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Supporting Information

Versatile phosphorescent color tuning of highly efficient borylated iridium(III) cyclometalates by manipulating the electron-accepting capacity of the dimesitylboron group

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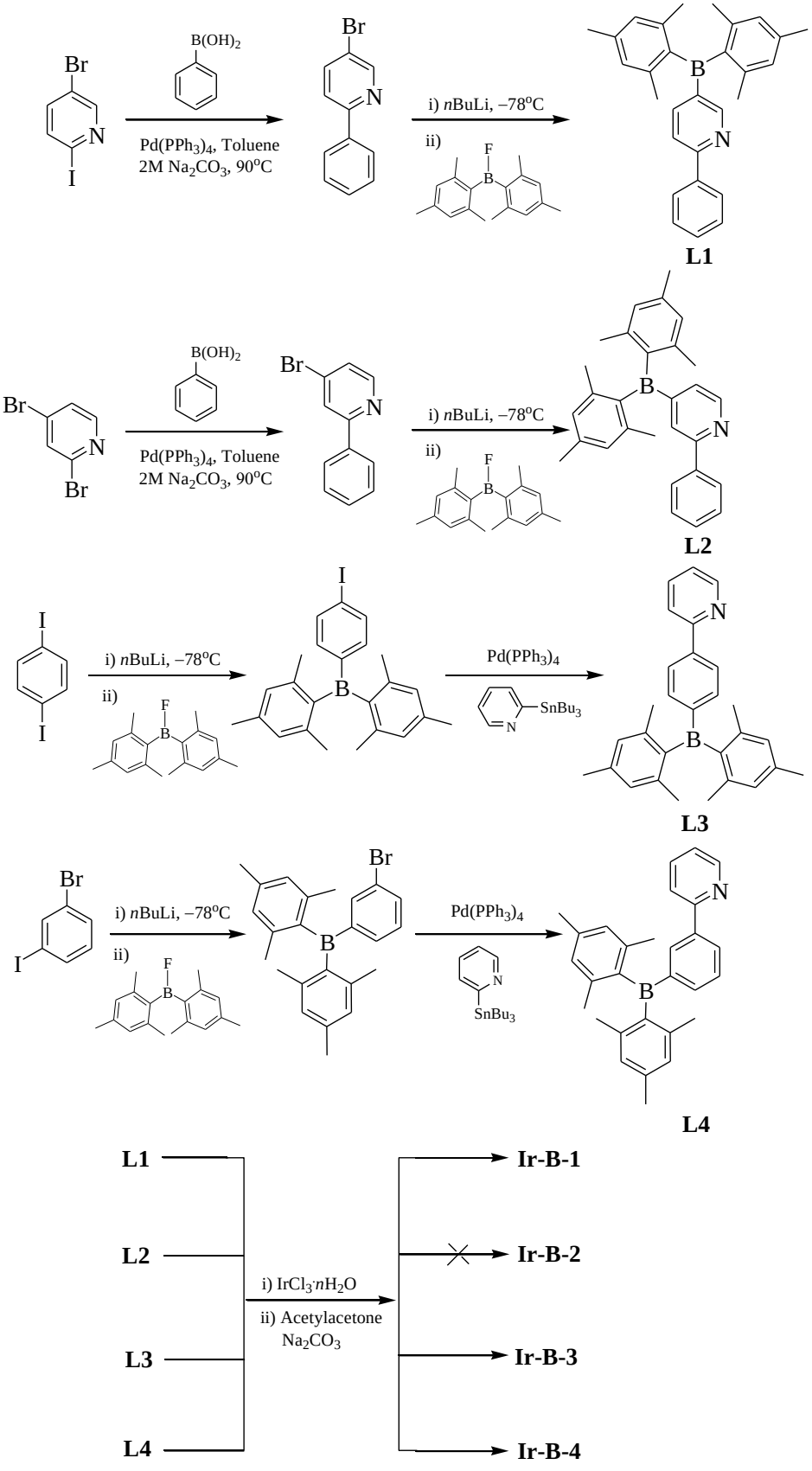
Experimental



Scheme S1. The synthetic protocols for the borylated Ir^{III} phosphors.

The detailed synthetic procedures for **L1**–**L4**, their intermediate compounds and complexes **Ir-B-3** and **Ir-B-4** are given as follows.

5-Bromo-2-phenylpyridine. Under a N_2 atmosphere, 5-bromo-2-iodopyridine (1.42 g, 5.00 mmol), phenylboronic acid (0.61 g, 5.00 mmol) and $Pd(PPh_3)_4$ (289 mg) were added to a mixture of toluene (40 mL) and 2 M Na_2CO_3 (30 mL). The reaction mixture was heated to 90 ^oC for 24 h under stirring. Then, the reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 (3 × 60 mL). The combined organic phase was washed with water (3 × 80 mL). The organic phase was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography eluting with CH_2Cl_2/hexane (1:8, v/v). The product was obtained as a white crystalline solid (1.05 g, 90%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.74 (d, *J* = 2.0 Hz, 1H, Ar), 7.97–7.94 (m, 2H, Ar), 7.87 (dd, *J* = 2.0, 8.4 Hz, 1H, Ar), 7.63 (d, *J* = 8.4 Hz, 1H, Ar), 7.50–7.42 (m, 3H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.87, 150.65, 139.31, 138.17, 129.34, 128.86, 126.74, 121.65, 119.30 (Ar). FAB-MS (*m/z*): 234 $[M]^+$. Anal. calcd. for $C_{11}H_8BrN$: C, 56.44; H, 3.44; N, 5.98; found: C, 56.12; H, 3.42; N, 5.68.

