Towards solution-processed top-emitting OLEDs using a phosphorescent iridium complex

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ABSTRACT
Phosphorescent inverted top-emitting OLEDs using green iridium complexes have been fabricated by spin coating and their performances compared to bottom-emitting OLEDs based on the same materials. Even if the current efficiency is lower, respectively 7.0 ± 1.1 $cd.A^{-1}$ and 12.9 ± 1.9 $cd.A^{-1}$, this paper demonstrates the feasibility to fabricate phosphorescent top-emitting OLEDs by using a solution process with a simple OLED structure and replacing indium tin oxide electrode by a low-cost reflective aluminum electrode. Optical characterization of the top-emitting OLEDs shows a low emission shift compared to the spectrum of bottom-emitting OLED. A low angle dependency of the electroluminescence peak wavelength is observed , showing it is possible to control and minimize the microcavity effects for solution-processed top-emitting OLEDs.
Keywords: Top-emitting organic light-emitting diodes (OLEDs), solution process, phosphorescent emitters

1. INTRODUCTION

Roll-to-roll printing technologies to fabricate organic light-emitting diodes (OLEDs) have been shown to be attractive to simplify the fabrication process and reduce its cost. For a few years, research on bottom-emitting OLEDs (BOLEDs) fabricated by solution process has been widely conducted. BOLEDs show a typical light extraction of only 25 % due to the glass substrate [1], [2]. On the other hand, top-emitting OLEDs (TOLEDs) show interesting properties for displays and lighting. They are more suitable for active-matrix OLED displays, using a thin-film transistor backplane. The TOLED structure allows the design of a large aperture for high resolution displays without any blocking from the wired metal lines and the opaque TFTs [3], [4]. Besides, inverted TOLEDs are highly promising in the case of a CMOS addressing circuit because they are easier to use than direct TOLEDs via a common anode addressing scheme. Nevertheless, research effort mostly focuses on evaporated inverted TOLEDs and only a few studies have been conducted to develop TOLEDs by solution process, whether direct or inverted structures [5], [6].

Iridium complexes have been widely used to fabricate bottom-emitting phosphorescent OLEDs (PhOLEDs), either by evaporation or by solution process[7]–[10]. Literature reports also top-emitting PhOLEDs based on them [11], [12]. Nethertheless, only thermal evaporation has been used for their fabrication. Iridium complexes are mainly used with the small-molecule tris(4-carbazoyl-9-ylphenyl)amine (TCTA), by evaporation or spin coating. However, Destouesse *et al.* reported the difficulty to deposit small molecules by a solution process depending on the roughness of the layer underneath, more specifically if nanoparticles were used [13]. By incorporating a small quantity of a polymer such as polystyrene in a small-molecule blend, the quality of film forming was improved leading to a lower dark current in solar cells. Large band gap polymers such as poly(N-vinylcarbazole) (PVK) are suitable as a host for iridium complexes [14]. Mixing PVK with iridium emitter instead of pure small molecule blend leads to a smoother layer and avoids pin-holes [15]. Besides, it has been shown that incorporating the electron transport material 2,2',2''-(1,2,5-benzenetriyl)tris[1-phenyl-1H-benzimidazole (TPBi) in TCTA:$Ir(mppy)_3$ leads to a stable efficiency roll-off for green iridium complexes [7]. This ternary blend was used for other iridium emitters, such as Ir(acac) [9]. TPBi has an effect on the morphology of the layer once deposited [8].

In this work, we report the performances of top-emitting PhOLEDs fabricated by a solution process, by using tris[2-(p-tolyl)pyridine]iridium(III) ($Ir(mppy)_3$) and tris[2-(phenylpyridinato-C^2, N]iridium(III) ($Ir(ppy)_3$) and a blend of two hosts: PVK and TPBi.

2. MATERIALS AND METHODS

BOLEDs and TOLEDs based on the same emissive material (iridium complex) were fabricated and characterized. Both structures are depicted in Fig. 1. The whole fabrication process is conducted in a clean room environment. The fabrication process used is based on our previous work studying Super Yellow polymer in both structures [6]. OLEDs are built on 25 by 25 mm^2 glass substrates, covered by an indium tin oxide (ITO) layer for BOLEDs and by a 140 nm thick aluminum layer for TOLEDs. ITO substrates and glass substrates, respectively used for BOLEDs and TOLEDs, are cleaned using an ultrasonic bath with acetone and isopropanol in sequence. Oxygen plasma treatment for 2 min at 300W is used in order to remove organic residues at the

surface and enhance the adhesion for the materials deposited on top. The aluminum electrode is deposited on top of the glass substrates by thermal evaporation under vacuum (10^{-7} mbars).

