Organic Electrochemical Transistors for Printed Digital Circuits

Marzieh Zabihipour
Copyright © 2024 Marzieh Zabihipour, unless otherwise mentioned.

This work is licensed under a Creative Commons Attribution Non-commercial 4.0 International License.

Printed in Sweden by LiU-Tryck, 2024

ISBN 978-91-7929-204-1 (PDF)
https://doi.org/10.3384/9789179292041
ISSN 0345-7524

Cover photo taken by Marzieh Zabihipour.
Dedicated to my loving family
Abstract

Organic electronics enables cost-effective production of flexible electronic devices with high throughput and easy processing compared to the conventional electronics. Organic electronics, therefore, has the potential to realize various innovative applications on a large scale, for example, flexible displays, smart windows, solar cells, electronic skin and implantable medical devices.

Many of the materials employed in the field of organic electronics can be processed from chemical solutions. This allows for making various types of inks and hence the possibility to use the traditional high-volume printing methods such as screen printing, inkjet printing and gravure printing for fabricating organic electronic devices on different surfaces. Screen printing has advantages over the other methods in terms of the range of ink viscosity, resolution, and controllable thickness of dry ink film.

For various applications envisioned for an integration of printed organic electronics with other technology platforms, a prolonged lifetime and low power consumption are desired. This requires an optimized design of the electronic components and circuits so that they can operate at reduced voltages to guarantee both the long lifetime and the low power consumption. This thesis focuses on designing fully screen printed vertically stacked organic electrochemical transistors (OECTs) and OECT-based circuits operating at low supply voltages and at the same time delivering high gain and low power consumption with long lifetime. The OECTs and OECT-based circuits employ poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) as the organic polymer in their channel. The multi-layered OECTs have a small footprint with a high manufacturing yield and performance uniformity across the printed area, making them suitable for complex printed circuits. Furthermore, various inverter designs based on the reliable and reproducible OECTs are developed and explored to target circuits that can perform at relatively low supply voltages, yet offering improved performance.
Populärvetenskaplig sammanfattning

Organisk elektronik möjliggör kostnadseffektiv produktion av flexibla elektroniska enheter i en enkel och snabb tillverkningsprocess jämfört med den konventionella elektroniken. Organisk elektronik har därför potential att realisera olika innovativa tillämpningar på stor skala, till exempel flexibla displayar, smarta fönster, solceller, elektronisk hud och implantbar medicinsk elektronik.

Många material som används inom organisk elektronik kan hanteras i form av kemiska lösningar. Detta möjliggör tillverkning av olika typer av elektroniskt bläck och därmed möjligheten att använda traditionella tryckmetoder såsom screentryck, bläckstråletryck och gravyrtryck för tillverkning av organisk elektronik på olika ytor. Screentryck har fördelar jämfört med de andra metoderna när det gäller intervallet för bläckviskositet, upplösning och kontroll över tjockleken hos den torkade bläckfilmen.

Acknowledgements

I am absolutely grateful to my supervisors, Isak Engquist and Magnus Berggren! You gave me a one-off opportunity to explore the emerging area of printed and organic electronics in a thriving environment. Besides the strong supervision, you entrusted me with the freedom and flexibility. Thank you for being so much generous and kind in every situation! It has been a truly rewarding experience.

My PhD thesis is an outcome of a close collaboration with RISE. Special thanks to Peter Andersson Ersman. I am lucky to have the experience of working with you. You are a role model for how the top-quality research must be done with the high standards of ethics. Whenever I needed help, you were there for drilling down into details. Words cannot express my gratitude.

I am greatly indebted to Jan Strandberg, Roman Lassnig, Deyu Tu, Per Janson, Daniel Simon and Robert Forchheimer for the fruitful collaboration. Your contributions have been fundamental in our joint research work. Thank you for also teaching me the invaluable skills along the way!

A lot of my time was spent at PEA, carrying out the experiments. I would like to thank Marie, Xin, and Astrid for the refreshing conversations. That made the whole experience much more enjoyable.

Thanks to all our LOE members for bringing the diversity of ideas and cultures. I also want to thank the TPE group, for regularly sharing the ongoing research and helping each other. The LOE administration must also be acknowledged for the smooth and swift administrative support.

My family and friends have been an endless source of love and encouragement. Special thanks to my parents who invested in my education throughout and gave me the confidence to travel abroad. More than anyone else, I would like to thank my husband. Besides the love, his inspirational attitude motivates me to continuously grow. Finally, the latest
addition in our family, little Sara, has brought a completely new feeling of joy and optimism to my life.

Thank you everyone!
List of Included Papers

Paper I:

High Yield Manufacturing of fully Screen-Printed Organic Electrochemical Transistors

Marzieh Zabihipour, Roman Lassnig, Jan Strandberg, Magnus Berggren, Simone Fabiano, Isak Engquist and Peter Andersson Ersman.

npj Flexible Electronics, 2020, 4 (15).

Contribution: Majority of the experimental work, characterization of devices and data analysis. Assisted in the screen printing. Wrote majority of the first draft and contributed to the final editing of the manuscript.

Paper II:

Designing Inverters Based on Screen Printed Organic Electrochemical Transistors Targeting Low-Voltage and High-Frequency Operation

Marzieh Zabihipour, Deyu Tu, Jan Strandberg, Magnus Berggren, Isak Engquist and Peter Andersson Ersman.

Advanced Materials Technologies, 2021, 6, 2100555.

Contribution: All experimental work. Large part of the data analysis. Assisted in the device manufacturing. Wrote majority of the first draft and contributed to the final editing of the manuscript.

Paper III:

xv
High-gain Logic Inverters Based on Multiple Screen Printed Organic Electrochemical Transistors

Marzieh Zabihipour, Deyu Tu, Robert Forchheimer, Jan Strandberg, Magnus Berggren, Isak Engquist and Peter Andersson Ersman.

Advanced Materials Technologies, 2022, 2101642.

Contribution: All experimental work. Assisted in transistor manufacturing. Wrote majority of the first draft and contributed to the final editing of the manuscript.

Paper IV:

Organic Electrochemical Transistors Manufactured by Laser Ablation and Screen Printing

Flexible and Printed Electronics, 2022, 7, 035018.

Marzieh Zabihipour, Per Janson, Magnus Berggren, Daniel T. Simon, Peter Andersson Ersman, Isak Engquist

Contribution: Large parts of characterization of devices. Wrote large parts of the first draft and contributed to the final editing of the manuscript.
Related work Not Included in the Thesis

Paper V:

Monolithic Integration of Display Driver Circuits and Displays Manufactured by Screen Printing

Peter Andersson Ersman, Marzieh Zabihipour, Deyu Tu, Roman Lassnig, Jan Strandberg, Jessica Åhlin, Marie Nilsson, David Westerberg, Göran Gustafsson, Magnus Berggren, Robert Forchheimer and Simone Fabiano

Flexible and Printed Electronics, 2020, 5, 024001.

Paper VI:

Electrical Current Modulation in Wood Electrochemical Transistor

Van Chinh Tran, Gabriella G. Mastantuoni, Marzieh Zabihipour, Leng-wan Li, Lars Berglund, Magnus Berggren, Qi Zhou, Isak Engquist

Proceedings of the National Academy of Sciences, 2023, 120 (18) e2218380120.

Paper VII:

mm-Wave Exposure Estimation Using Screen-Printed Metasurfaces

Johan Lundgren, Marzieh Zabihipour, Daniel Sjöberg, Isak Engquist, Mats Gustafsson
European Conference on Antennas and Propagation, EuCAP 2023, IEEE - Institute of Electrical and Electronics Engineers Inc.

