

Supplementary Information

High Efficiency Solution-Processed Green Thermally Activated Delayed Fluorescence OLEDs using Polymer-Small Molecule Mixed Host

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Experimental Section

Instrumentation

^1H nuclear magnetic resonance (NMR) spectra and ^{13}C NMR spectra were recorded using Varian Mercury 500 MHz spectrometers (Cambridge Isotope Laboratories), with a CDCl_3 solvent. The M_n and polydispersity index (PDI) of the polymer were determined relative to polystyrene (PS) standards by gel permeation chromatography (GPC; Agilent GPC 1200 series) using 1,2-dichlorobenzene (*o*-DCB). Mass spectrometry was performed using the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF/TOF™ 5800 system (AB SCIEX)) at the Korea Basic Science Institute (Seoul), to analyze the mass of the compounds. The absorption spectra of the hosts in toluene solutions and neat films were obtained using a UV-vis absorption spectrometer (Agilent 8453, photodiode array, $\lambda = 190$ -1100 nm). The fluorescence (298 K) and phosphorescence (77 K, delay time = 1.0 ms) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer. In the TRPL experiments, the film samples were housed in a cryostat (Janis, VPF-100) under a vacuum condition ($\leq \sim 10^{-2}$ mTorr) and were excited by 355 nm pulses produced by the third harmonic generation of 1064 nm from a Nd:YAG laser (Q-smart 850, Lumibird FR). The TRPL signals were detected using a photomultiplier tube (Hamamatsu photonics, R955) connected to a 100-MHz digital oscilloscope (DSO-X 3014A, Keysight). The absolute photoluminescence quantum yields (PLQYs) of the films were obtained using an integrating sphere (ILF-835) in an FP-8500 spectrofluorometer (JASCO). UV photoemission spectroscopy (UPS, Nexsa XPS system) was employed to determine the energy levels of the hosts with He I as the UV source (21.2 eV) at 2.0×10^{-7} Torr. The samples were prepared in the film state. The thermal properties of the hosts, such as the melting temperature (T_m) and glass transition temperature (T_g), were

estimated by differential scanning calorimetry (DSC, Mettler STAR^e). The decomposition temperature (T_d) was determined using thermogravimetric analysis (TGA, Mettler STAR^e) at a heating rate of 10 °C min⁻¹ under N₂.

Single carrier devices

To compare the charge carrier transport abilities, HODs and EODs using hosts were fabricated with a patterned ITO-coated glass (serving as the anode) with a sheet resistance of 10.0 Ω/sq (AMG Corp.). The HOD and EOD configurations used were as follows: ITO (150 nm)/PEDOT:PSS (40 nm)/PVK (20 nm)/EML (25 nm)/Al (100 nm) and ITO (150 nm)/EML (25 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm), respectively. PEDOT:PSS was deposited as received (annealed at 155 °C for 15 min), whereas PVK was dissolved in chlorobenzene (annealed at 130 °C for 20 min). The hosts which dissolved in toluene were spin-coated as required. TPBi, LiF, and Al were deposited using a thermal evaporator.

OLED device fabrication

OLED devices were fabricated using a patterned ITO-coated glass (150 nm) as the anode, with a sheet resistance of 10 Ω cm⁻². Synthesized hosts were used, and the green TADF emitter was made of *t*4CzIPN. The configuration of the OLEDs was as follows: ITO (150 nm)/PEDOT:PSS (40 nm)/PVK (20 nm)/host:*t*4CzIPN (25 nm, x wt %)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm). The PEDOT:PSS and PVK function as the hole injection and transport layers, respectively, whereas the TPBi and LiF function as the electron transport and injection layers, respectively. The Al acts as the cathode. x represents the various dopant concentrations at 6.0, 12.0, 18.0,

and 24.0 wt % and were used to optimize the device conditions. PEDOT:PSS was directly spin-coated on an ITO plate and annealed at 155 °C for 15 min, whereas PVK dissolved in chlorobenzene (0.5 wt%) was spin-coated before annealing at 130 °C for 20 min. The toluene solutions (0.2 wt%) of the emissive materials were deposited by spin coating onto the PVK layer to act as the emissive layer. These three steps were performed under ambient conditions before the substrates were moved into a vacuum chamber to deposit TPBi, LiF, and Al sequentially, using a thermal evaporator.