L1. Under a N_2 atmosphere, 5-bromo-2-phenylpyridine (0.87 g, 3.73 mmol) was added to dry ether (25 mL). The mixture was cooled to –78 ^oC under stirring. Then, 2.5 M *n*-BuLi (1.6 mL, 4.00 mmol) was added with a syringe dropwisely. After addition, the reaction mixture was stirred at this temperature for 0.5 h. Dimesitylboron fluoride (1.00g, 3.73 mmol) was added to the reaction mixture in one portion at –78 ^oC. The reaction mixture was warmed to room temperature slowly and stirred for 1 h before being quenched by adding water (20 mL). After extraction with CH_2Cl_2 (3 × 60 mL), the combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was firstly purified by column chromatography

eluting with hexane/CH_2Cl_2 (1:1, v/v). Then, further purification of the product was conducted with preparative TLC plates using hexane/ethyl acetate (45:1, v/v) as eluent. The product was obtained as a white solid (0.97 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.73 (d, *J* = 0.8 Hz, 1H, Ar), 8.10 (*d*, *J* = 6.8 Hz, 2H, Ar), 7.84 (dd, *J* = 1.2, 7.6 Hz, 1H, Ar), 7.74 (d, *J* = 8.0 Hz, 1H, Ar), 7.51–7.44 (m, 3H, Ar), 6.85 (s, 4H, Ar), 2.32 (s, 6H, CH_3), 2.05 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 159.47, 157.18, 144.50, 140.72, 139.13, 138.88, 129.59, 128.79, 128.35, 119.78 (Ar), 23.55, 21.23 (CH_3). FAB-MS (*m/z*): 403 $[M]^+$. Anal. calcd. for $C_{29}H_{30}BN$: C, 86.35; H, 7.50; N, 3.47; found: C, 86.15; H, 7.56; N, 3.29.

4-Bromo-2-phenylpyridine. Under a N_2 atmosphere, 2,4-dibromopyridine (2.05 g, 8.65 mmol) and phenylboronic acid (1.05 g, 8.65 mmol) and $Pd(PPh_3)_4$ (0.5 g, 0.43 mmol) were added to a mixture of bis(2-methoxy ethyl)ether (20 mL) and water (8 mL). The reaction mixture was stirred at 95 ^{o}C for 19 h. After being cooled to room temperature, water (60 mL) was added. Then, the mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were dried with anhydrous $MgSO_4$ and concentrated in volume. Purification by silica column chromatography using petroleum ether/diethyl ether (v/v, 5:1) afforded the title compound as a pale yellow oil (1.18 g, 58.3%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.51 (d, *J* = 5.2 Hz, 1 H, Ar), 7.97 (dd, *J* = 1.6 Hz, 8.4 Hz, 2 H, Ar), 7.90 (d, *J* = 1.2 Hz, 1H, Ar), 7.51–7.44 (m, 3 H, Ar), 7.40 (dd, *J* = 1.6 Hz, 5.2 Hz, 1 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.87, 150.33, 138.01, 133.47, 129.60, 128.86, 126.99, 125.24, 123.91(Ar). FAB-MS (m/z): 233, 235 $[M]^+$. Anal. calcd. for $C_{11}H_8BrN$: C, 56.44; H, 3.44; N, 5.98; found: C, 56.55; H, 3.64; N, 5.66.

L2. A solution of 4-bromo-2-phenylpyridine (0.87 g, 3.7 mmol) in 25 mL diethyl ether was cooled to -78 °C under nitrogen atmosphere, followed by addition of 1.5 mL *n*-BuLi (2.5 M). The

mixture was stirred for 30 min at -78 °C and dimesitylboron fluoride (1.0 g, 3.7 mmol) was added. Then the reaction solution was warmed to room temperature and stirred for 1 h. After adding 10 mL water, the mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried with anhydrous $MgSO_4$ and concentrated in volume. Purification by silica column chromatography using petroleum ether/diethyl ether (v/v, 6:1) afforded the title compound as a white solid (0.63 g, 41.9%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.71 (d, *J* = 4.4 Hz, 1 H, Ar), 7.94 (d, *J* = 7.6 Hz, 2 H, Ar), 7.46–7.37 (m, 3 H, Ar), 7.25 (d, *J* = 4.8 Hz, 1H, Ar), 6.85 (s, 4 H, Ar), 2.33 (s, 6 H, Me), 2.01 (s, 12 H, Me). ^{13}C NMR(100 MHz, $CDCl_3$, δ): 157.11, 149.50, 140.92, 139.72, 139.52, 128.84, 128.64, 128.49, 127.06, 127.04, 125.25 (Ar), 23.50, 21.27 (Me). FAB-MS (m/z): 403 $[M]^+$. Anal. calcd. for $C_{29}H_{30}BN$: C, 86.35; H, 7.50; N, 3.47; found: C, 86.15; H, 7.75; N, 3.17.

(4-Iodophenyl)dimesitylborane. To a stirred solution of 1,4-diiodobenzene (1.8 g, 5.5 mmol) in 30 mL of THF cooled to –78 ^{o}C under stirring, 2.5 M *n*-BuLi (1.7 mL, 4.2 mmol) was added with a syringe dropwisely. The mixture was stirred for 30 min at –78 ^{o}C before the addition of dimesitylboron fluoride (1.0 g, 3.7 mmol). Then, the reaction mixture was allowed to warm to room temperature slowly and stirred for 2 h before being quenched by adding water (15 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). All organic portions were combined and dried with $MgSO_4$. After removing the solvents, the residue was purified by chromatography on a silica column to give a white solid (1.26 g, 75.3%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, *J* = 8.0 Hz, 2H, Ar), 7.49 (d, *J* = 8.0 Hz, 2H, Ar), 6.82 (s, 4H, Ar), 2.31 (s, 6H, Me), 1.99 (s, 12H, Me); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 140.77, 138.94, 137.67, 137.29, 128.24, 100.41 (Ar), 23.43,

21.22 (Me). FAB-MS (*m/z*): 452 $[M]^+$. Anal. calcd. for $C_{24}H_{26}BI$: C 63.75, H 5.80; found: C 63.55, H 5.96.

