Phenylpyrimidine-Based Iridium Complex for High-Performance Green-Yellow Phosphorescent Organic Light-Emitting Diodes

Y Bi¹, X Y Zhang¹*, H Li² and T Wang²

¹School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, P.R. China
²Jilin OLED Material Tech Co., Ltd

*Correspondings: zhangxiyan@cust.edu.cn

Abstract. In this work, a phenylpyrimidine-based green-yellow iridium complex, (bpp)Ir(acac), is prepared. Tert-butyl group is introduced to weaken the intermolecular interaction and endow (bpp)Ir(acac) with favorable physical properties. Phosphorescent device which utilizes (bpp)Ir(acac) as the luminescent guest material displays high efficiencies (73.9 cd/A, 84.8 lm/W, 21.2%), low efficiency roll-off (from 100 to 10000 cd/m²: 5.1%), relatively low concentration sensitivity (from 5% to 12%) and very stable electroluminescent spectra (from 1 cd/m² to maximum luminance). As a consequence of the results proved that (bpp)Ir(acac) is a good phosphorescent material.

Keywords: Phosphorescent emitter • Iridium complex • Phenylpyrimidine

1. Introduction

As the most widely used luminescent guest material in practical organic light-emitting diodes (OLEDs), the iridium(III) complex has achieved great development in the past decades [1-3]. Until now, part of green, yellow and red iridium complexes have been used in commercial OLEDs [4-6]. Despite these achievements, for the iridium complex, some aspects still need to be improved. First, high-performance green-yellow iridium complex is not enough. In contrast to the green and yellow iridium complexes, the researches of green-yellow iridium complex are very rare. At the same time, only a few green-yellow iridium complexes report device efficiency more than 80 lm/W [7-9]. Second, concentration sensitivities of the iridium complex should be lowered. Currently, most of these materials are subjected to concentration quenching [10, 11]. In order to improve device property, the doped concentration must be accurately controlled. Third, the comprehensive property of iridium complex should be enhanced. For most of previous reported high-performance iridium complexes, the prominent parameters are limited [12, 13]. For commercial application, much more prominent parameters are needed. To the solve above problems, basic method is designing novel molecular structure. Therefore, developing new green-yellow iridium complex with low concentration quenching and excellent device performance is still highly important.

Here, we developed a new phenylpyrimidine-based green-yellow iridium complex ((bpp)Ir(acac)) by introducing the tert-butyl group to weaken the intermolecular interaction and endow it with favorable physical properties: (1) amorphous film could be formed uniformly and lowered molecular crystallization; (2) excellent photoluminescence quantum yield (93.94%) was resulted into a high exciton utilization efficiency; (3) the doped concentration influence on performance of iridium complex was decreased. Favorable physical properties brought about high device performance.
(bpp)\(_2\)Ir(acac)-doped phosphorescent device displayed high efficiencies, very stable electroluminescent spectra, relatively low efficiency roll-off and concentration sensitivity. All above results proved that (bpp)\(_2\)Ir(acac) was a good phosphorescent material.

2. Experimental Section

2.1. Synthesis

\( [(\text{bpp})_2\text{Ir(μ-Cl)}]_2 \): The bpp ligand (12 g), iridium chloride hydrate (8 g), 2-ethoxyethanol (200 mL) and distilled water (100 mL) were sequentially added to the three-neck round-bottom flask. After degassed thoroughly, the mixture was stirred at 140 °C for 24 hours and a lot of solid produced. After cooled down to the room temperature, the mixture was filtered by using buchner funnel and the wet filter cake was washed from ethanol and petroleum ether in turn. After dried in an oven, compound (11 g, 91% yield) was obtained.

