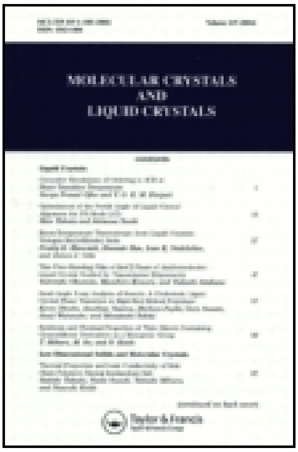

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Synthesis and Electroluminescent Properties of Ir(III) Complexes Containing Alkenyl Pyridine Ligands

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The synthesis and electroluminescent properties of two red Ir(III) complexes based on alkenyl pyridine derivatives, **(BzPP)$_2$Ir(acac)** *and* **(IQP)$_2$Ir(acac)** *are reported. Multilayered, organic light-emitting diodes (OLEDs) were fabricated using* **(BzPP)$_2$Ir(acac)** *as dopant material. A maximum luminance was 6996 cd/m^2 at 12 V, a maximum luminous and power efficiency were 8.54 cd/A, and 8.16 lm/W, respectively, were achieved. This device showed the deep red emission with the CIE coordinates of (0.66, 0.34) at 10 V.*

Keywords Alkenyl pyridine derivatives; phosphorescent OLEDs; red-Ir(III) complexes

1. Introduction

Electrophosphorescence can make use of both singlet and triplet excitons due to strong spin-orbital coupling of heavy-metal ions in phosphorescent compounds, thereby theoretically achieving 100% of internal quantum efficiency differently from electrofluorescence [1]. Since conventional red fluorescent emitters are not as good as green or blue fluorescent emitters, much research is focused on achieving higher efficiency from red phosphorescent devices. For the most part, Ir(III) complexes have been used as red phosphorescent emitters [2–8] since it exhibits the suitable triplet band gap and life time for the efficient OLEDs when doped in host materials such as CBP derivatives. Recently, success in the use of alkenyl pyridines for cyclometalation with Ir(III) in Paulos groups prompted them to design new ligand systems for Ir(III) complexes that lead to the emission of light with different colors [9]. Among those, in a device containing green iridium complex (PP)$_2$Ir(acac) based on propenylpyridine ligand as a dopant, the maximum luminous and quantum efficiencies were 43.9 cd/A and 10.6%, respectively, which are in the similar range of those using the well-known Ir(ppy)$_3$.

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In this paper, as a continuing effort to develope the efficient phophorescent Ir(III) complexes based on the alkenylated ligands for OLED, red phosphorescent Ir(III) complexes, **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$,** are synthesized and their electrophosphrescent properties are investigated. In **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$,** the different groups such as benzoylpyridine and isoquinoline were introduced in the ligands of Ir(III) complexes in stead of pyridine moiety in $(PP)_2Ir(acac)$. Presumably, these extended π-conjujation of **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$** would lead to the red-shifts of the emission spectra of **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$** in comparison with $(PP)_2Ir(acac)$. As will be seen in below, iridium complexes **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$** show the efficient red phosphorescence and a device using **$(BzPP)_2Ir(acac)$** as a dopant exhibits the efficient red emission.

2. Experimentals Details

2.1. Material and Synthesis

5-Benzoyl-2-bromopyridine [7] was synthesized as previously reported. Liagnds, **$(BzPP)_2Ir(acac)$,** and **$(IQP)_2Ir(acac)$** were prepared according to modified literature procedures [7, 11]. ^{1}H- and ^{13}C-NMR were obtained using a Varian (Unity Inova 300Nb) spectrometer at 300 MHz. Low- and high-resolution mass spectra were recorded using either a Jeol JMS-AX505WA spectrometer in the FAB mode. UV-Vis spectra were measured with a Shimadzu UV-1650PC spectrometer. Photoluminescence spectra were obtained on an Amincobrowman series 2 luminescence spectrometer. The phosphorescent quantum yield was determined in a CH_2Cl_2 solution (10^{-5} M) at 293 K against fac-$Ir(ppy)_3$ as a reference ($\Phi = 0.40$) [10]. The energy levels were measured with a low-energy photo-electron spectrometer (Riken Keiki, AC-2).

