

Supporting Information for

Blue phosphorescent iridium(III) complexes containing carbazole-functionalized phenylpyridine for organic light-emitting diodes: Energy transfer from carbazolyl moieties to iridium(III) cores

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Experimental procedure – Syntheses

Materials: The chemicals were obtained commercially from Aldrich Chemical Co. and used without further purification unless otherwise noted. IrCl₃·3H₂O was purchased from Alfa Aesar. All solvents were purified and freshly distilled prior to use according to literature procedures. 9-(6-Bromohexyl)carbazole and 2-(2',4'-difluorophenyl)-4-methylpyridine were prepared following the literature methods.¹

2-(2',4'-difluoro-3'-hexylcarbazolylphenyl)-4-methylpyridine (HL): Lithium diisopropylamide (2.0 g, 20 mmol) was added to a solution of 2-(2',4'-difluorophenyl)-4-methylpyridine (4.0 g, 20 mmol) in 50 mL of THF. The mixture solution was stirred for 1 h. 9-(6-Bromohexyl)carbazole (6.6 g, 20 mmol) was added to the solution, and stirred for 1 h at room temperature. The mixture extracted with ethyl acetate (80 mL × 3 times) and dried over anhydrous magnesium sulfate. The crude product was subjected to flash column chromatography (ethyl acetate : *n*-hexane = 1 : 8) to give **HL** as yellow oil. Yield : 38 % (3.40 g). ¹H NMR (300 MHz, CDCl₃) δ 8.56 (d, 1H, *J* = 5.1Hz), 8.11 (d, 2H, *J* = 6.6Hz), 7.77-7.69 (m, 1H), 7.52-7.38 (m, 4H), 7.23 (t, 2H, *J* = 7.8Hz), 7.08 (d, 1H, *J* = 4.5Hz), 6.95 (t, 1H, *J* = 7.2Hz), 4.31 (t, 2H, *J* = 7.2Hz), 2.72 (t, 2H, *J* = 7.5Hz), 2.41 (s, 3H), 1.89 (t, 2H, *J* = 7.2Hz), 1.61 (t, 2H, *J* = 6.9Hz), 1.44 (t, 4H, *J* = 3.9Hz). ¹³C NMR (CDCl₃) δ 172.70, 165.48, 163.98, 163.28, 161.23, 160.02, 159.69, 157.72, 156.67, 151.75, 149.73, 148.11, 147.95, 147.22, 146.41, 145.71, 140.32, 137.85, 128.28, 128.04, 125.52, 123.16, 122.71, 120.26, 118.71, 114.22, 113.38, 110.47, 108.49,

42.90, 29.31, 29.01, 28.79, 26.93, 21.47. MALDI-TOF MS: m/z 454.32.

(L)₂Ir(acac) (1): The cyclometalated Ir(III) chloride-bridged dimer was prepared by the modified method of Nonoyama.² The iridium(III) trichloride hydrate (2.0 g, 6 mmol) and the cyclometalating ligand **HL** (9.25 g, 21 mmol) were dissolved in a mixed solvent of 2-ethoxyethanol/water (20 mL; 3:1 v/v). The mixture was heated at 130 °C under nitrogen condition for 24 h. The reaction mixture was cooled to room temperature and the precipitates were collected. The products were washed with ethanol and hexane, and dried in vacuum (3.84 g, 64%). The dimeric iridium(III) complexes (1.14 g, 0.5 mmol), sodium carbonate (0.5 g, 5 mmol) and acetylacetone (acac) (0.15 g, 1.5 mmol) were dissolved in 2-ethoxyethanol (30 mL), and refluxed for 24 h. The mixture extracted with dichloromethane (50 mL × 3 times) and dried over anhydrous magnesium sulfate. The crude product was subjected to flash column chromatography (methanol : heaxane = 1 : 5) to give **1** as yellow solid. Yield: 67 % (0.40 g). ¹H NMR (300 MHz, CDCl₃) δ 8.26 (d, 2H, J = 5.8Hz), 8.09 (d, 4H, J = 7.2Hz), 8.05 (s, 2H), 7.34-7.47 (m, 10H), 7.21 (t, 4H, J = 7.9Hz), 6.98 (d, 2H, J = 6.3 Hz), 5.64 (d, 2H, J = 9.6Hz), 5.21 (s, 2H), 4.25 (t, 4H, J = 6.9Hz), 2.57 (s, 6H), 2.49 (t, 4H, J = 7.2Hz), 1.84 (t, 4H, J = 7.5Hz), 1.77 (s, 6H), 1.34-1.56 (m, 12H). ¹³C NMR (CDCl₃) δ 192.30, 184.96, 177.60, 174.54, 170.02, 165.33, 162.82, 161.16, 159.59, 157.63, 151.95, 149.45, 147.61, 146.74, 140.59, 128.69, 125.77, 123.74, 123.99, 12.69, 120.51, 118.84, 115.03, 110.48, 109.01, 108.87, 100.80, 43.17, 29.56, 29.24, 28.95, 27.18, 2.47, 21.82. MS (MALDI-TOF): m/e 1198.90 (M). Anal. Calcd for C₆₅H₆₂F₄IrN₄O₂: C, 65.09; H, 5.21; N, 4.67. Found: C, 64.86; H, 5.99; N, 4.43.

