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On the mode of operation in electrolyte-gated thin film transistors based on different substituted polythiophenes

Henrik Toss [a], Clément Suspène [b], Benoît Piro [b], Abderrahim Yassar [c], Xavier Crispin [a], Loïg Kergoat [a], Minh-Chau Pham [b], Magnus Berggren [a,*]

[a] Department of Science and Technology (ITN), Linköpings Universitet, Campus Norrköping, Bredgatan 34, 601 74 Norrköping, Sweden
[b] Univ. Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France
[c] LPICM, UMR CNRS 7647, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France

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ABSTRACT

Organic Thin Film Transistors (OTFT), gated through an aqueous electrolyte, have extensively been studied as sensors in various applications. These water-gated devices are known to work both as electrochemical (Organic ElectroChemical Transistor – OECT) and field-effect (Organic Field-Effect Transistor – OFET) devices. To properly model and predict the response of water-gated OTFT sensors it is important to distinguish between the mechanism, field-effect or electrochemical, by which the transistor is modulated and thus how the gate signal can be affected by the analyte. In this present study we explore three organic polymer semiconductors, poly-(3-hexyl-thiophene) (P3HT), poly-(3-carboxy-pentyl-thiphene) (P3CPT) and a co-polymer P3HT–co-poly-(3-ethoxypentanoic acid-thiophene) (monomer ratio 1:6, P3HT–COOH15) in water-gated OTFT structures. We report a set of transistor characteristics, including standard output parameters, impedance spectroscopy and current transients, to investigate the origin of the mode of operation in these water-gated OTFTs. Impedance characteristics, including both frequency and voltage dependence, were recorded for capacitor stacks corresponding to the gate/electrolyte/semiconductor/source structure. It is shown that P3HT as well as P3HT–COOH15 both can function as semiconductors in water gated OTFT devices operating in field-effect mode. P3CPT on the other hand shows typical signs of electrochemical mode of operation. The –COOH side group has been suggested as a possible anchoring site for biorecognition elements in EGOFET sensors, rendering P3HT–COOH15 a possible candidate for such applications.

1. Introduction

Presently, there is a tremendous activity to explore organic semiconducting materials because they can be processed from solution at low temperature [1–8] hence, traditional printing technologies can be adapted to manufacture printed sensors and detectors. Such types of devices represent an important corner stone for applications such as distributed monitoring and medical surveillance. The printed sensors are typically comprised of bio-recognition elements and a signal transducer device; which could e.g. be an organic thin film transistor. The OTFTs typically run either in a field-effect (OFET) or an electrochemical (OECT) mode of operation, i.e. current modulation is due to either charge polarization occurring along the aqueous electrolyte–semiconductor interface or chemical doping occurring within the bulk of the semiconductor channel [1–3,6,9–11].

* Corresponding author. Tel.: +46 11 36 36 37.
E-mail address: magnus.berggren@liu.se (M. Berggren).

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Organic Thin Film Transistors (OTFT) hosting antibodies, peptides or enzymes have been developed for applications in aqueous and physiological media and have been studied extensively in the past [1–5,7,12–17]. The bio-recognition elements can be either attached to the surface of the gate in a top-gate configuration (Fig. 1a) [2–3,5,7,18]; or on the surface of the semiconductor in a bottom gate structure using a solid insulator layer (Fig. 1b) [19–23].

