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Enhanced Performance of Single Layer MEH-PPV Polymer Light Emitting Diodes

Effect of Alq_3 Electron Transporting Layer and LiF:Al Cathode Contact on Single Layer MEH-PPV Polymer LEDs

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Abstract: Poly (2-methoxy-5-(2'-ethylexyloxy)-1,4-phenylene vinylene) (MEH-PPV) is the most important polymeric material, which can be used to make commercially stable light-emitting devices (LEDs) in the red-orange region. In the present work, we have improved the performance of simple polymer light-emitting devices (PLEDs) based on MEH-PPV. We experimentally investigated the performance of different LEDs *viz.* ITO/MEH-PPV/Al, ITO/ MEH-PPV/Al and ITO/MEH-PPV/Alq3/Al and found that the performance of monolayer PLEDs can be improved by the use of bilayer PLED and also by improving the cathode contact so that it can inject a large number of electrons into poor hole conducting polymers.

***Index Terms* - Electronic polymer, polymer light emitting diodes, electro-luminescence, thin films**

I. INTRODUCTION

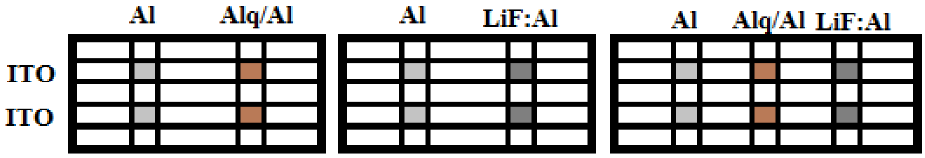
Since their discovery in 1990, the poly-phenylene vinylene (PPV) and their derivatives are finding good use as electroluminescent materials [1] [2]. However, these polymeric materials suffer some of the drawbacks that hinder their commercialization as active light-emitting material [3]. Two most important problems are listed below:

1. PPV and most of its derivatives act as good hole transporter as compared to electrons [4]. This leads to unbalanced recombination of holes and electrons, which limits their efficiency.
2. Highest Occupied Molecular Orbital (HOMO) levels of these materials lying around 3*eV*; this makes it difficult to have near ohmic cathode contact. Most researchers used Al or Ca for this purpose. Aluminum (work function at 4.3*eV*) proved to be good cathode contact but results in a high potential barrier for electron emission. Calcium (work function at 2.0*eV*) proved to be a good electron emitter but it forms clusters, Ca^{2+} ions, and oxides, which deteriorate the lifetime of the device.

In this paper, we present the enhanced performance of the monolayer polymeric light-emitting device (PLED) *viz.* ITO/MEH-PPV/Al, by counteracting both of the above problems. MEH-PPV offers easy processability as compared with other derivatives of PPV. The first problem has been counteracted by the use of a bilayer structure in place of monolayer structure. We inserted an electron-transporting layer (ETL) of Alq_3 with MEH-PPV, which acts as a hole transporting layer (HTL). The second problem of cathode contact is improved by inserting the LiF buffer layer in between MEH-PPV and Al. We then measured the current-voltage and current-light intensity characteristics of ITO/MEH-PPV/Alq_3/Al and ITO/MEH-PPV/LiF:Al devices and compared them with basic device viz. ITO/MEH-PPV/Al.

II. EXPERIMENTAL DETAILS

MEH-PPV $(C_{18}H_{28}O_2)_n$ powder having molecular weight distribution 40,000-70,000 was obtained from Sigma-Aldrich (JAPAN). It was dissolved in *p*-xylene, at a concentration of ~8mg/mL and then properly mixed by using ultrasonic agitator (at 50 Hz) for about three hours at a temperature of 50ºC. This solution of MEH-PPV then spin-coated on patterned ITO-glass. The speed of spinner was kept in the range 1500-2000rpm and the duration of the spin was kept at 20sec. We then made ITO/MEH-PPV/Al and ITO/MEH-PPV/Alq3/Al devices on the same substrate over the same MEH-PPV layer [device set A]. For the deposition of Al and Alq_3/Al layers over ITO/MEH-PPV, we used a thermal evaporation process. One boat containing Alq_3 and a filament containing Al wire was placed in the vacuum chamber (at 10^{-5} torrs). The evaporation of Alq_3 was followed by that of Al. Proper masking was also done to obtain the desired structure. We also made buffered cathode device ITO/MEH-PPV/LiF:Al with basic device ITO/MEH-PPV/Al on the same substrate by using similar procedure [device set B]. All three types of devices are also made on the same MEH-PPV coated substrate [device set C]. The thickness of the MEH-PPV layer in all samples was found to be 2000±5%Å using talystep and that of Al and LiF was ~80nm. The cross-section of these devices is shown in **Fig. 1**.



