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Charge transfer through amino groups-small molecules interface improving the performance of electroluminescent devices



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Ali Kemal Havare^{a,*}, Mustafa Can^{b,*}, Cem Tozlu^c, Mahmut Kus^d, Salih Okur^e, Şerafettin Demic^e, Kadir Demirak^e, Mustafa Kurt^f, Sıddık Icli^g

^a Electrical and Electronics Engineering, Toros University, Mersin, Turkey

^b Department of Engineering Sciences, Izmir Katip Celebi University, Izmir, Turkey

^c Department of Energy Systems Engineering, KMU, Karaman, Turkey

^d Department of Chemical Engineering, Selcuk University, Konya, Turkey

^e Department of Materials Science and Engineering, Izmir Kâtip Celebi University, Izmir, Turkey

^f Department of Physics, Ahi Evran University, Kırşehir, Turkey

^g Energy Department, Ege University, Izmir, Turkey

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ABSTRACT

A carboxylic group functioned charge transporting was synthesized and self-assembled on an indium tin oxide (ITO) anode. A typical electroluminescent device [modified ITO/TPD (50 nm)/Alq₃ (60 nm)/LiF (2 nm)/(120 nm)] was fabricated to investigate the effect of the amino groups-small molecules interface on the characteristics of the device. The increase in the surface work function of ITO is expected to facilitate the hole injection from the ITO anode to the Hole Transport Layer (HTL) in electroluminescence. The modified electroluminescent device could endure a higher current and showed a much higher luminance than the nonmodified one. For the produced electroluminescent devices, the I-V characteristics, optical characterization and quantum yields were performed. The external quantum efficiency of the modified electroluminescent device is improved as the result of the presence of the amino groups-small molecules interface.

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1. Introduction

Historical background of the electroluminescent device extends to 1960s, to the observation of electroluminance from organic materials. W. Helfrich and his friends have demonstrated the phenomenon of electroluminance through the process of charge injection, using the electroluminescence of anthracene crystal and a hole and electron injecting electrode [1–4]. These initial studies are considered to be the fundamental studies of the field of organic electronic devices. Possible modifications of inorganic electrodes (anode or cathode) have also attracted much attention in the studies of organic semiconductor devices in the last decade [5–10]. These applications of organic electronic devices are based on different properties of organic/inorganic hetero-junctions with strong chemical interactions [11–13]. In electroluminescent devices, the efficient hole transporting from electrode to the electroluminescence organic material is one of the most critical

parameters [14–16]. The electrodes having a high work function, which prevents the movement of charge carriers between the organic materials and the electrode interface, is one of the main current issues in the design of organic devices [17–19]. The work function of ITO alloy, used in optoelectronic applications and also known as transparent conductive glass, was measured using Kelvin Probe and ultraviolet photon spectroscopy (UPS) and was found to vary between 4.2 and 4.4 eV [20,21]. These values are suitable for enhancing via surface chemical processes, so that the work function of ITO can be further tuned between 3.9 and 5.1 eV. Many studies were performed in recent years focusing on the modifications of ITO surface using different methods, thus achieving the desired levels of the work function [22–25]. Modifying the surface of ITO with self-assembled monolayer (SAM) techniques had been shown to increase the charge transfer at the organic/metal interfaces [26–29]. The work function of ITO can be thus tuned by using SAM between 4.8 and 5.2 eV [30–33]. Particularly to facilitate the transfer of charge carriers with SAM technique, molecular structures with high oxidation potential need to be synthesized. SAM molecules make chemical bound with the groups on the surface of the substrate and thus change their physical and chemical



^{*} Corresponding authors. *E-mail addresses: alikemal.havare@toros.edu.tr* (A.K. Havare), mustafacan80@ yahoo.com (M. Can).

properties. In this way, SAM molecules allow achieving better matching of the organic semiconductor-metal interfaces.

In this work, we synthesized MK116 and MK118 SAM molecules and reported theoretical and experimental works on how MK116 and MK118 SAM molecules affect the performance of electroluminescent devices, as an injection layer at the interface of an organic-HTL/ITO anode electrode. Furthermore, the electrochemical properties of the MK116 and MK118 molecules are obtained with respect to HOMO and LUMO energy levels using cyclic voltammetry (CV), and their photophysical properties are obtained using UV spectrophotometer. Atomic Force Microscopy (AFM) is used to further characterize the surface morphology of SAMmodified ITO.