\( (\text{bpp})_2\text{Ir(acac)} \): \([(\text{bpp})_2\text{Ir(μ-Cl)}]_2 \) (10 g, 7.7 mmol), sodium carbonate (7 g, 66 mmol) and 2-ethoxyethanol (200 mL) were added to the three-neck round-bottom flask. After degassed for three times, pentane-2,4-dione (3.1 g, 30.8 mmol) was added under nitrogen. The mixture was heated to reflux for 24 hours and then allowed to cool to ambient temperature. The mixture was filtrated by using buchner funnel and the wet filter cake was flushed by petroleum ether. The mixture was dried in an oven. The crude product (5.1 g, 51% yield) was obtained. The compound was further purified in a vacuum sublimation. The synthesis process was described in Figure 1. 1H NMR (400 MHz, CDCl\(_3\), δ): 9.03 (d, J = 4 Hz, 2H), 7.75 (d, J = 4 Hz, 2H), 7.66 (d, J = 4 Hz, 1H), 7.64 (d, J = 4 Hz, 1H), 6.84 (ddd, J = 8 Hz, 2H), 6.76 (ddd, J = 8 Hz, 2H), 6.34 (dd, J = 8 Hz, 2H), 5.26 (s, 1H), 1.79 (s, 6H), 1.49 (s, 18H). 13C NMR (400 MHz, CDCl\(_3\), δ): 28.61, 29.66, 37.71, 100.99, 109.00, 120.97, 125.48, 130.96, 133.72, 142.71, 151.12, 156.92, 174.49, 178.28, 184.99. MS: 714.55 [M]+ (calcd: 713.90). Anal. Calcd for C\(_{33}\)H\(_{37}\)IrN\(_4\)O\(_2\): C 55.52, H 5.22, N 7.85; found: C 55.61, H 5.18, N 7.83.

3. Results and Discussion

3.1. Thermal Properties

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to measure thermal properties of (bpp)\(_2\)Ir(acac) (Figure 2 and Table 1). (bpp)\(_2\)Ir(acac) showed good thermal stability. Its decomposition temperature (Td) (corresponding to 5% weight loss) was 479 °C. From DSC thermograms, no glass transition was not observed. High thermal stability was favorable for practical application.

![Figure 1. The synthesis process of (bpp)\(_2\)Ir(acac).](image)
Figure 2. (a) TGA curve and (b) DSC thermograms of (bpp)$_2$Ir(acac).

3.2. Electrochemical Properties and Theoretical Calculation
The electrochemical properties of (bpp)$_2$Ir(acac) were studied by cyclic voltammetry (CV). The result was shown in Figure 3. (bpp)$_2$Ir(acac) exhibited reversible oxidation behavior and no reduction wave was detected. From the oxidation wave, the highest occupied molecular orbital (HOMO) energy level of (bpp)$_2$Ir(acac) was determined to be $-5.33$ eV. The lowest unoccupied molecular orbital (LUMO) energy level of (bpp)$_2$Ir(acac) was calculated to be $-3.00$ eV according to the HOMO and absorption spectra.

Figure 3. Cyclic voltammetry curve of (bpp)$_2$Ir(acac).

3.3. Photophysical Properties
The absorption and photoluminescence (PL) spectrum ($10^{-5}$ M) of (bpp)$_2$Ir(acac) in degassed dichloromethane(CH$_2$Cl$_2$) solution as well as the phosphorescence spectrum ($10^{-5}$ M) in degassed 2-methyltetrahydrofuran solution at 77 K were exhibited in Figure 4a. According to some previous reported iridium complexes [14, 15] and calculation results, the strong energy absorption band below 350 nm were due to the spin-allowed ligand-centered (LC, $\pi \rightarrow \pi^*$) transitions of the cyclometalated ligands. However, because of the spin-orbit coupling of the iridium atom, the absorption bands from 350 to 480 nm were assigned to the mixed MLCT, LLCT and ILCT transitions. From onset of absorption spectra, the energy gap (Eg) was 2.33 eV.

