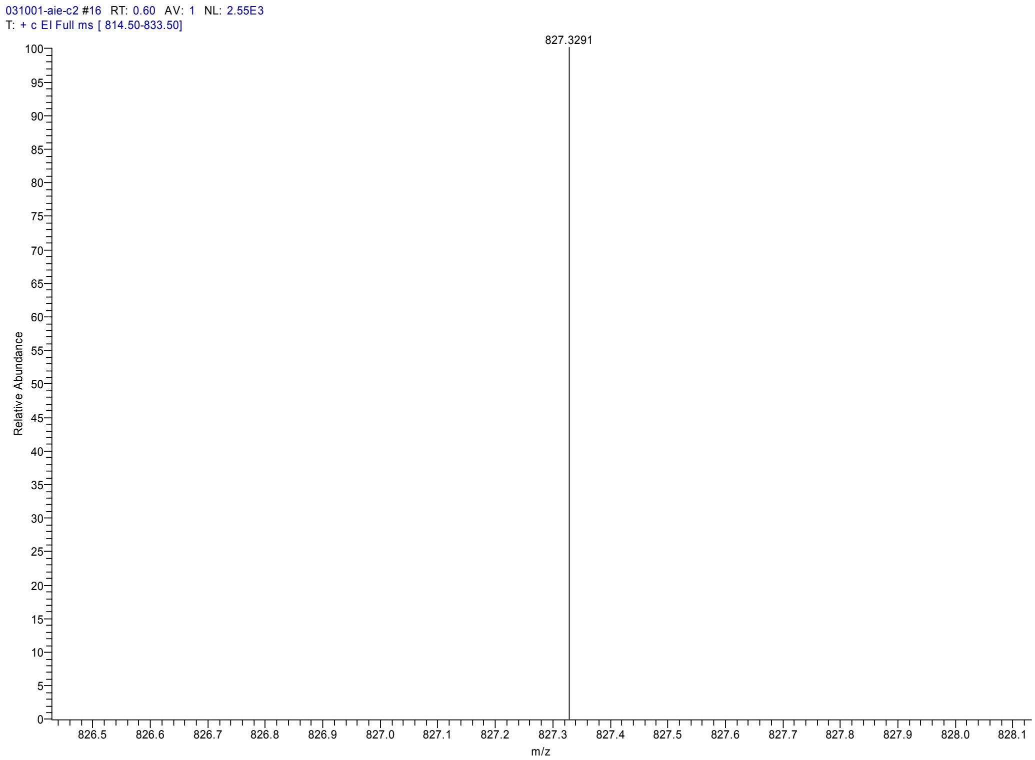


Fig. S4 EI-mass spectrum of 2CzTPEPCz.



Mass: 827.3291 Relative Intensity: 100.0 RDB: 44.0 Composition: C_{62} H_{41} N_3
Theoretical Mass: 827.3295 Delta [ppm]: -0.4 Delta [mmu]: -0.4

Fig. S5 High resolution mass spectrum of 2CzTPEPCz.