L3. Under a N_2 atmosphere, (4-iodophenyl)dimesitylborane (0.55 g, 1.22 mmol) and 2-(tributylstannyl)pyridine (0.49 g, 1.34 mmol) were added in dry toluene (35 mL) in the presence of $Pd(PPh_3)_4$ (70 mg, 0.061 mmol). The reaction was allowed to proceed at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a separating funnel and CH_2Cl_2 (150 mL) was added. The mixture was washed with water (3 × 100 mL). The organic phase was dried over $MgSO_4$. The solvent was then removed and the residue was purified by column chromatography eluting with CH_2Cl_2/hexane (3:1, v/v). The title product was obtained as a white solid (0.33 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): δ (ppm) 8.72–8.70 (m, 1H, Ar), 7.97 (d, *J* = 8.4 Hz, 2H, Ar), 7.78–7.76 (m, 2H, Ar), 7.64–7.62 (m, 2H, Ar), 7.27–7.24 (m, 1H, Ar), 6.84 (s, 4H, Ar), 2.32 (s, 6H, Mes), 2.03 (s, 12H, Mes); ^{13}C NMR (100 MHz, $CDCl_3$, δ): δ (ppm) 157.17, 149.76, 146.36, 142.31, 141.69, 140.85, 138.71, 136.78, 128.17, 126.39, 122.47, 121.02 (Ar), 23.45, 21.22 (Mes). FAB-MS (*m/z*): 403 $[M]^+$. Anal. calcd. for $C_{29}H_{30}NB$: C 86.35, H 7.50, N 3.47; found: C 86.21, H 7.63, N 3.39.

(3-Bromophenyl)dimesitylborane. To a solution of 1-bromo-3-iodobenzene (1.10 g, 3.88 mmol) in dry ether (30 mL) cooled to –78 ^{o}C under stirring, 2.5 M *n*-BuLi (1.5 mL, 3.73 mmol) was added with a syringe dropwisely. Before dimesitylboron fluoride (1.00g, 3.73 mmol) was added to the reaction mixture in one portion, the reaction mixture was stirred for 30 min at –78 ^{o}C. Then, the reaction mixture was allowed to warm to room temperature slowly and stirred for 2 h before being quenched by adding water (15 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 60 mL) and the combined organic phase was dried over $MgSO_4$. The residue was purified by

column chromatography using hexane as eluent to give the product as a white solid (0.85 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.62-7.57 (m, 2H, Ar), 7.42-7.40 (m, 1H, Ar), 7.23 (t, *J* = 7.6 Hz, 1H, Ar), 6.82 (s, 4H, Ar), 2.31 (s, 6H, CH_3), 1.99 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.13, 139.09, 138.24, 134.55, 129.81, 128.30, 127.03, 122.90 (Ar), 23.43, 21.22 (CH_3). FAB-MS (*m/z*): 404, 406 $[M]^+$. Anal. calcd. for $C_{24}H_{26}BBr$: C 71.14, H 6.47; found: C 71.04, H 6.86.

L4. To a stirred solution of (3-bromophenyl)dimesitylborane (1.0 g, 2.5 mmol) and 2-(tributylstannyl)pyridine (1.0 g, 2.7 mmol) in toluene (30 mL) was added $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol). The mixture was heated to 110 ^{o}C and stirred under a nitrogen atmosphere for 18 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography using dichloromethane/hexane (v/v, 1:1) as eluent to give **L2** as a yellow jelly product (0.7 g, 69.4%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.67 (d, *J* = 4.8 Hz, 1H, Ar), 8.19 (d, *J* = 7.6 Hz, 1H, Ar), 8.03 (s, 1H, Ar), 7.72 (t, *J* = 8.0 Hz, 1H, Ar), 7.62 (d, *J* = 8.0 Hz, 1H, Ar), 7.56 (d, *J* = 6.0 Hz, 1H, Ar), 7.48 (t, *J* = 7.2 Hz, 1H, Ar), 7.24-7.20 (m, 1H, Ar), 6.83 (s, 4H, Ar), 2.32 (s, 6H, CH_3), 2.02 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.54, 149.39, 146.32, 141.61, 140.87, 138.82, 138.73, 137.04, 136.91, 134.29, 130.78, 128.62, 128.22, 122.04, 121.01 (Ar), 23.50, 21.23 (CH_3). FAB-MS (*m/z*): 403 $[M]^+$. Anal. calcd. for $C_{29}H_{30}BN$: C, 86.35; H, 7.50; N, 3.47; found: C, 86.20; H, 7.83; N, 3.27.

General procedure for the synthesis of Ir-B-3 and Ir-B-4. Under a N_2 atmosphere, each appropriate organic ligand and 0.4–0.5 equiv of $IrCl_3 \cdot nH_2O$ was heated to 110 ^{o}C in a mixture of 2-ethoxyethanol and water (3:1, v/v) for 16 h. Then the reaction mixture was cooled to room temperature and water was added. The cyclometalated Ir(III) μ-chloro-bridged dimer was formed

as a precipitate which was collected and dried under vacuum. The dimeric Ir complex, 2.5 equiv of acetylacetone and 10 equiv of Na_2CO_3 were added to 2-ethoxyethanol and the mixture was heated to 110 ^oC for 12–15 h. After cooling to room temperature and the addition of water, the colored precipitate was collected by filtration and washed with water and dried. The crude product was chromatographed on a silica column using an appropriate eluent to produce a pure sample of each of the title iridium complexes after solvent evaporation and drying.

Ir-B-3: (Yield 30.0%).^{1}H NMR (270 MHz, $CDCl_3$, δ): δ (ppm) 8.32 (d, J = 5.4 Hz, 2H, Ar), 7.57 (d, J = 8.1 Hz, 2H, Ar), 7.45–7.38 (m, 4H, Ar), 6.95–6.87 (m, 4H, Ar), 6.66 (s, 8H, Ar), 6.08 (s, 2H, Ar), 5.22 (s, 1H, acac), 2.31 (s, 12H, Me), 1.79 (s, 6H, acac), 1.74 (s, 24H, Me); ^{13}C NMR (67.5 MHz, $CDCl_3$, δ): δ (ppm) 184.34 (acac), 167.30, 148.28, 147.85, 145.20, 142.04, 141.44, 140.45, 137.33, 135.69, 128.76, 127.49, 122.65, 121.64, 119.00 (Ar), 100.33, 28.82 (acac), 23.32, 21.36 (Me). FAB-MS (*m/z*): 1096 $[M]^+$. Anal. calcd. for $C_{63}H_{65}N_2B_2O_2Ir$: C 69.04, H 5.98, N 2.56; found: C 68.96, H 6.01, N 2.55.

