

Supplementary Information for:

Synthesis of dimesitylborane-substituted phenylcarbazoles as bipolar host material and green PHOLED performances with substitu te position of boron atom

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General Procedure:

Chemicals were commercially purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated SiO_2 (IB2-F) and visualized by UV light. Column chromatography was conducted using SiO_2 (60-200 mesh) from Fisher Scientific. Melting points were determined on MEL-TEMP, model 1102D. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 300 NMR spectrometer using CDCl_3 , as the solvent, except where noted. Mass spectra obtained on Agilent Technology 6100 Series Electrospray Ion Trap mass spectrometer (ESI-MS) and Applied Biosystems, Voyager-DE Matrix-Assisted Laser Desorption Ionization Mass Spectrometer (MALDI-TOF). Photophysical properties of the synthesized compounds were analyzed using ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectrometer. The synthesized host materials were dissolved in tetrahydrofuran at a concentration of 1.0×10^{-4} M for UV-Vis and PL measurements. Triplet energy analysis of the host materials were carried out using low temperature PL measurement in liquid nitrogen (77 K). Their energy levels were measured using cyclic voltammetry (CV). Cyclic voltammetry measurement of organic materials was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Ag/AgCl electrode was used as the reference electrode and Pt was the counter electrode. High performance liquid chromatography (HPLC) analysis of the synthesized materials was carried out using HPLC from Younglin Instrument. Glass transition temperature of the materials was measured using a differential scanning calorimeter (DSC; Melter-Toledo DSC 820) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Thermogravimetric analysis (TGA) was conducted with a Mettler-Toledo TG50 at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere.

Synthesis:

3-(dimesitylboryl)-9-phenyl-9*H*-carbazole (1). 3-bromo-*N*-phenylcarbazole (4g, 12.42 mmol) was dissolved in dried THF (70ml) under nitrogen atmosphere and the solution cooled down to $-78 \text{ }^\circ\text{C}$. *n*-BuLi (2.5M in hexanes 6ml, 14.91mmol) dropped slowly to the solution. The solution was stirred for 1h at $-78 \text{ }^\circ\text{C}$, followed by the addition of dimesitylboron fluoride (3.35g, 12.5mmol) dissolved in THF (10ml). The reaction mixture was slowly warm up to room temperature and was then stirred for 12h. The mixture was diluted with dichloromethane and washed with distilled water and brine three times. The combined organic layer was dried over anhydrous MgSO_4 and filtration. The crude material was purified by silica column chromatography (SiO_2) eluting with a mixture of DCM : *n*-hexane (1:5; v/v) to give a white solid (2.01g, 33%): m.p. 226.0-227.0 $^\circ\text{C}$; ^1H NMR δ 8.39 (s, 1H), 8.13 (d, 1H), 7.66-7.58 (m, 4H), 7.52-7.47 (m, 1H), 7.42 (d, 2H), 7.35-7.28 (m, 3H), 6.87 (s, 4H), 2.36 (s, 6H), 2.08 (s, 12H); ^{13}C NMR δ 144.1, 143.9, 142.1, 141.8, 141.0, 138.2, 137.3, 139.9, 130.9, 130.1, 128.2, 127.8, 127.1, 126.2, 124.0, 123.1, 120.9, 120.7, 110.5, 109.4, 20.4, 20.2; MS (MALDI-TOF): m/z = 491.3497 [M]⁺ (calcd. m/z = 491.28).

9-(4-bromophenyl)-9*H*-carbazole (2). Carbazole (10g, 59.85mmol), 1,4-dibromobenzene (14g, 60.00mmol), potassium carbonate (24g, 179.55mmol), CuI (5.71g, 29.93mmol) and 18-crown-6 (0.8g, 2.99mmol) were dissolved in DMF (180ml) under nitrogen atmosphere. The

reaction mixture was stirred for 12h at 130 °C. The mixture extracted to dichloromethane. The solution washed with distilled water and brine. The combined organic mixture dried over anhydrous MgSO₄ and filtration. The crude material was purified by silica column chromatography (SiO₂) eluting with *n*-hexane to give a white solid (7.0g, 36%): m.p. 134-135 °C; ¹H NMR δ 8.18 (d, 2H), 7.76 (d, 2H), 7.50-7.41 (m, 6H), 7.40-7.32 (m, 2H); ¹³C NMR δ 140.70, 136.89, 133.23, 128.83, 126.22, 123.59, 121.00, 121.53, 120.34, 109.67; ESI-MS: m/z = 320.2 [M-H]⁺ (calcd. m/z = 321.02).

