Computational Modelling of Organic Bioelectronic Devices and Materials

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Description of the cover page: Depicts the structure of the PEDOT:Tos film in contact with water (+ions) included in the thesis by Najmeh Delavari, LiU.

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Abstract

Bioelectronics being the intersection field between electronics and biology, aims to investigate the transduction between electronic signals and ionic signals within a biological environment. Organic materials such as conducting polymers are extensively utilized in the fabrication and development of bioelectronic devices due to their ability to conduct both electrons and ions. In addition, organic materials offer advantages compared to their inorganic traditional counterparts, including being flexible, solution processable and printable as it is an easy strategy for the fabrication process. These unique properties make organic conductor materials a good match for a wide range of organic bioelectronic applications such as organic transistors and biosensors interacting with biological/physiological systems and pave the way for more developments in the state-of-the-art technology of organic bioelectronics. Many of the organic bioelectronic devices function in contact with a biological system, usually an electrolytic medium, where mostly ionic transport occurs. Therefore, understanding the structural, morphological, and electronic properties of materials and devices used for organic bioelectronics applications is the topic of strong current interest.

This thesis is focused on two levels of computational investigations: studying bioelectronic devices and studying materials used for bioelectronic applications. The former includes modelling of electrolyte-gated organic field effect transistors (EGOFET), whereas the latter provides theoretical insights into morphological changes, ion injection, water intake, and self-assembly of conducting polymers. In the part of the thesis addressing the device modelling we first proposed an EGOFET model based on the Nernst-Planck-Poisson equations to describe, on equal footing, both the polymer and the electrolyte regions within the device. Using the developed model, we modelled and analysed experimentally measured current–voltage characteristics of the device (the output and transfer curves), where a semi-qualitative agreement between the experimental and calculated results was achieved. In a follow-up study, we demonstrated that Nernst-Planck-Poisson modelling represents a powerful tool allowing quantitative device design, modelling and analysis enabling us to forecast the influence of geometrical parameters as well as the materials used as electrolyte and the organic semiconductor for the case of a printed EGOFET.

To explore the ion exchange phenomena at the interface of conducting polymers with aqueous electrolytes, we provided a detailed atomistic understanding of the water intake, swelling, and ion injection during cyclic voltammetry. By combining the molecular dynamics simulations with experimental measurements such as e-QCM (electrochemical quartz crystal microbalance), UV–VIS–NIR absorption spectroscopy, and XPS (X-ray photoelectron spectroscopy) we demonstrated that the PEDOT:Tos film underwent significant changes in morphology and mass during the redox processes. Finally, we studied the self-assembly of polythiophene based polymers with glycol and alkyl side chains deposited on the gold surface. Using molecular dynamics simulations, we investigated the diffusion of the molecules and analysed their conformations. We explored how different side chains interact with each other and how they influence the conjugated polymers self-assembly.
We believe that the knowledge we acquired from our studies, combining experimental investigations with computational insights, provided an important understanding of the fundamental molecular processes at the material and device level that could help a practical enhancement in the field of organic bioelectronics.
Populärvetenskaplig Sammanfattning


Bioelektronik, som kombinerar elektronik med biologi, syftar till att undersöka gränssnitten mellan elektroniska signaler i elektroniska komponenter och jonsignaler hos levande organismer. Organska material, särskilt ledande polymerer, används i stor utsträckning vid tillverkning och utveckling av bioelektroniska enheter, tack vare deras förmåga att leda både elektroner och joner. Dessutom har organiska material flera fördelar jämfört med sina traditionella oorganiska motsvarigheter, som till exempel att vara flexibla och processbara i lösningsmedel. Det gör det möjligt att printa materialet, vilket ger en ytterligare fördel eftersom det förenklar tillverkningsprocessen. Dessa unika egenskaper gör att organiska ledarmaterial passar utmärkt till ett brett spektrum av organiska bioelektroniska applikationer, såsom organiska transistorer och biosensorer som interagerar med biologiska/fysiologiska system och banar väg för fortsatt utveckling inom den senaste teknologin för organisk bioelektronik.

Många av de organiska bioelektroniska enheterna är kompatibla med biologiska system, vanligtvis genom ett elektrolytiskt medium där överföring av signaler framför allt sker genom joner. Därför finns det ett stort aktuellt intresse för en förståelse av strukturella, morfologiska och elektroniska egenskaperna hos de material och anordningar som används för organiska bioelektroniktillämpningar.

Molekyldynamik (MD) är en beräkningsmetod som används brett för att studera atomers och molekylers fysiska rörelse samt morfologien och strukturen hos komplicerade system som består av miljontals atomer. MD gör det möjligt att simulera och förutsäga den dynamiska utvecklingen av ett system av partiklar och få detaljerad morfologisk information som inte är tillgänglig genom konventionella experimentella tekniker. På grund av detta kallas det ibland "beräkningsmikroskopi". En annan teknik som används för att modellera enheter är finita elementmetoden, som är den vanligaste numeriska tekniken för att lösa tekniska och matematiska problem inom fysik och industri.

Denna avhandling är huvudsakligen inriktad på två nivåer av beräkningsundersökningar: studier av bioelektroniska enheter respektive studier av material som används för bioelektroniktillämpningar. Den förra inkluderar modellering av en specifik typ av transistor baserad på ett gränssnitt mellan ledande polymer och ett elektrolytiskt medium,
medan den senaste ger teoretiska insikter om morfologiska förändringar, joninjektion, vattenintag och självorganisering av ledande polymerer.


Vi tror att den kunskap vi har fått från våra studier, genom att kombinera experimentella undersökningar med beräkningsinsikter, har bidragit med en viktig förståelse för de grundläggande molekylära processerna på material- och enhetsnivå som skulle kunna innebära en praktisk förbättring inom området organisk bioelektronik.
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List of Included Publications

Publication I
Nernst–Planck–Poisson analysis of electrolyte-gated organic field-effect transistors
Najmeh Delavari, Klas Tybrandt, Magnus Berggren, Benoît Piro, Vincent Noël, Giorgio Mattana, and Igor Zozoulenko
Contribution: Carrying out COMSOL simulation, Analysis of simulation results, Writing computational part of the manuscript

Publication II
All-inkjet-printed, coplanar electrolyte-gated organic field-effect transistors on flexible substrates: fabrication, modeling and applications in biodetection
Khalil Chennit, Najmeh Delavari, Samia Mekhmoukhen, Laure Fillaud, Samia Zrig, Benoît Piro, Vincent Noël, Igor Zozoulenko, Giorgio Mattana
Submitted to journal Advanced Materials Technologies
Contribution: Carrying out COMSOL simulation, Analysis of simulation results, Writing computational part of the manuscript

Publication III
Water Intake and Ion Exchange in PEDOT:Tos Films upon Cyclic Voltammetry: Experimental and Molecular Dynamics Investigation
Najmeh Delavari, Johannes Gladisch, Ioannis Petsakourakis, Xianjie Liu, Mohsen Modarresi, Mats Fahlman, Eleni Stavrinidou, Mathieu Linares, and Igor Zozoulenko
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Contribution: Carrying out MD simulation, Analysis of MD results, Writing MD part of the manuscript

Publication IV
Molecular Dynamics Study of Diffusion and Self-Assembly of Polyythiophenes with Glycol and Alkyl Side Chains Deposited on a Metallic Surface
Najmeh Delavari, Mathieu Linares, Igor Zozoulenko
In manuscript
Contribution: Carrying out simulations, Data analysis, Writing manuscript
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1. Introduction

