

**Supporting information for**

**Red, green, and blue radio-luminescent polymer dots doped with heteroleptic tris-cyclometalated iridium complexes**

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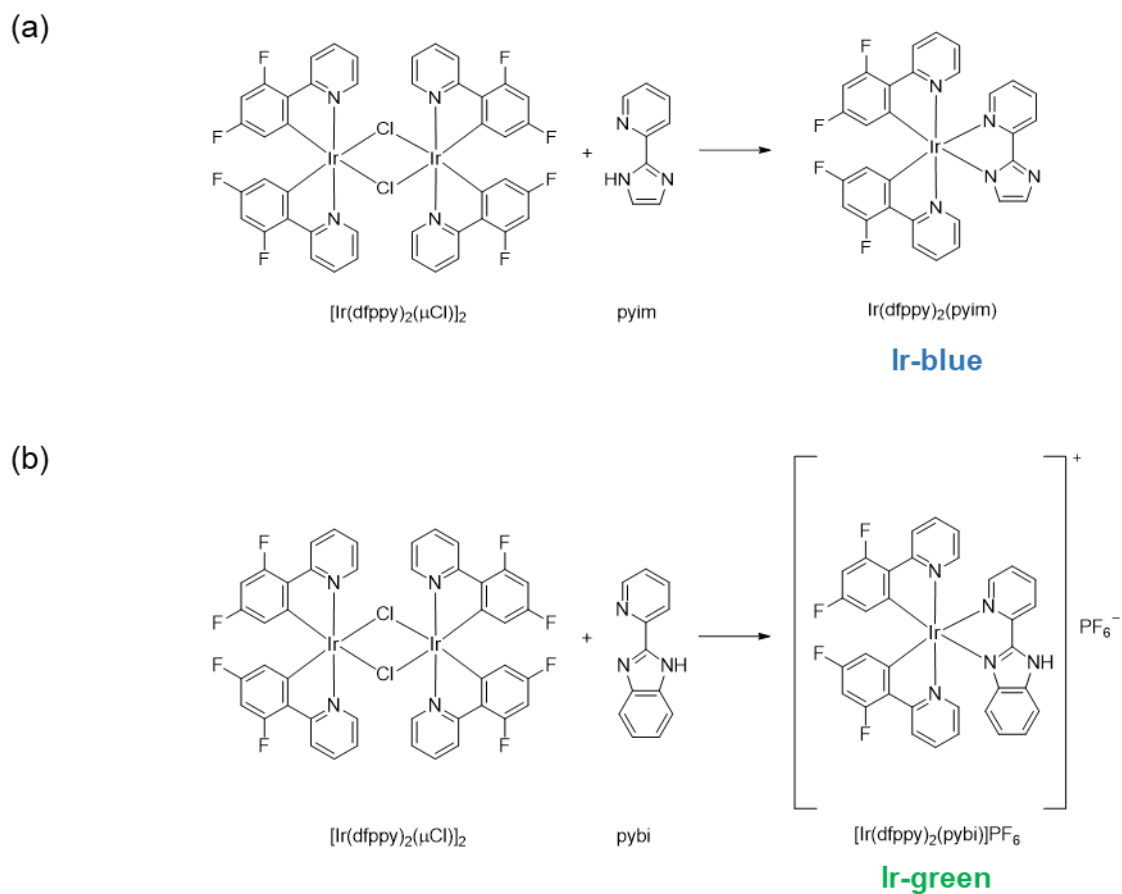
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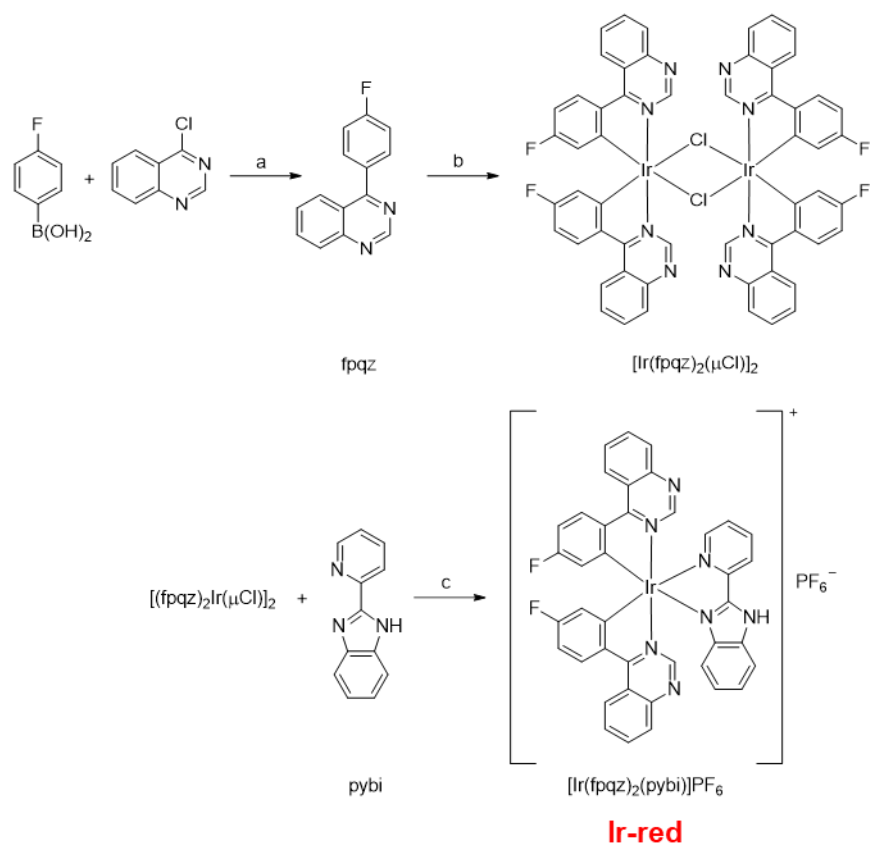
