

Charge transport materials for the manufacture of OLEDs

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Abstract

OLEDs are becoming established as a commercially viable flat panel display technology of choice of the 21st century because of its lightweight, fast response time, lower thickness than LCD's and potentially low cost (1-2). For the OLEDs to function effectively, highly thermally stable materials, which offer high efficiency and long operational lifetimes are required. To achieve long lifetime, highly stable charge (both holes and electrons) transporters are essential. OLED-T provides these materials as well as fluorescent and phosphorescent dopants. This paper reports a unique patented hole injector (E9363) and an electron transporter (E246) that increases the lifetime and efficiency and reduces operating voltage. Further, an electron injector, EEI-101, which evaporates at a very low temperature of 300 °C as opposed to the conventional LiF, which requires 580 °C, is also presented.

1. Objectives and Background

Electron transporters and electron injectors are integral parts of most OLED's and they facilitate efficient electron injection. The requirement of a good electron transporter is that it should prolong life, increase the efficiency and lower the operating voltage at a useful luminance. It is now widely accepted by major manufacturers that an electron transporter with higher mobility than Alq₃ is required (3-6) for early commercialisation of AM-OLEDs. We, at OLED-T, have been focussing our attention on OLED materials (both fluorescent and phosphorescent), hosts, hole injectors, electron transporters and electron injectors that offer long lifetime and high efficiency (7). We report here a unique patented novel electron transporter and an electron injector. We have discovered an electron transporter (a metal complex, E246[®]) that increases the lifetime and efficiency and reduces the operating voltage for R, G and B devices.

Further, E246[®] has been validated on both ULVAC and Tokki vacuum systems. We also report a patented electron injector (EEI-101[®]), which evaporates at 300 °C as opposed to the conventional

LiF, which evaporates at 580 °C in vacuo. We have also developed a transparent hole injector (E9363) which requires a temperature of only 390 °C to have an evaporation rate of 2 Ås⁻¹ as opposed to 460 °C for CuPc to achieve the same rate. Furthermore, E9363 provides longer lifetime than CuPc.

2. Experimental and Results

2.1. Physical Properties

A selected number of physical properties of the hole injector E9363 is compared with CuPc and 2-TNATA in Table 1. The absorption spectra of thin films of CuPC, 2-TNATA and E9363 are compared in Figure 1 and the evaporation rate vs. temperature profile is shown in Figure 2. A selected number of physical properties of the electron transporter E246 is compared with that of Alq₃ in Table 2.

Table 1: Selected physical properties of hole injectors.

Material	T _g (°C)	T _m (°C)	ϕ _{WF} (eV)	Temperature required to achieve 2 Ås ⁻¹
E9363	-	> 400	-5.4	390 °C
CuPC	-	> 400	-5.3	460 °C
2-TNATA	118	254	-5.3	370 °C

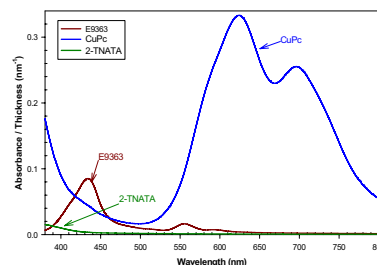


Figure 1: Absorption spectra of hole injectors.

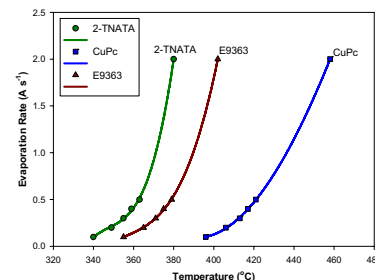


Figure 2: Evaporation rate vs. temperature profiles in solciet.

Table 2: Selected physical properties of electron transporters.

Material	T_m (°C)	HOMO (eV)	LUMO (eV)	Photoluminescence maximum (nm)
E246	388	- 5.6	- 2.9	537
Alq ₃	414	- 5.7	- 2.9	520

We have carried out extensive thermal stability tests on E246 by heating the E246 (5 g) in a BN crucible for 2 days in our Solciet (ULVAC) OLED production machine. Temperature, pressure and evaporation rate vs. time profiles for Day 1 and Day 2 are shown in Figures 3 and 4 respectively. In-situ q-mass spectroscopy has been carried out on E246 (15 g) in a titanium crucible on a Tokki OLED machine at 320°C over a continuous period of 19 hours. The spectral out-put at t = 0 and t = 19 h are shown in Figures 5a-b.

