# The doping effect of cesium-based compounds on carrier transport and operational stability in organic light-emitting diodes

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## ARTICLE INFO

## ABSTRACT

The doping effect of cesium compounds (i.e., $Cs_2CO_3$, $CsN_3$ and CsF) doped electron injection layer (EIL) on charge transport properties and operational stability of organic light-emitting diodes (OLEDs) was systematically investigated in this work. It has been found that device characteristics and lifetime are highly dependent on the doping constituent materials. The doping of cesium compounds in EIL can improve the charge injection and transport of OLEDs, due to the increase in conductivity and reduction in electron injection barrier. Apart from the difference in electrical characteristics, the operational stability of OLEDs is strongly influenced by the doping mechanism of different cesium compounds in the EILs. The OLED device using $Cs_2CO_3$ as the n-type dopant for the EIL shows a superiority in both electrical property and operational lifetime.

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## 1. Introduction

Organic light-emitting diodes (OLEDs) have become one of the mainstream candidates for realizing the high-quality information flat displays. To obtain highly efficient and low-voltage OLEDs, optimization of charge injection and carrier transport is critically important towards the improvement of device performance [1,2]. Significant effort has been devoted in recent years to improving the carrier injection from electrodes to organic transporting layers, and to overcoming the limitations of low bulk conductivity using a variety of different materials processing strategies [3–7]. A widely used method for improving electron injection and transport is to employ low-work-func-

tion metals, either as individual layer in contact with cathode or as n-type conductive dopants in the organic electron-injection layers (EILs), which can help to reduce the injection barrier at the electrode/organic interface and provide excellent electron injection from cathode to organic layer [7–10]. However, the direct adoption of such reactive metals (e.g., Li, Cs) is quite complex and requires additional experimental conditions.

Accordingly, alkali metal compounds, including cesium carbonate ($Cs_2CO_3$), cesium fluoride (CsF), cesium azide ($CsN_3$), etc., were extensively utilized in OLEDs as n-type dopants in EILs to facilitate electron injection and transport from a wide range of metal electrodes and reduce the Ohmic losses in these layers [2,10–17]. Compared to reactive metals, the application of these cesium compounds as n-type dopants exhibits superior beneficial effects, not only on electron-transporting properties but also on material handling process with air-stability and low deposition

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temperature [10,17–19]. Recently, some attempts have been made to elucidate the physical mechanisms of cesium compound doping for electron-transport enhancement [11,12,15–20]. It has been demonstrated that each of cesium compounds exhibits its special characteristics as an n-type dopant. For instance, $Cs_2CO_3$ will partially decompose with the product of cesium oxide ($Cs_2O$) during the thermal evaporation [14,20], while $CsN_3$ has been confirmed to generate Cs and nitrogen ($N_2$) [15,17].

In addition to high efficiency, long-term operational stability is equally important for realizing the further application of OLEDs as a low-cost and sustainable technology. The lifetime of OLEDs can be determined by many factors, including dark spots and morphological defects [21], electrochemical and environmental aging occurring at the interface or inside the organic active layer, and so on [22,23]. Among them, the oxidization caused by the diffusion of moisture and oxygen molecules from the cathode is a common problem for all types of OLEDs. Meanwhile, the insertion of EILs will not only enhance the charge injection from the cathode, but also block the direct contact between the cathode and organic active layer, which suggests that the EILs may also work as a buffer layer to suppress the oxygen and moisture diffusion through cathode into the device. However, despite the overwhelming work dedicated to the utilization of cesium compounds as n-type dopants in organic devices, the detailed comparison of the merits of different cesium compounds is not yet fully clarified. Hence, it is necessary to elucidate the contribution of cesium compounds in EILs of OLEDs for both device performance and operational stability.

Here, we have compared OLEDs using various cesium compounds doped tris (8-hydroxyquinolonato) aluminum ($Alq_3$) layer as the EILs. The detailed contribution of cesium compounds (e.g., $Cs_2CO_3$, $CsN_3$, and CsF) as the n-type dopants on the device performance and operational stability was systematically investigated based on the measurements of current density–voltage–luminance, electroluminescent efficiency, capacitance–voltage, and lifetime measurement. Finally, the superiority of each cesium compound in electron injection ability and operational stability was analyzed with the consideration of different doping mechanisms.