9-(4-(dimesitylboryl)phenyl)-9H-carbazole (3). 9-(4-bromophenyl)-9H-carbazole (4g, 1.42mmol) dissolved in dried THF under nitrogen atmosphere and the solution cooled down to -78 °C. *n*-BuLi (2.5M in hexanes 6ml, 14.91mmol) was dropped over a period of 30min to a solution. The solution was stirred for 1h at -78 °C, followed by the addition of dimesitylboron fluoride (3.35g, 12.5mmol) dissolved in THF (10ml). The reaction mixture was slowly warmed up to room temperature and was then stirred for 12h. The mixture was diluted with dichloromethane and washed with distilled water and brine three times. The combined organic layer dried over anhydrous MgSO₄ and filtration. The crude material was purified by silica column chromatography (SiO₂) eluting with a mixture of CHCl₃ : *n*-hexane (1:5; v/v) to give a white solid (1.7g 28%): m.p. 265-266 °C; ¹H NMR δ 8.18 (d, 2H), 7.89 (d, 2H), 7.61 (d, 2H), 7.55 (d, 2H), 7.47-7.43 (m, 2H), 7.35-7.31 (m, 2H), 6.91 (s, 4H), 2.37 (s, 6H), 2.14 (s, 12H); ¹³C NMR δ 144.8, 141.7, 141.0, 140.2, 138.9, 138.1, 128.9, 126.1, 126.0, 123.9, 120.3, 120.2, 110.0, 23.9, 21.1; MS (MALDI-TOF): m/z = 491.3951 [M]⁺ (calcd. m/z = 491.28).

Fabrication of PHOLED device and measurements

The device structure of green PHOLEDs was indium tin oxide (ITO, 150 nm)/ poly(3,4-ethyl enedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/ *Tris*(4-carbazoyl-9-ylphenyl)amine (TCTA, 20 nm)/ *N,N'*-dicarbazoyl-3,5-benzene (mCP, 10 nm)/New Host: *Tris*[2-phenylpyridinato-C²,N]iridium (Ir(ppy)₃) (25 nm, 10 %)/4-(triphenylsilyl) phenyldiphenylphosphine oxide (TSPO1, 35 nm)/LiF (1 nm)/Al (200 nm). The doping concentration of Ir(ppy)₃ was 10%. The device performances of the green PHOLEDs was measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer.

