

*Supporting information:*

**A Universal Thermally Activated Delayed Fluorescence Host with Short Triplet Lifetime for Highly Efficient Phosphorescent OLEDs with Extremely Low Efficiency Roll-off**

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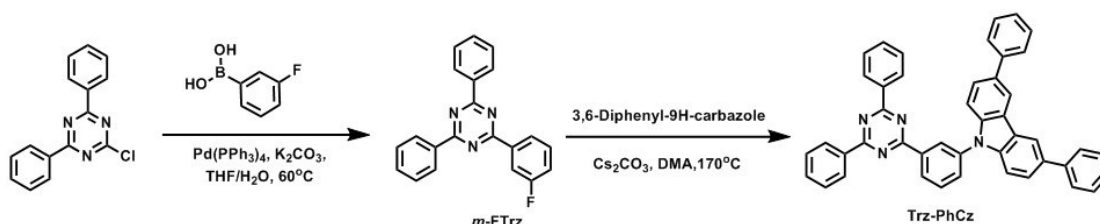
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## General Information

All reactions were performed under nitrogen atmosphere unless otherwise stated. Dry tetrahydrofuran (THF) and toluene (Tol) were purified by PURE SOLV (Innovative Technology) purification system.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in chloroform-*d* ( $\text{CDCl}_3$ ) on a Bruker 400 MHz and Agilent DD2-600 MHz NMR spectrometer at room temperature. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a Bruker ultraflextreme MALDI-TOF spectrometer. UV-vis absorption spectra were recorded on Cary 60 spectrometer (Agilent Technologies). PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of  $5^\circ\text{C min}^{-1}$  under nitrogen. The glass transition temperatures ( $T_g$ ) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of  $5^\circ\text{C min}^{-1}$  under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature ( $T_d$ ). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene ( $\text{Fc}^+/\text{Fc}$ ) as the external standard. The oxidative scans were performed using 0.1 M *n*- $\text{Bu}_4\text{NPF}_6$  ( $\text{TBAPF}_6$ ) in deoxygenated with nitrogen dichloromethane as the supporting electrolyte. A conventional three-electrode configuration consisting of a Pt-wire counter electrode, an Ag/AgCl reference electrode, and a Glassy-Carbon working electrode was used. The cyclic voltammograms were obtained at a scan rate of  $0.1 \text{ V s}^{-1}$ .



Scheme S1. Molecule structures and design strategy of host materials.

### Synthesis and characterization

#### 2-(3-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (*m*-FTrz):

A mixture of (3-fluorophenyl)boronic acid (1.20 g, 8.57 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (1.90 g, 7.14 mmol), potassium carbonate (1.96 g, 14.25 mmol) and tetrakis(triphenylphosphine)palladium (0.400 g, 0.35 mmol) in 75 mL hydrofuran and 15 mL water under nitrogen was refluxed for 12 h. After cooling down to room temperature, the product was extracted with dichloromethane ( $3 \times 50$  mL) and washed with water. The combined organic phase was dried over anhydrous sodium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 1: 5 dichloromethane/ petroleum as eluent to afford a white solid (3.02 g, 83%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (d,  $J = 7.3$  Hz, 4H), 8.57 (d,  $J = 7.7$  Hz, 1H), 8.46 (d,  $J = 10.0$  Hz, 1H), 7.63 (t,  $J = 7.2$  Hz, 2H), 7.59 (t,  $J = 7.4$  Hz, 4H), 7.55 (d,  $J = 5.8$  Hz, 1H), 7.31 (t,  $J = 6.9$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  171.76, 170.56, 163.93, 162.30, 138.68, 138.63, 135.95, 132.67, 130.16, 130.11, 128.97, 128.67, 124.59, 119.43, 119.29, 115.74, 115.59. MALDI-TOF-MS  $m/z$ :  $[\text{M}]^+$  calcd. for  $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{N}$ , 328.12, found, 328.14.

#### 9-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-3,6-diphenyl-9H-carbazole (Trz-PhCz):

Under nitrogen atmosphere 3,6-diphenyl-9H-carbazole (0.59 g, 1.84 mmol) was added to a two necked round bottom flask equipped with a reflux condenser. Addition of cesium carbonate (1.00g, 3.06 mmol) followed by DMA (50 mL) resulted in a suspension, which was stirred for 30 min at room temperature. Afterwards, 2-(3-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (0.50 g, 1.53 mmol) was poured in all in once and reaction mixture was stirred at 170°C for 48 hours. The black mixture was diluted with water and crude product was extracted with dichloromethane ( $3 \times 50$  mL). Organic phases were dried over anhydrous sodium sulfate and solvent was removed

under reduce pressure. Trz-PhCz (0.67 g, 70%) was isolated as yellow solid after purification by column chromatography on silica gel using 1: 5 dichloromethane/petroleum as eluent.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.04 (s, 1H), 8.91 (t,  $J = 3.7$  Hz, 1H), 8.78 (d,  $J = 7.1$  Hz, 4H), 8.46 (d,  $J = 1.5$  Hz, 2H), 7.85 (dd,  $J = 3.8, 2.0$  Hz, 2H), 7.77 (d,  $J = 7.2$  Hz, 4H), 7.72 (dd,  $J = 8.5, 1.7$  Hz, 2H), 7.62 (t,  $J = 7.3$  Hz, 2H), 7.58 – 7.55 (m, 6H), 7.51 (t,  $J = 7.7$  Hz, 4H), 7.38 (t,  $J = 7.4$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  171.82, 170.83, 141.81, 140.81, 138.51, 138.12, 135.90, 133.78, 132.68, 130.89, 130.29, 129.00, 128.80, 128.66, 128.10, 127.44, 127.31, 126.64, 125.83, 124.10, 118.91, 110.14. MALDI-TOF-MS  $m/z$ :  $[\text{M}]^+$  calcd. for  $\text{C}_{45}\text{H}_{30}\text{N}_4$ , 626.25, found, 626.39.

