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Improved efficiency and colour purity of blue electrophosphorescent devices by codoping a fluorescent emitter

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Abstract

Improved efficiency and colour purity of blue electrophosphorescent devices based on bis[(4,6-difluorophenyl)-pyridinato-N,C^2](picolinato)Ir(III) (FIrpic) were demonstrated by codoping a fluorescent emitter 2,5,8,11-tetra-*t*-butyl-perylene (TBPe). The optimized device codoped with 8 wt% FIrpic and 0.15 wt% TBPe shows a maximum current efficiency and power efficiency of 11.6 cd A^{-1} and 7.3 lm W^{-1}, which were increased by 20% and 40%, respectively, compared with that of the reference device. Also, a blue shifted electroluminescent spectrum of the codoped devices was observed with doping concentration of TBPe, leading to improved colour purity of the devices. The improved efficiency and colour purity of the codoped devices were attributed to the simultaneous emission of the two emitters.

1. Introduction

Since the first demonstration of electroluminescence (EL) from organic bilayer devices in 1987 [1], much effort has been focused on improving the performance of the organic light-emitting devices (OLEDs). Notably, the use of phosphorescent materials has been a major breakthrough in boosting the EL efficiency [2]. The phosphorescent devices can harvest both the singlet and triplet excitions, leading to a maximum internal quantum efficiency of 100% as compared with its fluorescent counterparts that only a 25% maximum internal quantum efficiency can be theoretically obtained [2–4]. High efficiency organic green and red phosphorescent devices based on cychometalated iridium complexes have been reported in the literature [4–9]. However, the development of high efficient blue phosphorescent devices lags far behind that of the green and red ones. One of the most well known blue phosphorescent emitters is bis[(4,6-difluorophenyl)-pyridinato-N,C^2](picolinato)Ir(III) (FIrpic), and high efficiency was demonstrated by endothermic energy transfer from $4,4'$-N,N'-dicarbazole-biphenyl host [10]. Unfortunately, the endothermic transfer efficiency is strongly affected by the defects in the host that limit device efficiency, operating temperature and long-term operational stability. High efficiency and colour purity are two important issues in developing blue phosphorescent devices. Although high external quantum efficiency based on FIrpic has been reported, the light emission was far from saturated and the efficiency should be further improved for practical applications. Thus, many methods have been adopted to improve the performance of blue electrophosphorescent devices, including optimizing device configuration [11–14] and synthesizing new efficient blue emission materials [15–17].

Phosphor and fluorophore codoped OLEDs have drawn particular interest since reported by Baldo *et al* [18]. Among the two dopants, the phosphor has a higher emission energy than the fluorophore, and this strategy is generally adopted in yellow and red emission devices [19, 20]. After excitation, almost all the excited energy of the phosphors is transferred to the fluorophores, and the emissions are predominantly coming from the fluorophores, finally a dramatically improved fluorescent emission is observed.

In this report, FIrpic and a traditional blue fluorescent emitter, 2,5,8,11-tetra-*t*-butyl-perylene (TBPe) which has a

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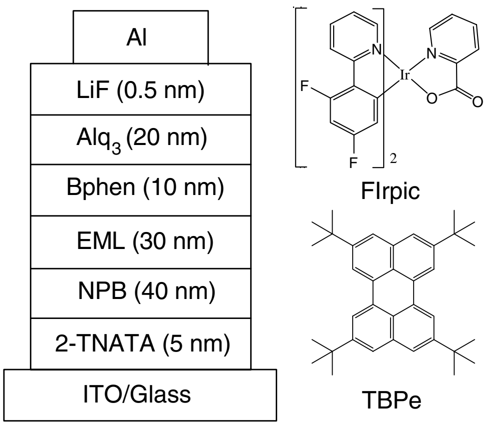

Figure 1. The structure of the blue OLEDs and the chemical structures of FIrpic and TBPe.

higher emission energy than that of FIrpic [21, 22], were codoped into N,N'-dicarbzolyl-3.5-benzene (mCP), which acted as the emitting layer (EML). By elaborately modulating the concentrations of FIrpic and TBPe, simultaneous emission of the two emitters can be realized, which leads to improved efficiency and colour purity of the blue electrophosphorescent devices.