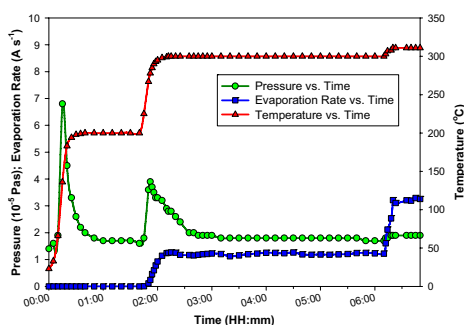


Figure 3: Evaporation rate and pressure vs. temperature profiles of E246 in solciet (Day 1).

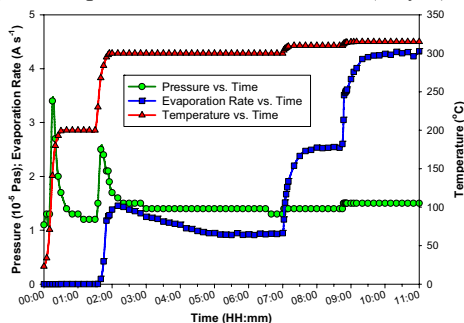


Figure 4: Evaporation rate and pressure vs. temperature profiles of E246 in solciet (Day 2).

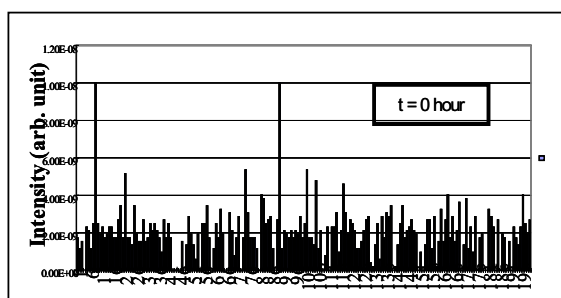


Figure 5a: Q-mass of E246 in solciet t = 0.

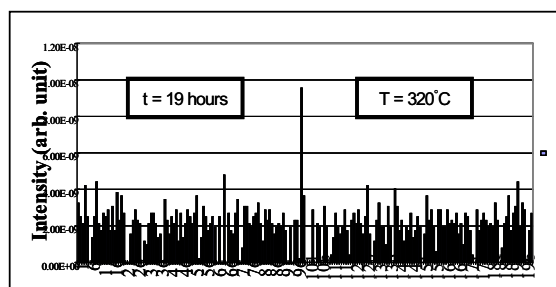


Figure 5b: Q-mass of E246 in solciet at t = 19 hours.

DSC (Figure 6), UV-Visible spectroscopy of the thin films made in Day 1 and Day 2 (Figure 7), UV-Vis. Spectroscopy of dichloromethane solutions of E246 before and after evaporation tests at 300°C for 16 hours (Figure 8), fluorescent spectroscopy of dichloromethane solutions of E246 (before and after evaporation tests, Figure 9) have been carried out to ensure that the chemical composition of E246 has not changed during the oled manufacture.

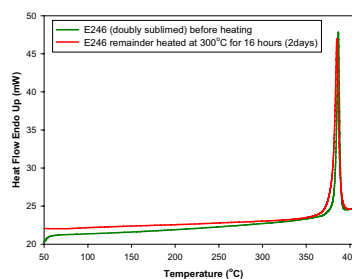


Figure 6: DSC of E246 before and after evaporation test.

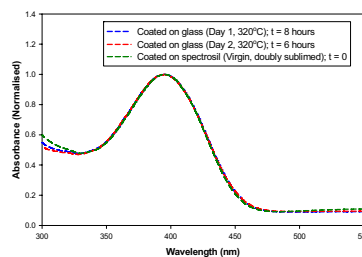


Figure 7: UV-vis absorption spectra of thin films of E246 after Day 1 and Day 2 of evaporation tests.

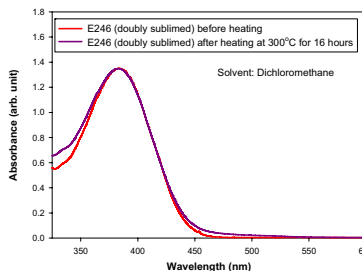


Figure 8: UV-vis absorption spectra of E246 before and after evaporation test.

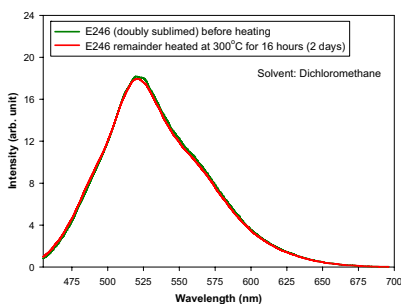


Figure 9: Fluorescent spectra of E246 before and after evaporation test.