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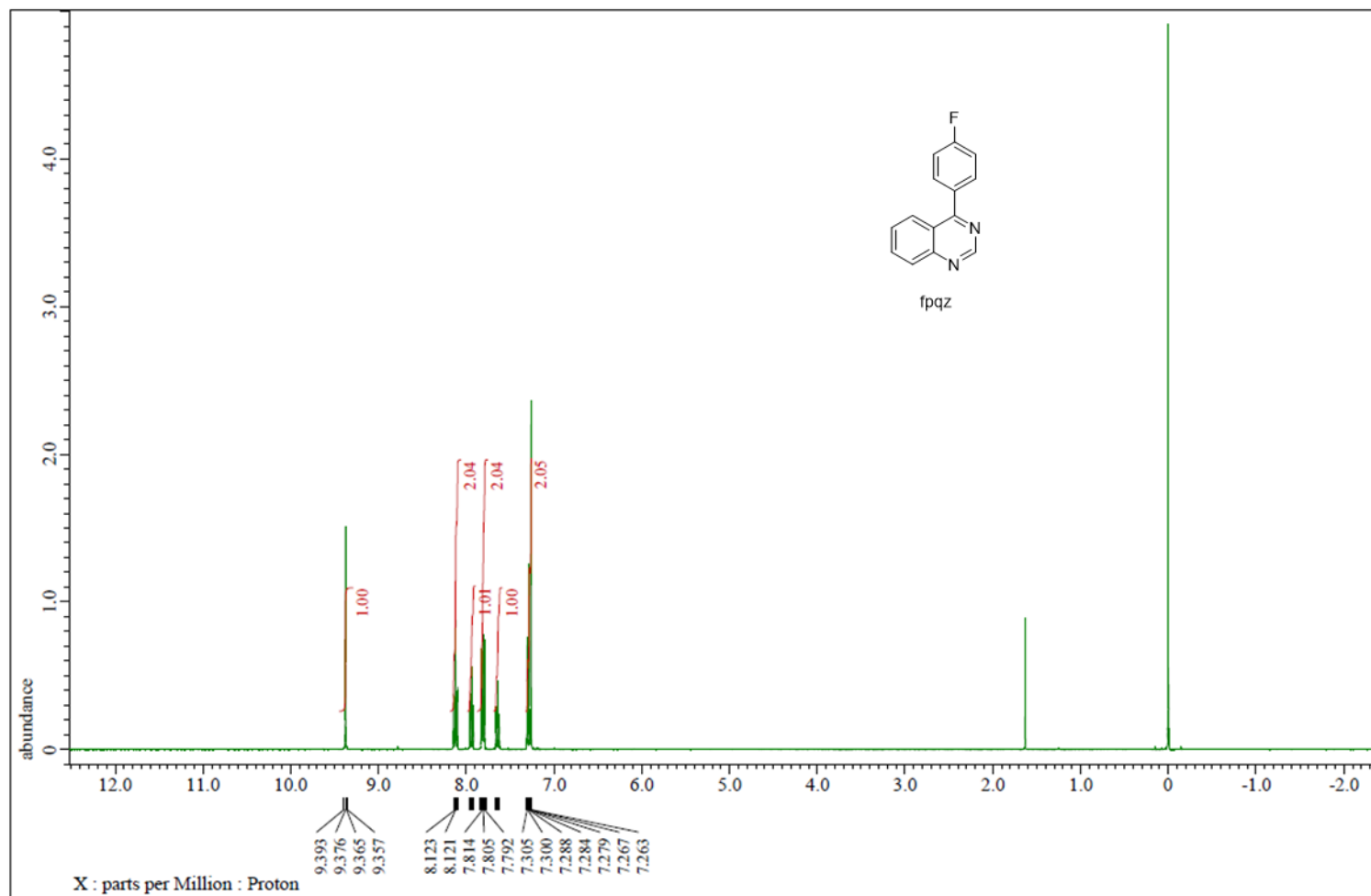
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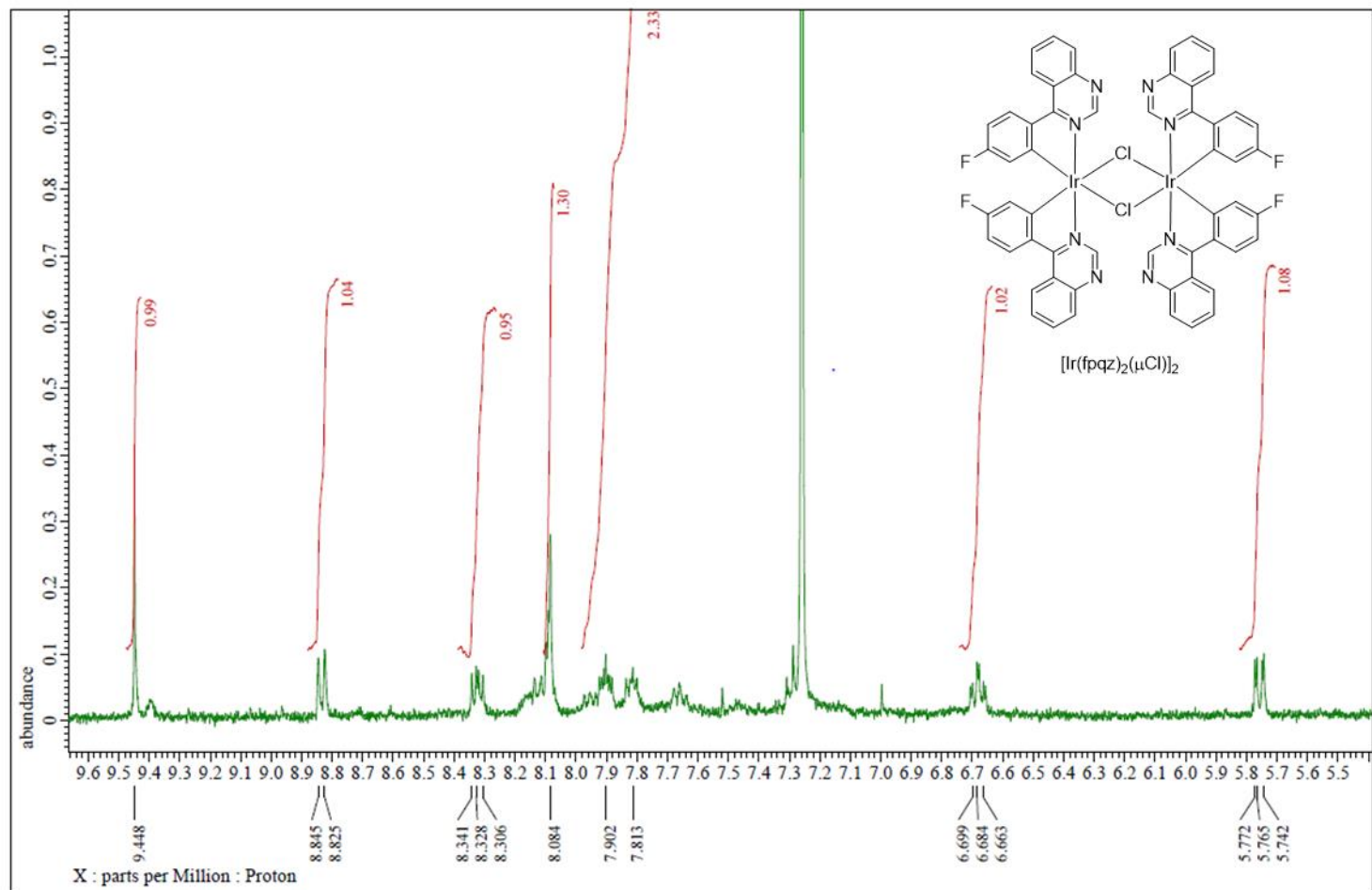
**Figure S1.** Synthetic schemes and chemical structures of heteroleptic tris-cyclometalated iridium complexes and ligands. (a) **Ir-blue** and (b) **Ir-green**.