Materials and Synthesis

For synthesizing the donor polymer and acceptor molecule, all reagents and solvents were purchased from Aldrich, Alfa Aesar, and TCI and were used without further purification. Compounds **1**, **2**, **3**, and **4** as well as 9,9-Diphenyl-9,10-dihydroacridine were prepared according to the literature.^{S1-S4}

Synthesis of 9,9-diphenyl-10-(4-vinylbenzyl)-9,10-dihydroacridine (1, Bn-DPAc)

NaH dispersed in paraffin liquid (55 % (0.39 g, 9.0 mmol) and 9,10-Dihydro-9,9-diphenylacridine (1.0 g, 3.0 mmol) were dissolved in N,N-Dimethylformamide (DMF) (20 mL) to remove the generated H₂ gas by purging N₂ at room temperature (RT) for 30 min. Thereafter, 4-vinylbenzyl chloride (0.85 mL, 6.0 mmol) was added dropwise into the mother mixture and stirred for 4 h under a N₂ atmosphere at RT. The mixture was extracted with water (100 mL) and dichloromethane (DCM, 3 × 100 mL). The organic layer was dried over anhydrous sodium sulfate. The concentrated solution was purified by silica gel column chromatography (DCM:hexane = 1:4 v/v). The target compound **1** was collected as a white

powder (yield: 1.1 g, 80.1%). ^1H NMR (500 MHz, CDCl_3) δ ppm 7.19 - 7.24 (m, 8 H), 7.12 (t, $J=6.41$ Hz, 2 H), 6.92 - 6.98 (m, 4 H), 6.84 - 6.91 (m, 6 H), 6.81 (d, $J=8.35$ Hz, 2 H), 6.61 - 6.70 (m, 1 H), 5.68 (d, $J=17.55$ Hz, 1 H), 5.19 (d, $J=10.91$ Hz, 1 H), 5.03 (s, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ ppm 146.20, 141.66, 136.78, 136.46, 136.20, 131.58, 130.47, 130.02, 127.60, 127.13, 126.67, 126.44, 126.31, 120.04, 113.54, 113.31, 57.06, 50.23. MALDI-TOF: m/z 449.22 [M^+]. Elemental Anal. Calcd. For ($\text{C}_{34}\text{H}_{27}\text{N}_1$): C, 84.32; H, 10.27; N, 5.41. Found: C, 84.36; H, 10.26; N, 5.38.

Synthesis of (2, P(Bn-DPAc))

P(Bn-DPAc) was prepared by free-radical polymerization using azobisisobutyronitrile (AIBN) as an initiator. Monomer **1** (0.50 g, 1.1 mmol), AIBN (5.4 mg, 0.030 mmol), and chlorobenzene (3.5 mL) were all mixed in a sealed tube under a N_2 atmosphere. The mixture was then stirred at 80 °C for 48 h. After cooling to RT, the mixture was precipitated with MeOH, and the solid precipitate was filtered. For purification, Soxhlet extraction was conducted with acetone, hexane, and DCM in succession. **P(Bn-DPAc)** was obtained as a white solid. (yield: 392 mg, 78.4 %): $M_n = 7.43$ kDa, PDI = 2.05). Elemental Anal. Calcd. For ($\text{C}_{36}\text{H}_{33}\text{N}_1$) $_n$: C, 90.15; H, 6.93; N, 2.92. Found: C, 89.96; H, 6.85; N, 3.11.

Synthesis of 2-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-4,6-diphenyl-1,3,5-triazine (5, tPTRZ)

Compound **3** (388 mg, 1.0 mmol), compound **4** (262 mg, 1.1 mmol), potassium carbonate (276 mg, 2 mmol), and tetrakis (triphenylphosphine)palladium(0) were dissolved in a solution of toluene (12 mL), distilled water (4.5 mL), and methanol (3 mL). The mixture was stirred

overnight under N₂ atmosphere at 90 °C. The mixture was extracted using distilled water (100 mL) and DCM. The organic layer was dried over anhydrous sodium sulfate. The concentrated solution was purified by silica gel column chromatography (DCM:hexane = 1:5 v/v). The product solution was concentrated, and precipitation occurred in hexane. The target **tPTRZ** was collected as a white powder (yield: 362 mg, 78.2 %). ¹H NMR (500 MHz, CDCl₃) δ ppm 8.83 (d, *J*=8.55 Hz, 2 H), 8.80 (d, *J*=6.56 Hz, 4 H), 7.81 (d, *J*=8.55 Hz, 2 H), 7.67 (d, *J*=8.54 Hz, 2 H), 7.57 - 7.64 (m, 6 H), 7.53 (d, *J*=8.54 Hz, 2 H), 1.39 (s, 9 H). ¹³C NMR (125 MHz, CDCl₃) δ ppm 171.63, 171.49, 151.19, 145.07, 137.47, 136.33, 134.90, 132.49, 129.46, 128.98, 128.64, 127.15, 126.93, 125.91, 34.65, 31.36. MALDI-TOF: *m/z* 428.25 [M⁺]. Elemental Anal. Calcd. For (C₃₁H₂₇N₃): C, 84.32; H, 6.16; N, 9.52. Found: C, 84.35; H, 6.17; N, 9.54.