The same process is conducted for both OLED structures to deposit the layers on top of ITO (BOLED) and Al (TOLED). First, zinc oxide nanoparticles (ZnO NPs) supplied by *Genes'ink* are spin-coated on top of ITO and Al at 2500 rpm for 90s, followed by an annealing under vacuum at 100°C for 10 min. A blend of polyethylenimine-ethoxylated (PEIE) as electron injection material provided by *Sigma-Aldrich* and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) from *Lumtec*, as hole blocking material, is prepared in isopropanol as described in literature [16] and spin-coated at 1000 rpm for 60s. The annealing time and temperature are the same as the one for ZnO.

Two iridium complexes were tested: $Ir(mppy)_3$ and $Ir(ppy)_3$, provided respectively by *Lumtec* and *Sigma-Aldrich*. $Ir(mppy)_3$ is more soluble due to its methyl group. However, both emitters have been widely used to fabricate solution-processed BOLEDs in literature. Both materials are incorporated with a ratio of 13 wt% in the co-host blend made of PVK and TPBi with a 1:1 weight ratio. The total concentration of the two hosts is 10 $mg.ml^{-1}$ and they are mixed in a blend of toluene:o-dichlorobenzene with a volume ratio of 1:1. The solution is prepared in the glovebox and stirred overnight at room temperature. The solution is spin-coated at 2000 rpm for 60s and the layer formed is annealed at 90°C for 10 min. The layer thickness is about 60 nm.

N,N'-Di(1-naphthyl)-*N,N'*-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) is deposited by thermal evaporation at a rate of 0.1 $nm.s^{-1}$ under vacuum (10^{-8} mbars), followed by the evaporation of a 10 nm thick molybdenum oxide layer at a rate of 0.03 $nm.s^{-1}$. As a top electrode, 70 nm and 15 nm of silver (Ag) are evaporated, respectively for BOLEDs and TOLEDs. The OLED active area is 5x5 mm^2. A capping layer of 25 nm thick MoO_x is evaporated on top of Ag in TOLED structure in order to increase the transmittance of the semi-transparent electrode and the light out-coupling. Finally, a glass substrate is glued on top of the OLED with *UHU Endfest* glue as a barrier encapsulation to prevent oxygen and moisture from degrading the OLED.

The electroluminescence spectrum is measured with an *Andor SR-500i* spectrometer and current density-voltage-luminance (JVL) characteristic are recorded using two Source Measure Units (SMUs), *Keithley 2400*, and a silicon photodiode. Angle-dependent spectra are measured by using a self-made goniometer in order to quantify the microcavity effects on the optical performances of the device.

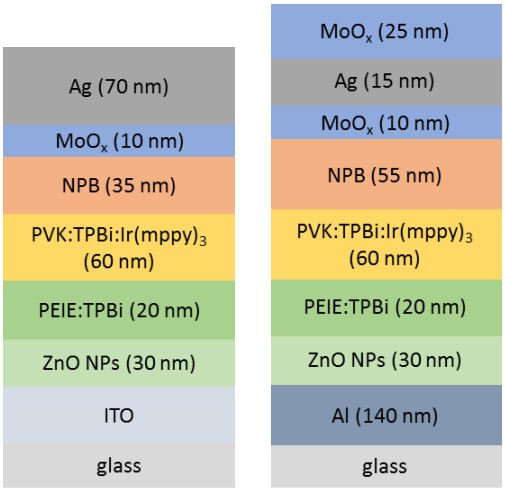

Figure 1. Bottom-emitting (left) and top-emitting (right) OLEDs based on iridium complex.

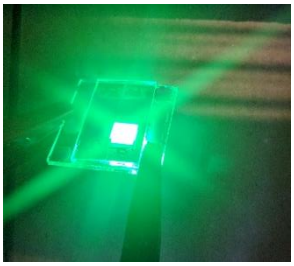

Figure 2. Top-emitting OLED based on iridium complex.