Polymers make up the building blocks of such a wide range of our contemporary world, that is enough to look around to see a variety of polymer-based products. With the advent of polymers, we have witnessed them replacing many customary products that were conventionally made with different materials such as metals, stones, etc. But this is just the rise of the polymer era and every day we expect to see novel products of these materials that are released to the market. Therefore, no peak can be imagined for them thanks to their capabilities to be low-cost, light weight, relatively easy solution processibility and exceptional bio-related properties. In the past, perhaps few people thought that polymers would ever be considered an electrically conductive material. Since the advent of polymers, these materials have initially been used as electrical insulators. However, over the past few decades, discovery of conducting polymers with high conductivity has broken the boundaries of this notion. It was in 2000 that Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa won the Nobel Prize in Chemistry for the discovery and development of conductive polymers.\(^1\)

High electrical conductivity of polymers was investigated and proved back in 1970s.\(^2,3\) In the meanwhile, combined electronic and ionic conductivity has been observed in polymers.\(^4-6\) In addition, organic materials and conducting polymers offer tremendous advantages compared to their inorganic counterparts, i.e., solid-state-electronics. Some of the characteristics that make organic electronics material unique include flexibility, printability, and relatively low-cost investment.\(^7\) There are some other features that support the fact that organic electronic materials are considered as the active material in organic bioelectronic devices, such as, defining functionality (translating chemical bio signals into electronics) at the material level, transparency, being soft and able to self-assemble. In addition, the most important feature is that organic electronic materials are both electronically and ionically conductive.\(^8\) All these unique features and characteristics, make organic electronic materials a promising candidate for a wide variety of applications like organic photovoltaic solar cells\(^9\) (OPV), organic light-emitting diodes\(^10,11\) (OLED), Organic electronic transistors\(^12,13\) (OECT) and electrolyte-gated organic field-effect transistors\(^14,15\) (EGOFET). What all organic bioelectronic devices share in common is the ions; and organic electronic materials provide the functionality at the material level where ionic-electronic coupling of bio signals and electronic signals is defined.

The path of ion transport is paved by several factors such as material used for doping the conjugated polymer, the arrangement and morphology of the conjugated polymer and the chain length itself. That is, in bioelectronics the main focus is always to facilitate the transport of electrons as well as ions which is the main charge carrier in the biological environment. Therefore, finding materials with higher abilities in ion transport and ion exchange would be interesting. Besides, the morphology and self-arrangement of the polymers play a significant role in the transport phenomena. The focus of this thesis is to provide computational insights
into a better understanding of the fundamental molecular processes within organic bioelectronics materials and devices.
2. Aim and Outline of the Thesis

Conjugated polymers have gained special attention due to their dual conduction capabilities in conducting both electronic and ionic charges. That is, they have been used in a wide spectrum of applications and techniques in the field of bioelectronics where ion transport turns out to be the topic on great interest. The aim of this thesis is to provide a theoretical understanding of the underlying molecular processes taking place within the material and device for organic bioelectronics applications.

This thesis consists of two parts. The first part (part I) describes the scope of the thesis where basic theoretical foundations are presented. This chapter starts with an introduction of organic electronics and bioelectronics with the focus on the relevant conjugated polymer-based materials and devices. Then fundamentals of device modelling used in this thesis are described. Lastly, fundamentals of molecular dynamics simulations and computational techniques are presented.

The second part (part II) of the thesis contains the results of our works and projects in the form of scientific publications. These publications mainly include two levels of computational investigations: studying bioelectronic devices (publication I and publication II) and studying materials used for bioelectronic applications (publication III and publication IV).

Publication I proposes a new approach for modelling of electrolyte-gated organic field effect transistors (EGOFET). In a follow-up study, publication II demonstrates that Nernst-Planck-Poisson modelling represents a powerful tool allowing quantitative device design, modelling, and analysis for the case of a printed EGOFET. In publication III, theoretical insights into the morphological changes, ion exchange, and water intake of a conducting polymer compound are combined with experimental measurements. Finally, publication IV presents investigations on the effect of the side chain type and length on the diffusion and self-assembly of polythiophene-based conjugated polymers with glycol and alkyl side chains deposited on a gold surface using molecular dynamics simulations.
3. Organic Electronics and Bioelectronics

3.1. Conducting Polymers

Polymers are large molecules that are made up of a large number of smaller repeating units called monomers. They have many types and applications and are abundantly utilised in everyday life, investigated in science, and industry. Until about 40 years ago, perhaps no one imagined that a polymer (conventionally known as plastic) could conduct electricity. Polymers were considered non-conductive materials and even were used as electrical insulation coatings. However, these notions have changed since the early 1970s, when it was shown that conjugated polymers can be conductive.

Conjugated polymers are a group of polymers with alternated single and double bonds in their chain made of unsaturated monomers. These polymers can be conductive and transport electrons/holes along the backbones of their chains. This amazing discovery opened a new branch in the science of polymers called conductive polymers, which sparked interest in further research over the decades. Conjugated polymers are proved to be a promising candidate for many applications due to their unique interesting properties. They benefit from being low cost, having low density, easy structural modifications, optical properties, combined with many other interesting features making them proper materials for a vast variety of specific applications. These features have led researchers to make extensive efforts to eliminate some of the disadvantages of these materials, such as low solubility and improve their structural properties. Conjugated polymers have an undeniable role in industry, medicine, and bio-related research. The importance of these materials is such that they are called “21st-century materials”.

As mentioned, the essential characteristic of conductive polymers lies in their conjugation, that is, alternating single and double carbon bonds through the polymer backbone structure. It is well known that these conjugated bonds are responsible for the charge transport in the polymer. That is, carbon atoms of the backbone have a strong chemical bond, referred to as localised sigma bonds. Moreover, each double bond also holds a delocalised pi bond (see Figure 1) where the interaction between the electrons is weaker compared to the sigma bonds. Since pi orbitals are delocalised throughout the chain of conjugated pi bonds, the electrons are relatively free to move. Thus, the overlap of pi orbitals of carbon atoms is the key to the charge carriers movement across the polymer backbone chain.
However, being conjugated is not enough for a polymer to be a good conductor. Morphological and structural disorders can disrupt charge transport over the length of polymer chain.\textsuperscript{25–27} That is, some conjugated polymers demonstrate low electrical conductivity in their pristine state (undoped). Therefore, they need to be doped with an appropriate material in order to be conductive. In solid-state physics, electrical properties of materials are defined by their electronic band structure where the valence band being the highest energy state where electrons exist at absolute zero temperature, and the conduction band being the lowest vacant energy state. A conjugated polymer can be doped either positively or negatively. In positive doping electron removal from valence band occurs which corresponds to addition of positive charge carriers as holes, whereas negative doping corresponds to addition of an electron to the conduction band. Thus, there are p-type and n-type conjugated polymers where charge carriers are the absent electrons (referred as holes) and added electrons, respectively. As a matter of fact, p-type conjugated polymers are much more common than n-types due to their higher stability at ambient conditions.\textsuperscript{28} Depending on the material used as a dopant, the arrangement of the conjugated polymer and chain length, conductivity of a polymer compound could change significantly.

The conductivity of conjugated polymers can be enhanced by increasing the density of the charge carriers.\textsuperscript{29} This is usually governed during the doping process where a high amount of dopant is added. There are a few numbers of ways for doping conjugated polymers, namely chemical doping, and electrochemical doping.

