

Tuning Threshold Voltage in Organic Electrochemical Transistors by Varying Doping of the Conjugated Polymer p(g3T2-T)

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Preface

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Abstract

Organic Electrochemical Transistors (OECTs) exhibit advantageous properties, such as high transconductance and steep-slope switching, while operating at very low voltages. Although, their switching speed is comparatively slower than solid-state devices, it remains sufficient for applications in bioelectronics [1]. The gold standard conjugated polymer for p-type OECTs is PEDOT:PSS. However, its main drawback lies in its depletion-mode operation, which requires power to turn off the device. To minimize power consumption and improve stability, efforts have been made to the design conjugated polymers that allow accumulation-mode devices. One such polymer, 3-(2-(2-methoxyethoxy)ethoxy)thiophene (p(g3T2-T)) has demonstrated negative threshold voltages close to zero and high transconductance [2]. Furthermore, by doping p(g3T2-T) at various levels and drop-casting it as a gate, it has been possible to fine-tune the threshold voltage [3]. This study aims to adapt a microstructuring method for fabricating side-gated OECT devices that comprise different doping levels of F₄TCNQ and F₆TCNNQ in p(g3T2-T) and a solid-state electrolyte [4], the latter is deposited by inkjet printing. Additionally, the study aims to adjust the threshold voltage by utilizing these varying doping levels, while analyzing the stability and performance of the doped devices.

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Chapter 1

Introduction

The field of organic electronics has witnessed significant advancements in recent years due to its potential biocompatibility, mechanical compliant, and other application-specific characteristics. Among the numerous types of organic devices, Organic Electrochemical Transistors (OECTs) have attracted considerable attention due to their unique capabilities such as high transconductance and steep-slope switching at low operation voltages, which give them potential for use in energy storage, bioelectronics, and neuromorphic devices.

Accumulation-mode transistors, devices that are normally in the OFF state at zero-gate-biased condition, rely on the use of undoped conjugated polymers. In contrast, the ability to precisely control and tune the threshold voltage of an OECT can be achieved by manipulating the doping level of the mentioned conjugated polymer as shown by Tan et al. [3]. However, they fabricated devices that did not follow a complete microstructuring technique, limiting their integration into circuits.

The primary objective of this research is to address this missing information by developing a microstructuring method to fabricate accumulation-mode OECTs with controlled doping levels and enable their seamless integration into circuits. However, during the pursuit of this objective, it was identified that stability of the polymer and dopants in an electrochemical environment may pose challenges that need to be addressed as well. Therefore, this research project specifically aims to:

1. Characterize 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene (p(g3T2-T)) with varying doping levels of F₄TCNQ and F₆TCNNQ. This involves modifying the conjugated polymer film with different concentrations of dopant and analyzing their electronic structure, morphology and electrical properties using techniques such as UV-Vis spectroscopy, Ultraviolet Photoelectron Spectroscopy (UPS), Van Der Pauw method, Electrical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV),
2. fabricate OECT devices, which involves utilizing the conjugated polymer at different doping levels, and adapting an existing method that combines electrode patterning techniques, spin-coating, photolithography and inkjet printing. The devices will be carefully optimized to ensure reproducibility and stability,

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3. assess doped polymer stability in OECTs, which involves performing conductivity measurements over time and selecting an electrolyte composition that allows a stable performance, and
4. investigate the shift in threshold voltage through electrical characterization of the fabricated OECT devices with varying doping levels of F₄TCNQ and F₆T₂CNNQ.

The thesis is structured as follows: Chapter 1 provides an overview of organic electronics and the importance of the OECT threshold voltage, and outlines the motivation, goals, and structure of the thesis. Chapter 2 presents a comprehensive review of the relevant background information on Organic Semiconductors (OSCs), Organic Mixed Ionic Electronic Conductors (OMIECs), and Organic Electrochemical Transistors, and relevant research on tuning the threshold voltage of OECTs. Chapter 3 illustrates the Experimental Methods used in this research, describes the materials, equipment, software, and procedures to chemically dope the films and characterization method employed in the study. Finally, it outlines the fabrication and characterization process of OECT devices. In Chapter 4, the experimental results obtained are presented, from the characterization of the conjugated polymer at different doping levels and fabricated OECT devices. Analysis of the relationship between the doping level and the shift in threshold voltage. Finally, it discusses the implications of the findings and their relevance to the field. Lastly, Chapter 5 provides a summary of the research objectives and the extent to which they were achieved, suggests future research direction, and potential applications.

Chapter 2

Background

2.1 Organic Semiconductors

Unlike inorganic semiconductors, organic semiconductors are lightweight, easy to chemically tune, mechanically flexible, and offer low-cost and low-temperature processing. All of these characteristics are responsible for the increased attention to this type of material in the field of organic electronics.

2.1.1 Electronic Structure and Transport

Organic semiconductors are π -conjugated molecules that comprise mostly carbon and hydrogen atoms, with alternating multiple (sp^2 hybridization) and single (sp hybridization) bonds. The wavefunction of the sp^2 orbitals overlap so that electrons are delocalized. Based on the size of the conjugated system, organic semiconductors can be divided into conjugated polymers and small molecules. The latter have the advantage that their synthesis and low molecular mass allows to obtain them high purity material [5].

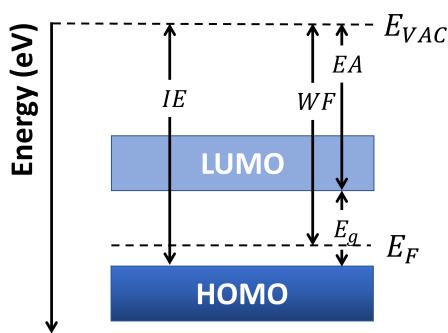


FIGURE 2.1: Energy level diagram of an p-type doped organic semiconductor.

The energy structure of organic semiconductors comprises a highest occupied molecular orbital (HOMO) state and a lowest unoccupied molecular orbital (LUMO) state, which are analogous to the valence and conduction bands, respectively, from

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inorganic semiconductors. The difference between these energy levels corresponds to the energy gap (E_g) of the material, as illustrated in Figure 2.1. Additionally, we can define i) the Fermi level (E_F) using the material's work function (WF), ii) the ionization energy (IE), also referred as ionization potential (IP), using the HOMO energy, and iii) the electron affinity (EA), using the LUMO energy.

Organic semiconductor materials can also be classified based on whether their ground state is degenerate or non-degenerate. In the former case, the term “degenerate” describes monomers that have equivalent energy states in the ground state. In contrast, in the latter case, the ground state exhibits non-degeneracy, which is commonly observed due to the energy difference of aromatic (benzoid) and quinoid structures [6], as exhibited in Figure 2.2.

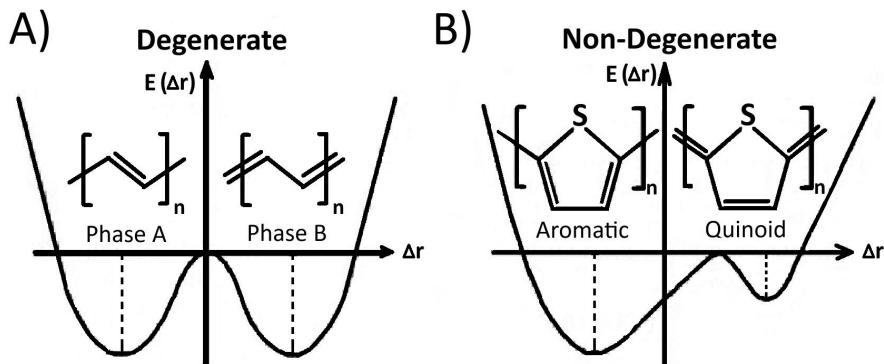


FIGURE 2.2: Potential energy change (electronic plus lattice distortion energy) in A) degenerate and B) non-degenerate ground-state-conjugated polymers. Extracted from reference [7].

In electronic transport theory for organic semiconductors, the concept of polarons is introduced. This quasiparticle effectively captures the alteration of the bond-length alternation pattern induced by the movement of charge carriers (electrons or holes) [8]. This alteration can be observed, for instance, when transitioning from Phase A to Phase B in degenerate molecules, or from aromatic to a quinoid structure in non-degenerate molecules.

2.1.2 Molecular Doping

The basic principles of molecular doping are similar than in inorganic materials. A donor or acceptor entity is added to generate electrons or holes, as shown in Figure 2.3. While n-type dopants donate electrons to the LUMO state, the p-type dopants extract electrons from the HOMO state, thus creating holes [9]. In other words, the Fermi level E_F of the polymer will shift towards the LUMO (or HOMO) level when there is n-type (or p-type) doping. This shift can be quantified using spectroscopy techniques such as Ultraviolet Photoelectron Spectroscopy (UPS) [10], although it may be somewhat limited by the penetration depth of the exciting electrons.

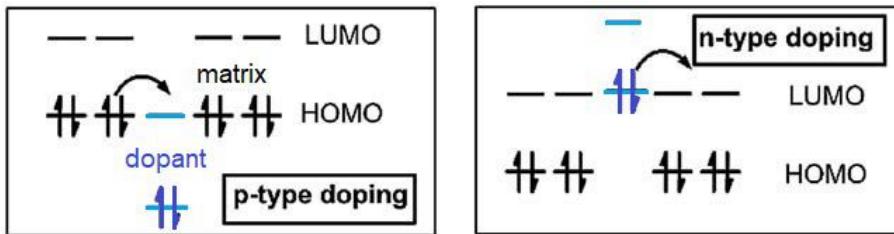


FIGURE 2.3: Schemes for p-type (left) and n-type (right) doping processes.

When doping occurs, the formation of a new quasiparticle named bipolaron occurs. For instance, if p-type dopants are introduced to a degenerate molecule (as depicted in Figure 2.4), electrons are removed from double bonds. Focusing on a single event, this removal leaves one carbon positively charged, with an adjacent carbon atom possessing an unpaired electron. This unpaired electron moves along the polymer chain until it encounters another unpaired electron from a separate doping event. When they come together, they form a double bond, resulting in the creation of two charged polarons: a bipolaron [11].

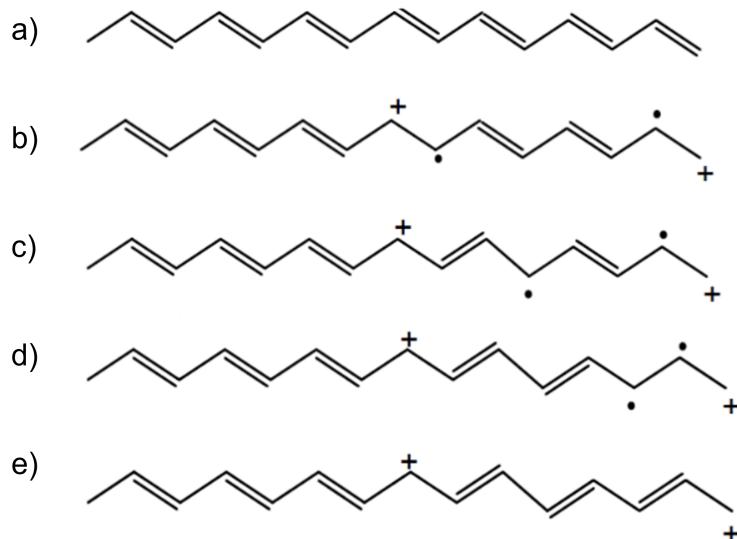


FIGURE 2.4: a) Structure of degenerate molecule. b) Electron extraction via doping. c) Unpaired electron shifting down. d) Unpaired electrons meet. e) Formation of double bond and two charged polarons: bipolaron.

The energy levels generated upon the formation of polarons and bipolarons in non-degenerate molecules are illustrated in Figure 2.5. As the doping density increases, the amount of bipolaron states also increases. Their overlapping leads to the formation of bipolaron bands, and the energy difference between the two in-gap states i and i^* , as shown from Figure 2.5B to D, decreases.

In addition to these new electronic states, the doped polymer will also exhibit

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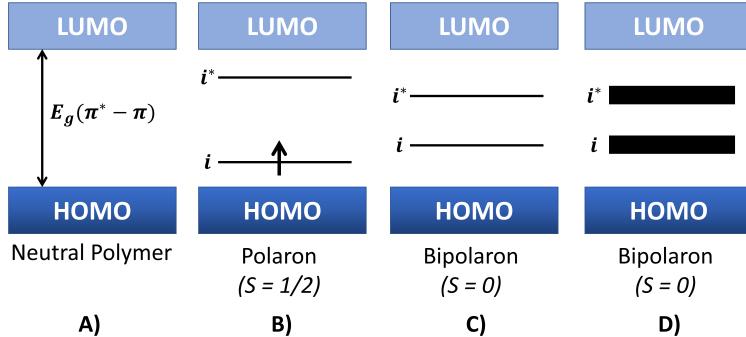


FIGURE 2.5: Potential energy change of aromatic and quinoid in the non-degenerate ground-state A) neutral conjugated polymer, and formation of B) polaron, C) bipolaron, and D) bipolaron bands upon doping. Extracted from reference [7].

distinct optical transitions that could be revealed through UV-Vis-NIR spectroscopy. In this technique, absorption peaks indicate the presence of these optical transitions. However, these transitions may not be precisely quantified or clearly defined [7].

The use of small molecules as dopants for organic materials is commonly reported. Some strong acceptor (or electron-deficient) molecules that are widely used include 2,3,5,6 tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) or 1,3,4,5,7,8 hexafluoro-7,7,8,8-tetracyanonaphthoquinodimethane (F_6TCNNQ), both of which are also relevant to this work. The latter exhibits a higher electronic affinity (-5.3 eV) than F_4TCNQ (-5.2eV), indicating that it can abstract electrons more efficiently, specially from polymers with low ionization potential ($IP < 5eV$) [12].

Among the various methods of molecular doping for conjugated polymers, Jacobs et al. conducted a comparison between solution-mixed and solution-sequential doping of P3HT, a thiophene-based polymer, doped with F_4TCNQ . These doping methods are considered straightforward and easy, especially when compared to other techniques such as vapor-phase doping [13]. Their research showed that solution-mixed films tend to have considerably rougher surface than solution-sequential films, which can negatively impact their conductivity [14]. The fact that solution-sequential doped films exhibit better homogeneity also makes them more compatible with microstructuring processes such as photolithography. Reason why it is going to be used in this work and will be further detailed in Section 3.5.1. However, this advantage comes at the expense of having less control over the doping levels when compared to solution-mixed films [15].

2.2 Organic Mixed Ionic/Electronic Conductors (OMIECs)

Organic Mixed Ionic/Electronic conductors are a class of organic semiconductors that allow the conduction of electrons (or holes) and ions. This feature sets them apart from other organic semiconductors. Commonly designed with polar side

2.2. Organic Mixed Ionic/Electronic Conductors (OMIECs)

chains, OMIECs have been identified as a promising class of materials for the field of bioelectronics [16]. Initially investigated for batteries and super-capacitors [17] [18], where the primary objective was to induce charges in a semiconducting polymer, OMIECs have rapidly expanded their scope to include other applications, among them, our focus: OECTs.