$(BzPP)_2Ir(acac)$ (Yield of 53%): ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.49 (s, 2H), 8.06 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 7.0$ Hz, 3H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 6.9$ Hz, 2H), 7.29 (d, $J = 9.7$ Hz, 2H), 6.77 (s, 2H), 5.19 (s, 1H), 1.78 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) : δ ppm 193.1, 189.8, 185.1, 174.7, 151.3, 138.7, 137.7, 132.5, 129.7, 128.7, 126.1, 117.8, 100.7. FAB-MS (*m/z*): 736 [M^+]. HRMS-FAB$^+$ calcd for $C_{35}H_{31}IrN_2O_4$: 736.1913, found: 736.1911. mp: 193°C

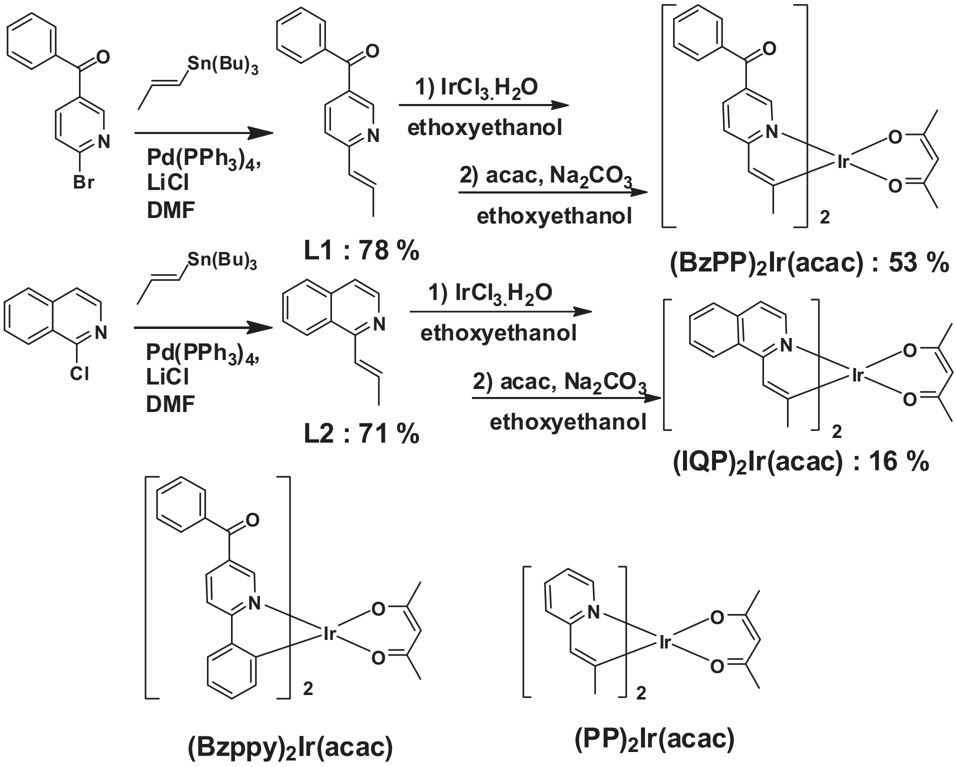
$(IQP)_2Ir(acac)$ (Yield of 16%): ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.27 (d, $J = 8.1$ Hz, 2H), 8.03 (d, $J = 6.3$ Hz, 2H), 7.76 (d, $J = 7.8$ Hz, 2H), 7.62–7.58 (m, 2H), 7.56–7.48 (m, 4H), 7.21 (d, $J = 6.6$ Hz, 2H), 5.19 (s, 1H), 1.84 (s, 6H), 1.83 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 186.9, 184.7, 171.9, 140.6, 136.4, 130.8, 127.5, 126.7, 124.7, 12.4, 115.3, 100.6, 29.1, 28.5. FAB-MS (*m/z*): 628 [M^+]. HRMS-FAB$^+$ calcd for $C_{29}H_{27}IrN_2O_2$: 628.1702, found: 628.1697. mp: 114°C

