Enhanced properties of organic electroluminescent devices with cesium chloride ultra-thin layer

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ABSTRACT

The effect of various positions and thicknesses of cesium chloride (CsCl) layer in organic light-emitting diodes is investigated. The basic device configuration is indium–tin–oxide (ITO)/N,N'-bis-(1-naphthl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB)/tris (8-hydroxyquinoline) aluminum (Alq_3)/aluminum (Al). The following results are demonstrated. When the CsCl layer is placed at the Alq_3/Al interface and closer to the Al cathode inside Alq_3 layer, the effective barrier to electron injection is reduced due to the reaction between Cs and Al. As a result, the injection of electrons and holes is more balanced and the efficiency is enhanced from 1.83 to 3.49 cd/A. And as an electron injection layer, CsCl can be comparable with lithium fluoride (LiF). If the distance of the CsCl layer is more than 20 nm from Alq_3/Al interface inside Alq_3 layer, the luminance and efficiency are enhanced but the injection is not increased, which is attributed to trap sites induced by the CsCl layer. The decrease of luminance and efficiency is observed when the CsCl layer is located at the NPB/Alq_3 interface. The reason is exciton quenching due to charge transfer from metal Cs to organic material Alq_3. The CsCl layer inside NPB layer plays a role of hole blocking. More balanced injection of carriers is expected. Subsequently, both luminance and efficiency are enhanced by 34% and 60%, respectively. When the cathode of lithium fluoride (LiF)/Al is used, the device efficiency is also improved from 4.0 to 5.0 cd/A by inserting the CsCl layer inside NPB layer. However, the improvement is not observed for the device with the CsCl layer inserted inside Alq_3 layer in LiF/Al-OLED.

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1. Introduction

In the last decade, organic light-emitting diodes (OLEDs) have been extensively investigated as the potential next generation technology for flat-panel display [1] and solid-state lighting [2,3]. The interest in this technology has been triggered due to the reports of new breakthroughs in device efficiencies, lifetimes, and achievable colors, including white [4].

To improve the device performance, it is desirable that the number of holes and electrons is in perfect balance in OLEDs. In a typical OLED, the mobility of holes in the hole transporting layer (HTL) is a few orders of magnitude higher than that of electrons in the electron transporting layer (ETL) [5–7]. Therefore, the carriers are unbalanced in the emissive region, which decreases the device efficiency. Enhancing electron-injection into the ETL or reducing the number of hole in the HTL can help to improve the electron–hole balance in the OLEDs. For physicists, the balance of carriers

is commonly improved by electrode modification. The modification of the anode [8–11] is capable of tuning hole injection (e.g. blocking holes at the HTL side) so that proper charge balance can be achieved. Consequently, device's efficiency is increased. On the other hand, cathode modification, which can improve minority carrier (electron) injection, is another of commonly used approaches. Many chemical stable alkaline metal compounds have been selected to improve the electron injection performance, inserted between Al cathode and the ETL [12–14] or doped in the ETL [15–17].

Additionally, the device performance has also been improved by inserting alkaline metal compounds inside HTL [18] or ETL. A study by Han et al. [19] showed that a 0.3-nm-thick LiF layer inside tris (8-hydroxyquinoline) aluminum (Alq_3, ETL) can improve the electroluminescent (EL) efficiency.

In previous works [20–22], we reported the efficiency and EL intensity improvements of OLEDs with potassium chloride (KCl), rubidium chloride (RbCl) or cesium chloride (CsCl) inserted inside Alq_3 layer. In this work, we carried out systematic studies on the effect of CsCl in OLEDs. With the optimization of CsCl thickness at the Alq_3/Al interface, electron injection is improved with results of enhancements of luminance and efficiency and can be compared

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with that of OLED with LiF at Alq_3/Al interface. What is more, both efficiency and luminance of OLEDs are improved by inserting CsCl layer inside Alq_3 and NPB layers. However, the device performance is deteriorated if the CsCl is located at NPB/Alq_3 interface.

2. Experiment

For the device fabrication, indium tin oxide (ITO) substrates (20 Ω/square) were cleaned using a routine procedure included sonication in detergent, de-ionized water, acetone and alcohol, and finally irradiated in an UV-ozone chamber for 10 min.

NPB was used as a hole transporting layer (HTL), and Alq_3 was used as a bi-functional (electron transport and emissive layer, ETL&EML) layer. The molecular structures of the materials used in the experiment are referred to Ref. [23]. The procedure of device fabrication was detailed described in our previous work [20].

Four groups of devices (Groups A–D) were fabricated in the experiment.

Group A: ITO/NPB(40 nm)/Alq_3(60 nm)/CsCl(0.0, 0.3, 0.5, 0.7, 1.0 and 1.5 nm)/Al, labeled as devices A0–A5, respectively.
Group B: ITO/NPB(40 nm)/Alq_3(60 − x nm)/CsCl(0.5 nm)/Alq_3 (x nm)/Al, where x = 10, 20, 30, 40, 50 and 60, named as B1–B6, respectively, and ITO/NPB(40 nm)/Alq_3(60 nm)/Al (device B0) for reference.
Group C: ITO/NPB(40 − y nm)/CsCl(0.5 nm)/NPB(y nm)/Alq_3(60 nm)/Al, where y = 10, 20 and 30, labeled as devices C1–C3, respectively, and ITO/NPB(40 nm)/Alq_3(60 nm)/Al (device C0) for reference.

