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Ultra high-efficiency multi-photon emission blue phosphorescent OLEDs with external quantum efficiency exceeding 40%

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ABSTRACT

We developed high-efficiency multi-photon emission (MPE) blue phosphorescent OLEDs with external quantum efficiency exceeding 40% at 100 cd m^{-2}. In these MPE devices, we used a blue phosphorescent emitter, FIrpic and pyridine-containing electron-transporters, B3PyPB and B3PyMPM, B4PyMPM. We also used a well-known electron-transporter, BCP for comparison. We used a combination of TAPC/MoO_3/Al/Liq layers as the charge-generation layer unit. An optimized MPE device showed an extremely high current efficiency of over 90 cd A^{-1} and a high power efficiency of over 40 lm W^{-1} at 100 cd m^{-2} without any outcoupling enhancement.

1. Introduction

Organic light-emitting device (OLEDs) has been expected to realize energy-saving general lighting and usher in an era of new lighting designs, such as transparent lighting panels and luminescent wallpapers [1,2]. The primary requirements for general lighting are threefold: (i) power efficiency (PE) at high brightness (>3000 cd m^{-2}), which is greater than that of a fluorescent tube, (ii) color rendering index (Ra)>80, (iii) operational stability at high-brightness. From this perspective, a tandem OLED, so-called multi-photon emission (MPE) OLED is recognized as a key technology for use in general lighting, because we can obtain high-brightness at low current density leading to an OLED with high efficiency and long life [3]. MPE device consists of multiple emissive units connected with charge generation layer (CGL). In this device, each CGL generates electrons and holes upon voltage application. Injected holes and electrons recombine in each emissive layers (EML). Therefore, extremely high external quantum efficiency (η_{ext}) can be obtained.

Among three primary colors, development of a stable blue phosphorescent emitter and related materials is still one of the biggest hurdles from material side. While from device side, realization of a stable and high-performance blue phosphorescent OLED is a major obstacle to overcome. A performance of a white OLED strongly depends on that of a blue unit contained therein, therefore, development of a blue phosphorescent OLED based on a MPE structure is one of the most challenging issues. Moreover, a concept of MPE blue phosphorescent OLED potentially provides a key solution for a stability issue in a blue phosphorescent OLED. However, because the use of wide-energy-gap materials with high triplet energy (E_T) is imperative for realizing a high-efficiency blue phosphorescent OLED, effective electron-injection from a CGL to an

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electron-transport layer (ETL) with high-lying electron affinity (E_a) level can be a hurdle to reduce a driving voltage.

Recently, we have developed several types of pyridine-containing multifunctional ETLs [4]. By using these ETLs, we have demonstrated high-performance phosphorescent OLEDs with η_{ext} of ~30%. Further, by using a combination of *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)$_3$] and a pyridine-containing ETL, ultra high-efficiency MPE green phosphorescent OLEDs with an extremely high current efficiency (η_c) over 250 cd A^{-1} have been developed [5]. In this study, by using a blue phosphorescent emitter, iridium(III) bis[(4,6-difluorophenyl)-pyridinate-*N*,$C^{2\prime}$]picolinate (FIrpic) and a pyridine-containing ETL, we successfully developed ultra high-efficiency MPE blue phosphorescent OLEDs with $\eta_{ext,100}$ exceeding 40%. For a CGL unit, we introduced a combination of 1,1-bis[4-[*N*,*N*-di(*p*-tolyl)amino]phenyl]cyclohexane (TAPC)/MoO_3/Al/8-quinolinolato lithium (Liq) layers. An optimized MPE OLED showed an extremely high $\eta_{c,100}$ of over 90 cd A^{-1} and a high $\eta_{p,100}$ of over 40 lm W^{-1} without any outcoupling enhancement techniques.

2. Experimental

All organic materials were purified by temperature-gradient sublimation in vacuum. The substrates were cleaned with ultra-purified water and organic solvents, and then dry-cleaned for 30 min by exposure to an UV-ozone ambient. The organic layers were deposited onto the ITO substrate under the vacuum (~10^{-5} Pa), successively. Liq, LiF and Al were patterned using a shadow mask with an array of 2 mm × 2 mm openings without breaking the vacuum (~10^{-5} Pa). All devices were encapsulated immediately after preparation under a nitrogen atmosphere using epoxy glue and glass lids. The EL spectra were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density–voltage and luminance–voltage characteristics were measured using a Keithley source measure unit 2400 and a Minolta CS200 luminance-meter, respectively. External quantum efficiencies were calculated from the front luminance, current density and EL spectrum.