2. Experimental methods

New molecules with a functional COOH acid group given in Fig. 1 are coated onto ITO surface with SAM technique in this study.

The synthesis of the sensitizers is described below and the synthesis procedure is briefly presented. 1-) Synthesis of 1-(hexyloxy)-4-iodobenzene: A mixture of 4-iodophenol (18 g; 81 mmol), potassium carbonate (15.8 g; 113 mmol), 18-crown-6 (4.3 g; 16 mmol) was prepared in 250 ml of anhydrous acetone. After reaction was heated to 50 °C, bromohexane (15.7 ml; 113 mmol) was added to the solution. Final mixture was refluxed overnight. The organic layer was extracted with equal amount of diethyl ether and distilled water. The solvent was removed under reduced pressure using a rotary evaporator to obtain liquid. The final product was purified by elution with CH₂Cl₂/Hexane on silica gel column (transparent liquid). ¹H NMR (CDCl₃): 7.57 (d, 2H), 6.70 (d, 2H), 3.95 (t, 2H), 1.37 (m, 8H), 0.92 (t, 3H). 2-) Synthesis of 4-bromo-N,N-bis[4-(hexyloxy)phenyl]aniline: A mixture of 4-bromoaniline (4.34 g; 25.2 mmol), 1-(hexyloxy)-4-iodobenzene (19 g; 63 mmol) and KOH, (22 g; 403 mmol), CuI (0.78 g; 4.05 mmol) in 1,10-Phenanthroline (0.73 g. 4.05 mmol) was prepared in anhydrous toluene. The final solution was refluxed for 24 h. After reaction



Fig. 1. Chemical structure and synthesis procedure of the MK-116 and MK-118 molecules.

was cooled down, the residue was repeatedly extracted by 1:1 vol ratio of water-ethyl acetate mixture. The final product was purified by elution with CH₂Cl₂/Hexane (1:5 vol ratio) on silica gel column (yellowish substance). ¹H NMR (CDCl₃): 7.27 (d, 2H), 7.03 (s, 4H), 6.85 (d, 6H), 3.94 (t, 4H), 1.81 (m, 4H), 1.49 (m, 4H), 1.37 (m, 8H), 0.96 (t, 6H). 3-) Synthesis of (4-{bis [4-(hexyloxy) phenyl] amino}phenyl)boronic acid: 4-bromo-N,N-bis[4-(hexyloxy)phe nyl]aniline (2 g; 3.81 mmol) was dissolved in anhydrous THF (10 ml) and the mixture was cooled down –78 °C. n-BuLi (1.6 M; 3.8 mL; 6.11 mmol) was added to solution and the mixture was stirred for 1 h at -78 °C. After the dropwise addition of B(OMe)₃ (4.48 mL; 40 mmol) to the system, final mixture was stirred overnight at room temperature. The reaction was completed and the residue was repeatedly extracted by 1:1 vol ratio of water-ethyl acetate mixture. The final product was purified by elution with Ethylacetate/Hexane (1:1 vol ratio) on silica gel column (White solid substance). ¹H NMR (DMSO-*d*₆): 7.68 (s, 2H), 7.58 (d, 2H), 6.98 (d, 4H), 6.86 (d, 4H), 6.67 (d, 2H), 3.90 (t, 4H), 1.71 (m, 4H), 1.38 (m, 4H), 1.27 (m, 8H), 0.86 (t, 6H). 4-) Synthesis of methyl 4'-{bis [4-(hexyloxy) phenyl] amino}biphenyl-4-carboxylate: (4-{bis [4-(hexyloxy) phenyl] amino}phenyl)boronic acid (245 mg, 0.5 mmol), methyl 4-iodobenzoate (130 mg, 0.5 mmol), Pd(dppf) Cl₂ (15 mg, 0.02 mmol) was dissolved in anhydrous DME (10 mL). After reaction was heated to 50 °C, 2 mL K₂CO₃ (1 M) was added and final solution was stirred at 90 °C for 20 h. The organic layer was extracted with equal amount of water (30 mL)dichloromethane (30 mL) mixture. The solvent was removed under reduced pressure using a rotary evaporator and the final product was purified by elution with CH₂Cl₂/Hexane on silica gel column (Green Substance). ¹H NMR (CDCl₃): 8.10 (d, 2H), 7.63 (d, 2H), 7.47 (d, 2H), 7.11 (d, 4H), 7.01 (d, 2H), 6.87 (d, 4H), 4.43 (m, 3H), 3.97 (t, 4H), 1.89 (m, 4H), 1.51 (m, 12H), 0.99 (m, 6H). 5-) Synthesis of 4'-{bis [4-(hexyloxy) phenyl] amino}biphenyl-4-carboxylic acid (MK-116):A mixture of methyl 4'-{bis [4-(hexyloxy) phenyl] amino}biphenyl-4-carboxylate (0.12 g; 1 mmol) and 1 mL of 2 N NaOH was prepared in 150 ml of anhydrous THF/MeOH solution and the system was refluxed for 3 h. After the reaction was cooled down to room temperature. 1 mL of 2 N HCl was added to system. The solution was filtrated and green particles were collected. ¹H NMR (CDCl₃): 7.79 (d, 2H), 7.18 (d, 2H), 7.10 (d, 2H), 6.87 (d, 4H), 6.77 (d, 2H), 6.69 (d, 4H), 3.81 (t, 4H), 1.71 (m, 4H), 1.41 (m, 4H), 1.32 (m, 8H), 0.89 (t, 6H); FT-IR (KBr, cm⁻¹): -OH, 3465; C=O, 1691; (C-H, aliphatic), 2932 and 2858; C=C-H, 3037; -C=C-, 1600; (C=C, Ph) 1506 and 1473; C-O, 1239.

