

Enhancing Carrier Mobility in Organic Light Emitting Diode Based Polyfluorene by Self-Assembled Monolayers Technique on Indium Tin Oxide

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Abstract: An organic compound (1'-4-iodophenyl) trihidroksilane (OH-IPhSi) functionalized as hole transporting material was synthesized and used as interface self-assembled monolayers (SAM) on ITO film. To analyze the effect of a SAM layers on the characteristics an organic light emitting diode (Organic LED), a typical Organic LED device (ITO/OH-IPhSi/polymer/LiF/Al) was fabricated. The SAM-treatment ITO device performed a higher mobility than the bare ITO device. The carrier mobility properties were calculated by space-charge-limited current measurements (SCLC) technique for polyfluorene (PFO) polymer Organic LED devices.

İndiyum Kalay Oksit Üzerinde Kendiliğinden Organize Tek Tabaka Tekniği ile Polifluoren Tabanlı Organik Işık Yayan Diyotun Taşıyıcı Mobilitesinin Geliştirilmesi

Anahtar Kelimeler

Organik LED,
Polifluoren,
Kendiliğinden Organize Tek Tabaka

Özet: Hole taşıma malzemesi olarak işlev gören bir organik bileşik (1'-4-iyodofenil) trihidroksilane (OH-IPhSi) sentezlendi ve indiyum kalay oksit (ITO) anodu üzerinde kendinden organize tek tabaka (KOT) olarak kaplandı. Bir KOT katmanının, bir organik ışık yayan diyot (Organik LED) üzerindeki etkisini araştırmak için, tipik bir Organik LED cihazı (ITO / OH-IPhSi / polimer / LiF / Al) yapılmıştır. KOT ile modifiye edilmiş cihaz, çıplak ITO cihazından daha yüksek bir mobilite göstermiştir. Bunun yanı sıra, yüklerin mobilite özelliklerinin, polifluoren (PFO) polimer Organik LED cihazları için space charge limitli akım (SCLC) tekniği kullanılarak hesaplanmıştır.

1. Introduction

Organic LEDs has become important in recent years owing to the possible applications as commercial devices in organic electronic industry such as mobile phones and display screen etc.[1-4]. The interfacial phenomena is important for performance and stability of an organic LEDs. An assortments of interfacial modifications have been taken to both cathode/organic and anode/organic junctions to enhance the charge injection, and device performance[5]. The modification of indium tin oxide (ITO) anode/hole transport layer (HTL) interface play a significant role about hole injection. One of the novel treatment techniques is to use SAM between anode and HTL. The SAM layer is used for surface modification in order to enhance the carrier mobility and has had a powerful potential to improve the interfacial compatibility between the hydrophilic ITO

and hydrophobic organic layers[6, 7]. Moreover, the other functions of SAMs in Organic LED: as increase the work function of ITO, a current blocking layer and enhance the stability of HTL layer and the adhesion [8, 9].

In this study, we investigated the electrical properties of SAM treatment ITO surface to elucidate the performance of ORGANIC LED devices. The new generation OH-IPhSi -SAM molecule was synthesis to modified ITO surface. Two different standard Organic LED devices were fabricated which is the structure ITO/PFO/LiF/Al and ITO/OH-IPhSi /PFO/LiF/Al to compare their electrical characteristics by means of carrier mobility via SCLC method. SCLC measurements have been used to evaluate carrier mobility under steady state of current in an organic layer [10-12].

2. Material and Method

2.1. Materials and Preparation of ITO

The polyfluorene (PFO, 99%) and ITO films with a surface resistivity of 15-25 Ω /sq were purchased from Sigma Aldrich. Al metal with a purity of 99% was used as cathode contact material in the Organic LED devices. The synthesis of SAM material (a trihydroxysilane derivative) was carried out by a previously published procedure [J. Ohshita, A. Yamashita, T. Hiraoka, A. Shinpo, and A. Kunai, *Polymeric Organosilicon Systems*. 27. Preparation and Reactions of Poly[(ethoxysilylene)phenylenes] and Thermal Properties of the Resulting Polymers, *Macromolecules*, 1997, 30, 1540-1549.] and it is depicted in Scheme 1.

