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Organic thin films as active materials in field effect
transistors and electrochemical sensing

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Abstract

This PhD thesis is focused on Organic Electronics, an emerging field where different disciplines converge to gain insights into the properties of organic materials and their applications. Under the present work different organic materials have been realized and analysed for application both in Organic Field Effect Transistors and electrochemical sensing with Organic Electrochemical Transistors.

An overview about Organic Electronic is reported with the most recent advancement of the last years: a state of the art of research about Organic Field Effect Transistors (OFETs) and Organic Electrochemical Transistors (OECTs) is given, with an overview on the emerging Organic Bioelectronics. The main motifs of the research performed are reported along the discussion.

In the application of the supersonic molecular beam epitaxy method, thin films of Copper Phthalocyanine have been grown, reaching an unprecedented order in the crystalline structure, as the characterization by Raman spectroscopy and AFM have shown.

A modified-pentacene molecule (2,3-CN₂-TIPS-Pn films) has been used as active layer for the building of an OFETs device, which showed an ambipolar behaviour with balanced electrons and holes mobility on the order of $2 \cdot 10^{-3} \text{cm}^2/\text{Vs}$. The charge transport properties of 2,3-CN₂-TIPS-Pn films show the effectiveness of TIPS-Pn functionalization with cyano e⁻ withdrawing groups to promote e⁻ transport while maintaining equivalent h⁺ transport.

A second OFET device has been realized with tetracene organic thin films deposited on different dielectrics substrates: the devices have been characterized and the mobility measured. For the tetracene film deposited on the polystyrene substrate, we have found a mobility of $2 \cdot 10^{-1} \text{cm}^2/\text{Vs}$, the highest retrieved up to now in literature for tetracene.

The molecular structures of all the organic molecules used, have been deeply investigated by means AFM analysis and XRD-advanced algorithm tools. For the films made with the TIPS molecule, the GIXRD analysis revealed a favourable arrangement of the molecules in the TFT channel. The XRD analysis performed on the tetracene films revealed interesting correlation between the mobility of the film and the AFM and structural parameters: in particular the polystyrene film shows the best surface coverage and the highest alpha phase percentage of the molecular structure.

New insights into the device physics of OECT have been discovered: in the sensing experiments with OECTs, the role of the gate electrode has been investigated. This clarified the two working principles an OECT can operate (faradaic or non-faradaic mode). We found that an OECT can switch between these two modes of operation simply changing the metal wire acting as gate electrode. In particular the faradaic operational mode lead to the possibility to exploit the transistor as a halide sensor, able to detect Na⁺ ions in solution with a sensibility up to 10 μM.

Then the role of electrolyte has been studied with micellar structures, which open unexplored horizons for the application of OECT with a new class of electrolytes. The ability of micelles to dope/dedope efficiently the PEDOT:PSS permitted to investigate the doping process of the polymer, that is one of the main issue today in organic electronics. The modulation signals have been correlated with the surface charge of the micelles, measured by the zeta-potential techniques and the injection of micelles into the polymer structure has been probed by an optical spectroscopy measurement, performed in-situ during the OECT current acquisition. As a consequence of the micelle experiment,

bilayer structure, like liposomes, have been tested and detected for the first time with an OECT. Although this experiment is currently in progress, it seems particularly promising, mainly because the opportunity to exploit the ability of liposomes to trap and release drugs in a controlled way.

A new nanoparticles-based sensor has been developed, able to detect the presence in solution of iron-oxide magnetic nanoparticles functionalised with different polymeric coatings: we provide the ability of OECTs to detect and monitor selectively, with an appropriate choice of the electrolyte, different nanosystems. We demonstrate an on-line sensing based on OECTs, with an easy sampling/sample preparation, for the detection of functionalized magnetic nanoparticles.

OECTs have promising applications in bioelectronics as well as in nanomedicine or neuroscience. They are becoming an ideal platform for both in-vitro and in-vivo biomedical applications, as well as for the development of protocells inside miniaturized electro-chemical laboratory.

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Publications

In the following, a summary of my experiences and publications during the 3 PhD years, organized in publications in peer-reviews journals, contribution at national and international conferences with posters or oral presentation, and finally the PhD-schools I have attended.

Publications in peer-reviewed journals.

Paper 1.

F.M. Mohammadi, **G. Tarabella**, N. Coppedè, F. Barbero, S. Iannotta, F. Cicoira, C. Santato. "Playing with Electronic and Ionic Transport in Functional Organic Films".
RCS Chemical Science. In press.

Paper 2.

D. Isik, Y. Shu, **G. Tarabella**, N. Coppedè, S. Iannotta, L. Lutterotti, F. Cicoira, J.E. Anthony and C. Santato. "Ambipolar organic thin film transistors based on a soluble pentacene derivative".
Appl. Phys. Lett. 2011, 99, 023304.

Paper 3.

G. Tarabella, C. Santato, S.Y. Yang, S. Iannotta, G.G. Malliaras, F. Cicoira. "Effect of the gate electrode on the response of organic electrochemical transistors".
Appl. Phys. Lett. 2010, 97, 123304.

Paper 4

N. Coppedè, M. Castriota, E. Cazzanelli, S. Forti, **G. Tarabella**, T. Toccoli, K. Walzer and S. Iannotta. "Controlled Polymorphism in Titanyl Phtalocyanine on Mica by Hyperthermal Beams: a Micro-Raman Analysis".
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- [1] G. Tarabella *et al.* "OECT with micellar electrolytes", *submitted*.
- [2] G. Tarabella *et al.* "Structural GIXRD analysis of Tetracene thin films grown on different substrates: morphology and transport correlations", *submitted*.

Proceedings

C. Ress, L. Odorizzi, C. Collini, L. Lorenzelli, S. Forti, C. Pederzoli, L. Lunelli, L. Vanzetti, N. Coppedè, T. Toccoli, **G. Tarabella**, S. Iannotta. "Comparative Bioaffinity Studies for In-Vitro Cell Assays on MEMS-Based". *Sensors and Microsystems. Lecture Notes in Electrical Engineering*, 2010, Volume 54, Part 2, 83-87. DOI: 10.1007/978-90-481-3606-3_13

National and international conferences.

- [1] **G. Tarabella**, N. Coppedè, L. Lutterotti, S. Bertolazzi, F. Cicoira, C. Santato. "Structural GIXRD analysis of Tetracene thin films grown on different substrates: morphology and transport correlations". XL National Conference of Italian Association of Crystallography. September 19-22, 2011, Siena (Italy). *Accepted as oral*
- [2] A. Romeo, **G. Tarabella**, N. Coppedè, R. Mosca and S. Iannotta. "Organic Electrochemical Transistors for monitoring functionalized magnetic nanoparticles". X Congresso Nazionale Materiali Nanofasici. September 6-8, 2011, Bologna (Italy). *Accepted as oral*
- [3] F. Cicoira, **G. Tarabella**, C. Santato, S. Iannotta and G.G. Malliaras. "Effect of the Gate Electrode on the Response of Organic Electrochemical Transistors". MRS Spring meeting, Organic Bioelectronic Symposium. April 25-29, 2011, San Francisco (USA). *Accepted as oral*

[4] **G. Tarabella**, L. Lutterotti, S. Bertolazzi, J. Wuensche, N. Coppedè, S. Iannotta, F. Cicoira, C. Santato. "On the correlation between structure, morphology, and charge transport in organic molecular films: the tetracene case". SPIE 2011 Optics + Photonics. August 21-25, 2011, San Diego (USA).
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[5] F. Cicoira, **G. Tarabella**, S. Iannotta, G.G. Malliaras. "Organic Bioelectronics with Electrochemical Transistors". International Conference on Organic Electronics. June 22-24, 2011, Rome (Italy).
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Posters at international conferences:

[1] **G. Tarabella**, F. Cicoira, N. Coppedè, C. Santato, S.Y. Yang, G.G. Malliaras, S. Iannotta. "Organic electrochemical transistors applied in biosensing". The 6th International Conference on Microtechnologies in Medicine and Biology (MMB 2011). May 4-6, 2011, Lucerne (Switzerland).

[2] N. Coppedè, T. Toccoli, **G. Tarabella**, K. Walzer, M. Castriota, E. Cazzanelli, S. Iannotta. "Titanyl Phthalocyanine thin films polymorphism and order control by Supersonic Molecular Beam Deposition growth". ElecMol 2008: Fourth International conference on Molecular and Organic Electronics. December 8-12, 2008, Grenoble (France).

PhD schools attended.

1. *Atomic Force Microscopy Advanced School*. May 2009 – June 2009.
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2. *Computational Thermofluidodynamics*. 5-10 September 2009
Unione Italiana Termofluidodinamica (UIT), Siena.

3. *National School of Bioinorganics Chemistry*. 3-6 July 2011
University of Siena.

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1. Introduction

In this chapter, an outline of the current “state of the art” in Organic Electronic (OE) is given. OE is the branch of electronic based on π -conjugated molecules and polymers [1-3]. Since the discovery of conducting polymers in 1977 by A. J. Heeger, A. G. MacDiarmid and H. Shirakawa, awarded of the Nobel Prize in Chemistry in 2000, tremendous efforts have been devoted to OE research on π -conjugated materials and device development [4]. OE devices, among which the most well known are light-emitting diodes, field-effect transistors and solar cells, are being fabricated since more than three decades. Significant advancements in chemical tailoring and synthesis, materials processing as well as device engineering, are driving the fabrication of devices with improved performance and reproducibility. The enormous interest in OE has been originally motivated by the unique properties of organic materials, such as easy of processing, tunability of electronic properties through chemical design and synthesis, and the promise of flexible and cost effective devices. Recent achievements have opened new horizons in OE. A few examples are: the observation of high charge carrier mobility in organic single crystals [5], the discovery of metallic conduction at organic interfaces [6], the fabrication of organic field effect transistors able to operate in water [7], the observation of cell growth on organic materials [8], the fabrication of light emitting transistors [9, 10, 11], and the coupling of electronic and ionic conduction in organic semiconductors (OSs) [12-17]. I will discuss in particular OSs capable to sustain both electronic and ionic conduction since the coupling of electronic and ionic conduction has been exploited in various classes of devices such as light emitting electrochemical cells, electrochromic devices, and electrolyte-gated transistors. Here, the focus is on the progress on electrolyte-gated transistors, which are of great interest for low power electronics and bioelectronics.

In particular the interest on these subject is motivated by the novel boosting development of organic electronics that exploits the ionic-to-electronic transduction/amplified conduction that selected organic materials can exhibit, to produce a wide range of devices with potential applications in electronics, chemical/biological sensing and bio-electronics. Examples of such devices are electrolyte-gated transistors (electrolyte-gated organic field effect transistors, EG-OFETs, and organic electrochemical transistors, OECTs) and miniaturized bio-laboratories making use of surface, physico-chemical properties of which are controlled electronically. EG-OFETs (based on molecules and polymers) can be operated at low voltage (about 1 V or below), giving unprecedented charge carrier densities. OECTs can be operated in aqueous environment as efficient ion to- electron converters, thus providing an interface between the world of biology and electronics. For this reason, they open exciting opportunities for applications in biosensing. Biocompatible organic conducting polymers, operating in aqueous environment can be interfaced with biological systems. By exploiting conducting polymer properties such as electrochemical switching and combined electronic and ionic transport, it is possible to use these polymers as platforms where cells can adhere and proliferate and as a playground to novel biomedical and neuronal interfaces. This is a challenging field of research, whose most recent developments I am going to summarize in this chapter, the first development of which is the result of the exciting combination and convergence of different disciplines such as Materials Science, Physics, Chemistry, Electrochemistry, Organic Electronics, and Biology and more recently Medicine.

The chapter is organized in five sections:

1.1 Introduces the basic questions and evolution of organic materials for electronics, discusses the concepts of electrolyte-gated organic transistors and the difference between electrostatic and electrochemical doping.

1.2 deals with electrolyte-gated organic field-effect transistors (EG-OFETs), whose working principle is based on electrostatic doping. This part is divided in three sections where I discuss: EG-OFETs based on organic thin films (*section 1.2.1*), EG-OFETs based on organic single crystals (*section 1.2.2*), and the working mechanisms of EG-OFETs (*section 1.2.3*).

1.3 deals with organic electrochemical transistors (OECTs) whose working principle relies in electrochemical doping.

1.4 deals briefly with the recent demonstration of electrochemically doped organic light emitting transistors.

1.5 reports the most recent developments in organic bioelectronic.

The relevance state of the art for the present work is briefly discussed in the following sections and the reader is referred to some of the reviews articles already published by several authors for more detailed overview [3, 17-19, 20, 21].

1.1 Organic Electronics

Conjugated organic semiconductors

In this introduction an overview about organic semiconductor is reported. This summary has been written following the Nobel lecture of A.J. Heeger [4]. A polymer is a large molecule composed of the repetition of a structural unit, which is the monomer. Because most of the polymers are soluble in aqueous or organic solvents, they can be handled easily in solution phase by standard techniques as spin coating, molding or drop casting.

The conducting polymers are a special class of polymers able to conduct charges, more often holes, but also electrons, and they include the special class of conducting ions in addition to holes or electrons.

Conducting polymers are carbon-based molecular semiconductors, whose distinct property is the *conjugation*: the bonding in the molecule or along the polymer backbone consists of alternating single and double carbon-carbon bonds (**Figure 1.1**) [1].



Figure 1.1 The conjugation property of conducting polymers consists in the alternating single-double carbon bond along the polymer chain.

The conjugated molecular structure leads to one unpaired electron per carbon atom (the π electron). In the π bonding the carbon orbitals are in the sp^2p_z configuration and the orbitals of successive carbon atoms along the polymer backbone overlap. The overlapping leads to the electron delocalization that permits the charges mobility along the polymer chain. Polymers then can exhibit semiconducting or metallic properties [4]. As a result the electronic structure of conducting polymers is given by the chain symmetry, that is the number and kind of atoms within the repeat unit.

Polyacetylene (PA) is an example of conjugated polymer ($-CH_n$) (**Figure 1.2**), in which each carbon atom is bonded to two neighboring carbons and one hydrogen atom by a σ bonding, with a π electron on each carbon.

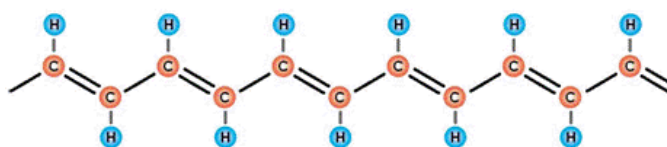


Figure 1.2 Structure of Polyacetylene (PA).

The structure of PA, due to the Peierls Instability, has two carbon atoms in the repeat unit $(-CH=CH)_n$, thus, the π band is divided into π and π^* bands, each holding two electrons per atom (spin up and down). As a result the π band is filled and the π^* is empty. The energy band gap is defined by the energy difference between the highest occupied state in the π band and the lowest unoccupied state in the π^* band. The alternated structure of PA characterizes in general conjugated polymers. Because no partially filled bands are present in conjugated polymers, they exhibit typically semiconducting behavior.

Organic semiconductors are divided essentially in two types: conjugated polymers and conjugated small-molecules [22]. Other examples of conjugated polymers, as well as PA, are polythiophene (PT), poly(3-hexyl) thiophene (P3HT), polyethylenedioxythiophene (PEDOT), polypyrrole (PPy) or

polyparaphenylene (PPP).

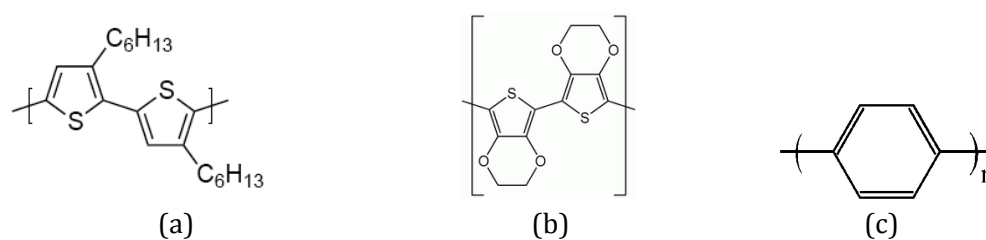


Figure 1.3 Examples of conjugated polymers: **(a)** P3HT, **(b)** PEDOT and **(c)** PP.

Among the small-molecule organic semiconductors, the most widely studied materials include tetracene, pentacene, sexithiophene and copper phthalocyanine (**Figure 1.4**).

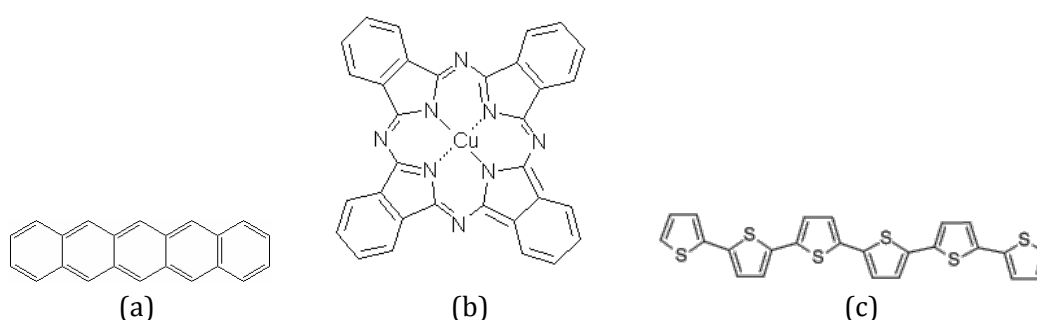


Figure 1.4. Examples of small-molecule organic semiconductors, (a) pentacene (b) copper phthalocyanine and (c) sexithiophene.

The electrical conductivity of conducting polymers can be controlled over the full range from insulator to metal, and can be realized by a reversible doping of the polymer. The doping could be of different types, among them the most well established are: the chemical and electrochemical doping, and the photochemical and interfacial doping (**Figure 1.5**). Concurrent with the doping the electrochemical potential (Fermi level) is moved into a region of energy where there is a high density of electronic state, while the charge neutrality is maintained by the introduction of counter ions. The electrical conductivity result from the existence of charge carriers (hole or electrons) and from the ability of these to move along the π bonds of the polymer backbone. As a result, doped conjugated polymers are good conductors because charge carriers have been introduced into the electronic structure by doping and because the attraction of an electron in one repeat unit to the nuclei in the neighboring units leads to a carrier delocalization along the polymer chain and to charge-carrier mobility.

Chemical doping relies on the charge-transfer redox reaction, which could be an oxidation (p-type doping) or a reduction (n-type doping) [23-25]. It is an efficient way to dope organic materials but difficult to control. Electrochemical doping gives the opportunity to obtain intermediate homogeneous doping levels: in this kind of doping an electrode supplies the redox charge to the polymer, while ions diffuse in and out of the polymer from an electrolyte. The ions compensate the electronic charge. Importantly, the doping level is determined by the voltage between the polymer and the electrode (the gate, in the case of OECTs): at the stationary condition (electrochemical equilibrium) that voltage defines the doping level.

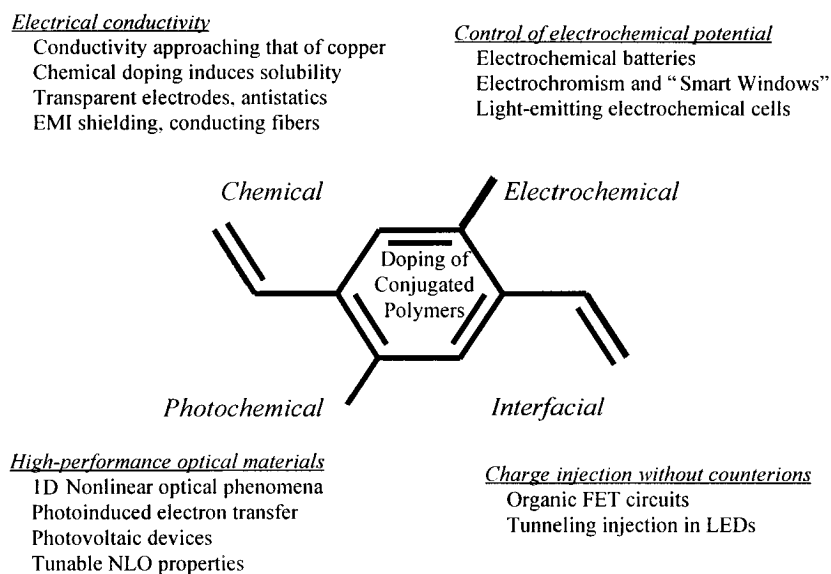


Figure 1.5 Types of doping in conjugated polymers. Reprinted with permission from [4] @ Wiley.

An OECT, as an organic electrochemical device, schematically represents a standard layout to explain the electrochemical doping process in a conjugated polymer. The polymer is in contact with a working electrode on one side, and a ground electrode on the other side, and with an ionically conductive electrolyte, the last being in turn in contact with another electrode (the counter electrode, or the gate in OECT). A bias between the working and ground electrodes controls the injection of charges (electrons) into the polymer. The ions from the electrolyte act as counter-ions that neutralize the charge of polarons, in order to maintain the electro neutrality of the system. Under the bias applied, charges move along the polymer backbone causing a moving local distortions of the conjugated molecular structure of the polymer: it is exactly the movement of local geometrical defect that generates the electrical current in the polymer.

Among the very wide range of molecules used as organic semiconductors, acenes play a particular relevant role. They are an extended class of polycyclic aromatic hydrocarbons made of fused benzene rings.

In particular naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) are the smaller acenes with 2 and 3 fused benzene rings, respectively. Tetracene ($C_{18}H_{12}$) and pentacene ($C_{22}H_{14}$) are the larger and most studied acenes [26-28] with 4 and 5 fused benzene rings. Due to their electronics properties, these molecules are under intense study, in particular they are promising organic semiconductors as active layer in organic field effect transistors. Electronic properties of acenes improve with the size of the molecule (number of rings), like carrier mobility [29] and band width [30], while reorganization energy decreases [31]. In Chapter 3, two experiments involving thin films of tetracene and a modified molecule of pentacene, as active layers in organic filed effect transistor, will be discussed.

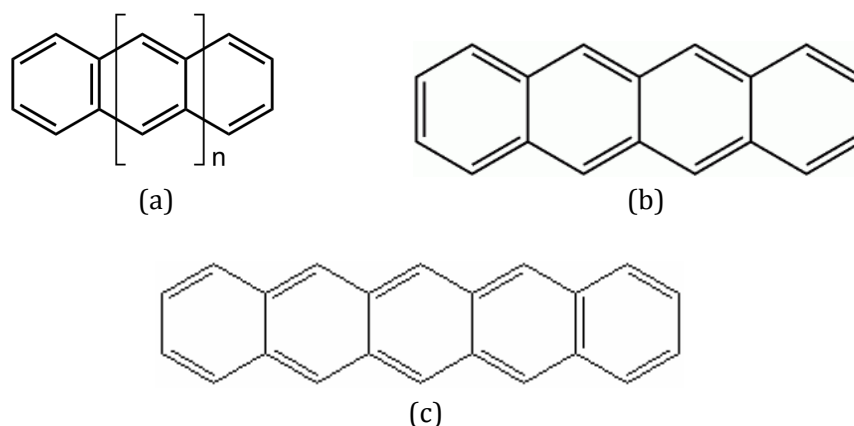


Figure 1.6 (a) structure of acenes (b) tetracene molecule structure with $n=4$ fused benzene rings and (c) pentacene molecule structure with $n=5$.

OFETs are a main area where efforts are being focused, and acenes have already found application in front-panel displays, RFID tags and sensors or solar cells [32, 33]. Indeed, the FET is an ideal platform to study organic semiconductors and measure their performance in terms of the charge carrier mobility, $I_{on,off}$ and V_{th} (μ , that is the drift velocity of charges per unit electric field, expressed as $\text{cm}^2/\text{V}\cdot\text{s}^{-1}$). The charge mobility in particular μ is calculated from the equation of the transistor transfer characteristic (I_{ds} vs. V_g):

$$I_{ds} = \frac{WC_i}{2L} \mu (V_G - V_0)^2$$

where W and L are the width and channel length, respectively, V_G is the gate applied voltage and V_0 the threshold voltage. C_i is the capacitance of the gate insulator.

FET performance is strongly dependent on the structure and morphology of the molecular films and becomes optimum for single crystals. A challenging experimental question is to form films with very high degree of order and possibly free of defects. Organic thin films structure is very sensitive to the deposition technique, deposition conditions and substrate properties. In fact the strong anisotropy, typical of organic π -conjugated molecules, gives rise an assembly in the films which is very sensitive to the molecule-substrate and molecule-molecule interaction. Major consequences are the formation of several structure and poly-types that differ very closely in energy, and hence very difficult to control during the growth of the film, so that is difficult to make films with the single well defined extended crystal structure free of defect. Different crystal structures differ only slightly in energy, making the coexistence possible. Summary, the structure, morphology and also texture determine the conductive properties of the organic film: more the film is well ordered more the conduction can be improve. To realize organic thin films the SuMBE method has been exploited because of the improved and unprecedented control on the growth that it can yields in film deposition.

Tetracene

The Tetracene molecule is widely investigated in organic electronics thanks to its charge transport and electroluminescence properties [26, 27].

The first light emitting OFET has been fabricated with tetracene semiconducting film and single crystals [34]. More, for tetracene single crystal, the hole mobility has been reached up to $2.4 \text{ cm}^2/\text{Vs}$ [35] and ambipolar light-emitting transistors have been shown [36]. The hole mobility in thin films has improved up to $0.1 \text{ cm}^2/\text{Vs}$ [26].

Pentacene

Pentacene is one of the most studied molecule among organic semiconductors, and is considered as a prototypal system to study and better understand the properties of these systems [2]. The ability to form ordered films with good electronic properties (comparable with those of amorphous silicon) make this compound very interesting for applications in electronic devices, also in VCSI technology [37]. However, performances of devices realized with these compounds are still far to be fully understood. This is mainly due to a lack of knowledge of the growth processes and of the formation of the interfaces with both metal contacts and dielectric substrates [38].

Pentacene (C₂₂H₁₄) is a planar molecule with typical dimensions of 16.6 Å and 7.4 Å. The interesting electronic properties of this compound are mostly due to its π -conjugated orbitals, which are strongly delocalized over the entire structure. Moreover the overlapping of π -orbital among neighbouring molecules determines the conduction phenomena that make pentacene appreciable for devices applications [39], showing a p-type semiconductor characteristic [40]. In its bulk phase pentacene has a triclinic structure (space group P1) and a density of 1.32 g/cm³. There are two molecules per unit cell arranged in a herringbone configuration [41].

In films having a lower dimensionality, the interaction of the molecules with the substrate induces strain in the crystalline structure, causing modification of the crystalline form. The anisotropy of the molecules give rise to the possibility to crystallize in different structures having small energetic differences, with nucleation of grains of different structural composition [42]. Typically these modifications are strongly related to substrates nature, both in terms of its structure, order and interface formation [43].

Electrolytes

Electrolytes are conductive liquids containing free ions. They can be liquids, but also solid or in gel form. Common electrolytes are simple salts in water, where the salt (solute) dissociates in positive and negative ions in water (solution). The degree of dissociation defines the strength of an electrolyte: strong electrolytes are almost completely dissociated, while weak electrolytes are only partially ionized. Organic electronic makes use of different kind of electrolytes, like simple electrolytes, ionic liquids, ion gels, polyelectrolytes, polymer electrolytes. Under this thesis I will introduce a new class of *micellar electrolyte*. Simple electrolytes are salts dissolved in a solvent liquid medium, like water or alcohol, whose molecules surround the ions salt, forming a solvation shell. They are very common in electrochemical transistors. The choice of solvent is very important in electrochemical experiments because it interacts directly with ions and, in sensing applications, with the elements to detect.

A salt in the liquid state is called ionic liquid (IL). We will have the opportunity to introduce ionic liquids with a concrete example in the following of this chapter. They are already used in electrochemical devices and it seems very promising for sensing applications. Usually an IL has a high ionic conductivity, up to 0.1 S cm⁻¹. They are very stable and in electrochemical operational permit to use higher voltages than a simple salt. The evolution of ionic liquids in the solid state are the ion gels: using a polymer blend (a block co-polymer or a polyelectrolyte) is possible to realize a gel structure of the ionic liquid, which becomes available for application as solid electrolyte. The conductivity of an ion gel is similar to that of ionic liquids. Polymers with an electrolyte group in the monomeric unit are called polyelectrolytes. When a polyelectrolyte is immersed in a solvent, like water, the electrolyte group dissociates from the polymer backbone, leaving a charged polymer chain and the counterions in the solvent. The counterions are the free ionic charged in a solid polyelectrolyte, moving in the polymeric fixed matrix: for this polyelectrolytes are ionic conductors, called polycations or polyanions in depending on whether free ions are positive or negative. In Chapter 1 we have already seen an application of electrochemical transistors using a polymer electrolyte, in that case the PEO

(poly(ethylene oxide)) [44]. A polymer electrolyte is a solvent-free solid electrolyte, consisting of a salt dissolved into a polymer matrix acting as a solvent. For example, the PEO is a sodium or lithium salt dissolved in the PEO matrix (Figure X). Ionic conductivity of polymer electrolytes range usually from 10^{-8} to 10^{-4} S cm $^{-1}$.

In the follows I refer as micellar electrolyte an ionic surfactant used as electrolyte. The ionic surfactant is completely dissociated at low concentration, while at the critical micellar concentration in water (cmc_w), ions aggregate to form micellar structures of spherical shape. At the increasing of concentration, beyond the second critical micellar concentration (cmc_2), the shape can be changed from spherical to rod-like. Recently, also the pre-micellar critical concentration (pmcc_w) has been quantified [45]. Common ionic surfactants are CTAB, DTAB or SDS: in their micellar state they are widely used mainly in biology. The detailed experiment, making use of a micellar electrolyte in a OECT, is reported in Chapter 4. For the first time a cationic surfactant has been used as an electrolyte in organic electrochemical transistor. The electrolyte shows excellent capabilities for current modulation and it appears as a very promising tool to improve the sensing performance of EOCT.

