Efficient green electroluminescent devices based on iridium complex with wide energy gap complexes as sensitizers

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ABSTRACT

In this work, electroluminescent (EL) performances of a green iridium complex $(tfmppy)_2Ir(tpip)$ were significantly improved by utilizing wide energy gap iridium complexes FK306 and FIrpic as sensitizers. Due to the low-lying energy levels, the co-doped FK306 or FIrpic molecules function as electron trappers, which are helpful in balancing holes and electrons on $(tfmppy)_2Ir(tpip)$ molecules and in broadening exciton recombination zone. Consequently, the co-doped devices displayed high EL efficiencies and slow efficiency roll-off. Compared with FIrpic, FK306 acts as a more effective sensitizer because of its relatively lower energy levels. Consequently, highly efficient green EL device with maximum current efficiency, power efficiency and brightness up to 102.29 cd/A (external quantum efficiency (EQE) of 25.3%), 88.67 lm/W and 96,268 cd/m^2, respectively, was realized by optimizing the co-doping concentration of FK306. Even at the practical brightness of 1000 cd/m^2, EL current efficiency up to 92.93 cd/A (EQE = 23%) can still be retained.

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1. Introduction

Since the reports by Ma et al. [1] and Thompson et al. [2] in 1998 on electroluminescence (EL) originating from a triplet excited state, transition metal complexes have been extensively investigated due to their potential application in the area of organic light-emitting devices (OLEDs). Transition metal complexes can be used to harvest both singlet and triplet excitons, thus are advantageous for achieving 100% internal quantum efficiency [3,4]. Among the previous reported transition metal complexes, iridium(III) (Ir(III)) complexes are most interesting because of their high phosphorescent efficiency and relatively short excited state lifetime [5–7]. In recent decades, many groups have given their attention to novel Ir(III) complexes design and device structures optimization [8–12]. Although significant enhancement of maximum

electroluminescent (EL) efficiency has been achieved, the EL efficiency roll-off with increasing current density is quite severe in most reported phosphorescent OLEDs due to triplet-triplet annihilation (TTA), triplet-polaron annihilation, and electric field induced dissociation of excitons, which detrimentally degrades the device performances for practical applications, particularly at high brightness [13,14]. Therefore, suppress the annihilation of triplet excitons and enhance the recombination probability of holes and electrons are important for improving the EL performances of Ir(III) complexes.

Previously, Che et al. demonstrated an effective device design strategy to improve the EL performances of red platinum(II) (Pt(II)) complex by co-doping wide energy gap Ir(III) complex with low-lying energy levels into electron dominant light-emitting layer (EML) as electron trapper and energy transfer ladder [15]. The low-lying LUMO level and matched triplet energy of co-doped Ir(III) complex are helpful in balancing carriers' distribution, broadening exciton recombination zone, and facilitating energy transfer from host to emitter molecules. Consequently, high EL efficiency with slow efficiency roll-off, high brightness and even long device lifetimes were realized by the optimized co-doped devices. Recently,

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we reported the significantly improved EL performances of a red Ir(III) complex realized by co-doping a wide energy gap rare earth europium(III) (Eu(III)) complex into the light-emitting layer as electron trapper and energy transfer ladder [16]. By optimizing the co-doping concentration of Eu(III) complex, highly efficient red OLEDs with current efficiency and power efficiency as high as 58.98 cd/A and 61.73 lm/W, respectively, were obtained. Even at the high brightness of 1000 cd/m^2, a high current efficiency of 51.94 cd/A still could be retained. Very recently, we further confirmed the efficacy of this device design strategy in improving the EL performances of a red Ir(III) complex by utilizing a wide energy gap blue Ir(III) complex as the sensitizer [17]. Compared with red complexes, the relatively wider energy gaps and higher triplet energies of blue and green complexes make it more difficult to select appropriate sensitizer with matched energy levels and triplet energy.

In this work, we aim to improve the EL performances of an excellent green Ir(III) complex (tfmppy)$_2$Ir(tpip) (iridium(III)bis(2-(4-trifluoromethylphenyl)pyridine) tetraphenylimidodiphosphinate) by utilizing wide band gap and low-lying energy levels Ir(III) complexes FK306 (iridium(III)bis[4-(tert-butyl)-2,6-diuoro-2,3-bipyridine]acetylacetonate) and FIrpic (iridium(III)bis[(4,6-difluorophenyl)pyridinato-N,C$^{2'}$]picolinate) as sensitizers. To broaden the recombination zone and balance the distribution of holes and electrons on emitter molecules, the selected sensitizers were minutely co-doped into the electron-dominant EML. Compared with reference device, the co-doped devices displayed higher brightness and higher EL efficiency with slower EL efficiency roll-off. By optimizing the concentration of co-doped sensitizers, efficient green EL device with maximum current efficiency, power efficiency and brightness up to 102.29 cd/A (external quantum efficiency (EQE) of 25.3%), 88.67 lm/W and 96,268 cd/m^2, respectively, was realized. Even at the high brightness of 1000 cd/m^2, a current efficiency as high as 92.93 cd/A (EQE = 23%) can still be retained.

