

# Influence of Exciton-Polaron Quenching Occurring at the Interface Mixing Zone on the Operational Lifetime of Solution-Processed OLED

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## ABSTRACT

*The serious driving voltage rise in hole only device in this work could be an evidence of negative effect of exciton-polaron quenching (EPQ) to cause device degradation. Strong deterioration of device lifetime was observed when the recombination zone coincides with the interface mixing zone, where higher degree of EPQ occurs. On the other hand, the device lifetime was improved by a factor of 8 as the recombination was confined away from interface mixing zone of full solution-processed device.*

## 1 INTRODUCTION

Organic light emitting diodes (OLEDs) are used extensively in mobile display, television, and lighting applications, and have received tremendous attention due to its superior image quality. However, the current manufacturing technology for color patterning has too much limitation to prepare large area or high resolution display. Thus, there has been lots of interests on solution-processed OLEDs because it may realize potentially low costs in manufacture of large-area display compared to vacuum-deposition ones. However, its short operational lifetime is a serious issue needed to be solved before commercialization. There are several important factors which may limit the operational lifetime of solution-processed devices including unavoidable interface mixing, carrier accumulation at the interface resulting in exciton – polaron quenching (EPQ), low film density, difficulty of electron transport materials processing, etc. The academic literature contains only few scientific studies of the lifetime of solution-processed OLED. Especially, in the case when the recombination zone occurs at the interface mixing region, the non-radiative charge recombination is accelerated resulting in higher driving voltage for a certain luminance.

One of the several methods for minimizing is reducing the exciton and polaron densities in the recombination zone. Higher electron mobility host will result in charge accumulation on the HTL side of EML, and vice versa. The high density of excitons can be generated where charge accumulation around the point of injection of the lowest mobility carrier. Furthermore, being considered as one of the main demerits of solution-processed OLEDs is the difficulty in forming well-defined multi-layer structure when more than one layer were spin-coated

sequentially, even cross-linkable HTL (x-HTL) was utilized, leading to an unavoidable interface mixing effect. If the charges pile-up at this mixed interface, a higher degree of EPQ could be generated and hence strong deterioration of device lifetime could occur.

In this study, we investigated the effect of EPQ which affects the operational lifetime of the solution processed OLEDs. Especially, we compared the operational stability of the devices with recombination zone formed at the interface between x-HTL/EML and/or EML/EBL. We first analyzed the the main cause of device failure by using hole only devices (HOD). In particular, in this study, we have identified which cases have the greatest effect on the stability of the device when only exciton and polaron are formed, and when exciton and polaron are formed simultaneously. Full devices were then fabricated with different recombination zones. The device lifetime significantly depends on the recombination zone where significantly different degrees of EPQ occurred.

## 2 EXPERIMENT

### 2.1 Material

We used a x-HTM supplied by Duksan Neolux, Co., Ltd<sup>23</sup> as a cross-linkable HTL material. GH (Green host) was utilized as host material in hole only devices and full devices, purchased from AlphaChem Co., Ltd. DIC-TRZ was also used as a host material and an exciton blocking layer (EBL). Ir(mppy)<sub>3</sub> was used as a phosphorescent green dopant for the EML, purchased from Lumtec. Molybdenum oxide (MoO<sub>3</sub>) (Sigma-Aldrich) as a material for the electron blocking layer in HODs, Aluminium (Al) as a cathode were purchased from commercial suppliers and used without any purification.

### 2.2 Device Fabrication

For device fabrication, PEDOT:PSS was spin-coated onto ITO glass and annealed at 150 °C for 20 min. Subsequently, the x-HTM was dissolved in toluene at 0.5 wt%, then spin-coated and cross-linked at 220 °C for 30 min. For the EML coating procedure, solutions of 1 wt% DIC-TRZ in chlorobenzene, 1 wt% GH in chlorobenzene and 0.5 wt% of green dopant Ir(mppy)<sub>3</sub> in chlorobenzene were utilized. We mixed the host materials with the green dopant in a 9:1 weight

ratio. Then, the mixed solutions were spin-coated (one step, 3000 rpm, 30 s) onto the x-HTL and dried at 100 °C for 15 min. DIC-TRZ as EBL, LG201 mixed with lithium quinolate (LiQ) (mixing ratio = 1:1) as an ETL, LiQ as an EIL, and Al as cathode were successively thermally deposited in a vacuum condition under  $10^{-7}$  Torr.

