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New red phosphorescent iridium(III) complex with 4-tert-Butylphenyl-boronic acid of organic borane

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ABSTRACT

A new phosphorescent (CQ-BP)₂Ir(acac), (CMQ-BP)₂Ir(acac), (BQ-BP)₂Ir(acac) was synthesized for organic light-emitting diodes (OLEDs). OLEDs using phosphorescent iridium(III) complexes attract enormous attention because they allow highly efficient electro phosphorescence. The donor-acceptor type ligands for the Iridium(III) complexes were synthesized by Suzuki coupling reaction. The ligands through changes in oxidative addition materials (electron-acceptor) and organic borane (electron-donor) to get the red color were to study the appropriate Iridium(III) complexes. Oxidative addition materials were used such as 2-chloro-4-methylquinoline, 1-chloroisoquinoline and 2-bromoquinoline. 4-tert-Butylphenyl-boronic acid was used as organic borane. The dopant was synthesized by Nonoyama reaction. Red dopants were observed with an emission peak at approximately 600 nm. Iridium(III) complexes were measured by nuclear magnetic resonance (NMR), UV-visible spectroscopy and photoluminescence (PL). The phosphorescence emission maxima were dependent on the electron density of donor and acceptor moiety of the ligands.

KEYWORDS

red dopant; iridium(III) complex; OLED; phosphorescent

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention in scientific and industrial utilization due to their merits in low operating voltage, wide range of self-emissive materials, high contrast, fast response time, wide-viewing angle, ultrathin structure and light weight [1–10]. In particular, heavy metal ions, such as Pt(III), Ru(III), and Ir(III) have been employed for the synthesis of high emission phosphorescent materials to utilize for the solar-cells and the OLEDs. OLEDs composed of glass substrate, transparent conductor (ITO), electron injection layer (EIL), electron transfer layer (ETL), emission material layer (EML), hole transfer layer (HTL), hole injection layer (HIL) and metal cathode [11–14]. We has been studying phosphorescent iridium(III) complex dopants for the EML layer. The excitons formed in EML are composed of 25% singlet and 75% triplets [15]. Which enable both nearly 100% internal device quantum efficiency. Such promising features prompted the development of a number of novel phosphorescent Iridium(III) complexes. In this paper, we report synthesis and emission properties of novel red-emitting iridium complexes through changed

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electron-donor and electron-acceptor of ligand and measure characteristic respectively [16–18].

2. Experimental

2.1. General information

All reactions and manipulation were carried out under N_2 with the use of standard inert atmosphere. Solvents were dried by standard procedures. All column chromatography was performed under standard atmosphere with the use of silica gel (230–400 mesh, Sigma-Aldrich) as the stationary phase in a column of 30 cm long and 2.0 cm diameter. The 1H NMR spectra were measured by using a Bruker DRX 400 spectrometer in deuterated chloroform solution. 500 MHz UV-visible absorption spectra were recorded on an Agilent8453 UV-Vis spectrophotometer. All measurements were carried out room temperature. For expect phosphorescent emission energy and electronic state of newly designed iridium complex, we used Gaussian 08 program. Gaussian 08 program performs structure optimization and time-dependent density functional theory (TD-DFT) calculations HF and DFT.

2.2. Synthesis of ligand

1-(4-(tert-butyl)phenyl)isoquinoline

A mixture of 4-tert-Butylphenylboronic acid (2.00 g, 11.234 mmol), 1-Chloroisoquinoline (2.02 g, 12.357 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.112 mmol, 1 mol%), Potassium carbonate (33.17 g, 240 mmol), tetrahydrofuran (120 mL), water (60 mL) was headed under nitrogen atmosphere at $80^\circ C$ for 24-hour (This reaction is Suzuki coupling reaction). After cooling to room temperature, the crude reaction product was poured into water, extracted with dichloromethane. And extract is concentrated under vacuum. The product was purified by column chromatography to obtain a dark-red powder with yield of 61.2% and dried in vacuum to yield light-green solid product with 79.4% yield.

1H NMR ($CDCl_3$, 500MHz): δH (ppm) 8.42(d, 1H), 8.22(d, 2H), 7.92(d, 1H), 7.63(d, 1H), 7.49(d, 1H), 7.42(d, 1H), 7.41(d, 1H), 7.10(d, 1H), 1.35(s, 1H)

2-(4-(tert-butyl)phenyl)-4-methylquinoline

A mixture of 4-tert-Butylphenylboronic acid (2.00 g, 11.234 mmol), 2-chloro-4-methylquinoline (2.19 g, 12.357 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.112 mmol, 1 mol%), Potassium carbonate (33.17 g, 240 mmol), tetrahydrofuran (120 mL), water (60 mL) was headed under nitrogen atmosphere at $80^\circ C$ for 24 h. hours (This reaction is Suzuki coupling reaction). The abstraction and purification process are the same as the method described above. Yield: 87.3%.

