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Water-gated phthalocyanine transistors: Operation and transduction of the peptide–enzyme interaction

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ABSTRACT

The use of aqueous solutions as the gate medium is an attractive strategy to obtain high charge carrier density (10^{12} cm^{-2}) and low operational voltages (<1 V) in organic transistors. Additionally, it provides a simple and favorable architecture to couple both ionic and electronic domains in a single device, which is crucial for the development of novel technologies in bioelectronics. Here, we demonstrate the operation of transistors containing copper phthalocyanine (CuPc) thin-films gated with water and discuss the charge dynamics at the CuPc/water interface. Without the need for complex multilayer patterning, or the use of surface treatments, water-gated CuPc transistors exhibited low threshold (100 ± 20 mV) and working voltages (<1 V) compared to conventional CuPc transistors, along with similar charge carrier mobilities (1.2 ± 0.2) x 10^{-3} cm^2 V^{-1} s^{-1}. Several device characteristics such as moderate switching speeds and hysteresis, associated with high capacitances at low frequencies upon bias application (3.4 −12 μF cm^{-2}), indicate the occurrence of interfacial ion doping. Finally, water-gated CuPc OTFTs were employed in the transduction of the biospecific interaction between tripeptide reduced glutathione (GSH) and glutathione S-transferase (GST) enzyme, taking advantage of the device sensitivity and multiparametricity.

1. Introduction

Interfacing electrolytes with organic semiconductors has been an interesting and effective approach for achieving high charge carrier density (typically 10^{12} cm^{-2}) and low voltage operation (<1 V) in organic thin-film transistors (OTFT) [1,2]. Such virtuous device characteristics are attributed to the high capacitance of the electrolyte/semiconductor interface (~10^{-6} F cm^{-2}) which exceeds typical values for thin-film dielectrics (e.g. high-k oxides, self-assembled monolayers – SAMs, polymer films) commonly used in conventional OTFTs [1]. In this sense, several different electrolytes (e.g. ionic liquids, polyelectrolytes, polymer electrolytes, ion gels, aqueous solutions) have been exploited as the "gate dielectric" in such electrolyte-based thin-film devices [1]. The use of aqueous solutions as the dielectric medium offers an additional advantage over such variety of choices – a benign environment to produce biosensors and related bioelectronic applications using OTFTs [2,3].

In a water-gated OTFT, a drop of water or buffer solution is placed in contact with the organic active layer over the whole transistor channel area [2–4]. An immersed top-gate electrode sets the electrical potential that controls the motion of ionic species and, consequently, the number of charge carriers in the transistor channel by two different mechanisms, named field-effect gating and electrochemical doping [2,5–7]. The former is based on the accumulation of charge carries in the semiconductor film due to the formation of an electric double layer at the solid/liquid interface, similarly to the field-effect process in conventional OTFTs [6]. The latter, on the other hand, relies on the penetration of electrolyte ions into the organic semiconductor bulk, causing its electrochemical doping and, therefore, changes to the transistor channel current [6]. The coexistence of these two mechanisms in the same device is also likely to occur [6,7]. Such hybrid operation mode becomes an interesting feature to probe the mechanisms related to the accumulation and transport of charges in organic thin-films [6,7].

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Organic transistors gated with aqueous solutions have been realized for several semiconducting and conducting polymers, such as different polythiophenes [5,8–10], and small molecule semiconductors (e.g. rubrene [5], sexithiophene [11] and pentacene [12]). However, no water-gated transistors have been reported so far using metallophthalocyanines, a class of molecules widely exploited in organic electronics [13,14] that have been reported, in general, to be resistant to water and air exposure in a thin-film structure [15,16]. Copper phthalocyanine (CuPc), has been assigned as one of the most interesting molecules to study thin-film structural properties [17], optical phenomena [18], charge transport mechanisms [15] as well as to be used in electroluminescent devices [19], sensors [20], photovoltaics [21] and OTFTs [14,22]. Concerning CuPc OTFTs, research efforts have been reported for almost two decades, mostly exploiting different chemical modifications (e.g. SAM assembly and polymer coating) of the Si/SiO_2 gate dielectric surface [23–29], and the use of high-k oxides as the gate insulating layer [30–34]. Such variety of strategies aims at the modification of the CuPc/dielectric interface to obtain better device characteristics. Nevertheless, none of them has considered the direct gating of a metallophthalocyanine transistor in water to achieve improved OTFT performance. The latest advances in CuPc as well as other phthalocyanine-based transistors have been recently reviewed [14].