Electrolyte gating

The principle of electrolyte gating, although still poorly exploited in electronics, is known since almost 60 years. Interestingly, the first transistor fabricated by Shockley, Bardeen and Brattain was based on electrolyte gating [46]. Electrolyte-gated transistors can be divided in two main classes: EG-OFETs and OECTs. Electrolyte-gated organic transistors consist of source and drain electrodes as well as a channel containing the organic active material (an OS or an organic conductive polymer) in contact with a gate electrode *via* an electrolyte solution (Figure 1.7). It is important to notice that the gate electrode and the transistor channel are connected ionically but isolated electronically. Different designs and fabrication techniques can be used for these devices depending on the nature of the materials employed (e.g. solid *versus* liquid electrolyte).

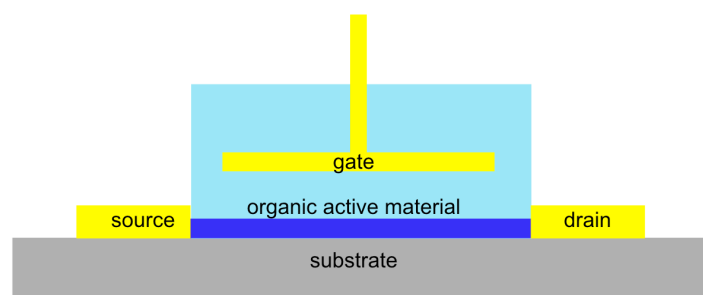


Figure 1.7 Device structure of an electrolyte gated transistors. The device includes source and drain electrodes, an organic active material and a gate electrode. The gate electrode and the organic active material film are connected ionically *via* the electrolyte.

Depending on the nature of the organic active material and the electrolyte, a similar transistor structure can be exploited for two types of devices, with a different working mechanism. If the organic active material is not electrochemically active (i.e. if the organic active material is not involved in electron transfer reactions being paralleled by electrolyte ions redistribution to ensure electroneutrality), the application of a gate voltage induces the formation of an electrical double layer (EDL) at the electrolyte/OS interface [47]. This is the EG-OFET (Figure 1.8). To briefly illustrate the concept of EDL we remind the case of EDLs formed at electrode/electrolyte interfaces in electrochemical cells. When an electrical bias is applied between two electrodes immersed in an electrolyte, the electrolyte ions move towards electrodes driven by the electric field. Eventually, ions form a charged plane at the electrode, called the Helmholtz plane. The Helmholtz plane and the

electrode surface are oppositely charged: this is the EDL. If one of the electrodes is replaced by an OS incorporated between source and drain electrodes, the system works as a field effect transistor (FET) where the formation of the EDL is responsible for the electrostatic doping of the semiconductor. EDLs are able to accumulate a high density of charge carriers with small gate bias applied (below 1 V), because of their nanoscale thickness (of the order of a few nm).

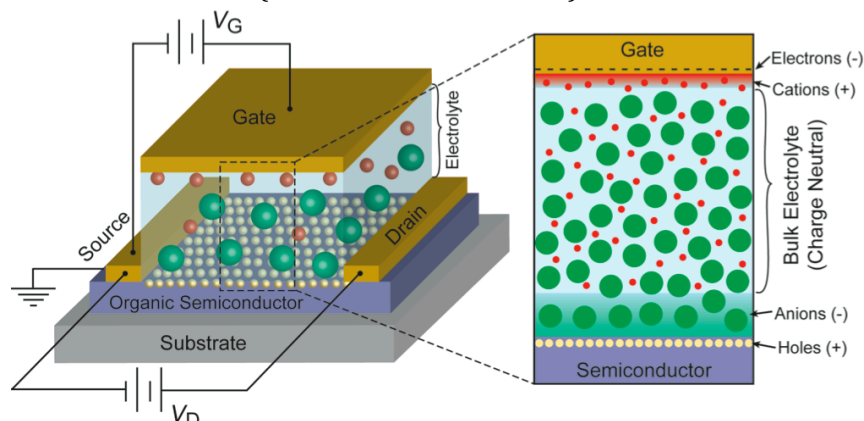


Figure 1.8 Device structure and working principle of an electrolyte-gated organic field effect transistor. The gate voltage (V_G) and the drain voltage (V_D) are applied relatively to the grounded source electrode. Applying a V_G causes ion migration within the electrolyte dielectric layer, resulting in the formation of electrical double layers (EDLs) at the gate/electrolyte and electrolyte/semiconductor interfaces. The charge-neutral electrolyte region forces nearly all of the electrostatic potential applied in the vertical direction (V_G) to be dropped across these two double-layer “capacitors”.

DOI: 10.1002/adma.200800617. Reprinted with permission from [47] © Wiley.

For this reason electrolyte gate dielectrics can be used to decrease the operating voltage (typically ranging from |20 V| to |40 V| for the commonly employed 100-300 nm-thick SiO_2 gate dielectric). In this context, the use of electrolyte dielectrics is an alternative to other approaches to decrease the OFET operating voltage, such as *high-k* [48] or ultrathin gate dielectrics [49]. For instance, EDL capacitances per unit area are in the order of $10 \mu\text{Fcm}^{-2}$ and can be as high as $500 \mu\text{Fcm}^{-2}$, whereas the typical capacitance of a 200 nm-thick SiO_2 dielectric is of the order of tens of nFcm^{-2} . The EDL approach, with gate electrolytes such as LiClO_4 solutions or ionic liquids, has permitted the fabrication of low-voltage organic transistors based on both small molecules and polymers.

A different scenario is possible if the organic active material is electrochemically active. In this case, the application of a gate bias induces a reversible redistribution of ions within the film and the electrolyte. This, together with charge injection from source and drain, results in electrochemical doping/de-doping of the transistor channel, accompanied by a change in conductivity of the organic active material. The change in conductivity depends upon the applied gate bias. This scenario describes OECTs. The organic active material in OECTs is typically a conducting polymer, whose conductivity varies upon doping/de-doping. Examples of organic active materials for OECTs are the commercially available Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) [18], polypyrroles, and polyanilines. OECTs can be operated in aqueous environment as efficient ion to electron converters (**Figure 1.9**), thus providing an interface between the worlds of biology and electronics. For this reason, OECTs open exciting opportunities for applications in biosensing, which has the potential to become a main thrust of OE and to play a pivotal role in the emerging field of organic bioelectronics [17].

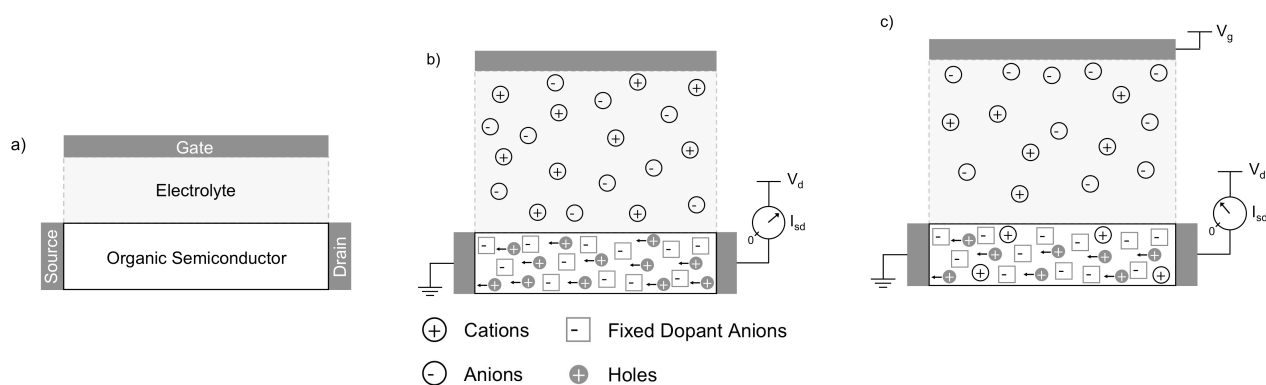


Figure 1.9 Device structure and working principle of an organic electrochemical transistor (OECT) working as ion-to-electron converter. **(a)** Scheme of an OECT labeled with appropriate naming conventions. **(b)** OECT without gate voltage applied. The current is determined by the intrinsic conductance of the organic semiconductor. **(c)** OECT with gate voltage (V_g) applied. The current is determined by the extent to which the organic semiconductor is de-doped.

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1.2. Electrolyte-gated OFETs

In OFETs (**Figure 1.10**) the OS is in contact with the source (S) and drain (D) electrodes, whereas it is isolated electronically with respect to the gate electrode (G).

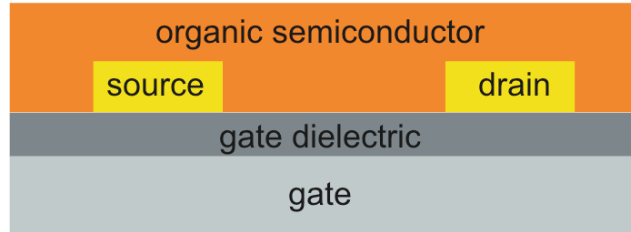


Figure 1.10 Device structure of a bottom gate, bottom contact organic field effect transistor.

The region of the OS film delimited by the S and D electrodes defines the transistor channel whose geometry is characterized by the inter-electrode distance (channel length, L) and the electrode width (W). On application of an appropriate gate-source bias (V_{gs}), charge carriers are injected from the S and D electrodes into the transistor channel, where they move under the action of a drain-source bias (V_{ds}). The current flowing between S and D (I_{ds}) is modulated by V_{gs} . OFETs can be of n- and p-type: the majority carriers are electrons (holes) in n-type (p-type) OFETs [48]. The figures of merit in OFETs are the mobility (μ), the threshold voltage (V_{th}), the I_{on}/I_{off} ratio, and the subthreshold swing (SS) [51]. The mobility ($\text{cm}^2/\text{V}\cdot\text{s}$) is the drift velocity of the charge carriers per unit of applied electric field. The threshold voltage can be calculated from the intercept of the square root of I_{ds} plotted versus V_{gs} at constant V_{ds} , in the *saturation* region of the transistor. I_{on}/I_{off} is the ratio between the maximum current (ON current) and the minimum current (OFF current) in the plot $\log(I_{ds})$ versus V_{gs} at constant V_{ds} (transfer curves). The subthreshold swing is defined as $dV_{gs}/d\log_{10}I_{ds}$ in the subthreshold region and indicates how abruptly the transistor switches on.

1.2.1. Electrolyte-Gated OFETs based on Organic Thin Films

One of the first examples of EG-OFETs (**Figure 1.11**) was based on a pentacene thin films gated by a solid electrolyte (LiClO_4 dissolved in high molecular-weight polyethylene oxide, PEO) [52].

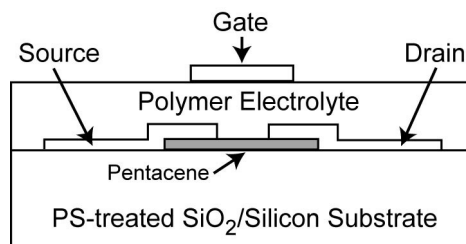


Figure 1.11 Device structure of a top contact electrolyte-gated pentacene field effect transistor. DOI:10.1063/1.1880434. Reprinted with permission from [52] © American Institute of Physics.

The specific capacitance of the gate dielectric was $5 \mu\text{F}/\text{cm}^2$. I_{ds} was modulated by four orders of magnitude applying V_{gs} lower than $|2\text{V}|$. The FET mobility was in the $10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$ range, the subthreshold swing was $180 \text{ mV}/\text{decade}$ at $V_{ds} = -1 \text{ V}$. The relatively low FET mobility was attributed to the rough dielectric surface. Successively, the same group reported of finite regions of highconductivity in n-type N,N' -dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C8) and p-

type pentacene thin film OFETs gated by electrolyte dielectrics (LiClO₄/PEO) [53]. From the transfer characteristics (I_{ds} versus V_{gs} , for a fixed V_{ds}) charge carrier densities higher than 10^{14} charge carriers/cm² were obtained for both PTCDI-C8 (**Figure 1.12**) and pentacene (**Figure 1.13**) OFETs. Shimotani *et al.* observed a similar behavior of the conductivity in single crystal FETs (see Section 2.2) [54].

A limitation of EG-OFETs is their low switching speed, originated by the low ion mobility. To improve the switching speed of EG-OFETs, Lee *et al.* explored the use of an *ion gel electrolyte* dielectric having both large capacitance and high ion mobility (resulting in significantly shorter polarization times) [55]. The ion gel dielectric consisted of a combination of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, (BMIM)(PF₆), with the triblock copolymer (poly(styrene-*block*-ethylene oxide-*block*-styrene, SOS). Top-gated poly(3-hexylthiophene) (P3HT) FETs employing this ion gel showed larger I_{ds} at considerably reduced driving voltages in comparison with SiO₂-gated FETs. The hole FET mobility of P3HT was 0.6 cm²/V·s. The EG-OFETs response time was in the order of 1 ms when switching from OFF to ON at 100 Hz. In a successive study [56], ion gels based on SOS and three different imidazolium ionic liquids, were used as gate dielectrics in P3HT EG-FETs.

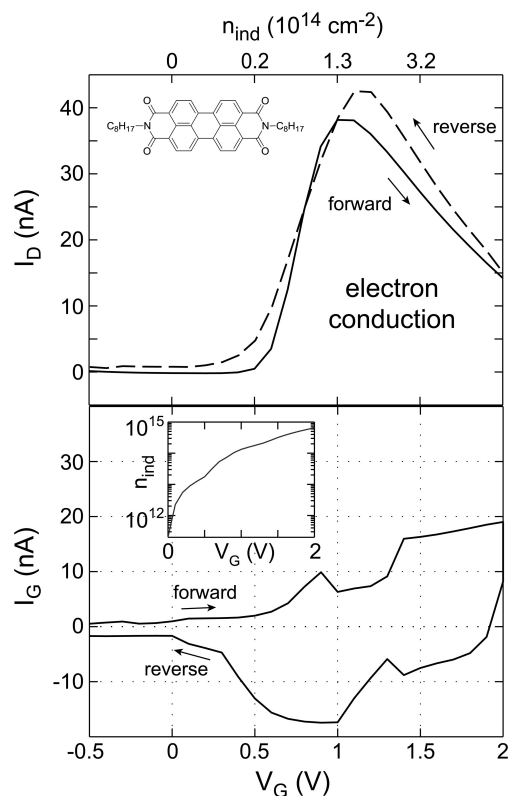


Figure 1.12

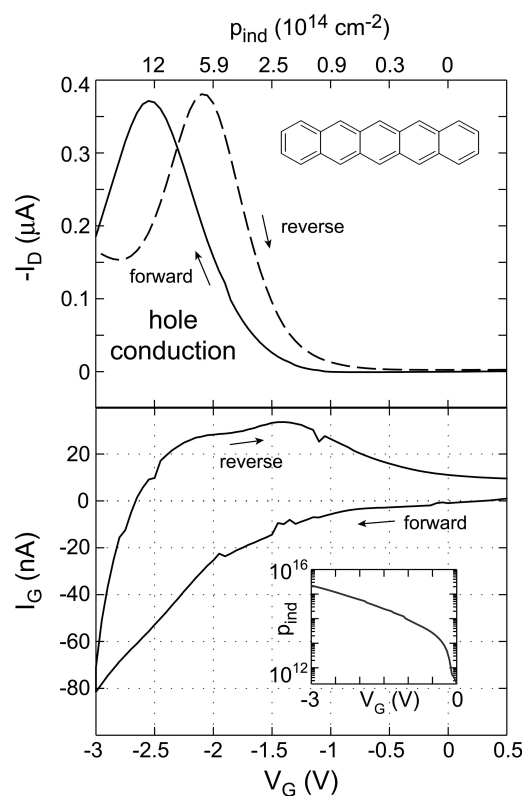


Figure 1.13

Figure 1.12 Source-drain current (I_D , top panel) and source-gate current (I_G , bottom panel) versus gate voltage (V_G) measured simultaneously for a PTCDI-C8 OFET gated by a polymer electrolyte at 295 K. The drain-source voltage was +0.5 V and the V_G sweep rate was 40 mV/s. Estimated induced electron densities (n_{ind}) were obtained by integrating I_G versus time for the forward sweep. Inset in the lower panel shows the evolution of n_{ind} (charges/cm²) with V_G for the forward sweep.

DOI: 10.1021/ja051579+. Reprinted with permission from [53]© American Chemical Society.

Figure 1.13 Source-drain current (I_D , top panel) and source-gate current (I_G , bottom panel) measured simultaneously for a pentacene OFET gated by a polymer electrolyte at 310 K. The drain-source voltage was -0.5 V. V_G was swept at 50 mV/s. Estimated induced hole densities (p_{ind}) were obtained by integrating I_G versus time for the forward sweep. Inset in the lower panel shows the evolution of p_{ind} (charges/cm²) with V_G for the forward sweep.

DOI: 10.1021/ja051579+. Reprinted with permission from [53]© American Chemical Society.

The ionic liquids employed were: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ((EMIM) (TFSI)), (BMIM) (PF₆) and 1-ethyl-3-methylimidazolium n-octylsulfate ((EMIM) (octOSO₃)), whose room temperature ionic conductivities are 9.4×10^{-3} , 1.6×10^{-3} and 6.6×10^{-4} S cm⁻¹ respectively. The ion gels showed specific capacitances between 38 and 43 $\mu\text{F cm}^{-2}$ at 10 Hz. All the dielectrics resulted in EG-OFETs where the mobility was close to 1 cm²/Vs. The high specific capacitance of (EMIM) (TFSI)-based ion gels resulted in higher $I_{\text{ON}}/I_{\text{OFF}}$ ratios and shorter response times. The high conductivity of (EMIM) (TFSI) was also used to achieve operating frequencies as high as 1 kHz, a remarkably high value for EG-OFETs. Aerosol printing was used to deposit ion gel dielectrics incorporated in fully solution processable EG-OFETs fabricated on polyimide substrates [57]. These EG-OFETs employed Au S and D electrodes processed from soluble nanoparticles, a P3HT transistor channel deposited by spin coating, an aerosol-printed poly(styrene-block-methylmethacrylate-block-styrene)/(EMIM) (TFSI) gel gate dielectric and a spin coated PEDOT:PSS top gate. These EGOFETs showed high mobility, high $I_{\text{ON}}/I_{\text{OFF}}$ ratios and promising operational and environmental stability. Electrolyte dielectrics with high capacitance and good surface smoothness were obtained mixing the block copolymer SOS with LiClO₄ [58]. The capacitance was shown to depend upon Li concentration (O/Li) in SOS/LiClO₄. The capacitance was 4.5 $\mu\text{F/cm}^2$ at 10 Hz and 1.5 $\mu\text{F/cm}^2$ at 1000 Hz with Li concentration (O/Li) between 3:1 and 48:1.

1.2.2. EG-OFETs Based on Organic Single Crystals

Electrolyte gating has also been achieved in OFETs based on organic single crystals. For rubrene and tetracene single crystal EG-OFETs, the crucial fabrication step was the introduction of an insulating buffer layer (about 50 Å-thick) between the organic single crystal and the LiClO₄/PEO gate dielectric (**Figure 1.14**), to protect the single crystal from solvents used during the solution processing of the gate dielectric [59].

Rubrene FETs displayed I_{ds} modulation of approximately five orders of magnitude for a range of V_{gs} of only 3 V. Tetracene FETs did not perform as well as rubrene transistors: the FET mobility was about 2×10^{-3} cm²/V·s for rubrene and 5×10^{-5} cm²/V·s for tetracene and the turn-ON voltage was about $V_{gs} = 0.4$ V for rubrene and about $V_{gs} = -1.6$ V for tetracene (the turn-on voltage V_{ON} is determined as the V_g at which the current abruptly increases in the semilog plot of the transfer characteristics). The difference was ascribed to a higher degree of interfacial trapping in tetracene FETs.

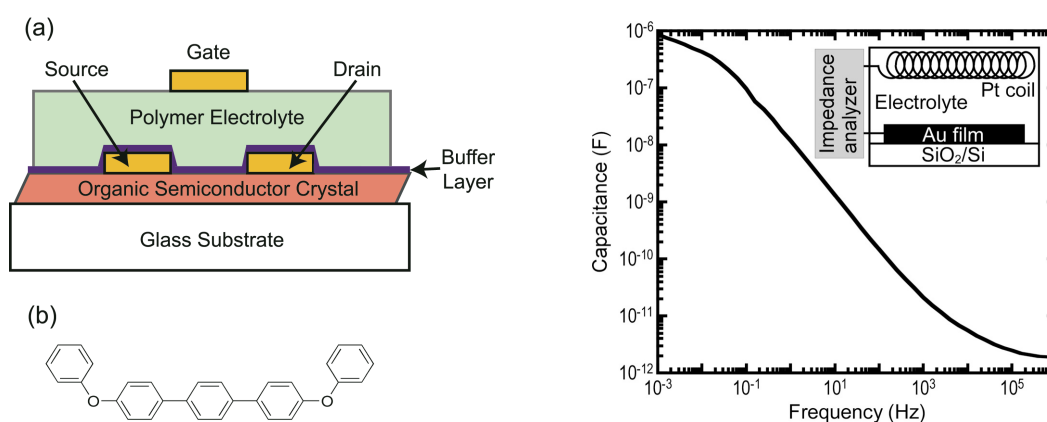


Figure 1.14 (left) (a) Device structure of a polymer gated organic single crystal transistor. **(b)** Molecular structure of the buffer layer material, 4,4'- diphenoxy-(1,1';4',1'') terphenyl (DPTP). DOI: 10.1063/1.2204846. Reprinted with permission from [59]© American Institute of Physics.

Figure 1.15 (right) Capacitance of the LiClO₄ /PEO solution plotted against ac voltage frequency obtained by electrochemical impedance measurements. The inset shows the experimental configuration used. DOI: 10.1063/1.2387884. Reprinted with permission from [54]. © American Institute of Physics.

Shimotani *et al.* reported on comparative studies of electrolyte and SiO₂-gated FETs of rubrene single crystals [54]. The capacitance of PEO/LiClO₄, measured by electrochemical impedance (**Figure 1.15**), was 15 μF/cm² at 1 mHz, i.e. about two orders of magnitude larger than that associated to 100 nm-thick SiO₂. The charge accumulated at the electrolyte/ and SiO₂/rubrene interfaces were compared, measuring I_{ds} in the range -1.2 V < V_{gs} < 0 V for the electrolyte-gated FETs and -50 V < V_{gs} < 50 V for the SiO₂-gated FETs. Plots of I_{ds} versus the number of carriers per molecule (q) showed that the maximum q in electrolyte-gated FETs was 27 times larger than in SiO₂-gated FETs. For the same value of q , I_{ds} in electrolyte-gated FET was lower than in SiO₂-gated FETs. This clearly indicated that mobility in electrolyte-gated FETs was lower (**Figure 1.16**).

Takeya *et al.* reported on a rubrene single crystal dual-gate FET using SiO₂ and a polymer gel electrolyte as the gate dielectrics [60]. The electrolyte was placed on top of the single crystal, whose opposite side was gently attached to a SiO₂ substrate. The electrolyte was PEO (molecular weight 50,000)/LiClO₄ mixed with N-methyl-2-pyrrolidone, which increases the viscosity of the solution. With SiO₂ the FET mobility was between 0.5 and 0.9 cm²/Vs whereas with the electrolyte the mobility was between 0.1 and 0.01 cm²/Vs. This difference was attributed to the different quality of the two OS/gate dielectric interfaces.

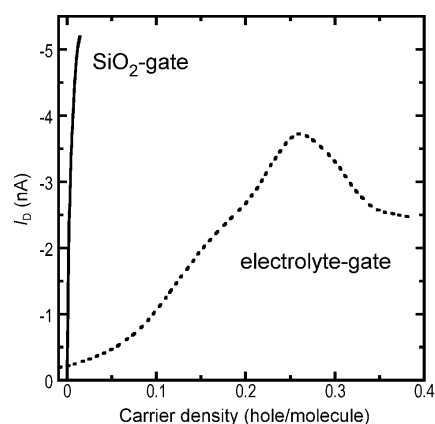


Figure 1.16 Drain current (I_D) of SiO₂ gated-OFET (solid line) and electrolyte gated OFET (dashed line) for a rubrene organic single crystal, plotted as a function of the accumulated hole density.

DOI: 10.1063/1.2387884. Reprinted with permission from [54]. © American Institute of Physics.

1.2.3. How do Electrolyte-Gated OFETs work?

A number of studies on the working mechanism of electrolyte-gated transistors have been reported. Actually, current modulation in electrolyte-gated OFETs can be explained by two possible mechanisms: *electrostatic* and *electrochemical* (**Figure 1.17**), as discussed in [61]. Current modulation in EG-OFETs was studied employing two different polymer electrolytes and three different polymer semiconductors. PEO/LiClO₄ and PEO/LiTFSI were employed as the electrolyte dielectrics. Solution processed P3HT, poly(3,3'-didodecylquaterthiophene) (PQT-12) and poly(9,9'-dioctylfluorene-co-bithiophene) (F8T2) were used as the semiconductors. These EG-OFETs showed high charge carrier density ($2 \cdot 10^{14}$ holes/cm²), and high hole mobility (up to 3.4 cm²/V·s for P3HT). At the same time small I_{ds} hysteresis were observed for both electrolytes, suggesting an electrostatic doping mechanism. An electrochemical doping mechanism would have led to a greater hysteresis for LiTFSI-gated transistors, making use of larger anions.

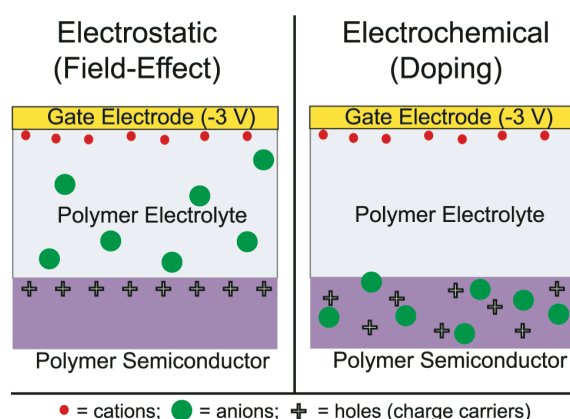


Figure 1.17 Cross-sections of polymer electrolyte-gated polymer semiconductor transistors showing the difference between electrostatic (left) and electrochemical (right) doping.

DOI: 10.1021/ja0708767. Reprinted with permission from [61] ©American Chemical Society.

Hamedi *et al.* [62] reported on an electrolyte-gated transistor based on P3HT for e-textile applications (**Figure 1.18**). A viscous mixture of ionic liquids, specifically 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) ((bmim)(Tf₂N)) and poly(1-vinyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) (poly(ViEtIm)(Tf₂N)), was used as the electrolyte dielectric. Time resolved electrical measurements revealed that the transistor channel forms in two steps: a first step

attributable to the formation of EDLs responsible for the electrostatic doping, followed by a second step attributable to the electrochemical doping. This study points to the possible co-existence of the two doping mechanisms, electrostatic and electrochemical, in EG transistors. Herlogsson *et al.* reported on low-voltage ring oscillators based on polyelectrolyte-gated transistors [63]. In this polyanionic electrolyte, the anions are effectively non mobile and could not enter the semiconductor, a novel polythiophene derivative, P(TOTTT16) [64]. These results would support the electrostatic doping mechanism. The effect of ion currents on poly(styrene-sulfonic acid) (PSS:H) gated P3HT OFETs was studied by means of a series of measurements performed at different relative humidity (RH) [65].

The drain current resulted from an electronic contribution from I_{ds} and an ionic contribution from the gate-drain current, i.e. the current crossing the electrolyte layer between the gate and the drain. Data collected at different RH values showed that, at low V_{gs} , RH strongly influences I_{ds} whereas, at high V_{gs} , I_{ds} is almost independent on RH. The electronic contribution is relatively small (i.e. the ionic contribution is predominant) at low V_{gs} , whereas it is predominant at high V_{gs} , at low RH values. Above 50% RH, the ionic and the electronic contribution are comparable. Fundamental studies on the polarization mechanism of PSS:H were reported in [66] in view of the relevance of this polyelectrolyte in electrolyte-gated transistors [67, Said, #832].

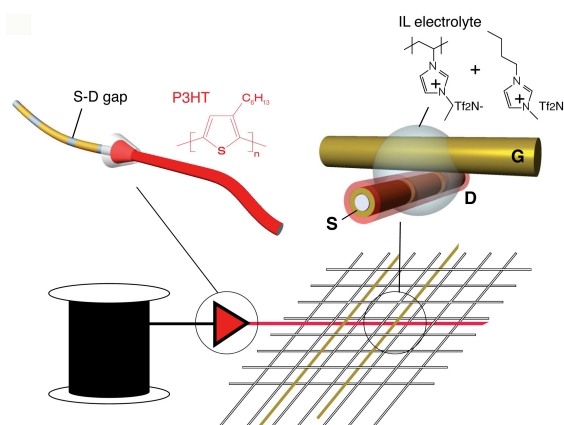


Figure 1.18 Electrolyte-gated organic transistor on weaving fibers: the semiconductor polymer P3HT was coated on the top of the fiber (top left); the transistor was fabricated at a fiber junction (top right), the source (S) and drain (D) contacts being formed along one fiber and the gate (G) at the junction with a second fiber in correspondence of the transistor channel in the first fiber.
DOI: 10.1002/adma.200802681. Reprinted with permission from [65] © Wiley.

Capacitors made of a thin PSS:H layer (80 nm), sandwiched between two Ti electrodes, were characterized with impedance spectroscopy at various RH levels (10% to 80% RH) at room temperature. RH affects the mobility and the amount of dissociated protons in the electrolyte. At high frequencies ($f > 120$ kHz, 10% RH) the capacitive behavior is attributed to the dipolar relaxation of the polyelectrolyte; at intermediate frequencies ($800 \text{ Hz} < f < 120 \text{ kHz}$, 10% RH) to ionic relaxation; at low frequencies ($f < 800 \text{ Hz}$, 10% RH) to the formation of EDLs at polyelectrolyte/metal electrode interface. Importantly, the formation of the EDL with a capacitance of $10 \mu\text{F}/\text{cm}^2$ at 1 MHz, observed between 60% and 80% RH, demonstrates the potential of using such an electrolyte dielectric to obtain OFETs that operate at 1 MHz at a driving voltage as low as 1 V.