In a new version of the OTFT sensors, the electrolyte media carrying the analyte, is located between the gate and the semiconducting channel. In other words, the electrolyte serves as gate-insulator for the transistor (Fig. 1c). In this case, the drain current modulation and the transistor performance rely on the electric field established across the semiconductor–aqueous media interface. For these electrolyte-gated OTFTs (EGOTFTs) a capacitance is built up as charge is injected into the organic semiconductor (OSC) at the interface, to compensate for the charges stored within the Helmholtz layer of the electrolyte. The properties of this electric double layer interface, and the corresponding capacitance, are thus crucial to the transistor characteristics. It is attractive to anchor sensor receptors directly at the OFET channel, since the receptor reaction can cause modulation of the trap density, morphology, dipoles, etc., thus causing control of the drain current. Assuming that the bio-recognition element is located on the surface of the semiconductor, upon reaction with the analyte, the charge capacity and dynamics of the Helmholtz double-layer is expected to be modified; which should results in a variation of the static and/or dynamic transistor responses. The speed of EGOFETs gated via water is primarily dictated by the ion diffusion rate and concentration of the aqueous electrolyte. For OECTs the speed of operation is typically governed by ion migration within the bulk semiconductor and thus appears relatively slower than the EGOFETs [11]. One strategy to immobilize the bio-recognition element along the surface of the OSC channel surface is to utilize molecular anchors, such as carboxyl groups [24–25]. Similar methods have been applied in EGOTFT-sensors in the past. In those cases the anchoring sites have either not been attached directly to the semiconductor or the mechanism of transistor actuation has been unclear. The inclusion of anchoring sites on the semiconducting polymer may affect the mode of operation of the OTFT [11]. Previous studies on solid electrolyte gated OTFTs, i.e. using architectures not appropriate for sensors, indicate that the chemical nature of the semiconducting polymers is crucial since it affects the operation mechanisms. The EGOTFTs typically run either in a field-effect (OFET) [26] or an electrochemical (OECT) mode of operation P3CPT, [11], i.e. current modulation is due either to charge polarization occurring along the aqueous analyte–semiconductor interface or chemical doping occurring within the bulk of the semiconductor channel.

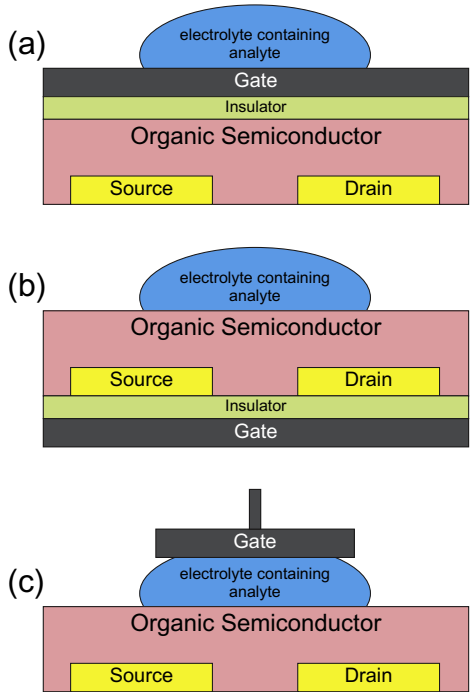

Fig. 1. Three different possible set-ups for sensors with amplification of the sensing signal through OTFTs. The sensing elements are tentatively located; on the gate but separate from the OSC (a), on/in the OSC but separate from the gate (b), and on either the gate or the OSC or in between the gate and the OSC (c).

Here, we investigate the impact of the bio-recognition anchoring groups on the mode of operation of EGOTFTs for bio-sensor applications. Three different polythiophene derivatives with various ratio of anchoring groups are compared: poly-(3-hexyl-thiophene) P3HT (Fig. 2a), poly-(3-carboxy-pentyl-thiphene) P3CPT (Fig. 2b) and a random co-polymer P3HT–co-poly-(3-ethoxypentanoic acid-thiophene) (monomer ratio 1:6, i.e. ~15% –COOH side chain end groups, P3HT–COOH15 [27,28]) (Fig. 2c) are compared.

2. Experimental

2.1. Production of devices

The capacitor and transistor devices are fabricated according to the same process protocol; the only difference is the bottom metal electrode pattern. The top electrode of the capacitor stack is identical to the gate electrode of the transistors. Capacitor and transistor devices (see Fig. 3) are fabricated on Si-wafers with a thick (10,000 Å) thermally grown oxide layer on top. As the first process step, a thin attachment layer of Ti (50 Å) is vacuum evaporated on the oxide surface. Then, a 500 Å layer of Au is vacuum evaporated on top of the Ti attachment layer. The patterned Au electrodes are then generated using standard UV–photolithography (Suss MA/BA 6 mask and bond aligner and soda lime glass masks with patterned chromium from Delta Mask) followed by chemical wet etching (I/KI in H_2O for Au and NH_3/H_2O_2 in H_2O for Ti etch). Electrode patterns for capacitors and transistors are generated, $1 * 1\ mm^2$ patterns for the capacitors and interdigitated electrodes with channel length (L) of 2 μm and width (W) of 2–10 mm for the transistors. P3HT is purchased from Sigma (electronic grade, 15,000–45,000 u)