Paper VIII:

Real-Time Near-Field mmWave Measurements Using Screen-Printed Metasurfaces and IR Camera

Johan Lundgren, Torleif Martin, Hamza Khalid, Marzieh Zabihipour, Deyu Tu, Isak Engquist, Daniel Sjöberg, Mats Gustafsson

(Submitted to IEEE Transactions on Antennas and Propagation, 2024)
# Table of Contents

Abstract........................................................................................................ vii  
Populärvetenskaplig sammanfattning......................................................... ix  
Acknowledgements........................................................................................ xi  
List of Included Papers.................................................................................... xiv  
Related work Not Included in the Thesis.................................................... xvi  
Table of Contents ............................................................................................ xix  
Part I: Background .......................................................................................... 1  
1 Introduction.................................................................................................. 2  
   1.1 Organic Electronics............................................................................ 2  
   1.2 Printed Electronics........................................................................... 3  
   1.3 Printed Organic Electrochemical Transistors................................. 4  
   1.4 Aim of the Thesis............................................................................ 5  
   1.5 Outline of the Thesis...................................................................... 7  
2 Conjugated Polymers................................................................................... 9  
   2.1 Structure........................................................................................... 9  
      2.1.1 Hybridization............................................................................ 9  
      2.1.2 σ Bonds............................................................................... 11  
      2.1.3 π Bonds............................................................................. 11
2.1.4 Doping and Charge Transport ........................................ 12

2.2 Specific Material ........................................................................ 15
  2.2.1 PEDOT:PSS ........................................................................ 15

3 Electrochemical Devices based on PEDOT:PSS .................. 18
  3.1 Organic Electrochemical Transistors (OECTs)................................. 18
    3.1.1 Structure .......................................................................... 18
    3.1.2 Operation mechanism .................................................... 21
  3.2 Logic Circuits ........................................................................... 24
    3.2.1 Standard Inverter ................................................................ 24
    3.2.2 Inverters with Variable resistor(s) ...................................... 26
    3.2.3 Cascade-Coupled Inverter .................................................. 30
    3.2.4 Ring Oscillators .................................................................. 30

4 Methods ............................................................................................. 32
  4.1 Materials ................................................................................... 32
  4.2 Manufacturing ............................................................................ 32
    4.2.1 Screen Printing Principles ................................................... 33
      4.2.1.1 Alignment ...................................................................... 38
    4.2.2 Laser Ablation .................................................................... 39
  4.3 Profilometry ................................................................................ 42
  4.4 Electrical Characterization .......................................................... 42

xx
4.4.1 Transfer Measurements ..............................................43
4.4.2 Output Characteristics .............................................43
4.4.3 Dynamic Switching ..................................................43

5 Conclusions and Outlook ................................................ 45
References ...........................................................................48
Part II: Papers ........................................................................61
Part I: Background
1 Introduction

1.1 Organic Electronics

Our daily lives are becoming more and more dependent on electronic products due to a rapid evolution of technology. The fast developments in science and technology have made it feasible to integrate electronic products with other technology platforms like the Internet of Things (IoT), or even interface electronics with other fields, such as biology (referred to as bioelectronics)\(^1\)\(^{-10}\) to realize novel applications. The conventional electronics is mostly based on inorganic materials (such as silicon and metals), which is expensive, rigid and inflexible. Furthermore, the device production requires immense amounts of energy since it typically relies on various vacuum deposition processes. Various emerging applications have new requirements that cannot be addressed with the pricey and inflexible silicon-based electronics. To meet the newly emerging requirements, the field of organic (carbon-based) electronics started a common pathway to offer manufacturing of flexible electronic devices based on cheap abundant materials using simple and high-throughput fabrication methods. Organic electronics is capable of producing electronic devices from non-traditional materials on flexible substrates with multiple functionalities in a variety of advanced applications\(^11\)\(^{-20}\). That is, a mass production of flexible electronic devices in large volumes and at low unit costs is feasible. This is how organic electronics is distinctive from conventional electronics.

The developments in the field of material science paved the way for the advent of novel electronics to the market. Organic electronics\(^21\)\(^{-30}\) is often based on organic molecules and polymers with electronic functionalities that, by different means, can be switched from a conducting to a non-conducting character\(^31\)\(^{-40}\). Polymers have historically been considered as plastics, that is, electrically insulating. For a long time, they have therefore been used as insulating materials in electronic products and industries. However, in the 1970s, it was reported for the first time that polymers may exhibit considerably high electrical conductivity\(^41\). Since then,
activities to further develop electrically conducting polymers and organic materials were initiated. The polymeric materials are ideal candidates for a high volume production of electronics and show advantages in terms of solution processability and flexibility, thereby helping to enable large area, lightweight and low cost electronic devices. Organic electronic materials can be processed from a solution at room temperature and their opto-electronic properties can be modified through chemical engineering. Most of these materials are responsive to electrochemical switching and can conduct both electronic and ionic currents. One of the most well-studied active materials used in organic electronic devices is the conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS)\textsuperscript{32,43}, wherein both the optical absorption characteristics and the electrical conductivity are governed by the oxidation state, which in turn can be controlled by electrochemical switching.

During the past decades, organic electronic materials and various electronic applications have been developed and demonstrated. Some of the organic electronic devices reported in literature are light emitting diodes (LEDs)\textsuperscript{33}, organic thin film transistors (OTFTs)\textsuperscript{18,44}, solar cells\textsuperscript{45}, and memory devices\textsuperscript{35,46–49}. Some of them are also commercially available in the market\textsuperscript{48,50}.

1.2 Printed Electronics

Within the field of organic electronics it is possible to define the device functionality at molecular levels, prepare materials from a solution and produce electronic devices on flexible substrates\textsuperscript{51}. Due to the solution processable nature of conducting polymers, it is feasible to make inks and, hence, use the traditional high-volume printing methods to develop various organic electronic device concepts. Printed electronics focuses on the manufacturing of electronic components by means of printing techniques\textsuperscript{52} on different types of substrates. The printing processes are used to transfer a stack of layers onto a substrate, and thereby create an electronic component with a certain functionality\textsuperscript{53}. There are several printing methods that may be used in the manufacturing of printed electronic devices and systems, such as gravure printing, flexography, offset printing,
screen printing and inkjet printing. In this context, the screen printing method is one of the most commonly used techniques\textsuperscript{54-60}.

The radio frequency identification (RFID) tag technology is a classic example of printed electronics where a printing process plays an essential role in the mass production\textsuperscript{61}. The combination of printing processes and organic electronic materials allows for the manufacturing of low-cost, large area electronics on different types of flexible substrates, and the resulting components and systems can be coupled to a variety of IoT applications.

1.3 Printed Organic Electrochemical Transistors

Organic electrochemical transistors (OECTs) belong to a class of transistors based on organic materials that shows several advantages compared to the other types of transistors, e.g., simple fabrication, relatively low operation voltages (~1 V) and reasonably high ON/OFF current ratios\textsuperscript{56,62}. PEDOT:PSS is one of the most promising conducting polymers used as the channel material in OECTs. Various types of OECTs and OECT-based devices relying on PEDOT:PSS have been developed\textsuperscript{56}. PEDOT:PSS-based OECTs can be used in various applications, including chemical and biological devices\textsuperscript{63,64}, neural interfaces and neuromorphic systems\textsuperscript{6,65-67} and printed electronic applications\textsuperscript{58,68}. In this thesis, the PEDOT:PSS-based devices are explored for applications within printed electronics.

Figure 1 shows a brief history of the development of PEDOT:PSS-based OECTs towards printed OECT-based integrated circuits. In the mid-1980s, Wrighton et al.\textsuperscript{69} developed OECTs for the first time. The operation of OECTs relies on reversible doping and dedoping of the conducting polymer in the channel. PEDOT was explored as an electronic ink in the early 1990s\textsuperscript{42,43,70}. PEDOT can be doped with different anionic counterions and its properties depend on the type of counterions\textsuperscript{71}. One of the commonly used counterions incorporated into PEDOT is the PSS anion. The aqueous form of PEDOT:PSS allows for a simple deposition of thin films by using the printing techniques\textsuperscript{72}. This made it easy to utilize the printing techniques in fabricating PEDOT:PSS-based OECTs. In 2002,
the first step in demonstrating OECT-based circuits was initiated by employing PEDOT:PSS-based OECTs as addressing transistors and pixel drivers in printable active matrix electrochromic displays. After three years, in 2005, the PEDOT:PSS-based OECTs were manufactured and explored in logic gates, exemplified by inverters, NAND gates, NOR gates and ring oscillators. Thereafter, in 2007, printable active matrix addressed displays were further explored by developing electrochemical smart pixels in which the PEDOT:PSS-based OECTs were relying on a vertically stacked architecture, to enable individual addressing of display pixels in a more compact design. A few years later, in 2015, the PEDOT:PSS-based lateral OECTs were utilized in screen printed logic gates and integrated logic circuits. After that, in 2019, a large scale integration of fully screen printed digital circuits with more than 100 OECTs was reported, demonstrating that multilayered PEDOT:PSS-based OECTs may be used to provide a unique technology for IoT applications.

