

Synthesis and Photoluminescence of a New Red Phosphorescent Iridium(III) Quinoxaline Complex

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Abstract: A new cyclometalated iridium(III) complex with the formula $[\text{Ir}(\text{DPQ})_2(\text{acac})]$ (DPQ=2,3-diphenylquinoxaline; acac=acetylacetonate) was prepared. The structure of the complex was confirmed by Elemental Analysis (EA), ^1H NMR, and mass spectroscopy (MS). The UV-vis absorption and photoluminescent properties of the complex were investigated.

Keywords: Phosphorescence, iridium complexes, charge transfer, 2,3-diphenylquinoxaline, luminescence.

Much attention has been paid to the phosphorescent materials in recent years for their potential application as highly efficient electroluminescent (EL) emitters in organic light emitting diodes (OLEDs)¹⁻². Heavy metal complexes, particularly those containing Pt and Ir, where strong spin orbit coupling leads to singlet-triplet state mixing, can result in high efficiency electrophosphorescence in OLED³⁻⁵. Among the many kinds of metal complexes, iridium complexes are the most effective and show intense phosphorescence at room temperature⁶. The iridium complexes used in electroluminescent (EL) devices are octahedral with a 3^+ oxidation state and the observed luminescence is the emission from a triplet MLCT(metal-to-ligand charge-transfer) state or a ligand-based $^3(\pi-\pi^*)$ excited state. The organic ligands in the complexes are generally a heterocycle that coordinates to the metal center *via* the formation of an Ir-N and Ir-C bond. Both the EL efficiency and the emission wavelength of Ir complex based devices are affected greatly by this organic ligand⁷. Thus, the design and synthesis of new organic ligands for Ir complexes is highly desirable in order to improve the efficiency and the color purity of Ir complex based EL devices. In this paper, we will report the synthesis and luminescence property of a new red phosphorescent iridium(III) quinoxaline complex.

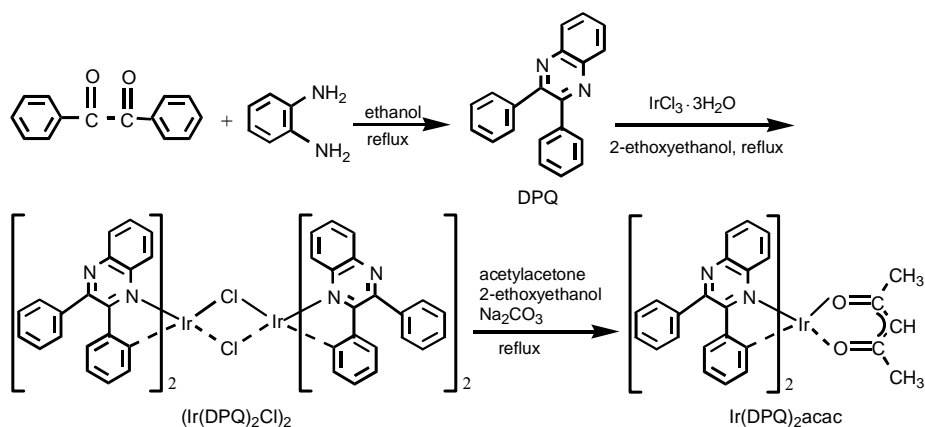
Experimental

Preparation of 2,3-diphenylquinoxaline (DPQ): DPQ (**Scheme 1**) was conveniently prepared from benzil and diamine in refluxing ethanol⁸.

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Preparation of Ir(DPQ)₂Cl₂: DPQ (1.24 g, 4.4 mmol) was dissolved in 2-ethoxyethanol (20 mL) in round-bottomed flask. Iridium trichloride hydrate [IrCl₃ · 3H₂O] (0.705 g, 2 mmol) and water (6 mL) were then added to the flask. The reaction mixture was refluxed under nitrogen atmosphere for 24 h. After cooling to room temperature, the precipitate was collected by suction and washed with ethanol, acetone, and then dried in vacuum to give a cyclometallated Ir-chloro-bridged dimer (Ir(DPQ)₂Cl)₂ (**Scheme 1**) as black brown powder.

