Interface Study of the Intermediate Connectors in Tandem Organic Devices

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Abstract

We have demonstrated several effective intermediate connectors in tandem organic light-emitting devices (OLEDs) using doped or nondoped organic p-n heterojunction. The influence of n-type or p-type organic layer in intermediate connectors on device performance has been investigated based on the understanding of interfacial electronic structures.

1. Introduction

In the last decade, there has been widespread research and commercial interest in organic light-emitting diodes (OLED), because they are useful for applications in next-generation flat panel displays and solid-state lighting. Research has amply revealed the existence of a tradeoff between the operation lifetime and driving current density for OLEDs. To achieve high brightness, an OLED must be operated at a relatively high current density, thus resulting in a reduced lifetime. To increase the luminous efficiency and lifetimes of OLEDs a tandem (or stacked) structure can be fabricated, where all of the individual electroluminescent (EL) units are electrically connected in series by inserting an intermediate connector between adjacent EL units [1-7].

The intermediate connector plays a critical role in the performance of tandem OLEDs. For a tandem OLED, the intermediate connector should facilitate effective electron injection and hole blocking into one of the connected EL units while performing the exact opposite role for the other connected emitting unit. Meanwhile, the intermediate connector must be highly transparent for light transmission, maintain low series resistance for a minimal electrical loss, as well as guarantee deposition compatibility and stability. Thus understanding the physical properties of the intermediate connector is not only important fundamentally, but also crucial to developing high-efficiency organic (opto)electronic devices with a tandem structure.

In this work, we have carried out systematic investigations on tandem OLEDs [8-11], and demonstrated several effective intermediate connectors for tandem OLEDs using doped or nondoped organic p-n heterojunction. By combining interface study and device fabrication, we investigate the influence of n-type or p-type organic layer in intermediate connectors on device performance and provide physical insights for exploring new structures as an effective intermediate connector with reduced drive voltage, improved voltage stability, and improved power efficiency for tandem OLEDs.

2. Experimental

The tandem OLEDs were fabricated onto cleaned and UV-ozone treated ITO-coated glass substrate (30Ω/□) with two individual EL units, each consisting of a hole-transporting layer (HTL) and an electron-transporting layer (ETL). The two EL units were separated by an intermediate connector with a variety of organic heterostructures. For comparison, standard devices with a single EL unit were also prepared. The organic and metal layers were thermally evaporated at a base pressure of 8×10^{-6} Torr. Deposition rates of different layers were monitored with a quartz oscillating crystal and controlled to be 1–2 Å/s for both organics and metals, while the dopant and host materials were co-evaporated with a rate ratio of 0.2 to 1 Å/s. A shadow mask was used to define the cathode and to make four 0.1 cm^2 devices on each substrate.

TABLE 1. OLED layer structures

Device or Units	Layer structures
A	ITO/EL1/Mg:Alq_3 (10 nm, 10 vol%)/m-MTDATA (20 nm)/EL2/Mg:Ag (200nm)
B	ITO/EL1/Alq_3 (10 nm)/F_4-TCNQ:m-MTDATA (20 nm, 5 vol%)/EL2/Mg:Ag (200nm)
C	ITO/EL1/ Mg:Alq_3 (10 nm, 10 vol%)/F_4-TCNQ:m-MTDATA (20 nm, 5 vol%)/EL2/Mg:Ag (200nm)
D	ITO/EL1/Mg:Ag (200nm)
EL1	NPB (60 nm)/Alq_3 (40 nm)
EL2	NPB (60 nm)/Alq_3 (40 nm)
E	ITO/EL3/Mg:Alq_3 (10 nm)/WO_3 (4 nm)/EL4/Ca (15 nm)/Ag (100 nm)
F	ITO/EL3/Yb:Alq_3 (10 nm)/WO_3 (4 nm)/EL4/Ca (15 nm)/Ag (100 nm)
G	ITO/EL3/Ca:Alq_3 (10 nm)/WO_3 (4 nm)/EL4/Ca (15 nm)/Ag (100 nm)
H	ITO/ EL4/Ca (15 nm)/Ag (100 nm)
EL3	NPB (70 nm)/Alq_3 (40 nm)
EL4	NPB (70 nm)/Alq_3 (50 nm)