2.2 Device Manufacture and Performance

2.2.1. HIL (E9363):

We established the superior quality of our hole injector, E9363, by fabricating devices with Alq₃ as a host doped with our proprietary green dopant (E036) and Alq₃ as the etl and comparing the devices with E9363, CuPc and 2-TNATA as HILs. Figure 10 shows the luminance vs. voltage for devices ITO/HIL(20 nm)/ α -NPB(50 nm)/Alq₃: E036(40 nm : 0.1 nm)/Alq₃(20 nm)/LiF(0.3 nm)/Al.

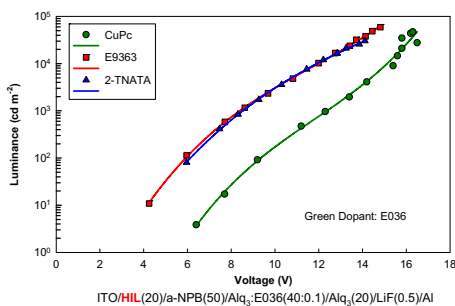


Figure 10: Green device performance (L vs. V); E9363 vs. CuPc and 2-TNATA as hole injectors.

Lifetime measurements on these devices were made at 1200 cdm^{-2} under constant current drive (Figure 11). The performance of devices of ITO/HIL(20nm)/ α -NPB (65 nm)/CBP : EPhosA (20 nm:0.5 nm)/BCP (6 nm)/Alq₃(55 nm)/LiF(0.3 nm)/Al where HIL is CuPc or E9363 are shown in Figures 12a-b.

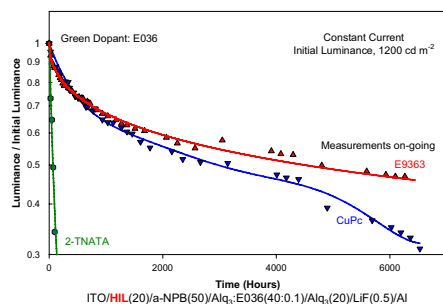


Figure 11: Green device lifetime; E9363 vs. CuPc and 2-TNATA as hole injectors.

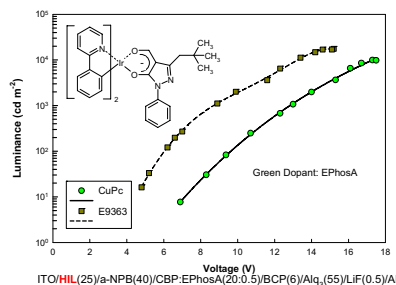


Figure 12a: Phosphorescent green device performance (L vs. V); E9363 vs. CuPc as a hole injector.

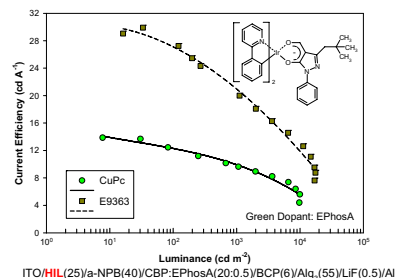


Figure 12b: Phosphorescent green device performance (η_1 vs. L); E9363 vs. CuPc as a hole injector.

2.2.2 ETL (E246):

Red devices were made as follows: ITO/E9363(20 nm)/ α -NPB(50 nm)/Alq₃(60 nm) : E047 (0.7 nm, red dopant)/ETL(30 nm)/LiF(0.3 nm)/Al where the etl is either Alq₃ or E246. The performance of these devices is shown in Figures 13a-b.

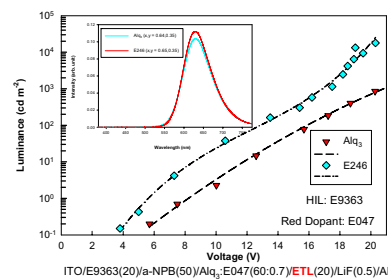


Figure 13a: Red device performance (L vs. V); E246 vs. Alq₃ as an electron transporter.

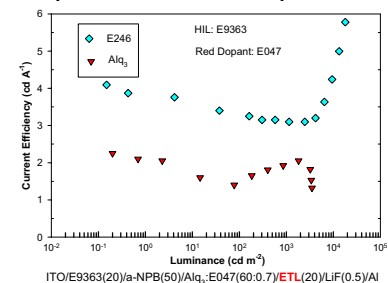


Figure 13b: Red device performance (η_1 vs. V); E246 vs. Alq₃ as an electron transporter.