1H NMR ($CDCl_3$, 500MHz): δH (ppm) 8.22(d, 2H), 8.16(d, 1H), 7.95(d, 1H), 7.75(t, 1H), 7.59(t, 1H), 7.41(d, 1H), 7.00(s, 1H), 2.61(s, 1H), 1.35(s, 3H),

2-(4-(tert-butyl)phenyl)quinolone

A mixture of 4-tert-Butylphenylboronic acid (2.00 g, 11.234 mmol), 2-bromoquinoline (2.57 g, 12.357 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.112 mmol, 1 mol%), Potassium carbonate (33.17 g, 240 mmol), tetrahydrofuran (120 mL), water (60 mL) was headed under nitrogen atmosphere at $80^\circ C$ for 24 h. hours (This reaction is Suzuki coupling reaction). The abstraction and purification process are the same as the method described above. Yield: 83.4%.

¹H NMR (CDCl₃, 500MHz): δH(ppm) 8.22(d, 2H), 8.10(s, 1H), 8.06(t, 1H), 7.98(d, 1H), 7.78(t, 1H), 7.6(t, 1H), 7.41(t, 2H), 7.35(d, 1H), 1.35(d, 3H)

2.3. Synthesis of dimer

Dimer [(CQ-BP)₂IrCl]₂ diiridium(III)

The cyclometalated iridium (III) μ -chloride-bridged dimer, [(CQ-BP)₂Ir(μ -Cl)]₂ (II) was prepared using a slight modification of the Nonoyama reaction step 1. Iridium (III) chloride hydrate (1.331 g, 4.457 mmol) and Ligand (2.330 g, 8.915 mmol) was added a 3:1 in mixture of 2-ethoxyethanol and water. The reaction is required under nitrogen atmosphere. The mixture was heated to reflux for 27-hour at 135 C. The solution was cooled to room temperature, and leaves the flask in ice bath 2 hours. The crude reaction product was poured into water, extracted with dichloromethane. And extract is concentrated under vacuum. yield: 95.7%.

Dimer [(CMQ-BP)₂IrCl]₂ diiridium(III)

The cyclometalated iridium (III) μ -chloride-bridged dimer, [(CMQ-BP)₂Ir(μ -Cl)]₂ (II) was prepared using a slight modification of the Nonoyama reaction step 1. Iridium (III) chloride hydrate (1.464 g, 4.902 mmol) and Ligand (2.7 g, 9.804 mmol) was added a 3:1 in mixture of 2-ethoxyethanol and water. The reaction is required under nitrogen atmosphere. The mixture was heated to reflux for 27-hour at 135 C. The purification process is the same as the method described above. yield: 89.1%.

Dimer [(BQ-BP)₂IrCl]₂ diiridium(III)

The cyclometalated iridium (III) μ -chloride-bridged dimer, [(BQ-BP)₂Ir(μ -Cl)]₂ (II) was prepared using a slight modification of the Nonoyama reaction step 1. Iridium (III) chloride hydrate (1.399 g, 4.687 mmol) and Ligand (2.45 g, 9.374 mmol) was added a 3:1 in mixture of 2-ethoxyethanol and water. The reaction is required under nitrogen atmosphere. The mixture was heated to reflux for 27-hour at 135 C. The purification process is the same as the method described above. yield: 96.7%.

2.4. Synthesis of iridium(III) complexes

(CQ-BP)₂Ir(acac)

Dimer (3.11 g, 2.072 mmol) were dissolved in 2-ethoxyethanol (124.40 mL). 5 equivalent acetylacetone (1.037 g, 10.361 mmol) and sodium carbonate (2.864 g, 20.722 mmol) is placed. Reactants refluxed under nitrogen atmosphere for 21-hour at 130°C (Fig. 1). After cooling to room temperature, the crude reaction product was poured into water, extracted with

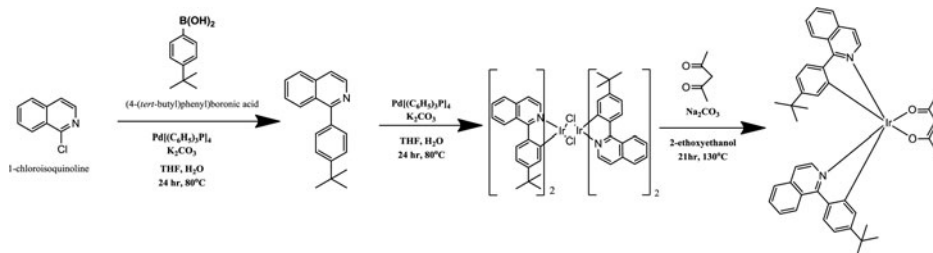


Figure 1. Synthetic route of (CQ-BP)₂Ir(acac).

