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# A red tandem organic light-emitting diode based on organic photovoltaic-type charge generation layer

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ABSTRACT

In this paper, a significant enhancement in current efficiency of a red tandem organic light-emitting diode (OLED), which is based on an organic photovoltaic-type charge generation layer (CGL) of fullerene carbon 60/copper (II) phthalocyanine, is introduced. The CGL can absorb a part of photons, radiated from emission zone, then form excitons, which are dissociated into free charges. It induces in lower driven voltage and better efficiency of tandem OLED. Compared with single emitter-unit OLED and tandem OLED with bulk heterojunction CGL, the luminous efficiency boosts remarkably with increasing current density and shows rather slower roll-off. Our results demonstrate that the organic photovoltaic heterojunction, consists of two matched n- and p-type organic semiconductors, is a promising CGL for tandem OLEDs with high efficiency.



## 1. Introduction

In recent years, organic light-emitting diodes (OLED) have gained remarkable attention because of the appealing commercial interest for flat panel display, next generation and flexible displays, especially, indoor low power lighting source, and so on [1–4]. In the past decade, a substantial achievement has been undertaken to improve both efficiency and lifetime of OLEDs to satisfy the requirements of manufacture production [5–7]. Tandem OLEDs, which contain multiple electroluminescence (EL) units stacked with intermediate connectors in adjacent EL units, can potentially achieve both high efficiency and long driving time. In tandem OLEDs, the intermediate connector usually acts as a charge generation layer (CGL), which is very vital for device performance of tandem OLEDs. As the most important part in the tandem OLEDs, the CGL structures are classified into four types, which are metal/metal [8], n-type doped layer/p-type doped layer [9], n-type doped layer/electron acceptor/hole transporting layer (HTL) [5,10] and hetero-junction [11,12], respectively. However, several problems have limited CGLs' application. Such as, some metal oxides used in CGLs form complexes with the migrated n-dopants from the adjacent electron transporting layer during driven process, inducing a significant degradation in performance and increasing of driven voltage [13,14]. To avoid the performance degradation and the higher driven voltage, more and more researches on organic CGL have been focused. Additionally, since that only about 20% of emission light generated in recombination zone can be out-coupled in OLEDs, the remaining 80% is mainly wasted through substrate mode, waveguide mode and surface plasmon mode [15,16]. So, it is important to utilize the wasted part of emission light for improving the efficiency of tandem OLED.

To solve above problems, we designed a novel type of tandem OLED, in which the organic photovoltaic (OPV) is introduced as CGL. In this work, this special OPV-type CGL can not only absorb internal radiation partially but also favor charge generation, leading to enhancement of EL performance. The combination of fullerene carbon 60 ($C_{60}$)/copper (II) phthalocyanine (CuPc) was selected to

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constitute the CGL of tandem OLED. Furthermore, in order to improve injection efficiency of charges generated in CGL to adjacent emissive units, the molybdenum trioxide ($MoO_3$) and LiF films at two sides of $C_{60}$/CuPc are used as interface-modification layers.

## 2. Material and methods

In this work, the N,N′-dicarbazolyl-4–4'-biphenyl (CBP) acted as the host materials of red emitter of the Bis(1-phenyisoquionoline) (acetylacetonate)iridium (III) ($Ir(piq)_2acac$). The N,N′-bis-(3-naphthy)-N,N'-biphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) was used as hole transporting layer in each EL unit, and the 4,7-diphenyl-1,10-phenanthroline (Bphen) worked as electron transporting layer in each EL unit. In our work, the OPV-type CGL contained multi-layers of LiF/$C_{60}$/CuPc/$MoO_3$. The red tandem OLED (device A in Table 1) with the configuration of indium tin oxide (ITO)/$MoO_3$(3 nm)/NPB(40 nm)/CBP:$Ir(piq)_2acac$(30 nm, 8% by volume)/Bphen(30 nm)/LiF(1 nm)/$C_{60}$(5 nm)/CuPc(5 nm)/$MoO_3$(3 nm)/NPB(40 nm)/CBP: $Ir(piq)_2acac$ (30 nm, 8% by volume)/Bphen(30 nm)/LiF(1 nm)/Al(150 nm) was fabricated. And the red single emitter-unit OLEDs (device R in Table 1) with the configuration of ITO/$MoO_3$(3 nm)/NPB(40 nm)/CBP:$Ir(piq)_2acac$ (30 nm, 8% by volume)/Bphen(30 nm)/LiF(1 nm)/Al(150 nm) was also fabricated. Fig. 1 presents the schematic diagrams of cross sectional view of a tandem OLED. Prior to device fabrication, the ITO glasses were well cleaned with acetone and isopropanol in an ultrasonic solvent bath. After drying, the ITO glasses were treated with UV ozone for 15 min before loading into the vacuum chamber. Each layer grew in succession by vacuum evaporation with a base pressure of less than $5 \times 10^{-4}$ Pa without breaking vacuum. The evaporating rates were controlled at 0.1–0.2 nm $s^{-1}$ for the organic layers and 5–10 nm $s^{-1}$ for the Al cathode, respectively. The active emission area of each OLED was $3 \times 3$ mm.

After fabrication, the current-voltage-luminance characteristics were measured by Keithley 2400 source measurement unit and Topcon BM-7A luminance measurement unit. And the EL spectra were measured by a Spectra Scan PR655 spectrophotometer. The absorption and transmission spectra of $C_{60}$ and CuPc film were measured by HITACHI U-3900 UV–vis scanning spectrophotometer. All measurements were carried out in ambient atmosphere at room temperature.