(L)₂Ir(pic-N-oxide) (2): This compound was prepared by the similar method as that of **1** using picolinic acid N-oxide (pic-N-oxide). Yield: 37% (0.23 g). ¹H NMR (300 MHz, CDCl₃) δ 8.53 (d, 1H, J = 5.7Hz), 8.29 (d, 1H, J = 6.9Hz), 8.19 (d, 4H, J = 6.9Hz), 8.03 (s, 1H), 7.87 (t, 1H, J = 7.8Hz), 7.71 (d, 1H, J = 4.8Hz), 7.36-7.48 (m, 6H), 7.19-7.28 (m, 5H), 6.96 (d, 1H, J = 6.0Hz), 6.74 (d, 1H, J = 4.5Hz), 5.80 (d, 1H, J = 9.6Hz), 5.56 (d, 1H, J = 9.3Hz), 4.27 (t, 4H, J = 7.5Hz), 2.49-2.53 (m, 10H), 1.86 (t, 4H, J = 7.2Hz), 1.34-1.58 (m, 12H). ¹³C NMR (CDCl₃) δ 173.01, 165.76, 164.27, 163.71, 161.56, 160.11, 158.00, 152.04, 150.06, 148.48, 148.51, 147.51, 146.78, 140.63, 138.15, 128.57, 128.30, 125.82, 124.38, 123.55, 123.03, 120.59, 118.95, 114.44, 114.28, 111.22, 110.71, 108.94, 43.23, 29.64, 29.30, 29.07, 27.21, 22.36, 21.79. MS (MALDI-TOF): m/e 1237.90 (M). Anal. Calcd for C₆₆H₅₈F₄IrN₃O₃: C, 64.06; H, 4.72; N, 5.66. Found: C, 64.58; H, 4.81; N, 5.39.

(L)₂Ir(biim) (3): The dimeric iridium(III) complexes (1.14 g, 0.5 mmol) and biimidazole (biim) (0.20 g, 1.5 mmol) were dissolved in a mixed solvent of methanol/dichloromethane (30 mL; 2:3

v/v). The mixture was refluxed for 8 h. The crude product was subjected to flash column chromatography (methanol : dichloromethane = 1 : 20) to give **3** as yellow solid. Yield: 76% (0.47 g). ^1H NMR (300 MHz, CDCl_3) δ 8.09 (d, 4H, $J = 7.5\text{Hz}$), 8.04 (s, 2H), 7.35-7.48 (m, 10H), 7.22 (t, 4H, $J = 8.1\text{Hz}$), 7.01 (s, 2H), 6.76 (d, 2H, $J = 6.0\text{Hz}$), 6.41 (s, 2H), 5.78 (d, 2H, $J = 9.3\text{Hz}$), 4.26 (t, 4H, $J = 7.2\text{Hz}$), 2.51 (s, 6H), 1.86 (t, 4H, $J = 7.5\text{Hz}$), 1.36-1.54 (m, 16H). ^{13}C NMR (CDCl_3) δ 164.93, 163.49, 161.33, 160.22, 157.90, 149.78, 149.18, 148.61, 141.95, 140.59, 128.21, 126.74, 125.78, 123.78, 123.02, 120.58, 118.92, 114.07, 113.83, 111.35, 111.05, 108.82, 100.20, 43.15, 29.55, 29.23, 28.99, 27.19, 22.45, 21.74. MS (MALDI-TOF): m/e 1233.22 (M-Cl). Anal. Calcd for $\text{C}_{66}\text{H}_{60}\text{ClF}_4\text{IrN}_8$: C, 62.47; H, 4.77; N, 8.83. Found: C, 62.37; H, 4.91; N, 8.77.

