

Supporting Information for “Inter-ligand energy transfer and related emission change in the cyclometalated heteroleptic iridium complex: Facile and efficient color tuning over the whole visible range by the ancillary ligand structure”

Youngmin You and Soo Young Park*

School of Materials Science & Engineering, Seoul National University, San 56-1,

Shillim-Dong, Kwanak-Gu, Seoul 151-744, Korea

* parksy@snu.ac.kr

Synthesis. Materials obtained from commercial supplier were used without further purification. Anhydrous tetrahydrofuran (THF) was distilled with sodium and benzophenone under nitrogen atmosphere. All glass wares, syringes, magnetic stirring bars and needles were dried in the convection oven at least 4 hours. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F₂₅₄, Merck Co.) were developed and the spots were seen under UV light at 254 and 365 nm, or stained with *p*-anisaldehyde. Silica column chromatography was done with silica gel 60 G (particle size 5~40 μ m, Merck Co.).

2-(2,4-Difluorophenyl)pyridine (*dfppy*). 2-Bromopyridine (2.01 mL, 21.1 mmol), 2,4-difluorophenylboronic acid (4.00 g, 25.3 mmol) and tetrakis(triphenylphosphine)palladium(0)

(0.732 g, 0.633 mmol) were added to round-bottomed flask with reflux condenser and dissolved to 50 mL of THF. After 30 mL of aqueous 2N Na₂CO₃ was delivered, reaction mixture was heated at 70 °C for 1 day. The cooled crude mixture was poured onto water and extracted with CH₂Cl₂ (50 mL × 3 times) then dried over anhydrous magnesium sulfate. Finally silica column purification (*n*-hexane : EtOAc = 5 : 1) gave transparent liquid (4.07 g, 21.0 mmol) in quantitative yield. TLC, *R_f* = 0.5 (*n*-hexane : EtOAc = 5 : 1); ¹H-NMR δ 6.89 (m, 1H), 7.1 (m, 1H), 7.28 (m, 1H), 7.75 (m, 2H), 8.00 (m, 1H), 8.71 (d, *J* = 3.5, 1H) ; HRMS (EI) calculated M⁺ 191.0544; observed M⁺ 191.0546.

[(*dfppf*)₂Ir(*μ*-Cl)]₂. IrCl₃·H₂O·HCl (Aldrich) (0.702 g, 2.35 mmol) and *dfppy* (2.00 g, 10.5 mmol) were dissolved in 2-EtOEtOH : H₂O = 60 mL : 20 mL, and refluxed at 140 °C for 20 hr. After cooling, yellow precipitate was filtered and washed with acetone : ethanol = 60 mL : 60 mL. The washed product was recrystallized in *n*-hexane : toluene = 10 mL : 25 mL to give yellow fine crystal (2.28 g, 1.88 mmol) in 85 % yield. HRMS (FAB) calculated M⁺ 1216.0509; observed M⁺ 1216.0499.

General synthetic procedure for heteroleptic iridium complex. [(*dfppf*)₂Ir(*μ*-Cl)]₂ (0.500 g, 0.411 mmol), sodium carbonate (0.479 g, 4.52 mmol) and 2.6 equivalent ancillary ligand were dissolved in 30 mL of 2-EtOEtOH. After degassed, the reaction vessel was maintained under nitrogen condition. Temperature was raised to 140 °C and the reaction mixture was

stirred for 12 hr. Then cooled crude mixture was poured to EtOAc (150 mL) and extraction with water (100 mL \times 3 times) was performed to remove 2-EtOEtOH. Silica column purification with EtOAc and recrystallization in ether : *n*-hexane = 10 mL : 40 mL gave fine crystal.