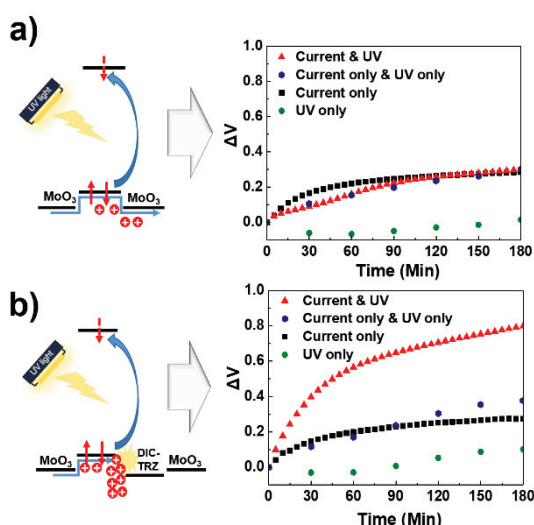
### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of Exciton Polaron Quenching on Device Stability

The charge accumulation near the interface accelerates the interaction between exciton and polaron, and hence the occurrence of EPQ. This EPQ not only gives rise to reduction of the internal quantum efficiency but also the degradation of operational lifetime. The mechanism of device deterioration due to EPQ was investigated by analyzing the rising in driving voltage  $\Delta V(t)$  needed to drive a current with density of  $20 \text{ mA cm}^{-2}$  when devices were exposed to the following condition: (1) UV irradiation only (the wavelength 365nm was chosen as to minimize the damage caused by UV absorption); (2) Current flow only ( $20 \text{ mA cm}^{-2}$ ); (3) Current flow and UV irradiation (365nm) simultaneously.

**HOD A:** ITO/MoO<sub>3</sub> (10nm)/GH:Ir(mppy)<sub>3</sub> (10%)/ MoO<sub>3</sub> (10nm)/Al (100nm)

**HOD B:** ITO/MoO<sub>3</sub> (10nm)/GH:Ir(mppy)<sub>3</sub> (10%)/ DIC-TRZ (5nm)/ MoO<sub>3</sub> (10nm)/Al (100nm)



**Fig. 1** The device degradation mechanism and changes in  $V_d$  value versus time at  $20 \text{ mA cm}^{-2}$  in a) **HOD A** (without DIC-TRZ layer) and b) **HOD B** (with DIC-TRZ layer)

Both devices were first subjected to UV irradiation for 3 hours resulting in a small increase in driving voltages which were 0.016V and 0.08V for **HOD A** and **HOD B**, respectively (Fig. 1). The increases in  $V_d$  were attributed to photo-degradation of ITO/organic interface leading to a gradual deterioration in charge injection across the interface<sup>[1]</sup>. The increases in  $V_d$  when only current flow exhibit almost the same behavior for devices

without and with DIC-TRZ which were 0.275V and 0.285, respectively. Particularly, when simultaneously exposing devices to both current flow and UV irradiation, a remarkable different phenomenon in  $\Delta V$  between **HOD B** (with DIC-TRZ) and **HOD A** (without DIC-TRZ) were observed. In **HOD A**, the increase in driving voltage was 0.299V which was not significant different from the case of current flow only ( $\Delta V=0.275\text{V}$ ). Meanwhile, in **HOD B**, the  $V_d$  dramatically increases and reaches  $\Delta V=0.8\text{V}$  after 3 hours. This fast increase is superior all other exposing conditions used in this device. Interestingly, this increase in  $V_d$  is also much higher than that of algebraic sum of  $\Delta V$  values in 2 individual cases of only current and only UV, which was  $\Delta V=0.37\text{V}$  as shown in Fig. 1b.

These significant differences suggest that when simultaneously exposing to both current flow and irradiation, some interaction between them occurs leading to degradation and hence much faster rising in  $V_d$ . This could be attributed to the interaction between charges and excitons and hence, quenching occurred in the device. In addition, the degradation of the dopant due to bonding dissociation should be considered. The exciton formed on GH molecule may be reductively quenched by electron transfer from nearby dopant molecule to form radical ion of GH and radical cation of dopant. These radical ion pairs may recombine to become neutral. However, there a certain probability that, before recombination, the weak bonds in the dopant molecules may undergo the dissociation<sup>[2]</sup>. The high energy polarons formed due to EPQ surpassed the bond dissociation energy of the bonds and increased the probability that they will be cleaved. The dissociation of weak bonds in dopant molecules probably lead to device degradation

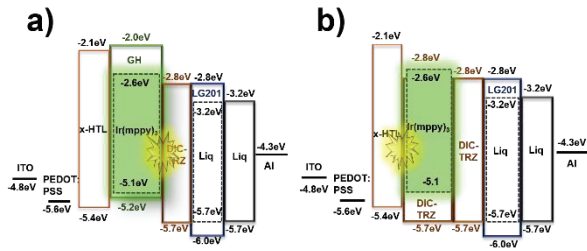
#### 3.2 Full device characteristics and lifetime with different recombination zones

As previously observed, if exciton is intensively generated where charge accumulation takes place, that is, when recombination occurs where charge accumulation occurs, the deterioration of the device occurs more seriously. So, we designed the following two devices.