(A) Device Set A (B) Device Set B (C) Device Set C

Figure 1. Cross-section for (A) device set A, which contains ITO/MEH-PPV/Al and ITO/ MEH-PPV/Alq_3/Al devices and (B) device set B, which contains ITO/ MEH-PPV/Al and ITO/ MEH-PPV/LiF:Al devices (C) device set C which contains ITO/ MEH-PPV/Al, ITO/ MEH-PPV/Alq_3/Al and ITO/ MEH-PPV/LiF:Al devices.

We then measured the J-V characteristics of devices in set A and B and recorded light emission using a Si-photodetector. For J-V characterization we used Keithley's source meter.

III. RESULTS & DISCUSSION

3.1 Device Set A

The device set A contains ITO/MEH-PPV/Al and ITO/ MEH-PPV/Alq3/Al devices. For a typical set of device set A, the J-V characteristics for these devices are shown in **Fig. 2**.

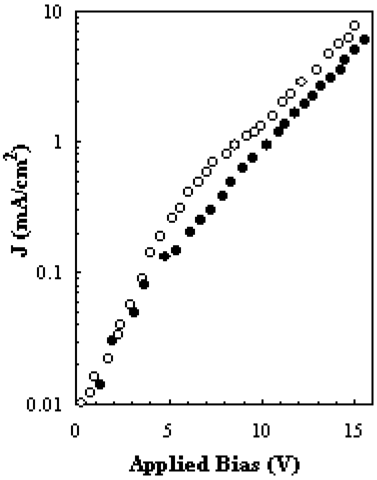


Figure 2. J-V characteristics for ITO/MEH-PPV/Al (○) and ITO/MEH-PPV/Alq_3/Al (●) devices in device set A.

The current density for ITO/MEH-PPV/Alq_3/Al device is found to be less than that for ITO/MEH-PPV/Al especially for voltages greater than 2.5V. The less current density in the bilayer device can be attributed inclusion of the hole blocking layer of Alq_3. The LUMO level for Alq_3 is at 3.0 eV [5], which is the same as that for MEH-PPV. Hence electrons have a similar barrier at the Alq_3/Al interface as that was at MEH-PPV/Al interface in monolayer device.

The light detected, by Si-photodetector from the LEDs in the device set A, is plotted as a function of current density flowing through them is shown in **Fig. 3**. Light intensity for the bilayer device is found to be higher than that for monolayer devices at the same value of current density. The monolayer device is made of MEH-PPV which is a good hole transporter therefore electron and holes recombine together and form exciton in the area near to Al-cathode. Aluminum has a lower electron affinity (0.4 eV) [6]; therefore electrons get attracted towards the cathode and thereby excitons get dissociated. This results in poor electroluminescence from monolayer devices.

In the ITO/MEH-PPV/Alq3/Al device, the barrier to electron injection at the Alq_3/Al interface is very large therefore a relatively small number of electrons is injected. However, the barrier to hole injection at the ITO/MEH-PPV interface is much smaller and large numbers of holes are injected. MEH-PPV is an efficient hole transporter, but Alq_3 layer acts as a hole blocking layer, therefore holes accumulate at MEH-PPV/Alq3 interface. On the other hand, Alq_3 is an efficient electron-transporting material, but MEH-PPV acts as an electron blocking layer, and so electrons accumulate at the MEH-PPV/Alq_3 layer. So the recombination of electrons and holes takes place near the interface away from electrodes. So the loss of excitons due to electrodes capturing of carriers is minimized and hence a high light-emitting efficiency can be achieved.