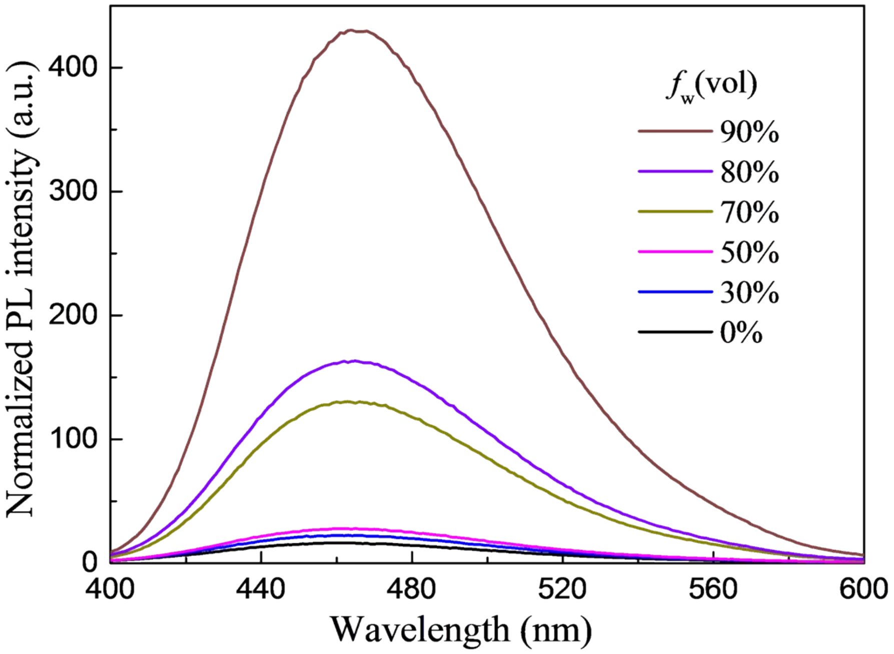


Fig. S6 PL spectra of blue fluorescent 2CzTPEPCz in THF/water mixtures with different water fractions f_w(vol).

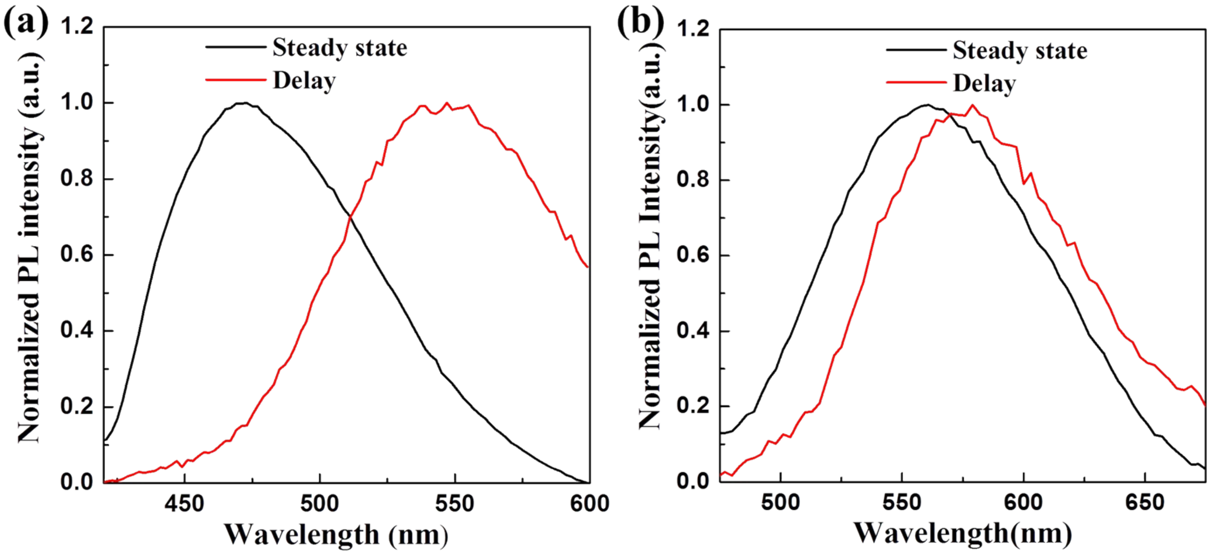


Fig. S7 Time-resolved PL spectra of (a) blue fluorescent 2CzTPEPCz film and (b) yellow TADF OPDPO film recorded at 11 K.

