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Highly efficient blue organic electrophosphorescence devices using a trifluorine-replaced iridium complex

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1. Introduction

ABSTRACT

Highly efficient blue phosphorescent organic light-emitting devices have been achieved by using a new emitter Iridium complex, bis[(3,4,5-trifluorophenyl)-pyridinato- N,C^2 '] picolinate (F_3 Irpic). For a mCP:4%F₃Irpic device, blue emission with a maximum power efficiency of 18.1 lm/W has been realized, which is much higher than those of FIrpic based devices. The emission peak was located at 480 nm with a subpeak at 511 nm. By using an optimized device structure with a better host material, performance of the device can be further increased to give a maximum power efficiency of 33.7 lm/W.

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White organic light-emitting devices (OLEDs) have drawn much attention due to their applications as backlights for liquid-crystal displays and as solid-state light sources [1–4]. For these applications, high efficiency and long life-time are important. Phosphorescent OLEDs have been shown to harvest 100% of the excitions generated by electrical injection, corresponding to a four times increase in efficiency compared to that achievable in singletharvesting fluorescent OLEDs [5]. For this reason, white phosphorescent OLED has been a focus of intense research. Meanwhile, one bottleneck for further enhancing the efficiency of white phosphorescent OLEDs is the performance of blue phosphorescent emitters. Although many blue phosphorescent emitters have been reported [6–15], till now, iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N,C^{2'}] picolinate (FIrpic) is still the best and most widely used blue phosphorescent emitter. In a typical device with FIrpic doped in a 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) host, a maximum power efficiency of 7.7 lm/W with emission peaks centered at 472 and 500 nm are usually achieved [6].

Due to the high triplet energy level of FIrpic, many new materials with high triplet energies have been designed and used as its host. Examples include *N*,*N'*-dicarbazolyl-3,5-benzene (mCP), 4,4'-bis(9-carbazolyl)-2,2'-dimethyl-biphenyl (CDBP), *p*-bis-(triphenylsilyly)benzene (UGH2) [16–19]. By using mCP instead of CBP, power efficiency has been increased to 8.9 lm/W [19]. However, efficiency of blue phosphorescent OLEDs is still far below the requirements needed for solid state lighting applications. New blue phosphorescent emitters of high performance are obviously still in great demand.



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In this paper, highly efficient blue phosphorescent OLEDs have been achieved by using a new emitter, iridium(III) bis[(3,4,5-trifluorophenyl)-pyridinato- $N,C^{2'}$] picolinate (F_3 Irpic). Using the typical mCP host, blue emission with a maximum power efficiency of 18.1 lm/W has been realized. The power efficiency can be further increased to 33.7 lm/W by using a host of UGH2. Performance of the device is among the best reported for blue OLEDs.

2. Experimental details

The cyclometalating ligand 1-(3,4,5-trifluorophenyl)pyridine was prepared via a Suzuki coupling reaction between 1-bromopyridine and 3.4.5-trifluorophenyl boronic acid. Synthesis of the final Ir complex involved two key steps. In the first step, IrCl₃ was reacted with excess of the synthesized ligands to produce a chloro-bridged Ir dimer. This dimer can be readily converted to the monomeric complex F₃Irpic by replacing the bridging chlorides with Picolinic Acid in the presence of Na₂CO₃. The synthetic pathway towards the preparation of F₃Irpic is outlined in Scheme 1. The identity was confirmed by 1H-nuclear magnetic resonance, elemental analysis, and mass spectrometry. MS (m/z): 730; ¹H NMR (Acetone, 300 MHz): δ : 7.16–7.21 (t, 1H), δ : 7.36–7.40 (t, 1H), 7.65-7.66 (d, 2H), 7.75-7.88 (m, 2H), 7.92-8.00 (m, 3H), 8.13-8.20 (m, 4H), 8.67-8.69 (d, 1H). Anal. Calcd. for IrC₂₈H₁₄N₃O₂F₆: C, 46.03; H, 1.93%; N, 5.75%. Found: C, 45.63; H, 2.00%; N, 5.70%.

Absorption and photoluminescence spectra were recorded, respectively with a Perkin–Elmer Lambda 2S UV– Vis spectrophotometer and a Perkin–Elmer LS50B luminescence spectrophotometer. The highest occupied molecular orbital (HOMO) value of the Ir complex was measured via ultraviolet photoelectron spectroscopy (UPS). The lowest unoccupied molecular orbital (LUMO) value was determined from the difference between the HOMO energy and the band gap determined from the optical absorption edge. OLEDs were fabricated by vacuum deposition on ITOcoated glass substrates with a sheet resistance of 30Ω / square. Before deposition, the ITO substrate was first carefully cleaned, dried in an oven at 120 °C, and then treated with UV-ozone before loaded into a deposition chamber. Organic layers were then sequentially deposited onto the ITO substrate at a rate of 2–4 Å/s and a pressure below 5×10^{-6} mbar. Electroluminescence (EL) spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer. Current–voltage–luminescence characteristics were measured with a computer-controlled Keithley 236 source meter under ambient conditions.

3. Results and discussion

Iridium(III) bis[(3,4,5-trifluorophenyl)-pyridinato-N,C^{2'}] picolinate (F₃Irpic) was synthesized in house. The molecular structure of F₃Irpic (Scheme 1), which has been confirmed with ¹H nuclear magnetic resonance, mass spectrometry and elemental analysis, is similar to that of FIrpic except for the three fluorine atoms substituted at the 3,4,5-position of the phenylpyridine ligand. Fig. 1 shows the absorption and photoluminescence (PL) spectra of F₃Irpic in dilute dichloromethane solution. The PL spectrum of F₃Irpic shows a blue emission with a main emission peak centered at 479 nm and a smaller peak at 509 nm. The shape of the PL spectrum is similar to that of FIrpic except for a red-shift of 8 nm [18]. On the other hand, the photoluminescence quantum yield of F₃Irpic in chloroform solution was measured to be 0.67 using FIrpic (Φ_f : 0.50) as a calibration standard, which is higher than that of FIrpic. The higher PL quantum yield of F₃Irpic should be attributed to more fluorine atoms substituted in the ligand than FIrpic [20].

