

Phosphorescent iridium(III) complexes with hetero ($\hat{C}N$) ligands [☆]

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Abstract

In order to improve luminescence efficiency, it is necessary to design a phosphorescent material which is capable of transferring the excited energy without triplet–triplet (T–T) annihilation. For this purpose, new types of metal complexes were designed with different species of ($\hat{C}N$) ligands. Herein, Ir(ppy)₂(piq), Ir(ppy)₂(piq-F) and Ir(ppy)₂(piq-CF₃) were designed and prepared, where ppy, piq, piq-F and piq-CF₃ represent 2-phenylpyridine, 1-(phenyl)isoquinoline, 1-(4'-fluorophenyl)isoquinoline and 1-(4'-trifluoromethylphenyl)isoquinoline, respectively. These Ir(III) complexes having two different ligands (hetero-Ir complexes) are expected to have a high luminescence efficiency by intramolecular energy transfer from the energy absorbing ligand to the luminescent ligand leading to a decrease in quenching or energy deactivation. To compare luminescent characteristics of these hetero-Ir complexes, homo-Ir complexes Ir(ppy)₃, Ir(piq)₃, Ir(piq-F)₃ and Ir(piq-CF₃)₃ were prepared and investigated photophysically.

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1. Introduction

Since organic light-emitting devices (OLED) were developed in 1987 [1,2], materials for the devices and device fabrication have been extensively studied [3,4]. Along with this development, design and synthesis of luminescence dopants have been intensively studied. Luminescent materials are generally classified into two groups, fluorescent and phosphores. OLEDs based on phosphorescent emitters can significantly improve electroluminescence performance, because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100% [5]. However, most of the phosphorescent materials have a long lifetime (>10 μ s), which causes saturation of emissive sites

at increasing currents. Therefore, it is necessary to develop phosphorescent materials that can have high efficiency by avoiding triplet–triplet (T–T) annihilation.

Among luminescence dopants, green luminescent ones have been more successfully developed than red or blue ones. In 2001, Baldo et al. made a green phosphorescent dopant, (ppy)₂Ir(acac), with an internal quantum efficiency of nearly 100%. On the other hand, it is not easy to find a red phosphorescent dopant with high external quantum efficiency, even at high current.

In order to improve luminescence efficiency by avoiding T–T annihilation, a metal complex having a different species of plural ligands has been proposed [6]. When a metal complex having three ligands including one luminescent ligand is placed in an excited state, the excited energy can be transferred from two ligands to one luminescent ligand.

Herein, we report efficient phosphorescent emitters having different ligands, Ir(ppy)₂(piq), Ir(ppy)₂(piq-F) and Ir(ppy)₂(piq-CF₃). Since the homo-Ir complexes, Ir(ppy)₃, Ir(piq)₃ and Ir(piq-F)₃, are identified as being placed in

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the MLCT excited state, they are known to have high phosphorescence efficiency in EL emissions at 514 nm, 620 nm and 595 nm, respectively [7]. In our earlier result, PL emission of Ir(piq-CF₃)₂(acac) occurred at 612 nm. In this study we made hetero-Ir(III) complexes that exhibit red-shift luminescence compared to Ir(ppy)₂(acac). Ir(ppy)₂(acac) has been known to have nearly 100% internal quantum efficiency. Thus, in the hetero-complexes, ppy ligand was employed to harvest both singlet and triplet excitons efficiently and a fluorinated phenylisoquinoline(piq) ligand was introduced as a luminescent ligand. In other words, absorption occurs at the ppy ligand and then energy transition occurs from ppy to the ligand having a much lower HOMO value. We also studied the phosphorescence mechanism of the hetero-Ir(III) complexes, as compared with homo-Ir(III) complexes.

2. Experimental section

2.1. Synthesis and characterization

All reagents were purchased from Aldrich Co., except Ir(III) trichloride hydrate (IrCl₃ · H₂O), which was purchased from Strem Co. and used without further purification. All reactions were carried out under a nitrogen or argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-mesh, Merck Co). Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A (capillary column) at Seoul National University, Korea.

2.1.1. Synthesis of ligands (*L* = piq, piq-F, piq-CF₃)

Phenylisoquinoline ligands piq, piq-F and piq-CF₃ were obtained from the reaction of 1-chloroisoquinoline with the corresponding substituted phenylboronic acids by Suzuki coupling.

