

## Supplementary Information

### **New Hole Transport Styrene Polymers Bearing Highly $\pi$ -Extended Conjugated Side-Chain Moieties for High-Performance Solution-Processable Thermally Activated Delayed Fluorescence OLEDs**

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### **Experimental**

#### ***Instrumentation***

We recorded <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra using Varian Mercury 500-MHz spectrometers in CDCl<sub>3</sub> solvent. Mass spectrometry was performed using MALDI-TOF MS instrument (Bruker Daltonics). Differential scanning calorimetry (DSC, Mettler 821 Instrument) and thermogravimetric analysis (TGA) using TGA Q500 V20.13 build 39 were performed to observe the thermal properties of the hole transport materials (HTMs).

Absorption spectra of the HTMs were measured using an UV-vis spectrophotometer (HP 8453,  $\lambda$  = 190-1100 nm). Photoluminescence (PL) spectra were also recorded at room temperature (298K) and at low temperature 77K. (Hitachi F-7000 and Thermo FA-357

fluorescence spectrophotometer) Triplet energies were obtained from the onset wavelength of the low-temperature PL spectra measured at 77 K. In order to measure the oxidation potential of the HTMs in the film state, cyclic voltammetry was used at a scan rate of 50 mV s<sup>-1</sup> using a potentiostat (EA161, eDAQ).

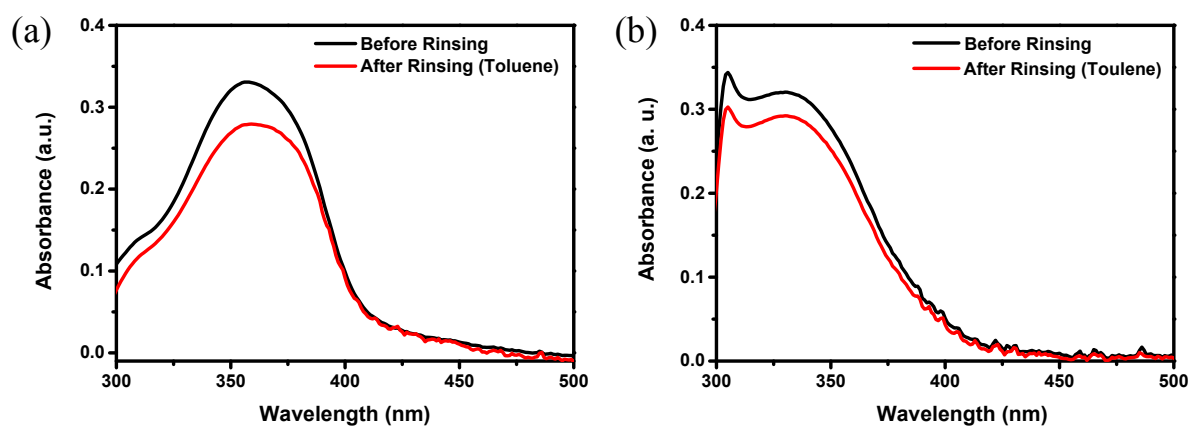
### ***Space-charge-limited current (SCLC) method for measuring hole mobility***

The hole mobilities of the HTMs were measured using SCLC method after being fabricated in a typical device structure of ITO/PEDOT:PSS (40 nm)/**2DMFCz**, **2DBFCz** or PVK film (100nm)/MoO<sub>3</sub> (10 nm)/Ag (100 nm). The mobility was calculated according to  $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$ , where  $J$  is the current density;  $\epsilon_0$  is the permittivity of the HTL;  $\epsilon_r$  is the relative dielectric constant;  $\mu$  is the hole mobility; and  $L$  is the thickness of the HTL. The internal voltage is  $V = V_{\text{appl}} - V_{\text{bi}} - V_{\text{a}}$ , where  $V_{\text{appl}}$  is the voltage applied to the device;  $V_{\text{bi}}$  is related to the work-function difference between two electrodes; and  $V_{\text{a}}$  is the voltage drop.

