

Supporting Information

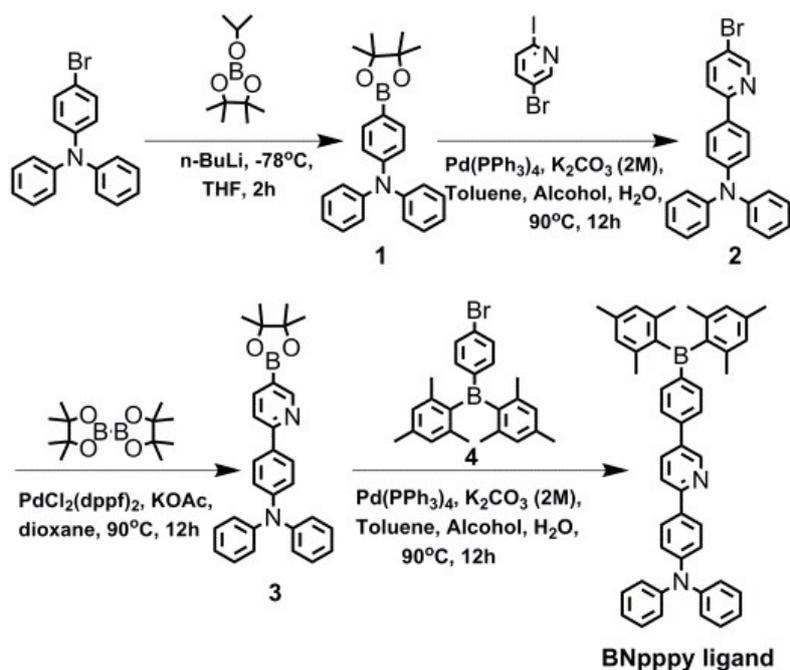
Two novel neutral and ionic Ir(III) complexes based on the same bipolar main ligand: a comparative study of photophysical properties and the application in solution-processed red organic light-emitting diodes

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Scheme S1. Synthetic routes of **BNpppy** ligand

The synthesis of *N,N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**1**). It was modified from a previous procedure. A mixture of 4-bromo-*N,N*-diphenylaniline (2.00 g, 6.2 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.64 g, 6.5 mmol), KOAc (1.66 g, 16.8 mmol), Pd(dppf)Cl₂ (135.50 mg, 0.166 mmol) and dioxane (60.0 mL) were placed into an evacuated round bottom stirred for 16 h at 90 °C under nitrogen. After cooling to room temperature, the solution was extracted with dichloromethane and washed with water and brine. The organic layer was dried over MgSO₄, and the solvents were removed in vacuo. The crude material was purified by column chromatography over silica gel (PE: DCM = 4:1) to obtain white solid (1.70 g, yield: 74%). ¹H NMR (300 MHz, CDCl₃): δ = 7.67 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 4H), 7.13 – 7.00 (m, 8H), 1.33 (s, 12H). ¹³C NMR (126 MHz, CDCl₃): δ = 150.61, 147.44, 135.86, 129.28, 124.99, 123.35, 121.83,

83.43, 24.61.

The synthesis of 4-(5-bromopyridin-2-yl)-N,N-diphenylaniline(2). A mixture of N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (742.00 mg, 2 mmol), 5-bromo-2-iodopyridine (568.00 mg, 2 mmol), Pd(PPh₃)₄ (50.00 mg, 0.04 mmol), K₂CO₃ (816.00 mg, 6 mmol), toluene (6.0 mL), H₂O (3.0 mL) and EtOH (3.0 mL) were placed into an evacuated round bottom stirred for 12 h at 80 °C under nitrogen. After cooling to room temperature, the solution was extracted with dichloromethane and washed with water and brine. The organic layer was dried over MgSO₄, and the solvents were removed in vacuo. The crude material was purified by column chromatography over silica gel (PE: DCM = 20:1) to obtain the yellow solid (641.60 mg, yield: 80%). ¹H NMR (300 MHz, DMSO): δ = 8.70 (d, *J* = 1.8 Hz, 1H), 8.05 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 4H), 7.09 (t, *J* = 8.9 Hz, 6H), 7.00 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 155.52, 150.54, 149.08, 147.34, 139.10, 131.66, 129.35, 127.58, 124.90, 123.44, 122.87, 120.81, 118.37.

The synthesis of N,N-diphenyl-4-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)aniline(3). A mixture of 4-(5-bromopyridin-2-yl)-N,N-diphenylaniline (802.00 mg, 2 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.52 g, 6 mmol), KOAc (1.18 g, 12 mmol), Pd(dppf)Cl₂ (120.00 mg, 0.16 mmol) and dioxane (60.0 mL) were placed into an evacuated round bottom stirred for 16 h at 90

°C under nitrogen. After cooling to room temperature, filtered, and the filtrant was washed with EtOAc. The organics were then washed with sat. NaHCO₃, sat. NH₄Cl and brine, dried over MgSO₄, filtered and removed in vacuo. The crude material was then taken up in hexanes, the insolubles filtered off and the filtrate concentrated, obtained white-yellow foam (852.00 mg, yield: 95%). ¹H NMR (500 MHz, DMSO): δ = 8.83 (s, 1H), 8.06 (t, *J* = 7.4 Hz, 3H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 4H), 7.13 (m, 6H), 7.05 (d, *J* = 8.6 Hz, 2H), 1.35 (s, 12H). ¹³C NMR (126 MHz, CDCl₃): δ = 158.98, 155.15, 148.83, 147.25, 142.98, 132.57, 129.28, 128.01, 124.80, 123.38, 122.95, 119.05, 83.97, 24.69.

The synthesis of (4-bromophenyl)dimesitylborane(4). A mixture of 1,4-dibromobenzene (567.00 mg, 2.4 mmol) and THF (24.0 mL) were placed into an evacuated round bottom stirred under nitrogen, after cooling to -78 °C, n-BuLi (2.5 M in hexanes, 1.65 mL, 2.64 mmol) was added to the solution dropwise over 15 min and the mixture was stirred for 2 h at -78 °C under nitrogen, then dry fluorodimesitylborane (708.00 mg, 2.64 mmol) in THF (5.0 mL) was added to the reaction mixture dropwise, then continue reaction at -78 °C for 1 h. After that, temperature was raised slowly to ambient temperature and kept stirring overnight. The distilled water was added to the reaction mixture to quench the procedure, the solution was extracted with dichloromethane and washed with water and brine. The organic layer was dried over MgSO₄, and the solvents were removed in vacuo. The crude material was purified by column chromatography over silica gel (PE: DCM = 15:1) to

obtain the white solid (708.60 mg, yield: 75%). ¹H NMR (500 MHz, DMSO): δ = 7.63 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.83 (s, 4H), 2.26 (s, 6H), 1.92 (s, 12H). ¹³C NMR (126 MHz, CDCl₃): δ = 140.78, 138.94, 138.60, 137.77, 136.28, 131.30, 128.28, 127.35, 23.40, 21.19.