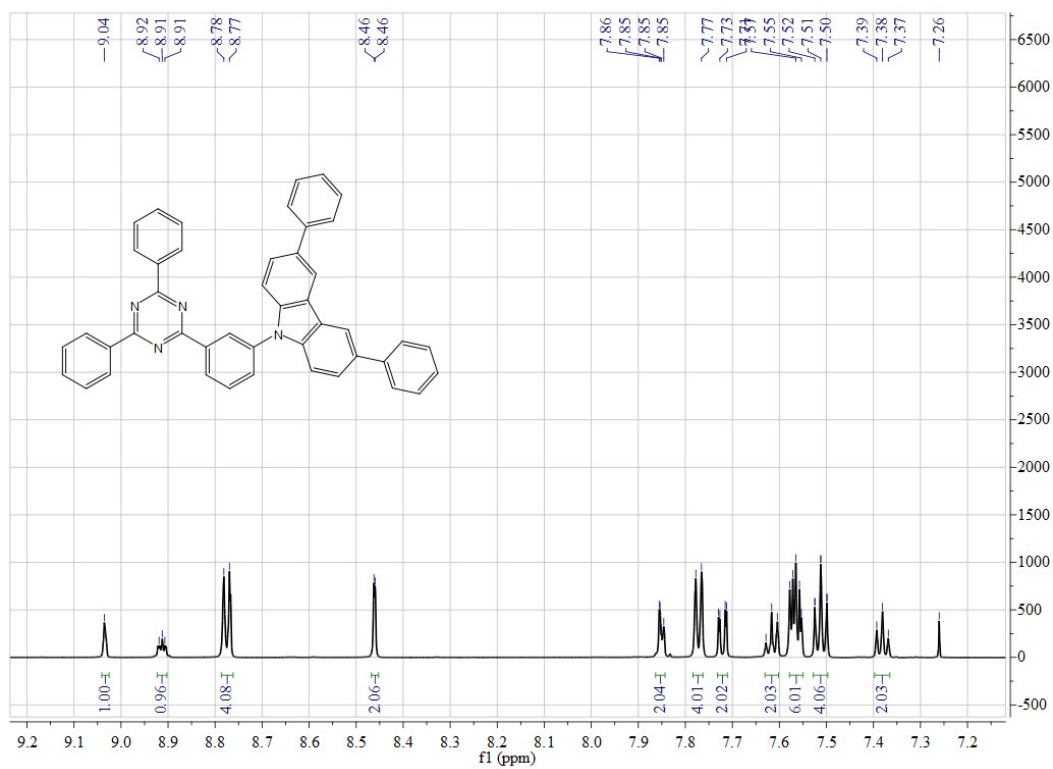


Fig. S1.  $^1\text{H}$  NMR spectrum of **Trz-PhCz** ( $\text{CDCl}_3$ ).

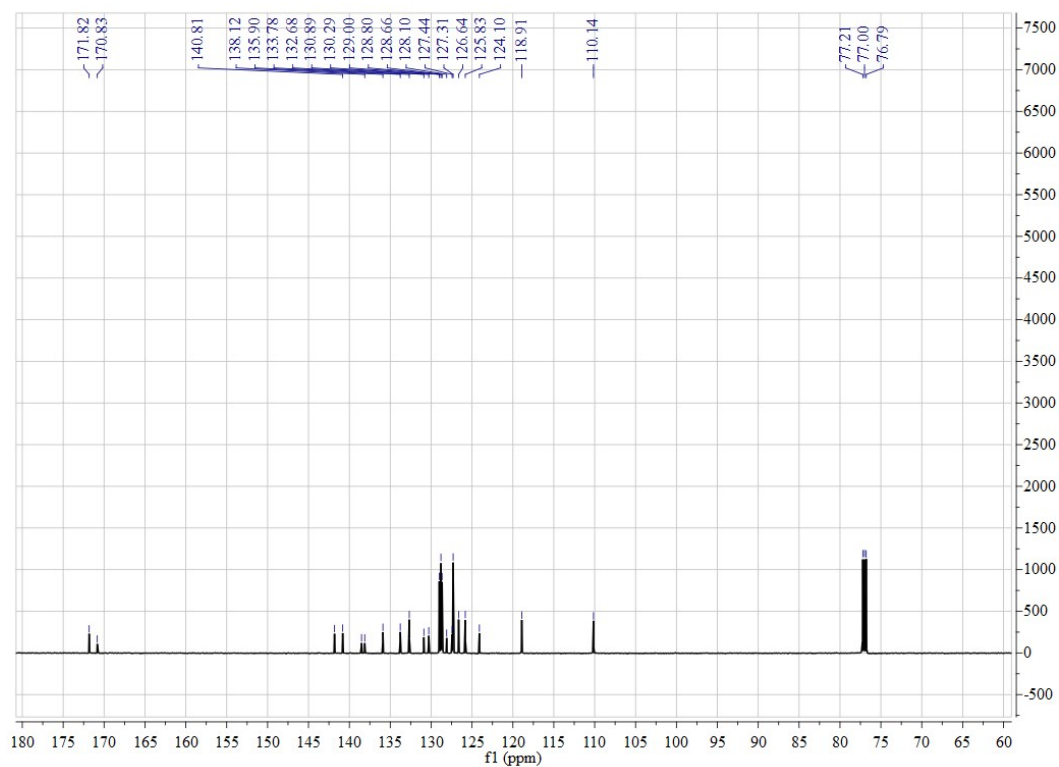


Fig. S2.  $^{13}\text{C}$  NMR spectrum of **Trz-PhCz** ( $\text{CDCl}_3$ ).

