

## Synthesis and luminescent properties of a novel green-emitting iridium complex

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**Abstract.** A novel cyclometalated iridium complex bis[(4-(2-(4-Diphenylamino -phenyl)-benzoinidazol-1-ylmethyl)-phenyl)-diphenyl-amine]iridium(acetylacetonate) Ir(DBPA)<sub>2</sub>(acac) is designed and synthesized, and the thermo-stability and photo-physical properties of iridium complex Ir(DBPA)<sub>2</sub>(acac) are researched in detail. The complex is functionalized by a bulky non-planarity substituent, thus the phosphorescent concentration quenching in solid state is substantially suppressed, and Ir(DBPA)<sub>2</sub>(acac) exhibits bright green-emitting in both solution and solid. The maximum emission peak in pure solid is about 516 nm, which is slightly blue-shifted in comparison with that in solution. Moreover, the complex Ir(DBPA)<sub>2</sub>(acac) exhibits high photoluminescent efficiency and short excited lifetime, indicating it has potential application in fabricating nodoped electrophosphorescence device.

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**Key words:** molecule design, iridium complex, photoluminescence

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## 1 Introduction

Nodoped phosphorescent organic light-emitting devices (NPOLEDs) have received an increasing interest because they can simplify the fabrication process and decrease the cost for mass production compared with dopant counterparts [1, 2]. Unfortunately, phosphorescent-based emitters have some intrinsic disadvantages, such as concentration quenching and triplet-triplet (T-T) annihilation, which make them become either weakly emissive or even not emissive at all in solid state [3-5], and several phosphorescent materials are synthesized as neat emitters [6, 7]. A solution to the NPOLEDs, either in materials or devices perspective, is highly needed. Recently, many researchers have turned to explore the possibility of new phosphor materials which can be vacuum-deposited as pure films with

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highly luminescent efficiency [8-10]. For example, Burn and co-workers have developed a class of phosphorescent dendrons composed of an iridium core, meta-bonded phenylene dendrons, and 2-ethylhexyloxy surface groups. However, the first-generation dendrons are not sufficient enough to prevent the interactions between the emissive cores, and higher-generation dendrons usually cause significant reduction in charge mobility [8, 9]. Huang *et al.* synthesized a new iridium complex containing carbazole functionalized  $\beta$ -diketonate and applied it in NPOLEDs successfully [10]. Moreover, the performances of these recent reported NPOLEDs are comparable with, or better than, the doped OLEDs reported to date. It is thus an important consideration of further obtaining emitters with suppressed self-quenching effect.

In this paper, we attempted to synthesize a green emitting iridium(III) complex bis[(4-(2-(4-Diphenylamino-phenyl)-benzoinidazol-1-ylmethyl)-phenyl)-diphenylamine]iridium (acetylacetonate) [Ir(DBPA)<sub>2</sub>(acac)] with reduction of concentration quenching effect, which is suitable for NPOLEDs. We designed this molecule to have bulky non-planarity substituent, thus the phosphorescent concentration quenching in solid state can be substantially suppressed, and hole transporting group, triphenylamine, was introduced to the molecule to increase the hole-transporting property. The chemical structure and synthetic route of iridium (III) complex Ir(DBPA)<sub>2</sub>(acac) are depicted in Fig. 1. Even as our anticipation, the iridium complex Ir(DBPA)<sub>2</sub>(acac) exhibits highly efficiency phosphorescent emission in solid state, and we discussed its photoluminescent (PL) properties in detail, which indicating that it has potential application in NPOLEDs.

## 2 Experiments

### 2.1 Apparatus

<sup>1</sup>H NMR spectra were recorded on a Bruker AVANVE 300 MHz spectrometer. Element analyses were performed using a Vario Element Analyzer. The UV-visible absorption spectra was obtained on a shi-madzu-UV-3101 scanning spectrophotometer. Steady state PL spectra were measured with a RF-5301Pc spectrofluorophotometer. Thermalgravimetric analyses (TGA) was performed using an SDT 2960 Simultaneous DSC-TGA of TA instruments, and the heating rate was 10°C min<sup>-1</sup> under nitrogen. The PL decays of the complex in solution and pure solid excited by laser pulse at wavelength 355 nm were measured by a quanta ray DCR-3 pulsed Nd: YAG laser system. The PL quantum yield of the complex was measured in dilute solution by comparing fluorescence intensities (integrated areas) of a standard sample (quinine sulfate) and the unknown sample according to the following equation:

