



## Synthesis of a highly phosphorescent emitting iridium(III) complex and its application in OLEDs

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### ARTICLE INFO

#### Article history:

Received 11 March 2008

Received in revised form 12 May 2008

Accepted 23 May 2008

Available online 29 May 2008

#### Keywords:

Iridium complex

Synthesis

Phosphorescent materials

OLED

### ABSTRACT

A rigid ligand benzo[de]benzo[4,5]imidazo[2,1- $\alpha$ ]isoquinolin-7-one (biio) was designed and conveniently synthesized, and the corresponding bis-cyclometalated iridium complex (biio)<sub>2</sub>Ir(acac) (acac = acetylacetonate) was prepared. The light emitting and electrochemical properties of this complex were studied. The complex has the characters of simply synthetic procedure and strong phosphorescence. The electroluminescent device using this complex as dopant was fabricated. The device had the structure of ITO/NPB (40 nm)/Ir complex:CBP (7%, 30 nm)/BCP (15 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Al (100 nm). The maximum emission of the device was at 496 nm. The maximum brightness of the device can reach 79640 cd m<sup>-2</sup> with an external quantum efficiency of 12.1% and a maximum current efficiency of 31.7 cd A<sup>-1</sup>.

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### 1. Introduction

One of the most important research subjects in the development of organic light-emitting diodes (OLEDs) is the development of phosphorescent metal complexes due to their extremely high efficiency as electroluminescent emitters [1–5]. The strong spin-orbit coupling induced by a heavy-metal ion, such as Os, Ir, and Pt promotes an efficient intersystem crossing (ISC) between the singlet and the triplet excited state manifold. Therefore, both singlet and triplet excitons can be harnessed and then strong electroluminescence with an internal efficiency theoretically approaching to 100% can be achieved [6–10]. In particular, cyclometalated iridium(III) complexes show high phosphorescent efficiencies and relatively short lifetimes, and thus behave as one of the most promising class of phosphorescent dyes in OLEDs. These Ir complexes generally contain two cyclometalated ligands and a bidentate, monoanionic ancillary ligand, or with three cyclometalated ligands. Both the luminescent efficiency and emission wavelength of iridium complexes can usually be tuned by the introduction of substituent groups with different electronic effects or variations of the conjugation system on ligands. Therefore, design of cyclometalated ligands for Ir complexes is of great importance in order to achieve high efficiency and color purity for OLEDs [11–13]. We have reported two red emitters based on rigid quinoxaline derivative-Ir complexes, Ir(DBQ)<sub>2</sub>(acac) and Ir(MDQ)<sub>2</sub>(acac), and very

high external quantum efficiency and brightness (reached to 12.4% and 73,870 cd m<sup>-2</sup>) were achieved [14]. Very recently, we have synthesized two iridium complexes (DBA)<sub>2</sub>Ir(acac) and (BA)<sub>2</sub>Ir(acac) with rigid dihydro-benzo[*c*]acridine (DBA) and benzo[*c*]acridine (BA) ligands and high efficiencies were exhibited [15]. Some Os, Cu complexes based on rigid ligands have been used in fabrication of OLEDs and also showed fine electroluminescent characters [16,17]. Considering the rigidity of the ligand may be one of the factors for increasing fluorescence efficiency of Ir complexes, we decided to design some ligands with rigid structures.

In this article, a rigid ligand benzo[de]benzo[4,5]imidazo[2,1- $\alpha$ ]isoquinolin-7-one (biio) was synthesized by a very simple method and the cyclometalated complex (biio)<sub>2</sub>Ir(acac) based on this compound was prepared. The results showed that the complex (biio)<sub>2</sub>Ir(acac) had a strong phosphorescent property, and the device based on this complex gave a very high brightness and external quantum efficiency.