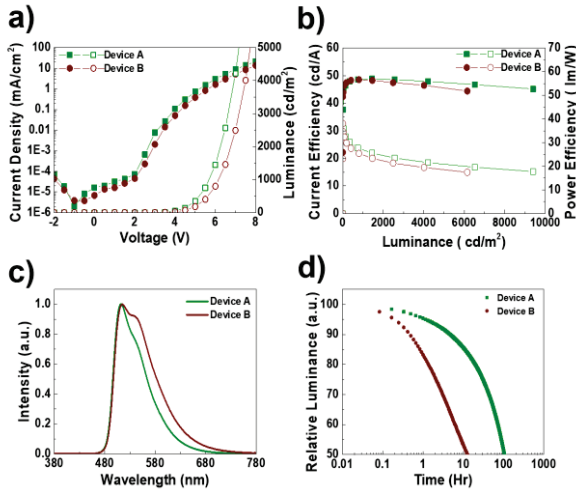
**Device A:** ITO//PEDOT:PSS (40nm)/ x-HTL(17nm)/ GH:Ir(mppy)<sub>3</sub>(10%,30nm)/ DIC-TRZ (5nm)/ LG201:LiQ (1:1)(45nm)/ LiQ (1nm)/Al (100nm)

**Device B:** ITO//PEDOT:PSS (40nm)/ x-HTL(17nm)/ DIC-TRZ:Ir(mppy)<sub>3</sub>(10%,30nm)/ DIC-TRZ (5nm)/ LG201:LiQ (1:1)(45nm)/ LiQ (1nm)/Al (100nm)

Although x-HTM is used, some uncrosslinked HTM is mixed with EML, so the hole injection is excessive, so the interface between x-HTM/EML is assumed to be rich in polaron in both devices. On the other hand, **Device A** was designed so that the recombination zone is biased to the right interface of the EML, and **Device B** is designed so that the recombination zone is biased to the interface that is rich in polaron.



**Fig. 2** Energy band diagram of devices a) with GH utilized as host material (**Device A**) and b) with DIC-TRZ was used as host material (**Device B**)



**Fig. 3** a) Current density-voltage-luminance, b) Current and power efficiency-luminance, c) Normalized electroluminescence spectra of devices, and d) Half-lifetime for an initial luminance at 1000 cd m<sup>-2</sup> of investigated devices.

Fig. 2 shows the energy band diagram of full devices. Meanwhile, a thin layer of DIC-TRZ was inserted between EML and ETL in the two devices to serve as exciton blocking layer (EBL).

Fig. 3 and Table 1 summarize the performances of those devices. The current density (J) - voltage (V) - luminance (L) characteristics were shown in Fig. 3a. The operating voltages ( $V_{on}$ ) at which the luminance was 1000 cd m<sup>-2</sup> were 5.7V and 6.2V for **Device A** and **Device B**, respectively. **Device A** also exhibits slightly higher current density than the other. The current and power efficiency as a function of luminance were shown in Fig. 3b. At a constant luminance of 1000 cd m<sup>-2</sup>, the current and power efficiency were 48.4 cd A<sup>-1</sup> and 26.8 lmW<sup>-1</sup> for **Device A**, 48.8 cd A<sup>-1</sup> and 24.9 lmW<sup>-1</sup> for **Device B**, respectively. The maximum current and power efficiencies were 48.6 cd A<sup>-1</sup> and 38.0 lmW<sup>-1</sup> for **Device A**, 48.9 cd A<sup>-1</sup> and 35.8 lmW<sup>-1</sup> for **Device B**, respectively. These values were not significantly different between the two devices. **Device A** has much narrower electroluminescence spectrum as compared to **Device B** (Fig. 3c). Surprisingly, the half-lifetime for an initial luminance of 1000 cd m<sup>-2</sup> of **Device A** was 105 hours surpassing

that of **Device B** which was only 12.7 hours (Fig. 3d). The remarkable difference in half-lifetime could be attributed to shipment of recombination zone to the x-HTM/EML interface where extensive interface mixing exists as aforementioned.

**Table 1**

Summary of device characteristics of the full devices measured at 1000 cd m<sup>-2</sup>

	Operating Voltage (V)	CE (cd A <sup>-1</sup> )	PE (lm W <sup>-1</sup> )	Color (CIE 1931)	FWHM (nm)	T <sub>50</sub> (hr)
Device A	5.7	48.4	26.8	(0.299, 0.625)	68.0	105
Device B	6.2	48.8	24.9	(0.345, 0.600)	86.0	12.7

#### 4 CONCLUSION

The lifetime of full device where recombination zone occurred in the EBL-side of EML shown the much higher stability which was 8 times longer in lifetime as compared to device having recombination zone coincided with interface mixing zone. It is clear in this work that EPQ can be accelerated by interface mixing resulting in much shorter lifetime which is one of the main demerits of solution-processed devices. The interface mixing between HTL and EML may result in inflow in excessive polaron to be the source of unwated exciton-polaron quenching interaction which accelerates the device degradation.

#### REFERENCES

- [1] Q. Wang, G. Williams, H. Aziz, "Photo-degradation of the Indium Tin Oxide (ITO)/Organic Interface in Organic Optoelectronic Devices and a new Outlook on the Role of ITO Surface Treatments and Interfacial Layers in improving Device Stability," *Org. Electronics*, Vol. 13, pp. 2075-2082 (2012).
- [2] S. Kim, H. J. Bae, S. Park, W. Kim, J. Kim, J. S. Kim, Y. Jung, S. Sul, S.G. Ihn, C. Noh, S. Kim & Y. You, "Degradation of blue-phosphorescent organic light emitting devices involves exciton-induced generation of polaron pair within emitting layers," *Nat. Communications* 9, 1211 (2018).

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