2.2. Device Fabrication and Characterization

OLEDs using red dopants in the emitting layers were fabricated by vacuum (10^{-7} torr) thermal evaporation onto pre-cleaned ITO coated glass substrates. The structure was as follows: ITO/ NPB (30 nm)/ CBP: 8% **$(BzPP)_2Ir(acac)$** (30 nm) / BCP (10 nm)/ Alq_3 (40 nm) / Liq (2 nm) / Al. All of the optical and electrical properties of OLEDs such as the current density, luminance, luminous efficiency and CIE coordinate characteristics were measured with Keithley 236, LS-50B, and MINOLTA CS-100A, respectively.

3. Results and Discussion

Scheme 1 outlines the structures and synthetic processes of the Ir(III) complexes, **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$**. The ligands were synthesized in moderate yield via the Stille cross coupling reaction. The Ir(III) complexes were obtained by cyclometalation of the ligands with $IrCl_3$ and subsequent reaction with acetylacetone [11].



Scheme 1. Synthetic route to **$(BzPP)_2Ir(acac)$**, **$(IQP)_2Ir(acac)$** and structure of $(Bzppy)_2Ir(acac)$, $(PP)_2Ir(acac)$.

Figure 1 depicts the X-ray crystal structure of **$(BzPP)_2Ir(acac)$**. The molecular structure revealed the central iridium center to be coordinated by two anionic N^C ligands and one chelating acac anion. The coordination around the Ir center was a distorted octahedral with the *cis*-O,O, *cis*-C,C, and *trans*-N,N chelate disposition.

Figure 2 shows the UV-Vis absorption and photoluminescence spectra of the orange-red dopants in the CH_2Cl_2 solution. For Ir(III) complexes, the higher energy absorption peaks below 450 nm were assigned to spin-allowed $^1\pi$-π^* transitions of the cyclometalated ligands [12]. Common to all other Ir(III) complexes, there was a weak but well- resolved peak near 400 nm with lower extinction coefficients, which can be interpreted as arising from a spin-orbit coupling, together with an admixture of ^{1}MLCT and ^{3}MLCT states. The maximum emission wavelength (λ_{max}) of **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$** appeared at 606 and 596 nm, respectively. Interestingly, compared to $(PP)_2Ir(acac)$ ($\lambda_{max} = 536$ nm), there are red-shifts in the PL spectra of **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$** (*ca.* 70 and 60 nm, respectively). This is likely due to the increase in π-conjugation length by