Ir-B-4: (Yield 23.3%). ^{1}H NMR(400 MHz, $CDCl_3$, δ): 8.49 (d, J = 5.6 Hz, 2H, Ar), 7.71 (d, J = 8.0 Hz, 2H, Ar), 7.67–7.63 (m, 4H, Ar), 7.11 (t, J = 7.2 Hz, 2H, Ar), 6.75–6.71 (m, 10H, Ar), 6.20 (d, J = 7.6 Hz, 2H, Ar), 5.26 (s, 1H, acac), 2.28 (s, 12H, Me), 1.93 (s, 24H, Me), 1.83 (s, 6H, acac); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 184.84 (acac), 168.30, 158.56, 148.23, 144.82, 142.12, 140.70, 137.76, 137.66,136.95, 132.65, 131.83, 127.86, 121.44, 118.82 (Ar), 100.44, 28.74 (acac), 23.38, 21.16 (Me). FAB-MS (*m/z*): 1096 $[M]^+$. Anal. calcd. for $C_{63}H_{65}N_2B_2O_2Ir$: C 69.04, H 5.98, N 2.56; found: C 69.15, H 5.93, N 2.58.

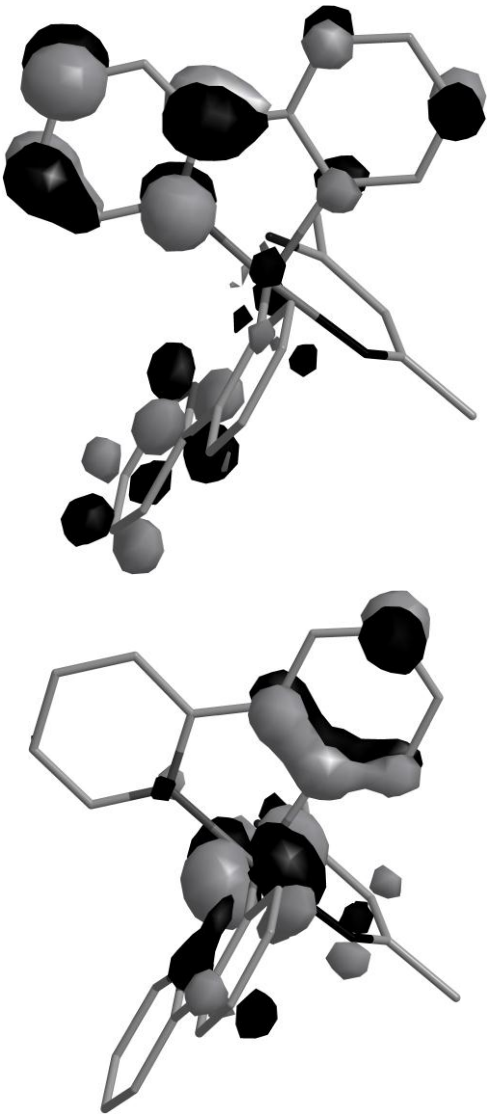


Figure S1. Plots of the LUMO (up) and HOMO (down) for **[Ir(ppy)$_2$(acac)]**.

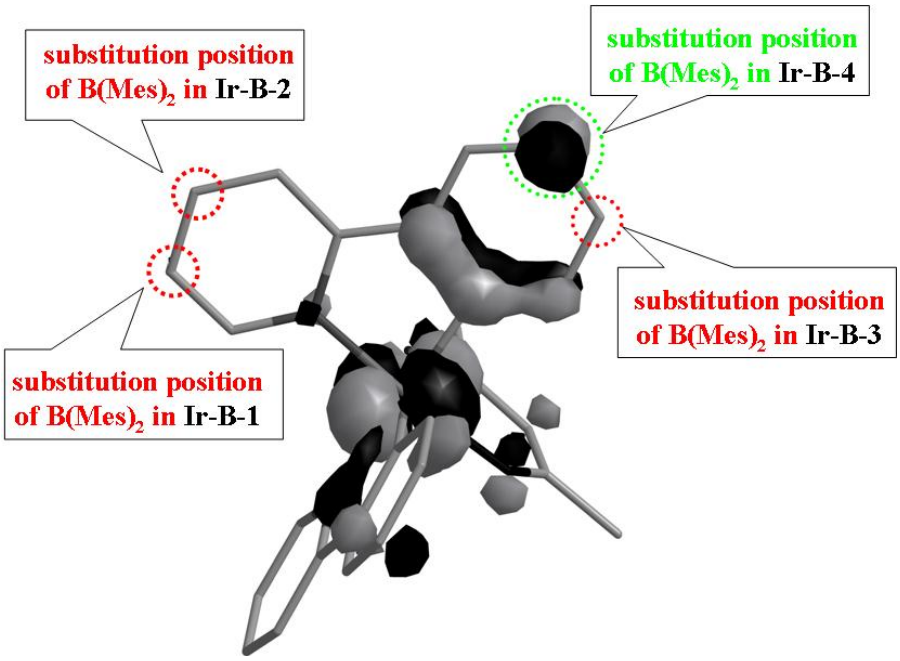


Figure S2. The electronic features as indicated by the HOMO patterns of **[Ir(ppy)$_2$(acac)]** for the substitution position of the B(Mes)$_2$ moieties in the concerned borylated Ir^{III} phosphors.