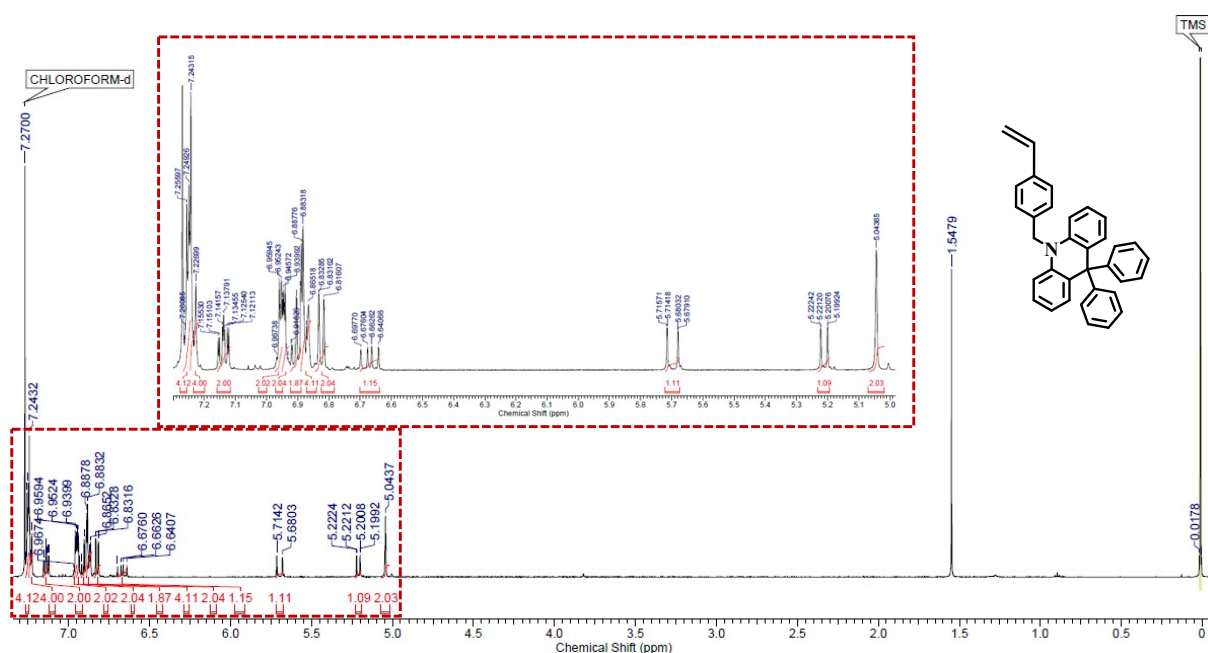
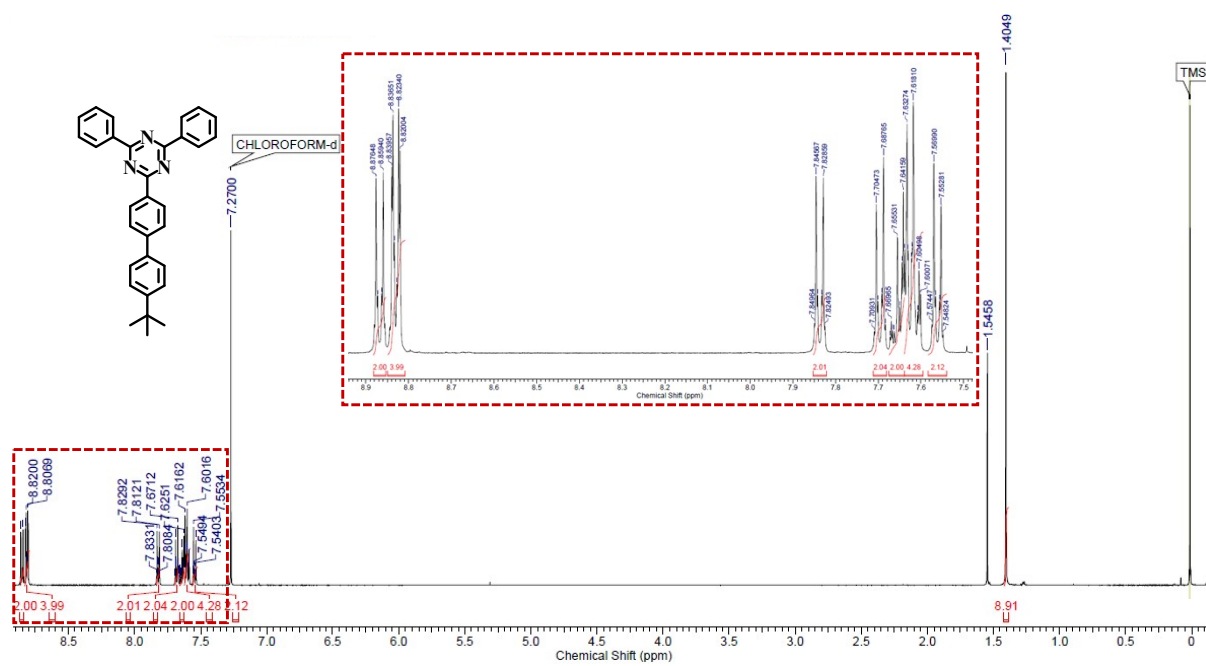


