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Highly efficient single-layer organic light-emitting devices using cationic iridium complex as host

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ABSTRACT

Highly efficient single-layer organic light-emitting devices (OLEDs) based on blended cationic Ir complexes as emitting layer have been demonstrated using narrow band gap cationic Ir complex $[Ir(Meppy)_2(pybm)](PF_6)$ (**C1**) as guest and wide band gap cationic Ir complex $[Ir(dfppy)_2(tzpy\text{-}cn)](PF_6)$ (**C2**) as host. As compared with single cationic Ir complex emitting layer, these host–guest systems exhibit highly enhanced efficiencies, with maximum luminous efficiency of 25.7 cd/A, external quantum efficiency of 8.6%, which are nearly 3-folds of those of pure **C1**-based device. Compared with a multilayer host-free device containing **C1** as emitting layer and TPBI as electron-transporting and hole-blocking layer, the above single-layer devices also show 2-folds enhancement efficiencies. The high efficiencies achieved in these host–guest systems are among the highest values reported for ionic Ir complexes-based solid-state light-emitting devices. In addition, a white-similar emission with CIE of (0.36, 0.47) has also been achieved with luminous efficiency of 4.2 cd/A as the **C1** concentration is 0.1 wt.%. The results demonstrate that the ionic Ir complexes-based host–guest system provides a new approach to achieve highly efficient OLEDs upon single-layer device structure and solution-processing technique.

1. Introduction

Organic light-emitting devices (OLEDs) based on phosphorescent Ir complex as guest have received great attention due to continuous advance toward practical applications both in solid-state lighting and color displays [1–14]. For the purpose of low production cost and large area displays, single-layer device structure and solution-based technologies present distinct advantages [15–17]. Recently, tremendous effort has been made in the development of neutral Ir (III) complexes-based OLEDs, in which Ir (III) complexes have been primarily used as phosphorescent emitters dispersed in a fluorescent host material (such as poly(*N*-vinylcarbazole) (PVK)) to produce highly efficient organic electroluminescence [18–25]. The presence of hydrophobic host is indispensable for these devices for transporting charge as well as minimizing phase aggregation of Ir complexes in solid state. However, the introduction of hydrophobic materials also makes the carrier transportation unbalanced, requiring multilayer structure, for example, hole-transporting (HT) layer, emissive layer (EML), and electron-transporting (ET) layer, thus the devices fabrication become complicated.

Compared with neutral Ir complex, ionic Ir complex shows the advantages of minimized carrier injection barrier for electron and hole as well as balanced carrier injection and transportation due to mobile ions contained

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in emissive layer which can form ohmic contact with each electrode under applied voltage [26]. However, it is still very scarce for ionic Ir complexes-based OLEDs because of absence of suitable host. The usually used polymer or small molecule hosts are hydrophobic and not effective for ionic Ir complexes because of poor compatibility between the hydrophobic hosts and hydrophilic ionic dopants. Thus, ionic Ir complexes are typically fabricated to host-free Light-emitting electrochemical cells (LECs), in which phase aggregation is moderately suppressed by interaction of the Ir complexes because of their intrinsic ionic nature. However, the efficiencies of ionic Ir complex based host-free devices are always lower than those of neutral Ir complexes based on polymer or small molecule host doping system because of moderate concentration quenching [27]. Qiu et al. reported solution-processed OLEDs based on ionic Ir complexes doped in PVK:OXD-7 (1,3-bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene) with maximum efficiencies of 5.2 cd/A [28]. The efficiencies of these devices can be further improved by introducing electron-transporting (ET) layer (such as 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI)) [29,30]. However, the introduction of TPBI layer will confine the device area and increase the fabrication cost.

For further decreasing concentration quenching of ionic Ir complexes, the development of new host materials with good compatibility with the ionic Ir complex emitters is still a highly desirable and pursued task. Actually, ionic Ir complex itself can be acted as matrix to host narrower band gap ionic Ir emitters to further decrease concentration quenching of emitters [5] and the resulted system show better compatibility than that of hydrophobic hosts due to the same ionic nature. Furthermore, phosphorescent nature of ionic Ir complex host also helps to improve the device efficiency.

