Novel Organic Electron Injectors for the Enhancement of Lifetime, Efficiency and Reduction in Operating Voltage in OLEDs

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Abstract

Both PM-OLEDs and AM-OLEDs are now in production. However, manufacturers are still concerned about life-time, voltage drift, operating voltage and efficiency in order to develop larger displays. Most material suppliers seem to be focussing on emitters and the benefits of introducing suitable charge transporters have been largely unexplored. OLED-T has developed a novel organic electron injector (Trade Name: EI-101) which evaporates at a very low temperature of 300℃ as opposed to the conventional LiF which requires 580℃. EI-101 has been found to increase the lifetime by up to 12%, reduce the voltage drift by up to 61% and increase the efficiency by up to 15%. The material can be handled in air and in situ Q-mass spectroscopy on extended thermal evaporation has confirmed its high stability for use in mass production.

1. Introduction

Almost all the OLED panel manufacturers employ an electron injector (e.g. LiF, KF, CsF) or a low work function metal (e.g. Li, Cs) or both [1-5].
Electron injectors facilitate efficient electron injection and lower the work function of the organics/Al interface. Amongst the electron injectors, the manufacturers seem to prefer LiF.
LiF (or any other metal fluoride) requires high temperature (above 580°C) and thus in turn, it requires expensive high temperature crucibles (e.g. BN). It also requires relatively long time to deposit, thus affecting the underlying organic layers. LiF is also hygroscopic. Further, the ionic metal fluorides cause significant voltage drift. We have developed a series of organic electron injectors which can be handled in air and they only require a temperature of 300^0C to evaporate. We discuss one such proprietary material (EI-101) in detail here. Further, EI-101 has been tested under production conditions (W crucible) for a continuous period of 14 hours at 5 A/s and no decomposition peaks were observed on in-situ q-mass spectra.

2. Experimental

EI-101 has a melting point of 358^oC (Differential Scanning Calorimetry, Figure 1) and is stable up to 350^oC in air (Thermogravimetry, Figure 2).

HOMO-LUMO levels of EI-101 were determined by both AC-II and cyclic voltammetry to be -5.4 eV and -2.5 eV.

Evaporation tests (Figure 3) and device fabrications were carried on our OLED vacuum deposition machine (Solciet) purchased from (ULVAC, Japan). In-situ Q-mass spectroscopy was carried out by heating EI-101 in a tungsten crucible in an OLED production equipment (Figure 4). We present the results for red (phosphorescent), green (fluorescent) and blue (fluorescent) devices here.

The device structure for the blue devices is as follows:

ITO/HI (E9363, 20 nm)/HTL (α-NPB, 65 nm)/Blue host (EH007, 25 nm)): Blue Dopant (E1384, 0.5 nm)/ETL (E246, 20 nm)/EI (either LiF or EI-101 (0.5 nm)/Al (150 nm).

The device structure for the red devices are:

ITO/HI (50 nm)/ α-NPB (105 nm)/Host + Red Dopant (30 nm:2.5 nm)/ETL (25 nm)/EI (1 nm)/Al

The device structure for the green devices are :
ITO/HI (80 nm)/α-NPB (30 nm)/Host + Green Dopant (25 nm:0.2 nm)/ETL (35 nm)/EI (0.5 nm)/Al

3. Results and Discussion

The peak on the DSC (Figure 1) of 366°C is invariant on repetitive cycling between room temperature and 399°C indicates that the material is highly stable and does not undergo decomposition on melting. TGA (Figure 2) indicates that EI-101 does not decompose on heating to 350°C under an atmosphere of nitrogen.

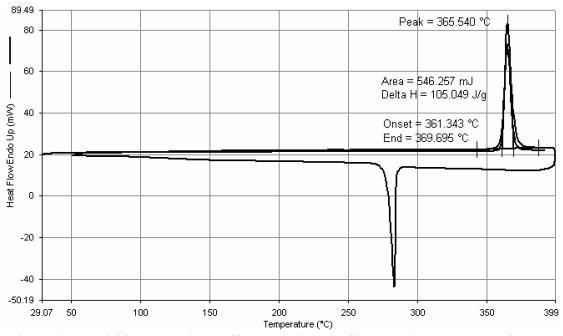


Fig. 1. Differential Scanning Calorimetry of EI-101.