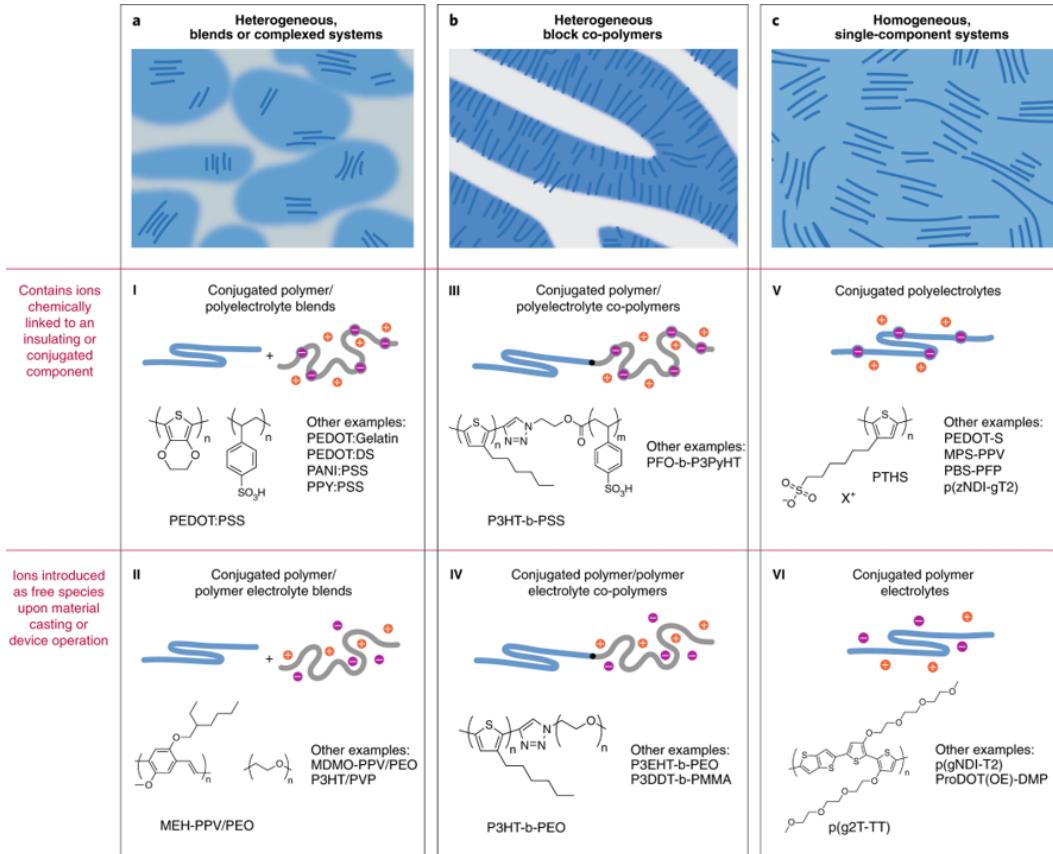


FIGURE 2.6: **OMIECs classes.** a) Heterogeneous blends of a conducting conjugated polymer with (I) a polyelectrolyte or (II) an ion-solvating polymer electrolyte. b) Heterogeneous block copolymers of a conducting conjugated polymer with (III) a polyelectrolyte or (IV) an ion-solvating polymer electrolyte. c) Fully conjugated (V) polyelectrolytes and (VI) ion-solvating polymer electrolytes. Extracted from reference [19].

Paulsen et al. classified OMIECs into six different categories based on whether they “*intrinsically contain ionic charge*” (I, III, V) or not (II, IV, VI), the latter group comprises materials that “*contain polar moieties that can solvate ions*”. Another distinguishing factor among these categories is whether the conjugated system is composed of a single material (homogeneous, type V and VI) or a two-component, more complex systems or block co-polymer materials (heterogeneous, type I, II, III, IV)[19]. A schematic representation is shown in Figure 2.6.

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2.2.1 Processes in OMIECs

2.2.1.1 Ionic-electronic interactions

The presence of electronic charges in OMIECs requires also the presence of excess ionic charge, so charge in the system remains in balance. In the case of types II, IV, and VI OMIECs, a phenomenon known as stabilizing electrochemical doping is achieved through the presence of mobile ions that act as free charges. Conversely, other types of OMIECs have these stabilizing charges chemically bound and fixed, making them inherently doped.

The degree of coupling between electronic charges and excess ionic charges in OMIECs can be modulated by applying a bias when connected through an electrolyte [19]. This fundamental principle forms the basis of OECTs, which will be discussed further in Section 2.3.

2.2.1.2 Electronic transport

Electronic charge transport mechanisms present in OMIECs include thermally-activated hopping and band-like transport, as depicted in Figure 2.7. These mechanisms are not different from those observed in other conjugated polymers.

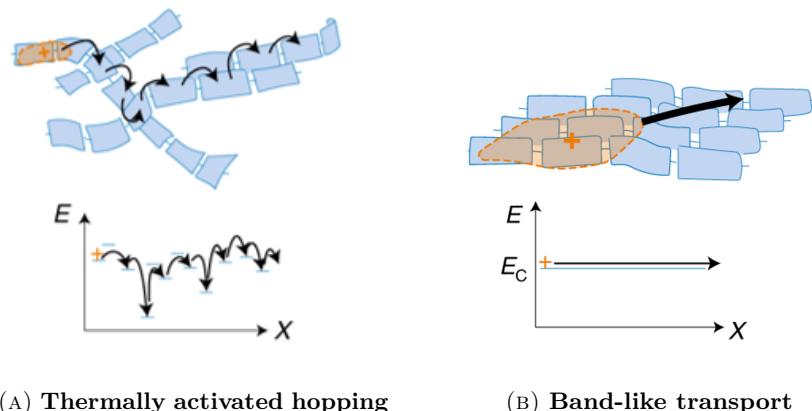


FIGURE 2.7: Schematic representation of electronic charge transport mechanisms: A) Thermally-activated hopping transport and B) band-like transport, where the electronic charge carrier is relatively localized and delocalized, respectively. Extracted from reference [19].

Thermally-activated hopping, as its name implies, is driven by thermal energy and is limited by the degree of structural disorder. In this mechanism, weakly-bonded electrons in delocalized π -orbital move along adjacent π -orbitals within the length of the conjugated polymer, or even between molecules where there is sufficient π - π overlapping. This mechanism predominates when there is a low electronic charge carrier density and a low density of accessible hopping states, resulting in low mobility and electrical conductivity [19].

2.2. Organic Mixed Ionic/Electronic Conductors (OMIECs)

In contrast, band-like transport, typically occurs in OMIECs with increasing doping levels. In this case, the activation energy of charge hopping decreases, and carrier mobility increases. This leads to diffuse band-like charge transport within the polymer-stacking [20].

2.2.1.3 Ionic transport

While transport of anions and cations in OMIECs shares some similarities with the transport of electrons and holes, it is a more complex process, since ions can be “*multi-valent, and form pairs and larger clusters; moreover, they are sensitive to solvent and solvation*” [19].

Ion transport in dry OMIECs of type I, III, and V is unipolar because these ions are fixed on a polyelectrolyte. In contrast, in type II, IV, and VI OMIECs, both anions and cations are mobile. When OMIECs come into contact with an electrolyte, they tend to swell, allowing the penetration of excess ions from the electrolyte. Therefore, both mobile anions and cations contribute to ion transport to ensure electroneutrality.

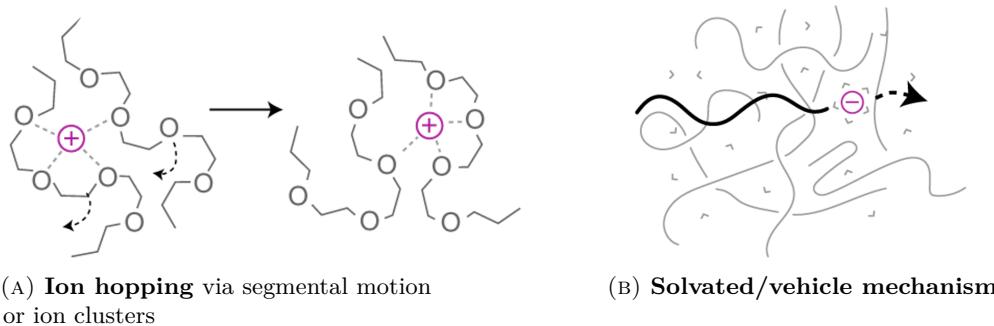


FIGURE 2.8: Schematic representation of ionic charge transport mechanisms: A) Ion hopping via segmented motion and B) vehicular solvated-ion transport. Extracted from reference [19].

There are two types of ionic charge transport in OMIECs: ion hopping and vehicular solvated-ion transport. In dry or minimally hydrated OMIECs, ion hopping assisted by segmental motion of the OMIEC side chains or backbone is the primary mechanism, as shown in Figure 2.8A. However, when OMIECs are in contact with a solvent or liquid electrolyte, both mechanisms are present, with solvated ion vehicle transport being the predominant mode. For instance, in water-based electrolytes, proton diffusion occurs via the Grotthuss mechanism, where protons within water molecules diffuse through neighboring molecules. This involves a transfer of ionic effects through the hydrogen-bonded network, as shown in Figure 2.8B.

Due to the existing ionic-electronic coupling, both ionic and electronic transport in OECTs and other OMIEC-electrolyte-based applications are not independent but are rather complex and must consider side effects such as hydration and electrolyte swelling [19], as will be further discuss in Section 2.3.

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2.3 Organic Electrochemical Transistors

Organic Electrochemical Transistors are composed of metallic source, drain and gate electrodes, an organic conjugated polymer channel (specifically an OMIEC as described in previous sections), and an electrolyte that bridges the channel and the gate, as illustrated in Figure 2.10A. OECTs are devices that have received increasing attention due to their mechanical compliance, biocompatibility, and sensitivity to biochemical signals [21].

2.3.1 Device Physics

Although the structural configuration of OECTs differs from conventional metal-oxide-semiconductor field-effect transistors (MOSFETs), understanding the operation of the latter can provide insight into how OECTs function. In contrast to MOSFETs, where an insulator is used, OECTs are coupled with an electrolyte, as shown in Figure 2.9. When a gate voltage is applied, instead of polarizing the dipoles in the insulator and creating a field that causes accumulation of carriers at the interface of the semiconductor/insulator, as is the case with MOSFETs, in OECTs, the gate voltage drives ions to penetrate the bulk of the channel. Consequently, accumulation of carriers occurs throughout the whole volume of the OMIEC film. This mechanism explains the large gate-channel capacitance observed in these devices compared to MOSFETs and why the drain current takes into account a volumetric capacitance [22].

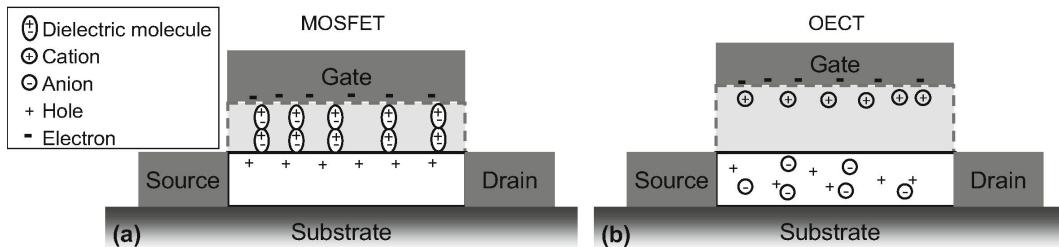


FIGURE 2.9: Comparison of p-type A) MOSFET and B) OECT, where the light-gray region represents an insulator and electrolyte, respectively. Extracted from reference [22]

Bernards and Malliaras implemented a model based on a p-type depletion-mode OECT (based on PEDOT:PSS as it is widely studies and fabricated material, further discussion in the following section) [23]. The model divides the behavior of the OECT into two circuits: an electronic circuit (comprising the source-channel-gate structure) and an ionic circuit (comprising the gate-electrolyte-channel structure).

The electronic circuit is treated as a *variable* resistor and is thus modeled using Ohm's law. Its variability arises from the fact that when a positive gate voltage is applied, de-doping of the semiconductor occurs, which is analogous to the compensation doping observed in silicon. Cations from the electrolyte penetrate the polymer, compensating for an acceptor.

Meanwhile, the ionic circuit consists of a resistor that represents the flow of ions in the electrolyte, connected in series with a capacitor representing the storage of ions in the channel, as shown in Figure 2.10B [1][23].

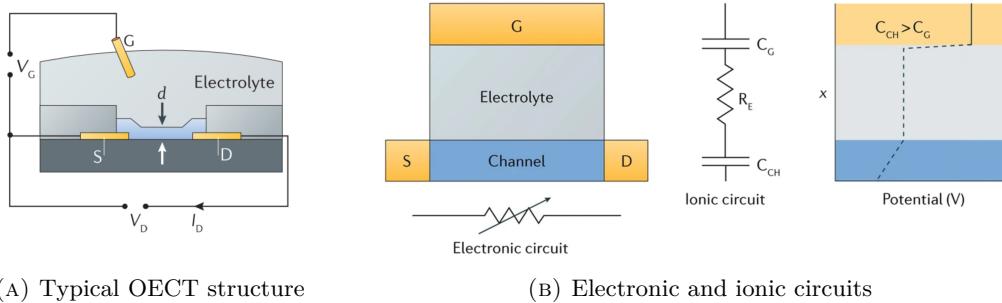


FIGURE 2.10: A) Typical structure of an organic electrochemical transistor. B) (Left) Electronic circuit modelled as a resistor with a variable resistance. (Right) Ionic circuit consisting of channel (C_{CH}) and gate (C_G) capacitors, coupled with a resistor corresponding to the electrolyte (R_E). Extracted from reference [1].

Finally, the drain current I_D for the steady state behavior of the OECT can now be described using the following equation:

$$I_D = \begin{cases} -\mu C^* \left[\frac{Wd}{L} \frac{V_{GS} - V_{Th}^2}{2V_{Th}} \right] & |V_{DS}| < |V_{GS}| - |V_{Th}| \\ -\mu C^* \frac{Wd}{L} \left[1 - \frac{V_{GS} - 1/2V_{DS}}{V_{Th}} \right] V_{DS} & |V_{DS}| > |V_{GS}| - |V_{Th}| \end{cases} \quad (2.1)$$

where μ is the charge mobility, C^* is the volumetric capacitance and W , d and L are the width, thickness and length of the channel. V_{GS} , V_{DS} and V_{Th} correspond to the gate, drain and threshold voltage, respectively. Parameters will be further discuss in Section 2.3.3.

2.3.2 Operation Modes

Analogous to conventional MOSFETs, depending on whether the device requires a gate potential to be turned ON, OECTs exhibit two operation modes: depletion and enhancement (the latter often referred to as accumulation in the context of OECTs). The operation modes are closely linked to the nature of the channel material.

As illustrated in Figure 2.11A and B, the polymer can be either intrinsically doped (conductive) or undoped (insulating). In the first scenario, the OMIEC already possesses anions that induce charges within its backbone. Consequently, to turn off the device, cations need to be injected to counteract this effect. Conversely, for an insulating polymer channel, a zero-gate biased OECT will have no charges induced in its backbone, resulting in the OFF state. To transition to the ON state, a gate voltage is required to drive anions into the polymer and induce charges.