## 3. Results and discussion

### 3.1. Structure design of OPV-type CGL

As shown in Fig. 1, the possible hole–electron pairs formed at the $C_{60}$/CuPc interface. In addition, considering the energy level between the each side EL unit and the intermediate that the highest occupied molecular orbital (HOMO) of CuPc is 5.3 eV, which is only 0.1 eV lower than the HOMO of NPB (5.4 eV). At the same time, the lowest unoccupied molecular orbital (LUMO) of $C_{60}$ is 3.7 eV, which is 0.7 eV higher than the LUMO Bphen (3.0 eV). It is indicated that holes can transport to the HOMO of NPB and electrons can transport to the LUMO of Bphen. In order to decrease the difficulty of electronic extraction, LiF and $MoO_3$ buffers are introduced to modify $C_{60}$ and CuPc, respectively. Therefore, in the CGL with structure of $C_{60}$/CuPc, the bounded electron–hole pairs can be separated into free electrons and holes, which transport along the LUMO of $C_{60}$ and the HOMO of CuPc, respectively, and inject into the corresponding EL units by adjacent layers finally.

To identify OPV function of $C_{60}$/CuPc CGL in our work, we measured the UV–vis absorption spectrum of double layers of $C_{60}$/CuPc and PL spectrum of $Ir(piq)_2acac$ film. It can be seen in Fig. 2 (a) that above two spectra overlap in the range of 600–700 nm, which indicates the red emission of $Ir(piq)_2acac$ can be absorbed by of $C_{60}$/CuPc. It suggests that the $C_{60}$/CuPc CGL possibly exhibits OPV function in our work.

In order to investigate the effect of thickness variation of $C_{60}$ and CuPc in OPV-type CGL on device performance of tandem OLEDs, we researched the properties of different thickness of $C_{60}$ and CuPc. For optical properties of OPV-type CGL, we compared the light transparency of different thickness of $C_{60}$/CuPc. As shown in Fig. 2(b), the transmittance of 5 nm, 10 nm and 20 nm thickness of both $C_{60}$ and CuPc are 96.177%, 93.77% and 91.562% at 625 nm, respectively. Clearly, the OPV-type CGL with the structure of $C_{60}$(5 nm)/CuPc(5 nm) exhibits the highest transmittance.

Following, electrical properties of OPV-type CGL were also studied. The inversion devices with different thickness of $C_{60}$ and CuPc were fabricated. The device structures were ITO/Bphen(30 nm)/LiF(1 nm)/$C_{60}$(x nm)/CuPc(x nm)/$MoO_3$(3 nm)/NPB(40 nm)/Al(150 nm) (x = 5, 10, 20 nm). As expressed in Fig. 3, it can be seen that the voltages of three devices are 13.7 V (x = 5 nm), 15.8 V (x = 10 nm) and 20.1 V (x = 20 nm) when the current density is 200 mA $cm^{-2}$. From it, we can find when the thickness of $C_{60}$ and CuPc are 5 nm, the current density of device is the best at the same voltage. It is suggested that the increasing of thickness will bring the difficulty of electronic extraction [17]. So, the device (x = 10 nm or 20 nm) requires a greater driven voltage to reach the same current density than that of the device (x = 5 nm). Considering both optical and electrical properties, we can get the optimized structure of OPV-type CGL, which is $C_{60}$(5 nm)/CuPc(5 nm).

### 3.2. Device performance

#### 3.2.1. EL spectra

In order to investigate the effect of OPV-type CGL on EL spectra of OLEDs, we compared the EL spectra of devices R and A. As expressed in Fig. 4, the EL spectrum of tandem OLEDs with OPV-type CGL (device A) shows red emission peak located at 625 nm corresponding to the emission of $Ir(piq)_2acac$, which is nearly identical with that of single emitter-unit OLED (device R). It is indicated that OPV-type CGL have little influence on EL spectra relative to single emitter-unit OLED.

**Table 1**
The device structure of all OLEDs.

| | Device | Structure |
|---|---|---|
| Red single emitter-unit OLED | R | ITO/$MoO_3$(3 nm)/EL unit[a]/LiF(1 nm)/Al(150 nm) |
| Green single emitter-unit OLED | G | ITO/$MoO_3$(3 nm)/EL unit[b]/LiF(1 nm)/Al(150 nm) |
| Red tandem OLED | A | ITO/$MoO_3$(3 nm)/EL unit[a]/LiF(1 nm)/$C_{60}$(5 nm)/CuPc(5 nm)/$MoO_3$(3 nm)/EL unit[a]/LiF(1 nm)/Al(150 nm) |
| Red tandem OLED | B | ITO/$MoO_3$(3 nm)/EL unit[a]/LiF(1 nm)/$C_{60}$:CuPc(10 nm, 50% by volume)/$MoO_3$(3 nm)/EL unit[a]/LiF(1 nm)/Al(150 nm) |
| Green tandem OLED | C | ITO/$MoO_3$(3 nm)/EL unit[b]/LiF(1 nm)/$C_{60}$(5 nm)/CuPc(5 nm)/$MoO_3$(3 nm)/EL unit[b]/LiF(1 nm)/Al(150 nm) |

[a] Red EL unit: NPB(40 nm)/CBP:$Ir(piq)_2acac$(30 nm, 8% by volume)/Bphen(30 nm).
[b] Green EL unit: NPB(40 nm)/CBP:$Ir(ppy)_3$(30 nm, 8% by volume)/Bphen(30 nm).