



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



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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 electroluminescence from organic materials. W. Helfrich and his friends have demonstrated the phenomenon of electroluminescence 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 bond with the groups on the surface of the substrate and thus change their physical and chemical

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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 SAM-modified 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

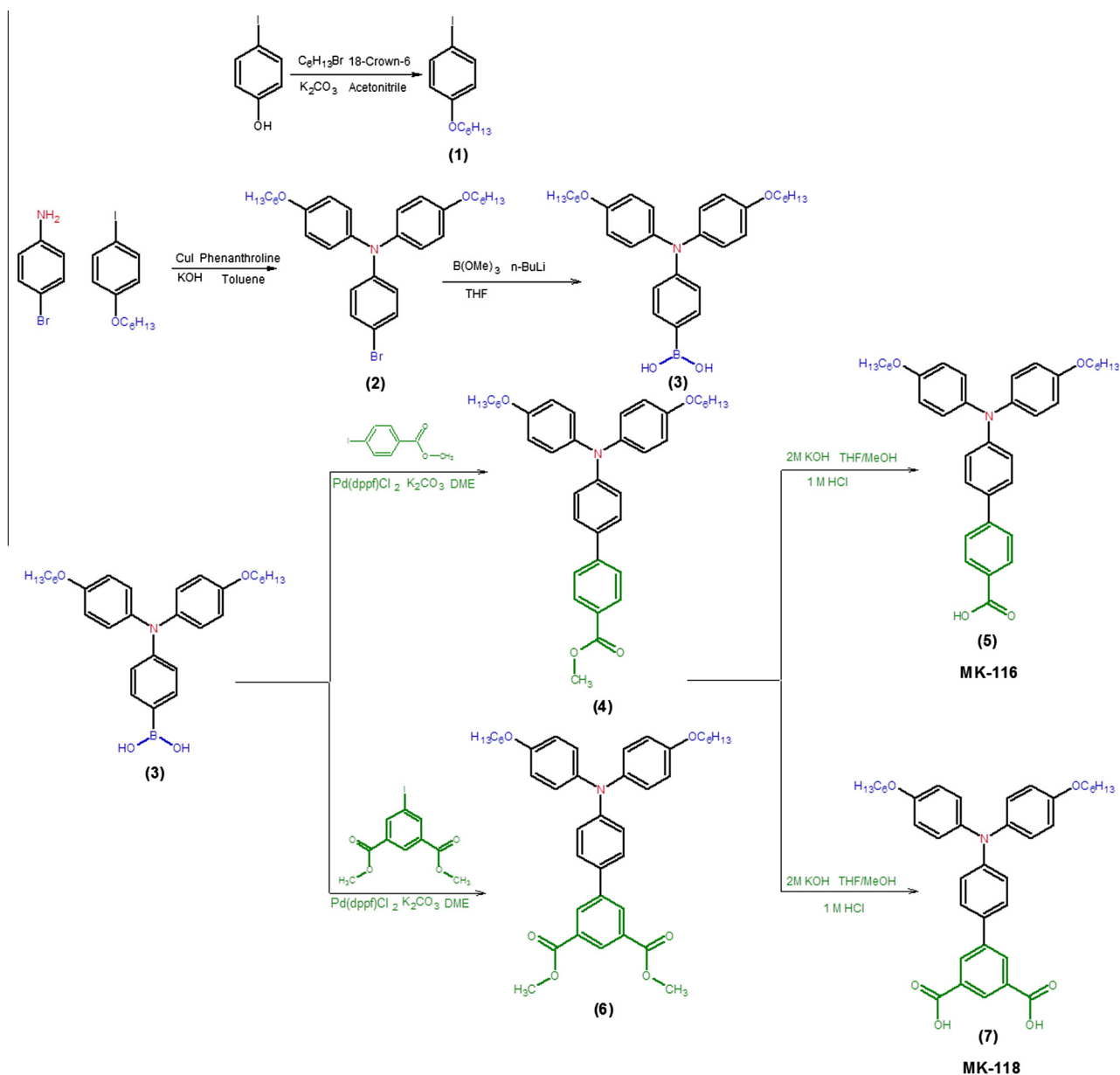


Fig. 1. Chemical structure and synthesis procedure of the MK-116 and MK-118 molecules.

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