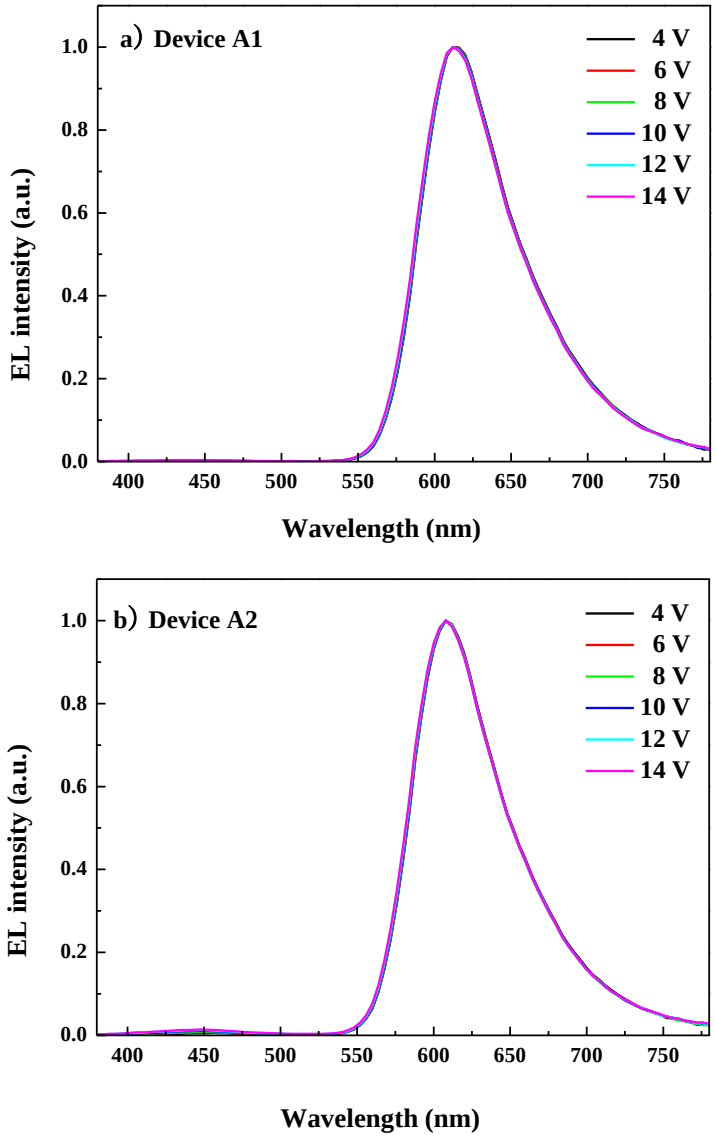


Figure S3. The EL spectra for devices **A1** and **A2** at different driving voltages.

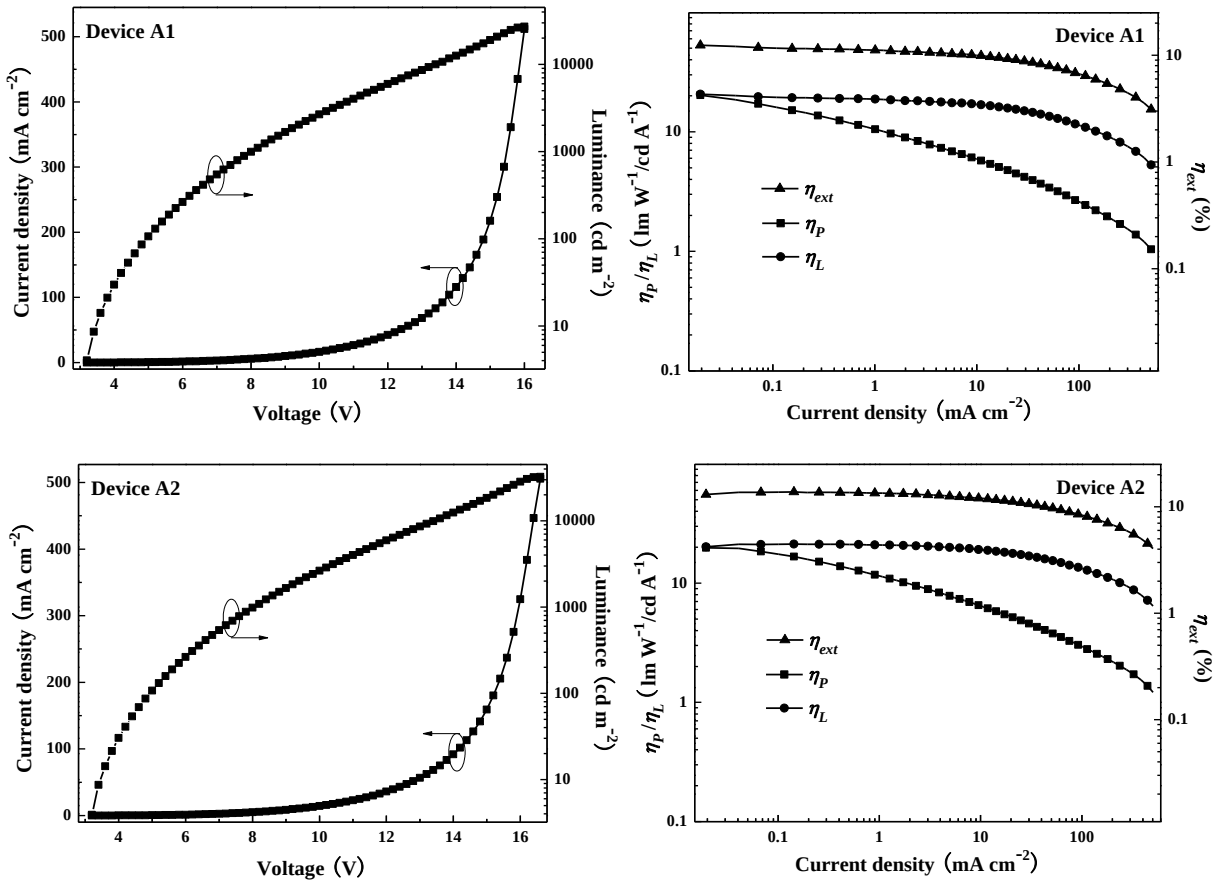


Figure S4. The *L–V–J* curves and the efficiency versus current density relationship for devices **A1** and **A2**.

