Supporting Information

Saturated-Blue-Emitting [3+2+1] Coordinated Iridium(III) Complexes for Vacuum-Deposited Organic Light-Emitting Devices

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Contents

EXPERIMENTAL SECTION

Materials. Reagents and solvents employed were commercially available without further purification.

Characterization Method. NMR spectra (^{1}H, ^{19}F NMR) were recorded on a 400 NMR spectrometer (Bruker). Chemical shifts in ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm.

The absorption and phosphorescence spectra were performed using a UV-vis spectrophotometer (Cary 5000 UV–vis–NIR, Agilent, USA) and a spectrofluorometer (Edinburgh Instruments Ltd FS5), respectively. Electrochemical measurements were performed with a PalmSens4 electrochemical work station with platinum-carbon as working electrode, platinum wire as the counter electrode, and a saturated calomel electrode (SCE) in saturated KCl aqueous solution as the reference electrode. The cyclic voltammogram was referenced to the ferrocene/ferrocenium couple at a scan rate of 100 mV s^{-1}. Thermogravimetric analysis (TGA) was performed on a Mettler TGA2 thermogravimeter by measuring the weight loss from 25°C to 100°C at a rate of 10°C/min under nitrogen. After 15 minutes, heating from 100°C to 800°C at a rate of 10°C/min under nitrogen.

Device Fabrication. The ITO (indium-tin oxide) coated glass substrates were first cleaned in deionized water, acetone, and ethanol, then dried in an oven and treated by ultraviolet ozone exposure for 20 min. Device fabrication were performed with a FS-450(Suzhou Fangsheng) chamber. All organic layers were thermally evaporated at a rate of 0.5-1.5 Å s^{-1} at a pressure of *ca*. 7.5 ×10^{-7} Torr. A Liq layer (2.5 nm) was

deposited at a rate of 0.2 Å s^{-1}. The Al cathode was deposited at a rate of 4 Å s^{-1}; the active area of the diode segments was 3×3 mm^2. The PHOLEDs devices performance including EL spectra, current density-voltage-luminance (*J-V-L*) curves and Commission Internationale de L'Eclairage (CIE) coordinates were characterized by a Keithley 2400 semiconductor characterization system.

Materials Synthesis

N-(3,4-dimethylphenyl)-3-nitropyridin-2-amine: 2-Chloro-3-nitropyridine (3.0 g, 18.9 mmol), 3,4-dimethylaniline (2.8 g, 22.7 mmol), and triethylamine (2.4 g, 23.6 mmol) were refluxed with 50 mL of 2-propanol for 24 h. Afterward, the reaction mixture was concentrated and extracted with diethyl ether. *N*-(3,4-dimethylphenyl)-3-nitropyridin-2-amine (2.2 g, 48%) was obtained: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 8.51 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.46 (dd, *J* = 4.5, 1.8 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 8.3, 4.5 Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H).

N-(3,4,5-trimethylphenyl)-3-nitropyridin-2-amine: 2-Chloro-3-nitropyridine (3.0 g, 18.9 mmol), 3,4,5-trimethylaniline (3.1 g, 22.7 mmol), and triethylamine (2.4 g, 23.6 mmol) were refluxed with 50 mL of 2-propanol for 24 h. Afterward, the reaction mixture was concentrated and extracted with diethyl ether. 3-nitro-*N*-(3,4,5-trimethylphenyl)pyridin-2-amine (4.4 g, 91%) was obtained: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.50 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.46 (dd, *J* = 4.5, 1.8 Hz, 1H), 7.23 (s, 2H), 6.77 (dd, *J* = 8.3, 4.4 Hz, 1H), 2.31 (s, 6H), 2.17 (s, 3H).

3-(3,4-dimethylphenyl)-3H-imidazo[4,5-b]pyridine: *N*-(3,4-dimethylphenyl)-3-nitropyridin-2-amine (4.86 g, 12.4 mmol), formic acid (122 g, 2.66 mol), ammonium

chloride (11.2 g, 0.21 mol), and iron powder (100 mesh, 11.7 g, 0.21 mol) were suspended in 40 mL of 2-propanol and refluxed for 48 h. Afterward, the reaction mixture was concentrated to dryness, washed with 200 mL of a saturated aqueous NaHCO$_3$ solution, and extracted with dichloromethane; organics were dried over MgSO$_4$, and volatiles were removed. The product was obtained in 86% yield (3.85 g): ^{1}H NMR (400 MHz, Chloroform-d) δ 8.46 (dd, J = 4.8, 1.4 Hz, 1H), 8.30 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.43 (dd, J = 8.0, 2.3 Hz, 1H), 7.33 – 7.29 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H).

3-(3,4,5-trimethylphenyl)-3H-imidazo[4,5-b]pyridine: N-(3,4,5-trimethylphenyl)-3-nitropyridin-2-amine (7.72 g, 30.0 mmol), formic acid (183.6 g, 3.99 mol), ammonium chloride (16.6 g, 0.31 mol), and iron powder (100 mesh, 17.3 g, 0.31 mol) were suspended in 80 mL of 2-propanol and refluxed for 48 h. Afterward, the reaction mixture was concentrated to dryness, washed with a saturated aqueous NaHCO$_3$ solution, and extracted with dichloromethane; organics were dried over MgSO$_4$, and volatiles were removed. The product was obtained in 71% yield (5.03 g): ^{1}H NMR (400 MHz, Chloroform-d) δ 8.45 (dd, J = 4.8, 1.5 Hz, 1H), 8.27 (s, 1H), 8.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.32 (s, 2H), 7.29 (dd, J = 8.1, 4.8 Hz, 1H), 2.38 (s, 6H), 2.24 (s, 3H).

1-methyl-3-(3,4-dimethylphenyl)-3H-imidazo[4,5-b]pyridin-1-ium iodide (pmpMe$_2$): 3-(3,4-dimethylphenyl)-3H-imidazo[4,5-b]pyridine (3.85 g, 17.2 mmol) and methyl iodide (2.4 g, 17.2 mmol) were dissolved in 20 mL of THF and stirred at 60 °C for 72 h in Schlenk tube. Afterward, the precipitate was filtered, washed with diethyl ether, and dried in vacuo. The product was obtained in 38% yield (2.37 g): ^{1}H NMR (400

MHz, DMSO-d6) δ 10.33 (s, 1H), 8.81 (d, J = 4.7 Hz, 1H), 8.68 (dd, J = 8.4, 1.4 Hz, 1H), 7.87 (dd, J = 8.4, 4.7 Hz, 1H), 7.67 (s, 1H), 7.62 (dd, J = 8.0, 2.3 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 4.18 (s, 3H), 2.36 (s, 6H).

1-methyl-3-(3,4,5-trimethylphenyl)-3H-imidazo[4,5-b]pyridin-1-iumiodide(pmpMe₃): 3-(3,4,5-trimethylphenyl)-3*H*-imidazo[4,5-b]pyridine (5.0 g, 21.2 mmol) and methyl iodide (3.0 g, 21.2 mmol) were dissolved in 20 mL of THF and stirred at 60 °C for 72 h in Schlenk tube. Afterward, the precipitate was filtered, washed with diethyl ether, and dried in vacuo. The product was obtained in 74% yield (5.96 g): ¹H NMR (400 MHz, DMSO-d6) δ 10.32 (d, J = 2.5 Hz, 1H), 8.81 (dd, J = 4.8, 1.4 Hz, 1H), 8.67 (d, J = 8.4 Hz, 1H), 7.87 (dd, J = 8.4, 4.8 Hz, 1H), 7.54 (s, 2H), 4.18 (s, 3H), 2.38 (s, 6H), 2.25 (s, 3H).

1-benzyl-3-(3,4-dimethylphenyl)-3H-imidazo[4,5-b]pyridin-1-ium bromide (pmpMe₂Bz): 3-(3,4-dimethylphenyl)-3H-imidazo[4,5-b]pyridine (9.8 g, 43.7 mmol) and benzyl bromide (7.5 g, 43.7 mmol) were dissolved in 20 mL of THF and stirred at 110 °C for 24 h in Schlenk tube. Afterward, the precipitate was filtered, washed with diethyl ether, and dried in vacuo. The product was obtained in 31% yield (5.4 g, %): ¹H NMR (400 MHz, Chloroform-d) δ 11.76 (s, 1H), 8.71 (dd, J = 4.7, 1.3 Hz, 1H), 8.21 (dd, J = 8.5, 1.4 Hz, 1H), 7.84 (d, J = 2.4 Hz, 1H), 7.78 (dd, J = 8.1, 2.4 Hz, 1H), 7.67 (dd, J = 7.5, 2.0 Hz, 2H), 7.58 (dd, J = 8.4, 4.7 Hz, 1H), 7.38 – 7.34 (m, 4H), 6.28 (s, 2H), 2.38 (s, 3H), 2.34 (s, 3H).

1-benzyl-3-(3,4,5-trimethylphenyl)-3H-imidazo[4,5-b]pyridin-1-ium bromide(pmpMe₃Bz): 3-Phenyl-3*H*-imidazo[4,5-b]pyridine (5.8 g, 24.4 mmol) and

benzyl bromide (4.2 g, 24.4 mmol) were dissolved in 20 mL of THF and stirred at 110 °C for 24 h in Schlenk tube. Afterward, the precipitate was filtered, washed with diethyl ether, and dried in vacuo. The product was obtained in 74% yield (7.4 g): ^{1}H NMR (400 MHz, Chloroform-d) δ 11.68 (s, 1H), 8.70 (d, J = 4.4 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 7.68 –7.66 (m, 4H), 7.57 (dd, J = 8.4, 4.7 Hz, 1H), 7.40 – 7.32 (m, 3H), 6.29 (s, 2H), 2.39 (s, 6H), 2.24 (s, 3H).

General Synthesis of Iridium Complexes. Under the protection of N_2, **pbib** (0.90 mmol, 435.9 mg) and [Ir(COD)Cl]$_2$ (0.45 mmol, 300.0 mg) were added to a mixture of triethylamine (1 mL) and acetonitrile (15 mL) in Schlenk tube. The suspension was heated at 90 °C for 12 h. After cooling, the solvent was removed off by rotary evaporation to give yellow solid. Then the yellow solid was dissolved in 2-ethoxyethanol (10 mL), and NHC precursors (0.90 mmol) and triethylamine (1 ml) was added to the solution and heated at 150°C under N_2. After cooling to room temperature, 2-ethoxyethanol was distilled under the low pressure. The crude product was purified by silica gel column to afford the intermediate product. Then, the intermediate product was recrystallized in CH_2Cl_2/diethyl ether.

Under the protection of N_2, the intermediate product and the double molar quantity of AgCN were dissolved in a round-bottom flask containing 20 mL of N,N-dimethylformamide (DMF). The suspension was heated at 100 °C under N_2 for 2 h. After cooling, the solvent was filtered and removed off by rotary evaporation to afford the crude product. The crude product was purified by silica gel column to afford the expected product. Then, the expected product was recrystallized in CH_2Cl_2/diethyl

ether.

(pbib)Ir(pmpMe₂)I: Under the protection of N_2, **pbib** (0.90 mmol, 435.9 mg) and [Ir(COD)Cl]₂ (0.45 mmol, 300.0 mg) were added to a mixture of triethylamine (1 mL) and acetonitrile (10 mL) in Schlenk tube. The suspension was heated at 90 °C for 12 h. After cooling, the solvent was distilled by rotary evaporation to give yellow solid. Then the yellow solid was dissolved in 2-ethoxyethanol (10 mL), and **pmpMe₂** (0.90 mmol, 328.7 mg) and triethylamine (1 ml) was added to the solution and heated at 150°C for 24 h under N_2. After cooling to room temperature, 2-ethoxyethanol was distilled under the low pressure. The crude product was purified by silica gel column (eluent = dichloromethane/petroleum ether 3:1 v/v) to afford the expected product (376.2 mg, 47%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.47 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 2H), 7.32 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.24 – 7.20 (m, 3H), 6.67 (d, *J* = 2.1 Hz, 2H), 5.57 (s, 1H), 4.80 (s, 3H), 3.50 – 3.43 (m, , 2H), 3.40 – 3.33 (m, 2H), 2.14 (s, 3H), 1.82 (s, 3H), 1.43 – 1.34 (m, 2H), 1.10 – 0.99 (m, 2H), 0.83 – 0.73 (m, 2H), 0.58 – 0.48 (m, 8H). ESI-MS m/z [**(pbib)Ir(pmpMe₂)I**+H]⁺ calcd for $C_{35}H_{40}IIrN_7$ 878.2019, found 878.2008.

(pbib)Ir(pmpMe₂)CN: Under the protection of N_2, (pbib)Ir(pmpMe₂)I (0.34 mmol, 300.0 mg) and the double molar quantity of AgCN (0.68 mmol, 91.6 mg) were dissolved in a round-bottom flask containing 20 mL of *N,N*-dimethylformamide (DMF). The suspension was heated at 100 °C under N_2 for 2 h. After cooling, the solvent was filtered and removed off by rotary evaporation to afford the crude product.

The crude product was purified by silica gel column (eluent = dichloromethane/ethyl acetate 3:1 v/v) to afford the expected product. Then, the expected product was recrystallized in CH_2Cl_2/diethyl ether (251.5 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.54 (s, 1H), 8.49 (dd, J = 5.0, 1.4 Hz, 1H), 7.82 (dd, J = 8.0, 1.4 Hz, 1H), 7.46 (d, J = 2.1 Hz, 2H), 7.39 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 6.71 (d, J = 2.1 Hz, 2H), 5.60 (s, 1H), 4.60 (s, 3H), 3.38 – 3.25 (m, 4H), 2.14 (s, 3H), 1.80 (s, 3H), 1.42 – 1.34 (m, 2H), 1.10 – 0.99 (m, 2H), 0.83 – 0.74 (m, 2H), 0.59 – 0.48 (m, 8H). ^{13}C NMR (125 MHz, Chloroform-d) δ 191.62, 163.72, 146.85, 145.64, 145.25 (2C), 143.34, 136.16, 136.06, 132.41, 129.60, 129.01 (2C), 128.81, 128.74, 128.26, 122.89, 119.06 (2C), 117.70, 117.48, 116.20, 115.85 (2C), 107.65 (2C), 52.56, 50.86 (2C), 33.03, 19.81 (2C), 19.79, 19.76, 13.44 (2C). **[(pbib)Ir(pmpMe₂)CN+H]**[+] calcd for $C_{36}H_{40}IrN_8$ 777.3005, C 55.51; H 5.43; N14.38; found 777.2993, C 54.64; H 5.048; N 13.7.

(pbib)Ir(pmpMe₃)I: Under the protection of N_2, **pbib** (0.90 mmol, 435.9 mg) and [Ir(COD)Cl]₂ (0.45 mmol, 300.0 mg) were added to a mixture of triethylamine (1 mL) and acetonitrile (10 mL) in Schlenk tube. The suspension was heated at 90 °C for 12 h. After cooling, the solvent was distilled by rotary evaporation to give yellow solid. Then the yellow solid was dissolved in 2-ethoxyethanol (10 mL), and **pmpMe₃** (0.90 mmol, 341.3 mg) and triethylamine (1 ml) was added to the solution and heated at 150°C for 24 h under N_2. After cooling to room temperature, 2-ethoxyethanol was distilled under the low pressure. The crude product was purified by silica gel column (eluent = dichloromethane/petroleum ether 3:1 v/v) to afford the expected product (426.9 mg, 53%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.77 (s, 1H), 8.50 (dd, J = 4.9, 1.4 Hz, 1H),

7.76 (dd, J = 8.0, 1.2 Hz, 1H), 7.47 (d, J = 2.1 Hz, 2H), 7.32 (dd, J = 8.0, 4.9 Hz, 1H), 7.18 (s, 3H), 6.70 (d, J = 2.0 Hz, 2H), 4.72 (s, 3H), 3.31 – 3.18 (m, 4H), 2.27 (s, 3H), 1.89 (s, 3H), 1.40 – 1.30 (m, 2H), 1.20– 1.08 (m, 5H), 0.65 – 0.51 (m, 10H). ESI-MS m/z [**(pbib)Ir(pmpMe₃)I**-I]⁺ calcd for $C_{36}H_{41}IrN_7$ 764.3053, found 764.3055.

(pbib)Ir(pmpMe₃)CN: Under the protection of N_2, (pbib)Ir(pmpMe₃)I (0.34 mmol, 300.0 mg) and the double molar quantity of AgCN (0.68 mmol, 91.6 mg) were dissolved in a round-bottom flask containing 20 mL of *N,N*-dimethylformamide (DMF). The suspension was heated at 100 °C under N_2 for 2 h. After cooling, the solvent was filtered and removed off by rotary evaporation to afford the crude product. The crude product was purified by silica gel column (eluent = dichloromethane/ethyl acetate 3:1 v/v) to afford the expected product. Then, the expected product was recrystallized in CH_2Cl_2/diethyl ether (244.7 mg, 91%).[^1]H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.54 (dd, J = 5.0, 1.4 Hz, 1H), 7.82 (dd, J = 8.1, 1.5 Hz, 1H), 7.53 (d, J = 2.1 Hz, 2H), 7.37 (dd, J = 8.0, 5.0 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.22 – 7.20 (m, 2H), 6.76 (d, J = 2.1 Hz, 2H), 4.51 (s, 3H), 3.20– 3.08 (m, 4H), 2.30 (s, 3H), 1.91 (s, 3H), 1.34 – 1.28 (m, 2H), 1.17 – 1.12 (m, 2H), 1.08 (s, 3H), 0.66 – 0.54 (m, 10H). ESI-MS m/z [**(pbib)Ir(pmpMe₃)CN**+H]⁺ calcd for $C_{37}H_{42}IrN_8$ 791.3162, C 55.58; H 5.31; N 14.40, found 791.3158, C 54.30; H 5.50; N 14.78.

(pbib)Ir(pmpMe₂Bz)Br: Under the protection of N_2, **pbib** (0.90 mmol, 435.9 mg) and [Ir(COD)Cl]₂ (0.45 mmol, 300.0 mg) were added to a mixture of triethylamine (1 mL) and acetonitrile (10 mL) in Schlenk tube. The suspension was heated at 90 °C for 12 h. After cooling, the solvent was distilled by rotary evaporation to give yellow solid. Then

the yellow solid was dissolved in 2-ethoxyethanol (10 mL), and **pmpMe₂Bz** (0.90 mmol, 354.9 mg) and triethylamine (1 ml) was added to the solution and heated at 150°C for 24 h under N_2. After cooling to room temperature, 2-ethoxyethanol was distilled under the low pressure. The crude product was purified by silica gel column (eluent = dichloromethane/petroleum ether 3:1 v/v) to afford the expected product (445.8 mg, 55%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.48 (s, 1H), 8.43 (dd, J = 4.9, 1.4 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.44 (d, J = 2.1 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.25 – 7.18 (m, 4H), 6.74 (s, 2H), 6.65 (d, J = 2.1 Hz, 2H), 5.66 (s, 1H), 3.44 – 3.37 (m, 2H), 3.31 – 3.24 (m, 2H), 2.13 (s, 3H), 1.81 (s, 3H), 1.26 – 1.14 (m, 2H), 0.89 – 0.78 (m, 2H), 0.67 – 0.56 (m, 2H), 0.44 – 0.30 (m, 8H). ESI-MS m/z **[(pbib)Ir(pmpMe₂Bz)Br-Br]**$^+$ calcd for $C_{41}H_{43}IrN_7$ 826.3209, found 826.3208.

(pbib)Ir(pmpMe₂Bz)CN: Under the protection of N_2, (pbib)Ir(pmpMe₂Bz)Br (0.55 mmol, 500.0 mg) and the double molar quantity of AgCN (1.11 mmol, 148.0 mg) were dissolved in a round-bottom flask containing 20 mL of *N,N*-dimethylformamide (DMF). The suspension was heated at 100 °C under N_2 for 2 h. After cooling, the solvent was filtered and removed off by rotary evaporation to afford the crude product. The crude product was purified by silica gel column (eluent = dichloromethane/ethyl acetate 3:1 v/v) to afford the expected product. Then, the expected product was recrystallized in CH_2Cl_2/diethyl ether (423.7 mg, 90%).^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (s, 1H), 8.49 (dd, J = 5.0, 1.4 Hz, 1H), 7.83 (dd, J = 8.1, 1.4 Hz, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 2.1 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.22 (d, J = 7.4 Hz, 2H), 6.69 (d, J = 2.1 Hz, 2H), 6.36 (s, 2H), 5.60 (s, 1H), 3.24 – 3.12 (m, 4H),

2.13 (s, 3H), 1.79 (s, 3H), 1.20 – 1.10 (m, 2H), 0.88 – 0.75 (m, 2H), 0.68 – 0.55 (m, 2H), 0.43 (t, J = 7.1 Hz, 6H), 0.37 – 0.27 (m, 2H). ESI-MS m/z [**(pbib)Ir(pmpMe$_2$Bz)CN**+H]$^+$ calcd for $C_{42}H_{44}IrN_8$ 853.3318, C 58.99; H 5.42; N13.10, found 853.3325, C 54.54; H 4.80; N 12.89.

(pbib)Ir(pmpMe$_3$Bz)Br: Under the protection of N$_2$, **pbib** (0.90 mmol, 435.9 mg) and [Ir(COD)Cl]$_2$ (0.45 mmol, 300.0 mg) were added to a mixture of triethylamine (1 mL) and acetonitrile (10 mL) in Schlenk tube. The suspension was heated at 90 °C for 12 h. After cooling, the solvent was distilled by rotary evaporation to give yellow solid. Then the yellow solid was dissolved in 2-ethoxyethanol (10 mL), and **pmpMe$_3$Bz** (0.90 mmol, 367.5 mg) and triethylamine (1 ml) was added to the solution and heated at 150°C for 24 h under N$_2$. After cooling to room temperature, 2-ethoxyethanol was distilled under the low pressure. The crude product was purified by silica gel column (eluent = dichloromethane/petroleum ether 3:1 v/v) to afford the expected product (386.5 mg, 47%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.72 (s, 1H), 8.44 (dd, J = 5.0, 1.4 Hz, 1H), 7.76 (dd, J = 8.1, 1.5 Hz, 1H), 7.62 (dd, J = 7.5, 2.1 Hz, 2H), 7.48 (d, J = 2.1 Hz, 2H), 7.25 – 7.21 (m, 4H), 7.19 – 7.15 (m, 3H), 6.73 (s, 2H), 6.69 (d, J = 2.0 Hz, 2H), 3.22 – 3.09 (m, 4H), 2.26 (s, 3H), 1.90 (s, 3H), 1.23 – 1.14 (s, 5H), 0.92 – 0.81 (m, 2H), 0.56 – 0.40 (m, 10H). ESI-MS m/z [**(pbib)Ir(pmpMe$_3$Bz)Br**-Br]$^+$ calcd for $C_{42}H_{45}IrN_7$ 840.3366, found 840.3373.