Synthesis of 4-{bis [4-(hexyloxy) phenyl] amino} phenyl) boronic acid was already mentioned in the procedure of MK-116. 6-) Synthesis of dimethyl 4'-{bis [4-(hexyloxy) phenyl] amino}biphe nyl-3,5-dicarboxylate: A mixture of (4-{bis [4-(hexyloxy) phenyl] amino}phenyl)boronic acid (245 mg, 0.5 mmol), dimethyl 5iodoisophthalate (160 mg, 0.5 mmol), Pd(dppf)Cl₂ (15 mg, 0.02 mmol) was prepared in 12 ml of anhydrous DME. The mixture was heated to 50 °C before the addition of 2 mL K₂CO₃ (1 M). The mixture was refluxed at 90 °C for 26 h. The organic layer was extracted with equal amount of dichloromethane and distilled water. The solvent was removed under reduced pressure using a rotary evaporator to obtain solid. The final product was purified by elution with CH₂Cl₂/Hexane on silica gel column (Green Substance). ¹H NMR (CDCl₃): 8.58 (s, 1H), 8.39 (s, 2H), 7.46 (d, 2H), 7.08 (d, 4H), 7.00 (d, 2H), 6.85 (d, 4H), 3.94 (s, 10H), 1.77 (s, 4H), 1.46 (s, 4H), 1.27 (s, 8H), 0.91 (s, 6H). 7-) Synthesis of 4'-{bis [4-(hexyloxy) phenyl] amino}biphenyl-3,5-dicarboxylic acid (MK-118): A mixture of dimethyl 4'-{bis [4-(hexyloxy) phenyl] amino} biphenyl-3,5-dicarboxylate (0.17 g; 1 mmol) and (1 mL of 2 N) NaOH was refluxed in THF/MeOH solution. After the reaction was cooled to room temperature, (1 mL) 2 N HCl was added to system. The solution was filtered and green particles were collected. ¹H

NMR (CDCl₃): 13.61 (s, 2H), 8.33 (s, 1H), 7.90 (s, 1H), 7.47 (s, 1H), 6.90 (m, 2H), 6.74 (m, 10H), 3.91 (s, 4H), 1.81 (s, 4H), 1.41 (s, 12H), 0.97 (s, 6H); FT-IR (KBr, cm⁻¹): –OH, 3466; C=O, 1702; (C–H, aliphatic), 2933 and 2863; C=C–H, 3040; –C=C–, 1602; (C=C, Ph) 1506 and 1468; C–O, 1239.

2.1. Theoretical and experimental calculations of HOMO-LUMO energy levels

Charge transfer takes place throughout the layer of the electroluminescent device from the Fermi level of the electrode to the HOMO-LUMO energy levels of the materials. The alignment of the work function of the electrode and the energy level of the charge-transport states in the electroluminescent organic material is essential to obtaining efficient and balanced charge injection at low voltages in electroluminescent devices. Determination or calculation of the HUMO-LUMO energy levels of a synthesized molecule is important to decide whether materials are appropriate for a electroluminescent device. The theoretical HOMO-LUMO levels of the MK116 and MK118 are calculated here using **Gaussian 09** program, and the electronic charge distribution is shown in Fig. 2.

