

Electrical properties of SAM-modified ITO surface using aromatic small molecules with double bond carboxylic acid groups for OLED applications



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ABSTRACT

5-[(3-Methylphenyl)(phenyl)amino]isophthalic acid (5-MePIFA) and 5-(diphenyl)amino]isophthalic acid (5-DPIFA) organic molecules were synthesized to form self-assembled monolayer on indium tin oxide (ITO) anode to enhance hole transport from ITO to organic hole transport layers such as TPD. The modified surface was characterized by scanning tunneling microscopy (STM). The change in the surface potential was measured by Kelvin probe force microscopy (KPFM). Our Kelvin probe force microscopy (KPFM) measurements showed that the surface potentials increased more than 100 mV with reference to bare indium tin-oxide. The results show that the threshold voltage on OLEDs with modified ITO is lowered significantly compared to OLEDs with unmodified ITO. The hole mobility of TPD has been estimated using space-charge-limited current measurements (SCLC).

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1. Introduction

Technological applications of semiconducting organic light emitting diode (OLED) devices have unquestionable importance. There are many advantages of OLED displays such as more brightness, contrast, resolution, faster response time, larger viewing angle, low consuming energy besides flexible, thin panel applications and incredible light weight. Besides these advantages, many technological milestones have been investigated in detail. These researches are focused to improve performance and stability of OLED displays. The energy level alignment and charge injection in OLED device is a significant step to elucidate these organic semiconductors and to optimize their performance. The weak bonding at the organic/inorganic interface in OLEDs due to incompatible structural difference is one of the limiting parameters for the stability and performance of OLEDs. Therefore one of the most important issues in OLED devices is to be able to control electrode/organic interface and the differences between the work function of the anode (ITO) and HOMO level of the organic semiconducting hole

transport layer (HTL) material. This difference can cause high turn on voltage, low efficiency and restricts hole-injection [1,2]. Recently in literature, self-assembled monolayers (SAMs) are used to establish a compatible interface between hydrophilic ITO surface and hydrophobic hole transport layer (HTL) surface [3,4]. Important improvements have been achieved increasing the stability and efficiency of OLEDs by using SAM technique by chemical covalent bonding with Si group over alkyl chains to TPD molecules and ITO surface [4]. But an exponential decrease in tunneling current was observed due to increase of tunneling barrier distance with increasing alkyl chain length and filled sigma-bond of alkyl chains and lack of π -bond for free carrier transport. It is shown that smaller threshold voltage was obtained in tunneling IV measurements since the charge carrier increases conductivity over the inelastic tunneling mechanism over aromatic molecules with respect to alkyl structures [4]. The π -conjugated molecular structure helps to increase the charge transfer in aromatic groups with respect to alkyl groups. In this work, carbon based aromatic SAM molecules with carboxylic acid functional ends have been synthesized and used to modify ITO surface to enhance charge transport in OLEDs. Three different methods are used to characterize ITO surface. The modified surface was investigated by scanning tunneling microscopy (STM). The change in the surface potential was measured by Kelvin

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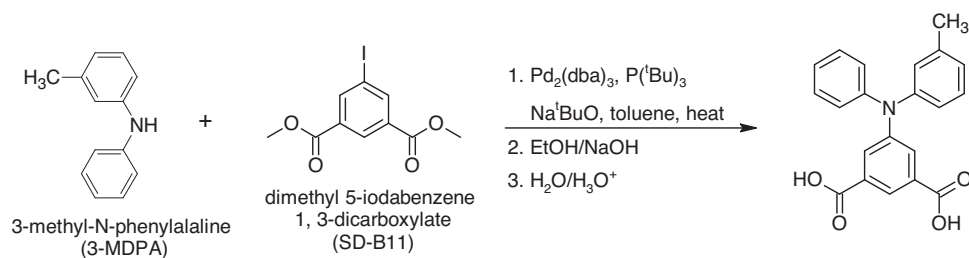


Fig. 1. Synthesis procedure of a double bond carboxylic acid based (MePIFA) SAM molecule.

probe force microscopy (KPFM). The Schottky barrier parameters have been obtained using Richardson thermionic emission analysis. Space-charge-limited current (SCLC) technique [5,6] was used to evaluate carrier mobility under steady state current in an organic layer.