Scheme 1 The synthetic routes of [Ir(DPQ)₂(acac)]



Preparation of Ir(DPQ)₂(acac): (Ir(DPQ)₂Cl)₂ (0.7 g, 0.44 mmol), acetylacetonone (0.12 mL, 1.1 mmol), and sodium carbonate (0.32 g, 3.0 mmol) were refluxed under nitrogen atmosphere in 2-ethoxyethanol (10 mL) for 12 h. After cooling to room temperature, the precipitate was filtrated and washed with water, ethanol, and ether to give the desired product Ir(DPQ)₂(acac). Yield 78.6%. ¹H-NMR (CDCl₃, δppm) 1.62(s, 6H), 4.69(s, 1H), 6.44(d, 2H, J=8Hz), 6.51(t, 2H, J=8Hz), 6.61(t, 2H, J=8Hz), 7.07(d, 2H, J=8Hz), 7.48(t, 2H, J=8Hz), 7.63(m, 8H), 8.10(s, 4H), 8.13(d, 2H, J=8Hz), 8.26(d, 2H, J=8Hz). Anal. calcd. for C₄₅H₃₃IrN₄O₂(%): C:63.2, H:3.89, N:6.56. Found(%): C:62.6, H:3.94, N:6.28. HRMS: Calcd. for C₄₅H₃₃IrN₄O₂ 852.22; Found 852.34.

¹H-NMR spectra were measured on a Bruker ARX 400 spectrometer in CDCl₃ using tetramethylsilane as an internal reference. UV-Vis absorption spectra were recorded using a Shimadzu UV-2550 spectrophotometer. Emission and excitation spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. Elemental analysis was performed on an Elementar Vario EL instrument. Mass spectra were measured on a Bruker BIFLEX III mass spectrophotometer.

Results and Discussion

The UV-vis absorption spectra for free ligand and the iridium complex are shown in **Figure 1**. There are three major absorptions at 230, 245, and 343 nm in the UV-Vis spectrum of the free ligand. The former two bands appear to be (π - π^*) absorptions, and

the latter one to be ($n-\pi^*$) absorption of the free ligand. In the UV-Vis absorption spectrum of the Ir complex, there are five major absorptions at 236, 285, 378, 476, and 625 nm. The former three bands resemble the spectrum of the free ligand, whereas the latter two absorptions are likely due to $^1\text{MLCT}$ and $^3\text{MLCT}$.⁶

Figure 1 The UV-Vis absorptions of ligand and the complex in CH_2Cl_2 at room temperature (concentration = 10^{-5} mol/L)

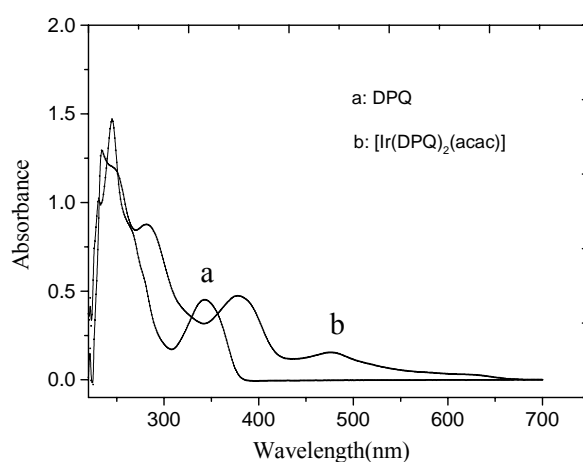
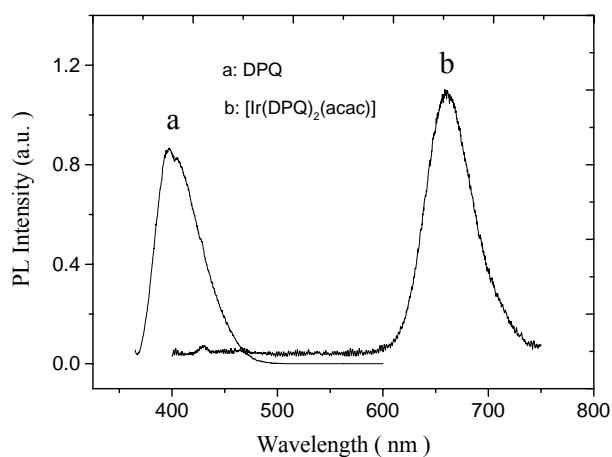


Figure 2 The photoluminescence spectra of ligand and the complex in CH_2Cl_2 at room temperature (concentration = 10^{-5} mol/L, excitation at 378 nm).



The photoluminescence spectra for the free ligand and the iridium complex are shown in **Figure 2**. It can be seen from **Figure 2** that the Ir complex shows strong photoluminescence at 660 nm, which is much red shifted from that of the free ligand (at 397 nm). From this observation and by comparison with those of known iridium

complexes^{6,9}, it is clear that the observed emission of the iridium complex is phosphorescent in nature.

In conclusion, we have successfully synthesized a new ligand, DPQ, and have used the ligand to synthesize the iridium complex [Ir(DPQ)₂(acac)]. The complex shows strong photoluminescence at 660 nm. Further studies on its electrophosphorescence property are in progress.

Acknowledgments

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