Synthesis and Characterization of heteroleptic Iridium Complex with Phenylpyridine and 5'-methyl-diphenylquinoline

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Abstract

New heteroleptic tris-cyclometalated iridium complex, $Ir(ppy)_2(dpq-5CH_3)$, was prepared, where ppy and dpq-5CH$_3$ represent phenylpyridine and 2(5'-methyl)-4-diphenylquinoline, respectively. The heteroleptic iridium complex shows high luminescence efficiency by the intramolecular energy transfer from the energy absorbing ppy ligands to the luminescent dpq-5CH$_3$ ligand leading to a decrease on quenching or energy deactivation.

1. Introduction

Since organic light-emitting devices (OLED) were developed in 1987, materials for the devices and device fabrication have been extensively studied.[1-3] Greater success has been achieved in the development of a green emitter than that of a red one in fluorescent and phosphorescent displays. Organic light-emitting diodes (OLEDs) based on phosphorescent materials 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%. Thompson et al. have developed electrophosphorescent OLEDs with a high efficiency approaching 100% of the internal quantum efficiency, which utilize both singlet and triplet excitons produced at the emitting layer doped with the phosphorescent dopants.[4, 5] A heavy metal such as Ir or Pt in their complex forms is known to induce intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states. The spin-forbidden nature of radiative relaxation from the triplet excited state has then been changed to allow, resulting in high phosphorescent efficiencies. Thus, Ir complexes are known to have high photoluminescence (PL) efficiency and a relatively short excited state lifetime which minimizes quenching of triplet emissive states.[6, 7]. In order to improve the luminescence efficiency by avoiding T-T annihilation, the metal complex having a different species of plural ligands has been proposed.[8] The metal complex has been designed to transfer the energy of exciton smoothly between ligands placed in its excited states. When a metal complex having one luminescent ligand among three ligands is placed in the lowest excited state, the excited energy is transferred from the other two ligands to one luminescent ligand.

The purpose of the present study[9, 10] is to design and to synthesize the high efficient heteroleptic tris-cyclometalated iridium complex having different species of ligands, [$Ir(ppy)_2(dpq-5CH_3)$] for red OLED devices. In addition to the increase the phosphorescent efficiency, the phosphorescent mechanism of the heteroleptic iridium complex having different ligands is studied in comparison with those having the homoleptic iridium complexes having the same species of ligands.

2. Experimental section

2.1 Synthesis and characterization
All reagents were purchased from Aldrich Co., except iridium(III) trichloride hydrate ($IrCl_3 \cdot H_2O$), 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). The synthesis method is shown Fig. 1.

2.1.1. Synthesis of ligands (dpq and dpq-5CH$_3$)
6-methyl-2,4-diphenyl-quinoline (dpq-5CH$_3$): This compound was prepared similarly from the reaction of 5-methyl-2-aminobenzophenone (2.112g, 10.0 mmol)

with acetophenone (1.169 g, 10.0 mmol) in 30 ml of glacial acetic acid according to the procedure described above. (Yield: 2.42 g, 74%)
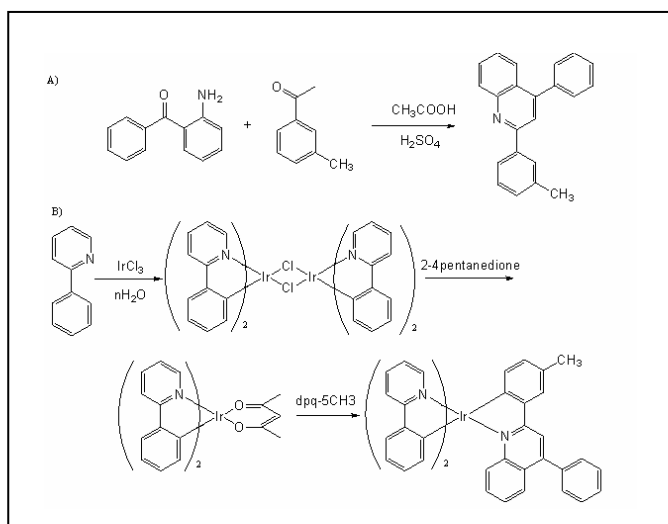
Fig. 1. (a) Synthesis of the dpq-5CH₃ ligand. (b) Synthesis of heteroleptic tris-cyclometalated iridium(III) complex [Ir(ppy)₂(dpq-5CH₃)].