1.3. Organic Electrochemical Transistors (OECTs)

OECTs can be fabricated using high throughput processes, such as optical lithography and screen printing, which make them viable for mass production. The working principle of OECTs has been already described in 1.1. It is worth to notice that there are two regimes of operation for OECTs: the non-Faradaic regime (capacitive) and the Faradaic regime. In the non-Faradaic regime, the application of V_{gs} induces only a transient current in the electrolyte. In the Faradaic regime, a steady-state current due to reduction/oxidation (redox) reactions is sustained in the electrolyte. As a consequence, the OECT gate-source current (I_{gs}), which results from capacitive effects and/or from redox reactions at the gate electrode, is a fingerprint of the OECT regime of operation. Examples of Faradaic regime of operation are glucose sensors based on OECTs, employing a PEDOT:PSS transistor channel, PEDOT:PSS source and drain electrodes, and a Pt gate electrode immersed in phosphate buffer saline solution (PBS). In the first reported glucose sensor based on OECTs [68], the enzyme glucose oxidase (GOx) was added (*free-floating*) to detect the presence of glucose in the electrolyte. The drain current showed a weak modulation upon application of a gate bias (at $V_{ds} = 0.2$ V), which remained unchanged after addition of the enzyme GOx. Addition of glucose to the PBS caused a dramatic increase in current modulation. The sensor response was shown to depend linearly on gate voltage for glucose concentrations between 0.1 and 1 mM. The sensor response to glucose is due to an electrochemical effect. Oxidation of glucose by GO_x produces H_2O_2 , which can be oxidized to O_2 at the Pt electrode. This reaction is accompanied by de-doping of the PEDOT:PSS channel caused by an increase of the electrolyte potential [50, 69]. Successively, the effect of the OECT device geometry on sensing of H_2O_2 , i.e. the species detected during glucose sensing, was investigated [70]. The response of PEDOT:PSS OECTs to peroxide concentrations between 10^{-6} M and 1 M was evaluated for devices with different channel area (A_{ch})/gate area (A_g) ratios, fabricated with a new patterning approach (**Figure 1.19**). Devices with small gate surface areas showed lower background signal and higher sensitivity. The minimum and maximum detectable analyte concentration appeared to be independent on A_{ch}/A_g .

Lin *et al.* investigated the device physics of OECTs based on a redox active and ion-permeable conjugated polymer [71]. The two main goals of the work were i) detailing the gate electrode processes and their influence on the transfer characteristics of the OECTs and ii) demonstrating conductivity modulation associated to non-Faradaic gate electrode processes. The OECT used in this work consisted of a 200 nm thick cationically functionalized polyacetylene channel, sandwiched between two Au electrodes. The upper gold electrode was thin enough (10-15 nm) for the polyacetylene layer to be ion-permeable.

The electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile (CH_3CN); Pt wires of variable areas were used as gate electrodes. A reference Ag/Ag^+ electrode was incorporated into the device. The channel active material potential and gate electrode potential were measured with respect to the reference electrode. Conductivity modulation of the OECT channel was achieved through Faradaic processes taking place at the gate electrode (electrolyte reduction) or through the non-Faradaic (capacitive) charging of the EDL at the gate/electrolyte interface. A study on the effect of the cation type (H^+ , K^+ , Na^+ , Ca^{2+} and Al^{3+}) and concentration as well as of gate electrode material ($Ag/AgCl$, Pt, Au) on the response of PEDOT:PSS OECTs was reported by Lin *et al.* (**Figure 1.20**) [72]. With an $Ag/AgCl$ gate electrode, they observed similar OECT response with the different cations. The increase of the cation concentration induced a gate voltage shift in transfer curves towards lower voltages with a logarithmic dependence on the concentration. Different sensitivities to cations concentration were found, depending on the Faradaic ($Ag/AgCl$ electrode) or capacitive (or non-Faradaic, Pt and Au electrodes) device operation.

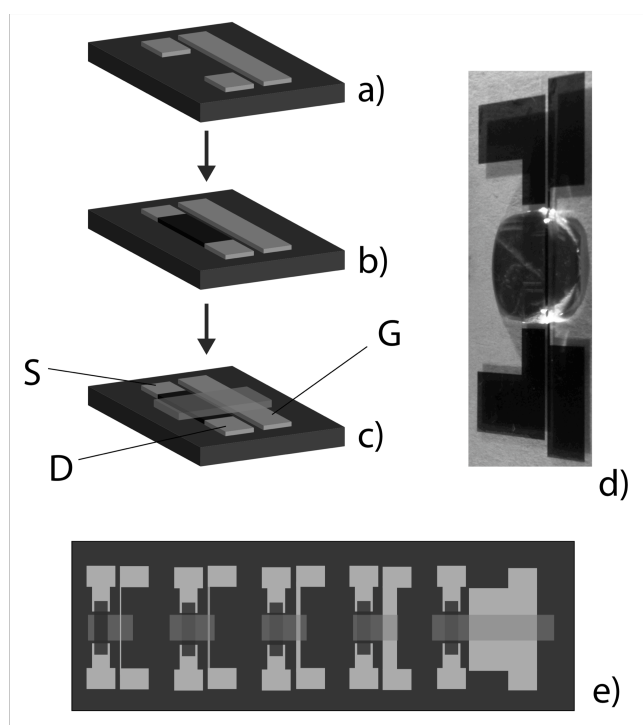


Figure 1.19 (a–c) Sequence of the patterning process, (d) optical image of a device with $A_{ch}/A_g = 40$, and (e) layout of organic electrochemical transistors (OECTs) with $A_{ch}/A_g = 40, 10, 5, 1$ and 0.2 (from left to right) on the same substrate. The patterning process involves the definition of Pt source (S), drain (D), and gate (G) electrodes, a PEDOT:PSS channel, and a hydrophobic self assembled monolayer which confines the electrolyte over the channel and gate electrode.

DOI: 10.1002/adma.200902329. Reprinted with permission from [70] © Wiley.

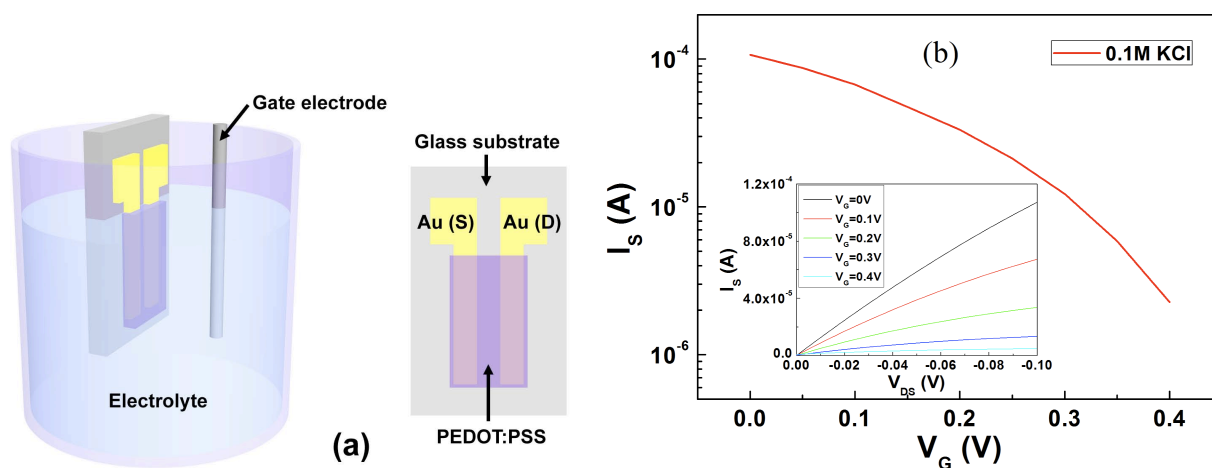


Figure 1.20 (a) PEDOT:PSS organic electrochemical transistor (OECT) device structure. (b) Transfer characteristics of the OECT measured in 0.1 M KCl solution. A commercial Ag/AgCl (saturated KCl) electrode was used as the gate electrode. Inset: OECT output characteristics measured in 0.1 M KCl. DOI: 10.1021/am100154e. Reprinted with permission from [72] © American Chemical Society.

The effect of the gate electrode material on the response of OECTs operating in a halide electrolyte was investigated by Tarabella *et al.* in [73]. OECT making use of Ag gate electrodes (Ag OECTs) lead to larger current modulation compared to OECTs making use of Pt gate electrodes (Pt OECTs). The results were explained considering the different OECT regimes of operation that characterize Ag and Pt OECTs: Faradaic (for Ag OECT) and non-Faradaic (for Pt OECT). Because the electrolyte solution potential (V_{sol}) determines the OECT current modulation, the different way the materials affect V_{sol}

explains the origin of these different behaviors: under the non Faradaic regime $V_{sol} < V_{gs}$, due to the EDL formed at the gate electrolyte interface, whereas $V_{sol} \approx V_{gs}$ under Faradaic mode, where no potential drop occurs at the interface.

PEDOT:PSS based OECTs have been integrated with a microfluidic channels for the development of a multi-analyte sensor [74]. The simultaneous detection of glucose and lactate was demonstrated thanks to the microfluidic layout, yielding the possibility to transport liquids into separate reservoirs.

Figure 1.21 shows the sensor layout consisting of one input reservoir and four separated measurement reservoirs, each containing a planar OECT. The microfluidic channels, where the aqueous analytes flow without the application of external pressures, are defined by a patterning technique consisting of sequential deposition of a tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (FOTS) layer, photolithography, oxygen plasma etching, and lift off. The OECTs were fabricated by patterning a PEDOT:PSS channel by using the parylene lift-off technique [75]. The sensors were exposed to different solutions (PBS, with glucose or lactate) and showed good sensing properties as well as good selectivity.

A new strategy for glucose sensing was demonstrated using a room temperature ionic liquid (RTIL) as an integral part of a sensor based on a planar OECT entirely made of PEDOT:PSS [76]. A hydrophilic virtual well, based on a patterned self-assembled monolayer of FOTS, was used to confine the electrolyte/analyte solution and to have it in contact with both the transistor channel and the gate electrode. The RTIL (in this case the hydrophilic triisobutyl(methyl)-phosphonium tosylate) including the enzyme glucose oxidase (GOx) and the redox mediator bis (n5-cyclopentadienyl)iron (ferrocene, Fc) was placed on the virtual well. A glucose solution in PBS was successively added. The working mechanism of the OECT was explained as follows: glucose is oxidized in solution whereas the GOx enzyme is reduced and cycles back with the help of the redox couple Fc/Fc^+ , which shuttles electrons to the gate electrode.

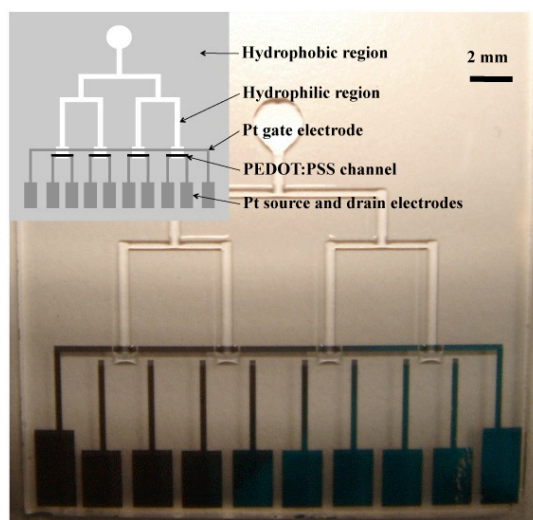


Figure 1.21 Microfluidic sensor layout, including four organic electrochemical transistors, with a drop of aqueous analyte solution spread across the microfluidic system.

DOI: 10.1039/b811606g. Reprinted with permission from [74] © Royal Society of Chemistry.

This OECT permitted to detect glucose concentrations in the range 10^{-7} M to 10^{-2} M. To understand the working mechanism of OECTs it is of paramount importance to determine to which extent the electrolyte ions enter the polymer channel. To prove that the conductivity of the OECT polymer channel is related to the ionic flux in and out the polymer, electrical measurements were performed simultaneously to grazing incidence X-ray fluorescence [44]. The latter permitted to detect the presence of metal ions into a polyaniline (PANI) film.

The device was constituted by a transistor channel made of a PANI film deposited onto an insulating support, a silver wire gate electrode and a gel of PEO/RbCl as the electrolyte (**Figure 1.22**). X-ray fluorescence spectra were acquired during device operation. The conductivity of the polymer was found to depend on the ionic flux between PANI and the electrolyte: under a negative V_{gs} bias, Rb^+ ions enter the polymer thin film, reducing the PANI to its insulating state (OECT OFF state). Under a positive V_{gs} bias, ions leave the polymer film, flowing back into the electrolyte: PANI undergoes an oxidation process and its conductivity increases (OECT ON state). The highest X-ray fluorescence signal of Rb^+ was found in correspondence of the lowest polymer conductivity, in agreement with the proposed interpretation.

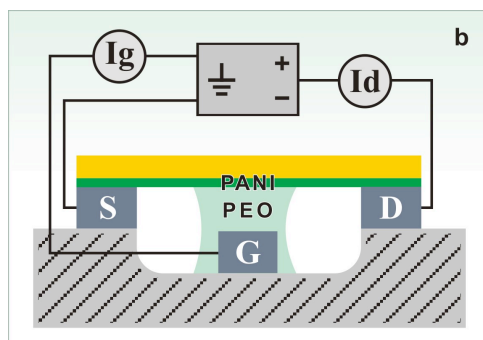


Figure 1.22 Device structure of the organic electrochemical transistor used in [44]. DOI: 10.1021/am900464k. Reprinted with permission from [44] © American Chemical Society.

OECTs can also be applied in e-textiles [77]. Wire Electrochemical Transistors (WECTs) were fabricated by using PEDOT:PSS coated (**Figure 1.23**) polyamide monofilaments fibers (100 μm in diameter). WECTs were realized adding a solid polymer electrolyte at the junction of two suspended PEDOT:PSS coated fibers. Surface energy drives the electrolyte coverage of two coated fibers at their junction, where it covers both fibers. Since OECT operation does not depend on the shape of the electrolyte/polymer interface, WECTs can work as well as planar OECTs, despite the completely different layout. WECTs show (i) operating voltage insensitive on the channel-gate distance, (ii) low-voltage operation, and (iii) no sensitivity to vertical/horizontal displacement of the fibers. Based on the crossed fiber geometry, two standard electronic logic circuits were realized: an inverter and a multiplexer.

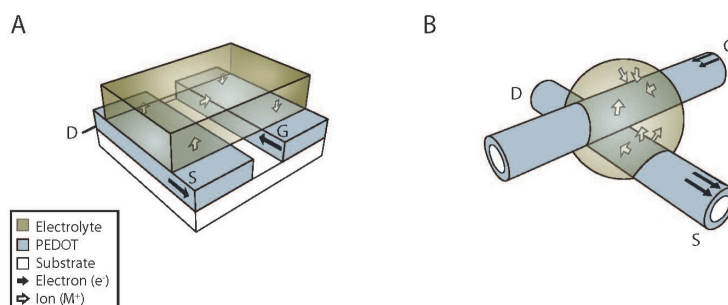


Figure 1.23 Device structure of a planar (left) and wire (right) PEDOT:PSS electrochemical transistor [77]. DOI:10.1038/nmat1884. Reprinted with permission from [77] © MacMillan Publisher Ltd.

Starting from models originally developed by Bernardis *et al.* [50, 69], an important contribution has been given in understanding the role played by geometrical and materials parameters in establishing

OECT performance [78]. Simulations of OECT modulation with three different Ach/Ag ratios (0.01, 1, and 100) were carried out. These simulations showed that for non-Faradaic operation, a maximum OECT response is achieved by using gate electrodes with surface areas much larger than channel surface areas. For OECT working in Faradaic regime, the opposite is true, in agreement with experimental data reported in [70].

1.4. Electrochemically doped organic light emitting transistors

Light emitting devices based on OSs can also benefit from combined electronic and ionic transport. Electrochemical doping, representing an interesting approach to obtain ohmic contacts (i.e. contacts where the injection efficiency is unity) at metal/semiconductor interfaces [79], has been indeed employed in light emitting electrochemical cells (LEECs) [80, Pei, #837]. LEECs are devices where electroluminescence can be generated from OSs at relatively low operating voltages (about 3V). LEECs are commonly based on an organic light emitting polymer (LEP), a salt (source of cations and anions), and an ion-conducting agent, embedded in between two electrodes. The working principle of LEECs is such that when an electrical bias is applied to the device, mobile ions redistribute so that EDLs form at the metal/LEP interfaces, lowering the h^+ and e^- injection barriers. Light is generated by the radiative recombination of the e^- - h^+ pairs (excitons) in the organic layer. Different LEEC architectures have been demonstrated, different classes of materials have been investigated, and different models have been proposed to describe their underlying physics. Interestingly, Sariciftci *et al.* [81] extended the LEEC approach to three-electrode light emitting devices, to demonstrate the first organic electrochemical light emitting transistors (**Figure 1.24**).

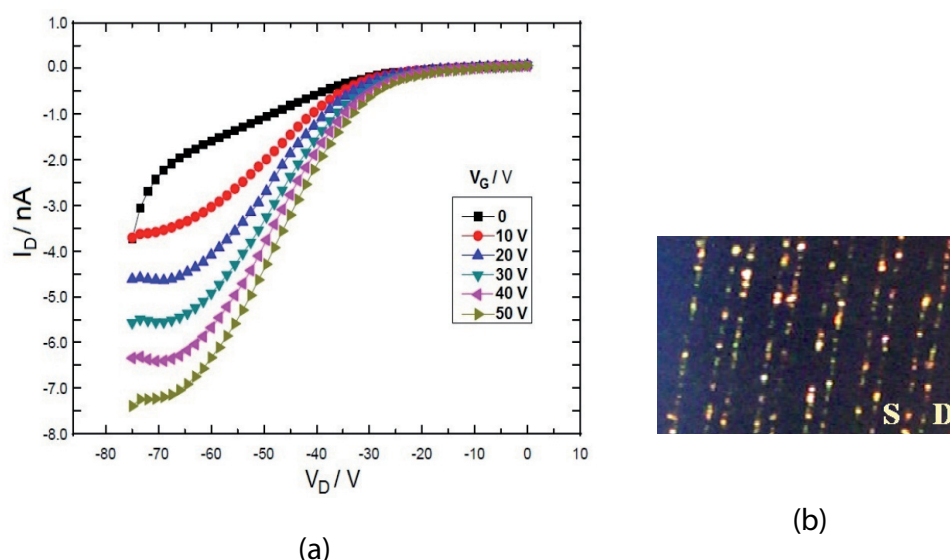


Figure 1.24 (a) Output characteristics of an organic electrochemical light emitting transistor. Reprinted with permission from [81]. DOI:10.1063/1.3464558 © American Institute of Physics. (b) Optical image of an operating organic electrochemical light emitting transistor. DOI:10.1063/1.3464558. Reprinted with permission from [81] © American Institute of Physics.

In principle, compared to two-electrode devices such as LEECs, the three-electrode configuration could help the balance of the e^- and h^+ mobility, through the application of a suitable V_{gs} . This is relevant to achieve a *centered* emission zone in the transistor channel, far from metal electrodes that induce the quenching of the light emission. Previously, electrochemical doping had been applied to transistors based on the phenyl-substituted poly(para-phenylene vinylene) copolymer Superyellow; in

these devices no e- injection was detected [82]. Exclusive p-type conduction was also observed after the application of electrochemical interface doping, a modified version of electrochemical doping, to tetracene-light emitting field effect transistors [83]. Besides electrochemically doped light emitting transistors, we consider that an extremely interesting opportunity to explore electroluminescence generated by OSs at high charge carrier density and low operating voltages might be offered by electrolyte-gated light emitting field effect transistors.

1.5. Organic bioelectronics

Biocompatibility and possibility to operate in an aqueous environment with a number of organic conducting polymers offer the opportunity to interface OECTS based on PEDOT:PSS with biological systems. By exploiting the unique properties of conducting polymers, such as electrochemical switching and combined electronic/ionic transport, it is possible to transduce biological signals into electrical signals and vice versa. Polymers can be also used as platforms where cells can adhere and proliferate in a controlled manner. For these reasons, organic conducting polymers are being investigated in a variety of bioelectronics applications, such as biosensors as well as lab-on-a-chip systems. OECTs have been successfully applied as biosensors for the detection of glucose [68, 84], DNA [85, 86], Cells [87, 88], immunosensor [89], enzymes [74] and neurotransmitters [90]. In the following the most advanced results published in the recent years are reported. A recent review reports useful Tables with a summary of the OFET and OECT application as chemical and biological sensors [21].

1.5.1. Glucose sensing

The application of OECT in glucose sensing has been already reported previously, in regard to the faradaic/non-faradaic discussion of the regime of operation of OECT. The first work from Malliaras' group [68] inspired also the successive works, also regarding the modeling of OECTs developed by Bernards [50], which many papers referred to in the successive years [70, 84].

1.5.2. DNA sensors

The first OECT based on PEDOT, used as a label-free DNA sensor, has been reported by Krishnamoorthy in 2004 [85]: the device was able to detect the complementary target DNA in PBS solution down to 8×10^{-8} g/ml. The sensing mechanism is based on the immobilization of ss-DNA probe (single strand) on the PEDOT during the polymerization: the hybridization of DNA causes the modification of PEDOT structure chains that induces the variation in conductivity.

Lin *et al.* realized [86] a flexible microfluidic device able to detect complementary DNA targets at concentration down to 1nM. Interestingly, the transfer characteristics of the transistor are almost the same independently on the bending state. The detection limit has been improved up to 10pm upon application of a pulsed bias to the gate electrode that enhanced the DNA hybridization.

1.5.3. Cells-based biosensor

The control of the adhesion and density of stem cells (c17.2 cell line) on PEDOT:p-toluenesulfonate (tosylate) films has been achieved through the modulation of the PEDOT:tosylate oxidation state [91]. Adhesion is an essential event for cells since the seeding density is regulated by the adhesive properties of the substrate. PEDOT:tosylate films were patterned into two equally sized electrodes. The application of a potential difference between these electrodes induced an electrochemical reaction: the negatively (positively) biased electrode is reduced (oxidized) to the neutral (fully oxidized) state. Water contact angles, measured along the reduced and oxidized film surfaces were 30° and 58° , respectively. The origin of the electronic control of the wettability of PEDOT:tosylate surfaces was attributed to a change in the binding characteristics between tosylate and PEDOT at the surface. Experiments performed in with c17.2 neural stem cells revealed that oxidized (hydrophilic) PEDOT:tosylate surfaces increased cell adhesion compared to reduced PEDOT:tosylate surfaces. The origin of the wettability switching in electrochemically active polymers for applications in cell biology and medicine was further investigated [92]. Polypyrrole surface microstructures, including pillar and

mesh-like patterns, were realized on PEDOT:PSS films by photolithography. The microstructured surfaces were electrochemically switched from dewetting to wetting (water contact angle from 129° to 44°). This switching was originated from surface topography and surface tension effects, influenced by the oxidation state of the polypyrrole. Electronic control on the density of (Madin-Darby canine kidney) epithelial cells on PEDOT:tosylate was demonstrated using an OECT employing a channel of PEDOT:tosylate and an aqueous NaCl electrolyte [93]. V_{ds} and V_{gs} were used to control the degree of PEDOT:tosylate reduction along the transistor channel. The electrochromism of PEDOT:tosylate permitted to visually monitor the change of electrochemical state (reduced or oxidized) along the OECT channel (**Figure 1.25**) [93].

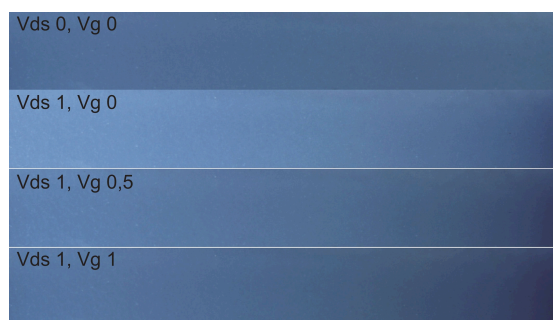


Figure 1.25 Electrochromic gradient along the PEDOT:Tosylate organic electrochemical transistor channel corresponding to different electrical bias applied.

DOI: 10.1002/adma.200901191. Reprinted with permission from [93] © Wiley.

Fluorescence microscopy revealed that the cell density decreased moving towards the more oxidized region of PEDOT:tosylate. A rather different result was obtained by Wan *et al.*, who investigated the possibility to control the density along a PEDOT:tosylate surface gradient of two cell lines, representative models of normal and cancerous cells [87]. Cell adhesion was mediated by the adhesion protein fibronectin. By applying an electrical bias at the opposite sides of an indium tin oxide (ITO) film on glass substrate (**Figure 1.26**), where a PEDOT:tosylate film had been previously deposited, a redox gradient was established within the PEDOT:tosylate stripe. The adhesion of normal and cancerous cell lines were tested on this type of surface. Images acquired by fluorescence microscopy revealed that the density of both normal and cancerous cells was higher towards the oxidized side of the PEDOT:tosylate stripe, despite the higher concentration of adsorbed fibronectin on the reduced side.

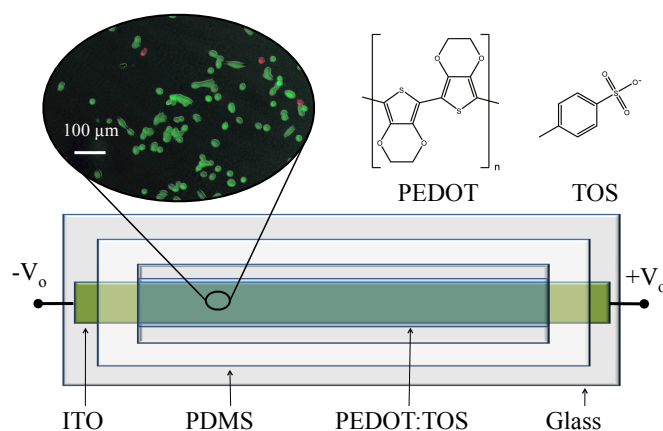


Figure 1.26 Device structure employed in [87]: ITO on glass/PEDOT:Tosylate and PDMS well as reservoir containing the cell growth medium. The inset shows the living (uncircled) and dead (circled) cells after the live/dead assay. DOI: 10.1039/b911130a. Reprinted with permission from [87] © Royal Society of Chemistry.

Another example of organic bioelectronic device based on organic conducting polymers is an electrophoretic ion pump, which was used to electronically control Ca^{2+} delivery [94]. This pump exploits the combined ionic/electronic transport properties of PEDOT:PSS to translate electronic signals into ion fluxes and it acts as an actuator to pump ions (K^+ , Ca^{2+}) from one electrolyte (AB in **Figure 1.27**) to another (CD). The device has four PEDOT:PSS electrodes (A,B,C and D); the bridge between B and C is a PEDOT:PSS over-oxidized area that permits ionic conduction (not electronic). The working principle of the pump is the following: V_{BC} drives the ion transport whereas V_{AB} and V_{CD} regenerate the B and C electrodes. When V_{BC} is applied, the final result is a net flux of ions from the reservoir electrolyte AB to the target electrolyte CD. The pump was used to demonstrate the controlled delivery of Ca^{2+} to (HCN-2) neuronal cells.

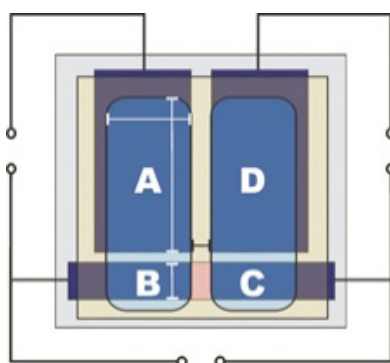


Figure 1.27 Structure of the ion-pump discussed in [95] with indicated the electrodes (A,B,C,D), the reservoirs (AB and CD), and the bias applied (V_{AB} , V_{CD} and V_{BC}).

DOI:10.1038/nmat1963. Reprinted with permission from [95] © MacMillan Publisher Ltd.

Organic conducting polymers were also incorporated in biomedical devices for delivery of neurotransmitters *in-vitro* and *in-vivo* [95]. Three different neurotransmitters, glutamate (Glu), aspartate (Asp), and amino butyric acid (GABA) were tested, at first using a planar device geometry. The source electrolyte was filled with the testing neurotransmitter, which was transported by electrophoresis from the anode to the cathode (**Figure 1.28a**) through an over oxidized channel, to be finally delivered into the target electrolyte. By measuring the evolution of the neurotransmitter concentration in the target electrolyte, the experiment proved the delivery capability of the device. A different syringe-like device (**Figure 1.28b**) was fabricated for *in-vivo* testing. The syringe was used to stimulate astrocytes cells. After astrocytes cells bind the Glu neurotransmitter, ion channels open such that Ca^{2+} ions enter the cell membrane. Indeed, after activation of the Glu, an increase of Ca^{2+} intracellular concentration was recorded, probing the successful delivery of the neurotransmitter. Encouraging results were obtained from *in-vivo* experiment carried out on the auditory system of guinea pig.

Electrospun organic nanofiber structures were used to study cell growth in a complex 3D environment [96]. To achieve uniform and conformal coatings, vapor phase polymerization (VPP) of PEDOT:tosylate was employed to cover poly(ethyleneterephthalate) (PET) nanofibers. Contact angle measurements were used to investigate the wettability of the surfaces: the uncoated PET nanofibers were found to be strongly hydrophobic (contact angle 147°), whereas VPP-PEDOT:tosylate surfaces were found to be more hydrophilic (contact angle 62°). Experiments showed that (SH-SY5Y) cells cultured on the 3D surfaces formed neuritis, a result indicating neural cell viability and adhesion. Moreover, upon application of an electrical bias in the 1.5 - 3.0 V range, the VPP-PEDOT:tosylate coated PET nanofibers were electrochemically switched to induce Ca^{2+} signalling in (SH-SY5Y) neuroblastoma cells.