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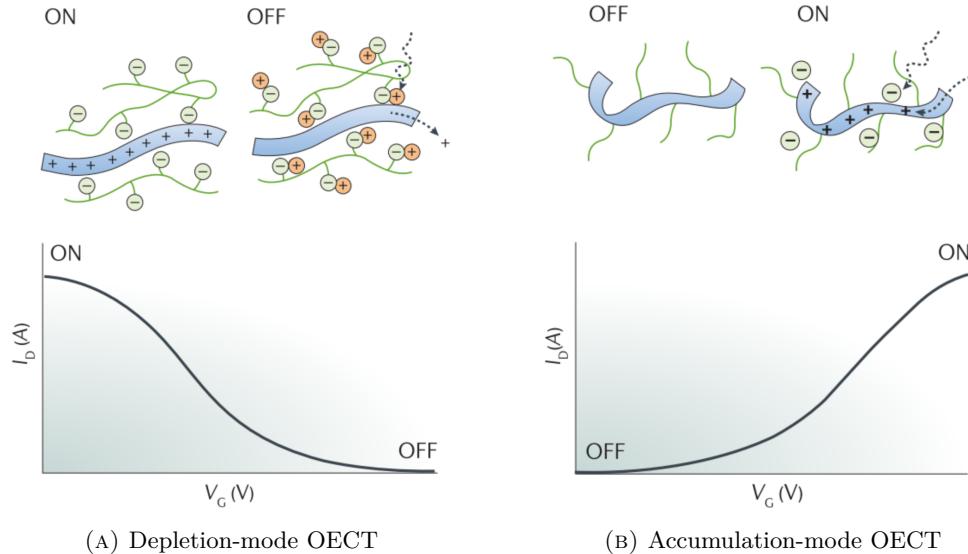


FIGURE 2.11: (A) Transfer curve showing depletion-mode operation of a p-type OECT with a conducting polymer channel. (B) Transfer curve showing accumulation-mode operation of a p-type OECT with an insulating polymer channel. Images extracted from reference [1].

2.3.2.1 Standard material for depletion-mode OECTs

Poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate) (PEDOT:PSS) is a “*degenerately doped*” [23] or conductive polymer that is widely used in various applications in organic electronics. Classified as type I OMIEC, as seen in Figure 2.6, it is a blend between a conjugated polymer (PEDOT) and a polyelectrolyte (PSS), the latter possesses chemically linked ions and serves as a polymeric acid template to allow dispersable suspensions [19].

Due to its commercial availability, operational stability, and relatively high performance, PEDOT:PSS became a standard material for p-type OECTs. However, its main drawback lies in its depletion-mode operation.

With the aim of minimizing power consumption, there is a strong interest in fabricating high-performance accumulation-mode devices [2][15][24][25]. These devices offer the advantage of dissipating less static power when the device is not in operation, due to low OFF current [16].

2.3.2.2 Prospective materials for accumulation-mode OECTs

PEDOT:PSS has not been ruled out as a possible accumulation-mode OECT, Keene et al. employed a series of amines to de-dope PEDOT:PSS and achieve OECTs with negative turn-on voltages [25]. However, synthetically modifying PEDOT:PSS in a controlled manner remains a challenge.

2.3. Organic Electrochemical Transistors

In parallel to these efforts, researchers are also working on the design of new conjugated polymers with the aim of not only having accumulation-mode OECTs but enhancing their performance. Nielsen et al. reported a series of semiconducting polymers with triethylene glycol (TEG) side chains, some of which demonstrated good performance. Among the five thiophene- and benzodithiophene-based polymers, they found out that the one with a backbone consisting of 2,2'-bithiophene (blue) polymerized with other thiophene molecule (green), named as **g2T-T**, as seen in Figure 2.12, exhibited the highest performance [2].

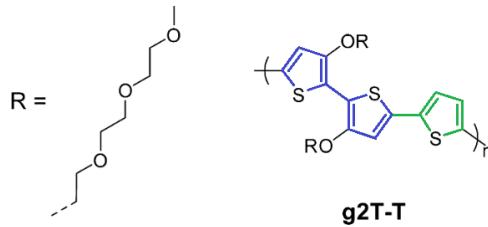


FIGURE 2.12: Chemical structure of polymer with backbone g2T-T, R representing the side chain. Extracted from reference [2].

Moser et al. conducted a study using the same backbone (g2T-T) to investigate the impact of the length of the ethylene glycol (EG) side chain on the performance of OECTs [26]. They found that reducing the side chain length maximized both the capacitance and mobility of the OECTs. However, a shorter side chain is less favorable for ion-polymer interaction.

Their research suggested an optimum-side-chain length of 3 monomers, compared to 2, 4 and 6 monomer. OECTs based on 3-(2-(2-methoxyethoxy)ethoxy) thiophene ($p(g3T2-T)$) exhibited a turn-on voltage close to zero and superior performance compared to other thiophene-based species (as seen in Figure 2.13 and Table 2.1), even surpassing PEDOT:PSS-based OECTs [24].

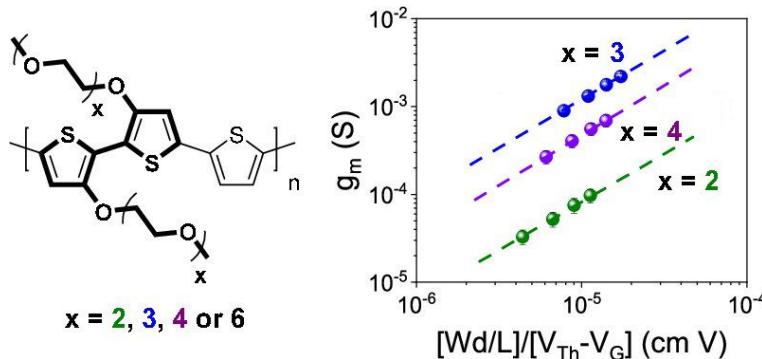


FIGURE 2.13: (Left) Chemical structure of the repeat units for $p(gxT2-T)$. (Right) Transconductance vs channel geometry and operating parameters of $p(gxT2-T)$ for $x = 2, 3$ and 4 . Extracted from reference [26].

The structure of the polymer was designed to have a backbone that warrants

2. BACKGROUND

reversibility during electrochemical redox reactions and good electronic transport, while the side chains enhance its stability in aqueous electrolytes and facilitate efficient transport of both ionic and electronic charge carrier [27].

Under the classification presented in Figure 2.6, p(g3T2-T) can be categorized as a type VI OMIEC that consists of a conjugated polymer with ions introduced as free species. Whereas, PEDOT:PSS contains ions that are chemically linked to the polyelectrolyte (PSS). This structural distinction results in p(g3T2-T) displaying larger magnitudes of ionic-electronic coupling and volumetric capacitance compared to biphasic OMIECs like PEDOT:PSS [19]. Understanding these structural characteristics is crucial for addressing the challenges associated with achieving stable OEETs, as it will be further addressed in this thesis.

TABLE 2.1: Volumetric capacitance (C^*) of OEETs channel materials including p(g2T2-T), p(g3T2-T), p(g4T2-T) and PEDOT:PSS using a 0.1 NaCl electrolyte and Ag/AgCl pellet electrode.

Polymer	C^* (Fcm^{-3})	Reference
p(g2T2-T)	8±2	[26]
p(g3T2-T)	211±18	[26]
p(g4T2-T)	192±10	[26]
PEDOT:PSS	39	[24]

2.3.3 Important Figures of Merit

2.3.3.1 Transconductance

Transconductance is considered as the most important parameter for measuring the amplification capability of any transistor. It is calculated as the first-order derivative of the output current (drain current) with respect to the input voltage (gate-source voltage), expressed as $g_m = \partial I_D / \partial V_{GS}$. Bernards and Malliaras derived this parameter in their mathematical model for depletion-mode p-type OEETs [23], as discussed in Section 2.3.1. When considering both n-type and p-type OEETs, the transconductance can be expressed as follows:

$$g_m = \frac{Wd}{L} \mu C^* |(V_{th} - V_G)|, \quad (2.2)$$

where W , L and d are the channel width, length, and thickness, respectively, μC^* denotes the product of mobility and volumetric capacitance, while V_G and V_{th} stand for the gate voltage and threshold voltage, which will be further discussed in the following subsections.

Typically, the maximum transconductance ($g_{m,max}$) is reported, which falls into the saturation regime. Inal et al. reported the maximum transconductance for various channel materials with different device geometry parameters. They used an Ag/AgCl pellet as reference/gate electrode and 0.1M NaCl as electrolyte. Their results showed that OEETs with polymerized g2T backbones exhibited the best

performance, achieving transconductance values ranging from 1 to 30 mS, depending on the geometry (Figure 2.14A) [24].

2.3.3.2 μC^* product

The parameter μC^* is considered the most important for benchmarking OEET channel materials because it represents both the ionic and electronic transport properties [24]. It is the product of two important parameters, μ , the electronic mobility, and C^* , the volumetric capacitance, the latter encloses the ion penetration, transport, and storage ability of the OMIEC film.

Along with the transconductance, Inal et al. determined the values of μC^* by calculating the linear slope of the maximum transconductance and channel geometry (Figure 2.14A), using Equation 2.2. They correlated their results with independent calculations of both parameters and found that polymerized g2T backbones exhibited the highest μC^* value of $261 \pm 29 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$. Among the materials that showed a close 1:1 relationship for both methods of calculation of the μC^* product, polymerized g2T backbones stood out (Figure 2.14B) [24].

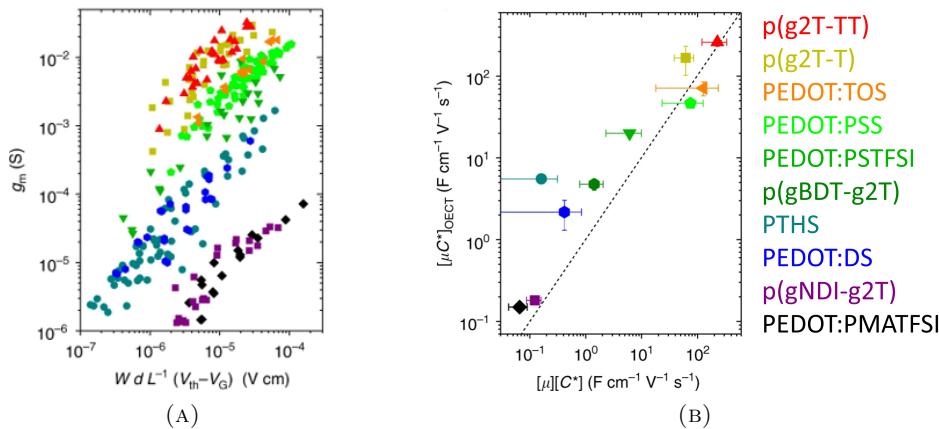


FIGURE 2.14: A) Plot of μC^* product calculated by the linear slope between transconductance and channel geometry. B) Calculated slope from A) in function of the product of independent determination of μ and C^* , dotted line represents the 1:1 relation between both methods of calculation. Extracted from reference [24].

Calculating the electronic mobility (μ) independently is challenging due to the presence of ionic species. This calculation is normally performed in transient regimes, taking advantage of ions' lower mobility, but it is outside the scope of this work.

One method to calculate the volumetric capacitance (C^*) is by performing Electrochemical Impedance Spectroscopy (EIS). Equation 2.3 is used to calculate the capacitance (C) based on the imaginary part of impedance (Z^{img}) at low frequency ranges where the capacitance should describe a plateau. The calculated capacitance is then divided by the film volume to obtain C^* [28].

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$$C = \frac{1}{2\pi \cdot f \cdot |Z^{img}|}, \quad (2.3)$$

It is important to note that the capacitance (C) can be potential-dependent when electrochemical doping is modulated in OECTs with an applied bias [24].

2.3.3.3 Threshold voltage

The threshold voltage (V_{th}) in an OECT can be determined from the steady-state transfer characteristics (I_D vs V_{GS}). To calculate V_{th} , you can plot the square root of I_D as a function of V_{GS} and extrapolate the linear portion of the slope, where it intersects the x-axis. This value of V_{th} represents the “film’s readiness for ion penetration” in OECTs [28].

Controlling or shifting the threshold voltage is desirable, specially for integrating transistors into circuits to meet specific requirements for operation, noise margins, and power consumption. There are different approaches to achieve this. One approach is the chemical de-doping of PEDOT:PSS, as discussed in previous sections, which can shift the threshold voltage to negative values characteristic of accumulation-mode OECTs [25].

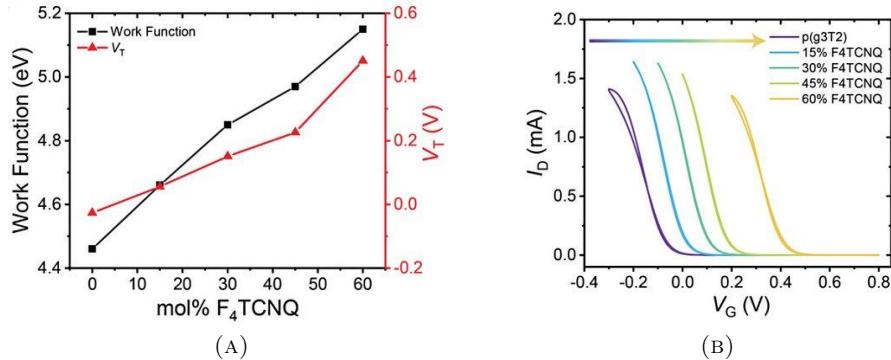


FIGURE 2.15: Controlling OECT threshold voltage by chemical doping of p(g3T2-T) gate electrode with F_4TCNQ . A) Plot of threshold voltage and gate work function for doped gates of different dopant concentrations. B) Transfer curves of p(g3T2-T) channel OECT with p(g3T2-T) gates of various F_4TCNQ dopant concentrations. . Extracted from reference [3].

Another approach, explored by Tan et al., involves tuning the doping level of the gate to shift the threshold voltage. They used p(g3T2-T) and achieved a 400 mV change in threshold voltage with a 60% molar ratio of F_4TCNQ dopant, as shown in Figure 2.15. This approach offers advantages such as i) protecting the material from oxidation by bringing the Fermi level towards the highest occupied molecular orbital, and ii) avoiding interference with the channel which helps to maintain the transconductance unaffected [3].

2.3.4 Side Reactions

2.3.4.1 Water uptake and swelling

Water uptake and swelling are important side reactions that occur when OMIECs come into contact with water-based electrolytes. Even in the pursuit of solid-state OECTs, precursors may contain a certain degree of water content [4][29], making it necessary to understand the impact of water-related side reactions.

Water uptake in OMIECs causes their increase of mass (swelling) and changes in morphology. This water uptake occurs because OMIECs need to compensate for their intrinsic doping, and as a result, “*the effect of doping-induced hydration on the OMIEC morphology must be taken into account when designing OECTs*” [30].