2. Experimental

2.1. Synthesis of SAM molecules

In this work, 5-[(3-methylphenyl)(phenyl)amino]isophthalic acid (MePIFA) and 5-(diphenyl) amino]isophthalic acid (DPIFA) aromatic small molecules with double bond carboxylic acid have been used as self-assembly monolayer (SAM). The synthesis procedures for SAM molecules are described below. For MPPBA molecule, to a solution of dimethyl 5-iodobenzene 1,3-dicarboxylate (0.5 g, 1.56 mmol) and 3-methyl-N-phenylalanine (0.29 g, 1.56 mmol) in toluene (1.5 ml), Na^tBuO (0.18 g, 1.87 mmol), $\text{Pd}_2(\text{dba})_3$ (0.033 g, 36 μmol) and P^tBu_3 (0.032 g, 36 μmol) were added in the given sequence and then followed by adding toluene (1.0 ml) again. After that, while keeping the solution under vigorous mixing, it was heated in oil bath till it reached a temperature of 100 °C and this solution was kept overnight. Thereafter the solution of ammonia (NH_3) (1 N, 15 ml) was added and mixture was stirred at room temperature. This mixture was extracted with chloroform (CHCl_3) (50 ml). At the end, the crude material was obtained and ethanol (18 ml) was added. In an aqueous solution of sodium hydroxide (NaOH) (1 N, 18 ml), this crude material was boiled for an hour. Finally deionized water (22 ml) and hydrochloric acid (HCl) (1 M, 22 ml) were added to the cooled mixture at room temperature. To obtain MePIFA SAM molecule, the collapsing material was collected by filtering and then dried under vacuum (Fig. 1).

For DPIFA molecule, to a solution of dimethyl 5-iodobenzene 1,3-dicarboxylate (0.5 g, 1.56 mmol) and diphenylamine (0.26 g, 1.56 mmol) in toluene (1.5 ml), Na^tBuO (0.18 g, 1.87 mmol), $\text{Pd}_2(\text{dba})_3$ (0.033 g, 36 μmol) and P^tBu_3 (0.032 g, 36 μmol) were added in the given sequence and then again toluene (1.0 ml) was added. After that, while keeping the solution under vigorous mixing, it was heated in oil bath to reach a temperature of 100 °C

and this solution was waited overnight. Thereafter, the solution of ammonia (NH_3) (1 N, 15 ml) was added and the mixture was stirred at room temperature. This mixture was extracted with chloroform (CHCl_3) (50 ml). At the end, crude material was obtained and ethanol (18 ml) was added. In an aqueous solution of sodium hydroxide (NaOH) (1 N, 18 ml) this crude material was boiled for an hour (Fig. 2).

Finally deionized water (22 ml) and hydrochloric acid (HCl) (1 M, 22 ml) were added into the cooled mixture at room temperature. To obtain 5-(diphenyl)amino]isophthalic acid (DPIFA) SAM molecule, the collapsing material was collected by filtering and dried under vacuum.

2.2. Preparing SAM layer

ITO glasses were first cleaned with ultrasonic bath successively for 15 min in detergent solution, and then washed with deionized water, acetone and 2-propanol. After drying in N_2 stream, the substrates were then treated in oxygen plasma for 30 min to activate the ITO surface. ITO glasses were used immediately after oxygen plasma treatment to form SAM. ITO coated glass substrates were dipped into 1 mM methanol solution of MePIFA and DPIFA at 20 °C and kept for 48 h to form SAM on ITO surface. A chemical bonding was constituted on the hydroxyl-rich ITO surface from the carboxylic acid head group of these SAM molecules. The substrates were then rinsed with methanol to remove the residual molecules from the ITO surface and finally dried in a stream of N_2 gas.

