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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Contents

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 semiconductor 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-(2-methoxyethoxy)ethoxy)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 comprises different doping levels of F_4TCNQ and F_6TCNNQ 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.

List of Figures and Tables

List of Figures

List of Tables

List of Abbreviations and Symbols

Abbreviations

OECT	Organic Electrochemical Transistor
Vth	Threshold Voltage
CV	Cyclic Voltammetry
EIS	Electrical Impedance Spectroscopy
UPS	Ultraviolate Photoelectron Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy

Symbols

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 due to its 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 constrast, the ability to precisely control and tune threshold voltage of an OECT can be achieve by manipulating the doping level of the mentioned conjugated polymer [3]. Tan et al. 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 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 F_4TCNQ and F_6TCNNQ. This involves chemically modifying the conjugated polymer 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), Atomic Force Microscopy (AFM), 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,

3. assess doped polymer stability in OECT, which involves performing conductivity measurements over time and selecting an electrolyte composition that allows an stable performance, and

4. investigate the shift in threshold voltage through electrical characterization of the fabricated OECT devices with varying doping levels of F_4TCNQ and F_6TCNNQ.

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 doped 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.

By addressing the aforementioned research goals and following the proposed thesis structure, this study aims to contribute in adapting an existing protocol to the conjugated material p(g3T2-T), in understanding the doping-dependent tuning of OECT threshold voltage and establish a foundation for the development of high-performance organic electronic devices.

Chapter 2

Background

2.1 Organic Semiconductors

Semiconducting properties of conjugated polymers built by alterning 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 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]

2.1.2.1 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 folow Hucke´s rule. Hene it is aromatic compound

2.2.3 Electrochemical Doping

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

Chapter 3

Experimental Methods

3.1 Materials

3.2 Equipmment

3.3 Software

3.4 Experimental Procedures

3.4.1 Conjugated polymer films

3.4.2 Fabrication of Organic Electrochemical Transistors

Chapter 4

Results and Discussion

4.1 Doped Conjugated Polymer films

4.1.1 Polaron and Bipolar formation

4.1.2 Workfunction increase

4.1.3 Redox properties with Solid State Electrolyte

4.2 Organic Electrochemical Transistors

4.2.1 Channel and gate morphology

4.2.2 Channel conductivity

4.2.2.1 Under inert conditions

4.2.2.2 Under ambient conditions

4.2.3 Threshold voltage shift

4.2.4 Important figure of merit

Chapter 5

Conclusion and Outlook

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. Rozylowicz, 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