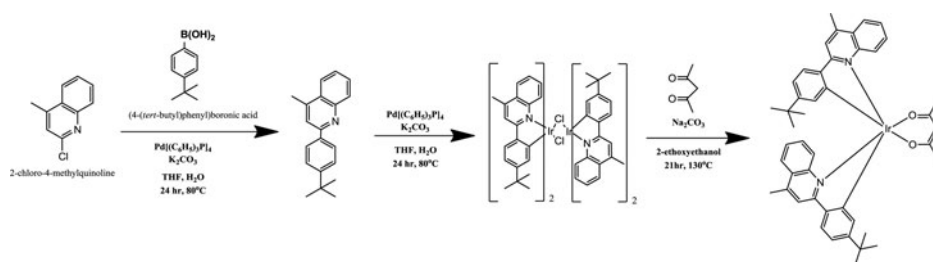


Figure 2. Synthetic route of (CMQ-BP)₂Ir(acac).

dichloromethane. And extract is concentrated under vacuum. The product was purified by column chromatography to obtain a red powder with yield of 74.3%.

¹H NMR (CDCl₃, 500MHz): δ H(ppm) 8.22(d, 1H), 8.10(d, 2H), 8.06(d, 2H), 7.98(d, 1H), 7.78(t, 2H), 7.60(d, 2H), 7.56(s, 2H), 7.41(d, 2H), 7.35(d, 2H), 2.24(s, 1H), 1.35(s, 6H), 1.27(d, 1H)

(CMQ-BP)₂Ir(acac)

Dimer (3.4 g, 2.184 mmol) were dissolved in 2-ethoxyethanol (136 mL). 5.0 equivalent acetylacetone (1.093 g, 10.922 mmol) and sodium carbonate (3.019 g, 21.844 mmol) is placed. Reactants refluxed under nitrogen atmosphere for 21-hour at 135°C (Fig. 2). The abstraction and purification process are the same as the method described above. Yield: 67.4%.

¹H NMR (CDCl₃, 500MHz): δ H(ppm) 8.22(d, 2H), 8.16(d, 2H), 7.95(d, 2H), 7.75(t, 2H), 7.59(s, 2H), 7.56(d, 2H), 7.41(d, 2H), 7.0(s, 2H), (d, 1H), 5.75(d, 1H), 2.61(s, 2H), 2.24(s, 1H), 1.35(s, 6H), 1.27(d, 1H)

(BQ-BP)₂Ir(acac)

Dimer (3.4 g, 2.265 mmol) were dissolved in 2-ethoxyethanol (136 mL). 5.0 equivalent acetylacetone (1.134 g, 11.327 mmol) and sodium carbonate (3.131 g, 22.654 mmol) is placed. Reactants refluxed under nitrogen atmosphere for 21-hour at 135°C (Fig. 3). The abstraction and purification process are the same as the method described above. Yield: 46.8%.

¹H NMR (CDCl₃, 500MHz): δ H(ppm) 8.22(d, 2H), 8.18(d, 2H), 7.92(d, 2H), 7.63(d, 2H), 7.56(s, 2H), 7.49(t, 2H), 7.42(t, 2H), 7.41(s, 2H), 7.02(d, 2H), 5.75(d, 1H), 4.08(t, 1H), 2.24(s, 1H), 1.35(s, 6H), 1.27(d, 1H),

3. Results and discussion

The maximum PL emission of (CMQ-BP)₂Ir(acac), (BQ-BP)₂Ir(acac) and (CQ-BP)₂Ir(acac) were observed at 591 nm 596.5 nm, 623.5 nm respectively (Fig. 4 and Table 1).

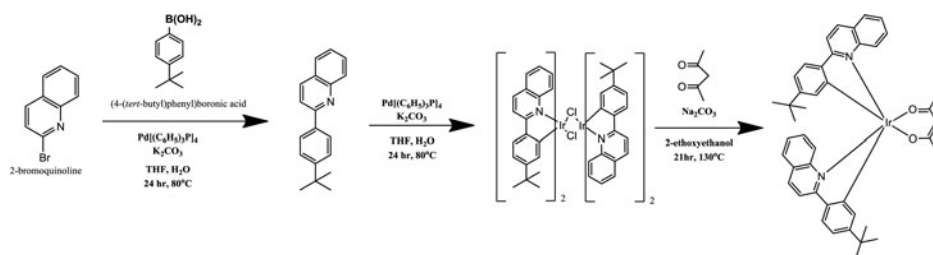


Figure 3. Synthetic route of (BQ-BP)₂Ir(acac).

