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# A highly efficient, transparent and stable charge generation unit based on a p-doped monolayer

Jun Liu, Jing Wang, Saijun Huang, Xindong Shi, Xinkai Wu, Gufeng He *

*National Engineering Lab for TFT-LCD Materials and Technologies, Department of Electronic Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China*

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ABSTRACT

We demonstrate a highly efficient, transparent and stable charge generation unit (CGU) combining a p-doped hole transporting layer (HTL) with an electron extraction layer (EEL). The CGU exhibits high optical transparency of over 90% and good stability with little voltage variation under stress. We propose a working mechanism of CGU based on an investigation of the CGU-only devices excluding the influences of emitters. Holes and electrons are generated in the p-doped layer, while the EEL facilitates electron injection into the adjacent electron transporting layer. It is expected that this CGU is a promising candidate for easy-fabrication, low-power-consumption and high-stability tandem white OLED for future display and lighting application.



## 1. Introduction

Tandem organic light-emitting diodes (OLEDs) have attracted wide attention because of their excellent properties such as enhanced current efficiency and extended lifetime as compared to conventional OLEDs [1–6]. Both current efficiency and operating voltage scale linearly with the number of stacked electroluminescent (EL) units, which are connected vertically in series with charge generation unit (CGU). Under an electric field, holes and electrons generated in CGU inject into the adjacent EL units, and then recombine with electrons from the cathode side and holes from anode side in individual EL unit, respectively. Therefore, an effective CGU to generate hole and electron carriers is crucial for an efficient tandem OLED.

The CGU used in tandem OLEDs can be typically classified into three categories: organic/metal oxide (or metal) heterojunction, bulk heterojunction and organic/organic heterojunction. An organic/metal oxide junction is usually composed of an n-doped electron transporting layer (ETL) and transition metal oxides (TMOs) such as vanadium oxide ($V_2O_5$) [2,7], molybdenum trioxide ($MoO_3$) [8–11] and tungsten trioxide ($WO_3$) [12–14]. Yang et al. proposed a thermal diffusion charge generation model based on studying 4,7-diphenyl-1,10-phenanthroline (BPhen): cesium azide ($CsN_3$)/$MoO_3$ bilayer as CGU. $MoO_3$ acted as holes and electrons resource due to spontaneous electron transfer from various defect states to the conduction band, and BPhen:$CsN_3$ extracted electrons and blocked the leakage of holes [9]. However, the fabrication of metal oxide film requires high thermal evaporation temperature. Recently, Chen et al. used a bulk heterojunction consisting of zinc phthalocyanine (ZnPc) and fullerene ($C_{60}$) as organic bipolar CGU [15]. In addition to a significant enhancement in luminance and current efficiency, the power efficiency was almost twice increased. However, the working mechanism is not fully understood and the transmittance of CGU is low due to strong absorption of ZnPc and $C_{60}$. In the organic/organic junctions, n-doped layer/p-doped layer is wildly used. The p-doped layer in CGU is usually formed by doping an organic HTL with Lewis acid

* Corresponding author. Tel.: +86 21 34207045; fax: +86 21 34204371.
*E-mail address:* gufenghe@sjtu.edu.cn (G. He).

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**Table 1**
Layer structures of the OLED devices.

| Devices or units | Layer structures |
|---|---|
| Device A | ITO/**EL-G**/Liq(1 nm)/Al(1 nm)/NPB(40 nm)/**EL-R**/Liq(1 nm)/Al(100 nm) |
| Device B | ITO/**EL-G**/NPB:F4-TCNQ(1%, 40 nm)/ **EL-R**/Liq(1 nm)/Al(100 nm) |
| Device C | ITO/**EL-G**/**CGU**/**EL-R**/Liq(1 nm)/Al(100 nm) |
| Device D | ITO/**EL-G**/NPB(40 nm)/**EL-R**/Liq(1 nm)/Al(100 nm) |
| Device E | ITO/**EL-R**/Liq(1 nm)/Al(100 nm) |
| Device F | ITO/**EL-G**/Liq(1 nm)/Al(100 nm) |
| **CGU** | Liq(1 nm)/Al(1 nm)/NPB:F4-TCNQ(1%, 40 nm) |
| **EL-G** | NPB(40 nm)/$Alq_3$(60 nm) |
| **EL-R** | NPB(40 nm)/$Alq_3$:DCJTB(1%, 20 nm)/$Alq_3$(40 nm) |

as $FeCl_3$ [16] or strong electron acceptor as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) [17,18], while the n-doped layer is often prepared by an ETL doped with low-work-function metals (e.g., Li, Cs, and Mg) [5,19,20]. Kröger et al. suggested a working mechanism of such n–p junction. Charge generation process takes place at the interface of the junction, and electrons are tunneled from the filled highest occupied molecular orbital (HOMO) states of HTL to the lowest unoccupied molecular orbital (LUMO) states of ETL through a narrow depletion zone at the interface [21]. However, a proper interlayer (e.g., CuPc [22] and HAT-CN [5]) is often required to prevent chemical reaction or dopant inter-diffusion at the n-p junction to suppress high voltage rise during operation. In addition, both of two-step doping and interlayer increase the complexity of CGU's fabrication.