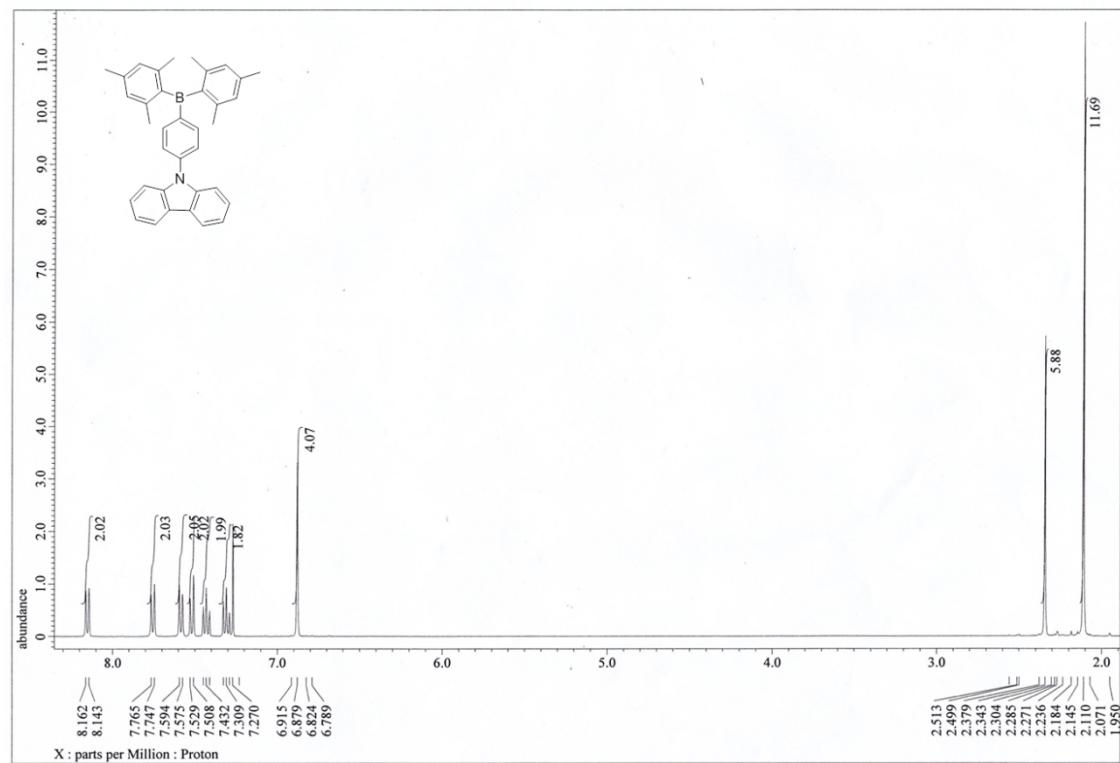
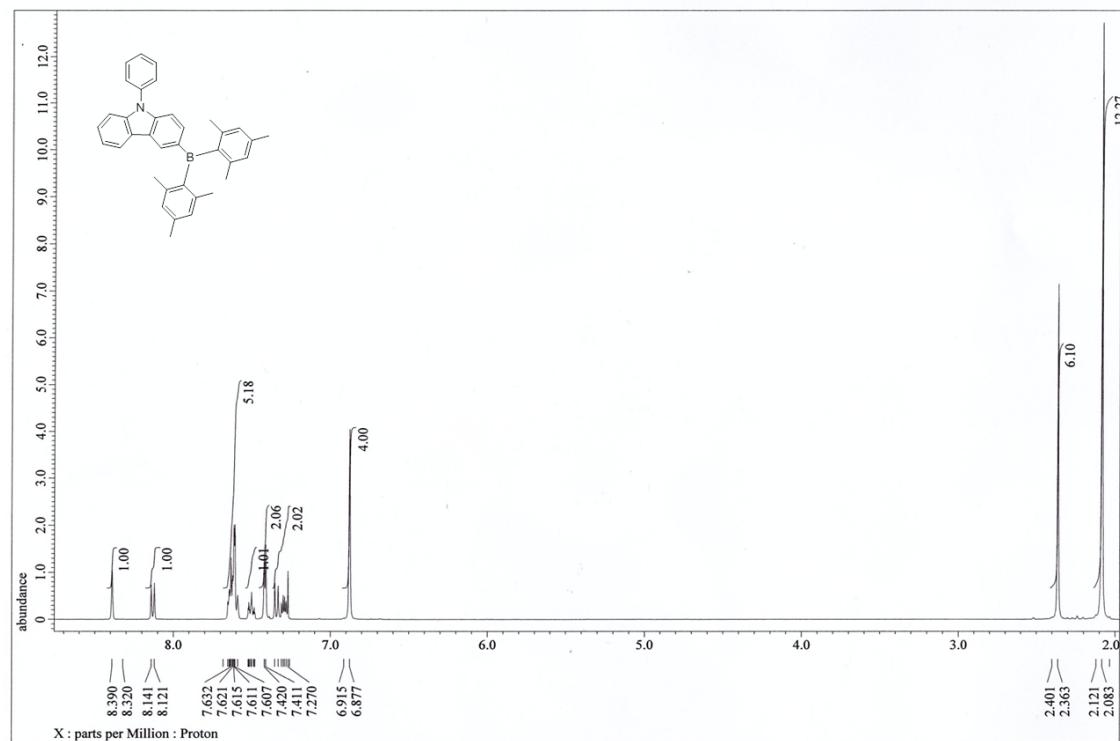


Figure S1. ^1H NMR spectra of **1** and **3**.