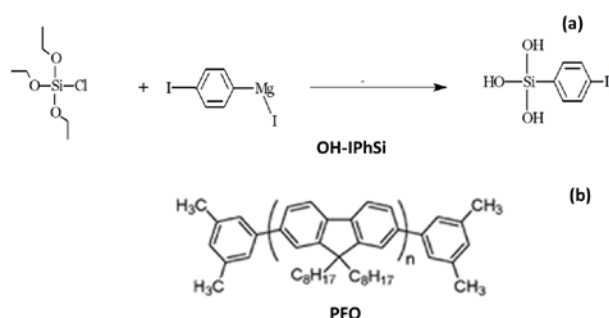


Figure 1. Synthetic pathway and structure of SAM molecule OH-IPhSi (a), and structure of PFO polymer (b).

The aim of the development of the ITO surface is to remove the impurities and to obtain reactive ITO surface as well as to increase the interactions between ITO and SAM interface. In order to refrain to any contamination that may prevent bounding of SAM on ITO, the tools are carefully cleaned in all steps fabricating the device process. The ITO substrates were cleaned by the following procedure; firstly, the films are bathed in an ultrasound solution of ultrapure water for 30 min, and then they are rinsed in pure NaOH (30%) for 20 min after that they are immersed in pure sulphuric acid (98%) during 20 seconds. The final step, the films are rinsed again in an ultrasound bath of ultrapure water for 2 min. These treatments are performed in order to provide ITO surface more hydrophilic and reactive to help formation of SAM properly. ITO coated glasses (2.5x2.5 cm) were kept in 1mM OH-IPhSi chloroform solution for 24 hours in order to let the formation of SAM film on ITO. Then the glasses were rinsed to remove uncoated organic material and then dried slowly by Nitrogen.

2.2. The formation of Organic LED layers

The layers of the Organic LED devices were formed by thermal evaporation. The active polymer polyfluorene (PFO) film is coated by spinning onto the ITO/OH-IPhSi substrate. Metal layer, aluminum (Al), was evaporated at a rate of 1 \AA /s under a base pressure of 5×10^{-6} mbar. The structure of Organic

LED devices are in the configuration of ITO/PFO (70 nm)/LiF(5 nm)/Al (120 nm) and ITO/ OH-IPhSi /PFO (70 nm)/LiF (5nm)/Al (120nm).

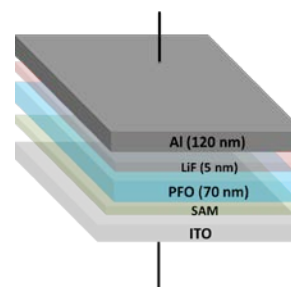


Figure 2. The structure of Organic LED device layer by layer.

3. Result

In our study, Polymer Organic LEDs create lights by various steps as follows. By forward bias, positive charge carrier (holes) are tunneling from the anode to the highest occupied molecular orbital (HOMO) of PFO at the same time negative charge carriers are injected from the cathode to the lowest unoccupied molecular orbital (LUMO) of PFO (Figure 3). In this heterostructure device, interface barrier leads to an injection-limited current. Hole injections is able to be tunneling (Fowler–Nordheim injection) or be thermionic emission injection[13]. As a result, the injection of hole or electrons between layers is the first step to form light. Therefore, enhancing the interface between the contacts and the organic layer becomes critical to obtain better device performance.

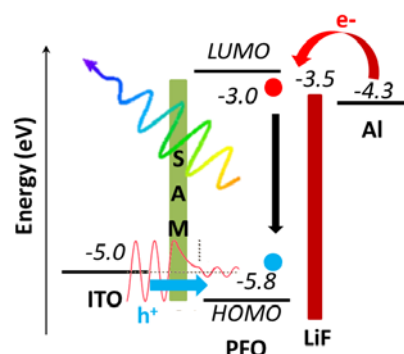


Figure 3. The energy diagram of polymer Organic LED.