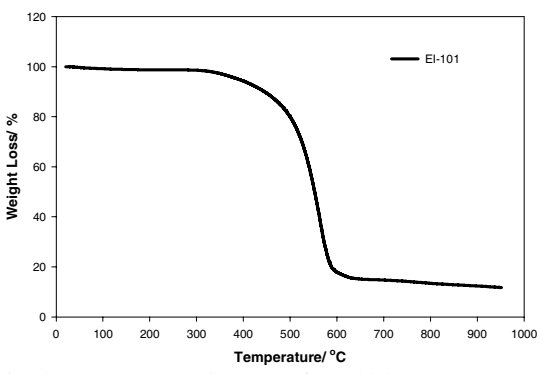


Fig. 2. Thermogravimetry of EI-101.

Figure 3 compares the evaporation rate vs. temperature profiles for EI-101 and LiF. EI-101 evaporates at 300°C to give a rate of 0.1 As^{-1} whereas a temperature of 580°C is required to achieve the same rate. This is explained by the more organic nature of EI-101 as opposed to the fully ionic LiF. The low temperature evaporation capability of EI-101 help alleviate the damage caused by LiF to the underlying organic layers.

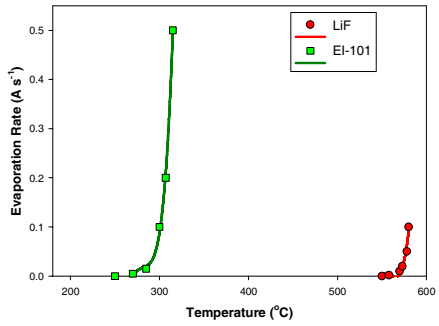


Fig. 3. Evaporation rate - temperature profiles: EI-101 vs. LiF.

In-situ Q-mass spectroscopy (Figure 4) shows no decomposition peaks in the range 60-380 (M/Z, amu) despite heating at 340°C for 12 hours (Evaporation Rate, 5 As^{-1}).

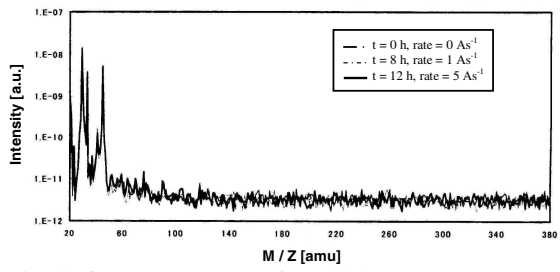
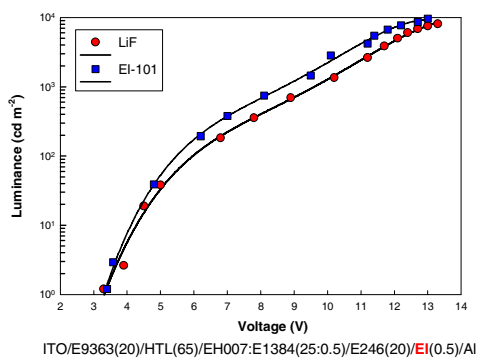


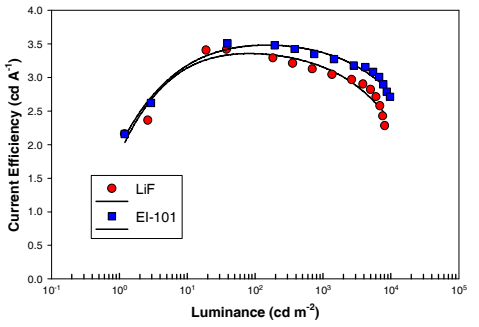
Fig. 4. Q-Mass spectra of EI-101.

Figures 5-8 compare the performance of blue devices of EI-101 with that of LiF. Figure 9 shows the life-time data of blue devices for EI-101 and LiF at 3000 cdm^{-2}. It is immediately apparent that EI-101 enhances the efficiency and reduces the operating voltage. Life time is also increased by 12% and the voltage drift reduced from 1.4 V to 0.8 V (measured over a period 1600 hours (Initial luminance, 3000 cdm^{-2}) on replacing LiF with EI-101.