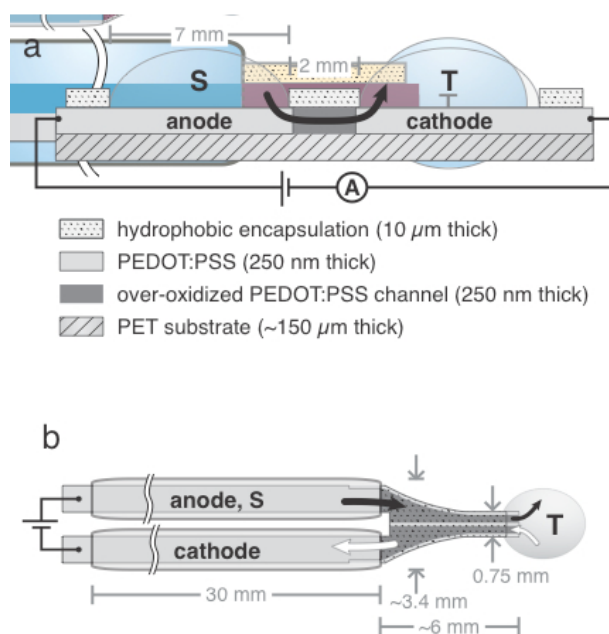


Figure 1.28 Planar device architecture of the ion-pump (a) and a novel syringe-like architecture (b) discussed in [96]. DOI: 10.1038/NMAT2494. Reprinted with permission from [96] © MacMillan Publisher Ltd.

Recently, an article from *Lin et al* [88] reports a very interesting application of Organic Electrochemical Transistors (OECTs) as cell-based biosensor, in which cells activity has been *in-vitro* monitored for two kind of cells lines: human esophageal squamous epithelial cancer cells (KYSE30) and fibroblast cells (HFF1). Preliminary, device characterization results in a stable performance in culture medium. First, the OECT device showed a stable performance in a standard cell culture medium (Dulbecco's Modified Eagle Medium, DMEM). That is done by measuring the transfer and output characteristics of the transistors. Secondly, the OECT device has shown also an excellent biocompatibility in culture medium. *The biocompatibility of PEDOT:PSS has been found excellent because the cells densities on PEDOT:PSS are identical to or even better than on silica.* Then, two experiments have been carried out: cell detachment, that is the investigation of cells detachment under trypsin treatment and the mechanism analysis of the voltage shifts produced by the cells detachment; cell morphology, that is the investigation of morphological change of cells on the OECT response under addition of retinoic acid. It was found that the device is sensitive to the *change of surface charge and to the morphology of adherent cells.* Trypsin treatments can induce morphological and detachment of cells from the substrate very quickly. The transfers characteristics of the EOCT of the cells in culture medium before and after trypsin treatment, reveals a gate voltage shift of -150mV for the cancer cells and -70mV for the fibroblast cells: this last lower shift voltage has been attributed to the weaker surface coverage on the active layer seen for the fibroblast cells. The effective capacitance (per unit area) of the transistor has been estimated by impedance analyzer measurements. The effective capacitance is related to the capacitance at the two interfaces: gate/electrolyte and electrolyte/polymer, and it has been found very stable in low voltage range. In fact the relative change of the effective capacitance before and after the trypsin treatment is less than 2%. From the governing equations of OECT [50] is possible to calculate that the gate voltage shift induced by trypsin is less than 10mV. Because 10mV is $\ll$ 150mV this means that the **effective gate voltage** shift is due mainly by the voltage off-set. Thanks to this valuation is possible to estimate the potential change at the electrolyte/polymer interface due to the cell detachment, that is about -65mV

in the similar range of the Zeta potential of the attached cancer cells [97]. Finally, retinoid acid is an anti-cancer drug that can induce morphological change of cancer cell lines more slowly than trypsin. More it can induce the rupture of cells. Upon addition of retinoic acid with no cells on the polymer channel, the OECT gives no response. Retinoic acid induces a morphological change and then the rupture of cells: after 7 hours has been observed that most of the cells are dissolved and detached from the device and a gate voltage shift is observed.

1.5.4. Neurotransmitter sensors

Hao Tang [90] used an OECT based on PEDOT:PSS for the first time as dopamine sensor. Dopamine is one of the neurotransmitters playing key functions in the renal, hormonal and central nervous systems, but present with very low clinical concentration levels (μM or nM concentrations). OECT is able to detect dopamine in PBS solution with a detection limit lower than 5 nM . Sensing properties of the organic transistor have been tested with different gate electrode (Au, Pt and Graphite GE) and with gate electrode modified with multi-walled carbon nanotubes (MWCT)-chitosan (CHIT) hybrid. Pt-electrode gives the highest sensitivity in the OECT response, even if the cause of the best effect yields by the Pt material is not yet clear at this time. Figure X shows the transfer characteristic (I_{ds} vs. V_g) with the electrolyte only (PBS, curve I) and with the addition of $2\mu\text{M}$ of dopamine (curve II) causing the gate voltage shift.

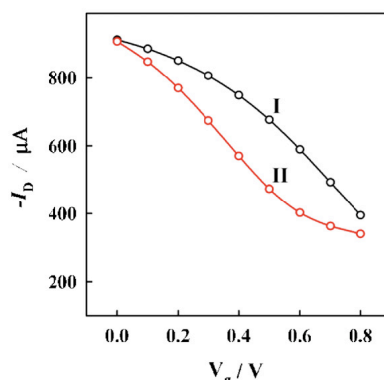


Figure 1.29 OECT response with and without Dopamine injected. Reprinted with permission from [90] © Elsevier.

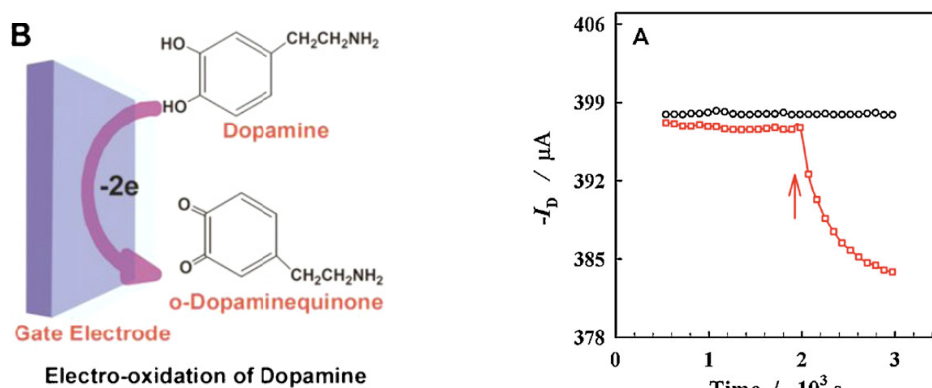


Figure 1.30 Proposed dopamine sensing mechanism (left) and a real-time measurement (right). Reprinted with permission from [90] © Elsevier.

The sensing mechanism is explained by the electro-oxidization of dopamine to o-dopaminequinone at the surface of the gate electrode that makes OECT working under faradaic regime (**Figure 1.29**). The

potential drop at the gate/electrolyte decreases, respect to a capacitive dropping, and the effective gate voltage (V_g^{eff}), that ultimately is the potential applied on the PEDOT:PSS channel, increases. A real-time detection of dopamine clearly shows the sensing capability of the OECT (**Figure 1.30**).

Conclusion

The field of research that studies the combined ionic and electronic transport in organic materials offers unique opportunities for fundamental investigations and technological applications. With respect to basic research, the field provides new insights in a variety of domains such as (i) charge carrier transport in high charge carrier density conditions, as generated by gating through electrolyte dielectrics, (ii) ions penetration and motion into polymers, as related to polymer electrochemical doping/de-doping, (iii) surface properties of conducting polymers to be employed as platforms for cell adhesion and proliferation, (iv) charge carrier injection and transport in light emitting organic semiconductors. With respect to applied research, high performance OE devices based on mixed ionic and electronic transport have been demonstrated. EG-OFETs can be operated at low voltages and exhibit high charge carrier mobility. Making use of OE devices, a wide range of bioelectronic applications is possible, including OECTs for biosensing and electrophoretic ion pumps.

2. Experimental.

2.1. SuMBE

Supersonic Molecular Beam Deposition (SuMBD) approach is based on the kinetic properties of a under expanded neutral gas, seeded with the selected organic molecules, which expands in a ultra high vacuum chamber in controlled conditions. Supersonic beams have become very popular as the ideal environment to study free molecules, preferred to others for their narrow velocity distribution and for the strong cooling effects, that allow the investigation of both the spectroscopy of large cold molecules [98]. In Molecular Beam deposition, where Knudsen cells are used, the evaporating material is characterized by the temperature T_0 and it is in thermal equilibrium with its vapors at a pressure P_0 . In these conditions the vapor dynamics can be described by the classical kinetic theory of gases, and on the bases of this theory their angular and velocity distributions. Instead, the case of Supersonic Beam Deposition, a continuous free jet is generated by a gas at high pressure flowing outside a narrow nozzle into a vacuum chamber environment (**Figure 2.1**). In this case, the flow can be approximated by an isentropic expansion with negligible heat conduction and viscous effect. The gas inside the source, seeded by sublimated organic molecules, is characterized by thermalized conditions (P_0, T_0), it flows through the nozzle into the outside chamber at lower pressure P_v , driven by the pressure gradient ($P_0 - P_v$). The gas starts from thermal small velocities determined by the thermodynamic equilibrium in the stagnation state and accelerates for the pressure gradient, as the cross section decreases, toward the source exit.

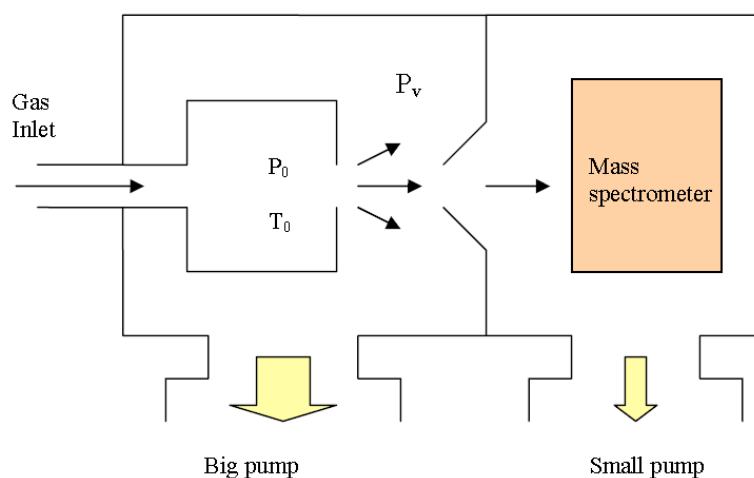


Figure 2.1 Basic scheme of a molecular beam apparatus with an inlet gas at a defined pressure. The flow may reach supersonic speed and the seeded molecules during the expansion experience a high number of hits with the molecules of the carrier gas. In this process, in dependence of their masses, the heavier organic molecules gain in kinetic energy, which may reach tens of eV, and form a focused supersonic beam, that reaches the substrate and grows an organic molecule thin film.

The main characteristics of the organic molecules distribution in the beam are a narrower velocity distribution and the cooling of internal degrees of freedom as reported in **Figure 2.2**.

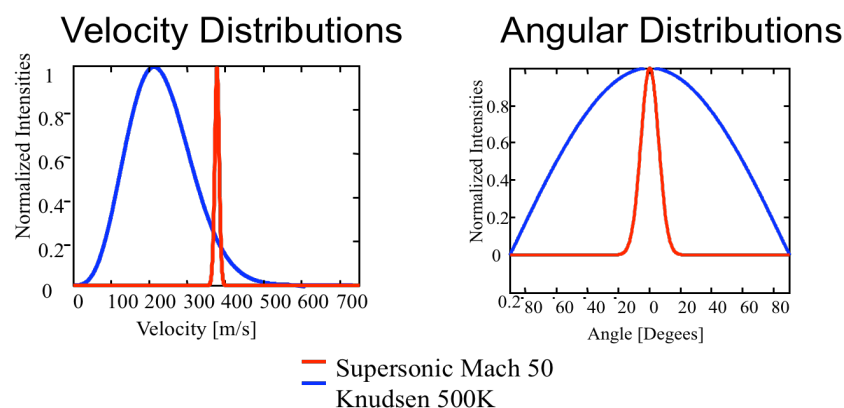


Figure 2.2 Velocity distribution and angular distribution of SuMBD beam compared to a Knudsen cell. Supersonic molecular beam deposition is based on the controlled expansion in high vacuum of a carrier gas (He, Ar, Kr), seeded by the organic molecules.

The molecular beam properties, when properly selected and skimmed, can be tuned in terms of kinetic energy, alignment, and directionality. Such parameters play a critical role in the growth of the organic films. From the experimental point of view SuMBD basically consists of a differentially pumped supersonic beam, a TOF mass spectrometer, and a deposition chamber. The supersonic beam source, placed in a high vacuum chamber, is made of a quartz tube with a micrometric nozzle at the front end (typically $50 \div 130$ mm in diameter). An inert carrier gas (helium in this experiment) is injected in the quartz tube at a controlled pressure ($2 \div 3$ bar). Inside the tube, a vessel with the organic material powder is used to sublimate by Joule heating the molecules, dispersing them at very low concentrations into the gas, and expanding both through the source nozzle into the deposition chamber. A conical skimmer selects the central part of the beam, which proceeds to the sample in a ultra high vacuum chamber. By changing the working parameters (nature and pressure of the carrier gas, sublimation temperature, nozzle diameter, and temperature), it is possible to finely control key properties of molecules in the supersonic beam such as kinetic energy, momentum, and cooling of the internal degrees of freedom typically induced by expansion.

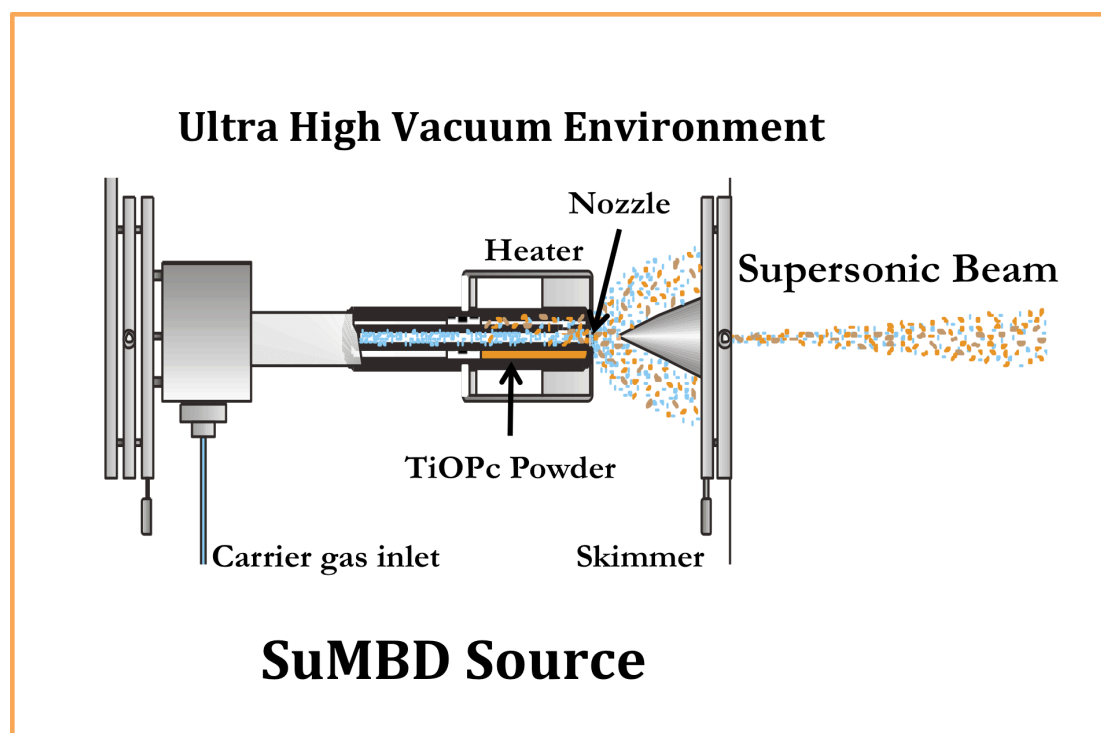


Figure 2.3 Scheme of the SuMBD source the organic molecule are reported in orange while the carrier gas is reported in blue.

The source typically operates using a He carrier gas pressure in the range of 100 ÷ 200 kPa. The central part of the beam is selected by skimming the free jet expansion via a sharp edged conical collimator, which separates the source from the deposition chambers (base pressure 10⁻⁸ mbar). Here, the molecular beam is intercepted by the substrate, the temperature of which can be varied from -100 up to 350 °C, with a stability of about 1 °C. SuMBD in the last few years has been already successfully used as a high controlled growth technique for organic molecules [99, 100] showing a unique ability to control structure and morphology in the growth of thin films [101] and consequently in achieving improved performances in devices applications [102]. Kinetic activated surface processes have also been explored to produce functional layers [103].

2.2 OECT fabrication and characterization

A description of the device OECT fabrication is reported, following a known protocol [75] that has been set up in IMEM during the first year. In **Figure 2.4** the OECT device structure is reported. An OECT consists of a conducting polymer channel in contact with an electrolyte that has a gate electrode immersed in it (**Figure 2.4a**).

At present, the majority of OECTs employ poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate), PEDOT:PSS, a degenerately doped *p*-type semiconductor, as the conducting polymer. Upon application of a drain-source voltage (V_{ds}), holes drift within the transistor channel generating a *drain-source* current (I_{ds}) (this is the *on state*). When a positive gate-source voltage (V_{gs}) is applied, cations (M^+) from the electrolyte enter the PEDOT:PSS channel and de-dope it according to the equation below [104], thereby decreasing I_{ds} (this is the *off state*, [50]):



The fabrication of OECTs consists of patterning a film of parylene on a glass substrate by optical lithography and oxygen Reactive Ion Etching (RIE), followed by spin coating of a 4/1 mixture of PEDOT:PSS (Clevios PH500, Starck GmbH)/ethyleneglycole and, finally, parylene lift-off [105, Yang #225, DeFranco #275]. The OECT channel is defined by the contact region between the electrolyte (here an aqueous halide solution), confined into a polymethyldisiloxane (PDMS) well, and the PEDOT:PSS film. The external parts of the PEDOT:PSS film act as source and drain electrodes. A metal wire (Pt or Ag) immersed into the electrolyte at a fixed depth of 2 mm acts as the gate electrode. OECT characteristics are evaluated using two Keithley 2400 SourceMeters with an home-made data acquisition software. The OECT response is expressed as the current modulation:

$$\frac{\Delta I}{I_0} = \frac{|I_{ds,off} - I_{ds,on}|}{|I_{ds,on}|}$$

where $I_{ds,off}$ is the *off* current (that is when $V_{gs} > 0$ V), and $I_{ds,0}$ is the *on* current (that is $V_{gs} = 0$ V).

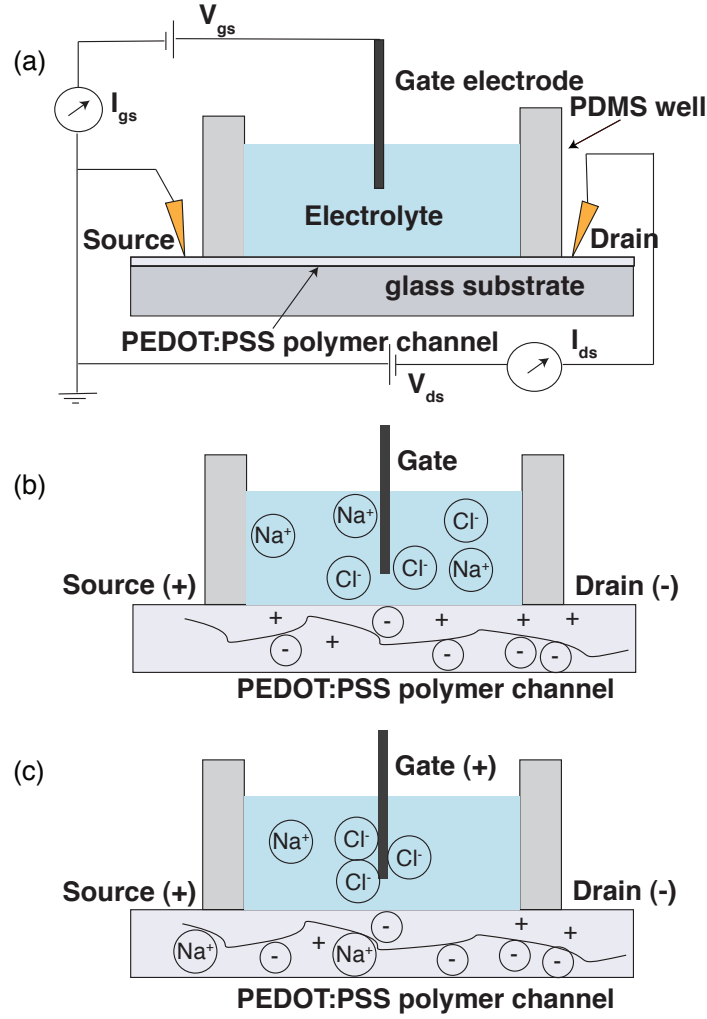


Figure 2.4 (a) Device structure and electrical circuit of a PEDOT:PSS OEET. (b, c) OEET working principle. Circles filled with indicate PSS⁻ ions and + indicate mobile holes. (b) Being PEDOT:PSS a hole conductor, the application of a negative V_{ds} bias generates a drain-source hole current I_{ds} . (c) Upon application of a positive V_{gs} , the electrolyte ions redistribute in solution. Part of these ions enter the PEDOT:PSS channel, thus affecting I_{ds} (de-doping process).

2.3. Spin Coating

Spin coating is a fast and easy method to realize thin films from a solution. In our work it has been engaged to make the PEDOT:PSS thin film on the patterned glass substrate for the realization of the transistor channels. The glass-substrate is attached on a chuck base using vacuum pump and the polymer solution is spun out onto the substrate, which then is rotated at a desired speed, measured in rounds for minute (RFM). The rotation distributes the polymer over all the entire substrate, resulting in a homogenous polymer film. The homogeneity results from the optimization of the velocity speed and the material polymer deposited on the substrate, this is a delicate operation whose set up has been quite time-consuming. Spin speed, polymer concentration, and characteristics of the solvent are all parameters affecting the thickness and morphology of the spinned polymer film.

2.4. Dynamic Light Scattering and Zeta Potential

Dynamic Light Scattering (DLS) is the technique used for determining particle size: during this PhD work it has extensively used, mainly dealing with coated-nanoparticles as well as micellar structures. DLS measurement is based on the Brownian motion of particles inside a fluid. Brownian motion is due to the random movement of particulates under the interaction with solvent molecules. The velocity of the Brownian motion is retrieved starting from the Rayleigh scattering of a laser source by the particulates and depends on the translational diffusion coefficient (D), which is a property of the particle in a specific solvent. The size measured by DLS is not the absolute size of the particle, but the hydrodynamic diameter (d), that is the size of an equivalent spherical particle with the same D . It is calculated from the Stokes-Einstein formula:

$$d(H) = \frac{kT}{3\pi\eta D}$$

where $d(H)$ is the hydrodynamic diameter, D is the translational diffusion coefficient, k is the Boltzmann constant, T the absolute temperature and η the viscosity of the medium. Solvent concentration, types of ions and surface coating are all parameters affecting strongly the diffusion coefficient.

The Zeta Potential is a technique used to valuate the particle surface charge. When a particle in a liquid medium develops a net surface charge, the surrounding distribution of solvent ions is modified: the concentration of counter ions close the particle surface increases, leading to the formation of a double layer around the particle. The layer is formed by two parts: the inner one, more strongly bounded, called the Stern layer, and the outer, where the solvent ions are weaker bounded to the particle, called the diffusion layer. The external boundary of the diffusion layer is the zeta potential, often referred also as the surface of hydrodynamic shear. Zeta potential gives information about the stability of a colloidal system and depends strongly on the ionic strength of the medium, the concentration and the pH of solution. The measurement of the zeta potential value is performed by the laser Doppler electrophoresis technique: briefly, upon application of an electric field between two electrodes, the charged particles move toward the opposite charge electrode, the movement causes the fluctuation of the scattered laser light with a frequency proportional to the particle velocity. The zeta potential measurements have been performed in our experiments with OECTs to valuate the surface charge of nanoparticles as well as the cationic micelles.

2.5. Quantitative XRD texture analysis

This section is an introduction to Quantitative Texture Analysis (QTA) from X-Ray Diffraction data. In a powder sample, the distribution function of grain orientation is usually assumed to be isotropic: that is all grain orientations occur with the same probability. In thin polycrystalline films however, certain crystallographic lattice planes can occur with a greater probability than others: this is called preferred orientation or texture. The crystallites in a polycrystalline sample have different chemical compositions, phases, shapes and size, and more their orientations are usually quite different within the sample. Therefore a quantitative description of the elements of a sample depends on a great number of parameters, and statistical description is necessary to achieve the main goal, e.g. to find the Orientation Distribution Function (ODF) [106].

The QTA is based on an extended-Rietveld method of parameters refinement and the overall procedure is called as “combined analysis”, respect to the classical one [107].

The idea underlying the method is to describe the sample by a set of physical parameters and using them to fit the diffraction and spectra, collected at different position by tilting the sample [108]. Then the physical parameters of the sample, that is layer thickness, phase composition, texture, residual stresses, crystal structure and microstructure (crystallites size and microstrains), are optimized by the extended-Rietveld refinement process [109]. This method is fully integrated in the software MAUD (Materials Analysis Using Diffraction), a program entirely written in Java by Luca Lutterotti [110], and in the following I am going to give more details about the computational methods employed. During my PhD work different organic thin film samples have been analyzed with Maud. The samples on which I have performed the analysis are the following:

1. **Modified Pentacene** thin films (TIPS);
2. **Tetracene** thin films deposited on different polymeric substrates.

All the XRD raw-data (2-dim CCD camera images) have been collected at the Synchrotron facilities Elettra in Trieste, in two different sessions in December 2009 and in March 2010. The spectra obtained can be processed by a Rietveld texture analysis.

2.5.1. Diffraction and Rietveld analysis.

The general principles of the classical Rietveld method are already reported in literature [109, 111]. The method is based on the non-linear least squares fitting of the acquired diffraction spectra. The goal of the Rietveld method is to minimize the residual function *WSS* (*Weighted Sum of Square*):

$$WSS = \sum_i w_i (I_i^{exp} - I_i^{calc})^2, \quad \text{where } w_i = \frac{1}{I_i^{exp}}$$

and refine the crystal structure of the compound, like cell parameters, atomic positions and Debye-Waller factors. The calculated I_i^{calc} intensity at the point i in a power diffractometer, for a spectrum collected at a sample orientation (χ, ϕ) , is given by the following formula (1):

$$I_i^{calc}(\chi, \phi) = bkg_i + I_0 \sum_{n=1}^{N_{phases}} \frac{f_n}{V_n^2} \sum_{k=1}^{N_{hkl}} m_{k;n} L_{k,p}(2\theta) |F_{k;n}|^2 S_{k;n}(2\theta_i - 2\theta_{k;n}) P_{k;n}(\chi, \phi) A_i(\chi, \phi) \quad (1)$$

The spectrum depends on:

1. **Phases:** crystal structure, microstructure, quantity, cell volume, texture, stress, chemistry composition;
2. **Instrument:** beam intensity, Lorentz-polarization, background, resolution, aberrations, radiation;
3. **Sample:** position, shape, dimension, orientation, layers.

Each of these quantities is written in term of refinable parameters. In equation (1) the first term is the background value, the second term represents the diffraction peaks depending on different terms:

- diffraction intensity, that determines the height of the peaks;
- line broadening ($S_{k;n}(2\theta_i - 2\theta_{k;n})$) that determines the shape of the peaks;
- number (N_{hkl}) and positions ($2\theta_{k;n}$) of the peaks.

The background function is a polynomial function:

$$bkg(2\theta_i) = \sum_{n=0}^{N_b} a_n (2\theta_i)^n$$

where N_b is the polynomial degree. In Maud is possible to choice the N_b value in case of complex background. For more complex background again also the interpolation method is implemented.

In the intensity expression of equation (1) the term S_n is a scale factor for each phase:

$$S_n = I_0 \sum_{n=1}^{N_{phases}} \frac{f_n}{V_n^2}$$

where I_0 is the beam intensity depending on the measurement, f_n is the phase volume fraction and V_n is the phase volume cell. The term $L_{k,p}(2\theta)$ is the Lorentz-polarization factor that depends on the geometry, detector, beam size/sample volume, and has specific formula for the configuration used, as for the Bragg-Brentano instrument:

$$L_p = \frac{1 + P_h \cos^2 2\theta}{2(1 + P_h) \sin^2 \theta \cos \theta}$$

The structure factor $F_{k;n}$ is expressed by:

$$|F_{k,j}|^2 = m_k \left| \sum_{n=1}^N f_n e^{-B_n \frac{\sin^2 \theta}{\lambda^2}} (e^{2\pi i(hx_n + ky_n + lz_n)}) \right|^2,$$

where m_k is the multiplicity of the k reflection, often expressed separately in the intensity expression (as in equation (1)), f_n is the atomic scattering factor and B_n the temperature factor (or Debye-Waller), N is the number of atoms and (x_n, y_n, z_n) the coordinates of the n^{th} atom. Worth to remember here that the atomic scattering factor in X-Ray diffraction decreases with the diffraction angle and is proportional to the number of electrons, while the Debye-Waller factor has a function to accelerate the decreasing of f_n . The absorption factor A_i in case of thin films, as in the case of our analysis on organic thin films, depends on 2θ . For Bragg-Brentano geometry $A_i = 1/2\mu$, where μ is the linear absorption coefficient of the sample.

The profile shape function is:

$$S_{k;n}(2\theta_i - 2\theta_{k;n})$$

and can be express by different analytical function: Gaussian, Cauchy (also called Lorentzian), Voigt or Pseudo-Voigt (PV) function, Pearson VII. Although the different line profile functions usable in profile broadening analysis, there are today indications supporting the use of the Voigt function, resulting from the convolution of a Lorentzian and a Gaussian contribution. One reason is that the convolution of two Voigt function is a Voigt function, this enabling an easier separation of instrumental and sample effects from the experiment.