(pbib)Ir(pmpMe$_3$Bz)CN: Under the protection of N$_2$, (pbib)Ir(pmpMe$_3$Bz)Br (0.51 mmol, 465.6 mg) and the double molar quantity of AgCN (1.01 mmol, 135.7 mg) were dissolved in a round-bottom flask containing 20 mL of *N,N*-dimethylformamide

(DMF). The suspension was heated at 100 °C under N_2 for 2 h. After cooling, the solvent was filtered and removed off by rotary evaporation to afford the crude product. The crude product was purified by silica gel column (eluent = dichloromethane/ethyl acetate 3:1 v/v) to afford the expected product. Then, the expected product was recrystallized in CH_2Cl_2/diethyl ether (401.7 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.48 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.60 (s, 2H), 7.52 (d, *J* = 2.1 Hz, 2H), 7.29 – 7.25 (m, 5H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 2.1 Hz, 2H), 6.36 (s, 2H), 3.06 – 2.95 (m, 4H), 2.26 (s, 3H), 1.88 (s, 3H), 1.20 – 1.08 (m, 2H), 1.05 (s, 3H), 0.90 – 0.79 (m, 2H), 0.55 – 0.40 (m, 10H). ESI-MS m/z [**(pbib)Ir(pmpMe₃Bz)CN**+H]$^+$ calcd for $C_{43}H_{46}IrN_8$ 867.3475, C 59.06; H 5.31; N 13.12, found 867.3477, C 57.52; H 5.36; N 13.51.
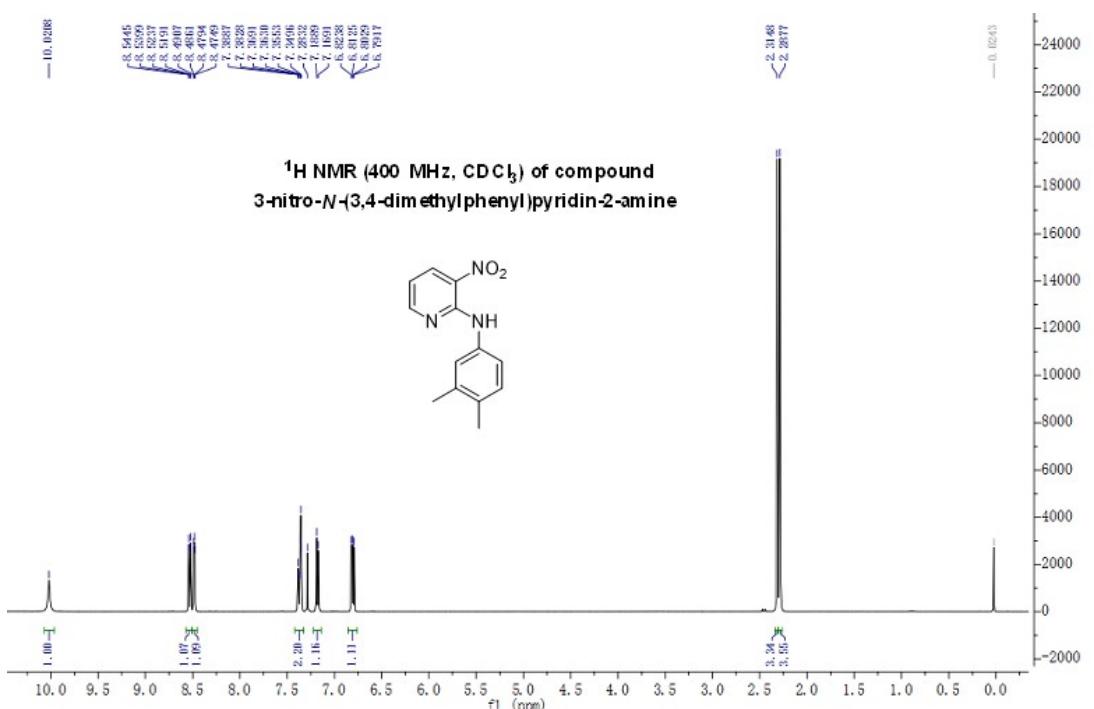
Figure S1. [^1]H NMR (400MHz, CDCl$_3$) of compound ***N-(3,4-dimethylphenyl)-3-nitropyridin-2-amine***
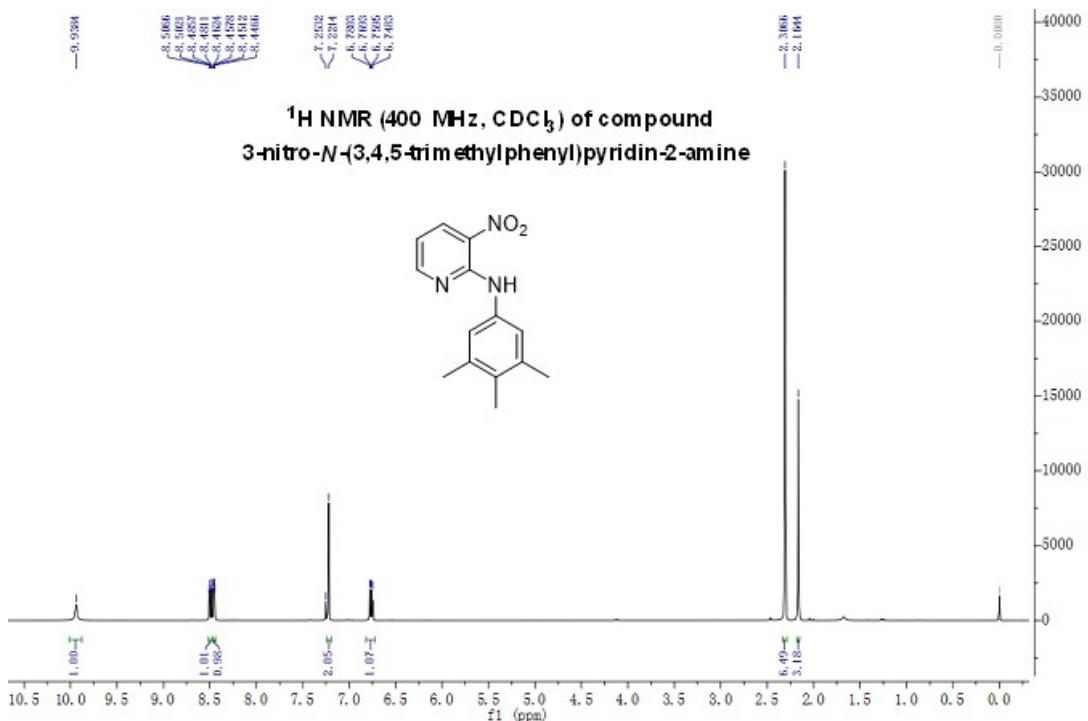
Figure S2. [^1]H NMR (400MHz, CDCl$_3$) of compound ***N-(3,4-dimethylphenyl)-3-nitropyridin-2-amine***
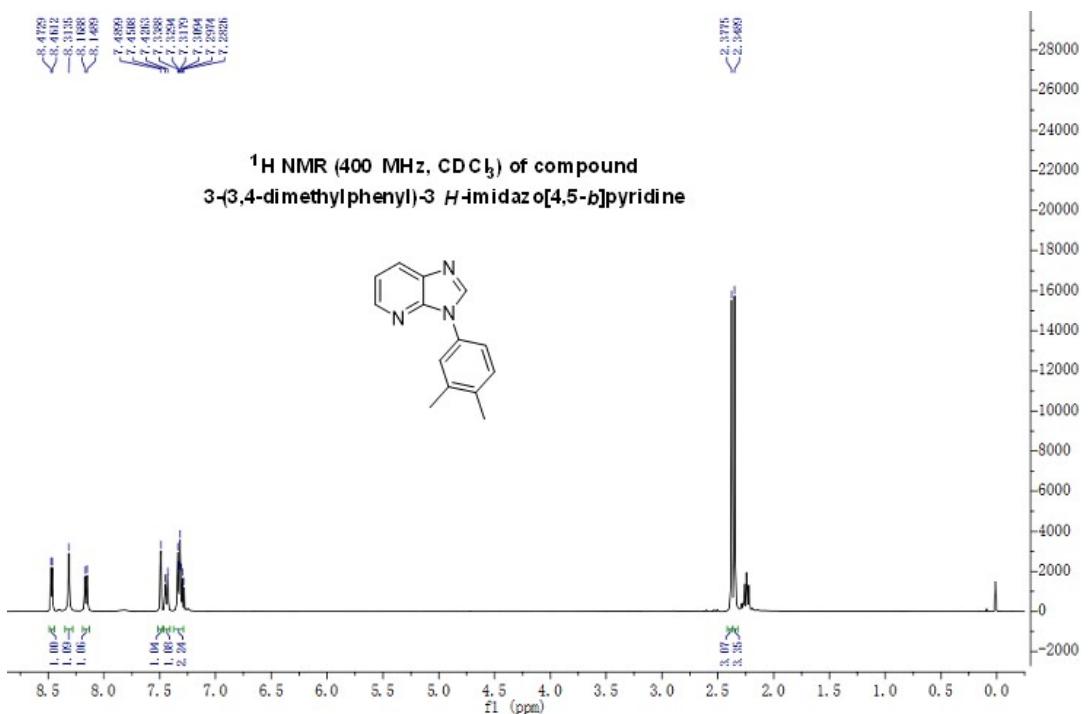
Figure S3. ^{1}H NMR (400MHz, CDCl$_3$) of compound **3-(3,4-dimethylphenyl)-3H-imidazo[4,5-b]pyridine**
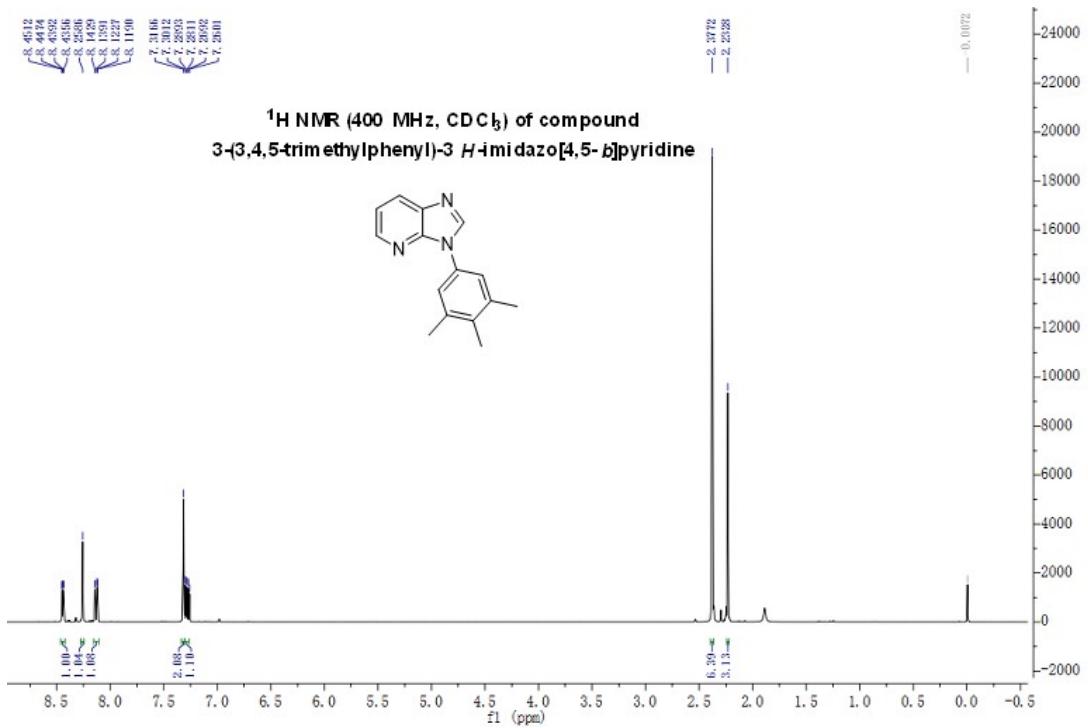
Figure S4. ^{1}H NMR (400MHz, CDCl$_3$) of compound **3-(3,4,5-trimethylphenyl)-3H-imidazo[4,5-b]pyridine**
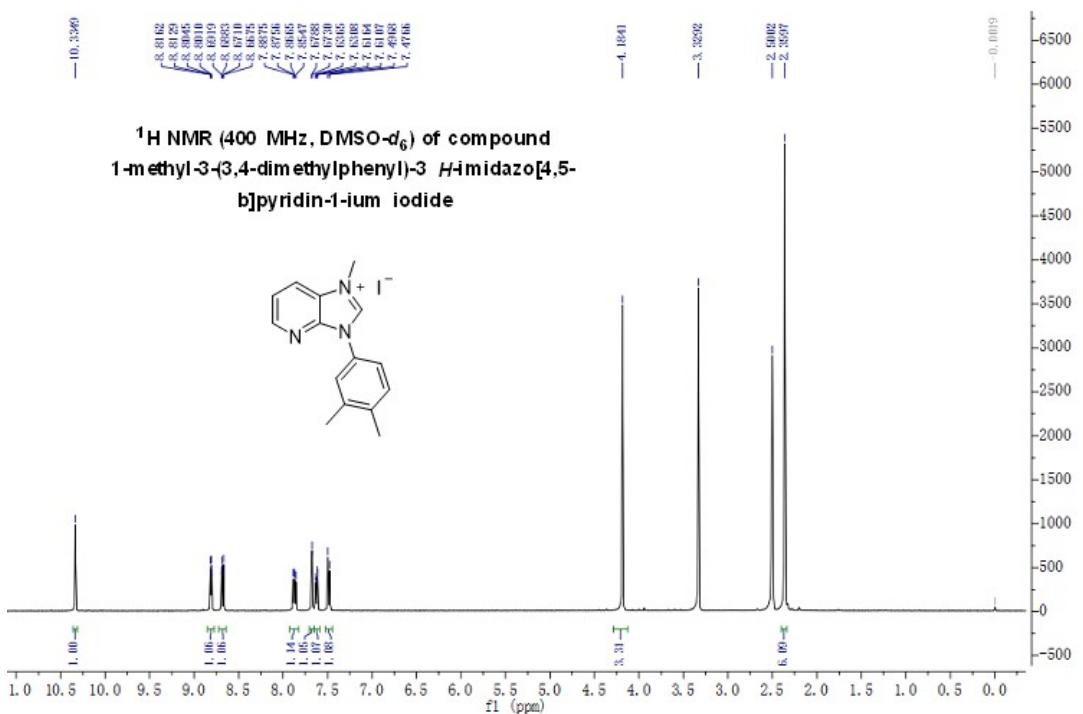
Figure S5. ^{1}H NMR (400MHz, CDCl$_3$) of compound ***pmpMe$_2$***
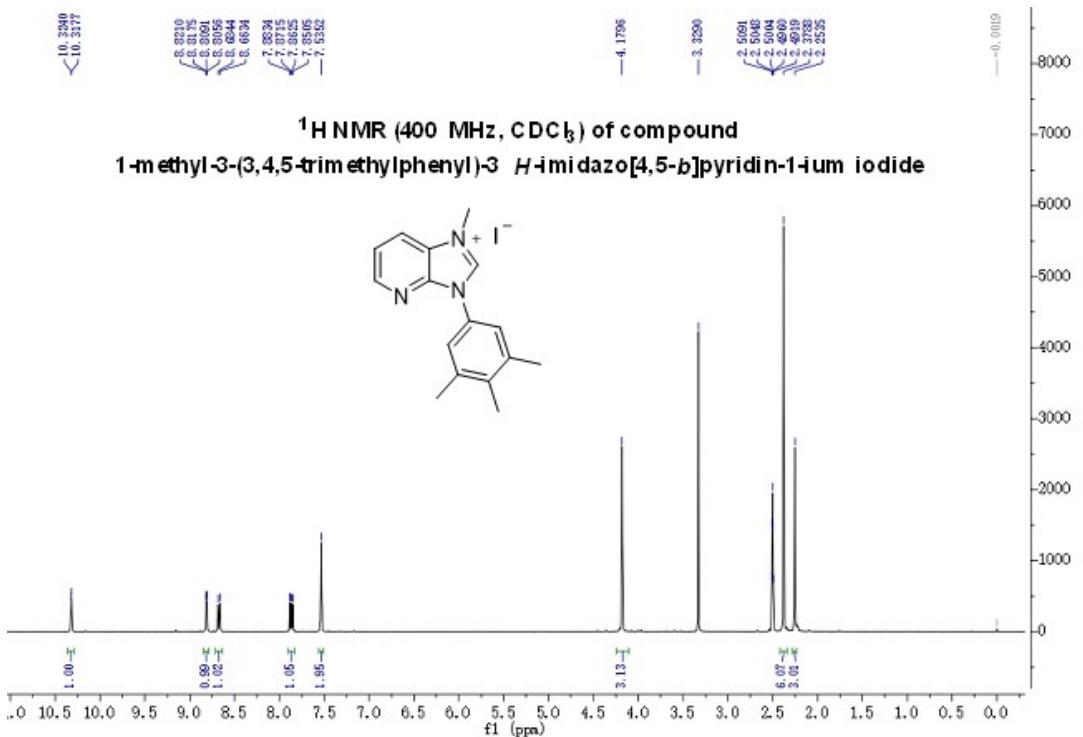
Figure S6. ^{1}H NMR (400MHz, CDCl$_3$) of compound ***pmpMe$_3$***
