

Synthesis and Photoluminescence of a Novel Iridium Complex (BuPhOXD)₂Ir(acac) with Unit of 1, 3, 4-Oxadiazole

Zhong Lian WU¹, Mei Xiang ZHU¹, Yu LIU^{1,2}, Jian LIU¹, Jian Ren LI¹,
Yu Ping YANG¹, Quan GAN¹, Wei Guo ZHU^{1*}

¹College of Chemistry, Xiangtan University, Xiangtan 411105

²Department of Chemistry, Qiongzhou University, Wuzhishan 572200

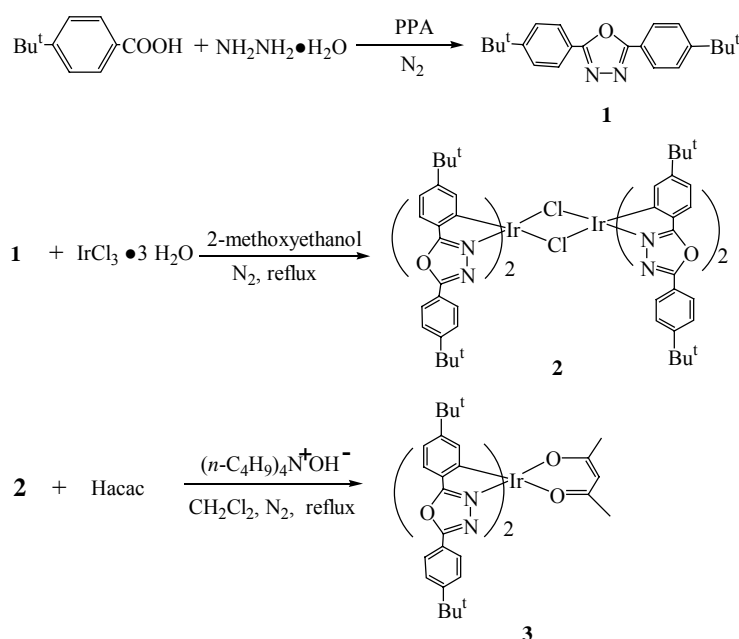
Abstract: A novel cyclometalated iridium complex with 1, 3, 4-oxadiazole moiety was synthesized and characterized. Its UV and photoluminescent properties were studied. The strong UV absorption intensity around 462 nm attributed to spin-forbidden triplet metal–ligand charge transfer band and photoluminescence at 518 nm were observed. This indicated that achieved iridium complex could be used as an efficient electrophosphorescent material.

Keywords: Iridium complex, 1, 3, 4-oxadiazole, synthesis, photoluminescence.

Organic/polymer light-emitting diodes(LEDs) have been attractive worldwide because of their potential application to large area displays and backlights for recent years. Much effort has been made to improve the emission efficiency for organic/polymer LEDs by employing high-efficiency emission materials and novel device architectures. According to the spin statistical rule, recombination of charge carriers can produce both singlet and triplet exciton, so fluorescence-based LEDs have only an upper limit for the internal quantum efficiency (QE_{in}) of 25%. However, phosphorescence-based LEDs using phosphorescent emitter can reach 100% of QE_{in} due to enough intensities of both singlet and triplet exciton to emit light in principle. It is considered to be a promising candidate to achieve high emission efficiency.

Cyclometalated complexes of Pt(II)¹, Os(II)² and Ir(III)³⁻⁶ were widely employed as electrophosphorescent emitters. Among these complexes, iridium complex was one of the most effective emitters as it has relatively short lifetime between 1 to 14 μ s. Much highly efficient phosphorescent polymer LEDs based on these guest metallic complexes doped into host matrix have been reported. Gong *et al.* reported the devices fabricated by doping tris[9, 9-dihexyl-2-(pyridyl-2')fluorene]iridium(III) [Ir(DPF)₃] into a blend of poly(vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1, 3, 4-oxadiazole (PBD) had an external quantum efficiency (QE_{ext}) as high as 10% for yellow–green light emission⁷. Zhu *et al.* reported QE_{ext} of 5.1% and luminous efficiency (LE) of 12cdA⁻¹ by employing *fac*-tris(2-(4-*tert*-butyl)-phenyl pyridine) iridium [Ir(Bu-PPy)₃]