In chemical doping, a neutral polymer (P) is exposed to chemical compounds that are either electron acceptors (A) or electron donors (D):

$$P + A \rightarrow P^* + A^-$$

$$P + D \rightarrow P + D^*$$
That is, by oxidation or reduction, an electron is removed or added during doping process, thus making the polymer chain positively (p-type) or negatively charged (n-type). For p-type conducting polymers, the holes on the backbone of the polymer are compensated by negatively charged dopants. As an instance, in PEDOT:Tos, Tosylates are the molecular counterions that compensate for the electronic charges on the PEDOT backbone.

In electrochemical doping, the polymers are doped using electrodes:

\[ P + e^- \rightarrow P^- \]
\[ P^+ - e^- \rightarrow P \]

That is, doping takes place in an electrochemical setup where injection of charge carriers occurs by applying a potential to the conjugated polymer. \(^{30}\) Electrochemical doping can be operated using either liquid or solid electrolyte and it is sensitive to the potential window applied. By monitoring these parameters, a desired conductivity can be achieved in the conjugated polymers.

The study of polymer morphology as a physical phenomenon is an interesting topic in the realm of organic electronics. It aims at investigating polymers structures and understanding the morphology of the polymers at a large scale. Some polymers have amorphous structure, while others maintain crystalline or semi-crystalline arrangements. \(^{31}\) Different arrangements of the polymers are due to different strengths in the molecular interactions (electrostatic and Van der Waals) which vary with the chain length. Depending on what type of morphology a conducting polymer possesses, a good or poor charge transport may happen. An effective \(\pi\)-\(\pi\) stacking lead to a better transport in semi-crystalline domain and it is important to connect those domains with longer chains. That is, the morphology of the conjugated polymer plays a role on the charge transport being the key factor in the operation of polymer electronic devices. \(^{32}\)

Poly(3,4-ethylenedioxythiophene), best known as PEDOT, is one of the most widely used derivatives of thiophene. EDOT is polymerized to produce a conductive polymer with various applications in science and industry of organic electronics, such as organic field-effect transistors\(^{33}\), thermoelectric devices\(^{34}\), organic electrochemical transistors\(^{12}\) (OECT), electrochromic displays\(^{35}\), smart surfaces for cell control\(^{36-39}\), source and drain electrodes\(^{40}\), electrodes in contact with neuronal interfaces\(^{41}\), supercapacitors\(^{42}\), implanted drug delivery devices\(^{43}\) (i.e., organic electronic ion pumps), organic light-emitting diodes\(^{10}\), and many other applications. Compared to other conductive polymers, PEDOT has been one of the most studied due to its outstanding advantages such as physical and chemical stability, high conductivity, easy synthesis method, good compatibility with other materials, excellent electrocatalytic activity, transparency, and biocompatibility.\(^{44-48}\) Specifically, PEDOT is well-known for being highly conductive with the electric conductivity exceeding 1000 S cm\(^{-1}\).\(^{34,47-49}\) When oxidized, PEDOT is rather transparent in the visible range and when reduced, changes
colour to dark blue.\textsuperscript{50} Presenting both electronic and ionic conductivity, PEDOT can also function as a mixed conductor.\textsuperscript{49,51,52}

As a result of oxidative polymerization in the presence of negative counterions, PEDOT is categorized as a p-type organic semiconductor. The positive charge carriers on oxidized PEDOT (usually in the form of polaron/bipolarons defined as “a combination of charge carrier together with the geometrical distortion of the polymer chain that it creates”\textsuperscript{53}) need to be electronically stabilized. This will be governed during the polymerization process where adding negatively charged polystyrene sulfonate (PSS) or molecular counterions such as tosylate compensates for the positive charge on the PEDOT.\textsuperscript{47–49,54–58} The latter (PEDOT:Tos) has attracted lots of attention because it is highly conductive and is showing semi-metallic behaviour.\textsuperscript{56,59–61} In addition, PEDOT:Tos has gained great attention to be used where electronic devices come to a close contact with a physiological/ biological environment.\textsuperscript{62–66}

### 3.2. Bioelectronics

Intersection between biology and electronics represents the research field of bioelectronics. The origin of bioelectronics is traced back to the 19\textsuperscript{th} century when Luigi Galvani discovered “animal electricity” by applying a voltage to a dead frog’s leg and observing it twitching.\textsuperscript{67} Later, it was evident that the ions and charged compounds in the animal’s body was the reason for the dead leg twitching. Since then, the field has progressed considerably and there has been a great range of applications within electronics and biological interfaces. When merged with organic materials, the field of organic bioelectronics is established. Over the last few decades, organic materials and in particular conducting polymers have become an indispensable part of many bioelectronic devices. This originates mainly from the fact that organic materials are soft and considered biologically compatible materials\textsuperscript{6} compared to conventional materials used in solid-state electronic devices. In addition, they have the advantage of transporting ions which is the main signal within biological systems. Thus, when it comes to building an interface with biological systems, organic materials come as a priority. Also, being low-cost, flexible, printable on soft transparent substrates, solution-processable, and having a high electronic and ionic conductivity makes polymer-based organic electronic devices an extensively studied and explored materials in organic bioelectronic applications. The field of organic bioelectronics takes the advantage of organic electronics in an extensive range of applications such as biosensing\textsuperscript{68–70}, neural interfaces\textsuperscript{71}, and drug delivery devices.\textsuperscript{72–74}

Among all organic bioelectronic devices, in this thesis we focus on the electrolyte-gated organic field-effect transistors.
3.3. Electrolyte-Gated Organic Field-Effect Transistor

Nowadays, transistors have become one of the most important components of modern electronics, and it is almost impossible to imagine a world without them. Transistors are utilised either as amplifiers and voltage stabilizers (regulators) or switches and electronic gates.

Field-effect transistors (FET) are a type of transistors in which control of the current is performed by an electric field. In these transistors, only one type of charge carrier (free electron or hole) is involved in generating the electric current. Field effect transistors have three terminals, namely, the source, drain, and the gate where the gate controls the flow of current passing through the source to the drain. A FET that has an organic material as the semiconductor is referred as an organic field-effect transistor (OFET).

Electrolyte-gated organic field-effect transistors (EGOFET) differ from conventional OFETs by using an electrolyte as the gate insulating material. Due to a high permittivity of the electrolyte, EGOFETs tend to have a higher capacitance than their conventional non-electrolytic counterparts. Therefore, the operating voltage in these devices is considerably smaller than in the OFETs (< 2 V) that makes them ideal for sensing and biosensing applications within liquid environments.75

The working principle of an EGOFET is as follows. A voltage is applied to the gate electrode and a voltage to the drain electrode with the source terminal being grounded. In an EGOFET with a p-type organic semiconductor, upon negative polarization of the gate, the positive charges in the electrolyte are attracted toward the electrolyte-gate interface, while negative charges migrate to the electrolyte-semiconductor interface. This leads to the formation of an accumulation layer of holes at the nano-meter-thick distance from the interface within the semiconductor region resulting in the formation of electric double layer (EDL) at both interfaces (see Figure 2). The holes as charge carriers within the semiconductor are homogeneously distributed across the channel length. Now, by applying a negative potential to the drain electrode (V_D), a current could flow throughout the channel.
The performance of the EGOFET device is generally described by the basic traditional equations used to explain the operation of metal-oxide-semiconductor field-effect transistors (MOSFET). The set of equations employed are listed below:

\[ I_D = \frac{W}{L} C_{TOT} \mu (V_{GS} - V_{TH}) V_{DS} \]  
\[ I_{D-SAT} = \frac{W}{2L} C_{TOT} \mu (V_{GS} - V_{TH})^2 \]

where \( I_D \) is the current flowing between the source and drain electrodes (drain current), \( W \) is the channel width, \( L \) is the channel length, \( C_{TOT} \) is the total gate-semiconductor capacitance per unit area, \( \mu \) is the mobility of the charge carriers, \( V_{DS} \) is the drain-source voltage, \( V_{GS} \) is the gate-source voltage and \( V_{TH} \) is the threshold voltage (i.e. the minimum gate voltage necessary to induce the formation of a conductive channel between source and drain). The two equations above, represent two different regimes: First the linear regime where the transistors output current \( I_D \) depends linearly on the value of \( V_{DS} \). Second, the saturation regime where \( I_D \) reaches an ideally constant (i.e. not depending on \( V_{DS} \)) value named saturation current \( I_{D-SAT} \). The former regime applies for small \( V_{DS} \) values, while the latter describes the behaviour of the drain current when \( V_{DS} \) increases.