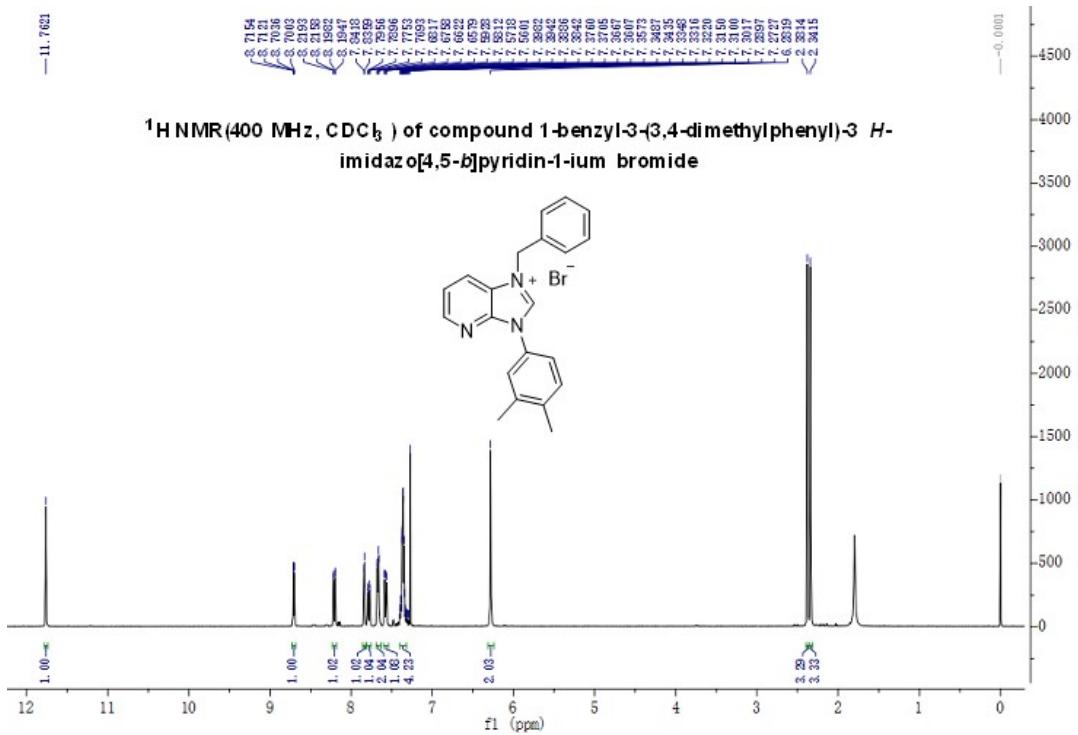
Figure S7. ^{1}H NMR (400MHz, CDCl$_3$) of compound ***pmpMe$_2$Bz***
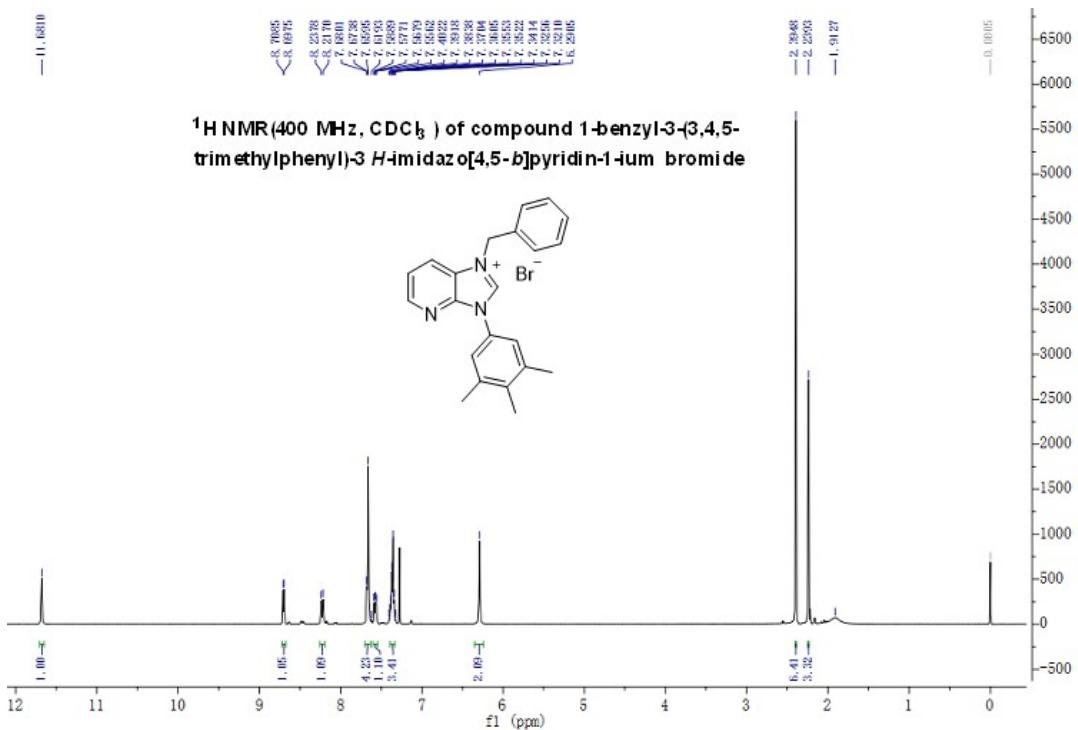
Figure S8. ^{1}H NMR (400MHz, CDCl$_3$) of compound ***pmpMe$_3$Bz***
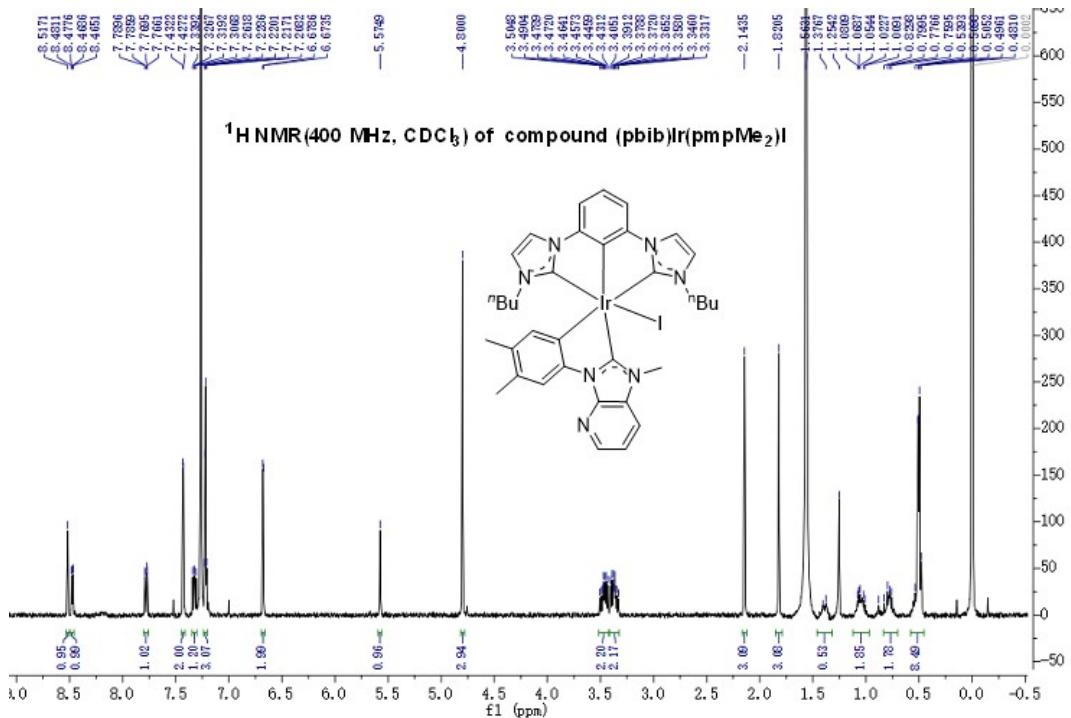
Figure S9. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_2$)I]*
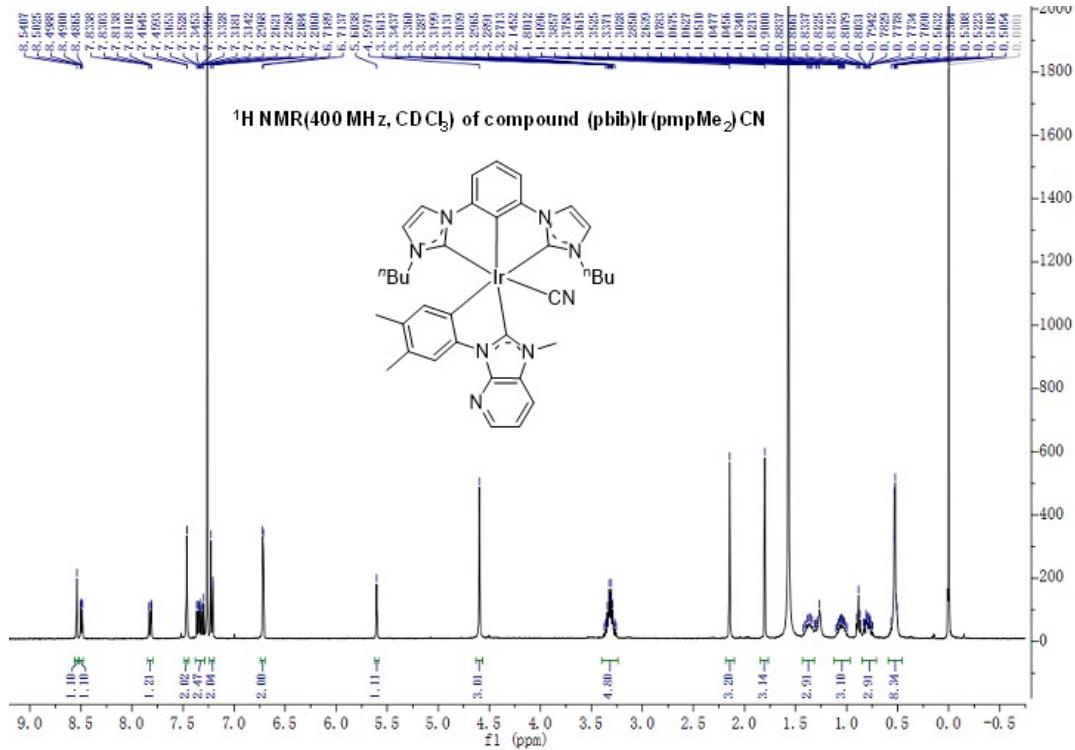
Figure S10. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_2$)CN]*
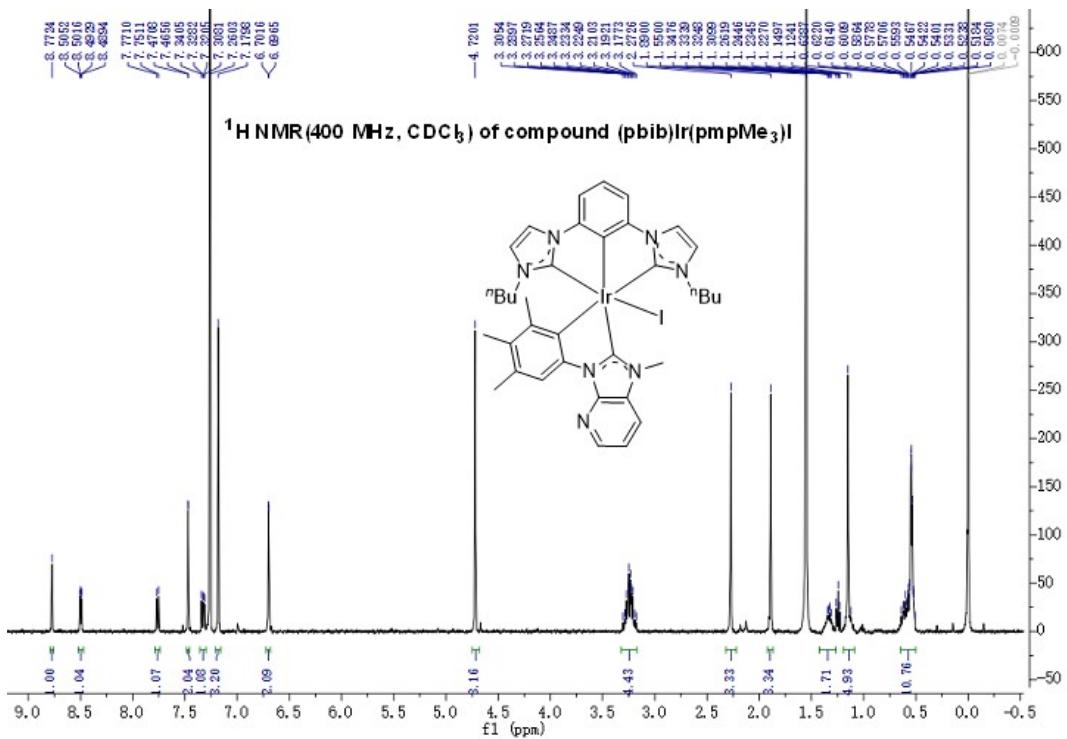
Figure S11. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_3$)I]*
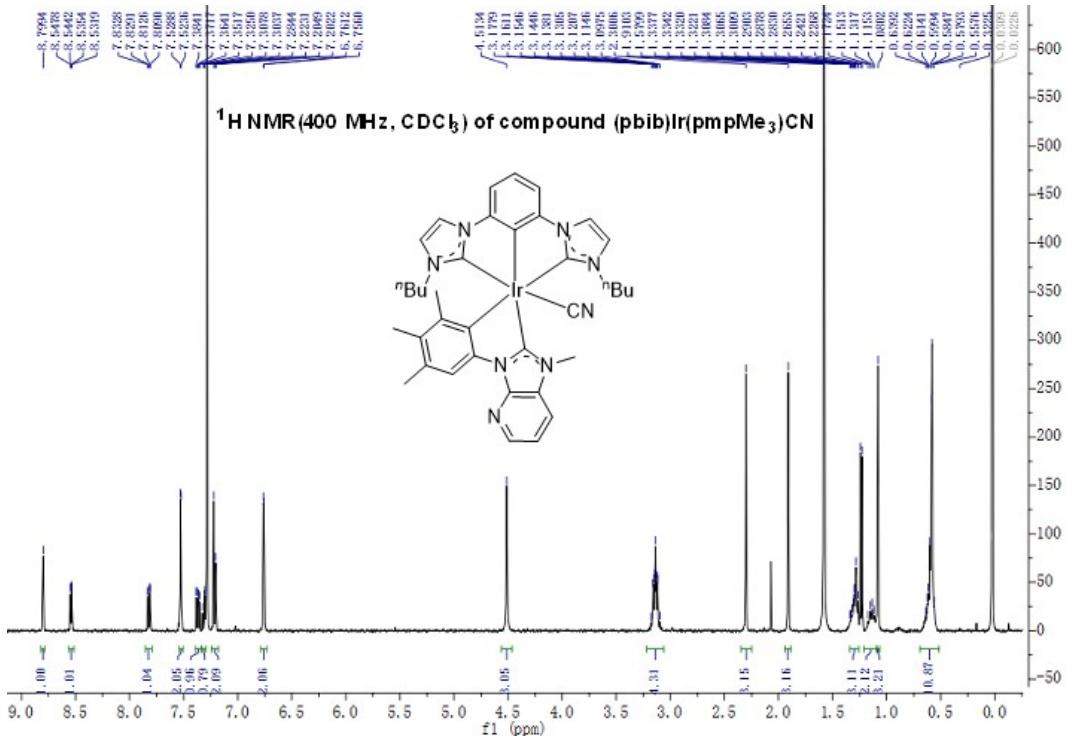
Figure S12. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_3$)CN]*
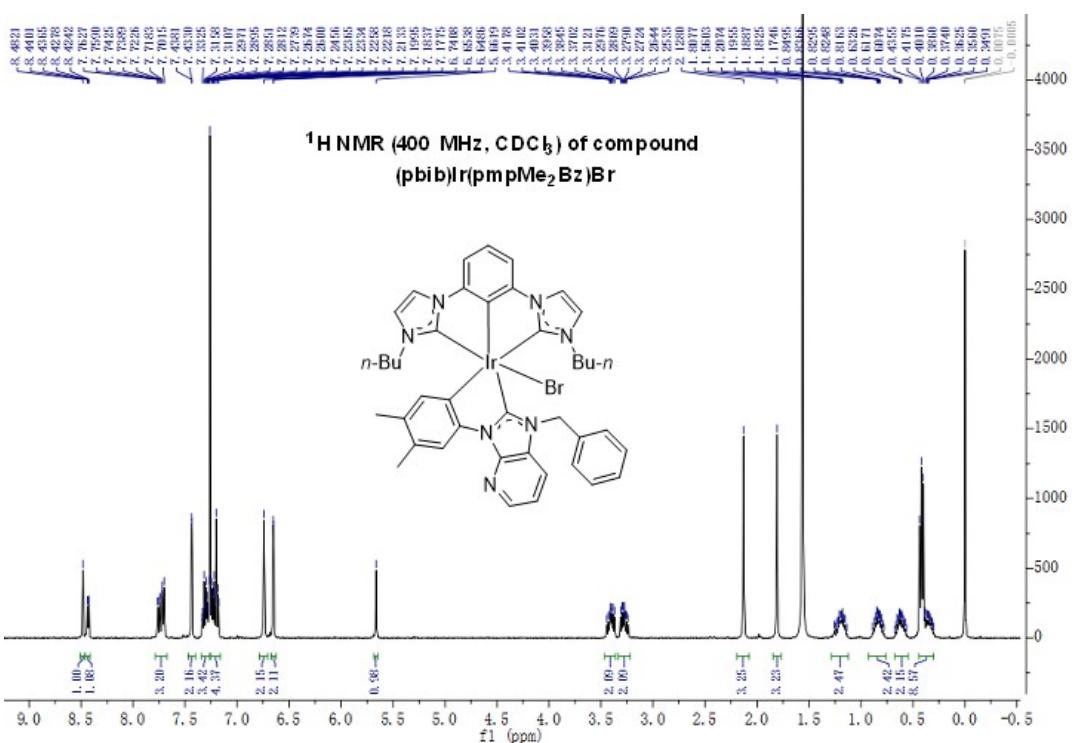
Figure S13. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_2$Bz)Br]*
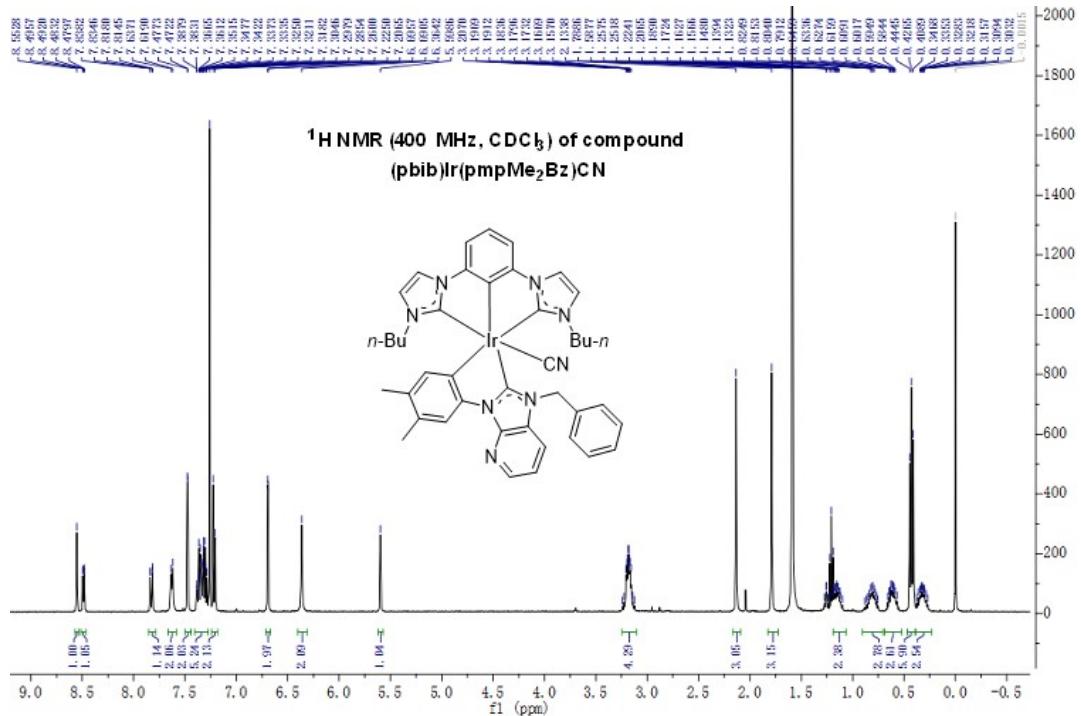
Figure S14. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_2$Bz)CN]*
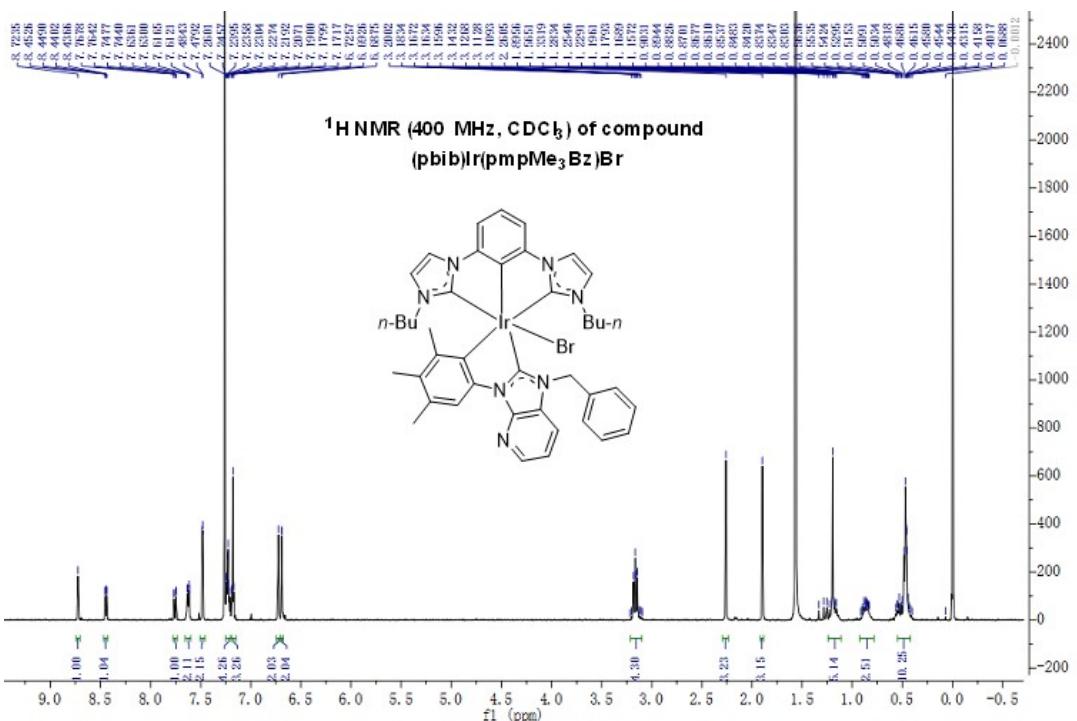
Figure S15. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_3$Bz)Br]*
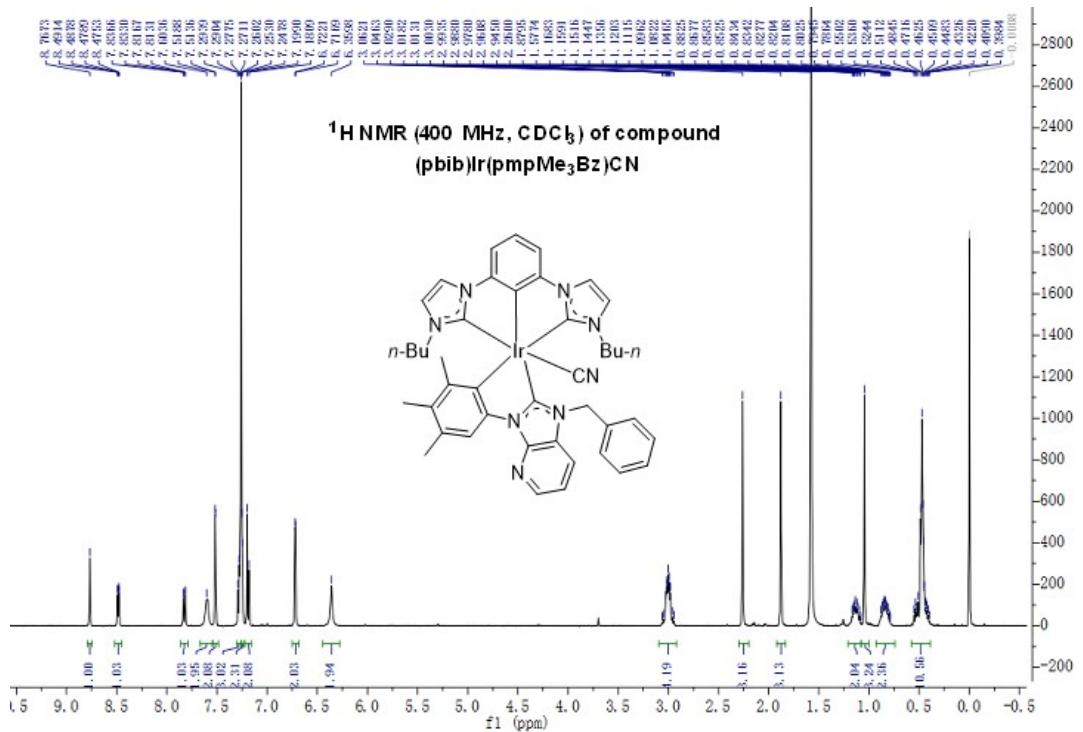
Figure S16. ^{1}H NMR (400MHz, CDCl$_3$) of compound *[(pbib)Ir(pmpMe$_3$Bz)CN]*
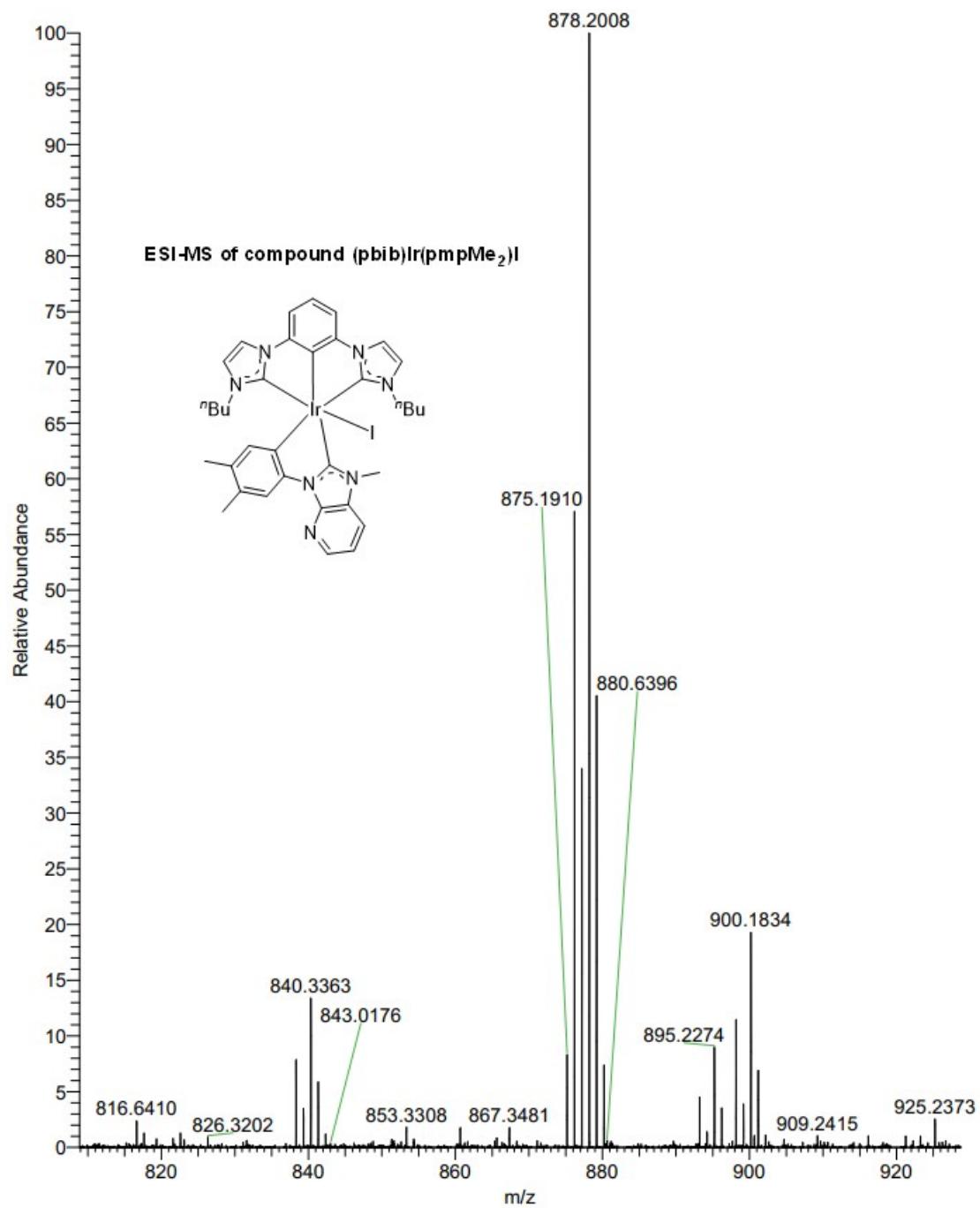
Figure S17. ESI-MS of compound *[(pbib)Ir(pmpMe₂)I]*
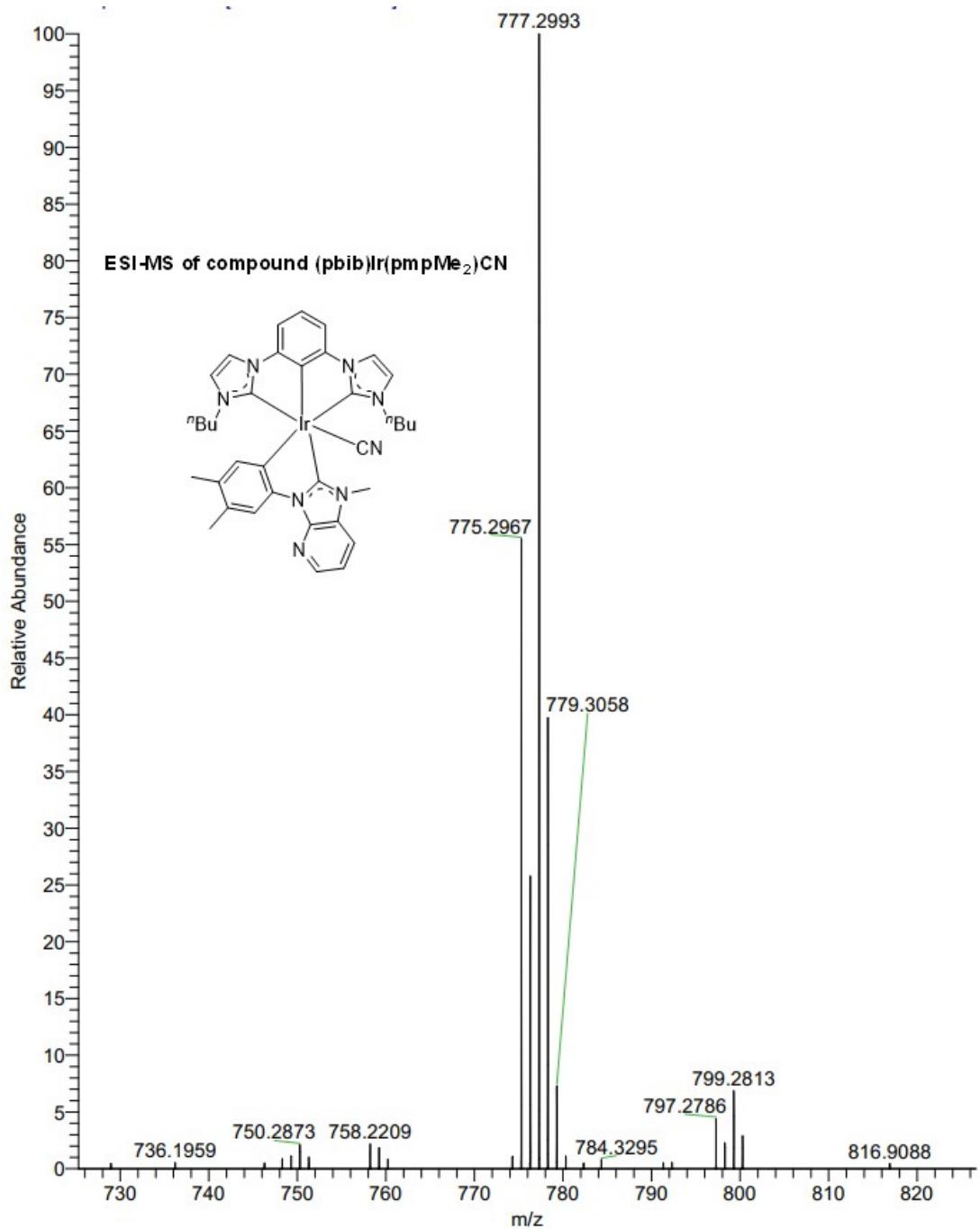
Figure S18. ESI-MS of compound *[(pbib)Ir(pmpMe₂)CN]*
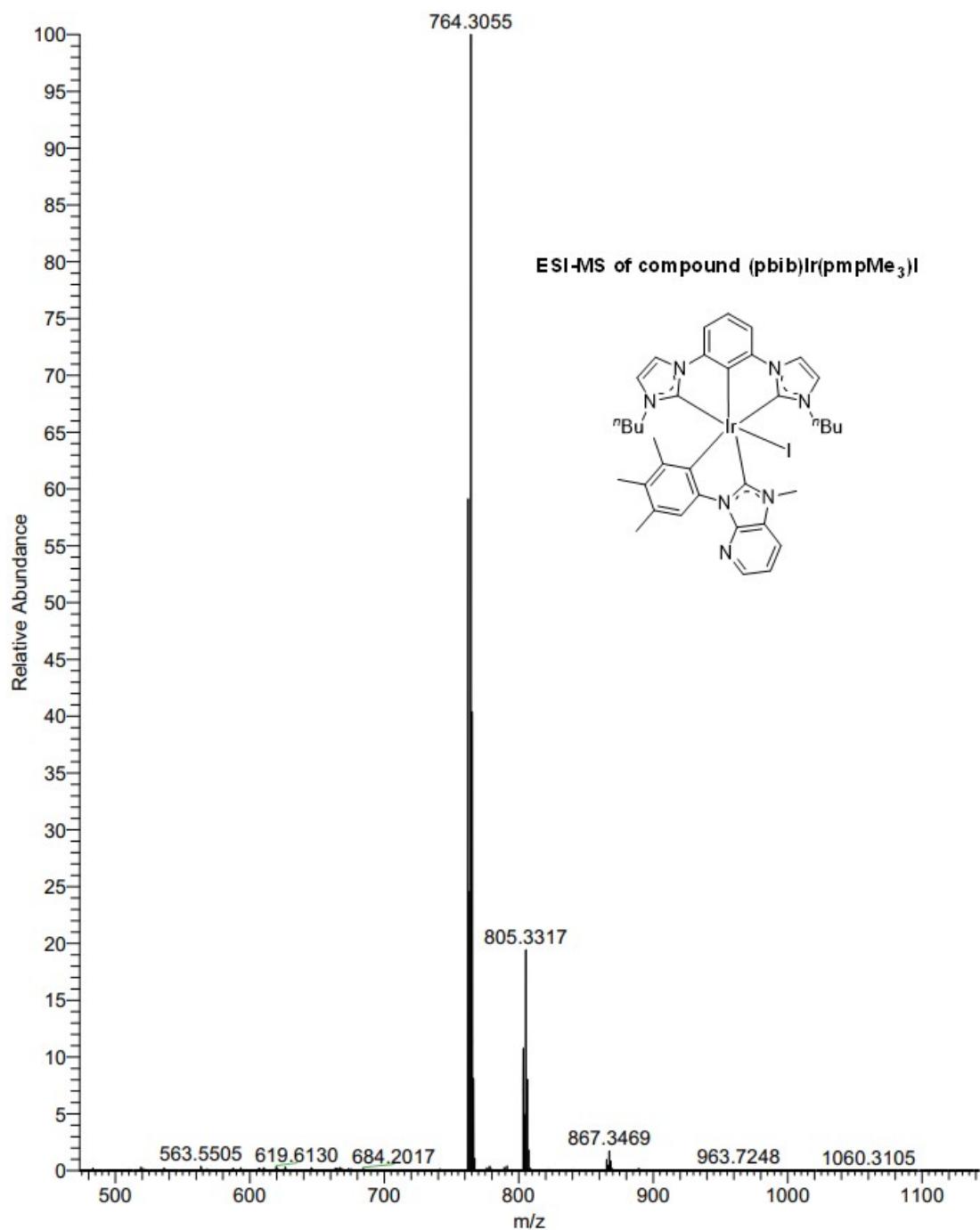
Figure S19. ESI-MS of compound *[(pbib)Ir(pmpMe₃)I]*
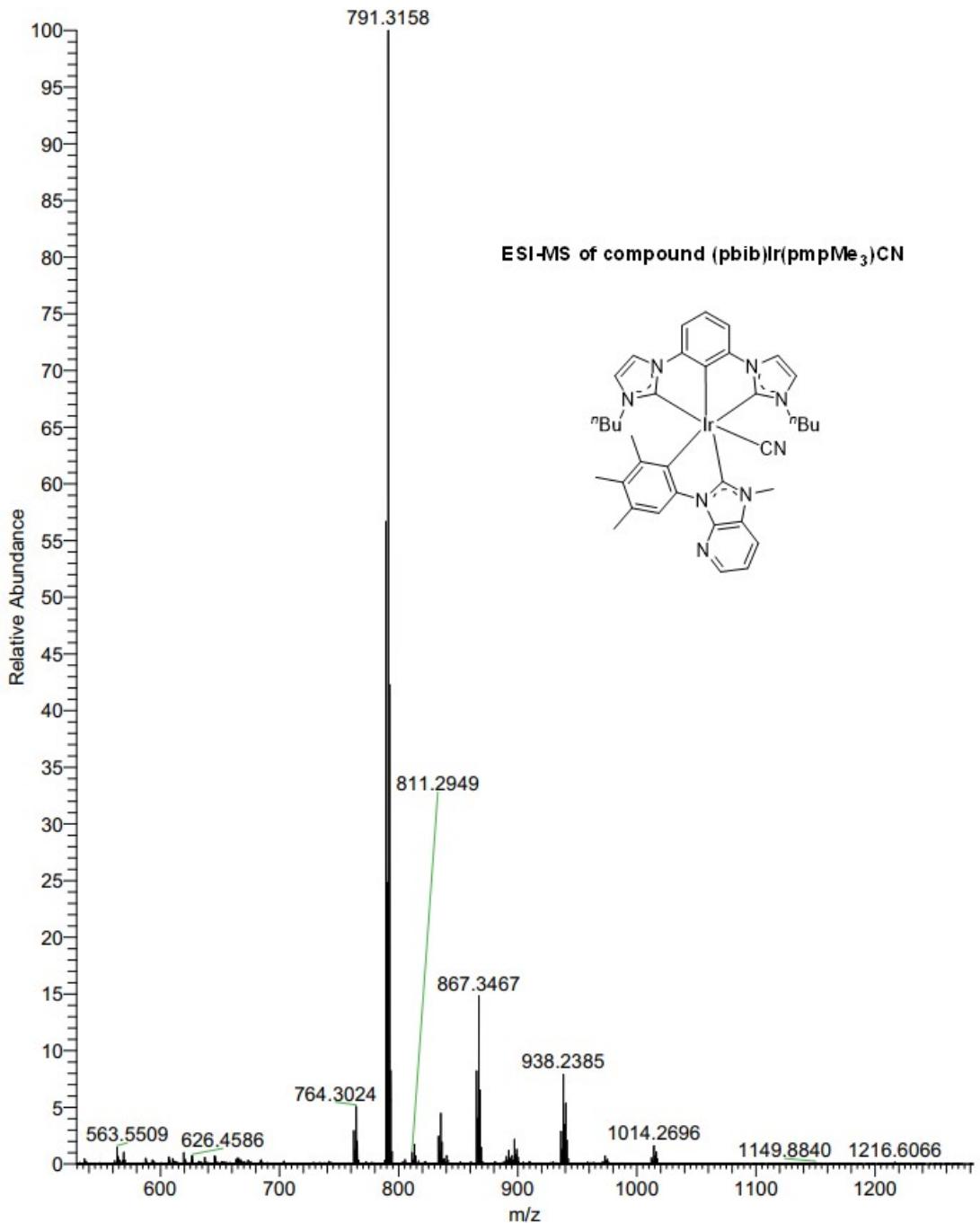
Figure S20. ESI-MS of compound *[(pbib)Ir(pmpMe₃)CN]*
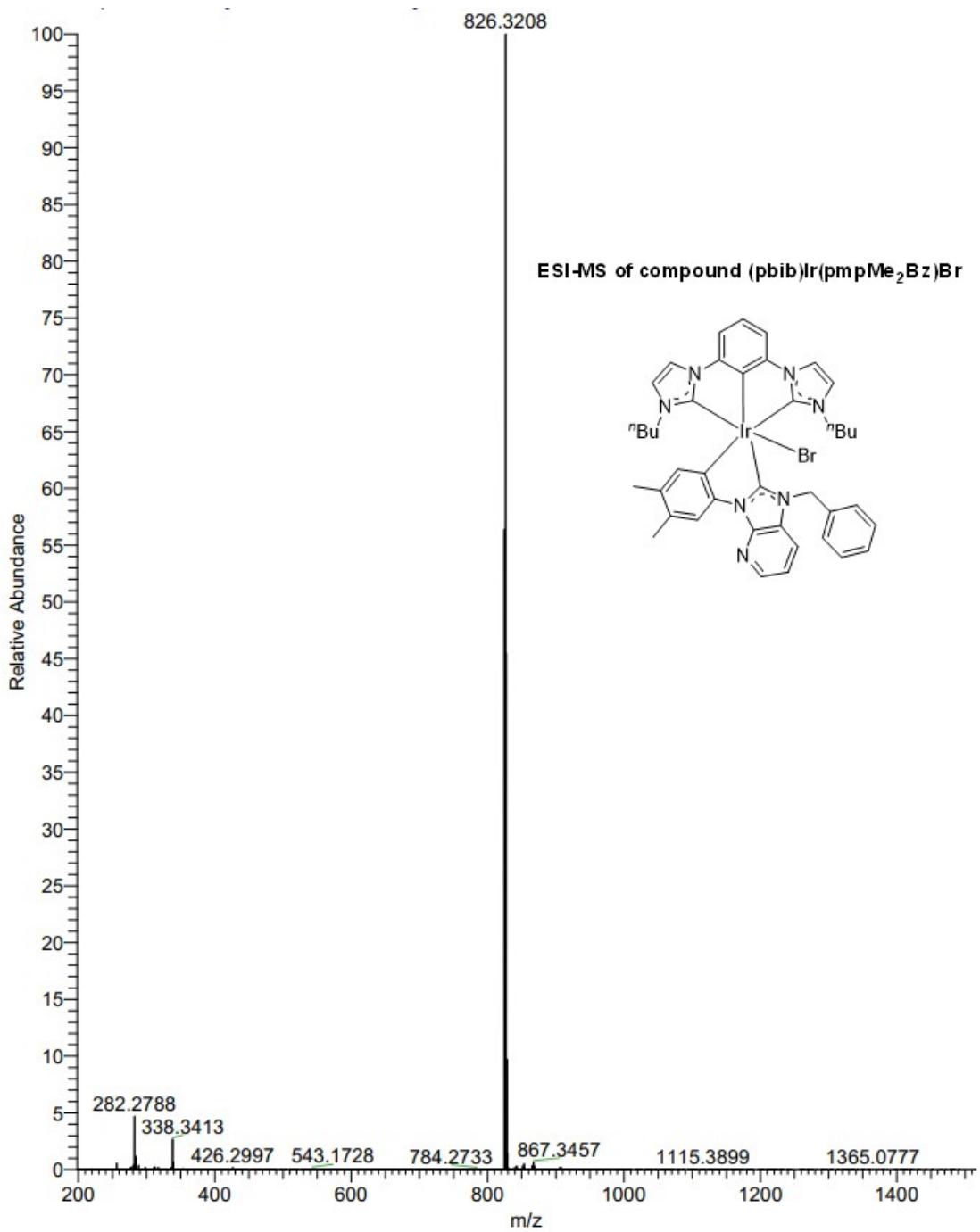
Figure S21. ESI-MS of compound *[(pbib)Ir(pmpMe₂Bz)Br]*
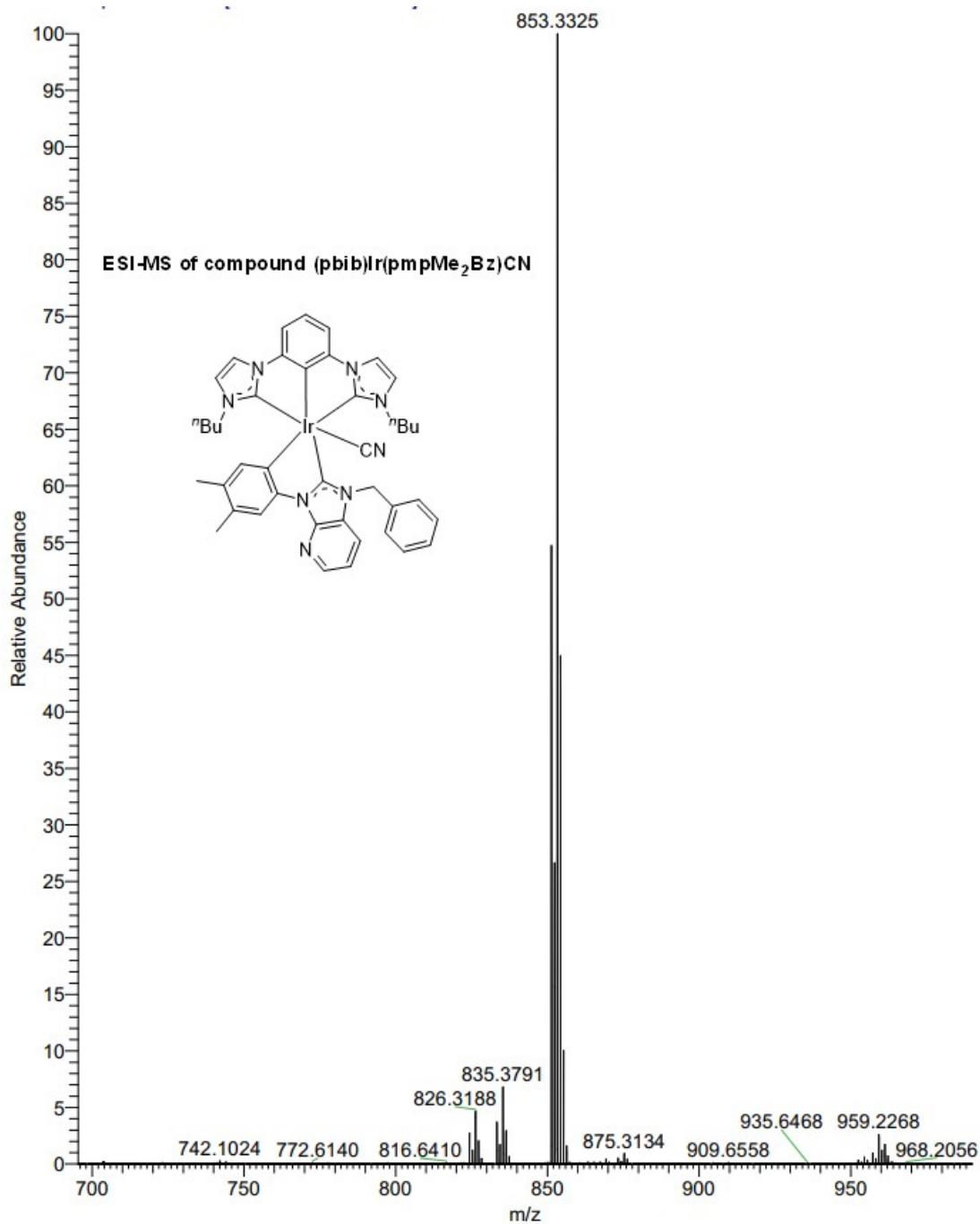
Figure S22. ESI-MS of compound *[(pbib)Ir(pmpMe₂Bz)CN]*
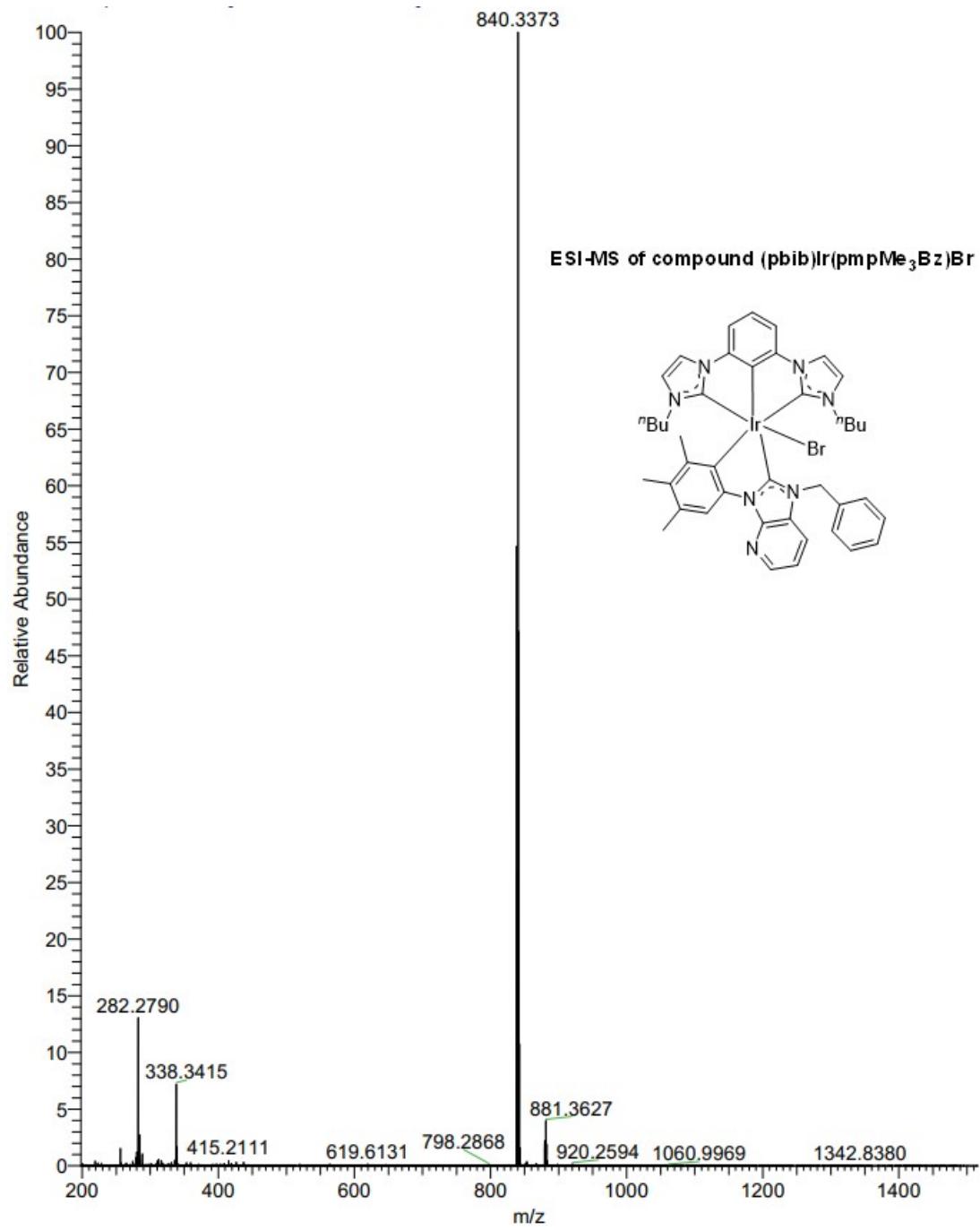
Figure S23. ESI-MS of compound *[(pbib)Ir(pmpMe₃Bz)Br]*
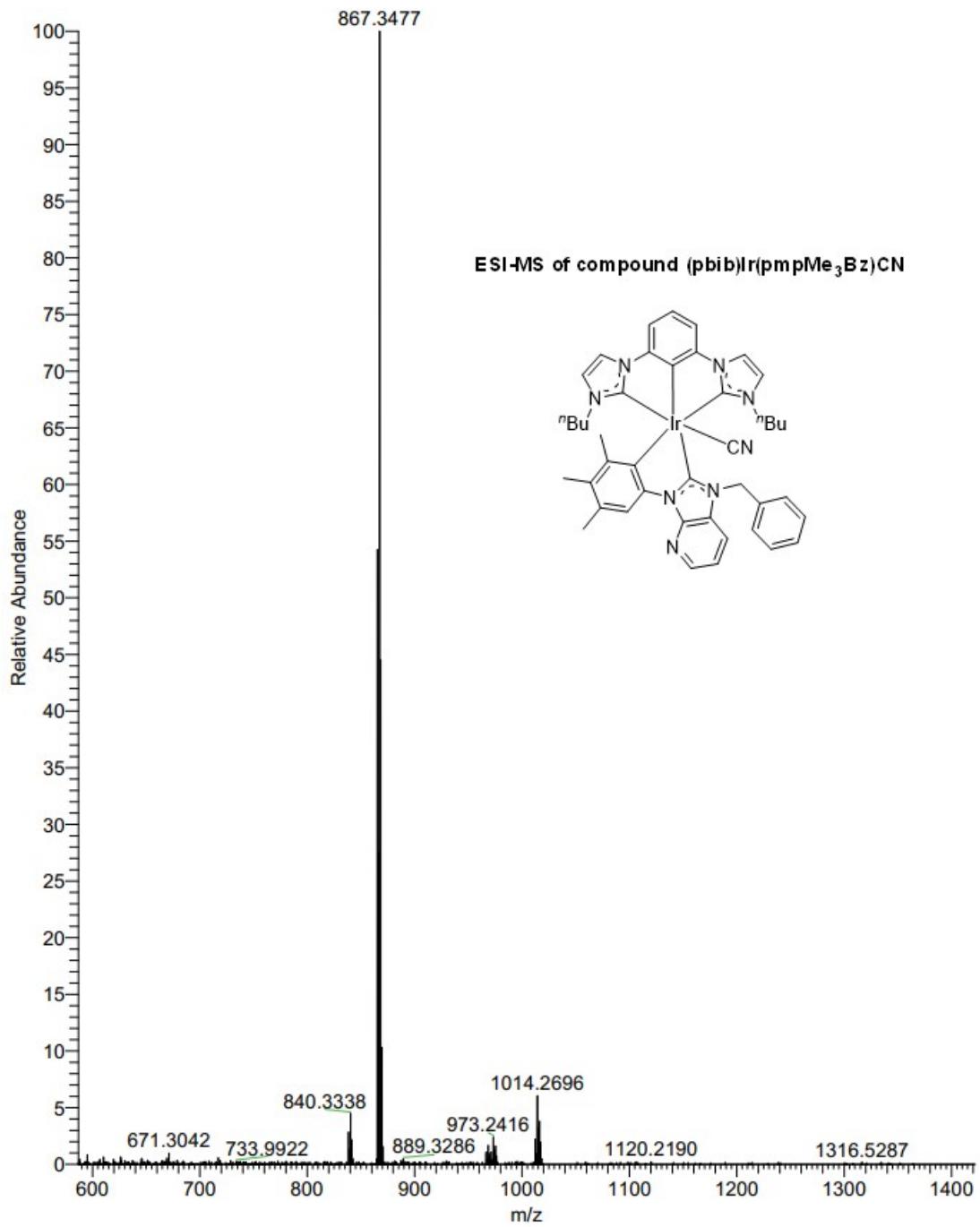
Figure S24. ESI-MS of compound *[(pbib)Ir(pmpMe₃Bz)CN]*