3. RESULTS AND DISCUSSION

The JVL characteristics are shown Fig. 3. The turn-on voltage (V_{on}) of TOLED based on $Ir(mppy)_3$ is slightly lower than V_{on} of BOLED based on the same emitter, respectively 2.2 V and 2.5 V. The different electrodes used in both architectures may explain this. Using PEIE polymer surface modifier allows to reduce the work function of ITO and Al and use these materials as cathode. Zhou *et al.* [17] measured the work function of ITO/PEIE and Al/PEIE by Kelvin Probe and show that for a 10 nm thick PEIE layer, the work function was reduced from 4.6 eV to 3.6 eV for ITO and 3.4 eV to 2.75 eV for Al. We explain the lower V_{on} shown in this work by a better electron injection from Al. V_{on} of TOLED based on $Ir(ppy)_3$, around 2.3 V, is also low despite different HOMO-LUMO levels for both emitters, -5.4/-2.4 eV for $Ir(mppy)_3$ and -5.8/-2.8 eV for $Ir(ppy)_3$. However, both TOLED structures show a higher leakage current than BOLED. The luminance increases faster with voltage for BOLED. For the same current density, the luminance is also lower. For 20 $mA.cm^{-2}$, the luminance is 2200 $cd.m^{-2}$, 1400

cd.m^{-2} and 1200 cd.m^{-2} for respectively BOLED, TOLED (Ir(mppy)$_3$) and TOLED (Ir(ppy)$_3$). The efficiencies, shown in Fig. 3, are higher for the BOLED than both TOLEDs. TOLED with Ir(ppy)$_3$ shows a lower roll-off compared to the other fabricated structures.

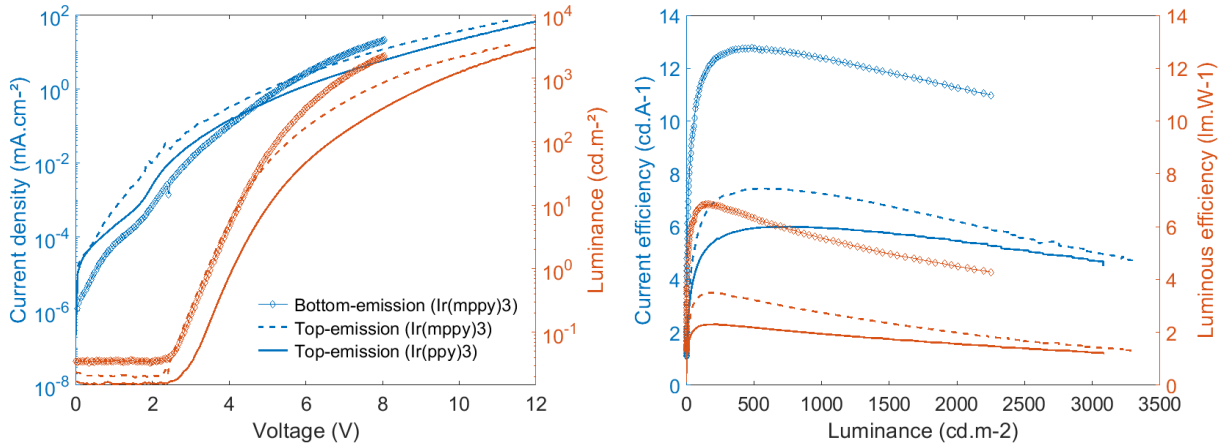

Figure 3. Current density-voltage-luminance characteristics, current efficiency and luminous efficiency of solution-processed bottom-emitting PhOLED and top-emitting PhOLED, based on Ir(mppy)$_3$ and Ir(ppy)$_3$.

Table 1 summarizes the performances of the three OLED architectures. BOLED shows the highest maximal current efficiency, 12.9 ± 1.9 cd.A^{-1}; while TOLEDs reach 7.0 ± 1.1 cd/A with Ir(mppy)$_3$ and 5.4 ± 1.3 cd/A with Ir(ppy)$_3$. The standard deviation for current efficiency is similar for both architectures, about 14.7% and 15.7% for BOLED and TOLED using Ir(mppy)$_3$.

Table 1. Performances of bottom-emitting and top-emitting OLEDs based on iridium complexes (Ir(mppy)$_3$ and Ir(ppy)$_3$)).