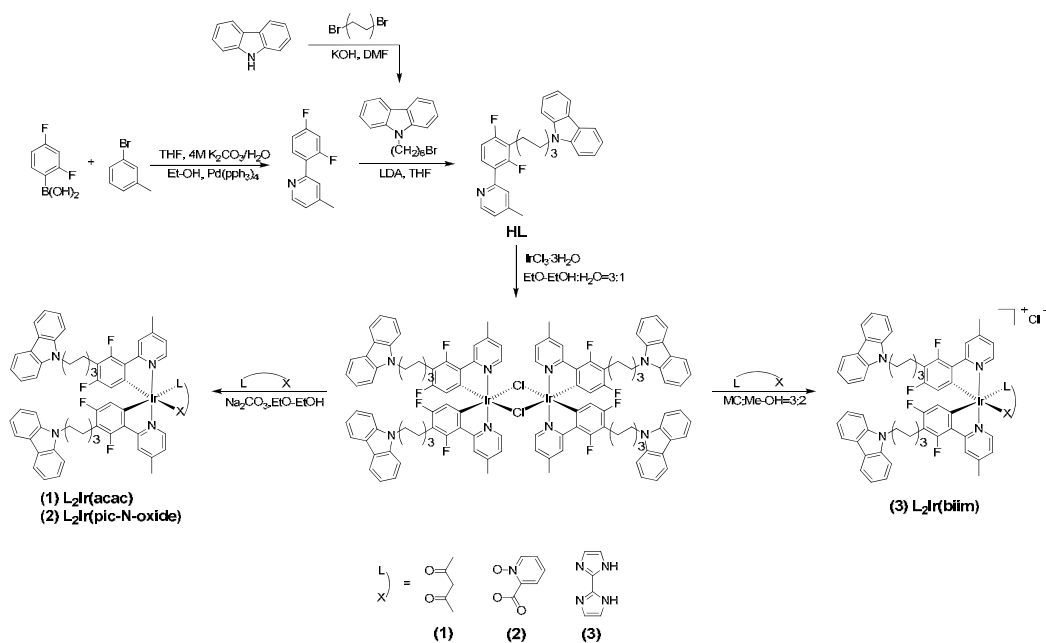
Characterization: ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz spectrometer, and CDCl_3 was used as a solvent. Chemical shifts are reported in parts per million (ppm) relative to residual CDCl_3 at 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR. MALDI-TOF mass spectra were obtained in linear negative mode using a Kratos Compact MALDI I (Shimadzu). The UV-visible spectra were recorded on a Jasco V-570 spectrophotometer. The photoluminescence spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The equation $\Phi_s = \Phi_r(\eta_s^2 A_r I_s / \eta_r^2 A_s I_r)$ was used to calculate quantum yields, where the symbols have their usual meanings.³ The thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851 analyzer under a N_2 atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Cyclic voltammetry (CV) was carried out with a Bioanalytical Systems CV-50W voltammetric analyzer at potential scan rate of $50 \sim 100\text{ mV s}^{-1}$ in a 0.1 M solution of tetra(*n*-butyl)ammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous dichloromethane. An Ag/AgNO_3 (0.1 M) electrode was used as the reference electrode and a Pt wire was used as the counter electrode. The working electrode was a Pt disc electrode (0.2 cm^2). The potentials are reported relative to a ferrocene/ferrocenium ($\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$) redox couple used as an internal reference (0.45 V vs SCE).⁴ Electrochemical experiments were performed under a N_2 atmosphere at room temperature.

X-ray Crystallography: X-ray intensity data were collected at room temperature on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Structure was solved by applying the direct method using a SHELXS-97 and refined by a full-matrix least-squares calculation on F^2 using SHELXL-97.⁵ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and were riding on their respective carbon atoms ($B_{\text{iso}} = 1.2 B_{\text{eq}}$ and $1.5 B_{\text{eq}}$).