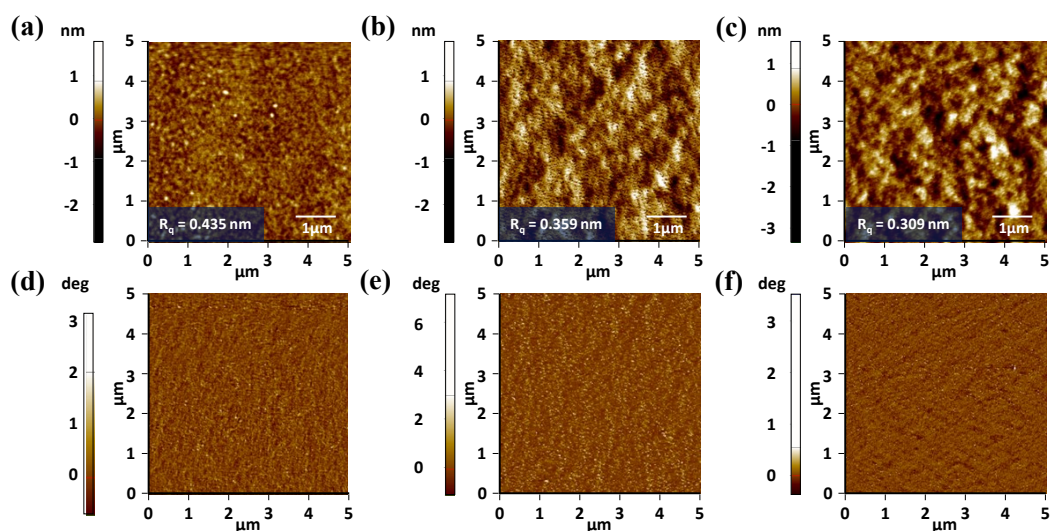
### ***Green TADF-OLED Fabrication and Measurements***

The green TADF device structure comprises ITO/PEDOT: PSS (40 nm)/poly-(9-vinylcarbazole) (PVK, 20 nm) or **2DMFCz**, **2DBFCz** (20nm)/ EML (host: IAPC, dopant: t4CzIPN (15 nm, 3 wt. % and 9 wt. %))/TPBi (40 nm)/LiF (0.8 nm)/Al (100 nm). Prior to device fabrication, the ITO-coated substrates were washed with isopropanol. PEDOT: PSS (40 nm) was deposited on the ITO-coated substrates at spin rate of 4000 rpm for 40 s and then annealed at 155 °C for 15 min. The 0.5 wt. % PVK [Sigma-Aldrich,  $M_n = 1,100.0$  kDa, polydispersity = 3.19] solution was prepared from a chlorobenzene solvent, spin-coated on top of the ITO/PEDOT: PSS, and subsequently annealed at 130 °C for 20 min. The emitting layers were prepared from a toluene solution of IAPC and t4CzIPN and spin-coated at 3000 rpm for

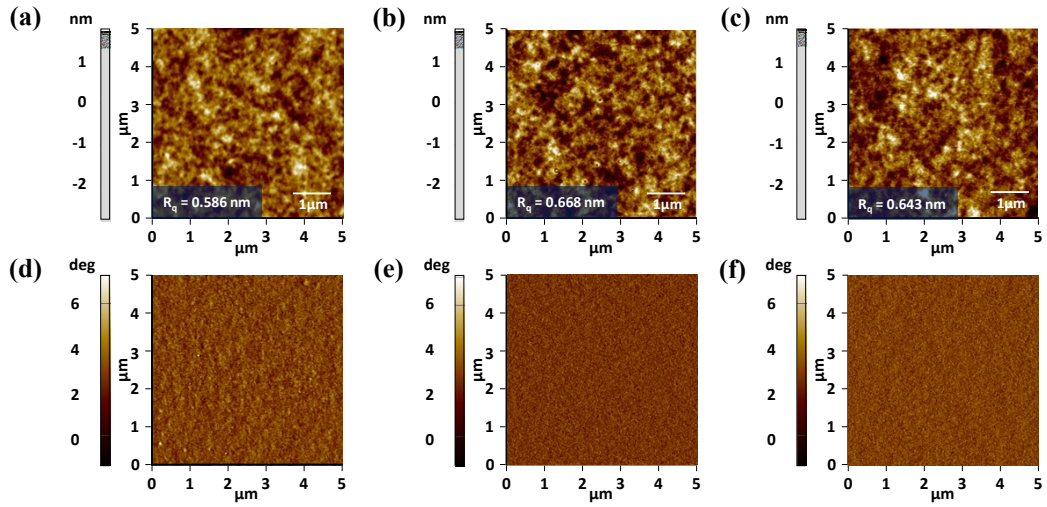
30 s. TPBi with a thickness of 40 nm was deposited under high vacuum conditions. Finally, LiF and Al electrodes were produced by vacuum deposition. The characteristics of the OLED device were measured with a Keithley SMU 236 instrument and a SpectraScan PR-655 colorimeter.