(bpp)$_2$Ir(acac) displayed green-yellow emission (540 nm) in CH$_2$Cl$_2$ solution ($10^{-5}$ M). Its phosphorescence spectrum at 77 K possessed nearly same main emission peak (539 nm) (Figure 4a). From the first vibronic peak, the lowest triplet excited state (E_T) energy level was 2.30 eV. The transient photoluminescence decay property of (bpp)$_2$Ir(acac) in degassed CH$_2$Cl$_2$ solution ($10^{-5}$ M) was measured (Figure 4b). Using the curve fitting method, phosphorescence lifetime of (bpp)$_2$Ir(acac) was calculated to be 1591.6 ns. Meanwhile, the measurement result of photoluminescence quantum yield (PLQY) in degassed CH$_2$Cl$_2$ solution ($10^{-5}$ M) was 93.94%.
**Figure 4.** (a) Room-temperature UV-Vis absorption, PL and phosphorescence spectrum of (bpp)$_2$Ir(acac). (b) Transient PL decay profile of (bpp)$_2$Ir(acac) in degassed CH$_2$Cl$_2$ solution.

**Table 1.** Physical properties of (bpp)$_2$Ir(acac).

| Compound    | $T_d$ [°C] | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | $\Phi$ [%] | $\tau$ [ns] | HOMO/LUMO [eV] | $E_g$/ ET [eV] |
|-------------|------------|----------------------|---------------------|-------------|-------------|----------------|----------------|
| (bpp)$_2$Ir(acac) | 479        | 359, 405, 476        | 540                 | 93.94       | 1591.6      | -5.33/-3.00    | 2.33/2.30      |

3.4. Electroluminescent Properties

To illustrate the electroluminescent performance of (bpp)$_2$Ir(acac), doped devices configuration consisting of [ITO/HATCN (150 Å)/TAPC (600 Å)/TCTA (50 Å)/mCP: 5-12% (bpp)$_2$Ir(acac) (400 Å)/TPBI (400 Å)/LiF (15 Å)/Al] (Y1 for 5%; Y2 for 8%; Y3 for 12%) were fabricated, respectively. The luminance (L)-voltage (V)-current density (J) characteristics, power efficiencies versus luminance curves, electroluminescent (EL) spectra and external quantum efficiencies (EQE) of these devices were shown in Figure 5 and the parameters were summarized in Table 2.

These doped devices displayed green-yellow emission with two peaks (Figure 5d). The emission peaks at different doped concentrations were as following: 541 and 573 nm for 5%; 545 and 574 nm for 8%; 545 and 574 nm for 12%, respectively. With increasing of different doped concentration from 5% to 12%, the EL spectra only showed tiny difference. The maximum current ($\eta_c$ max), power ($\eta_p$ max) and external quantum ($\eta_{ext}$ max) efficiencies of these devices were as following: 71.7 cd/A, 80.4 lm/W, 20.3% for Y1; 73.9 cd/A, 84.8 lm/W, 21.2% for Y2; 67.1 cd/A, 75.0 lm/W, 19.5% for Y3. At the same time, efficiencies roll-off of these devices were not serious. From 100 to 10000 cd/m$^2$, the roll-off of current efficiencies were calculated to be 3.1% for Y1, 5.1% for Y2, 4.6% for Y3. Finally, (bpp)$_2$Ir(acac)-based devices showed very low concentration sensitivity (Table 2). The improvements of above performance parameters were related with the alkyl groups in (bpp)$_2$Ir(acac) molecule. The tert-butyl and methyl groups could weaken the intermolecular interaction and brought about several favorable properties: (1) amorphous film could be formed uniformly and lowered molecular crystallization; (2) excellent photoluminescence quantum yield (93.94%) was resulted into a high
exciton utilization efficiency; (3) the doped concentration influence on performance of iridium complex was decreased.

Figure 5. (a) L-V-J curves of Y1, Y2, Y3. (b) ηc-ηe curves of Y1, Y2, Y3. (c) EQE-L curves of devices Y1, Y2, Y3. (d) EL spectra of Y1, Y2, Y3 at the luminance of 100 cd/m².