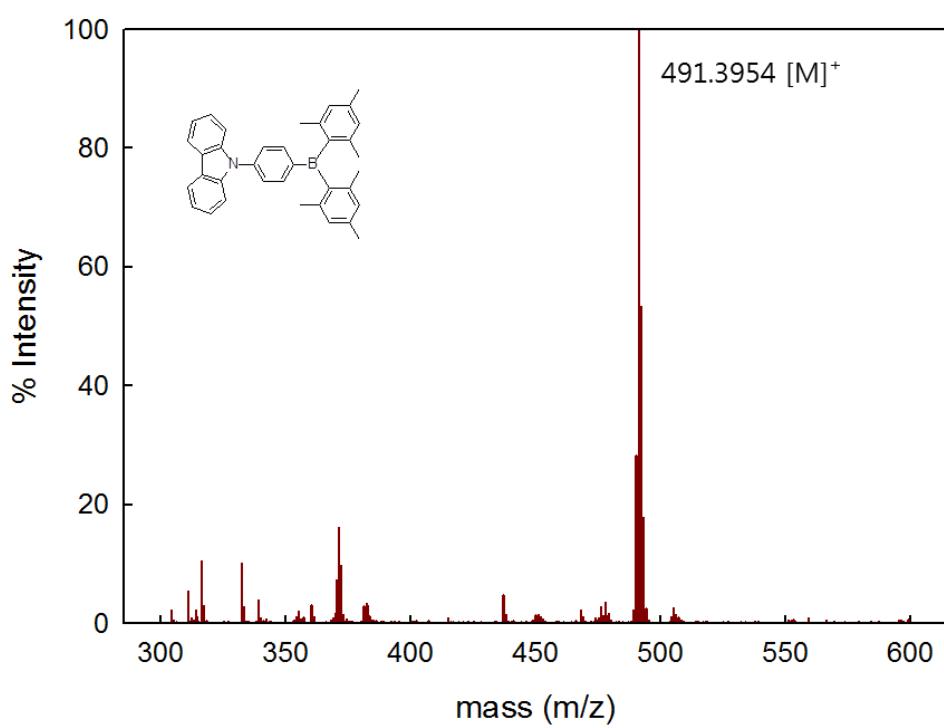
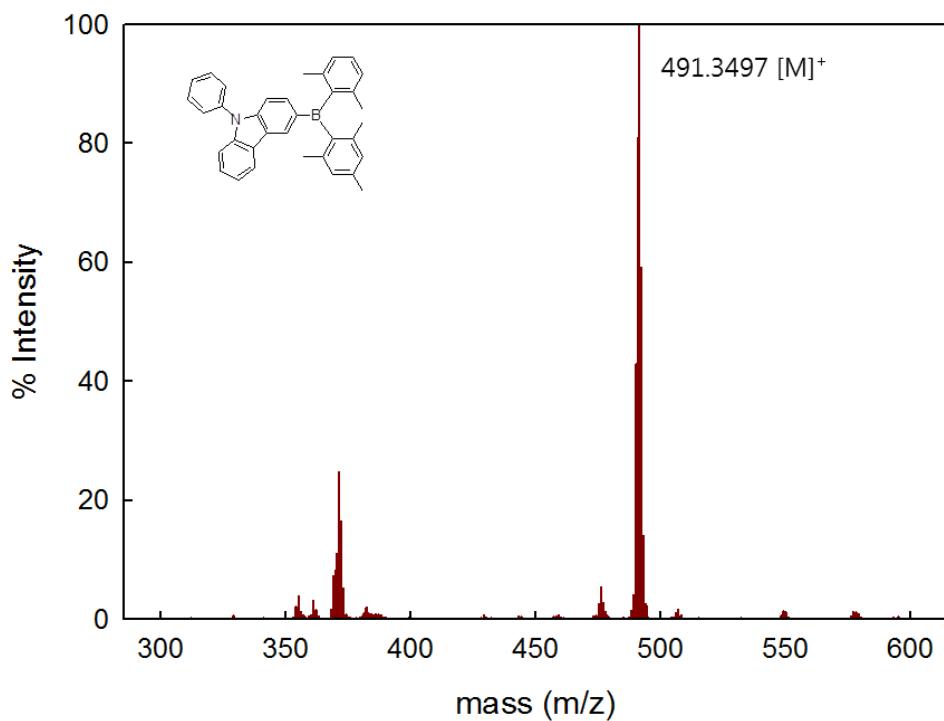