Figure 1. A brief history of the development of OECT and OECT-based digital circuits based on PEDOT:PSS.

1.4 Aim of the Thesis

In many of the targeted applications for printed organic electronics, such as power-efficient IoT devices, the system needs to be powered by printed
energy sources, e.g. batteries\textsuperscript{75,76}, solar cells\textsuperscript{77} or thermoelectric generators\textsuperscript{78,79}. Thus, the organic digital components and circuits, such as logic gates based on OECTs, should be operated at a low voltage and preferably also show stable operational lifetime characteristics to address the growing demands for the power efficient electronic circuits. The importance of low-voltage operating devices is not only due to minimizing the power consumption but also to reduce the device degradation and expand the operational lifetime. Furthermore, for OECT-based circuits it is important that the operation of every single standalone OECT is predictable and stable. This is because a printed logic circuit is typically composed of tens or even hundreds of OECTs\textsuperscript{59} and the overall performance of the circuit is dependent on the individual performances of the OECTs.

Indeed, the OECT technology benefits from inherent assets of OECTs such as the simple device design, easy manufacturing, low operational voltage, and compatibility with flexible and large-area substrates\textsuperscript{80}. Due to such properties, combined with the solution processibility of conducting polymers, printing methods can be exploited in the fabrication of OECTs and OECT-based devices. A typical OECT architecture includes several layers printed on top of each other, such as source and drain electrodes, channel material, insulator and electrolyte. Printing such multilayered structures can be challenging since a misalignment between the layers may lead to non-operational or malfunctioning devices. This becomes even more critical for printed circuits, where small and more compact dimensions of the printed features are preferred. For printed OECTs, the channel size has an impact on the switching performance, and it also contributes to the overall size of the printed devices. Hence, the importance of the printing alignment gets even more pronounced when targeting miniaturized OECT-based circuits.

The objective of the thesis is to address two major challenges regarding OECT-based digital circuits: i) printing small-sized OECTs with predictable and reliable performance on a large area and ii) implementing the printed OECTs into elemental digital circuit units (i.e., inverters) with the aim of establishing circuits with a satisfactory performance while operating at low voltages.
1.5 Outline of the Thesis

This thesis has two parts. Part I contains the necessary background information and concepts to understand the scientific work of the thesis. Part II includes the scientific papers that are the main contributions of this thesis.

The remainder of Part I has three chapters. Chapter 2 describes conjugated polymers and their characteristics. Chapter 3 reviews electrochemical devices based on PEDOT:PSS. Chapter 4 covers the methods we have used for the manufacturing and characterization of the devices described in the thesis. Finally, Chapter 5 presents conclusions and some directions for future research.

Part II includes four scientific publications.

Paper I investigates the manufacturing yield and stable switching performance of almost 800 OECTs. The devices are fully screen printed and contain six printed layers and relatively small channel dimensions. The achievable channel dimensions of the fully screen printed OECTs are investigated without compromising on the manufacturing yield. The main contribution of this work is the reliability of the screen printed OECTs across flexible large-area substrates.

In Paper II, screen printed OECTs are incorporated into inverter structures. An inverter design with a reasonable balance between its propagation delay, power consumption and voltage gain is proposed as a suitable design for general printed electronic applications. The OECT-based inverters are investigated for low-voltage and high-frequency operation, operational lifetime stability, power consumption and voltage gain. One of the key contributions is that the developed OECT-based ring oscillators show faster signal propagation in comparison with the OECT-based ring oscillators previously reported in the literature.

In Paper III, novel OECT-based inverter designs with variable resistance values are developed. The tunability of the resistor ladder is achieved by incorporating at least one additional OECT in the inverter design. The performance of the inverters in terms of voltage gain and output voltage
levels is studied at lowered supply voltages. The major contribution of this publication is that the novel inverter designs have delivered higher voltage gain, while operating at lower supply voltages, as compared to the inverters relying on the PEDOT:PSS-based OECTs and a printed resistor ladder with static resistance values, which have been previously reported in the literature.

In Paper IV, laser ablation is employed to assist the screen printing process. The main objective is to enable shorter OECT channel lengths to further improve the switching performance of the OECTs. 200 OECTs are produced by the screen printing technique with an additional laser ablation step, and the manufacturing yield of the resulting devices is investigated. Besides the achievement of a high manufacturing yield and the shortened channel lengths by including the laser ablation process, the ON/OFF ratio is also improved.
2 Conjugated Polymers

2.1 Structure

All polymers, being synthesized in laboratories or being available in nature, consist of repeated molecular units called monomers that are coupled to one another and result in long chains of polymeric materials. In our body cells, the protein called DNA is a natural polymer while plastics like polyethylene terephthalate (PET) are the synthetic examples. As mentioned earlier, since the discovery of the charge transport in organic materials\(^8\), the semiconducting behavior can be realized for polymers with a specific polymeric structure. Most polymers consist of a backbone chain of carbon atoms where each carbon atom has only two unpaired electrons in the valence shell in the ground state \((1s^2 \ 2s^2 \ 2p^2)\). As described in coming sections, the essential structure of conducting polymers relies on their conjugated systems where conjugation is defined as alternation of single and double carbon bonds with overlapping p orbitals.

2.1.1 Hybridization

Having two unpaired valence electrons for a carbon atom suggests that it could only form two covalent bonds, while in practice a carbon atom can make single, double or triple bonds. To explain this, it should be mentioned that compared to the core electrons \((1s)\), the four valence electrons \((2s^2 \ 2p^2)\) are located farther from the nucleus which allow the molecular formation. When two carbon atoms approach each other to bond and make a molecule, their atomic orbitals overlap, or hybridize, and new hybrid molecular orbitals are formed. The concept of hybridization was proposed by Linus Pauling in 1931\(^8\) and is schematically illustrated in Figure 2 where the hybrid orbital shape is inherited from combination of the shapes of both s and p orbitals. Depending on the bonding of carbon atoms in different molecules, there are three hybridization alternatives. That is, the hybridization of the 2s orbital with one, two or three of the 2p orbitals results in sp, sp\(^2\) and sp\(^3\) hybrid orbitals, respectively. As Figure 2 suggests, the shape of hybrid orbitals is unsymmetrical around the
nucleus and is strongly oriented in a specific direction which make it feasible to form stronger bonds than the s and p orbitals. Carbon atoms that form only single bonds use four equivalent sp³ hybrid orbitals. Due to the spatial symmetry of the four equal hybridized orbitals, the tetrahedral structure is formed which is the characteristics of sp³-hybridized materials. When forming carbon-carbon double bonds, carbon has three equivalent sp² orbitals that are trigonally positioned in the same plane as the nucleus (planar geometry) and one unhybridized p orbital which is perpendicular to the sp² plane. In the case of forming carbon-carbon triple bonds, carbon has two equivalent sp orbitals with linear geometry perpendicular to the two remaining unhybridized p orbitals.

Figure 2. The concept of hybridization.
The hydrocarbon molecules ethane (C₂H₆), ethene (C₂H₄) and ethyne (C₂H₂) molecules, are examples of carbon-carbon bonds with sp³, sp² and sp hybridization, respectively.

2.1.2 σ Bonds

When two hybridized atoms approach each other by head-on overlap, i.e., the axial overlapping of atomic orbitals, they form a strong bond called sigma (σ) bond. The scheme in Figure 3 shows electron clouds of two p-orbitals forming a σ bond. Electrons in σ bonds occupy the region centered between nuclei and form strong bonds. The four C-H bonds in methane molecule which are sp³ hybridized are examples of σ bonds.

![Figure 3. The overlap of the electron clouds in σ and π bindings between two p-orbitals.](image)

2.1.3 π Bonds

When bonds between two atoms are formed by sideways overlap of p orbitals, the so-called pi (π) bond is formed. This bond is illustrated in Figure 3. Consider ethene (C₂H₄) molecule in which there are four...
hydrogen and two carbon atoms. The s orbital and two p orbitals of each carbon atom combine and make three sp\(^2\) hybrid orbitals. These three hybrid orbitals participate in three \(\sigma\) bonds, two with hydrogens and one with the other carbon, while the remaining electron in the p\(_z\) orbital of each carbon atom interact by sideways overlap and form a \(\pi\) bond. That is, carbon atoms that are taking part in forming a double bond are sp\(^2\) hybridized and consist of one \(\sigma\) bond and one \(\pi\) bond. The interaction by sideways overlap of two unhybridized p orbitals, i.e., the bonding orbitals that are perpendicular to the molecule plain, give rise to a \(\pi\) bond. Because of the sideways overlap, the \(\pi\) bond electrons compared to electrons in \(\sigma\) bonds (head-on overlap of atomic orbitals), have weak coulomb interaction with the cores and are less localized or associated with the atom and can move easily between atoms in presence of an applied electric field. This electron delocalization governs the electrical conductivity in carbon-based organic \(\pi\)-conjugated polymers.