The two aforementioned equations analytically describe the current-voltage characteristic of an EGOFET in different operational regimes as explained. During recent years, several other analytical methods for modelling organic electronic devices have been reported.
Although all those methods provide a useful insight to the physical characteristics of EGOFETs, they often lack a phenomenological explanation of what has been experimentally observed. In this context, a numerical approach based on the Nernst-Planck-Poisson equations could thoroughly contribute to the understanding of the physical and operational phenomena of the EGOFETs and provide an accurate description of their experimental behaviour in terms of current–voltage characteristics and parameters. This approach, which is based on finite element method, offers additional advantages including the possibility of generating a spatial map of the physical response of the system at desired location, being relatively low-cost, and the rapid calculation time for most applications. Herein, we utilise this method to describe the electrical behaviour of EGOFETs (See section 3. Device modelling).

3.4. Water Intake and Ion Exchange

The term ion exchange is referred to the exchange of ions between an electrolyte solution and a compound which in this case is a polymer film. Specifically, ion exchange is a process in which certain ions in the polymer film are replaced by the ions in the electrolyte solution. Conducting polymers are extensively used in many state-of-the-art electronic and bioelectronic applications and devices, such as sensors/biosensors, drug delivery devices, OECTs, EGOFETs, and a lot more. Many of these devices function upon oxidation and reduction processes, which significantly affects the morphology of their active material. In the cyclic voltammetry condition, when a conjugated polymer is in contact with an electrolytic medium, a penetration of the ions from the electrolyte into the polymer film changes its morphology. The ions penetrate the polymer film to compensate for the charges that are inserted to or released from the film. This may lead to adsorption of ions on the surface of the polymer film or swelling of the polymer itself. In either case, studying the morphological change of the polymer film is the question of great interest, because these changes correlate significantly with the device performance; as several studies have been conducted during the last years, to address various aspects of the water intake, swelling, and ion injection in conducting polymers.\textsuperscript{5,84–88}

3.5. Diffusion and Self-Assembly on a Metallic Surface

Being recognised as “mixed” conductors, conjugated polymers have been heavily studied and utilised in bioelectronic devices and applications.\textsuperscript{89,90} Several attempts have been initiated to manipulate the molecular design of conjugated polymers with the aim of improving their electronic and ionic conductivities.\textsuperscript{87,91–97} Many of these manipulations have been focused on
the strategies to enhance the molecular design, such as regulating the type and length of the side chains attached to the conjugated polymers’ backbone. Specifically, conjugated polymers with thiophene-type backbones and ethylene glycol-based side chains are getting more and more attention. This is mainly due to the fact that a good electronic conductivity is governed by thiophene backbone, whereas ion diffusion and water intake is facilitated by polar hydrophilic glycolated side chains. Conjugated polymers with glycolated side chains demonstrated a comparable performance with the polymers with the similar backbones but with alkylated side chains, while the former exhibited higher functionality due to better water and ion intake. That is, conjugated polymers with glycolated side chains cause high ionic diffusion and outstanding performance in organic electrochemical transistors. Recently, experimental investigations on the molecular conformation of the self-assembled polymer arrays on the gold surface has been carried out. However, theoretical investigations of the self-assembly of these conjugated polymers on a metallic surface that could provide an insight into the role of the side chains in the molecular arrangement of the polymers is not available in the literature. Thus, studying the diffusion and self-assembly of polythiophenes with glycol (pgBTTT) and alkyl side chains (pBTTT) deposited on gold surface would provide us with the basic theoretical foundation and the thorough understanding of the process of the self-assembly in these types of conjugated polymers.
4. Device Modelling

4.1. Drift-Diffusion Equations

Drift-diffusion equations represent one of the most widely used models in describing transport phenomena in semiconductor devices. In this model, a nonlinear system of partial differential equations is solved numerically. Drift-diffusion model is considered to be used as a predictive tool, so that to reduce the load of laboratory fabrications and tests by means of numerical simulations at a relatively lower cost.

Drift-diffusion model is based on three main equations as listed below:

\[ J_i = -D_i \left( \nabla c_i + f c_i \nabla V \right) \]  
\[ \nabla J_i = -\frac{dc_i}{dt} \]  
\[ \nabla \cdot (-\varepsilon \nabla V) = \rho \]

Equation 3 represents the drift-diffusion equation where \( c_i \), \( D_i \), and \( J_i \) are the concentration, diffusion coefficient and the flux of charge carriers, respectively. \( f = \frac{F}{RT} \) (\( F \) the Faraday constant, \( R \) the ideal gas constant, \( T \) the temperature), and \( V \) the electrostatic potential within the system. This equation governs the diffusion and drift contributions to the flux by considering the motion of the charge carriers due to the electric field and the gradient in charge carrier concentration, respectively. Equation 4 represents the continuity equation that relates the changes in concentrations to the fluxes. Finally, by solving the Poisson equation (Equation 5) coupled with the other equations above, transport phenomena is described within the system under study where \( \varepsilon \) is the permittivity of the medium.

4.2. Finite Element Method

Finite Element Method, or FEM for short, is the most common numerical technique for solving engineering problems and mathematical problems in physics. This technique is for solving partial differential equations based on one, two, or three spatial variables depending on the definition of the problem.

FEM is used in problems such as structural analysis, heat transfer, fluid dynamics, etc. To solve such problems through analytical methods, one must obtain the solution of several boundary
value problems for partial differential equations. Physical phenomena have equations that
govern them and describe their conditions. These equations are often in the form of
differential equations and are often nonlinear and complex due to the complex conditions in
the model and its surroundings. In these cases, the usual analytical methods presented under
the heading "Differential Equations" are no longer applicable. Therefore, other methods are
used to solve these equations, which are called numerical methods. Finite element method is
also a numerical method that can be used to numerically solve differential equations. In this
method, to simplify the problem, the whole area in which the equations must be solved is
divided into smaller components, each component being called an element. As the name
implies, each individual domain—an element—has a finite number of points. Hence, the
abbreviation for this method is FEM: Finite Element Method.

The FEM consists of the following main steps:

- First, geometry of a large complex body is divided into smaller and simpler bodies
called finite elements. This spatial discretization comes as a result of a discretized
model called mesh. The elements are interconnected via nodes that can be nodal
points, boundary lines, or boundary surfaces depending on the dimensionality of the
problem defined, that is, 1D, 2D, or 3D, respectively (see Figure 3).
- The next step is the interpolation of the field variables over the element. That is, an
interpolation function is used to interpolate the solution inside the element according
to the nodal points values.
- Then the elements properties are found by deriving governing equations for each
element.
- Finally, having each element well-defined, a global system of equations for the whole
body is derived by assembling all the elements equations. That is, all discretized local
elements are combined to give an assembly for the whole computational region.