Similarly, the matching energy level of each layer is an important point to balance the hole and electrons in emissive layer to enhance the device performance. The problem of the multilayers' structure in Organic LED device is mismatch of energy level may prevent holes and electrons injection from anode and cathode contacts. Modification of ITO anode by SAM and Al cathode by LiF is popular solutions to overcome these kinds of difficulty. SAM-OH-IPhSi form an extra HOMO levels on ITO surface and it is shifted the HOMO level of ITO toward HOMO of PFO after modification. So that OH-IPhSi layer may aid the holes to tunnel from fermi energy level of ITO to the HOMO of PFO (Figure 3.). The easiest way to understand how to SAM layer affect hole injection on

the performance of the Organic LED device is to measure Current-Voltage (I-V) and calculate the hole mobility by Space charge limited current (SCLC).

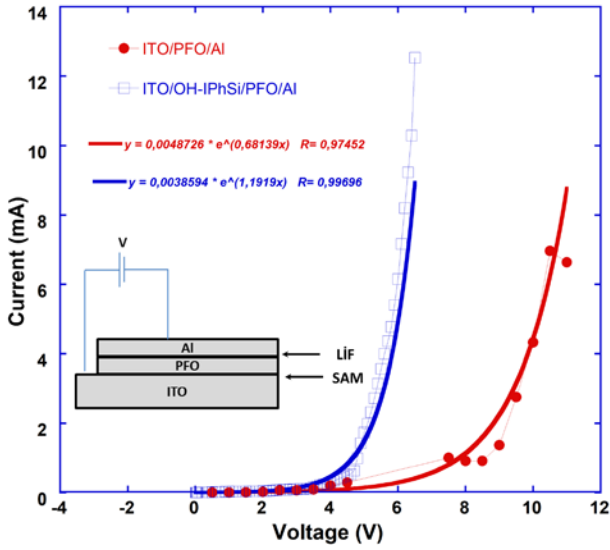


Figure 4. The current (I)-Voltage (V) characteristic of ITO/PFO/LiF/Al and ITO/OH-IPhSi/PFO/LiF/Al Organic LED device.

The current (I)- Voltage (V) characteristics of the Organic LED with and without SAM treatments were shown in Figure 4. The turn-on voltage of the OH-IPhSi- Organic LEDs is lower than bare one that implies the hole injection is increased by SAM interface between ITO and the PFO layer (Figure 4.). The curve of J-V is fitted to see in detail the increasing current density for each device by exponential curve fit. When the current density becomes 1 mA, the voltage of ITO/PFO/LiF/Al and ITO/OH-IPhSi/PFO/LiF/Al is 2 V and 3.1 V, respectively (Figure 5(a)). It can be seen easily from Figure 5(a) that the OH-IPhSi -modified Organic LED device shows higher current density for the same voltage. It means that OH-IPhSi-SAM layer let more holes to get tunneling from ITO to HOMO level of PFO and at the same time the balance of holes and electron are adjusted in emissive layer (PFO layer). As well as the logarithmic curve fit of J-V characteristic data also shows that OH-IPhSi-SAM layer increases hole injections at the interface of ITO and organic layer (Figure 5(b)). The turn-on voltages for both modified ITO with OH-IPhSi and bare ITO devices are compared.