2.1.4 Doping and Charge Transport

The important aspect of conjugated polymers in their neutral forms is their \(\pi\) electrons associated to their \(\pi\) orbitals. These electrons characterize the alternation of single and double carbon-carbon bonds in conjugated polymers. The conductivity range of conjugated polymers in their neutral form spans from an almost insulating (~10\(^{-10}\) S/cm) to a semiconducting state (~10\(^6\) S/cm). This low conductivity makes it favorable to enhance their charge carrier concentration to achieve higher electrical conductivity. Upon doping procedure and introducing further charges in polymers, their conductivity can approach that of metals which makes them beneficial in electronic applications. For example, a conductivity of 10\(^3\) S/cm was observed for doped polyacetylene\(^84\). In conjugated polymers, it is the \(\pi\) conjugated system that makes them straight and rigorous, however, some factors like chemical defects or structural disorder/torsion disturbs the conjugation along the chain.

In doping of conjugated polymers, the added charges can be considered as the oxidation or reduction of organic polymers. That is, despite doping of inorganic materials which includes adding impurities as electron donors or acceptors, doping for the organic materials involves oxidation or
reduction of the polymer material resulting in charge transfer between the polymer and the neutralizing dopant counterions. A dopant counterion has the opposite charge and locally stabilizes the charge in the polymer. This results in changing the conjugation length over a few monomer units. Conjugated polymers can be p-doped through the oxidation process, i.e., withdrawing electrons from the π bonds of the backbone and making the polymer positively charged. The positive charge can move in the polymeric system and create an electrical current. On the other hand, conjugated polymers can be n-doped with introducing electrons into the π system of the polymer backbone via the reduction mechanism where the motion of the added electrons generates the electrical current.

Upon doping and adding charges to a polymer chain, carbon bonds rearrange themselves. For example, adding a hole to a conjugated polymer (p doping) causes a π bond to be broken and create a distortion and consequently a rearrangement in the polymer structure. This readjustment is more pronounced close to the location of the additional charge. The additional charge carrier that is followed by the structural distortion of the polymer is referred to as a polaron. Polarons can be either positive (a radical cation) or negative (a radical anion). Figure 4 exemplifies positive and negative polarons for polythiophene. By coupling two polarons a so-called bipolaron with a charge of +2 or -2 is formed. That is, removing another electron from a positive polaron result in a bipolaron with +2 charge whereas injecting another electron to a negative polaron forms a negative bipolaron.
Although polarons are delocalized over a few monomer units compared to the rest of the neutral polymeric system, they can be regarded as a delocalized charge bundles that can break bonds and spread along the polymer chain. While polaron (the charge package) is travelling in the neighborhood of charge neutralizing dopant counterions, it swaps the conjugated bond arrangement. Charge transport by polarons through conjugated polymers occurs either by intra- or inter-chain transport. When charge transport happens due to carriers travelling along one polymer
chain, it is intra-chain whereas hopping of carriers between different chains of the polymeric system results in inter-chain transport.

2.2 Specific Material

The oxidatively p-doped polymers are more common in device applications because the majority of the current n-doped polymers are reactive with oxygen and, hence, unstable in ambient atmosphere. This motivated scientists to utilize p-type organic semiconductors more and due to this most of research have been conducted based on them.

2.2.1 PEDOT:PSS

The poly(3,4-ethylenedioxythiophene) (PEDOT) mixed with the poly(styrene sulfonate) (PSS) as the counterion results in a conjugated polymer abbreviated to PEDOT:PSS. The intrinsic form of PEDOT cannot be dissolved in water. The highly electronegative sulfonate group in PSS dopants generates positive charges along the PEDOT chain. This way, as shown in Figure 5, the PEDOT mixed with PSS' counterions are stable in water emulsions. PEDOT:PSS is a polythiophene derivative that was developed in late 1980s. Since then, it has found lots of applications in electronics due to being chemically stable in the oxidized state. Since the oxidation of a polymer chain is referred to as p-doping, PEDOT:PSS is a p-type semiconducting polymer with the conductivity of $10^{-5}$ S/cm in its neutral form. Figure 5 shows the polaronic structure of PEDOT:PSS in which an electron is removed (inducing one positive charge) and a single doped form of the polymer is created. The positive charge is compensated by the negative charge from one of the sulfonate groups of PSS:H. Also Figure 5 depicts the modification that occurs in the conjugation over several monomers upon doping.
The intrinsic form of PEDOT:PSS is a blend of doped (oxidized or PEDOT\(^+\)) and undoped (neutral or PEDOT\(^0\)) entities. Electrochemical doping of PEDOT:PSS happens according to the reaction below where PEDOT:PSS can be reversibly switched between its conducting (PEDOT\(^+\)) and semiconducting (PEDOT\(^0\)) forms:

\[
PEDOT^+\cdot PSS^- + M^+ + e^- \rightleftharpoons PEDOT^0 + M^+: PSS^- \]

In the above reaction, the mobile cation and electron is represented with \(M^+\) and \(e^-\), respectively. The PEDOT reduction process is shown by the arrow to the right while the left pointed arrow indicates the oxidation reaction. Because PEDOT is a low band gap (~1.6 eV)\(^9\) polymer which greatly absorbs the red portion of the visible spectrum, it has a blue color\(^4\). PEDOT in its doped form (PEDOT\(^+\)) has a translucent bluish
color while the undoped state (PEDOT\textsuperscript{0}) is less transparent due to a dark blue color. This color changing upon oxidation and reduction is referred to as electrochromism. Due to the electrochromic property, PEDOT is utilized in printed displays\textsuperscript{42,43,97–101} and smart windows\textsuperscript{102,103}. It is noted that since PEDOT has high conductivity of 10\textsuperscript{-5} S/cm in the neutral form\textsuperscript{99}, it can be used as an electrode material in electrochemical devices. In the papers of this thesis PEDOT:PSS is used as the active material in both the standalone electrochemical transistors as well as the transistors used in logic gates.
3 Electrochemical Devices based on PEDOT:PSS

Electrochemical devices are a class of systems in which both ions and electrons serve as signal carriers. Working principle of such devices is based on electrochemical modulation of active materials. In this context, conductive polymers (e.g., PEDOT:PSS) are good candidates for electrochemical devices due to their capability in conducting both ions and electrons. From an electronic point of view, electrochemical devices including transistors, inverters, oscillators, and other types of logic gates are the elemental parts of complex and advanced electrochemical logic circuits.

3.1 Organic Electrochemical Transistors (OECTs)

3.1.1 Structure

Transistors are electronic devices with three terminals mainly utilized as ON/OFF switches or as signal amplifiers in the field of electronics. The current flowing between source and drain terminals is controlled via the potential applied to the third terminal, called the gate. The working principle of all types of transistors is based on conductivity modulation of a semiconductor material. The source and drain electrodes are bridged by the semiconductor route referred to as the channel. The field effect transistors (FETs) are a popular type of transistor in which the channel is separated from the gate electrode via a dielectric layer. By using organic semiconductor in the channel another version of transistors called organic field effect transistors (OFETs) is realized. Instead, if the dielectric material is replaced by an electrolyte layer, an electrolyte gated field effect transistor (EGOFET) is made. The replacement of the dielectric material with an electrolyte layer leads to increased capacitance and reduced operating voltage. OECTs are organic electronic devices working based on electrochemical switching (doping-dedoping) of a conductive polymer (e.g., PEDOT:PSS) as the channel material. In the mid-1980s, the OECT was developed by Wrighton and colleagues.
contrast to FETs, both OECTs and EGOFETs employ an electrolyte in their structure. OECTs are sometimes denoted as electrolyte-gated transistors.

