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Improving mobility and electrochemical stability of a water-gated polymer field-effect transistor

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ABSTRACT

Water-gated organic transistors have attracted considerable attention in the field of biosensors, thanks to their capability of operating in the aqueous environment typical of biological systems at very low voltages (~1 V). Some examples have been recently reported in the literature, employing different organic materials as the active semiconducting layer, ranging from small molecules to single crystals. Here we report on water-gated polymer-based organic-field effect devices using poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (pBTTT) as the active layer. Very promising electronic performances, in terms of mobility and operating voltages are obtained; notably, the charge carrier mobility is in the order of 0.08 cm^2/V s, which is of the same order of magnitude of values reported for single-crystal based water-gated devices, and consistent with values reported for solid-state polymer dielectric transistors. Moreover, the pBTTT-based device shows improved electrochemical stability, as compared to previously reported polymer based water-gated devices. Importantly, good functioning of the device is demonstrated also when water is replaced by physiological-like solutions. Critical to the transistors operation, besides the good transport properties of the active material, is the key-role played by alkyl side chains and ordered morphology of the polymer at the interface with the liquid environment, which we highlight here for the first time. Our contribution overall provides a useful step towards the development of bio-organic sensors, with enhanced properties in terms of sensitivity and stability, and for a successful exploitation of organic based field effect transistors in biotic/abiotic interfaces.

1. Introduction

Electrolyte-gated Organic Field Effect Transistors (EG-OFETs), organic transistors where an electrolyte, in particular aqueous saline solutions, is utilized as the gating medium, have recently attracted growing attention in view of their use in the field of biosensors and biosystems [1,2]. Water-gated techonology indeed fulfil the two fundamental requirements needed for the realization of disposable biosensing systems [3–5], i.e. the possibility to operate (i) in an aqueous environment, typical of biological systems, and (ii) at low voltages (~1 V), which requires high gate capacitance values, in the order of few μF. Organic π-conjugated semiconductors offer several advantages for the use as active materials in liquid-gated configurations: their chemical structure can be modified and functionalized to

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be adapted to a wider range of uses; they are soft materials, minimally invasive in contact with a biological tissue and compatible with the deposition on flexible and biocompatible substrates; devices can be disposable and easily upscaled. While various examples of EG-OFETs based on evaporated small molecules thin films and single crystals have been demonstrated in the recent past [6–8], so far only a few solution-processed semiconducting polymers, namely poly(3-hexylthiophene) (P3HT) and a few of its derivatives, have been shown to work in a water-gated device [7,9–11]. P3HT has been used in a water-gated structure in its pristine form [9,12] or blended with PMMA [13]. The chemical synthesis of a polythiophene derivative bearing carboxylic acid moieties (poly [3-(5-carboxypentyl)thiophene-2,5-diyl] (P3PT–COOH)) has allowed biosensing applications by incorporating probe molecules either in direct contact with the semiconducting polymer [7], or through the prior formation of a lipid bilayer on the semiconducting material [14].

One of the main drawbacks of water-gated polymer FETs reported so far in the literature is the limited charge carriers' mobility, of the order of 10^{-3} cm^2/V s, which frustrates, in terms of sensing capability, the high gate capacitive coupling of the device. Moreover the well-known environmental instability of P3HT based FETs [15–17] and of devices based on conjugated polymers characterized by low ionization energies, represents a strong limit for transistor applications. This makes the development of higher mobility water-gated polymer FETs, characterized by improved stability and capability of working also in contact with saline solutions typical of the biological environment, highly desirable.

In this work, we report a water-gated, low-voltage polymer FET based on poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (pBTTT, chemical structure in Fig. 1a) [18]. Liquid–crystalline pBTTT has been preliminarily used as semiconducting layer in a liquid-gated structure by Al Naim et al. [19], however a detailed electrical characterization of the device, in terms of mobility and electrochemical stability, as well as a detailed understanding of the polymer/electrolyte interface phenomena, is still missing. Here, we show, through electrical characterization, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) investigations, that the pBTTT-based water-gated device results in increased charge carriers' mobility, at levels comparable with single-crystal based water-gated devices, and improved electrochemical stability, as compared to previously demonstrated polymer-based devices. Moreover, we demonstrate that enhanced performances can be explained by a combined effect of a high degree of order within the polymeric film, which are preserved in contact with the water medium, higher ionization energy and the key protective role of alkyl-side chains at the interface with water. Importantly, such improved performances enable the operation of pBTTT based transistors also when a water based NaCl solution (0.2 M) is adopted as the gating medium.

Our results represent a clear indication of the importance of the polymer physical–chemical properties and morphology in establishing an optimal interface with the water environment, and constitute a useful guideline for further development of water-gated polymer FETs for biosensors and biomedical devices.

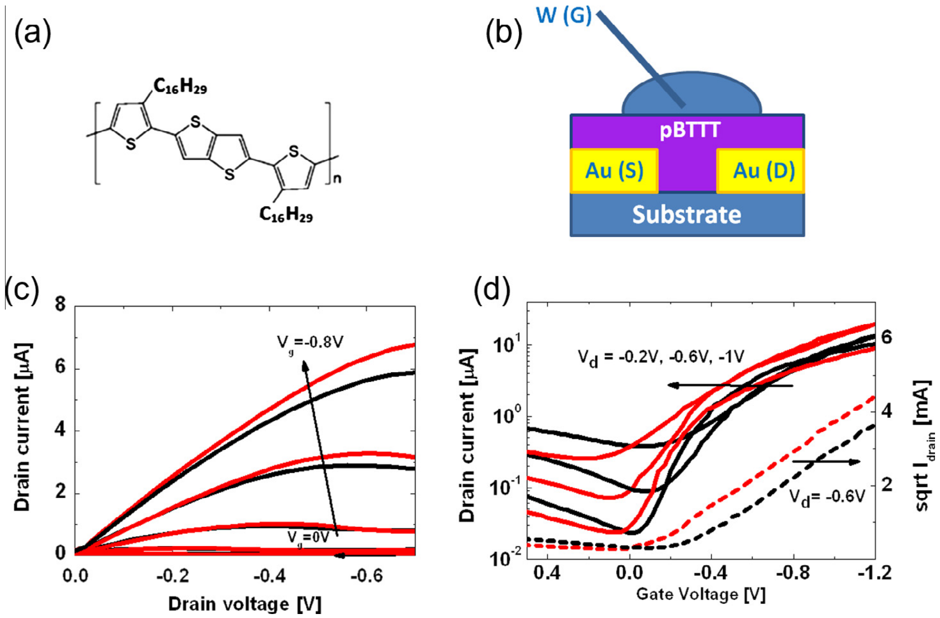

Fig. 1. (a) Chemical structure of pBTTT. (b) Schematic section of the water-gated organic transistor. Electrical characteristics of the devices: (c) output curves of annealed (black lines) and non-annealed (red lines) pBTTT-based water-gated transistors with a tungsten gate electrode; (d) transfer curves of the same transistors in logarithmic scale (solid lines, left axis), and square root of the drain current at drain voltage $V_d = -0.6$ V (dashed lines, right axis). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)