The device shows diode characteristic current that the charges flow is ruled by Ohm's law once the external electric field is less than 10^4 V/cm, injected charge density is less than intrinsic current flow density. That is because the mobilities in organic luminescent materials are low. Charge injection into low mobility organic materials inherently leads to charge accumulations in the organic layer. The formed charge partially keeps out the applied electric field, leading to its redistribution. With the application of high external field ($>10^5$ V/cm), the

injected current density is higher than intrinsic charge density near the electrode/organic interface because of low carrier mobility. Thus, the internal electric field is improved by the space charges and the current density J is governed by the SCLC[11, 12] and can be described as,

$$J = \frac{9}{8} \epsilon \epsilon_0 \frac{E^2}{L} \quad (1)$$

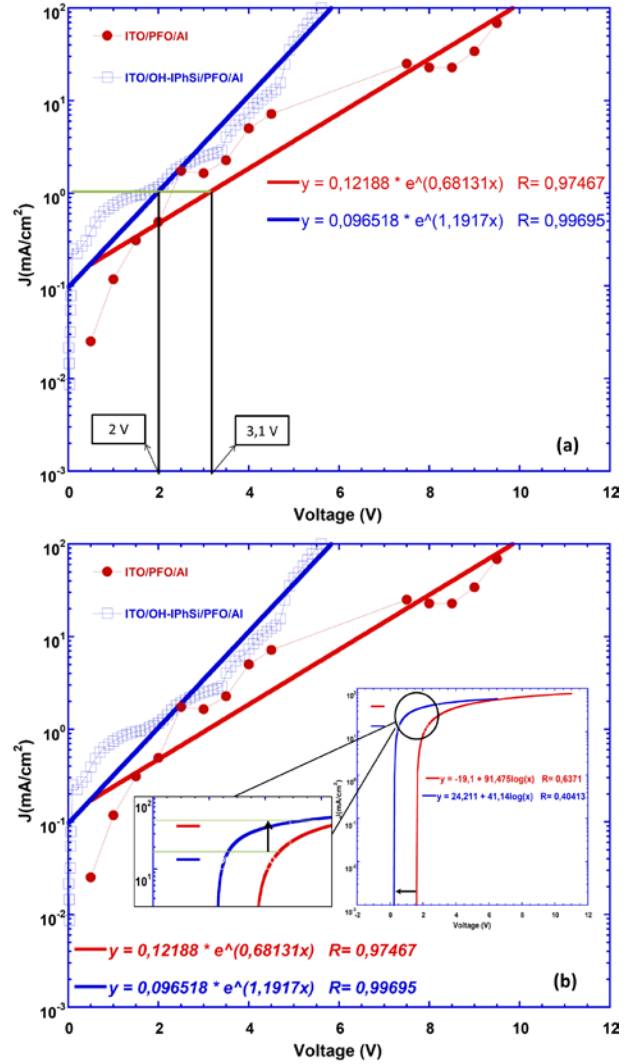


Figure 5. The current density (J)-Voltage (V) characteristic of ITO/PFO/LiF/Al and ITO/OH-IPhSi/PFO/LiF/Al Organic LED device with exponential curve fit (a), and logarithmic curve fit (b).

L is the thickness of the organic layer, ϵ_0 and ϵ are the permittivity of the free space and the relative dielectric constant, respectively (Figure 6(a)). Arbitrarily located dipoles in the organic layers and randomly interaction and collision each charge lead to decreases the hole mobility μ . Thus, the mobility concerning the electric field and is defined by Poole-Frenkel equation[14],

$$\mu(E) = \mu_0 \exp(\beta \sqrt{E}) \quad (2)$$

Table 1. The maximum current, current density, the logarithm of J/E^2 for ITO/ OH-IPhSi/PFO/LiF/Al and ITO/PFO/LiF/Al device

	Turn on Voltage	J (mA/cm ²)	ln J/E ² (900 V/cm ²)	μ (cm ² /Vs)
ITO/PFO/LiF/Al	7	56.5 (7 V)	-31.3	4.5x10 ⁻⁶
ITO/ OH-IPhSi/PFO/LiF/Al	4.5	54.3(4.5 V)	-29.2	4.3x10 ⁻⁷

β is Poole-Frenkel factor and μ_0 is the zero-field mobility. From the combinations of equa. (1) and (2), the field dependent SCLC [15, 16] is described by

$$J = \frac{9}{8} \epsilon \epsilon_0 \frac{E^2}{L} \mu_0 \exp(\beta \sqrt{E}) \quad (3)$$

The carrier mobility is an important parameter for all electronic devices in terms of performance. It is calculated the hole mobility of ITO/ OH-IPhSi/PFO/LiF/Al and ITO/PFO/LiF/Al using SCLC technique (Figure 6(b)).