In Maud a PV function is implemented, and the explicitly expression is reported in the following formula:

$$PV(2\theta_i - 2\theta_k) = I_j \left[\eta_k \left(\frac{1}{1 + S_{i,k}^2} \right) + (1 - \eta_k) e^{-S_{i,k}^2 \ln 2} \right]$$

where:

$$S_{i,k} = \frac{2\theta_i - 2\theta_k}{\omega_k}$$

In the PV function the shape parameters ω and η are expressed by the Caglioti and Gaussianity formula:

$$\omega^2 = W + V \tan \theta + U \tan^2 \theta \quad (\text{Caglioti})$$

$$\eta = \sum_{n=0}^{N_g} c_n (2\theta)^n \quad (\text{Gaussianity})$$

By the Maud interface is possible to add or remove terms in each of these functions.

Next, before the discussion about the texture analysis, that needs a more detailed explanation, is important to express the quality refinement factors, called also refinement estimators, that gives us an indication about how well the recalculated spectra from fitting is matching the experimental spectra.

The Weighted Sum of Square have been already reported before:

$$WSS = \sum_i w_i (I_i^{exp} - I_i^{calc})^2, \quad \text{where } w_i = \frac{1}{I_i^{exp}}$$

The two main parameters giving information about the quality of the fitting are the two R-indices R_{wp} and the R_{exp} , defined as:

$$R_{wp} = \sqrt{\frac{(N - P)}{\sum_{i=1}^N [w_i I_i^{exp}]^2}}, \quad \text{where } w_i = \frac{1}{\sqrt{I_i^{exp}}}$$

$$R_{exp} = \sqrt{\frac{\sum_{i=1}^N [w_i (I_i^{exp} - I_i^{calc})]^2}{\sum_{i=1}^N [w_i I_i^{exp}]^2}}, \quad \text{where } w_i = \frac{1}{\sqrt{I_i^{exp}}}$$

where N is the number of points and P the number of parameters.

R_{exp} is the minimum R_{wp} value reachable using a certain number of refineable parameters. In order to be reliable it needs a valid weighting scheme. The R_{wp} factor is the more reliable for the evaluation of our analysis. The R_{wp} absolute value does not depend on the absolute value of the intensities, but on the background: with a high background is more easy to reach very low values, while increasing the number of peaks (sharp peaks) is more difficult to get a good value. In general we can set establish that for $R_{wp} < 0.1$ correspond to an acceptable refinement with a medium complex phase. For a complex phase (monoclinic to triclinic) a value $R_{wp} < 0.15$ is good, finally for a highly symmetric compound (cubic) with few peaks a value $R_{wp} < 0.08$ start to be acceptable.

The goodness of fit is defined as:

$$G.of.F. = \frac{R_{wp}}{R_{exp}}$$

2.5.2. Texture analysis.

The basic concept in texture analysis is the Orientation Distribution Function (ODF). The ODF, analytically $f(g)$, represents the statistical distribution of the orientations of the crystallites in a polycrystalline sample:

$$\frac{dV(g)}{V} = \frac{1}{8\pi^2} f(g) dg$$

where $dg = \sin\beta d\beta d\alpha d\gamma$ is the orientation element, defined by three Euler angles $g = \{\alpha, \beta, \gamma\}$. V is the irradiated volume of the sample and $dV(g)$ is the volume of crystallites whose orientation is between g and $g+dg$ [106].

For example, a sample with a randomly-oriented crystallites has an ODF of 1 m.r.d. (multiples of random distribution) for all the g values. In any sample a fraction of the total volume is randomly oriented, (V_r) while the other fraction will have an preferred orientation component $f_c(g)$. The random fraction of the sample produces a background in the ODF, called “phon” (or also “fon”). That means that, after calculation, the minimum value of the ODF identifies with the random value fraction of the sample.

The texture of a phase is explicitly expressed in the equation of intensity (1) by the term $P_{k,n}(\chi, \phi)$ of the calculated intensity, that is a factor changing the intensity of different peaks as function of their (h k l) miller indices and orientation angles (χ, ϕ). By collecting a sufficient number of spectra at different tilting angles, is possible, in principle, to reconstruct by fitting the entire three-dimensional orientation distribution function. For the organic thin film samples that I have analysed, no more than a few peaks, usually two or three, are present in the spectra, leading the necessity to acquire more spectra at more tilting angles. The ODF so obtained can be used to predict and verify anisotropic macro properties of the sample.

The fundamental equation of quantitative texture analysis expresses the texture in terms of the ODF:

$$P_h(\varphi) = \frac{1}{2\pi} \int f(g) d\varphi$$

this equation representing the fact that each pole figure (that is a 2-dim figure) is a projection along a certain path (φ) of the ODF (that is a 3-dim object) [107].

There are different methods to solve the fundamental equation of QTA, each working with completely different strategy: the March-Dollase function, spherical harmonics and component method, also called standard function, WIMV and Extended-WIMV.

Each of these methods is full implemented in Maud. The first method, that is also the more common, called *harmonic*, is based on the expansion of the function in spherical harmonics [112]: this method has been implemented into the Rietveld procedure by Popa [113].

Another method, developed by Matthies (the Williams-Imhof-Matthies-Vinel, WIMV), consists of dividing the function in a finite number of regular cells, inside of which the ODF is described by discrete value [106]. The algorithm is based on the numerical refinement of the ODF [107, 108], is optimized for traditional pole figure analysis and wants to find the best ODF reproducing the pole figure texture values, by maximizing the ODF minimum value and the texture sharpness. When inserted into a Rietveld loop, the WIMV method required two additional steps: first, the extraction of the pole figures, and second, the interpolation of these texture weights in a regular grid. Therefore for sharp texture and coarse irregular coverage, the ODF values retrieved are non-optimized. To

overcome these problems a modified method has been derived from WIMV, called Extended-WIMV. The new algorithm, also called entropy-modified method, can be used with irregular pole figures coverage and includes smoothing based on a concept similar to the tube projection of the ADC (Arbitrary-defined cells) method (see below) [108, 114]. The iteration scheme for the ODF refinement is based on the entropy maximization algorithm [115] that includes the reflections weights:

$$f^{(n+1)}(g) = f^{(n)}(g) \prod_{m=1}^{M_{hkl}} \left(\frac{P_{hkl}(g^{-1}, h_m)}{P_{hkl}^{(i)}(g^{-1}, h_m)} \right)^{\lambda_i \frac{w_{hkl}}{M_{hkl}}}$$

here M_{hkl} is the number of division points for the discretization of the integral of all the orientations around the scattering vector for the pole figure (hkl) and $P_{hkl}^{(i)}(g^{-1}, h_m)$ is the calculated pole figure value from iteration (i) for the reflection Miller indices (hkl) . The method has been successfully tested [108, 116, 117] and is fully integrated in Maud, it has been used for the analysis of organic films reported in Chapter 3.

The Arbitrary-Defined Cells (ADC) method.

The ADC method is an WIMV-modified method in which, the pole figures from the ODF cells are calculated using a projection tubes (instead of a projection path) depending on the pole figure cells concerned. In this way the calculation takes into account for each cell volume, resulting in a better smoothing.

Entropy maximization method.

For entropy in this context we mean the texture “disorder”, that is texture entropy. Similarly to the formalism defined from information theory [118], the entropy estimator in texture is written as:

$$S = \sum_i f(g_i) \ln f(g_i)$$

resulting in the iterative algorithm:

$$f^{(n+1)}(g) = f^{(n)}(g) \prod_{m=1}^{M_{hkl}} \left(\frac{P_{hkl}(g^{-1}, h_m)}{P_{hkl}^{(i)}(g^{-1}, h_m)} \right)^{\frac{\lambda_i}{M_{hkl}}}$$

that is the same of the E-WIMV method but without the weights.

Standard Function

Another texture model implemented in Maud is the Standard Function, also called component method. This method is useful particularly for very strong texture, and applications will be shown in Chapter 3. In a sample with strong texture a large number of crystallites have the same orientation distribution and ODF can be described by a small number of g orientations: if this is the case the ODF can be write by simple functions, leading to a large reduction of data. If $f^c(g)$ is the part of the ODF representing the texture component centered at the orientation g^c , then ODF can be written as:

$$f(g) = F + \sum_c I^c f^c(g)$$

where F is the part of the ODF randomly oriented and I^c is the fraction of crystallites oriented along the component g^c of the distribution $f^c(g)$, that can be represented by any functions, that are what we call standard functions and we can control by Maud interface.

In Maud there are two standard functions available: a fiber and a spherical component, both being a linear combination of a Gaussian and Lorentzian standard functions.

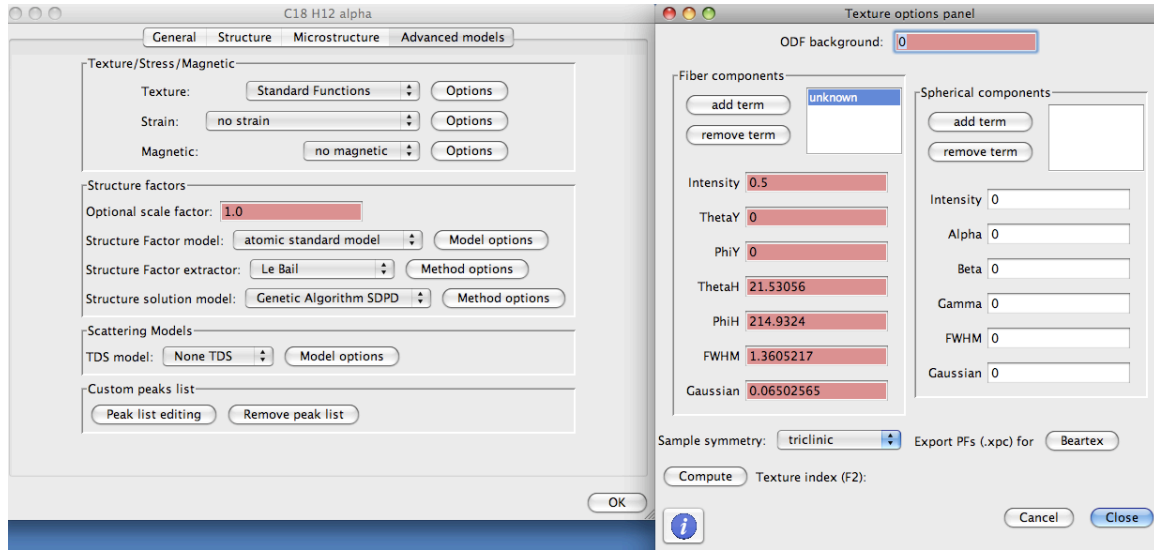


Figure X. Texture model implemented in Maud. In the example a fiber or a spherical component are available under the Standard Function model.

Following the convention from [106], the Gauss spherical component is defined as:

$$f(S, \tilde{\omega}) = N(S)e^{Scos\tilde{\omega}} \geq 0$$

$$0 \leq \tilde{\omega} = \tilde{\omega}(g_0, g) \leq \pi$$

$$0 \leq S \leq \infty$$

where:

$$N(S) = [I_0(S) - I_l(S)]^{-1}$$

$$I_l(x) = \frac{1}{\pi} \int_0^\pi e^{xcost} \cos l t dt$$

$I_l(x)$ being the modified Bessel function, g and g_0 are the eulerian coordinates in the ODF space, g_0 being the position of the maximum of the spherical component.

The Lorentz spherical component is:

$$f(t, \tilde{\omega}) = (1 - t^2) \frac{(1 + t^2)^2 + 4t^2 \cos^2(\tilde{\omega}/2)}{(1 + t^2)^2 - 4t^2 [\cos^2(\tilde{\omega}/2)]^2} > 0, \quad t < 1$$

A fiber component is obtained integrating a Gauss spherical component around the fiber axis n :

$$f(S, \bar{n}, g_0, g) = N(S) I_0 \left(S \frac{1+z}{2} \right) e^{\frac{S(z-1)}{2}}, \quad z = (\bar{n} \cdot g_0^{-1} \cdot g \cdot \bar{n})$$

The main disadvantage of standard function is that a definition of the starting components is required, for example by another method of analysis: for the organic thin films discussed in Chapter 3 the starting components have been found by testing some components and restricting the ranges after checking the resulting fitting, as explained in the following section regarding the reconstructed pole figures.

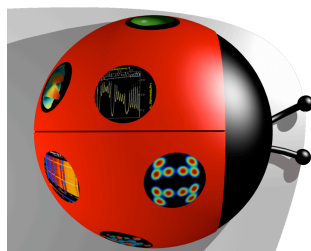
Reconstruction of plot figures

The best and quickest way to check for the angle orientation of the c axis respect to the sample (or whatever axis) in Maud is looking at the pole figures, which gives information about the ODF independent on the model used to represent texture. With the pole figures we can do it the same for whatever texture model. In the following I refer about the case of ours analyses on organic thin films, where I have always used the standard function model that permit to derive the pole figures also from some of its parameters. As a general procedure in Maud to plot the pole figure, the starting point is to plot a reconstructed pole figure to check where the sharp fiber texture pole is located respect to the sample normal (the sample normal is in the centre of the pole figure). For example, in the case of the tetracene analyses it is easy to see that the texture fiber pole is in the centre of the pole figure for the (00l). This means the c axis is exactly perpendicular to the sample surface unless it is a triclinic sample for which the c axis is not perpendicular to the 00l plane (and for the tetracene it is triclinic). For the tetracene, we just get that the 00l planes are parallel to the sample surface.

There are 5 principal parameters in a fiber component defined in the defined standard functions as we used in the analyses with Maud:

- **thetaY** (angle inclination or polar angle of the fiber component axis respect to the normal to the sample; goes from 0 to 90); it was zero in our analyses
- **phiY** (azimuthal angle of the fiber component; from 0 to 360, the zero is the east direction in the pole figure and positive rotation is counter-clockwise); in our analyses being $\text{thetaY} = 0$, phiY can be any value
- **thetaH** (azimuthal angle of the crystal axis oriented along the fiber texture axis; the zero is for the c axis)
- **phiH** (polar angle for the oriented crystal axis in the cell setting; 0-360, when thetaH is 90 and $\text{phiH} = 0$, the oriented axis is the a axis, except for the triclinic and trigonal with non hexagonal axes).
- FWHM, Full Width at Half Maximum, this gives the mean deviation in degrees of the texture from the oriented axis (the distribution of the orientation along the fiber axis is described by a gaussian+lorentzian component with a certain FWHM that it is refined along with the fraction of gaussianity). As an example, being $\text{thetaY}=0$, it is possible to get the orientation of the c axis with a simple computation from the cell parameters and thetaH , phiH . In the most simple case, being $\text{phiH} = 0$, and thetaH being for example 21 deg, then the orientation of the c axis respect to the sample normal is 21 deg. Instead if the angle in the cell between the a and c axis is 110 deg, then $110 - 21$ will give 89 deg and this means that the a axis is 1 deg off from being parallel to the sample surface (or 1 deg off from being normal to the sample normal). If phiH is not zero, then should just to play with the angles. Saying the $\text{phiH} = 0$ is the same than saying that a is in the plane defined by c and the texture direction.

3. Molecular Organic films for Organic Electronics



In this chapter, the study performed on different organic thin film samples is presented. The chapter is organized in three sections, each regarding a different experiment.

3.1 Titanil Phthalocyanine (CuPc) thin films, deposited by Supersonic Molecular Beam Epitaxy, have been analysed by different techniques, including AFM, Micro-Raman and Maud. This work has been published on *Journal of Chemical Physics C*.

3.2 Modified-Pentacene thin films (TIPS), this experiment has been carried out in collaboration with the Polytechnique de Montréal, and has been published on *Applied Physics Letter* **97**, 123304 (2010).

3.3 Tetracene thin films deposited on different polymeric substrates, in collaboration with the Polytechnique de Montréal. At this time the work has been submitted.

3.1. Controlled Polymorphism and growth of Titanyl Phthalocyanine

The polymorphism of titanyl phthalocyanine films, grown on atomically flat mica substrates, has been systematically studied by micro-Raman spectroscopy, correlating structure and optical properties. Different growth regimes, using hyperthermal seeded supersonic beams, have been explored as a function of the substrate temperature. Specific signatures in micro-Raman spectra, correlated to different phases, are identified and discussed. We demonstrate the unprecedented ability to grow crystalline films at low temperature, with improved structural order, and we show that different regimes lead to grain dimensions in a range from the nanometric to the micrometric scale. The local micro-Raman analysis, carried out on crystallites with regular shapes, allows discriminating different structural phases of the single crystalline grains. We provide evidence that different growth regimes are achieved and controlled, paving the way to phase selection, which is envisaged as a key feature to improve device performance.

Phthalocyanines are stable oligomer macrocyclic compounds, with distinctive optical properties, including an intense absorption in the visible region and a p type π -conjugated semiconductor behavior in the solid state [119]. These characteristics make them attractive for important applications in optoelectronics [120], photovoltaics [121], spintronics [122], and for sensing [123], devices. On this basis, the scientific community is devoting widespread efforts to study their structure and morphology and to control their properties in the solid state. A better control on the growth of phthalocyanine thin films is crucial to improving their transport and optical properties, and many studies are devoted to this topic, approaching different growth techniques for different kinds of phthalocyanine molecules.

Among all different metal phthalocyanines, titanyl phthalocyanine (TiOPc) [124, 125], is of particular interest for optoelectronic and photovoltaic applications, especially because its absorption spectrum in the visible, with a band centered at 860 nm in its stable crystalline phase, extends toward the infrared.

As is typical for metal phthalocyanines in general, TiOPc films are characterized by a strong polymorphism [126]. Their peculiar, nonplanar, and polar structure gives rise to several crystalline phases, different from those typical of the planar MPC. The main stable crystal structures of TiOPc have been characterized by means of X-ray diffraction (XRD) by W. Hiller et al. [126] in the early 80s and have been identified as phase I (sometimes also referred to as β , monoclinic, with the $P21/c$ space group and number of molecules per unit cell $Z = 4$) and phase II (also called α , triclinic, with the $P1$ space group and $Z = 2$), grown as single crystals by CVD [127]. Another polymorph, called phase Y, is sometimes reported and described as a crystal structure similar to phase I, with a different tilting angle of the molecules in the a - b plane [128], and up to date, only polycrystalline films of phase Y have been grown.

The presence of different polymorphic structures makes the development of growth methods particularly important, enabling appropriate control of the crystalline phase [129], so that device performances can be improved [130-132]. TiOPc films have been grown with different methods: Langmuir-Blodgett (LB) and spin-coating have been used in combination with post-deposition treatments to obtain a selective production of film in phases I, II, and Y [133].

The phase selection was achieved by exposing films to vapors of solvents, such as chlorobenzene or xylene, followed by annealing processes. However, the best results in terms of phase control are achieved by organic molecular beam deposition (OMBD) [134, 135].

At about 50 °C (on several different substrates, including sapphire and PTFE), only amorphous films can be grown [134], whereas above 100 °C, the simultaneous presence of amorphous and crystalline regions (phases I and II) is observed. At higher temperatures and on appropriate crystalline substrates (such as sapphire), films grow preferentially in phase II.

We have previously shown, by morphological and structural studies of TiOPc thin films on disordered substrates, such as quartz [100], that the kinetic energy, supplied to the molecules by the supersonic expansion, has a remarkable ordering effect [136, 137]. In particular, we found that increasing the kinetic energy leads to larger uniform grains with respect to OMBD. A very interesting question that could not be studied on an amorphous substrate is the role played by molecule-surface interactions and the kinetic energy of the impinging molecule, which can be better investigated on a crystalline surface. In the present paper, we explore the formation of TiOPc crystalline phases on atomically flat mica. The aim is to clarify the role of the substrate surface order on the growth mechanism on a surface where the energies of interaction are similar.

Besides the XRD, TiOPc crystalline phases have been characterized by UV-visible spectroscopy [138, 139] showing features that can be precisely and unambiguously associated with the different crystalline phases. A few papers report Raman scattering studies [140, 141] where evidence of the phase dependence of peak position and intensity are discussed.

In a previous paper [137], UV-visible spectra has been correlated to the micro-Raman analysis, identifying, for both the spectroscopic techniques, well-defined fingerprints of amorphous and crystalline phases.

In this experiment, dealing with an atomically flat mica substrate, the presence of the substrate features makes the UV-visible spectroscopy useless, while the XRD becomes quite cumbersome to interpret. We take advantage of the correlations, defined in our previous work, between Raman spectra features and amorphous or crystalline phases, to investigate the structural properties of the films. Henceforth, as shown in the following, micro-Raman analysis, correlated also to the morphology of the films studied by AFM and optical microscopy, allows a precise identification of the phase in TiOPc film and grains.

Spanning a wide range of deposition conditions, we show here that hyperthermal beams give an unprecedented control on the growth, producing crystalline films with a defined structure and phase, even at room temperature. This is a remarkable result, which further confirms the perspective of the

supersonic molecular beam deposition (SuMBD) approach as a promising method for the synthesis of controlled organic functional films.

Film Growth.

Thin films have been grown by a supersonic beam deposition apparatus, already detailed elsewhere [142]. In brief, it consists of a differentially pumped supersonic beam, a TOF mass spectrometer, and a deposition chamber. The supersonic beam source is realized by a quartz tube, closed at the front end, with a nozzle typically 50-130 μm in diameter, placed in a high-vacuum chamber. An inert carrier gas (helium in this experiment) is supplied in the source at a controlled pressure.

The organic material is seeded by Joule heating sublimation into the gas at very low concentrations. The seeded gas flows through the nozzle into the vacuum chamber, generating a supersonic expansion. By changing the working parameters (nature and pressure of the carrier gas, sublimation temperature, nozzle diameter, and temperature) we are able to finely control the kinetic energy, the momentum, and the degree of cooling regarding the internal degrees of freedom of the molecules in the beam [143].

The source typically operates with a He carrier gas pressure at 1000-2000 mbar. By skimming the free jet expansion, it is possible to select the central part of the beam via a sharp-edged conical collimator, which separates the source chamber from the deposition chamber (base pressure = 10^{-7} mbar). Finally, the molecular beam is intercepted by the substrate for the deposition of the film. Alternatively, a third chamber, which is connected through another skimmer along the beam path, allows the film growth under ultra-high-vacuum (UHV) conditions. The temperature of the substrate may be controlled from -115 up to 250 $^{\circ}\text{C}$, with a stability of about ± 1 $^{\circ}\text{C}$.

The TiOPc films have been grown in a temperature range from 25 to 220 $^{\circ}\text{C}$ on atomically flat mica (previously characterized by atomic force microscopy (AFM)). A quartz microbalance measures the deposition rate, which is fixed for all the samples at 0.5 nm/min. The source operating conditions have been tuned to keep the same high kinetic energy of 15 eV for all the films deposited. The in-line time-of-flight mass spectrometer (TOF-MS) with laser multiphoton ionization, achieved by the fourth harmonic of a Nd:YAG laser (266 nm), monitors the intensity, purity, and stability of the beam. The duration of the deposition has been set to produce films of the same nominal thickness (~ 20 nm). We used a TiOPc material coming from the same batch (Syntec - Sensient GmbH, Wolfen, Germany) for all experiments. It was purified by repeated vacuum gradient sublimation cycles, after which the TOF-MS mass spectra did not show any significant residual contamination. Amorphous reference samples were also prepared by a home-made evaporator operating under high-vacuum conditions (10^{-7} mbar). We used the same TiOPc powder in a tantalum boat and the same mica substrates, producing samples with a thickness up to 1 μm .

Characterization Techniques.

A Nanoscope IIIa (Digital Instruments) AFM was used in tapping mode to study the topography of the samples. The Raman measurements were carried out by a microprobe setup (HORIBA-Jobin-Yvon, model Labram) equipped with a CCD detector and a He-Ne laser (632.8 nm emission). The highest resolution grating with 1800 grooves/mm was used for the reported measurements. We could estimate the resulting uncertainty of the peak position to be about 1 cm^{-1} for the narrow peaks and about 3 cm^{-1} for the broader bands, by taking into account the resolving power of the grating, the pixel size of CCD, and the errors in the correction procedure of the drift in the monochromator frequency setting (performed by subtracting the apparent position of the laser line, monitored at regular time intervals). Two objectives have been used to collect the spectra: a 100X and a 50X long working distance. The laser power out of the 50X objective was about 5 mW, and the diameter of the focused spot was about 3-4 μm . Therefore, the irradiance for the unfiltered laser beam was of the order of 50

kW/cm². When neutral filters of variable optical density (OD) are used, the laser power impinging the samples can be reduced to the following amounts: 50% for the OD 0.3 filter, 25% for the OD 0.6, 10% for the OD 1, and 1% for the OD 2. Proper filters were chosen to have a good signal-to-noise-ratio without excessive heating, to have Raman measurements at temperatures not far from RT: typically, the OD 0.6 filter was adopted with the 50X objective and the OD 1 filter with the 100X objective. A special X-Y stage for spectral mapping has been used to point out and map the interesting zones of the samples.

Morphology of TiOPc Thin Films.

The films deposited on the mica substrates present quite different morphologies, as a function of the substrate temperature, with crystalline grain dimensions typically in the range of tens of nanometers up to a temperature of about 100-130 °C. The AFM images of TiOPc films grown at increasing substrate temperature, from 25 to 220 °C (**Figure 3.1**), confirm the ability of SuMBD to control the dimension of the crystallites [131, 132].

The typical texture of room -temperature (RT) grown samples (**Figure 3.1a**) is characterized by a uniform distribution of small grains, having typical lateral dimensions smaller than 50 nm and heights up to 10 nm. Above 130 °C, the regular-shaped crystalline grains exhibit increasing sizes in the micrometer range and can be imaged by the optical microscopy of the Raman apparatus (**see Figure 3.1b-d**). With this approach, we characterize the single crystalline grain and identify the structural properties with respect to the geometrical shape of the grain. The film roughness and the height scales measured by tapping mode atomic force microscopy are very different: the min-max height scale is 14 nm for films grown at 25 °C and becomes 60 nm for films grown at 160 °C or higher. The rms roughness changes from 2 nm for films deposited at 25 °C to 13 nm for films grown at 160 °C [136].

Two structural classes of crystallites may be identified: the first one, where crystallites present a flat large area, usually with a rectangular base and with very steep side walls, and the second, characterized by a thin needle-like shape. These characteristics may be observed, at substrate temperatures ranging from 150 to 220 °C, also with the optical microscope.

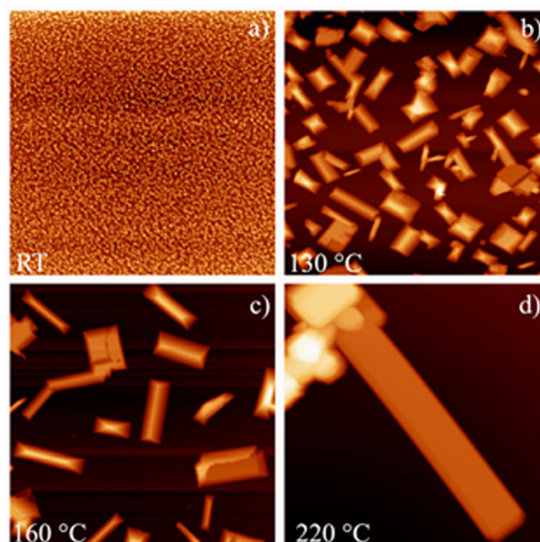


Figure 3.1 AFM images (5x5 μm^2) of TiOPc thin films deposited by supersonic molecular beams on mica at different substrate temperatures: (a) 25 (b) 130 (c) 160 and (d) 220 °C.

Besides the formation of microcrystals growing at increasing temperature, we gained experimental evidence about a wetting layer deposited in the region between the microcrystals. In fact, when this region is explored by AFM, a significant roughness is measured [131]. In **Figure 3.2** (insets), we have compared the rms roughness of the region between large grains of TiOPc (inset a) with that of the

clean mica substrate (inset b).

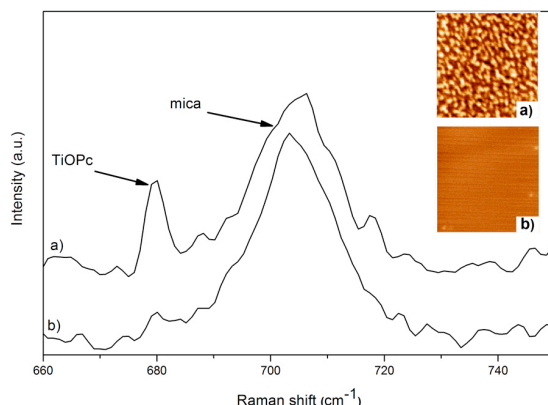


Figure 3.2 (a) Raman spectrum of a thin film of TiOPc grown by SuMBD on the substrate at 220 °C. The signal has been collected in a zone between micrograins. The macrocycle peak is clearly visible. (b) Raman spectrum of the mica substrate in a nondeposited zone. AFM images of the two different zones are shown in the insets.

In the first case, we found a value of 1.7 ± 0.3 nm, whereas in the second case, we have roughness data typical of an atomically flat surface. The difference suggests the presence of a very thin layer of TiOPc between the larger grains (wetting layer), which is confirmed by micro-Raman spectra, acquired through a long collection time. **Figure 3.2** shows that the strongest peak of TiOPc, the macrocycle mode at 680 cm^{-1} , is observable together with the typical Raman spectrum of mica (Figure 3.2, spectrum a). The spectrum of bare mica is also reported for comparison (Figure 3.2, spectrum b). Obviously, the very weak Raman signal coming from a few layers is not enough to characterize the structure of this wetting layer. Its presence is, anyhow, very interesting and quite important for device fabrication, confirming the structural continuity of the film and allowing the electronic transport between the grains.

Micro-Raman Analysis of the TiOPc Thin Films.

The Raman spectra of solid TiOPc contain many peaks associated with vibrations of different molecular groups. In principle, the interaction between the molecules in the solid state changes for different crystalline phases and causes different types of distortions and modifications in the vibrational modes. Raman spectroscopy is very useful to analyze the dependence of the spectral parameters of the vibrational modes on the structural properties. However, only a few Raman peaks are very sensitive to the various ordered or disordered structures exhibited by the TiOPc films.

Table 3.1 lists the positions of the main Raman features for the different phases observed. The same features are also reported for a typical OMBD grown film, which has an amorphous structure at room temperature.