Finally, there are four types of devices in Group D:

Device D1: ITO/NPB(40 nm)/Alq_3(60 nm)/CsCl(0.5 nm)/Al.
Device D2: ITO/NPB(40 nm)/Alq_3(60 nm)/LiF(0.5 nm)/Al.
Device D3: ITO/NPB(20 nm)/CsCl(0.5 nm)/NPB(20 nm)/Alq_3(60 nm)/LiF(0.5 nm)/Al.
Device D4: ITO/NPB(40 nm)/Alq_3(30 nm)/CsCl(0.5 nm)/Alq_3(30 nm)/LiF(0.5 nm)/Al.

The structures and labels of all devices are shown in Table 1.

The overlap between ITO and Al electrodes was 9 mm^2 as the emissive size of devices. Current–voltage–luminance characteristics were recorded by using a Keithley source measurement unit (Keithley 2410) with a silicon photodiode (Newport Optical Power Meter Model 1830-C) calibrated by PR-650 spectrometer. The EL spectra were measured using a charge-coupled device (CCD) spectrometer. All the measurements were carried out under ambient atmosphere at room temperature.

3. Results and discussion

The first section of this part will be described by CsCl as an electron injection layer (EIL) with various thicknesses. In the second and third section, the attention will be directed to the characteristics of devices with a CsCl layer inserted inside Alq_3 and NPB layers, respectively. Finally, the electron injection property of LiF/Al and CsCl/Al is compared and the effect of LiF/Al cathode on the performance of devices with a CsCl layer inside organic layer will be discussed.

3.1. CsCl as an electron injection layer

In this section, we describe the effect of the deposition of a thin layer of CsCl between Alq_3 and the Al cathode [22]. In order to investigate the effect of the thickness of CsCl layer on the device performance, the devices with different CsCl layer thicknesses (Group A: ITO/NPB(40 nm)/Alq_3(60 nm)/CsCl(0.0, 0.3, 0.5, 0.7, 1.0 and 1.5 nm)/Al) were prepared.

Table 2 illustrates the properties of devices with various CsCl thicknesses, ranging from 0.3 to 1.5 nm. It can be seen from Table 2 that even for the device with a thickness of only 0.3 nm of CsCl (device A1), the current density and luminance increase dramatically compared to the reference device without any CsCl (device A0). The current densities for the devices with a CsCl layer are more or less identical under all forward biases. For instance, at a bias of 10 V, the current densities are 111.9, 114.0, 124.7, 114.0 and 107.7 mA/cm^2 for devices A1–A5, respectively. The highest current density of 124.7 mA/cm^2 is observed for the device with 0.7 nm CsCl layer (device A3). This device reaches a maximum luminance of 20,944 cd/m^2, which is very close to what is observed from the device A2 with 0.5 nm CsCl layer (20,990 cd/m^2).

The improved performances can be ascribed to the inserted CsCl layer. The reaction between Cs and Al can be considered to be a heavily doped n-type semiconductor with an intrinsically low work function [24], which reduces the work function of the cathode. Consequently, the barrier for electron injection is reduced and the number of electrons is increased in the emissive region. The charge carrier balance in the OLED is improved and leads therefore to a superior performance (e.g. efficiency, luminance). What is more, the improved properties of OLEDs can be attributed that the holes leakage to the cathode are blocked by CsCl due to its deep HOMO (the highest occupied molecular orbital) of 8.6 eV [25].

The current efficiency and luminous efficiency increase significantly from the device A0 (reference device) to the device A1 (0.3 nm CsCl), and they reach maximums of 3.49 cd/A and 2.40 lm/W for the device A2 (0.5 nm CsCl), respectively. After that they decrease with the increase of CsCl thickness. The results indicate that the optimum thickness of CsCl as an electron injection

Table 1
The structures and labels of the OLEDs in the experiment. x and y are the distance of cesium chloride (CsCl) layer away from the Al cathode and the NPB/Alq_3 interface, respectively.

Groups	Devices					
Group A	A0 (w = 0)	A1 (w = 0.3)	A2 (w = 0.5)	A3 (w = 0.7)	A4 (w = 1.0)	A5 (w = 1.5)
	ITO/NPB(40 nm)/Alq_3(60 nm)/CsCl(w nm)/Al					
Group B	B1 (x = 10)	B2 (x = 20)	B3 (x = 30)	B4 (x = 40)	B5 (x = 50)	B6 (x = 60)
	ITO/NPB(40 nm)/Alq_3(60 − x nm)/CsCl(0.5 nm)/Alq_3(x nm)/Al					
Group C	C1 (y = 10)		C2 (y = 20)		C3 (y = 30)	
	ITO/NPB(40 − y nm)/CsCl(0.5 nm)/NPB(y nm)/Alq_3(60 nm)/Al					
Group D	D1	D2	D3	D4		
	ITO/NPB(40 nm)/ Alq_3(60 nm)/ CsCl(0.5 nm)/Al	ITO/NPB(40 nm)/ Alq_3(60 nm)/LiF (0.5 nm)/Al	ITO/NPB(20 nm)/CsCl(0.5 nm)/ NPB(20 nm)/Alq_3(60 nm)/ LiF(0.5 nm)/Al	ITO/NPB(40 nm)/Alq_3(30 nm)/ CsCl(0.5 nm)/Alq_3(30 nm)/ LiF(0.5 nm)/Al		