In OECTs the channel conductivity modulation is not a surface effect which is induced by the field effect. Instead, upon the doping state of the channel, mobile ions (M$^-$ anions and M$^+$ cations) from the electrolyte layer can migrate in and out of the whole bulk of the channel material. For the PEDOT:PSS-based OECTs the conductivity of PEDOT:PSS in the channel can be tuned by the gate voltage ($V_G$). This is due to the switching ability of PEDOT:PSS upon electrochemical oxidation and reduction$^{68,112-114}$ occurring in the whole volume of the channel. In Figure 6, simplified structures of vertically and laterally stacked OECTs based on PEDOT:PSS are schematically illustrated. All three electrodes are based on PEDOT:PSS and the PEDOT:PSS gate electrode is connected to the channel via an electrolyte layer. As demonstrated in Figure 6, the area between the source and drain electrodes which is covered by the electrolyte defines the channel area (width × length). The channel dimension (width, length and thickness) plays a major role in switching behavior of OECTs. The OECT’s channel area is correlated to its channel resistance. That is, for an identical thickness of PEDOT:PSS in the channel, a longer channel is more resistive due to covering more squares and subsequently higher sheet resistance while a wider channel gives a much larger current throughput$^{115}$ due to having only a fraction of a square in the channel. Similarly, the channel thickness can adjust the OECT’s performance, i.e., the channel capacitance is proportional to the channel thickness and OECTs get slower as their channel thickness increase$^{72}$. Therefore, the response time of OECTs is dependent on their channel thickness because the channel capacitance scales with the volume and the channel resistance for a certain channel thickness scales with the channel area$^{116}$.

In the lateral OECT design shown in Figure 6a, the source, drain and gate electrodes are in the same plane making it a simple design in which the three OECT’s electrodes can be printed in one step. However, in the vertical configuration (Figure 6b), only the source and drain electrodes are
in the same plane and the electrolyte vertically bridges the bottom channel and top gate electrode.

**Figure 6.** (a), The structure of laterally stacked OECTs based on PEDOT:PSS. (b) The structure of vertically stacked OECTs based on PEDOT:PSS.
Although the lateral OECT configuration is manufactured by using a minimum printing steps, it results in larger footprint and longer switching time\textsuperscript{105}, compared to the vertical OECT designs\textsuperscript{56}. Due to this, the vertical OECT designs are preferred and utilized throughout this thesis.

3.1.2 Operation mechanism

Transistors with a highly resistive channel, operate in a so-called enhancement mode. Such transistors are in their OFF state at a zero $V_G$ (normally-OFF) while applying a voltage to the gate turns the transistor channel into a conductive (ON) state. On the other hand, a transistor with a conductive channel which is in the ON state upon apply no $V_G$ (normally-ON), has a depletion mode type operation.

Because the pristine state of PEDOT:PSS is oxidized (p-type), in OECTs that are based on PEDOT:PSS, without applying any $V_G$, the channel is in the conductive state. That is, PEDOT:PSS OECTs are p-channel transistors and operates in a depletion mode. Upon applying a positive $V_G$ to the gate, mobile cations in the electrolyte enter the OECT channel and reduce the PEDOT channel. As a result, channel conductivity declines. The electroneutrality needs to maintain during electrochemical switching. This can be accomplished by the movement of ions or counterions into or out of the PEDOT:PSS channel. In the case of PSS anion, which is a large and immobile counterion, instead cations can easily go in and out of polymer during switching to balance electronic charges. Therefore, when the doping state of PEDOT changes, mobile cations move in or out of the PEDOT:PSS channel, to provide charge balance to PSS\textsuperscript{−}.

Switching an OECT on and off occurs by transferring ions in and out of the bulk of channel polymer. This means that in OECTs the conductivity state of PEDOT:PSS in the channel regulates the current which passes from the source to the drain through the channel. A ratio between the drain-source currents ($I_D$) passing through the channel at ON (when $V_G = 0$ V) and OFF (when $V_G >$ threshold voltage $> 0$ V) states of OECTs is denoted as ON/OFF ratio. This ratio represents the capability of OECTs to modulate current, i.e., the switchability of the PEDOT:PSS channel and the ability to suppress parasitic reactions. The ON/OFF ratio of more
than $10^4$ has been observed and reported for PEDOT:PSS-based OECTs$^{115}$. The current level at ON and OFF states of OECT may differ, depending on the OECT’s channel dimension$^{115}$ and also the voltage applied to the drain electrode ($V_D$). Figure 7 exemplifies typical performance of PEDOT:PSS-based OECTs in terms of transfer and output characteristics.
Figure 7. (a) An OECT’s typical behavior in a transfer measurement with a fixed $V_D = -1$ V and recording $I_D$-$V_G$ and $I_G$-$V_G$ curves, (b) OECT’s output characteristics ($I_D$-$V_D$).

As illustrated in Figure 7a, for the transfer measurement upon applying higher $V_G$ to the OECT’s gate electrode the channel gets reduced and the current level ($I_D$) drops (forward sweep). Again, by lowering the $V_G$ to low values (backward
sweep) the $I_D$ will be high and the OECT will be back to its ON state (Figure 7a). The gate current ($I_G$) in Figure 7a shows the redox reactions at the gate electrode. In the forward direction, the $I_G$ peak (which occurs at $V_G \approx 1.1$ V in Figure 7a) indicates when the PEDOT:PSS channel has been fully reduced. Figure 7b shows OECT’s output characteristics in which the linear (for low $V_D$) and saturated (for elevated $V_D$) regimes are observed for different $V_G$ values.

3.2 Logic Circuits

Transistors are employed in logic circuits as signal switches due to having low and high impedance states in their channel. For instance, transistors are the constituents found in inverters and logic gates. In an inverter (also called as a NOT gate), the incoming voltage signals (input voltage; $V_{IN}$) arrives to the transistor’s gate terminal and gets inverted at an outgoing node (output voltage; $V_{OUT}$). This inverter sometimes is referred to as a voltage inverter since it deals with a voltage signal. Inverters are the fundamental building blocks in digital electronics which can be modified to more complicated logic gates such as NAND or NOR gates. Similarly, these gates can be used as basic elements to develop even more advanced and complex circuits. The OECT-based inverters are the logic components studied in this thesis.

3.2.1 Standard Inverter

The standard inverter structures based on PEDOT:PSS OECTs comprises an OECT and a resistor network\textsuperscript{56,59,68,105,106}. Figure 8 schematically illustrates the voltage divider structure of an inverter using the p-type depletion mode OECT which employs PEDOT:PSS as the channel material. As shown in the figure, the inverter is fed by two voltage supplies ($V_+$ and $V_-$) connecting to the two ends of the resistor ladder. The inverter’s resistor ladder includes three resistors called $R_1$, $R_2$ and $R_3$. The OECT’s source electrode is connected to the ground while the drain side is attached between $R_2$ and $R_3$ components. The voltage applied to the OECT’s gate electrode ($V_{IN}$ or $V_G$) defines the ON or OFF state of the OECT.
Figure 8. The standard structure of an OECT-based inverter.

For proper operation of inverters and other logic circuits, the $V_{\text{IN}}$ levels corresponding to logic "0" or "LOW" ($V_{\text{IN,L}}$) and logic "1" or "HIGH" ($V_{\text{IN,H}}$) are important parameters defining the corresponding $V_{\text{OUT}}$ levels ($V_{\text{OUT,H}}$ and $V_{\text{OUT,L}}$ levels). Upon applying $V_{\text{IN,L}}$ to the OECT’s gate, $V_{\text{OUT,H}}$ defined by $V_+$, $R_1$, $R_2$ and the OECT’s channel resistance in the ON-state ($R_{\text{Ch,ON}}$) is achieved. Alternatively, by employing $V_{\text{IN,H}}$ to the gate electrode, the $V_{\text{OUT,L}}$ specified by $V_+$, $R_1$, $R_2$, $R_3$ and $V_-$ due to the high impedance of the OECT channel in the OFF-state ($R_{\text{Ch,OFF}}$) is attained. In addition, the $V_{\text{OUT}}$ can be written as a function of current passing through the OECT ($I_D$) and the resistor ladder. The current passing through the $R_3$ component, denoted as $I_3$, can be written as

$$I_3 = \frac{V_D - V_-}{R_3} \quad (1)$$

Also, the current passing through $R_1$ and $R_2$ is equal to

$$I_3 + I_D = \frac{V_+ - V_D}{R_1 + R_2} \quad (2)$$
From equation (1) and (2), $I_3$ can be described as:

$$I_3 = \frac{(V_+ - V_-) - I_D(R_1 + R_2)}{R_3} = \frac{(V_+ - V_-) - I_D(R_1 + R_2)}{R_1 + R_2 + R_3} \quad (3).$$

Therefore, $V_{OUT}$ can be specified as:

$$V_{OUT} = V_+ - R_1(I_3 + I_D) = \left( V_+ - R_1 \frac{V_+ - V_-}{R_1 + R_2 + R_3} \right) - \frac{R_1 R_3}{R_1 + R_2 + R_3} I_D \quad (4)$$
in which $I_D$ can be either non-zero (at OECT’s ON state or when applying $V_{IN,L}$) or almost zero (at OECT’s OFF state or upon using $V_{IN,H}$).