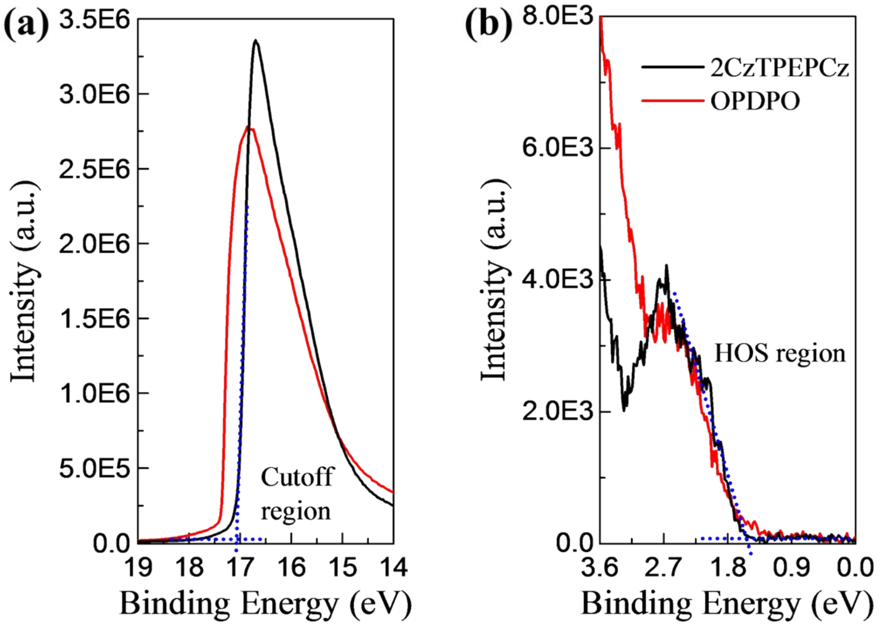


Fig. S8 Ultraviolet photoelectron spectroscopy (UPS) spectra of 2CzTPEPCz and OPDPO in (a) the cutoff regions and (b) the highest-occupied states regions. The dotted blue lines in (a) and (b) determine two energy points of 17.08 eV and 1.56 eV for 2CzTPEPCz, and thus the HOMO of 2CzTPEPCz can be determined by subtracting the energy separation by 21.22 eV and calculated to be 21.22 − (17.08 − 1.56) = 5.7 (eV). The HOMO of OPDPO is calculated to be 5.5 eV by using the same method.

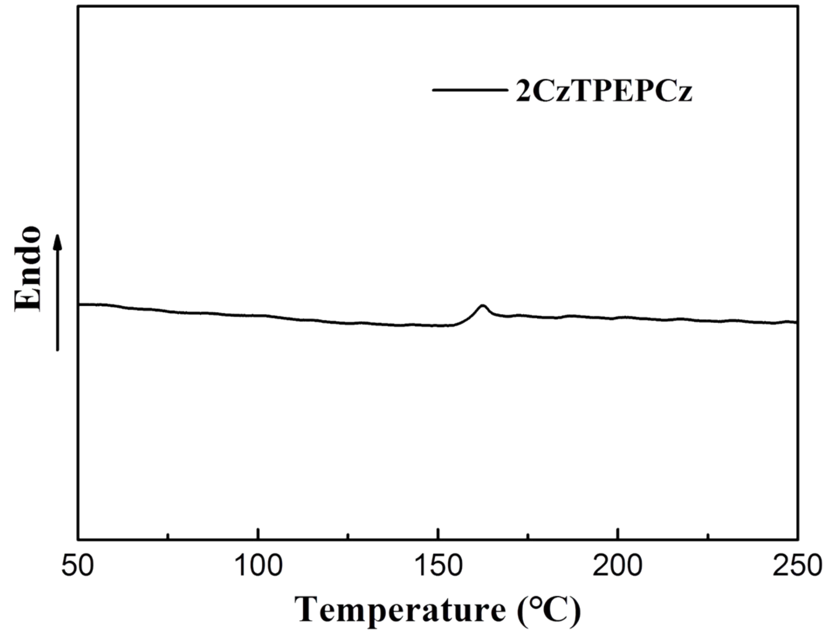


Fig. S9 Differential scanning calorimetry curve of blue fluorescent 2CzTPEPCz measured at the second heating cycle at a temperature rate of 10 K/min, under nitrogen atmosphere, showing the glass transition temperature (T_g).

