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Highly efficient red electrophosphorescent device based on a new iridium complex with trifluoromethyl-substituted 2-benzo[*b*]thiophen-2-yl-pyridine ligand

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Abstract

We report a new red Ir(III) complex, $(btfmp)_2Ir(acac)$, with the trifluoromethyl-substituted 2-benzo[*b*]thiophen-2-yl-pyridine ligand. Efficient red electrophosphorescence with CIE coordinates ($x = 0.69$, $y = 0.29$) independent on current density was observed from the $(btfmp)_2Ir(acac)$ doped devices. The electroluminescent (EL) spectrum has a maximum at $\lambda_{max} = 648$ nm. Maximum external quantum efficiency of 9.6% at current density of 0.125 mA/cm^2 and 3.7% at $J = 100$ mA/cm^2 were obtained.

Keywords: Electrophosphorescence; Red light emitting; Iridium complex; Organic light-emitting devices (OLEDs)

1. Introduction

The organic light-emitting diodes (OLEDs) using phosphorescent dopants have attracted much attention due to their high external quantum efficiency in recent years [1–4]. Cyclometalated heavy metal complexes used as guest in phosphor dye-doped OLEDs have been reported [5–7]. For the red phosphor, the first example was based on PtOEP doped in CBP [1], achieving an external quantum yield of 5.6% [8]. More recently, efficient red EL emission has been reported from phosphor $(btp)_2Ir(acac)$, reaching 7.0% at low current [3]. But comparing with green phosphors, the red emitters of high efficiency are more desirable for commercial full displays.

Fluorination is an effective way to enhance both electron mobility and thermal stability of organometallic complexes [9], which are important for fabrication and performance of solid film devices [10]. It has been reported that fluorinated complexes exhibited markly improved EL efficiency partly due to excellent volatility which aids device processing [11,12].

In this work, we report a new red light emitting Ir(III) complex $[(btfmp)_2Ir(acac)]$ using 2-benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridine as the ligand, and its application for OLEDs. The trifluoromethyl substitution at this position influenced the electron extent of delocation between the pyridyl and benzo[*b*]thiophen-2-yl rings, which was supposed to tune the electron structure and hence to result in efficient host-to-guest energy

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transfer, an improved EL efficiency based on the new Ir(III) complex has been obtained.

2. Experimental

2-Chloro-5-trifluoromethyl-pyridine, benzo[*b*]thiophene-2-boronic acid, CBP, NPB, BCP, and $IrCl_3 \cdot nH_2O$ were from Aldrich, and used without further purification. Thermogravimetric analysis (TGA) was performed by a TGA 2950 thermal analyzer (TA Co.) under N_2 stream with a scanning rate of 10 °C/min. Absorption spectrum was measured on UV–VIS–NIR scanning spectrophotometer. EL spectra were measured with a F-4500 Fluorescence Spectrometer. Brightness–current–voltage (*B–I–V*) characteristics were measured by using a 3645 DC power supply combined with a 1980A Spot Photometer. External quantum efficiency was calculated from the luminance, current density, and EL spectrum according to standard method [13].

2.1. Synthesis and characterization of ligand

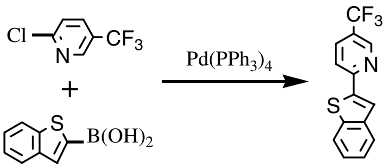
2-Benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridine (Scheme 1) was synthesized according to literature procedure [14]. The white product with the yield of 75% was obtained.

^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.80 (s, 1H), 7.80 (m, 5H), 7.3 (t, 2H). Anal. Found: C, 60.09; H, 2.693; N, 4.913. Calcd.: C, 60.22; H, 2.867; N, 5.018.

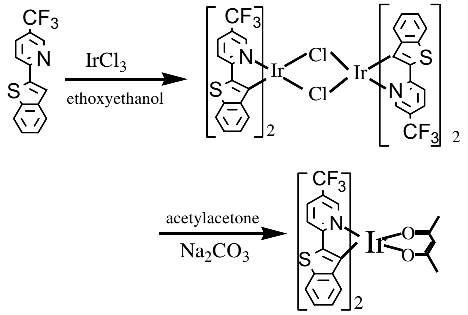
2.2. Synthesis and characterization of iridium complex

Bis(2-benzo[*b*]thiophen-2-yl-5-trifluoro methyl-pyridinato-$N,C^{3'}$) iridium (acetyl acetonate) [$(btfmp)_2Ir(acac)$] (Scheme 2) was obtained in two steps using standard procedure [15]. First, a cyclometalated Ir(III) *m*-chloro bridged dimer was synthesized by the reacting $IrCl_3 \cdot nH_2O$ and 2-benzo[*b*]thiophene-2-yl-5-trifluoromethyl-pyridine. Then, the dimer was reacted with acetylacetone in 2-ethoxyethanol. The red powder was afforded in 65% yield with train sublimation.

