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# The heteroleptic complexes containing 2,3-diphenylquinoline derivatives as phosphorescent materials

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#### Abstract

New types of heteroleptic iridium complexes were designed and synthesized with two different species of chelating ligands ( $\hat{C}$ N) in this study. Ir(ppy)<sub>2</sub>(4-Me-2,3-dpq), Ir(ppy)(4-Me-2,3-dpq)<sub>2</sub>, Ir(pq)<sub>2</sub>(4-Me-2,3-dpq) and Ir(pq)(4-Me-2,3-dpq)<sub>2</sub> were prepared, where ppy, 4-Me-2,3-dpq and pq represent 2-phenylpyridine, 4-methyl-2,3-diphenylquinoline and 2-phenylquinoline, respectively. According to our previous study, Ir(4-Me-2,3-dpq)<sub>2</sub>(acac) showed orange-red emission at 603 nm with the luminescence efficiency of 8.10 cd/A in electroluminescence (EL) spectra. On the other hand, Ir(ppy)<sub>2</sub>(acac), a green phosphor, has been known to have an outstanding efficiency of more than 45 cd/A. In order to improve the luminescence efficiency, it is necessary to design a phosphorescent material which is capable of transferring the excited energy efficiently and properly. The heteroleptic Ir(III) complexes containing two different kinds of ligands can 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. Thus, the luminescence characteristics of the iridium complexes prepared herein were investigated. Ir(ppy)<sub>2</sub>(4-Me-2,3-dpq), Ir(ppy)(4-Me-2,3-dpq)<sub>2</sub>, Ir(pq)<sub>2</sub>(4-Me-2,3-dpq)<sub>2</sub> and Ir(pq)(4-Me-2,3-dpq)<sub>2</sub> exhibited the emission maxima at 512, 512, 583, and 584 nm, respectively. Two different light-emitting mechanisms were suggested to explain these phenomena.

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# 1. Introduction

Organic light-emitting diodes (OLEDs) that involve phosphorescent metal complexes as an emitting material have been attracting a great deal of attention because they exhibit higher efficiency than OLEDs that use conventional fluorescent materials [1–9]. The purpose of the present study was the molecular design and synthesis of phosphorescent emitters based on heteroleptic iridium(III) phenylquinoline complexes [10]. The heteroleptic Ir(III) complexes containing two different kinds of ligands can have a high luminescence efficiency by intramolecular energy transfer from the energy-absorbing ligand to the luminescent ligand. However, relatively few hetero-

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leptic iridium complexes were reported so far [11–16], compared with the well-developed classes of homoleptic iridium complexes probably due to synthetic difficulty.

Our previous study showed that a 2,3-diphenylquinoline iridium complex,  $Ir(4-Me-2,3-dpq)_2(acac)$ , exhibited its photoluminescence (PL) emission at 604 nm with a luminescence efficiency of 8.10 cd/A. The quinoline-based iridium complexes possess relatively short phosphorescence lifetimes that suppress triplet-triplet (TT) annihilation which results in improved device quantum efficiency at a high current density [17]. The Thompson group reported that  $Ir(ppy)_2(acac)$  and  $Ir(pq)_2(acac)$  have emission peaks at 516 and 599 nm, with the life time of 1.6 and 2.0 µs, respectively [10,18]. In this study, we synthesized the heteroleptic complexes involving 4-Me-2,3 dpq and ppy/pq ligands, and investigated their luminescence properties.

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# 2. Experimental section

All reactions were carried out under a dry argon atmosphere.

## 2.1. Synthesis of ligand

#### 2.1.1. 4-Me-2,3-dpq

This dpq-ligand derivative was obtained according to the Friedlander reaction with 1-(2-amino-phenyl)-ethanone (1.352 g, 10.0 mmol) and 1,2-diphenyl-ethanone (1.962 g, 10.0 mmol) in 30 ml of glacial acetic acid. The solution was heated to reflux for 6 h at 110 °C. The reaction mixture was then cooled and dripped slowly under stirring into an ice-cold solution of 50% ammonium hydroxide (160 ml). The resultant dark-yellow precipitate was collected by filtration. The solid was chromatographed on a silica-gel column with dichloromethane (yield:80%).

