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Highly efficient blue and white phosphorescent OLEDs based on an iridium complex

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A new blue-emitting iridium complex, Iridium(III) bis [(2,3,4-trifluorophenyl) -pyridinato-N, $C^{2'}$] picolinate (Ir(tfpd)$_2$pic) has been designed, synthesized and used to fabricate blue phosphorescent organic light-emitting devices with a efficiency up to 41.4 lm/W (52.6 cd/A). Furthermore, by combining the blue phosphorescence of Ir(tfpd)$_2$pic and the yellow emission of iridium(III) bis [2-(2-naphthyl)-pyridine] (acetylacetonate) (Ir(npy)$_2$acac), highly efficient white emission with a maximum efficiency of 49.0 lm/W (54.5 cd/A) has been achieved. The results indicate that Ir(tfpd)$_2$pic is a promising blue phosphor for the applications in highly efficient blue and white OLEDs.

1. Introduction

White organic light-emitting diodes (WOLEDs) have drawn much attention for their applications in flat-panel displays and solid-state lightings [1]. WOLEDs can be classified into three types according to the emitters used: fluorescent devices (F-WOLEDs), phosphorescent devices (P-WOLEDs) and hybrid devices employing both fluorescent and phosphorescent emitters (F/P-WOLED) [2]. WOLEDs based on phosphorescent emitters have been shown to achieve an internal quantum efficiency of 100% as compare to the theoretical value of 25% in fluorescent OLEDs [3]. Recent works have reported impressive power efficiency up to 124 lm/W by utilizing three primary colors (RGB) phosphorescent materials and light out-coupling enhancement [4]. In fact, much recent progress on new materials, novel device structures, and light extraction methods have been developed to meet the requirements of WOLEDs [5]. Meanwhile, one bottleneck for further enhancement of the efficiency of WOLEDs is the low performance of the blue phosphorescent emitters. For instance, maximum power efficiencies for red and green monochromatic device have been reached 42.7 lm/W (Iridium(III) bis-(2-phenylquinolyl-N,$C^{2'}$) acetylacetonate, PQIr) [6], and 133 lm/W (tris-(phenylpyridine)Iridium, Ir(ppy)$_3$) [7], respectively. While, FIrpic (Iridium (III) bis [(4, 6-difluorophenyl)-pyridinato-N, $C^{2'}$] picolinate) and FIr6 (Iridium(III) bis-(4′, 6′-difluorophenylpyridinato) tetrakis (1-pyrazolyl) borate) are still the best and most frequently used blue phosphorescent emitters. Performance of FIrpic and FIr6 based devices are still below the requirements for applications in solid-state lightings [8]. Thus, development of high performance blue phosphorescent emitters is essential for further improvement of WOLEDs.

Fluorine substituted Ir(III) complexes have been used for designing blue phosphors due to their high quantum yields and color tunability. Conversion of C—H bonds in these complexes to C—F bonds may have several potential benefits, such as reduction of irradiative exciton decay, enhancement of photoluminescence (PL) efficiency and electron mobility etc. [9]. Tokito et al. reported two fluorine substituted Ir(III) complexes, in which pentafluorophenyl group is bound to either *meta*- or *para*- position of the phenyl ring. Interestingly, the small difference in the two complexes lead to significant difference in PL efficiency [9b]. Chen et al. synthesized a iridium complex, which is similar to FIrpic

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except for a *tert*-butyl substituted at the 4-position in pyridine. The material also shows much different EL performance compared with FIrpic [9c]. In our previous report, an Ir complex with a phenylpyridine ligand substituted by three fluorines at the *meta*-, *para*-positions gives a light blue emission peaked at 479 nm. An optimized device using the complex as dopant exhibits a maximum current efficiency of 37.6 cd/A [9d]. It can be seen that differences in the number of fluorine and their substitution positions can have considerable effects on the properties and performance in these Ir(III) complexes [10].

In this work, we designed and synthesized a new blue phosphor, Iridium(III) bis[(2,3,4-trifluorophenyl)-pyridinato-N,C$^{2'}$] picolinate (Ir(tfpd)$_2$pic). Highly efficient blue phosphorescent OLEDs were fabricated by using this new phosphor. By doping Ir(tfpd)$_2$pic into 9, 9-spirobifluoren-2-yl-diphenyl-phosphine oxide (SPPO1), blue emission with a maximum efficiency of 41.4 lm/W (52.6 cd/A) has been realized. Performances of the blue phosphorescent OLEDs are among the best-reported values. Furthermore, WOLEDs have been fabricated by using a simple dual-emissive-layer device structure, combining the blue emitting dopant Ir(tfpd)$_2$pic with a yellow phosphor, Iridium(III) bis [2-(2-naphthyl)-pyridine] (acetylacetonate) (Ir(npy)$_2$acac). Highly efficient white emission with a maximum efficiency of 49.0 lm/W (54.5 cd/A) has been achieved. These results suggest that Ir(tfpd)$_2$pic should be a promising blue phosphor for the applications in highly efficient blue and white OLEDs.