The synthesis of 4-(5-(4-(dimesitylboranyl)phenyl)pyridin-2-yl)-N,N-diphenylaniline (BNpppy). A mixture of **3** (448.00 mg, 1 mmol), **4** (405.00 mg, 1 mmol), Pd(PPh₃)₄ (50.00 mg, 0.04 mmol), K₂CO₃ (408.00 mg, 3 mmol), toluene (3.0 mL), H₂O (1.5 mL) and EtOH (1.5 mL) were placed into an evacuated round bottom stirred for 12 h at 90 °C under nitrogen. After cooling to room temperature, the solution was extracted with dichloromethane and washed with water and brine. The organic layer was dried over MgSO₄, and the solvents were removed in vacuo. The crude material was purified by column chromatography over silica gel (PE: DCM = 20:1) to obtain the yellow-green solid (614.40 mg, yield: 95%). ¹H NMR (300 MHz, DMSO): δ = 9.02 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 4H), 7.17 -7.02 (m, 8H), 6.86 (s, 4H), 2.28 (s, 6H), 1.98 (s, 12H). ¹³C NMR (126 MHz, DMSO): δ = 154.79, 148.08, 146.54, 140.98, 139.87, 139.66, 137.93, 136.07, 134.49, 132.27, 131.47, 129.13, 127.74, 127.21, 125.67, 124.24, 123.21, 121.81, 118.89, 22.51, 20.32; MALDITOF-MS m/z: Calculated: 646.352, Found: 646.417.

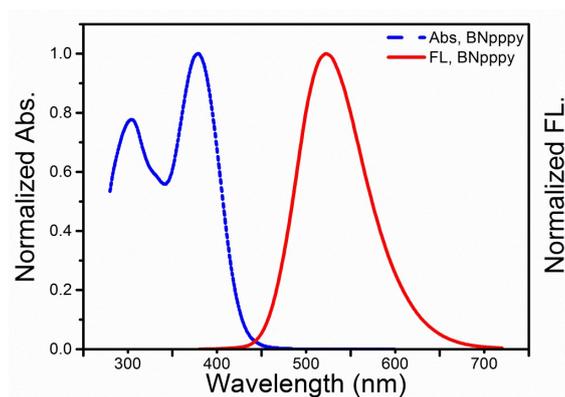


Figure S1. Normalized absorption and emission spectra of **BNpppy** ligand in the CH_2Cl_2 solution (10^{-5} M).

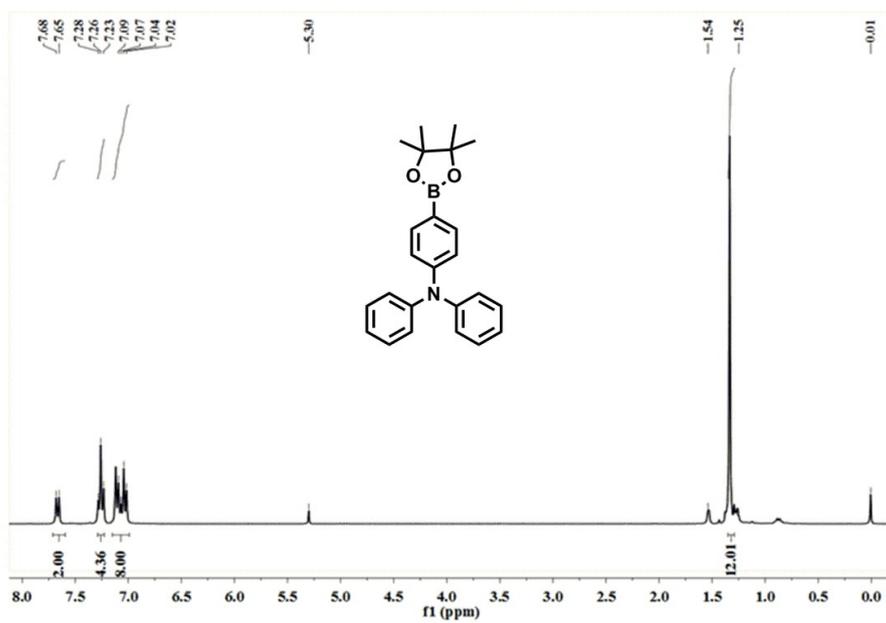


Figure S2. ^1H NMR Spectrum of compound **1**.

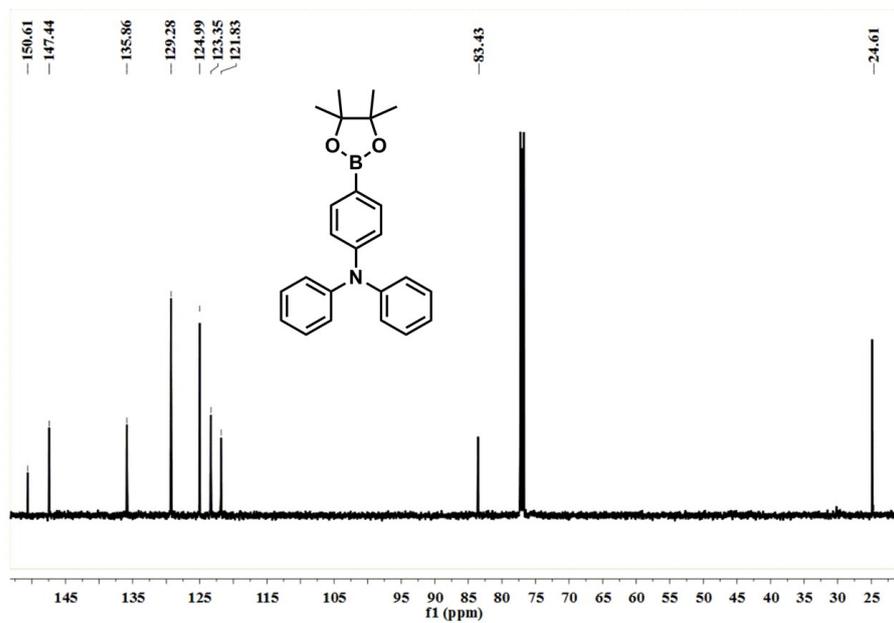


Figure S3. ¹³C NMR Spectrum of compound 1.