FIrmpic. *Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato-*N,C*^{2'}) (6-methylpicolinate)* (0.530 g, 91%). ¹H-NMR δ 1.99 (s, 3H), 5.37 (dd, *J* = 8.8, 2.2, 1H), 5.79 (dd, *J* = 8.9, 2.4, 1H), 6.39 (m, 2H), 6.99 (t, *J* = 7.5, 1H), 7.17 (t, *J* = 7.0, 1H), 7.31 (d, *J* = 7.7, 1H), 7.60 (d, *J* = 5.3, 1H), 7.79 (m, 2H), 7.86 (d, *J* = 7.7, 1H), 8.28 (m, 2H), 8.69 (d, *J* = 6.8, 1H); MS (FAB) *m/z* 710 (*M*⁺ + 1), 573, 154, 136. Anal. Calcd for C₂₉H₁₈F₄IrN₃O₂: C, 49.15; H, 2.56; N, 5.93. Found: C, 48.94; H, 2.44; N, 6.10.

FIrqnd. *Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato-*N,C*^{2'}) (quinaldinate)* (0.569 g, 93%). ¹H-NMR δ 5.43 (d, *J* = 8.8, 1H), 5.94 (d, *J* = 8.8, 1H), 6.47 (m, 2H), 6.86 (t, *J* = 6.6, 1H), 7.12 (t, *J* = 7.0, 1H), 7.38 (m, 1H), 7.59 (m, 2H), 7.69 (t, *J* = 8.3, 1H), 7.76 (t, *J* = 7.9, 1H), 7.89 (m, 2H), 8.19 (d, *J* = 8.8, 1H), 8.31 (d, *J* = 9.0, 1H), 8.44 (m, 1H), 8.53 (m, 1H), 8.67 (d, *J* = 5.0, 1H); MS (FAB) *m/z* 746 (*M*⁺ + 1), 573, 154. Anal. Calcd for C₃₂H₁₈F₄IrN₃O₂: C, 51.61; H, 2.44; N, 5.64. Found: C, 51.66; H, 2.34; N, 5.80.

FIrpca. *Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato-*N,C*^{2'}) (picolinamide)* (0.518 g, 91%). ¹H-NMR δ 5.61 (d, *J* = 9.0, 1H), 5.86 (d, *J* = 8.8, 1H), 6.44 (m, 1H), 6.94 (m, 1H), 7.12

(t, $J = 6.8$, 1H), 7.32 (m, 1H), 7.44 (d, $J = 5.1$, 1H), 7.74 (m, 4H), 7.88 (m, 1H), 8.26 (m, 3H), 8.85 (d, $J = 5.1$, 1H); MS (FAB) m/z 695 ($M^+ + 1$), 573, 136. Anal. Calcd for $C_{28}H_{17}F_4IrN_4O$: C, 48.48; H, 2.47; N, 8.08. Found: C, 48.74; H, 2.44; N, 8.30.

FIriq. Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato- $N,C^{2'}$) (isoquinolate) (0.593 g, 97%). 1H -NMR δ 5.58 (dd, $J = 8.5$, 2.3, 1H), 5.85 (dd, $J = 8.7$, 2.2, 1H), 6.46 (m, 2H), 6.91 (t, $J = 6.0$, 1H), 7.17 (t, $J = 6.4$, 1H), 7.42 (d, $J = 5.7$, 1H), 7.76 (m, 9H), 8.24 (d, $J = 8.6$, 1H), 8.31 (d, $J = 9.3$, 1H), 8.80 (d, $J = 6.2$, 1H), 10.23 (m, 1H); MS (FAB) m/z 746 ($M^+ + 1$), 573, 154. Anal. Calcd for $C_{32}H_{18}F_4IrN_3O_2$: C, 51.61; H, 2.44; N, 5.64. Found: C, 51.49; H, 2.54; N, 5.77.