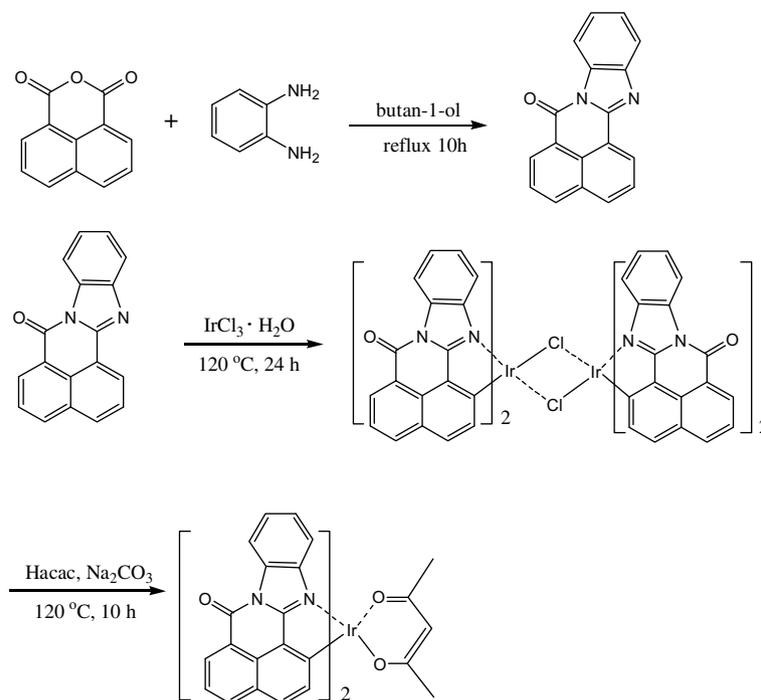
### 2. Results and discussion

#### 2.1. Synthesis of the complex (biio)<sub>2</sub>Ir(acac)

The cyclometalated ligand benzo[de]benzo[4,5]imidazo[2,1- $\alpha$ ]isoquinolin-7-one (biio) was conveniently prepared from 1,8-naphthalic anhydride and benzene-1,2-diamine by a nucleophilic substitution and condensation reaction [18]. Several solvents such as ethanol, 1-propanol, 2-propanol and butan-1-ol were tested and the results showed that in refluxing butan-1-ol, it gave the best yield.

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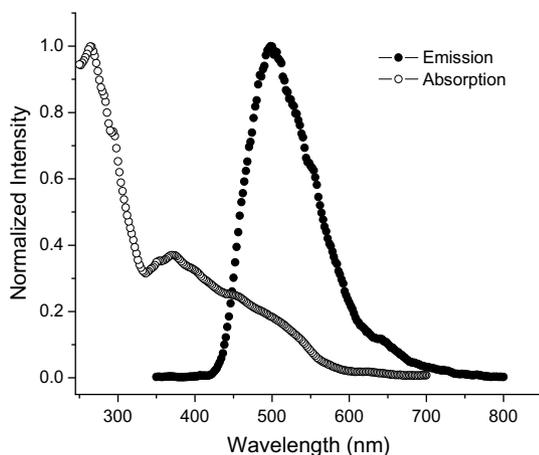


**Scheme 1.** Synthesis of the complex.

The complex  $(\text{biiO})_2\text{Ir}(\text{acac})$  was synthesized by a general procedure [19]. The reaction of iridium trichloride hydrate with ligand gave a Ir(III)  $\mu$ -chlorobridged dimer. The dimer reacted with acetylacetonate in the presence of  $\text{Na}_2\text{CO}_3$  in 2-ethoxyethanol then afforded the corresponding complex with moderate yield (Scheme 1).

## 2.2. Absorption, emission and electrochemical properties

As a specifically structured complex with rigid and electron withdrawing group substituted ligands,  $(\text{biiO})_2\text{Ir}(\text{acac})$  may have a great researching value, though there is a few literatures referred to this type of complex [20]. The absorption and photoluminescence (PL) spectra of the complex in dichloromethane at room temperature are shown in Fig. 1. In the UV–Vis spectra, there are four major absorptions at 265, 370, 449, 510 nm. The former two bands are assigned to be ligand based transitions, which closely resemble the absorption spectra of the free ligand, whereas the latter two



**Fig. 1.** Absorption and emission spectra of the complex.

absorptions are likely due to  $^1\text{MLCT}$  and  $^3\text{MLCT}$  [5,14]. The comparable intensities of  $^1\text{MLCT}$  and  $^3\text{MLCT}$  imply the presence of significant singlet–triplet coupling due to spin–orbital coupling which leads to efficient phosphorescence.