Data File D:\DATA\DAVID\2022-08-17\PMPME2-CN.D
Sample Name: pmpMe2-CN

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Acq. Operator   : SYSTEM                      Seq. Line :   1
Acq. Instrument : 1260 DAD+ELSD                Location : Vial 6
Injection Date  : 8/17/2022 1:54:06 PM             Inj :   1
                                          Inj Volume : 10.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\DAVID\2022-08-17\DAVID-20210927.M
Last changed    : 8/17/2022 1:57:47 PM by SYSTEM
                  (modified after loading)
Analysis Method : D:\DATA\DAVID\2022-08-17\DAVID-20210927.M (Sequence Method)
Last changed    : 8/17/2022 1:53:17 PM by SYSTEM
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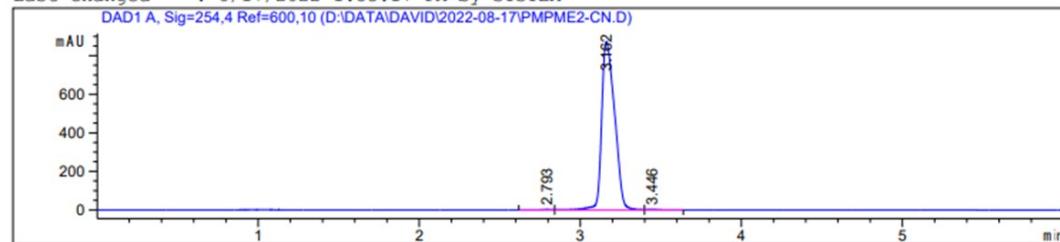


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================================================================
                    Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=600,10

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1   2.793 BV   0.0630    8.71559    1.91787   0.1775
  2   3.162 VV   0.0959 4887.47412  872.47058  99.5575
  3   3.446 VB   0.0617   13.00834    2.67865   0.2650

Totals :                4909.19805  877.06710


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                   *** End of Report ***
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Figure S25. The purity analysis by HPLC for [(pbib]Ir(pmpMe$_2$)CN]

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Data File D:\DATA\DAVID\2022-08-17\PMPME3-CN.D
Sample Name: pmpMe3-CN

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Acq. Operator   : SYSTEM                      Seq. Line :   2
Acq. Instrument : 1260 DAD+ELSD               Location : Vial 7
Injection Date  : 8/17/2022 2:01:01 PM             Inj :   1
                                          Inj Volume : 10.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 5.000 µl
Acq. Method     : D:\DATA\DAVID\2022-08-17\DAVID-20210927.M
Last changed    : 8/17/2022 1:57:47 PM by SYSTEM
Analysis Method : D:\DATA\DAVID\2022-08-17\DAVID-20210927.M (Sequence Method)
Last changed    : 8/17/2022 1:53:17 PM by SYSTEM
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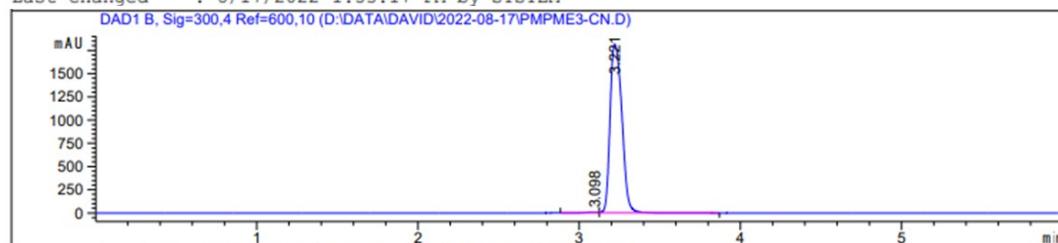


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================================================================
                    Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=600,10

Peak RetTime Type  Width     Area        Height     Area
 #    [min]        [min]   [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1   3.098 BV   0.0828   53.13431    8.75760   0.5728
  2   3.221 VB   0.0828 9223.09863 1814.93591  99.4272

Totals :                9276.23294 1823.69351


================================================================
                    *** End of Report ***
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Figure S26. The purity analysis by HPLC for [(pbib]Ir(pmpMe$_3$)CN]
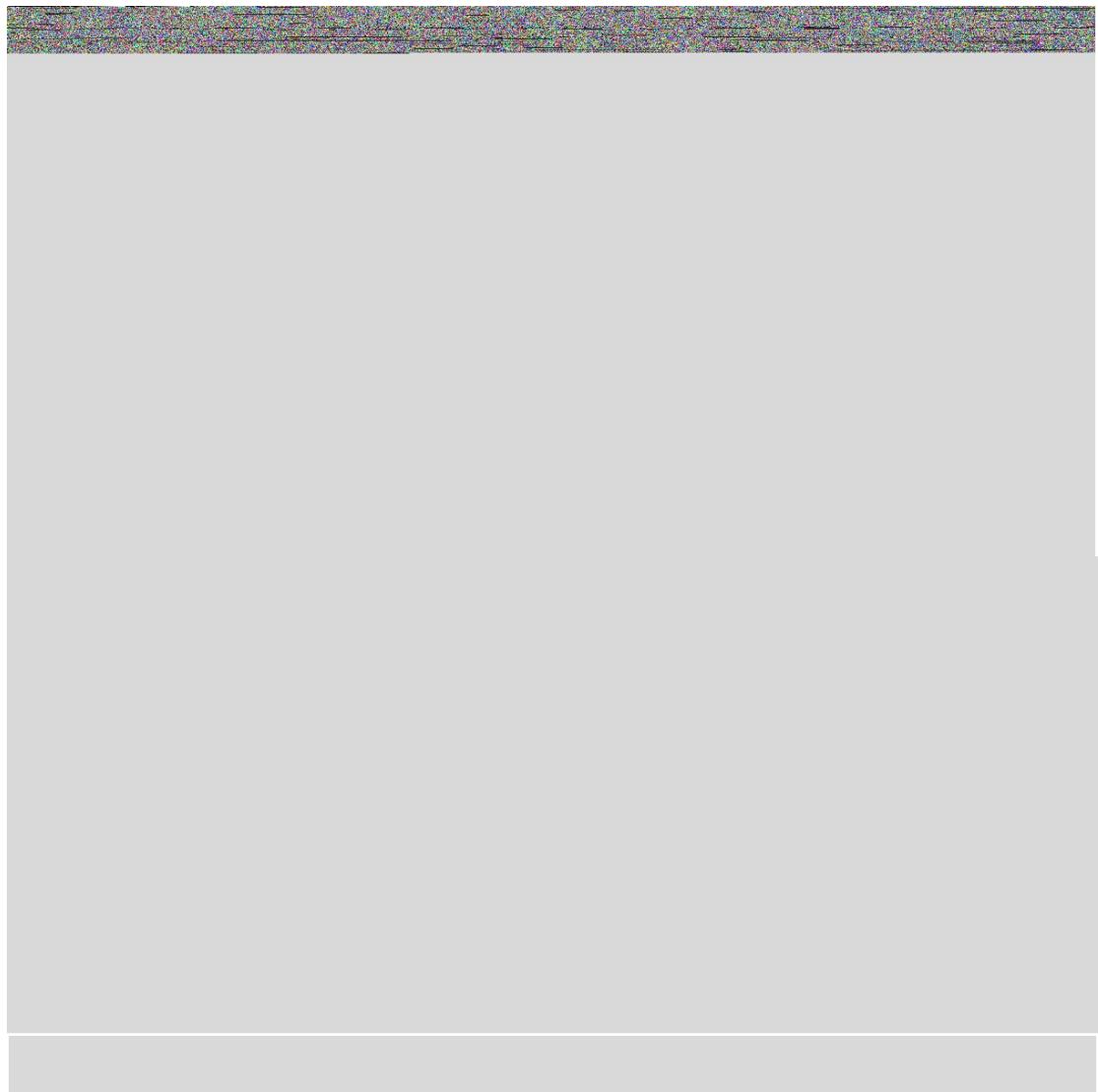
Figure S27. The purity analysis by HPLC for [(pbib]Ir(pmpMe$_2$Bz)CN]