3. Results and discussion

Prior to the fabrication of MPE device, we evaluated FIrpic-based conventional OLEDs using a pyridine-containing ETL. Based on our previous results of FIrpc-based OLEDs, first, we investigated the effect of ETLs on OLED performances. We used three types of ETLs with different E_a, such as 3,3″,5,5″-tetra(3-pyridyl)-1,1′;3′,1″-terphenyl (B3PyPB: E_a = 2.62 eV) [4c], bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PyMPM: E_a = 3.44 eV) and bis-4,6-(3,5-di-4-pyridylphenyl)-2-methylpyrimidine (B4PyMPM: E_a = 3.71 eV) [4a,e]. In addition, we also used a well-known electron-transporter, 2,9-dimethyl-4,7-diphenylphenanthroline (BCP) for comparison. For a hole-transport layer (HTL) and a host material, we used TAPC and 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA), respectively. These materials except BCP have higher E_T than that of FIrpic. Therefore, the triplet exciton quenching of FIrpic at the HTL/EML and/or EML/ETL interface(s) can be minimized. Then, we fabricated a blue phosphorescent OLED with a structure of [ITO (130 nm)/TAPC (60 nm)/TCTA: 7 wt% FIrpic (5 nm)/TCTA: FIrpic 20 wt% (5 nm)/ETL (20 nm)/ETL: 25 wt% Liq (35 nm)/Liq (1 nm)/Al (100 nm)]. Here, we used double emission layer with different doping concentrations for a better carrier balance (Fig. 1) [2g,4c].

EL spectra showed an emission only from FIrpic with no emission from neighboring materials (inset in Fig. 2(b)). The current density–voltage–luminance (*J*–*V*–*L*) and the power efficiency–luminance (*PE*–*L*) characteristics are shown in Fig. 2(a) and (b), respectively. All the performances are summarized in Table 1. A reference OLED using BCP gave a very poor η_{ext} of ~5.6% and an η_p of ~10 lm W^{-1} probably because of two factors: (a) much lower E_T (2.63 eV) than that of FIrpic (2.77 eV) and (b) lower carrier balance of holes and electrons in the EML (see supporting information in detail). Among pyridine-containing ETLs, B3PyPB showed superior performances in FIrpic-based OLED despite the high-lying E_a of 2.62 eV. B3PyPB-based OLED showed much reduced driving voltage of 2.87 V at 100 cd m^{-2}, and gave an $\eta_{p,100}$ of 56.5 lm W^{-1} (51.6 cd A^{-1}, $\eta_{ext,100}$ 21.8%) at 100 cd m^{-2} and 43.2 lm W^{-1} (46.3 cd A^{-1}, $\eta_{ext,100}$ 19.6%) at 1000 cd m^{-2}, respectively. These are among the best performances in FIrpic-based OLEDs. Whereas B3PyMPM- and B4PyMPM-based OLEDs showed lower η_{ext} of ~15% and $\eta_{p,100}$ of ~30 lm W^{-1} indicating carrier imbalance in EML. Because these ETLs have much deeper E_a than that of B3PyPB, large excess of electrons can be injected in EML. Additionally, there is large barrier of 0.55 eV between TAPC (I_p = 5.60 eV) and FIrpic (I_p = 6.15 eV) in EML [6]. Thus, hole-injection to FIrpic can be more difficult than electron-injection. Considering B3PyMPM and B4PyMPM have comparable E_T to that of FIrpic, in order to maximize a FIrpic-based OLED, it is important for an ETL to possess not only high E_T but also high-lying E_a level.

With these data in hand, we tried to fabricate a MPE blue phosphorescent OLED using a combination of TAPC/MoO_3/Al/LiF layers as a CGL unit. In this CGL unit, holes and electrons are generated from TPAC/MoO_3 interface. A MPE device with a structure of [ITO (130 nm)/TAPC (60 nm)/TCTA: 7 wt% FIrpic (5 nm)/TCTA: FIrpic 20 wt% (5 nm)/B3PyPB (55 nm)/LiF (1 nm)/Al (1 nm)/MoO_3 (5 nm)/TAPC (60 nm)/TCTA: 7 wt% FIrpic (5 nm)/TCTA: FIrpic 20 wt% (10 nm)/B3PyPB (55 nm)/LiF (1 nm)/Al (80 nm)] was fabricated. Although this device gave an $\eta_{c,100}$ of 45.5 cd A^{-1}, this device did not work well as a MPE device, and showed much higher driving voltage of 16.2 V at 100 cd m^{-2}, which is 5.6 times higher than 1 unit device. An $\eta_{p,100}$ of 8.9 lm W^{-1} ($\eta_{ext,100}$ 21.5%) at 100 cd m^{-2} was obtained. These results suggest that a CGL with LiF should be improved to reduce a driving voltage of a MPE device. To improve CGL unit, we investigated three CGL only devices [5,7] with a structure of: [ITO/B3PyPB (50 nm)/X/TAPC (50 nm)/Al], (A) X = none, (B) X = LiF (1 nm)/Al (1 nm)/MoO_3 (5 nm), (C) X = Liq (1 nm)/Al (1 nm)/MoO_3 (5 nm). In a CGL only device, hole-injection from anode ITO is blocked by B3PyPB due to the deep I_p of 6.67 eV.