Figure 3 schematic view of the types of finite elements. a) 1D- nodal points, b) 2D- boundary lines, and
c) 3D- boundary surfaces.
4.3. **COMSOL Multiphysics**

Designing complex devices that combine different physics requires solving complex equations that cannot be solved analytically. Here is where the finite-element-method-based software play a role. COMSOL Multiphysics is an excellent example designed to calculate multi-physical problems and is widely used in science and industry.

Using COMSOL Multiphysics, we performed numerical analysis by solving related partial differential equations. The modules we utilised for our study are Transport of Diluted Species and Electrostatics as implemented in the software.

**4.3.1. Transport of Diluted Species**

Mass transfer studies the physical processes involving diffusive and/or convective transport of chemical species in a physical system. The transport of species could be due to differences either in the potential or concentration of the species. Transport of Diluted Species module is designed to model transport phenomena in a diluted environment occurring due to diffusion, convection, or migration in the electric field. Fick’s law describes the diffusion contribution, convection becomes important for a flow field, and drift contribution is governed by migration of the charge carriers in an electric field. The dependent variable for the module is the concentration of species in mol/m³. Transport of Diluted Species module supports transport phenomena in 1D, 2D, 3D, and axisymmetric models in 1D and 2D.

The module is based on Nernst-Planck equations that account for the transport of all the charged species involved in the system, as described in section 3.1.

**4.3.2. Electrostatics**

The Electrostatics module can be utilised for calculating the electric field, electric displacement, and electric potential distribution in dielectric materials where the distribution of electric charges is known. Since the problems studied in this module are static, our tasks are solved in a stationary solver. However, there is a possibility to use this module for Frequency Domain and Time Dependent modes. Like any other module in COMSOL, Electrostatics module can be coupled with other modules, as well. The equation solved in this module is Gauss’s law, which solves the electric potential in the form of a scalar field (Equation 7). The dependent variable for the module is the electric potential $V$, that is defined by:

$$E = -\nabla V$$

(Equation 6)
The Gauss’s law is represented as:

\[ \nabla \cdot D = \rho \tag{7} \]

with \( D = \varepsilon_0 \varepsilon_r E \), where \( D \) is the electric displacement, \( E \) the electric field, and \( \varepsilon_0 \) and \( \varepsilon_r \) are permittivity of vacuum and dielectric constant of the material, respectively.

The Electrostatics module supports for 1D, 2D, 3D, and axisymmetric models in 1D and 2D.\(^{306}\)

### 4.3.3. Mesh

In the finite element method, the computational domain contains discretized elements referred to as “mesh”. An appropriate meshing is essential to the proper analysis of the model. The finer the meshing, the better approximation of the geometry, thus, the lower the error in the simulations. There is also an issue of wasting too many resources that can be tackled by a proper meshing strategy where a very fine mesh is defined at the boundaries or domains of interest and a coarser mesh implemented in other areas (e.g., in the bulk). In many simulations software packages, meshing is done manually, including setting the mesh size, number of boundary layers and its growth rate. This could become time consuming and increase the possibility of an error in some cases. COMSOL automatically applies optimal settings for volumetric, surface, and boundary mesh size according to the geometry and physics of the problem. The user can qualitatively determine the overall mesh size (coarse, normal, fine, etc.). However, there is an option for the user to change mesh settings manually, as well.

### 4.3.4. Solver

Solver defines the process of solving the problem in COMSOL Multiphysics. COMSOL has many advantages over other simulation software in terms of the solver selection. COMSOL, by default and according to the physics of the problem, selects the “best solver” as implemented within the package.

When solving a multiphysical model, there are two approaches that can be used as a descriptive solution to solve the (usually nonlinear) equation system. The Fully Coupled approach constitutes a large single system of equations that is solved for all unknowns and includes all couplings between the unknowns together in a single iteration. On the other hand, the Segregated approach does not solve for all unknowns at the same time. Instead, it divides the problem into two or more segregated steps. Each step usually represents a single physic (module), but sometimes even a single physic can be divided into steps, and sometimes a step
can include several physics. The single segregated steps are smaller than the complete system of equations formed with the *Fully Coupled* approach. *Segregated* steps are solved sequentially, in a single iteration, so less memory is required. The software automatically selects the *Segregated* approach for many cases, especially 3D models. On the other hand, for most 2D models, the *Fully Coupled* approach is used by default. Such that the user is only required to determine the type of study (stationary, time dependent, etc.). These default settings are selected for the overall reliability and strength of the solution. However, if necessary, the user can manually change the type of solver, solution settings, and even how to discrete variables. A significant advantage of COMSOL compared to other packages is the possibility of parametric solution and optimization of the model. Using a parametric solution, the user can check for changes in the output solutions of the model as a result of changes in one or more input parameters. That is, the sensitivity of the model to changes in its parameters can be investigated.
5. Molecular Dynamics Simulations

5.1. Background

Molecular dynamics (MD) is a computational technique that is widely used to study the physical motion of atoms and molecules as well as the morphology and structure of complex systems consisting of millions of atoms. MD allows to simulate and predict the dynamic evolution of a system of a large number of particles. MD is a powerful tool making possible to obtain detailed morphological information that is not accessible via conventional experimental techniques. Because of this it is sometimes referred to as “computational microscopy”.

The MD simulations are based on classical physics, in particular, on Newton's equation of motion. That is, for a system of N particles, the following equations are solved:

\[ m_i \frac{d^2 r_i}{dt^2} = F_i, \quad i = 1, \ldots, N \]  

(8)

where \( m_i \) is the mass of particle \( i \), \( r_i \) coordinates of particle \( i \), and \( F_i \) is the force felt by particle \( i \) from \( N-1 \) other particles. After letting the system to evolve over a short period of time, the forces are recalculated as below:

\[ F_i = -\frac{\partial U(r_1, \ldots, r_N)}{\partial r_i} \]  

(9)

where \( U \) is the potential between particles. Having the new force calculated, new positions are extracted using Newton’s equation of motion. Performing the above procedure with small enough time steps repetitively provides the trajectory of the system, that is the position and velocities of particles as a function of time.

5.2. Techniques and Procedures

The whole procedure of performing a molecular dynamics simulation can be divided into four steps:

1. Preparing inputs: initial conditions including initial coordinates and velocities of all the particles present in the system must be available. The exact positions come from the
initial structure while initial velocities are randomly assigned to each particle according to the Maxwell-Boltzmann distribution at a defined temperature.

2. Calculating forces: force is the spatial derivative of the potential. Potentials in MD describe two types of interactions, namely, non-bonded and bonded.

3. Reconfiguration: new positions and velocities are calculated by integrating Newton’s equation of motion, following the evolution of the system for a short period of time.

4. Generating output: Energies, positions, velocities, and other information are saved as the result of the simulation in trajectory and energy profiles.

The above-mentioned procedure is repeated until the total time of the simulation is reached.

5.2.1. Preparing Inputs

To perform a simulation, we need to build the molecule first, that is finding the \((x,y,z)\) position of all atoms present in the system. Initial configuration of the system must be selected carefully since an improper choice will influence and pollute the results.

In the very first stage, the atoms’ coordinates as well as their velocities are defined. Atomic coordinates are obtained from the initial structure and velocities are assigned according to the Maxwell-Boltzmann distribution at a specific temperature. Maxwell-Boltzmann distribution, a probability distribution utilized for assigning velocity to particles at equilibrium at a given temperature \(T\), is described as follows:

\[
f(v_i) = \left(\frac{m_i}{2\pi k_B T}\right)^\frac{3}{2} e^{-\frac{m_i v_i^2}{2 k_B T}}
\]  

(10)

where \(m_i\) is the mass of particle \(i\), and \(k_B\) is the Boltzmann’s constant.

