



Large enhancement of hole injection in pentacene by modification of gold with conjugated self-assembled monolayers

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ABSTRACT

Planar diodes with gold electrodes and a pentacene semiconductor layer were made and electrically characterized. The gold electrodes were modified with self-assembled monolayers of biphenylthiol and biphenylthiol substituted with a terminal fluorine atom (fluorobiphenylthiol). Atomic force microscopy of the pentacene layer reveals large morphological similarities when the film is grown on gold modified with either of the two kinds of self-assembled monolayer. This is at variance with the significant increase of the current observed when the gold electrodes are treated with fluorobiphenylthiol, with a bulk mobility rising up to $1 \text{ cm}^2/\text{V s}$, while the treatment with biphenylthiol leads to a substantial decrease of the current. These results are interpreted in terms of adjustment of the injection barrier height as a result of the interface dipole induced by the self-assembled monolayer.

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1. Introduction

Charge injection from the conducting electrodes into the organic semiconductor is becoming a crucial issue as the performance of organic electronic devices improves. Efficient charge injection is mainly controlled by the barrier height at the electrode–semiconductor interface. An elegant way to lower the barrier was introduced by the pioneering work by Campbell and coworkers [1], in which a self-assembled (SAM) bearing an appropriate electrical dipole moment is deposited on top of the electrode prior to the deposition of the semiconductor layer. The efficacy of the method has been now largely proven by numerous studies [2–7], and the validity of its interpretation confirmed by quantum mechanical simulations [8]. However, although the benefit of SAMs in diodes is now largely recognized, there is still controversies about the origin of the improvement they bring in organic field-effect transis-

tors (OFETs). In diodes, when a very thin organic semiconductor layer is sandwiched between two electrodes, the effect of the contacts largely predominates. This is not the case in transistors, which adopt a planar geometry with contacts made of two parallel metal stripes deposited on a planar substrate. Under such circumstances, the area of the contact is substantially reduced as compared to than in a diode. Moreover, the total current flowing in an OFET combines charge carrier injection at electrodes and charge carrier transport that takes place in a very thin conducting channel close to the semiconductor–insulator interface, so that the morphology of the semiconductor at this interface plays a crucial role in the overall performance of the device. Under such circumstances, SAMs can play an alternative beneficial role as a promoter for a more favorable morphology for charge carrier transport in the conducting channel. A mere analysis of the device through its output and transfer characteristics does not allow for disentangling the respective roles of injection barrier lowering [9–11] and better morphology [12–14] in the improvement brought by the SAMs. Actually, it is most probable that both play a role [15,16]. More sophisticated tech-

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niques, such as the transmission line method (TLM), which consist of measuring the transfer characteristic of similar devices with various channel lengths, have recently been successfully used to separate the respective roles of charge carrier injection and charge carrier transport [17]. In some cases, improved charge carrier transport is observed together with a degradation of charge carrier injection, which may account for the controversial results reported earlier. Another instructive piece of information was drawn by the work by Stadlober et al. [18], in which the barrier height of gold was changed through an oxidative treatment. However, the main origin of improved performance in that case comes from a better morphology of the pentacene layer on both the electrodes and the conducting channel.

Most early works dealing with the modification of metal electrodes with SAMs involved molecules based on alkanes. Alkanes are known to lead to well-organized two-dimensional structures only for chain lengths above a certain value of the number of carbon atoms. The dark side of this feature is that long alkyl chain are also electrically insulating, thus preventing efficient electric charge injection. For this reason, most recent works use conjugated molecules including a phenyl moiety, such as thiophenols [11,16]. However, most of the works dealing with the effect of SAMs in OFETs lack for the morphological characterization that has been developed in the surface-science community for determining the orientation of the molecules in the SAMs. The techniques involve Infrared Reflection–Absorption Spectroscopy (IRRAS), X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) [19,20].