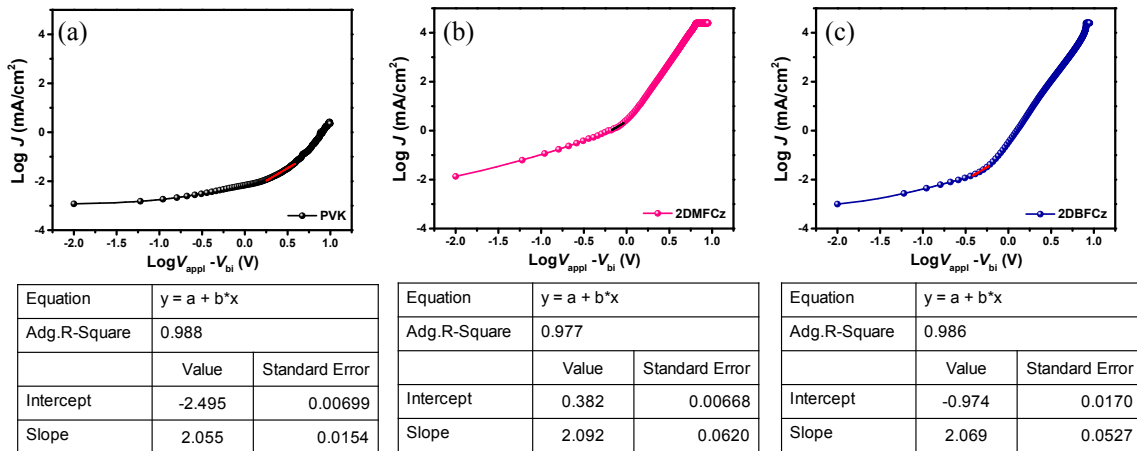
**Fig. S1.** Absorption spectra of **2DMFCz** and **2DBFCz** in thin film states before and after solvent rinsing. Solvent: toluene.



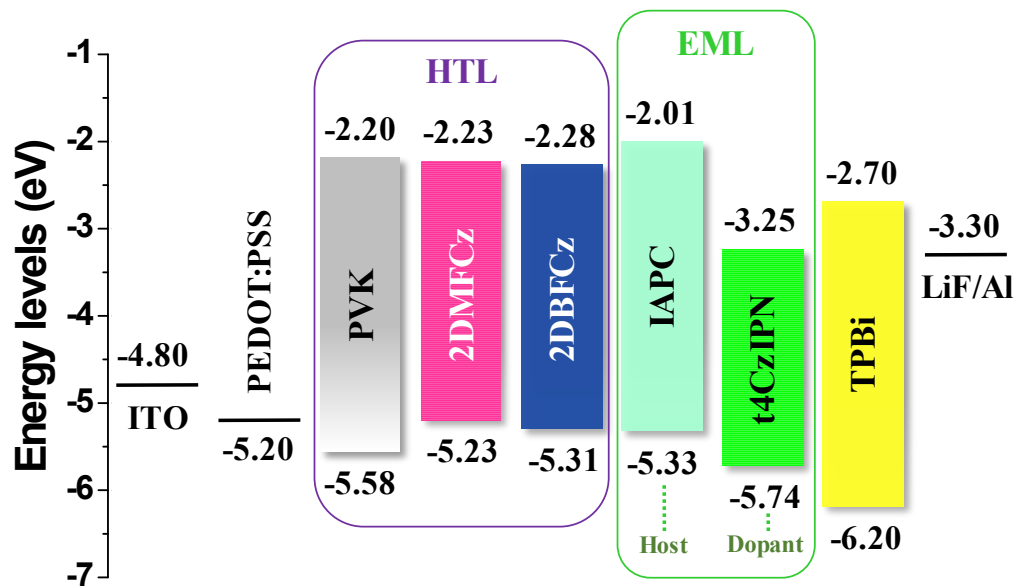
**Fig. S2.** AFM height (a, b, c) and phase (d, e, f) images ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) of PVK (a, d), **2DMFCz** (b, e), and **2DBFCz** (c, f) films.