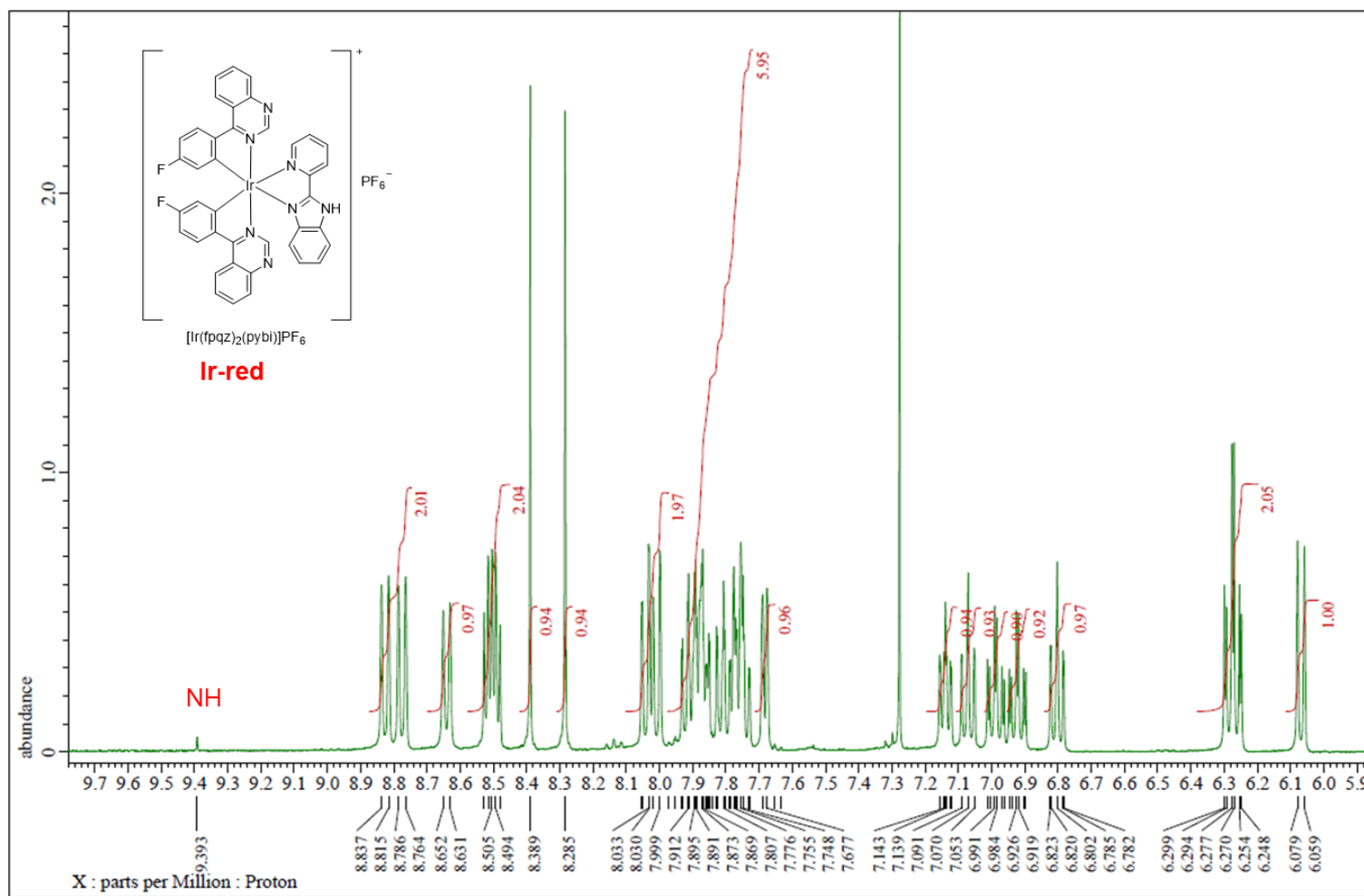
**Figure S2.** Synthetic schemes and chemical structures of heteroleptic tris-cyclometalated iridium complexes and ligands for **Ir-red**.