Simulating a real complex system is a challenging task since it requires a massive amount of computational time and resources. Therefore, in molecular dynamics we aim for modelling the complex processes occurring in nature as accurately as possible by taking some approximations into account. One of the techniques that is widely used in molecular simulations is the periodic boundary conditions (PBC). PBCs are used to simulate a portion of a larger sample. Consider a cubic box (unit cell) that is repeated in all directions and forms a periodic array of boxes (super cell) that are periodic copies of the original box. During the simulations, particles are free to move in the unit cell. When a particle leaves any boundary of the unit cell, it is going to reappear on the opposite side of the cell. Using periodic boundary conditions, a small system representing the behaviour of a large system can be simulated. Figure 4 represents a unit cell that is surrounded by its translated copies.
Using PBC, we can perform simulations with a finite number of particles while maintaining a reasonable representation of an infinite real system.

5.2.2. Calculating Forces

In molecular dynamics, atoms are modelled as hard spheres with no internal degrees of freedom. However, they have specific properties such as charge and mass and can interact with each other. Molecules are described as a combination of these charged balls linked by bonds. To perform a molecular dynamics simulation, a potential function that describes the interaction between atoms and molecules in the system must be available.

Set of the potentials that act on each particle depending on its spatial position is called force field. In other words, a force field is a collection of mathematical equations designed to investigate the interactions of the system of atoms and molecules. The force acting on each particle is the negative derivative of the potential energy $U$.

$$ F = -\nabla U $$ (11)
The potential energy comprises two main contributions, namely bonded and non-bonded interactions. Bonded interactions involve the interactions between covalently bonded atoms while non-bonded interactions involve interactions between atoms in the same molecule not connected by covalent bonds as well as with atoms in other molecules.

\[ U = U_{\text{bonded}} + U_{\text{non-bonded}} \]  

(12)

### 5.2.2.1. Bonded Interactions

Bonded potentials contribution of the potential energy involves the interactions between two, three, and four covalently bonded atoms, that is, the bonds, angles, and dihedral terms, respectively (see Figure 5).

![Figure 5 Schematic representation of bonded interactions considered in MD simulations. a) two-body spring bond, b) three-body spring angle, c) four-body proper dihedral angle (torsion) and d) four-body improper dihedral angle.](image)

Bonds, angles, and dihedrals contributions are derived from the harmonic oscillator approximation,

\[
U_{\text{bonded}} = \sum_{\text{bonds}} \frac{1}{2}K_b(r_{ij} - r_0)^2 + \sum_{\text{angles}} \frac{1}{2}K_\theta(\theta_{i,j,k} - \theta_0)^2 + \sum_{\text{improper}} \frac{1}{2}K_d(d_{i,j,k,l} - d_0)^2 + \sum_{\text{tortion}} K_d(1 + \cos(n\phi_{i,j,k,l} - \phi_0))
\]  

(13)
where $K_b$, $K_\theta$, and $K_d$ are the force constants, respectively. $r_0$, $\theta_0$, and $d_0$ are the equilibrium values, namely the equilibrium distance, equilibrium angle and equilibrium dihedral angle, respectively.

5.2.2.2. Non-bonded Interactions

Non-bonded potential term involves interactions between all $(i,j)$-pairs of atoms, usually neglecting the pairs already involved in the bonded term. The main contributions to the non-bonded potential are the van der Waals interactions and the electrostatics.

\[
U_{\text{non-bonded}} = \sum_{i<j} 4\varepsilon_{i,j} \left[ \frac{\sigma_{i,j}^{12}}{r_{i,j}} - \left( \frac{\sigma_{i,j}^6}{r_{i,j}} \right)^6 \right] + \sum_{Coulomb} \frac{q_i q_j}{4\pi \varepsilon_0 \varepsilon_1 r_{i,j}}
\]  

(14)

The van der Waals force, a distance-dependant force, is the sum of the repulsive and attractive forces between atoms. The van der Waals force is described by the Lenard-Jones potential where $C_{i,j}^{12} = 4\varepsilon_{i,j}\sigma_{i,j}^{12}$ is the repulsive term at close distances and $C_{i,j}^6 = 4\varepsilon_{i,j}\sigma_{i,j}^6$ is the attractive term at farther distances. Although van der Waals forces are relatively weak compared to covalent bonds or electrostatic interactions, they play a fundamental role in molecular dynamics.

The electrostatic forces are described by Coulomb potentials. $q_i$ and $q_j$ are the atomic charges and, $\varepsilon_0$ and $\varepsilon_1$ are the vacuum electric permittivity and relative permittivity of the material, respectively.

5.2.3. Update Configuration

Newton’s equation of motion is utilized in molecular dynamics simulations. Forces are derived from the potential energy and with that the acceleration of the particles is calculated. The new positions and velocities are calculated by numerical integration of Newton’s equations of motion and the trajectory of the particles in the system is predicted over a defined period. In the following, we will mention some of the most popular numerical approximations and integration algorithms for molecular dynamics simulations.
5.2.3.1. Finite Difference Methods

Given the current positions and velocities at time $t$, the positions and velocities at the later time $t + \Delta t$ is predicted. Considering a Taylor expansion of the position vector in time, the equations are solved on a step-by-step basis:

$$r(t + \Delta t) = r(t) + dr(t)\Delta t + \frac{1}{2} \frac{d^2 r(t)}{dt^2} \Delta t^2 + \frac{1}{6} \frac{d^3 r(t)}{dt^3} \Delta t^3 + \frac{1}{24} \frac{d^4 r(t)}{dt^4} \Delta t^4 \ldots$$

(15)

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2} a(t)\Delta t^2 + \frac{1}{6} b(t)\Delta t^3 + \frac{1}{24} c(t)\Delta t^4 \ldots$$

(16)

$$v(t + \Delta t) = v(t) + a(t)\Delta t + \frac{1}{2} b(t)\Delta t^2 + \frac{1}{6} c(t)\Delta t^3 \ldots$$

(17)

$$a(t + \Delta t) = a(t) + b(t)\Delta t + \frac{1}{2} c(t)\Delta t^2 \ldots$$

(18)

where $r$, $v$, and $a$ are the position, velocity, and acceleration, respectively. The algorithm to follow is: first, positions, velocities, and accelerations at the time $t + \Delta t$ is calculated using the initial values. Second, from the new positions, the forces and then accelerations of each particle are predicted.

There is no absolute choice for the value of the time-step $\Delta t$. A large $\Delta t$ may end up having an unstable system. On the other hand, if $\Delta t$ is too small, the time of the calculations will increase which might not be computationally efficient. Therefore, finding the optimum value of $\Delta t$ for the system would be beneficial to both system under study and the resources.

5.2.3.2. Leap-Frog Integrator

Leapfrog integration is a method for numerically integrating Newton’s equations of motion.\textsuperscript{108}

This method differs from other available methods in a number of important ways, including, being fast, accurate, and long-time stable.

The leap-frog algorithm is applied to obtain position and velocities from an already available state. The positions are updated every $\Delta t$ step:
\[ r(t + \Delta t) = r(t) + v\left(t + \frac{\Delta t}{2}\right)\Delta t \]  

(19)

while the velocities are updated every \(\frac{\Delta t}{2}\) step and “leap” ahead the positions:

\[ v\left(t + \frac{\Delta t}{2}\right) = v\left(t - \frac{\Delta t}{2}\right) + a(t)\Delta t \]  

(20)

Since velocities are not acquired at the same time as the positions, the current velocities can be attained by an estimation:

\[ v(t) = \frac{v\left(t + \frac{\Delta t}{2}\right) + v\left(t - \frac{\Delta t}{2}\right)}{2} \]  

(21)

5.2.4. Generating Output

Finally, all the information related to the positions, velocities, and energies for each time-step is calculated and written in the trajectory and energy files. Different properties of the system are going to be analysed based on the output files.

