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# Efficiency improvement of organic light-emitting diodes using 8-hydroxy-quinolinato lithium as an electron injection layer

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## Abstract

Organic light-emitting diodes (OLEDs) using tris-(8-hydroxy-quinolinato) aluminum ($Alq_3$) as an emitter, 8-hydroxy-quinolinato lithium (Liq) as an electron injection layer, were prepared. Experimental results show that the efficiency of device with Liq is three times higher than that without Liq. The device using Liq as an injection layer is less sensitive in efficiency to the Liq thickness than that using LiF. In addition to the $Alq_3$ based devices, Liq is also very effective as an electron injection layer for 4,4′-bis(2,2-diphenylvinyl)-1,1′-biphenyl based blue OLED and poly (2-methoxy,5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene) based orange polymer OLED.

*Keywords:* Organic light-emitting diode; Efficiency; Improvement; 8-Hydroxy-quinolinato lithium

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## 1. Introduction

Tang and Van Slyke [1] reported double layer organic light-emitting diodes (OLEDs) with high luminance and low operating voltage. It is one of the key factors to enhance efficiency and stability of the OLED for the application. Much effort has been made to improve OLED performance by modifying its structure to achieve an effective and balanced injection of the carriers. The carrier injections from electrodes are dependent on the energy barrier heights at the interfaces between electrodes and organic layers [2,3]. In most OLEDs, the barrier height for holes is relatively lower than that for electrons, and the mobility of holes in an organic layer is larger by orders of magnitude than that of electrons; therefore, the injection and transportation of holes are more easily than that of electrons. To achieve a balanced injection of carriers, it is common to use low-work-function metals such as Li, Ca, Mg, etc., to enhance electron injection into organic materials. However, such metals are not stable in air and need to be protected in the device processing, and sometimes may react with and diffuse into organic material and deteriorate the device [4].

Many studies [5–7] showed that a thin insulating layer such as LiF, CsF, $CaF_2$, $BaF_2$ MgO, etc., deposited between an organic layer and Al cathode can drastically enhance the electron injection and the electroluminescent (EL) efficiency. The drawbacks for processing these insulating materials are that they need quite high temperature for evaporation and accurate control of thickness usually less than 2 nm. Endo et al. [8] reported that an introduction of thin lithium quinolate complex layer such as 8-hydroxy-quinolinato lithium (Liq) between (tris-(8-hydroxy-quinolinato) aluminum) ($Alq_3$) and Al can improve electron injection. Schmitz et al. [9] demonstrated that the improve-

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ment by using Liq is similar to that by using LiF. Liu et al. [10] once reported that the performance tolerance of Liq device to the injection layer thickness is better than that of the LiF device. All these bilayer cathodes are environmentally stable relative to the reactive metal cathodes and are considered to be compatible with mass production processing. However, the mechanism behind this enhancement of electron injection is not fully understood. In addition, the application of Liq to other emissive materials has nearly been reported and it is worthy of study.

In this article, we use Liq as an electron injection layer for several emissive materials, and investigate the effect of thin Liq layer on the injection of electron. A dipole model is proposed to interpret the mechanism.

## 2. Experimental details

Indium tin oxide (ITO) with thickness of 60 nm and sheet resistance of about 50 Ω/sq was used as the substrate for OLEDs. ITO substrates were cleaned by sonication successively in a detergent solution, acetone and deionized water, and followed by air-plasma treatment. The device structure is ITO/TPD (*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′biphenyl-4,4′diamine)/$Alq_3$/Liq/Al. For comparison, control devices with the structures of ITO/TPD/$Alq_3$/LiF/Al and ITO/TPD/$Alq_3$/Al were also prepared. TPD and $Alq_3$ were used as the hole transport and emissive layer, respectively. Thicknesses of TPD and $Alq_3$ were both 50 nm if not specifically indicated elsewhere. The thickness of either Liq or LiF was varied in the range 0.3–5 nm. In the further experiment, devices with structures of ITO/TPD/DPVBi (4,4′-bis (2,2-diphenylvinyl)-1,1′-biphenyl, 50 nm)/cathode and ITO/PEDOT (poly(ethylene dioxythiophene), 50 nm)/MEH-PPV (poly(2-methoxy,5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene), 120 nm)/cathode were also made to test the effect of Liq and LiF on the performance of DPVBi and MEH-PPV based devices, here cathodes were Liq (0.5 nm)/Al, LiF (0.5 nm)/Al and Al, respectively.