Figure S2. MALDI-Tof spectra of **1** and **3**.

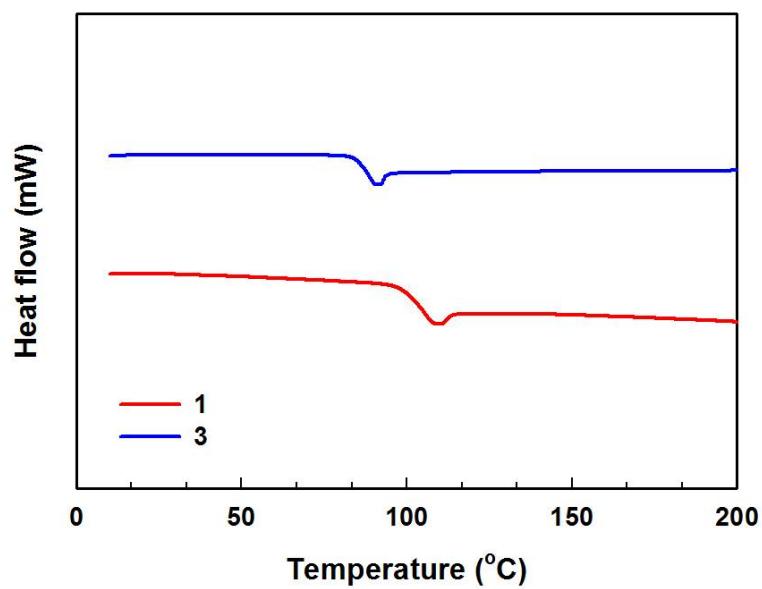


Figure S3. DSC thermograms of **1** and **3**.

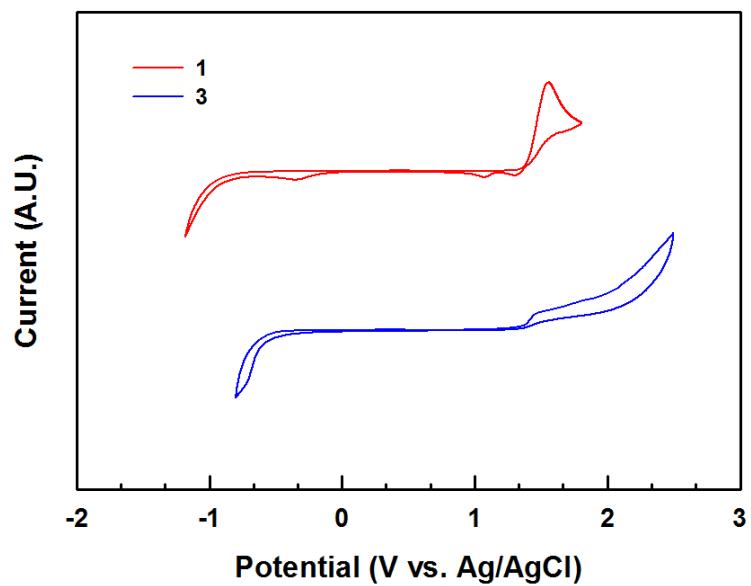


Figure S4. CV results of **1** and **3**.