$$\phi_{unk} = \phi_{std} \cdot I_{unk} / A_{unk} \cdot A_{std} / I_{std} \cdot \eta_{unk}^2 / \eta_{std}^2 \quad (1)$$

where  $\phi_{unk}$  is the luminescence quantum yield of the sample;  $\phi_{std}=0.546$  is the luminescence quantum yield of quinine sulfate [11],  $I_{unk}$  and  $I_{std}$  are the integrated fluorescence

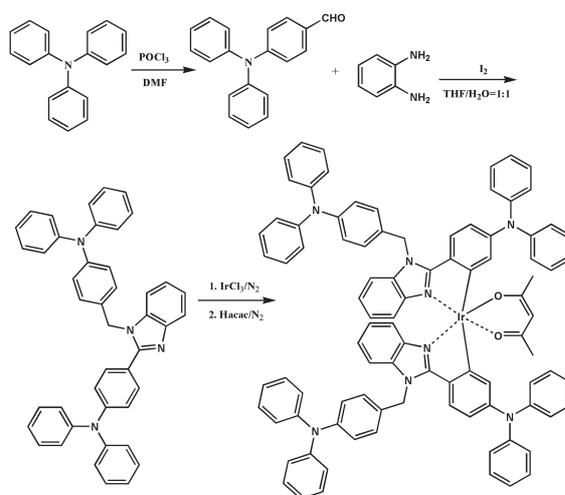


Figure 1: The chemical structure and synthetic route of iridium (III) complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$ .

intensities of the unknown sample and quinine sulfate, respectively;  $A_{unk}$  and  $A_{std}$  are the absorbance of the unknown sample and quinine sulfate at the wavelength of excitation. The  $\eta_{unk}$  and  $\eta_{std}$  are the refractive indices of the corresponding solvents (pure solvents were assumed).

## 2.2 Synthesis

**4-Diphenylamino-benzaldehyde:** Phosphorus oxychloride (3.8 mL, 0.04 mol) was added dropwise to a stirred 6.2 mL (0.08 mol) of *N, N*-dimethyl formamide (DMF) at 0°C. The mixture was stirred at 0°C for 1 h and additionally stirred at room temperature for 1 h. After the addition of 10 g (0.04 mol) of triphenylamine dissolved in dichloroethane, the mixture was stirred at 90°C for 2 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with 2 N NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column (ethyl acetate/*n*-hexane) 1/3 to produce 6.2 g of yellowish solid, 60 % yield.  $^1\text{H}$  NMR (acetone- $d_6$ , 300 MHz)  $\delta$  [ppm]: 10.12 (s, 1H), 7.72 (d, 2H), 7.43-7.37 (t, 4H), 7.24-7.17 (t, 6H), 6.98-6.94 (d, 2H).

**DBPA [12]:** 1,2-phenylenediamine (10.0 mmol), 4-Diphenylamino-benzaldehyde (20.0 mmol), and iodine (0.2 mmol) was dissolved in 20 mL THF:H<sub>2</sub>O (*V/V*=1:1). The resulting mixture was stirred at 80°C for 5 h, then extracted with CH<sub>2</sub>Cl<sub>2</sub> and purified by column chromatography on silica gel with ethyl acetate/petroleum ether (*V/V*=1:10) as eluent to yield white powder. Yield: 5.263 g (85 %).  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  [ppm]: 5.427 (s, 2H), 6.984 (d, 6H), 7.046 (d, 2H), 7.084 (m, 4H), 7.116 (m, 8H), 7.150 (m, 3H), 7.232 (m, 3H), 7.308 (d, 6H).