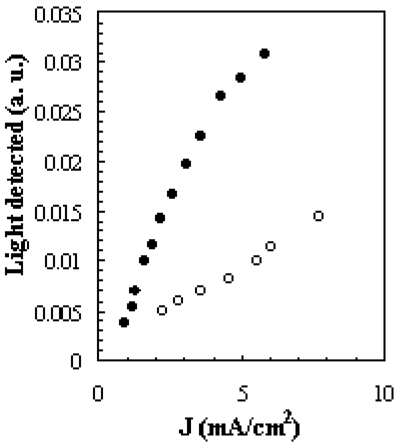


Figure 3. Emitted light intensity recorded by Si photodiode vs. current density flowing through polymer LEDs ITO/MEH-PPV/Al (○) and ITO/MEH-PPV/Alq_3/Al (●) in device set A.

3.2 Device Set B

Device set B contains ITO/MEH-PPV/Al and ITO/MEH-PPV/LiF:Al devices. The J-V characteristics for these devices are shown in **Fig. 4**. It can be observed that the current density for ITO/MEH-PPV/Al at any bias voltage is lower than that of ITO/MEH-PPV/LiF:Al. For example, Al cathode requires approximately 12V to generate a current density of 32mA/cm2 while LiF:Al requires only 9.6 V to do so.

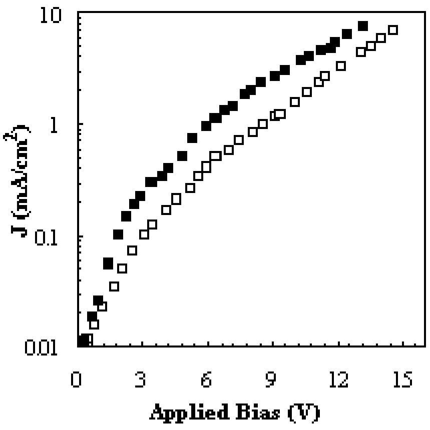


Figure 4. J-V characteristics for ITO/MEH-PPV/Al (□) and ITO/MEH-PPV/LiF:Al (■) devices in set A.

This higher current density for LiF:Al cathodes as compared to Al cathodes, can be attributed to the decrease in the work function of Al. However, the reasons for this decrease in work function are a subject of debate. Initially, this decrease was attributed to the decrease in the surface potential of Al due to the dipole moment of LiF [7], later it was proposed that the decrease work function of Al is caused by dissociation of LiF and production of free Li [8]. The ultraviolet photoelectron spectroscopy (UPS) studies show evidence of doping of the organic, which is consistent with the production of free Li [9].

Fig. 5 shows the light detected by Si-photodiode vs. the current density flowing through devices. The light output is found to be directly proportional to the injected current. The slope of the curve measures the EL efficiency of diodes. It is found that the efficiency of ITO/MEH-PPV/LiF:Al is six times higher than that for ITO/MEH-PPV/Al. In ITO/MEH-PPV/Al device ITO/MEH-PPV contact can be assumed to be ohmic because of low difference between the HOMO level of MEH-PPV and work function of ITO [10]. But MEH-PPV/Al contact is non-ohmic; therefore electrons, which can tunnel through this barrier, can contribute to exciton formation and light emission. When LiF:Al cathode formed over MEH-PPV, Al attacks and dissociates it to form AlF3, releasing metallic Li. Since the Fermi level of Li (work function 3.0 eV) is the same as the LUMO level of MEH-PPV (3.0 eV), Li will dope the MEH-PPV, creating an ohmic contact for electron injection. The higher electron injection will result in a high density of excitons in the active polymer layer and hence higher emission of light will result. This explains why we got higher efficiency by LiF:Al cathodes as compared to simple Al cathode.

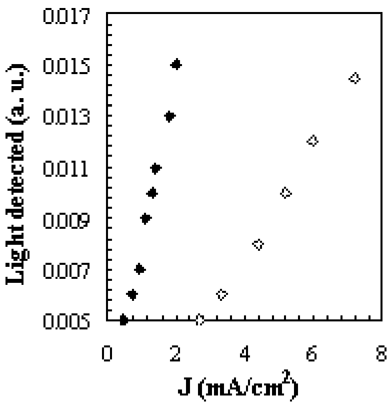
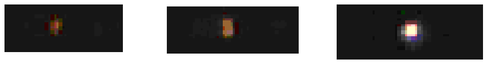


Figure 5: Emitted light intensity recorded by Si photodiode vs. current density flowing through polymer LEDs with Al (◇) and LiF:Al (◆) cathodes in set A.