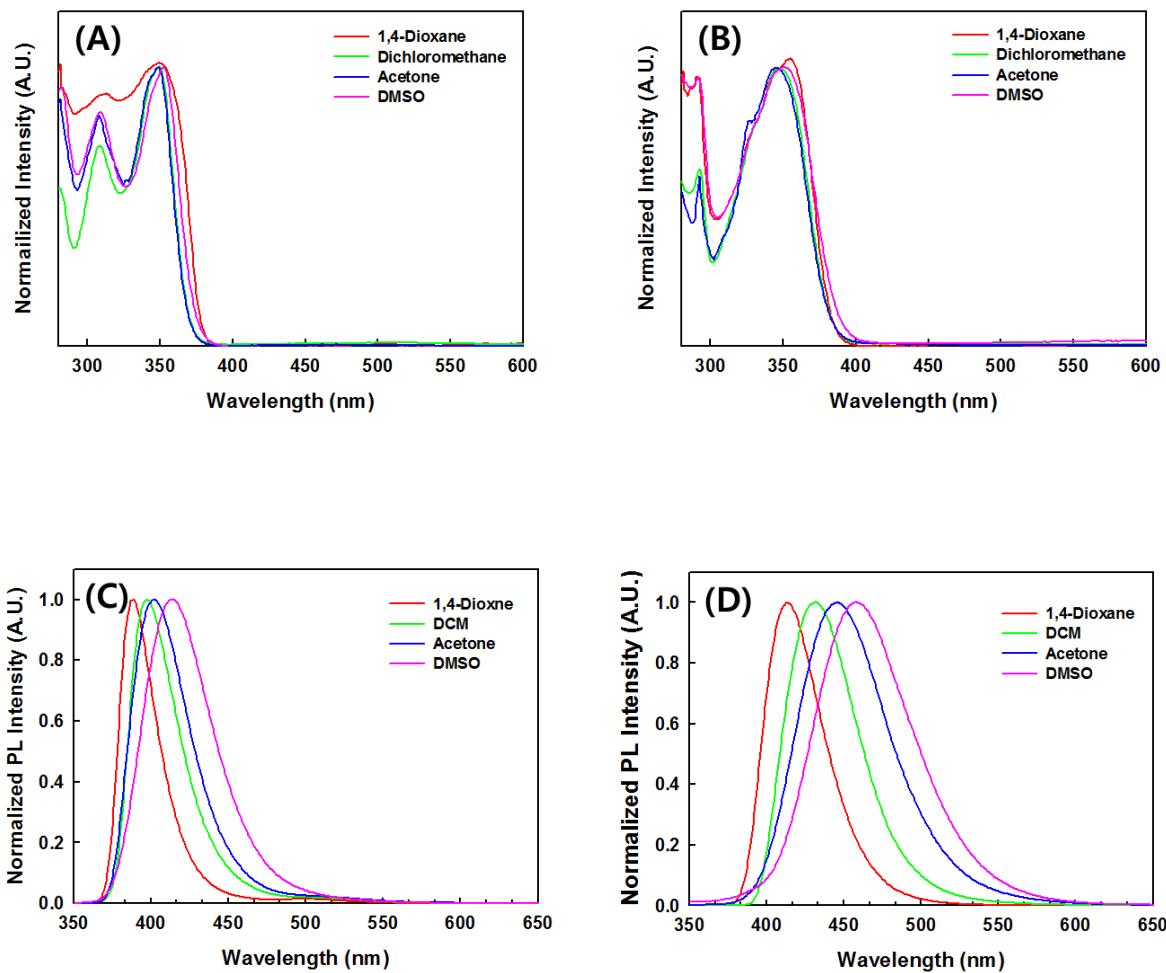


Figure S5. Room-temperature absorption and PL spectra of **1** and **3** in various organic solvents (excited at 330 nm). (A) Absorption spectra for **1**; (B) Absorption spectra for **3**; (C) PL spectra for **1**; (D) PL spectra for **3**.