Data File D:\DATA\DAVID\2022-08-17\PMPME3BZ-CN.D
Sample Name: pmpMe3Bz-CN

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Acq. Operator   : SYSTEM   Seq. Line :   4
Acq. Instrument : 1260 DAD+ELSD   Location : Vial 9
Injection Date : 8/17/2022 2:14:49 PM   Inj :   1
                                            Inj Volume : 10.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 5.000 µl
Acq. Method   : D:\DATA\DAVID\2022-08-17\DAVID-20210927.M
Last changed   : 8/17/2022 1:57:47 PM by SYSTEM
Analysis Method : D:\DATA\DAVID\2022-08-17\DAVID-20210927.M (Sequence Method)
Last changed   : 8/17/2022 1:53:17 PM by SYSTEM

==
                      Area Percent Report
==
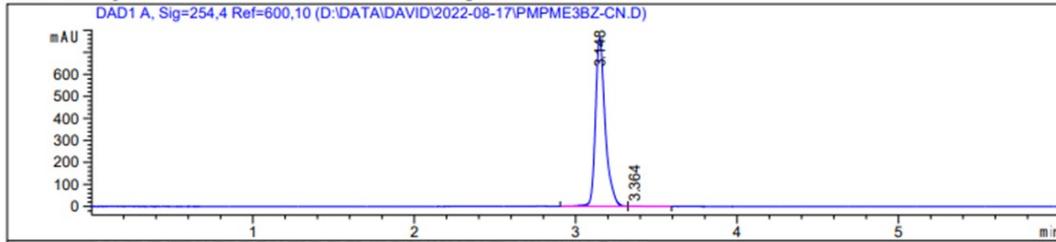
Sorted By   :   Signal
Multiplier   :   1.0000
Dilution   :   1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=600,10

Peak RetTime Type Width   Area   Height   Area
 #   [min]   [min]   [mAU*s]   [mAU]   %
----|-------|----|-------|----------|----------|--------|
  1   3.148 BV   0.0628 3202.55469 766.21381 99.7321
  2   3.364 VB   0.0613   8.60180   1.73595   0.2679

Totals :   3211.15649 767.94975

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                      *** End of Report ***

Figure S28. The purity analysis by HPLC for [(pbib]Ir(pmpMe$_3$Bz)CN]
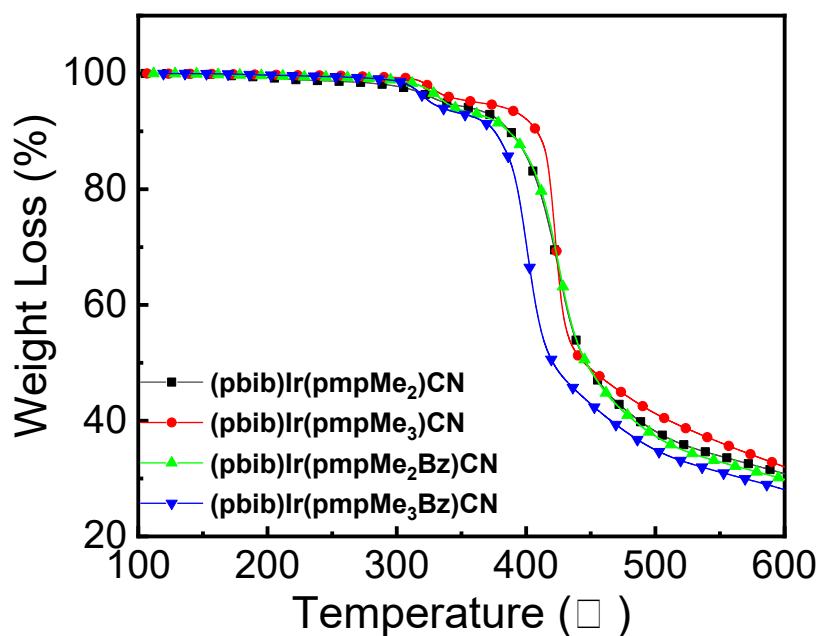
Figure S29. The thermogravimetric analysis (TGA) curves for the [3+2+1] coordinated iridium(III) complexes.

Table S1. Thermal properties of the [3+2+1] coordinated iridium(III) complexes.

Complex	$T_d{}^a$/°C
[(pbib)Ir(pmpMe₂)CN]	337
[(pbib)Ir(pmpMe₃)CN]	363
[(pbib)Ir(pmpMe₂Bz)CN]	337
[(pbib)Ir(pmpMe₃Bz)CN]	326

[a] Decomposition temperature (T_d) is defined as the temperature at which the complex shows a 5 % weight loss.
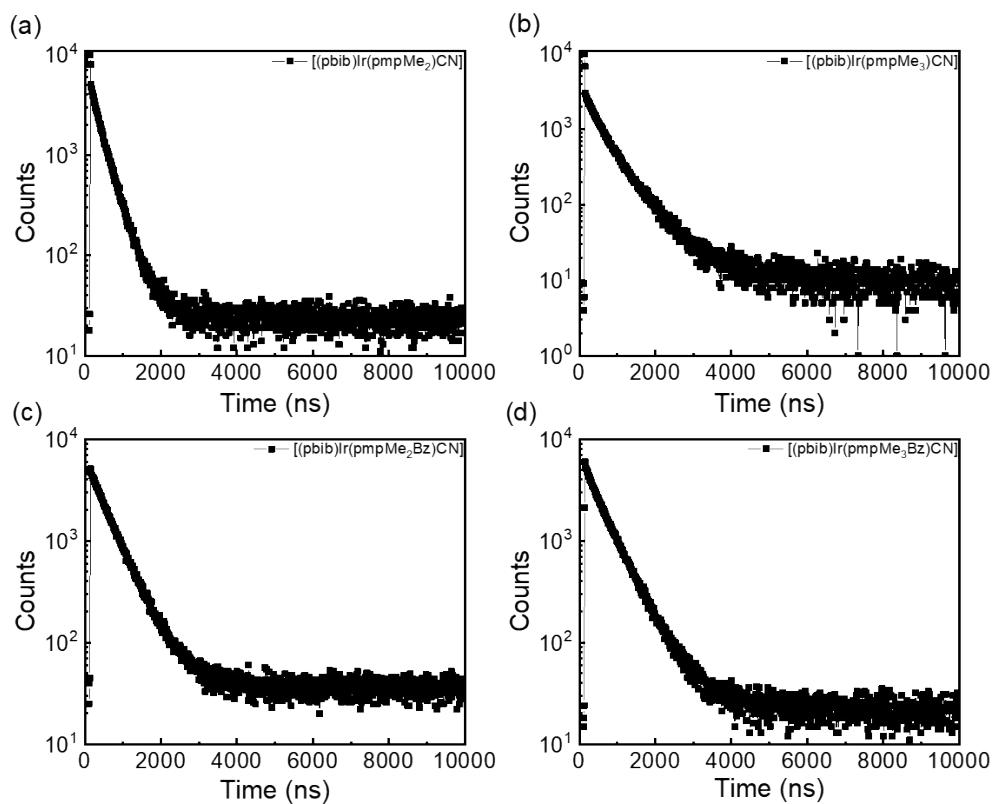
Figure S30. Time-resolved photoluminescence decay profiles of the [3+2+1] coordinated iridium(III) complexes in degassed toluene at 298 K.
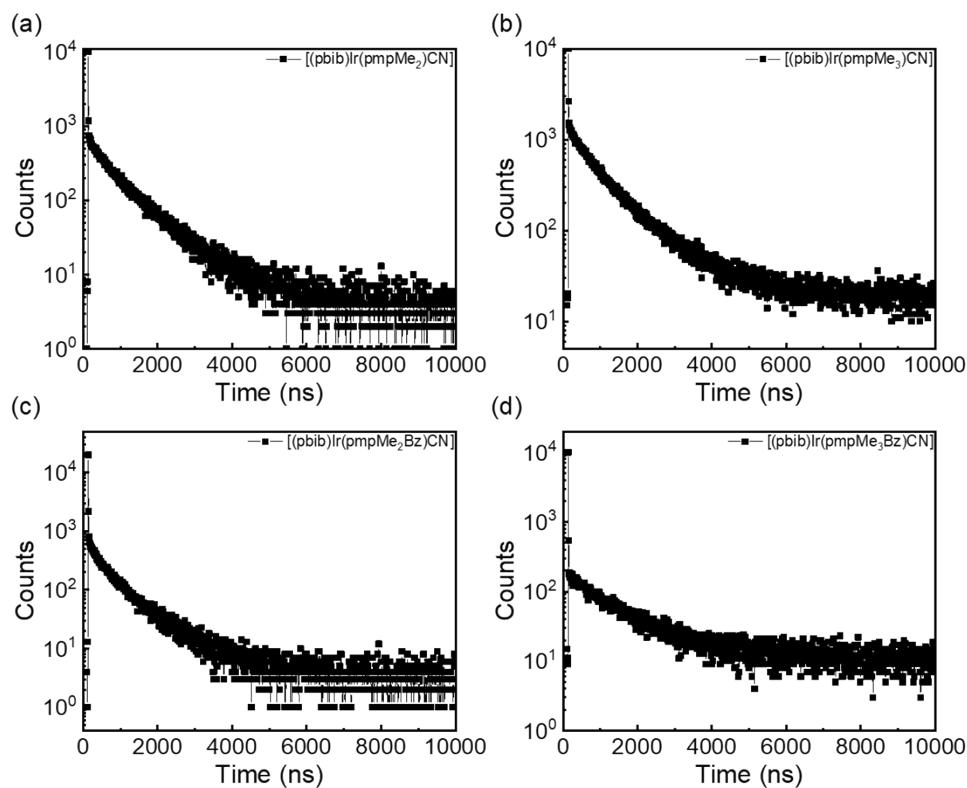
Figure S31 Time-resolved photoluminescence decay profiles of 20 wt % iridium complexes doped into DPEPO at 298 K
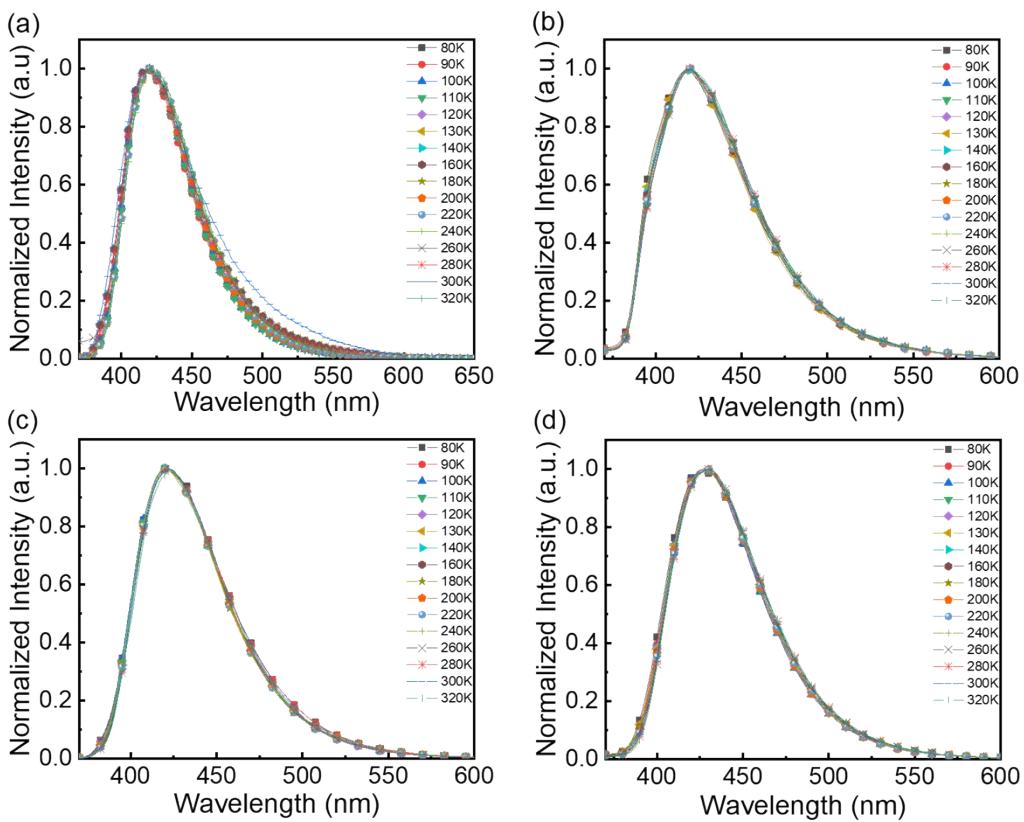
Figure S32 Normalized emission spectra of (a) *[(pbib)Ir(pmpMe₂)CN]*, (b) *[(pbib)Ir(pmpMe₃)CN]*, (c) *[(pbib)Ir(pmpMe₂Bz)CN]*, (d) *[(pbib)Ir(pmpMe₃Bz)CN]*, in degassed toluene upon increasing temperature from 80 K to 320 K.
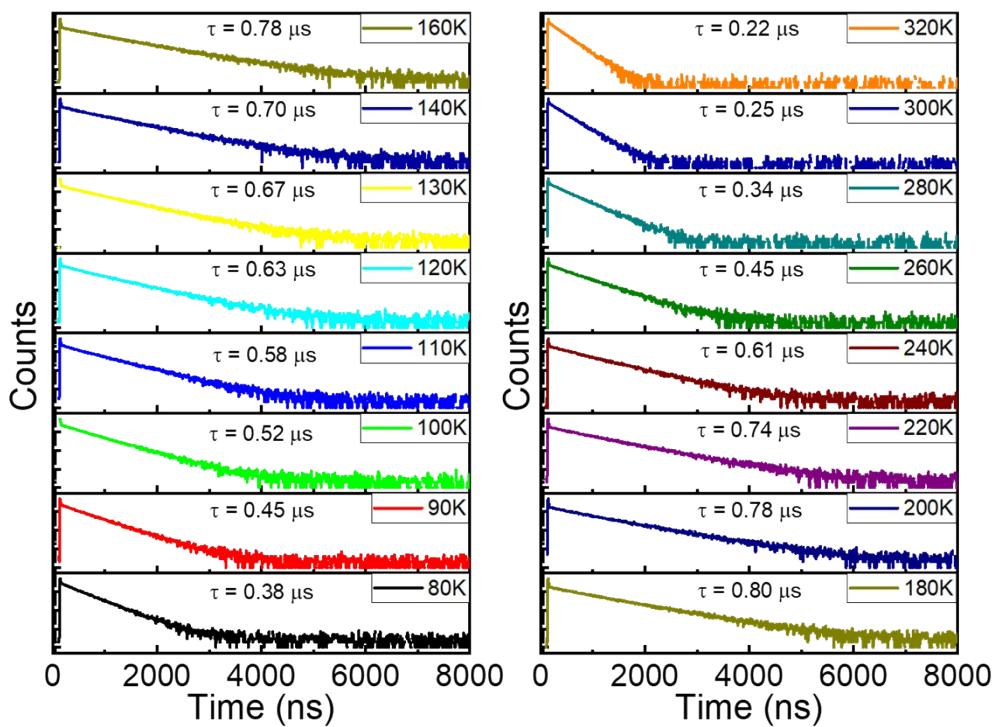
Figure S33 Time-resolved photoluminescence decay profiles of **[(pbib)Ir(pmpMe₂)CN]** in degassed toluene upon increasing temperature from 80 K to 320 K.
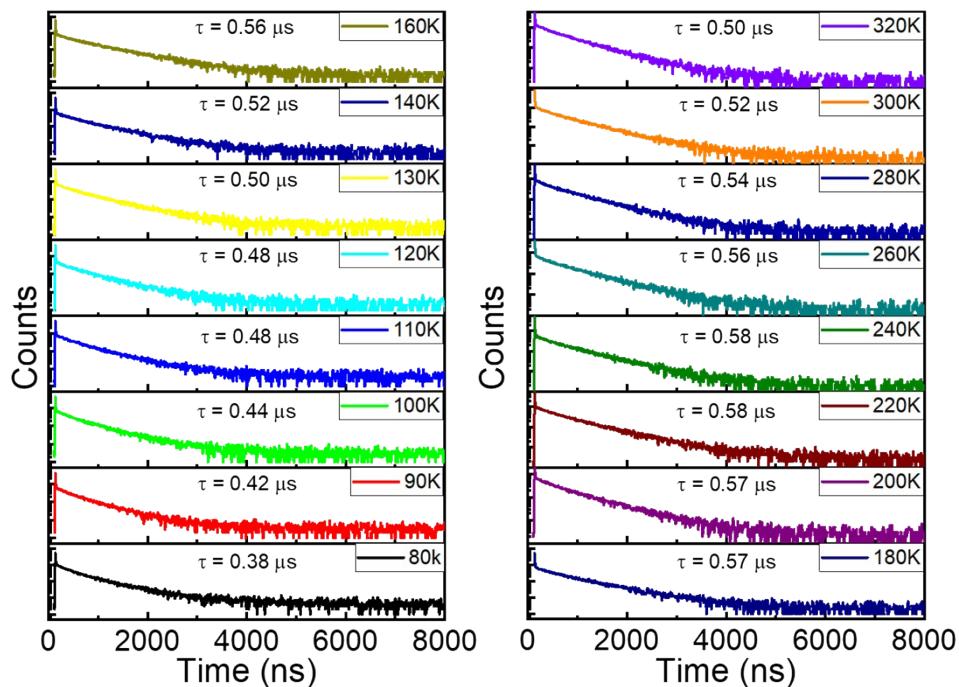
Figure S34 Time-resolved photoluminescence decay profiles of **[(pbib)Ir(pmpMe₃)CN]** in degassed toluene upon increasing temperature
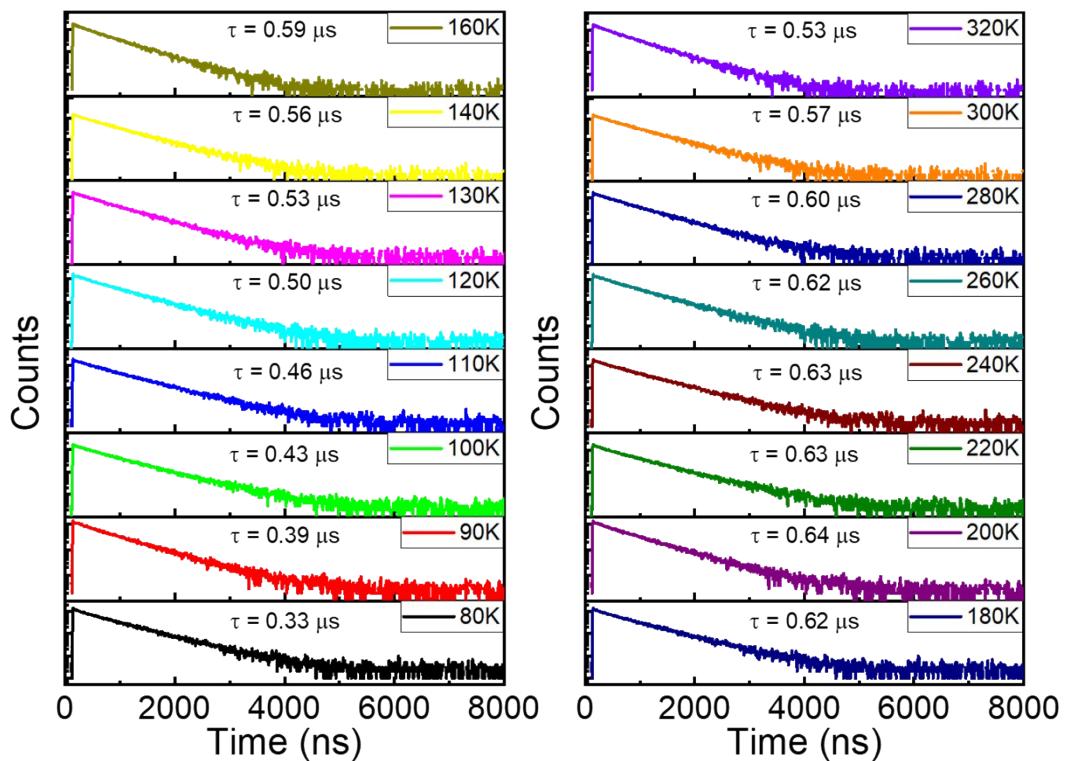
from 80 K to 320 K.

