

## A new synthesis method and photophysical properties of Ir(C<sup>^</sup>N)<sub>3</sub> cyclometalated iridium phosphorescent complexes

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Received September 25, 2015, Revised October 13, 2015

A new convenient synthesis method with excellent yields for Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub> is developed using [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)] as an efficient starting material. Their structures are fully characterized by elemental analysis, <sup>1</sup>H-NMR and ESI-MS. The photophysical properties of both compounds are studied by UV-visible spectra and photoluminescence spectra.

**Keyword:** iridium, cyclometalated complexes, synthesis, phosphorescent, Ir(C<sup>^</sup>N)<sub>3</sub>.

### INTRODUCTION

Neutral cyclometalated iridium phosphorescent complexes with Ir(C<sup>^</sup>N)<sub>3</sub> and Ir(C<sup>^</sup>N)<sub>2</sub>(LL) types are the most promising phosphorescent materials in organic light-emitting devices (OLEDs)[1-4]. Tris-cyclometalated iridium complexes have attracted considerable attention due to a potential application in OLED [5]. Several experimental procedures[5-6] have been developed for their synthesis using IrCl<sub>3</sub>·nH<sub>2</sub>O, Ir(acac)<sub>3</sub>, [Ir(acac)(coe)<sub>2</sub>] or the chlorinated bridged dimer as a precursor, their synthesis often requires harsh reaction conditions to proceed so that they can not be widely be applied in OLED. Therefore, developing the new synthesis route for Ir(C<sup>^</sup>N)<sub>3</sub> type phosphorescent complexes is very worthy and interesting. [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)] has a rich coordination and reaction chemistry due to the presence of a coordinated water ligand [7-9], which has a better reaction activity than Ir(acac)<sub>3</sub> for preparing Ir(C<sup>^</sup>N)<sub>3</sub> type phosphorescent complexes. In this contribution, a new convenient synthesis method with excellent yields for Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub> is developed using [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)] as a new precursor.

### EXPERIMENTAL

#### General considerations

All manipulations were performed in an atmosphere of high purity argon using conventional Schlenk techniques. All reagents and solvents in this study were used without further purification. [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)] was synthesized

from IrCl<sub>3</sub>·nH<sub>2</sub>O and NaHCO<sub>3</sub> in refluxing acetylacetone according to the literature[10]. NMR spectra were obtained on a Bruker AV400 using tetramethylsilane as an internal reference. Mass spectrometry studies were carried out on an Autospec 3000 Instrument. Elemental analyses for C, H, and N were performed using a Carlo-Ebra Instrument. UV-visible absorption spectra were measured on a Cary 50Bio spectrophotometer. The photoluminescence (PL) spectra were recorded on an F-7000 spectrometer in CH<sub>2</sub>Cl<sub>2</sub>.

#### Synthesis of Fac-Ir(ppy)<sub>3</sub>

[(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)] (2 g, 3.94 mmol) and 2-phenylpyridine (3.67 g, 23.66 mmol) were refluxed under an inert gas atmosphere in 50 mL of glycerol for 24 h. After the mixture was cooled to room temperature, 50 mL of 1M HCl solution and 50 ml of methanol were added and stirred for 30 min and then filtered to yield the crude product. The crude product was flash chromatographed on a silica column using dichloromethane to yield 80% (2.06 g) product. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>), ppm: 8.52(d, 1H), 7.84(d, 1H), 7.72(t, 1H), 7.52(d, 1H), 7.13(t, 1H), 6.77(t, 1H), 6.63(t, 1H), 6.27(d, 1H). ESI-MS: m/z = 655(M+1), 501(Ir(ppy)<sub>2</sub>+1) Anal. Found: C 60.45, H 3.62, N 6.45. Calcd: C 60.53, H 3.69, N 6.42.