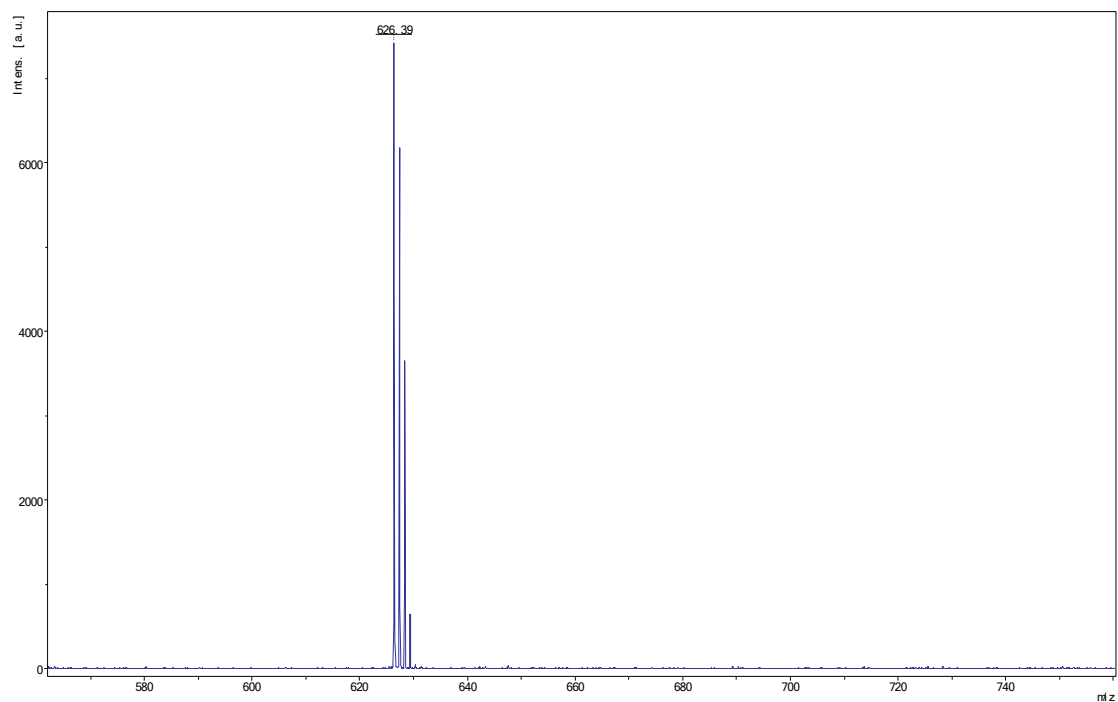


Fig. S3. MALDI-TOF-MS spectrum of **Trz-PhCz**.

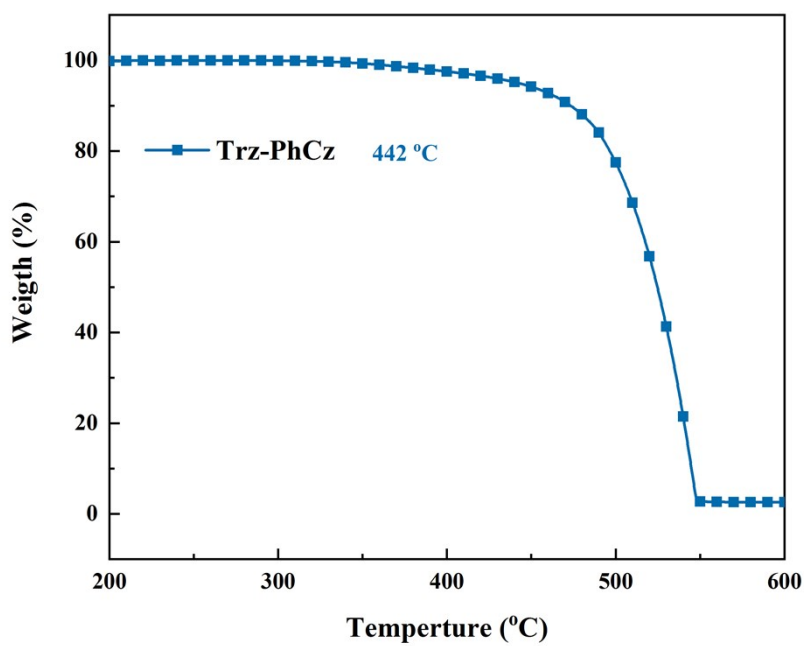


Fig. S4. Thermogravimetric analysis (TGA) curve of **Trz-PhCz**.

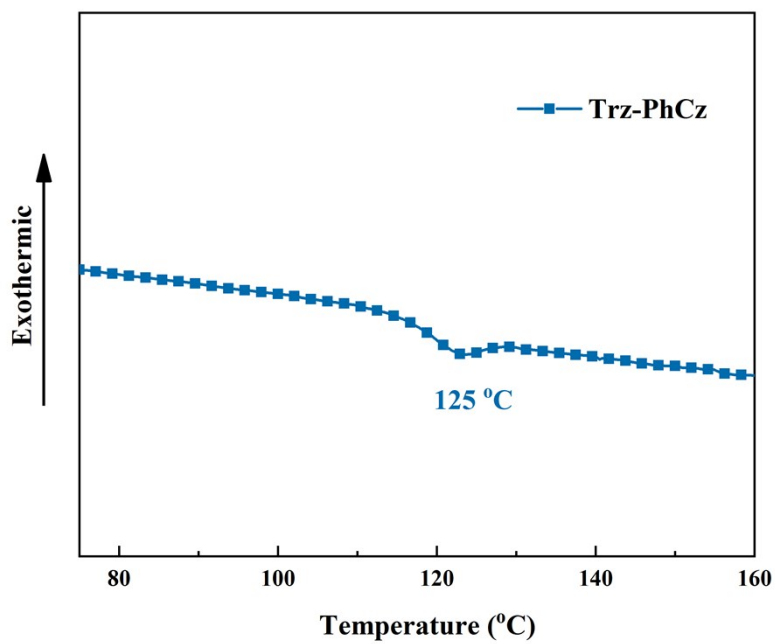


Fig. S5. Differential scanning calorimetry (DSC) curve of **Trz-PhCz**.

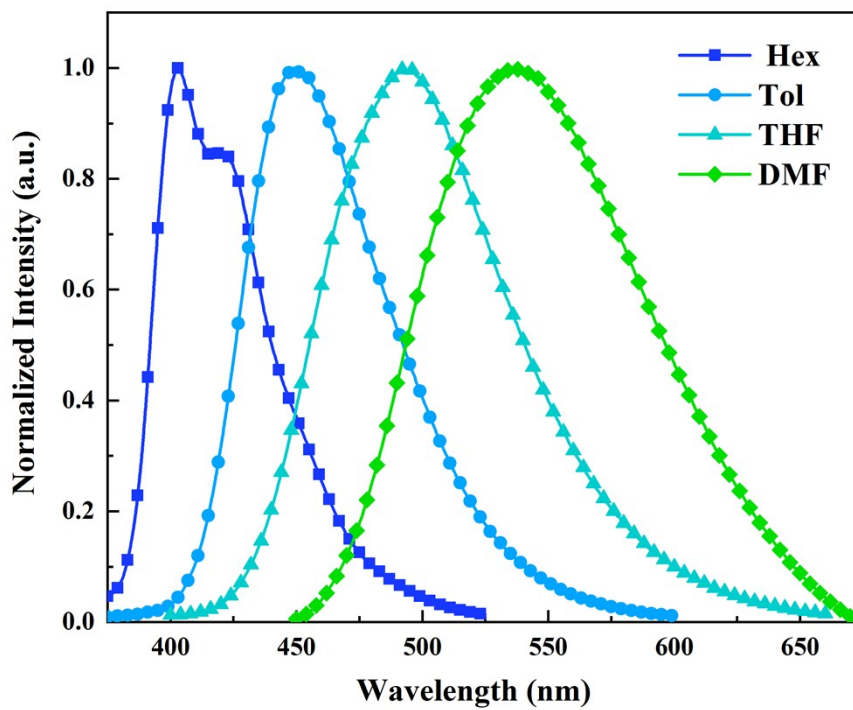


Fig. S6. Fluorescence spectra of **Trz-PhCz** in various solvents at room temperature.