^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.56 (s, 2H), 7.65 (d, 2H), 7.60 (t, 2H), 7.10 (m, 4H), 6.79 (t, 2H), 6.16 (d, 2H), 5.25 (s, 1H), 1.75 (s, 6H). Anal. Found: C, 46.56; H, 2.455; N, 3.277. Calcd.: C, 46.85; H, 2.485; N, 3.313.



Scheme 1.



Scheme 2.

2.3. Device fabrication

Fig. 1 shows the chemical structures of materials used and the device configuration ITO/NPB/$(btfmp)_2Ir(acac)$:CBP/BCP/Alq_3/LiF/Al. The multilayered devices consisted of a 40 nm thick NPB (4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl) as a hole transporting layer, a 30 nm thick $(btfmp)_2Ir(acac)$ doped CBP (4,4′-*N*,*N*′-dicarbazole-biphenyl) as an emitting layer, a 20 nm thick BCP (2,9-dimethyl-4,7-diphenyl-phenanthroline) as a hole blocking layer, a 30 nm thick Alq_3 (tris(8-hydroxy quinolinato)aluminium(III)) as an electron transporting layer, and a 1 nm LiF followed by 200 nm aluminium cathode. The devices were successively deposited onto a ITO coated glass substrate with a sheet resistance of 20 Ω/□ in high vacuum of 5×10^{-4} Pa during one pump down. Prior to use, the ITO glass substrates were rinsed and degreased by sonication in a detergent solution, distilled water, and acetone. The substrates were treated by UV–ozone for 30 min before loading into a vacuum chamber [16].

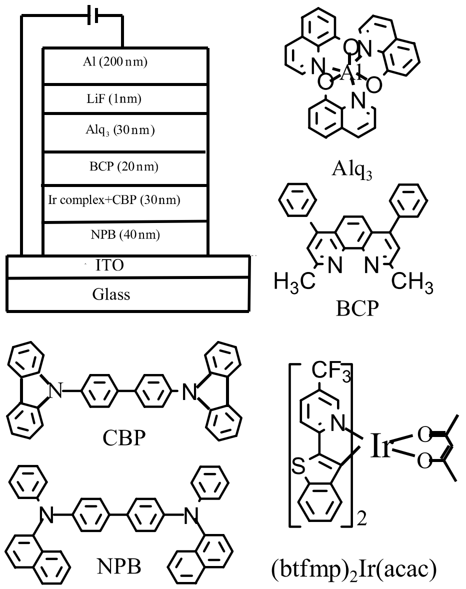


Fig. 1. Configuration of the device and chemical structures of materials used.

The emissive area of the device defined by the overlapping area of the cathode and the anode was 15 mm^2. All measurements were carried out in air at room temperature.

3. Results and discussion

Fig. 2 shows the absorption spectrum of the complex $(btfmp)_2Ir(acac)$ in CH_2Cl_2, which are similar with that of $(btp)_2Ir(acac)$ [15]. The intense absorption bands at higher energy were assigned to π–π* ligand-centered (LC) transitions, and low energy bands in the range of 460–560 nm to singlet and triplet MLCT transitions. The ^{1}MLCT and ^{3}MLCT were not well resolved, which has been observed from the complex $(bzq)_2Ir(acac)$ [6,15]. A large Stokes shift between the ^{3}MLCT absorption and emission bands was observed, so $(btfmp)_2Ir(acac)$ should emit from an excited state that is predominantly due to ^{3}(π–π*) [15,17].

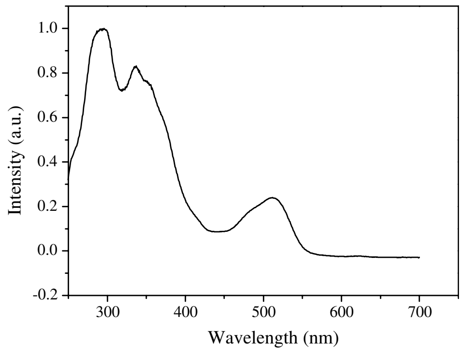


Fig. 2. The absorption spectrum of $(btfmp)_2Ir(acac)$ in CH_2Cl_2.

