



Functionalized p-dopants as self-assembled monolayers for enhanced charge carrier injection in organic electronic devices

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ABSTRACT

We demonstrate that electrical dopants can be modified with self-assembling groups to form injection layers in organic electronic devices. A strong p-type dopant has been modified in a one-step synthesis to form self-assembled monolayers on gold electrodes from solution. F_4TCNQ was functionalized with sulfur-containing triazole anchor groups via nucleophilic substitution in a simple substitution reaction. Assembly of functionalized dopants on gold surfaces was verified by ATR-FT-IR measurements. Pentacene-based bottom gate, bottom contact organic thin film transistors show a strongly improved performance. The effective mobility could be increased by a factor of three when electrodes were covered with a SAM of functionalized dopant.

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1. Introduction

The injection of charge carriers from electrodes into organic semiconductors is one of the limitations in the performance of electronic devices, such as organic field effect transistors (OFETs) or organic diodes. Despite improved charge carrier mobilities of the materials and downscaled channel lengths [1], contact resistances are still a challenge [2]. They essentially restrict the maximum driving current as well as the switching speed of those devices. The main reason for contact resistance in OFETs is the high energy barrier which charge carriers have to overcome during injection. This barrier can be considered as a Schottky barrier and is defined by the difference in energy levels of work function of the metal and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the adjacent semiconductor. Additional shifting of this barrier can be induced by interface dipoles [3].

In OFETs different geometries of source/drain and gate electrodes lead to different results in terms of scalability and driving operation. Bottom gate, top contact devices as well as top gate, bottom contact devices show far better performance due to their staggered structure and hence larger area of injection [4]. However, for industrial application bottom gate, bottom contact OFETs represent the geometry of choice since they can be structured with conventional, high resolution lithography, without effecting the semiconductor. Hence, these types of transistor now require new material approaches to improve injection and mobilities.

One common approach to enhance the performance of electronic devices is doping [5] of the organic semiconductor via co-evaporation of strong electron acceptors like F_4TCNQ or F_6TCNNQ [6]. Electrical doping using such dopants is widely used to improve the efficiency of organic light emitting diodes (OLEDs) [7,8] and organic solar cells [9,10]. These dopant molecules donate free charge carriers to the matrix material and hence increase the conductivity of the organic semiconductors. Due to this process, a quasi-ohmic contact is formed at the interface to a metal contact, eliminating any contact resistance [11,12]. Also evaporation of a monolayer of dopants between metal electrode and semiconductor [13] showed the potential to enhance

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charge carrier injection. Yet, a great drawback of this method is the unselective deposition of dopants on electrodes as well as gate oxides in the channel of OFETs if evaporated without suitable shadow masks. Dopants in the channel inevitably lead to bulk conductivity, lowering the on/off ratio of the transistor. Also the structural order is influenced, affecting the charge carrier mobility [14]. Thus, doping limits its minimum channel length of bottom contact OFETs.

Another option to improve charge carrier injection in organic devices is the treatment of electrodes with self-assembled monolayers (SAMs) [15,16] of different thiols, aromatic as well as aliphatic. They benefit from their high selectivity of anchor groups to suitable surfaces, which leads to a directed assembly exclusively on predefined metal electrodes without contaminating the channel region. Thus, they offer simplified processing, directly from solution and under ambient conditions, making expensive and complex techniques like evaporation in high vacuum chambers redundant.

A frequently investigated system of SAMs are thiols on gold surfaces [17]. The high affinity of the sulfur-group of those compounds to noble metals leads to very stable monolayers of high order. For the modification of electrodes in bottom-contact organic field effect transistors, aliphatic as well as aromatic thiols, bearing different chemical functionalities, are being described [18]. One explanation for improved injection of charge carriers through these SAMs is the change of interface dipole between electrode and semiconductor [3,19], accompanied with the alignment of work function of the metal and transport levels of the semiconducting material. Furthermore, as the growth of such SAM layer is self-limited to a monolayer thickness, charge carrier tunneling between the metal and the semiconductor through the interfacial SAM layer is easily possible [20].