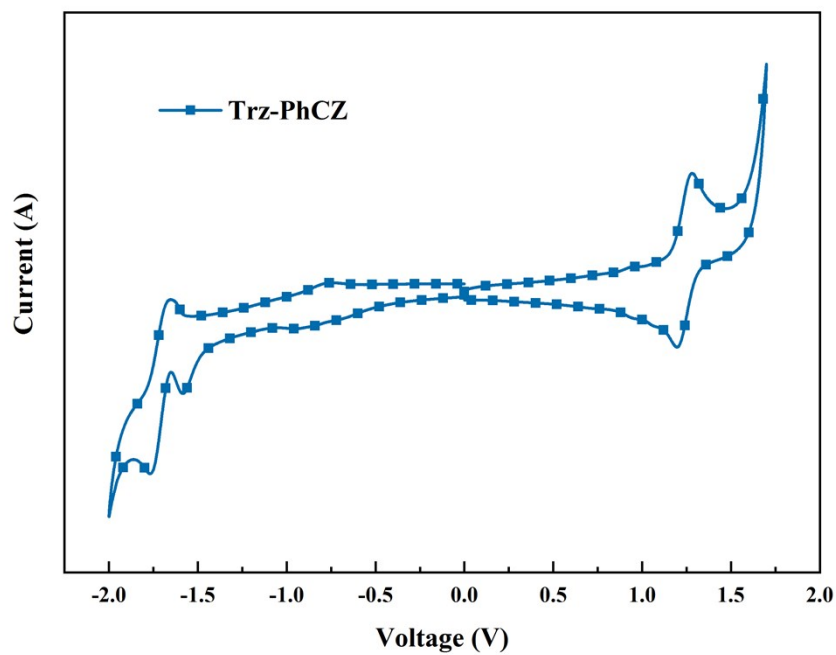


Fig. S7. Cyclic voltammogram curve of **Trz-PhCz**.

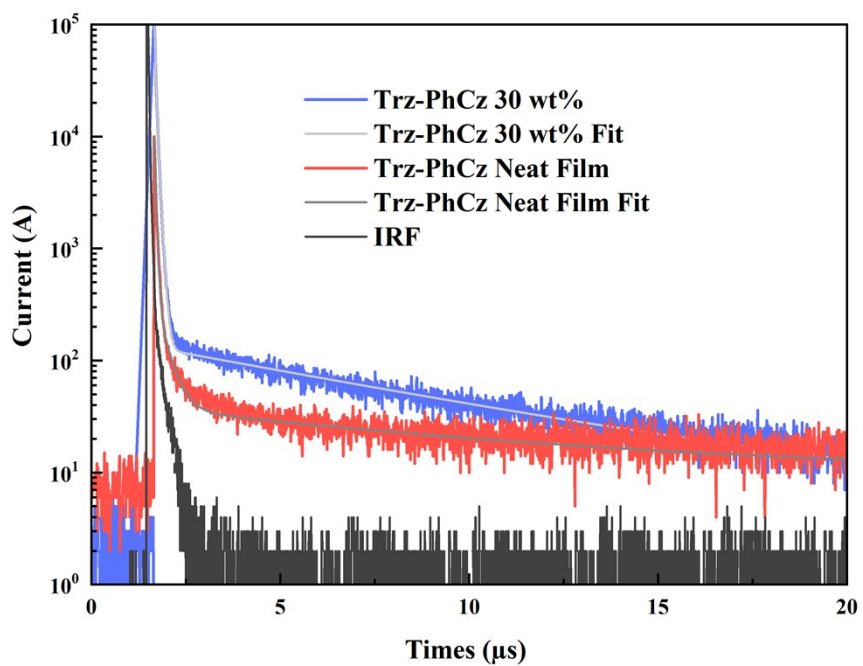


Fig. S8. Transient PL decay in Trz-PhCz 30 wt% film and neat film at room temperature.



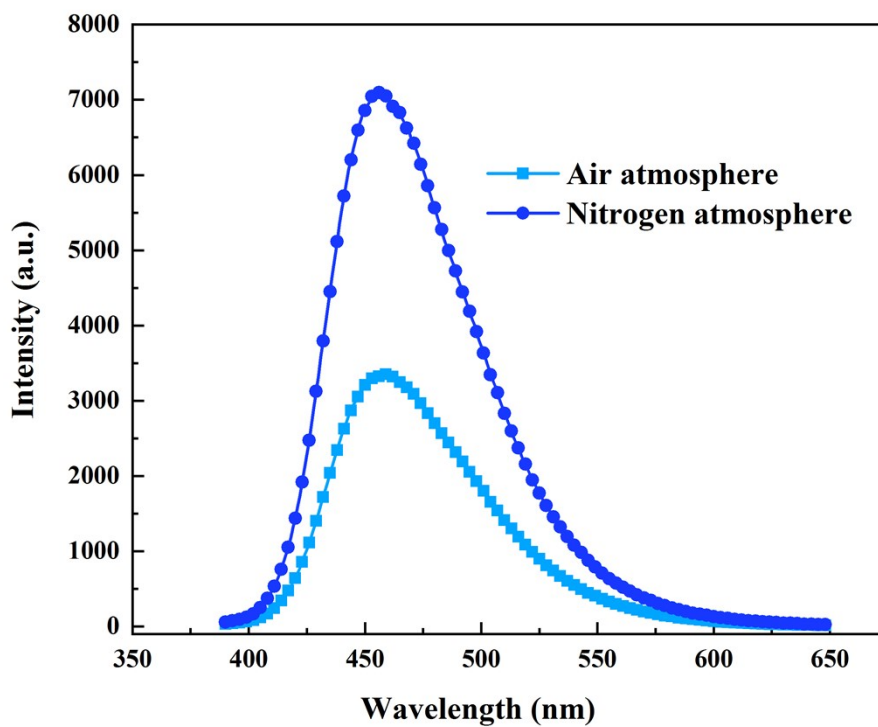


Fig. S9. PL spectra of the toluene solutions ( $1.0 \times 10^{-5}$  M) of **Trz-PhCz**