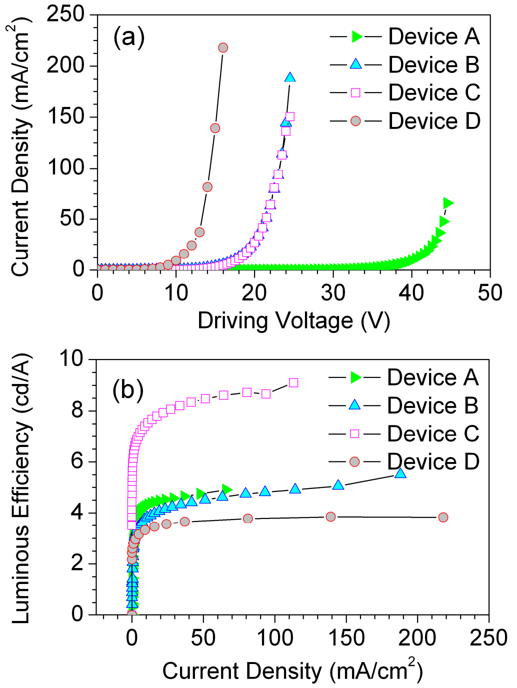

Fig. 1. (a) Current density as a function of the driving voltage, and (b) luminous efficiency versus current density for devices A–D.

The current density-voltage-luminance (*J–V–L*) characteristics and electroluminescence spectra were measured simultaneously with a programmable Keithley model 237 power source and a Photoresearch PR 650 spectrometer. The interface study was carried out in a VG ESCALAB 220i-XL photoelectron spectroscopy system, which consists of an analysis chamber interconnected to an evaporation chamber. Base pressures in the evaporation chamber and analysis chamber were 8×10^{-10} and 5×10^{-10} Torr, respectively. The ultraviolet photoelectron spectrum (UPS) measurements were performed by using an unfiltered He I (21.2 eV) gas discharge lamp with the sample biased at negative 4 V. The resolution of UPS measurements was 0.09 eV. All measurements were carried out in air at room temperature.

3. Results and discussion

In the early works, to achieve high brightness and high efficiency at low current density, tandem OLEDs were fabricated by stacking several individual EL units with the cathode and anode (e.g., Mg:Ag/ITO) as an intermediate connector [12]. The metal oxides have also been introduced in intermediate connectors, such as V_2O_5 [1], WO_3 [6], MoO_3 [7], and so on. However, using a metal or a metal oxide in an interconnecting layer invariably introduces fabrication complexity, due to the non-compatibility of the deposition methods of many kinds of metals and metal oxides with the organic layers. In contrast, organic–organic intermediate connectors can be formed using thermal evaporation methods with relatively low evaporation temperatures, and do not cause low optical transparency. Therefore, we report several organic p-n heterostructured intermediate connectors to produce high-efficiency tandem OLEDs. The detailed layer structures of OLEDs fabricated in this work are shown in Table 1.

3.1 Doped organic p-n heterostructure as the intermediate connector

We have investigated a bilayer intermediate connector of Mg-doped tris(8-hydrooxyquinoline) aluminum(III) (Alq_3) and tetrafluoro-tetracyanoquinodimethane (F_4-TCNQ)-doped 4,4',4"-tris{N,-(3-methylphenyl)-N-phenylamino}-triphenylamine (m-MTDATA) for application in tandem OLEDs. The *J-V* characteristics and luminous efficiency of three tandem OLEDs (Devices A-C as listed in Table 1) are shown in Fig. 1, together with that of a standard OLED having only one EL unit (e.g., Device D) for comparison. It is obvious that devices B and C perform similarly, while device A has little current flow until the driving voltage is above 35 V. It indicates that the current density of OLED with the utilization of F_4-TCNQ:m-MTDATA as the hole-injection contact was two orders of magnitude higher than that without the use of F_4-TCNQ, indicating the significance of F_4-TCNQ dopant in the intermediate connector. The luminous efficiency of device D, the reference device, is 3.5 cd/A, whereas those of devices A, B, and C are 4.5, 4.1, and 7.9 cd/A, respectively, at a current density of 20 mA/cm^2. The intermediate connector of device C led to a tandem OLED with a luminous efficiency twice that of a single-unit OLED. As the EL unit in devices A, B, and C is identical, it suggests that the intermediate connectors play a crucial role in determining the device performance of tandem OLEDs.