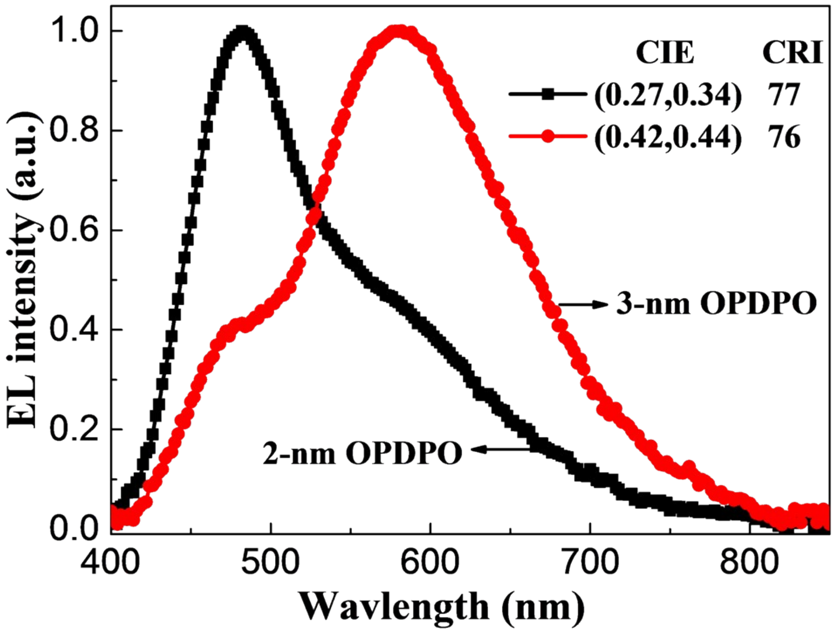


Fig. S10 EL spectra of the devices with different thickness of the OPDPO layer. The device configuration is: ITO/PEDOT:PSS(40 nm)/CBP(20 nm)/OPDPO(2 nm or 3 nm)/2CzTPEPCz (15 nm)/TPBI(40 nm)/Mg:Ag.

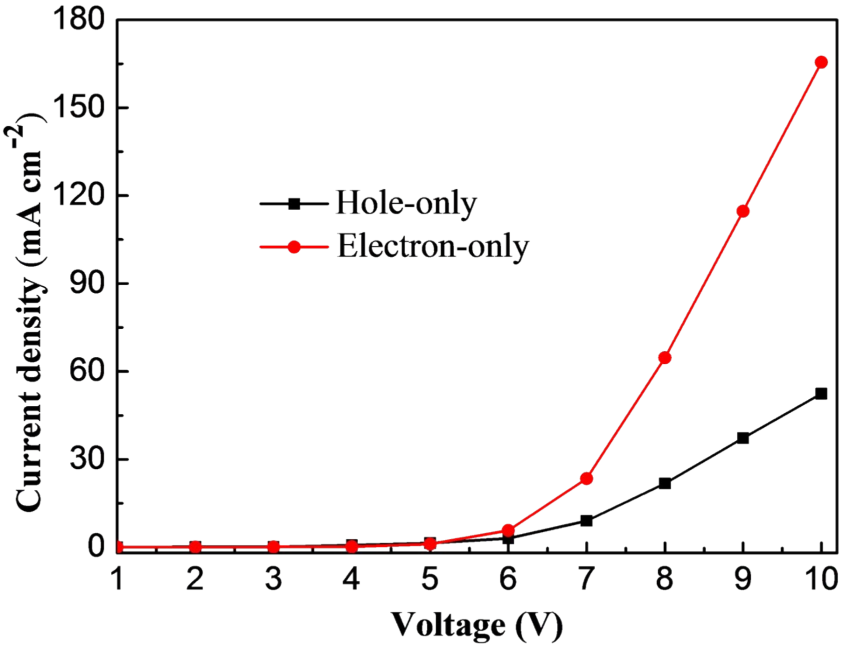


Fig. S11 Current density–voltage curves of the electron-only and hole-only devices. The hole-only device was: ITO/PEDOT:PSS(40 nm)/CBP(20 nm)/OPDPO(4 nm)/2CzTPEPCz(15 nm)/CBP(20 nm)/Ag, while the electron-only device was: ITO/TPBI(40 nm)/OPDPO(4 nm)/2CzTPEPCz(15 nm)/TPBI(40 nm)/Mg:Ag.