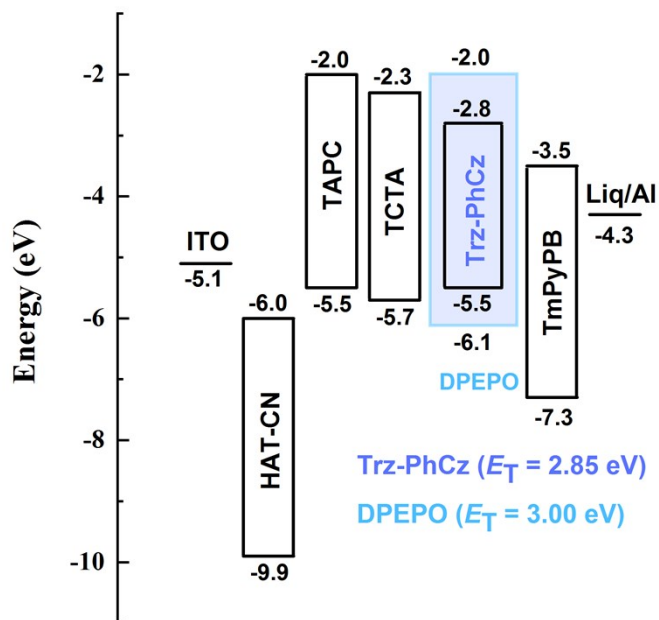


Fig. S10. Device structure and representative energy level diagram for **Trz-PhCz**-doped OLEDs

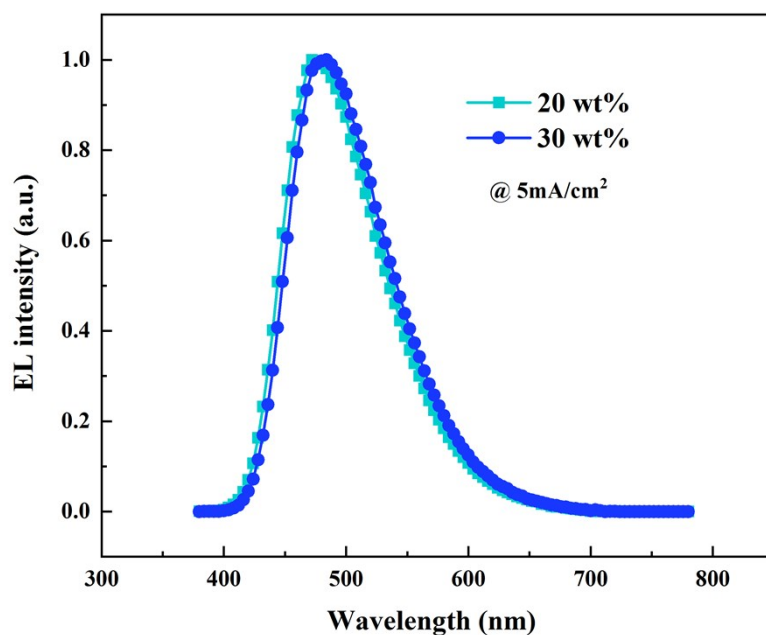


Fig. S11. EL spectra of **Trz-PhCz** -doped OLEDs hosted by DPEPO at 5 mA cm<sup>-2</sup>

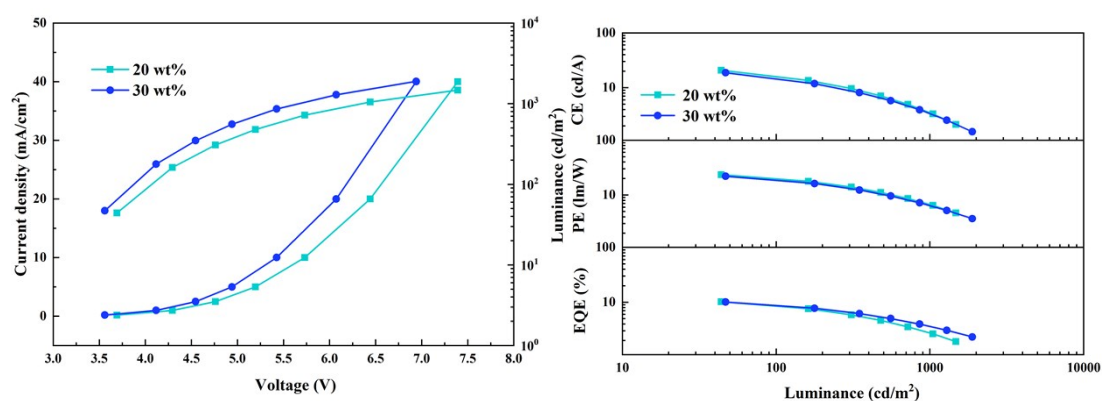


Fig. S12. *J-V-L* characteristics spectra (left) and EQE-current density curves (right) of **Trz-PhCz** -doped OLEDs hosted by DPEPO.

Table S1 Electroluminescence performance of **Trz-PhCz** doped device

Doping conc. [wt%]	V <sup>a</sup> [V]	CE <sup>b</sup> [cd/A]	PE <sup>b</sup> [lm/W]	EQE <sup>b</sup> [%]	CIE <sup>c</sup> [x, y]	λ <sub>EL</sub> <sup>d</sup> [nm]
20	3.6	18.7	22.0	10.1	(0.19, 0.32)	472
30	3.7	20.7	23.5	10.1	(0.20, 0.36)	484

<sup>a</sup> Voltage at 100 cd m<sup>-2</sup>.

<sup>b</sup> Maximum value.

<sup>c</sup> Commission Internationale de l'Eclairage coordinates measured at 5 mA cm<sup>-2</sup>.

<sup>d</sup> Measured at 5 mA cm<sup>-2</sup>.

Ignoring singlet internal conversion (IC) process, the main rate constants of Trz-PhCz in doped films can be determined by using the following equations:

$$k_p = 1/\tau_p \quad (S1)$$

$$k_r^s = k_p \Phi_p \quad (S2)$$

$$k_p = k_r^s + k_{ISC} \quad (S3)$$

$$k_d = \Phi_d / (\Phi_{ISC} \tau_d) \quad (S4)$$

$$k_{RISC} = k_p k_d \Phi_d / (k_{ISC} \Phi_p) \quad (S5)$$

$$\Phi_{ISC} = 1 - \Phi_p \quad (S6)$$

Where  $\Phi_p$  is the prompt fluorescent component of  $\Phi_{PL}$ .  $\Phi_d$  is the delayed fluorescent component of  $\Phi_{PL}$ .  $\tau_p$  is the lifetime of prompt fluorescent;  $\tau_d$  is the lifetime of delayed fluorescent.  $k_r^s$  is the rate constant of radiative transition from  $S_1$  to  $S_0$ ;  $k_p$ ,  $k_{ISC}$ ,  $k_d$  are the rate constants of prompt fluorescence, intersystem crossing and delayed fluorescence decay, respectively.  $\Phi_{ISC}$  and  $\Phi_{RISC}$  are the quantum efficiencies of ISC and RISC process, respectively. Absolute PL quantum yield in doped film (30% for Trz-PhCz) and neat film.

