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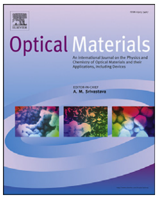

Functionalized organic semiconductor molecules to enhance charge carrier injection in electroluminescent cell

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ABSTRACT

Organic semiconductor (OSC) materials as a charge carrier interface play an important role to improve the device performance of organic electroluminescent cells. In this study, 4,4″-bis(diphenyl amino)-1,1':3′,1″-terphenyl-5'-carboxylic acid (TPA) and 4,4″-di-*9H*-carbazol-9-yl-1,1':3′,1″-terphenyl-5'-carboxylic acid (CAR) has been designed and synthesized to modify indium tin oxide (ITO) layer as interface. Bare ITO and PEDOT:PSS coated on ITO was used as reference anode electrodes for comparison. Furthermore, PEDOT:PSS coated over CAR/ITO and TPA/ITO to observe stability of OSC molecules and to completely cover the ITO surface. Electrical, optical and surface characterizations were performed for each device. Almost all modified devices showed around 36% decrease at the turn on voltage with respect to bare ITO. The current density of bare ITO, ITO/CAR and ITO/TPA were measured as 288, 1525 and 1869 A/m^2, respectively. By increasing current density, luminance of modified devices showed much better performance with respect to unmodified devices.

1. Introduction

Electroluminescent devices have a great interest during the past decade because of its advantages such as self-emission, wide viewing angle, low driving voltage, high efficiency, flexibility and especially potential applications in solid state lighting [1,2]. During this time, various methods have been used to enhance the efficiency. However, in order to get high efficiency from an OLED and electroluminescent cell devices, electrons and holes should be efficaciously injected from the corresponding electrodes into organic layers [3]. It is well known that a barrier has been occurred at the metal/organic interface of the devices because of the different energetic alignments of the metal work function and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the organic components. Reducing the energy barrier between the interfaces are desirable for higher charge injections and better charge recombinations [4,5]. That is the more charge injection, the increased chance of forming excitons and the more brightness [5].

Indium tin oxide (ITO) has been widely used as anode electrode in electroluminescent devices because of its low resistivity ($\sim 2 \times 10^{(-4)}$ Ω cm), high transparency (~90% at 550 nm) and high work function (~4.8 eV) [6–8]. In such devices, surface conditions of ITO has significant effects on turn on voltage, current efficiency and operation stability [9,10]. In this regard, there is an intense interest in modification of ITO to solve the contact problem between metal/organic interface [11,12]. Therefore, various methods have been used to modify ITO surface by different treatments,

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namely oxygen plasma [13,14], ultraviolet-ozone [15,16], poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)(PEDOT/PSS) [17], self-assembled monolayers (SAMs) [18,19] and ultra-thin buffer layer such as MoO3 [20,21], WO_3 [22], p-dopant [23]etc.

Recently, treatments with SAM molecules have been used to solve the contact problem between hydrophilic ITO surface and hydrophobic hole transport layer (HTL) [16,24]. SAM molecules are ultrathin films and formed on ITO surface by strong covalent bonding [25,26]. Furthermore, other function of SAM molecules in organic electronic applications were reported in literature as current blocking layer or a moisture penetration blocking layer [27,28], changing the work function of ITO [29,30], enhance charge injection rate [31], reduce the turn on voltage [32] and improve the adhesion between interfacing materials [31] and stability of hole transport layer [33,34].

In this paper, ITO was treated with OSC molecules to change the work function of ITO for a better charge injection and solve the contact problem between ITO and TPD [31,33,35]. However, the molecules may not be completely covered on ITO surface. Therefore, PEDOT:PSS was coated on SAM treated ITO surface to observe the change in device performance and the stability of SAM molecules. Beside, bare ITO and PEDOT:PSS coated onto ITO layer was used as reference devices for comparison.

2. Experimental

2.1. Synthesis of TPA

Suzuki cross-coupling procedure was used for the synthesis of this component. Methyl 3,5-dibromobenzoic acid (0.40 g, 0.62 mmol), 4-(diphenyl amino)phenylboronic acid (0.91 g, 1.35 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), and K_2CO_3 (0.69 g, 5.00 mmol) were dissolved in DME. Then the complete solution was degassed for 30 min and refluxed for 16 h under argon atmosphere. The reaction medium was cooled to room temperature and then extracted with dichloromethane. The organic phase was washed with water and brine solution, dried over sodium sulfate. Finally organic solvent was evaporated and the residue was purified by silica gel column chromatography (hexane: ethyl acetate, 1:2). A mixture of (4,4″-bis(diphenylamino)-(1,1’:3′,1″-terphenyl)-5’-yl)(methyl ester) (0.17 g; 1 mmol) and (1 mL of 2 N) KOH was refluxed in THF/MeOH mixture. After that the resulting mixture was cooled to room temperature, and then 2 N HCl (1 mL) was added to this mixture. The solution was filtered and the product was collected by filtration. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 8.23 (dd, H), 7.67–7.71 (dd, 2H), 7.56–7.59 (m, 8H), 7.41–7.43 (s, 8H), 7.10–7.12 (m, 12H).