2.1.2. Synthesis of heteroleptic Ir(III) complex : Ir(ppy)₂(dpq-5CH₃)
Cyclometalated Ir(III) μ-chloro-bridged dimers of the general formula, (ppy)₂Ir(μ-Cl)₂Ir(ppy)₂, were synthesized by the method reported by Nonoyama with slight modification.[11] IrCl₃•H₂O (1.490 g, 5 mmol) and H₂O (10 ml) were added to a solution of ppy (we bought this ppy ligands from sigma-aldrich. Product number=P33402-50G) (1.94 g, 12.5 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed at 120°C under argon for 12 h and then cooled to room temperature. The solution mixture was evaporated under vacuum slowly to obtain the crude product (ppy)₂Ir(μ-Cl)₂Ir(ppy)₂. The resultant precipitate was dissolved in dichloromethane and was filtered chromatographically on silica gel column with dichloromethane. The product portion was collected and dried in vacuum. (Ppy)₂Ir(μ-Cl)₂Ir(ppy)₂ (0.959g, 0.24 mmol) and 2,4-pentanedione (0.07 ml, d = 0.975, 0.84 mmol) were mixed with Na2CO3 (250 mg) in 2-ethoxyethanol (30 ml). The mixture was refluxed for 2 h. The solution was cooled to room temperature and the yellow solid was filtered. Ir(ppy)₂(acac) was obtained after the chromatographing on silica gel column with dichloromethane to yield a bright red powder. Ir(ppy)₂(acac) (845.14 mg, 1 mmol) and dpq or dpq-5CH₃ ligand (2 mmol) were dissolved in 20 ml

of glycerol and refluxed for 10 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 using CH₂Cl₂.

2.1.3. Synthesis of homoleptic Ir(III) complex : Ir(ppy)₃ and Ir(dpq-5CH₃)₃,
These complexes were prepared from Ir(acac)3 and the corresponding ligand by a reported procedure.[12] Ir(acac)₃ (245 mg, 0.5 mmol) and ppy (or dpq, dpq-5CH3) (2 mmol) were dissolved in 20 ml of glycerol and 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 using CH₂Cl₂.

2.2 UV-absorption and photoluminescence (PL) measurement
UV-Vis absorption spectra were measured on Hewlett Packard 8425A spectrometer. The PL spectra were obtained on Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of Ir(ppy)₂(dpq-5CH₃) were measured with a 10-5 M dilute solution in CH₂Cl₂.

2.3 Theoretical calculation
Calculations on the electronic ground states of Ir(ppy)3, Ir(ppy)₂(dpq-5CH₃), and Ir(dpq-5CH₃)₃ were carried out using Gaussian 98 with the B3LYP density functional theory (DFT). LANL2DZ [13] and 6-31G(d) [14] basis sets were employed for Ir and the other atoms, respectively. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). And the electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of metal 5d character in the occupied molecular orbitals related to those MLCT transitions. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the complexes, time-dependent density functional theory (TD-DFT) calculations using the B3LYP functional was performed at the respective ground-state geometry, where the basis set of ligands was changed to 6-31+G(d). (2 line spacing)

3. Results and discussion

The UV-vis absorption spectra of heteroleptic and homoleptic Ir(III) complexes were shown in Fig. 2. The overall profile of the absorption spectrum is red-shifted as ppy ligand was replaced with dpq-CH₃

ligand. Both [1]MLCT and [3]MLCT peaks are observed for these complexes. The absorption peaks of Ir(ppy)$_3$ is located at 380, 410, 460 and 490 nm. The absorption bands below 380 nm can be assigned to the spin-allowed [1]**π-π*** transition and the band around 410 nm to a spin-allowed [1]MLCT band and the band around 460 and 490 nm can be assigned to a spin-forbidden [3]MLCT band. MLCT absorption is allowed by the strong mixing between the π character of the ligand and the 5d character of the centric metal in HOMOs. MLCT absorption peaks of Ir(dpq-5CH$_3$)$_3$ are observed at 410, 457 and 516 nm. However, the MLCT absorption peaks of the heteroleptic Ir(ppy)$_2$(dpq-5CH$_3$) are observed at 410, 457, 490 and 516 nm where the MLCT peaks of both Ir(ppy)3 and Ir(dpq-5CH$_3$)$_3$ are located. In addition, the shape of absorption spectra of Ir(ppy)$_2$(dpq-5CH$_3$) are mixed with Ir(ppy)3 and Ir(dpq-5CH$_3$)$_3$. It provides the evidence that MLCT absorption of the Ir(ppy)$_2$(dpq-5CH$_3$) occurs at the ppy as well as dpq-5CH$_3$ ligands. Because HOMO energy level of Ir(dpq-5CH$_3$)$_3$ is similar with that of Ir(ppy)$_3$, MLCT absorption at both ppy and dpq-5CH$_3$ ligands is allowed as shown in Fig. 3.
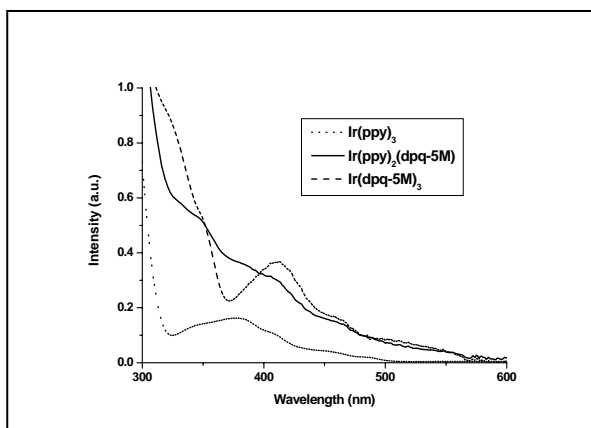
**Fig. 2. UV-vis absorption spectra of Ir(ppy)$_3$, Ir(dpq-5CH$_3$)$_3$ and Ir(ppy)$_2$(dpq-5CH$_3$).**
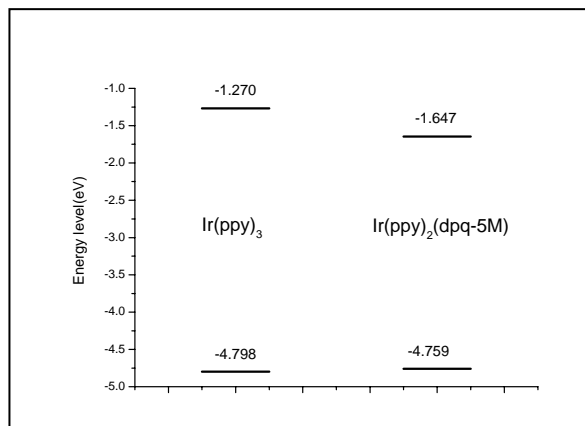
Fig. 3. HOMO and LUMO energy levels of Ir(ppy)$_3$ and Ir(ppy)$_2$(dpq-5CH$_3$).