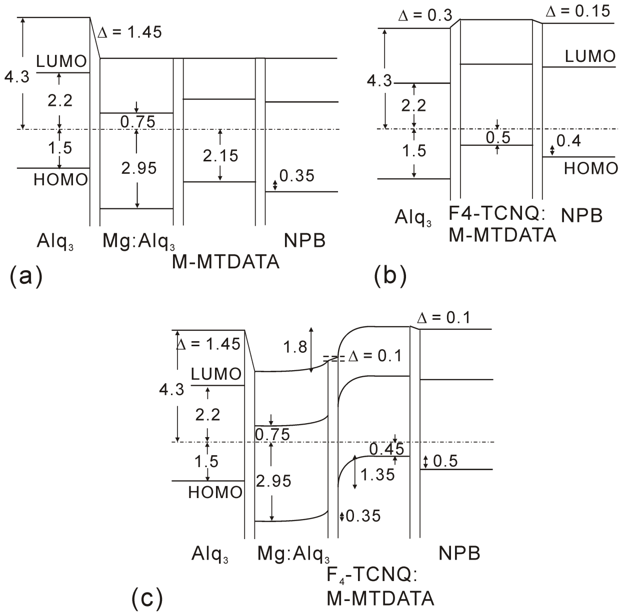

Fig. 2. Energy band diagrams for (a) Alq_3 /$Mg:Alq_3$/m-MTDATA/NPB, (b) Alq_3/F_4-TCNQ:m-MTDATA/NPB, and (c) Alq_3 /$Mg:Alq_3$ /F_4-TCNQ:m-MTDATA/NPB interfaces on UV-treated ITO substrates, respectively.

To understand the difference in luminous efficiency, we performed UPS experiments to investigate the interfacial electronic structures. Data are summarized as energy band diagram, shown in Fig. 2 for various intermediate connectors on UV-treated ITO substrates. The UPS measurements depict that the differences in device performance can be explained by the electronic structures of the intermediate connectors and the interface formation between the intermediate connectors and the neighboring EL units. It is demonstrated that controlled p-doping of hole-injection layer with F_4-TCNQ can substantially improve hole injection in conventional OLEDs with a single EL unit. The presence of both Mg and F_4-TCNQ dopants provides a better energy level matching, leading to the formation a bipolar heterojunction and thus effective charge spouting. Moreover, the insertion of $Mg:Alq_3$ between the Alq_3 and F_4-TCNQ:m-MTDATA, which helps to block the holes flowing from the ITO side simultaneously into the second EL unit and hence eliminate the leakage current. As a result, such an intermediate connector facilitates efficient carrier injection from the intermediate connector into the carrier-transporting layers [9,10].

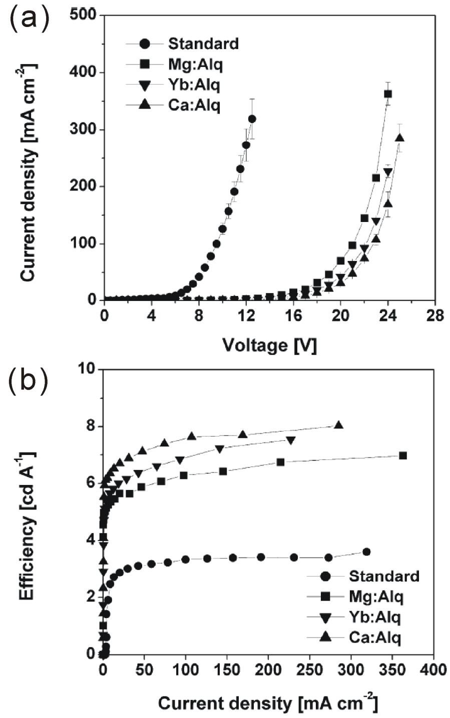

Fig. 3. (a) J–V and (b) luminous efficiency characteristics of tandem OLEDs with different metal-doped intermediate connectors.

