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A carbazole-functionalized Ir complex used in efficient single-layer electrophosphorescent devices ☆

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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ABSTRACT

The fabrication of electroluminescent devices that combine high device performance with simple device configuration remains an attractive challenge for their low costs and simple fabrication process. In this paper, a novel red phosphorescent iridium complex containing a carbazole-functionalized β-diketonate ligand, bis(1-phenylisoquinolinato-C2,N) iridium 1-(carbazol-9-yl)-5,5-dimethylhexane-2,4-diketonate ($Ir(piq)_2(CBDK)$), is designed, synthesized, and characterized. The electrophosphorescence of $Ir(piq)_2$(CBDK) as an emitter in organic light-emitting diodes was examined and compared with that of $Ir(piq)_2$(acac) (acac = acetylacetonate) without carbazolyl group. A series of single-layer devices containing different concentration gradients of $Ir(piq)_2(CBDK)$ as an emitting and hole-transporting material and 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene as an electron-transporting material were constructed. A maximum current efficiency of 9.9 cd A^{-1} and power efficiency of 7.8 lm W^{-1} were obtained, which is one of the best performances obtained for a single-layer device containing one material as a host.

1. Introduction

Organic light-emitting diodes (OLEDs) have been extensively researched because of their importance in flat-panel displays and lighting sources [1–5]. Among them, Phosphorescent organic light-emitting devices (PhOLEDs) can exhibit 100% internal quantum efficiency because phosphorescent materials harvest both triplet and singlet excitons for light generation [6,7]. Usually, to avoid triplet–triplet annihilation and improve the carrier-transporting ability of the emissive layer in PHOLEDs, phosphorescent materials are used as an emitting guest and are doped into host materials [8]. In addition, traditional devices employ a number of functional layers, including hole injection, hole transport, hole blocking, and electron transport layers to balance carrier transport for electron–hole recombination and confine the formation of excitons to the emissive layer. Such a multilayer structure leads to devices with higher performance whereas it uses more expensive materials and makes device fabrication complex. Therefore, electrophosphorescent devices should be simplified while their competitive performance is maintained for their low costs and simple fabrication process.

Single- or double-layer OLEDs have been reported recently by several researchers [9–12]. Most reported single-layer devices contain both hole-transporting and electron-transporting materials as dopants, such as *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB) and 2,7-bis(diphenylphosphoryl)spiro[fluorene-7,11′-benzofluorene] (SPPO21) [9] 4,4′,4″-tris(*N*-3-methylphenyl-*N*-phenyl-amino) triphenylamine (m-MTDATA) (or NPB) and bis(10-hydroxybenzo[h] quinolinato)beryllium (Bebq2) [10], where NPB and m-MTDATA were used as hole-transporting host materials, and Bebq2 and SPPO21 were used as electron-transporting host materials. Holes were directly injected from the ITO anode to the emitting layer through NPB or m-MTDATA, while electrons were injected from the cathode to the emitting layer through SPPO21 or Bebq2. The quantum efficiencies of these simple devices are comparable to those of common multilayer devices. It is obvious that the choice of suitable hole- and electron-transporting host materials is very important to balance injection and transport of holes and electrons in single-layer devices. In 2009, Lu et al. reported a single-layer red PHOLED, in which tris[1-phenylisoquinolinato-C2,N]iridium (III) ($Ir(piq)_3$) was doped in 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBi). The current and power efficiency of this device were about 3.7 cd A^{-1} and 3.2 lm W^{-1} (at 1 cd m^{-2}), respectively [11]. The low efficiency may be caused by the use of TPBi as a host material causing poor hole-injecting or transporting properties in the device. Therefore, the direct injection of charge carriers into the organic layer and high carrier mobility are important to simplify the structure of devices while maintaining a high efficiency.