Al cathode and organic materials except PEDOT and MEH-PPV were sublimed on the substrates by conventional resistive heating in the same vacuum chamber. The layer thicknesses were controlled by using a quartz crystal thickness monitor. The two polymer layers were deposited by spin casting, and the thicknesses were measured by a surface profiler (Tencor Alpha-step 500). The pressure of the chamber was below $1\times10^{-3}$ Pa. The electrical characteristics of the OLEDs were measured with a Keithley 2400 source meter and the radiance with a Libero PR650 spectra scan.

## 3. Results and discussion

Current density–voltage characteristics of $Alq_3$ based OLEDs with Liq (0.5 nm)/Al, LiF (0.5 nm)/Al and Al are presented in Fig. 1. The inset shows the luminance vs. current density characteristics. From the figure, it can be seen that the performances of the devices using either Liq or LiF as an injection layer are nearly identical; but they are far better than the device with an Al only cathode. For example, at a current density of 20 mA/cm$^2$, the devices using Liq/Al, LiF/Al and Al cathodes require driving voltages of 7.1, 7.8 and 14 V, and have luminance of 955, 926 and 314 cd/m$^2$, respectively. From the inset in Fig. 1, the luminance is approximately proportional to the injected current in the low current density region (2–200 mA/cm$^2$) and the slopes of the curves are the EL efficiencies. The efficiencies of the three devices are 4.8, 4.6 and 1.6 cd/A, respectively. It is also seen that the luminance of the three devices does not increase as quickly as the corresponding current density. This means that the EL efficiency decreases at higher voltages, and it may be attributed to the field-induced luminescence quenching [11].

As the thickness of Liq or LiF layer increases, the current density–voltage curves shift to higher voltage range and the efficiencies are lowered in both cases. For example, when the thickness of Liq or LiF increases to 2.5 nm from 0.5 nm, the operating voltages of Liq/Al and LiF/Al devices at 20 mA/cm$^2$ rise to 10.9 and 11.0 V from 7.1 and 7.8 V, and the efficiencies drop to 3.5 and 1.1 cd/A from 4.8 and 4.6 cd/A, respectively. These tendencies of dependence of the EL efficiency on the thickness of injection layer in the two devices are similar; but the variation of EL efficiency of Liq/Al device vs. thickness of injection layer is smaller than that of LiF/Al device. Fig. 2 shows the variations of EL efficiencies at a current density of 20 mA/cm$^2$ for Liq/Al and LiF/Al devices with different thicknesses of Liq and LiF. When the thickness of Liq or LiF is further increased to 5 nm, the EL efficiency of Liq/Al device drop to 2.0 cd/A (still better than that of Al only device), and that of LiF/Al device is already below 0.05 cd/A (more inferior to that of Al only device) and the device is extremely unstable. This

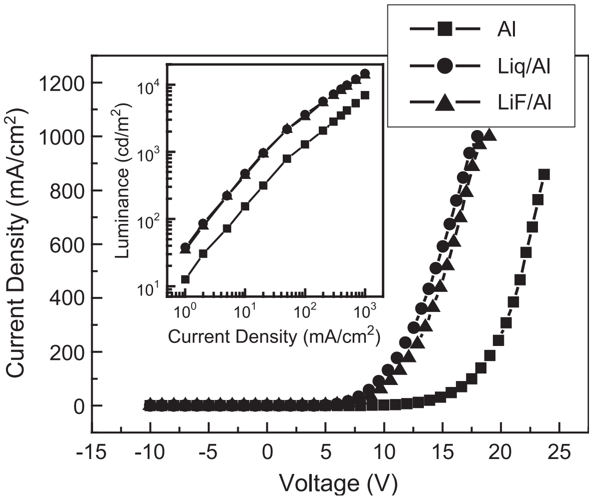


Fig. 1. Current density–voltage characteristics of TPD/$Alq_3$ devices with Liq (0.5 nm)/Al, LiF (0.5 nm)/Al and Al cathodes, respectively. The inset shows the luminance vs. current density characteristics.