FIrprz. Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato- $N,C^{2'}$) (pyrazinate) (0.538 g, 94%). 1H -NMR δ 5.52 (dd, $J = 8.8$, 2.6, 1H), 5.82 (dd, $J = 8.4$, 2.4, 1H), 6.47 (m, 2H), 7.03 (t, $J = 7.0$, 1H), 7.24 (m, 1H), 7.42 (m, 1H), 7.78 (m, 1H), 7.83 (t, $J = 8.3$, 1H), 8.27 (d, $J = 8.3$, 1H), 8.32 (d, $J = 8.8$, 1H), 8.70 (m, 1H), 8.74 (d, $J = 2.7$, 1H), 9.50 (d, $J = 1.3$, 1H); MS (FAB) m/z 697 ($M^+ + 1$), 573, 154. Anal. Calcd for $C_{27}H_{15}F_4IrN_4O_2$: C, 46.62; H, 2.17; N, 8.05. Found: C, 46.60; H, 2.32; N, 8.10.

FIrprza. Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato- $N,C^{2'}$) (pyrazinamide) (0.519 g, 91%). 1H -NMR δ 5.56 (d, $J = 6.4$, 1H), 5.83 (d, $J = 8.4$, 1H), 6.46 (m, 2H), 7.00 (t, $J = 6.2$, 1H), 7.17 (t, $J = 6.2$, 1H), 7.42 (d, $J = 4.4$, 1H), 7.71 (m, 1H), 7.79 (t, $J = 7.5$, 2H), 8.28 (m,

2H), 8.63 (d, $J = 3.9$, 1H), 8.80 (d, $J = 5.0$, 1H), 9.44 (s, 1H); MS (FAB) m/z 696 ($M^+ + 1$), 573, 154. Anal. Calcd for $C_{27}H_{16}F_4IrN_5O$: C, 46.68; H, 2.32; N, 10.08. Found: C, 46.94; H, 2.32; N, 9.86.

FIrqnx. *Iridium (III) bis(2-(2,4-difluorophenyl)pyridinato- $N,C^{2'}$) (quinoxalinate)* (0.533 g, 87%). 1H -NMR (600 MHz) δ 5.41 (dd, $J = 6.5, 2.1$, 1H), 5.94 (d, $J = 6.5, 2.1$, 1H), 6.45 (m, 1H), 6.54(m, 1H), 6.91 (t, $J = 6.4$, 1H), 7.17 (t, $J = 6.4$, 1H), 7.49 (t, $J = 7.5$, 1H), 7.54 (d, $J = 5.7$, 1H), 7.72 (m, 2H), 7.82 (m, 2H), 8.21 (d, $J = 4.2$, 1H), 8.23 (d, $J = 4.2$, 1H), 8.33 (d, $J = 4.3$, 1H), 8.64 (d, $J = 2.9$, 1H); MS (FAB) m/z 747 ($M^+ + 1$), 573, 154. Anal. Calcd for $C_{31}H_{17}F_4IrN_4O_2$: C, 49.93; H, 2.30; N, 7.51. Found: C, 49.94; H, 2.53; N, 7.86.

Characterization. 1H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ at 300 MHz (JEOL, JNM-LA 300 or Bruker, Avance DPX-300). Chemical shifts were recorded by ppm. Multiplicity was denoted by s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet). Coupling constants (J) were in hertz (Hz). Mass spectra (MS) were obtained with JEOL, JMS-AX505WA using direct insertion probes (DIP) method. Elemental analysis (EA) was performed with CE Instrument, EA1110. Absorption spectra of solution and doped PMMA film (spin coated film on precleaned glass substrate under 1500 rpm with 3 wt% solution in 1,2-dichloroethane) were recorded with SHIMAZU, UV-1650PC from 250

nm to 650 nm with 0.2 nm increments. Photoluminescence spectra were obtained with SHIMAZU, RF 5301 PC Spectrophotometer which was corrected in the range of 372 ~ 700 nm. Absorption and PL spectra of iridium complexes in solution were measured under nitrogen saturated condition. Cyclic voltametric experiments were carried out with a Model 273A (Princeton Applied Research) using three electrode cell assemblies. The measurements were done in CH₂Cl₂ solution with tetrabutylammonium tetrafluoroborate as supporting electrolyte at a scan rate of 50 mV/s and nitrogen condition. Each oxidation potential was calibrate with ferrocene as a reference. Dmol³ module installed within Accelrys Materials Studio was used for DFT calculation. Ground state geometry optimization and single point calculation were done with BLYP functional and DNP basis set under effective core potential. SCF tolerance was maintained within 10⁻⁶.