2. Experimental details

The devices were fabricated on pattered indium tin oxide (ITO) coated glass substrates with a sheet resistance of $25\,\Omega\,\mathrm{sq}^{-1}$ by thermal evaporation in vacuum chamber at 3×10^{-4} Pa. The devices have a structure of ITO/2-TNATA (5 nm)/NPB (40 nm)/mCP : FIrpic : TBPe (30 nm)/Bphen (10 nm)/$\mathrm{Alq_3}$ (20 nm)/LiF (0.5 nm)/Al (100 nm), as shown in figure 1. Here, 4, 4′,4″,-tris[2-naphthyl(phenyl) amino]-triphenylamine (2-TNATA), N, N'-diphenyl-N, N'-bis (1-naphthyl)-(1, 1′-benzidine)-4, 4′-diamine (NPB), 4,7-diphenyl-1,10-phenanthroline(Bphen) and tris(8-hydroxyquinoline)aluminium ($\mathrm{Alq_3}$) act as hole-injection layer, hole-transporting layer, exciton-blocking layer and electron-transporting layer, respectively. The doping concentration of FIrpic in the EML was fixed at 8 wt%, while the concentration of TBPe was varied from 0 to 0.5 wt%. Deposition rates and thicknesses of the layers were monitored *in situ* using oscillating quartz monitors. The evaporating rates were kept at 0.5–1 $\mathrm{\AA\,s^{-1}}$ for organic layers and LiF layer, and 10 $\mathrm{\AA\,s^{-1}}$ for Al cathode, respectively. EL spectrum and CIE coordinates of the devices were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The luminance–current–voltage (L–I–V) characteristics were measured with a 3645 dc power supply combined with a spot photometer and were recorded simultaneously with measurements. All the measurements were carried out at room temperature under ambient conditions.

3. Results and discussions

Figure 2 shows the normalized EL spectra of the devices codoped with different concentrations of FIrpic and TBPe at 8 V, for comparison, the EL spectrum of the 0.15 wt% TBPe monodoped device is also shown. The EL spectrum of the 8 wt% FIrpic monodoped device presents an emission peak at 473 nm and a shoulder at about 500 nm, while the 0.15 wt% TBPe monodoped device shows an emission peak at 460 nm with a low emission band of mCP due to the incomplete energy transfer to TBPe. With increasing doping concentration of TBPe, the emission peak of the devices reveals an apparently blue shift, and the emission peaks of the 0.15 wt%, 0.25 wt% and 0.5 wt% TBPe codoped devices locate at 470 nm, 468 nm and 465 nm, respectively. Also, a decreased shoulder emission of FIrpic at about 500 nm with the doping concentration of TBPe was also observed. Correspondingly, the CIE coordinates of the devices shift from (0.145, 0.329) of the 8 wt% FIrpic monodoped device to (0.129, 0.218) of the 8 wt% FIrpic and 0.5 wt% TBPe codoped device, as shown in figure 3.

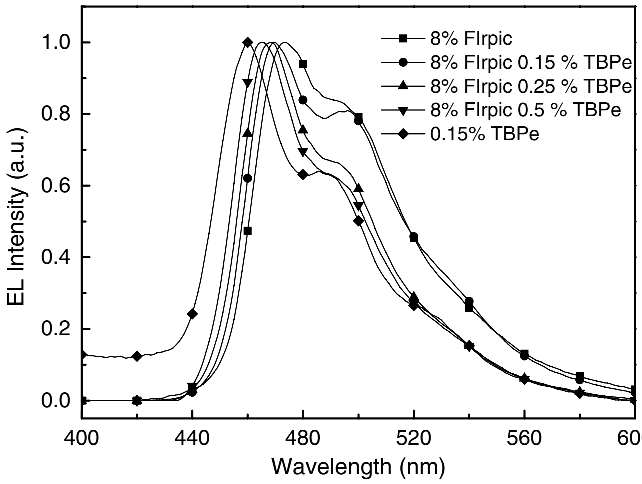

Figure 2. EL spectra of the devices doped with different concentrations of FIrpic and TBPe.

