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Efficient red electrophosphorescence from a fluorene-based bipolar host material

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1. Introduction

Phosphorescent organic light-emitting diodes (OLEDs) attract a great deal of attention because they can theoretically approach 100% internal quantum efficiency by harnessing both singlet and triplet excitons [1–6]. In these phosphorescent devices, the organometallic phosphors are commonly doped into appropriate host materials to prevent concentration quenching and achieve high efficiency [1,2]. The past few years have witnessed the development of blue and green phosphorescent OLEDs exhibiting high external quantum efficiencies (EQEs) and

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ABSTRACT

We have prepared efficient red organic light-emitting diodes (OLEDs) incorporating 2,7bis(diphenylphosphoryl)-9-[4-(*N*,*N*-diphenylamino)phenyl]-9-phenylfluorene (POAPF) as the host material doped with the osmium phosphor Os(fptz)₂(PPh₂Me)₂ (fptz = 3-trifluoromethyl-5-pyridyl-1,2,4-triazole). POAPF, which possesses bipolar functionalities, can facilitate both hole- and electron-injection from the charge transport layers to provide a balanced charge flux within the emission layer. The peak electroluminescence performance of the device reached as high as 19.9% and 34.5 lm/W – the highest values reported to date for a red phosphorescent OLED. In addition, we fabricated a POAPF-based white light OLED – containing red-[doped with Os(fptz)₂(PPh₂Me)₂] and blue-emitting {doped with iridium(III) bis[(4,6-difluorophenyl)pyridinato- $N,C^{2'}$] picolinate, FIrpic} layers – that also exhibited satisfactory efficiencies (18.4% and 43.9 lm/W).

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power efficiencies (PEs) [4,7–12]. There are, however, far fewer reports describing high-performance red phosphorescent OLEDs. Being one of the primary colors, red emission from OLEDs is important for applications in fullcolor displays and solid state lighting [13–19]. For future device applications, it will be essential for OLEDs to exhibit efficient, saturated red emissions.

Since Baldo et al. developed the concept of phosphorescent OLEDs [1], the carbazole derivative 4,4'-N,N'-dicarbazolebiphenyl (CBP) has been used widely as a host material for red phosphorescent OLEDs [3,20–27] because of its suitable triplet energy (E_T) and good hole-transporting ability. Because CBP has a wide band gap (E_g), injecting carriers are often required to overcome the large energy barriers between the charge transport layers and its highest occupied molecular orbital (HOMO) and/or lowest unoccupied molecular orbital (LUMO). In addition, the poor match between the energy levels of CBP and the red triplet dopants usually results in direct charge trapping within the emitting layer (EML). Therefore, red phosphorescent devices based on CBP often require high operation voltages and provide unsatisfactory PEs. To break free from these constraints, several attempts have been made recently to use host materials possessing narrower band gaps [28–30] or bipolar characteristics [31–33] to improve the charge injection and electroluminescence (EL) performance of red phosphorescent OLEDs. Nevertheless, the PEs of the red electrophosphorescence remain far below those reported for blue- or greenemitting devices [3,20–27].

In this paper, we report the fabrication of efficient red phosphorescent OLEDs incorporating the bipolar host 2,7-bis(diphenylphosphoryl)-9-[4-(N,N-diphenylamino) phenyl]-9-phenylfluorene (POAPF) doped with the efficient red-emitting phosphor $Os(fptz)_2(PPh_2Me)_2$ (fptz = 3-trifluoromethyl-5-pyridyl-1,2,4-triazole); Fig. 1 presents their chemical structures. This charge-neutral osmium complex has been used previously as a phosphor in red-emitting devices displaying high EQEs [22,34]. The relatively low oxidation potential of Os(fptz)₂(PPh₂Me)₂, however, results in severe charge trapping in devices using CBP as the host, resulting in high driving voltages and unsatisfactory PEs. POAPF, which contains an electronrich triphenylamine group and an electron-deficient bis(diphenylphosphoryl)fluorene unit [35-37], has recently been developed as a host material exhibiting bipolar characteristics [38] that not only provide suitable frontier orbital energies for facile hole- and electron-injection but also improve the balance of charge flux in the emission layer. Moreover, the triplet energy (E_T) of POAPF is estimated to be 2.72 eV - a value that is sufficiently high for POAPF to act as a host material for red, green, and even blue phosphorescent emitters. Indeed, blue phosphorescent OLEDs based on POAPF doped with FIrpic can exhibit high values of EQE and PE [38]. We expected that POAPF could also be utilized as a host for the red-emitting Os(fptz)₂(PPh₂Me)₂, thereby improving charge injection and enhancing charge balance to result in highly efficient red phosphorescent devices.

2. Experimental

The bipolar host molecule POAPF [38] and the red phosphorescent emitter $Os(fptz)_2(PPh_2Me)_2$ [22] were prepared using previously reported procedures. The hole-



Fig. 1. Chemical structures of POAPF and Os(fptz)₂(PPh₂Me)₂.

transport material 4,4'-bis(3-methylphenylphenylamino)biphenyl (TPD), the conventional host material CBP, and the electron-transport material 4,7-diphenyl-1,10phenanthroline (BPhen) were all purchased from LumTec Corp. and used without further purification.

The oxidation and reduction potentials were measured, respectively, in anhydrous CH_2Cl_2 and anhydrous DMF, containing 0.1 M TBAPF₆ as the supporting electrolyte, at a scan rate of 50 mV/s against a Ag/Ag⁺ (0.01 M AgNO₃) reference electrode, with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.

The EL devices were fabricated through vacuum deposition (10^{-6} torr) of the materials onto ITO glass (sheet resistance: 25Ω /square). All of the organic layers were deposited at a rate of 1.0 Å/s. The cathode was completed through thermal deposition of LiF (15 Å; deposition rate: 0.1 Å/s) and then capping with Al metal (100 nm) through thermal evaporation (deposition rate: 4.0 Å/s). The current–voltage–luminance relationships of the devices were measured using a Keithley 2400 source meter and a Newport 1835C optical meter equipped with an 818ST silicon photodiode. The EL spectrum was obtained using a Hitachi F4500 spectrofluorimeter.

3. Results and discussion

Fig. 2 presents the current density-voltage (I-V) characteristics of the hole-only devices having the configuration indium tin oxide (ITO)/TPD (30 nm)/host material (30 nm)/TPD (30 nm)/Al (100 nm) and the electron-only devices having the configuration ITO/BPhen (30 nm)/host material (30 nm)/BPhen (30 nm)/LiF (15 Å)/Al (100 nm). Here, "host material" refers to either the bipolar host POAPF or the conventional host CBP. Because of the high LUMO energy level (-2.20 eV) of TPD in the hole-only devices and the low HOMO energy level (-6.40 eV) of BPhen in the electron-only devices, injections of electrons and holes were prohibited in the hole- and electron-only devices, respectively; accordingly, the measured I-V characteristics were dominated by holes and electrons, respectively. Fig. 2 reveals that the POAPF-based devices exhibited lower turn-on voltages and higher current densities than did the CBP-based devices under the same bias.



Fig. 2. Current density–voltage (*I–V*) curves of (a) hole- and (b) electrononly devices.

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