Recently, Su et al. reported self-doping ionic Ir complexes in LECs based on green-emitting $[Ir(dFppy)_2(SB)]^+(PF6)^-$ as the host and orange-emitting $[Ir(ppy)_2(SB)]^+(PF6)^-$ as the guest with high quantum efficiency of 10.4% [31]. Efficient white [32] and red-emitting [33] LECs were also achieved under this self-doping strategy by blending blue–green- and red-emitting ionic Ir complexes with CIE of (0.35, 0.39) with quantum efficiency of 3.3% and 3.62%, respectively. Recently, near-infrared LECs using ionic Ir complex as host and fluorescent ionic NIR emitting dyes as guest were also reported with quantum efficiency of 1.24% [34].

However, these devices exhibit much lower brightness (<100 cd/m^2) and comparatively long turn-on time [35] (>30 min) which greatly obstruct its practical applications.

In this work, we demonstrate highly efficient single-layer, solution-processed OLEDs based on ionic Ir complexes host–guest system by using narrow-band gap $[Ir(Meppy)_2(pybm)](PF_6)$ (**C1**) as guest and wide-band gap $[Ir(dfppy)_2(tzpy\text{-}cn)](PF_6)$ (**C2**) as host. Our previous work [36] had shown that the incorporation of cyanogen group in the side chain of the ancillary ligand significantly improved the device efficiencies. The resulted devices exhibit high brightness and much enhanced EL efficiencies as compared with those of pure **C1** or **C2**-based devices (three times enhancement to **C1**), giving a peak LE of up to 25.7 cd/A, which is among the highest values reported for ionic Ir complexes-based solid-state light-emitting devices [27,37–44].

2. Results and discussions

2.1. Synthesis

The Ir dimer was synthesized using literature procedure [45] by reacting of $IrCl_3{\cdot}3H_2O$ and 2.5 equiv 2-(4-methylphenyl)pyridine in a mixture of 2-ethoxyethanol and water (3/1, v/v) at 110 °C overnight under argon. After being cooled to room temperature, the resulting precipitate was filtered off, then washed with water, methanol and ethyl ether, and finally dried to afford the desired product.

The ionic Ir complexes $[Ir(Meppy)_2(pybm)](PF_6)$ (**C1**) and $[Ir(dfppy)_2(tzpy\text{-}cn)](PF_6)$ (**C2**) were synthesized by the reaction of dimeric Ir complex with ancillary ligand in 1,2-ethanediol under argon according to our articles published earlier [36,46], as shown in Scheme 1 (where Meppy is 2-(4-methylphenyl)pyridine, dfppy is 2-(2,4-difluorophenyl)pyridine, pybm is 2,2-dimethyl-6-(2-(pyridin-2-yl)-1H-benzo[d]imidazol-1-yl)hexanenitrile, and trzpy-cn is 2,2-dimethyl-6-(3-(pyridin-2-yl)-4H-1,2,4-triazol-4-yl)hexanenitrile).

2.2. Optical properties

The absorption and photoluminescence (PL) spectra of the complexes in films are depicted in Fig. 1. **C2** show intense absorption with peaks around 250 nm and 370 nm, corresponding to spin-allowed ligand-to-ligand (π–π^*) and metal-to-ligand charge transfer (MLCT) transitions, respectively. **C1** exhibit similar absorption peaks as **C2**, with π–π^* transitions at 253 nm but much stronger MLCT absorption at around 350 nm than that of **C2**.

The PL of **C1** show a broad and almost featureless emission spectrum peaked at 588 nm, suggesting a predominant characters of MLCT transition excited states. **C2** exhibit a vibronic structure emission spectrum with two peaks at 456 nm and 486 nm, respectively, indicative of much more characters of LC $^3\pi$–π^* transitions. The slight overlap between emission of **C2** and absorption of **C1** (see Fig. 1) suggests energy transfer from **C2** to **C1** could occur.

The normalized PL spectra of blended **C1**–**C2** films with different **C1** concentration from 0.1 wt.% to 2 wt.% are shown in Fig. 2. The spectra of pristine **C1** and **C2** films are also investigated for comparison. The blended films show two major peaks at 458 nm and 530 nm at **C1** concentration from 0.1 wt.% to 0.25 wt.% due to incompletely energy transfer from **C2** to **C1** at low **C1** concentration. With the increase of **C1** concentration, the emission intensity weakens at 458 nm and enhances at 530 nm. At **C1** concentration of 2 wt.%, most of the **C2** emission is quenched as seen by the peak intensities at 458 nm due to a completely energy transfer. The efficient energy transfers achieved at such a low guest concentration (2 wt.%) suggest the main contribution is from a long-range Förster energy transfer [47] instead of Dexter in this