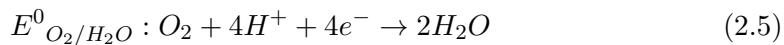
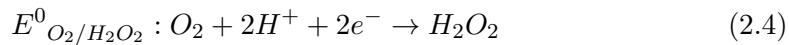
Savva et al. conducted a study to investigate the influence of water on the performance of PEDOT:PSS OECTs. They found that water uptake led to a 10-13% increase in mass under non-biased conditions. Interestingly, the concentration of water played a role in the ionic charging rate. While lower concentrations of water (NaCl_{aq} 10 mM, 100mM, 1M, and 6M) led to faster ionic charging, the fastest response time was achieved with NaCl_{aq} 1 M. This was attributed to attractive forces between counter ions, which hindered the drift of anions and delayed the injection of ions from the electrolyte [31].

Another study by Savva et al. showed that a certain level of hydration is necessary for facile ionic transport, but can have a negative impact on electronic charge transport, particularly in glycol-based side chains [30]. These side chains are commonly used in accumulation-mode OECTs, where ionic transport is already enhanced through side-chain engineering [27].

2.3.4.2 Oxygen Reduction Reaction (ORR)

The Oxygen Reduction Reaction (ORR) is a common undesirable side reaction that occurs under environmental conditions, especially in devices fabricated with polymers having low ionization potential (IPs). The use of OMIECs with low IPs is frequent in accumulation-mode OECTs.

The ORR is a non-capacitive faradaic reaction that takes place between the OMIEC and molecular oxygen, involving electron-transfer. This reaction can yield either hydrogen peroxide (H_2O_2) or water (H_2O), as described in 2.4 and 2.5, or it can result in the oxidation (p-doping) of the OMIEC which acts as the catalyst [16].



As represented in Figure 2.16, η_1 and η_2 represent the free energy difference between reactants and the reaction products H_2O_2 and H_2O , respectively. If this free energy difference is negative, indicating that the reaction requires an energy input, the ORR is endergonic, while a positive free energy difference makes it exergonic

2. BACKGROUND

(spontaneous). For instance, to prevent the formation of oxygen peroxide, a polymer with higher IP ($> 4.9\text{eV}$) would be required.

In the context of OECTs, where polymers like PEDOT:PSS and p(g3T2-T) are used, it is important to recognize that these materials exhibit exergonic reactions under environmental conditions. Therefore, it is crucial to consider the impact of the ORR on device stability and performance, particularly in applications where long-term reliability is essential.

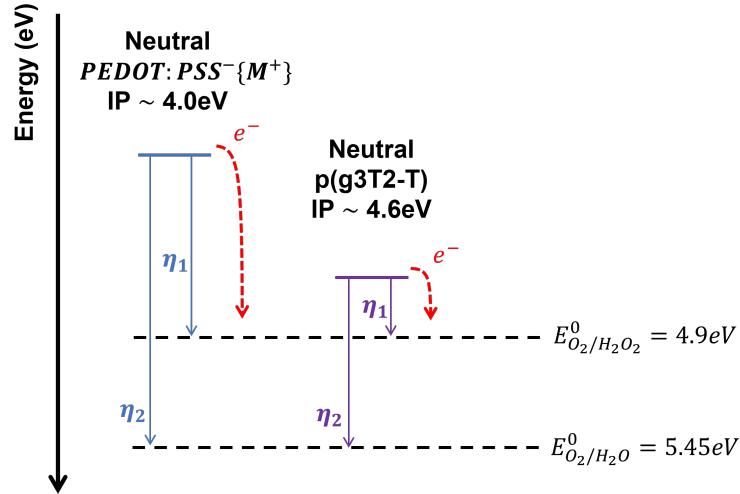


FIGURE 2.16: Simplified mechanism of two- and four-electron Oxygen Reduction Reactions with neutral states of OMIECs: p(g3T2-T) and PEDOT:PSS. The free energy difference between reactant and the reaction products is represented by η . Image adapted from reference [16], where values are defined from cyclic voltammetry measurements using Ag/AgCl as reference electrode and NaCl as electrolyte.

Chapter 3

Experimental Methods

3.1 Materials

All reactives were purchased from commercial suppliers.

- Chromium etchant: High purity ceric ammonium nitrate, Standard, Sigma Aldrich
- Gold etchant: HHPAA (2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone), 98%, Standard, Sigma Aldrich
- Developer: AZ 726 MIF Developer, Merck performance Materials GmbH
- EG: Ethylene glycol, \geq 95%, Sigma Aldrich
- [EMIM][EtSO₄]: (1-Ethyl-3-methylimidazolium ethyl sulfate), \geq 95%, Sigma Aldrich
- MBBAm: (N,N'-Methylenebisacrylamide), 99%, Sigma Aldrich
- NIPAm: (N-Isopropylacrylamide), 97%, Alfa Aesar
- Sacrificial Layer 1: Sacrificial Layer 1 (SL1), Orthogonal Inc
- Photoresist: AZ 1518 Photoresist, Merck Performance Materials GmbH & Microchemical GmbH
- Photoresist for undoped species: NLOF 2020, commercial negative-tone photoresist, Microchemical
- Orthogonal Photoresist for doped species: OSCoR 4020 Photoresist, Orthogonal Inc.
- Developer for SL1: Developer HF 7300, Orthogonal Inc.
- Orthogonal Developer for OSCor 4020: Orthogonal Developer 103a, Orthogonal Inc.

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- Orthogonal Stripper: Orthogonal Stripper 900, Orthogonal Inc.
- p(g3T2-T): 3-(2-(2-methoxyethoxy)ethoxy)thiophene from Professor Iain McCulloch, Chemistry Research Laboratory, University of Oxford.
- Dopants: 1,3,4,5,7,8-hexafluorotetracyanonaphthoquinodimethane ($F_6\text{TCNNQ}$) and 1,3,4,5-tetrafluorotetracyanonaphthoquinodimethane ($F_4\text{TCNQ}$), 97%, Sigma Aldrich.
- Adhesion promoter: Silane A174 (3-(Trimethoxysilyl)propyl methacrylate), TCI.

3.2 Equipment

- Baking: All baking steps were carried out on a Stuart SD160 digital hotplate (Stuart Equipment, UK).
- Electrical characterization (ambient): Device characterization under ambient conditions was performed on a Everbeing C-6 Probe Station (Everbeing Int'l Corp., Taiwan), connected to a Keithley 4200-SCS Semiconductor Characterisation System (Keithley Instruments, USA).
- Electrical characterization (glovebox): Device characterization was performed in a nitrogen-filled glovebox. Probing needles were connected to two Keithley 236 Source Measure Units (Keithley Instruments, USA).
- Cyclic voltammetry and Impedance measurements: Measurements were carried out by using a Metrohm Autolab PGSTAT302N potentiostat/galvanostat (Metrohm AG, Switzerland).
- Micrographs: Micrographs were taken on a Nikon Eclipse LV100ND microscope, equipped with a DS-Fi2 camera (Nikon, Japan).
- Photolithography: Photolithography was carried out on a SÜSS Microtec MJB4 maskaligner system (SÜSS Microtec AG, Germany).
- Photomasks: Photomasks were custom made by Compugraphics Jena in a 4-inch format (soda-lime glass covered with chromium) and held several mask designs (Compugraphics Jena GmbH, Germany).
- Plasma cleaning: O_2 -plasma cleaning was performed by using a Harrick PDC-002 plasma cleaner (Harrick Plasma, USA), connected to a Leybold Heraeus Combitron CM 330 Vacuum Gauge Controller (Leybold GmbH, Germany).
- Plasma etching: O_2 -plasma etching was performed by using a Diener electronic ATTO plasma cleaner (Diener electronic GmbH & Co. KG, Germany).
- Profilometry: Profilometry was performed on a Veeco Dektak 150 surface profiler (Veeco Instruments Inc., USA).

- Film resistance measurements: The film resistance was measured using a linear four-point probe system (Lucas four-point probe connector) connected to a multimeter (Keithley 2010 Multimeter).
- Transmittance and Reflectance measurements: Measurements were performed with UV-Visible-NearInfraRed Spectroscopy on a SolidSpec-3700 UV-Vis-NIR spectrometer using an integral sphere from Shimadzu.
- Energy of HOMO/HBEC cutoff measurements: Measurements were done using Ultraviolet Photoelectron Spectroscopy (UPS) on a PHOIBOS 100 from Specs, a Helium plasma discharge lamp (UVS10/35, Specs).
- Spincoating: Samples were coated with a SAWATEC SM-180-BT spincoater (SAWATEC AG, Switzerland).

3.3 Software

- Data processing: All data was processed by customized scripts written in Python. Files import and manipulation was done by using OS [32] and CSV [33] modules. Mathematical computations (e.g. fits, integration) were carried out by employing the NumPy [34], SciPy [35], and PeakDetect [36] libraries. Visualisations were performed using the Matplotlib library [37]. All is compiled in the following GitHub Repository: **marivelasco25/Thesis.git**.
- Electrical characterization: Measurements were performed by controlling SMUs through the in-house developed SweepMe! software (<https://sweep-me.net/>).
- Profilometry: Profilometry was performed by using the Dektak software (Veeco Instruments Inc., USA).
- Cyclic voltammetry: Measurements were performed by using the NOVA software (Metrohm AG, Switzerland). Parameters were fixed and are described in the following table:

TABLE 3.1: Cyclic Voltammetry parameters.

Parameter	Value
Start/Stop potential	0 V
Upper vertex potential	1 V
Lower vertex potential	-1 V
Number of scans	10
Scan rate	0.1 V/s

- Impedance measurements: Measurements were performed by using the NOVA software (Metrohm AG, Switzerland) in potentiostatic mode. Parameters were fixed and are described in the following table:

3. EXPERIMENTAL METHODS

TABLE 3.2: Electrochemical Impedance Spectroscopy parameters.

Parameter	Value
Initial frequency	10^5 Hz
Final frequency	10^{-1} Hz
Frequencies per decade	10
Amplitude (V_{RMS})	0.01 V

3.4 Photomask

The employed photolithography mask for OECT fabrication depict a specific layout of gold electrodes, as illustrated in Figure 3.1. Detailed information about the photolithography process is provided in the following section.

This layout accommodates 14 devices, each with a channel length of 70 μm and a 20 μm overlap on both sides. The channel width is set at 190 μm . Additionally, the gate electrode dimensions describes a length of 190 μm and a width of 220 μm , with a gate-channel distance of 30 μm . All 14 devices will be located within a glass sample substrate measuring $2.5 \times 2.5 \text{ cm}^2$.

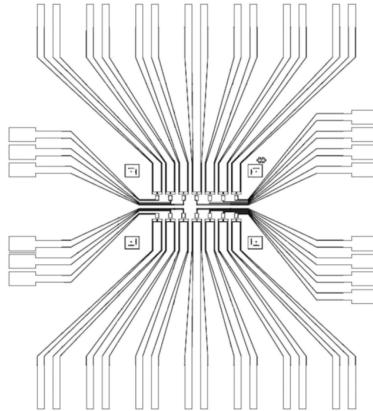


FIGURE 3.1: Used photomask for fabricated OECT gold electrodes.

3.5 Experimental Procedures

All fabrication steps were performed under standard cleanroom conditions.

3.5.1 Preparation of Films

Dynamic spin-coating of p(g3T2-T). In contrast to the approach described in reference [3], which employed drop-casting for the deposition of undoped and doped p(g3T2-T) films, our objective is to enable photolithography and facilitate a miniaturization process. To achieve this, uniform films are needed. The BioSens group members at IAPP had previously established dynamic spin-coating method

3.5. Experimental Procedures

due to the high volatility of p(g3T2-T) solvent, chloroform. Substrates were cleaned through sequential steps of ultrasonic bath in acetone for 15 minutes, IPA rinse, N₂ drying, and 5 minutes of O₂ plasma etching (0.3 mbar). Then, 70 μ L of 10 mg/mL of p(g3T2-T) mixed at 60°C for 20 minutes, was applied using dynamic spin-coating at 3000 RPM for 60s, yielding approximately 70nm thick films. The samples were then dried at 80°C.

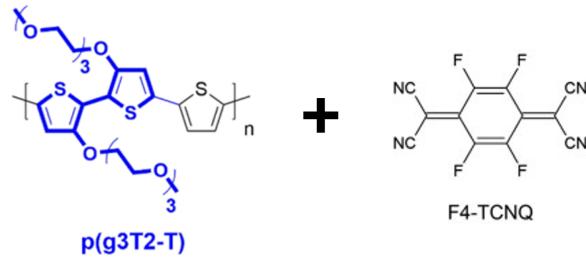


FIGURE 3.2: Chemical structures of the repeat units of p(g3T2-T) and F₄TCNQ dopant.

Dynamic spin-coating of F₄TCNQ dopant. Different doping levels of p(g3T2-T) were achieved by dynamic spin-coating 140 μ L of dopants at different concentrations (5, 10 and 20 mg/mL, as seen in Figure 3.3), previously mixed in acetonitrile at 60°C for 20 minutes. The samples were then dried at 80°C.

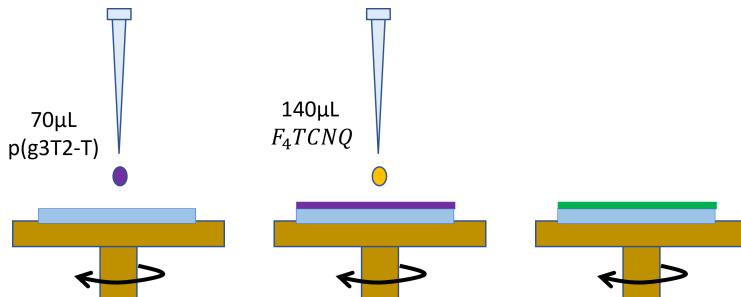


FIGURE 3.3: Dynamic spin-coating process to obtain undoped and doped films of p(g3T2-T)).

3.5.2 Doping Characterization of Films

Profilometer. The films were scratched 4 times to remove part of material, and measure the cavity depth to obtain the film thickness.

Four-point probe. Sheet resistance and resistivity were calculated following reference [38], via equations:

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$$R_s = \frac{\pi}{\ln(2)} R = 4,53R \quad [\Omega/sq], \quad (3.1)$$

where R is the resistance measured with the four-point probe setup, and

$$\rho = R_s t \quad [\Omega.cm], \quad (3.2)$$

where t is the thickness of the film.

UV-Vis-NIR Spectroscopy. After the preparation of the films onto quartz substrates, transmittance (T) and reflectance (R) was measured using the UV-Vis-NIR Spectrometer in the range of 285 to 1600 nm. Then, absorption (A) was calculated via

$$A = 1 - T - R, \quad (3.3)$$

and normalized with respect to the incoming light [39]. Additional measurements were taken, after some days of storage under ambient conditions to check its stability in air.

Ultraviolet Photoelectron Spectroscopy. After the preparation of the films, the energy of the highest occupied molecular orbital cutoff (E_{HOMO}) and the high binding energy cutoff E_{HBEC} was measuring using UPS. The pressure in the chamber during measurements was about $5 \cdot 10^{-9}$ mbar, while the base pressure is in the range of $10 \cdot 10^{-10}$ mbar. The workfunction (WF) and ionization energy (IE) are calculated by using the following equations:

$$WF = h\nu - E_{HBEC} \quad [eV], \quad (3.4)$$

$$IE = h\nu - (E_{HBEC} - E_{HOMO}) \quad [eV], \quad (3.5)$$

where $h\nu = 21.22eV$, the main He I excitation line of the Helium plasma discharge lamp [40].

