

Tuning of Organic Electrochemical Transistor Threshold Voltage by varying doping of semiconducting polymer p(g3T2-T)

Marielena Velasco Enriquez

Thesis submitted for the degree of
Erasmus Mundus Master of Science
in Nanoscience and Nanotechnology,
graduation option Nanoelectronics

Supervisors:

Prof. Dr. Karl Leo
Prof. Dr. Steven De Feyter

Assessor:

PD Dr.rer.nat.habil. Hans Kleeman

Assistant-supervisor:

Anton Weissbach

© Copyright KU Leuven

Without written permission of the supervisors and the author it is forbidden to reproduce or adapt in any form or by any means any part of this publication. Requests for obtaining the right to reproduce or utilize parts of this publication should be addressed to Faculteit Ingenieurswetenschappen, Kasteelpark Arenberg 1 bus 2200, B-3001 Leuven, +32-16-321350.

A written permission of the supervisors is also required to use the methods, products, schematics and programmes described in this work for industrial or commercial use, and for submitting this publication in scientific contests.

Preface

I would like to thank everybody who kept me busy the last year, especially my promoter and my assistants. I would also like to thank the jury for reading the text. My sincere gratitude also goes to my wife and the rest of my family.

Marielena Velasco Enriquez

Contents

Preface	i
Abstract	iii
List of Figures and Tables	iv
List of Abbreviations and Symbols	v
1 Introduction	1
1.1 Motivation	1
1.2 Goal	1
1.3 Structure of the Work	2
2 Background	5
2.1 Organic Semiconductors	5
2.1.1 Electronic structure	5
2.1.2 Electronic transport: Hopping mechanism	5
2.1.3 Doping	5
2.2 Organic Mixed Ionic/Electronic Conductors (OMIECs)	6
2.2.1 A widely used material: PEDOT:PSS	6
2.2.2 Other thiophene-based polymers	6
2.3 Organic Electrochemical Transistors (OECTs)	6
2.3.1 Device physics	6
2.3.2 Operation modes	6
2.3.3 Important figures of merit	6
2.3.4 Requirements to avoid undesirable side reactions	6
2.3.5 Building block for neuromorphic and bioelectronic applications	7
Bibliography	9

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 for p-type OECT devices 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 semiconducting polymers that allow accumulation-mode devices. One such polymer, 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene (p(g3T2-T)) has demonstrated 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 OECT devices that incorporate a solid electrolyte [4] along with different doping levels of p(g3T2-T). Additionally, the study aims to adjust the threshold voltage by utilizing these varying doping levels.

List of Figures and Tables

List of Figures

List of Tables

List of Abbreviations and Symbols

Abbreviations

OECT	Organic Electrochemical Transistor
V _{th}	Threshold Voltage
CV	Cyclic Voltammetry
EIS	Electrical Impedance Spectroscopy
UPS	Ultraviolet Photoelectron Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy

Symbols

42	“The Answer to the Ultimate Question of Life, the Universe, and Everything” according to [?]
c	Speed of light
E	Energy
m	Mass
π	The number pi

Chapter 1

Introduction

The field of organic electronics has witnessed significant advancements in recent years, with organic electronic devices exhibiting promising characteristics for various applications. One key component of these devices is the Organic Electrochemical Transistor (OECT), which has attracted considerable attention due to its unique capabilities and potential for use in biosensors, energy storage and neuromorphic devices. The OECT's operation relies on the modulation of its threshold voltage, which determines its switching behavior and performance.

Explain the progress on the design in new conjugated polymers for enhancement-mode OECTs.

1.1 Motivation

The ability to precisely control and tune threshold voltage of an OECT is of great importance in reducing power consumption, optimizing device performance and expanding their applications. By manipulating the doping level of the conjugated polymer p(g3T2-T), we can potentially achieve significant shifts in the threshold voltage, leading to improved device characteristics such as sensitivity, response time, and stability. Understanding the relationship between the doping level and threshold voltage shift is crucial for the design and fabrication of high performance OECTs.