In this research, we propose a highly efficient, transparent and stable CGU based on a p-doped monolayer, which is easily formed by doping F4-TCNQ in [N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB). Holes and electrons are generated at the HOMO of NPB and LUMO of F4-TCNQ, respectively. Instead of conventional n-doped layer, an easy-fabricating ultrathin bilalyer Liq (1 nm)/Al (1 nm) acting as an electron extraction layer (EEL) is introduced to assist electron tunneling into the adjacent ETL at the anode side. The application of CGU Liq/Al/NPB:F4-TCNQ in tandem OLED results in more than twofold improvement in the current efficiency. Moreover, our CGU exhibits high optical transparency of over 90% in the main visible region, and good stability with operating voltage almost constant after 100 h at current density of 10 mA/cm$^2$. This work demonstrates that the p-doped monolayer combined with ultrathin bilayer is a promising candidate for tandem OLED.

## 2. Experimental

The OLEDs were fabricated by thermal evaporation under a base vacuum of about $10^{-6}$ torr. The active area defined by the overlap of the ITO anode and the Al cathode was 3 mm × 3 mm. Devices A to D are composed of a green EL unit (EL-G) at the anode side and a red EL unit (EL-R) at the cathode side with different intermediate layers (ILs) to connect them, namely Liq (1 nm)/Al (1 nm) (device A), NPB:F4-TCNQ(1%, 40 nm) (device B), Liq (1 nm)/Al (1 nm)/NPB:F4-TCNQ (1%, 40 nm) (device C) and none (device D). All of devices have the same total thicknesses so that the microcavity effects in these devices are the same. For comparison, two reference devices with single EL-G (device E) and EL-R (device F) are also prepared respectively. The EL-G consists of an HTL of NPB and an ETL of tris(8-hydroxyquinoline) Aluminum ($Alq_3$), while the EL-R consists of an HTL of NPB, a light-emitting layer (EML) of $Alq_3$ doped with 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7,-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) and an ETL of $Alq_3$. The detailed layer structures of the devices or units are shown in Table 1. Fig. 1 illustrates the schematic diagram of reference and tandem devices structures. Current density–voltage (*J*–*V*) and current efficiency–current density (CE–*J*) characteristics were measured with a computer controlled Keithley 2400 Source Meter and BM-7A Luminance Colorimeter. Capacitance–voltage (*C*–*V*) measurement was performed using a Keithley 4200 semiconductor characterization system.

## 3. Results and discussions

Fig. 2a shows *J*–*V* and CE–*J* characteristics of tandem OLEDs with different ILs (device A–D) and reference device E and device F. It can be seen that both device A with IL of Liq/Al and device D without IL require higher driving voltage than device B with IL of NPB:F4-TCNQ. However, the driving voltage of device C with Liq/Al/NPB:F4-TCNQ as IL decreases significantly at the same current density. Fig. 2b shows current efficiency–current density (CE–*J*) characteristics of tandem OLEDs with different ILs (device A–D) and reference device E and device F. The current efficiencies of device A–D and the reference device E and device F measured at current density of 20 mA/cm$^2$ are about 4.6, 2.6, 8.0, 3.0, 2.0, and 4.5 cd/A, respectively. The current efficiency of device C is more than the sum (6.5 cd/A) of those of device E and device F, indicating that IL of Liq/Al/NPB:F4-TCNQ functions well as CGU for high current efficiency tandem OLEDs.

Fig. 3 shows the EL spectra of OLEDs with different ILs (device A–D), together with reference device E and device F at a current density of 5 mA/cm$^2$. In device D without IL, holes from anode can transport through $Alq_3$ layer into the EL-R unit, and then be captured by the HOMO (5.28 eV) of DCJTB. On the other hand, electrons from the cathode can be trapped by DCJTB due to its relative low LUMO level (3.03 eV) compared to that of $Alq_3$ (2.85 eV). Therefore, the EL of device D is dominated by red emission at 615 nm, indicating the recombination zone is located in the EL-R unit. For device A with IL of the bilayer Liq/Al, the EL peak is at 520 nm corresponding to $Alq_3$ emission, inferring that the location of recombination zone is only in the EL-G unit at the anode side. This means that electrons reach the EL-G unit, while holes from anode are blocked by IL of the bilayer Liq/Al. In device B, the p-doped monolayer NPB:F4-TCNQ is used. Due to the close level between the HOMO (5.52 eV) of NPB and the LUMO (5.24 eV) of F4-TCNQ [23,24], electrons at the filled HOMO states of NPB transfer into the unoccupied LUMO states of F4-TCNQ, leading to the generation of holes and electrons at the NPB's HOMO