Synthesis of piq. 1-Chloroisoquinoline (0.899 g, 5.5 mmol), phenylboronic acid (0.699 g, 5 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.196 g, 0.17 mmol) were placed in a mixture of toluene (20 ml), ethanol (10 ml) and 2 N sodium carbonate aqueous solution (20 ml). The reaction mixture was heated to reflux for 15 h at 135 °C. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction was dried over anhydrous MgSO₄, filtered and pumped dry. The residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:7). The product was collected and dried in vacuum to yield a white powder with 64% yield.

Ligands piq-F and piq-CF₃ were prepared from the reaction of 1-chloroisoquinoline with 4-fluorophenylboronic acid and 4-(trifluoromethyl)phenylboronic acid by a similar procedure, respectively.

piq: Yield (0.68 g, 60%), **piq-F:** Yield (0.72 g, 64%), **piq-CF₃:** Yield (0.85 g, 62.5%).

2.1.2. Synthesis of complexes

The cyclometalated Ir(III)μ-chloro-bridged dimer, (ppy)₂Ir(μ-Cl)₂Ir(ppy)₂, was synthesized by the method reported by Nonoyama with slight modification.

Ir(ppy)₂(piq), Ir(ppy)₂(piq-F), Ir(ppy)₂(piq-CF₃).

Synthesis of Ir(ppy)₂(acac). To a flask containing IrCl₃ · H₂O (1.49 g, 5 mmol) and ppy (1.78 ml, 2.5 mmol (2.5 eq)) was added a 3:1 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 15 h and cooled to room temperature. The solution mixture was slowly evaporated under vacuum to obtain the crude product (ppy)₂Ir(μ-Cl)₂Ir(ppy)₂. The yellow solid was filtered and washed with ethanol. This chloride-bridged dimer (2 mmol) was then placed in a 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL). 2,4-Pentanedione (0.68 ml, *d* = 0.975, 6.8 mmol (3.4 eq)) was added and the reaction mixture was refluxed for 2 h at 135 °C. The solution was cooled to room temperature and poured into 30 ml of 2 N HCl. The yellow solid was filtered and washed with water, followed by purification by silica gel column chromatography by using CH₂Cl₂ to afford a dark yellow powder of Ir(ppy)₂(acac).

Ir(ppy)₂(acac): Yield (2.130 g, 71%).

Synthesis of Hetero-Ir(III) complexes. General Procedure. Ir(ppy)₂acac (0.600 g, 1 mmol) and a cyclometalating ligand (piq-F, piq-2F, piq-CF₃ = 2.3 mmol (2.3 eq)) were dissolved in 20 mL of glycerol in a 50 ml flask. The mixture was refluxed for 10 h at 210 °C. The reaction mixture was poured into 30 ml of 2 N HCl to give the crude solid. Column chromatography on silica followed by recrystallization in CH₂Cl₂/CH₃OH yielded a red powder of the hetero Ir complexes.

Ir(ppy)₂(piq): Yield (0.536 g, 76%), **Ir(ppy)₂(piq-F):** Yield (0.448 g, 62%).

Ir(ppy)₂(piq-CF₃): Yield (0.534 g, 69%).

Synthesis of homo-Ir(III) complexes: Ir(ppy)₃, Ir(piq)₃, Ir(piq-F)₃ and Ir(piq-CF₃)₃.

These complexes were prepared from Ir(acac)₃ and the corresponding (CN) ligand by a reported procedure [8]. Ir(acac)₃ (245 mg, 0.5 mmol) and (CN) ligands (ppy, piq, piq-F and piq-CF₃, 2 mmol) were dissolved in 20 ml of glycerol and the mixture was refluxed for 12 h. After cooling, 20 ml of 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography by using CH₂Cl₂.

2.2. Optical measurements

UV–vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV–vis and PL spectra of iridium complexes were measured in 10⁻⁵ M dilute CH₂Cl₂ solution.

2.3. Theoretical calculation

Computationally, the electronic ground states of ppy, piq and piq-F ligands and of Ir(ppy)₂(piq), Ir(ppy)₂(piq-F)

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