**Figure S3.**  $^1\text{H}$  400 MHz NMR spectrum of fpqz in  $\text{CDCl}_3$ .



**Figure S4.**  $^1\text{H}$  400 MHz NMR spectrum of  $[\text{Ir}(\text{fpqz})_2(\mu\text{Cl})_2]$  in  $\text{CDCl}_3$ .



**Figure S5.**  $^1\text{H}$  400 MHz NMR spectrum of **Ir-red** in  $\text{CDCl}_3$ .

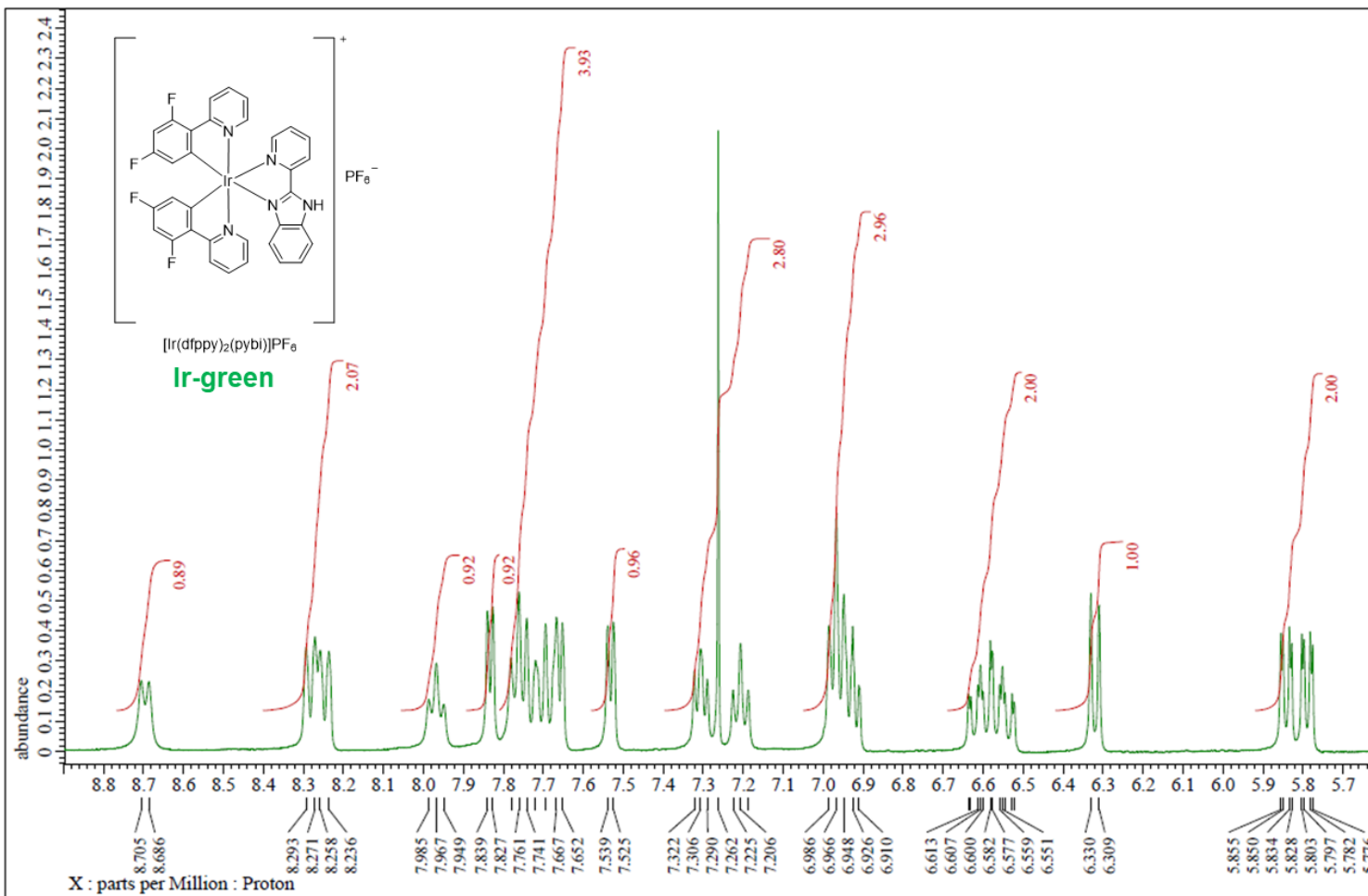
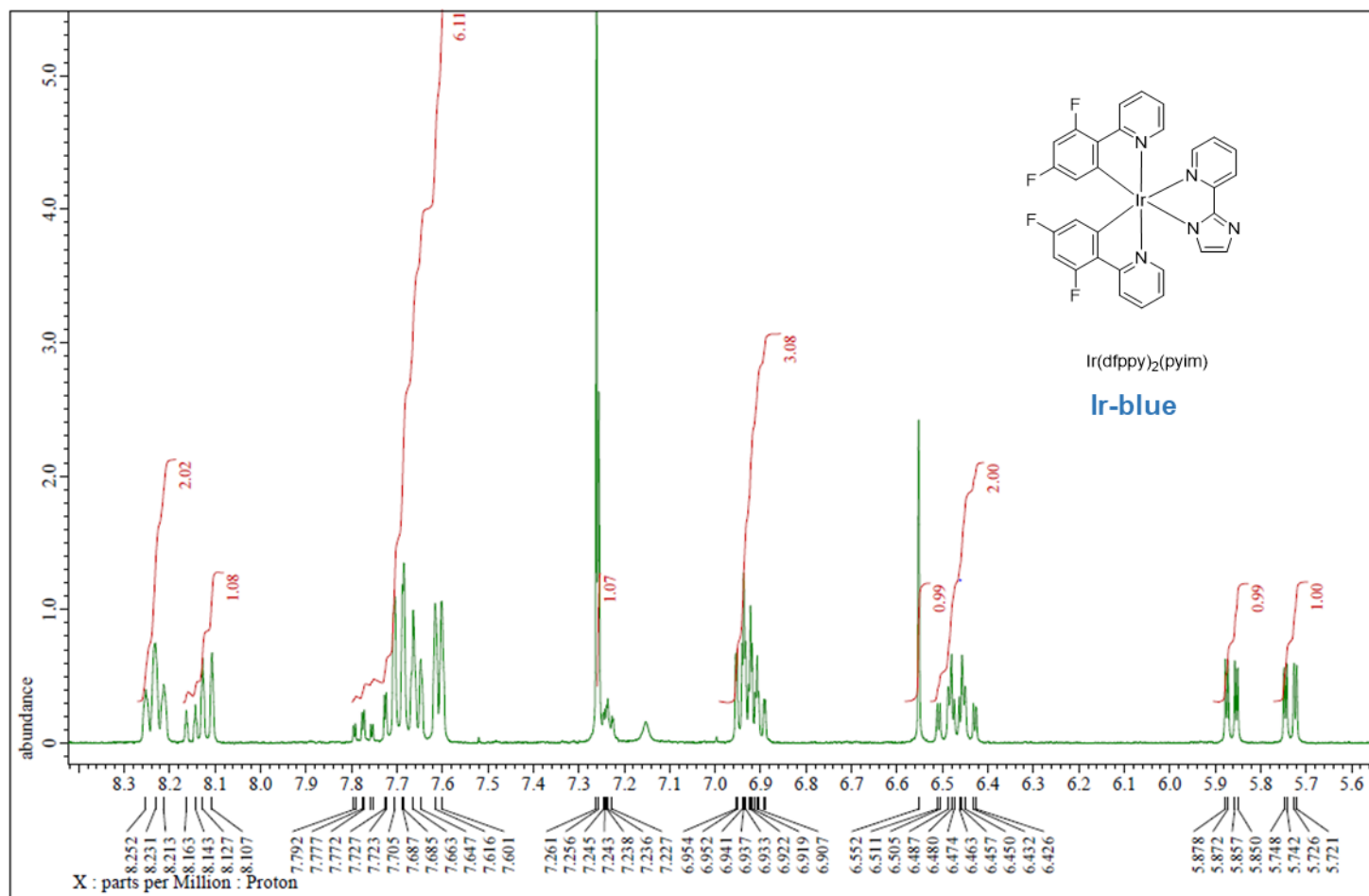
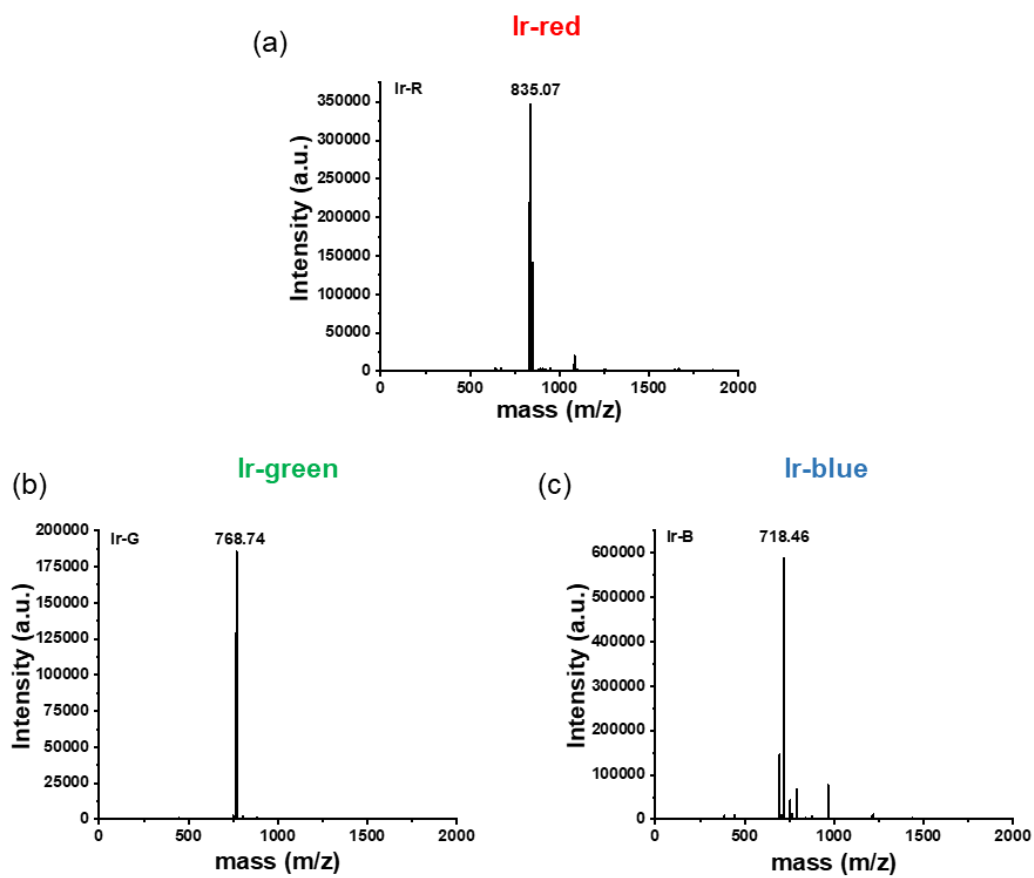