3.2 Influence of the n-type layer on the intermediate connector

While the characteristics of tandem OLEDs using different intermediate connectors have been reported; performance of the intermediate connectors cannot be directly compared due to the differences in their individual device configurations and preparation processes. In this work, we also investigated the influence of n-type organic layers in intermediate connectors on the performance of tandem OLEDs [8]. Here, the n-type organic layers were prepared by doping different reactive metals (Yb, Ca, and Mg) into Alq_3 (devices E-G), while keeping the p-type layer (WO_3) of the intermediate connectors unchanged. Figure 2 depicts the current J–V characteristics and current efficiency for the devices with different metal dopants in the intermediate connectors. It is shown that all the tandem OLEDs show a doubled current efficiency, but require a higher driving voltage to achieve the same current density, as compared to the standard device (device H).

Contrary to common belief, device characteristics were found to be insensitive to metal work functions, as supported by the UPS results (see Fig. 4) that the LUMO of all metal-doped n-type layers studied here have similar energy levels. This suggests that the electron injection barriers from the intermediate connectors are not sensitive to the metal dopant used. On the other hand, it was found that performance of the n-type layers depends on their electrical conductivities which can be improved by using an electron-transporting host with higher electron mobility. This effect is further modulated by the optical transparency of constituent organic layers.

3.3 Non-doped organic p-n heterostructure as the intermediate connector

In addition, it is useful to replace the doped organic layer in the organic heterojunction intermediate connector by a nondoped organic layer to make tandem OLEDs with improved voltage stability, as well as to simplify the fabrication process. We explored the feasibility of replacing the doped organic layers by a fully non-doped organic system of copper hexadecafluorophthalocyanine ($F_{16}CuPc$)/copper phthalocyanine (CuPc) as an intermediate connector for deep-blue electrofluorescent tandem OLEDs [11]. The pure organic intermediate connector showed superior optical transparency (~100%), resulting in minimal microcavity effect in the devices.

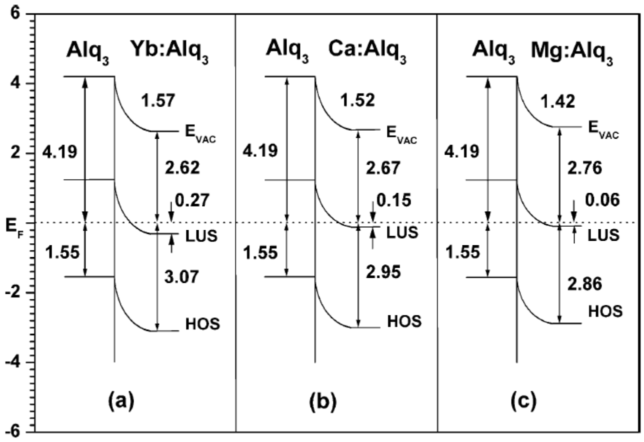

Fig. 4. Energy level diagrams for (a) Alq_3/Yb:Alq_3, (b) Alq_3/Ca:Alq_3, and (c) Alq_3/Mg:Alq_3 intermediate connectors, respectively.

4. Summary

We have investigated several effective intermediate connectors in tandem OLEDs using doped or nondoped organic p-n heterojunction. Electronic structures, including relevant electron energy levels, of the various intermediate connectors were studied by UPS to discuss their working mechanisms. It is revealed that p-type doped organic films with F_4-TCNQ can be used to replace the metal oxides as the p-type layer in the intermediate connector. By systematically varying the metal dopants for n-type organic layer in the intermediate connectors, we have identified the important factors affecting the performance of tandem OLEDs.

5. References

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