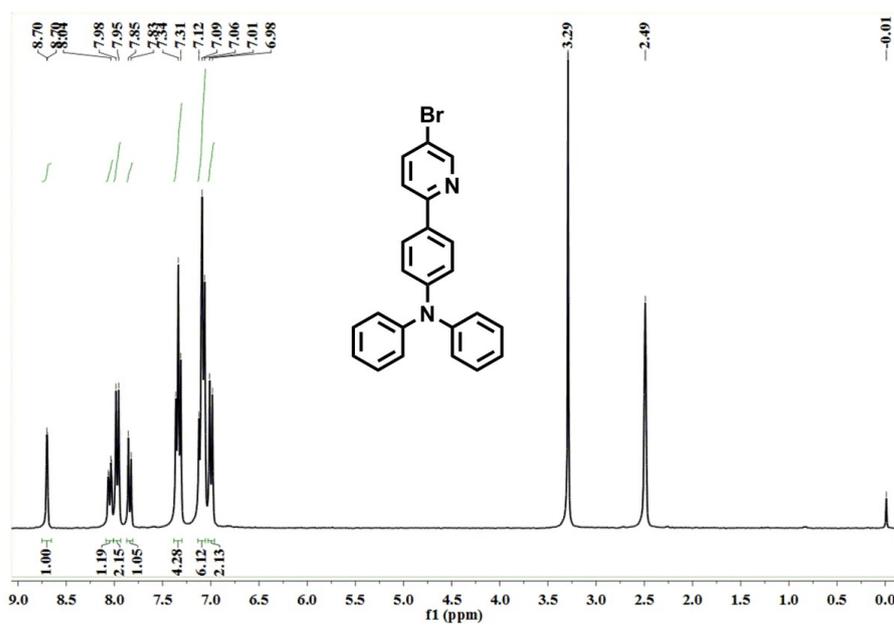


Figure S4. ¹H NMR Spectrum of compound 2.

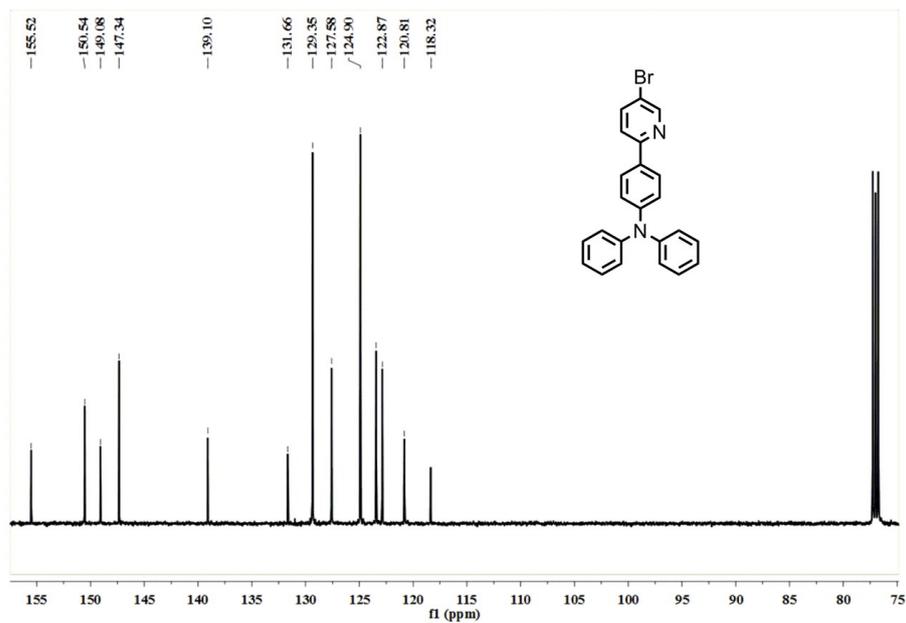


Figure S5. ^{13}C NMR Spectrum of compound 2.

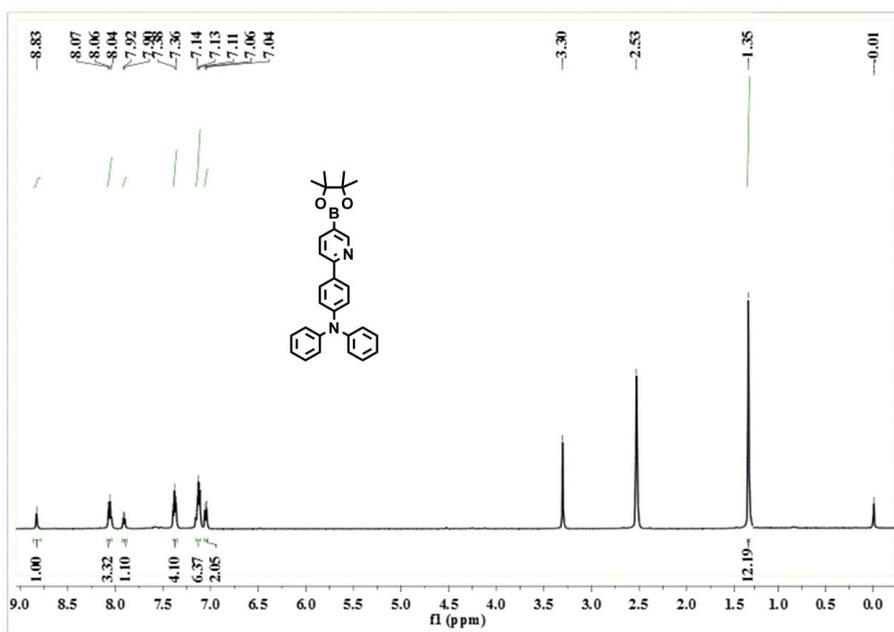


Figure S6. ^1H NMR Spectrum of compound 3.

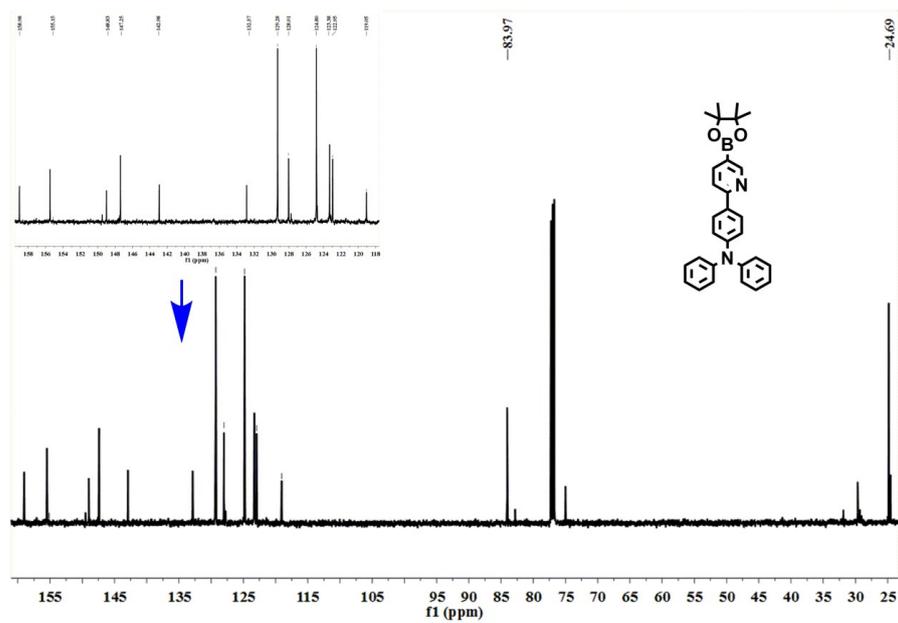


Figure S7. ^{13}C NMR Spectrum of compound 3.