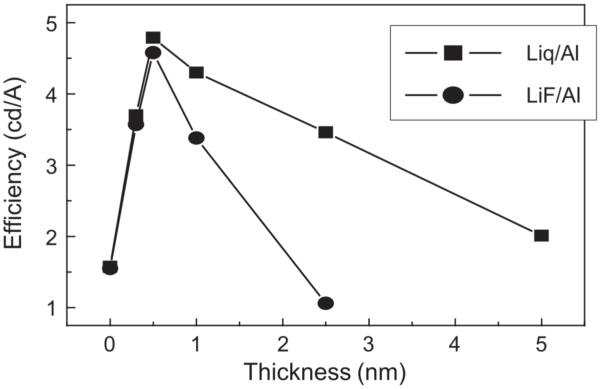


Fig. 2. Variations of EL efficiencies at current density of 20 mA/cm$^2$ for TPD/Alq$_3$/Liq/Al and TPD/Alq$_3$/LiF/Al devices with different thicknesses of Liq and LiF, respectively.

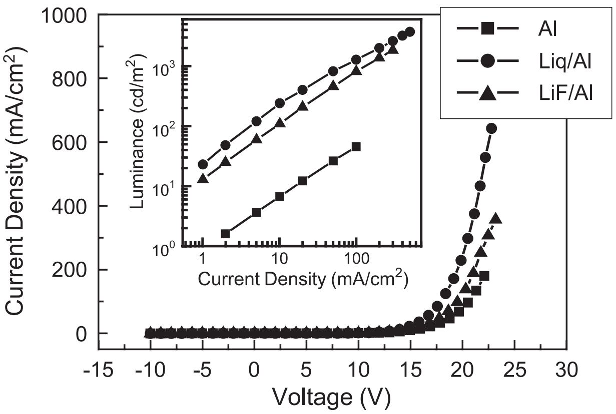
means that the device performance by using Liq as an injection layer is less sensitive to Liq thickness. This property of Liq would be very important in the mass production. The difference may be attributed to the fact that Liq is an organic semiconductor [9] and LiF an insulator.

In order to verify whether Liq is suitable to apply to other organic/metal interfaces, EL devices with structures, ITO/TPD/DPVBi/cathode and ITO/PEDOT/MEH-PPV/cathode, were prepared, where the cathodes are Liq/Al, LiF/Al and Al, respectively. Current density–voltage characteristics of DPVBi and MEH-PPV based EL devices with Liq (0.5 nm)/Al, LiF (0.5 nm)/Al and Al only are shown in Fig. 3a and b, respectively. The insets show the luminance vs. current density characteristics of the corresponding devices. It is found that both Liq and LiF are effective on enhancing the electron injection in both kinds of devices. At a current density of 20 mA/cm$^2$, the driving voltages of DPVBi based devices with Liq/Al, LiF/Al and Al cathodes are 14.8, 15.9 and 16.8 V, respectively, the luminance of the three devices are 416, 208 and 12.2 cd/m$^2$ (corresponding efficiencies are 2.1, 1.0 and 0.06 cd/A), respectively. These values of MEH-PPV based devices are 11.0, 12.0, 13.1 V, and 108, 20.7, 6.9 cd/m$^2$ (corresponding efficiencies are 0.54, 0.10 and 0.035 cd/A), respectively. In other words, voltage drops of 2.0 and 1.0 V, efficiency improvements by factors of about 35 and 17 for driving DPVBi devices at 20 mA/cm$^2$ are obtained by inserting thin layer of Liq and LiF between DPVBi and Al, respectively. In MEH-PPV based devices, corresponding voltage drops are 2.1 and 1.0 V, factors of efficiency improvement are about 15 and 3, respectively. It is obviously that using Liq as an electron injection layer is more efficient than LiF in the enhancement of the EL efficiency for TPD/DPVBi and PEDOT/MEH-PPV devices.

From the obtained experimental results, it can be seen that the enhancements of device performance are very different in the three kinds of OLEDs. They strongly depend on the kinds of organic materials and device structures. Comparing Liq (0.5 nm) with LiF (0.5 nm), it can be found that the performance enhancements of Alq$_3$ based device are similar, but in the latter two cases, LiF is inferior to Liq. This difference could not be explained from the energy level of three kinds of organic materials. We guess that the compatibility of Liq is better than that of LiF in DPVBi and MEH-PPV based devices.