2. Experimental

All the organic materials used in this study were obtained commercially from Luminescence Technology Corp. and used as received except for (tfmppy)$_2$Ir(tpip), which was synthesized and purified in our laboratory. Indium-tin-oxide (ITO) coated glass with a sheet resistance of 10 Ω/sq was used as the anode substrate. All the organic layers were deposited with the rate of 0.1 nm/s under high vacuum (≤2.0 × 10^{-5} Pa). The EMLs were prepared by co-evaporating dopant(s) and host material from two or three individual sources, and the doping concentrations were modulated by controlling the evaporation rates of dopant(s). MoO$_3$, LiF and Al were deposited in another vacuum chamber (≤8.0 × 10^{-5} Pa) with the rate of 0.01, 0.01 and 1 nm/s, respectively, without being exposed to the atmosphere. Current density-brightness-voltage (J-B-V) characteristics were measured by using a programmable Keithley source measurement unit with a silicon photodiode. The EL spectra were measured with a calibrated Hitachi F-7000 fluorescence spectrophotometer. The EQE was calculated based on the photo energy measured by the photodiode, the EL spectrum and the current pass through the device [18].

3. Results and discussion

Device structure and HOMO/LUMO level diagrams are depicted in Fig. 1(a). Here, di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) was utilized as hole transport/electron block layer (HTL/EBL) due to its high hole mobility (1 × 10^{-2} cm^2 V^{-1} s^{-1}) and high-lying LUMO level (−1.8 eV) [19], while 1,3,5-Tri(m-pyrid-3-yl-phenyl) benzene (TmPyPB) was utilized as hole block/electron transport

layer (HBL/ETL) due to its low-lying HOMO level (−6.7 eV) and high electron mobility (1 × 10^{-3} cm^2 V^{-1} s^{-1}) [20]. To facilitate the balance of holes and electrons on emitter molecules, double-EMLs device structure was adopted by choosing p-type material TcTa (4,4′,4″-tris(carbazole-9-yl)triphenylamine) and bipolar material 26DCzPPy (2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine) as the host materials of EML1 and EML2, respectively [20,21]. A green Ir(III) complex (tfmppy)$_2$Ir(tpip) was doped into EMLs as emitter, while the widely used blue Ir(III) complex FK306 or FIrpic was co-doped into electron dominant EML2 as sensitizer [15]. The molecular structures of FK306, FIrpic and (tfmppy)$_2$Ir(tpip) were also shown in Fig. 1(a). In this case, the HOMO and LUMO levels (−5.44 and −2.98 eV, respectively) of (tfmppy)$_2$Ir(tpip) are within those of TcTa and 26DCzPPy [22]; therefore, carrier trapping will be the dominant EL mechanism of these devices [23].

As shown in Fig. 1(b), our previous reports have demonstrated that the stepwise HOMO levels of TAPC (−5.5 eV), TcTa (−5.8 eV), and 26DCzPPy (−6.1 eV) are beneficial for the hole injection and transport, while the stepwise LUMO levels of TmPyPB (−2.7 eV), 26DCzPPy (−2.6 eV), and TcTa (−2.4 eV) are beneficial for the injection and transport of electrons [24]. Therefore, balanced distribution of carriers (holes and electrons) within wide recombination zone could be expected. In addition, the 0.6 eV LUMO level discrepancy between TAPC/TcTa and the 0.6 eV HOMO level discrepancy between TmPyPB/26DCzPPy ensure that holes and electrons would be well confined within EMLs [24]. Within EML1, most holes and electrons will be well trapped by (tfmppy)$_2$Ir(tpip) molecules. Within EML2, as shown in Fig. 1(b), electrons will be preferentially trapped by FK306 or FIrpic molecules because of their lower LUMO levels (−3.6 or −3.47 eV) than those of 26DCzPPy (−2.6 eV) and (tfmppy)$_2$Ir(tpip) (−2.98 eV). On the other hand, holes will be trapped by (tfmppy)$_2$Ir(tpip) molecules because of its higher HOMO level (−5.44 eV) than those of 26DCzPPy (−6.1 eV), FK306 (−6.3 eV) and FIrpic (−6.15 eV). However, the transfer of holes from TcTa or 26DCzPPy to FK306 or FIrpic molecules will be insignificant because the HOMO levels of FK306 (−6.3 eV) and FIrpic (−6.15 eV) are 0.2 and 0.05 eV lower than that of 26DCzPPy (−6.1 eV), respectively.

To optimize the doping concentration of (tfmppy)$_2$Ir(tpip) and the thickness of 26DCzPPy, a series of single-EML devices with the structure of ITO/MoO$_3$ (3 nm)/TAPC (50 nm)/(tfmppy)$_2$Ir(tpip) (x wt %):26DCzPPy (y nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) were firstly fabricated and examined. Experimental results indicated the optimized doping concentration of (tfmppy)$_2$Ir(tpip) and the optimized thickness of 26DCzPPy are 8 wt% and 15 nm, respectively. This device (defined as single-EML reference device (S-RD)) displayed the maximum current efficiency, power efficiency and brightness up to 87.51 cd/A, 72.70 lm/W and 62,251 cd/m^2, respectively. At the brightness of 1000 cd/m^2, EL current efficiency of 85.59 cd/A was retained. Detailed EL performances of these devices are summarized in Tables S1 and S2, Figs. S1 and S2 in Supplementary Data.

To reduce the roll-off of EL efficiency, a series of double-EMLs devices with the structure of ITO/MoO$_3$ (3 nm)/TAPC (50 nm)/(tfmppy)$_2$Ir(tpip) (x wt%):TcTa (y nm)/(tfmppy)$_2$Ir(tpip) (x wt %):26DCzPPy (z nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) were also fabricated and examined. These devices were conceived to possess the broadened recombination zone and improved balance of carriers. In a recent paper, the high efficacy of this device design strategy has been demonstrated [24]. The characteristics of these devices were shown in Tables S3 and S4, Figs. S3 and S4 in Supplementary Data. The optimal concentration was 8 wt%, and the optimal thicknesses of EML1 and EML2 were 5 and 15 nm, respectively. This device was defined as double-EMLs reference device (D-RD) which gave the maximum brightness and current