Green devices were made as follows: ITO/CuPc (20 nm)/Alq₃(40 nm): C545T (0.4 nm)/ETL (20 nm)/LiF (0.3 nm)/Al where the etl is either Alq₃ or E246 (Figures 14 a-b).

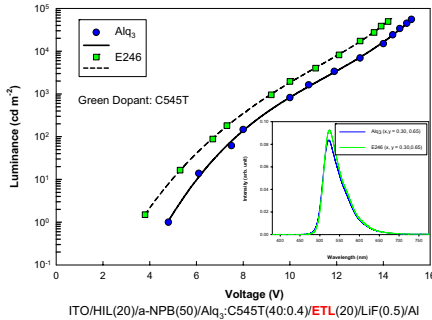


Figure 14a: Green device performance (L vs. V); E246 vs. Alq₃ as an electron transporter.

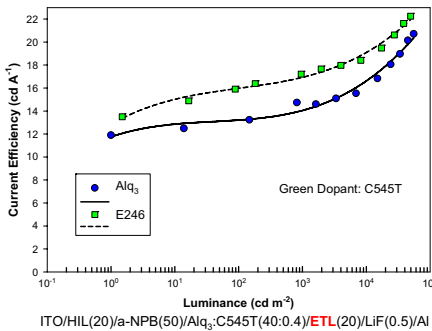


Figure 14b: Green device performance (η_i vs. L); E246 vs. Alq₃ as an electron transporter.

Blue devices made as follows: ITO/E9363(30 nm)/α-NPB(50 nm)/EH007(blue host, 25 nm);perylene (0.02 nm, blue dopant)/ETL(20 nm)/LiF(0.3 nm)/Al (Figures 15.1 a-b) or ITO/HIL/blue host(EH007): blue dopant/ETL/LiF (0.3 nm)/Al (Figures 15.2 a-b) where the ETL is either Alq₃ or E246.

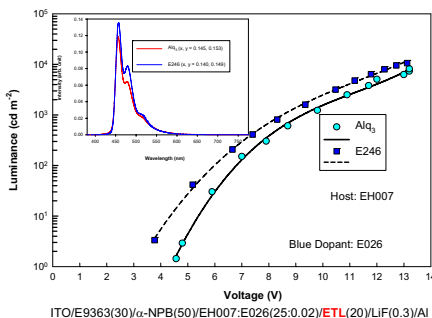
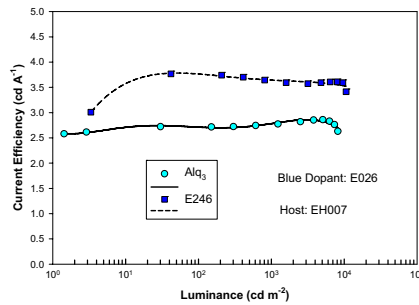


Figure 15.1a: Blue device performance (L vs. V); E246 vs. Alq₃ as an electron transporter.



ITO/E9363(30)/α-NPB(50)/EH007:E026(25:0.02)/ETL(20)/LiF(0.3)/Al

Figure 15.1b: Blue device performance (η_i vs. L); E246 vs. Alq₃ as an electron transporter.

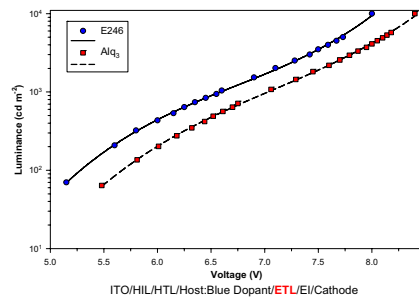


Figure 15.2a: Blue device performance (L vs. V); E246 vs. Alq₃ as an electron transporter.

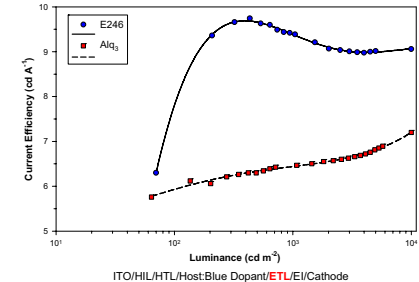


Figure 15.2b: Blue device performance (η_i vs. L); E246 vs. Alq₃ as an electron transporter.