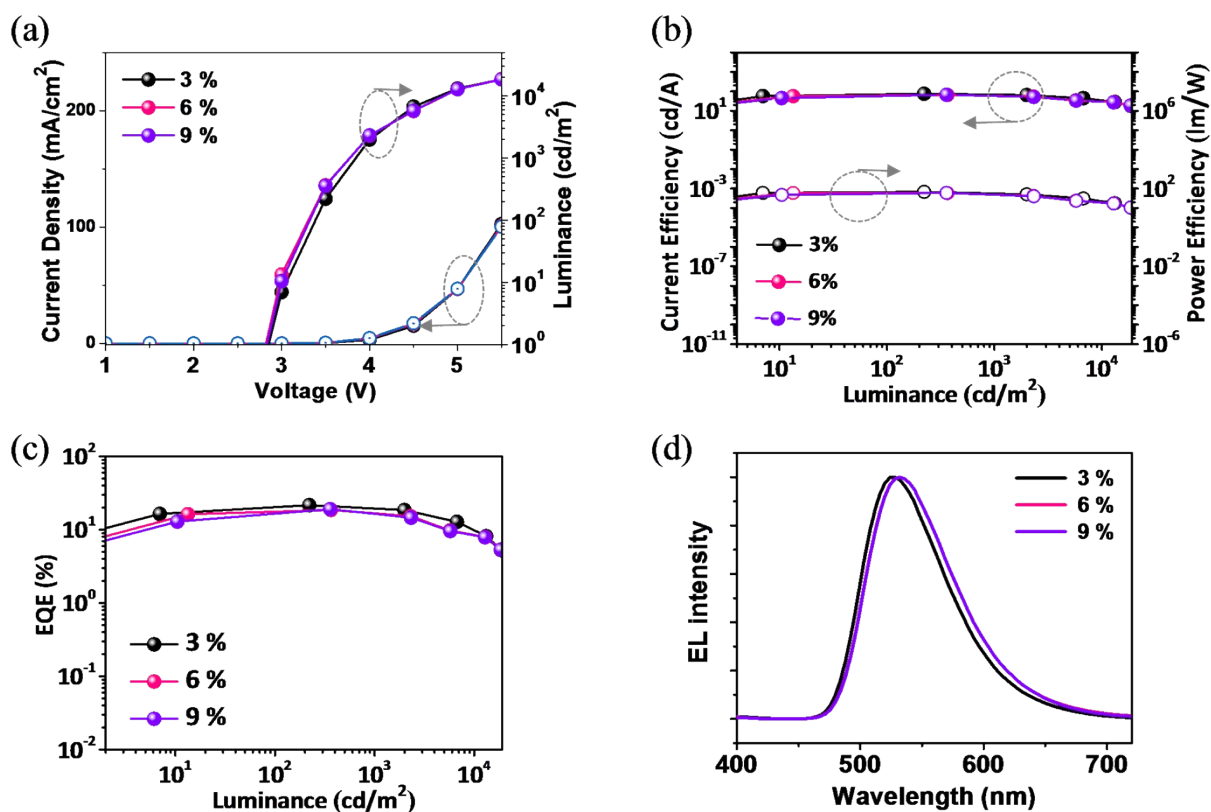
**Fig. S3.** AFM height (a, b, c) and phase (d, e, f) images ( $5 \mu\text{m} \times 5 \mu\text{m}$ ) for emitting layers which were deposited on PVK (a, d), **2DMFCz** (b, e), and **2DBFCz** (c, f) films.