Achieving the restored $V_{IN}$ and $V_{OUT}$ levels ($V_{IN,L} = V_{OUT,L}$ and $V_{IN,H} = V_{OUT,H}$) is the ideal operation for inverters. The performance of the OECT-based inverter greatly depends on the switching behavior of the OECT, i.e., the ON/OFF ratio, $R_{CH,ON}$, $R_{CH,OFF}$ and the gate voltage at which the OECT gets OFF (also referred to as switching voltage). Furthermore, there are other key parameters associated with the inverter’s performance such as $V_{OUT}$ window, voltage gain ($\partial V_{OUT}/\partial V_{IN}$), propagation delay and lifetime which are considerably linked to $V_{IN}$ levels, the resistor ladder and supply voltages.

### 3.2.2 Inverters with Variable resistor(s)

In organic electronics, inverters qualified to operate at relatively low supply voltages, yet offering high voltage gain and enlarged $V_{OUT}$ windows than the respective $V_{IN}$ window are desired. The voltage windows (i.e., the $V_{IN}$ and $V_{OUT}$ windows) are defined as the difference between their respective digital “High” and “LOW” voltage levels. Since circuits developed based on standard PEDOT:PSS-based OECTs result in low voltage gain\textsuperscript{105,106} and sometimes not obtaining output voltage levels that are coinciding with those of the input, the utilization of OECTs in logic circuitry can be challenging.

Let’s consider the inverter from a voltage gain perspective. The voltage gain ($\partial V_{OUT}/\partial V_{IN}$) shows the ability of inverters to enhance a voltage
signal from its input to the output. That is, an inverter with a high voltage gain represents a high voltage enhancement ability. In the following, the voltage gain and its dependency on different parameters is described.

The relationship between the transconductance and the differential form of the drain current can be written as

$$
\frac{dI_D}{dV_{IN}} = \frac{\partial I_D}{\partial V_{IN}} dV_{IN} + \frac{\partial I_D}{\partial V_{DS}} dV_{DS} = g_m dV_{IN} + g_d dV_{DS} \quad (5)
$$

where $g_m$ is the OECT’s transconductance and $g_d$ is the drain conductance. Besides, based on the current passing through $R_1$ and $R_2$, $V_{DS}$ can be presented as below

$$
V_{DS} = V_{OUT} \left(1 + \frac{R_2}{R_1}\right) - \frac{V_+ R_2}{R_1} \quad (6).
$$

Then, by using equation (5) and (6) in the differential form of equation (4), the voltage gain can be expressed as

$$
Voltage \ gain = \frac{\partial V_{OUT}}{\partial V_{IN}} = \frac{R_1 R_3 g_m}{(R_1 + R_2 + R_3) + R_3 (R_1 + R_2) g_d} \quad (7).
$$

The OECT inside the inverter structure experiences different $V_{DS}$ levels depending on the selection of resistor values, supply voltages and/or $V_{IN}$ levels (Figure 8). This $V_{DS}$ level typically has high value (e.g., $V_{DS} < -1 \text{V}$). At a relatively high $V_{DS}$ (e.g., $V_{DS} > -0.2 \text{V}$) a PEDOT:PSS-based OECT operates in the saturation region\textsuperscript{105,106,113,117,118}. For an OECT operating in its saturation region, $I_D$ is independent of $V_{DS}$ (Figure 7b) and hence the drain conductance ($g_d$) is zero. Therefore, equation (7) can be shortened to\textsuperscript{119}:

$$
Voltage \ gain = -\frac{R_1 R_3}{R_1 + R_2 + R_3} g_m \quad (8).
$$

From the above equation it is noticeable that to get a high voltage gain for the inverter, it is essential to enhance the resistances (cf. equation (6) and (8)) and/or the OECT’s transconductance. To improve the $g_m$, the bulk doping (the capacitance per volume) can be enhanced. This not a
simple approach as it requires modifying the OECT design (e.g., OECTs with wider channels) or changing the electrolyte properties or the material applied in the OECT’s channel. The alternative to achieve high voltage gain is increasing the resistances in the resistor ladder. Although this way the voltage gain gets improved, it negatively affects the switching speed (due to the RC component). Instead, a low resistance would correspond to a high gm but it risks not obtaining the expected $V_{OUT}$ window. Therefore, a trade-off between the $g_m$ and the resistor ladder is essential to augment the voltage gain (equation 8).

From the $V_{OUT}$ window standpoint, there is usually sequential signal transmission in digital circuits where the $V_{OUT}$ signal attained from one inverter (or other logic circuit) is utilized as the $V_{IN}$ signal for the next inverter stage. In such cases, if the $V_{OUT}$ signal diminishes after propagation through a few stages, ultimately the attenuated voltage signal is not able to switch the rest of inverters in the sequence. Therefore, it is essential that the $V_{OUT}$ window is of a certain size to satisfy safe logic propagation between stages.

To attain inverters capable of operating at low voltages with improved performance in terms of voltage gain and $V_{OUT}$ window, variable resistors in the inverter structure are introduced. By introducing variable resistors, the concern can be circumvented. To get a variable resistor in the inverter structure, a resistor is connected between the OECT’s gate and the source electrodes so that when current is passing through the resistor a voltage bias is created at the gate of the coupled OECT. That is, depending on the resistance and the drain current travelling through the OECT channel, the coupled OECT experiences a particular voltage range across its channel. For a given set of supply voltages, a gate voltage range is expected for the OECT which is coupled with the fixed resistance. Therefore, the combination of a fixed resistance and the channel resistance ($R_{ch}$) of the coupled OECT creates a variable resistance in the inverter structure. In Figure 9a, the scheme of variable resistor is illustrated.
Figure 9. (a) A variable resistor achieved by combination of a fixed resistor (R) and OECT’s channel resistance (R_{Ch}) (b) Inverters with variable R_{1} and R_{3}.

Figure 9b schematically shows an inverter with two variable resistors which is derived from the standard inverter structure. For instance, in Figure 9b, by assuming I_{1} as the current going through the fixed R_{1}, the gate voltage range for the coupled OECT is defined by V_{+} - (I_{1} \times R_{1}). This
implies that when the gate voltage increases, the $R_C$ also increases since the coupled PEDOT:PSS OECT works in the depletion mode.

3.2.3 Cascade-Coupled Inverter

As mentioned earlier, inverters are fundamental components of digital circuits. There are some simple inverter-based configurations that provide practical assessment on circuit operation. One configuration is so-called cascade-coupled inverters. We can design a cascade of two or more stages by connecting several inverters in series. Figure 10 illustrates cascade-coupled inverters with several stages.

![Cascade-coupled inverters](image)

**Figure 10.** Cascade-coupled inverters.

3.2.4 Ring Oscillators

Another simple method to evaluate circuit performance is to make ring oscillator circuits. A ring oscillator is formed by connecting an odd number of inverters in a loop such that the $V_{OUT}$ of the last inverter (last stage) is fed back into the $V_{IN}$ node of the first inverter (first stage). The ring oscillator provides a simple method to measure the inverter propagation delay. For a ring oscillator with $N$ inverters ($N$ must be an odd number) the $V_{OUT}$ signal oscillates with frequency of $1/2Nt_p$ where $t_p$ is the propagation delay for each stage. Figure 11 exemplifies ring oscillator structures consisting of five inverters.
Figure 11. Ring oscillator structure consisting of five inverters.

The circuit shown in Figure 11 results in a waveform that oscillates with frequency of $1/10t_p$. 
4 Methods

This chapter briefly describes methods employed in this work to fabricate and characterize the devices.