Fig S1. ¹H NMR spectra of **Bn-DPAc (1)**



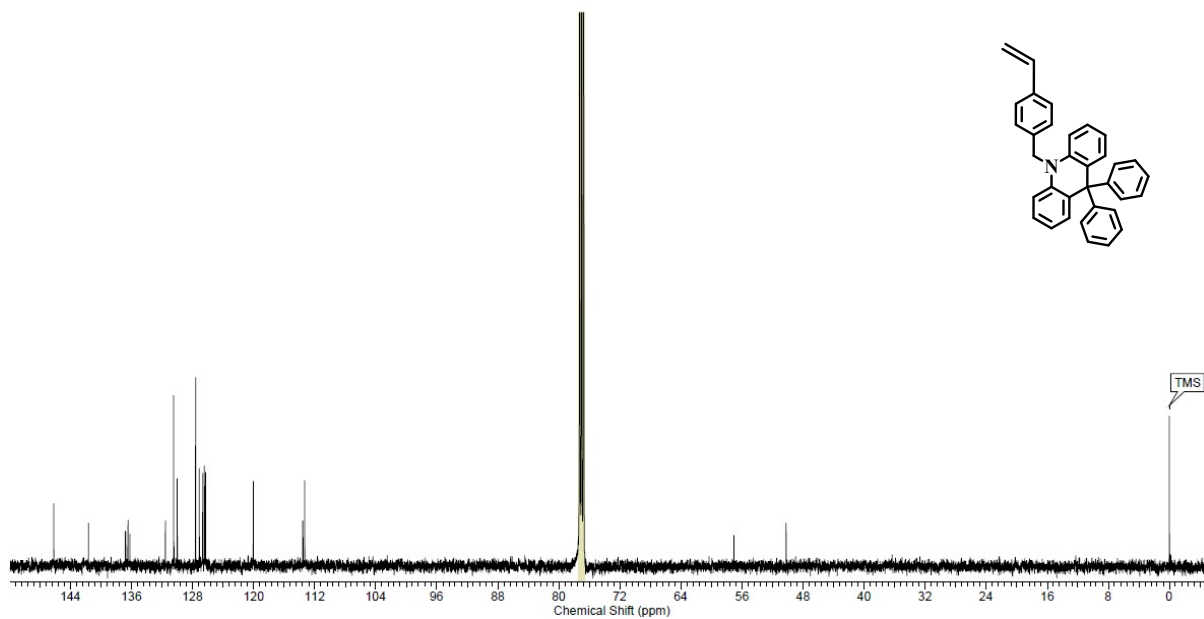


Fig S4. ^{13}C NMR spectra of **Bn-DPAC (1)**

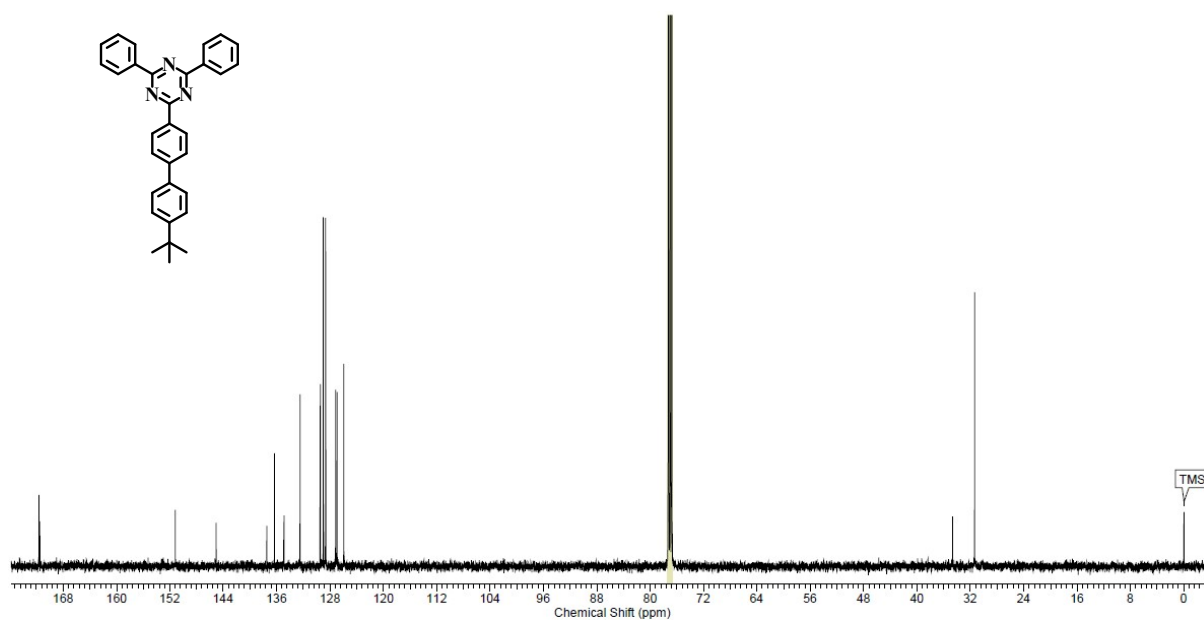