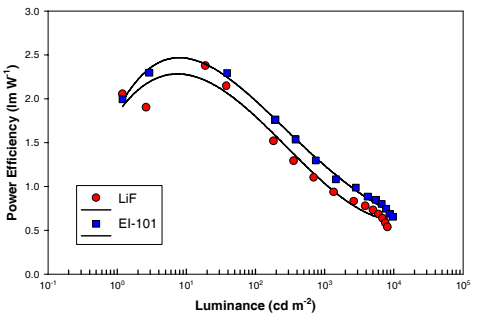
ITO/E9363(20)/HTL(65)/EH007:E1384(25:0.5)/E246(20)/EI(0.5)/Al

Fig. 5. Blue devices (L vs. V): EI-101 vs. LiF.



ITO/E9363(20)/HTL(65)/EH007:E1384(25:0.5)/E246(20)/EI(0.5)/Al

Fig. 6. Blue devices (η_I vs. L): EI-101 vs. LiF.



ITO/E9363(20)/HTL(65)/EH007:E1384(25:0.5)/E246(20)/EI(0.5)/Al

Fig. 7. Blue devices (η_P vs. L): EI-101 vs. LiF.

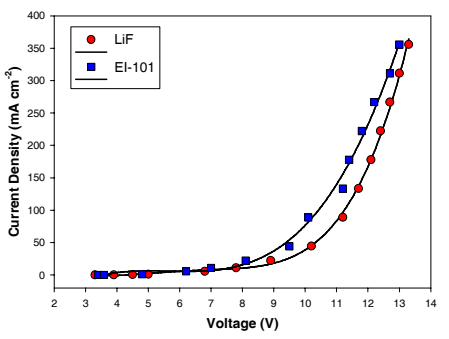
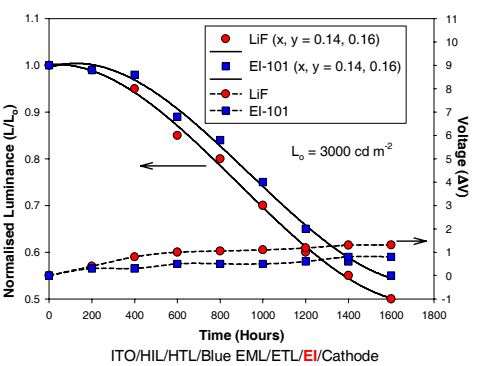


Fig. 8. Blue devices (J_d vs. V): EI-101 vs. LiF.



ITO/HIL/HTL/Blue EML/ETL/EI/Cathode

Fig. 9. Blue devices (L vs. t): EI-101 vs. LiF; initial luminance (L_o), 3000 cdm^{-2}.

Performance data for the phosphorescent red devices and fluorescent green devices are summarised in Tables 1 and 2 respectively.

Phosphorescent red (CIE, 0.65, 0.35) devices show substantial improvement of over 12% in both current and power efficiencies with a slight reduction in operating voltage for a given luminance (Figure 10). Although, there is no difference in the extent of voltage drift over a period 800 hours at 3000 cdm^{-2}, the life time lengthened from 650 hours to 730 hours on substituting EI-101 for LiF.

TABLE 1. Performance of Red Devices: Comparison of EI-101 with LiF

EI	Voltage at 20 mAcm^{-2}	Luminance / cdm^{-2} at 20 mAcm^{-2}	Efficiency / cdA^{-1}	Efficiency / lmW^{-1}	CIE (x, y)
LiF (1 nm)	4.3 ± 0.1 V	3940	19.7	14.5	(0.65, 0.35)
EI-101 (1 nm)	4.4 ± 0.1 V	4530	22.2	16.3	(0.65, 0.35)

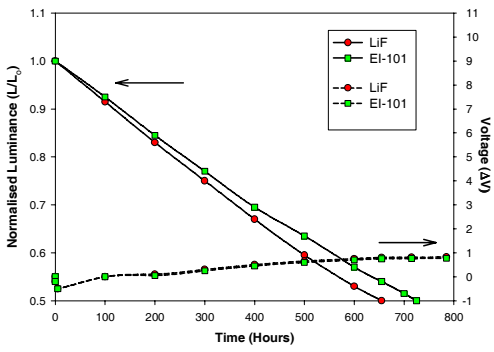


Fig. 10. Red devices of EI-101, (L vs. t): EI-101 vs. LiF; initial luminance (L_o), 3000 cdm^{-2}.