Figure S35 Time-resolved photoluminescence decay profiles of **[(pbib)Ir(pmpMe₂Bz)CN]** in degassed toluene upon increasing temperature from 80 K to 320 K.
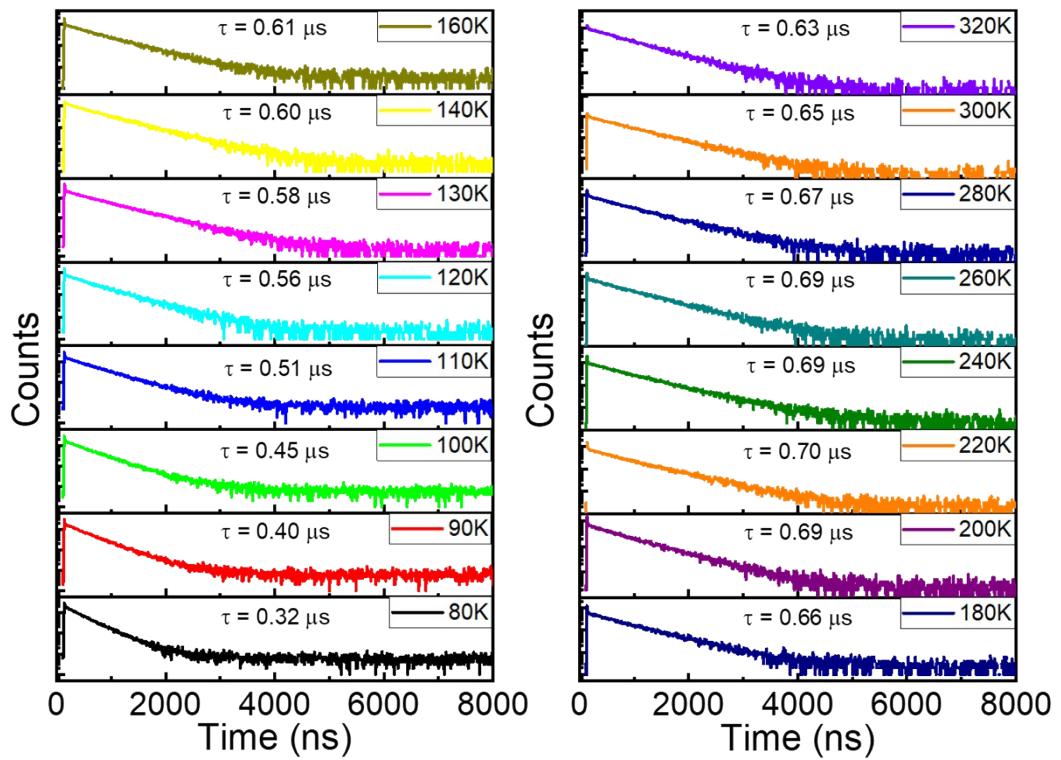
Figure S36 Time-resolved photoluminescence decay profiles of **[(pbib)Ir(pmpMe₃Bz)CN]** in degassed toluene upon increasing temperature from 80 K to 320 K.
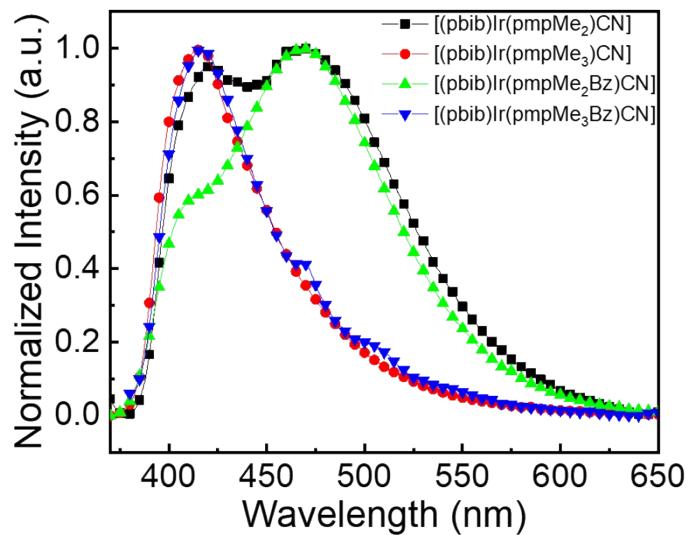
Figure S37 Normalized emission spectra of iridium(III) complexes in powder at 298 K.
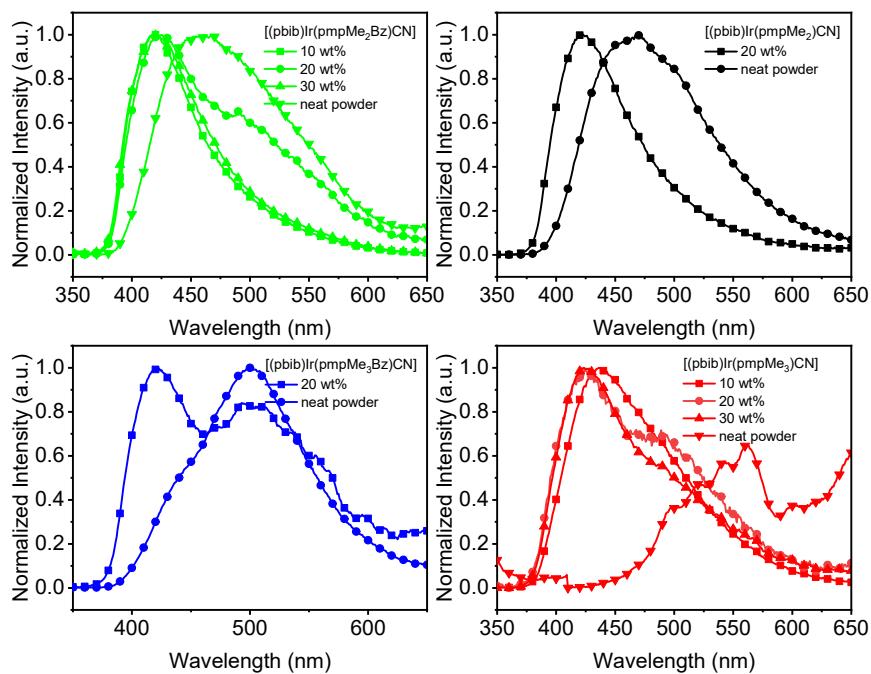
Figure S38 Normalized emission spectra of iridium(III) complexes doped in DPEPO at 298 K.
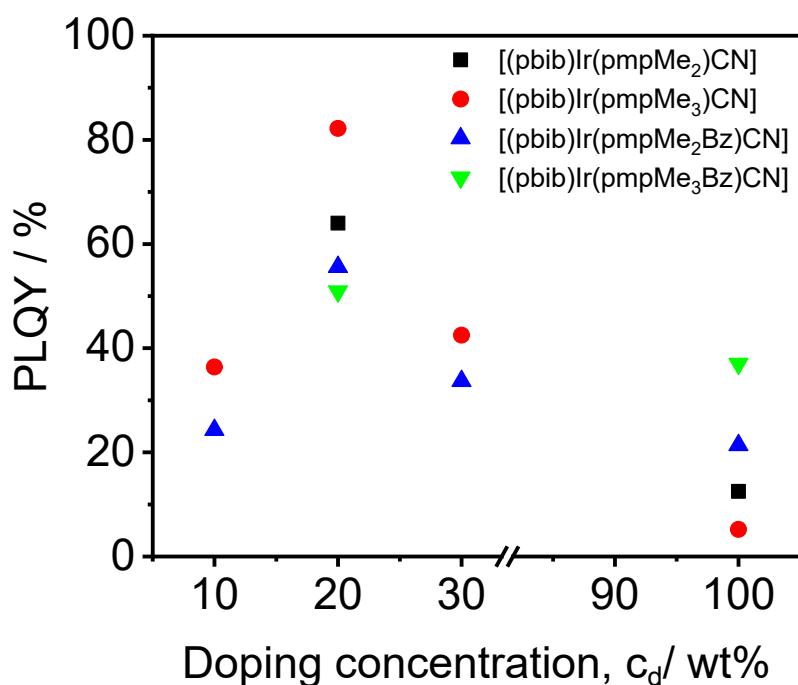
Figure S39 PLQY vs doping concentration for vacuum-deposited doped films of the iridium complexes in DPEPO

Table S2. Solid state emission data for the iridium(III) complexes doped in DPEPO.

Complex	C_D / wt%	λ / nm	ϕ_{PL} / %
[(pbib)Ir(pmpMe$_2$)CN]	20	423	64.0
	100	469	12.5
[(pbib)Ir(pmpMe$_3$)CN]	10	436	36.4
	20	424	82.2
	30	423	42.5
	100	560	5.2
[(pbib)Ir(pmpMe$_2$Bz)CN]	10	420	24.3
	20	425	55.6
	30	419	33.7
	100	462	21.4
[(pbib)Ir(pmpMe$_3$Bz)CN]	20	421	50.9
	100	501	37.0

Computational Details

All calculations were performed with the Gaussian 16 program suite.[1] By density functional theory (DFT), the ground-state (S_0) geometries of the iridium(III) complexes were fully optimized in toluene with the hybrid B3LYP functional,[2-5] in conjunction with the conductor-like polarizable continuum model (CPCM).[6, 7] At the same level of theory, time-dependent density functional theory[8-10] (TDDFT) calculations were performed on the optimized S_0 geometries to compute the singlet-singlet transitions in the absorption spectra of the iridium(III) complexes. In order to investigate the emissive states of the complexes, the geometries of the lowest-lying triplet excited states (T_1) have been optimized with the unrestricted UB3LYP/CPCM method. The vibrational frequencies of all the stationary points have been computed and all of them were verified as minima (NIMAG = 0) on the potential energy surface. The Cartesian coordinates of the optimized geometries of both the S_0 and T_1 states were given in Tables S4–S11. In all the calculations, the LanL2DZ basis set with effective core potential[11-13] (ECP) was employed for Ir with f-type polarization functions ($\zeta = 0.938$),[14] whereas the 6-31G(d,p) basis set[15-17] was applied to all other elements (C, H, and N). A pruned (99,590) grid was used for numerical integration.
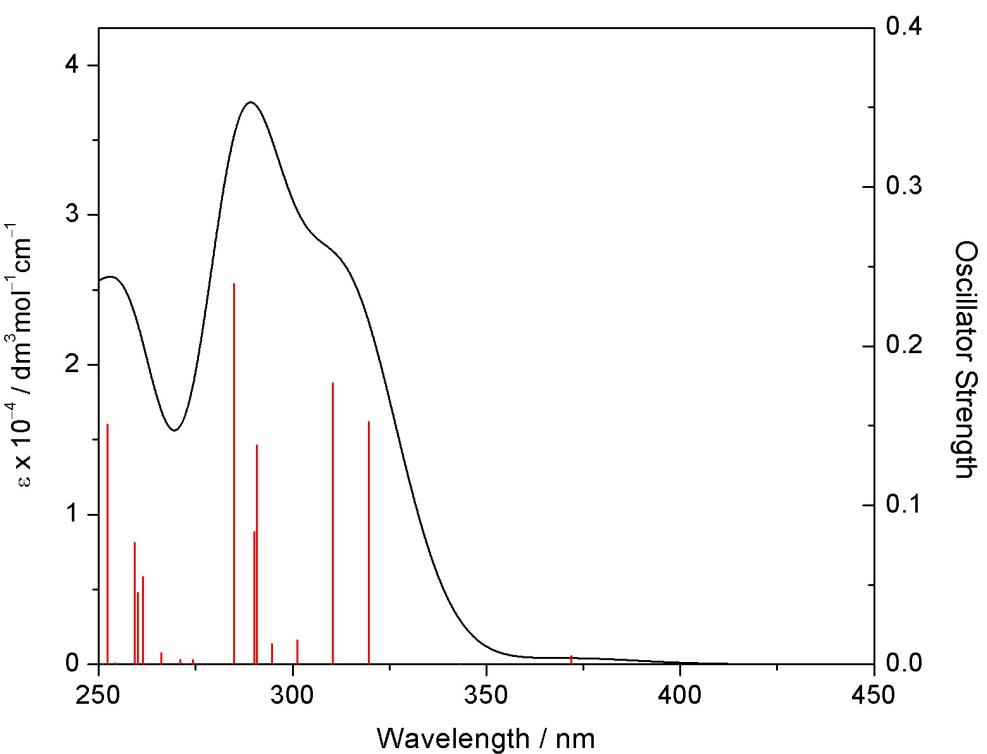
Figure S40 Simulated UV-Vis spectrum of **[(pbib)Ir(pmpMe₂)CN]** computed by
TDDFT/CPCM using toluene as the solvent.
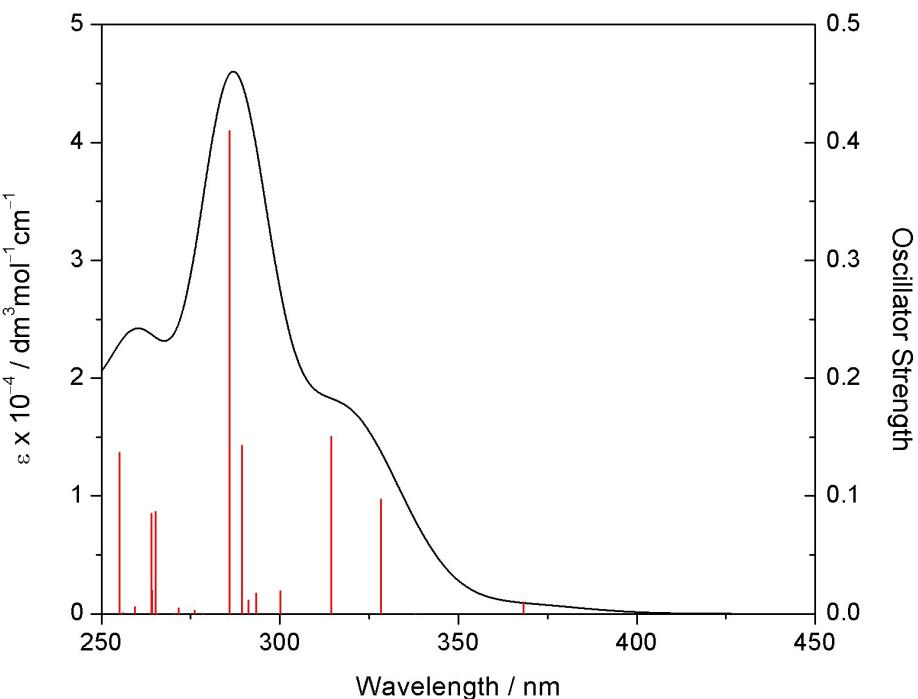
Figure S41 Simulated UV-Vis spectrum of **[(pbib)Ir(pmpMe₃)CN]** computed by
TDDFT/CPCM using toluene as the solvent.
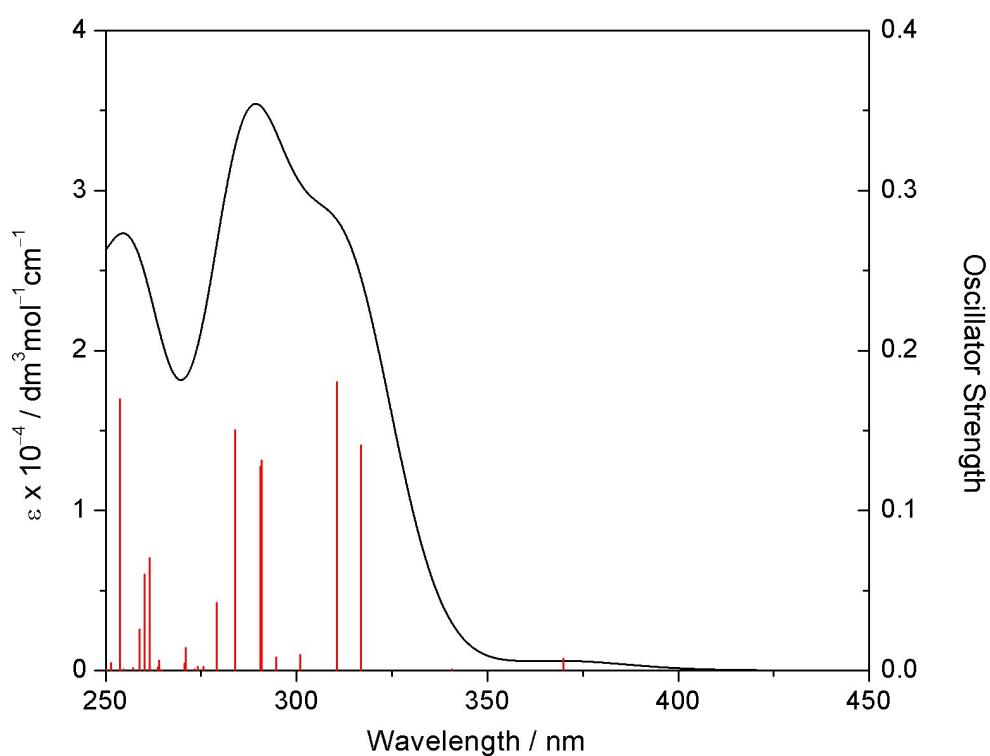
Figure S42 Simulated UV-Vis spectrum of **[(pbib)Ir(pmpMe₂Bz)CN]** computed by TDDFT/CPCM using toluene as the solvent.
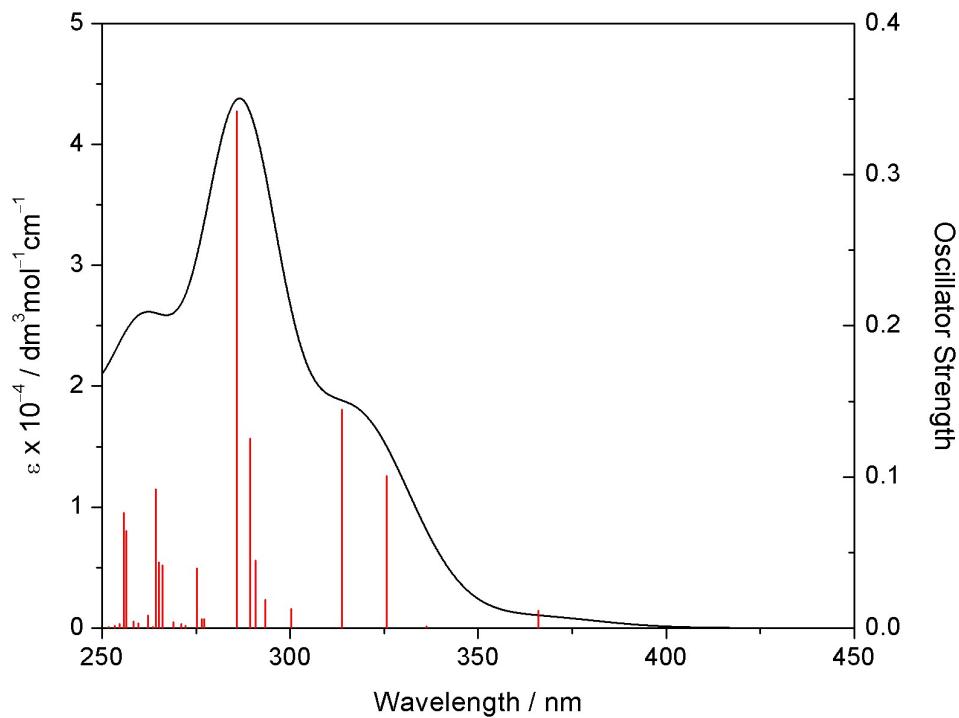
Figure S43 Simulated UV-Vis spectrum of **[(pbib)Ir(pmpMe₃Bz)CN]** computed by TDDFT/CPCM using toluene as the solvent.

Table S3 The first fifteen singlet excited states (S_n) of the four iridium(III) complexes computed by TDDFT/CPCM using toluene as the solvent.

Complex	S_n	Excitation[a] (Coefficient)[b]	Vertical excitation wavelength (nm)	f^c
[(pbib)Ir(pmpMe$_2$)CN]	S_1	H→L (0.70)	372	0.005
	S_2	H–1→L (0.70)	343	0.000
	S_3	H–2→L (0.69)	320	0.153
	S_4	H–3→L (0.65)	310	0.177
	S_5	H→L+1 (0.67)	301	0.015
	S_6	H→L+3 (0.50) H–1→L+1 (−0.48)	295	0.013
	S_7	H–1→L+1 (0.49) H→L+3 (0.48)	291	0.138
	S_8	H→L+2 (0.57) H–4→L (−0.32)	290	0.083
	S_9	H–4→L (0.59) H→L+2 (0.33)	285	0.239
	S_{10}	H–5→L (0.69)	277	0.000
	S_{11}	H–1→L+3 (0.64)	274	0.003
	S_{12}	H–1→L+2 (0.66)	272	0.000
	S_{13}	H–2→L+1 (0.52) H–3→L+1 (0.43)	271	0.003
	S_{14}	H→L+4 (0.61)	266	0.007
	S_{15}	H–7→L (0.68)	266	0.000
[(pbib)Ir(pmpMe$_3$)CN]	S_1	H→L (0.70)	368	0.010
	S_2	H–1→L (0.70)	338	0.000
	S_3	H–2→L (0.70)	328	0.097
	S_4	H–3→L (0.66)	314	0.150
	S_5	H→L+1 (0.66)	300	0.019
	S_6	H–1→L+1 (0.50) H→L+3 (−0.48)	293	0.018
	S_7	H–4→L (0.49) H→L+2 (0.45)	291	0.012
	S_8	H→L+3 (0.49) H–1→L+1 (0.47)	289	0.143
	S_9	H→L+2 (0.49) H–4→L (−0.45)	286	0.410
	S_{10}	H–5→L (0.69)	278	0.000
	S_{11}	H–2→L+1 (0.63)	276	0.003
	S_{12}	H–1→L+3 (0.62)	272	0.005
	S_{13}	H–1→L+2 (0.66)	270	0.000
	S_{14}	H–2→L+3 (0.55) H–3→L+3 (0.31)	266	0.000
	S_{15}	H–2→L+2 (0.60)	265	0.087
[(pbib)Ir(pmpMe$_2$Bz)CN]	S_1	H→L (0.70)	370	0.008
	S_2	H–1→L (0.69)	341	0.001
	S_3	H–2→L (0.69)	317	0.141

	S_4	H–3→L (0.65)	311	0.180
	S_5	H→L+1 (0.67)	301	0.010
	S_6	H→L+5 (0.46)	295	0.008
		H–1→L+1 (0.45)		
	S_7	H→L+2 (0.47)	291	0.131
		H–1→L+1 (−0.34)		
	S_8	H–1→L+1 (0.39)	290	0.127
		H→L+2 (0.34)		
		H→L+5 (−0.34)		
	S_9	H–4→L (0.63)	284	0.151
	S_{10}	H→L+3 (0.63)	279	0.042
	S_{11}	H–5→L (0.67)	276	0.002
	S_{12}	H–1→L+5 (0.52)	274	0.003
	S_{13}	H–1→L+2 (0.59)	273	0.001
	S_{14}	H→L+4 (0.45)	271	0.014
		H–2→L+1 (−0.34)		
	S_{15}	H–3→L+1 (0.39)	271	0.004
		H→L+4 (−0.38)		
		H–2→L+1 (−0.36)		
[(pbib)Ir(pmpMe₃Bz)CN]	S_1	H→L (0.70)	366	0.012
	S_2	H–1→L (0.69)	336	0.001
	S_3	H–2→L (0.69)	326	0.101
	S_4	H–3→L (0.66)	314	0.145
	S_5	H→L+1 (0.66)	300	0.013
	S_6	H–1→L+1 (0.49)	293	0.019
		H→L+5 (−0.43)		
	S_7	H→L+2 (0.52)	291	0.045
		H–4→L (−0.33)		
	S_8	H→L+5 (0.45)	289	0.126
		H–1→L+1 (0.43)		
	S_9	H–4→L (0.55)	286	0.342
		H→L+2 (0.37)		
	S_{10}	H–5→L (0.68)	277	0.006
	S_{11}	H–2→L+1 (0.61)	276	0.006
	S_{12}	H→L+3 (0.62)	275	0.039
	S_{13}	H–1→L+2 (0.49)	272	0.002
		H–1→L+5 (0.38)		
	S_{14}	H–1→L+2 (0.44)	271	0.003
		H–1→L+5 (−0.40)		
	S_{15}	H→L+4 (0.64)	269	0.004

[a] Orbitals involved in the major excitation (H = HOMO and L = LUMO).

[b] The coefficients in the configuration interaction (CI) expansion.

[c] Oscillator strengths.
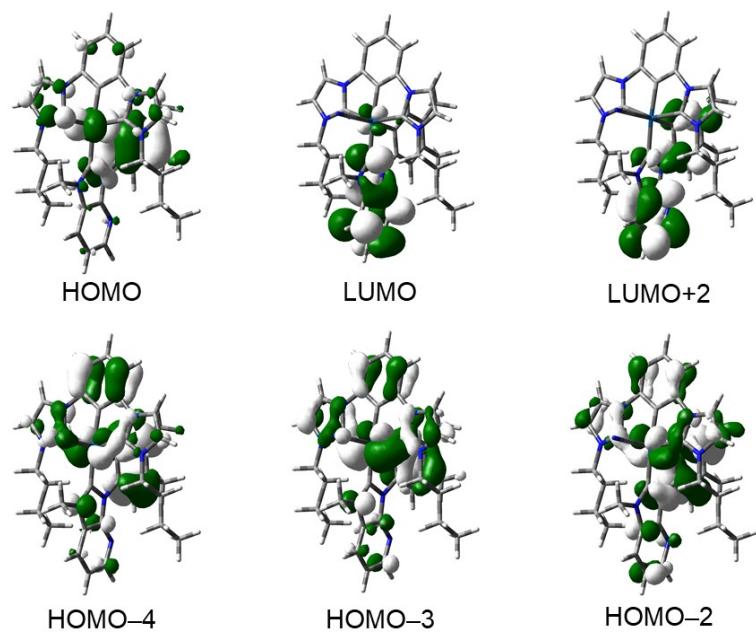
Figure S44 Spatial plots of (isovalue = 0.03) of selected molecular orbitals of **[(pbib)Ir(pmpMe₂)CN]** at the optimized B3LYP ground-state geometry.
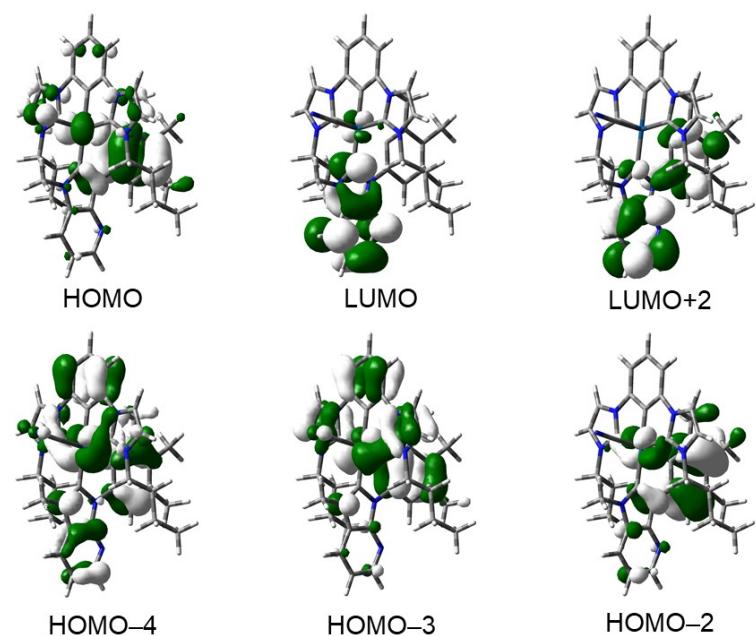
Figure S45 Spatial plots of (isovalue = 0.03) of selected molecular orbitals of **[(pbib)Ir(pmpMe₃)CN]** at the optimized B3LYP ground-state geometry.
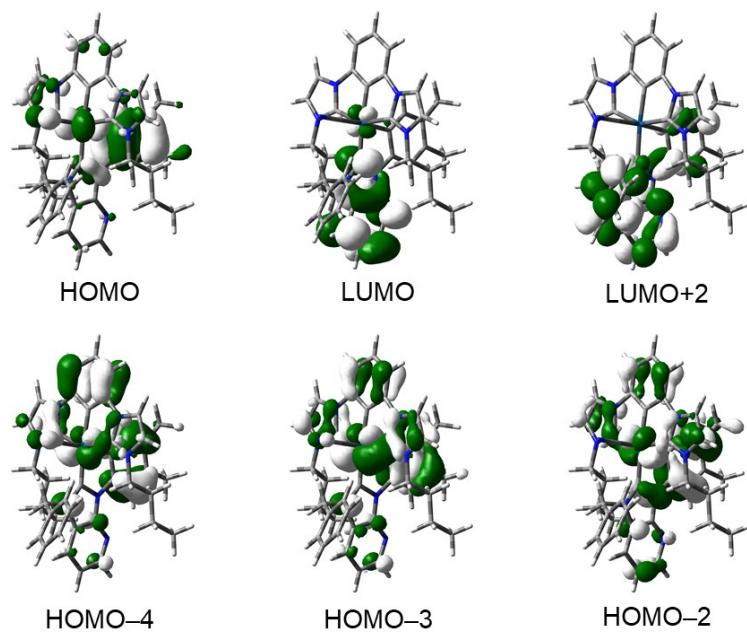
Figure S46 Spatial plots of (isovalue = 0.03) of selected molecular orbitals of **[(pbib)Ir(pmpMe₂Bz)CN]** at the optimized B3LYP ground-state geometry.
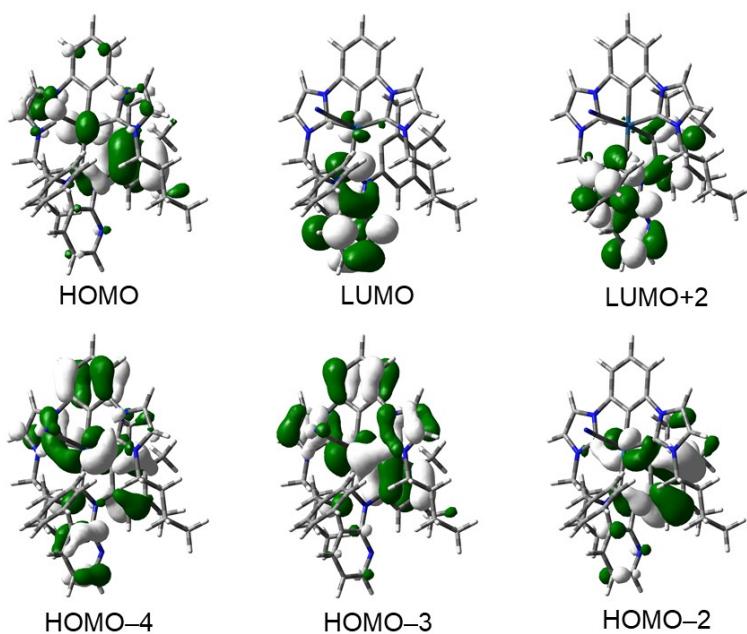
Figure S47 Spatial plots of (isovalue = 0.03) of selected molecular orbitals of **[(pbib)Ir(pmpMe₃Bz)CN]** at the optimized B3LYP ground-state geometry.