#### Synthesis of Ir(piq)<sub>3</sub>

The synthesis procedure of Ir(piq)<sub>3</sub> was the same for Ir(ppy)<sub>3</sub> except that 1-phenylisoquinoline was used in place of 2-phenylpyridine in the same molar amount: yield 72% (2.28 g). Anal. Found: C 67.12, H 3.74, N 5.20. Calcd: C 67.15, H 3.76, N 5.22. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>), ppm: 8.92(d, 1H), 8.16(d, 1H), 7.93(t, 1H), 7.78(t, 2H), 7.48(d, 1H),

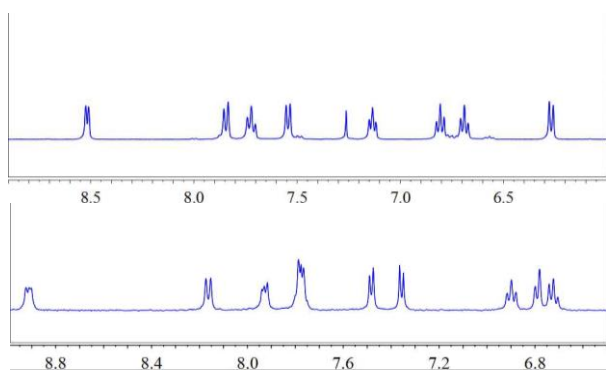
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7.36(d, 1H), 6.90(t, 1H), 6.79(d, 1H), 6.72(t, 1H).  
ESI-MS: m/z = 827(M+23), 425(M/2+23).

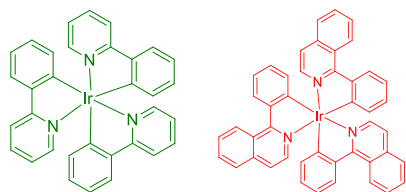
## RESULTS AND DISCUSSION

### Synthesis and characterization of Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub>

Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub> were synthesized by reacting [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)] with corresponding cyclometalated ligands (see scheme 1). And their structures were confirmed by element analysis, ESI-MS (see experiment section) and <sup>1</sup>H-NMR (see Figure 1). The results match those reported for Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub>[11-12] and the molecule structures shown in Figure 2.



**Fig. 1.** <sup>1</sup>H-NMR of Ir(ppy)<sub>3</sub> in CDCl<sub>3</sub> (above) and Ir(piq)<sub>3</sub> in DMSO-*d*<sub>6</sub> (below).

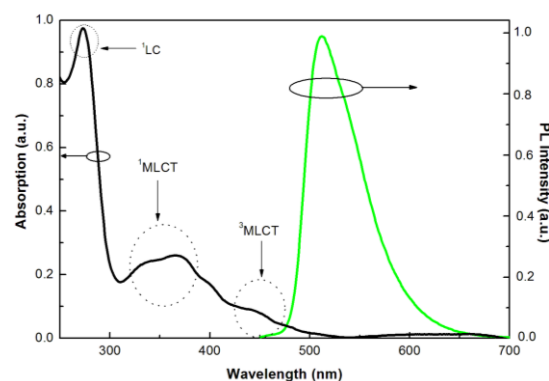


**Fig. 2.** Molecular structures of Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub>.

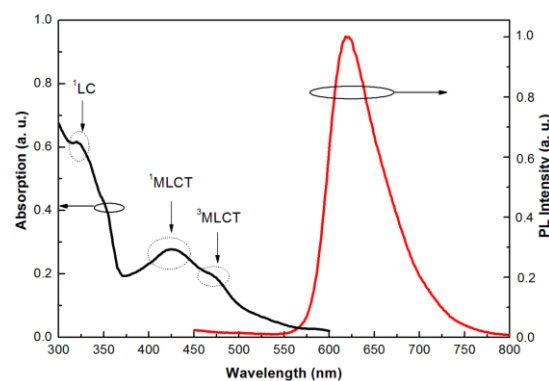
### Photophysical properties of Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub>