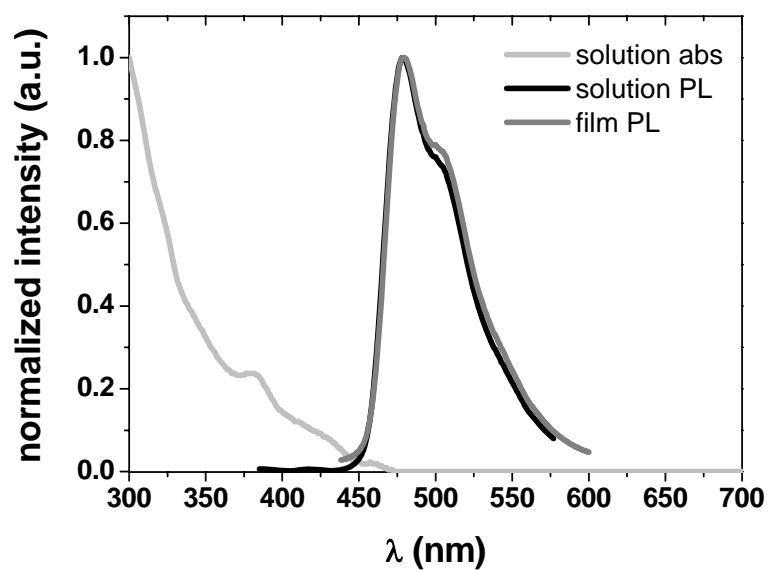


Figure S-1. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in CH_2Cl_2) and film (PMMA film doped by 5 wt% of iridium complex) of Flrmpic.

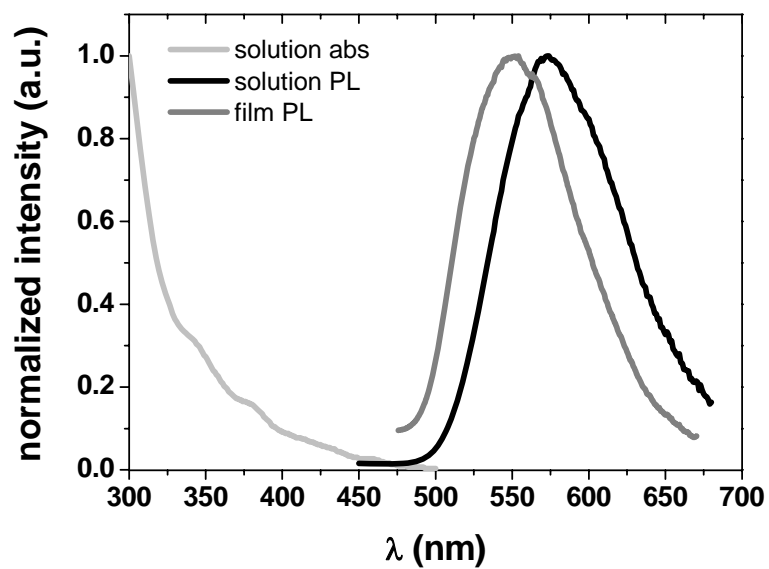


Figure S-2. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in CH_2Cl_2) and film (PMMA film doped by 5 wt% of iridium complex) of Flrqnd.