Device fabrication: Organic light-emitting devices using Ir(III) complexes **1**, **2** and **3** as dopants in emitting layers were fabricated. The ITO (indium tin oxide)-coated glass substrates were precleaned and treated for 20 min using UV-ozone. The surface of the ITO substrate was modified by spin-coating conducting PEDOT:PSS (CLEVIOS PH500), with a thickness of around 40 nm, and baked at 120 °C for 10 min under a N₂ environment. A 70 nm-thick emitting layer was prepared by spin-coating in chlorobenzene solution at 8 wt % of Ir(III) complexes doped into the host (PVK:OXD-7:UGH3 = 2:1:1 w/w), where PVK is poly(*N*-vinylcarbazole), OXD-7 is 1,3-bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene and UGH3 is 1,3-bis(triphenylsilyl)benzene. A 20 nm-thick layer of OXD-7 was spin-coated on the top of emitting layer and annealed at 80 °C for 60 min. Ba and Al were evaporated at a base pressure of 5×10^{-8} Torr. The film thickness was determined with an α -Step IQ surface profiler (KLA Tencor, San Jose, CA, USA). In order to determine the device characteristics, the EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current density-voltage-luminance (J-V-L) changes were measured using a current/voltage source meter (Keithley 238) and an optical power meter (CS-1000, LS-100).

References

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Scheme S1. Synthetic scheme of ligand and Ir(III) complexes.

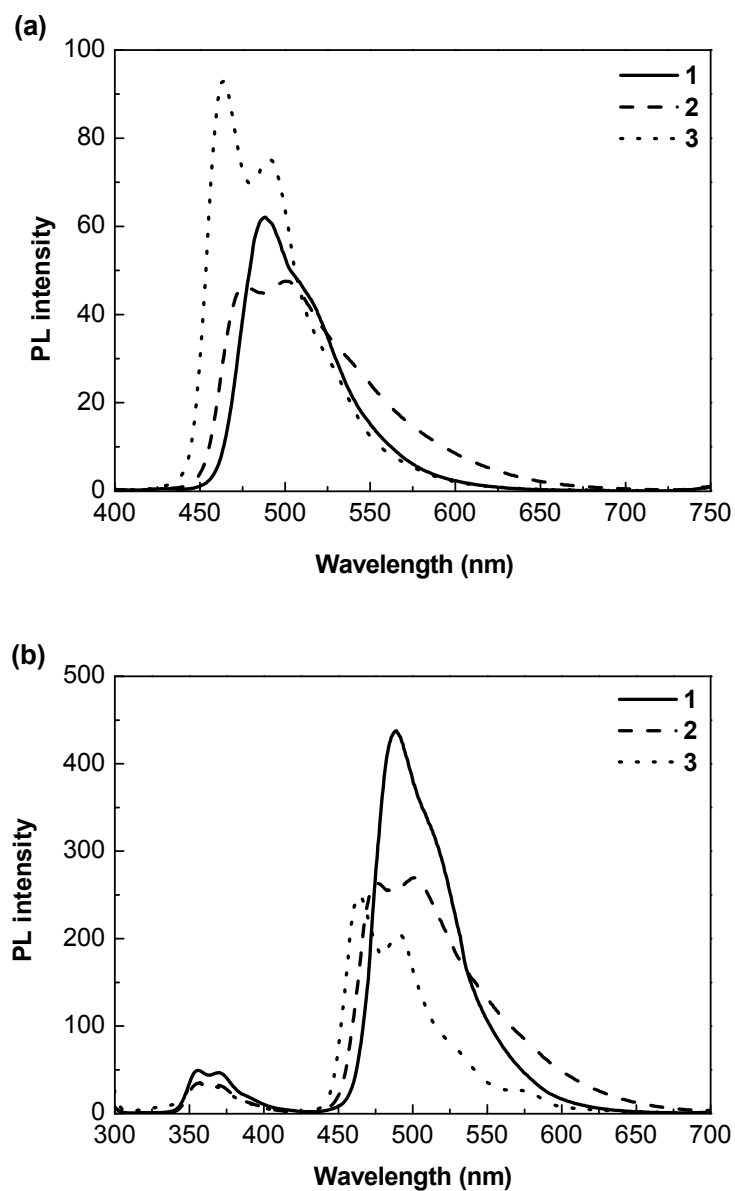


Fig. S1 Photoluminescence spectra of complexes in solution (1.0×10^{-5} M in CH_2Cl_2) excited at 380 nm (a) and 290 nm (b).