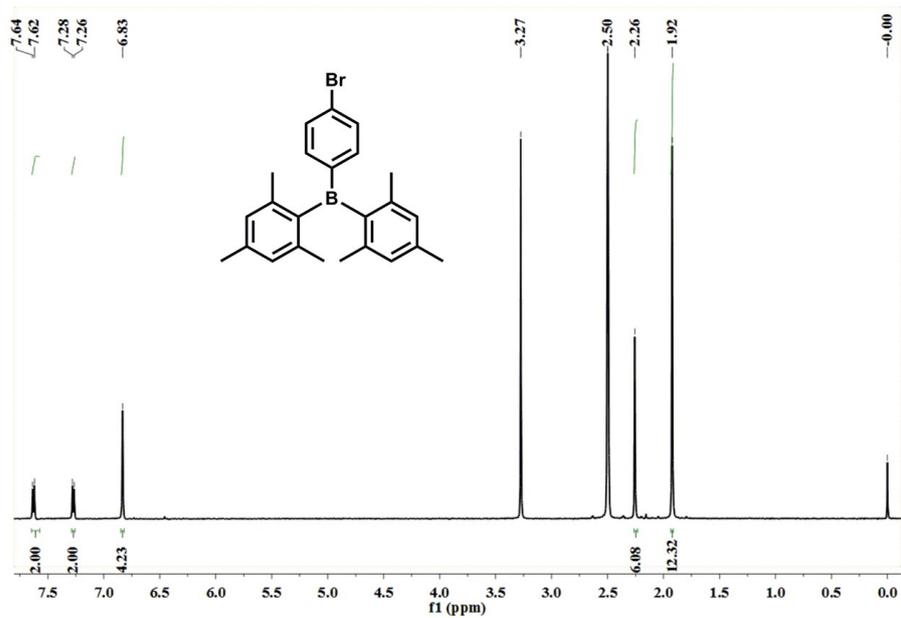


Figure S8. ^1H NMR Spectrum of compound 4.

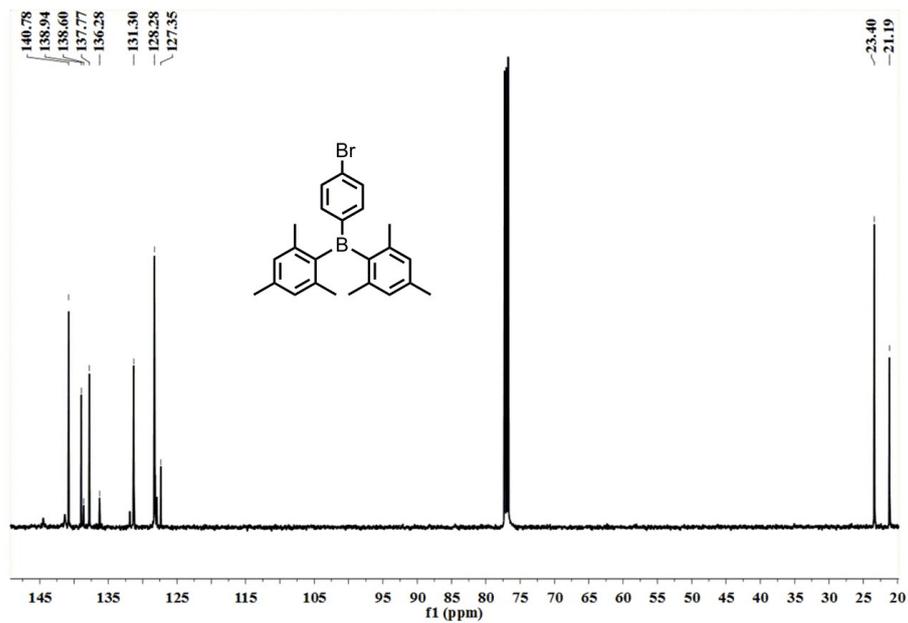


Figure S9. ¹³C NMR Spectrum of compound 4.

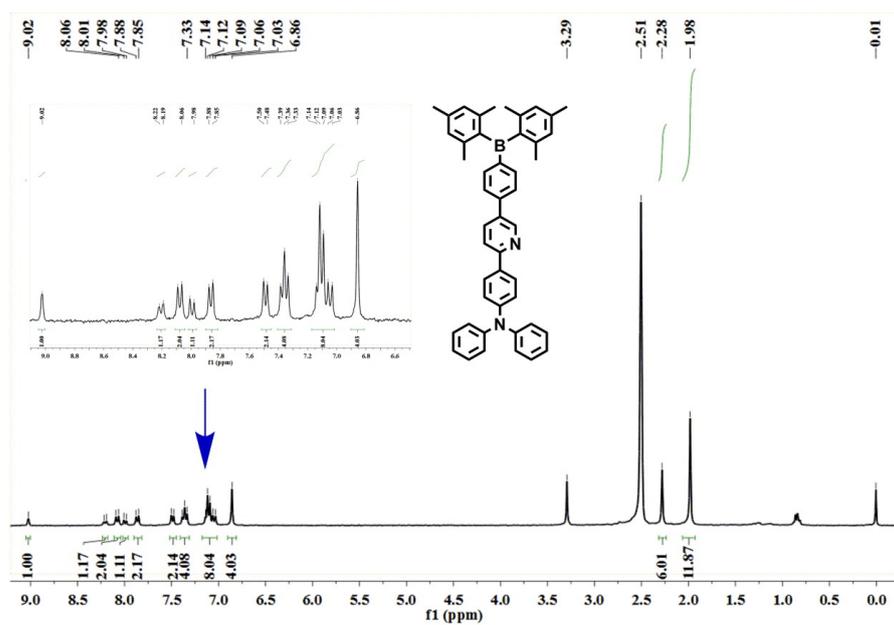


Figure S10. ¹H NMR Spectrum of compound BNppy.