In this study we present an approach which combines both, the improved charge carrier injection via molecular doping and the selective self-assembly on electrodes by chemically attaching an anchor group to a dopant. The aim is to (a) improve the injection of charge carriers and thus increase the on-state current and the effective mobility in OFETs and (b) avoid the generation of free charge carriers in the channel of these devices by selective assembly, exclusively on electrodes. For this purpose, dopant molecules are functionalized with either thiol- or disulfide-anchor groups to allow their assembly on noble metal surfaces. In particular, we present the synthesis and application of a sulfur-functionalized F_4TCNQ derivative with doping character which allows for simple processing from solution and offers selective assembly on gold electrodes. We show that the modified dopant significantly improves current injection in pentacene-based diodes and OFETs.

2. Results

2.1. Synthesis approach

F_4TCNQ as well as F_6TCNNQ are strong electron acceptors and their chemical modification is very challenging because of their high oxidation potential and the formation

of many undesired side products. To our knowledge, a functionalization of these molecules, especially with sulfur-containing reactants has not been reported before.

Since it is known that $TCNQ$ (Tetracyanoquinodimethane) quickly undergoes substitution at one or two cyano-groups when exposed to primary or secondary amines [21], we aimed to use this reaction to functionalize F_4TCNQ or F_6TCNNQ . As the doping strength is reduced with the loss of one or two electron withdrawing cyanogroups, a spacer group compensating this effect is required, containing a primary or secondary amine for the reaction with the dicyanomethylidenyl moiety and a thiol or a disulfide anchor for later assembly on gold. Hence, we initially calculated the approximated relative position of energy levels of the potential reaction products of different sulfur-containing amines with F_4TCNQ , using *MOPAC2009* (Molecular Orbital Package), a semiempirical quantum chemistry program. The calculations showed the possible applicability of sulfur-functionalized triazole groups as a spacer between dopant an anchor because of their low effect on the LUMO level of dopant. With their secondary amine, the substitution should occur at the cyanogroups of the dopant and the resulting product is expected to have a doping strength in the range of the initial dopant.

2.2. Synthesis route

Based on our theoretical considerations the most promising anchor groups with the lowest effect on the LUMO level of the resulting functionalized dopant are represented by commercially available triazoles 1-(4-pyridyl)-1H-1,2,4-triazole-3-thiol (**3a**) and 5-(3-pyridyl)-4H-1,2,4-triazole-3-thiol (**3b**) as shown in Fig. 1. Beside the possibility of substitution of Fluorine, we primarily expected the formation of thioethers **5a** and **5b**, rather than the free thiols (**4a**) and (**4b**) (Fig. 1) because of the high nucleophilicity of the sulfur. Thioethers are known to attach to gold surfaces as well [22], yet only coordinate to the metal instead of undergoing a chemical reaction as thiols do.

To avoid a chemical reaction of the sulfur to the F_4TCNQ prior to the assembly, we used a two-step process for assembly of the product on the gold surface. Examples in the literature [23] show the practicability of chemical reactions on SAMs on metal surfaces. Initially the triazole thiol was to be attached to gold surface and subsequently the secondary nitrogen should undergo a reaction with the dicyanomethylidenyl moiety as shown in Fig. 2.

2.3. Proof of assembly

The respective triazole thiol is dissolved in acetonitrile to give a 1 mM solution and a glass substrate, covered with 40 nm of gold is immersed into the solution over 24 h at room temperature. The substrates are rinsed with pure acetonitrile and dried in a nitrogen stream. Subsequently the surface is investigated via ATR-FT-IR. The spectrum indicates the complete coverage of the gold surface since the specific signal as at 1734 cm^{-1} , which is detected on every pure gold sample and presumably refers to a carbonyl containing impurity, is no longer visible (see Fig. 3, yellow graph). The triazole thiol covered gold substrates

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