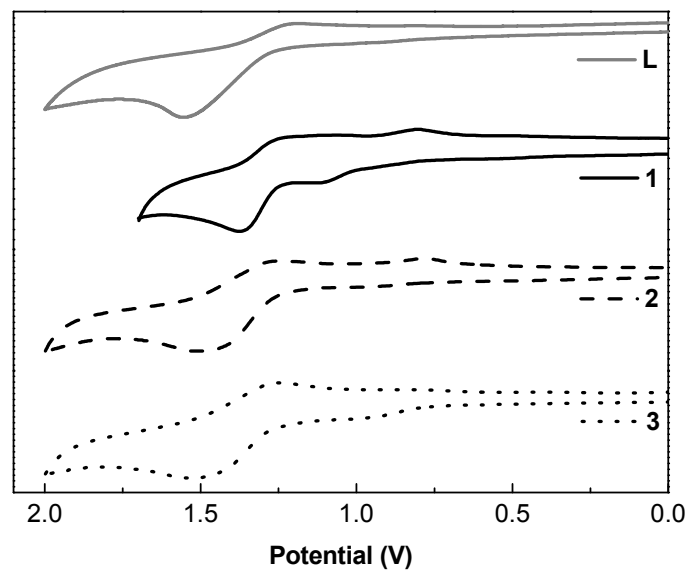


Fig. S2 Cyclic voltammograms of ligand and Ir(III) complexes.

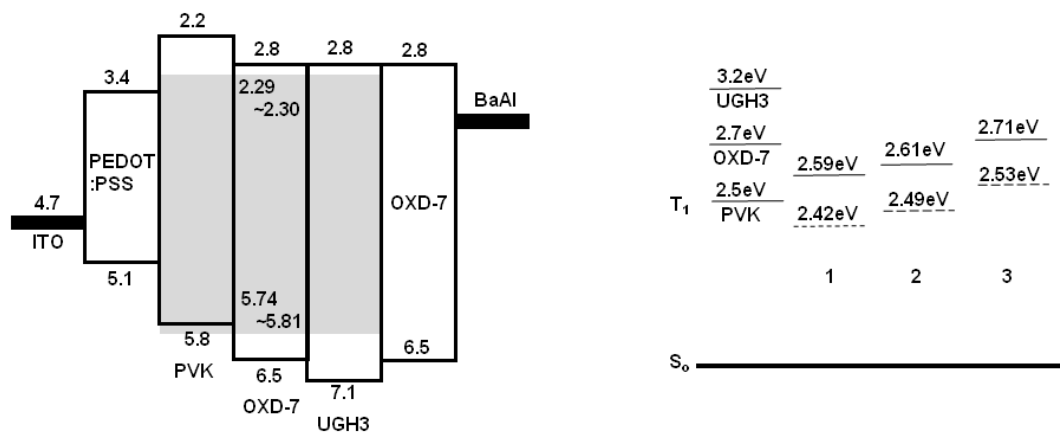


Fig. S3 Energy levels and triplet energy of materials in EL study.

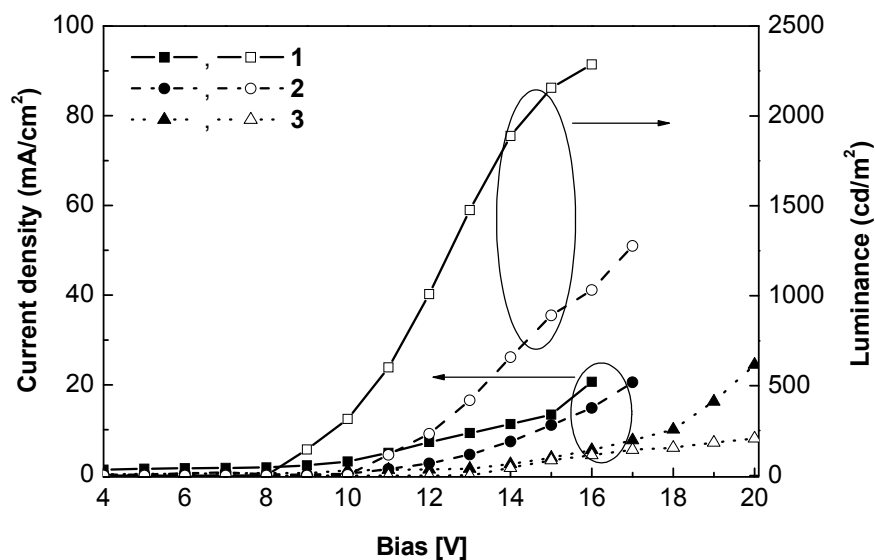


Fig. S4 Current (■,●,▲) and luminance (□,○,△) versus voltage curves of Ir(III) complexes.