Figure S6.  $^1\text{H}$  400 MHz NMR spectrum of **Ir-green** in  $\text{CDCl}_3$ .

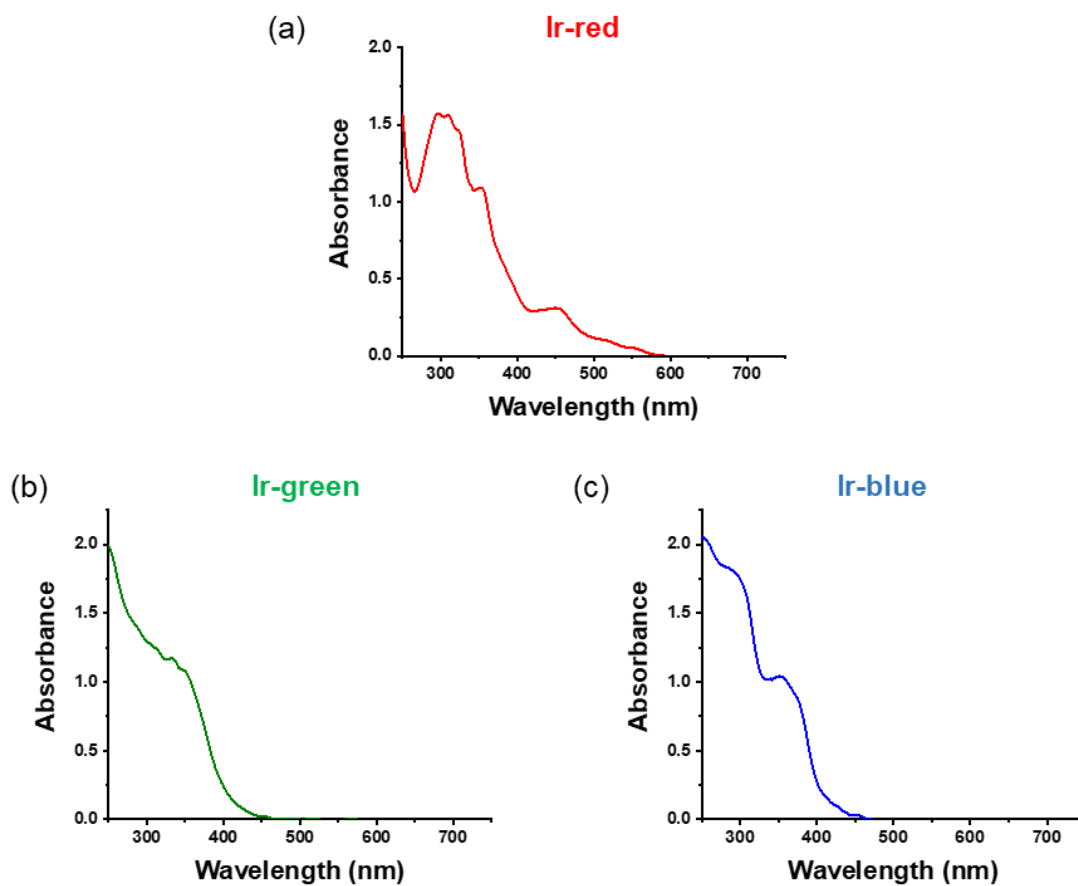


**Figure S7.**  $^1\text{H}$  400 MHz NMR spectrum of **Ir-blue** in  $\text{CDCl}_3$ .

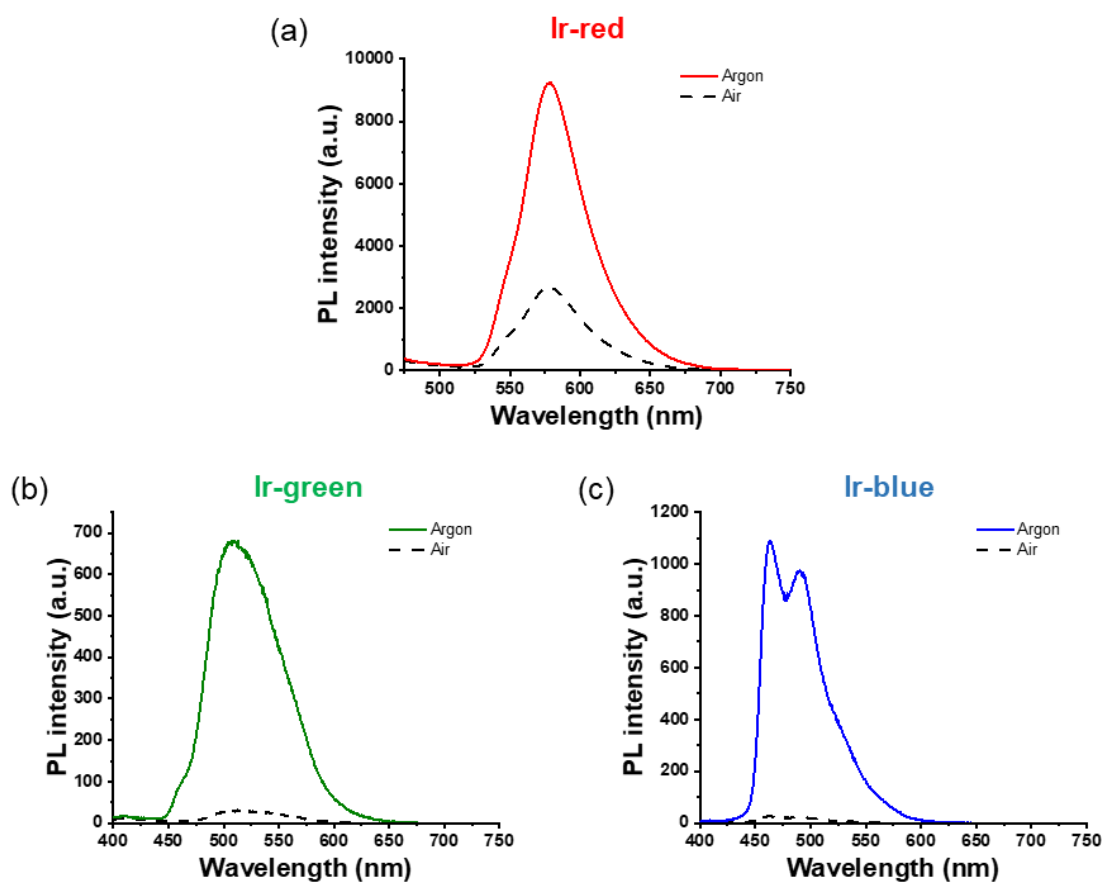




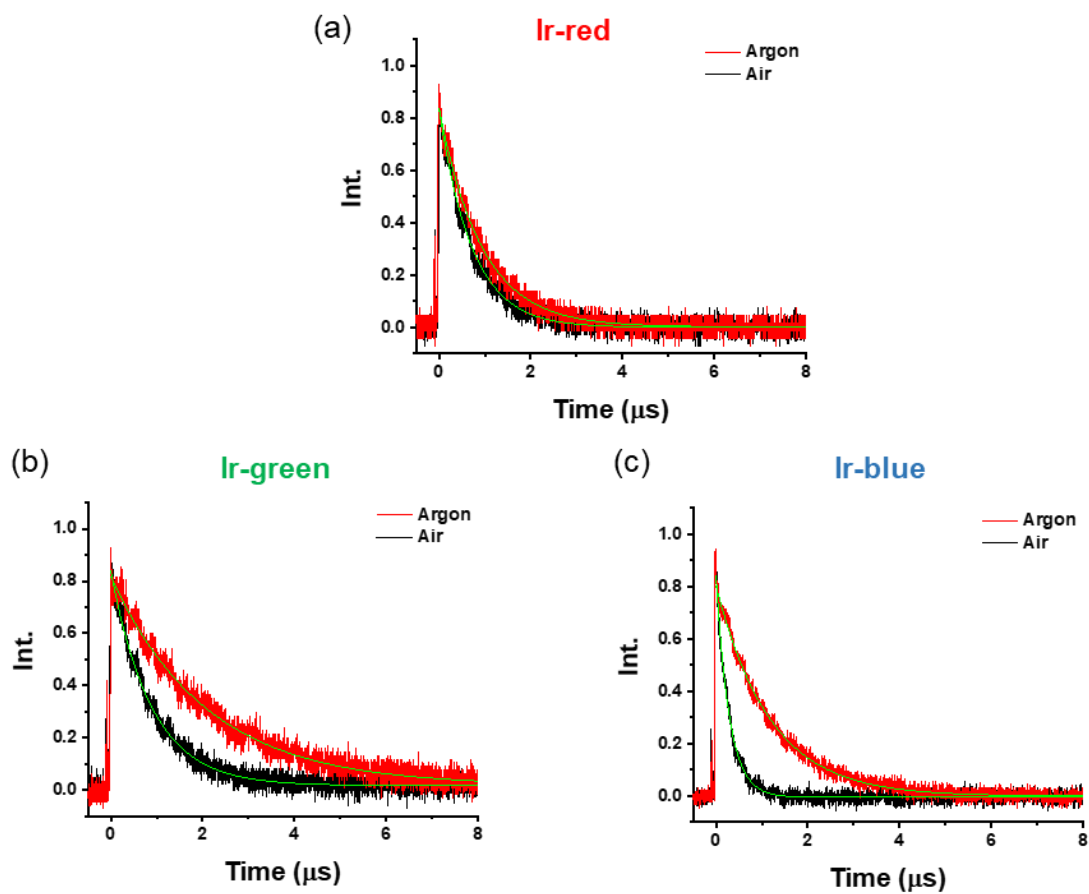
**Figure S8.** MALDI-TOF mass spectra for (a) **Ir-red**, (b) **Ir-green**, and (c) **Ir-blue**.