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In 2006, we reported a novel red phosphorescent iridium complex containing a carbazole-functionalized β-diketonate ligand, bis(dibenzo[f,h] quinoxalinato-N,C2) iridium (III) (1-(carbazol-9-yl)-5,5-dimethylhexane-2,4-diketonate) (Ir(DBQ)$_2$(CBDK)) [13]. The high electroluminescence (EL) performance observed from Ir(DBQ)$_2$(CBDK) was mainly attributed to the carbazole-functionalized β-diketonate ligand which improved its carrier-transport properties and reduced triplet–triplet annihilation. Encouraged by this result, in this work, the red phosphorescent complex bis [1-phenylisoquinolinato-C2,N] iridium (III) (1-(carbazol-9-yl)-5, 5-dimethylhexane-2,4-diketonate) (Ir(piq)$_2$(CBDK)) was designed, synthesized and characterized for single-layer electrophosphorescent devices. Using Ir(piq)$_2$(CBDK) as the guest doped in TPBi, the single-layer device with the structure ITO/Ir(piq)$_2$(CBDK):TPBi/ Mg$_{0.9}$Ag$_{0.1}$ (200 nm)/Ag (80 nm) was prepared. The device with the same structure using Ir(piq)$_2$(acac) (acac = acetylacetonate) as guest was also fabricated for comparison. As expected, the EL performance of Ir(piq)$_2$(CBDK) in the single-layer device was much better than that of Ir(piq)$_2$(acac). Moreover, it was demonstrated that the concentration of Ir(piq)$_2$(CBDK) in TPBi determines the hole or electron conductivity of the emitting layer and remarkable EL performances could be achieved using a concentration gradient to realize balanced charge transport in the emitting layer. A maximum current efficiency of 9.9 cd A^{-1} and power efficiency of 7.8 lm W^{-1} were obtained, which is one of the best performances obtained for a single-layer device containing one material as a host.

2. Experimental

2.1. General information

Ir(piq)$_2$(acac) [14] and Alq$_3$ [15] were synthesized according to literature procedures and sublimed twice prior to use. TPBi was purchased from Lum-Tec, and was used as received. NPB and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Aldrich and used after a single sublimation. Chromatographic separation was performed on silica gel (200–300 mesh). ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer using Me$_4$Si as an internal reference. Mass spectra were recorded on a ZAB-HS and BIFLEX III spectrometers. Elemental analyses were performed on a VARIO EL analyzer. Photoluminescence (PL) spectra were recorded on an Edinburgh Analytical Instruments FLS920 spectrometer. Absorption spectra were measured on a Shimadzu UV-3100 UV–Vis spectrometer. Cyclic voltammetry was performed with a computer controlled CHI600C electrochemical workstation. All measurements were performed at room temperature using a conventional three electrode configuration consisting of a one compartment electrolysis cell with a platinum button as a working electrode, platinum wire as a counter electrode, and Ag/AgCl reference electrode. Cyclic voltammograms were obtained at a scan rate of 50 mV s^{-1} in HPLC grade dichloromethane. The concentration of each complex was 1.0 mM and each solution contained 0.1 M tetrabutylammonium hexafluorophosphate (nBu$_4$NPF$_6$, TBAP) as a supporting electrolyte. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated by reference to the energy level of the ferrocene/ferrocenium redox couple of −4.8 eV. X-ray diffraction data were collected on a Rigaku MicroMax-007 CCD diffractometer by the ω scan technique at 131 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A multiscan absorption correction was applied to the intensity data. Structures were solved using direct methods, and heavy atoms were located from the E-map. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package.

2.2. Fabrication and measurement of OLEDs

Patterned anodes with a sheet resistance of 7 Ω/sq were obtained commercially. Before loading into the deposition chamber, the ITO-coated glass substrates were rinsed with organic solvent and deionized water and then treated with UV ozone. The organic and metal layers were deposited in different vacuum chambers under a base pressure better than 8×10^{-5} Pa. The emissive area of the device, defined as the overlapping area of the cathode and anode, was 9 mm^2. The thickness of the deposited layer and speed of evaporation of individual materials were monitored with quartz crystal monitors. Deposition rates were maintained at 0.05–0.2 nm s^{-1} for organic materials and 0.2–0.3 nm s^{-1} for the Mg$_{0.9}$-Ag$_{0.1}$ alloy. All electrical testing and optical measurements were performed under ambient conditions. EL spectra were measured with a Spectra Scan PR650. The current density–voltage (*J*–*V*) and luminance–voltage (*L*–*V*) characteristics were measured using a computer-controlled Keithley 2400 sourcemeter with a calibrated silicon diode.