3.5.3 Fabrication of Organic Electrochemical Transistors

Photolithographically patterned substrates with gold contacts for source, drain and gate were obtained using mask layout illustrated in Figure 3.1. The steps outlined in references [4] and [41] were followed, which is also represented in Figure 3.4.

Then p(g3T2-T) films were deposited following the procedure described in the previous section. The patterning of doped-p(g3T2-T) channel adopted a procedure similar to the one described in references [4][41], which involves the use of PEDOT:PSS. However, some modifications in the exposure and developing times were made. In contrast, the patterning of undoped-p(g3T2-T) samples, required a different protocol. A sacrificial layer is introduced to ensure proper cross-linking with photoresist. Both processes are detailed in the following:

3.5. Experimental Procedures

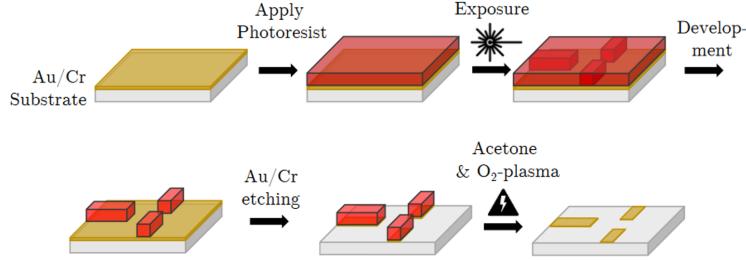


FIGURE 3.4: Visualization of the workflow for Au-contacts patterning. Image modified based on reference [41].

Patterning undoped-p(g3T2-T). Patterning of the p(g3T2-T) was achieved with photolithography, as shown in Figure 3.5. First, a fluoropolymer Sacrificial Layer 1 (SL1) was spin-coated at 6000 RPM for 60 s, followed by a baking step for 180 s at 113°C. Before the deposition of photoresist, a O₂ plasma cleaning step was applied for 60 s to promote adhesion. Then, NLOF 2020 photoresist was spin-coated at 3000 RPM for 60 s and baked for another 60 s at 113°C. Exposure of negative resist was performed for 12 s by shadowing all areas except the ones of interest. After post-baking for 60 s at 113°C, NLOF was developed by rinsing the sample in AZ MIF 726 for 20 s and wash off in DI water (carried out extra times if necessary). Next, SL1 was developed using HF 7300 developer for 45 s and spin rinsed at 3000 RPM (carried out extra times if necessary). Excess of p(g3T2-T) was removed by O₂-plasma etching for 180 s. The sample was placed in Orthogonal Stripper 900 overnight at room temperature, to complete the removal. Finally, ultrasonication in acetone was added for 15 min the next day.

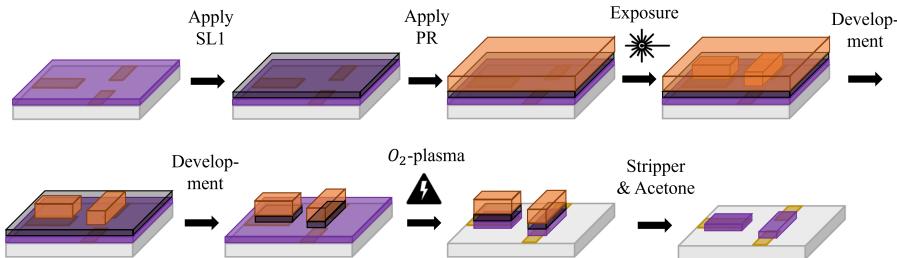


FIGURE 3.5: Visualization of the workflow for patterning undoped p(g3T2-T).

Patterning doped-p(g3T2-T). Patterning of the doped-p(g3T2-T) was achieved with photolithography, as shown in Figure 3.6. First, the orthogonal photoresist OSCoR 4020 was spin coated at 3000 RPM for 60 s and baked for another 60 s at 103°C. Exposure of negative resist was performed for 20 s with shadowing all areas except the ones of interest, one extra cycle was added if using higher dopant concentration (10 mg/mL). After post-baking for 60 s at 103°C, OSCoR was

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developed using Orthogonal Developer 103a for 45 s and spin rinsed at 3000 RPM for 60 s (carried out extra times if necessary). Excess of doped-p(g3T2-T) was removed by O₂-plasma etching for 180 s. The sample was placed in Orthogonal Stripper 900 overnight at room temperature.

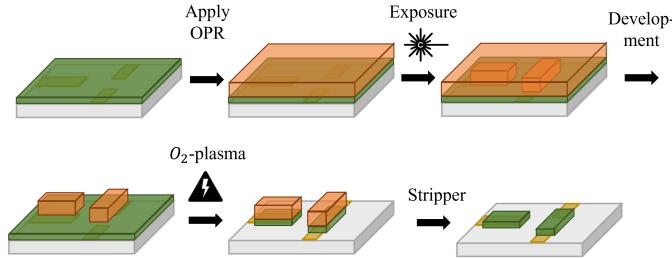


FIGURE 3.6: Visualization of the workflow for patterning doped p(g3T2-T).

3.5.3.1 Influence of Doping on OEET Channel

OEET with undoped- and doped-p(g3T2-T) channel. A solid-state electrolyte precursor was prepared according to the details provided in Table 3.3. Next, 20 μ L of this precursor were drop-casted to the patterned samples, both undoped and doped, covering all 14 devices in the sample. Finally, a Ag/AgCl pellet was installed and used as gate (Figure 3.7). Transfer characteristics were measured under ambient conditions with a V_{GS} swept backwards from 1.0 V to -0.8 V.

TABLE 3.3: Composition of the solid-state electrolyte [4].

Component	Amount	Function
H ₂ O	1.0 mL	dilution
[EMIM][EtSO ₄]	1.5 mL	ionic liquid
MBBAm	20 mg	crosslinker
NIPAm	750 mg	monomer
HPAA	200 mg	photoinitiator
EG	1.5 mL	increase viscosity, ensures good print
Triton	1 drop	surfactant, ensures good print

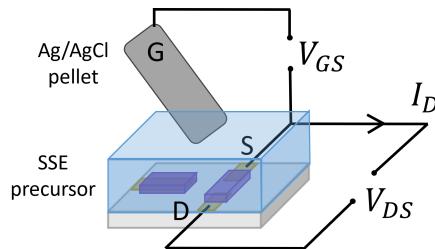


FIGURE 3.7: Representation of experimental setup for measuring threshold voltage shift of a single OEET under ambient conditions. Scheme is not drawn to scale.

3.5.3.2 Stability on Air of p(g3T2-T)

In this subsection, stability tests were conducted on both undoped and doped p(g3T2-T) samples. These samples were doped with F₆TCNNQ, following same procedure described in subsection 3.5.1. The channel conductivity was measured before and after patterning and after contact with SSE while a fixed biased drain-source voltage was maintained, under N₂ and ambient conditions.

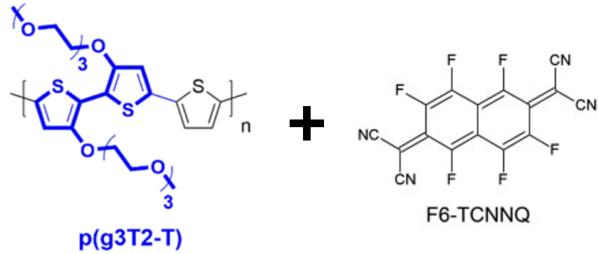


FIGURE 3.8: Chemical structures of the repeat units of p(g3T2-T) and F₆TCNNQ dopant.

Channel conductivity measurements. Undoped-p(g3T2-T) sample was measured in N₂ then ambient conditions immediately after spin-coating onto substrate with patterned gold contacts. Then, sample was measured after patterning process (as described in previous section). Finally, upon drop-casting solid-state electrolyte precursor. The doped-p(g3T2-T) channel was measured after patterning and upon drop-casting solid-state electrolyte precursor.

3.5.3.3 Reverse Oxidation of Undoped-p(g3T2-T)

By electrochemical dedoping. Undoped-p(g3T2-T) samples onto patterned-gold-contacts substrates were prepared. The solid-state-electrolyte precursor was dropcast onto the 14 devices, one device source-drain was negatively-biased and applied a positive gate voltage. Channel conductivity was monitored. Finally, other devices on the sample were measured to detect any effect of the process.

By heating. An undoped-p(g3T2-T) solid-OECT, whose fabrication will be described in the following subsection 3.5.3.4, was exposed to ambient conditions, devices were clearly oxidized. The sample was placed on a hot plate at 120°C, brought back to glovebox, and measured the following day.

3.5.3.4 Solid-OECTs using Undoped-p(g3T2-T)

After following the patterning steps for undoped-p(g3T2-T) from Subsection 4.5. Three different methods of applying the solid-state electrolyte precursor were tested. Then, transfer characteristics were measured at a constant V_{DS} of -0.1V, and a V_{GS} swept backwards from 1.0 V to 1.0 V at a scanning rate of 0.083 V/s. Cyclic

3. EXPERIMENTAL METHODS

voltammetry and electrochemical impedance spectroscopy were performed by short-circuiting source and drain to probe between channel and gate. Parameters were fixed as described in Section 3.3, and measurements were taken one day after the fabrication.

Application of adhesion promoter. An adhesion promoter, consisting of reactants detailed in Table 3.4, was applied to the substrate. The sample was placed in a Petri dish at 50°C and covered for 20 min. Subsequently, it was thoroughly rinse with ethanol and dried on a hot plate at 100°C for a minimum of 10 min. The composition and application steps of adhesion promoter was previously established by Biosens group members at IAPP.

TABLE 3.4: Composition of adhesion promoter.

Component	Amount
SilaneA174	30 μ L
Etolol	3mL
Acetic acid	60 μ L

OECT with drop-casted Solid-State Electrolyte. Solid-state electrolyte precursor was drop-casted and then exposed for 2 cycles of 60 s in a mask aligner, as shown in Figure 3.9A. No adhesion promoter was applied in this sample.

OECT with photopatternable Solid-State Electrolyte. After the application of the adhesion promoter, the solid-state electrolyte precursor was drop-casted onto the sample, followed by the placement of a Teflon foil to prevent contact with the mask, which would shadow all areas except the ones of interest in the negative resist. The sample was then exposed for 2 cycles of 60 s in a mask aligner. Removal of excess, non-cross-linked precursor was careful blown off with a N₂ gun, as shown in Figure 3.9B, following references [4][41].

OECT with inkjet-printed Solid-State Electrolyte. After the application of the adhesion promoter, the solid-state-electrolyte precursor was ink-jet printed and expose for 2 cycles of 60 s in mask aligner, as illustrated in Figure 3.9C. Parameters and procedure for ink-jet printing was previously established by members of BioSens group at IAPP.

3.5.3.5 Solid-OECTs using Doped-p(g3T2-T)

OECT with inkjet-printed Solid-State Electrolyte. After the deposition of films and dopant (F₆TCNNQ), films were stored in glovebox over the weekend to let dopants soak and dry. Then, the patterning steps for doped-p(g3T2-T) from Subsection 4.5 were followed with no extra cycles in exposure times. Solid-state electrolyte precursor was ink-jet printed as described in the previous subsection.

3.5. Experimental Procedures

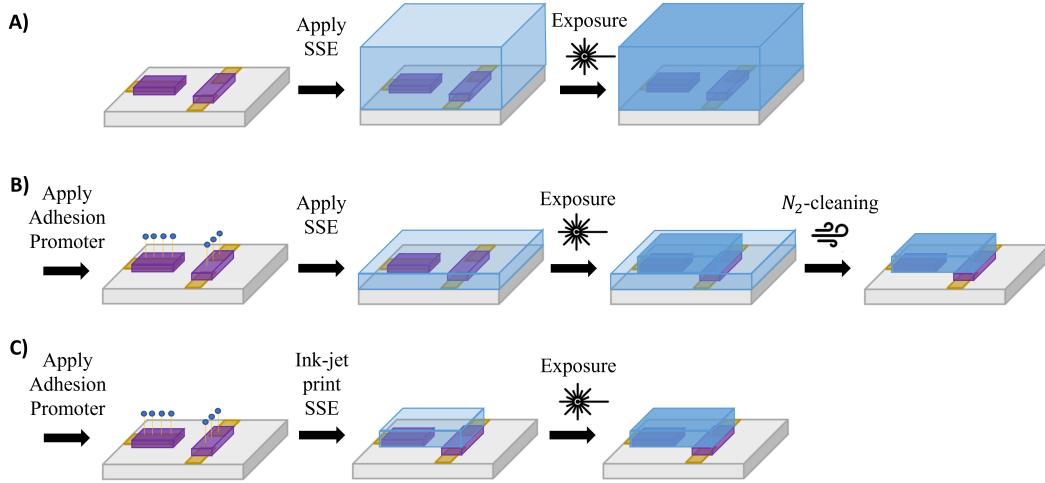


FIGURE 3.9: Visualization of the workflow for solid-OECT fabrication with undoped p(g3T2-T) by A) drop-casting SSE, B) photopatterning SSE, C) ink-jet printing SSE.

Then, transfer characteristics were measured at a constant V_{DS} of -0.1V, and a V_{GS} swept backwards from 1.0 V to 1.0 V at a scanning rate of 0.083 V/s. Cyclic voltammetry and electrochemical impedance spectroscopy were performed by short-circuiting source and drain to probe between channel and gate. Parameters were fixed as described in Section 3.3, and measurements were taken one day after the fabrication.

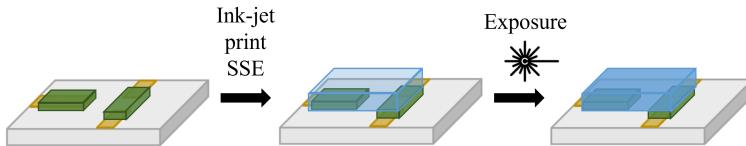


FIGURE 3.10: Visualization of the workflow for solid-OECT fabrication with doped p(g3T2-T) by ink-jet printing SSE.

Chapter 4

Results and Discussion

4.1 Doping Characterization

Upon increasing the dopant concentration deposited on top of the p(g3T2-T) film and subsequent baking, the reflection hue, as depicted in Figure 4.1 shift toward more yellowish tones.

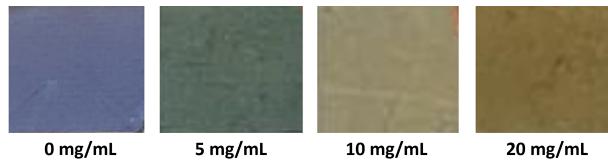


FIGURE 4.1: Color change upon increasing dopant concentration from 0 to 20 mg/mL.

4.1.1 Thickness, Sheet Resistance and Resistivity

Sheet resistance and resistivity, as shown in Table 4.1, were calculated using equations 3.1 and 3.2, respectively, as described in previous chapter. The film thickness was determined through profilometer measurements, resulting in an approximate thickness of 70 nm.