Water-gated OTFTs present a number of attractive characteristics for applications in bioelectronics that transcend the simple favorable aqueous environment. These characteristic include intrinsic signal amplification ability, potentiometric sensitivity, multiparametricity (i.e. the possibility to monitor a sensing event using different device parameters such as threshold voltage, drain current, I_{ON}/I_{OFF} ratio, etc.), low operational voltages and the possibility to incorporate novel and specific functionalities through the controlled surface engineering of the device. Kergoat et al., for example, reported the detection of DNA using water-gated OTFTs based on a polythiophene-derivative containing carboxyl side chains [35]. The DNA probes are grafted on the semiconductor surface and the device undergoes changes in the output curves when DNA immobilization and hybridization take place [35]. Buth et al. modified the surface of α-sexithiophene (α6T)-based devices using controlled oxidative processes and (3-aminopropyl)triethoxysilane (APTES) functionalization to anchor penicilinase enzyme [36]. The α6T OTFTs gated in a buffer solution exhibited changes in the source-drain current upon the titration of penicillin in different concentrations [36]. Cramer et al. reported the use of pentacene water-gated OTFTs as electrical stimulators and transducers of neuronal cellular activity [37]. When murine stem cells adhered on the device surface differentiate into neurons, electrical signals can be recorded following the cell stimulation [37]. Casalini et al. exploited the functionalization of the gate electrode instead of the semiconductor surface [38,39]. Using poly(3-hexylthiophene)-based devices, they have shown the detection of dopamine down to picomolar concentrations [38]. In another example, pentacene water-gated transistors were used to probe the specific interaction between cytokine antibodies and antigens [39]. In both cases they monitored changes on the device transfer curve during the sensing event at the gate electrode [38,39]. Recently, Mulla et al. reported the chiral differential detection of odorant molecules based on changes of gate electrode capacitance also using water-gated OTFTs [40].

Due to the striking capability of water-gated OTFTs to sense different species at the device surfaces, an attractive possibility relies on the transduction of the interaction between reduced glutathione (GSH) and glutathione S-transferase (GST). GSH is an ubiquitous tripeptide (γ-Glu-Cys-Gly) that possesses a variety of functions, including redox-buffering, antioxidant activity and cellular detoxification ability [41]. The detoxification of cells, for example, occurs by the conjugation of GSH with xenobiotics, i.e. non-naturally produced chemicals (such as pesticides, drugs and carcinogens) by an organism, a process that is catalyzed by GST enzymes [42,43]. Despite its protective function, the detoxification ability of GSTs may become a drawback in some cases, leading to undesired drug resistance effects [43]. Consequently, an increase of the GST levels can be related to drug resistance, which is of great relevance in cancer therapy, for instance [44,45]. Variable expressions of GSTs have been recognized in renal, gastric and pulmonary cancer as well, which makes their determination highly relevant [44,46]. Finally, the GSH-GST interaction has been widely exploited in the immobilization of several GST-fused proteins onto solid surfaces for different biotechnological purposes, such as pull-down assays [47,48], protein arrays [49,50], and related applications [51]. To the best of our knowledge, however, just a couple of approaches utilizing transistors to probe/explore the GSH-GST interaction have been reported so far [52–54]. Such strategies rely on minute changes in the conductance of inorganic transistors employing laborious multi-functionalization steps onto the semiconductor surface [52–54]. Here, we propose an alternative method, based on organic devices using a simpler surface modification strategy – the direct sensing of the GSH-GST pair on the transistor gate electrode.

In this work, we report the fabrication and successful operation of CuPc OTFTs gated with aqueous electrolytes. The charge dynamics at the CuPc/water interface in addition to the device ability to transduce the GSH-GST biospecific interaction are discussed. CuPc has been chosen as the prototypical molecular semiconductor due to its wide usage in OTFTs [23–34], vast literature regarding its chemical and electronic properties [55,56], reported evidence suggesting its stability in aqueous environments [15,16], and its novelty as the active layer in water-gated OTFTs.

2. Materials and methods

2.1. Device fabrication

Water-gated transistors of CuPc were fabricated in a bottom-contact top-gate configuration as schematically depicted in Fig. 1.

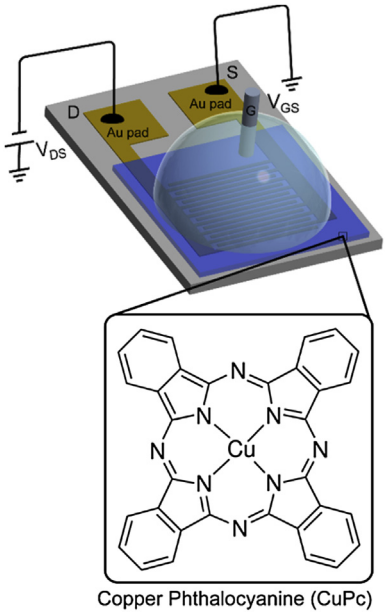

Fig. 1. The water-gated OTFT layout and the CuPc molecular structure.