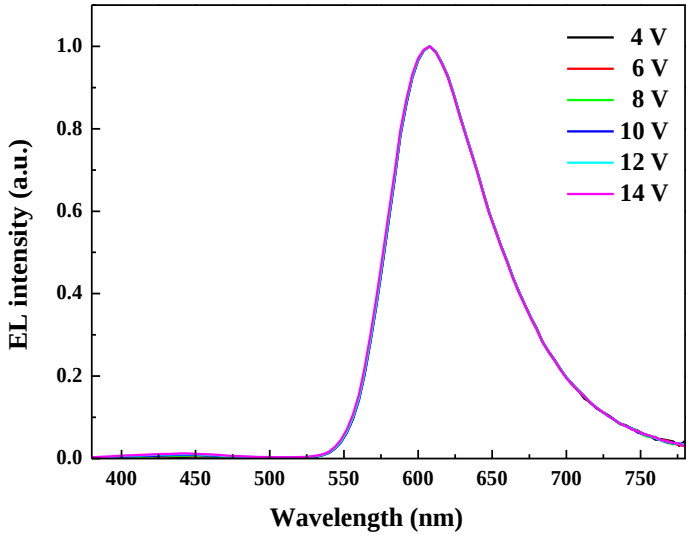


Figure S5. The EL spectra for the optimized device made from **[Ir(MDQ)$_2$(acac)]** at different driving voltages.

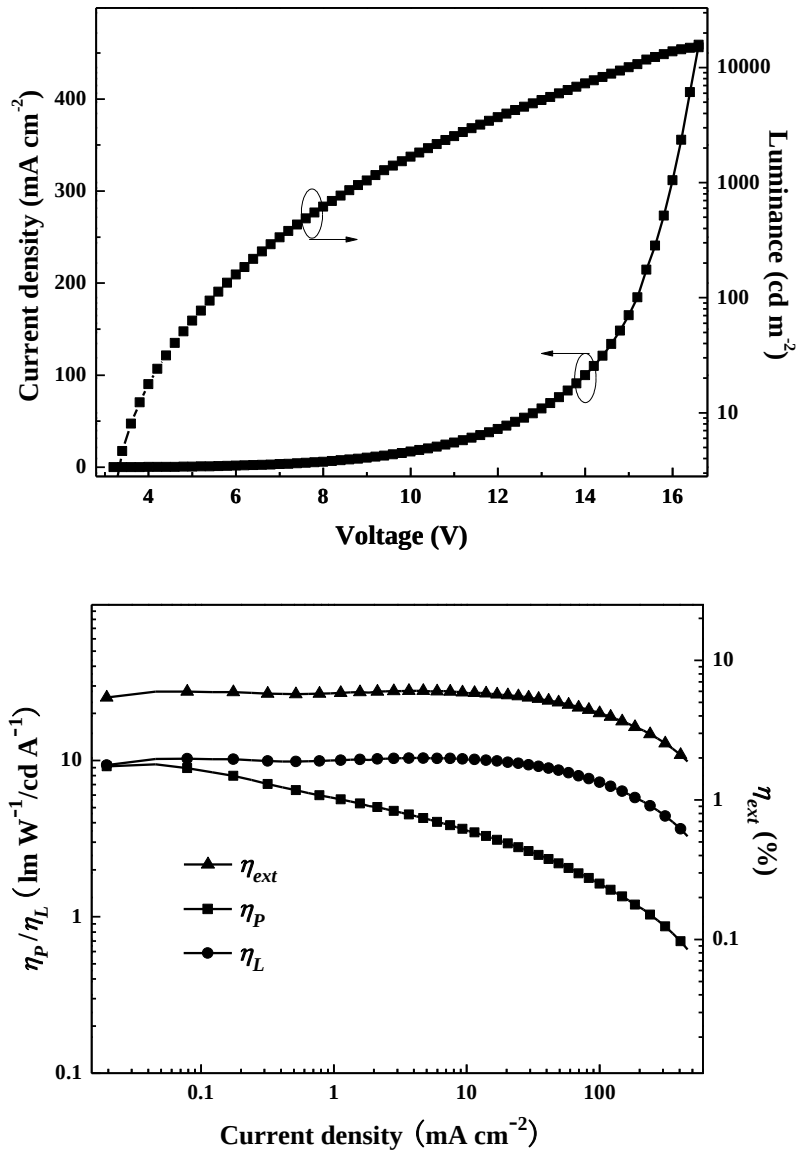


Figure S6. The *L–V–J* curves and the efficiency versus current density relationship for the optimized device made from **[Ir(MDQ)$_2$(acac)]**.