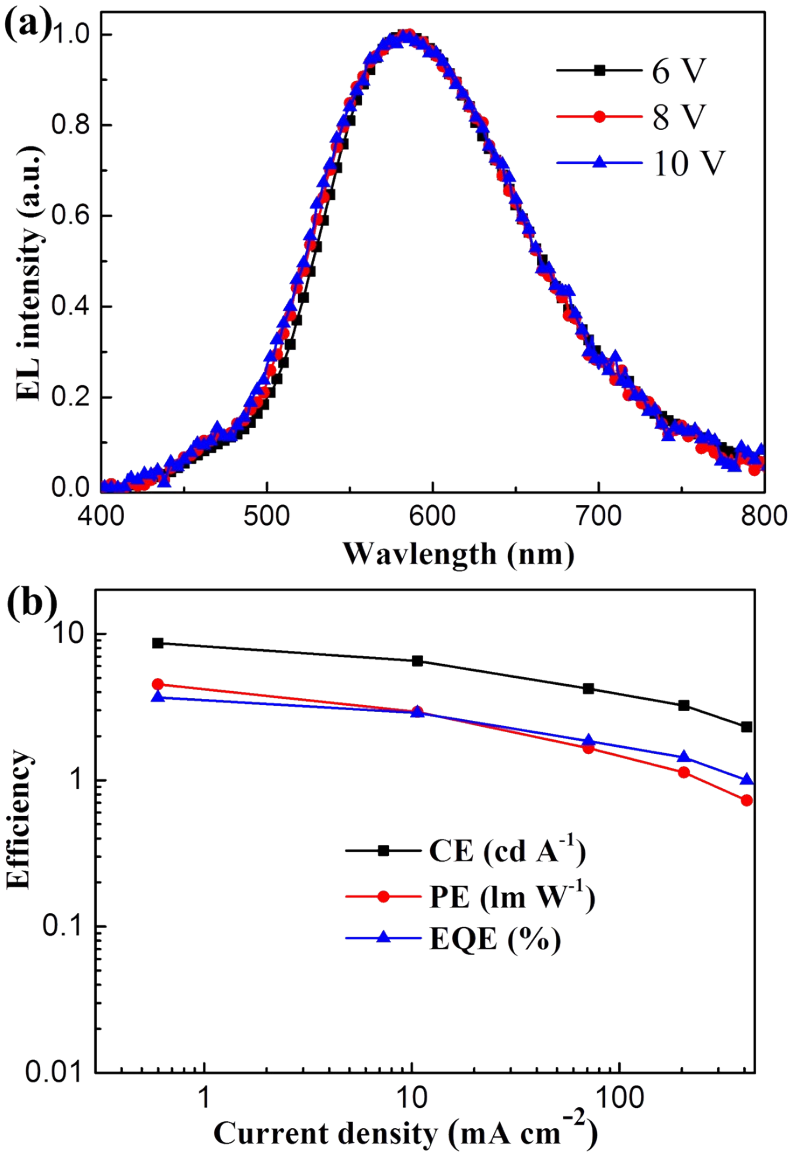


Fig. S12 (a) Normalized EL spectra and (b) EL performance of device S fabricated with a configuration of ITO/PEDOT:PSS(40 nm)/CBP(20 nm)/2CzTPEPCz (15 nm)/OPDPO(4 nm)/TPBI(40 nm)/Mg:Ag.

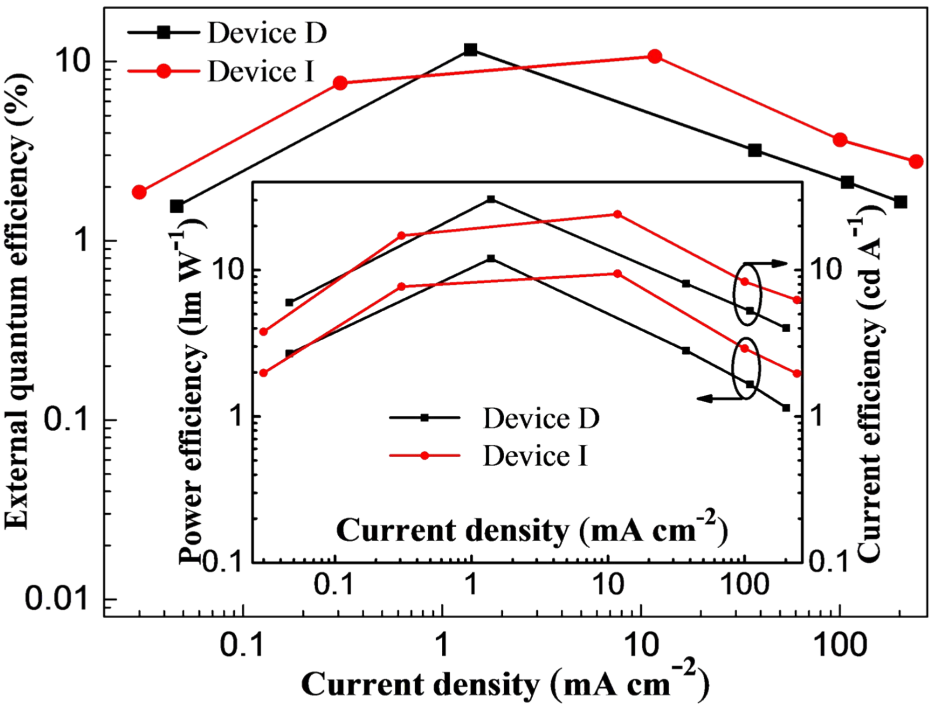


Fig. S13 External quantum efficiency–current density curves of devices D and I. Inset: power efficiency–current efficiency–current density curves.