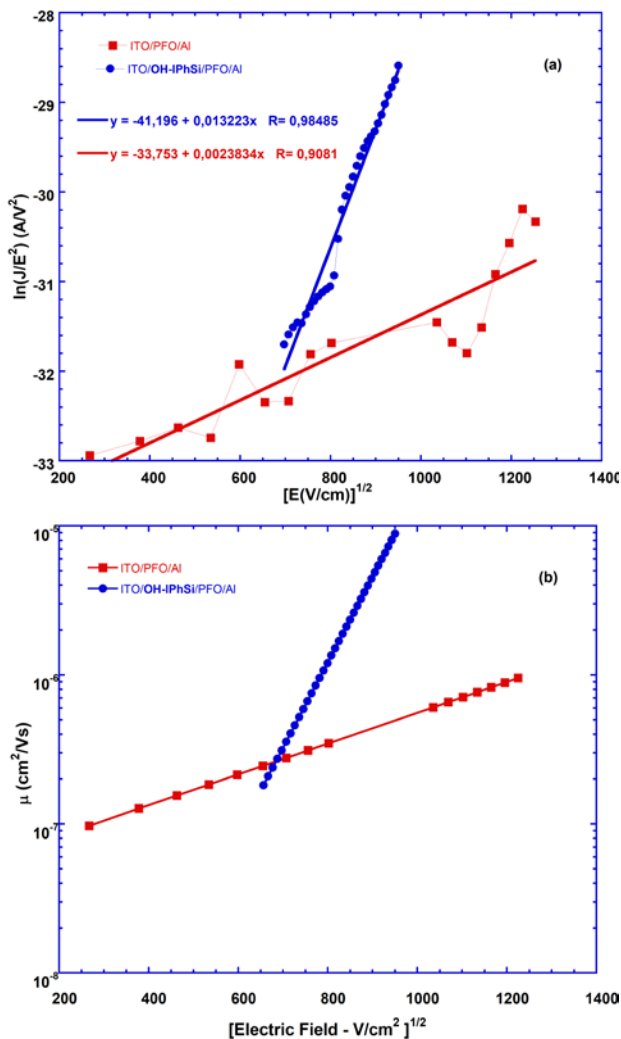


Figure 6. The square root of the applied electric field versus the logarithm of J/E^2 for ITO/ OH-IPhSi/PFO/LiF/Al and ITO/PFO/LiF/Al structure (a), the carrier mobility μ of these devices (b).

4. Discussion and Conclusion

SAM modification on the device leads to have better performance comparing to unmodified one. SAM layer cause lower the barrier of charge injection and

improve the interfacial layers the between metal contacts and organic layer (Figure 3). It is obvious that ITO/OH-IPhSi/PFO/LiF/Al device indicate the current increases faster than nonmodified device by the linear fitting of $\ln(J/E^2)$ curve (Figure 6(a)). There is a correlation between J-V characteristic results and hole mobility result, the carrier mobility is 4.5×10^{-6} cm²/Vs of OH-IPhSi modified Organic LED device and 4.3×10^{-7} cm²/Vs of ITO/PFO/LiF/Al at 900 V/cm electric field. (Figure 6(b)). 10 times higher mobility is obtained by modifying ITO surface with respect to bare one. The literature is showed that the hole mobility of the organic diodes are changes between 10^{-6} and 10^{-3} cm²/Vs under the electric field and all the results are found in this study is consistent with the literature[16-19].

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