* E-mail: zwg18@263.net

Scheme 1 The synthesis of BuPhOXD and (BuPhOXD)₂Ir(acac)

doped into poly(2-(6'-cyano-6'-methylheptyl-oxy)-1,4-phenylene) (CN-PPP) for green light emission⁶. It is obvious that the structure of cyclometalated organic ligand of iridium complexes influences both the EL efficiency and the emission wavelength in phosphorescence-based polymer LEDs.

The derivatives of 1,3,4-oxadiazole were a type of excellent electron-transporting and hole blocking materials in LEDs⁸. Hence, we synthesized a novel bis-cyclometalated iridium complex **3**, iridium(III) bis[2,5-bis(4-*tert*-butylphenyl)-1,3,4-oxadiazole(C², N)] acetylacetonate [(BuPhOXD)₂Ir(acac)], containing 2,5-bis(4-*tert*-butylphenyl)-1,3,4-oxadiazole (BuPhOXD) ligand **1**, expecting to adjust hole-electron balance property and increase the emission efficiency for phosphorescence-based polymer LEDs, employing oxadiazole moiety into iridium complexes. The photoluminescence (PL) and ultraviolet (UV) properties of (BuPhOXD)₂Ir(acac) were studied at the first time. It was found that this new iridium complex exhibited excellent PL property and good solvency. The synthesis of BuPhOXD and (BuPhOXD)₂Ir(acac) is depicted in **Scheme 1**.

Experimental

2,5-Bis(4-*tert*-butylphenyl)-1,3,4-oxadiazole BuPhOXD **1** was synthesized according to literature⁹.

Synthesis of (BuPhOXD)₂Ir₂Cl₂ **2**: Iridium trichloride hydrate (18 mg, 0.51 mmol), compound **1** (500 mg, 1.5 mmol), sodium chloride (105 mg, 1.8 mmol, benchmark) and 2-methoxyethanol (15 mL) were added into a three-neck flask (50 mL). The mixture was refluxed for 24 h under inert gas atmosphere, then cooled to room temperature, and the

colored precipitate was filtrated and washed with anhydrous ethanol. The yielded crude product was dried in vacuum and purified by column chromatography (silica gel, methanol) to provide a yellow powder with yield of 63.0%. ¹H NMR (400 MHz, CDCl₃, δ_{ppm}): 7.87(d, 8H, J=8.4 Hz), 7.43(d, 4H, J=8.4 Hz), 7.30(d, 8H, J=8.4 Hz), 6.89(dd, 4H, J=1.6, 7.8 Hz), 6.48(d, 4H, J=1.2 Hz), 1.34(s, 36H), 0.98(s, 36H).

Synthesis of (BuPhOXD)₂Ir(acac) **3**: A solution of **2** (147 mg, 0.082 mmol), acetylaceton (19 mg, 0.19 mmol) and tetrabutylammionium hydroxide (26 mg, 0.19 mmol) in dichloromethane (10 mL) was refluxed for 10 h under inert gas atmosphere. Then the solvent was evaporated in vacuum to give yellow solid. The crude product was purified by column chromatography (silica gel, dichloromethane) to obtain an orange yellow powder in yield of 85%. ¹H NMR (400 MHz, CDCl₃, δ_{ppm}): 8.15(d, 4H, J=8.4 Hz), 7.59(d, 4H, J=8.4 Hz), 7.48(d, 2H, J=8 Hz), 6.94(dd, 2H, J=1.6, 7.8 Hz) , 6.64(d, 2H, J=1.2Hz), 5.26(s, 1H), 1.90(s, 6H), 1.40(s, 18H), 1.11(s, 18H). IrC₄₉H₅₇N₄O₄ Calcd. (%) C 61.42, H 6.00, N 5.85. Found(%): C 60.61, H 6.09, N 5.59.