The PL spectra of the homoleptic and heteroleptic complexes in CH$_2$Cl$_2$ also reflected their absorption patterns, exhibiting red-shifted emissions by dpq-5CH$_3$ substituted iridium complexes compared to Ir(ppy)$_3$ as shown in Fig. 4. Ir(ppy)$_2$(dpq-5CH$_3$) and Ir(dpq-5CH$_3$)$_3$ showed the maximum emission at 619 and 616 nm, respectively, while Ir(ppy)$_3$ exhibited the maximum emission at 513 nm. It is suggested that, as in the case of heteroleptic Ir(ppy)$_2$(dpq-5CH$_3$), the electron withdrawing groups, [Ir(ppy)$_2$], in Ir(ppy)$_2$(dpq-5CH$_3$) is expected to contribute to a significant decrease in the π^* acceptor orbital energy of the dpq-5CH$_3$ ligand and therefore, the energy of the [3]MLCT (dpq-5CH$_3$ $\leftarrow$ Ir) state in Ir(ppy)$_2$(dpq-5CH$_3$) becomes small, giving rise to markedly red-shifted phosphorescence.

In the luminescent mechanism of Ir(ppy)$_2$(dpq-5CH$_3$), the excitation energy is quickly inter-ligand energy transferred from two ppy ligands to one luminescent dpq-5CH$_3$ ligand. This is because the triplet energy state of Ir(ppy)$_3$ is higher than that of Ir(dpq-5CH$_3$)$_3$ and because the energy transfer time from ppy to dpq-5CH$_3$ within ns time scale is shorter than the radiative lifetime of Ir(ppy)$_3$. It allow a monochromatic luminescent color and to improve the luminescent by the efficient energy absorption.
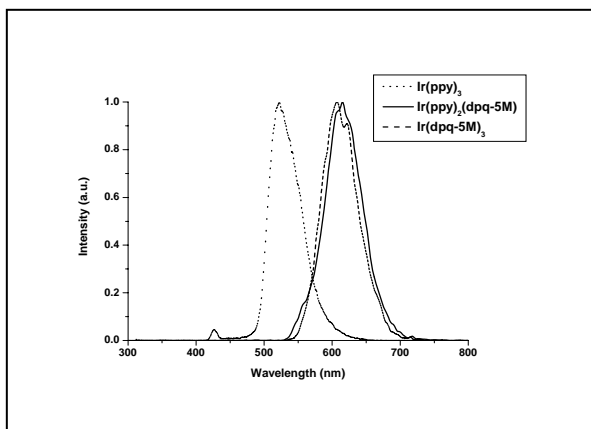
Fig. 4. PL spectra of Ir(ppy)$_3$, Ir(dpq-5CH$_3$)$_3$ and Ir(ppy)$_2$(dpq-5CH$_3$).

4. Summary

we report the detailed synthesis and photophysical properties of the phosphorescent tris-cyclometalated iridium (III) complexes having a different species of plural (C^N) ligands in order to improve the luminescence efficiency by avoiding T-T annihilation. Ir(dpq-5CH$_3$)$_3$ and Ir(ppy)$_2$(dpq-5CH$_3$) were studied their photophysical properties for the application in OLEDs. In the case of Ir(ppy)$_2$(dpq-5CH$_3$), the excited energy is absorbed from both ppy and dpq-5CH$_3$ ligands and the excited energy of ppy is transferred to dpq-5CH$_3$ ligand. As a result, Ir(ppy)$_2$(dpq-5CH$_3$) allows a high efficiency luminescence and a red emission color originated from dpq-CH$_3$ ligand because it harvest the excited energy from both two ppy and dpq-CH$_3$ ligands and it improve the luminescence efficiency by avoided the T-T annihilation by decreasing the number of the luminescent ligand.

5. References

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