Table S4 Relative energies of the lowest triplet excited states (T_1) of the iridium(III) complexes optimized at the B3LYP level.

Complex	$\Delta E(T_1-S_0)/cm^{-1}$ $(\lambda/nm)^a$
[(pbib)Ir(pmpMe$_2$)CN]	24654 (406)
[(pbib)Ir(pmpMe$_3$)CN]	24769 (404)
[(pbib)Ir(pmpMe$_2$Bz)CN]	24635 (406)
[(pbib)Ir(pmpMe$_3$Bz)CN]	24798 (403)

[a] Energy difference between the lowest triplet excited state (T_1) and the ground state (S_0) at the corresponding optimized geometries in toluene solution.

Table S5 Cartesian coordinates of the optimized S_0 geometry of **[(pbib)Ir(pmpMe₂)CN]** in toluene.

C	2.895796	0.000079	-0.123395	H	-2.103524	-0.890731	-3.918955
C	3.571031	1.197437	0.079397	H	-2.103606	0.889544	-3.919155
C	3.571135	-1.197175	0.079659	H	-0.598299	-0.000485	-3.572760
C	4.909009	1.227279	0.476899	C	0.235341	0.000178	1.293794
C	4.909113	-1.226815	0.477179	C	-1.166498	0.000126	1.420380
C	5.561756	0.000281	0.669875	C	0.939202	0.000379	2.506334
H	5.444231	2.158510	0.636276	C	-1.830780	0.000273	2.649623
H	5.444411	-2.157965	0.636772	C	0.316395	0.000528	3.764124
H	6.602862	0.000361	0.977267	C	-1.092208	0.000477	3.837662
C	2.933479	-3.666864	-0.103680	C	1.153146	0.000738	5.022790
C	1.761988	-4.260571	-0.445238	H	0.950555	-0.878182	5.648017
H	3.886933	-4.092609	0.162695	H	2.220366	0.000747	4.784514
H	1.500416	-5.303234	-0.529863	H	0.950486	0.879817	5.647770
C	1.761524	4.260563	-0.445831	C	-1.807022	0.000628	5.169181
C	2.933091	3.667029	-0.104235	H	-1.546952	-0.878318	5.772584
H	1.499827	5.303186	-0.530547	H	-1.546900	0.879672	5.772415
H	3.886493	4.092917	0.162097	H	-2.892051	0.000645	5.033072
C	1.409015	-2.022548	-0.543577	H	-2.914114	0.000231	2.681133
N	2.709629	-2.301553	-0.164943	H	2.026718	0.000422	2.481007
N	0.845423	-3.245331	-0.713840				
C	1.408840	2.022487	-0.544026				
N	2.709429	2.301686	-0.165443				
N	0.845087	3.245187	-0.714363				
C	-0.551096	3.493818	-1.078102				
H	-0.565997	4.343305	-1.769059				
H	-0.899811	2.616287	-1.623760				
C	-1.443018	3.769223	0.137933				
H	-1.402811	2.903223	0.809030				
H	-1.038096	4.621542	0.699131				
C	-2.895388	4.058681	-0.262602				
H	-3.277021	3.229343	-0.873010				
H	-2.925817	4.949556	-0.904526				
C	-3.814125	4.262050	0.946402				
H	-4.838370	4.487820	0.632591				
H	-3.846140	3.362087	1.570066				
H	-3.466794	5.090887	1.573571				
C	-0.550759	-3.494155	-1.077451				
H	-0.899530	-2.616846	-1.623432				
H	-0.565637	-4.343902	-1.768087				
C	-1.442636	-3.769147	0.138711				
H	-1.037679	-4.621268	0.700184				
H	-1.402411	-2.902918	0.809511				
C	-2.895019	-4.058750	-0.261668				
H	-3.276675	-3.229629	-0.872356				
H	-2.925469	-4.949852	-0.903276				
C	-3.813711	-4.261692	0.947442				
H	-4.837966	-4.487580	0.633748				
H	-3.466353	-5.090302	1.574894				
H	-3.845710	-3.361505	1.570784				
C	1.529906	-0.000334	-2.656617				
N	1.869126	-0.000537	-3.779373				
Ir	0.960456	-0.000065	-0.679031				
C	-1.094999	-0.000191	-0.982870				
C	-3.215992	-0.000185	-0.132045				
C	-3.296828	-0.000383	-1.539801				
C	-4.542667	-0.000539	-2.152960				
C	-5.457255	-0.000283	0.094769				
C	-5.646914	-0.000483	-1.292485				
H	-4.658874	-0.000692	-3.231436				
H	-6.318005	-0.000247	0.758689				
H	-6.654324	-0.000596	-1.694065				
N	-1.859178	-0.000077	0.171487				
N	-4.254126	-0.000132	0.696586				
N	-1.993900	-0.000375	-2.020369				
C	-1.678498	-0.000520	-3.444963				