Raman shift (cm ⁻¹)				
RT OMBD peaks positions	phase II SuMBD peaks @ 80 °C	narrow crystal SuMBD peaks @ 220 °C	flat crystal SuMBD peaks @ 220 °C	assignment
1528.6				pyrrole stretch
1512.6	1512.1	1512.8	1507.5	pyrrole stretch, <i>a</i> ₁
1451.1	1453.9	1452	1453.4	isoindole stretch
1433.3	1436	1434		isoindole stretch, <i>a</i> ₁
1343.7	1347.3	1338	1345.5	pyrrole stretch, <i>a</i> ₁
			1337.2	
1304.7	1306	1303.3		C–H bend
1209.8	1211	1211		C–H bend
1192.6	1194.2	1196		C–H bend
1143.7	1151.4	1143	1149.5	pyrrole ring breathing
1106.9	1108.7	1106.5		C–H bend
949.1	940.5	939		TiO stretch
830.5	838.2	836		macrocycle stretching, <i>a</i> ₁
749.7	751.2	751	751	macrocycle stretching, <i>e</i>
678.7	679.6	677.5	678.5	macrocycle breathing, <i>a</i> ₁

TABLE 3.1: Raman Peak Positions of the Principal Structures of TiOPc Thin Films Reported. The first column presents the peak position of the OMBD deposited thin film on the room-temperature substrate and the second column, the 80° C SuMBD deposited thin film. The third and fourth columns present the peak positions of the two different shapes of crystallites in the samples deposited with the substrate at 220° C.

The different molecular vibrational modes have been labeled following a procedure similar to that reported in [140]. In particular, as indicated in **Figure 3.3**, the spectral features above 1000 cm⁻¹ are associated with the pyrrole, isoindole, and C-H vibrational modes, whereas the features in the 650-850 cm⁻¹ region are due to the macrocycle vibrations [137]. In **Figure 3.3**, we report comparatively a micro-Raman spectra of the TiOPc films deposited by SuMBD on the mica substrate at 80 °C (top) and a spectrum of a TiOPc film grown by the OMBD technique (bottom) on a RT substrate.

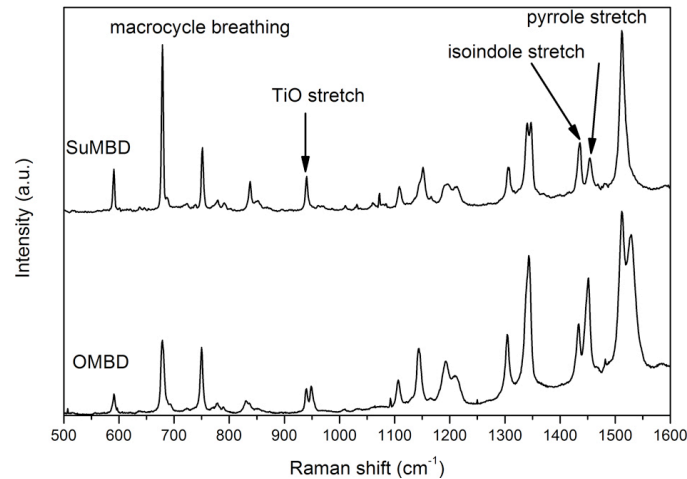


Figure 3.3. Comparison of Raman spectra from a TiOPc thin film grown by SuMBD at 80 °C (upper spectrum) and a TiOPc thin film grown by OMBD at room temperature (lower spectrum). In the upper part of the figure, the assignments of the principal modes are indicated.

For the first film, the kinetic energy of the molecules in the beam is 15 eV, whereas for the second one, the typical kinetic energy is thermal (~0.05 eV).

The general spectral shape of the TiOPc Raman scattering presents some characteristic differences between the two films. In particular, the position of the pyrrole stretching peak in the region of 1505-1530 cm⁻¹ is very sensitive to the crystalline structure. In the bottom spectrum of Figure 3.3, this peak

presents a strong component at 1531 cm^{-1} , a high-frequency value assigned in the literature to amorphous films [137, Mizuguchi, #879], and also a clearly separated component at 1512 cm^{-1} , a typical value of a crystalline structure [137]. A very similar pattern is observed in the TiO stretching mode, where, together with a main peak at 949 cm^{-1} (amorphous character), a smaller feature appears at 939 cm^{-1} (crystalline character).

Other Raman features indicating the prevalent amorphous character of typical OMBD films come from the intensity ratios: a lower relative intensity is observed in the macrocycle breathing mode (680 cm^{-1}) with respect to the pyrrole stretching band.

Besides that, the isoindole stretching mode at 1434 cm^{-1} is weaker than that at higher frequency (1450 cm^{-1}). A third relevant marker is the FWHM (full width at half-maximum) that is significantly larger for many of the peaks of the amorphous phase. In particular, the peak of the macrocycle breathing mode, being isolated and well-resolved, allows for the best quantitative evaluation of this parameter.

On the contrary, the SuMBD film spectrum shows all the typical characteristics of the crystalline structure: the presence of only the 1512 cm^{-1} component for the pyrrole stretching and of only the lower frequency (939 cm^{-1}) component for TiO stretching. Furthermore, the higher intensity ratio between the macrocycle breathing and the pyrrole stretching modes together with a higher intensity of the lower frequency component in the isoindole stretching is clearly observed. To study the correlations between the different Raman signatures and the structural phases, we carried out a detailed analysis of typical spectra of TiOPc films, measured at different substrate temperatures, taking also into account their typical morphological shape. At RT, the mean size of the grains deposited by SuMBD is typically in the range of nanometric dimensions, whereas samples with substrate temperatures ranging from 200 to $220\text{ }^{\circ}\text{C}$ reveal the presence of micrometric crystallites.

In particular, for the sample grown at $220\text{ }^{\circ}\text{C}$, the shape of the crystallites can be distinguished by using optical microscopy. The distinction between the two crystal classes, resulting from the AFM analysis in a previous work [100], can be summarized as “flat, large, and squared” crystallites against “long and narrow” crystallites.

Figure 3.4a,b reports the spectra of the two different kinds of crystallites. The narrow and long ones (needle-like) (**Figure 3.4a**) present the typical phase II spectral markers: the pyrrole stretching position at 1512 cm^{-1} , a very strong macrocycle peak with the nearby satellites all having a comparable intensity, and the higher intensity of the 1434 cm^{-1} peak among the modes of the isoindole stretching. For the flat and square crystallites, different spectra of a crystalline phase have been found (see **Figure 3.4b**). The observed red shift of the pyrrole stretching mode toward $1506\text{--}1509\text{ cm}^{-1}$ is symptomatic of a different structural organization because it is quite different than in the amorphous and phase II structures.

In addition, the macrocycle mode has an intensity comparable to that of the pyrrole stretching one, while the nearby modes have quite different intensities, and finally, the strongest peak of the isoindole region is the one at 1453 cm^{-1} . All this evidence indicates a crystal phase different from phase II. Further studies, possibly including other structural analyses, are needed to better characterize this phase. To have a clear and more detailed comparison between the crystalline phases and to determine the effect of the kinetic energy of the molecules on film growth, we analyze the spectral shape of the pyrrole peak between 1500 and 1550 cm^{-1} for SuMBD samples, grown at various substrate temperatures, compared with a OMBD samples grown at RT (**Figure 3.5**).

The samples deposited at RT by OMBD present two clearly distinct components (1531 and 1512 cm^{-1}), indicating a strong presence of amorphous phases, but also the coexistence of some crystalline structures.

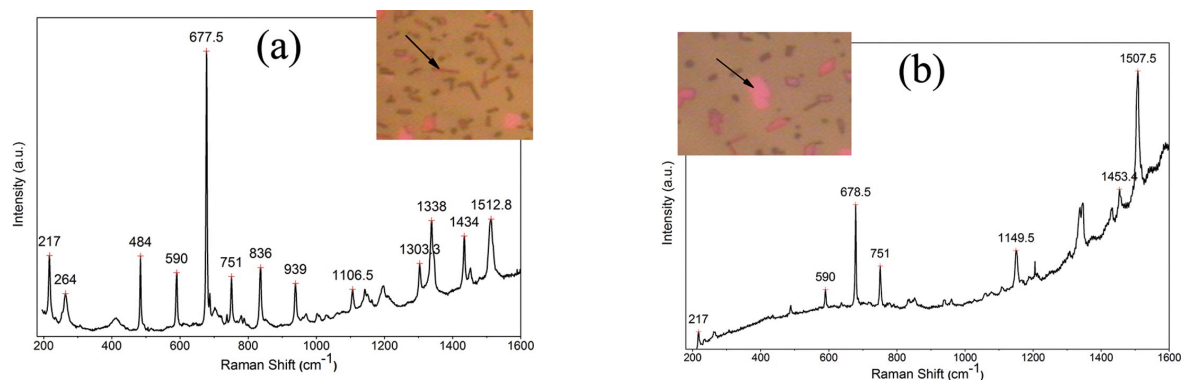


Figure 3.4. Micro-Raman spectra of TiOPc grown on the mica substrate at 220 °C by SuMBD, for crystals of different morphologies shown in the center of the optical images of the insets: (a) a long narrow single crystal and (b) a large flat crystal.

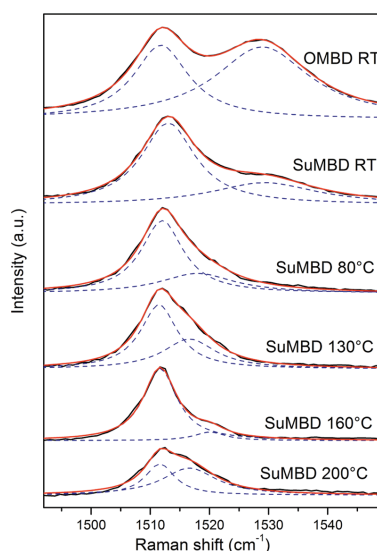


Figure 3.5 Evolution of the pyrrole mode peak for different growth temperatures. The component at about 1530 cm^{-1} is heavily reduced by using the SuMBD technique, and it disappears for the samples grown at higher temperatures.

The SuMBD-deposited samples at RT present also two peaks, but with a very different intensity ratio between them: a very strong peak at 1512 cm^{-1} , characteristic of the crystalline structure, and a shoulder, much lower in intensity, at 1530 cm^{-1} , typical of an amorphous structure. The dominant presence of the amorphous phase for OMBD deposition is in agreement with the literature [131, Saito, #878] and is typical for depositions made in thermodynamic equilibrium. On the contrary, in the SuMBD deposition at RT, the crystalline peak at 1512 cm^{-1} is dominant with respect to that attributed to the amorphous phase (1531 cm^{-1}). For SuMBD deposition at higher temperatures, 130-200 °C, the peak at 1531 cm^{-1} is completely absent, and if we analyze the underlying components obtained by a specific fitting procedure of the 1512 cm^{-1} peak in **Figure 3.5**, we can observe a shoulder present at 1516-1518 cm^{-1} in all these spectra (see **Figure 3.5**). Keeping into account the fact that, for completely crystalline spectra, there is a total absence of the 1531 cm^{-1} peak (amorphous phase), this shoulder could be associated with the minority presence of a different crystalline phase or to a distortion of some crystallite structure in phase II.

Figure 3.6 shows the TiO stretching peaks in the spectral range of 935-955 cm^{-1} , comparing a typical OMBD spectrum with SuMBD spectra for different growth temperatures. The presence

of a peak at 949 cm^{-1} is characteristic of the amorphous structure, while the peak at 939 cm^{-1} is characteristic of the crystalline phase II. In the OMBD deposition at RT, the evidence of a strong 949 cm^{-1} peak confirms the relevant presence of amorphous character.

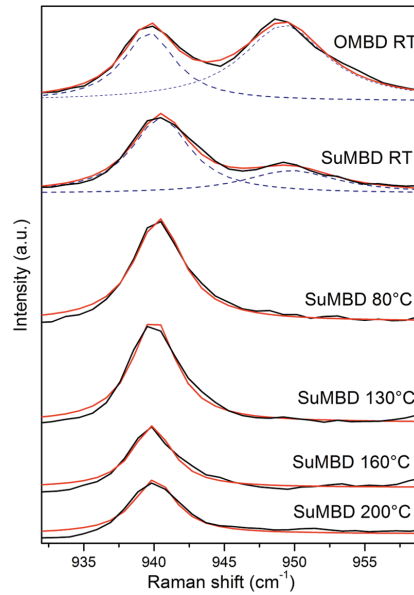


Figure 3.6 Evolution of the TiO mode peak for different growth temperatures. The component at 949 cm^{-1} is heavily reduced by using the SuMBD technique, and it disappears for the samples grown at higher temperatures.

SuMBD-deposited samples at RT present a much lower intensity in the 949 cm^{-1} peak, confirming the crystalline dominance of the structure. When the substrate temperature is increased to 80°C , the SuMBD-deposited samples do not present any more an evidence of the 949 cm^{-1} peak, and the same behavior is valid for the higher deposition temperatures.

Figure 3.7 reports the dependence of the fwhm versus the substrate temperature of the 678 cm^{-1} macrocycle breathing mode, both for the SuMBD TiOPc and for RT OMBD films over different substrates (mica, Si/SiO₂, quartz).

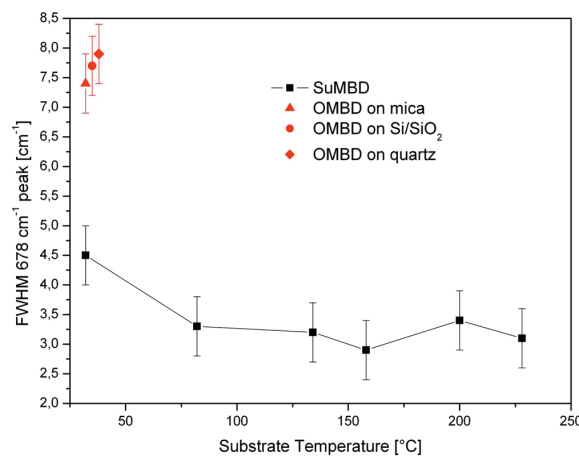


Figure 3.5. FWHM of the macrocycle breathing mode (MBM) at 678 cm^{-1} for TiOPc thin films grown by SuMBD at increasing substrate temperatures on mica (black) and for films grown by OMBD at RT (red) on different substrates (mica, Si/SiO₂, quartz).

The OMBD films grown close to RT show an FWHM that is independent, within the experimental errors, from the substrate over which

they are grown. The significantly larger FWHM of the 678 cm⁻¹ peak for the OMBD films confirms their amorphous character, whereas the SuMBD RT samples show a quite lower FWHM, indicating a dominant crystalline character, which is also confirmed by the growth by SuMBD at higher temperatures, also reported in **Figure 3.7**. The temperature dependence toward a narrower FWHM observed for SuMBD growth (see **Figure 3.7**) is consistent with a trend of increasing crystallinity with respect to RT.

Conclusions

The growth of TiOPc thin films on mica has been studied as a function of the substrate temperature, exploring the ability to control polymorphisms by supersonic molecular beam growth. Our combined AFM and micro-Raman study demonstrates that this is a viable and promising approach. In particular, we prove that the growth of polycrystalline films is achievable in temperature ranges where conventional techniques produce only amorphous films. However, the crystallinity of the deposited films as a function of substrate temperature exhibits a quite different trend for TiOPc on mica, with respect to the behaviour previously observed for a quartz substrate [137]. On this last substrate, a good crystallinity of SuMBD grown films occurs at high substrate temperatures (>200 °C), as expected. A “forbidden range” (150 °C > T > 50 °C) is present for lower temperatures, giving dominant amorphous phases, while a surprising increase of crystallinity occurs for substrate temperatures even lower (<50 °C). On a mica substrate, instead, the structural evolution appears as a monotonic increase of crystallinity for substrate temperatures just above RT. Even for RT deposition, the amorphous fraction appears strongly reduced with respect to the OMBD reference sample, grown at the same temperature. For higher substrate temperatures, the analysed Raman markers do not reveal any appreciable presence of the amorphous phase. This different structural evolution demonstrates the relevance of the substrate characteristics. This is possibly due to a sort of “registry” effect caused by the ordering interaction of the mica surface, which is, of course, absent in the quartz substrate, where only the molecular self-assembly takes place. Besides this basic description, some additional questions arise, however, about the TiOPc structures growing during the SuMBD deposition: a weak spectral contribution at about 1516-1520 cm⁻¹ is observed for deposition temperatures where the amorphous component of the film is no longer present (>80 °C), which could be associated with the formation of a phase with a strained structure.

Moreover, in samples grown on high T substrates, microcrystals having different morphologies and different Raman spectra can be found in the same film. The ones with a needle-like shape show the characters of well-known phase II, while large and flat microcrystals clearly present a different phase. The low-frequency value of the pyrrole stretching mode suggests a relaxed structure, with a minimum amount of strain. Obviously, more sophisticated structural investigations, with microscopic resolution, are necessary to gain a more complete understanding.

Finally, a combination of the micro-Raman spectroscopy and the AFM roughness analysis provides quite strong evidence for the presence of a very thin wetting layer, deposited on mica in the regions between the crystal grains. This layer could be very interesting in the prospective of innovative device applications. The observed ability to grow controlled crystalline phases in organic TiOPc thin films paves the way to an improved class of organic field effect transistors, for a molecule that has already been shown to be particularly well-suited for organic electronics [144].

The ability to improve crystalline quality at temperatures close to RT opens new perspectives for fully organic devices, in particular, over plastic substrates. In fact, as shown here, tuning the energy of the incoming molecules up to a hyperthermal regime results in a viable and effective way to control the structure and morphology of the films directly during growth.

We brought here strong indications that such control can be pushed up to the point of making a specific crystalline phase to become dominant in the growth process. This has been already shown to

be very important to producing TiOPc films with the desired electronic properties and high carrier mobility in particular [144]. Moreover, these particular properties are useful in organic spintronic applications [122], where the structural order and the p-orbital conjugation are crucial for the final performance of the device. Our aim is, therefore, now to implement such concepts in the fabrication of TiOPc-based OFETS, including flexible plastic substrates.

3.2. Ambipolar organic thin film transistors based on pentacene derivatives.

In this section the results obtained with a pentacene derivative molecule, the 2,3-dicyano-6,13-bis-(triisopropylsilylethynyl)pentacene (2,3-CN2-TIPS-Pn) have been reported. This work has been done in collaboration with the Polytechnique de Montréal, where the molecule has been synthesized and the OFET device realized with ambipolar conductive properties.

My contribution to this work regarded the analysis by the Maud software of the XRD spectra of the molecule, collected at the synchrotron radiation source in Trieste. The ambipolar charge transport observed in this material is well balanced; the values of the hole and electron mobility are both about $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$. The position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 2,3-CN2-TIPS-Pn with respect to the work function of the Au charge-injecting electrode and the arrangement of the molecules in the film, as deduced by grazing incidence x-ray diffraction analysis, contributes to explain the charge transport properties of 2,3-CN2-TIPS-Pn films.

We have already mentioned that organic thin films transistors (OTFTs) are interesting devices for low-cost and flexible electronics [27, 145]. Among the large number of organic semiconductors employed in OTFTs, pentacene is one the most studied molecule, having a hole mobility (μ_h) as high as $\sim 6 \text{ cm}^2/\text{Vs}$ [22]. Soluble pentacene derivatives for OTFTs have been demonstrate, with 6,13-bis(triisopropylsilylethynyl) exhibiting $\mu_h > 1 \text{ cm}^2/\text{Vs}$ [146]. At present, there is an intense research effort to demonstrate ambipolar OTFTs based on soluble pentacene derivatives [20, 147, 148]. Ambipolar OTFTs, relevant for complementary logic and light-emitting transistors, require injection of holes (h^+) and electrons (e^-), which translate into a good matching between the energy levels of the organic semiconductor and the work function of the electrodes used for h^+ and e^- injection [149-151]. Since this matching is rarely observed, ambipolar OTFTs are usually based on blends or heterostructures (bilayers) at different p- and n-type semiconductors [22, 152]. In pentacene derivatives that already possess good hole transport properties, substitution with electron withdrawing groups, such as nitrile group, is expected to lower the position of the Lowest Unoccupied Molecular Orbital (LUMO) energy level. In turn, this is expected to promote electron transport in bottom contact OTFTs, where metals with high work functions are typically used for source/drain electrodes.

Here, I report about OTFTs based on solution processed 2,3-dicyano-triisopropylsilylethynyl-pentacene (2,3-CN2-TIPS-Pn), a cyano substituted pentacene based on 6,13-bis TIPS-Pn [153, 154]. The molecular structure is shown in **Figure 3.8**. The transistor shows ambipolar transport properties, which are in agreement with predictions from theoretical calculations [155]. The film forming properties of 2,3-CN2-TIPS-Pn have been investigated, and the structure properties of the resulting films has been characterized by atomic force microscopy (AFM) and grazing incidence x-ray diffraction (GIXRD). The ambipolar properties and the AFM analysis have been carried out at the École Polytechnique de Montréal, while the GIXRD calculations have been fully performed under this work.

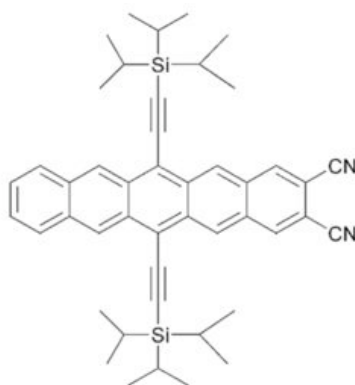


Figure 3.8 Molecular structure of 2,3-CN2-TIPS-Pn molecule.

In the following I report the summary of all the results, already published in *Applied Physics Letters* **99**, 023304 (2011) (Appendix X), and the details of the TIPS-XRD data, collected at the synchrotron radiation source in Trieste, and analysed by the Maud software. The film texture and the molecular packaging obtained for the 2,3-CN2-TIPS-Pn have been correlated with the film charge transport properties.

Experimental

In **Figure 3.9** the device structure is reported: bottom contact / bottom gate 2,3-CN2-TIPS-Pn TFTs were prepared on Au source. The drain electrodes were photolithographically patterned on SiO₂ (195 nm thick and with $C_i = 1.77 \cdot 10^{-4} \text{ F/m}^2$), thermally grown on heavily n-doped Si (resistivity 0.001 – 0.005 Ω/cm), which served as the gate electrode.

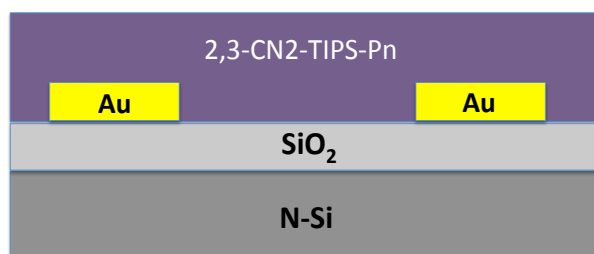


Figure 3.9 OTFT structure in bottom gate / bottom contact configuration.

Prior to film deposition, TFT substrates, cleaned with standard solvent procedures and UV/ozone exposure, were treated with hexamethyldisilazane (HMDS). Films of 2,3-CN2-TIPS-Pn were spin-coated from 10 mg/ml pre-heated chlorobenzene solutions (800 rpm for 15 sec. then 2000 rpm for 45 sec.) and annealed for 1 h at 100° C in a N₂ glove box. The TFT characteristics were measured in a vacuum probe station directly linked to the glove box, using a semiconductor parameter analyser (Agilent B1500A). Film morphology was studied with a Veeco 3100 AFM, in tapping mode, in ambient conditions, using Si cantilevers.

GIXRD images were collected at the XRD1 beamline of the Elettra Synchrotron in Trieste (Italy) at grazing angles from 0° to 13° (after that no diffraction figures were detectable) using a 165 mm CCD detector from MarResearch. Images were analysed by a modified Rietveld method, accounting for absorption and geometrical effects at the specific grazing angle [110].

An AFM image of the thin film is shown in **Figure 3.10**. The solution deposited 2,3-CN2-TIPS-Pn uniformly wets the HMDS modified substrate surface, a key requirement for the application of 2,3-

CN2-TIPS-Pn films into TFT devices.

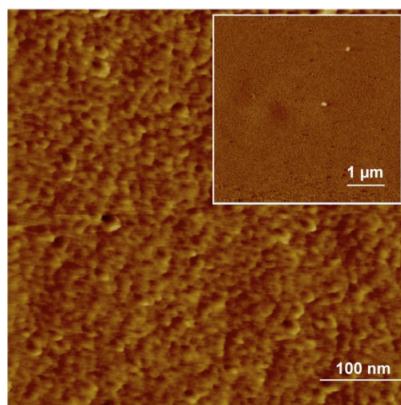


Figure 3.10 AFM topographical image (1 μm x 1 μm) of 2,3-CN2-TIPS-Pn film on HMDS-treated SiO₂. In the inset a (5 μm x 5 μm) zoom of the sample. RMS = 1.56 nm.

Next, in **Figure 3.11** the output (I_{ds} vs V_{ds}) and the transfer (I_{ds} vs V_{gs}) characteristics of 2,3-CN2-TIPS-Pn TFTs are reported. The curves show well-balanced ambipolar transport of the device.

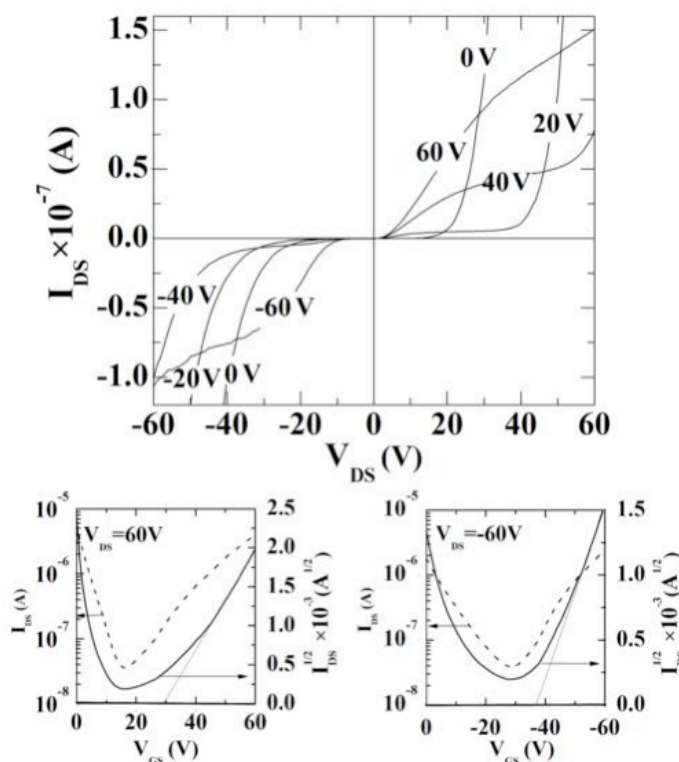


Figure 3.11 TFT characteristics of 2,3-CN2-TIPS-Pn films: output curves (I_{ds} vs V_{ds}) for V_{gs} = 0, 20, 40, 60 V in the p- and n-type regions (top); transfer curves (I_{ds} vs V_{gs}) at saturation for V_{ds} = 60 V (bottom left); transfer curves at saturation for V_{ds} = -60 V (bottom right). The ratio of channel width/channel length is 10 μm / 1880 μm .

The value of the mobility, as extracted from the transfer curves at saturation, was $\sim 2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for e^- and h^+ . The threshold voltage, V_{T} , was 29 and -36.5 V, respectively, for e^- and h^+ transport. Ambipolar transport in 2,3-CN2-TIPS-Pn can be explained, at least partially, by observing the position of the LUMO and highest occupied molecular orbital (HOMO) of 2,3-CN2-TIPS-Pn with respect to the work function of the Au injecting electrode ($\Phi_{\text{Au}} \sim 4.4 \text{ eV}$) [156]. The LUMO and HOMO levels of 2,3-

CN2-TIPS-Pn, deduced by cyclic voltammetry measurements, are located at about -3.63 and -5.44 eV¹, leading to estimated injection barriers of about 0.77 eV for e⁻ and 1.04 eV for h⁺. Clearly, e⁻ injection from Au is more favorable for 2,3-CN2-TIPS-Pn than for pentacene, where the injection barrier is about 2.1 eV high. At the same time, the h⁺ injection barrier, although larger than for pentacene, is low enough to permit h⁺ injection, thus offering the possibility to observe ambipolar transport [157]. We would like to emphasize that in 2,3-CN2-TIPS-Pn OTFTs, the ambipolar transport is balanced, differently to what frequently observed in ambipolar OTFT where h⁺ and e⁻ mobility can differ by a few orders of magnitude.

It is well recognized that the thin film structural properties play a primary role in establishing film transport properties [158, 159].

To gain insight into the structure and the molecular arrangement in the crystalline domains forming the polycrystalline films, we carried out a GIXRD analysis (**Figure 3.12**).

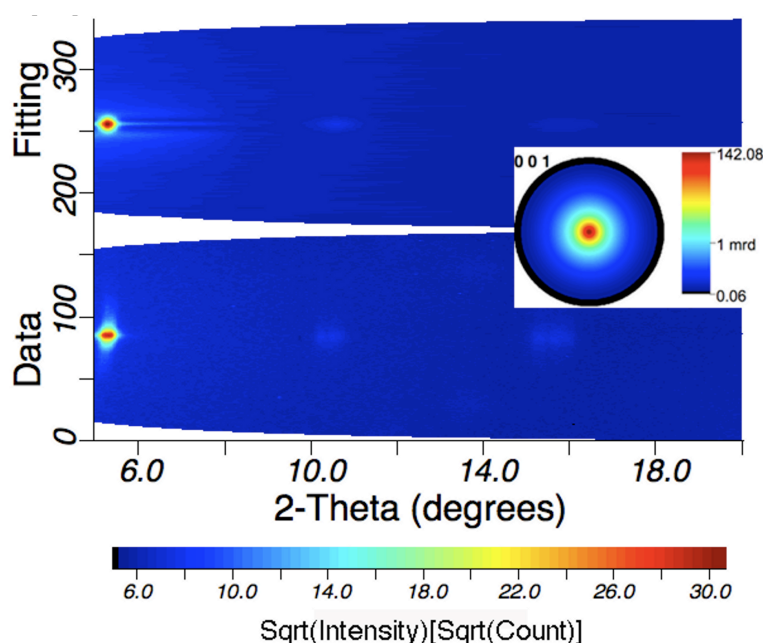


Figure 3.12 Rietveld fit of one of the x-ray diffraction images collected at an incident angle of 2°. The principal spot is due to the (001) diffracting plane parallel to the sample surface. The bottom 2D pattern represents the experimental data; the recalculated pattern is on top. The three spots (001/002/003 reflections) are aligned in the diffraction plane normal to the sample surface. As we move out of it (moving vertically in the image), the strong texture causes a rapid decrease of the intensity. The inset reports the recalculated pole figure showing the strong 001 orientation (mrd: multiple of random distribution, values in log scale).