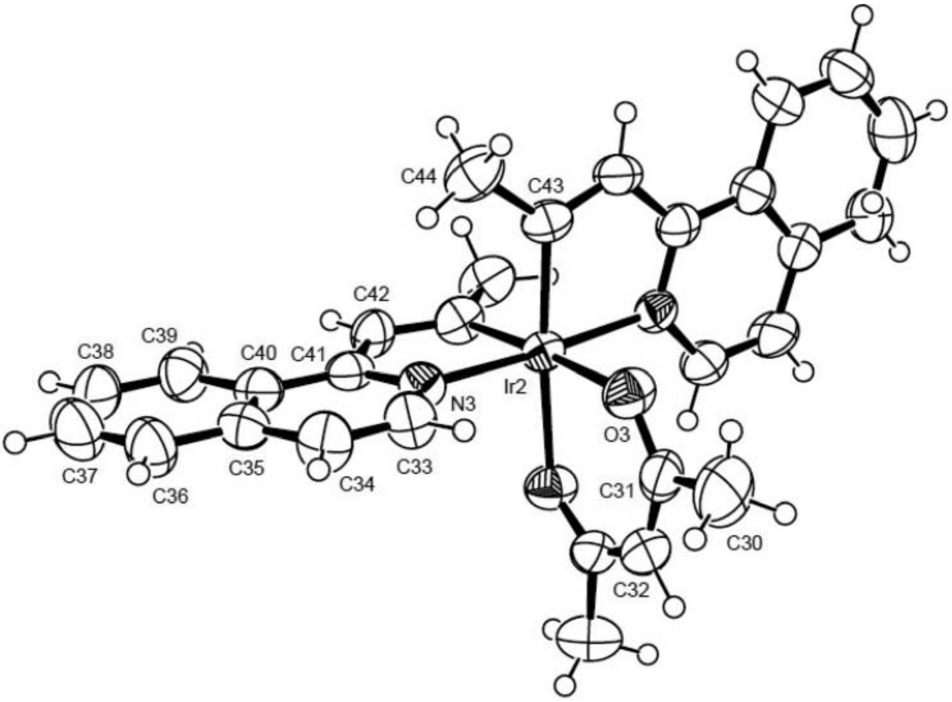


Figure 1. X-ray crystal structure of **(BzPP)$_2$Ir(acac)**.

benzoylpyridine and isoquinoline groups. Additionally, there was a red-shift (10 nm) in the PL spectra of **(BzPP)$_2$Ir(acac)** compared to that of **(IQP)$_2$Ir(acac)**. The emission quantum yields of **(BzPP)$_2$Ir(acac)** and **(IQP)$_2$Ir(acac)** were 0.45 and 0.27, as determined with Ir(ppy)$_3$ (0.40)[10] used as a reference.

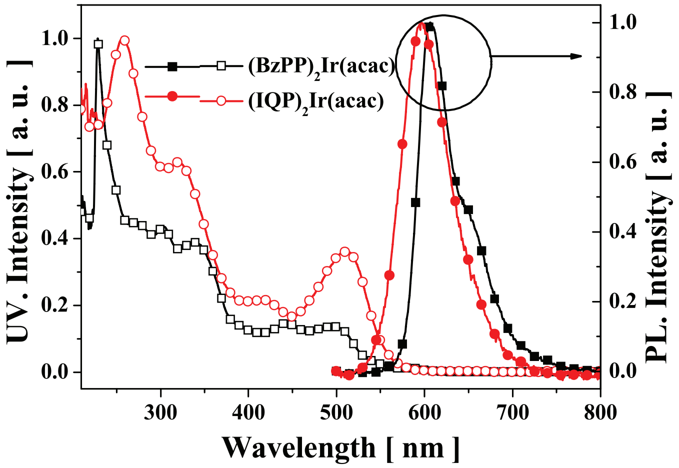


Figure 2. The absorption and emission spectra of **(BzPP)$_2$Ir(acac)**, **(IQP)$_2$Ir(acac).**

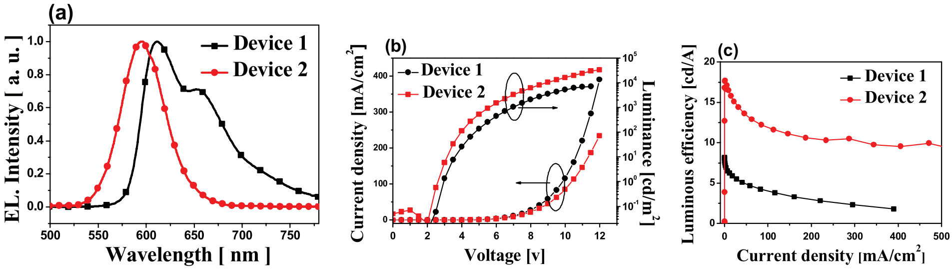


Figure 3. (a) EL spectra (b) *J-V-L,* (c) LE vs. current density relationship of devices **1** and **2**.

The HOMO energy levels were measured with an AC-2 photoelectron spectrometer and the LUMO levels calculated by subtracting the corresponding optical band gap energies from the HOMO values. The HOMO and LUMO energy levels for **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$** varied from −5.20 to −5.48 eV and −2.99 to −3.22 eV, respectively.

