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# A new iridium(III) complex with efficient photo- and electro-luminescent properties

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Cyclometalated iridium(III) complexes have attracted considerable attention in material research due to their outstanding performance in organic light-emitting diodes (OLED) [1-4]. The strong spin-orbit coupling induced by a heavy-metal ion 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 [5-8]. The Ir(III) complexes reported generally contain two cyclometalated ligands and a bidentate, monoanionic ancillary ligand, or with three cyclometalated ligands. Both the luminescent efficiency and emission colors of Ir(III) complexes can be tuned by introduction of substituents with different electronic effects or variations of the conjugation system on ligands [9–13]. Thus, manipulation of the skeletal arrangement as well as the substituent groups of the cvclometalating ligand may represent a promising venue for the development of highly phosphorescent Ir(III) complexes. Although a wide range of Ir(III) materials have been reported, the number of highly phosphorescent imidazole-based cyclometalated Ir(III) complexes is still rare [13,14]. 1,3,5-tris(N-phenylbenz-imidazole-2-yl)benzene (TPBI), a commonly used electron transporter and hole blocker, is a derivative of benzoimidazole compounds. Therefore, benzoimidazole(bi)-based cyclometalated iridium complexes may have good electron transporting ability, which is highly desirable in designing high efficiency OLEDs [15]. In this paper, a rigid ligand 2phenylphenanthro[9,10-d]imidazole (pi) was synthesized by a very simple method, and the OLED device based on this cyclometalated complex Ir(pi)<sub>2</sub>(acac) gave good brightness and efficiency.

## ABSTRACT

A new complex of  $Ir(pi)_2(acac)$  (L=2-(4-bromophenyl)-1-ethyl-1H-phenanthro[9,10-d]imidazole) was designed and synthesized. Its molecular structure was determined by a single-crystal X-ray diffraction analysis. The Ir(III) complex showed characteristic phosphorescence with an emission of 570 nm and a high quantum efficiency of 28%. A high performance yellow OLEDs was successfully fabricated by using this Ir(III) complex as dopant. © 2011 Elsevier B.V. All rights reserved.

> The 2-(4-bromophenyl)-1H-Phenanthro[9,10-d]imidazole ligand was easily obtained from the reaction of phenanthrequinone, NH<sub>4</sub>Ac and the p-bromobenzaldehyde in HAc solvent. Additional alkylation by EtBr afforded 2-(4-bromophenyl)-1-ethyl-1H-Phenanthro[9,10-d] imidazole (pi) (Scheme 1). Ir(pi)<sub>2</sub>(acac) was obtained in moderate condition from the above ligand by a conventional two-step sequence [14]. In the first step a chloro-bridged dimmer was formed by the reaction of pi with IrCl<sub>3</sub>. Then, this dimmer was cleaved by treatment with acac in the presence of  $Na_2CO_3$  to produce the complex  $Ir(pi)_2$ (acac). Yellow solid, yield: 24%. Anal. Calc. for C<sub>51</sub>H<sub>39</sub>Br<sub>2</sub>IrN<sub>4</sub>O<sub>2</sub> (%): C, 56.10; H, 3.60; N, 5.13. Found: C, 56.08; H, 3.66; N, 5.15. <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz}): \delta (ppm) = 8.84 - 8.77 (m, 4H), 8.59 (d, J = 8.3 \text{ Hz},$ 2H), 8.47 (d, *I*=8.2 Hz, 2H), 7.71 (t, *I*=8.4 Hz, 2H), 7.69-7.62 (m, 4H), 7.48 (t, *J*=7.8 Hz, 2H), 7.34 (t, *J*=7.8 Hz, 2H), 7.20 (s, 2H), 7.17 (d, *I* = 8.4 Hz, 2H), 5.37 – 5.16 (m, 4H), 4.21 (s, 1H), 2.05 (t, *I* = 7.1 Hz, 6H), 1.13 (s, 6H). MS (FAB): m/e 1090.3 (M<sup>+</sup>).

> The structure of  $Ir(pi)_2(acac)$  was confirmed by single crystal X-ray diffraction study (Fig. 1). The iridium resides in an approximately octahedral environment and the two nitrogen atoms of pi ligands exhibit cis–C–C and trans–N, N chelated dispositions. The Ir—C bonds 1.987(2) Å and Ir—O bonds 2.150(2) Å are similar to those of (fbi)<sub>2</sub>Ir (acac) (Ir–C, 2.006(4) Å; Ir–O, 2.145(6) Å) [13]. However, the Ir—N bonds 2.076(2) Å are a little longer than the Ir—N bonds (2.038(3) Å) in (fbi)<sub>2</sub>Ir(acac) possibly due to the more steric congestion of pi ligand. The Phenanthro[9,10-d]imidazolyl ring is approximately coplanar with the phenyl ring (the dihedral angle between the two planes is 4.0(0.1)°). The dihedral angles between the chelating ring of Ir–C–C–C–N and phenyl ring is 5.2°.