The absorption and emission spectroscopic behaviors of Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub> are studied at room temperature in CH<sub>2</sub>Cl<sub>2</sub>. Figure 3 shows the UV-vis absorption and photoluminescence spectra of Ir(ppy)<sub>3</sub>. The absorption band observed at 273 nm is related to spin-allowed  $\pi$ - $\pi^*$  transitions (corresponding to ligand centered states, <sup>1</sup>LC) of the cyclometalated ppy ligands. The broad and unresolved absorption band at lower energy,

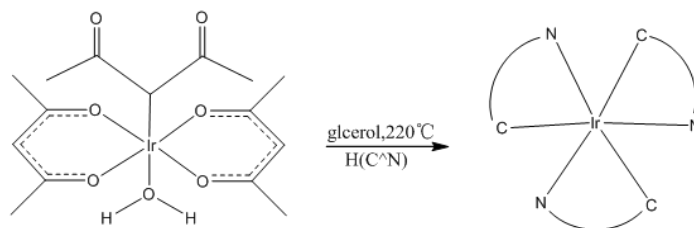
peaking at 367nm, is assigned to spin-allowed d- $\pi^*$  transitions (corresponding to metal-to-ligand charge transfer states, <sup>1</sup>MLCT), whereas absorptions at wavelengths between at 430 nm and 500 nm involve <sup>3</sup>MLCT states. The emission at ambient temperature shows a maximum peak at 512 nm. The UV-vis absorption and photoluminescence spectra of Ir(piq)<sub>3</sub> are also given in Figure 4. In the range below about 350 nm, the band is related to spin-allowed  $\pi$ - $\pi^*$  transitions (<sup>1</sup>LC), and the two lower-energy bands appear in the region of about 370-550 nm are tentatively assigned to the <sup>1</sup>MLCT and <sup>3</sup>MLCT transitions. The maximum emission peak of Ir(piq)<sub>3</sub> is at 619 nm.



**Fig. 3.** Absorption and photoluminescence spectra of Ir(ppy)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature.



**Fig. 4.** Absorption and photoluminescence spectra of Ir(piq)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature.



**Scheme 1.** Synthesis route of Ir(C<sup>N</sup>)<sub>3</sub> type phosphorescent complexes.



Comparing the absorption and emission spectra of Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub>, both compounds show similar spectral features which agree with the reports in the literature [12-15]. Differently, the absorption and emission peaks of Ir(piq)<sub>3</sub> have a red shift due to the bigger conjugation degree of piq than that of ppy.

## CONCLUSION

In conclusion, The advantages of the herein described synthetic procedures are that the complexes Ir(ppy)<sub>3</sub> and Ir(piq)<sub>3</sub> can be obtained in high yields by a convenient method starting from [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)]. The general usefulness of the described procedures for the synthesis of closely related cyclometalated iridium complexes will be examined by us in the near future.

**Acknowledgments:** The authors are grateful to Yunnan Provincial Science Foundation (Grant No. 2015IB019) and Kunming Science Foundation (Grant No.2016KJJH059) P.R.China for the financial support.

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## НОВ МЕТОД ЗА СИНТЕЗАТА И ФОТО-ФИЗИЧНИ СВОЙСТВА НА Ir(C<sup>N</sup>)<sub>3</sub> ЦИКЛОМЕТАЛИРАНИ ИРИДИЕВИ ФОСФОРЕСЦЕНТНИ КОМПЛЕКСИ

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<sup>2</sup>Държавна ключова лаборатория по нови технологии за пълно оползотворяване на метали от платиновата група, Кунминг'ска лаборатория за благородни метали, Кунминг 650106, Юнан, КНР

Постъпила на 25 септември 2015 г.; коригирана на 13 октомври 2015 г.

(Резюме)

Създаден е нов удобен метод за синтеза на Ir(ppy)<sub>3</sub> и Ir(piq)<sub>3</sub> с отличен добив. Като изходен материал е използван [(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)Ir(H<sub>2</sub>O)]. Тяхната структура е напълно охарактеризирана чрез елементен анализ, <sup>1</sup>H-NMR и ESI-MS. Фотофизичните свойства на двете съединения са изучени чрез UV-Vis спектри и фотолуминисцентни спектри.