$\text{Ir}(\text{DBPA})_2(\text{acac})$  [12]: a flask containing  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (243 mg, 0.68 mmol) and 2.5-3 equiv each cyclometalated ligand DBPA was added a 3:1 mixture of 2-ethoxyethanol and water (25 mL). Under a  $\text{N}_2$  atmosphere, the mixture was refluxed for 48 h and cooled to room temperature. A small quantity of water was added to precipitate an orange solid. Then the precipitate was washed with ethanol and hexane for several times. The dried chloro-bridged dimer was mixed with anhydrous sodium carbonate (216 mg, 2.04 mmol) in a two-neck flask. 2-ethoxyethanol (25 mL) and Hacac (202 mg, 2.04 mmol) were added and the mixture was refluxed for 16 h. The solution was cooled to room temperature and a small quantity of water was added. The colored solid was collected by filtration. The crude product was chromatographed using an appropriate eluent to produce a pure sample of iridium complex. Yield: 0.830 g (80 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  [ppm]: 2.07 (d, 6H), 3.547 (m, 1H), 5.549 (s, 4H), 6.850 (d, 6H), 6.854 (d, 6H), 6.902 (m, 4H), 7.037 (m, 16H), 7.183 (m, 8H), 7.196 (m, 10H), 7.203 (d, 12H). Anal. Calcd for  $\text{C}_9\text{H}_7\text{N}_3\text{O}_2\text{Ir}$ : C 73.16, H 4.82, N 7.34. found: C 72.93, H 5.17, N 7.58.

### 3 Results and discussion

#### 3.1 Thermal property

TGA was performed on complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$  in  $\text{N}_2$  atmosphere to investigate its stable characteristics, and the TGA trace is presented in Fig. 2. Complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$  began to lose weight when it was heated up to  $277^\circ\text{C}$ , which should be attributed to the loss of the acac ligand (theoretical weight loss 6.49%, observed 8.32%).  $\text{Ir}(\text{DBPA})_2(\text{acac})$  began to dramatically disassociate or sublime at  $368^\circ\text{C}$ , and totally decomposed at  $570^\circ\text{C}$ , which is due to liberation of the DBPA ligand. The result indicates that thermostability of the complex is well, which makes devices fabricated by vacuum evaporation more feasible.

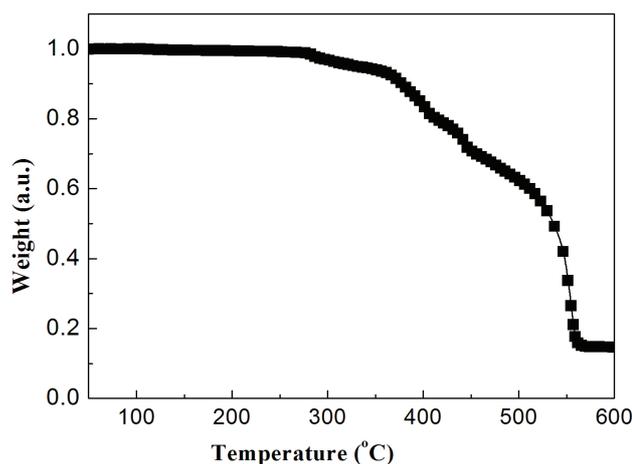


Figure 2: The TGA curve of the complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$ .

### 3.2 Photophysical properties

The absorption and emission spectra of complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$  in dichloromethane solution with the concentration  $1.0 \times 10^{-4} \text{ mol/L}$ , and emission spectrum in solid state at 298 K are shown in Fig. 3. Intense multiple absorption bands appearing in the ultraviolet part of the spectrum between 222 and 370 nm are assigned to the spin-allowed  $\pi - \pi^*$  transitions of the intraligand. The broad weak absorption bands at 392 nm and 433 nm are assigned to the transitions from the ground state to the singlet metal-ligand-charge-transfer ( $^1\text{MLCT}$ ) and triplet MLCT ( $^3\text{MLCT}$ ) excited states. From the emission spectra of  $\text{Ir}(\text{DBPA})_2(\text{acac})$ , it can be seen that the complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$  exhibits brightly green emission in both pure solid and solution. The emission maximum in solution with the concentration  $1.0 \times 10^{-4} \text{ mol/L}$  is 520 nm and a shoulder at 556 nm. while the main peak in pure solid is 516 nm with a shoulder at 550 nm, which is just slightly blue-shifted in comparison with that in solution. Herein, it is thus expected that the introduction of steric hindrance group which is connected by inert spacer of methyl into ligand may supply a shield for excited molecule, preventing quenching caused by molecular interaction. So the emission in pure solid can be considered the same as that of single molecule, and the moving of emission peak in solution and pure solid is relatively small.