2.3. Chemical materials

The ITO coated glass, with a surface resistivity 15–25 Ω/sq , slides were purchased from Sigma Aldrich. Alq_3 (tris-(8-hydroxyquinoline) aluminum) (99.995% trace metals basis, Aldrich) and TPD: [$-\text{C}_6\text{H}_4-4-\text{N}(\text{C}_6\text{H}_4\text{CH}_3)\text{C}_6\text{H}_5$] $_2$ (99%, Aldrich Co.) are used as emitting layer and HTL, respectively, without further purification. In the experiments, Al (evaporation slug, diam., 99% trace metals basis (Aldrich) was used as contact material. We synthesized MePIFA and DPIFA molecules as to form a (SAM) monolayer on an ITO anode.

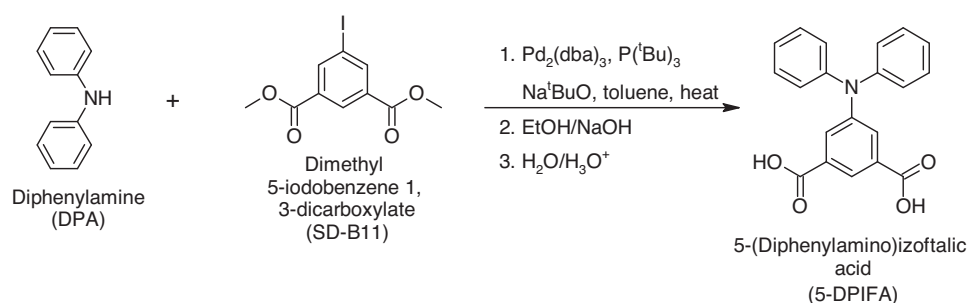


Fig. 2. Synthesis procedure of a double bond carboxylic acid based (DPIFA) SAM molecule.

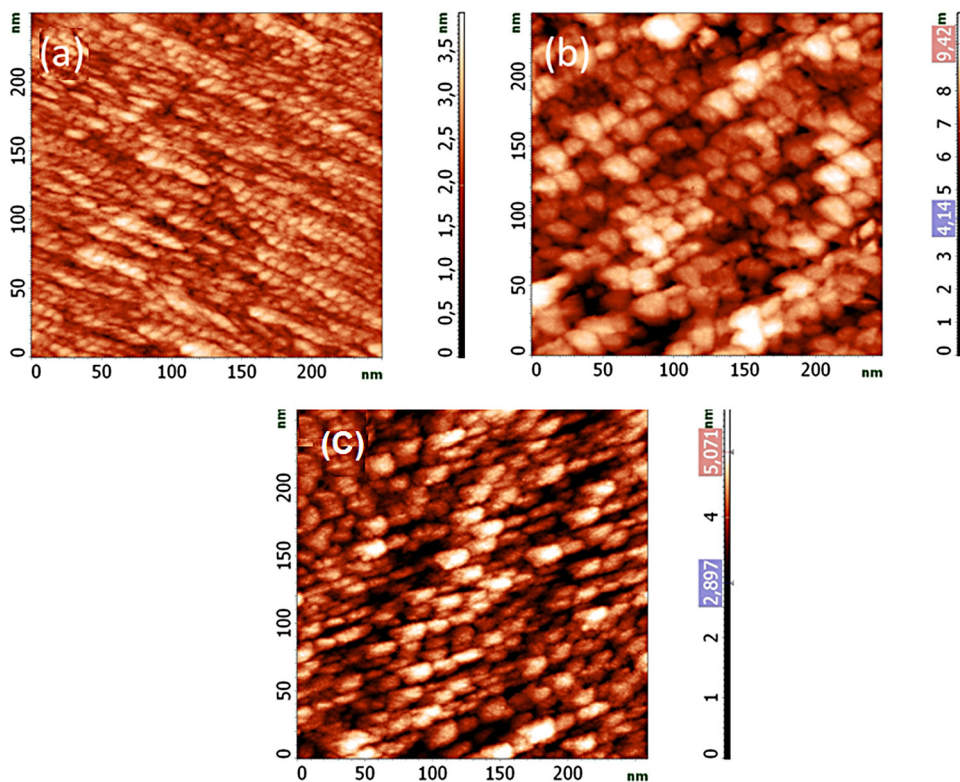


Fig. 3. STM images of bare ITO (a) of DPIFA-modified (b) and of MePIFA-modified ITO (c).