Fig S5. ^{13}C NMR spectra of *t***PTRZ (5)**

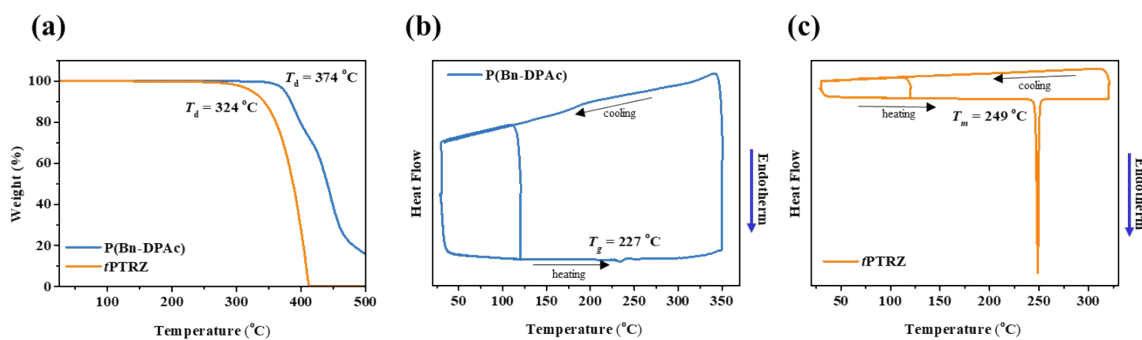


Fig S6. (a) TGA and DSC curves of (b) P(Bn-DPAc) and (c) tPTRZ measured under the N_2 condition.