Upon irradiation with 360 nm light, the complex gave a strong photoluminescence in dichloromethane at 496 nm. It was sure that the observed emission of this iridium complex was phosphorescent in nature based on the previously reported cyclometalated iridium complexes. Larger conjugation may bring on a longer emitting wavelength [21,22]. Our previous reports showed that when the rigid ligands such as DBQ, MDQ, DBA and BA were adopted, because of the extended conjugation in the corresponding iridium complexes, the long emitting wavelength (more than 600 nm) was shown and therefore some red emitting materials were obtained [14,15]. To the complex  $(\text{biiO})_2\text{Ir}(\text{acac})$ , the short emitting wavelength (less than 500 nm) may be related to the electron withdrawing effect of carbonyl group. The stabilization of the HOMO (highest occupied molecular orbital) by this effect leads to a shortened emitting wavelength. It sustains the conclusion that the emitting wavelength is affected by the electronic effect of functional groups on the ligand, which was also confirmed by Burn et al. through molecular orbital calculations [23]. It was also shown that the emitting wavelength can be modulated by the introduction of some special groups. Using  $\text{Ir}(\text{ppy})_2(\text{acac})$  as a reference which has a emission quantum yield of 0.34 [5], the emission quantum yield of  $(\text{biiO})_2\text{Ir}(\text{acac})$  was determined as 0.65. It was a base to get a high efficient electroluminescent device.

The electrochemical behavior of this Ir metal complex was investigated by cyclic voltammetry (CV). The conventional three-electrode configuration consists of platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire quasi-reference electrode. The ferrocene/ferrocenium couple was used as internal reference. The cyclic voltammograms (CVs) were made in a one-compartment glass cell in dichloromethane containing  $1 \times 10^{-3}$  M complex and 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte. Fig. 2 depicts a typical CV of the complex, where the potential is cycled at  $50 \text{ mV s}^{-1}$ .

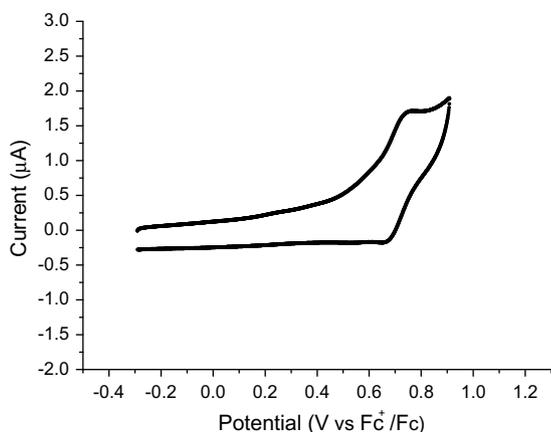


Fig. 2. Cyclic voltammogram of the complex  $(\text{biiio})_2\text{Ir}(\text{acac})$ .

The complex exhibited a one-electron oxidation wave during the anodic scan in  $\text{CH}_2\text{Cl}_2$  solution, with the half-wave oxidative potential of 0.71 V. On the basis of the onset potential of the oxidation, we can roughly estimate the highest occupied molecular orbital (HOMO) energy level of this Ir complex with regard to the energy level of the ferrocenium/ferrocene redox couple (being approximately 4.8 eV negative to the vacuum level) [24]. All the cyclic voltammetry data are listed in Table 1.

Yang and co-workers have reported an Ir complex  $(\text{tbi})_2\text{Ir}(\text{acac})$  which is also based on a benzoimidazo derivative ligand 1-hexyl-2-*p*-tolyl-1H-benzo[d]imidazole [25]. Compared with  $(\text{tbi})_2\text{Ir}(\text{acac})$ , the complex  $(\text{biiio})_2\text{Ir}(\text{acac})$  has a decreased HOMO energy level of  $-5.30$  eV (Table 1). Though the extension of  $\pi$ -conjugation in  $(\text{biiio})_2\text{Ir}(\text{acac})$  may bring a decrease of the energy gap and lead to a red shift of the PL spectrum [21,22], we observed not a red but a little blue shift emission from the PL spectrum of  $(\text{biiio})_2\text{Ir}(\text{acac})$ . We presume that the introduction of carbonyl group into the ligand framework may increase the energy gap by decreasing the HOMO energy level and therefore bring a shorter emitting wavelength.