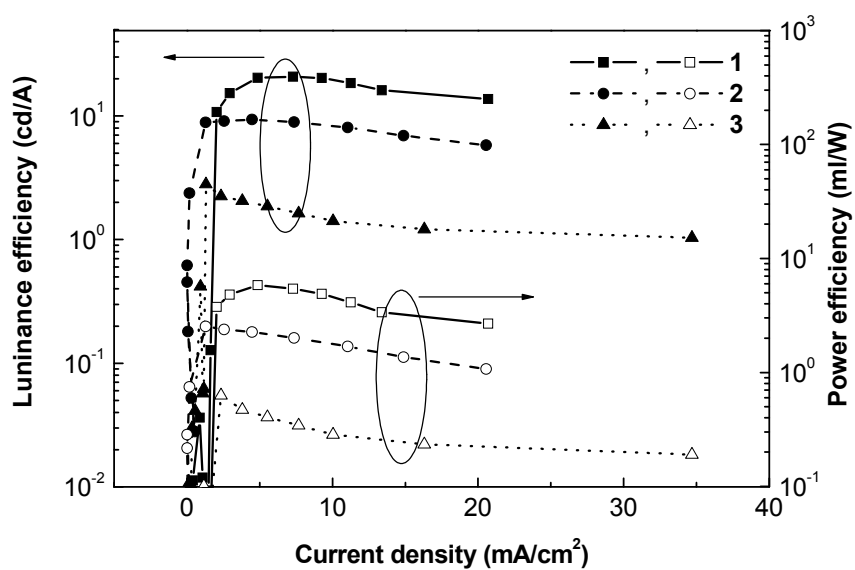


Fig. S5 Luminance efficiency (■,●,▲) and power efficiency (□,○,△) versus current density of Ir(III) complexes.

Table S1. Thermal and photophysical properties for Ir(III) complexes^a

Complex	Absorption λ_{max} [nm] $\epsilon (\times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$	Emission λ_{max} [nm]			Φ_{sol} [%] ^c	Φ_{film} [%] ^c	T_{d} [°C]
		MC	77K	Film ^b			
L	285(1.57), 297(0.1), 316(0.2), 336(0.3), 349 (0.3)	355, 369	-	-	-	-	-
1	284(3.8), 297(2.2), 311(1.9), 336 (1.1), 350(0.9), 361(0.5), 398(0.2), 434(0.2)	487, 508	478, 512	487	25.7	32.5	362
2	287(4.4), 297(2.1), 306(1.9), 322(1.7), 335(1.2), 348(1.2), 364(0.3), 388(0.4), 422(0.3)	474, 501	469, 498	475, 498	26.1	30.1	378
3	284(6.2), 297(3.9), 311(3.4), 337(1.5), 349(1.4), 373(0.8), 404(0.4), 435(0.1)	464, 491	457, 490	463, 491	15.8	19.8	347

^aAll data were measured in CH₂Cl₂ (concentration = 1×10^{-5} M). ^bFilm was doped in PMMA with 5 wt % of Ir(III) complex, and measured at room temperature. ^cIr(ppy)₃ (0.40) was used as an external reference. ^d T_{d} is decomposition temperature at 5 % weight loss.

Table S2. Electrochemical properties for Ir(III) complexes

Complex	E_{ox} [V] ^a	HOMO [eV] ^b	LUMO [eV] ^c	ΔE_{UV} [eV] ^c
L	1.36	-5.78	-2.33	3.45
1	0.96, 1.32	-5.38, -5.74	-2.81, -2.29	2.57
2	0.93, 1.39	-5.35, -5.81	-2.73, -2.30	2.63
3	0.88, 1.39	-5.30, -5.81	-2.61, -2.30	2.69

^aData measured in CH₂Cl₂ containing 1×10^{-3} Ir(III) complexes. ^bPotential values were reported vs. Fc/Fc⁺. ^c E_{uv} collected by UV-Vis spectrophotometer.