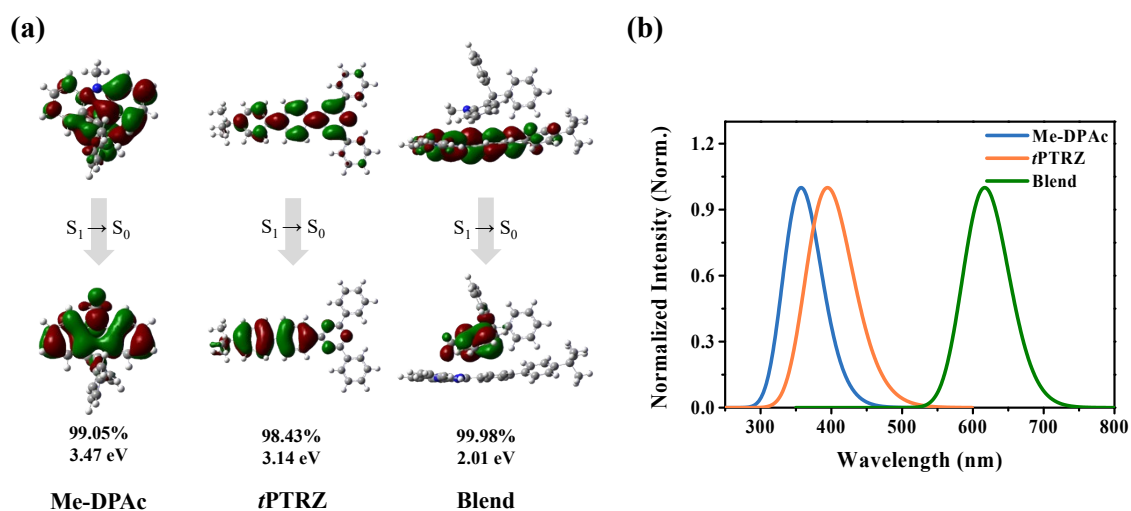


Fig S7. (a) Optimized geometries, emission energies, and (b) PL spectra of Me-DPAc, tPTRZ, and blend obtained by the DFT TD-opt method with B3LYP/6-31+g(d). Calculation of the blend was performed by adding the empirical dispersion term by d3 in the previous method.

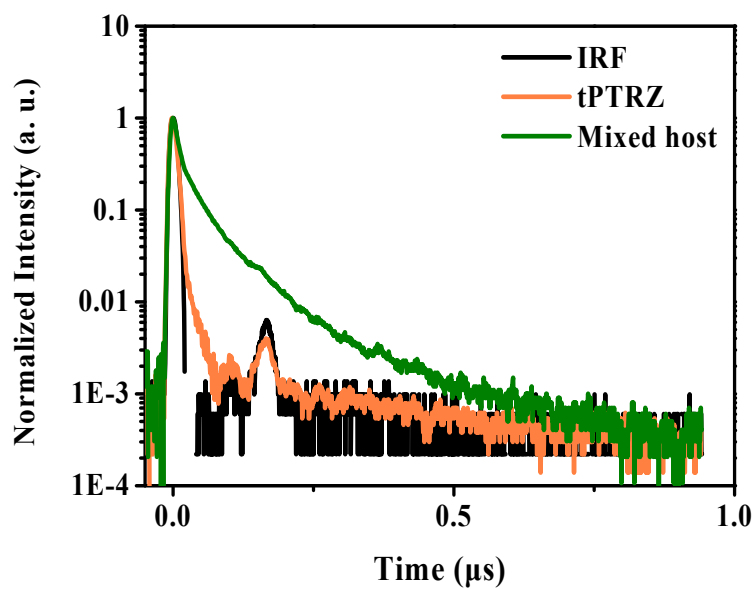


Fig S8. Transient PL of *t*PTRZ and mixed host (P(Bn-DPAc):*t*PTRZ = 1:1 wt%).

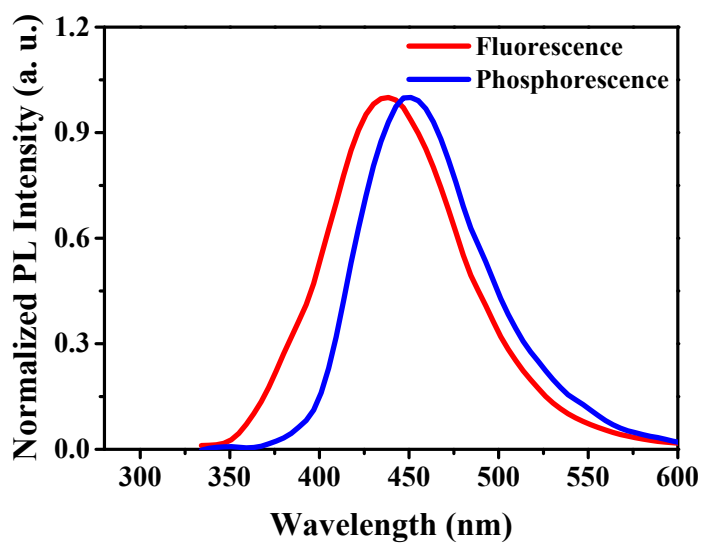


Fig S9. Fluorescence and phosphorescence (77 K) spectra of the mixed host in film states.

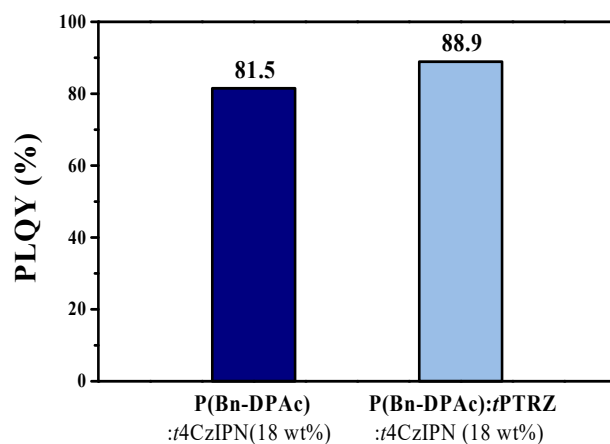


Fig S10. PLQY of P(Bn-DPAc):t4CzIPN (18 wt%) and mixed host (P(Bn-DPAc):tPTRZ):t4CzIPN (18 wt%).