The collected images were converted into 2D patterns. To obtain the phase content and texture, we further refined the images by use of the Rietveld methodology [110]. A triclinic structure was found

¹ Electrochemical analyses were performed with a BAS i-Epsilon voltammetric analyzer in a three electrode cell configuration consisting of silver wire as a pseudo reference electrode, platinum button as the working electrode, and platinum wire as counter electrode, using a 0.1M solution of tetrabutylammonium hexafluorophosphate in dichloromethane and a scan rate of 50 mV/s. Oxidation and reduction potentials were calibrated with respect to ferrocene/ferrocenium redox couple.

with a strong **fiber texture** perpendicular to the film surface with (00l) planes aligned parallel to it. From the texture and molecule orientation, we found that the pentacene backbone in the cell is located in a plane perpendicular to the substrate and that the long axis of the pentacene backbone is aligned parallel to the surface (**Figure 3.13**).

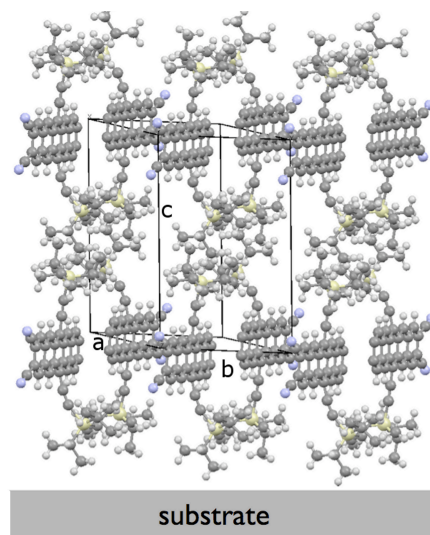


Figure 3.13 Proposed molecular arrangement of 2,3-CN2-TIPS-Pn on the substrate.

The TIPS groups are pointing towards and away from the substrate. The observed molecular arrangement forms a highly semiconducting channel that is favorable for charge transport between source and drain electrodes [160] thus contributing to explain the good performance of 2,3-CN2-TIPSPn TFTs.

In conclusion, we demonstrated solution deposited ambipolar TFTs based on 2,3-CN2-TIPS-Pn films with balanced e^- and h^+ mobility on the order of $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$. The charge transport properties of 2,3-CN2-TIPS-Pn films show the effectiveness of TIPS-Pn functionalization with cyano e^- withdrawing groups to promote e^- transport while maintaining equivalent h^+ transport. GIXRD characterization of the films revealed a favourable arrangement of the molecules in the TFT channel.

XRD texture analysis

In the following a detailed analysis of the XRD diffraction patterns has been reported, as analysed by the software Maud. This is the main contribution I have carried out to this work.

The TIPS thin films were measured at Elettra at the Synchrotron Radiation Source in Trieste (Italy), with a wavelength of $1.54 \text{ \AA}$. Images were recorded at 13 different omega tilt angles, rotating the sample around the axis normal to the beam in the same plane of the sample in 1 degree increments. A LaB_6 sample was used for the sample calibration in transmission mode, and then the 2-Dim images of thin films have been collected in reflection mode. The diffraction images of LaB_6 have been analysed by Maud in order to find the right instrument calibration parameters. **Figure 3.14** shows an example of diffraction image collected for the TIPS molecule. Intensity variations along Debye rings reveal already at this stage the presence of a texture.

The image data were entered into the program Maud, following a procedure already described in the Experimental Section (Chapter 2). In this case $180 \times 13 = 2340$ spectra were used for the refinement. The LaB_6 instrument parameters have been used as starting parameters, while the background has been modelled by an interpolated function. The sample has been modelled with a single layer of 65nm

with one phase. The starting crystallographic parameters has been used from the file .cif (Crystallography Information File) retrieved from *Org. Lett.*, 2005, 7 (15), 3163–3166 (“Synthesis and Characterization of Electron-Deficient Pentacenes”, Christopher R. Swartz, Sean R. Parkin, Joseph E. Bullock, John E. Anthony, Alex C. Mayer and George G. Malliaras), with a triclinic cell symmetry and space group P-1. The starting parameters being: Cell_length_a = 7.86230 (Å), Cell_length_b = 15.1731, Cell_length_c = 17.1191, Cell_angle_alpha = 74.7278, Cell_angle_beta = 85.9386, Cell_angle_gamma = 84.9098. The following (**Figure 3.15**) is the plot of the pentacene-modified molecules as plotted from the .cif file by the Mercury program.



Figure 3.14 Example of CCD raw data XRD image collected at the synchrotron facility

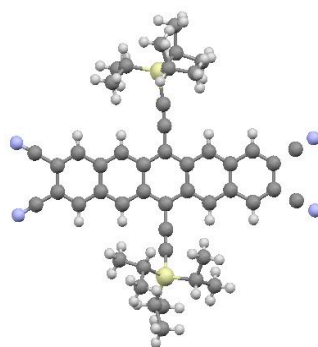


Figure 3.15 Structure of the TIPS molecule plotted by the Mercury program.

A first run of refinement used the following refinable parameters:

1. Omega sample orientation
2. Chi sample orientation
3. Incident intensity
4. Instrument angular calibration center x
5. Caglioti
6. Omega broadening

The corresponding parameters for all the other spectra have been set equal to the same values in the first one. Only the c-axis of the loaded phase has been set as refinable parameter.

Then a texture has been introduced and refined using a Standard Function with a fiber texture component. The Orientation Distribution Function is expressed by the pole figure, reconstructed in Maud. One single phase of the modified-pentacene has been identified, with a triclinic structure. The values of the c-axis parameters are after refinement is $c=17.27903 \text{ Å}$ ($c = 17.1191$ is the starting value), while the others parameters have been not refined. Modelling the texture with a fiber component normal to the surface sample and inclined by $(\text{Theta}, \text{Phi})=(14.21862, 250.70917)$ respect

to the crystallographic axis, we have found that for the single phase of the material, a strong fiber texture result, leading on the (a-b) plane of sample surface and more or less aligned along the 'a' axis. The molecule orientation in the cell presents the five benzene rings positioned horizontally on the (a-b) plane, while the lateral groups are along the c axis. This means that the lateral groups of (Si) result linked to the substrate and the orientation of the pentacene backbone is substantially different respect to pentacene non-modified films.

Crystallographic axis

Due to the strong texture and small thickness of the film (about 100nm) only information about their c-axis could be inferred, that is estimated after refinement to be about 17.28 Å (Angstrom).

Angular spread of grains

The angular spread of the grown film, telling the average misalignment between grains, has been expressed by the FWHM (Full Width at Half Maximum) of the orientation distribution simulated by a Gaussian function. This parameter has been used as a fitting parameter during the fitting of the diffraction images. CN film show a stronger alignment of FWHM=7.54 degrees. The crystallite size after refinement is **933.16565 Å**, and the distortions of the single grain is estimated very low: root Mean Square (rms) microstrain=0.0005.

2-dim plot

The figure below is the two-dimensional representation of one of the spectra collected at low angle. The reconstructed plot after fitting look good and the fitting parameters show a good level of convergence. In **Figure 3.16** (in the next page) the 2-Dim multiplots are reported at the varying of the tilting angle ω .

In **Figure 3.17** the reconstructed polar figure from fitting are reported as plotted by Maud. Because the normal to the substrate corresponds to the center of the pole figure, the peak at the center of the 001 pole figure clearly indicated the texture of film is almost normal to the sample surface. The very low value of the minimum (0.06 mrd) indicates that only the 6% of crystallites are randomly oriented.

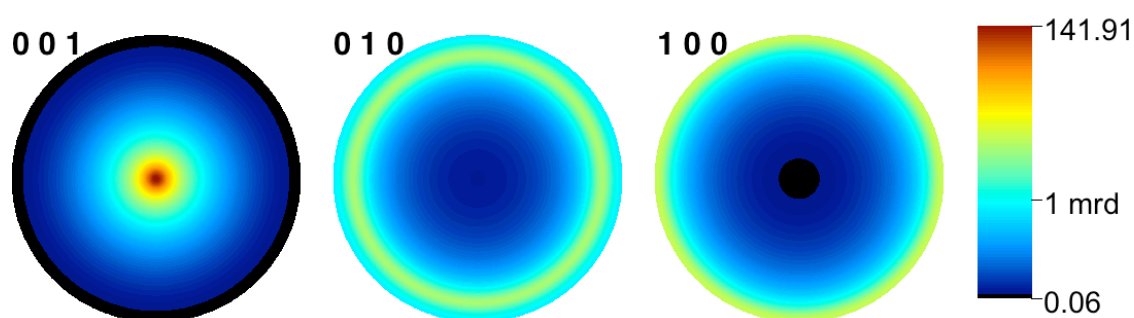


Figure 3.17. Reconstructed pole figures from fitting as plotted by the Maud software. The peak at the center of the 001 plane is clearly visible.

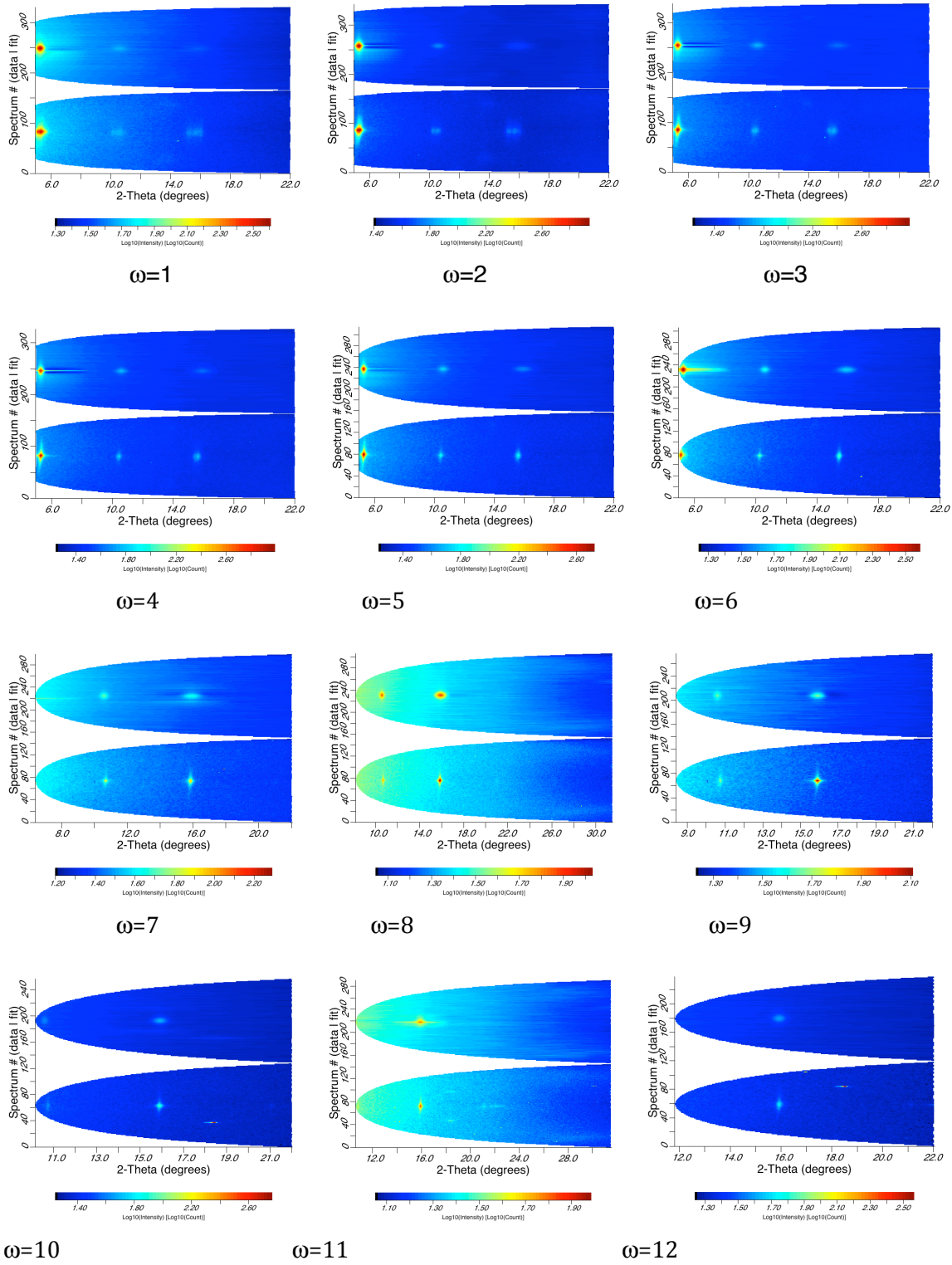


Figure 3.16 2-Dim multiplots at the varying of the tilting angle ω of the grazing incident analysis

3.3. XRD analysis of Tetracene thin film

In this experiment, the role of organic dielectric layers in determining/influencing the properties of polycrystalline tetracene films for application in OFETs, has been reported. The tetracene films were vacuum sublimed on six different dielectric substrates, namely bare SiO₂ (reference substrate), octadecyltrichlorosilane (OTS), hexamethyldisilazane (HMDS), paryleneC, polystyrene (PS) and polymethylmethacrylate (PMMA), all on SiO₂ (Figure 3.18). The effect of these different substrates on the organic film morphology has been investigated [161-163]. The substrates were kept at room temperature and the pressure inside the vacuum chamber was of 2.5×10^{-6} Torr. The objective is to understand the factors influencing charge transport and to find the correlations between the chemical and morphological properties of the gate dielectric (surface energy, surface roughness, surface chemistry, and dielectric constant), semiconductor film morphology and structure, and transport properties. We have found that all polymer dielectrics, in addition to the HMDS one, yield an increase of hole mobility of tetracene films with respect to the untreated SiO₂ substrate. The better performance has been achieved with the PS and PARY C dielectrics, as already reported [164]. Both AFM and GIXRD analysis have been carried out: AFM images of TC-films showed that the island density, size, shape, and substrate coverage, strongly depend on the substrate, while XRD data analysis give us information on the crystal and micro-structure of tetracene films deposited on the different gate dielectrics. In the following I am going to speak about the XRD analysis in more details.

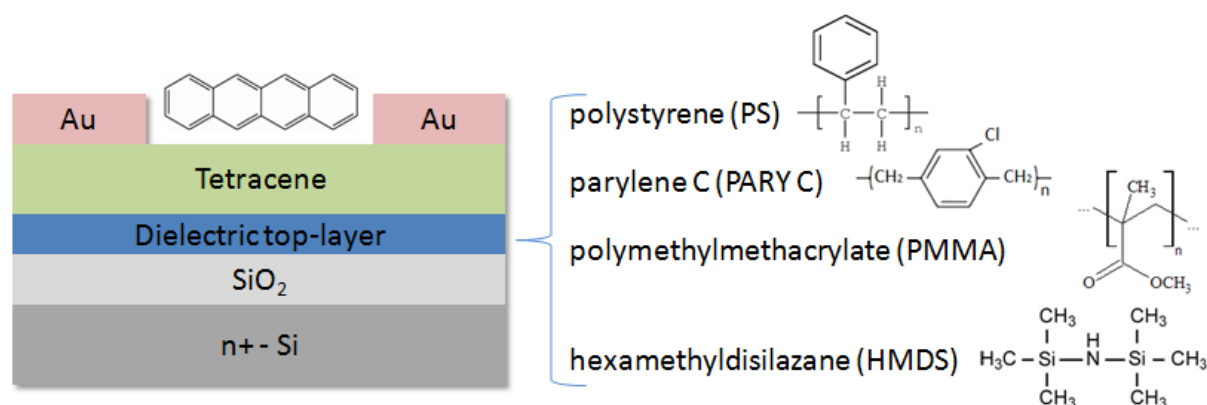


Figure 3.6. Left: Structure of the tetracene thin film transistors (with Au electrodes) and the samples for AFM and GIXRD studies (without Au electrodes) used in this work. Right: Molecular structures for the polymers and HMDS.

Tetracene-based p-type OFETs have been successfully fabricated, employing all the aforementioned dielectric layers, and measured the respective hole FET mobility. OFETs were fabricated in the bottom gate – top contact geometry depositing the source and drain electrodes by thermal evaporation of gold through a metal shadow masks. The hole mobility varies over more than one order of magnitude, depending on the dielectric substrates, ranging between $1 \cdot 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (bare SiO₂) and $2 \cdot 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (PS). The mobility value obtained on PS-based OFETs is the highest reported up to now for polycrystalline tetracene films. The interesting result is the remarkable variability of the hole mobility ascribed to different aspects of both the dielectric layers and the overgrown tetracene films.

The properties of the dielectric substrate surface influence the nucleation and growth process and consequently the final films' morphology and structure. Hence, the effect on film growth/morphology and charge transport had to be understood. The nucleation and growth process was investigated from the early stages of growth up to complete substrate surface coverage by means of ex-situ AFM. The growth and the morphology of the tetracene films were found to depend significantly on the dielectric

layer properties. Since the early stages of the growth, islands are formed with different densities, shapes and sizes. The dielectric substrate surface energy was observed to play a role in determining the islands density and shape. The dielectric substrate with the lowest surface energy, i.e. OTS treated SiO₂, presented the highest density of highly three-dimensional islands. We observed that treating the SiO₂ surface with OTS promotes the interfacial nucleation thus leading to increased substrate surface coverage, compared to bare SiO₂. However, the highly three dimensional shape of the tetracene islands on OTS can induce the formation of detrimental grain boundaries during coalescence. The trade-off between these two aspects could explain the moderate increase in hole mobility associated with the OTS treatment of the SiO₂ surface. On HMDS treated SiO₂, flat and large islands grow in a quasi “layer-by-layer” mode. This is expected to generate large and well-interconnected crystalline grains at the dielectric/semiconductor interface, where the charge transport occurs. The FET mobility is moderately higher than in the case of bare SiO₂ and OTS treated SiO₂. However, severe bias stress effects limit the performance of the corresponding OFETs. Tetracene thin films grown on PMMA show a hole FET mobility significantly lower compared to parylene C and PS. A Power Spectral Density analysis of the 50 nm thick tetracene films vacuum sublimed on the different dielectric substrates, revealed that the average size of tetracene grains on PMMA is significantly smaller than on the other polymer layers. Tetracene films on PS show low RMS roughness and the earliest complete substrate surface coverage: at 10 nm of nominal thickness the islands appear homogeneous in their shapes and tightly packed to each other. Well interconnected and ordered grains in the early stages of the growth represent a possible reason for the high hole FET mobility of tetracene on PS. The elaboration of the GIXRD data obtained from tetracene thin films deposited on the different substrates shed light on the possible correlation between the charge transport and film structure. This experiment has been carried out in collaboration with the École Polytechnique de Montréal, where the devices have been realized and characterized. Under this project I have been devoted to the XRD analysis of the thin film samples, that is reported in details in the following.

3.3.1 Texture analysis.

Tetracene thin films deposited on different dielectric surfaces (SiO₂, PS, PMMA, Parylene C, OTS, HDMS) have been characterized by GIXRD at the Synchrotron radiation source of Trieste, collecting diffraction pattern at different grazing incident angles in reflection mode. The analysis of the XRD diffraction pattern have performed trough the Maud software, based on the Rietveld method extended to give information about texture, phases amount, crystallites sizes and r.m.s. microstrains. Details about the algorithms have been discussed in the experimental section in Chapter 2.

Two different phases of the tetracene have been identified, but, due to the strong texture and small thickness of the film, only information about their c-axis could be inferred. The two phases where denominated alpha and beta and their percentage has been quantify in all samples. The beta phase shows a longer c axis respect to the alpha one. A strong fiber texture perpendicular to the sample surface and more or less aligned along the c axis, result for both phases.

Two slightly different types of textures have been discovered: the first one being a centered texture along the sample normal and the second one, a slightly tilted texture respect to the same normal, the former telling us that that the sample has grown *inclined*. Tetracene (TC) films on PMMA and Parylene-C substrates have an inclined texture, while TC films on SiO₂, PS, OTS, HDMS show a centered texture. TC on PMMA and SiO₂ has an amount of beta phase higher than alpha. For the TC film on Parylene C, OTS and HDMS the phases are equally present. TC film grown on PS substrate has the highest amount of Alpha phase: this could be correlated to the highest mobility recorded. The angular spread of the grown film, telling the average misalignment between grains, has been expressed by the FWHM (Full

Width at Half Maximum) of the orientation distribution simulated by a gaussian function. This parameter has been used as a fitting parameter during the fitting of the diffraction images. TC films on SiO₂ and PS show the stronger alignment (FWHM=1.36 and 2.04 degrees).

The theoretical model (crystallographic information file, .cif) for the alpha phase of the TC structure has been retrieved from the Centre for Molecular and Biomolecular Informatics (CMBI) database (<http://cheminf.cmbi.ru.nl/>); because of the lacking of the beta phase in the database, this has been reconstructed directly in the Maud software starting from the alpha phase crystallographic values. The values of the crystallographic cell for the alpha phase as retrieved from the database are: $a=6.008491$ Å, $b=7.403077$ Å, $c=13.71939$ Å, $\alpha=77.127$, $\beta=72.118$, $\gamma=85.792$.

The symmetry is triclinic and its own space group is P-1. The reconstructed beta Phase of TC has the crystallographic cell values $a=5.954351$ Å, $b=7.899832$ Å, $c=13.003217$ Å, $\alpha=77.127$, $\beta=72.118$, $\gamma=85.792$. We note that $c(\text{alpha})=13.71939$ Å and $c(\text{beta})=13.003217$, so the alpha phase shows a longer c-axis respect to the beta one. The instrument has been calibrated using a LaB₆ single crystal at 130mm of distance from the sample. In the **Figure 3.19a** the 2-dimensional multiplot of the texture analysis performed by the Maud software is reported.

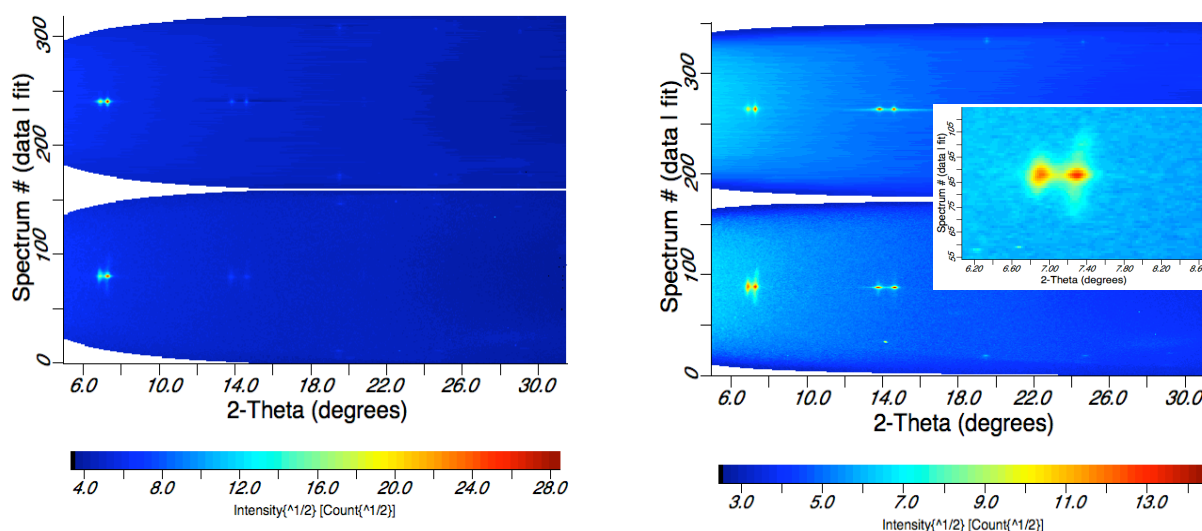


Figure 3.19 (a) 2dim multiplot of tetracene on SiO₂ substrate, at $\omega=4^\circ$ and (b) $\omega=5^\circ$. In the inset the zoom of the main reflection peaks of (001) reflections for alpha and beta phase.

The bottom blue plot represents the experimental data, while the upper one shows the experimental data, fitted respect to a theoretical model previously loaded. In the case of tetracene deposited on SiO₂ substrate, the sample has been analyzed by tilting the omega (ω) angle from $\omega=1$ to $\omega=9$ degrees, for a total of 9 images simultaneously fitted.

We have modeled the sample with a single layer of 65nm having a unknown a priori percentage of alpha and beta phase, for this the initial values have been fixed to 0.5 of volume fraction for both the phase: the Rietveld refinement is then able to quantify the exact amount of phases of the Tetracene film. The **Figure 3.19a** show the 2-dim multiplot acquired at the angle omega $\omega=4^\circ$, while the **Figure 3.19b** shows the same plot acquired at the angle omega $\omega=5^\circ$, that is one degree tilted.

We note that diffraction peaks at about 7 degrees in 2θ . After tilting peaks at 14 degrees in 2θ starts to appear, representing reflections from another crystallographic plane. The homogenous blue background represents a good homogeneity in the crystal distribution in the film. In the **Figure 3.19b** the zoom of the reflections at $\omega=5^\circ$ is reported. The amount of alpha phase found is about 43% while

the beta Phase is about 57%. The Tetracene film deposited on the Silicon Oxide substrate has an amount of beta phase higher than the Alpha Phase.

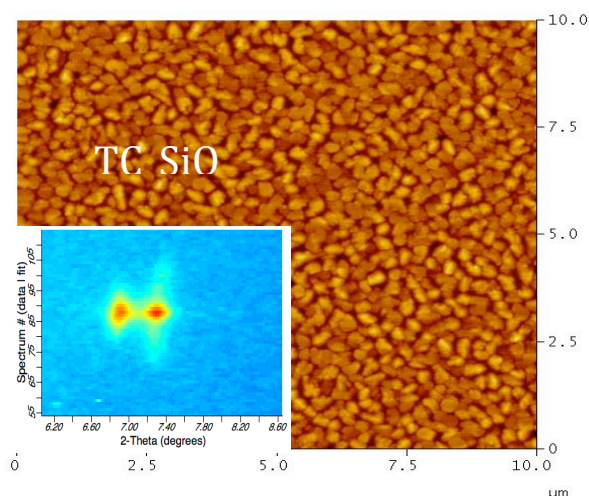


Figure 3.20 AFM of tetracene surface on SiO₂ substrate

The texture of the Tetracene thin film is known once we find the Orientation Distribution Function (ODF). We have so modeled the sample introducing the fiber component for a Fiber Texture: ThetaH and PhiH that are texture angles respect to the crystallographic axes. After refinement we have found the exact values of these components (Theta H=21.5306 and PhiH=214.9324) together with the angular spread (expressed as the FWHM) = 1.3605, representing a strong alignment along the texture direction. A strong fiber texture perpendicular to the sample surface and “more or less” aligned along the c axis, result for both the phases. This is the first type of texture we have discovered: as highlighted in the **Figure 3.19c** (zoom) this is a centered texture that means that the texture is normal to the sample – the film is grown normal to the sample surface. In the **Figure 3.20** the AFM of TC on SiO₂ at 35nm thickness together with the texture image is also reported. It is interesting comparing the AFM image of the surface with the reflection images, a trial sketched in Figure 3.20. Although we cannot inferred direct correlations at this stage of our analysis, it could be nevertheless a very challenging goal to compare images coming from so different experimental techniques.

In **Figure 3.21** the 2-dimensional multiplot of the texture analysis performed by the Maud software is reported for the PMMA substrate: it is shown the 2-dim multiplot acquired at the angle omega ω =4.5° degrees, while in **Figure 3.22** the same plot acquired at the angle ω =6.5° and ω =10.5° is reported. Again we note the two peaks are shown in the plot, at about 7 and 14 degrees, each one separated by the alpha and beta phases; after tilting reflections at 14 degrees in 2 θ starts to appear at 2 θ =6.5°, representing the reflection from another crystallographic plane, becoming dominant at ω =10.5°. The homogenous blue background represents a good homogeneity in the crystal distribution in the film. In the inset of **Figure 3.22b,c** the zoom of the reflections is reported.

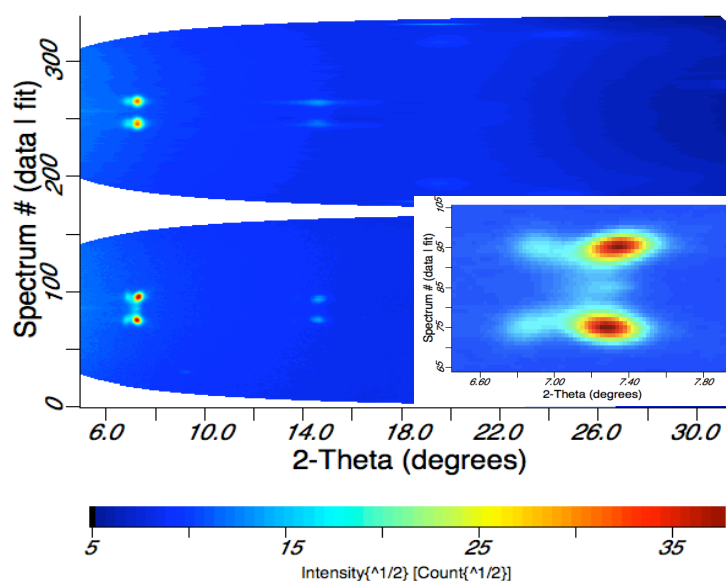


Figure 3.21 2dim multiplot of tetracene on PMMA substrate, at $\omega=4.5^\circ$. In the inset the zoom of the main reflection peaks of (001) reflections for alpha and beta phase.