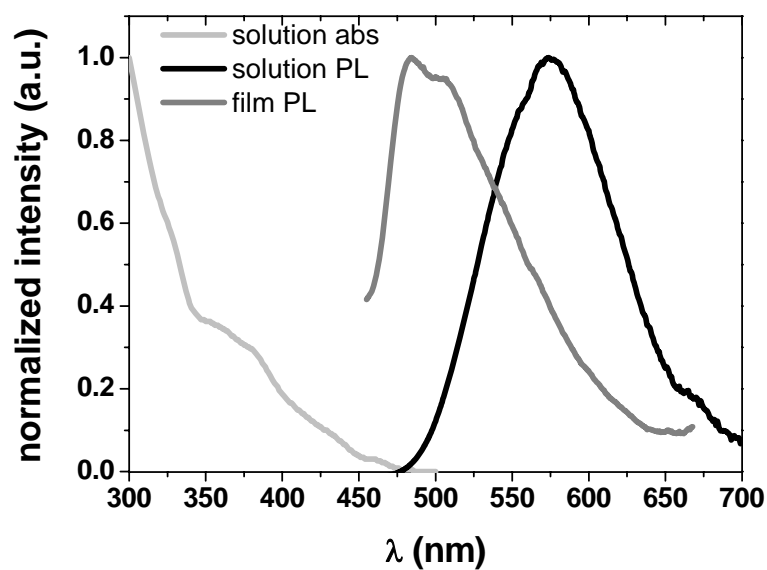


Figure S-3. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in CH_2Cl_2) and film (PMMA film doped by 5 wt% of iridium complex) of Flrpca.

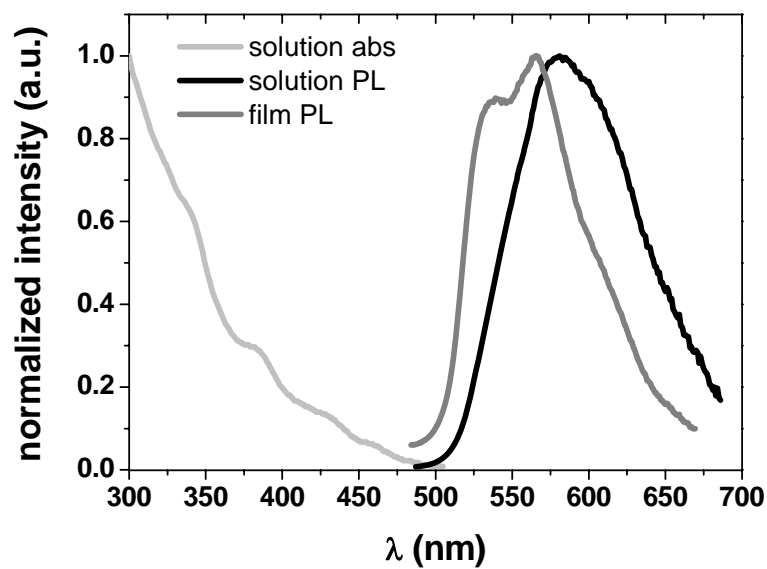


Figure S-4. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in CH_2Cl_2) and film (PMMA film doped by 5 wt% of iridium complex) of Flriq.