2.2.3 Electron Injector (EEI-101):

Figure 16 shows the evaporation rate vs. temperature for EEI-101 and LiF. The effectiveness of EEI-101 is illustrated by the following devices: ITO/E9363 (20 nm)/α-NPB(65 nm)/EH007:E1384(25 nm : 0.5 nm)/E246 (20 nm)/EI (0.3 nm)/Al, where EI is either EEI-101 or LiF (Figures 17 a-b).

3. Results and Discussion

Evaporation tests on E246: As the temperature was raised (Figure 3, Day 1), there is a slight pressure increase from 2×10^{-5} Pa to 3.5×10^{-5} Pa, then it stabilises around 2×10^{-5} Pa on evaporation at 1 \AA s^{-1} .

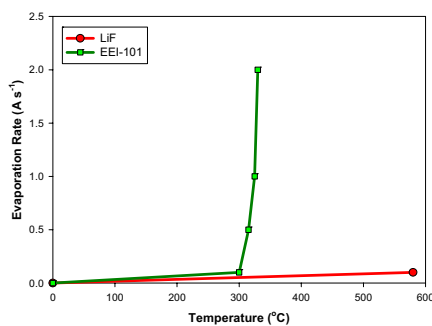


Figure 16: Evaporation rate vs. temperature profiles of electron injectors in solciet.

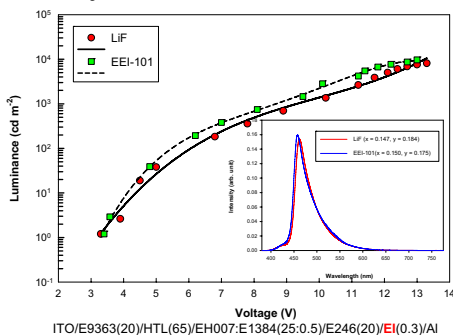


Figure 17a: Blue device performance (L vs. V); EEI-101 vs. LiF as an electron injector.

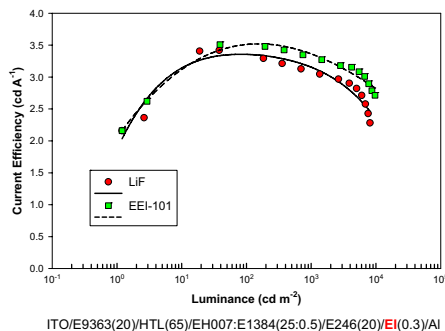


Figure 17b: Blue device performance (η_1 vs. L); EEI-101 vs. LiF as an electron injector.

On increasing the evaporation rate (by increasing the temperature) to 3 \AA s^{-1} , the pressure remains virtually constant. On day 2 (Figure 4), the pressure changes were even less marked than Day 1 even though the reaction rates were increased from 1 \AA s^{-1} (resident time, 5 hour) to 2.5 \AA s^{-1} (1 h) and then 4.5 \AA s^{-1} (1.5 h). In-situ q-mass spectroscopy of the vapours from E246 inside a Tokki OLED evaporator was carried out at an hourly interval. Figure 5 shows the q-mass spectra at $t = 0$ and $t = 19$ hours at 320°C which shows no evidence of any decomposition.

The DSC performed on E246 before and after heating at 300°C for 16 h shows that the E246 has identical m.pt. of $389 \pm 1^\circ\text{C}$ (Figure 6). UV-Vis.

Spectroscopy of thin films produced on Day 1 (8 h at 320°C , Day 2 (6 h, 320°C) and thin film produced from virgin E246 show that the films are identical (Figure 7). UV-vis. Spectroscopy and fluorescent spectroscopy of dichloromethane solutions of E246 (before and after heating at 300°C , 16 h) show that was no change in the characteristics of E246 on heat treatment/evaporation (Figures 8 and 9). All the above tests clearly demonstrate that E246 is very stable under manufacturing conditions.

The hole injector (E9363) gives lower operating voltage than CuPc and comparable performance to 2-TNATA as far as L vs. V is concerned. This is attributed to the high mobility and high W.F. of E9363. Lifetime measurements under constant current drive at an initial luminance of 1200 cd m^{-2} (Figure 11, fluorescent green devices) show that the half-life of 2-TNATA based devices is only 50 hours and that of CuPC is 2700 h. However, E9363 based devices give a half-life of 4590 h, demonstrating its superiority. The high mobility of E9363 is further illustrated by devices produced from our phosphorescent dopant, EPhosA where our HIL (E9363) is compared with CuPc (Figures 12a-b). At 100 cd m^{-2} , the efficiency of CuPc based devices is 12 cd A^{-1} whereas that with E9363 is 27 cd A^{-1} (an increase of 125%) and the corresponding operating voltages are 9.8 V and 6 V respectively.