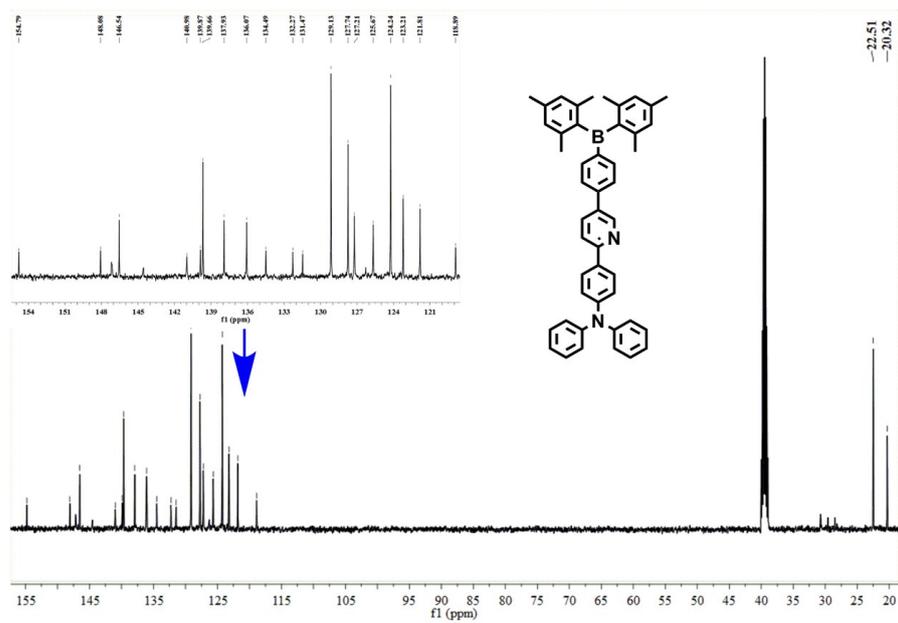


Figure S11. ^{13}C NMR Spectrum of compound **BNpppy**.

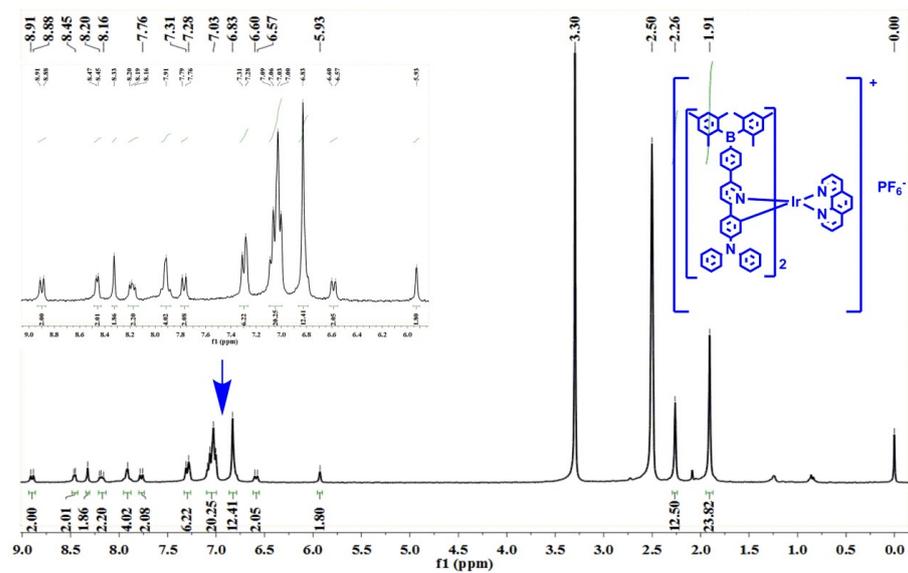


Figure S12. ^1H NMR Spectrum of complex $[(\text{BNpppy})_2\text{Ir}(1,10\text{-phenanthroline})]^+(\text{PF}_6)^-$ (**Ir-1**).

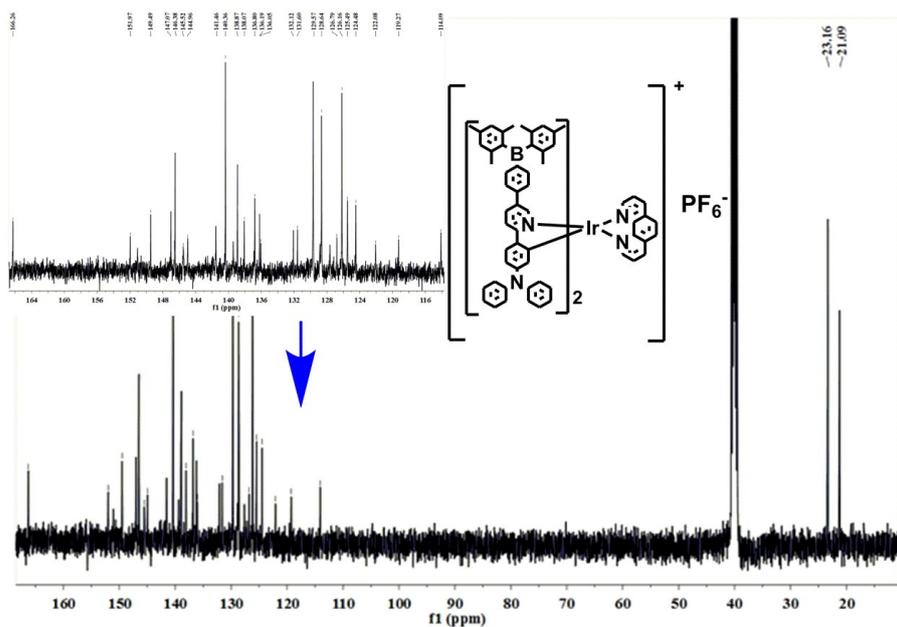


Figure S13. ^{13}C NMR Spectrum of complex $[(\text{BNpppy})_2\text{Ir}(1,10\text{-phenanthroline})]^+(\text{PF}_6^-)$ (**Ir-1**).