To explore the electroluminescent properties of **$(BzPP)_2Ir(acac)$** and **$(IQP)_2Ir(acac)$**, multilayer OLED devices were fabricated. Unfortunately, we did not fabricate a device employing **$(IQP)_2Ir(acac)$** because of its low melting point (114°C) as compared to **$(BzPP)_2Ir(acac)$** (193°C). Furthermore, **$(IQP)_2Ir(acac)$** has 108 g/mol lower molecular weight than **$(BzPP)_2Ir(acac)$**, therefore we expected that vacum thernal evaporation was not carried out. Figure 3(**a**) shows the normalized EL spectra for device with a device structure of ITO/ NPB (30 nm)/ CBP: 8% **$(BzPP)_2Ir(acac)$** (30 nm)/ BCP (10 nm)/ Alq (40 nm)/ Liq/ Al, where NPB is the hole-transporting layer, BCP the hole-blocking layer, Alq_3 the electron-transporting layer, and Liq/Al a composite cathode. Also, for the comparison, the control device using $(Bzppy)_2Ir(acac)$ [11, 13] as a dopant in CBP host at 8% doping concentration was fabricated. Electroluminescent data on devices using **$(BzPP)_2Ir(acac)$** and $(Bzppy)_2Ir(acac)$ was summarized in Table 1. This device **1** using **$(BzPP)_2Ir(acac)$** as a dopant gave red light with the emission maximum at 611 nm. The respective CIE coordinates was (0.66, 0.34). There was a red shift in the EL spectra of device **1** compared to that of reference device **2** with $(Bzppy)_2Ir(acac)$ and $(PP)_2Ir(acac)$ because the extended π-conjugation of ligand in **$(BzPP)_2Ir(acac)$** as compared to that of $(PP)_2Ir(acac)$. This trend of the CIE coordinates was well compatible with the PL spectra of **$(BzPP)_2Ir(acac)$** and $(PP)_2Ir(acac)$, indicating that the emission of device **1** came from the triplet excited state of the **$(BzPP)_2Ir(acac)$**.

The current density-voltage-luminance (*J-V-L*) characteristics and luminous efficiency (LE) of devices **1** and **2** were shown in Fig. 3, respectively. The maximum luminance of devices **1** and **2** were 6996 cd/m^2 and 24000 at 10 V, respectively. Also, device **1** showed maximum luminous efficiency, power efficiency, and external quantum efficiency of 8.16 cd/A, 8.54 lm/W, and 8.10% (5.86 cd/A, 2.38 lm/W, and 5.59% at 20mA/cm^2), respectively. Interestingly, compared to device using the known $(Bzppy)_2Ir(acac)$, device **1** showed the improved CIE coordinates of (0.66, 0.34), approaching the saturated red emission with the CIE coordinates of (0.67, 0.32), in spite of the similar EL efficiencies to each other. This study demonstrates that the phosphorescent Ir(III) complex based on the alkenylated pyridine ligand has the excellent properties for applications to red emitting materials in OLEDs.

Table 1. EL performances of device

Device	Dopant	V_{on}[a] [V]	L[b] [cd/m^2]	LE[c/d] [cd/A]	PE[c/d] [lm/W]	EQE[c/d] [%]	λ_{max}[e] [nm]	CIE[e] [*x*,*y*]
1	$(BzPP)_2Ir(acac)$	3.3	6996	8.16/5.86	8.54/2.38	8.10/5.59	611	0.66, 0.34
2	$(Bzppy)_2Ir(acac)$	4.0	24000	15.3/7.70	10.6/3.07	10.4 /6.55	594	0.61,0.38
3	$(PP)_2Ir(acac)$[f]	2.7	86000	36.2/	16.3/	8.70/	534	0.36, 0.62

[a] Turn-on voltage at 1 cd/m^2.
[b] Maximum luminance.
[c] Maximum values.
[d] At 20 mA/cm^2.
[e] At 8 V. [f] Ref 9.

4. Conclusion

We synthesized a series of alkenyl pyridine Ir(III) complexes and investigated their electroluminescent properties. An OLED device employing **(BzPP)$_2$Ir(acac)** as a dopant exhibits the best performance with a maximum luminance of 6996 cd/m^2 at 12 V, and a luminous efficiency of 5.86 cd/A at 20 mA/cm^2. Also, this device shows red emission with CIE coordinates of (0.66, 0.34) at 8.0 V. This highly efficient red emitting material **(BzPP)$_2$Ir(acac)** could be used in the OLED as a phosphorescent red emitter.

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