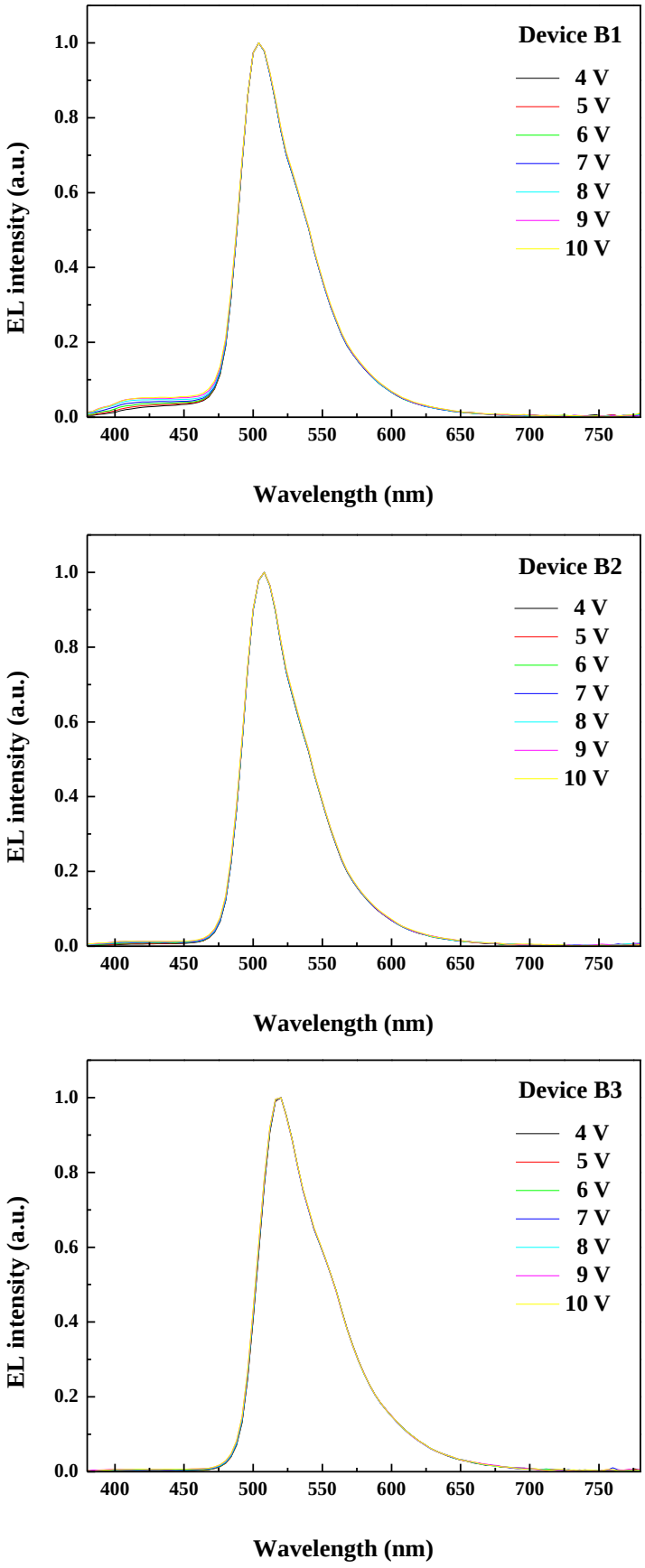


Figure S7. The EL spectra for devices **B1**–**B3** at different driving voltages.

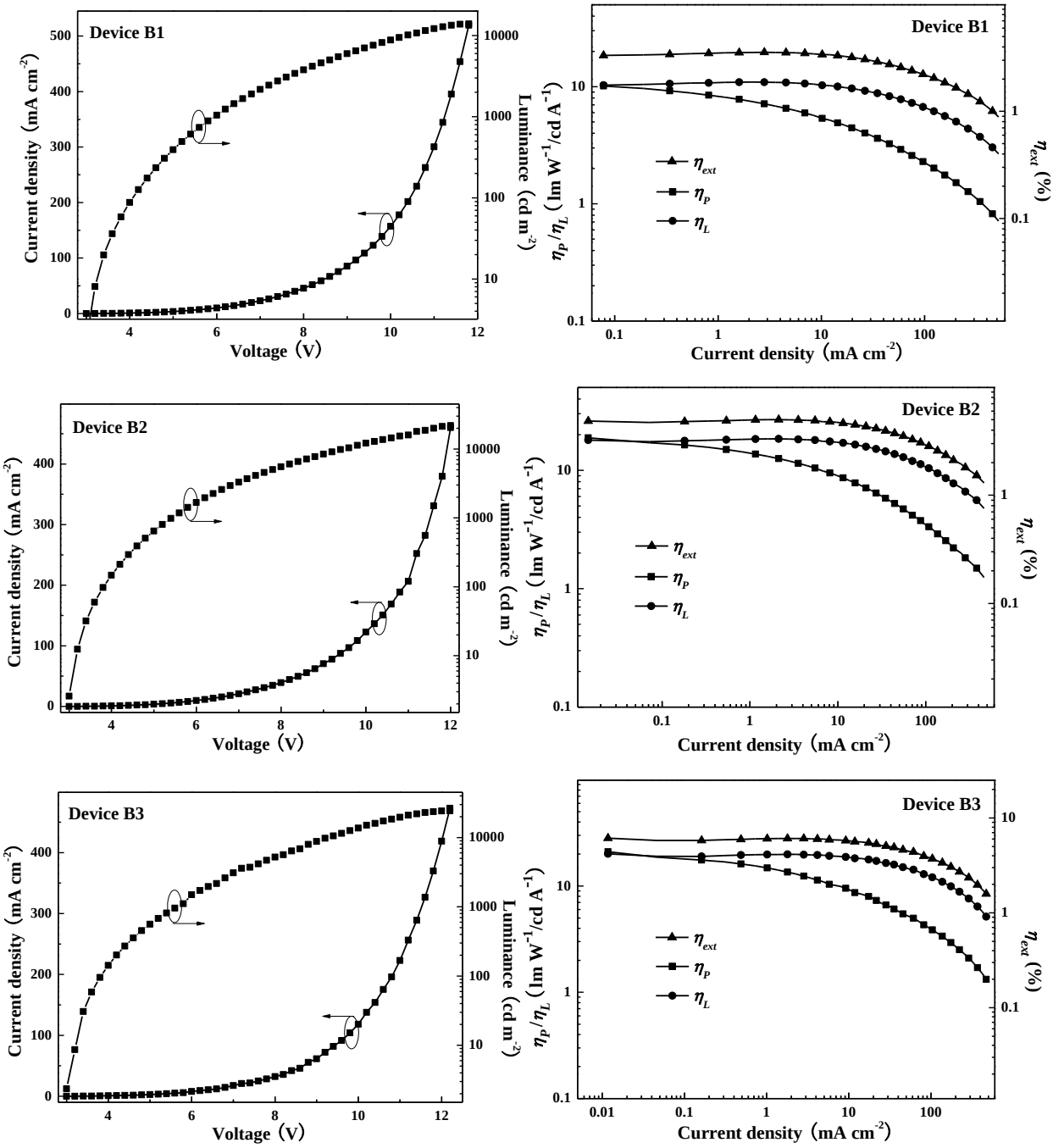


Figure S8. The *L–V–J* curves and the efficiency versus current density relationship for devices **B1**-**B3**.