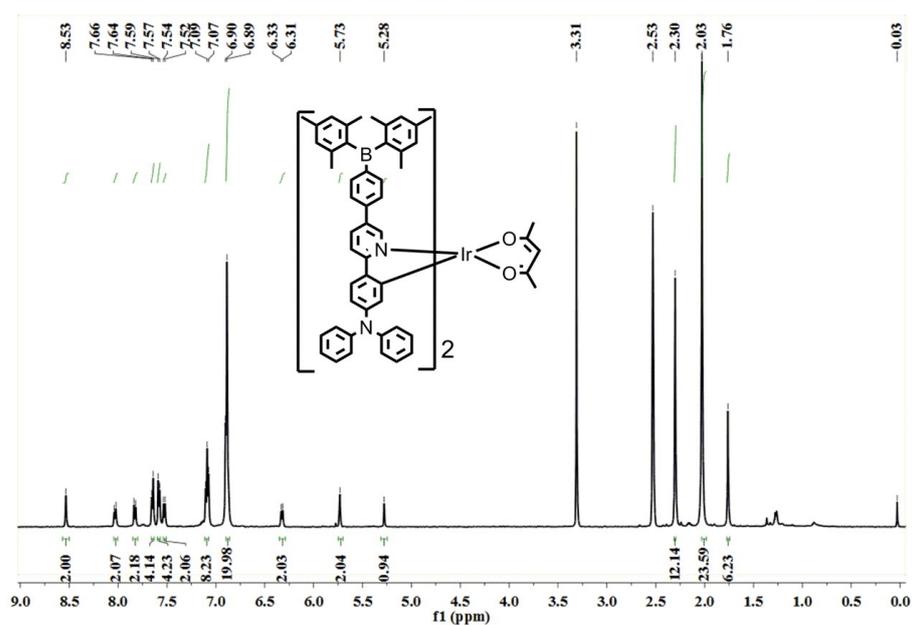


Figure S14. ^1H NMR Spectrum of complex $[(\text{BNpppy})_2\text{Ir}(\text{acac})]$ (**Ir-2**).

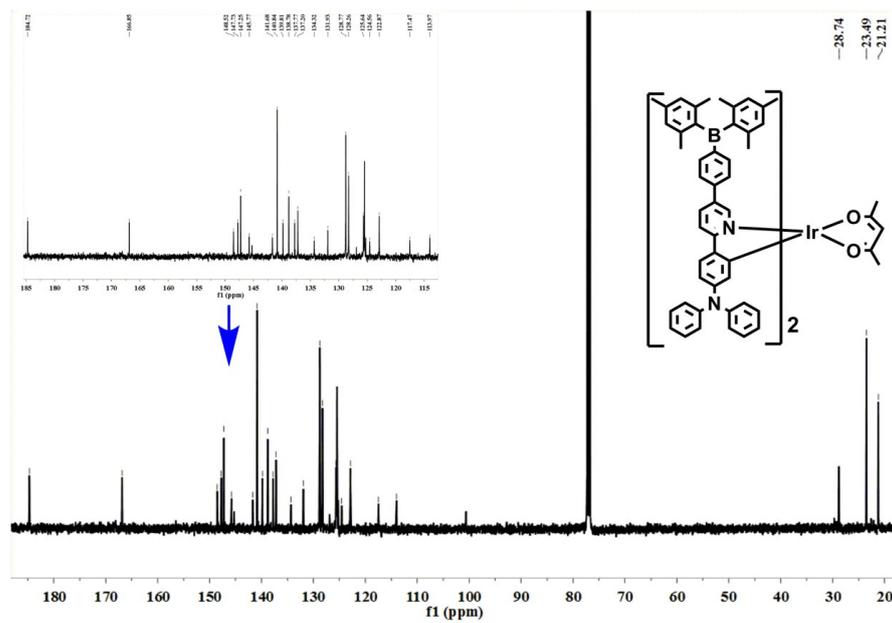


Figure S15. ^{13}C NMR Spectrum of complex $[(\text{BNpppy})_2\text{Ir}(\text{acac})]$ (**Ir-2**).

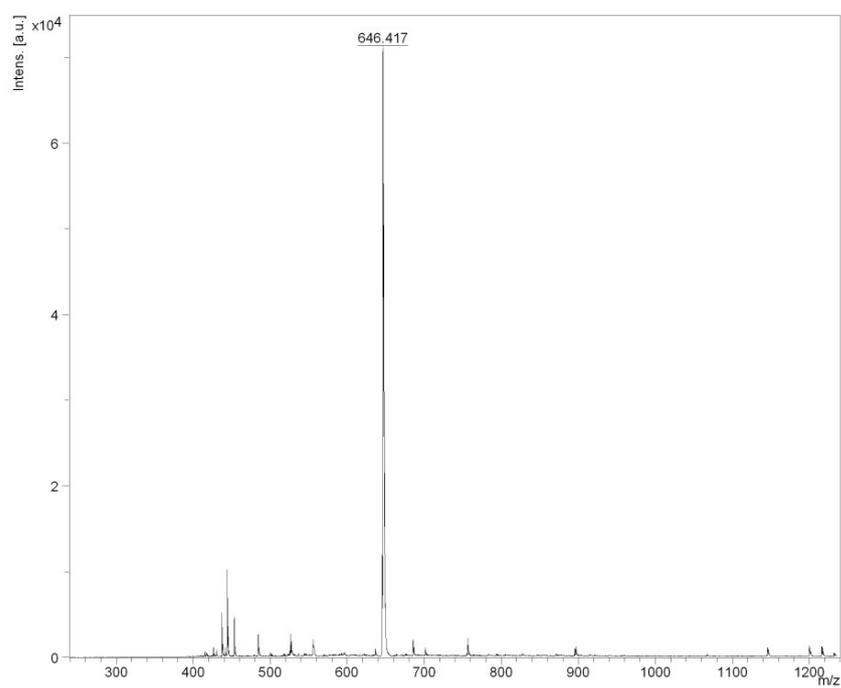


Figure S16. MALDI-TOF Spectrum of compound **BNpppy**.

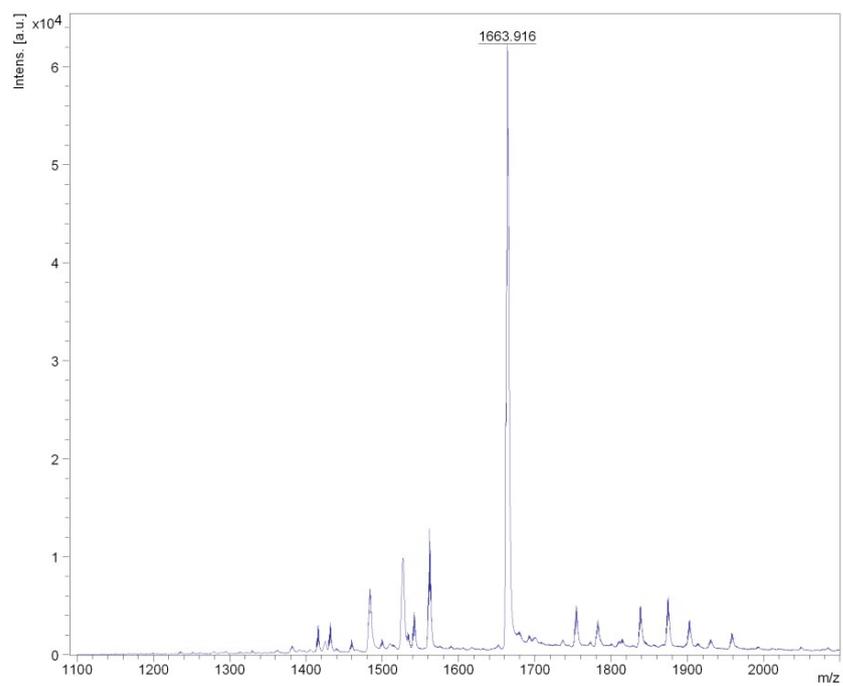


Figure S17. MALDI-TOF Spectrum of complex [(BNpppy)₂Ir(1,10-phenanthroline)]⁺(PF₆⁻) (**Ir-1**).