### 2.3. Electroluminescent properties

For studying electroluminescent properties of this iridium complex, device using complex  $(\text{biiio})_2\text{Ir}(\text{acac})$  as dopant emitter was fabricated. The device was prepared with the following structure: ITO/NPB(40 nm)/Ir-complex: CBP(7%, 30 nm)/BCP(15 nm)/Alq(30 nm)/LiF(1 nm)/Al(100 nm) in which ITO (indium tin oxide) was used as the anode, NPB (4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl) was used as the hole-transporting material, CBP (4,4'-*N,N'*-dicarbazole biphenyl) as the host, the iridium complex as the dopant, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as the hole blocker, Alq (tris(8-hydroxyquinolinato)aluminium) as the electron transporter, and LiF/Al as the cathode (Fig. 3).

The device had a maximum emission at 496 nm (Fig. 4), which resembled the PL spectrum of the complex. It showed that the energy transfer from the host material CBP to the Ir complex emitter was very efficient. At the voltages of 6, 8, 10 and 12 V, the device

Table 1  
The electrochemical behavior of  $(\text{biiio})_2\text{Ir}(\text{acac})$  and  $(\text{tbi})_2\text{Ir}(\text{acac})^a$

complex	$E_{1/2}$ (V)	$E_{\text{onset}}$ (V)	HOMO (eV) <sup>b</sup>	PL (nm)
$(\text{biiio})_2\text{Ir}(\text{acac})$	0.71	0.50	$-5.30$	496
$(\text{tbi})_2\text{Ir}(\text{acac})^a$	0.52	0.39	$-5.19$	500, 534

<sup>a</sup> The data of the complex  $(\text{tbi})_2\text{Ir}(\text{acac})$  were cited from lit. [25].

<sup>b</sup> Determined from the onset oxidation potential.

gave the almost completely superposed electroluminescence (EL) spectra. It indicated that the EL spectrum did almost not change when the voltage changed. It means that the EL spectrum of the device was independent of the applied voltage. The Commission International de l'Eclairage (CIE) coordinates were calculated to be (0.18, 0.54) based on the EL spectrum at an applied voltage of 8 V.

Figs. 5 and 6 show the luminance–voltage–current density curve and the power efficiency–current density–external EL quantum efficiency curve, respectively. The device showed a quite high efficiencies and brightness. At a voltage of 8.5 V (where the current density was  $11.4 \text{ mA m}^{-2}$ ), it gave a maximum external quantum efficiency of 12.1% and a maximum current efficiency of  $31.7 \text{ cd A}^{-1}$ ; at a voltage of 5 V, it gave a maximum power efficiency of  $16.5 \text{ lm W}^{-1}$ ; and at a voltage of 14 V, it gave a maximum brightness of  $79,640 \text{ cd m}^{-2}$ . These performances and the previous related reports [14,15] favored the supposition that the high rigidity of the ligand framework would significantly reduce the nonradiative transition and therefore enhance the emitting efficiency of the materials [17]. The rigid structure may be one of the factors for increasing fluorescence efficiency of Ir complexes, so OLEDs based on this rigid ligand–Ir complex could give a high brightness and efficiencies. The results may provide a useful reference for the design of new luminescent materials.

### 3. Conclusion

In summary, we designed and synthesized a new iridium complex  $(\text{biiio})_2\text{Ir}(\text{acac})$  with a rigid cyclometalated ligand *biiio*. The complex has the characters of simply synthetic procedure and strong phosphorescence. The maximum brightness of the electroluminescent device using this complex as dopant can reach  $79,640 \text{ cd m}^{-2}$  with an external quantum efficiency of 12.1% and a maximum current efficiency of  $31.7 \text{ cd A}^{-1}$ .

### 4. Experimental

#### 4.1. Reagents and instruments

Reagents were used as purchased without further purification.  $^1\text{H}$  NMR spectra was measured on a Bruker AVANCE 400 spectrometer in  $\text{CDCl}_3$  using TMS as an internal reference. Mass spectra (MS) were measured on a VG-ZAB-HS spectrometer with electron impact ionization. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. The UV-Vis spectra were recorded on VARIAN Cary 5000 spectrometer while PL spectra were recorded on Perkin-Elmer LS 50B luminescence spectrophotometer. CV measurements were carried out with a CHI660C electrochemical analyzer (CH Instruments) at room temperature. Current, voltage, and light-intensity measurements were made simultaneously using a Keithley 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photodiode.