As expected, the HOMOs of these molecules were localized mostly on the triphenylamine conjugated part, while the LUMOs mostly existed on the carboxylic acid, neighboring phenyl (or benzene) parts. There is one acceptor molecule-COOH group in the MK-116, while the MK-118 acceptor molecules have two COOH groups. The charge transfers from the triphenylamine group to the COOH acceptor group throughout the molecules on phenyl part. The experimental value of the HOMO energy level of the synthesized compound is obtained here using cyclic voltammetry. The experimental results for MK116 and MK118 molecules are above the theoretical calculations by approximately 0.5 eV.

2.2. Forming the layers of electroluminescent device

First a 1.5×1.5 cm section of ITO glass was cut, and a portion of the ITO layer was then removed with HCl + Zn²⁺ solution to prevent the device from being short circuited. After ITO samples were washed with soapy water, the samples were cleaned in an ultrasonic bath with acetone, isopropanol, ethanol and pure water for 15 min, respectively. Then, The ITO substrates are kept in the SAM solution with 0.1 mM in dimethyl sulfoxide for 3 h at room temperature 25 °C to modify ITO surface with SAM molecules. After cleaning, thermal evaporation technique was used to coat the organic and inorganic materials (electrical contacts). The TPD (50 nm), Alq₃ (40 nm) organic layers and LiF (2 nm), Al (120 nm) electrode layers of device are thermally evaporated on the SAM coated ITO surface under 4×10^{-6} Tor. The TPD and LiF layers are used as hole injection and electron injection layer. The structure of the complete electroluminescent device with the SAM layer, specifically ITO/SAM/TPD/Alq₃/LiF/Al, is shown in Fig. 3.

3. Results and discussion

HOMO energy level of the SAM/ITO surface was determined by cyclic voltammetry and the effect of the SAM molecules with different donor groups containing carboxylic acid derivatives on the charge transfer in electroluminescent device was investigated. The aim of this work was fixed on the heterogeneity problem in the electroluminescent device at the interface of ITO (inorganic) and TPD (organic) layers, using functional π -conjugated SAM molecules. The molecules synthesized for this purpose were critical for the energy-level alignment and significantly affected the balance charge injection in the electroluminescent device.



Fig. 2. The electronic charge distributions of MK116 and MK118 molecules. Molecular orbital diagrams of the calculated HOMO-LUMO energy levels are also shown.



Fig. 3. Fabricated standard electroluminescent device structure; SAM layer is between TPD and ITO anode electrode (ITO/SAM (MK116 or MK118)/TPD/Alq₃/LiF/Al).

3.1. Electrochemical properties by cyclic voltammetry

The cyclic voltammetry measurements of SAM molecules' properties both in liquid phase (in cell) and in solid phase (on ITO surface) were done. These two measurements provided the knowledge about the energy levels between the HTL materials and ITO. The electrochemical properties of MK116 and MK118 molecules were examined using cyclic voltammetry device (CH Instruments model CHI660B). Electrochemical studies were performed in chloroform and DMSO solutions. The scanning process was done with the speeds of 0.1–0.5 V/s.

The oxidation potential of MK116 in cell is 0.80 V and the oxidation potential of the MK118 in cell is 0.82 V (Fig. 4(a)). The point of view of MK118's electron affinity is higher due to the presence of two carboxylic acid groups (COOH) in MK118's chemical structure. This is expected to produce an effective electron transfer by binding the two acid groups of SAM molecules to the active surface of ITO. On the other hand, the oxidation potential of 0.67 V is obtained for MK116 and 0.70 V for MK118 molecules on ITO (Fig. 4(b)). Similar results are expected because of two electron affinity acceptor molecule groups (COOH) of MK118. According to these results, it is found that the presence of electrondonating groups coupled to the triphenylamine backbone reduces the oxidation potential of the molecules and the working potential of ITO. The band gap of the MK116 and MK118 was determined as 2.74 and 3.14, respectively by Gaussian 09 program.