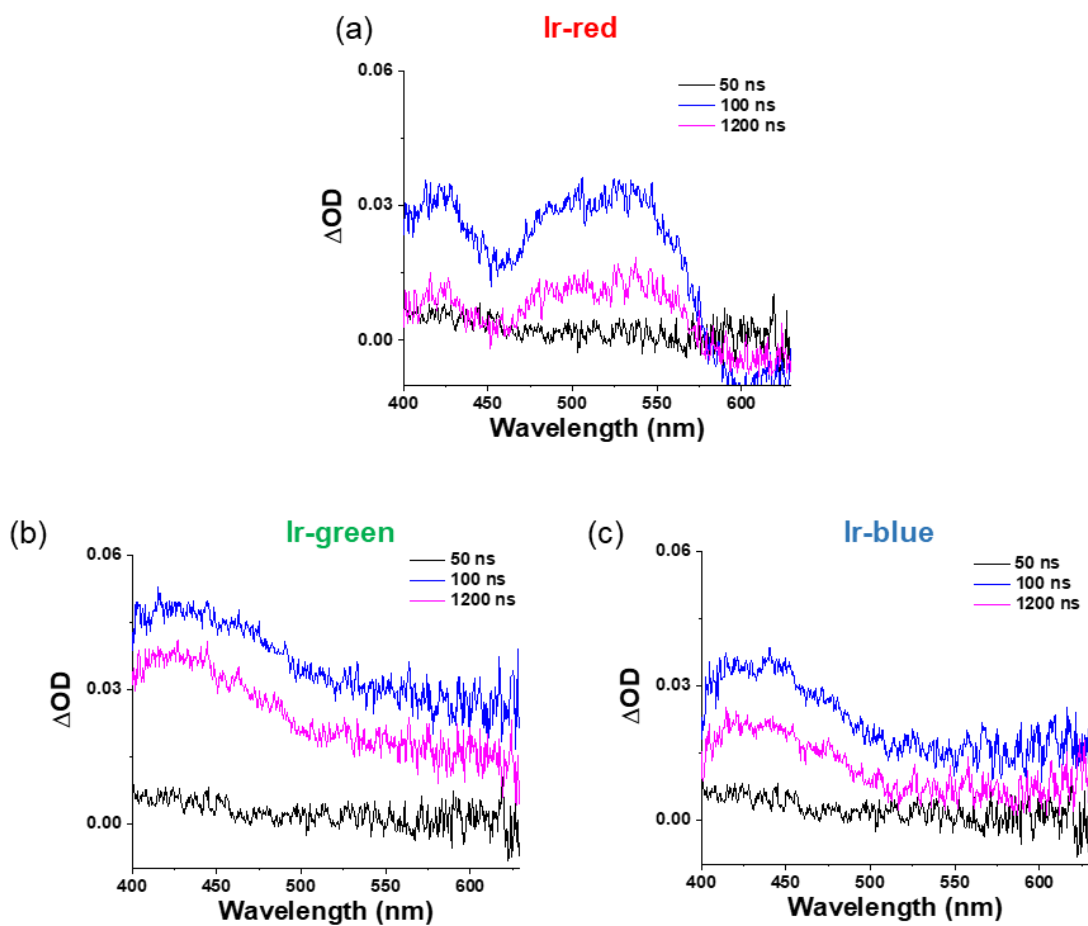
**Figure S9.** Absorption spectra of iridium monomer complexes in  $\text{CH}_2\text{Cl}_2$  solution of (a) **Ir-red**, (b) **Ir-green**, and (c) **Ir-blue**.



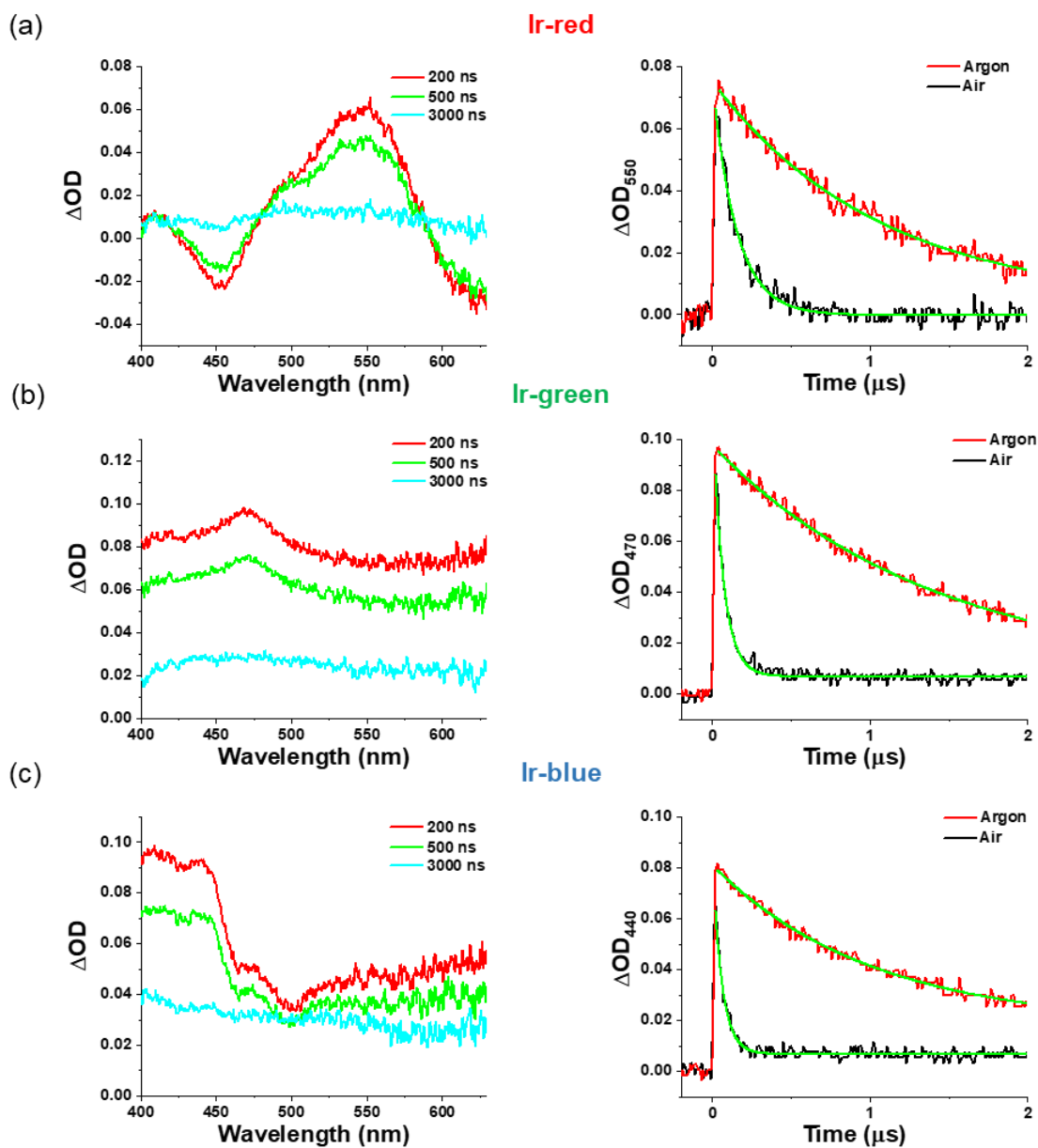
**Figure S10.** PL spectra of iridium monomer complexes in  $\text{CH}_2\text{Cl}_2$  solution. (a) **Ir-red**, (b) **Ir-green**, and (c) **Ir-blue** under argon (solid line) and air (dashed line).



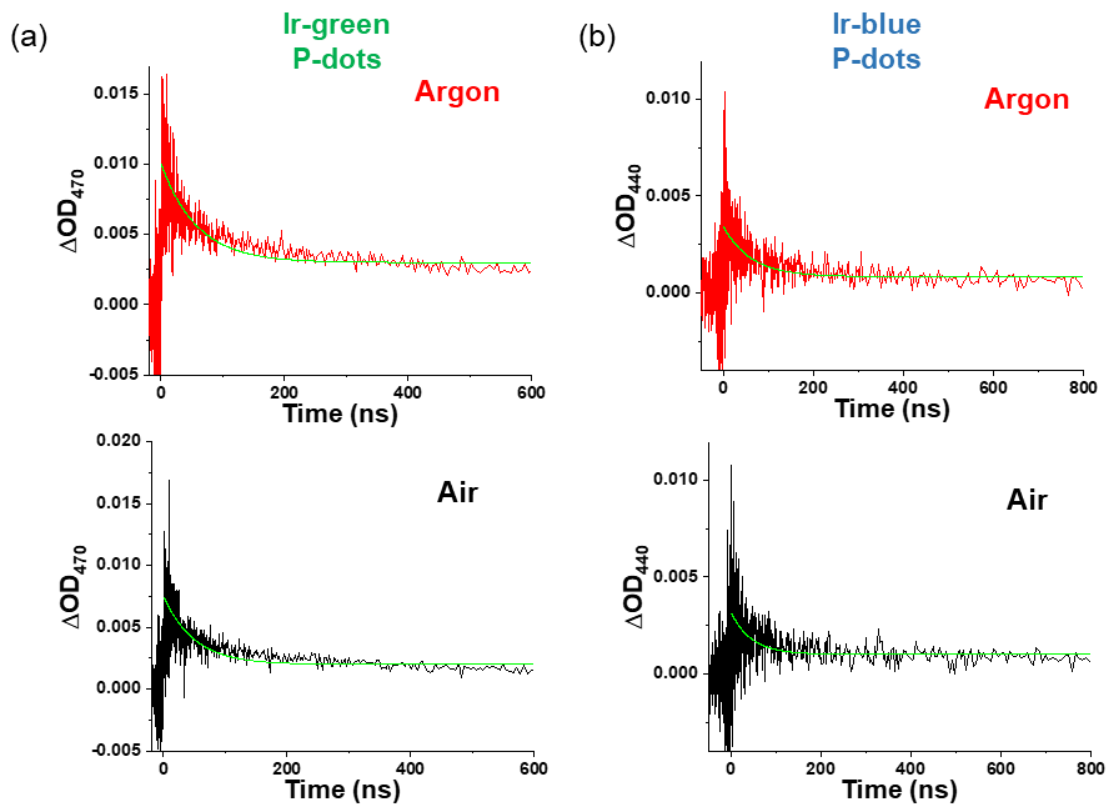
**Figure S11.** Lifetime of iridium monomer complexes in  $\text{CH}_2\text{Cl}_2$  solution. (a) **Ir-red**, (b) **Ir-green**, and (c) **Ir-blue** under air condition (black) and argon (red).