## 2.2. Synthesis of iridium(III) acac complexes

#### 2.2.1. $Ir(C^N)_2(acac)$

The cyclometallated Ir(III)  $\mu$ -chloro-bridged dimer,  $(C^N)_2 Ir(\mu$ -Cl)\_2Ir( $C^N$ ), was synthesized according to the Nonoyama method with a slight modification. The following reaction of the dimer with 2,4-pentandione gave Ir( $C^N$ )\_2(acac) (yield Ir(ppy)\_2(acac): 71%; Ir(pq)\_2(acac): 70%; Ir(4-Me-2,3-dpq)\_2(acac): 70%).



Fig. 1. Synthesis of the ligand and iridium complexes.

## 2.3. Synthesis of heteroleptic Ir(III) complexes

#### 2.3.1. $Ir(ppy)_2(4-Me-2,3-dpq)$

Ir(ppy)<sub>2</sub>(acac) (1 mmol) and 4-Me-2,3-dpq (2.3 mmol) 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 dichloromethane/hexanes yielded a yellow powder of Ir(ppy)<sub>2</sub>(4-Me-2,3-dpq) (yield 21%. FAB–MS: calculated 795; found 795).

2.3.2.  $Ir(ppy)(4-Me-2,3-dpq)_2$ ,  $Ir(pq)_2(4-Me-2,3-dpq)$ ,  $Ir(pq)_2(4-Me-2,3-dpq)$ ,  $Ir(pq)(4-Me-2,3-dpq)_2$ 

These heteroleptic complexes were prepared from the reaction of the corresponding dimer with the hetero-ligand, according to the procedure above.

Ir(ppy)(4-Me-2,3-dpq)<sub>2</sub>: yield 18%. FAB–MS: calculated 935; found 935.

Ir(pq)<sub>2</sub>(4-Me-2,3-dpq): yield 20%. FAB–MS: calculated 895; found 895.

Ir(pq)(4-Me-2,3-dpq)<sub>2</sub>: yield 19%. FAB–MS: calculated 985; found 985.

# 2.4. 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 CH<sub>2</sub>Cl<sub>2</sub> solution.

## 3. Results and discussion

The synthesis of ligands and heteroleptic iridium complexes was straightforward, according to the procedures reported by Friedlander and by Nonoyama with a slight modification, as summarized in Fig. 1.

The UV-Vis absorption spectra of heteroleptic complexes, Ir(ppy)<sub>2</sub>(4-Me-2,3-dpq) and Ir(ppy)(4-Me-2,3-dpq)<sub>2</sub>, and  $Ir(pq)_2(4-Me-2,3-dpq)$  and  $Ir(pq)(4-Me-2,3-dpq)_2$  were investigated and compared as shown in Fig. 2. The intense bands appearing between 200 and 320 nm are assigned to the spin-allowed  $(\pi \rightarrow \pi^*)$  transitions of the ligands in the complex. Due to the perturbation iridium metal, these transitions are shifted with respect to those of the free ligands. The bands extending into the visible region from 320 to 430 nm and the weak bands at the longer wavelength can be assigned to the spin-allowed metal-ligand chargetransfer band (<sup>1</sup>MLCT), and both spin-orbit couplings enhanced  ${}^{3}\pi - \pi *$  and  ${}^{3}MLCT$  transitions, respectively. In detail, triplet absorption peaks for Ir(ppy)<sub>2</sub>(4-Me-2,3-dpq) and Ir(ppy)(4-Me-2,3-dpq)<sub>2</sub> appeared at 456, 483, 520, and 581 nm, while the absorption peaks for Ir(pq)<sub>2</sub>(4-Me-2,3dpq) and  $Ir(pq)(4-Me-2,3-dpq)_2$  appeared at 440, 487, and 503 nm.