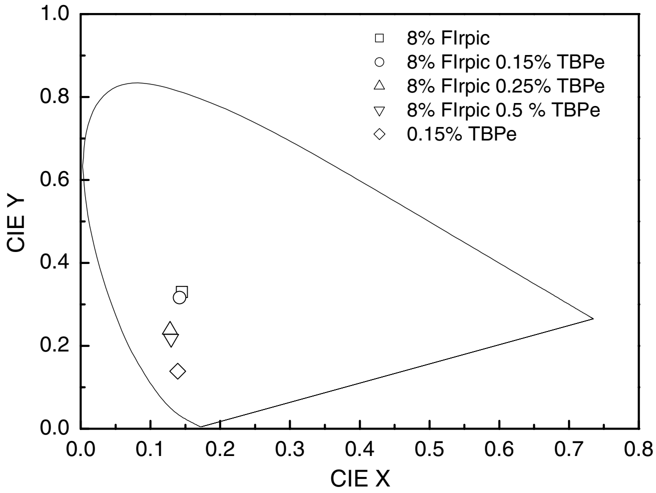

Figure 3. CIE coordinates of the devices doped with different concentrations of FIrpic and TBPe.

Figure 4 plots the I–V properties of the devices doped with different concentrations of FIrpic and TBPe. It can be found that the current density in the same drive voltage of the devices increases with the doping concentration of TBPe. It can be understood in terms of the schematic energy diagram

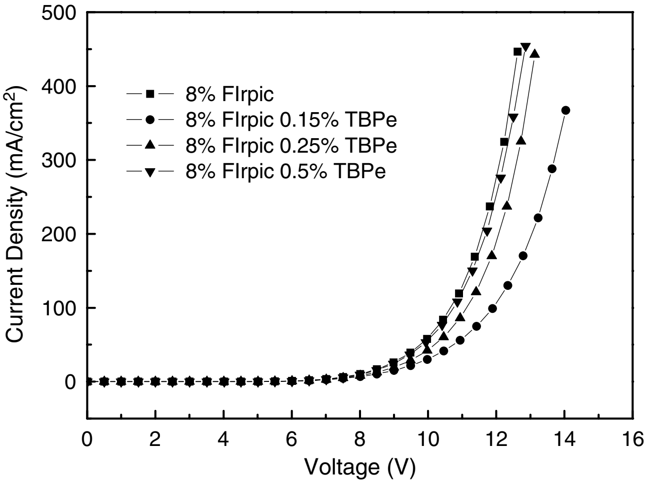

Figure 4. *I–V* properties of the devices doped with different concentrations of FIrpic and TBPe.

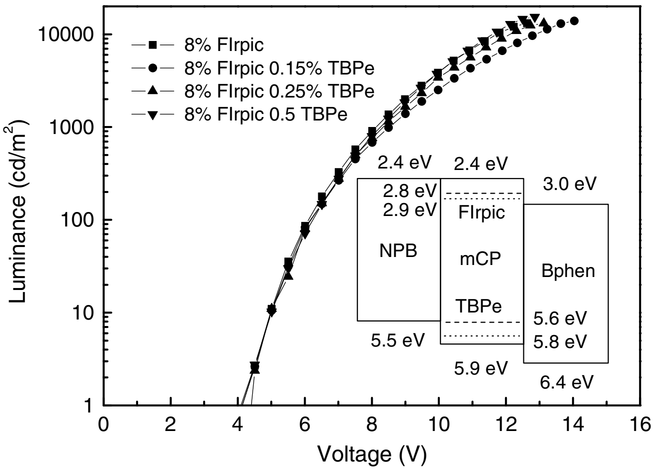

Figure 5. *L–V* properties of the devices doped with different concentrations of FIrpic and TBPe. Inset: schematic energy diagram of the OLEDs.