GC-MS data were obtained using Trace GC-MS-2000 Series System (Finnigan). ¹H NMR was performed on INOVA-400. The UV-Visable absorption spectra of solution of the ligand and iridium complexes were recorded with a HP-8453 UV Visible System. The PL spectrum was recorded on a fluorescence spectrophotometer (HITACHI-850). Elemental analysis(CHN) was measured on Harrios Elemental Analysis Instrument.

Results and Discussion

Figure 1 shows UV-Vis spectrum of BuPhOXD **1** and (BuPhOXD)₂Ir(acac) **3** in dichloromethane solution at 298 K. The intense absorption bands were observed in ultraviolet part of the spectra from 200 to 400 nm. The UV absorption peaks in dichloromethane were located at 294 nm from ligand **1**, and 294, 411 and 462 nm from iridium complex **3**, respectively. Comparing with UV spectrum of ligand **1**, the peak of iridium complex **3** at 294 nm was observed due to π-π* electron transition of ligand **1**, and the around 368nm was assigned to spin-allowed metal –ligand charge transfer band (¹MLCT).

Figure 1 UV-Vis spectrum of compound **1** and **3**

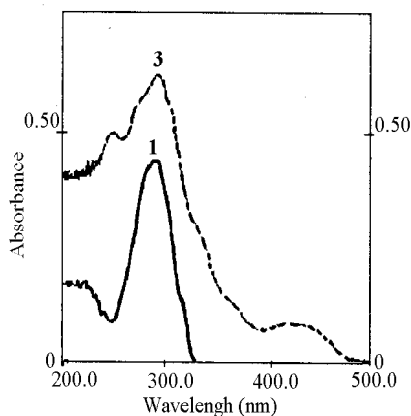
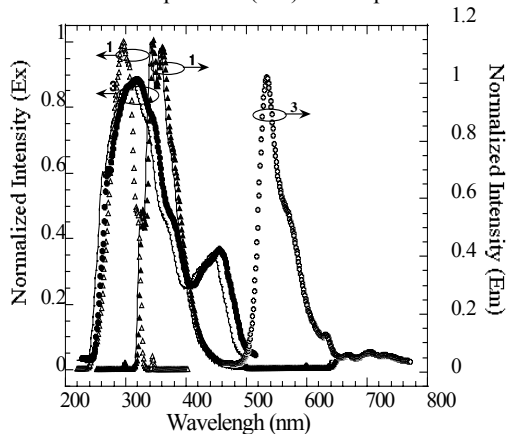


Figure 2 The excitation spectrum (Ex) and PL spectrum (Em) of compound **1** and **3**



Otherwise this cyclometalated complex **3** has the strong UV absorption intensity around 462 nm, which was typical for the spin-forbidden $^3\text{MLCT}$ as reported in the literature¹⁰. This implies that an efficient spin-orbit coupling arises in cyclometalated iridium complexes **3**.

The excited and photoluminescence (PL) spectrum of ligand **1** and complex **3** in chloroform were recorded, which were shown in **Figure 2**. Comparing PL spectrum of ligand **1** with complex **3**, ligand **1** has a maximum emission peak at 342 nm with shoulder peak at 356 nm, however, its iridium complex **3** has a maximum emission peak at 518 nm on the irradiation with 308 nm light. The PL resulted from triplet emission of iridium complex **3** based on the literature¹¹.

In conclusion, a novel cyclometalated iridium complex, $(\text{BuPhOXD})_2\text{Ir}(\text{acac})$, was achieved. Its UV absorption at 294, 411 and 462 nm and PL at 518 nm were observed. This indicated that it might be used as an efficient electrophosphorescent material. The electrophosphorescent properties of the iridium complex in phosphorescent polymer LEDs using iridium complex as guest doped into polymer host are investigated in progress.

Acknowledgments

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