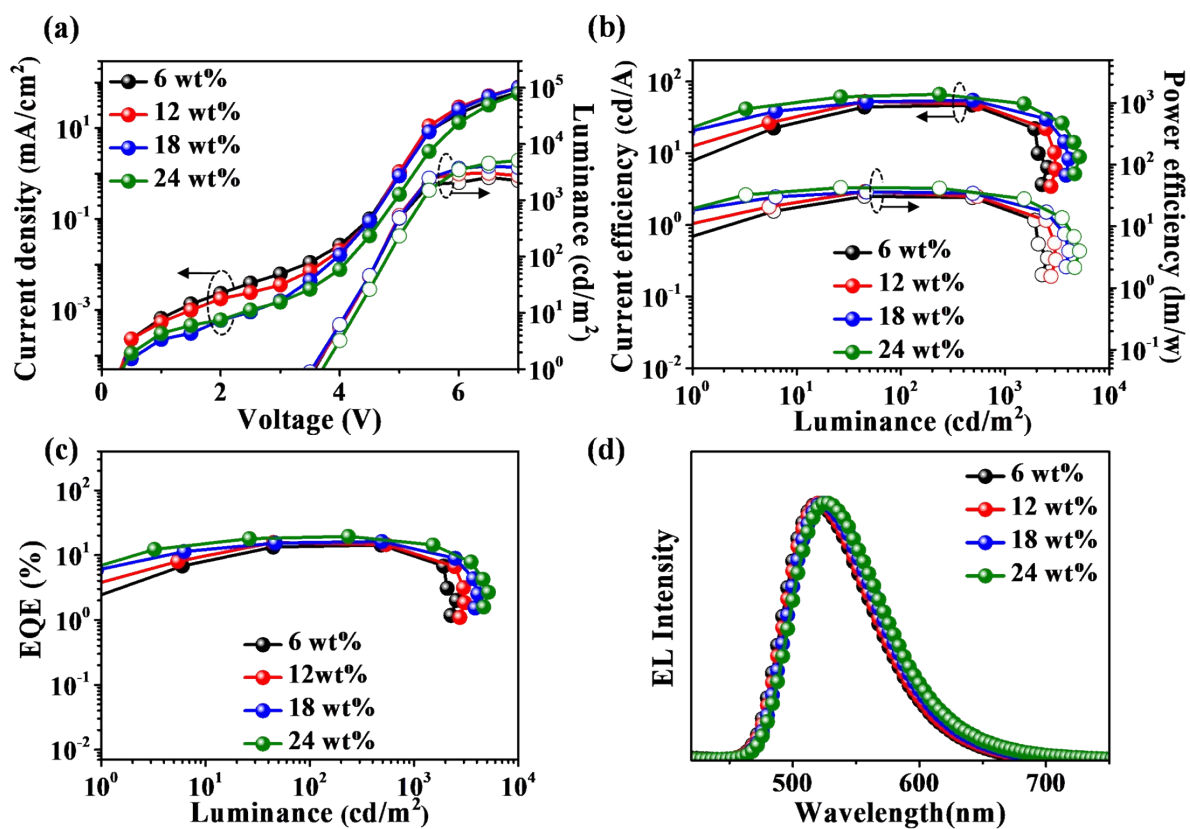


Fig S11. (a) J - V - L curves, (b) CE-luminance-PE curves, (c) EQE-luminance curves, and (d) EL spectra at a luminance of 1000 cd/m^2 for the solution-processed green TADF-OLED devices based on **P(Bn-DPAc)** with various doping concentration of the *t*4CzIPN emitter.