Table S2 The rate constant of **Trz-PhCz** doped device

Doping conc. [wt%]	$k_p$ [ $10^7$ s $^{-1}$ ]	$k_r^s$ [ $10^7$ s $^{-1}$ ]	$k_{ISC}$ [ $10^7$ s $^{-1}$ ]	$k_d$ [ $10^5$ s $^{-1}$ ]	$k_{RISC}$ [ $10^6$ s $^{-1}$ ]	$\Phi$ [%]	$\Phi_p/\Phi_d$ [%]
30	4.13	1.15	2.98	5.84	1.23	70	28/42
100	2.45	0.44	2.01	1.49	0.12	30	18/12

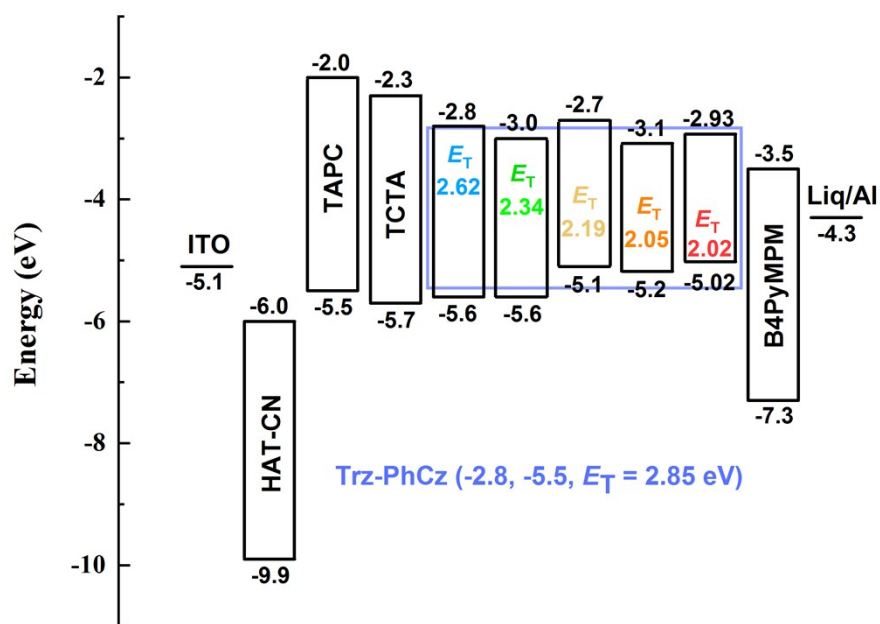


Fig. S13. Device structures and representative energy level diagram for **Trz-PhCz** hosted OLEDs

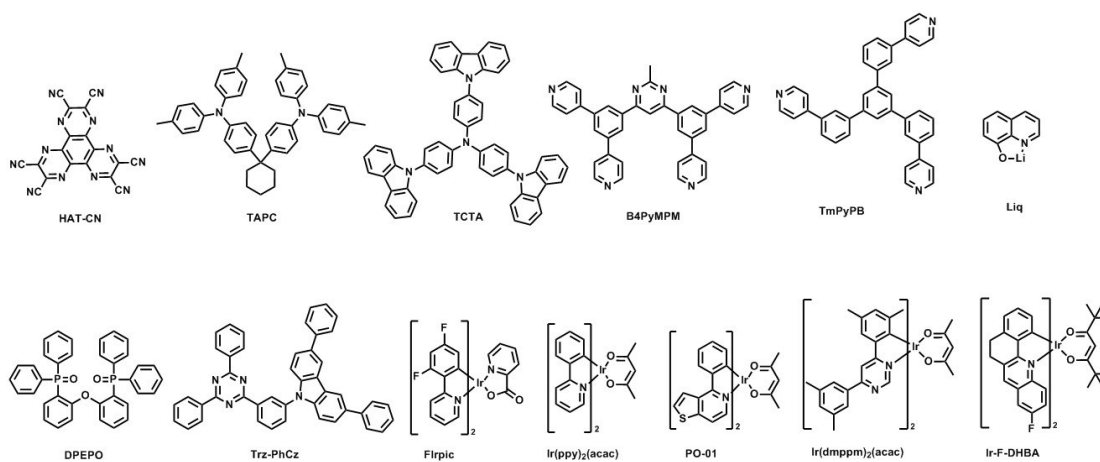


Fig. S14. Molecular structures of materials used in **Trz-PhCz** based device.

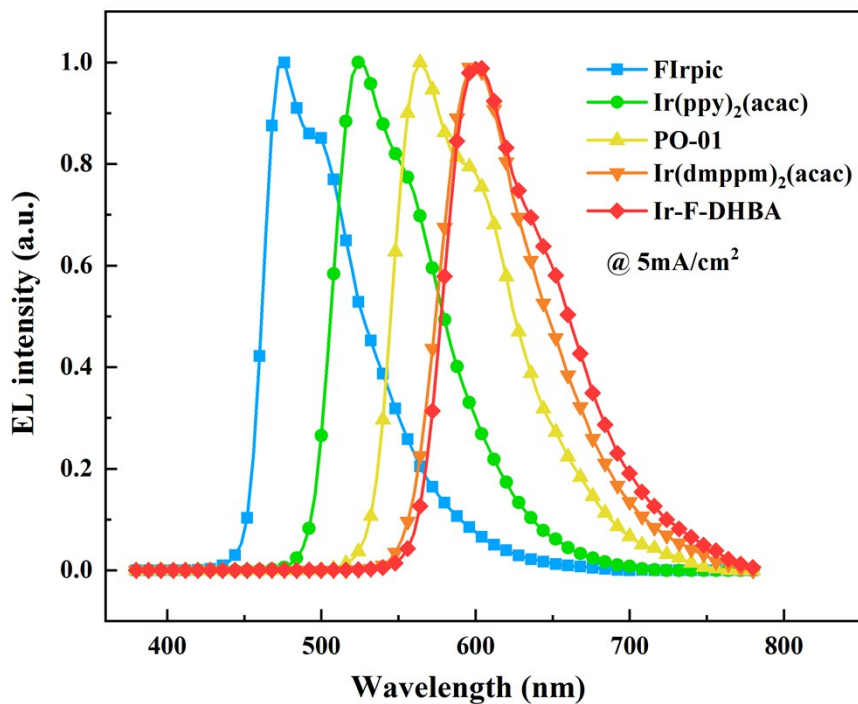


Fig. S15. EL spectra of FIrpc, Ir(ppy)<sub>2</sub>(acac), PO-01, Ir(dmppm)<sub>2</sub>(acac) and Ir-F-DHBA-doped PHOLEDs hosted by **Trz-PhCz** at 5 mA cm<sup>-2</sup>.