OLED structure	***Max. current efficiency (cd.A^{-1})***	***Max. luminous efficiency (lm.W^{-1})***	***Max. EQE (%)***	**EL peak (nm)**
Bottom-emission with Ir(mppy)$_3$	12.9 ± 1.9	5.8 ± 1.1	4.1 ± 0.6	520
Top-emission with Ir(mppy)$_3$	7.0 ± 1.1	3.2 ± 0.5	1.5 ± 0.3	540
Top-emission with Ir(ppy)$_3$	5.4 ± 1.3	1.7 ± 0.6	1.3 ± 0.4	550

The spectrum for every OLED is shown Fig. 4 and the EL peak wavelength in Table 1. BOLED EL peak (520 nm) is relatively similar to the literature (514 nm). TOLED EL peak is slightly shifted (540 nm). However, TOLED based on Ir(ppy)$_3$ has its EL peak closed to 550 nm, which is quite far from literature value (507 nm). The angle dependent spectrum was measured for TOLED based on Ir(mppy)$_3$ and the result is shown Fig. 4 from 0° to -80°. While the angle decreases, the emission spectrum is narrower. Nethertheless, a shift by only 20 nm can be observed for the EL peak, going from 540 nm at 0° to 520 nm at -80°. The microcavity is relatively well-adjusted.

4. CONCLUSIONS

Top-emitting OLEDs built from green iridium complexes (Ir(mppy)$_3$ and (Ir(ppy)$_3$) were fabricated by solution process and thermal evaporation. Their performances are lower than the bottom-emitting OLED built with the same emitter. Nevertheless, it is demonstrated that the optical properties are relatively well-optimized for Ir(mppy)$_3$. The electroluminescence spectrum is shifted by only 20 nm compared to the bottom-emitting OLED. By using another electrode than ITO as cathode, a better charge injection is obtained, allowing to reduce the fabrication cost and to overcome the brittleness issues of ITO.

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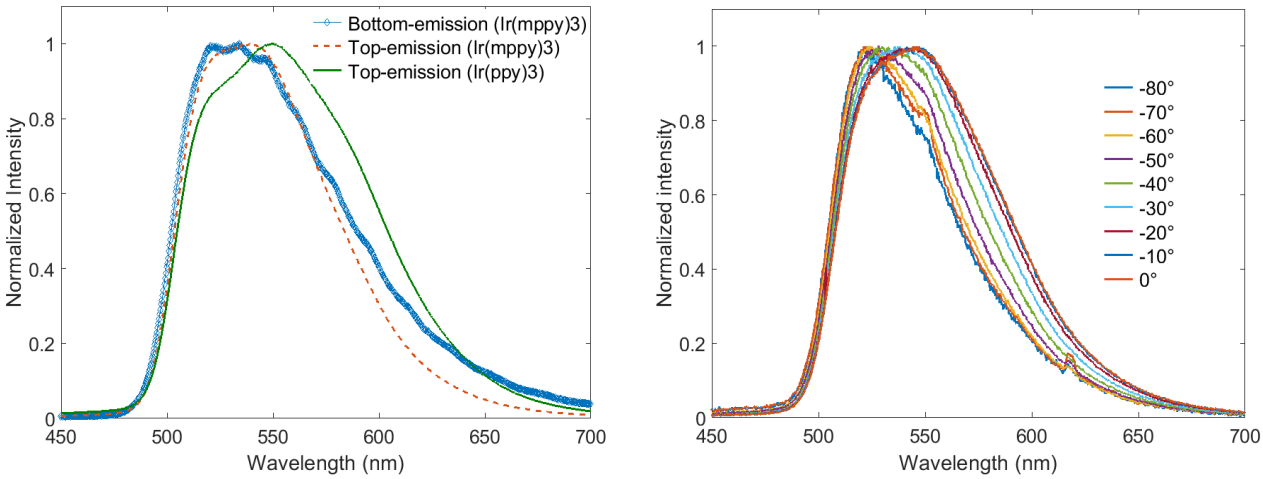

Figure 4. EL spectrum of solution-processed bottom-emitting and top-emitting PhOLEDs based on Ir(mppy)$_3$ and Ir(ppy)$_3$ (left) and angle-dependent spectra for solution-processed top-emitting PhOLEDs based on Ir(mppy)$_3$ (right).

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