

# 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 Master of Science in Electrical Engineering, option Electronics and Chip Design

**Supervisors:** 

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

**Assessor:** 

PD Dr.rer.nat.habil. Hans Kleeman

Assistant-supervisor:

Anton Weissbach

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### 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 wive and the rest of my family.

 $Marielena\ Velasco\ Enriquez$ 

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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 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

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# List of Abbreviations and Symbols

#### Abbreviations

LoG Laplacian-of-Gaussian MSE Mean Square error

PSNR Peak Signal-to-Noise ratio

#### **Symbols**

42 "The Answer to the Ultimate Question of Life, the Universe, and Everything" according to [?]

c Speed of light

E Energy

m Mass

 $\pi$  The number pi

### Chapter 1

### Introduction

The first contains a general introduction to the work. The goals are defined and the modus operandi is explained. The chapter should broadly contextualize your research and motivate your work.

### 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 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. Hene 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 Volumetric capacitance

#### 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]

# ${\bf 2.3.5} \quad {\bf Building\ block\ for\ neuromorphic\ and\ bioelectronic\ applications}$

### 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. 10252–10259, 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 Universitätsund 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