3.3 Device Set C

In order to visualize the contrast in light emission capabilities of ITO/MEH-PPV/Al, ITO/MEH-PPV/LiF:Al and ITO/MEH-PPV/Alq_3/Al, we made all three types of devices on same MEH-PPV layer and operated all of them at 10V. The photographs of one of these device set is taken using QHM350LM camera at a distance of ~15 cm. These photographs along with the photograph of sample are shown in **Fig. 6**. The results discussed above can be visualized from **Fig.6**. We also observed that light emission from ITO/MEH-PPV/Al and ITO/MEH-PPV/LiF:Al is orange-red but that of ITO/MEH-PPV/Alq_3/Al is greenish.



(A) **(B)** **(C)**

Figure 6: Photographs showing the light emission recorded by camera at 10 V for the devices made on set C viz. (A) ITO/MEH-PPV/Al, (B) ITO/MEH-PPV/LiF:Al and (C) ITO/MEH-PPV/Alq_3/Al.

IV. OBSERVED DEGRADATIONS IN DEVICES

The key element determining the technological impact of PLEDs is their stability. Observations presented in previous sections were done on freshly made PLEDs, but after ~40 days we observed following degradations mechanisms:

1. There is the formation of non-emissive dark spots, which degrades the light-emissive capability of PLEDs. The occurrence of these dark spots believed to be the result of degradation of the metal at polymer/metal interface initiated by pinholes on the cathode in the presence of significant Joule heating [11]. The electromigration of electrode material can also be the reason for these defects as proposed by Cumpston *et. al.* [12]. They proposed that the electromigration of electrode materials might occur in the areas where local conduction is high. This results in the inhomogeneity in the sample and then the loss of electrode continuity.

2. The light-emitting capability of PLEDs is found to degrade with time. There are many reasons, which can be attributed to this degradation. These reasons are summarized below:

   a. The photooxidation of the emissive polymeric layer can degrade the internal efficiency of PLEDs. However, it has been proposed by Yan *et. al.* that only exposure to oxygen cannot degrade the PPV derivatives [13]. The combination of exposure to light and oxygen together, however, leads to the addition of oxygen at the double bond in the vinyl groups [14]. The main source of oxygen is believed to be ITO anode from which oxygen diffuses into the polymeric layer [15].

   b. The migration of indium atoms from ITO, which occurs mainly during the operation of the devices, is also a noticeable problem that causes degradation of the device [16].

   c. Alq_3 is found to be unstable in the +1 oxidative state [17]. The hole migration, therefore, from the MEH-PPV to Alq_3 layer causes degradation when the injected electrons first charge the Alq_3 negatively.

As reported in ref. 18, the hole injection process degrades the ITO/PPV interface. A similar process is also expected at ITO/MEH-PPV interface. However, some methods to improve luminescence, reduce turn-on voltage, and stability in PLEDs have been recently suggested [19].

V. CONCLUSIONS

The light-emitting capability of monolayer polymer LED viz. ITO/MEH-PPV/Al can be enhanced if we insert LiF buffer layer between polymer and Al contact. This is the direct result of enhanced electron injection from LiF:Al cathode. The higher electron injection can also be observed from J-V characteristics of ITO/MEH-PPV/LiF:Al device, which shows a higher current density for

1. ITO/MEH-PPV/LiF:Al device as compared to ITO/MEH-PPV/Al at any given bias.

2. The efficiency of monolayer PLED, ITO/MEH-PPV/Al, can also be increased by using a bilayer structure ITO/MEH-PPV/Alq3/Al. The higher efficiency of bilayer PLED is attributed to balanced charge recombination at MEH-PPV/Alq3 interface. However, inclusion of Alq3 layer results in lower current density as compared to that of ITO/MEH-PPV/Al at any bias voltage.

LIMITATIONS

The present experimental study is performed on PLEDs that were made in open air laboratory atmosphere, however better results are expected with commercial grade equipment with better epoxy protection.

ACKNOWLEDGMENT

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