In this work, we use a geometry that stands in between the sandwiched diode used in organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPV) and the OFET, namely the planar diode, in which two similar electrodes are deposited on the same substrate (see Fig. 1). The interest of this structure over the conventional OFET is that the electrical current extends over the whole thickness of the semiconductor film, so that limitations due to interfacial defects do not intervene in the bulk conductance. The gold electrodes were modified with SAMs made of biphenylthiol (BPS) and a biphenylthiol modified by an end fluorine atom (FBPS). The chemical structure of BPS and FBPS is also shown in Fig. 1. The morphology of the film on the various substrates was investigated through atomic force microscopy (AFM).

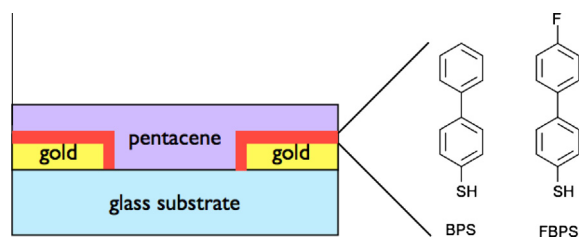


Fig. 1. Schematic view of the pentacene planar diodes. The chemical structure of the SAMs is shown on the right hand side.

2. Experimental methods

Biphenylthiol (full name: 4-phenylthiophenol, 97%) and fluorobiphenylthiol (full name: 4-(4-fluorophenyl) thiophenol, 97%) were purchased to Fluorochem and used without further purification.

Benzene and dichloromethane (Aldrich, HPLC grade) were distilled before use. Evaporated gold films on glass substrates (Arandee or home made) were cleaned ca. 30 times in a water–ethanol 50/50 vol.% mixture in an ultrasonic bath. They were then passed 3–6 times in an hydrogen flame during ca. 0.5 s, cooled under argon and immediately immersed in the thiol solution with a concentration ranging from 10^{-6} to 10^{-3} M. The adsorption time varied between 30 s and 24 h. A final cleaning step was performed in dichloromethane, and the sample dried under argon.

For the infrared reflection–absorption spectroscopy (IR-RAS) measurements, 2000 spectra were recorded with an argon purged FTIR spectrometer (Nicolet 860) at a grazing angle of 85° with a p-polarized IR beam. The reference spectrum was recorded on a flamed bare substrate.

Static contact angles were measured with ultra pure water and in air saturated with water vapor using a Digidrop (GBX, France).

AFM images were obtained in tapping mode using a Multimode scanning probe microscope setup driven by the Nanoscope IIIa electronics (Digital Instruments) and analyzed with the free software WSxM [21] (Nanotec Electrónica).

The glass substrates used for the planar diodes were cleaned following the same protocol as above. They were then dipped in a solution of octadecyltrichlorosilane (OTS) in hexadecane to render their surface hydrophobic. Two gold electrodes (2.5 mm long, separated by $50\ \mu\text{m}$) were vacuum evaporated at a base pressure of 2×10^{-4} Pa with a nominal thickness of 25 nm. Pentacene was vacuum evaporated at a base pressure of 10^{-5} Pa. The thickness of the film was 40 nm, as measured by a calibrated quartz microbalance. Fig. 1 gives a schematic view of the arrangement, together with the chemical structure of the molecules used for the SAMs. Current–voltage characteristics were recorded with a Keithley 4200 semiconductor characterization system.

3. Theoretical background

Here we briefly recall the model for charge injection at SAM modified electrodes first developed by Campbell and coworkers [1] for organic diodes, and more recently extended to organic field-effect transistors by our group [17,22] and others [9–11]. The basic concepts are depicted in Fig. 2 and can be found in recent review papers [23,24].

The idea behind the modification of the electrode by a SAM is to purposely play with the energy shift at the metal–semiconductor interface by deliberately introducing an interface dipole. As shown in Fig. 2, the direction of the dipole moment controls the direction of the energy shift. Namely, the electron barrier height is reduced when the dipole is directed from the metal to the semiconductor, while a reduction of the hole barrier requires a dipole oriented from semiconductor to the metal.

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