2.3. Synthesis of Ir(piq)$_2$(CBDK)

CBDK [13] and Piq [14] were synthesized following known literature procedures. Synthesis of Ir(piq)$_2$(CBDK): piq was dissolved in 2-ehtoxyethanol (10 ml) in a 50 ml round-bottomed flask. Iridium trichloride hydrate (1.0 mmol) and 3.0 mL of water were then added to the flask. After the mixture was stirred under nitrogen at 120 °C for 24 h, the mixture was cooled to room temperature and then the precipitate was collected and washed with ethanol, acetone, and dried in vacuum to give a cyclometallated Ir^{III}-μ-chloro-bridge dimer. In a 50 mL flask, the dimer complex (1.0 mmol), CBDK (2.0 mmol), and Na$_2$CO$_3$ (5.0 mmol) were dissolved in 2-ethoxyethanol (15 mL) and the mixture was then refluxed under a nitrogen atmosphere for 12 h. After cooling to room temperature, the precipitate was filtered off and washed with water. The rough product was purified by silica column chromatography with dichloromethane/petroleum ether (1:1, v/v), sublimed twice prior to use. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.08 (1H, d, *J* = 5.3 Hz), 8.96 (1H, d, *J* = 9.0 Hz), 8.37 (1H, d, *J* = 6.4 Hz), 8.26 (1H, d, *J* = 6.3 Hz), 8.21 (1H, d, *J* = 6.4 Hz), 8.16 (1H, d, *J* = 6.3 Hz), 8.02 (2H, d, *J* = 1.6 Hz), 8.00 (1H, t, *J* = 6.3 Hz), 7.90 (1 H, d, *J* = 6.3 Hz), 7.770–7.80 (2H, m), 7.68–7.70 (2H, m), 7.26–7.34 (2H, dd, *J* = 6.3 Hz), 7.14–7.18 (4H, m), 7.07 (2H, d, *J* = 7.5 Hz), 6.96 (1H, t, *J* = 7.6 Hz), 6.89 (1H, t, *J* = 6.8 Hz), 6.70 (1H, t, *J* = 6.8 Hz), 6.64 (1H, t, *J* = 6.8 Hz), 6.52 (1H, d, *J* = 0.96 Hz), 6.41 (1H, d, *J* = 1.1 Hz), 5.00 (1H, s), 4.68–4.72 (1H, d, *J* = 16.8 Hz), 4.46–4.50 (1H, d, *J* = 16.8 Hz), 0.50 (9H, s). *Anal.* calc. for C$_{50}$H$_{40}$IrN$_3$O$_2$: C, 66.20; H, 4.44; N, 4.63. Found: C, 66.33; H, 4.55; N, 4.47%. HRMS (ESI$^+$, CH$_3$OH) calc. for C$_{50}$H$_{40}$IrN$_3$O$_2$, 907.27 ([M+H]$^+$); found, 907.27.

3. Results and discussion

3.1. X-ray crystal structure of Ir(piq)$_2$(CBDK)

The single crystals of Ir(piq)$_2$(CBDK) suitable for X-ray diffraction were obtained from slow evaporation of a solution of Ir(piq)$_2$ (CBDK) in CH$_2$Cl$_2$ and C$_2$H$_5$OH.

Fig. 1 shows an ORTEP diagram of Ir(piq)$_2$(CBDK) (C$_{50}$H$_{40}$IrN$_3$O$_2$·CH$_2$Cl$_2$) obtained from X-ray analysis. Selected parameters of the molecular structure are listed in Table 1. Selected bond distances [Å] are: Ir(1)–N(2) 2.035(3), Ir(1)–N(3)2.028(3), Ir(1)–O(1) 2.141 (3), Ir(1)–O(2) 2.165(3), Ir(1)–C(31) 1.991(4), and Ir(1)–C(46) 1.974(4), and angles [°] are: O(1)–Ir(1)–O(2) 86.97(10), C(31)–