2.4. Fabrication of OLED devices

The SAM-modified ITO substrates were used immediately to prepare the OLED devices. The OLED devices were fabricated in a thermal evaporation coater of model NANOVAK Co., Turkey. Three OLED structures as ITO/SAM (MePIFA or DPIFA)/TPD (50 nm)/Alq₃ (60 nm)/Al (120 nm) and ITO/TPD (50 nm)/Alq₃ (60 nm)/Al (120 nm) without SAM layer were fabricated at same conditions. The organic layers were deposited at a rate of 0.5 Å/s under a base pressure of 4×10^{-5} Pa. High purity Al metal (99%) was thermally evaporated to form the top contact with a thickness of 120 nm in the pressure of 4×10^{-6} Torr. The deposition rate was 3 Å/s for aluminum contacts. The characteristics of the OLED devices were measured immediately by using 2400 KEITHLEY source meter. Ocean optics spectrometer was used to measure the light intensity of the OLEDs.

3. Results and discussion

3.1. STM results and the local contact potential difference via Kelvin probe

Topographic images taken by STM of the bare ITO and SAM-modified ITO substrates are given in Fig. 3(a)–(c). The surface roughness of bare ITO, DPIFA and MePIFA SAM-modified ITO surfaces are obtained as 0.450 nm, 0.963 nm and 0.534 nm, respectively. According to STM images, the SAM-modified ITO surfaces show more roughness compared to that of the bare ITO surface. Since extra formation or aggregation may occur on ITO surface due to both physical and chemical interactions with each SAM molecule. It was thought that methyl group on MePIFA led to form monolayer due to steric effect and this provides less roughness with respect to DPIFA. But DPIFA does not contain methyl group which increases both π – π and van der Waals interactions and these give

rise to formation of multilayers on ITO surface thus the roughness of DPIFA is higher than MePIFA and bare ITO.

Local contact potential difference (CPD) between self-assembled monolayer on ITO substrates and AFM conductive TiN tip was investigated with KPFM. The CPD (V_{CPD}) between TiN tip and sample is defined as follows:

$$V_{CPD} = \frac{\phi_{sample} - \phi_{tip}}{e}$$

where ϕ_{sample} and ϕ_{tip} are the work functions of the sample and TiN tip respectively. According to the equation it is easy to obtain the surface potential changing in terms of eV that is comparable to the work function of ITO and the HOMO level of HTL. Thus the local contact potential difference of bare ITO, ITO-DPIFA and ITO-MePIFA was measured as 0.036 V, 0.151 V and 0.127 V respectively, as shown in Fig. 4 by KPFM technique.

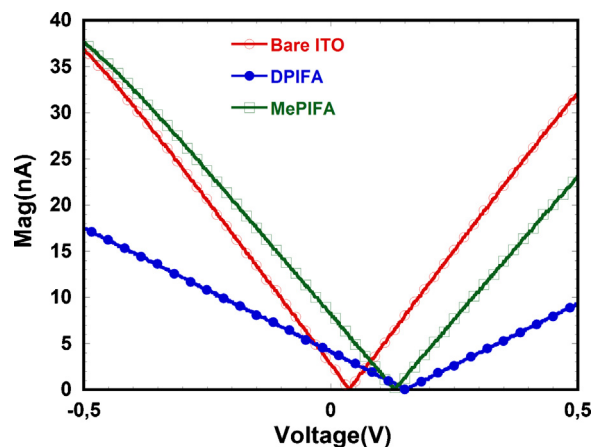


Fig. 4. The local contact potential difference of bare ITO and (ITO-SAM) by KPFM.