2.2. Synthesis of CAR

Compound CAR was synthesized by the following procedure described above for TPA molecule, by mixing 3,5-dibromobenzoic acid (0.40 g, 0.62 mmol), 4-(9H-carbazol-9-yl)phenylboronic acid (0.86 g, 1.33 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), and K_2CO_3 (0.69 g, 5.00 mmol). The crude product obtained, (4,4″-di(9H-carbazol-9-yl)-(1,1′:3′,1″-terphenyl)(methyl ester) (0.17 g; 1 mmol), and KOH (1 mL of 2 N) were refluxed in THF/MeOH solution. After cooling to room temperature, 2 N HCl (1 mL) was added to the resulting solution. The final suspension was filtered and the final product was collected by filtration. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.51(dd, H), 8,30–8,34 (dd, 4H), 8,00–8,04 (m, 6H), 7.70–7.65 (m, 16H).

2.3. Materials

4,4″-Bis(diphenylamino)-1,1′:3′,1″-terphenyl-5'-carboxylic acid (TPA) and 4,4″-di-*9H*-carbazol-9-yl-1,1′:3′,1″-terphenyl-5′-carboxylic acid (CAR) molecules (Fig. 1) were used as SAM materials. They were synthesized in the laboratory as described above. Beside the SAM materials, PEDOT:PSS was used as a reference hole injection layer. In addition, N,N′-diphenyl-N,N′-bis(3-methyphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) and tris-(8-hydroxyquinoline) aluminum (Alq_3) were used as HTM and EML respectively. Moreover, ITO and aluminum were used as anode and cathode materials, respectively.

2.4. ITO cleaning and activation

The ITO surface was sonicated in deionized water, acetone and isopropanol for 20 min, respectively. After that, ITO surface was

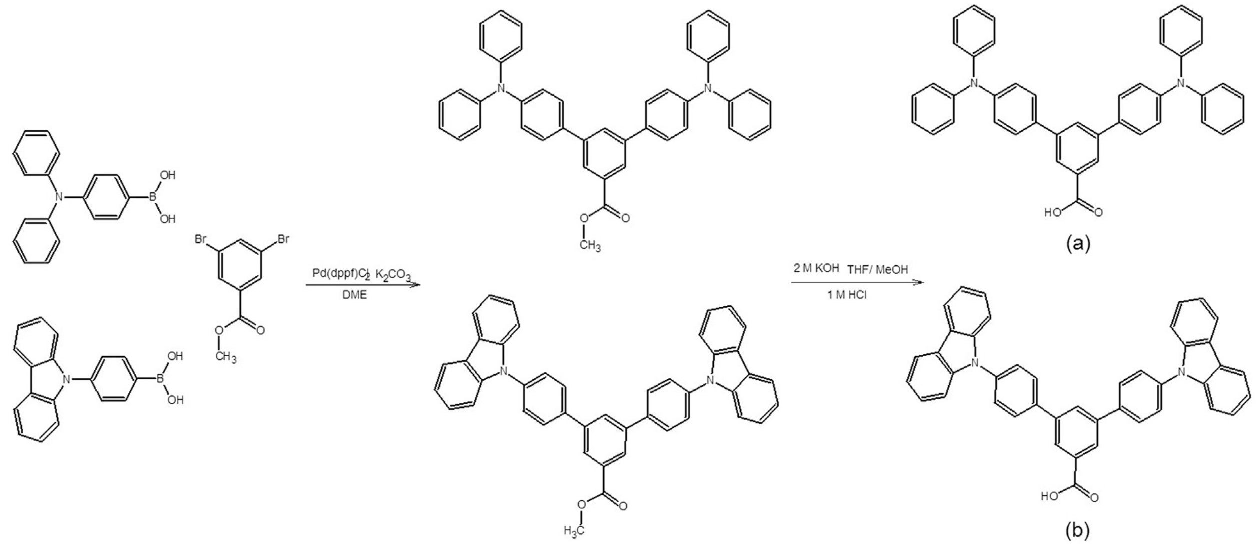

Fig. 1. Chemical structure of TPA (a) and CAR (b) SAM materials.