The absorption and emission spectra of  $Ir(pi)_2(acac)$  recorded in dichloromethane at room-temperature are shown in Fig. 2. In the absorption spectrum, the intense bands around 250–350 nm can be assigned to spin-allowed  ${}^1\pi$ – $\pi$ \* transitions of the ligand, which correlate

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Scheme 1. General synthetic route of ligand.

with the transition observed for the free pi. The absorption in the range of 365–400 nm corresponds to spin-allowed S°  $\rightarrow$  <sup>1</sup>MLCT transition. The broad band at 430 nm can be assigned to S°  $\rightarrow$  <sup>3</sup>MLCT transition and gains intensity by mixing with the higher lying <sup>1</sup>MLCT transition through the spin–orbit coupling of iridium(III). This mixing is strong enough in this complex that the formally spin forbidden <sup>3</sup>MLCT has an extinction coefficient that is almost equal to the spin allowed <sup>1</sup>MLCT transition [13].

The iridium complex showed characteristic phosphorescence with a high quantum efficiency of 28% in degassed CH<sub>2</sub>Cl<sub>2</sub> solutions upon irradiation with 430 nm light at an ambient temperature. The maximum emission peak was found to be dependent on the polarity of the solvent, which suggests the  ${}^{3}MLCT \rightarrow \pi$  transition of the emissive state. The complex shows broad and featureless transition with maximum at 570 nm in the photoluminescence (PL) spectrum (Fig. 2). It has been confirmed that the relative contribution of <sup>3</sup>MLCT vs ligand-based  ${}^{3}\pi-\pi^{*}$  transitions may affect the Stokes shifts between the <sup>3</sup>MLCT and emission bands as well as the phosphorescence spectral feature [16]. The significant Stokes shifts (140 nm) assist us in assigning the  ${}^{3}\pi$ - $\pi^{*}$  states as the dominant emitting state at room temperature in equilibrium with the other neighboring states. The excited state lifetime of Ir(pi)<sub>2</sub>(acac), measured at 298 K in degassed CH<sub>2</sub>Cl<sub>2</sub> solution, is 0.57 µs, comparable with that of benzoimidazole-based iridium complexes reported previously [13]. Furthermore, the emission band of complex Ir(pi)<sub>2</sub>(acac) is redshifted about 50 nm compared with that of  $Ir(bi)_2(acac)$  owing to the enlarged  $\pi$ -conjugation of Phenanthro[9,10-d]imidazolyl ring. The short excited state lifetime together with the high phosphorescence yield should be advantageous to highly efficient OLED devices.

The complex Ir(pi)<sub>2</sub>(acac) undergoes a reversible one-electron oxidation wave of 0.91 V vs Fc<sup>+</sup>/Fc [17] in CH<sub>2</sub>Cl<sub>2</sub>, which can be attributed to metal-centered Ir<sup>III</sup>/Ir<sup>IV</sup> oxidation process. As revealed



To demonstrate the basic electrophosphorescent properties of Ir  $(pi)_2(acac)$ , we fabricated the device with a multilayer configuration ITO/NPB (30 nm)/Ir $(pi)_2(acac)$ : CBP (5%) (30 nm)/BCP (10 nm)/AlQ (30 nm)/LiF (1 nm)/Al (200 nm) and investigated its electroluminescent (EL) performances. Fig. 3 (inset) shows the EL spectrum of the device at 10 V bias. The device had a maximum emission at 566 nm, 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. Moreover, the EL spectrum of the device was independent of the applied voltage. Fig. 3 shows the current density–voltage–brightness (*I–L–V*) characteristics of this device. A turn-on voltage of 4 V and a maximum brightness of 11232 cd/m<sup>2</sup> at 12 V were obtained. The calculated maximum current efficiency and power efficiency were 4.6 cd/A and 1.82 lm/W, respectively.



Fig. 1. Crystal structure of Ir(pi)<sub>2</sub>(acac).



Fig. 2. UV-vis and PL spectrum of  $Ir(pi)_2(acac)$  in  $CH_2CI_2$  solution at 298 K ( $c=1.0\times10^{-5}$  mol/L).



**Fig. 3.** The *I*-*L*-*V* characteristics of the device base on  $Ir(pi)_2(acac)$ . Inset: EL spectrum at 10 V of the device base on  $Ir(pi)_2(acac)$ .

In conclusion, a new iridium complex  $Ir(pi)_2(acac)$  with a rigid cyclometalated ligand 2-(4-bromophenyl)-1-ethyl-1H-phenanthro [9,10-d]imidazole was designed and synthesized. This complex has the characteristics of simply synthetic procedure and strong phosphorescence. Furthermore, the iridium complex could be used as an efficient dopant for fabricating yellow organic light-emitting diodes and gave a maximum brightness of 11232 cd/m<sup>2</sup> at 12 V.

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#### Appendix A. Supplementary material

CCDC 768352 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.05.030.

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