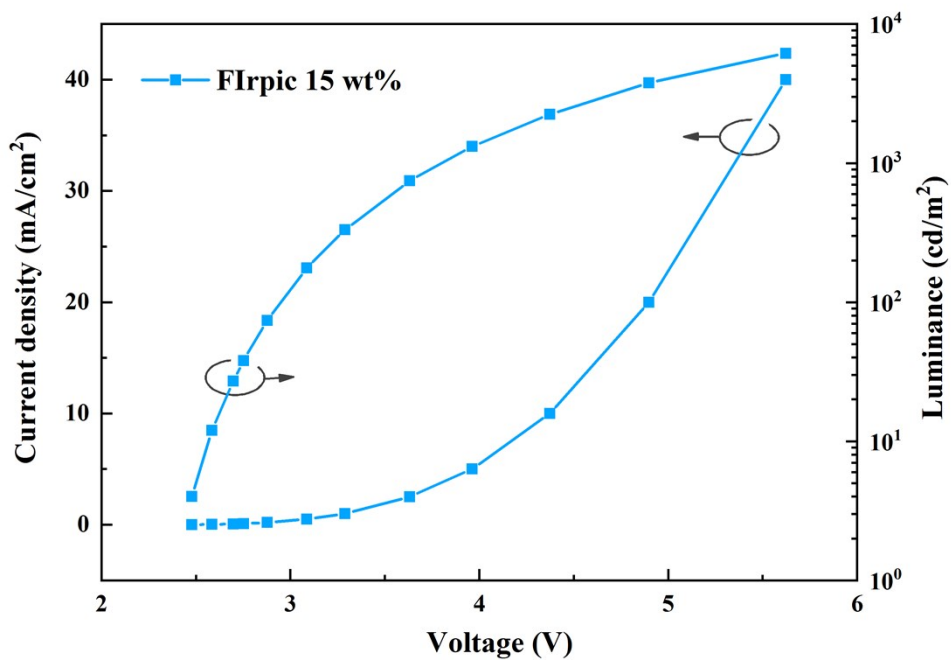


Figure S16. *J-V-L* characteristics spectra of FIrpc-doped PHOLEDs.

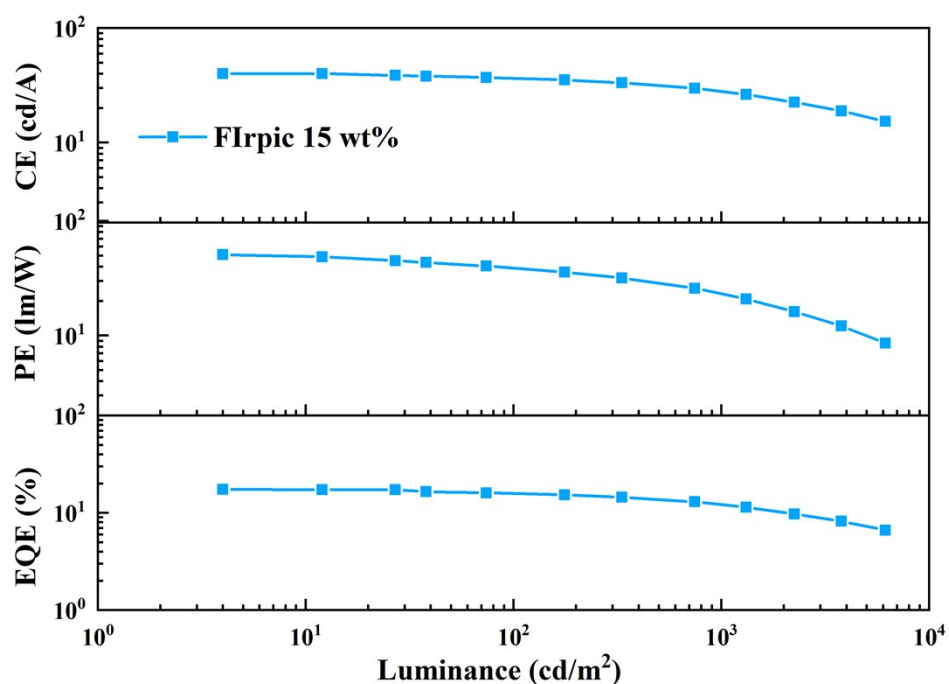


Figure S17 EQE-current density curves of FIrpic-doped PHOLEDs.

Table S3 Electroluminescence characteristics of FIrpic-doped PHOLEDs.

Device <sup>a</sup>	V [V] <sup>b</sup>	CE [cd A <sup>-1</sup> ] <sup>b</sup>	PE [lm W <sup>-1</sup> ] <sup>b</sup>	EQE [%] <sup>c</sup>	CIE [x, y] <sup>d</sup>
B	2.9	40	50.7	17.4/15.9/12.3	(0.18, 0.38)

<sup>a</sup> Device configuration: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)Trz-PhCz: FIrpic (15 wt %, 20 nm)/B4PyMPM (40 nm)/Liq (2 nm)/Al (120 nm);

<sup>b</sup> Voltages at 100 cd m<sup>-2</sup>.

<sup>c</sup> Efficiencies in the order of the maxima 100 cd m<sup>-2</sup> and 1000 cd m<sup>-2</sup>.