5.3. Force Fields

Force field is used to describe the parameters of bond lengths, bond angles, dihedrals, impropers, the non-bonding van der Waals and electrostatic interactions in a system of atoms and molecules. In other words, it is defined by the exact formulation of the potential energy and the choice of parameters. Parameters and constants such as force constants \((K_p, K_\theta, K_d)\) and equilibrium values \((r_0, \theta_0, d_0)\) are defined for each pair, triple, and quadruple of atoms in the force field. The charge \((q)\) and parameters of the Lenard-Jones potential \((\epsilon_{ij}, \sigma_{ij})\) are assigned to each atom, as well. Determination of these parameters demands considerable amount of work carried out by a combination of empirical and quantum mechanical calculations. Then the force field is tested to assure that it will successfully reproduce the properties of an experimentally characterized system.

Designing force fields is a complex task that is done by specialized scientific groups. Most of the current force fields are empirical with different fitting parameters. Therefore, there is no one good force field that is used for all systems. Depending on the system under study, there can be different useful force fields.
Here is a list of well-known force field categories that are widely used:

- All-at atom force fields
- United-at om force fields
- Coarse-grained force fields

All-at atom (AA) force fields provide parameters for every single atom in the system. While in united-at om (UA) force fields, hydrogen and carbon atoms in methyl groups are treated as one interaction center. Coarse-grained (CG) force fields group the atoms in specific beads to cut both complexity and computational cost down. CG is extremely useful when it comes to simulations of larger systems at longer time scales.

5.4. Ensembles in Molecular Dynamics

Thinking in terms of statistical mechanics, MD simulations are performed within certain constraints defined as ensembles. An ensemble is a large set of microscopic states within a system with given macroscopic properties. In MD, calculations can be done within several ensembles. NVE, a microcanonical ensemble where the total number of particles (N), the total volume (V), and the total energy (E) of the system is conserved. Microcanonical ensemble (NVE) is a convenient choice for MD. However, experiments are usually carried out within a canonical ensemble (NVT) where instead of the energy, the temperature (T) is conserved. Therefore, a method must be introduced to control the temperature, a thermostat. There is another ensemble used in MD, named as isothermal–isobaric ensemble in which the number of particles, temperature and pressure are kept constant (NPT). The mechanism to maintain a constant pressure is introduced by the barostat. There are more ensembles as well, namely the grand canonical ensemble ($\mu$VT) and isoenthalpic-isobaric ensemble (NPH). The former is a statistical ensemble where neither the energy nor the particle number are fixed. Instead, chemical potential ($\mu$), volume (V), and the temperature (T) are constant. While the in the latter (NPH), the number of particles (N), pressure (P), and enthalpy (H) are conserved.

5.4.1. Thermostat

Temperature as a statistical quantity is calculated based on positions and velocities of all the particles present in the system. Thermostat is an algorithm modifying the classical Newtonian molecular dynamics to generate an ensemble at a constant temperature. There is more than one solution for conserving the temperature in the system. So that the solution must be chosen based on the purpose one seeks. Among all, Berendsen thermostat is one of the most popular and straight-forward solutions.
The Berendsen thermostat\textsuperscript{111} couples the system to a heat bath with a reference temperature $T_{\text{ref}}$ and the temperature of the system is obtained:

$$
\frac{dT}{dt} = \frac{T_{\text{ref}} - T}{\tau_T}
$$

(22)

where $\tau_T$ is the time constant. Therefore, the temperature of the system is regulated to always be near the reference temperature.

5.4.2. Barostat

The barostat is an algorithm that modifies classical Newtonian molecular dynamics to generate another important statistical quantity, the pressure. For NPT ensembles, barostat is essentially required and must be accompanied with the thermostat.

The Berendsen barostat\textsuperscript{111} is a well-known fast and reliable algorithm to conserve the pressure in the system. The mechanism of the Berendsen barostat is very similar to the Berendsen thermostat. Berendsen barostat performs pressure coupling for a reference pressure $P_{\text{ref}}$ within each time-step:

$$
\frac{dP}{dt} = \frac{P_{\text{ref}} - P}{\tau_P}
$$

(23)

where $\tau_P$ is the time constant for pressure coupling. By this, there will be variations in the box size where the MD box is scaled at every time-step.

5.5. Implementation with GROMACS

GROMACS being one of the most popular software packages available, is widely used in the field of molecular dynamics.\textsuperscript{112-114} GROMACS is open-source and supports different types of forcefields. This makes the software powerful and flexible. The detailed information on the mechanism of the software can be found in the GROMACS manual where the authors elaborated all the concepts constructing the program.\textsuperscript{115}
6. Summary and outlook

Over the history of mankind, polymers have always been considered in everyday life consumables as wool, silk, cotton, and linen composed of natural polymers. However, conductivity was introduced to polymers quite recently during an accidental discovery in 1970s. Discovery of conducting polymers, opened a new horizon in polymer science and industry where many other fields of science became attracted to take the advantage of these new materials in their research and applications. An important example is the field of bioelectronics where conducting polymers are considered as an active material due to their ability in conducting both electronic and ionic charges.

This thesis provides a brief description of organic electronics materials and devices with potential applications in bioelectronics. We focused on developing a new approach for modelling of electrolyte-gated organic field effect transistors (EGOFET). This was for the first time that an EGOFET model was thoroughly investigated using the Nernst-Planck-Poisson equations to describe, on equal footing, both the polymer and the electrolyte regions of the EGOFET configuration (publication I: Nernst-Planck-Poisson analysis of electrolyte-gated organic field-effect transistors). EGOFETs are organic thin film transistors where the solid-state dielectric, which separates the gate electrode from the organic semiconductor in Organic Field-Effect Transistors (OFETs), is replaced by an electrolyte either in liquid or gel form. In EGOFETs, the application of a gate voltage induces the formation of two Electrical Double Layers (ELDs), one at the gate—electrolyte interface and the other one at the electrolyte—organic semiconductor interface; the latter is responsible for the accumulation of mobile electronic charges along the organic semiconductor surface, providing the desired transistor operation. The intrinsic presence of an electrolyte within EGOFETs structure, and their low biasing voltages, make them promising candidates for the next generation of sensors and bio-sensors application operating in aqueous environments. In publication I, we were able to obtain an accurate quantitative description of the electrical behaviour (current–voltage characteristics) of EGOFETs of an arbitrary geometry. With our model, we produced a spatial map of the physical response of the system at any location, such as the concentration of holes and ions, the distribution of electric potential, and the electric field (see Figure 6). Different operation regimes of the device, namely, the linear, pinch-off and saturation regimes, were depicted and analysed.
Figure 6 (a) Concentration profiles showing the formation of the electric double layers (cations at the gate and anions at the electrolyte—polymer interface) leading to accumulation of the holes in the channel. (b) The potential profile and (c) the electric field in the y-direction (along the cross-section of the device marked by a red dashed line in (a)). A zoomed view on the polymer–electrolyte interface: (d)–(f) the density of anions (blue) and holes (dark purple) for different drain voltages.

The experimentally measured current–voltage characteristics were modelled and analysed using the developed model, and semi-qualitative agreement between the experimental and calculated output and transfer curves was found. We performed simulations to predict the influence of a geometrical parameter such as the gate electrode area on the transistors’ electrical behaviour and demonstrated — both experimentally and via the model — that the performance of the EGOFET strongly depends on the gate electrode size.