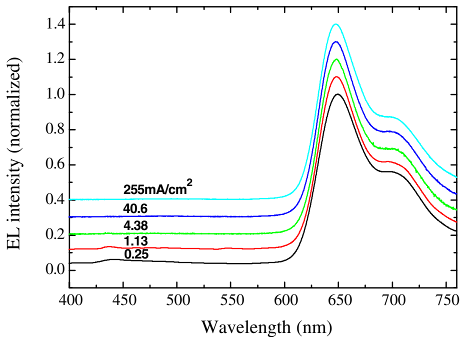


Fig. 3. Electroluminescent spectra of device doped with 7% $(btfmp)_2Ir(acac)$ at various drive current densities.

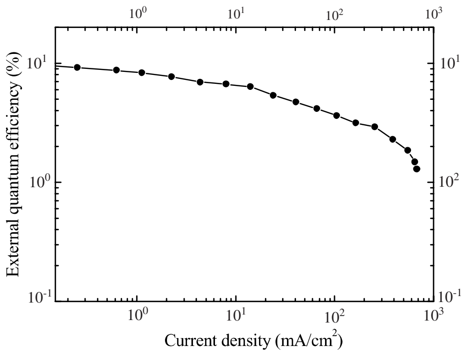


Fig. 4. External quantum efficiency (η_{ext}) vs. current density of EL device doped with 7% $(btfmp)_2Ir(acac)$.

The peak wavelength of phosphorescent emissions can be tuned by changing the substituents and their position [10,18]. In this work, substitution of an electron-with drawing group (trifluoromethyl) onto the 5-position of the pyridyl ring lowered the LUMO level, and reduced the HOMO–LUMO gap of the complex, and hence a 30 nm red shifted was observed comparing to that of $(btp)_2Ir(acac)$ [15].

In vacuum deposition process, OLED materials should be stable even at high temperature, because the decomposition products may contaminate the OLED and lead to poor device performance.

Thermogravimetric analysis (TGA) under 1 atm of flowing N_2 showed that the sublimation temperature of $(btfmp)_2Ir(acac)$ was 340 °C (the temperature is at point of 10% weight loss), about 30 °C lower than that of $(btp)_2Ir(acac)$, and suitable for thermal evaporation.

The EL spectra with a peak at 648 nm are shown in Fig. 3, corresponding to deep red light emission. The CIE color coordinates were $x = 0.69$, $y = 0.29$, independent of current density, even at $J > 255$ mA/cm^2. There was no blue emission from CBP host, indicating complete energy transfer from CBP host-to-guest $(btfmp)_2Ir(acac)$.

Table 1 summarizes the external quantum efficiency and maximum brightness of the devices doped with various ratio of $(btfmp)_2Ir(acac)$. When the concentration (wt%) of $(btfmp)_2Ir(acac)$ in CBP was 7%, a maximum external quantum efficiency of 9.6% at $J = 0.125$ mA/cm^2 and a maximum luminance of 4200 cd/m^2 at $J = 552$ mA/cm^2 were obtained.

Fig. 4 shows external quantum efficiency (η_{ext}) vs. current density for the device doped with 7%

Table 1
External quantum efficiency (%) and maximum brightness (cd/m^2) of the devices with various $(btfmp)_2Ir(acac)$ doped concentration

Devices	A	B	C	D
$(btfmp)_2Ir(acac)$ concentration in CBP (wt%)	5	6	7	8
External quantum efficiency (%) at J (mA/cm^2)	5.2 (1.8)	8.6 (0.127)	9.6 (0.125)	8.7 (0.089)
Maximum brightness (cd/m^2) at J (mA/cm^2)	3200 (632)	3600 (598)	4200 (552)	3400 (357)

$(btfmp)_2Ir(acac)$, the device showed a gradual decrease of η_{ext} with increasing current, which was attributed to T–T annihilation [19,20]. But, at $J = 100\,mA/m^2$, the $(btfmp)_2Ir(acac)$ doped device showed a relatively high $\eta_{ext} = 3.7\%$.

4. Conclusion

In summary, we report a new red iridium complex $[(btfmp)_2Ir(acac)]$ with trifluoro methyl-substituted 2-benzo[*b*]thiophen-2-yl-pyridine ligand. This study demonstrated that a CF_3 substituent at the 5-position of the pyridyl ring of 2-benzo[*b*]thiophen-2-yl-pyridine tuned the energy levels, and improved sublimation behavior of iridium complex. The deep red light emitting EL device based on the $(btfmp)_2Ir(acac)$ showed a peak external quantum efficiency of 9.6%. The EL efficiency can be further enhanced by choosing a suitable host material or optimization of the device structure.

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