The molecule stability tests of MK118 and MK116 molecules on the ITO surface were also done. These molecules were coated onto ITO, which was then verified by 30-50 cycles using the cyclic voltammetry (Fig. 5). These tests revealed that there was not any degradation of MK118 and MK116 on the ITO surface. HOMO levels for both molecules were calculated from the oxidation potentials. The values calculated for the HOMO levels were located at 5.16 and 5.20 eV, as shown in Table 1. The ITOcoated surface was used as a working electrode for the stability measurement. Modified ITO was used as a working electrode, a platinum wire as a counter electrode, and Ag wire as a reference electrode in acetonitrile supporting electrolyte, and 0.1 M TBAPF6 (tetra butyl ammonium hexa fluoro phosphate) was used in this method. These results showed that the MK116 and MK118 coating is very stable in terms of electrochemical compounds attached to the ITO surface.



Fig. 4. (a) The cyclic voltammetry results of MK116 (blue) and MK118 (red) in cell. (b) The cyclic voltammetry results of MK116 (red) and MK118 (blue) on ITO. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Stability of the SAM molecules on ITO surface determined by the cyclic voltammetry method. The oxidation and the reduction peaks of MK116 (red) and MK118 (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Photophysical properties

Photophysical properties of the synthesized compounds were determined using a UV spectrophotometer (Fig. 6). Absorption spectra of MK116 and MK118 molecules exhibited two distinct regions in the range of 300-450 nm (~UV region), attributed to

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Theoretical (HOMO-LUMO) and experimental (HOMO) energy levels.

Materials	Oxidation peak potentials (V)	Theoretical values ^a (eV)			Experimental values ^b (eV)
		Еномо	E _{LUMO}	$E_{gap}$	Еномо
MK116	$E_{Cell}^{ox} = 0.80$ $E_{TTO}^{ox} = 0.67$ (reversible)	-4.73	-1.33	2.74	-5.16
MK118		-4.69	-1.55	3.14	-5.20

^a Gaussian 09, 6-31G(d) set.

^b CH Instruments CHI660B cyclic voltammetry.



Fig. 6. Absorption graphs of the synthesized MK116 and MK118 molecules.

 $\pi$ - $\pi$ * transitions and intramolecular charge transfer between carboxyl acceptor group and triphenylamine-donor group localized conjugated structures [34–36]. MK118 (340 nm) shows hypsochromic(=blue) shift in absorption compared with MK116 (360 nm). This shift is due to the electron-donating effect of the attached triphenylamine donor group. The carboxyl-acceptors group is bonded to the ITO surface. The donor part of these molecules is known as hole transport materials (HTM). The HTMs usually make the absorption at UV region. According to the absorbance result, maximum absorption of the compounds was found to be below the visible region (<450 nm).

#### 3.3. Surface analysis of MK116 and MK118 layers

In this study, ITO surface was characterized using AFM and cyclic voltammetry. For determining the surface properties of the synthesized compounds, Ambiose Q-Scope 250 atomic force microscope was used. SAM molecules bind spontaneously to the ITO substrate in the solution prepared with specific concentration. Van der Waals force between SAM molecules enacts tilting of the molecules on the surface and, thus, the formations become a regular structure [37,38]. SAM molecules consist of functional groups with conjugated structure and charge transfer takes place via this structure. Oxide on the surface of ITO (XO₂) layer is wet etching or activated by oxygen plasma techniques. Hydroxyl groups on ITO surface and acidic functional groups in MK116 and MK118 molecule make strong chemical bond via COOH in solution during self-assembly (ester bond) and arrange properly on the surface [39]. Fig. 7 shows the AFM images of a bare ITO and a SAMmodified ITO. The observed RMS roughness before and after selfassembly was nearly identical, 8.6 nm for the bare ITO (Fig. 7(c)), 35.6 nm for MK116 (Fig. 7(a)) and 26.2 nm for MK118 (Fig. 7(b)), indicating that a uniform and flat layer is formed during the selfassembly process.

# 3.4. Electrical and optical characterization of electroluminescent devices

I-V characteristic of the electroluminescent device was done by using Keithley 236 and 6517. The optical properties of the electroluminescent device were measured by "QE65000 Ocean Optics" instrument. Characterization of the electroluminescent device (luminance and external quantum efficiency) was performed using the scavenger cells (integrating sphere). The external quantum



Fig. 7. AFM image of ITO modified with MK116 (a), MK118 (b) and bare ITO (c).

efficiency  $\eta_{ext}$  is found in terms of (cd/A) [40]. SAM molecules improved the performance of electroluminescent device in terms of turn-on voltage, luminance, and external quantum efficiency. According to this, the turn-on voltage of the electroluminescent device with the SAM molecules is 1.8 V for MK118, 1.8 V for MK116 and 7.0 V for bare ITO. The amino groups of the SAM structures facilitate the hole injection from the fermi energy level of ITO to HOMO level of TPD, as well as the similarity of chemical structure between MK116-MK118 and TPD increases the hole injection. As expected, the highest EQE is obtained as 7.07 (cd/A) from MK118 modified electroluminescent device. The measured EQE values of the devices are plotted in Fig. 8(a) against the current (mA), and the results are summarized in Table 2.