Fluorescent green (CIE, 0.28, 0.66) devices show only a marginal improvement with EI-101. However, the voltage drift is reduced from 0.8V to 0.05 V over 900 hours at an initial luminance of 8000 cdm^{-2} (Figure 11).

TABLE 2. Performance of Green Devices: Comparison of EI-101 with LiF

EI	Voltage at 50 mAcm^{-2}	Luminance / cdm^{-2} at 50 mAcm^{-2}	Efficiency / cdA^{-1}	Efficiency / lmW^{-1}	CIE (x, y)
LiF (1 nm)	6.7 ± 0.1 V	12150	24.3	11.3	(0.28, 0.66)
EI-101 (1 nm)	6.8 ± 0.1 V	12350	24.7	11.3	(0.28, 0.65)

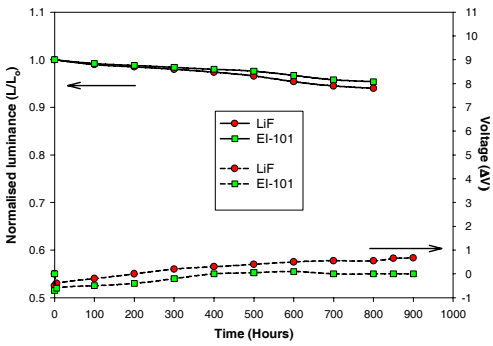


Fig. 11. Green devices (L vs. t): EI-101 vs. LiF; initial luminance (L_o), 8000 cdm^{-2}.

The thickness dependence of the electron injectors on the efficiency was investigated on blue devices (Figure 12). As the thickness of the EI layer increases, the efficiency decreases more sharply for LiF compared with EI-101. LiF is a poorly conducting ionic solid whereas EI-101 is much more conducting organic metal complex. This is a useful property as the thickness control of EI-101 is not as critical as LiF in production.

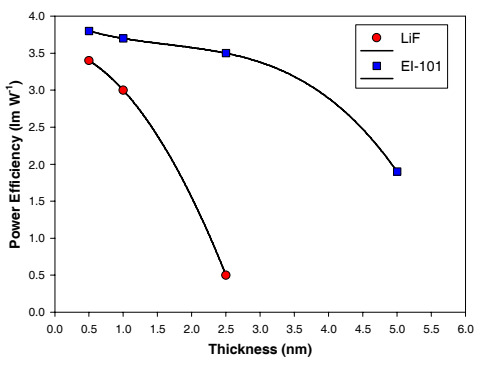


Fig. 12. Blue devices: Power Efficiency (lm/W^{-1}) vs. thickness (nm); EI-101 vs. LiF

It has also been found the EI-101 improves the performance of phosphorescent blue devices which will be published elsewhere.

4. Summary

The low temperature evaporable electron injector, EI-101 helps alleviate the thermal damage caused by high temperature required for the evaporation of LiF.

Table 3 summarises the device performance data obtained for red, green and blue devices. It has been demonstrated that EI-10I improves the efficiency, reduces the operating voltage for a given luminance, lengthens the life time and reduces the voltage drift.

EI-101 does not diminish the efficiency of devices up to a thickness of 2 nm whereas the LiF thickness has to be carefully controlled to 0.5 nm to achieve the optimum results. Thus, EI-101 allows manufacturers greater freedom of operation.
EI-101 is available in kg quantities from OLED-T.

TABLE 3. Improvement in Performance on Substituting LiF with EI-101

Parameter	Phosphorescent Red	Fluorescent Green	Fluorescent Blue
Current efficiency (cd/A) increase	7%	3%	9%
Power efficiency (lm/W^{-1}) increase	13%	0%	15%
Lifetime increase	12% at 3000 cdm^{-2}	7% at 8000 cdm^{-2}	12% at 3000 cdm^{-2}
Reduction in drift voltage during lifetime measurements	0	From 0.8 V to 0.05 V over 900 hours at 8000 cdm^{-2}	From 1.4 V to 0.8 V over 1600 hours at 3000 cdm^{-2}

5. Acknowledgements

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6. References

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