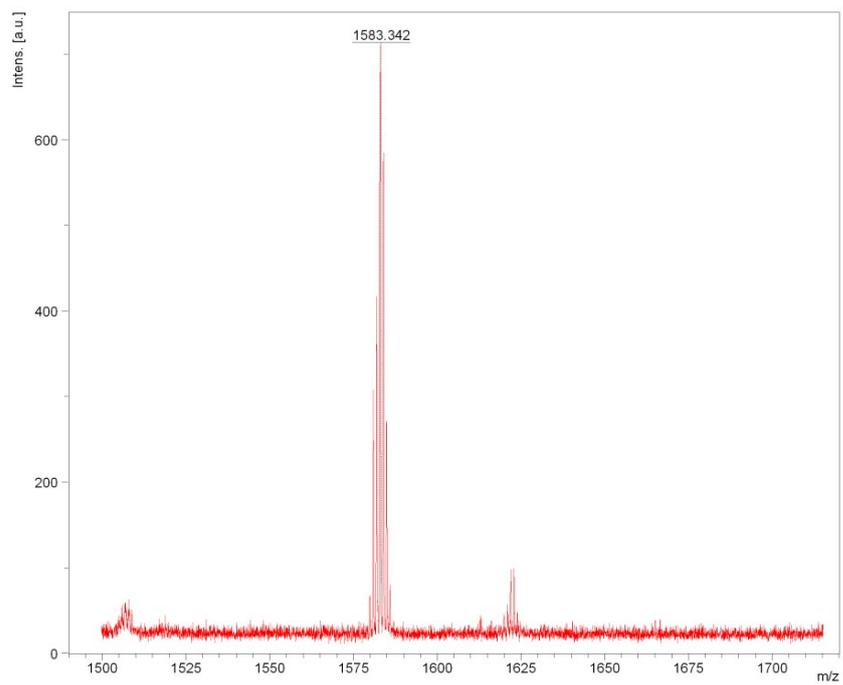


Figure S18. MALDI-TOF Spectrum of complex [(BNpppy)₂Ir(acac)] (**Ir-2**).

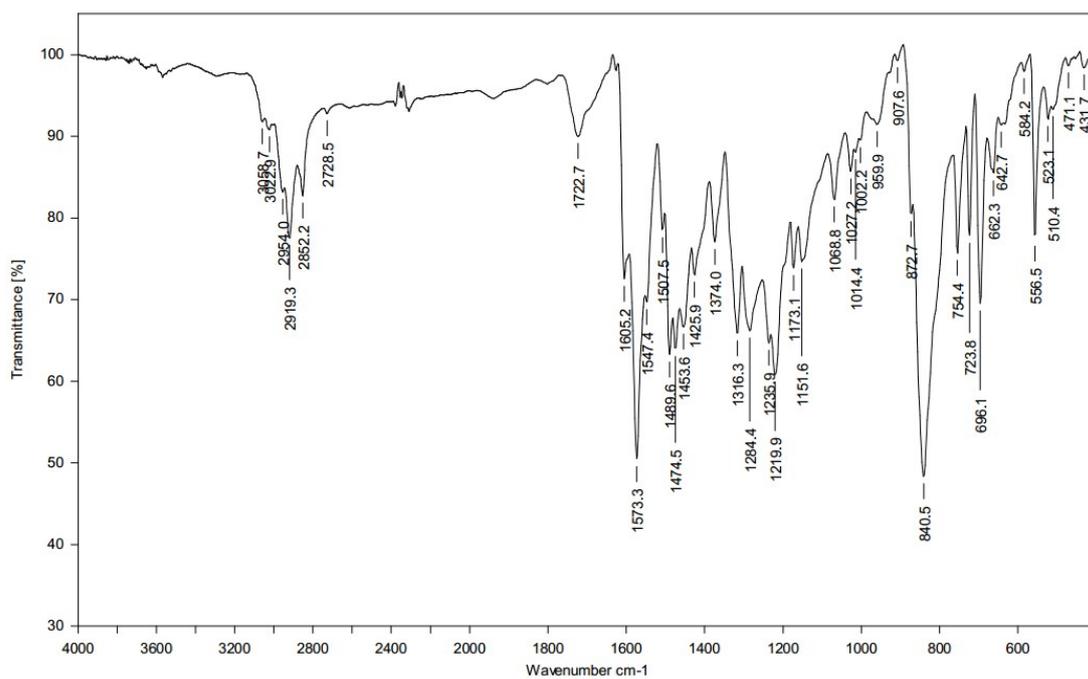


Figure S19. IR Spectrum of complex $[(\text{BNppy})_2\text{Ir}(1,10\text{-phenanthroline})]^+(\text{PF}_6)^-$ (**Ir-1**) in KBr film at 298 K.