of the device shown in the inset of figure 5. The data of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital levels of the materials were cited from the literature [6, 15, 23]. The higher HOMO level of TBPe (5.6 eV) compared with that of FIrpic (5.8 eV) and mCP (5.9 eV) would have acted as traps for holes transporting in the TBPe doped film, and the holes transportation in the doped film takes place in the form of hopping from one TBPe molecule to the other one. The trapped holes in the TBPe sites lead to a decreased current density of the devices in comparison with the FIrpic monodoped device. With increasing doping concentration of TBPe, the distance between TBPe molecules decreases, leading to increased current density of the devices. Figure 5 shows the *L–V* properties of the devices doped with different concentrations of FIrpic and TBPe. The *L–V* properties of the devices are almost identical, especially in low drive voltage. Taking into account the lower current density of the device with lower doping concentration of TBPe, a higher luminance in the same current density would be observed for the devices with lower doping concentration of TBPe.

Table 1 lists the EL performance of the devices doped with different concentrations of FIrpic and TBPe. The 8 wt% FIrpic monodoped device shows a maximum current efficiency and power efficiency of 9.6 cd A^{-1} and 5.2 lm W^{-1}, respectively, which were comparable to the report with the similar configuration [11]. The device codoped with 8 wt% FIrpic and 0.15 wt% TBPe shows a maximum current efficiency and power efficiency of 11.6 cd A^{-1} and 7.3 lm W^{-1}, which are 20% and 40% higher than that of the FIrpic monodoped device, respectively, as shown in figure 6. Compared with the efficiencies of the 8 wt% FIrpic and 0.15 wt% TBPe monodoped devices, it is interesting to find that the efficiency of the codoped device is almost the sum of that of the two monodoped devices. With increasing doping concentration of TBPe, the efficiency of the devices decreases gradually. At the TBPe doping concentration of 0.5 wt%, a current efficiency and power efficiency of 9.5 cd A^{-1} and 5.1 lm W^{-1} were found, which are comparable to the reference device. Further increase in the concentration of TBPe leads to further decreased efficiency (not shown here). Taking into account the lower photopic response of the human eye to the blue shifted EL spectrum, a more pronounced improvement of quantum efficiency was observed in the FIrpic and TBPe codoped devices. Yeh *et al* [16] reported a blue electrophosphorescent device with a maximum efficiency of 4.4 lm W^{-1} and CIE coordinate of (0.15, 0.24) based on iridium(III) bis(4,6-difluorophenylpyridinato)-5-(pyridine-2-yl)-1H-tetrazolate doped mCP. Comparing with their device, our codoped device with the same CIE coordinate has a little higher efficiency. Nevertheless, the efficiency of our devices is inferior to the iridium(III)bis(4′, 6′-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate based devices with a maximum efficiency of about 11.1 lm W^{-1} and CIE coordinate of (0.16, 0.26), which for the most part may be due to the difference in host materials [15].