4.1 Materials

OECTs and OECT-based inverters were printed on flexible PET substrates, Polifoil Bias purchased from Policrom Screen. The transistor channel and the gate electrodes are based on PEDOT:PSS (Clevios SV3 purchased from Heraeus). A screen printable and UV-curable electrolyte ink based on poly(diallyldimethylammonium chloride) dissolved in water (AFI VV009 provided by RISE Acreo) is employed to provide switching mechanism in the transistors. A screen printing carbon ink (7102 purchased from DuPont) is used to create the source and drain electrodes as well as the printed resistors for the inverters. A screen printable ink containing silver flakes (Ag 5000 purchased from DuPont) is utilized to lower the resistances in probe pads. A UV-curable insulator ink (5018 purchased from DuPont) is applied to separate layers.

4.2 Manufacturing

Among a wide range of printing methods, screen printing is one of the matured techniques in which a desired pattern is transferred through a screen onto a substrate. It is a mass production approach in fabricating large area flexible electronics. This printing technique is suitable with a variety of inks and substrates. There are variants of screen printing techniques such as flatbed sheet-fed screen printing, flatbed cylinder screen printing, rotational screen printing, cylindrical screen printing. Although the focus of this work is on the flatbed sheet-fed screen printing method, the laser ablation technique is used in one of the device fabrication steps to assist the manufacturing process (Paper IV).
4.2.1 Screen Printing Principles

The flatbed sheet-fed screen printing is the most common type of screen printing in which rectangular screens are employed. The screen is fabricated from a woven mesh (or pattern carrier) which is mounted on a frame (mesh holder) under a considerable tension. The woven mesh is usually made of polyester or stainless steel threads. There are holes between the threads in the mesh, and these holes can be blocked by using a photochemically defined emulsion (mask) coated on the nonprinting areas of the mesh. This way the desired pattern is established on the mesh. That is, the mesh contains binary features, i.e., printing and nonprinting areas, where the open areas allow the ink to be transferred to the substrate. To do printing, the ink is placed on top of the screen and a squeegee is applied to push the ink through the openings of the mesh. Figure 12 schematically illustrates the principle of flatbed screen printing method in top and cross sectional views. Figure 12a demonstrates that screen, squeegee and ink are the essential elements in the screen printing technique. As shown in Figure 12b, by the movement of the squeegee, the ink is pressed down and is transferred to the substrate through the openings of the mesh. As the squeegee moves along the screen, the mesh is pulled up away from the substrate due to the tension of the mesh. This way the ink is left on the substrate and the pattern is created. It is noted that to print electronic components which typically include multi-layer and multi-material structures, treatment of each layer is required to guarantee the desired function (e.g., minimal sheet resistance) without damaging previously deposited layers\(^3\). In screen printing method, depending on the nature of inks, various types of ink drying methods can be applied, e.g., thermal evaporation or ultraviolet (UV) curing.
Printing can be done by screen printers by which printing parameters such as the print gap (the gap between the screen mesh and the substrate), the squeegee speed, angle and the squeegee pressure can be controlled. Two screen printer machines are demonstrated in Figure 13 where one of them is equipped with a semi-automatic loading screen system (*DEK Horizon 03iX*) while the other one (*ATMA*) is equipped with an automatic screen positioning procedure. The screen printer used for fabrication of devices in this work is shown in Figure 13a.
To produce optimal screen printed films, considering factors such as printer settings, substrate preparation, screen options, squeegee types and ink rheology are substantial. In the following, fundamental background about screen, squeegee and ink together with their importance and effect on the printing quality is briefly explained.

The most important element dictating the printing resolution (line width) is the screen mesh. Each mesh is characterized by parameters such as the mesh openings and thread diameters. The more open the mesh, the less ink pass-through is blocked by the threads. The mesh openings are related to the mesh counts (mesh density) which is the number of mesh threads per centimeter. Thereby, a mesh is typically identified as $n\cdot d$ where $n$ is the mesh count and $d$ is the thread diameter in µm. For instance, a mesh named as 150-30 involves 150 threads/cm with a 30 µm thread diameter. To improve the device density and performance of electronic devices, a high resolution screen printing is desired. By using the screen printing, a printing resolution of 50-150 µm corresponding to a mesh resolution of 40-120 µm can be achieved\textsuperscript{14,125,126}. In this work, the fabrication of multi-layered devices is done by using meshes with standards polyester threads while the mesh counts are varied from 75 to 150 threads per cm and the thread diameters are ranged from 20 to 50 µm.
The squeegee and its movement can affect the thickness of the deposited layer. A squeegee with a sharp edge transfers less ink than a rounded edge squeegee. The movement of squeegee with low speed and high pressure may transfer more ink than high speed and low pressure.

Inks are fluids that have direct impacts on the printed film properties. Viscosity as a rheological property of inks is a key parameter in screen printing that represents the ink resistance to flow. It is the ink viscosity that specifies the ease/resistance at which the ink squeezes through the openings on the mesh. In screen printing, when an ink with an appropriate viscosity passes through the mesh, it leaves an even layer of defined thickness which resists spreading after deposition. Screen printable inks have high viscosity (low flow behavior after printing) with a broad viscosity range of 100-100,000 mPa s\textsuperscript{127}. This possibility to use inks of various viscosity makes screen printing a convenient technique.

The OECTs used in this work are built by six printed layers by using five different inks. Figures 14a-b schematically demonstrate the six printed layers building vertical OECTs together with the OECT’s cross-sectional view. The carbon connections are used as the drain and source contacts to minimize the reduction (blue) front. The carbon contacts also define the channel length since they are located at both ends of the channel (PEDOT:PSS). Figure 14c depicts a microscope image of a single OECT that is fabricated by only using screen printing method.
Figure 14. A vertically stacked OECT (a) The sequence of six printed layers. (b) The cross sectional view of the OECT schematically showing the multi-layered stack. (c) A microscope image of a fully screen-printed OECT.
4.2.1.1 Alignment

Digital cameras with rotary motors that are embedded in screen printers make it possible for the operator to optimize alignments. Printed electronic devices usually have multi-layer architectures which are realized by printing various layers onto the substrate. For a pattern that comprises different layers, each layer has its own mesh containing a part of the whole design. For printing each layer, the corresponding screen is placed on top of the substrate and the related ink is employed. For a multi-layered printing task, due to the topology of the previously printed layers, a good quality of printing can be challenging. Therefore, to print operational electronic devices with small dimensions, having good alignments between layers is vital. Figure 15 illustratively depicts printing of an image with two layers in which aligned and misaligned printing of layers are shown.

Figure 15. An illustration of aligned and misaligned printed layers for a two-layered image.
For a printed electronic device, when printing several consecutive layers on top of each other a misalignment between any of the layers negatively affects the device performance, i.e., leading to either a malfunctioning or a nonfunctional device. This even gets more critical when printed features are very small compared to the accuracy limitation provided by the printing method. The screen printer used for device fabrication in this work (Figure 13a) has alignment capability of +/- 25 µm. In paper I, manufacturing yield of fully screen printed OECTs are investigated in terms of their ON/OFF ratio where yield of 99.7% is achieved.

4.2.2 Laser Ablation

In this thesis, the OECT channel is formed by screen printing a PEDOT:PSS layer between the source and drain electrodes. As mentioned earlier, the OECT channel area plays a key role in the performance, i.e., OECTs with shorter channel lengths result in higher conductivity (lower channel resistance) in the ON state. In Figure 16 illustrates the side view scheme of a vertical OECT with its various layers. As shown in Figure 16, the channel length (L, indicated with the pink arrow) is specified by the separation between the source and drain carbon electrodes while the channel width (W, indicated with the yellow arrow) is defined by the width of the PEDOT:PSS layer.

![Figure 16](image)

**Figure 16.** The side view scheme of a PEDOT:PSS-based OECT with the printed layers.
In Paper I, Paper II and Paper III, the OECTs are fully screen printed with the smallest channel length of 80 µm. However, further reducing the channel length with the screen printing technique is challenging due to the lateral resolution limitation of this manufacturing method.