The performance data of fluorescent red, green and blue are given in Figures 13, 14 and 15 respectively. All the devices with E246 as etl operate at lower voltages than those with Alq_3 as etl. Table 3 below summarises the performance improvement on substituting Alq_3 with E246 at 100 cd m^{-2} .

Table 3: Improvements in performance by E246 over Alq_3 .

Parameter (%)	Red (Fluo.)	Green (Fluo.)	Blue (Fluo.)
Improvement in current efficiency	88	23	40
Reduction in operating voltage	20	12	8

The lifetime measurements were carried out at 1000 cd m^{-2} (red), 1200 cd m^{-2} (green) and 3000 cd m^{-2} (blue) which are shown in Figures 18, 19 and 20. It can easily be deduced that E246 doubles the lifetime of red devices and increases the lifetime of green by 1.25 fold or three fold if used as a host as well. The lifetime of blue devices is also more than doubled compared to Alq_3 . Figure 21 summarises the lifetime results of all the devices with fluorescent green

dopants for E9363 vs. CuPc. Vs. 2-TNATA and E246 vs. Alq₃.

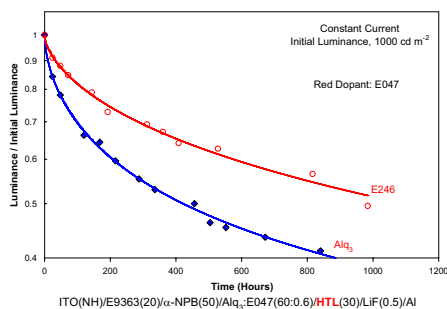


Figure 18: Red device lifetime; E246 vs. Alq₃ as an electron transporter.

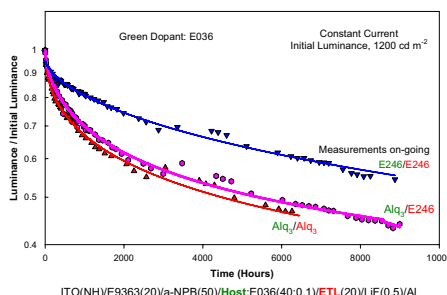


Figure 19: Green device lifetime; E246 vs. Alq₃ as a host and an electron transporter.

Electron injector, EEI-101 evaporates at much lower temperature of 300°C than LiF (580°C), thus making the deposition faster and energy consumption and equipment cost lower. In all other respects, EEI-101 is as effective as LiF as illustrated by the example in Figure 17 a-b.

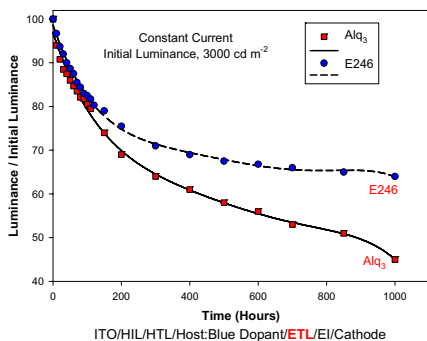


Figure 20: Blue device lifetime; E246 vs. Alq₃ as an electron transporter.

4. Conclusion

We have demonstrated that our hole injector, E9363, is superior to CuPc as far as the operating voltage and lifetimes are concerned. Substituting E246 for Alq₃ as an etl improves the efficiency, lifetime and colour co-ordinates.

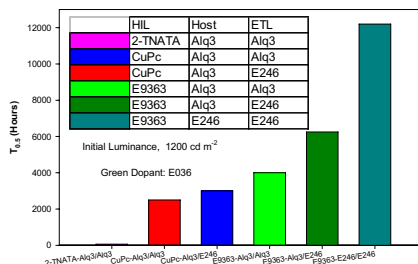


Figure 21: Green device lifetime at half-life ($T_{0.5}$); Different hole injectors and electron transporters.

The electron injector, EEI-101, evaporates at nearly 280°C lower than LiF. This should improve the productivity and saves costs on equipment design.

E9363, E246 and EEI-101 are available at a purity of 99.98% in kg quantities. E246 has been tested on two pre-production OLED equipment (Ulvac and Tokki) and shown to be stable on prolonged heating as determined by Q-mass spectroscopy. The low temperature evaporable electron injector, EEI-101 helps alleviate the thermal damage to organic layers caused by high temperature required for the evaporation of LiF and speed up production.

4. Acknowledgements

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5. References

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