TABLE 4.1: Sheet resistance and resistivity values for undoped and doped films of p(g3T2-T)

	Undoped	5 mg/mL	10 mg/mL	20 mg/mL
R_S (Ω/sq)	6.3M	104.6k	70.7k	49.4k
ρ (Ωcm)	44.1	0.73	0.49	0.35

Upon doping, a substantial decrease is observed in both sheet resistance and resistivity. However, this decrease is not as pronounced when higher dopant levels are introduced, as depicted in Figure 4.2. Nevertheless, when comparing the reduction

4. RESULTS AND DISCUSSION

among doped samples, a clear linear relationship becomes apparent with increasing the dopant concentration.

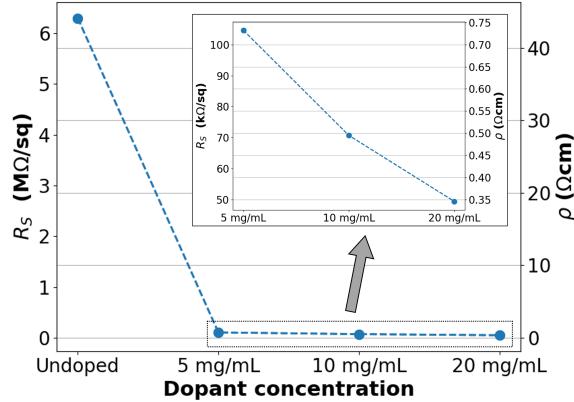


FIGURE 4.2: Sheet resistance and resistivity drop upon doping of p(g3T2-T). Inlet represents the quasi-linear drop of parameters as between doped samples.

4.1.2 Absorbance and Dopants Diffusion

The visible color hue shift can be quasi-quantitatively described by examining the absorbance spectra of the samples, as illustrated in Figure 4.3. In the case of undoped-p(g3T2-T), there is a prominent absorption peak at 588 nm (red), which diminishes with increasing doping concentration, indicative of oxidation. Notably, new absorption peaks emerge at around 860 nm, a consequence of polaron generation, leading to new optical transitions, as explained in Chapter 2, Section 2.1.2.

Tan et al. documented the appearance of new absorption peaks within the 300 to 600 nm range. The higher energy (lower wavelength) peak is generated by unreacted neutral dopant species (TCNQ^0), while the second is attributed to the new dopant anions (TCNQ^-), which induce charges in our polymer [3]. Additionally, it is worth noting that, after several days of storage, the initially dominant peak of unreacted neutral dopants diminishes in intensity relative to the anions peak. This observation suggests ongoing diffusion of dopants through the polymer over time.

Absorbance values are directly correlated with the density of states of these new optical transitions [11]. In our spectra, the absorbance value at 860 nm of the lowest-doped p(g3T2-T) sample (5 mg/mL) is relatively higher, around 40%. This might initially appear counterintuitive. However, as the doping concentration increases, the formation of bipolarons and bipolaron bands becomes energetically more favorable [42]. This phenomenon aligns with observations in the higher wavelengths, such as at 1600 nm, where absorbance increases in the more highly doped p(g3T2-T) sample.

Moreover, Tan et al. reported the formation of bipolaron in this specific context, evidenced by a shift to lower energies in the broad absorbance spectrum within the mid-IR region (wavenumbers $1000\text{-}1600\text{ cm}^{-1}$) [3]. Consequently, further analysis of

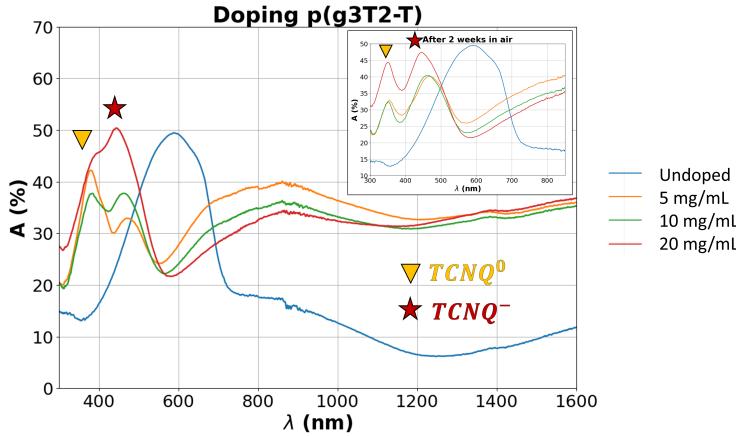


FIGURE 4.3: Spectra of undoped and doped-p(g3T2-T) at different doping levels, corresponding to samples on Figure 4.1. Inlet represents absorbance after two weeks of storage in ambient conditions.

hole bipolaron formation can be conducted with Fourier Transform InfraRed (FTIR) spectroscopy.

4.1.3 Workfunction

While the ideal preparation of films for studying electron energy levels with UPS involves working under inert conditions to prevent contamination, the current fabrication process of OECTs unavoidably exposes our films at ambient conditions. Therefore, measurements were conducted following deposition under these ambient conditions. Yet, it is possible to discern an increase in the workfunction, indicated by a shift of Fermi level of the polymer. This shift towards the HOMO level is more pronounced at higher dopant levels, as depicted in Figure 4.4, which is characteristic of p-type doping. Although some potential contamination prevented the measurement of samples with a dopant concentration of 20 mg/mL, the trend is clearly evident.

TABLE 4.2: Workfunction calculation from UPS measurements.

	Undoped	5 mg/mL	10 mg/mL
E_{HBEC} [eV]	17.35	16.47	16.36
E_{HOMO} (vs E_F)	4.28	3.27	3.24
WF [eV]	3.87	4.28	4.86

It is important to consider that UPS is a surface-sensitive measurement. The penetration depth of the ultraviolet-range electrons in UPS is approximately 2 nm, significantly less than our polymer thickness (approximately 70 nm). Consequently, this technique constrains our understanding of the diffusion of dopants throughout the entire volume of the polymer. While, we gained some insights into this matter in the previous subsection, further analysis could be undertaken using X-Ray Photoelectron Spectroscopy which offers a depth profiling mode.

4. RESULTS AND DISCUSSION

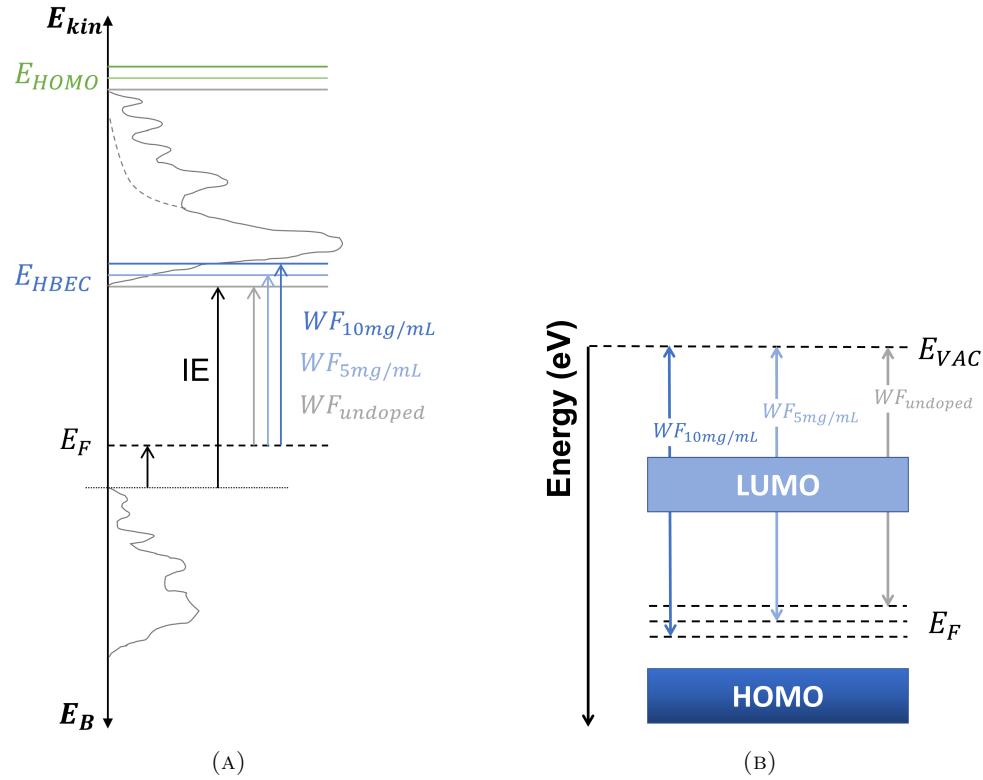


FIGURE 4.4: Graphical representation of A) the relationship between the binding energies E_B and the kinetic energy of the photoelectrons E_{kin} , and B) the Fermi level shift, upon doping.

4.2 Fabrication of Organic Electrochemical Transistors

The patterning process was successfully achieved with photolithography by using a mask that include a microstructure gate, suitable for studying OECTs with both channel and gate made of the same OMIEC material, commonly PEDOT:PSS. The result is displayed in Figure 4.5.

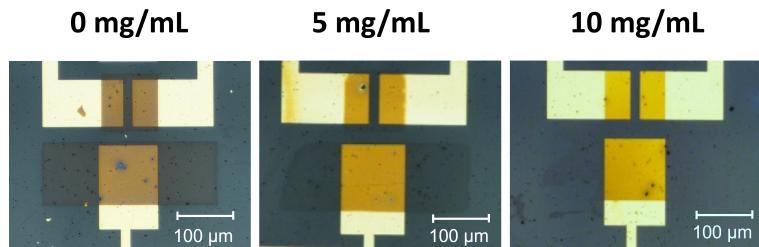


FIGURE 4.5: Micrographs of patterned channel and gate with p(g3T2-T) undoped, 5 mg/mL and 10 mg/mL dopants, following procedures explained in Section .

4.2.1 Influence of Doping on OEET Channel

Since our final goal is to study fully patterned solid-OEETs that will allow integrated circuits (IC). It was necessary to first understand the solely impact of the channel doping in our devices. Some hypothesis comes along, based on reference [3]:

1. The manipulation of channel doping will negatively impact transfer characteristics.
2. The introduction of ionic species (TCNQ^-) in p(g3T2-T) should create depletion-mode devices with positive threshold voltages. Since a higher positive gate biased would be needed to counteract these anions and turn OFF the device.

As explained in the last chapter, we paired our channel with a non-polarizable Ag/AgCl pellet as gate, a widely used gate to investigate OEET-based materials, and coupled with SSE precursor. Unfortunately, the sample that used solution with dopant concentration of 20 mg/mL exhibited doping homogeneity issues. While photolithography was still possible, it could not provide a fair basis for comparison with the other devices. Therefore, this sample will be omitted from this analysis.

The results shown in Figure 4.6, Figure 4.7 and Figure 4.8 correspond to the same device and same loop on each sample (undoped, 5 mg/mL and 10 mg/mL dopants) from the same batch of materials. After reporting the findings on the analysis of these devices, a more statistical study will be shown within the operating devices on each sample. An important consideration for the statistical analysis of this part is that besides the attempts to increase the yields, only 3 or 4 out of the 14 devices were operational on each sample. Further improvements on the photolithography process were needed, and were accomplished as it will be shown in further sections of this chapter.

Transfer characteristics are illustrated in Figure 4.6A, C, E which correspond to undoped, 5 mg/mL and 10 mg/mL dopants, respectively. A positive turn ON voltage is perceived in the undoped OEET device, which evidenced the fast oxidation (unwanted doping) of p(g3T2-T) under environmental conditions due to its low IP.

The drain current (I_D) of the undoped device shows higher values than doped devices, Hidalgo et al. reported that pristine p(g3T2-T) show oxygen reduction reaction activity in oxygen-saturated conditions, therefore, it is expected an increase of current within the polymer until saturation [43]. It will be necessary to control the oxidation state of the polymer among the different steps of the photolithography process, or somehow revert the oxidation of p(g3T2-T), this will be addressed in the following sections.

Gate current (I_G) is displayed in dotted lines and it is perceived that the drain OFF current ($I_{D,OFF}$) is dominated by this leakage current in all devices.

The higher dopant concentration device (10 mg/mL dopant) shows signs of breakage as going to more negative V_{DS} (Figure 4.6E and Figure 4.7D), therefore, this measurement will be disregard for calculating transconductance and threshold voltage.

4. RESULTS AND DISCUSSION

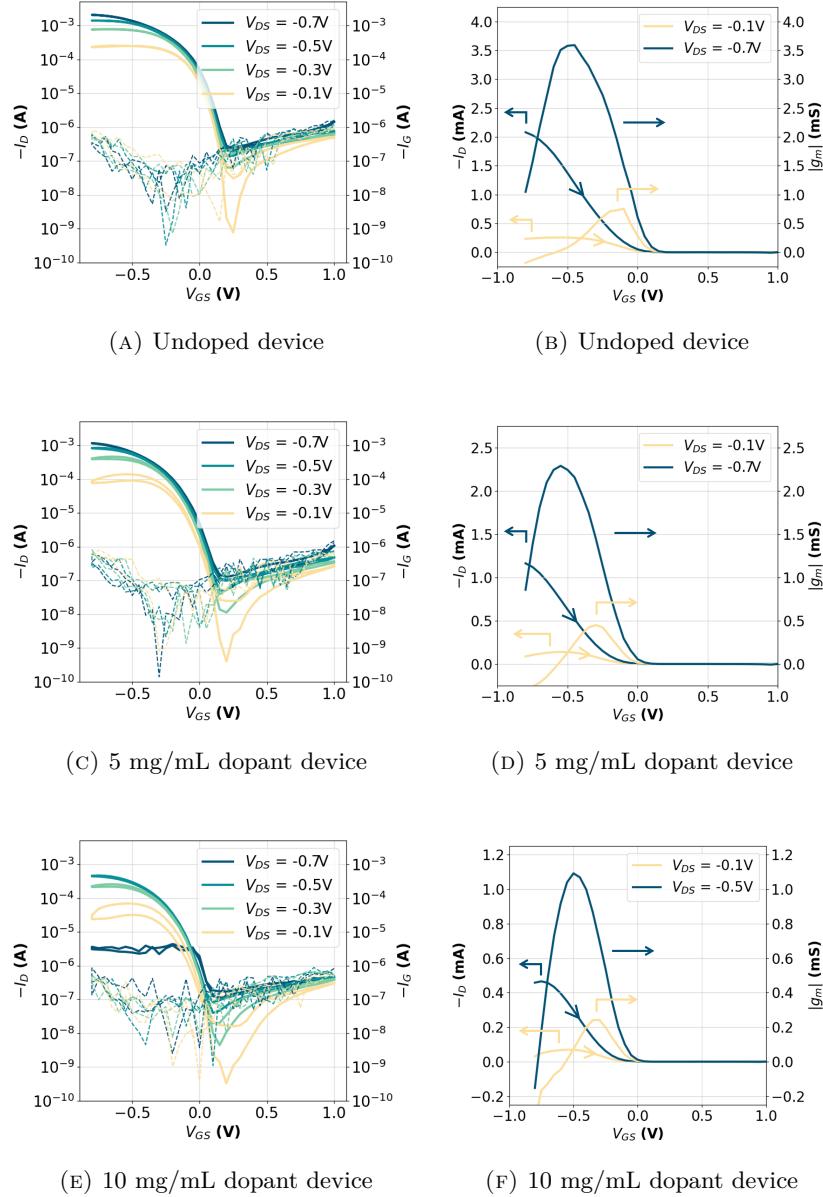


FIGURE 4.6: A), C), E) Transfer characteristics of all measured V_{DS} including the gate leakage current I_G B), D), F) Transfer curves (off-switching) with corresponding transconductance. Each group of graphs for undoped, 5 mg/mL and 10 mg/mL doped p(g3T2-T) channel, respectively.