<sup>d</sup> Commission International de l'Eclairage coordinates measured at 5 mA cm<sup>-2</sup>

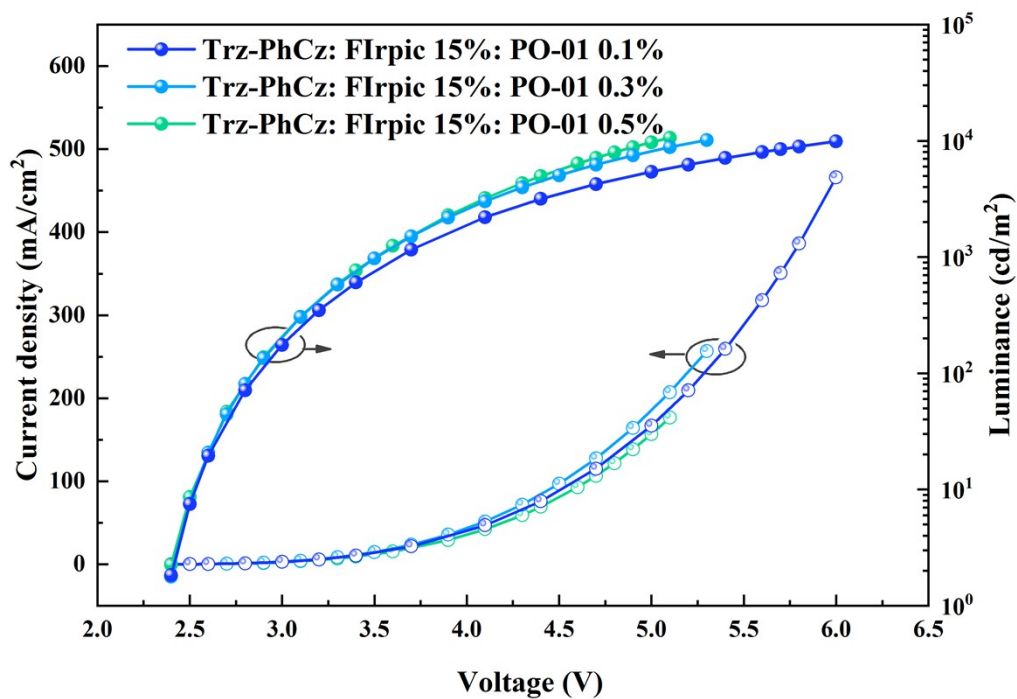


Figure S18. J-V-L characteristics spectrum of WOLEDs device.

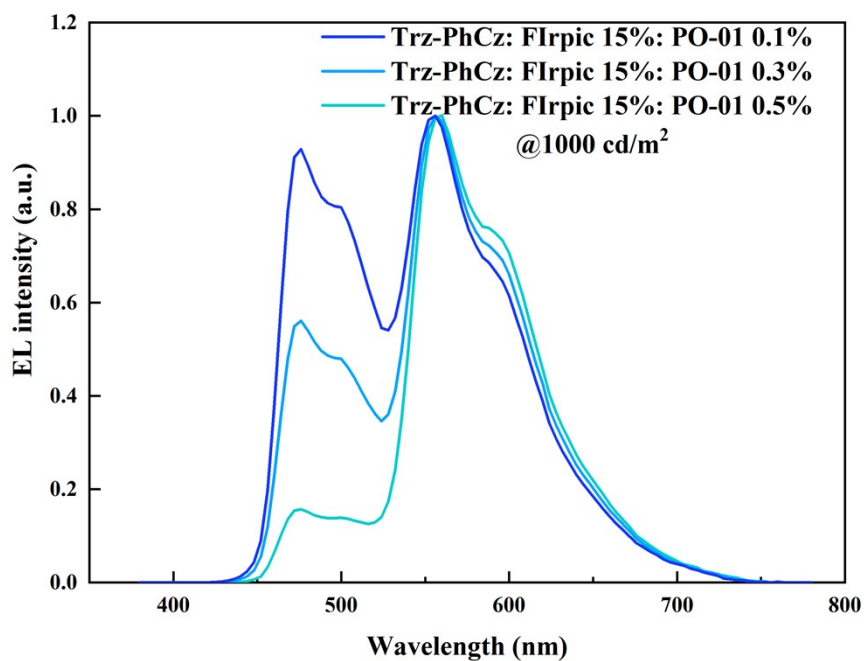


Fig. S19. EL spectra of WOLEDs device at 1000 cd/m<sup>2</sup>.

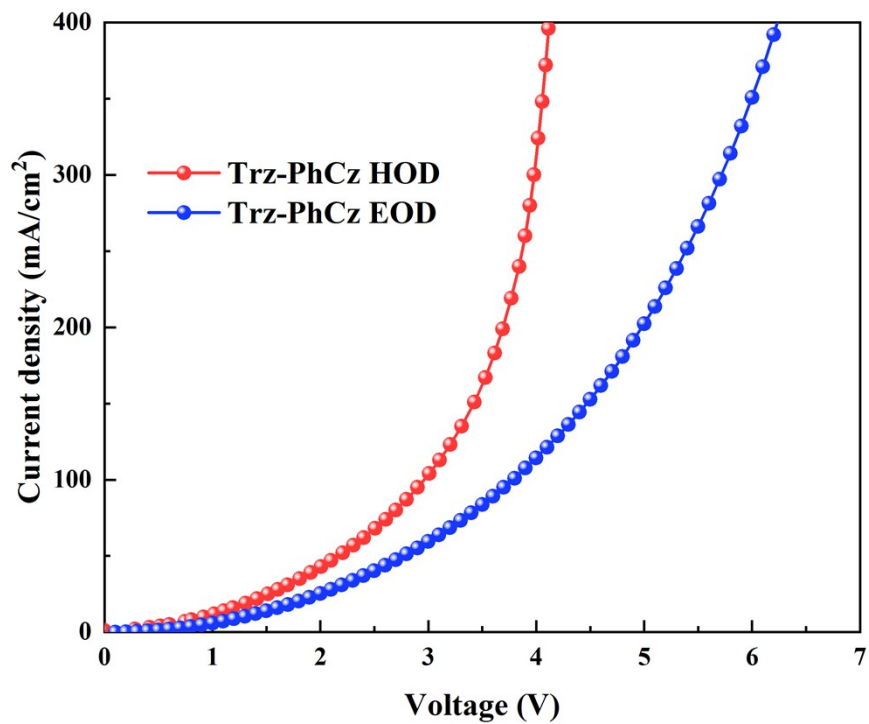


Fig. S20. Current density versus voltage characteristics of the hole-only devices (HODs) and electron-only devices (EODs).

Hole only device configuration: ITO/MoO<sub>3</sub> (10 nm)/Trz-PhCz (100 nm)/MoO<sub>3</sub> (10 nm)/Al (100 nm); electron only device configuration: ITO/TmPyPB (20 nm)/Trz-PhCz (100 nm)/TmPyPB (20 nm)/Liq (2 nm)/Al (100 nm).