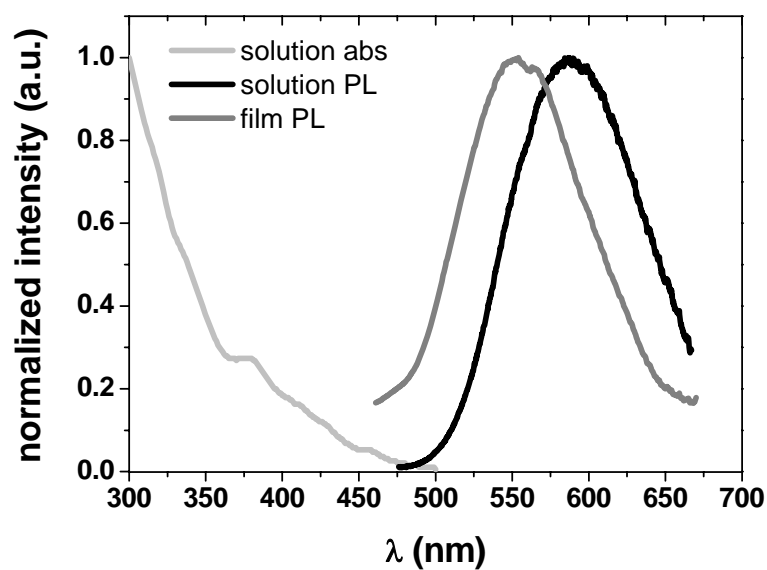


Figure S-5. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in CH_2Cl_2) and film (PMMA film doped by 5 wt% of iridium complex) of Flrprz.

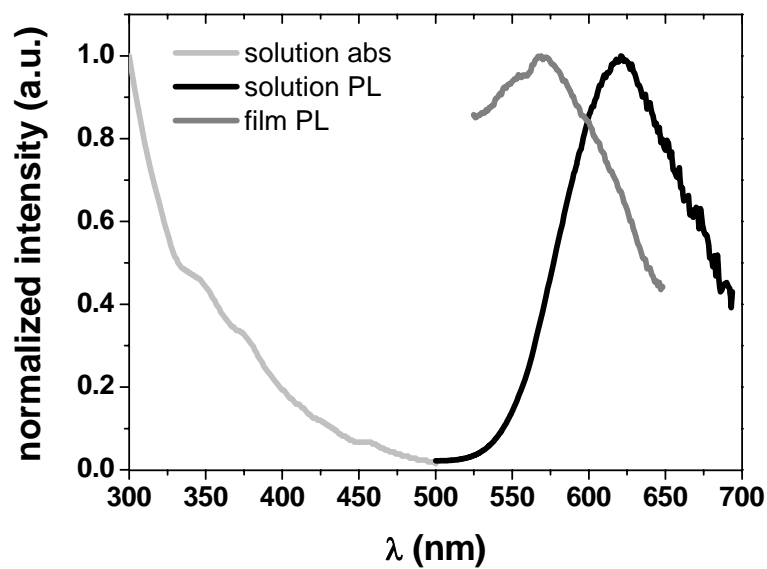


Figure S-6. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in CH_2Cl_2) and film (PMMA film doped by 5 wt% of iridium complex) of Flrprza.

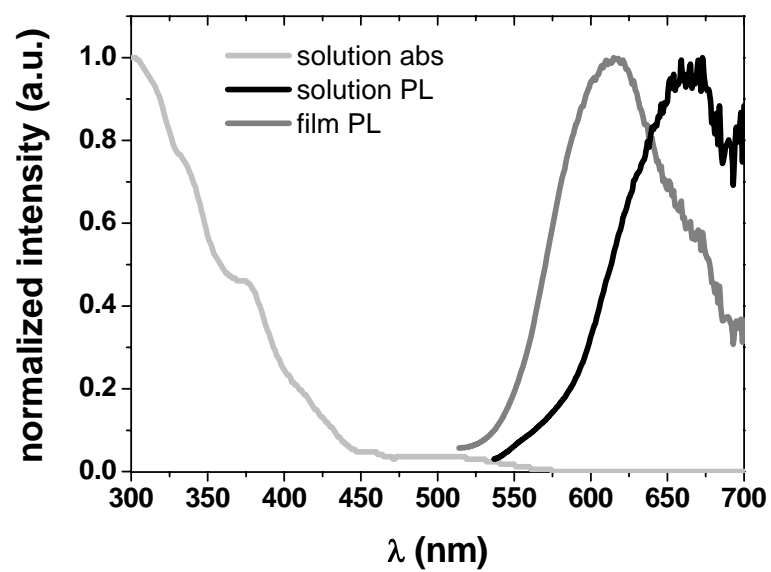


Figure S-7. Absorption and photoluminescence spectra of solution (1.0×10^{-5} M in MeCN) and film (PMMA film doped by 5 wt% of iridium complex) of FIrqnx.