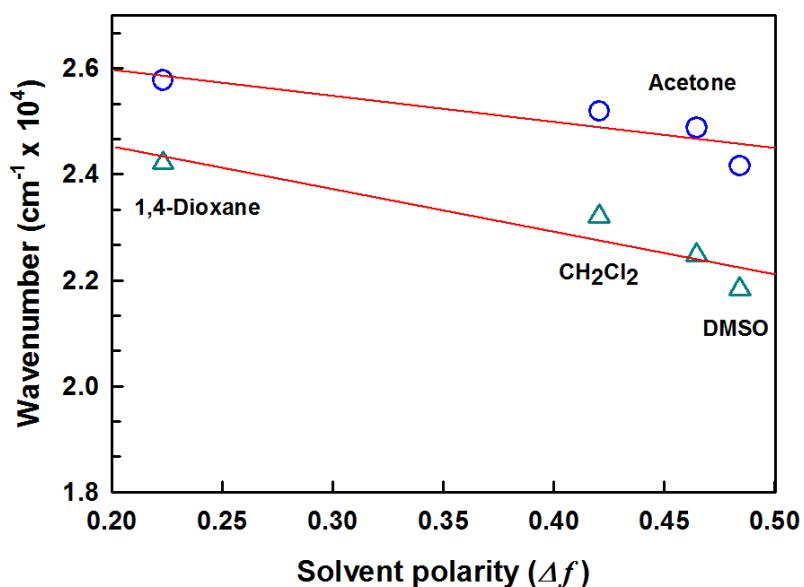


Figure S6. The plot of emission peak frequencies of **1** and **3** solutions as a function of solvent polarities. Δf is the solvent polarity parameter function and is generally expressed as $\Delta f = (\epsilon - 1)/(2\epsilon + 1)$, where ϵ denotes the static dielectric constant of the solvent.

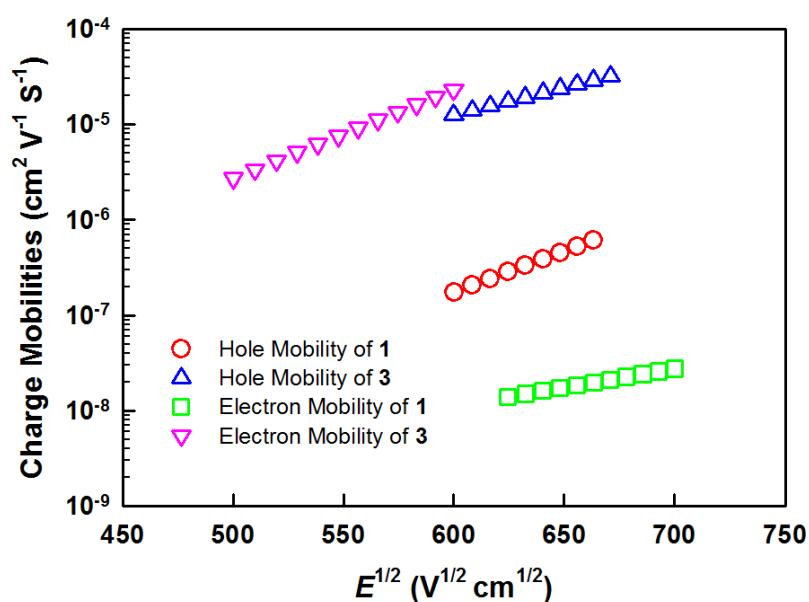


Figure S7. Hole and electron mobilities for **1** and **3** at various electric fields.

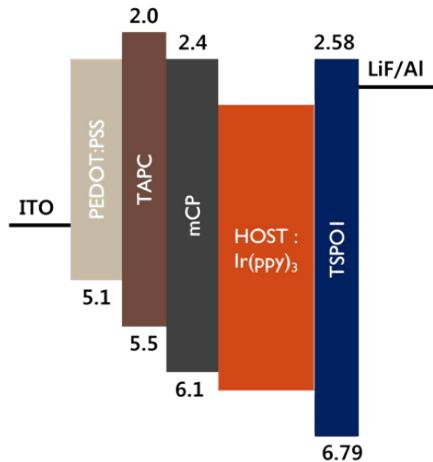


Figure S8. Energy diagram of **1** and **3** green PHOLED device.

Table S1. Physical properties of **1** and **3**.

Sample I D	HOMO	LUMO	Bandgap	T_g	PL	Triplet energy
1	-6.21 eV	-2.86 eV	3.35 eV	105 °C	400 nm	2.88 eV
3	-6.17 eV	-2.95 eV	3.22 eV	89 °C	430 nm	2.77 eV