In Figure 4.7, it can be perceived that doped devices exhibit minimum differences on $I_{D,OFF}$ but $I_{D,ON}$ decreases while increasing doping levels. This is reflected in the maximum transconductance values displayed in Table 4.3, a clear drop of $|g_{m,max}|$ is seen as doping level increases. From our initial hypothesis, this was expected and a

4.2. Fabrication of Organic Electrochemical Transistors

further analysis will be performed later with impedance measurements to calculate volumetric capacitance.

TABLE 4.3: Maximum transconductance values extracted from Figure 4.6B, D, F

$ g_{m,max} $ [mS] @	Undoped	5 mg/mL	10 mg/mL
$V_{DS} = -0.1$ V	0.75	0.45	0.24
$V_{DS} = -0.3$ V	2.01	1.31	0.74
$V_{DS} = -0.5$ V	2.90	1.97	1.09
$V_{DS} = -0.7$ V	3.59	2.23	

More importantly and what caught our attention, results displayed in Figure 4.7 and Figure 4.8 evidenced turn ON voltages and threshold voltages, respectively, **shifted towards negative values** as the dopant concentration increased in all V_{DS} values, **contradicting our initial hypothesis**. A sort of **compensation doping effect** is evidenced in the OECTs. Further investigation is needed to counteract this effect.

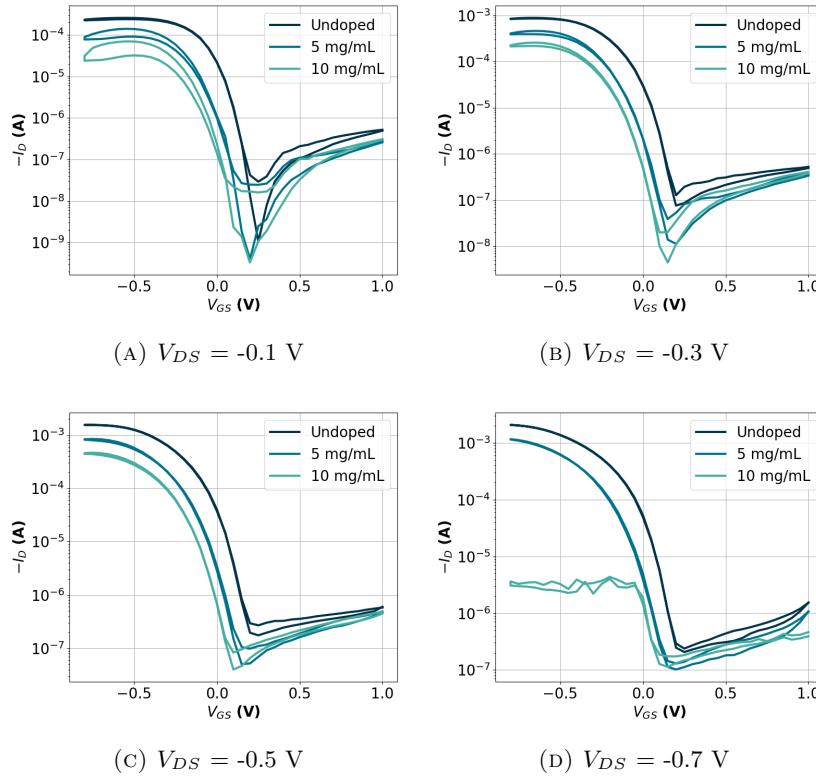


FIGURE 4.7: Transfer characteristics comparing undoped, 5 mg/mL and 10 mg/mL dopants devices, each graph represent a different V_{DS}

Additionally, threshold values showed lower variability among different values of V_{DS} with higher doping level (Figure 4.8). In the undoped species, the variability

4. RESULTS AND DISCUSSION

could be caused by ORR which should be different at different drain biased conditions. Whereas, in the doped species this variability should decrease since we are reducing ORR when doping by depleting reactive electrons from p(g3T2-T) with F₄TCNQ, hence assuring a better stability in air [3].

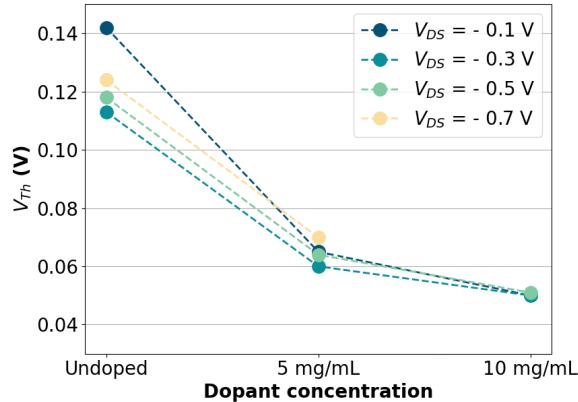


FIGURE 4.8: Threshold shift at different doping levels and V_{DS} , calculations were done using data shown in Figure 4.6.

Moreover, something that it is not shown in this report but it was perceived during analysis, there is higher repeatability of transfer characteristics with undoped OECT devices. The saturation of ORR in undoped species, as stated before, may maintain repeatability. However, variability in doped species needs yet to be further study.

4.2.2 Stability on Air of p(g3T2-T)

Channel conductivity of an undoped device was measured immediately after spin-coating exhibiting a value of 1 μS , after the patterning process described in previous sections, the conductivity increased three orders of magnitude yielding to approximate 1 mS. Although, μS values already represent a sign of oxidation, the patterning process oxidizes our material even more.

Measurements of I_D at -0.3 V of V_{DS} and no gate-biased exhibited a small decrease of 4%, and small increase of 15% within two hours in N_2 and air environment, respectively. Air stability is seeing after patterning but due to the unwanted doping.

Same study was performed with a doped device with 5 mg/mL of F₆TCNQ dopant, obtaining a higher level of doping than using F₄TCNQ, as it can be examined in Appendix A. The channel conductivity yielded to a value of 266 μS with a reduction of 1.2% within one hour in N_2 environment, and same value with minimal fluctuation of 1.0% within one hour in ambient condition. Showing a lower conductivity compared to the oxidized p(g3T2-T) but same stability in air, as stated in reference [3].

Interestingly, upon contact with SSE precursor, conductivity of both samples drops significantly, around six orders of magnitude, under N_2 environment, basically until reaching the sensitivity limits of our equipment and noisy signal is perceived,

4.2. Fabrication of Organic Electrochemical Transistors

as shown in Figure 4.9A. Our first hypothetical explanation relates to the fact that p(g3T2-T), as a type VI OMIEC, has no chemical binding with $TCNQ^-$ anions. Upon contact with the electrolyte, anions are dragged to it rather than staying in the backbone of the polymer (de-doping), leading to its original insulating state, which is actually required for accumulation-mode OECTs.

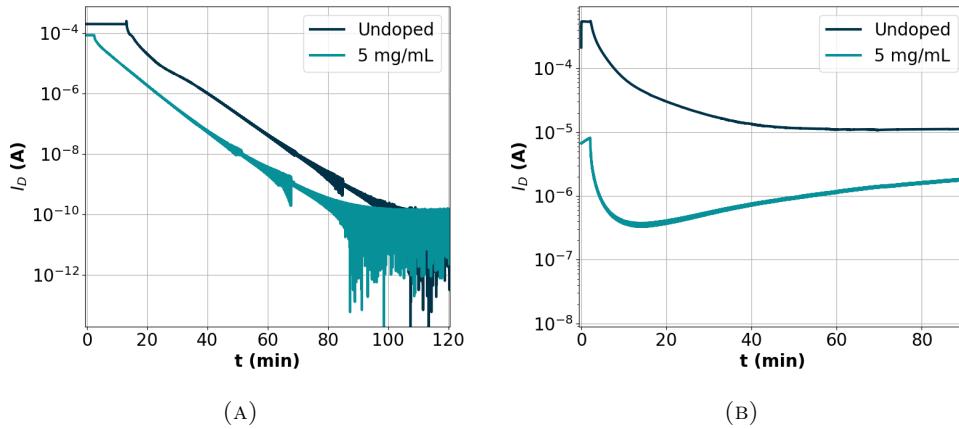


FIGURE 4.9: Drain current over time of undoped p(g3T2-T) coupled with SSE precursor under A) N_2 , and B) ambient environment.

On the other hand, as seen in Figure 4.9B, under ambient conditions, there is a smaller decrease of more than one order of magnitude for the undoped sample. The doped sample show a similar and faster drop in the first 15 minutes, but then a sudden increase of I_D is perceived. In both scenarios, ORR prevents a higher decrease of current, and the fluctuation seen in the doped species may be due to the simultaneous ORR and the de-doping.

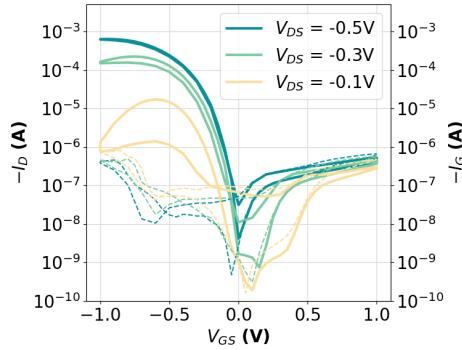


FIGURE 4.10: Transfer characteristics after electrochemical de-doping at different V_{DS} under ambient conditions

Transfer curves of the undoped device using an Ag/AgCl pellet as gate were measured under ambient conditions after de-doping in N_2 environment, as seen in

4. RESULTS AND DISCUSSION

Figure 4.10. The device is shifting its ON voltage and negative threshold voltages values, as shown in Table 4.4, to negative values. A visible sign of degradation is perceived at the end of the measurements when V_{DS} is -0.1 V.

TABLE 4.4: Threshold voltage extracted from Figure 4.10

V_{DS} [V]	V_{Th} [V]
-0.1	-0.18
-0.3	-0.15
-0.5	-0.13

In summary, the de-doping could become a method to obtain an accumulation-mode OECTs by reversing the oxidation of p(g3T2-T) and will be addressed in the following section.

4.2.3 Reverse Oxidation of Undoped-p(g3T2-T)

From the analysis above, the de-doping of the p(g3T2-T) took around two hours to obtain a fully insulating state of the polymer. However, we could speed up this process by applying a positive gate-biased on one of the devices.

Additionally, the use of high-temperature-baking step to revert oxidation of p(g3T2-T) was a method acknowledged by team mates of the Biosens group at IAPP, and is also going to be tested.

4.2.3.1 By Electrochemical Dedoping

De-doping under N_2 environment was performed by applying +1 V gate biased, p(g3T2-T) reached its insulating state in less than 300 seconds.

It was expected from the results above that this process was not reversible upon disconnection of gate. Figure 4.11A confirms this, after I_D drastically drops and gate is disconnected (grey arrows), the current remains low and leakage current is predominant. When connecting the gate again (gold arrows), a capacitive current jumps but later stabilizes to match the leakage current.

Now transfer curves using the p(g3T2-T) gate show a negative turn ON voltage after reversing oxidation. However, it is perceived that using the OMIEC gate instead of the Ag/AgCl pellet affects our “gating efficiency”, which was expected. Weissbach et al. demonstrated the Electrochemical Electrode Coupling (ECC) between channel and its electrode has stronger effects in device operation when micro-integrated polarizable gates (OMIECs) are used, causing saturation loss (as seen in Figure 4.11B) and threshold voltage roll-off when increasing V_{DS} [44], the latter was perceived during measurements. Therefore, from now on, V_{DS} will be fixed to - 0.1 V.

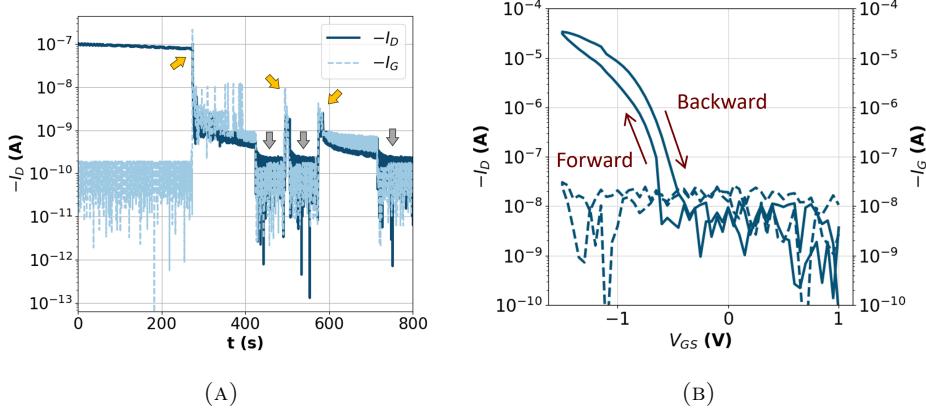


FIGURE 4.11: A) De-doping p(g3T2-T) using a gate biased of +1V, gold arrows indicate gate connection, while grey arrows indicate when gate was disconnected. B) Transfer characteristic at V_{DS} of -0.1 V using p(g3T2-T) gate coupled with SSE precursor.

4.2.3.2 By Heating

4.2.4 Solid-OECTs using Undoped-p(g3T2-T)

The fabrication of OECTs that used a solid-state electrolyte to enable IC and thermodynamics studies on these devices, were set by Weissbach et al. from the Biosens group at IAPP. The SSE comprises monomer units NIPAm and HHPA, seen in Section 3.3 on Chapter 3, which upon UV light exposure, cross-linking between them is triggered leading to the polymer poly(N-isopropylacrylamide) (PNIPAm), which is more precisely considered as a rigid gel [4].

Two types of OECTs were tested under N_2 environment and later expose to ambient conditions. In one type, SSE couples all fourteen devices of the sample, while in the other type, each device possesses a microstructure SSE. The latter strategy enhances the performance of OECTs since allows minimal leakage current and avoids device crosstalk, and it can be achieved by following a photolithography process as indicated in reference [4] or by ink-jet printing as implemented by team mates. Both methods are used under normal cleanroom conditions to test which can be implemented to minimize oxidation or allow reverse oxidation of p(g3T2-T) within the process.

Finally, a total of three samples will be analyzed in this section, it is expected to have major oxidation in the fully microstructure devices.

4.2.4.1 OECT with Drop-casted SSE

Patterning process at this point improved its yield, twelve out of the fourteen devices were patterned successfully, although with some differences in thickness as it is

4. RESULTS AND DISCUSSION

perceived by the reflection hue of the micrographs, leaving only seven operational devices.

Electrochemical de-doping of one device in the sample was done before exposure. Measurements of channel conductivity of the other devices indicated an impact of this process to neighbouring devices (a total of 5) since most of them had very low conductivity (in the order of nS). With one exception, that exhibited a conductivity in the order of the μ S, and threshold voltage of 0.0 V. Electrochemical de-doping to revert oxidation was intended on this device but after exposure (cross-linking of monomer units), it was not possible. Apparently, the formation of PNIPAm prevents the irreversible de-doping. An outcome that will become important for the fabrication of doped-devices and will be brought back in Section 4.2.5.