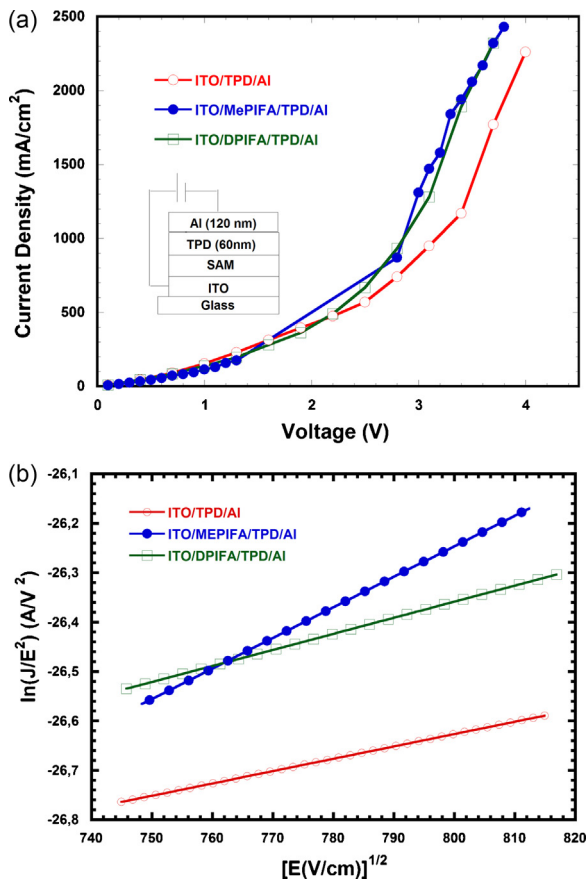


Fig. 5. Current density (J)–voltage (V) characteristic (a) and the logarithm of J/E^2 versus the square root of the applied electric field (b) for ITO/MePIFA/TPD/AI, ITO/DPIFA/TPD/AI and ITO/TPD/AI devices.

3.2. Space-charge-limited current technique

The schematic structure of hole only devices is shown in the inset of Fig. 5(a). The hole only devices with a structure of ITO/MePIFA or DPIFA SAM/TPD (50 nm)/Al (120 nm) were fabricated to compare hole mobility and current density versus voltage characteristic (J – V) of modified and unmodified ITO devices (Fig. 5(a)) by the space charge limited current (SCLC) technique. It can be seen that current density of modified ITO were increased with respect to the unmodified ITO when the ohmic current turn to the space charge limited current [7]. SCLC is expressed as

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{E^2}{L} \quad (1)$$

where E is the electric field, ε and ε_0 are the relative dielectric constant and the permittivity of the free space, respectively, and L is the thickness of the organic layer. The interaction of each hopping charge with randomly oriented dipoles on the surface of ITO occur in energetic disorder. It is one of the important case affecting the carrier mobility μ [8]. Therefore, the mobility depends on the electric field and can be expressed by a Poole–Frenkel equation as

$$u(E) = u_0 \exp(\beta\sqrt{E}) \quad (2)$$

where μ_0 is the zero-field mobility and β is Poole–Frenkel factor. From the combination of Eqs. (1) and (2), the field dependent SCLC can be easily expressed by

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \frac{E^2}{L} u_0 \exp(\beta\sqrt{E}) \quad (3)$$

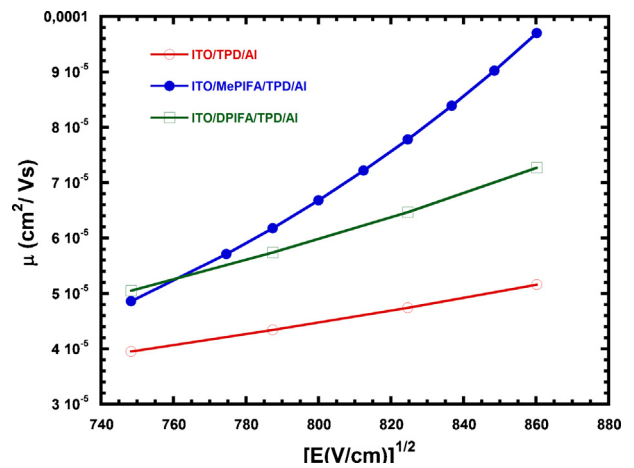


Fig. 6. The carrier mobility μ of ITO/MePIFA/TPD/AI, ITO/DPIFA/TPD/AI and ITO/TPD/AI.