## 2. Experimental methods

The OLED devices were fabricated on indium-tin-oxide (ITO)-coated glass substrates with a sheet resistance of 20 Ω/sq. As shown in Fig. 1, the OLED device is composed of a 40 nm-thick hole-transporting layer (HTL) of N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB), a 20 nm-thick green emitting layer of $Alq_3$ doped with green fluorescent dye of 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1)benzopyropyrano(6,7,8-i,j)quinolizin-11-one (C545T), a 20 nm-thick electron-transporting layer (ETL) of $Alq_3$, and a 10 nm-thick EIL of cesium compound-doped $Alq_3$ (i.e., $Cs_2CO_3$:$Alq_3$, $CsN_3$:$Alq_3$, or CsF:$Alq_3$). ITO and LiF (0.5 nm)/Al (100 nm) bilayer were used for the anode and cathode, respectively. The doping concentrations were 10 wt.% for cesium compounds
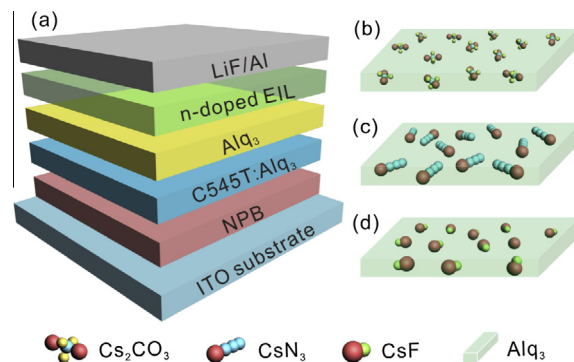


**Fig. 1.** Layer structure of OLEDs. (a) The device structure is composed of a hole-transport layer (HTL) of NPB, an emission layer of $Alq_3$ doped with 1 wt.% of the green fluorescent dye C545T, an electron-transport layer (ETL) of $Alq_3$, an electron-injection layer (EIL). The n-type doped EILs are formed by doping $Alq_3$ with 10 wt.% $Cs_2CO_3$ (b, $Cs_2CO_3$:$Alq_3$), $CsN_3$ (c, $CsN_3$:$Alq_3$), CsF (d, CsF:$Alq_3$), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in $Alq_3$ EIL and about 1 wt.% for C545T in $Alq_3$, respectively. Before loading into evaporation chamber, ITO substrates were subjected to a routine cleaning process, which were scrubbed with Decon 90 solution, ultrasonically cleaned with de-ionized water, dried in a closet, and finally exposed to ultraviolet (UV) ozone for 15 min. All the organic and metal layers were sequentially thermally deposited on top of the substrates in a high vacuum deposition system with a base pressure of $2 \times 10^{-6}$ Torr through shadow masks, while the deposition rate was kept to be 1–2 Å/s for organic layers and 5 Å/s for metal cathode. The thicknesses and deposition rates of different films were carefully controlled and calibrated using a quartz oscillating crystal situated near the substrates. The doping of organic layers was performed by thermal co-evaporation from independent sources, which were controlled via two quartz-crystal monitors. The overlap of ITO anode and Al cathode defines the active area of the device to be 10 mm². To minimize the influence due to different processing condition, OLEDs with four different EILs were fabricated in the same lot by changing the shadow masks. After fabrication, the devices were transported into an interconnected nitrogen-filled glove box for encapsulation without exposure to ambient condition. The device encapsulation was carried out with an epoxy-resin-sealed glass cap.

Most of the measurements were proceeding in the ambient condition. During testing, ITO substrate was used as the positive electrode to apply a constant bias. Current density–voltage–luminance ($J$–$V$–$L$) and luminance efficiency–current density–power efficiency characteristics of OLEDs were measured simultaneously with a programmable Keithley model 2400 power source and a PhotoResearch PR 655 spectrometer. Impedance spectroscopy (IS) measurement was performed to characterize the capacitance–voltage ($C$–$V$) properties through Keithley 4200-CVU Semiconductor Characterization System. A 30 mV amplitude AC signal superimposed on a DC bias was used to measure device capacitance as a function of AC frequency and DC bias. Conductivity was tested with a