1.2 Goal

The primary objective of this research is to investigate and characterize the tuning of the threshold voltage of an OECT by varying the doping level of the conjugated polymer p(g3T2-T). Specifically, we aim to:

1. Synthesize and characterize p(g3T2-T) with varying doping levels: This involves chemically modified the conjugated polymer with different concentrations of dopant and analyzing their structural and electrical properties using techniques such as UV-Vis spectroscopy, Ultraviolet Photoelectron Spectroscopy (UPS),

X-Ray Photoelectron Spectroscopy (XPS), Electrical Impedance Spectroscopy (EIS) and cyclic voltammetry (CV).

2. Fabricate OECT devices: Utilizing the synthesized polymer, we will design and fabricate OECT devices through a combination of electrode patterning techniques, material deposition, lithography and inkjet printing. The devices will be carefully optimized to ensure reproducibility and stability.
3. Investigate the shift in threshold voltage: through electrical characterization, we will measure the threshold voltage of the fabricated OECT devices with varying doping levels of p(g3T2-T) and the resulting threshold voltage shift.
4. Assess device stability: to evaluate stability of the OET devices, we will perform long-term measurements and examine the changes in their threshold voltage over time. This analysis will provide insights into the durability and reliability of the devices, essential for practical applications.

1.3 Structure of the Work

The thesis is structured as follows:

Chapter 1: Introduction

- Provides an overview of organic electronics and the importance of the OECT threshold voltage.
- Outlines the motivation, goals, and structure of the thesis.

Chapter 2: Background

- Presents a comprehensive review of relevant research on OMIECs, OECTs, and doping strategies.
- Highlights the current state-of-the-art in tuning the threshold voltage of OECTs

Chapter 3: Experimental work

- Describes the materials, chemical doping technique, and characterization method employed in the study
- Outlines the fabrication and characterization process of OECT devices

Chapter 4: Results and Analysis

- Presents the experimental results obtained from the chemical doping of the conjugated polymer and fabricated OECT devices
- Analysis the relationship between the doping level and the shift in threshold voltage

- Evaluates the stability of the undoped and doped material through long term measurements

Chapter 5: Discussion and Conclusion

- Discusses the implications of the findings and their relevance to the field
- Provides a summary of the research objectives and the extent to which they were achieved
- Suggests future reserach direction and potential applications

By addressing the aforementioned research goals and following the proposed thesis structure, this study aims to contribute to the understanding of the doping-dependent tuning of OECT threshold voltage and establish a goundation for the development of high-performance organic electronics devices.

Chapter 2

Background

2.1 Organic Semiconductors

Semiconducting properties of conjugated polymers built by alternating electron donor and acceptor moieties [5], esta cita facil la voy a sacar, are nowadays attracted for applications where fast computing is not relevant, in bioapplications

2.1.1 Electronic structure

Since inorganic semiconductors' band theory does not take into consideration the Coulomb and exchange electron-electron interaction, which play a major role in organic semiconductors, it is necessary to add new theoretical approaches. On one hand, the transport properties are better described in terms of a hopping mechanism and the optoelectronic properties are better described by the molecular orbital picture. [6]. Since the device under study in this work is a transistor and their transport properties in aqueous and quasi-solid environments, the theoretical approach used will be the hopping mechanism.

2.1.2 Electronic transport: Hopping mechanism

2.1.3 Doping

2.1.3.1 Doping mechanism

2.1.3.1.1 Molecular doping Use of small molecules Electron-deficient dopants such as 2,3,5,6tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) extract electrons from shallow HOMO p-type OMIECs, increasing hole concentration [7]

2.1.3.1.2 Electrochemical doping Important in OECT physics covered in a later section.

2.1.3.2 Measuring techniques to characterize doping

2.2 Organic Mixed Ionic/Electronic Conductors (OMIECs)

Commonly semiconducting polymers which are redox-active and can simultaneously conduct ions and electrons. Electronic charges accumulated on the conjugated polymer backbone result in secondary property changes in electrochemical potential and electronic conductivity, allowing OMIECs to be implemented in a variety of devices such as chemical sensors, organic electrochemical transistors, and energy storage electrodes [7]