**Figure S12.** The transient absorption spectra during pulse radiolysis (a) **Ir-red**, (b) **Ir-green**, and (c) **Ir-blue** under Ar condition in toluene.



**Figure S13.** Laser flash photolysis spectra and time profiles in acetonitrile, (a) **Ir-red**, (b) **Ir-green**, and (c) **Ir-blue** under air condition (black) and argon (red).



**Figure S14.** Time profile of P-dots measured by RIPT method for (a) Ir-green and (b) Ir-blue.

**Table S1. The absorption and photoluminescence wavelength maximum for iridium monomers and P-dots doped with iridium complexes.**

	Monomers (CH <sub>2</sub> Cl <sub>2</sub> )		Pdots (H <sub>2</sub> O)	
	Absorption <sup>a</sup> (λ, nm)	Emission <sup>b</sup> (λ, nm)	Absorption <sup>a</sup> (λ, nm)	Emission <sup>b</sup> (λ, nm)
<b>Ir-red</b>	300, 350, 450	580	300, 350, 450	580
<b>Ir-green</b>	290, 350	500, 530	295, 350	500, 530
<b>Ir-blue</b>	290, 350	465, 495	295, 350	465, 495

<sup>a</sup>. Measured at room temperature. <sup>b</sup>. Excited at 365 nm at room temperature.

**Table S2. The absolute photoluminescence quantum yields for iridium monomers and P-dots doped with iridium complexes in solution.**

	Monomers (Toluene)		Pdots (H <sub>2</sub> O)	
	$\Phi_{\text{Air}}$	$\Phi_{\text{Ar}}$	$\Phi_{\text{Air}}$	$\Phi_{\text{Ar}}$
<b>Ir-red</b>	0.13	0.64	0.02	0.02
<b>Ir-green</b>	0.04	0.36	0.13	0.14
<b>Ir-blue</b>	0.01	0.30	0.08	0.08



**Table S3. Photoluminescence lifetime in CH<sub>2</sub>Cl<sub>2</sub> and  $k_q$  for iridium complexes.**

	$\tau_{\text{Argon}} (\mu\text{s})$	$\tau_{\text{Air}} (\mu\text{s})$	$k_q (10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^a$
<b>Ir-red</b>	0.9	0.7	0.15
<b>Ir-green</b>	2.1	0.9	0.29
<b>Ir-blue</b>	1.2	0.3	1.2

<sup>a</sup>.  $k_q$  was determined by the equation as mentioned in the method section. In CH<sub>2</sub>Cl<sub>2</sub>, [O<sub>2</sub>] =  $2.2 \times 10^{-3}$  mol/L at 20 °C.<sup>1</sup> Diffusion-controlled rate constants in CH<sub>2</sub>Cl<sub>2</sub> is  $k_{\text{diff}} = 1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 20 °C.<sup>1</sup>

**Table S4. The triplet excited state lifetime in acetonitrile determined by laser flash photolysis.**

	$\tau_{\text{Argon}} (\mu\text{s})$	$\tau_{\text{Air}} (\mu\text{s})$	$k_q (10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^a$
<b>Ir-red</b>	1.1	0.15	3.0
<b>Ir-green</b>	1.4	0.07	7.1
<b>Ir-blue</b>	1.0	0.06	8.3

<sup>a</sup>.  $k_q$  was determined by the equation as mentioned in the method section. In acetonitrile, [O<sub>2</sub>] =  $1.9 \times 10^{-3}$  mol/L at 24 °C.<sup>1</sup> Diffusion-controlled rate constants in acetonitrile is  $k_{\text{diff}} = 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C.<sup>1</sup>

**Table S5. The hydrodynamic diameters and zeta potentials for P-dots.**

	Hydrodynamic diameter (nm)	Zeta potential (mV)
<b>Ir-red P-dots</b>	100	-29
<b>Ir-green P-dots</b>	97	-22
<b>Ir-blue P-dots</b>	91	-18

**Table S6. Averaged size determined by TEM images.**

	Averaged size (nm)
<b>Ir-red P-dots</b>	31
<b>Ir-green P-dots</b>	30
<b>Ir-blue P-dots</b>	27

**Table S7. Photoluminescence lifetime for P-dots in the absence or presence of oxygen molecules.**

	$\tau_{\text{Argon}}$ (ns)	$\tau_{\text{Air}}$ (ns)
<b>Ir-red P-dots</b>	34	33
<b>Ir-green P-dots</b>	50	34
<b>Ir-blue P-dots</b>	39	32

**Table S8. Triplet lifetime for P-dots in the absence or presence of oxygen molecules.**

	$\tau_{\text{Argon}}$ (ns)	$\tau_{\text{Air}}$ (ns)
<b>Ir-red P-dots</b>	-	-
<b>Ir-green P-dots</b>	58	50
<b>Ir-blue P-dots</b>	62	46

## **Materials and methods**

### **Materials.**

Dichlorotetrakis[3,5-difluoro-2-(2-pyridinyl)phenyl]diiridium(III) ( $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ ), 2-(1-H-imidazol-2-yl) pyridine (pyim), 4-chloroquinazoline, iridium(III) chloride hydrate ( $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ ) and 2-ethoxyethanol potassium hexafluorophosphate ( $\text{KPF}_6$ ), tetrahydrofuran (THF) and polyvinylcarbazole (PVK) polymer ( $M_w$ : 25,000-50,000) were purchased from Sigma-Aldrich (Tokyo, Japan). Poly(vinyl Alcohol) (PVA,  $n = \text{approx. } 1700$ ) and polyethylene glycol 200 ( $M_w$ : 200) were purchased from TCI (Tokyo, Japan). Polystyrene graft ethylene oxide functionalized with carboxylic end group (PEG-COOH,  $M_n$  total: 36,500,  $M_n$  of each branch: 4600) was purchased from Polymer Source Inc. (Quebec, Canada). All other starting materials and solvents were purchased from Fujifilm-Wako (Osaka, Japan). Reagents were used without further purification.