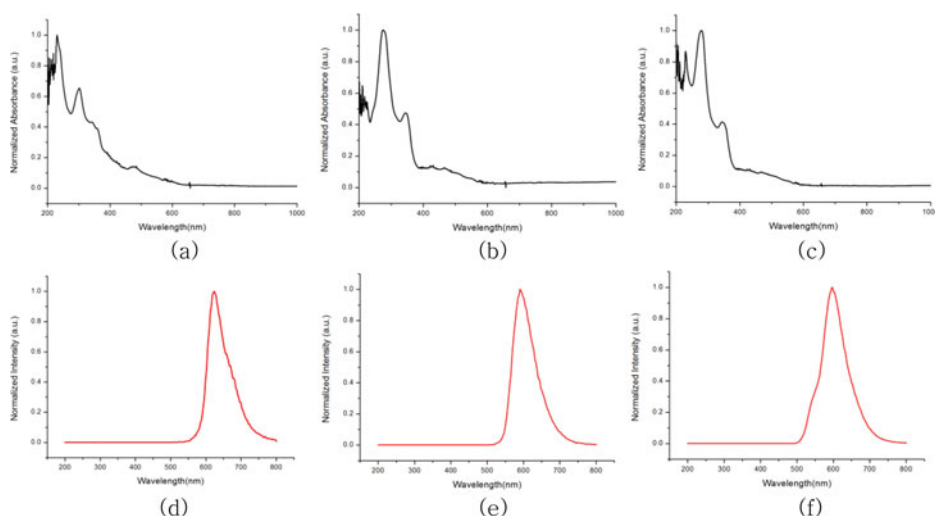


Figure 4. UV–visible absorption, and photoluminescence spectrum of Iridium(III) complexes in CH_2Cl_2 solution. (A) $(\text{CQ-BP})_2\text{Ir}(\text{acac})$, (B) $(\text{CMQ-BP})_2\text{Ir}(\text{acac})$, (C) $(\text{BQ-BP})_2\text{Ir}(\text{acac})$.

Table 1. UV–visible absorption, and photoluminescence spectrum peaks of Iridium(III) complexes.

Iridium complex	UV absorption spectrum		PL emission spectrum
	First peak	Second peak	Maximum peak
$(\text{CQ-BP})_2\text{Ir}(\text{acac})$	230nm	302nm	623nm
$(\text{CMQ-BP})_2\text{Ir}(\text{acac})$	275nm	345nm	591nm
$(\text{BQ-BP})_2\text{Ir}(\text{acac})$	279nm	344nm	596.5nm

The methyl group is electron donating group. The electron density of 2-chloro-4-methylquinoline is higher than 2-bromoquinoline in the pyridine ring. Therefore, the electron density in the pyridine ring is increased and the lowest unoccupied molecular orbital (LUMO) energy level is increased. Therefore, the HOMO-LUMO energy gap of $(\text{CMQ-BP})_2\text{Ir}(\text{acac})$ is increased and the emission wavelength is decreased. So wavelength of $(\text{CMQ-BP})_2\text{Ir}(\text{acac})$ is lower than $(\text{BQ-BP})_2\text{Ir}(\text{acac})$. At the same results, 1-chloroquinoline is more electron donating role than 2-bromoquinoline in the pyridine ring. So wavelength of $(\text{CQ-BP})_2\text{Ir}(\text{acac})$ is higher than $(\text{BQ-BP})_2\text{Ir}(\text{acac})$. [19]

4. Conclusion

As a result of a simulation using the Gaussian 09W program, $(\text{CQ-BP})_2\text{Ir}(\text{acac})$, $(\text{CMQ-BP})_2\text{Ir}(\text{acac})$, $(\text{BQ-BP})_2\text{Ir}(\text{acac})$ were predicted to emit luminance at 620nm, 598nm, 604.5 nm respectively. When Iridium(III) complexes were synthesized and had the maximum PL of $(\text{CQ-BP})_2\text{Ir}(\text{acac})$, $(\text{CMQ-BP})_2\text{Ir}(\text{acac})$, $(\text{BQ-BP})_2\text{Ir}(\text{acac})$ was observed at 623nm, 591nm, 596.5 nm at room temperature respectively. As a result, it was confirmed that $(\text{CQ-BP})_2\text{Ir}(\text{acac})$, $(\text{CMQ-BP})_2\text{Ir}(\text{acac})$, $(\text{BQ-BP})_2\text{Ir}(\text{acac})$ are suitable for red-emitting Iridium(III) complex.

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