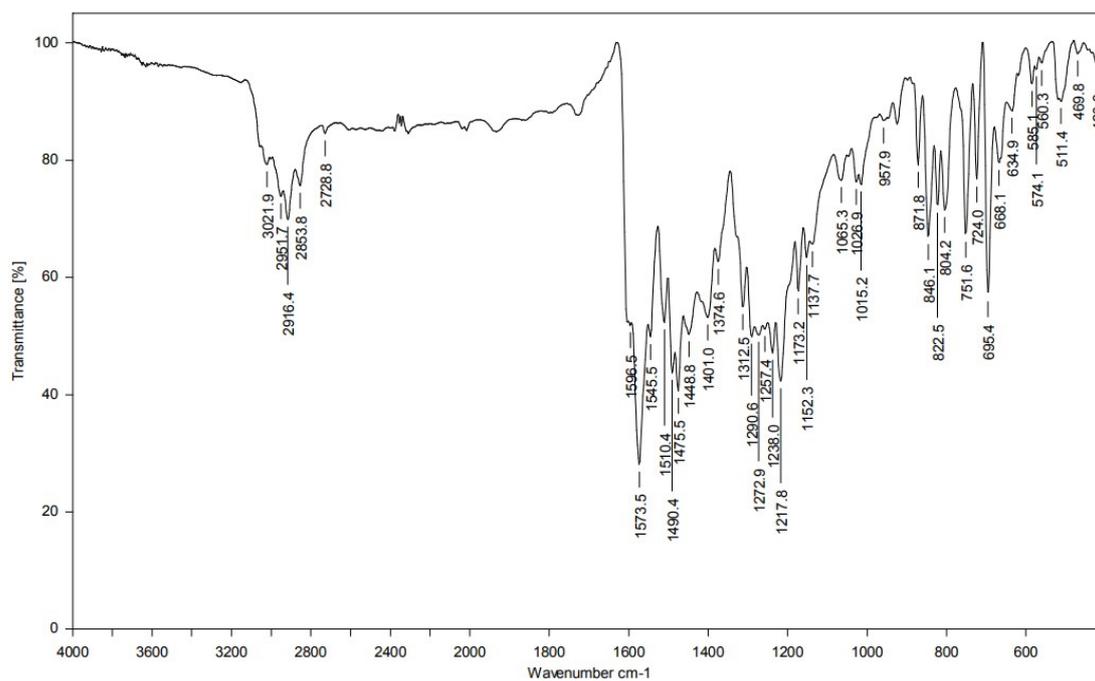


Figure S20. IR Spectrum of complex $[(\text{BNppy})_2\text{Ir}(\text{acac})]$ (**Ir-2**) in KBr film at 298 K.

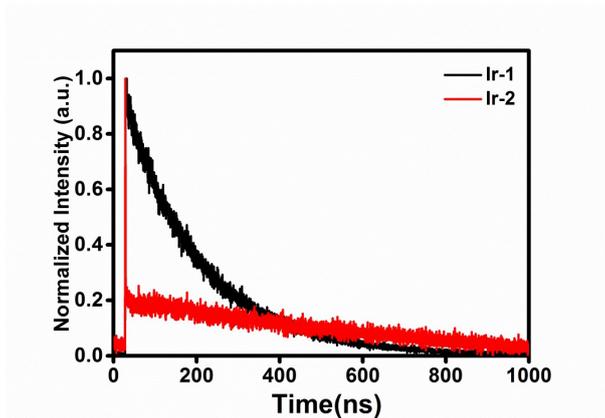


Figure S21. Decay of PL intensity (excited at 400nm) at room temperature of **Ir-1** and **Ir-2** in CH_2Cl_2 solution (10^{-5} M) under N_2 atmosphere.

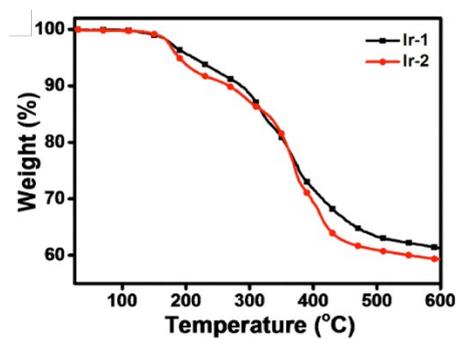


Figure S22. Thermal gravimetric analysis of **Ir-1** and **Ir-2** under nitrogen flow.

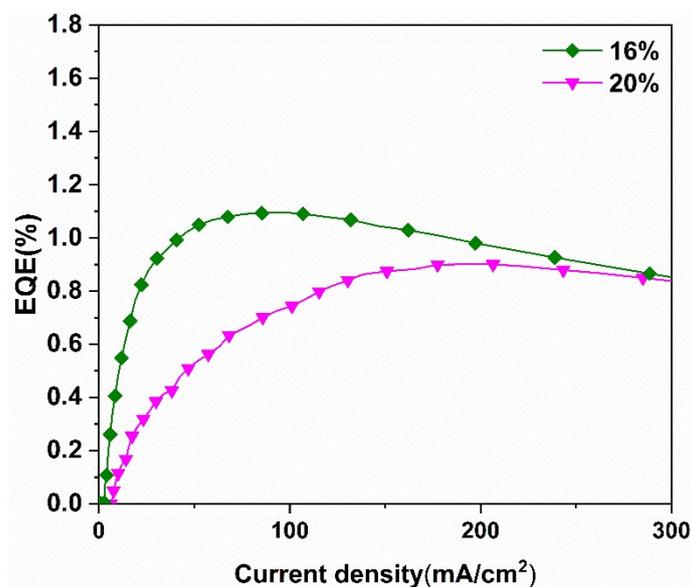


Figure S23. Current density-external quantum efficiency (J-EQE) curves of devices with 14 wt% and 20 wt% emitter doping level (Ir-2 in CBP).

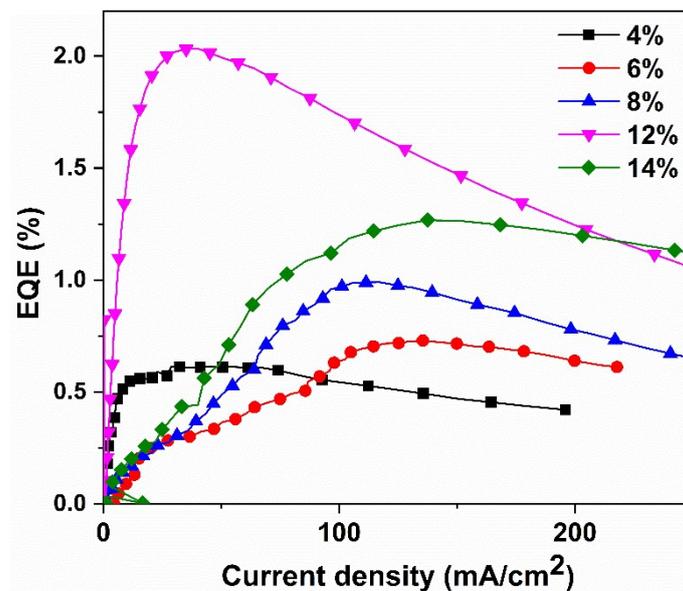


Figure S24. Current density-external quantum efficiency (J-EQE) curves of devices with 14 wt% and 20 wt% emitter doping level (Ir-2 in mCP).

In this work, 1,3-bis(N-carbazolyl)benzene (mCP) was selected as a host material. A series of solution-processed OLEDs have been fabricated by the configuration of indium tin oxide (ITO) / polyethylenimine ethoxylated (PEIE)-modified zinc oxide (ZnO) / mCP: x wt% Ir-2 complex / bis (dimethyl aniline) phenyl cyclohexane (TAPC) / molybdenum oxide (MoO_x) / Al. The current density-external quantum efficiency (J-EQE) curves of each device are showed in Figure S24.