#### 4.2. Synthesis of materials

##### 4.2.1. Synthesis of the cyclometalated ligand

1,8-Naphthalic anhydride (1.98 g, 10.0 mmol) and benzene-1,2-diamine (1.08 g, 10.0 mmol) were dissolved in 20 mL of butan-1-ol. After refluxed for 10 h, the solution was cooled to room temperature, the precipitate was collected. After recrystallised from butan-1-ol and ethanol, the pure product benzo[de]benzo[4,5]-imidazo[2,1- $\alpha$ ]isoquinolin-7-one was given with the yield of 85%. Yellow acicular solid. Mp  $190\text{--}192$  °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.96 (d,  $J = 9.6$  Hz, 1H), 8.86 (d,  $J = 9.6$  Hz, 1H), 8.62 (m, 1H), 8.35 (d,  $J = 10.8$  Hz, 1H), 8.21 (d,  $J = 11.3$  Hz, 1H), 7.84–7.96 (m,

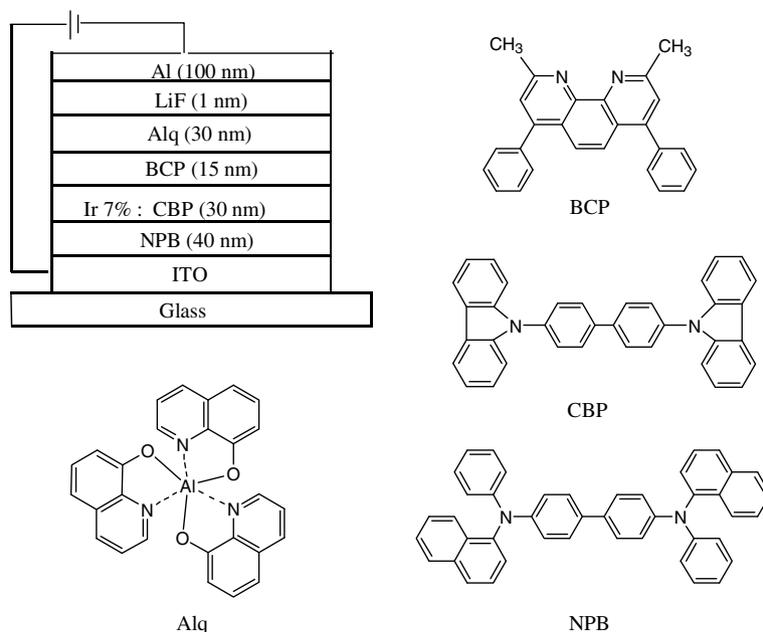


Fig. 3. Structure of the device and the molecular structures of the compounds used in the device.

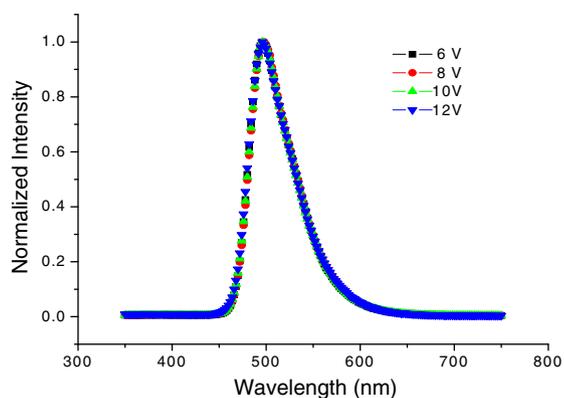


Fig. 4. Electroluminescence spectra of the device at various applied voltages.

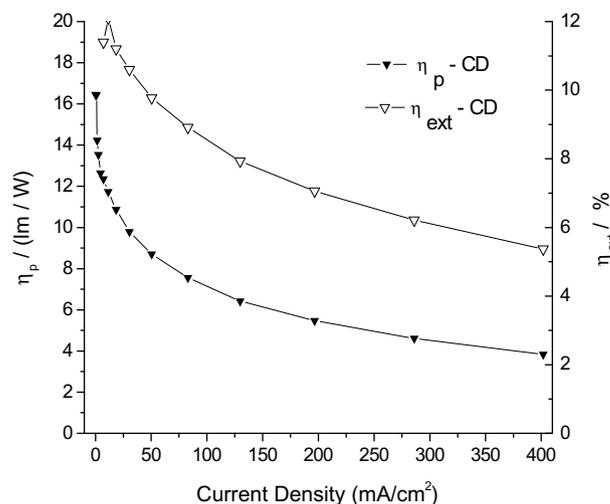


Fig. 6. Power efficiency ( $\eta_p$ )–current density–external quantum efficiency ( $\eta_{ext}$ ) characters of the device.