Table 2. The electroluminescent performance of (bpp)2Ir(acac)-based devices.

| Device | V_on [V] | L_max [cd m⁻²] | η(L) [cd A⁻¹] | ηp [lm W⁻¹] | ηext [%] | CIE (x,y) |
|--------|----------|----------------|---------------|-------------|----------|-----------|
| Y1(5%) | 2.4      | 34290          | 71.7, 47.6, 71.6, 69.5 | 80.4, 59.8, 80.4, 59.0 | 20.3, 13.6, 20.3, 19.6 | 0.42, 0.56 |
| Y2(8%) | 2.4      | 34910          | 73.9, 59.1, 73.9, 70.1 | 84.8, 74.3, 82.9, 59.5 | 21.2, 17.0, 21.2, 20.0 | 0.43, 0.55 |
| Y3(12%)| 2.4      | 29410          | 67.1, 59.8, 66.8, 64.0 | 75.0, 72.3, 72.4, 51.5 | 19.5, 17.6, 19.5, 18.6 | 0.43, 0.55 |

*In the order of maximum, then values at 100, 1000 and 10000 cd m⁻².

4. Conclusions
In conclusion, we had developed a novel phenylpyrimidine-based green-yellow iridium complex, (bpp)2Ir(acac). On the phenylpyrimidine ligand, the tert-butyl group was introduced to prevent the close packing of (bpp)2Ir(acac) molecules. Weak intermolecular interactions had contributed to the (bpp)2Ir(acac) with a high photoluminescence quantum yield (93.94%) and low concentration influence on material's property. Therefore, phosphorescent device which utilized (bpp)2Ir(acac) as emitter displayed high efficiencies (73.9 cd/A, 84.8 lm/W, 21.2%), low efficiency roll-off (from 100 to 10000 cd/m²: 5.1%), rather low concentration sensitivity (5%, 8%, 12%) and very stable electroluminescent spectra (from 1 cd/m² to maximum luminance). As a consequence of the results proved that (bpp)2Ir(acac) is a good phosphorescent material.
References

[1] Fang DQ, Sun Y, Chen YQ, Fu TC, Ali MU, He YW, Miao JS, Yan CY, Meng H 2020 Dyes Pigm 173 107990.
[2] Lu GZ, Tu ZL, Liu L, Zhang WW, Zheng YX 2019 J Mater Chem C 7 7273-78.
[3] Liu X, Yu Z, Yu MJ, Zhang XW, Xu YA, Lv P, Chu SQ, Liu CJ, Lai WY, Huang W 2019 ACS Appl Mater Interfaces 11 26174-184.
[4] Ning XW, Zhao CY, Jiang B, Gong SL, Ma DG, Yang CL 2019 Dyes Pigm 164 206-12.
[5] Peng T, Li GM, Ye KQ, Wang CG, Zhao SS, Liu Y, Hou ZM, Wang Y 2013 J Mater Chem C 1 2920-26.
[6] You CF, Liu DH, Zhu MB, Yu JT, Zhang B, Liu Y, Wang YF, Zhu WG 2020 J Mater Chem C 8 7079-88.
[7] Kim KH, Ahn ES, Huh JS, Kim YH, Kim JJ 2016 Chem Mater 28 7505-10.
[8] Yan ZM, Wang YP, Ding JQ, Wang Y, Wang LX 2017 J Mater Chem C 5 12221-7.
[9] Yan ZM, Wang YP, Wang JX, Wang Y, Ding JQ, Wang LX 2017 J Mater Chem C 5 10122-25.
[10] Li J, Liang F, Zhao Y, Liu XY, Fan J, Liao LS 2017 J Mater Chem C 5 6202-9.
[11] Liu BA, Dang FF, Feng Z, Tian ZZ, Zhao J, Wu Y, Yang XL, Zhou GJ, Wu ZX, Wong WY 2017 J Mater Chem C 5 7871-83.
[12] Han HB, Ma XF, Wu ZG, Zheng YX 2018 Mater Chem Front 2 1284-90.
[13] Xu QL, Liang X, Zhang S, Jing YM, Liu X, Lu GZ, Zheng YX, Zuo JL 2015 J Mater Chem C 3 3694-701.
[14] Dang WP, Yang XL, Feng Z, Sun YH, Zhong DK, Zhou GJ, Wu ZX, Wong WY 2018 J Mater Chem C 6 9453-64.
[15] Xu XB, Guo HR, Zhao J, Liu BA, Yang XL, Zhou GJ, Wu ZX 2016 Chem Mater 28 8556-69.