Codoping TBPe into the EML would increase the emitting site and hence the luminance. However, the lower triplet energy level of TBPe compared with that of FIrpic may result in the energy transfer from the FIrpic triplet to the TBPe triplet through the Dexter energy transfer mechanism, finally the triplet energy of TBPe is wasted due to the fluorescence nature of TBPe. Due to the higher singlet energy level of TBPe than the triplet energy level of FIrpic, energy transfer from the FIrpic triplet to the TBPe singlet is energetically unfavourable. Dexter energy transfer is a short-distance process where excitons diffuse from the donor to acceptor sites via intermolecular electron exchange. By precisely modulating the doping concentration of TBPe, the distance between FIrpic and TBPe molecules can be tuned beyond the Dexter energy transfer radius. As a result, energy transfer from FIrpic to TBPe can be avoided. The fact that the efficiency of the 8 wt% FIrpic and 0.15 wt% TBPe codoped device is the sum of that of the two monodoped devices indicating that the energy transfer from FIrpic to TBPe is totally avoided in this device and the emission comes from FIrpic and TBPe simultaneously. Given that the emission of FIrpic cannot be affected by the codoping of TBPe, an increase in EL efficiency would be expected with increasing doping concentration of TBPe in the concentration range of

Table 1. EL performance of the devices codoped with different concentrations of FIrpic and TBPe.

FIrpic ratio (wt%)	TBPe ratio (wt%)	Maximum η_c (cd A^{-1})	Maximum η_p (lm W^{-1})	Maximum luminance (cd m^{-2})	CIE coordinates at 8 V
8	0	9.6	5.2	13 170	(0.145, 0.329)
8	0.15	11.6	7.3	13 960	(0.142, 0.316)
8	0.25	10.3	5.2	13 060	(0.128, 0.238)
8	0.5	9.5	5.1	15 400	(0.129, 0.218)
0	0.15	2.2	1.4	3 290	(0.139, 0.139)

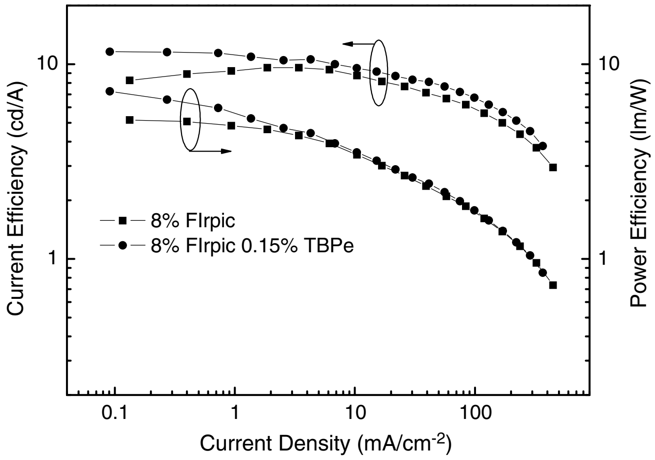

Figure 6. Current efficiency and power efficiency as a function of current density of the devices doped with different concentrations of FIrpic and TBPe.

our devices. However, with increasing doping concentration of TBPe from 0.15 to 0.5 wt%, a decrease rather than an increase in EL efficiency was observed. Thus, the decrease in the EL efficiency should be attributed to the energy transfer from the FIrpic triplet to the TBPe triplet, as normally found in the phosphor and fluorophore codoped devices with increasing doping concentration of the fluorophore [19, 20]. The distance between the FIrpic and TBPe molecules would be decreased with the TBPe doping concentration, which leads to increased energy transfer probability from the FIrpic triplet to the TBPe triplet and hence decreased emission from FIrpic, as found in the blue shifted EL spectrum and the decreased efficiency of the codoped devices.

4. Summary

In summary, improved efficiency and colour purity of the blue electrophosphorescent devices based on FIrpic were demonstrated by codoping a fluorescent emitter TBPe into the EML. The device codoped with 8 wt% FIrpic and 0.15 wt% TBPe shows a maximum current efficiency and power efficiency of 11.6 cd A^{-1} and 7.3 lm W^{-1}, respectively, which were increased by 20% and 40% compared with the reference device. A blue shift electroluminescent spectrum of the codoped devices was also observed, which leads to an improved colour purity of the devices. The improved efficiency and colour purity of the codoped devices were attributed to the simultaneous emission of the two emitters. The phosphorescent and fluorescent emitters codoped strategy has potential use in further improving the performance of the OLEDs.

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