From I-V results the turn-on voltage of MK116 and MK118 electroluminescent devices is lower than the bare one. This is due to the chemical structure of SAM interface and the structure of TPD being similar to each other. In view of energy band level window,



Fig. 8. The current-voltage results of the configuration of ITO/SAM/TPD/Alq₃/LiF/Al and external quantum efficiency results of the electroluminescent devices (a), the luminance results of the electroluminescent devices (b).

 Table 2

 The optoelectronic results of electroluminescent devices.

Device	Max luminance (cd/m ² )	Turn on voltage (V)	n _{ext} , Ex. quantum efficiency (EQE, cd/A) [40]
Bare ITO	57	7.00	0.47
ITO/MK116	1100	1.80	5.27
ITO/MK118	1390	1.80	7.07



Fig. 9. The color space chromaticity diagram for the SAM modified electroluminescent device. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the MK116 and MK118 interface layers formed extra HOMO energy levels on ITO and are measured as 5.16 eV and 5.20 eV. These energy levels take place between the ITO work function (4.8 eV) and the HOMO level of TPD (5.5 eV). In that case, the SAM interfaces in electroluminescent device help charge injection from ITO to HOMO energy level of TPD. Furthermore, because of the similar structure to TPD, the SAM layer decreases the defect at the interface and increases the charge carrier tunneling over  $\pi$ - $\pi$ * transitions.

According to luminance results, MK118-modified electroluminescent device shows the best performance (4 V, 1390 cd (Fig. 8 (b)). It is known that the efficient and balanced charge injection depends on the balance of electrons and holes on both sides of the electrodes in an electroluminescent device. In the literature, the hole mobility is shown to be lower than the electron mobility in organic semiconductors [41,42]. That is why we focused on the increase in the hole injection at the anode side of the electroluminescent device. In that point, TPD contains amino group known as an HTL material. The electronic and geometric structure of MK116 and MK118 is similar to TPD material due to the amino and phenyl groups. This structure is adequate to form an interface between ITO and TPD. This SAM modification leads to changing the surface energy of ITO and HOMO level of MK116 and MK118 to be closer to the HOMO level of TPD. Thus, the holes can tunnel more easily from the SAM layer to the HTL layer. In that case, the SAM modified molecules containing triphenylamine group allow the electroluminescent device to increase hole injection. The luminance-voltage of SAM modified electroluminescent device corresponds well with the idea described above. Luminance of MK116 and MK118 modified electroluminescent devices is higher than unmodified electroluminescent device (Fig. 8(b)). The differences between MK116 and MK118 are only in the number of carboxylic acid functional groups. The positions at 3 and 5 of two COOH groups at MK118 bond to ITO surface stronger than MK 116, which has only one carboxylic group. Furthermore, the electron affinity and  $\pi$ -conjugated bonds of the two carboxylic groups in MK118 produce more charge injection in comparison with MK116, which has only one COOH group. All of the above reasons show that MK118 enables better performance than MK116 in terms of the device's I-V characteristic, luminance and quantum efficiency.

The CIE XYZ color space was deliberately designed so that the Y parameter was a measure of the brightness or luminance of a color. The chromaticity of a color was then specified by the two derived parameters X and Y. In order for a electroluminescent device to be agreeable as an illumination source, it clearly must supply high-illumination-quality light source. We fabricated a typical green color electroluminescent device by using Alq₃ material as emissive layer. Alq₃ is well known in the literature as a green color material because of its high stability and good carrier transport properties [43]. The color space chromaticity diagram is given in Fig. 9 and the (X, Y) values were obtained as (0.26, 0.72) and the values are compatible with the literature [44,45]. Furthermore, it is possible to improve the purity green color by doping Alq₃ with different dopants materials [43]. It would allow to achieving green OLEDs exhibiting good color purity and high luminescence efficiency.