The improvement of OLED performance by inserting ultrathin film of insulators such as LiF, CsF, CaF$_2$, BaF$_2$, etc., between Alq$_3$/Al interface were usually attributed to tunneling injection. However, when GeO$_2$ [5] and CeF$_3$ [7], which are insulators, were inserted between Alq$_3$/Al interface, the device performance were deteriorated. This implies that tunneling model cannot completely explain the experimental results. In the present case, Liq is an organic semiconductor and LiF an insulator. Considering this fact, when Liq is used as an injection layer in Alq$_3$ based devices, the enhancement of the electron injection is very similar to that obtained by using LiF. The tunneling model should predict a strong dependence of the electron injection on the height of tunneling barrier and thus the kind of the insulating materials. The fact that electronically different materials both lead to enhanced electron injection (in the Alq$_3$ based devices, the enhancement of device performance

(a) DPVBi based devices



(b) MEH-PPV based devices

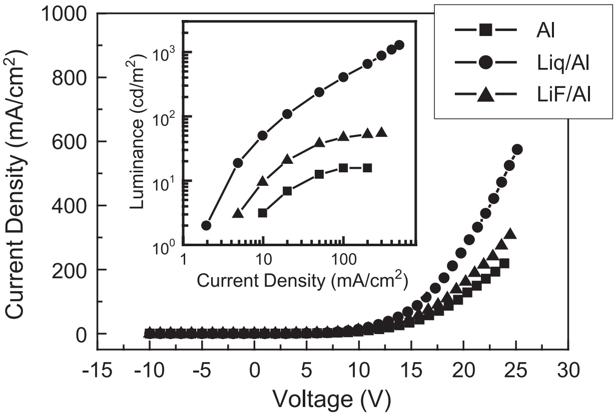


Fig. 3. Current density–voltage characteristics of DPVBi (a) and MEH-PPV (b) devices with Liq (0.5 nm)/Al, LiF (0.5 nm)/Al and Al cathodes, respectively. The insets show the luminance vs. current density characteristics.

is nearly identical) reveals that it is not reasonable to use tunneling model to explain the experimental results.

Another mechanism of ion dissociation and doping was once proposed to interpret the improvement of electron injection by using metal fluorides [12,13]. However, still some experimental results in the literatures [5,7] indicate that no evidence of dissociation of these metal fluorides was observed. In case of Liq, sufficient evidence of dissociation has not been reported.

Mori et al. [14] studied electronic structure of $Alq_3$/LiF/Al interface by ultraviolet photoelectron spectroscope and got a result that the barrier height for electron injection from Al to $Alq_3$ was reduced to 0.1 eV by the thin LiF layer. Hung et al. [5] measured the photoelectron emission and found that the energy bands of $Alq_3$ was bent downward by more than 1 eV when $Alq_3$ surface is in contact with LiF, thus lowering the electronic barrier height of $Alq_3$/Al interface. Their results are nearly the same, but still the underlying mechanism is not clear. It should be noted that in the formation of Liq molecule, the electron transfers from Li atom to quinolate ligand forming a polar Liq molecule, which is similar to metal halide. Thus Liq, LiF, CsF, $CaF_2$, $BaF_2$, MgO, etc., are all the molecules with strong polarity. Introducing ultrathin layer of these polar molecules may generate a dipole layer, which decreases the surface potential of the aluminum, thus lowering the electronic barrier height for electron injection. The dipole model was initially introduced by Campbell et al. [15] to explain the improvement of carrier injection in OLED and was suggested by several authors [5,7,16]. The dipole model may be used to explain the lowering of the effective barrier for electron injection by using Liq and metal fluorides. This saying needs further experimental confirmation.

## 4. Conclusions

In summary, in the devices with a structure of ITO/TPD/$Alq_3$/cathode, the efficiencies of the EL devices with Liq/Al and LiF/Al as cathodes are very similar, and far better than that with Al only cathode. The performance of the device with a Liq/Al cathode is less sensitive to the injection layer thickness than that of the device with a LiF/Al cathode. It would be very important in the mass production. Liq is also very effective to be used as an electron injection layer for DPVBi based blue OLED and MEH-PPV based orange polymer OLED. These results may be explained by the dipole model at the organic/metal interface.

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