Fig. 2. UV-Vis absorption spectra of the heteroleptic iridium complexes.

The photoluminescence PL spectra of the heteroleptic complexes are shown in Fig. 3. The emission maxima for both  $Ir(ppy)_2(4-Me-2,3-dpq)$  and  $Ir(ppy)(4-Me-2,3-dpq)_2$  appeared at 512 nm. Against our expectation, these emission peaks are similar to those of  $Ir(ppy)_3$  (514 nm). On the other hand, both  $Ir(pq)_2(4-Me-2,3-dpq)$  and  $Ir(pq)(4-Me-2,3-dpq)_2$  showed the PL peaks at 583 nm.

To explain these emission characteristics, the HOMO-LUMO levels of the related complexes,  $Ir(C^N)_2(acac)$ , where  $C^N = ppy$ , pq, and 4-Me-2,3-dpq, are investigated and the simple energy diagrams of these complexes are shown in Fig. 4. Based on the HOMO-LUMO levels of these related iridium complexes, two different luminescent mechanisms are suggested. In both  $Ir(ppy)_2(4-Me-2,3-dpq)$  and  $Ir(ppy)(4-Me-2,3-dpq)_2$ , MLCT absorptions occur at both ppy and 4-Me-2,3-dpq ligands because HOMO levels of  $Ir(ppy)_2(acac)$  and  $Ir(4-Me-2,3-dpq)_2(acac)$  are very similar [18,19]. However, for the photoluminescence the inter-ligand energy transfer (ILET) time from the ppy <sup>3</sup>MLCT state to the 4-Me-2,3 dpq <sup>3</sup>MLCT state and





Fig. 3. PL spectra of the heteroleptic iridium complexes in a  $10^{-5}\,M$   $CH_2Cl_2$  solution.

intra-radiative lifetime of the 4-Me-2,3-dpg ligand-based state can be longer than that of the ppy ligand-based state  $(16 \,\mu s)$ . As a result, the green emissions occur mainly from the <sup>3</sup>MLCT state of ppy in the complexes. On the other hand, the PL peaks of both Ir(pq)<sub>2</sub>(4-Me-2,3-dpq) and  $Ir(pq)(4-Me-2,3-dpq)_2$  (583 nm) show the hypsochromic shift, compared with those of Ir(pq)<sub>2</sub>(acac) (599 nm) and Ir(4-Me-2,3dpq)<sub>2</sub>(acac) (603 nm). A different light-emitting mechanism can explain these hypsochromic shifts. The ILET time from the 4-Me-2,3dpg <sup>3</sup>MLCT to the pq <sup>3</sup>MLCT states and intra-radiative lifetime of the 4-Me-2,3dpq <sup>3</sup>MLCT state of the heteroleptic complexes might be comparable and the emission from both states can be combined. Then, the energy gap can become larger due to combination of the transition from the higher LUMO of dpq-based energy state and the transition to the lower HOMO of pq-based energy state. As a result, the energy gap is extended, leading to a blue shift in the emission wavelength.



Fig. 4. The HOMO and LUMO levels of the related iridium complexes.

#### 4. Conclusion

The heteroleptic iridium complexes,  $Ir(ppy)_2(4-Me-2,3-dpq)$ ,  $Ir(ppy)(4-Me-2,3-dpq)_2$ ,  $Ir(pq)_2(4-Me-2,3-dpq)$  and  $Ir(pq)(4-Me-2,3-dpq)_2$ , were synthesized and their luminescence properties were investigated. The PL maxima of  $Ir(ppy)_x(4-Me-2,3-dpq)_y$  and those of  $Ir(pq)_x(4-Me-2,3-dpq)_y$  were observed at 512 and 583 nm, respectively. Two different light-emitting mechanisms were suggested for these emissions.

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