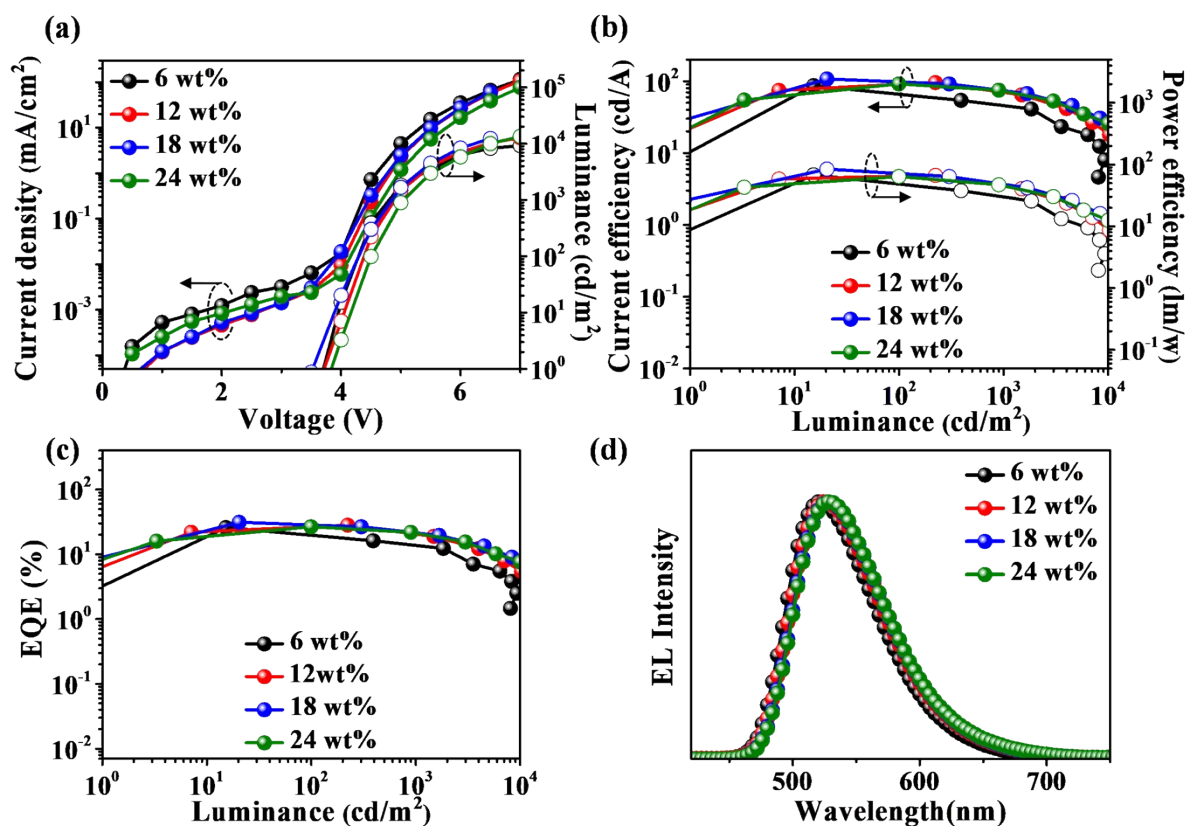


Fig S12. (a) J - V - L curves, (b) CE-luminance-PE curves, (c) EQE-luminance curves, and (d) EL spectra at a luminance of 1000 cd/m^2 for the solution-processed green TADF-OLED devices based on mixed host (**P(Bn-DPAc):*t*PTRZ = 1:1 wt%**) with various doping concentration of the *t*4CzIPN emitter.

Table S1. EL performance of the solution-processed green TADF-OLEDs based on different ratios of mixed host system.

EML (Host)	Mixed host Ratio	Dopant Conc. (wt%)	V_{on}^a (V)	$\eta_{c,max}^b$ (cd/A)	$\eta_{p,max}^c$ (lm/W)	L^d (cd/m ²)	$\eta_{ext,max}^e$ (%)	λ_{EL}^f (nm)	CIE ^g (x, y)
P(Bn-DPAc)	-	6	3.5	47.0	30.8	2553	14.4	520	(0.29, 0.58)
		12	3.5	52.6	36.7	3055	15.7	520	(0.30, 0.59)
		18	3.5	54.9	36.4	4079	16.2	524	(0.33, 0.60)
		24	3.6	66.5	42.7	5161	19.5	528	(0.32, 0.60)
P(Bn-DPAc) : tPTRZ	1 : 1	6	3.5	86.5	67.9	9269	25.9	520	(0.30, 0.59)
		12	3.6	95.6	66.8	12820	28.1	524	(0.32, 0.60)
		18	3.5	107.3	84.3	12360	31.2	528	(0.33, 0.60)
		24	3.6	91.7	64.0	16220	26.6	528	(0.33, 0.60)

^a Turn-on voltage at 1 cd/m². ^b Maximum CE. ^c Maximum PE. ^d Maximum luminance. ^e Maximum External quantum efficiency (EQE). ^f EL peak wavelength. ^g CIE color coordinates at 1000 cd/m².

References

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- S2. M. Godumala, J. Hwang, H. Kang, J. E. Jeong, A. K. Harit, M. J. Cho, H. Y. Woo, S. Park and D. H. Choi, *ACS Appl. Mater. Interfaces*, 2020, **12**, 35300-35310.
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