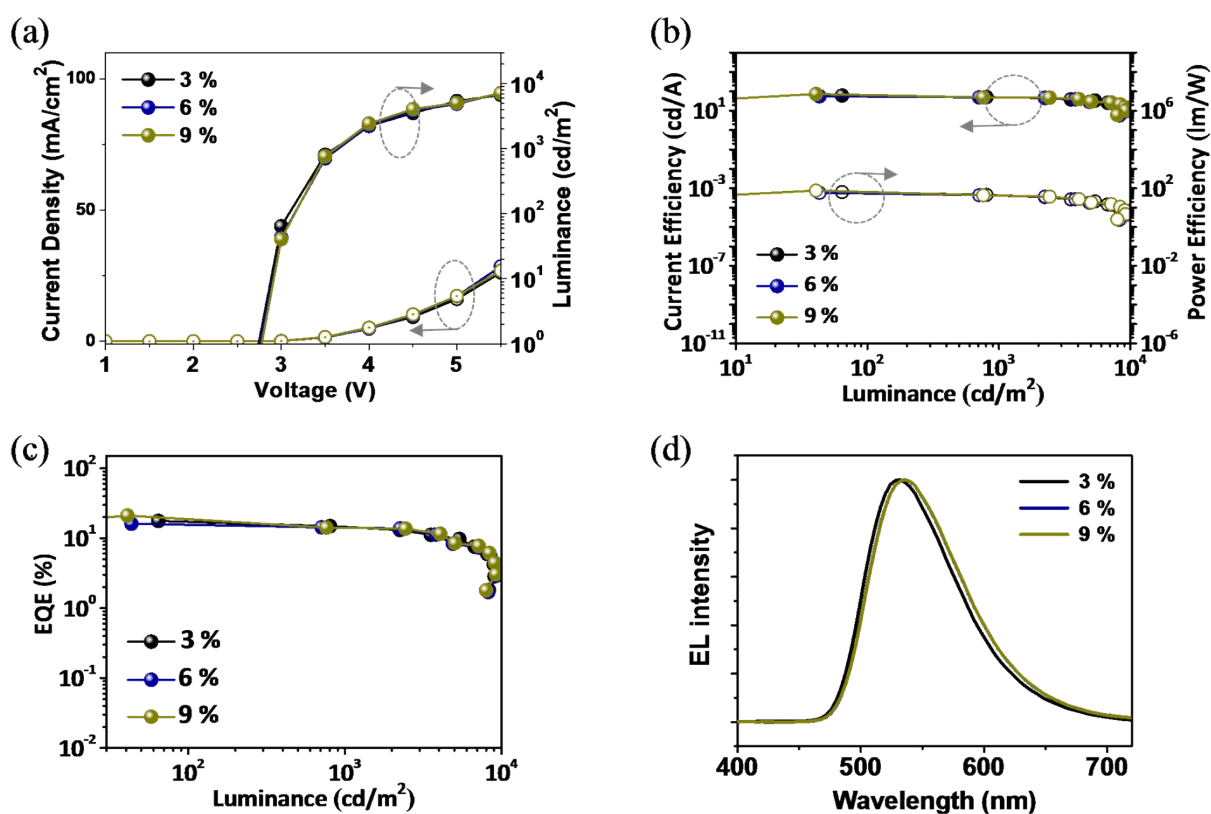
**Fig. S4.** Curve fitting results for calculating the mobility of the hole-only device. (a) PVK, (b) **2DMFCz**, (c) **2DBFCz**.



**Fig. S5.** Schematic energy level diagram of TADF-OLED device bearing PVK, 2DMFCz and 2DBFCz as HTL.



**Fig. S6.** (a) Current density–voltage–luminance ( $J$ – $V$ – $L$ ), (b) current efficiency–luminance–power efficiency (CE– $L$ –PE), (c) EQE–luminance (EQE– $L$ ) curves, and (d) EL spectra of solution-processed green TADF-OLED devices bearing **2DMFCz** as HTL. \*The doping concentration of the t4CzIPN dopant in the EML was examined in the range of 3–9 wt.%. IAPC was used as a host material.



**Fig. S7.** (a)  $J$ - $V$ - $L$ , (b)  $CE$ - $L$ - $PE$ , (c)  $EQE$ - $L$  curves, and (d) EL spectra of solution-processed green TADF-OLED devices bearing **2DBFCz** as HTL. \*The doping concentration of the t4CzIPN dopant in the EML was examined in the range of 3–9 wt.%. IAPC was used as a host material.

**Table S1.** Device performance of **2DMFCz**- and **2DBFCz**-based green TADF-OLED with various doping concentration. IAPC was used as a host material.

HTL	t4CzIPN Doping conc.	$V_{on}^a$ (V)	$CE_{max}^b$ (cd/A)	$PE_{max}^c$ (lm/W)	Luminance <sup>d</sup> (cd/m <sup>2</sup> )	$EQE^d$ (%)	$EL_{max}^g$	$CIE^h$ (x, y)
<b>2DMFCz</b>	3 wt. %	2.7	74.98	67.31	18550	21.60	528	(0.32, 0.60)
	6 wt. %	2.7	65.06	59.17	18680	18.61	532	(0.34, 0.60)
	9 wt. %	2.7	66.61	59.79	18480	19.05	532	(0.34, 0.59)
<b>2DBFCz</b>	3 wt. %	2.7	60.60	63.46	9026	17.67	532	(0.36, 0.59)
	6 wt. %	2.7	55.40	58.02	9323	16.10	536	(0.36, 0.59)
	9 wt. %	2.7	72.52	75.943	9221	21.11	536	(0.36, 0.59)

<sup>a</sup>Turn-on voltage at 1 cd/m<sup>2</sup>, <sup>b</sup>Maximum current efficiency, <sup>c</sup>Maximum power efficiency, <sup>d</sup>Maximum luminance, <sup>e</sup>Maximum external quantum efficiency, <sup>g</sup>EL peak wavelength, <sup>h</sup>Commission Internationale de L'Eclairage coordinates at 1000 cd m<sup>-2</sup>.