Table S6 Cartesian coordinates of the optimized S_0 geometry of **[(pbib)Ir(pmpMe3)CN]** in toluene.

```
C     2.928261   -0.000065   -0.021190      H    -1.475163   -0.889605   -4.326854
C     3.620604    1.197815    0.112347      H    -1.474617    0.890994   -4.326399
C     3.620517   -1.198006    0.112241      H    -0.044037    0.000117   -3.750617
C     4.981999    1.227022    0.418075      C    -0.080171   -0.000075    1.270709
C     4.981909   -1.227339    0.417969      C    -1.483584   -0.000078    1.097338
C     5.644639   -0.000190    0.572953      C     0.338568   -0.000187    2.626727
H     5.529394    2.157943    0.531008      C    -2.412977   -0.000190    2.136915
H     5.529236   -2.158311    0.530822      C    -0.587387   -0.000332    3.705201
H     6.703723   -0.000239    0.810956      C    -1.971954   -0.000326    3.460461
C     2.970945   -3.665329   -0.020936      C    -0.068398   -0.000485    5.128737
C     1.787386   -4.260344   -0.314212      H    -0.875874   -0.000823    5.861510
H     3.930364   -4.089600    0.225694      H     0.558419   -0.877582    5.331961
H     1.519377   -5.303365   -0.369258      H     0.557992    0.876842    5.332308
C     1.787659    4.260320   -0.313700      C    -3.002297   -0.000452    4.570968
C     2.971187    3.665196   -0.020524      H    -2.914463   -0.880967    5.218643
H     1.519713    5.303364   -0.368614      H    -2.914422    0.879884    5.218879
H     3.930637    4.089378    0.226141      H    -4.013335   -0.000375    4.154165
C     1.437798   -2.022470   -0.442785      C     1.801625   -0.000160    3.010876
N     2.749575   -2.300363   -0.098720      H     2.442258    0.000215    2.137503
N     0.865797   -3.247119   -0.572340      H     2.058174    0.877114    3.619374
C     1.437933    2.022484   -0.442557      H     2.058379   -0.877812    3.618750
N     2.749736    2.300254   -0.098491      H    -3.472515   -0.000172    1.914386
N     0.866002    3.247184   -0.571939
C    -0.544544    3.502186   -0.870468
H    -0.588798    4.355636   -1.555474
H    -0.921041    2.628917   -1.403937
C    -1.374981    3.773117    0.389327
H    -1.292906    2.907282    1.056135
H    -0.947870    4.630475    0.926179
C    -2.849353    4.048407    0.068323
H    -3.263194    3.200790   -0.493590
H    -2.924072    4.921868   -0.593791
C    -3.692267    4.280645    1.326335
H    -4.738837    4.477624    1.072647
H    -3.665428    3.403297    1.981622
H    -3.320670    5.137140    1.900323
C    -0.544755   -3.502004   -0.870946
H    -0.921194   -2.628634   -1.404291
H    -0.589034   -4.355345   -1.556086
C    -1.375238   -3.773094    0.388784
H    -0.948193   -4.630569    0.925501
H    -1.293129   -2.907377    1.055741
C    -2.849619   -4.048240    0.067697
H    -3.263398   -3.200493   -0.494067
H    -2.924373   -4.921573   -0.594582
C    -3.692574   -4.280666    1.325647
H    -4.739150   -4.477537    1.071898
H    -3.321039   -5.137290    1.899482
H    -3.665699   -3.403442    1.981099
C     1.818138    0.000126   -2.481837
N     2.327503    0.000171   -3.537860
Ir    0.995519    0.000034   -0.611249
C    -0.976957    0.000131   -1.251527
C    -3.216512    0.000128   -0.802806
C    -3.038748    0.000262   -2.200007
C    -4.148680    0.000378   -3.034447
C    -5.463215    0.000193   -0.997240
C    -5.393292    0.000338   -2.395504
H    -4.061081    0.000496   -4.115524
H    -6.431644    0.000162   -0.503314
H    -6.308793    0.000422   -2.976943
N    -1.933029    0.000049   -0.258293
N    -4.392469    0.000087   -0.183978
N    -1.671988    0.000247   -2.437437
C    -1.129419    0.000451   -3.791908
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C	2.806955	1.342258	-0.295975	H	-2.938476	0.268195	-2.902107
C	3.145882	2.273288	0.677700	H	-1.583675	1.288865	-2.386310
C	3.784293	0.911427	-1.184710	C	1.239984	-0.966380	0.892718
C	4.439819	2.786446	0.784321	C	0.110220	-1.766403	1.145785
C	5.094398	1.389812	-1.123978	C	2.402689	-1.346626	1.577516
H	4.712127	3.514906	1.542068	C	0.120692	-2.862526	2.012755
H	5.863464	1.058249	-1.815093	C	2.461791	-2.439744	2.455743
H	6.414220	2.717293	-0.065277	C	1.301323	-3.210223	2.678082
C	3.828955	-0.740267	-3.135512	C	3.758360	-2.781088	3.153348
C	2.851027	-1.516199	-3.667306	H	4.099411	-3.794916	2.907919
H	4.864433	-0.625265	-3.410906	H	4.552155	-2.084886	2.868819
H	2.873737	-2.208762	-4.493506	H	3.656646	-2.743447	4.245430
C	0.606294	3.272596	3.016967	C	1.316543	-4.395713	3.615283
C	1.890280	3.398436	2.597149	H	2.039365	-5.157966	3.297838
H	0.085060	3.741382	3.836290	H	1.598151	-4.106252	4.635645
H	2.700483	3.997981	2.978570	H	0.332932	-4.870962	3.664464
C	1.906315	-0.359921	-1.959743	H	-0.782424	-3.441416	2.166157
N	3.245267	-0.039594	-2.093328	H	3.311842	-0.768124	1.427439
N	1.686015	-1.270107	-2.942598	C	-3.498746	1.920212	-1.638690
C	0.831700	1.927218	1.204293	C	-4.829006	1.901932	-2.075430
N	2.020720	2.572300	1.493628	C	-3.066013	2.985182	-0.834983
N	-0.025280	2.374266	2.158296	C	-5.721711	2.906334	-1.693139
C	-1.407357	1.927005	2.346466	H	-5.168411	1.107583	-2.736332
H	-2.014403	2.809470	2.575105	C	-3.956415	3.987611	-0.449412
H	-1.749496	1.532175	1.390372	H	-2.021739	3.042139	-0.546016
C	-1.545004	0.873805	3.451825	C	-5.288322	3.947545	-0.871338
H	-0.926462	0.006770	3.192398	H	-6.750048	2.876737	-2.041722
H	-1.145632	1.277445	4.391555	H	-3.606262	4.810233	0.167651
C	-3.001670	0.437901	3.656498	H	-5.979109	4.731033	-0.573353
H	-3.412146	0.080935	2.702759				
H	-3.606790	1.308831	3.942631				
C	-3.146680	-0.661333	4.713630				
H	-4.195581	-0.942664	4.852034				
H	-2.594757	-1.561115	4.420998				
H	-2.758316	-0.332411	5.684247				
C	0.422345	-1.966841	-3.189370				
H	-0.376860	-1.318168	-2.829551				
H	0.307251	-2.066886	-4.273698				
C	0.357352	-3.338740	-2.508328				
H	1.205483	-3.949973	-2.843650				
H	0.476224	-3.201665	-1.427126				
C	-0.956712	-4.072866	-2.805196				
H	-1.803662	-3.432692	-2.524285				
H	-1.045142	-4.238966	-3.887448				
C	-1.066800	-5.410696	-2.066792				
H	-2.002706	-5.923105	-2.311771				
H	-0.240450	-6.079640	-2.332524				
H	-1.040653	-5.262516	-0.981791				
C	0.471967	2.179363	-1.709456				
N	0.231437	3.065651	-2.439098				
Ir	0.925641	0.636103	-0.425964				
C	-0.947975	-0.267891	-0.410392				
C	-2.335069	-1.906172	0.368907				
C	-3.053759	-1.113683	-0.550229				
C	-4.376419	-1.436306	-0.828501				
C	-4.095230	-3.260830	0.745976				
C	-4.895924	-2.545308	-0.151377				
H	-4.980826	-0.862808	-1.519860				
H	-4.503411	-4.120303	1.271781				
H	-5.922313	-2.854257	-0.316515				
N	-1.057429	-1.361502	0.428900				
N	-2.813831	-2.960383	1.019889				
N	-2.180781	-0.127891	-1.004125				
C	-2.522417	0.838520	-2.064837				

Table S8 Cartesian coordinates of the optimized S_0 geometry of [(pbib)Ir(pmpMe₃Bz)CN] in toluene.

C	-2.675501	-1.563184	-0.045077	H	2.891417	-1.078298	-2.911068
C	-2.939845	-2.358615	1.063129	H	1.560202	-1.923141	-2.104922
C	-3.617276	-1.493850	-1.065631	C	-1.096519	1.226049	0.652896
C	-4.143280	-3.052400	1.197215	C	0.098671	1.981139	0.657025
C	-4.837638	-2.166067	-0.983474	C	-2.193729	1.864290	1.286411
C	-5.084229	-2.937313	0.162560	C	0.237659	3.242544	1.234969
H	-4.360823	-3.670821	2.062828	C	-2.076249	3.143444	1.893854
H	-5.581943	-2.111373	-1.772168	C	-0.853888	3.838385	1.867921
H	-6.027191	-3.468331	0.246911	C	-3.284967	3.758993	2.569393
C	-3.747248	-0.256905	-3.298212	H	-4.081260	3.986744	1.848764
C	-2.847423	0.539429	-3.928460	H	-3.725374	3.080107	3.308730
H	-4.740107	-0.562117	-3.585295	H	-3.039479	4.688268	3.084601
H	-2.909190	1.062903	-4.869194	C	-0.676045	5.207797	2.490781
C	-0.454064	-2.523182	3.653313	H	-1.354307	5.952106	2.056901
C	-1.682669	-2.900182	3.218789	H	-0.863465	5.200077	3.571344
H	0.065071	-2.744733	4.572088	H	0.345521	5.567224	2.338784
H	-2.437072	-3.512785	3.684545	H	1.190338	3.754717	1.191276
C	-1.868832	-0.144843	-1.999498	C	3.503614	-2.358303	-1.291517
N	-3.144751	-0.668283	-2.120784	C	4.737892	-2.620972	-1.896987
N	-1.708242	0.594415	-3.127252	C	3.182534	-3.016522	-0.095707
C	-0.724433	-1.606474	1.595079	C	5.645481	-3.509617	-1.314264
N	-1.842770	-2.333231	1.965566	H	4.988743	-2.136124	-2.837906
N	0.116770	-1.736509	2.654085	C	4.088580	-3.900033	0.490228
C	1.413410	-1.071998	2.805533	H	2.211358	-2.851248	0.359438
H	2.125931	-1.810158	3.189449	C	5.324416	-4.146655	-0.115311
H	1.741567	-0.782644	1.807612	H	6.598919	-3.702471	-1.797648
C	1.343946	0.147526	3.732286	H	3.825731	-4.407184	1.414256
H	0.610024	0.853672	3.327944	H	6.027366	-4.837585	0.341025
H	0.976324	-0.166747	4.718107	C	-3.560236	1.218299	1.349600
C	2.703866	0.839680	3.888241	H	-3.596217	0.310305	0.759243
H	3.069932	1.148612	2.900637	H	-3.838580	0.957339	2.380112
H	3.438425	0.122195	4.278721	H	-4.341834	1.895556	0.984090
C	2.638768	2.062836	4.808417				
H	3.619500	2.539504	4.905228				
H	1.940389	2.809976	4.416053				
H	2.301009	1.786062	5.813683				
C	-0.539933	1.417640	-3.444899				
H	0.315908	0.967627	-2.940751				
H	-0.367761	1.344478	-4.523903				
C	-0.714968	2.880068	-3.019596				
H	-1.605477	3.294700	-3.510298				
H	-0.903255	2.910072	-1.940347				
C	0.509800	3.737700	-3.361637				
H	1.402232	3.298340	-2.896697				
H	0.684507	3.712313	-4.445963				
C	0.360302	5.189764	-2.896578				
H	1.243552	5.782685	-3.154971				
H	-0.510184	5.667258	-3.360652				
H	0.228599	5.240125	-1.810303				
C	-0.412107	-2.503732	-1.156103				
N	-0.196495	-3.544180	-1.651512				
Ir	-0.857940	-0.711000	-0.279469				
C	1.023601	0.119337	-0.547281				
C	2.507338	1.824992	-0.231824				
C	3.148006	0.807062	-0.965117				
C	4.468350	0.980919	-1.361492				
C	4.344418	3.132563	-0.250813				
C	5.068927	2.186625	-0.984789				
H	5.010186	0.226081	-1.918168				
H	4.814451	4.067517	0.043771				
H	6.098689	2.393134	-1.255294				
N	1.211488	1.367486	0.003873				
N	3.066707	2.973256	0.134576				
N	2.219484	-0.213012	-1.141965				
C	2.508777	-1.413991	-1.941307				

Table S9 Cartesian coordinates of the optimized T$_1$ geometry of **[(pbib)Ir(pmpMe$_2$)CN]** in toluene.

C	2.908225	-0.000727	-0.088415	H	-2.241019	-0.887919	-3.884331
C	3.586494	1.198761	0.092635	H	-2.241812	0.888594	-3.884563
C	3.585797	-1.200641	0.092453	H	-0.724886	0.001050	-3.580825
C	4.931296	1.226827	0.467294	C	0.237962	0.000082	1.269864
C	4.930576	-1.229541	0.467120	C	-1.214616	0.000288	1.400481
C	5.584617	-0.001560	0.652343	C	0.941097	0.000207	2.490431
H	5.472986	2.156691	0.612202	C	-1.865743	0.000342	2.657481
H	5.471722	-2.159741	0.611910	C	0.324438	0.000322	3.738088
H	6.630501	-0.001888	0.942851	C	-1.118129	0.000366	3.818258
C	2.958537	-3.671087	-0.141705	C	1.149962	0.000362	4.996548
C	1.791028	-4.264633	-0.502903	H	0.938366	-0.878237	5.618998
H	3.914257	-4.098355	0.114212	H	2.217485	0.000347	4.764429
H	1.539103	-5.306973	-0.616840	H	0.938374	0.879012	5.618929
C	1.793728	4.263851	-0.503097	C	-1.804301	0.000474	5.158301
C	2.960873	3.669589	-0.141902	H	-1.523963	-0.878261	5.751891
H	1.542473	5.306334	-0.617225	H	-1.523946	0.879296	5.751756
H	3.916918	4.096253	0.113810	H	-2.890284	0.000478	5.043194
C	1.421793	-2.031848	-0.539706	H	-2.948725	0.000416	2.684011
N	2.725552	-2.306602	-0.165018	H	2.026983	0.000141	2.459067
N	0.867776	-3.250699	-0.744467				
C	1.422972	2.031316	-0.539360				
N	2.726896	2.305257	-0.164702				
N	0.869814	3.250477	-0.744508				
C	-0.526138	3.485372	-1.127268				
H	-0.535521	4.295463	-1.863909				
H	-0.873302	2.574562	-1.616926				
C	-1.421908	3.826295	0.068625				
H	-1.381135	2.997996	0.786045				
H	-1.025815	4.710735	0.584944				
C	-2.875278	4.079361	-0.353510				
H	-3.241776	3.218627	-0.927674				
H	-2.911185	4.941048	-1.033751				
C	-3.805059	4.322718	0.839455				
H	-4.827498	4.529407	0.507779				
H	-3.839135	3.444836	1.493780				
H	-3.468949	5.176511	1.439060				
C	-0.528304	-3.484756	-1.127281				
H	-0.875183	-2.573326	-1.615984				
H	-0.538078	-4.294122	-1.864717				
C	-1.424056	-3.826492	0.068395				
H	-1.028129	-4.711427	0.583992				
H	-1.383075	-2.998778	0.786486				
C	-2.877502	-4.078944	-0.353854				
H	-3.243863	-3.217711	-0.927354				
H	-2.913613	-4.940114	-1.034738				
C	-3.807265	-4.323018	0.838975				
H	-4.829768	-4.529235	0.507202				
H	-3.471302	-5.177338	1.437912				
H	-3.841114	-3.445630	1.493976				
C	1.542270	0.000395	-2.621825				
N	1.864173	0.000887	-3.748897				
Ir	0.977194	-0.000165	-0.635389				
C	-1.106267	0.000356	-0.996359				
C	-3.263764	0.000763	-0.071026				
C	-3.354434	0.000918	-1.479039				
C	-4.627637	0.001175	-2.084200				
C	-5.511017	0.001204	0.199341				
C	-5.710774	0.001338	-1.172905				
H	-4.770684	0.001224	-3.157341				
H	-6.357457	0.001328	0.879885				
H	-6.728753	0.001556	-1.552856				
N	-1.892344	0.000436	0.215819				
N	-4.269184	0.000886	0.796748				
N	-2.070415	0.000729	-1.988927				
C	-1.800975	0.000601	-3.417838				

Table S10   Cartesian coordinates of the optimized T_1 geometry of **[(pbib)Ir(pmpMe$_3$)CN]** in toluene.

C	-2.889524	-0.404959	-0.057125
C	-3.357251	-1.707215	0.067415
C	-3.795370	0.648889	0.008749
C	-4.702417	-1.979035	0.323428
C	-5.151501	0.433810	0.258311
C	-5.583391	-0.890891	0.425218
H	-5.078027	-2.992215	0.430595
H	-5.865933	1.249456	0.316764
H	-6.633673	-1.081156	0.622463
C	-3.599013	3.194655	-0.192523
C	-2.526564	3.987336	-0.451439
H	-4.631138	3.445991	-0.010695
H	-2.450352	5.059841	-0.534644
C	-1.053531	-4.413251	-0.492480
C	-2.309502	-4.027503	-0.148630
H	-0.629868	-5.397477	-0.613859
H	-3.185249	-4.611386	0.082922
C	-1.774355	1.852004	-0.476859
N	-3.132664	1.890407	-0.206254
N	-1.425330	3.152637	-0.624772
C	-1.059341	-2.147839	-0.491828
N	-2.305643	-2.643453	-0.147745
N	-0.307318	-3.256410	-0.700792
C	1.106547	-3.262420	-1.089980
H	1.222844	-3.990060	-1.900361
H	1.322498	-2.272414	-1.493543
C	2.045748	-3.598562	0.073530
H	1.920200	-2.846595	0.861773
H	1.756890	-4.563771	0.510383
C	3.514145	-3.652569	-0.368732
H	3.784429	-2.705008	-0.851185
H	3.634186	-4.433189	-1.132108
C	4.473370	-3.917011	0.795789
H	5.509999	-3.973236	0.448938
H	4.414554	-3.114949	1.539472
H	4.237564	-4.861113	1.300372
C	-0.058993	3.626646	-0.862990
H	0.482273	2.796891	-1.321013
H	-0.110978	4.446326	-1.587124
C	0.640144	4.078329	0.423996
H	0.062360	4.886821	0.891405
H	0.642517	3.241135	1.132844
C	2.077389	4.548688	0.166818
H	2.642032	3.739617	-0.314435
H	2.065866	5.382763	-0.547857
C	2.797892	4.980178	1.447979
H	3.818872	5.312574	1.235431
H	2.272677	5.806839	1.940001
H	2.859003	4.151904	2.162547
C	-1.682538	-0.160047	-2.502595
N	-2.100183	-0.221714	-3.595604
Ir	-0.976747	-0.058944	-0.578028
C	1.023062	0.265596	-1.172113
C	3.283672	0.317609	-0.550667
C	3.176978	0.456435	-1.949548
C	4.349033	0.601727	-2.717724
C	5.545289	0.435089	-0.590643
C	5.549232	0.583378	-1.969226
H	4.336957	0.717133	-3.794108
H	6.477800	0.423387	-0.033883
H	6.501563	0.688281	-2.481735
N	1.962066	0.210768	-0.085569
N	4.402139	0.296225	0.164868
N	1.837635	0.417275	-2.282861
C	1.388505	0.551572	-3.659057
H	1.665210	1.536824	-4.052046
H	1.864428	-0.213504	-4.282123
H	0.309129	0.429036	-3.703502
C	-0.007187	0.058660	1.272446
C	1.455990	0.079869	1.174590
C	-0.507983	0.055642	2.608081
C	2.313047	-0.012084	2.293189
C	0.340525	-0.108057	3.718073
C	1.773540	-0.129860	3.553766
C	-0.236965	-0.257498	5.107449
H	0.483461	-0.683015	5.806605
H	-0.552945	0.710996	5.519958
H	-1.119379	-0.903172	5.108990
C	2.698370	-0.247838	4.738615
H	2.503788	0.529593	5.486310
H	2.581758	-1.212453	5.247814
H	3.740102	-0.161812	4.422141
C	-1.990108	0.210407	2.870812
H	-2.441785	0.861546	2.127717
H	-2.523183	-0.746982	2.826413
H	-2.180947	0.647256	3.853206
H	3.383464	0.018505	2.133797

Table S11 Cartesian coordinates of the optimized T$_1$ geometry of **[(pbib)Ir(pmpMe$_2$Bz)CN]** in toluene.

C	2.882711	1.209067	-0.335939
C	3.222166	2.241385	0.530255
C	3.859578	0.664556	-1.161010
C	4.526910	2.733034	0.604108
C	5.179693	1.117889	-1.126854
C	5.492943	2.153308	-0.232700
H	4.805087	3.538645	1.276869
H	5.952269	0.700304	-1.765414
H	6.513344	2.521147	-0.191086
C	3.882588	-1.151118	-2.963407
C	2.886190	-1.931841	-3.456530
H	4.926480	-1.095240	-3.225369
H	2.900884	-2.686129	-4.227090
C	0.641558	3.613409	2.631005
C	1.944947	3.639822	2.249501
H	0.111552	4.203742	3.361404
H	2.762477	4.257886	2.582886
C	1.953242	-0.616928	-1.867021
N	3.306135	-0.351806	-1.991227
N	1.718508	-1.590759	-2.779191
C	0.877567	2.039524	1.020509
N	2.083237	2.672793	1.268580
N	0.006939	2.632991	1.872536
C	-1.397574	2.248013	2.046632
H	-1.992893	3.165440	2.098997
H	-1.687915	1.709509	1.144180
C	-1.622656	1.381125	3.290346
H	-1.004616	0.478703	3.208614
H	-1.277607	1.919248	4.183271
C	-3.096660	0.989989	3.459388
H	-3.448154	0.496466	2.544327
H	-3.703479	1.898672	3.570382
C	-3.330081	0.063642	4.656832
H	-4.390937	-0.183414	4.764775
H	-2.780072	-0.876318	4.537843
H	-2.998471	0.529822	5.591820
C	0.423956	-2.242701	-3.000141
H	-0.340227	-1.546285	-2.653373
H	0.300994	-2.377021	-4.079836
C	0.300583	-3.583099	-2.267243
H	1.115989	-4.249109	-2.579070
H	0.429572	-3.409352	-1.192179
C	-1.051078	-4.261204	-2.527898
H	-1.861780	-3.563509	-2.281336
H	-1.147539	-4.478413	-3.600298
C	-1.232027	-5.550512	-1.720562
H	-2.191043	-6.027184	-1.946807
H	-0.438641	-6.273803	-1.941520
H	-1.208927	-5.344301	-0.644968
C	0.622566	1.968198	-1.903196
N	0.425790	2.769780	-2.735608
Ir	0.987613	0.555782	-0.442116
C	-0.967407	-0.260567	-0.423194
C	-2.410831	-1.863425	0.501642
C	-3.090025	-1.150249	-0.511786
C	-4.418455	-1.511611	-0.810851
C	-4.186886	-3.194777	0.947856
C	-4.941634	-2.569272	-0.033155
H	-5.008006	-1.015302	-1.568445
H	-4.607417	-4.002807	1.539340
H	-5.962011	-2.901507	-0.202591
N	-1.121193	-1.320647	0.548378
N	-2.887830	-2.857068	1.240513
N	-2.214419	-0.215982	-1.037080
C	-2.549451	0.655086	-2.170993

H	-3.031393	0.032168	-2.933667
H	-1.604380	1.021693	-2.573240
C	1.173012	-0.884066	0.993662
C	-0.028178	-1.657079	1.292272
C	2.306768	-1.232096	1.752335
C	-0.047778	-2.678591	2.273590
C	2.312611	-2.232442	2.720389
C	1.098961	-2.971495	2.984326
C	3.568698	-2.544164	3.488379
H	3.881169	-3.586631	3.347403
H	4.391603	-1.899520	3.170784
H	3.427726	-2.406612	4.567958
C	1.083270	-4.056183	4.028263
H	1.808260	-4.845839	3.795979
H	1.355250	-3.665039	5.016269
H	0.094693	-4.514008	4.104293
H	-0.970610	-3.218255	2.446876
H	3.231281	-0.689766	1.574116
C	-3.451344	1.827489	-1.820625
C	-4.818350	1.804948	-2.124856
C	-2.915538	2.973271	-1.213573
C	-5.641978	2.886465	-1.802692
H	-5.241862	0.944577	-2.636359
C	-3.736196	4.054483	-0.890182
H	-1.847391	3.025335	-1.029497
C	-5.103657	4.011564	-1.176676
H	-6.700040	2.850765	-2.046482
H	-3.304854	4.938724	-0.428999
H	-5.741121	4.855132	-0.927336

Table S12 Cartesian coordinates of the optimized T$_1$ geometry of [(pbib)Ir(pmpMe$_3$Bz)CN] in toluene.

|								
C	-2.747685	-1.460243	0.074479	H	2.853992	-0.885861	-3.066740
C	-2.967717	-2.256007	1.191926	H	1.495840	-1.746023	-2.319915
C	-3.727066	-1.393660	-0.911644	C	-1.069761	1.228291	0.677250
C	-4.172480	-2.935830	1.379594	C	0.210353	1.945022	0.751514
C	-4.948683	-2.054722	-0.776131	C	-2.158721	1.901747	1.301235
C	-5.156428	-2.813028	0.386160	C	0.385989	3.152972	1.465414
H	-4.358095	-3.554737	2.252307	C	-1.972200	3.068079	2.067595
H	-5.721567	-2.004682	-1.537218	C	-0.679350	3.706189	2.136922
H	-6.100090	-3.334184	0.512989	C	-3.129384	3.674625	2.827309
C	-3.920703	-0.194883	-3.165734	H	-3.801689	4.232980	2.160616
C	-3.033643	0.581197	-3.841086	H	-3.737561	2.906788	3.313786
H	-4.924920	-0.495370	-3.416233	H	-2.795203	4.368650	3.598979
H	-3.122327	1.085748	-4.790062	C	-0.475782	4.984984	2.909190
C	-0.304849	-2.619947	3.584241	H	-1.166069	5.771547	2.583150
C	-1.585007	-2.911937	3.237731	H	-0.646168	4.840540	3.983155
H	0.272507	-2.910612	4.447350	H	0.544219	5.353288	2.779721
H	-2.331076	-3.505608	3.740154	H	1.360843	3.623400	1.462862
C	-2.000285	-0.075464	-1.936037	C	3.426890	-2.297857	-1.547930
N	-3.284960	-0.590244	-2.000399	C	4.673594	-2.517003	-2.145232
N	-1.869539	0.640644	-3.079073	C	3.071313	-3.063014	-0.427571
C	-0.688246	-1.600829	1.596568	C	5.557799	-3.468328	-1.629028
N	-1.814183	-2.282689	2.026444	H	4.952475	-1.946802	-3.028416
N	0.225882	-1.821365	2.574484	C	3.953117	-4.010405	0.091955
C	1.578110	-1.255147	2.617589	H	2.090873	-2.929031	0.017270
H	2.274120	-2.065475	2.859475	C	5.201211	-4.213812	-0.505039
H	1.804123	-0.910796	1.608028	H	6.521464	-3.624889	-2.105524
C	1.705340	-0.113812	3.633023	H	3.661842	-4.601142	0.956128
H	0.989470	0.675265	3.372866	H	5.885751	-4.954161	-0.100869
H	1.423057	-0.479197	4.629458	C	-3.567529	1.363660	1.177557
C	3.124763	0.466336	3.681576	H	-3.695639	0.840216	0.235241
H	3.402723	0.832787	2.685637	H	-3.811153	0.652202	1.976742
H	3.836969	-0.332880	3.927252	H	-4.308591	2.165360	1.218272
C	3.260784	1.606248	4.695939				
H	4.281999	1.999720	4.714269				
H	2.588905	2.434977	4.446607				
H	3.013688	1.269431	5.709343				
C	-0.691729	1.436524	-3.436019				
H	0.152962	1.001108	-2.899617				
H	-0.518240	1.312739	-4.510029				
C	-0.851706	2.917872	-3.076256				
H	-1.729939	3.327590	-3.592797				
H	-1.052473	2.996931	-2.000751				
C	0.392671	3.739204	-3.436687				
H	1.268510	3.309351	-2.933627				
H	0.585438	3.655246	-4.514808				
C	0.259207	5.215945	-3.051752				
H	1.157693	5.778912	-3.323526				
H	-0.593785	5.682949	-3.557343				
H	0.109292	5.328218	-1.972258				
C	-0.545815	-2.421280	-1.197969				
N	-0.345001	-3.439315	-1.742106				
Ir	-0.935800	-0.643823	-0.248648				
C	0.994024	0.132954	-0.605410				
C	2.560499	1.818206	-0.157705				
C	3.148424	0.842247	-0.991070				
C	4.477137	1.029850	-1.418808				
C	4.430446	3.096162	-0.115435				
C	5.098010	2.205040	-0.943123				
H	4.997538	0.319385	-2.045986				
H	4.924036	3.993683	0.245683				
H	6.124914	2.418981	-1.225917				
N	1.243961	1.380653	0.065261				
N	3.133228	2.923304	0.300816				
N	2.203689	-0.136863	-1.236573				
C	2.459155	-1.276321	-2.121065				
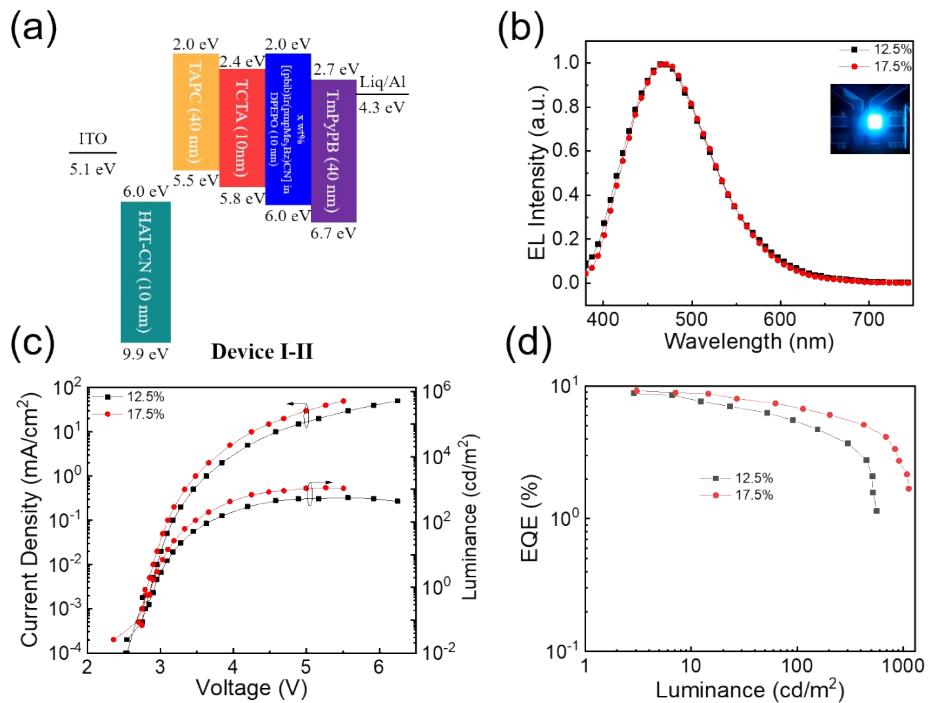
Figure S48 Device I-II based on [(pbib)Ir(pmpMe₃Bz)CN] as dopant (a) Energy diagram of the materials used in the OLEDs. (b) EL spectra of all devices. (c) Current density−voltage−luminance (*J*−*V*−*L*) characteristics. (d) EQE vs luminance.
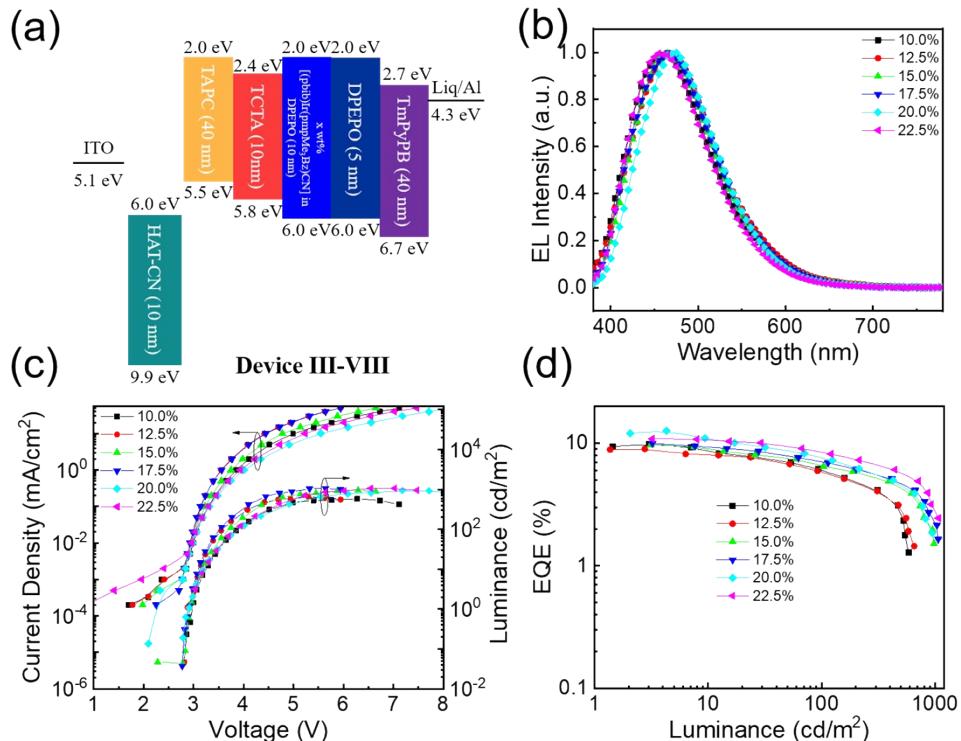
Figure S49 Device III-VIII based on [(pbib)Ir(pmpMe₃Bz)CN] as dopant (a) Energy diagram of the materials used in the OLEDs. (b) EL spectra of all devices. (c) current density−voltage−luminance (*J*−*V*−*L*) characteristics. (d) EQE
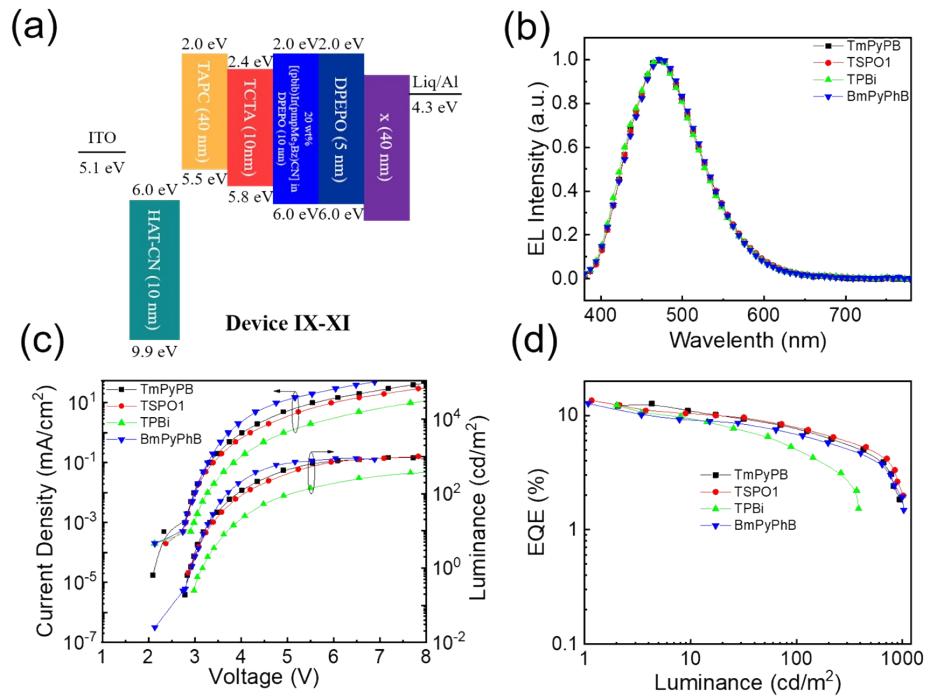
vs luminance.

Figure S50 Device IX-XI based on [(pbib)Ir(pmpMe₃Bz)CN] as dopant (a) Energy diagram of the materials used in the OLEDs. (b) EL spectra of all devices. (c) Current density−voltage−luminance (J−V−L) characteristics. (d) EQE vs luminance.

Table S13 Blue phosphorescent and TADF materials with lifetimes less than 1 μs

Complexes	τ(μs)	λ(nm)	PLQY	EQE(%)	CIE(x,y)	Ref
Ir(bpzb)(ppy)CN	0.0047	449,481,508	0.005	-		
Ir(dfbpzb)(ppy)Cl	0.00018	456,490,518	0.0004	-	-	
Ir(dfbpzb)(ppy)CN	0.0028	447,480,506	0.004	-		18
Ir(dmbpzb)(ppy)Cl	0.00079	460,493,522	0.0005	-		
Ir(dmbpzb)(ppy)CN	0.014	449,481,508	0.008	-		
fac-Ir(pmi)$_3$	0.4	-	0.02	-	-	
mer-Ir(pmi)$_3$	0.62	-	0.05	-	-	19
fac-Ir(pmb)$_3$	0.22	-	0.04	-	-	
mer-Ir(pmb)$_3$	0.015	-	0.002	-	-	
Ir2	0.63	470	0.95	8.9	0.15,0.23	20
mer-Ir(pmp)$_3$	0.8 ±0.1	465	0.78 ±0.05	14.4 ± 0.4	(0.16,0.15)	21
mer-Ir-1	0.67	470	0.95	24.8	(0.149,0.085)	22
MS-2	0.8	475,499,505	0.88	30.1	(0.15,0.38)	23
MS-17	0.6	462,475,488	0.88	31.2	(0.15,0.32)	
3DPyM-pDTC	0.27	464	0.98	31.9	(0.14,0.18)	24
MCz-BOBO	0.78	476	0.5	20.1	(0.13,0.20)	25
OBA-BrS	0.81	478	0.305	9.2	(0.29,0.46)	26
[(pbib)Ir(pmpMe$_2$)CN]	0.32	434	0.42	10.1	(0.20,0.30)	
[(pbib)Ir(pmpMe$_3$)CN]	1.10	426	0.61	11.2	(0.16,0.07)	This work
[(pbib)Ir(pmpMe$_2$Bz)CN]	0.68	428	0.44	11.7	(0.20,0.28)	
[(pbib)Ir(pmpMe$_3$Bz)CN]	0.78	434	0.39	13.5	(0.17,0.20)	

References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zarkrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16, Revision B.01*, Gaussian, Inc.: Wallingford CT, 2016.

2. Becke, A. D., Density-functional thermochemistry. 3. The role of exact exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648-5652.

3. Lee, C. T.; Yang, W. T.; Parr, R. G., Development of the colle-salvetti correlation-energy formula into a functional of the electron-density. *Phys. Rev. B* **1988**, *37* (2), 785-789.

4. Vosko, S. H.; Wilk, L.; Nusair, M., Accurate spin-dependent electron liquid correlation energies for local spin-density calculations - A critical analysis. *Can. J. Phys.* **1980**, *58* (8), 1200-1211.

5. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98* (45), 11623-11627.

6. Barone, V.; Cossi, M., Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A* **1998**, *102* (11), 1995-2001.

7. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V., Energies, structures, and electronic

properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* **2003**, *24* (6), 669-681.

8. Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J., An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules. *J. Chem. Phys.* **1998**, *109* (19), 8218-8224.

9. Bauernschmitt, R.; Ahlrichs, R., Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem. Phys. Lett.* **1996**, *256* (4-5), 454-464.

10. Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R., Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold. *J. Chem. Phys.* **1998**, *108* (11), 4439-4449.

11. Hay, P. J.; Wadt, W. R., Ab initio effective core potentials for molecular calculations - Potentials for the transition-metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82* (1), 270-283.

12. Wadt, W. R.; Hay, P. J., Ab initio effective core potentials for molecular calculations - Potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82* (1), 284-298.

13. Hay, P. J.; Wadt, W. R., Ab initio effective core potentials for molecular calculations - Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82* (1), 299-310.

14. Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G., A set of f-polarization functions for pseudo-potential basis-sets of the transition-metals Sc-Cu, Y-Ag and La-Au. *Chem. Phys. Lett.* **1993**, *208* (1-2), 111-114.

15. Hehre, W. J.; Ditchfie.R; Pople, J. A., Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **1972**, *56* (5), 2257-2261.

16. Hariharan, P. C.; Pople, J. A., The influence of polarization functions on molecular-orbital hydrogenation energies. *Theor. Chim. Acta.* **1973,** *28* (3), 213-222.

17. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A., Self-Consistent Molecular-Orbital Methods .23. A Polarization-Type Basis Set for 2nd-Row Elements. *J. Chem. Phys.* **1982**, *77* (7), 3654-3665.

18. Yang, L.; Okuda, F.; Kobayashi, K.; Nozaki, K.; Tanabe, Y.; Ishii, Y.; Haga, M.-a., Syntheses and phosphorescent properties of blue emissive iridium complexes with tridentate pyrazolyl ligands. *Inorg. Chem.* **2008**, *47* (16), 7154-7165.

19. Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R., Blue and near-UV phosphorescence from iridium complexes with cyclometalated pyrazolyl or N-heterocyclic carbene ligands. *Inorg. Chem.* **2005**, *44* (22), 7992-8003.

20. Cheng, W.; Wang, L.-D.; Zhou, Y.-Y.; Bian, Z.-Q.; Tong, B.-H.; Liu, Z.-W.; Wang, S., Blue iridium(III) complexes with high internal quantum efficiency based on 4-(pyridin-3-yl)pyrimidine derivative and their electroluminescent properties. *Dyes and Pigments* **2020**, *177*, 108257.

21. Lee, J.; Chen, H. F.; Batagoda, T.; Coburn, C.; Djurovich, P. I.; Thompson, M. E.; Forrest, S. R., Deep blue phosphorescent organic light-emitting diodes with very high brightness and efficiency. *Nat. Mater.* **2016**, *15* (1), 92-98.

22. Park, H. Y.; Maheshwaran, A.; Moon, C. K.; Lee, H.; Reddy, S. S.; Sree, V. G.; Yoon, J.; Kim, J. W.; Kwon, J. H.; Kim, J. J.; Jin, S. H., External Quantum Efficiency Exceeding 24% with CIEy Value of 0.08 using a Novel Carbene-Based Iridium Complex in Deep-Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* **2020**, *32* (29), 2002120.

23. Sarma, M.; Tsai, W.-L.; Lee, W.-K.; Chi, Y.; Wu, C.-C.; Liu, S.-H.; Chou, P.-T.; Wong, K.-T., Anomalously Long-Lasting Blue PhOLED Featuring Phenyl-Pyrimidine Cyclometalated Iridium Emitter. *Chem* **2017**, *3* (3), 461-476.

24. Rajamalli, P.; Senthilkumar, N.; Huang, P. Y.; Ren-Wu, C. C.; Lin, H. W.; Cheng, C. H., New Molecular Design Concurrently Providing Superior Pure Blue, Thermally Activated Delayed Fluorescence and Optical Out-Coupling Efficiencies. *J. Am. Chem. Soc.* **2017**, *139* (32), 10948-10951.

25. Agou, T.; Matsuo, K.; Kawano, R.; Park, I. S.; Hosoya, T.; Fukumoto, H.; Kubota, T.; Mizuhata, Y.; Tokitoh, N.; Yasuda, T., Pentacyclic Ladder-Heteraborin Emitters Exhibiting High-Efficiency Blue Thermally Activated Delayed Fluorescence with an Ultrashort Emission Lifetime. *ACS Materials Lett.* **2019**, *2* (1), 28-34.

26. Song, D.; Yu, Y.; Yue, L.; Zhong, D.; Zhang, Y.; Yang, X.; Sun, Y.; Zhou, G.; Wu, Z., Asymmetric thermally activated delayed fluorescence (TADF) emitters with 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (OBA) as the acceptor and highly efficient blue-emitting OLEDs. *J. Mater. Chem. C* **2019**, *7* (38), 11953-11963.