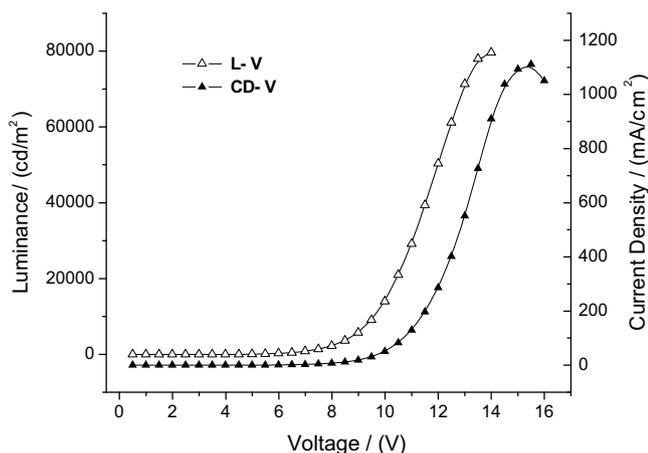


Fig. 5. Luminance –voltage –current density characters of the device.

3H), 7.53 (m, 2H). MS $m/z$ : 270.0 (5.4, M<sup>+</sup>), 255.0 (100), 256.1 (63.4), 128.0 (7.8), 127.0 (5.2), 77.0 (4.2). Anal. Calc. for C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>O: C, 79.99; H, 3.73; N, 10.36. Found: C, 79.45; H, 3.82; N, 10.17%.

#### 4.2.2. Synthesis of the complex

Benzo[de]benzo[4,5]imidazo[2,1- $\alpha$ ]isoquinolin-7-one (0.68 g, 2.5 mmol) was dissolved in 9 mL 2-ethoxyethanol, then iridium trichloride hydrate (0.34 g, 1 mmol) and 3 mL water were added. The mixture was stirred in a nitrogen atmosphere at 120 °C for 24 h, and then cooled to room temperature. The precipitate was collected and washed with ethanol, acetone, and then dried in vacuum. It gave the cyclometalated Ir(III)  $\mu$ -chlorobridged dimer. Then 0.20 g (2 mmol) acetyl acetone, 0.53 g (5 mmol) Na<sub>2</sub>CO<sub>3</sub> and the dimer were dissolved in 8 mL 2-ethoxyethanol and refluxed in a nitrogen atmosphere for 12 h. After cooling to room temperature, the precipitate was filtered off and washed with water, ethanol, and ether. The crude product was then sublimated at 300–320 °C and  $4 \times 10^{-3}$  Pa to give the pure complex. Yield: 72%. Brown powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 8.83 (d,  $J = 7.3$  Hz, 2H), 8.75 (d,  $J = 7.3$  Hz, 2H), 8.58 (d,  $J = 7.3$  Hz, 2H), 8.31 (d,  $J = 8.2$  Hz, 2H), 8.18 (d,  $J = 8.2$  Hz, 2H), 7.84–7.88 (m, 4H), 7.50–7.52 (m, 4H),

5.18 (s, 1H), 1.29 (s, 6H). Anal. Calc. for  $C_{41}H_{25}IrN_4O_4$ : C, 59.34; H, 3.04; N, 6.75. Found: C, 59.76; H, 3.12; N, 6.62%.

#### 4.3. OLED fabrication

The device was fabricated by vacuum deposition of the materials at  $1.3 \times 10^{-4}$  Pa onto a clean glass pre-coated with a layer of indium tin oxide with a sheet resistance of  $25 \Omega \text{ square}^{-1}$ . The deposition rate for the organic compounds was  $0.1\text{--}0.2 \text{ nm s}^{-1}$ . The cathode of LiF/Al was deposited by first evaporating LiF at a deposition rate of  $0.01 \text{ nm s}^{-1}$  and then evaporating aluminum at a rate of  $0.1\text{--}0.2 \text{ nm s}^{-1}$ .

#### Acknowledgements

Financial supports from the National Natural Science Foundation of China (Project Nos. 20772057 and 20773066) and the Natural Science Foundation of Jiangsu Province (Project No. BK2005139) are gratefully acknowledged.

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