### 4. Conclusions

As result, we focus on the effects of SAM interface on electroluminescent devices. Experimental results have shown that the improvement of charge transfer increases the performance of the electroluminescent device. The SAM-modified device could endure a higher current and showed a much higher luminance (1390 cd/  $m^2$ ) than the bare ITO device (57 cd/m²). The external quantum efficiency was shown to improve as the result of the presence of the SAM. The SAM molecules changed the work function of ITO after the modification. Therefore, the Fermi energy level of ITO approached the HTM material's HOMO energy level, so that the HOMO energy level of HTM (TPD) material (~5.4 eV) became closer to the work function of ITO used in the electroluminescent device. These results are consistent with the results obtained with the Kelvin Probe Microscopy (KPM) technique [46] and demonstrate that the ITO surface can be modified with SAM molecules.

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#### **Appendix A. Supplementary material**

¹H NMR spectra of initial compounds and MK molecules. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.optmat.2016.03.020.

#### References

- [1] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913-915.
- [2] M.A. Baldo, D. O'brien, Y. You, A. Shoustikov, S. Sibley, M. Thompson, S. Forrest, Nature 395 (1998) 151-154.
- [3] S. Van Slyke, C. Chen, C. Tang, Appl. Phys. Lett. 69 (1996) 2160–2162.
  [4] W. Helfrich, W. Schneider, Phys. Rev. Lett. 14 (1965) 229.
- [5] D. Boudinet, M. Benwadih, Y. Qi, S. Altazin, J.-M. Verilhac, M. Kroger, C. Serbutoviez, R. Gwoziecki, R. Coppard, G. Le Blevennec, Org. Electron. 11 (2010) 227-237
- [6] C.-G. Lee, S. Park, R.S. Ruoff, A. Dodabalapur, Appl. Phys. Lett. 95 (2009) 023304.
- [7] H. Ma, H.L. Yip, F. Huang, A.K.Y. Jen, Adv. Funct. Mater. 20 (2010) 1371–1388.
- [8] H. Park, P.R. Brown, V. Bulović, J. Kong, Nano Lett. 12 (2011) 133-140.
- [9] T.M. Khan, Y. Zhou, A. Dindar, J.W. Shim, C. Fuentes-Hernandez, B. Kippelen, ACS Appl. Mater. Interf. 6 (2014) 6202-6207.
- [10] F. Kaschura, A. Fischer, D. Kasemann, K. Leo, B. Lüssem, Appl. Phys. Lett. 107 (2015) 033301.
- [11] P.J. O'Brien, S. Shenogin, J. Liu, P.K. Chow, D. Laurencin, P.H. Mutin, M. Yamaguchi, P. Keblinski, G. Ramanath, Nat. Mater. 12 (2013) 118-122.
- [12] T. Satoh, M. Imanishi, T. Nishikawa, T. Mori, Jpn. J. Appl. Phys. 51 (2012) 035701.
- [13] M. Knupfer, H. Peisert, Phys. Status Solidi (A) 201 (2004) 1055-1074.
- [14] R.A. Hatton, S.R. Day, M.A. Chesters, M.R. Willis, Thin Solid Films 394 (2001) 291-296.
- J. Lee, B.-J. Jung, J.-I. Lee, H.Y. Chu, L.-M. Do, H.-K. Shim, J. Mater. Chem. 12 [15] (2002) 3494-3498.