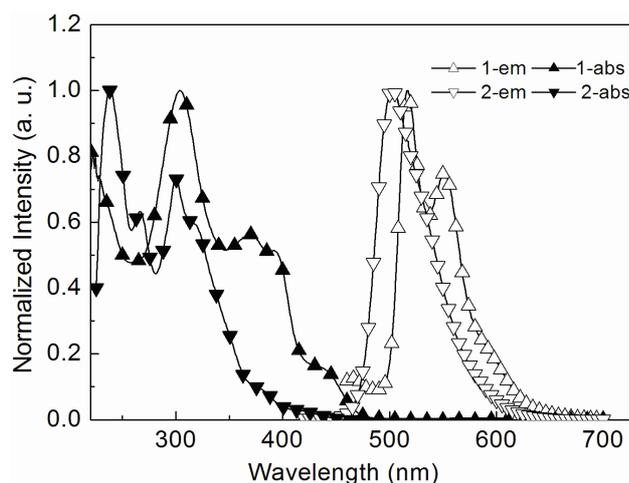


Figure 3: Absorption and emission spectra of  $\text{Ir}(\text{DBPA})_2(\text{acac})$  in  $\text{CH}_2\text{Cl}_2$  solution ( $1 \times 10^{-4} \text{ mol/L}$ ), and emission spectrum in solid state.

In order to testify this hypothesis, The excited state decays of the complex  $\text{Ir}(\text{DBPA})_2(\text{acac})$  in pure solid and in  $\text{CH}_2\text{Cl}_2$  solution ( $1 \times 10^{-5} \text{ mol/L}$ ) were measured, which is shown in Fig. 4. The excited state decays of  $\text{Ir}(\text{DBPA})_2(\text{acac})$  in pure solid and in  $\text{CH}_2\text{Cl}_2$  solution are monoexponential with excited state lifetime of 153.2 ns and 96.4 ns respectively. It is noteworthy that the excited lifetime under pure solid is longer than that under solution. It is thus confirmed that steric hindrance group triphenylamine which is connected by inert spacer of methyl into ligand may supply a shield for excited molecule, prevent-

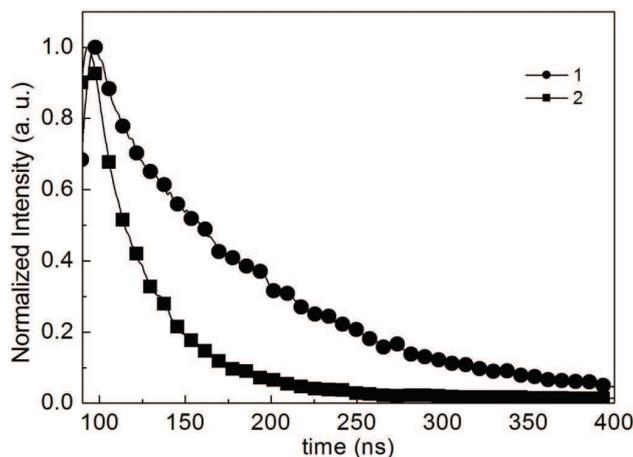


Figure 4: The excited state decays of Ir(DBPA)<sub>2</sub>(acac) in pure solid and in CH<sub>2</sub>Cl<sub>2</sub> solution ( $1 \times 10^{-5}$  mol/L).

ing quenching caused by molecular interaction, and the oxygen quenching and solvent quenching in solution make its excited lifetime becoming shorter than that in pure solid. Moreover, the phosphorescence quantum yield of Ir(DBPA)<sub>2</sub>(acac) is 0.71. These results all demonstrate it is favorable for fabricating NPOLEDs.

## 4 Conclusion

We have synthesized a new iridium complex Ir(DBPA)<sub>2</sub>(acac) containing steric hindrance group triphenylamine which is a hole transporting group, and the thermo-stability and photo-physical properties are researched in detail. A bright green emission with the main peak at 516 nm was obtained in pure solid. We found that the introduction of the steric hindrance fragment triphenylamine can supply a shield for excited molecule, preventing concentration quenching. Moreover, the complex Ir(DBPA)<sub>2</sub>(acac) has short excited state lifetime and high phosphorescence quantum yield, indicating that it has potential application in highly efficient NPOLEDs.

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