

Supporting Information

Reply to Comment on ‘Aggregation-induced phosphorescent emission (AIPE) of iridium(III) complexes’: origin of the enhanced phosphorescence

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Experimental Section

General Experiments. ^1H NMR spectra were recorded with Varian spectrometer at 400 MHz. All matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry experiments were performed on an Applied Biosystems 4700 proteomics analyzer (Applied Biosystems). The UV-visible spectra were recorded on Shimadzu UV-2550 spectrometer. Steady-state emission experiments were measured on an Edinburgh instrument Xe-900 spectrometer at room temperature. Lifetime studies were performed with an Edinburgh FL-920 photo-counting system with a hydrogen-filled as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using software package provided by Edinburgh Instruments. Measurement of the absolute photoluminescence (PL) efficiency was performed on LabsphereIS-080(8”), which contained an integrating sphere coated on the inside with a reflecting material barium sulfate, and the diameter of the integrating sphere was 8 inch. The wavelength range studied was from 400-700 nm.

Materials. Commercially available chemical reagents were used without further purification. 2-Phenylpyridine, 2'-hydroxyacetophenone (L1), 2-acetyl-1-tetralone (L2) and 1-benzoylacetone (L3) were obtained from Acros and used without further purification.

Synthesis of Iridium Complexes. The complex $\text{Ir}(\text{ppy})_2(\text{L1})$ was synthesized according to the previous literature.¹ A mixture of 2-ethoxyethanol and water (3:1, v/v) was added to a flask containing $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (1 mmol) and 2-phenylpyridine (ppy, 2.5 mmol). The mixture was refluxed for 24 h. After cooling, the yellow solid precipitate was filtered to give crude cyclometalated Ir(III) chlorobridged dimer. The crude chlorobridged dimer (0.2 mmol) was

mixed with Na_2CO_3 (1.4 mmol). 2-Ethoxyethanol and L1 (0.5 mmol) were added and then the mixture was refluxed for 12 h. After cooling to room temperature, yellow precipitate was collected by filtration and chromatographed using CH_2Cl_2 /petroleum ether (1:1, v/v) to afford the complex $\text{Ir}(\text{ppy})_2(\text{L1})$. ^1H NMR: (400 MHz, CDCl_3), δ (ppm): 8.74 (d, 1H), 8.37 (d, 1H), 7.86 (d, 2H), 7.73 (m, 3H), 7.56 (t, 2H), 7.47 (t, 1H), 7.21 (t, 1H), 7.07 (m, 2H), 6.83 (m, 2H), 6.71 (t, 2H), 6.31 (m, 2H), 6.21 (d, 1H), 2.33 (s, 3H). m/e 636.1.

Complex $\text{Ir}(\text{ppy})_2(\text{L2})$ was prepared by the similar procedure of $\text{Ir}(\text{ppy})_2(\text{L1})$. ^1H NMR: (400 MHz, CDCl_3), δ (ppm): 8.57 (t, 2H), 7.85 (t, 2H), 7.71 (m, 4H), 7.56 (t, 2H), 7.06 (m, 4H), 6.84 (m, 2H), 6.71 (t, 2H), 6.31 (m, 2H), 2.73 (t, 2H), 2.65 (t, 2H), 1.91 (s, 3H). m/e 688.1

Complex $\text{Ir}(\text{ppy})_2(\text{L3})$ was prepared by the similar procedure of $\text{Ir}(\text{ppy})_2(\text{L1})$. ^1H NMR: (400 MHz, CDCl_3), δ (ppm): 8.57 (d, 1H), 8.53 (d, 1H), 7.85 (t, 2H), 7.70 (m, 4H), 7.56 (t, 2H), 7.35 (t, 1H), 7.24 (t, 2H), 7.08 (m, 2H), 6.82 (m, 2H), 6.71 (t, 2H), 6.31 (m, 2H), 5.85 (s, 1H), 1.91 (s, 3H). m/e 662.1.

X-ray Crystallography Analysis. The single crystals of $\text{Ir}(\text{ppy})_2(\text{L1})$ and $\text{Ir}(\text{ppy})_2(\text{L2})$ were mounted on glass fiber and crystallographic measurement was carried out using a Rigaku Saturn CCD diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) under $-160 \text{ }^\circ\text{C}$. The crystal structures were solved by direct method and refined by full-matrix least-squares on F^2 values using the program SHELXS-97.² All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries. For the full-matrix least-squares refinements [$I > 2\sigma(I)$], the unweighted and weighted agreement factors of $R1 = \Sigma(\text{Fo}-\text{Fc})/\Sigma\text{Fo}$ and $wR2 = [\Sigma w(\text{Fo}^2-\text{Fc}^2)^2/\Sigma w\text{Fo}^4]^{1/2}$ were used. CCDC reference number 699183 and 699180 for $\text{Ir}(\text{ppy})_2(\text{L1})$ and $\text{Ir}(\text{ppy})_2(\text{L2})$, respectively.

The single crystals of $\text{Ir}(\text{ppy})_2(\text{L1})$ and $\text{Ir}(\text{ppy})_2(\text{L2})$ were analyzed to study the molecular packing structure.^{3, 4} For $\text{Ir}(\text{ppy})_2(\text{L1})$, the perpendicular distance of the 6-membered pyridyl ring N1C9C10C11C12C13 on another phenyl ring C14C15C16C17C18C19 was 3.4548 Å , while the perpendicular distance of the phenyl ring C14C15C16C17C18C19 on another pyridyl ring N1C9C10C11C12C13 was 3.4609 Å , and the average perpendicular value was 3.4579 Å . Similarly, for $\text{Ir}(\text{ppy})_2(\text{L2})$, the perpendicular distance of the phenyl ring C52C53C54C55C56C57 on another pyridyl ring N2C24C25C26C27C28 was 3.3465, while

the perpendicular distance of the pyridyl ring N2C24C25C26C27C28 on another phenyl ring C52C53C54C55C56C57 was 3.4609 Å, and the average perpendicular value was 3.4228 Å.

References

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