### **General methods.**

$^1\text{H}$  NMR (400 MHz) spectra were measured on JNM-ECS400 NMR spectrometer (JEOL, Tokyo, Japan). Chemical shifts (in ppm) were recorded in  $\text{CDCl}_3$  with tetramethylsilane ( $\delta = 0$  ppm) as an internal standard. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the ligands and iridium complexes was conducted by using Ultraflex III (Bruker, MA, USA) *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as matrix. The absorbance spectra were recorded using V630 UV-visible spectrophotometer (JASCO, Japan) at room temperature. The photoluminescence (PL) spectra were measured by FP-8200 fluorometer (JASCO, Japan) or Fluoromax (HORIBA, Kyoto, Japan). The photos were taken under room light and UV light (365 nm) by using PowerShot S100 (Canon, Japan). The hydrodynamic diameter and zeta potential of **P-dots** were measured by dynamic light scattering (DLS) with Zetasizer Nano ZS (Malvern Panalytical, Malvern, UK). The measurements were conducted in  $\text{H}_2\text{O}$  at room temperature. The morphologies of P-dots were observed by JEM-

ARM200F Cs-corrected field emission transmission electron microscope (TEM, JEOL, Tokyo, Japan). For sample preparation, the synthesized P-dots were sonicated for 1 min and 20  $\mu$ L of sample solution was dropped on the Cu grid. After drying completely, the samples were used for the TEM measurement. The TEM photographs were analyzed with ImageJ software by counting more than 100 particles.

#### **Synthesis of 4-(4-fluorophenyl)quinazoline (fpqz)**

4-Chloroquinazoline (3.0 mmol), 4-fluorophenylboronic acids (3.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.1 mmol) were mixed in 20 mL THF. Then 10 mL aqueous solution of 2 N  $\text{Na}_2\text{CO}_3$  (1 mol/L) was added into the mixture. The mixture was stirred at 70  $^\circ\text{C}$  for 20 h under argon atmosphere. After the reaction, the crude product was extracted by  $\text{CH}_2\text{Cl}_2$ , and then washed with water and dried using anhydrous  $\text{Na}_2\text{SO}_4$ . Finally, silica column chromatography (*n*-hexane/EtOAc = 7/1 as eluant) was used to give the pure product. Yield: 376 mg, 56%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.37 (s, 1 H), 8.12 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 17.2$  Hz, 2 H), 7.96-7.92 (m, 1 H), 7.84-7.79 (m, 2 H), 7.66-7.62 (m, 1 H), 7.73-7.27 (m, 2 H). MALDI-TOF MS (m/z):  $[\text{M}+\text{H}]^+$ , Found: 225.43, calculated: 225.07.

#### **Synthesis of $[\text{Ir}(\text{fpqz})_2(\mu\text{Cl})_2]$**

$\text{IrCl}_3$  (0.5 mmol) and cyclometalated ligand (1.2 mmol) were dissolved in a mixture of 2-ethoxyethanol (15 mL) and water (5 mL). The solution was stirred at 120  $^\circ\text{C}$  for 20 h under argon atmosphere. After cooling down to room temperature, water was added to produce red precipitation. The precipitation was filtered, washed with water, dried, and kept for the next step. Yield.: 104 mg, 62%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.45 (s, 1 H), 8.83 (d,  $J = 8$  Hz, 1 H), 8.33 (t,  $J = 6.8$  Hz, 1 H), 8.08 (s, 1 H), 7.90-7.81 (m, 2 H), 6.68 (t,  $J = 7.2$  Hz, 1 H), 5.75 (d,  $J = 9.2$  Hz, 1H) MALDI-TOF MS (m/z):  $[(\text{M}-2\text{Cl})/2]^+$ , Found: 640.14, calculated: 639.10.

### Synthesis of [Ir(fpqz)<sub>2</sub>(pybi)]PF<sub>6</sub> (Ir-red)

The iridium(III) chloro-bridged dimer [Ir(fpqz)<sub>2</sub>(μCl)]<sub>2</sub> (0.2 mmol) and ancillary ligand pybi (0.5 mmol) were stirred at 50 °C for 20 h under argon in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and methanol (10 mL). After the reaction, an aqueous solution of excess KPF<sub>6</sub> was added into the solution and the mixture was stirred for 2 h. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was finally purified by silica gel column chromatography to obtain pure product.

Yield: 253 mg, 65%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.39 (s, 1 H, NH), 8.80 (dd, *J*<sub>1</sub> = 8.8, *J*<sub>2</sub> = 11.6 Hz, 2 H), 8.64 (d, *J* = 8.4 Hz, 1 H), 8.52-8.48 (m, 2 H), 8.39 (s, 1 H), 8.28 (s, 1 H), 8.05-7.99 (m, 2 H), 7.93-7.73 (m, 6 H), 7.68 (d, *J* = 4.8 Hz, 1 H), 7.14 (td, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 7.2 Hz, 1 H), 7.07 (t, *J* = 6.8 Hz, 1 H), 6.99 (td, *J*<sub>1</sub> = 2.8, *J*<sub>2</sub> = 8.8 Hz, 1 H), 6.92 (td, *J*<sub>1</sub> = 2.8, *J*<sub>2</sub> = 8.8 Hz, 1 H), 6.80 (td, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 8.4 Hz, 1 H), 6.27 (td, *J*<sub>1</sub> = 2.4, *J*<sub>2</sub> = 9.2 Hz, 2 H), 6.07 (d, *J* = 8.0 Hz, 1 H). MALDI-TOF-MS (*m/z*): [M-PF<sub>6</sub>]<sup>+</sup> Found: 835.07, calculated: 834.18.

### Synthesis of [Ir(dfppy)<sub>2</sub>(pybi)]PF<sub>6</sub> (Ir-green)

Typically, [Ir(dfppy)<sub>2</sub>(μCl)]<sub>2</sub> (0.2 mmol) and ligand pybi (0.5 mmol) were dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1/1) and refluxed at 50 °C for 20 h. After cooling down to room temperature, the solvent was evaporated under vacuum. The crude product was re-suspended in 2 mL of MeOH, and dropped into 15 mL of KPF<sub>6</sub> (1.0 g, 5.4 mmol). After stirring for 2 h at room temperature, the product was extracted by CH<sub>2</sub>Cl<sub>2</sub>, and then washed with saturated NaCl solution and DI water twice. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. Finally, the product was purified by silica column chromatography.

Yield: 208 mg, 57%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.69 (d, *J* = 7.6 Hz, 1H, NH), 8.26 (dd, *J*<sub>1</sub> = 8.8, *J*<sub>2</sub> = 5.2 Hz, 2 H), 7.97 (t, *J* = 7.2 Hz, 1 H), 7.83 (d, *J* = 4.8 Hz, 1 H), 7.78-7.65 (m, 4 H), 7.53

(d,  $J = 6.4$  Hz, 1 H), 7.32-7.19 (m, 3 H), 6.98-6.91 (m, 3 H), 6.61-6.55 (m, 2 H), 6.32 (d,  $J = 8.0$  Hz, 1 H), 5.85-5.77 (m, 2 H). MALDI-TOF-MS ( $m/z$ ):  $[M-PF_6]^+$  Found: 768.74, calculated: 768.14.

### **Synthesis of Ir(dfppy)<sub>2</sub>(pyim) (Ir-blue)**

Typically,  $[Ir(dfppy)_2(\mu Cl)]_2$  (0.2 mmol), pyim (0.5 mmol) and  $Na_2CO_3$  (2 mmol) were dissolved in 20 mL  $CH_2Cl_2$ . The mixture was stirred at 40 °C for 20 h under argon. After the reaction was complete, the  $CH_2Cl_2$  solution was filtered to remove the inorganic salt. The solvent was removed under reduced pressure. The crude product was purified by silica column chromatography.

Yield: 158 mg, 55%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.23 (t,  $J = 8.0$  Hz, 2 H), 8.13 (q,  $J = 8.0$  Hz, 1 H), 7.79-7.59 (m, 6 H), 7.25-7.22 (m, 1 H), 6.95-6.89 (m, 3 H), 6.55 (s, 1 H), 6.51-6.43 (m, 2 H), 5.86 (dd,  $J_1 = 2.4$  Hz,  $J_2 = 8.0$  Hz, 1 H), 5.73 (dd,  $J_1 = 2.4$  Hz,  $J_2 = 8.0$  Hz, 1 H). MALDI-TOF-MS ( $m/z$ ):  $[M+H]^+$  Found: 718.46, calculated: 718.12.

### **Supporting reference.**

1. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T.; Editors, *Handbook of photochemistry - Third edition*. 2006; p 650 pp.