Current density versus voltage characteristic for modified and unmodified devices is shown in Fig. 5(a). The log of J/E^2 versus the square root of the applied electric field on ITO/MePIFA/TPD/AI and ITO/TPD/AI devices is shown in Fig. 5(b).

The $\ln(J/E^2)$ increased with increasing applied electric field (Fig. 5(b)). β (Poole–Frenkel) and μ_0 (zero-field mobility) can be obtained from the slope and intercept of a line fit to the linear part of J/E^2 versus $E^{1/2}$ plots. The values of μ_0 were found as 6.66×10^{-6} , 4.74×10^{-7} and 4.4×10^{-6} cm²/Vs for bare ITO, ITO/MePIFA and ITO/DPIFA, respectively. The values of β were found as 2.3×10^{-3} , 6.1×10^{-3} and 3.2×10^{-3} for bare ITO, ITO/MePIFA and ITO/DPIFA, respectively.

The mobility for MePIFA- and DPIFA-modified devices were increased compared with unmodified device (Fig. 6). For the electric field at 0.8 MV/s, the estimated hole mobility of bare and SAM-modified ITO with MePIFA and DPIFA were found as 4.95×10^{-5} , 6.60×10^{-5} , and 5.94×10^{-5} cm²/Vs, respectively. There is an important enhancement in hole mobility due to modification of SAM molecules. Both MePIFA and DPIFA SAM molecules form extra energy levels between HOMO and LUMO of TPD. That is the reason these energy levels help to increase tunneling in aromatic groups and contribute to increments of hole mobility.

The space-charge-limited current analysis results show that the charge mobility of TPD hole transport material on ITO was increased five times using an aromatic type MePIFA self-assembled monolayer.

3.3. The OLED characteristics

The turn-on voltages of OLED devices by unmodified bare ITO, SAM (MePIFA)-modified ITO and SAM (DPIFA)-modified ITO have been measured as 5 V, 10 V and 12 V, respectively (Fig. 7).

The brightness of OLEDs is achieved under a certain voltage of 18 V in Fig. 8. The extra energy levels between HOMO and LUMO of aromatic SAM molecules with π -conjugated structure led to create extra hole–electron couples at the interface. It helps to increase the EL intensity of SAM-modified OLED device (Fig. 8). Thus, SAM molecules increase the hole transport ITO surface to the HTL materials which is TPD.

The steric effect of the methyl group may as well as affect an uniform SAM-MePIFA layer on the whole surface of ITO [9]. So the device with SAM-MePIFA may increase the hole-current density and enhance the balance of charge carriers. This result indicates that electron–hole pairs for SAM-modified OLED devices

Table 1
The local contact potential difference (CPD) between self-assembled monolayer on ITO substrates and conductive AFM tip ($\Delta\Phi$), conductivity, hole mobility and optoelectronic properties of OLED devices.

Device	Poole–Frenkel factor β	Zero-field mobility μ_0 (cm^2/Vs)	Hole mobility μ (cm^2/Vs)	Surface potential (V)	OLED turn on voltage (V)
Bare ITO	2.3×10^{-3}	6.66×10^{-6}	4.95×10^{-5}	0.036	12
ITO/DPIFA	3.2×10^{-3}	4.40×10^{-6}	5.94×10^{-5}	0.151	10
ITO/MePIFA	6.1×10^{-3}	4.74×10^{-7}	6.60×10^{-5}	0.127	5

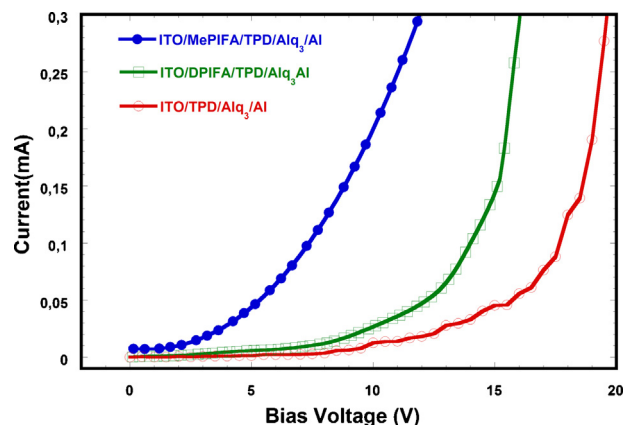


Fig. 7. Current–voltage characteristics for OLED devices made with SAM-modified ITO and bare ITO.