Transfer characteristics after and before exposure were measured, as seen in Figure 4.12B. Threshold voltage was calculated for the forward (from +1V to -1V) and backward (vice versa) scans, values are shown in Table 4.8, a small hysteresis is perceived but it is out of the scope of this work. Importantly, negative threshold voltages were calculated in all devices with low conductivity.

From the Bode plot illustrated in Figure 4.12C, shadowed area (low frequencies) was used to calculate the channel capacitance and volumetric capacitance are shown in Table 4.8. Very low values were obtained, that may represent still oxidation or defects (i.e. remains of photoresist).

Additionally, redox potentials are extracted from cyclic voltammetry (Figure 4.12D). Both the oxidation peak and two reduction peaks are exhibited in Table 4.8.

An important consideration for these measurements is that they are not an ideal CV measurement for characterizing the working electrode and where reference electrode is big enough to disregard its effects with the electrolyte. The peaks represent important operation points for our OEET, where electron transfer is more prominent. For instance, the oxidation peak could represent the oxidation of the gate as well as the reduction of the channel, and similar with the reduction peaks. Therefore, peaks outside the vicinity of 0 V, could represent some oxygen interaction or defects in our devices.

TABLE 4.5: Parameters extracted from the characterization of drop-casted SSE OEET

Parameters	Value	Parameters	Value
$V_{Th,forward}$ [V]	-0.21 ± 0.13	$V_{Th,backward}$ [V]	-0.17 ± 0.08
$C_{channel}$ [nF]	36 ± 10	C^* [Fcm^{-3}]	38 ± 10
V_{ox} [V]	0.68 ± 0.02	V_{red} [V]	$-1.0, -0.1$
$ g_{m,max} $ [mS]			

When sample was exposed to ambient conditions, a negative threshold voltage was maintained (-0.14 V with Ag/AgCl pellet), suggesting that drop-casted SSE creates a protective shell against molecular oxygen.

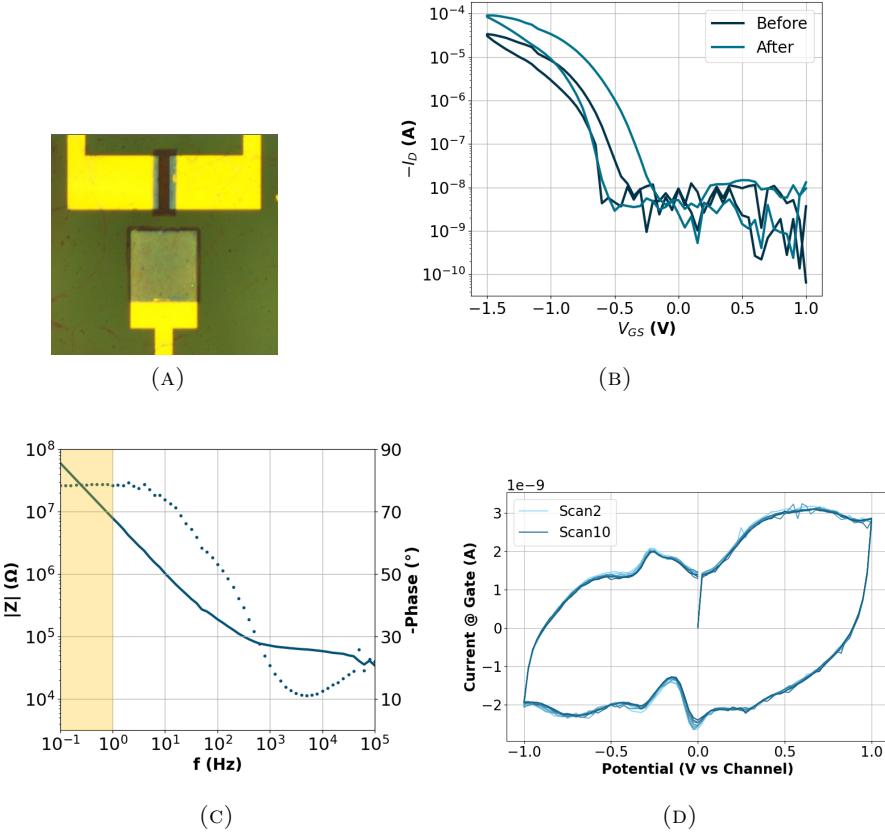
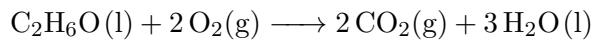


FIGURE 4.12: A) Micrograph of patterned device before application of SSE, B) transfer characteristics before and after exposure at V_{DS} of -0.1 V. And representative C) Bode plot obtained by EIS and C) redox behavior between Au/p(g3T2-T) and SSE using CV.

4.2.4.2 OECT with Photopatterned SSE

Ten out of fourteen operational devices were obtain for these trial, a micrograph of a representative device can be seen in Figure 4.13A. However, some devices that had an odd behavior due to some defects in the photolithography process will disregard from the analysis.

Microstructure SSE on top of device would require an adhesion promoter more than drop-casted SSE. In this particular case where removing non-crosslinked SSE precursor is done by using a N_2 gun, the risk of blowing off crosslinked SSE will not be as high with an adhesion promoter. Moreover, the ethanol rinsing as well as high temperature exposure will help to counterattack the oxidation of the polymer, the former would yield to the reaction describe in the following reaction:



4. RESULTS AND DISCUSSION

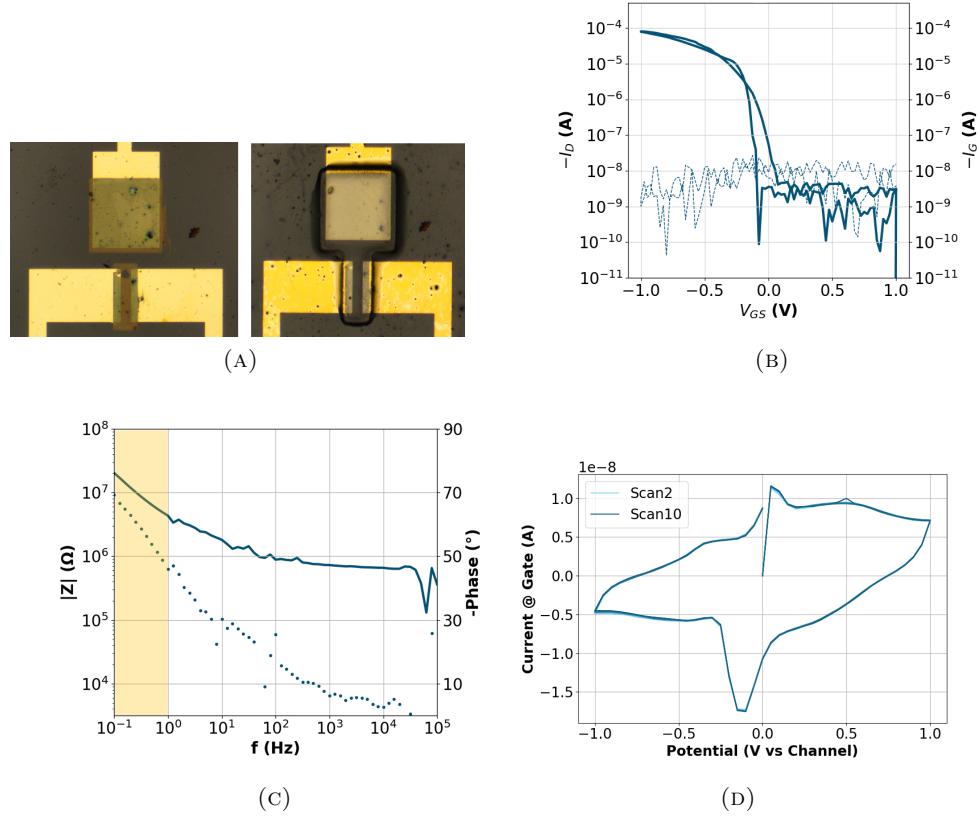


FIGURE 4.13: A) Micrograph of patterned device before and after application of SSE, B) transfer characteristics at V_{DS} of -0.1 V. And representative C) Bode plot obtained by EIS and C) redox behavior between Au/p(g3T2-T) and SSE using CV.

TABLE 4.6: Parameters extracted from the characterization of photopatterned SSE OECT

Parameters	Value	Parameters	Value
$V_{Th,forward}$ [V]	-0.08 ± 0.05	$V_{Th,backward}$ [V]	-0.09 ± 0.04
$C_{channel}$ [nF]	58.7 ± 24.4	C^* [Fcm^{-3}]	63.1 ± 26.2
V_{ox} [V]	0.04, 0.34	V_{red} [V]	-0.1, -0.2
$ g_{m,max} $ [mS]			

4.2.4.3 OECT with Inkjet-Printed SSE

4.2.5 Solid-OECTs using Doped-p(g3T2-T)

4.2. Fabrication of Organic Electrochemical Transistors

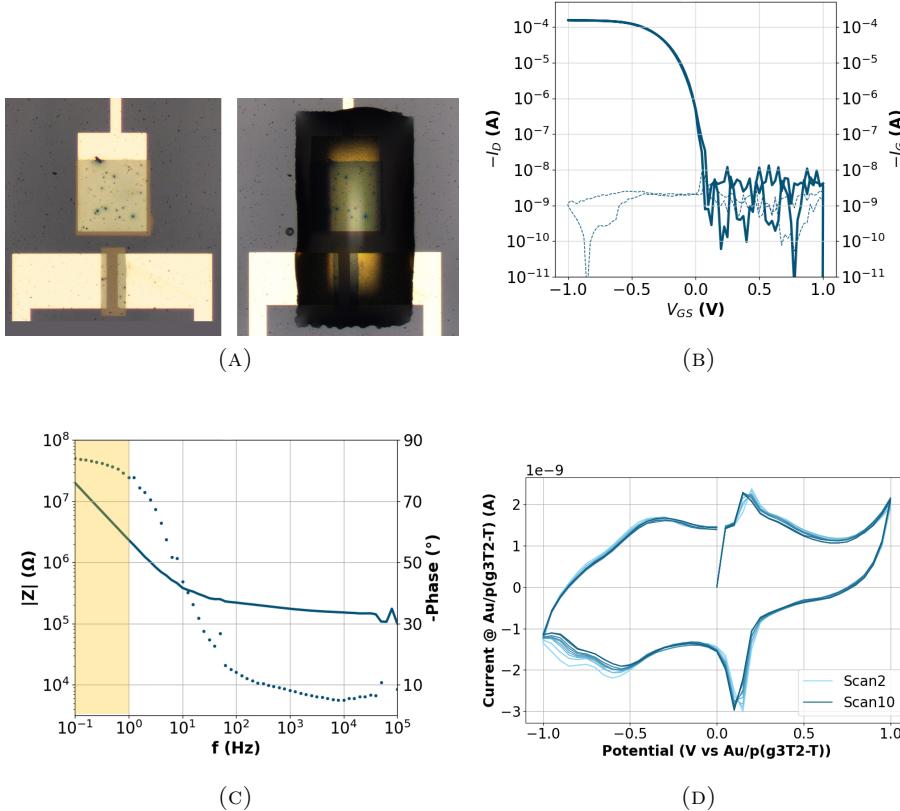


FIGURE 4.14: A) Micrograph of patterned device with printed SSE, B) transfer characteristics at V_{DS} of -0.1 V. C) Bode plot obtained by EIS and C) redox behavior between Au/p(g3T2-T) and SSE using CV.

TABLE 4.7: Parameters extracted from the characterization of printed SSE OEET

Parameters	Value	Parameters	Value
V_{Th} [V]	± 0.13	$ g_{m,max} $ [mS]	
$C_{channel}$ [nF]	36 ± 10	C^* [Fcm^{-3}]	38 ± 10
V_{ox} [V]	0.68 ± 0.02	V_{red} [V]	-1.0, -0.1

TABLE 4.8: Parameters extracted from the characterization of doped-p(g3T2-T) OEET

Parameters	Value	Parameters	Value
V_{Th} [V]	-0.1	$ g_{m,max} $ [mS]	
$C_{channel}$ [nF]		C^* [Fcm^{-3}]	
V_{ox} [V]	0.1	V_{red} [V]	0.0

4. RESULTS AND DISCUSSION

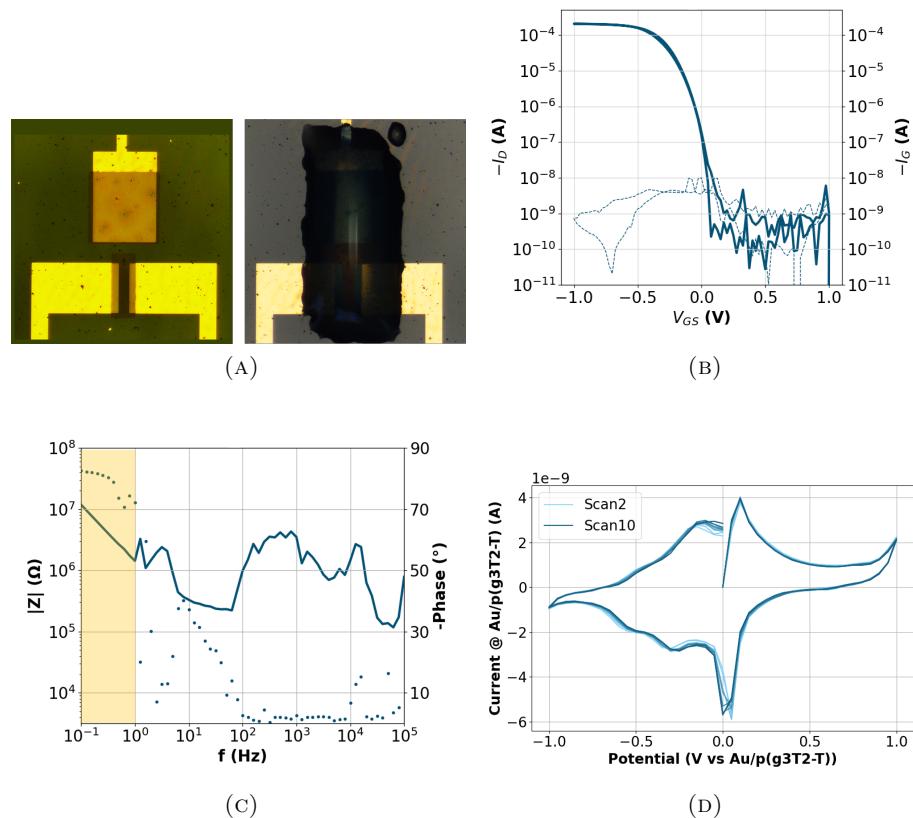


FIGURE 4.15: A) Micrograph of patterned device with printed SSE, B) transfer characteristics at V_{DS} of -0.1 V. C) Bode plot obtained by EIS and C) redox behavior between Au/p(g3T2-T) and SSE using CV.

Chapter 5

Conclusions and Outlook

Appendix A

Absorption of p(g3T2-T) Doped with F6TCNNQ

Appendix B

PEDOT:PSS vs Doped p(g3T2-T) as Channel

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