Lasers are influential tools which can be used in preparation, prototype fabrication and material processing. Laser cutting of screen printed patterns enables high resolution patterning, thus overcoming the limitation of the screen printing method. In context of OECT fabrication, laser patterning can be used to create small dimensions, for instance shortening the channel length and create wider channels with less resistivity. This approach is utilized in paper IV where the OECT’s channel length (the spacing between the source and drain electrodes) is formed by laser cutting of the previously screen printed carbon-based rectangle. Figure 17a illustratively shows the laser ablation approach used in paper IV to create OECTs with small channel lengths. This step is done by using a Speedy 300 industrial engraver (Trotec Laser GmbH), fitted with a 30 W CO₂ laser and a traveling speed of maximum 3.55 m/s mechanics. Figure 17b depicts the various layers of OECTs fabricated by a combination of laser ablation and screen printing.
Figure 17. Manufacturing OECTs using a combination of laser ablation and screen printing. (a) Forming the source and drain electrodes by laser ablating a previously screen printed carbon-based rectangle. (b) The exploded view of the OECT layers.
4.3 Profilometry

Profilometry is a way to obtain quantified information about thickness and roughness of samples. Profilometers can be categorized into two types, contact and non-contact. Contact profilometers collect profile information of samples by bringing the sample surface into contact with the stylus tip with a predefined force. In contrast, the working mechanism of non-contact profilometers is based on optical techniques, such as interferometry and confocal microscopy.

Although utilization of the optical profilometry can be challenging for transparent samples that reflect less amount of the incoming light, approximate values for the thickness and roughness can be achieved. For soft and sticky samples, applying contact profilometry can be tricky due to the risk of the stylus getting stuck or going into the sample. It is noted that when manufacturing OECTs, the requirements on thickness and roughness of the printed features are not critical, as compared to FETs fabrication. Thickness and roughness of the samples in this work is measured by employing a non-contact optical profilometer. This is also the motivation for choosing relatively coarse screen printing as the manufacturing method\textsuperscript{115}.

4.4 Electrical Characterization

Next step after design and fabrication of an electronic device is performing electrical characterization to evaluate the device performance. Most of the measurements are conducted in controlled environment at ~20 °C and ~50% relative humidity (RH). In the case of transistors, ON-current, OFF-current, switching voltage, switching time, leakage current are primary characteristics to evaluate among other properties. The equipment used to perfume the electrical characterization are Semiconductor Parameter Analyzer (Agilent 4155b) and Function Generator (Agilent 33120A). The main electrical characterization approaches commonly used for transistors are explained in the following sections.
4.4.1 Transfer Measurements

Transfer measurements is one of the most fundamental electrical characterization techniques used for transistors and other electronic components such as inverter. In the case of transistors, it basically includes recording the current that passes through the channel (drain current) versus the gate voltage while applying a fixed voltage to the OECT’s drain electrode. The gate voltage can be swept between two voltage levels with a desired voltage step. From this characteristic the ON/OFF ratio can be obtained (Figure 7a).

4.4.2 Output Characteristics

Output measurements is another way of presenting transistors’ performance in which the drain current is recorded versus the drain voltage for a given gate voltage (Figure 7b). In output characteristics of transistors, two distinctive regions occur for the drain current. At low drain voltage, the drain current has a linear relation with the drain voltage. That is, the transistor channel behaves as a resistor. However, at elevated drain voltages, the drain current remains constant even by increasing the drain voltage. This is called saturation region, i.e., independent of the applied drain voltage the drain current remains fixed and transistors behave as a constant current generator.

4.4.3 Dynamic Switching

In the dynamic switching measurements, the gate voltage is supplied from a function generator as a square wave alternating between two gate voltage levels at a certain frequency with a duty cycle of 50%. Then the transistor’s drain current which dynamically switches between the ON and OFF states is recorded over time by using the parameter analyzer. From dynamic switching behavior the switching time can be obtained. In case of logic gates (e.g., inverters), by running prolonged dynamic switching measurements, it is possible to observe the degradation of voltage levels over time and estimate the lifetime of the device.
5 Conclusions and Outlook

In this thesis, screen printed PEDOT:PSS-based organic electrochemical transistors (OECTs) and their application in digital logic inverters are investigated. Various designs of OECT-based inverters are explored, targeting low-voltage operating digital logic circuits within the field of organic printed electronics.

In Paper I, screen printing was employed to fabricate several hundreds of PEDOT:PSS-based OECTs including six vertically stacked layers and a relatively small footprint of each device (1\times1 \text{mm}^2, without probing lines) on large area flexible substrates, i.e. A4 size. Most of the printed OECTs had channel dimensions of 200\times200 \text{µm}^2. The manufacturing yield was assessed in terms of ON/OFF ratio, with an ON/OFF ratio > 400 as the yield criterion, and for the first time a manufacturing yield as high as 99.7\% was achieved for the fully screen printed OECTs. The reliable performance of screen printed OECTs across the printed area is the key contribution of this paper. In Paper II, screen printed OECTs with the channel dimensions of 150\times80 \text{µm}^2 are utilized to develop OECT-based inverter structures. The effect of three different resistor ladders (ranging from tens of kΩ to a few MΩ) were comprehensively investigated in terms of inverters, 3-stage cascade-coupled inverters and 3-stage ring oscillators. The resistor ladders were selected to extensively explore the inverter performance in terms of driving conditions with input voltage levels differing by about 1 V. It was shown that by increasing the resistor values in the ladder, the propagation delay is prolonged while a higher voltage amplification (~13-15) was obtained. Also, it was demonstrated that the lifetime is inversely proportional to the overall voltage strain applied to the inverter. One of the main contributions of this work is that the developed OECT-based ring oscillators have shown faster signal propagation than all printed OECT-based ring oscillators previously reported in the literature. Sometimes the utilization of OECTs in electronic logic circuits is challenging due to the resulting low voltage gain and low output voltage levels, even when operating at high supply voltages. This has brought us to Paper III, in which the inverter structure studied in Paper II was modified into different novel inverter designs. These
inverter designs were based on multiple screen printed OECTs and a resistor ladder, where the input signal was applied to one of the OECTs, while the additional one or two OECTs were employed to establish variable resistance values in the resistor ladder. The novel inverter designs can operate at relatively low supply voltages, yet offering high voltage gains and larger output voltage windows as compared to the respective input voltage window. In comparison with the inverter structures studied in Paper II, a threefold increase in the voltage gain (≈42) was achieved, even though lower supply voltages were used. By operating the inverters at low supply voltage levels (+/−2.5 V) and utilizing an input voltage window as low as 1 V, an output voltage window with almost 110% increment. The key contribution of this publication is that the novel inverter designs resulted in higher voltage gain while operating at lower supply voltages, in comparison with the inverters relying on static resistor ladders previously reported in the literature. Paper IV focused on the inclusion of a laser ablation step in the OECT manufacturing process, with the aim of minimizing the OECT channel area and thereby improve the switching performance. In this paper, the goal was to maintain a high manufacturing yield while making the channel length of the OECTs shorter. By this approach, 200 OECTs with the channel dimensions of 200×25 μm² were fabricated and an ON/OFF-based manufacturing yield of 89% was achieved. Here, an ON/OFF ratio > 1,000 was used as the yield criterion to define a functional device, and the highest recorded ON/OFF ratio was almost 600,000. The main contribution is to use laser ablation to achieve improved ON/OFF ratio by shortening the channel length, while at the same time maintaining a high manufacturing yield.

The low operation voltage, the large output voltage window and the capability to reach high voltage amplification turn these OECT-based inverters into promising candidates for further utilization in printed electronic applications. However, there are a few hurdles and challenges to overcome, such as the switching time of the circuits, footprint and the resolution limitations of the screen printing technique. After all, utilizing different manufacturing methods when printing and patterning the different layers needed in these devices should mitigate some of the challenges related to the manufacturing of OECTs with small channel dimensions and circuit footprints. For instance, the combination of screen and aerosol
jet printing can help to manufacture high performing devices by reducing the OECT’s channel size.
References


11. Williams, N. X., Bullard, G., Brooke, N., Therien, M. J. & Franklin, A. D. Printable and recyclable carbon electronics using...


20. Wegener, M. et al. Flexographic printing of nanoparticulate tin-


52. Perelaer, J. *et al.* Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic


62. Kawahara, J. *et al.* Flexible active matrix addressed displays


111. Kergoat, L., Piro, B., Berggren, M., Horowitz, G. & Pham, M.-C. Advances in organic transistor-based biosensors: from organic


121. Docking, S. & Sachdev, M. A method to derive an equation for the


Part II: Papers
Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

https://doi.org/10.3384/9789179292041