2.2.1 A widely used material: PEDOT:PSS

2.2.2 Other thiophene-based polymers

Thiophene is a planar conjugated ring structure consists of six delocalized pi-electrons. The aromatic nature arises from the four pi electrons and one unshared lone pair of electrons of the oxygen as six delocalized pi-electrons. It follow Hucke's rule. Hence it is aromatic compound

2.3 Organic Electrochemical Transistors (OECTs)

devices that are mechanically compliant, biocompatible, and are sensitive to biochemical modules [7]

2.3.1 Device physics

2.3.2 Operation modes

2.3.3 Important figures of merit

2.3.3.1 Transconductance

2.3.3.2 μC^* product

2.3.3.3 Threshold voltage

2.3.4 Requirements to avoid undesirable side reactions

Achieving effective charge transfer between the analyte and OMIEC requires appropriate alignment of the electrochemical potential of electrons on the OMIEC electrode and the redox specie. Failure to do so may result in the subsequent transfer of charges to other redox-active sinks in the environment, leading to undesirable side reactions and products that may interfere with the OMIEC's operation. Electrons flow from a region of higher to lower electrochemical potential. Hence, achieving electron transfer from redox-active species to the OMIEC requires the latter to have a deep LUMO (high electron affinity) [3]

2.3.5 Building block for neuromorphic and bioelectronic applications

Bibliography

- [1] J. Rivnay, S. Inal, A. Salleo, R. M. Owens, M. Berggren, and G. G. Malliaras, “Organic electrochemical transistors,” *Nature Reviews Materials*, vol. 3, no. 2, pp. 1–14, 2018. [Online]. Available: <https://www.nature.com/articles/natrevmats201786>
- [2] C. B. Nielsen, A. Giovannitti, D.-T. Sbircea, E. Bandiello, M. R. Niazi, D. A. Hanifi, M. Sessolo, A. Amassian, G. G. Malliaras, J. Rivnay, and I. McCulloch, “Molecular Design of Semiconducting Polymers for High-Performance Organic Electrochemical Transistors,” *Journal of the American Chemical Society*, vol. 138, no. 32, pp. 10 252–10 259, 2016.
- [3] S. T. M. Tan, G. Lee, I. Denti, G. LeCroy, K. Rozyłowicz, A. Marks, S. Griggs, I. McCulloch, A. Giovannitti, and A. Salleo, “Tuning Organic Electrochemical Transistor Threshold Voltage using Chemically Doped Polymer Gates,” *Advanced materials (Deerfield Beach, Fla.)*, vol. 34, no. 33, p. e2202359, 2022.
- [4] A. Weissbach, L. M. Bongartz, M. Cucchi, H. Tseng, K. Leo, and H. Kleemann, “Photopatternable solid electrolyte for integrable organic electrochemical transistors: operation and hysteresis,” *Journal of Materials Chemistry C*, vol. 10, no. 7, pp. 2656–2662, 2022.
- [5] C. Matt, “Electronic structure and morphology of organic semiconductors and the impact of molecular modifications,” doctoralThesis, Saarländische Universitäts- und Landesbibliothek, 2021, accepted: 2021-09-30T09:54:35Z. [Online]. Available: <https://publikationen.sulb.uni-saarland.de/handle/20.500.11880/31812>
- [6] L. Alcácer, *Electronic Structure of Organic Semiconductors: Polymers and small molecules*. Morgan & Claypool Publishers, Dec. 2018. [Online]. Available: <https://iopscience.iop.org/book/mono/978-1-64327-168-2>
- [7] S. T. M. Tan, “Organic Mixed Ionic Electronic Conductors for Electrochemical Devices,” Ph.D. dissertation, Stanford University, Palo Alto, CA, Dec. 2022. [Online]. Available: https://stacks.stanford.edu/file/druid:dc342qm3881/Organic%20Mixed%20Ionic%20Electronic%20Conductors%20for%20Electrochemical%20Devices_final-augmented.pdf