Our interesting findings in the first publication arouse a curiosity in further investigations on potential capabilities of our Nernst-Planck-Poisson modelling approach for EGOFETs. Therefore, publication II (All-inkjet-printed, coplanar electrolyte-gated organic field-effect transistors on flexible substrates: fabrication, modelling, and applications in biodetection), as a follow-up study, proposed our modelling approach to be employed as a powerful tool allowing quantitative device design, modelling, and analysis for the case of a printed EGOFET. In this publication, an example of all-inkjet-printed EGOFETs has been reported for the first time, by describing the fabrication protocol on flexible plastic substrates. We modelled the electrical behaviour of the all-inkjet-printed devices using the Nernst-Planck-Poisson
equations, and were able to achieve a good quantitative agreement between the simulation and experiments, outlining the attainable use of our modelling approach as a predictive tool for device design and optimisation. We calculated and analysed output and transfer curves based on the charge and potential distribution inside the device (see Figure 7). The calculated output and transfer curves showed not only qualitative, but rather good quantitative agreement with the experiment. The charge and potential distribution inside the device were calculated and analysed. In particular, it was shown that the “off-current” regime and the absence of the transistor action observed at low gate voltages $|V_{GS}| < 0.4 \text{ V}$ is an electrostatic effect related to the device geometry.

Figure 7 (a)-(c) and (e)-(g) Evolution of the charge carrier density (holes in red and anions in blue) at the electrolyte-semiconductor interface for different drain voltages $V_{DS} = 0, -0.2 \text{ V}, -0.5 \text{ V}$ as indicated by arrows. Top and bottom panels ((a)-(c) and (e)-(g) respectively) correspond to two representative gate voltages $V_{GS} = -0.7 \text{ V}$ and $-0.2 \text{ V}$. For convenience, the output curves for $V_{GS} = -0.7 \text{ V}$ and $-0.2 \text{ V}$ (the same as in Figure 6a) are shown in (d); Experimental data are shown in dots and simulated data are in empty squares.
We believe that this study may open an avenue to the development of the next generation of low-cost, flexible sensors and circuits, both through experimental studies and device modelling.

Over the last years, water intake, swelling, and ion injection in conducting polymers have attracted great attention in the literature, since these processes change the electrical and optical properties of the material and correlate significantly with the device performance. Typically, water intake and ion penetration are investigated under cyclic voltammetry conditions when the ions enter or leave the polymeric film to compensate for the charges that are inserted into or released from the film during oxidation or reduction. This phenomenon may lead to the adsorption of ions on the surface of the polymer film, thereby causing swelling of the film. Understanding those changes is crucial to enhance the design of future materials with improved performances. In publication III (Water Intake and Ion Exchange in PEDOT:Tos Films upon Cyclic Voltammetry: Experimental and Molecular Dynamics Investigation), we performed studies to better understand those phenomena in the PEDOT:Tos film during cyclic voltammetry. Combining our “computational microscopy” with experimental measurements (i.e., X-ray Photoelectron Spectroscopy (XPS) and electrochemical Quartz Crystal Microbalance (EQCM)), we provided an important understanding of the underlying molecular processes of the PEDOT:Tos film during cyclic voltammetry that has not been available before. We showed that the polymer film underwent significant changes in morphology and mass during the redox processes (see Figure 8). We observed that the film lost its mass during reduction as tosylate and Na\(^+\) ions were expelled, and gained mass during oxidation mainly due to the uptake of anions, i.e., tosylate and Cl\(^-\). Both e-QCM experiments, and simulations showed that a relative mass change between the most oxidized and reduced states was around 10–14%. The total film mass gradually decreased with increasing the cycle number, since the tosylates in the film were replaced by more agile Cl anions during cycling. MD simulations and XPS measurements confirmed that a portion of Tos is replaced by Cl\(^-\) during the voltammetry cycles. Moreover, MD simulations showed that during the redox process the volume of the film was gradually increased. Based on our calculations, we concluded that each ion brought ~4 water molecules into the polymer matrix. We believe that our molecular dynamics investigations combined with the experimental studies provided essential insights into the morphological changes, water intake and ion exchange of a well-known conducting polymer compound (PEDOT:Tos).
Figure 8 Changes in the PEDOT:Tos film composition (number of molecules) upon the first CV cycle with the corresponding molecular dynamics snapshots

Conjugated polymers with their exceptional capabilities in conducting both electronic and ionic charges have been extensively studied and employed in many bioelectronic devices and applications.\textsuperscript{52,90} Tuning the molecular design of conjugated polymers has also been investigated with the aim of improving their conductivity. Publication IV (\textit{Molecular Dynamics Study of Diffusion and Self-Assembly of Polythiophenes with Glycol and Alkyl Side Chains Deposited on a Metallic Surface}) is where we focused on regulating the type and length of the side chains attached to the conjugated polymers’ backbone. To this end, molecular dynamics simulations were performed to investigating the effect of the side chain type and length on the diffusion and self-assembly of conjugated polymers with glycol and alkyl side chains deposited on gold surface (pBTTT and pgBTTT, respectively). We found that the diffusion coefficient for alkylated sidechains decreased stepwise with the increase of the chain length $N$, while for glycolated sidechains the diffusion coefficient was rather independent on $N$. Moreover, pBTTT oligomers with shorter sidechains have the highest diffusion coefficient, whereas the diffusion coefficient of pgBTTT oligomers is rather independent on $N$. Investigating the score of elongation of the side chains, provided interesting information on their conformations on gold surface, where alkylated sidechains in pBTTT were found to be in more extended elongated structures while glycolated sidechains in pgBTTT were more twisted (see Figure 9a). This was correlated to the dihedral angle distribution of the CCCC and OCCO bonds in alkylated and glycolated sidechains, respectively. Molecular dynamics simulations demonstrated that two pBTTT oligomers are self-assembled and form
interdigitation of the side chains regardless of the sidechain length. In contrast, pgBTTT oligomers with short sidechains (N=12) did not form self-assembly. However, glycolated oligomers with longer sidechains (pBBTTT20) formed self-assembly, concluding that for pgBTTT, the sidechain length should be large enough to ensure sufficient interaction between the chains to drive the self-assembly. When deposited in an array configuration, both pBTTT19 and pgBTTT12 oligomers did form self-assembly (see Figure 9b) which found to be consistent with the experiments. We believe that our computational investigations provide the basic theoretical foundation on the effect of the type and length of the side chains in the molecular arrangement of the conjugated polymers on a metallic surface.

Looking forward, as a general statement, models can always be improved. There always remains neglected factors for the sake of simplicity or computational cost. For example, in modelling of EGOFET, we took the very first steps towards creating more accurate and comprehensive models. That is, we considered rather idealised conditions. Although our Nernst-Planck-Poisson modelling resulted in a good agreement between experimentally measured and calculated device characteristics, there are still several factors that have not been taken into account. Factors such as charge traps density in the semiconductor bulk and
at the semiconductor/electrolyte interface as well as the gate electrode leakage current are among them. These factors can be considered as challenges to be explored for further enhancements in the modelling of organic electronic devices.
References


101. Savagian LR, Österholm AM, Ponder Jr JF, Barth KJ, Rivnay J, Reynolds JR. Balancing charge storage and mobility in an Oligo (Ether) functionalized dioxythiophene copolymer...


115. Abraham M, Van Der Spoel D, Lindahl E, Hess B. GROMACS user manual version 5.0. 4. Sweden: Royal Institute of Technology and Uppsala University. Published online 2014.


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