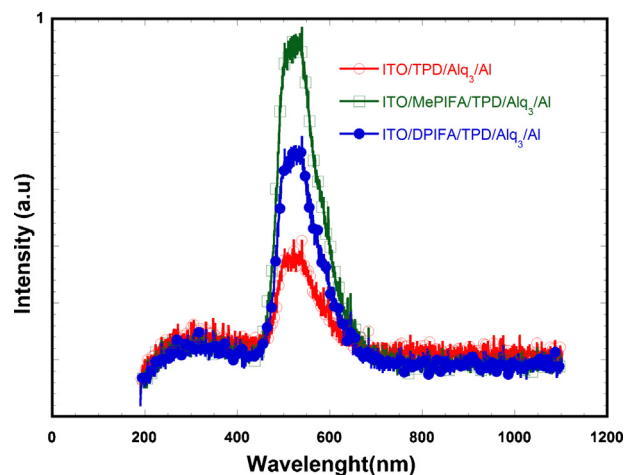


Fig. 8. EL spectrum of the ITO/SAM modified or unmodified/TPD/Alq3/Al devices.

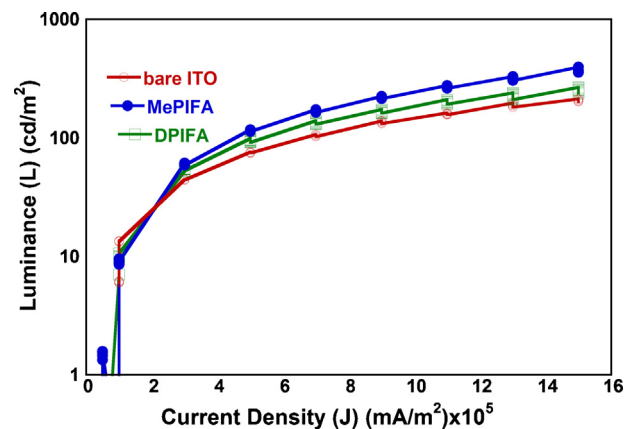


Fig. 9. Luminance (L)–current density (J) characteristics for OLED devices made with SAM-modified ITO and bare ITO.

were increased in the emitting zone, resulting in higher electroluminescence intensity compared to bare device.

Luminance versus current density characteristic for OLED devices made with SAM-modified ITO and bare ITO can be seen in Fig. 9. Luminance of SAM-modified OLED devices were increased compared to bare one. MePIFA and DPIFA SAM molecules have similar structure overlaying to TPD. This singularity of molecular structure helps to increase charge transfer in aromatic groups and provides higher luminance intensity with respect to the bare device. Table 1

4. Conclusions

Self-assembled monolayer (SAM) is used to modify the ITO surface and match the work functions of anode and the organic layers at the interface. Important improvements have been achieved to increase the charge transport in OLED devices by using SAM techniques. We believe that SAM molecules with π -conjugated structure to be used as tunnel barrier at the interface will help to increase tunneling charge density due to extra energy levels between HOMO and LUMO of aromatic molecules with respect to alkyl structures at the interface as a result of inelastic tunneling mechanism. The I – V results show that OLEDs with SAM-modified ITO have lower turn on voltages than OLED configurations without SAMs. The turn-on voltage for the SAM-modified OLED devices decreases for both devices in the order: SAM-modified ITO \leq bare ITO, which implies that the hole injection is enhanced by SAM layer. There are two kinds of effect of SAM modification on the device characteristics. One is the lowering the threshold of charge injection, and the other is the improvement of interfacial contact between the electrode and organics. The possible further optimization of SAM-modified OLEDs and theoretical understanding are under investigation.

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