1.1. Experimental details

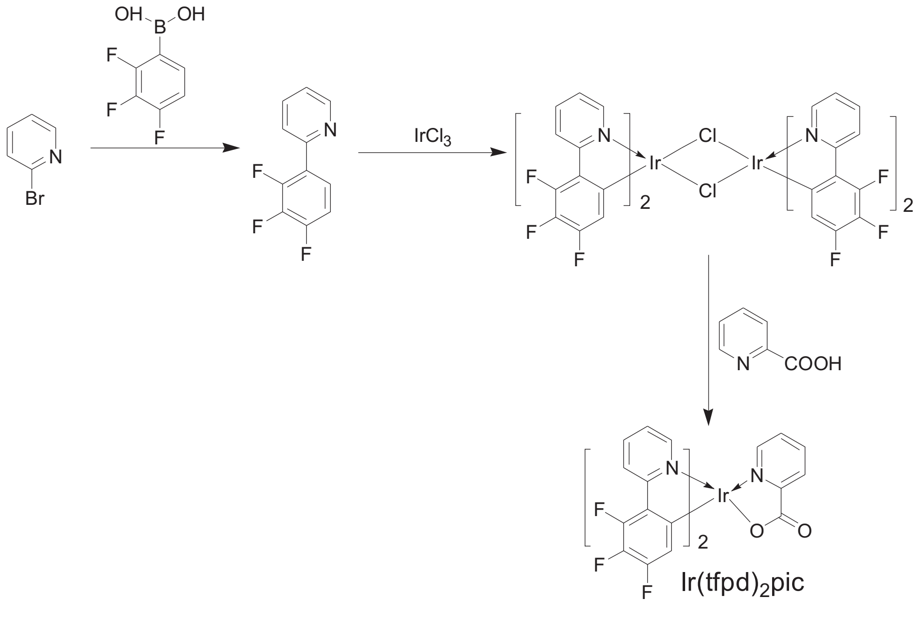
The cyclometalating ligand 1-(2,3,4-trifluorophenyl)-pyridine was prepared via a Suzuki coupling reaction between 1-bromopyridine and 2,3,4-trifluorophenyl boronic acid. Synthesis of the final Ir complex involved two key steps. In the first step, IrCl3 was reacted with excess of the synthesized ligands to produce a chloro-bridged Ir dimer. This dimer can be readily converted to the monomeric complex Ir(tfpd)2pic by replacing the bridging chlorides with picolinic acid in the presence of Na2CO3. The synthetic pathway toward the preparation of Ir(tfpd)2pic is outlined in Scheme 1. The molecular structure of Ir(tfpd)2pic has been confirmed with 1H nuclear magnetic resonance: (300 MHz, CDCl3) d: 5.53–5.58 (t, 1H), 5.80–5.85 (t, 1H),7.00–7.04 (t, 1H), 7.21–7.26 (t, 1H), 7.41–7.47 (m, 2H),7.77–7.85 (m, 3H), 7.95–8.00 (t, 1H), 8.23–8.35 (m, 3H). 8.73–8.75 (d, 1H); mass spectrometry (ESI$^+$):*m*/*z* 732.1(MH$^+$).Calcd for $C_{28}H_{14}O_2N_3F_6Ir$: 730.64. and elemental analysis: Anal. Calcd. For $C_{28}H_{14}O_2N_3F_6Ir$ C: 46.03%, H: 1.93%, N: 5.75%. Found: C: 45.89%, H: 1.95%, N: 5.59%.

Absorption and fluorescence 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) with a VG ESCALAB 220i-XL ultrahigh vacuum (UHV) surface analysis system). The lowest unoccupied molecular orbital (LUMO) value was determined from the difference between the HOMO energy and the energy gap determined from the optical absorption edge.

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 30 Ω/square were used as anode for OLEDs, all layers were deposited by vacuum thermal evaporation. Before successive deposition, the substrates were patterned by traditional lithography, cleaned and dried in an oven at 120 °C. *The ITO substrates were then treated with ultraviolet-ozone before loading into a deposition* chamber. All organic layers and cathode were sequentially deposited onto the ITO substrates under a base pressure of 10^{-6} *Torr. Current density-voltage-luminance (J-V-L) characteristics, CIE coordinates, and electroluminescent (EL)* spectra were measured with a programmable Keithley model 237 source and a Photo-research PR650 photometer.

2. Result and discussions

The molecular structure of Ir(tfpd)$_2$pic is similar to that of FIrpic except for one more fluorine atom at the 5-position of the phenylpyridine ligand. Fig. 1 shows an absorption and a photoluminescence (PL) spectra of Ir(tfpd)$_2$pic in a dilute CH_2Cl_2 solution at room temperature. The 254 nm absorption peak is attributed to the π-π* transition of the trifluorophenylpyridine ligand and the weak absorption peaks located at 365 and 430 nm are likely to be originated from the ^{1}MLCT (metal to ligand charge transfer) and ^{3}MLCT transitions, respectively [11]. The dilute Ir(tfpd)$_2$pic solution



Scheme 1. Synthetic routes of Ir(tfpd)$_2$pic.