- [16] M.S. Kim, Y.P. Jeon, Y. Kim, J. Noh, T.W. Kim, J. Nanosci. Nanotechnol. 15 (2015) 5062-5065
- [17] B. Delgertsetseg, N. Javkhlantugs, E. Enkhtur, Y. Yokokura, T. Ooba, K. Ueda, C. Ganzorig, M. Sakomura, Org. Electron. 23 (2015) 164-170.
- [18] H. Lei, P. Qin, W. Ke, Y. Guo, X. Dai, Z. Chen, H. Wang, B. Li, Q. Zheng, G. Fang, Org. Electron. 22 (2015) 173-179.
- [19] L. Lindell, C. Vahlberg, K. Uvdal, M. Fahlman, S. Braun, J. Elect. Spectrosc. Relat. Phenom. 204 (2015) 140-144.
- [20] Y. Park, V. Choong, Y. Gao, B. Hsieh, C. Tang, Appl. Phys. Lett. 68 (1996) 2699-2701.
- [21] J. Kim, B. Lägel, E. Moons, N. Johansson, I. Baikie, W.R. Salaneck, R. Friend, F. Cacialli, Synth. Met. 111 (2000) 311-314.
- [22] J.S. Kim, J.H. Park, J.H. Lee, J. Jo, D.-Y. Kim, K. Cho, Appl. Phys. Lett. 91 (2007) 112111.
- [23] C. Ganzorig, K.-J. Kwak, K. Yagi, M. Fujihira, Appl. Phys. Lett. 79 (2001) 272-274
- [24] H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, Science 345 (2014) 542-546.
- [25] S.A. Paniagua, E. Li, S.R. Marder, Phys. Chem. Chem. Phys. 16 (2014) 2874-2881.
- [26] P.J. Hotchkiss, S.C. Jones, S.A. Paniagua, A. Sharma, B. Kippelen, N.R. Armstrong, S.R. Marder, Acc. Chem. Res. 45 (2011) 337-346.
- [27] S. Das, J. Joslin, T. Alford, Sol. Energy Mater. Sol. Cells 124 (2014) 98-102.
- [28] W. Brütting, Semiconductors 6 (2005) 1-11.
- [29] S.K. Hau, H.-L. Yip, H. Ma, A.K.-Y. Jen, Appl. Phys. Lett. 93 (2008) 233304. [30] C.-C. Hsiao, C.-H. Chang, M.-C. Hung, N.-J. Yang, S.-A. Chen, Appl. Phys. Lett. 86 (2005) 223505.
- [31] N. Koch, A. Kahn, J. Ghijsen, J.-J. Pireaux, J. Schwartz, R. Johnson, A. Elschner, Appl. Phys. Lett. 82 (2003) 70-72.
- [32] J. Huang, P.F. Miller, J.S. Wilson, A.J. de Mello, J.C. de Mello, D.D. Bradley, Adv. Funct. Mater. 15 (2005) 290-296.
- [33] N. Koch, A. Vollmer, Appl. Phys. Lett. 89 (2006) 162107.
- [34] F. Zhang, Y.-H. Luo, J.-S. Song, X.-Z. Guo, W.-L. Liu, C.-P. Ma, Y. Huang, M.-F. Ge, Z. Bo, Q.-B. Meng, Dyes Pigm. 81 (2009) 224-230.
- [35] S. Qu, B. Wang, F. Guo, J. Li, W. Wu, C. Kong, Y. Long, J. Hua, Dyes Pigm. 92 2012) 1384-1393.
- [36] Y. Hong, J.-Y. Liao, J. Fu, D.-B. Kuang, H. Meier, C.-Y. Su, D. Cao, Dyes Pigm. 94 (2012) 481-489.
- [37] J.L. Fajín, F. Teixeira, J.R. Gomes, M.N.D. Cordeiro, Theoret. Chem. Acc. 134 (2015) 1–13.
- [38] T. Toledano, H. Sazan, S. Mukhopadhyay, H. Alon, K. Lerman, T. Bendikov, D.T. Major, C.N. Sukenik, A. Vilan, D. Cahen, Langmuir 30 (2014) 13596-13605.
- [39] D. Aswal, S. Lenfant, D. Guerin, J. Yakhmi, D. Vuillaume, Anal. Chim. Acta 568 2006) 84-108.
- [40] S.R. Forrest, D.D. Bradley, M.E. Thompson, Adv. Mater. 15 (2003) 1043-1048.
- [41] B. Sun, W. Hong, Z. Yan, H. Aziz, Y. Li, Adv. Mater. 26 (2014) 2636-2642.
- [42] C. Kanimozhi, N. Yaacobi-Gross, K.W. Chou, A. Amassian, T.D. Anthopoulos, S. Patil, J. Am. Chem. Soc. 134 (2012) 16532-16535.
- [43] M.-Y. Chang, Y.-K. Han, C.-C. Wang, S.-C. Lin, Y.-J. Tsai, W.-Y. Huang, J. Electrochem. Soc. 155 (2008) J365–J370.
- [44] P.N. Prasad, J.E. Mark, S.H. Kandil, Z.H. Kafafi, Science and Technology of Polymers and Advanced Materials: Emerging Technologies and Business Opportunities, Springer Science & Business Media, 2013.
- [45] A. Buckley, Organic Light-Emitting Diodes (OLEDs): Materials, Devices and Applications, Elsevier, 2013,
- [46] A.K. Havare, M. Can, S. Demic, S. Okur, M. Kus, H. Aydın, N. Yagmurcukardes, S. Tari, Synth. Met. 161 (2011) 2397–2404.