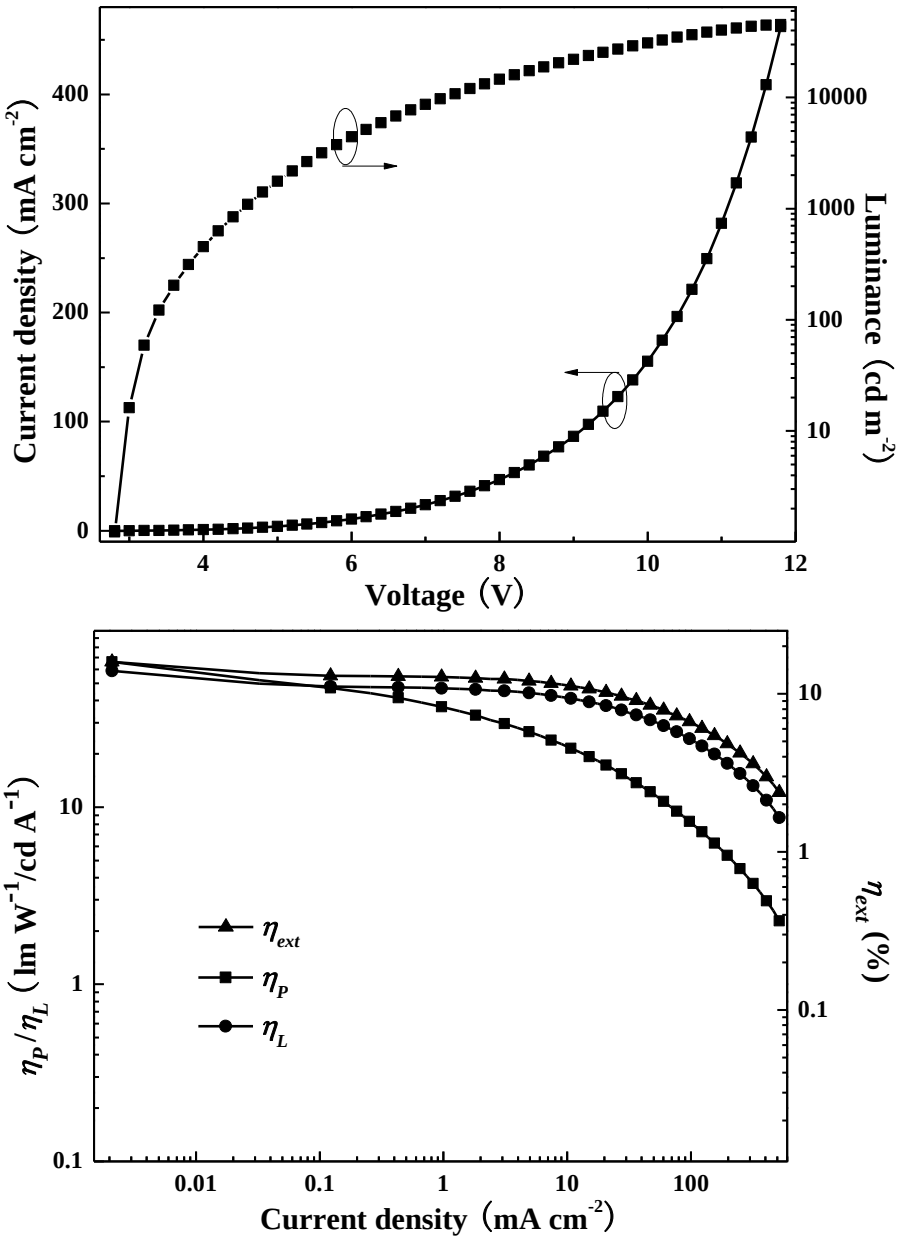


Figure S9. The *L*–*V*–*J* curves and the efficiency versus current density relationship for the optimized device **C** made from **[Ir(ppy)$_2$(acac)]**.

Table S1. EL performance data for the green phosphorescent OLEDs made from **Ir-B-4** and the optimized device of **[Ir(ppy)$_2$(acac)]**.

Device	Phosphor dopant	$V_{turn\text{-}on}$ (V)	Luminance L (cd m^{-2}) [a]	η_{ext} (%)	η_L (cd A^{-1})	η_P (lm W^{-1})	λ_{max} (nm) [d]
B1	**Ir-B-4** (5 wt.-%)	3.0	13901 (11.8)	3.6 (4.8) [a]	11.4 (3.0)	11.9 (3.0)	504
				3.5 [b]	10.8	8.3	(0.20, 0.57)
				3.4 [c]	10.3	5.4	
B2	**Ir-B-4** (8 wt.-%)	3.0	21876 (12.0)	5.0 (4.4)	18.0 (3.0)	18.8 (3.0)	508
				4.9	18.1	14.9	(0.24, 0.61)
				4.9	17.9	10.4	
B3	**Ir-B-4** (10	3.0	24334 (12.2)	6.1 (4.6)	20.1 (3.0)	21.0 (3.0)	508
	wt.-%)			6.0	19.5	16.1	(0.21, 0.62)
				6.0	19.4	10.8	
C	**[Ir(ppy)$_2$(acac)]**	2.8	45295 (11.8)	15.9 (2.8)	58.9 (2.8)	66.0 (2.8)	520
	(8 wt.-%)			13.0	47.8	44.9	(0.29, 0.64)
				12.4	45.7	31.7	

[a] Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. [b] Values collected at 100 cd m^{-2}. [c] Values collected at 1000 cd m^{-2}. [d] Values collected at 8 V and CIE coordinates (x, y) are shown in parentheses.