OLEDs were made by doping F_3 Irpic in mCP with a device structure of ITO/NPB (40 nm)/x% F_3 Irpic:mCP (30 nm)/BAlq (40 nm)/LiF (0.5 nm)/Al (80 nm). In the devices, ITO (indium tin oxide) and LiF/Al are the anode and the cathode, respectively; 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl amino] biphenyl (NPB) is the hole transporting layer (HTL), and aluminum





Fig. 1. Absorption and emission spectra of F_3 Irpic, inset is its molecular structure.

(III) bis(2-methyl-8-quinolinato)4-phenylphenolate (BAlq) is the electron transporting layer (ETL). The F_3 Irpic doped mCP layer is the emission layer (EML).

The devices with different concentration of F₃Irpic shows almost the same EL spectra (Fig. 2) as the PL spectrum (Fig. 1) of the Ir complex. Current and power efficiency of the best performing device (4% F₃Irpic in mCP) are shown in inset of Fig. 2. This device shows a maximum external quantum efficiency of 9.8%. The corresponding power (current) efficiency is 18.1 lm/W (25.9 cd/A), which is much higher than that of a similarly structured device using FIrpic dopant (7.5%, 8.9 lm/W) [19]. The good performance of the device should be attributed to the higher PL quantum yield of F₃Irpic than FIrpic. Current-brightnessvoltage characteristics of this F₃Irpic (4%):mCP device are shown in Fig. 3. It has a turn-on voltage (at a brightness of 1 cd/m^2) of 4.3 V and delivers a maximum brightness of 15000 cd/m² at a voltage of 13.5 V and a current density of 215 mA/cm². A schematic energy level diagram for the device is shown in the inset of Fig. 3. The HOMO level of F₃Irpic determined with UPS is 6.1 eV. The LUMO level as determined from the HOMO level and the optical absorption edge is 3.4 eV. As shown in the energy level diagram,



Fig. 2. EL spectra of the device at different doping concentrations, inset is the current efficiency–current density–power efficiency characteristics.



Fig. 3. *I*–*V*–*L* characteristics of the device, inset is the energy level diagram of the device.

the HOMO level of F_3 Irpic (6.1 eV) is lower than that of mCP (5.9 eV). This suggests that the F_3 Irpic might not be effective trap for the holes and thus decreases the chance of forming exciton in the phosphorescent emitter.

To address this problem, the mCP host was replaced by UGH2 which has a much larger energy gap. Chemical structure and the corresponding energy level diagram for the device are shown in Fig. 4. It can be noted that the HOMO and LUMO levels of the Ir complex are entirely bracketed by those of the UGH2 host. This suggests that the Ir molecules would be effective traps for both electrons and holes injected into the UGH2 layer. This is clear beneficial for exciton formation at the Ir molecules. It was found that the optimized device has a configuration of ITO/NPB (40 nm)/mCP (10 nm)/8% F₃Irpic:UGH2 (20 nm)/BAlq (40 nm)/LiF (0.5 nm)/Al (80 nm). The mCP layer is used as an interim layer to facilitate hole injection from the HTL into EML to overcome the large energy difference (1.8 eV) between NPB and UGH2.

Current efficiency-brightness-power efficiency characteristics of F₃Irpic:UGH2 device are shown in Fig. 5. This device shows blue emission (see inset of Fig. 5) with a peak centered at 482 nm and a sub-peak at 512 nm. The F₃Irpic:UGH2 device gives a maximum external quantum efficiency of 14.3%. The maximum power (current) efficiency of the device is 33.7 lm/W (37.6 cd/A), which is much higher than that of the F₃Irpic:mCP device. The high efficiency of the device is considered to arise from the following three aspects. Firstly, the high PL quantum yield of the F₃Irpic contributes to the high device efficiency; secondly, the good device structure can facilitate the injection and transport of electrons and holes; thirdly, the energy levels of F₃Irpic are entirely bracketed by UGH2, which induced the effective traps of the dopant for both electrons and holes injected into the host. Similar to other phosphorescent OLEDs, efficiency of the device decreases as the brightness increases. However, it is interesting to note that even at a brightness of 1000 cd/m², the efficiency of the device is still higher than 20 cd/A (9 lm/W). As far as we know, performance of this device is among the best values reported for blue OLEDs.

In summary, highly efficient blue phosphorescent OLEDs have been achieved by using a new emitter iridium(III)



Fig. 4. The chemical structure of UGH2; the energy level diagram of device II.



Fig. 5. The current efficiency-brightness-power efficiency characteristics of device II, the inset is the EL spectrum.

bis[(3,4,5-trifluorophenyl)-pyridinato- $N,C^{2'}$] picolinate (F₃Irpic). For a mCP:4%F₃Irpic device, blue emission with a maximum power efficiency of 18.1 lm/W has been realized, which is much higher than that of similarly structured FIrpic based device. The emission peak is located at 480 nm with a subpeak at 511 nm. By using an optimized device structure with a host of UGH2, performance of the device is substantially increased to give a maximum power efficiency up to 33.7 lm/W and an almost unchanged EL spectrum.

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