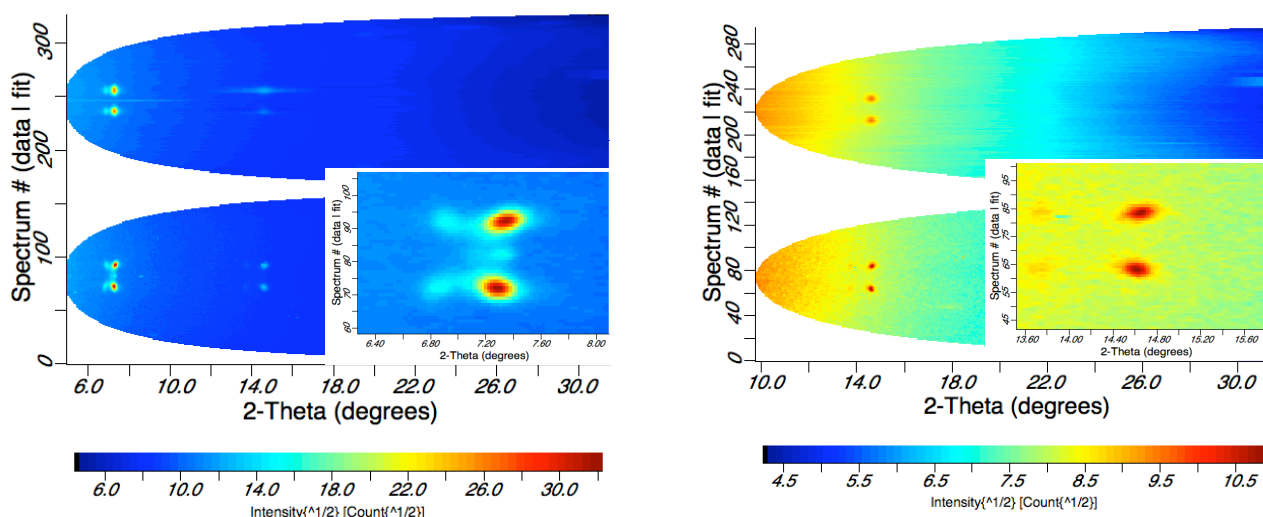


Figure 3.22 2dim multiplot of tetracene on PMMA substrate, at $\omega=6.5^\circ$ (a) and $\omega=10.5^\circ$ (b). In the inset the zoom of the main reflection peaks of (001) reflections for alpha and beta phase.

In these figures is highlighted the kind of texture we have found: that is a tilted texture. The amount of alpha phase found is about 10% while the beta phase is about 90%. For tetracene film grown on the PMMA substrate, we have found the fiber components after refinement ($\Theta_H=16.57$ and $\Phi_H=242$) together with the angular spread (expressed as the FWHM) found to be **5.72**, representing a weaker alignment along the texture direction respect what we found for the SiO_2 case. In this case a strong fiber texture perpendicular to the sample surface and inclined respect the c axis, result for both the phases. This is the second type of texture we have discovered: as highlighted in the **Figure 3.22** (zoom) this is a tilted texture that means that the texture is inclined respect to the normal to the sample – the film is grown inclined respect to the sample surface. The comparison of the PMMA-AFM image with the reflection images is sketched in **Figure 3.23**.

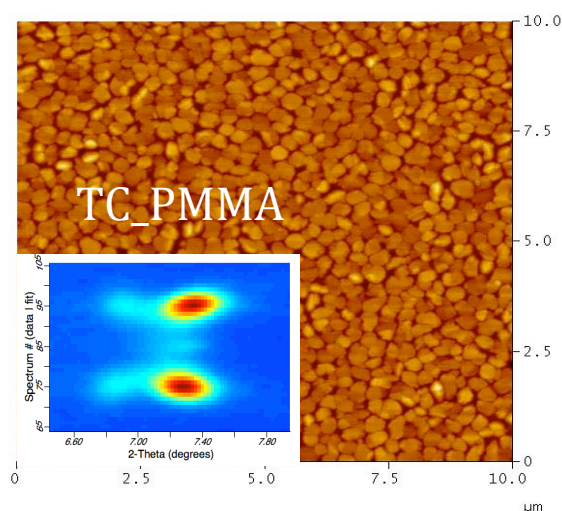


Figure 3.23 AFM of tetracene surface on PMMA substrate

The TC films grown on the Parylene-C substrate are a particular case for which we have found an *inclined* and *split* texture, as shown in the **Figure 3.24**. The texture parameters are $\Theta_H=21.53$, $\Phi_H=234$, $\text{FWHM}=1.36$ and $\text{Alpha}\% = 50$. All the data for all the samples are summarized in Table 1 at the end of this paragraph.

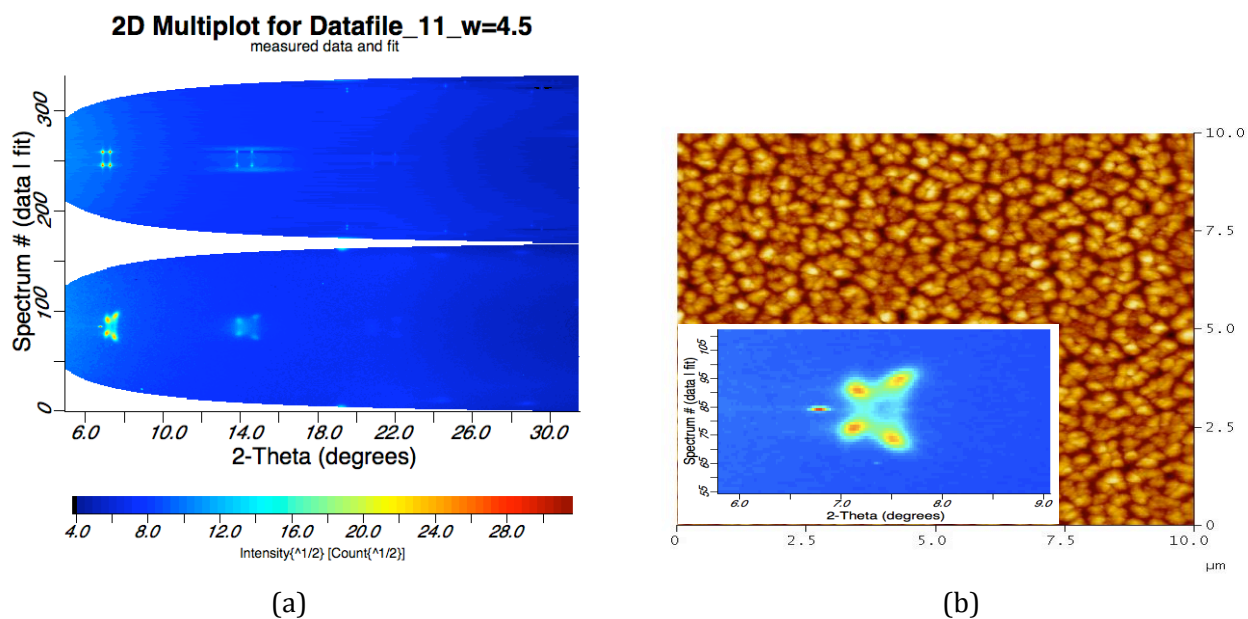


Figure 3.24 (a) 2-dim multiplot of tetracene on Parylene C substrate, at $\omega=4.5^\circ$, in the inset the zoom of the main reflection peaks of (001) reflections for alpha and beta phase. (b) the corresponding AFM image of the surface of TC film.

In **Figure 3.25** the AFM and zoom-reflection images of TC films for all the substrates are summarized. We can see that only tetracene film grown on PMMA and Parylene-C substrates both show an inclined texture. The Parylene C texture more is also splitted. SiO₂, PS, OTS and HMDS are instead a centered texture, that is the film is grown normal to the sample surface.

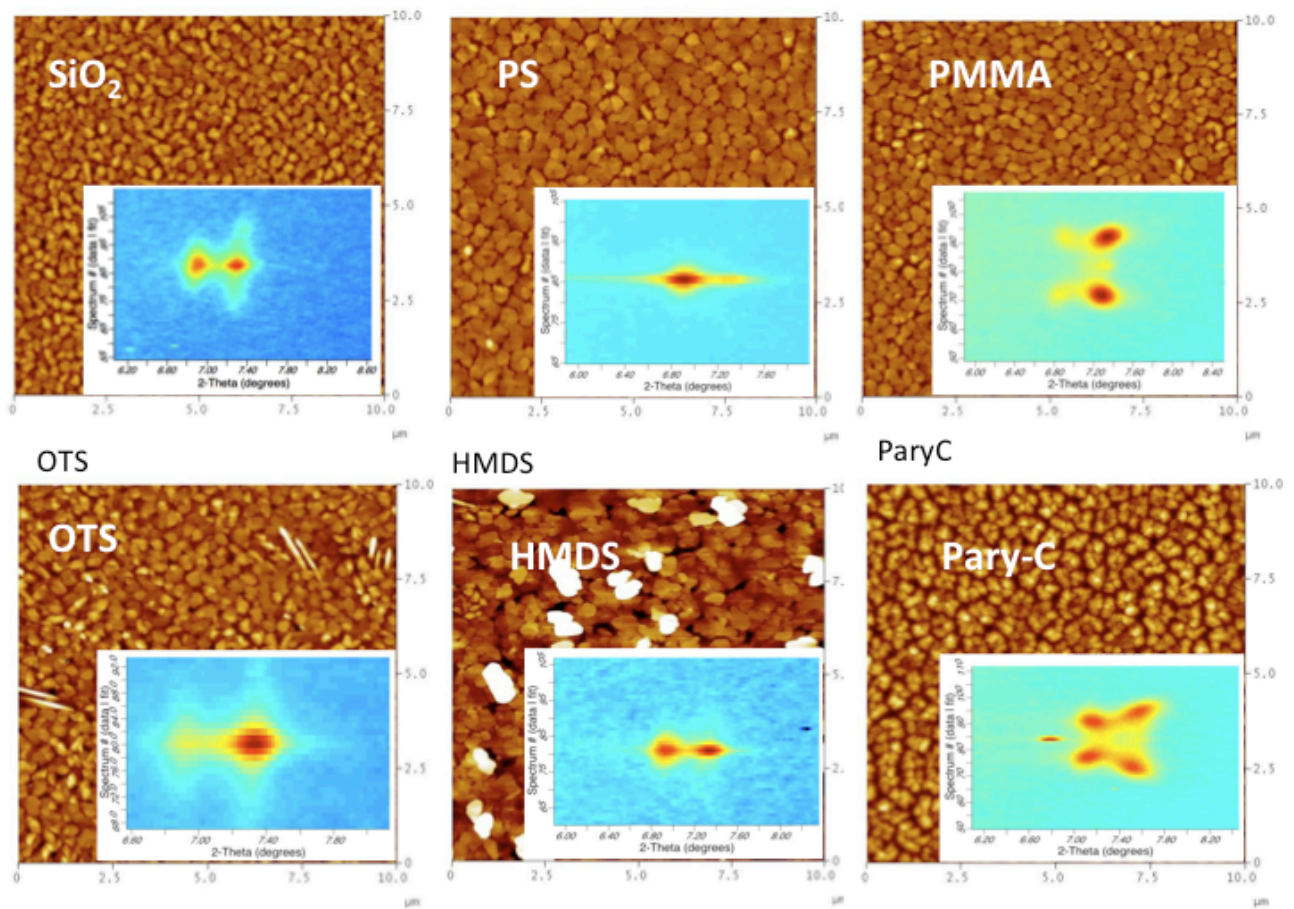


Figure 3.25 The figure with higher mobility (PS, HMDS and Parylene C) show from an AFM analysis a grain structure with higher grain size. PMMA, and SiO₂ show a grain size clearly smaller. The Parylene C is particular because there is a 3-dim grain grown and is completely different from the others: this is the same from the texture analysis, where the texture of Parylene C is completely different from the others.

Finally, in **Figure 3.26** is the representation of the ODF by the polar figures. The center of the polar figure corresponds to the normal to the substrate. For Parylene-C and PMMA we can note a ring at the center instead of a peak. The size of the ring is proportional to the inclination of the texture.

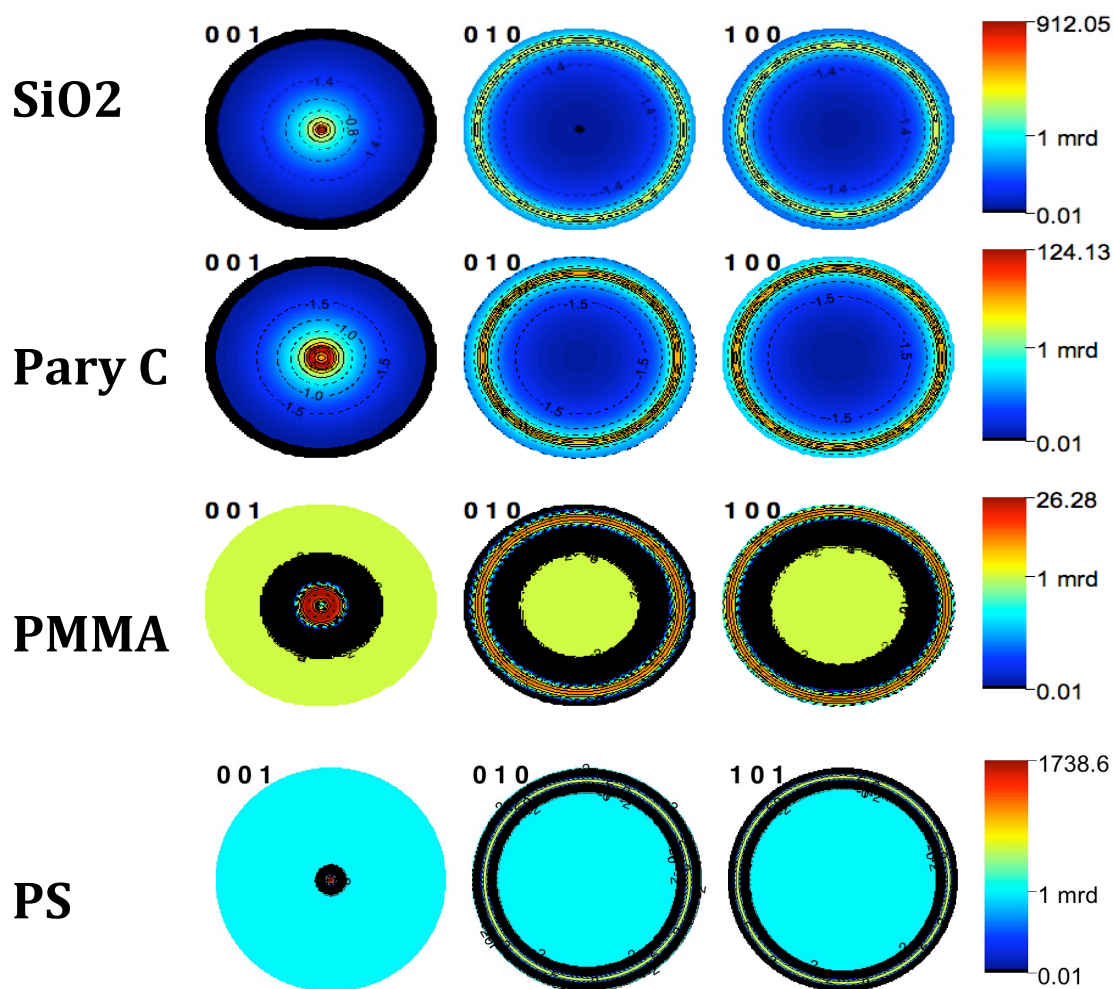


Figure 3.26. Reconstructed polar figures of tetracene film for the different substrates. The inclined texture for Pary-C and PMMA is clearly visible by the ring at the center of the pole figure, instead of a peak.

Correlations

With the AFM analysis, the parameters that have been found characterizing the films are particles area and roughness, while the GIXRD analysis gave information in terms of alpha and beta percentage, fibers components. The correlations between some of these quantities and between them and the OFET mobility are highlighted.

The plot of mobility as a function of alpha phase percentage reveals that the percentage of alpha phase is correlated to the OFET mobility: there is a “trend” of mobility to increase with the alpha phase percentage, the mobility achieving its highest value for the film grown on polystyrene, corresponding to the highest quantity of alpha phase (**Figure 3.27left**).

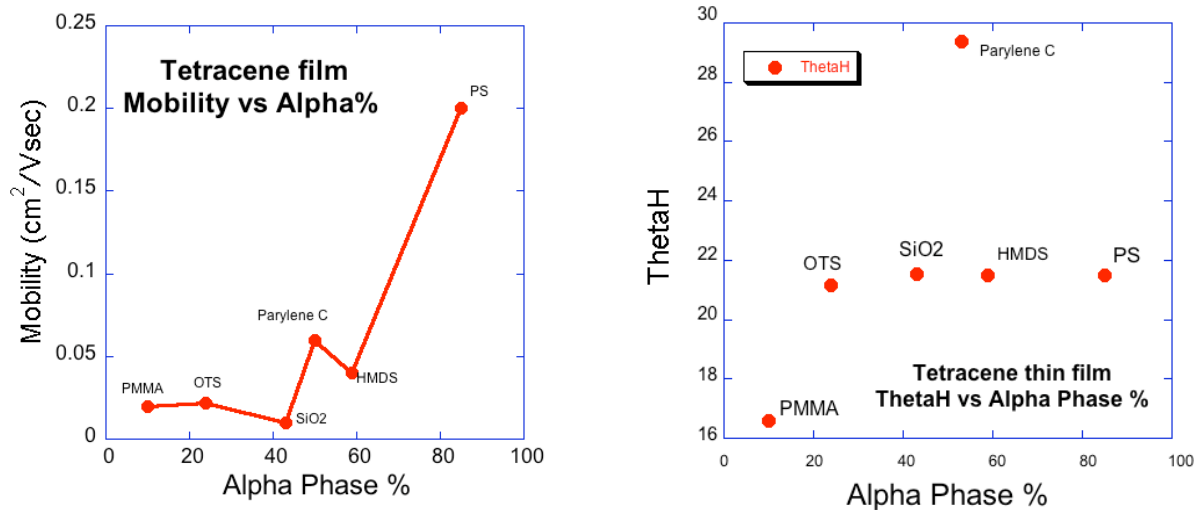


Figure 3.27 Mobility (left) and Theta H (right) as a function of Alpha Phase percentage.

Figure 3.27 (right) reports the it seems there is no significantly dependence of ThetaH on the alpha phase. But, except for the Parylene C, that is a special case of tilted and splitted texture, the PMMA case represents a case of the film with the lowest both alpha phase and ThetaH.

In **Figure 3.28** are plotted the fiber components of texture (PhiH and ThetaH) as a function of OFET mobility.

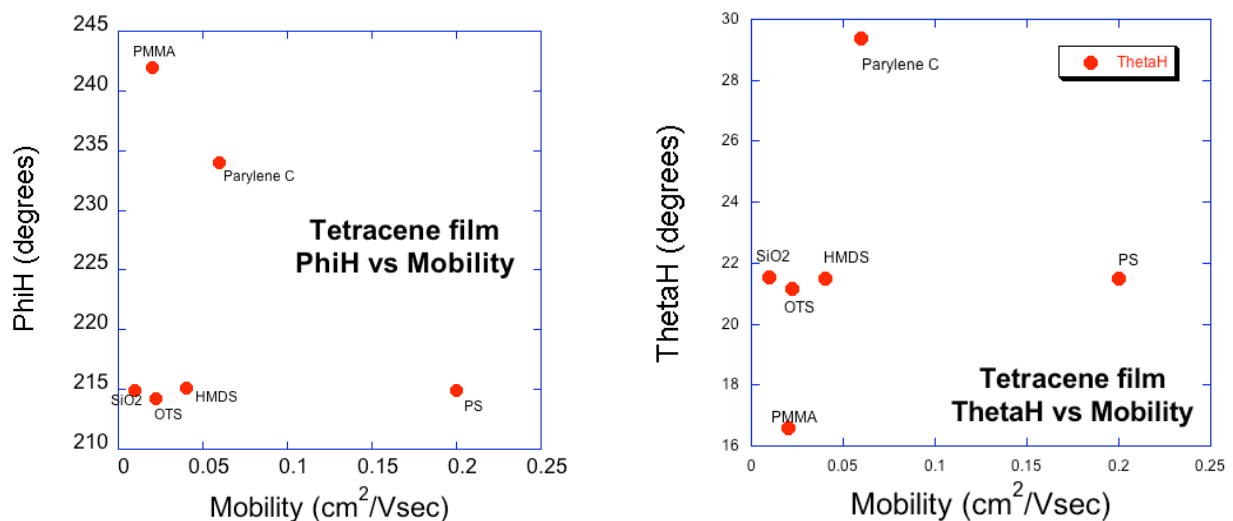


Figure 3.28. Fiber components of texture, PhiH and ThetaH, as a function of the OFET mobility.

In **Figure 3.29** the particle area as a function of the alpha Phase (a) and roughness (RMS) as a function of the OFET mobility are reported. Again the polystyrene substrate, having the higher alpha phase, shows the largest particle area.

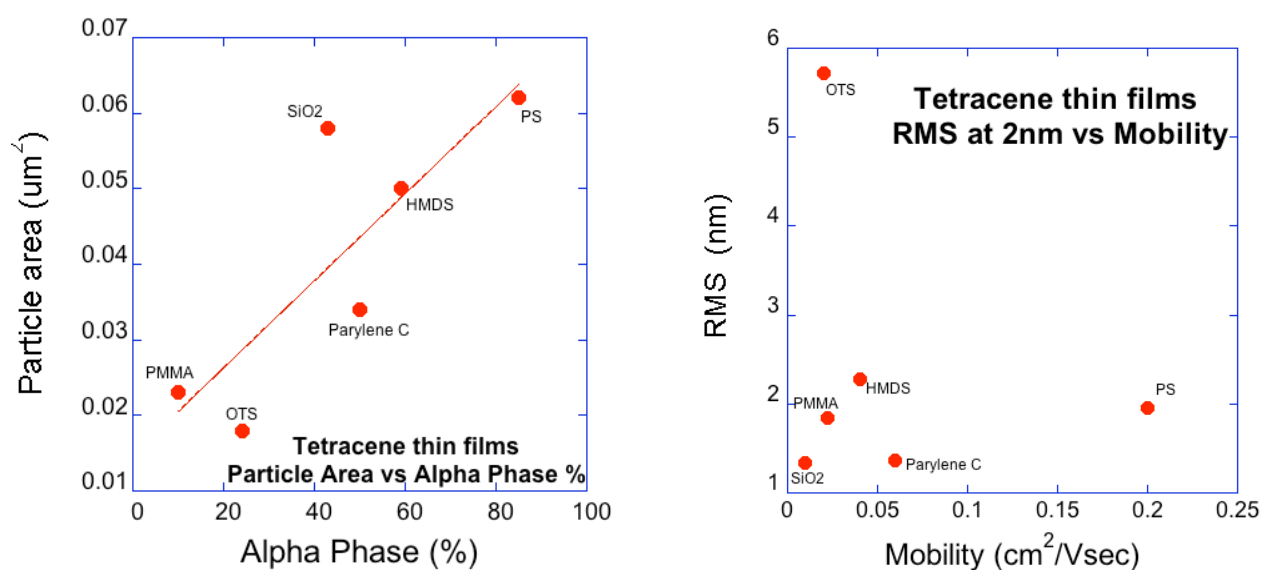


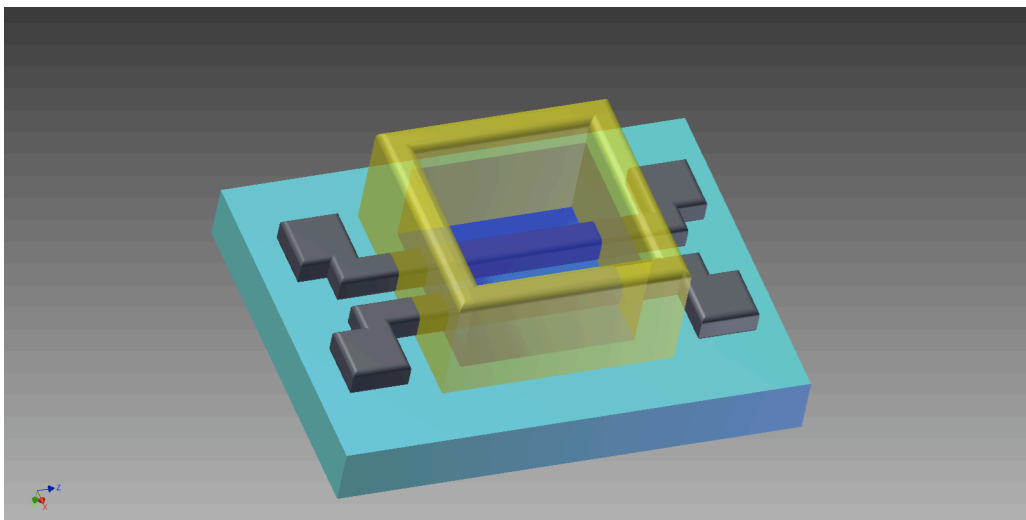
Figure 3.29. Plot of the Particle area as a function of the Alpha Phase (a) and Roughness (RMS) as a function of the OFET mobility.

Finally, the **Table 1** reports a summary of the texture parameters, alpha phase and mobility for each of the different substrates.

	SiO ₂	PMMA	OTS	HMDS	ParyC	PS
Kind	centered	inclined	centered	centered	Inclined	Centered
ThetaH	21.53	16.57	21.15	21.49	29.37	21.48
PhiH	214.9	242	214.19	215.09	234	214.9
FWHM	1.36	5.72	1.856	1.60	7.46	1.93
Mobility	0.01	0.02	0.022	0.04	0.06	0.2
Alpha%	43	10	24	52	53	90

Table 1. Data collected by the XRD texture analysis.

4. Organic Electrochemical Transistors: study of device physics and their application in biosensing.



Organic electrochemical transistors (OECTs) are attracting a great deal of interest for biosensing and bioelectronics applications. However, their **device physics** is not yet well understood. The ability of organic semiconductors to conduct *ionic* in addition to *electronic* charge carriers is being extensively exploited in light emitting electrochemical cells, electrochromic devices, and organic electrochemical transistors (OECTs) [12, 50, 70, 165].

The latter are of high interest for applications in bioelectronics and biosensing since they can be operated at low voltage in aqueous environment, enabling the transmission of signals between biological systems and electronics [17, 94, 166]. Moreover, simple processing and versatile geometry facilitate OECTs integration into lab-on-a-chip devices [15, 74]. In this chapter the application of OECTs as sensor device is reported. The goal of the experiments is the understanding of device physics of the transistor: the OECT response has been studied in depending on the gate electrode material and on the kind of electrolyte. The electrochemical transistor has been finally used as sensor device for bio-elements: nanoparticles and liposomes. Part of the work has been carried out at the University of Cornell during the summer 2009, in the laboratory of Prof. George Malliaras.

The chapter is organized in four sections, each of one concerning a different experiment:

4.1 The device physics of OECT has been studied with regards the role of the gate electrode material in halide sensing. This work has been published on *Applied Physics Letter* **97**, 123304 (2010).

4.2 The role of electrolyte on the OECT response has been investigated using a non-conventional (micellar) electrolyte, in this case a cationic surfactant, the Cetyl Trimethyl Ammonium Bromide (CTAB). At this time the work has been submitted to the *Journal of American Chemical Society*.

4.3 The sensing properties discovered in Section 3 have been extended to lipid bi-layers structures: lecithin liposomes have been detected in OECTs. This experiment has been carried out with the collaboration of Department of Pharmacy of Parma.

4.4 Finally, a great effort has been done to realize the sensing of functionalised magnetic nanoparticles with different polyelectrolytes coating. This experiment has been developed under the project Nanosmart of the Provincia Autonoma in Trento.

4.1. OECT sensing mechanism: the case of halide sensing.

Given that OECTs are rather new devices, their physics remains largely undiscovered. For instance, the role played by the gate electrode material in determining device performance has not been deeply investigated. In this experiment, the effect of the gate electrode material on the response of OECTs employing a halide electrolyte has been analyzed. By comparing the characteristics of OECTs having Pt gate electrodes (hereafter named as **Pt OECTs**) with OECTs having Ag gate electrodes (hereafter named as **Ag OECTs**). We demonstrate that Ag OECTs show a larger modulation in I_{ds} than Pt OECTs upon application of the same V_{gs} . This effect is due to a change in the OECT regime of operation from capacitive, in Pt OECTs, to Faradaic, in Ag OECTs. Our findings provide details on the OECT working mechanism.

The plot of $\Delta I/I_0$ versus V_{gs} for OECTs using 0.1 M NaCl_(aq) (**Figure 4.1a**) highlights the different responses for Ag OECTs and Pt OECTs. The important point here is that Ag OECTs display a higher modulation throughout all the investigated V_{gs} range.

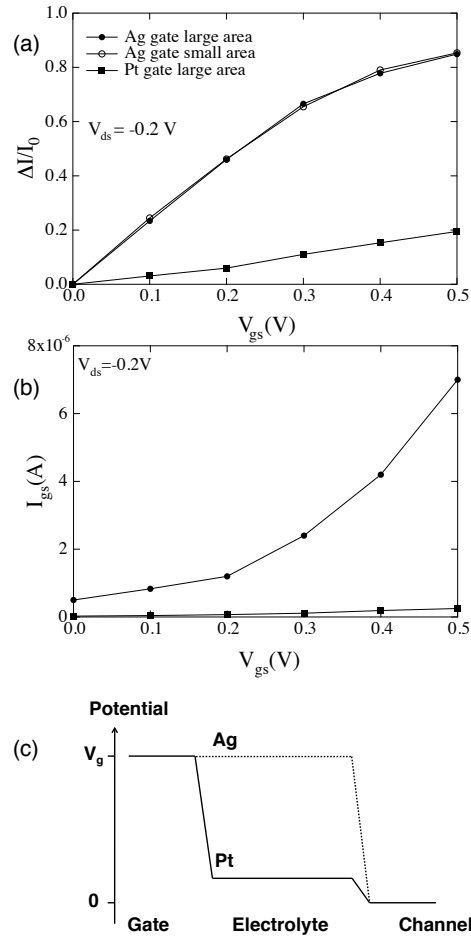
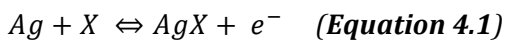


Figure 4.1. (a) $\Delta I/I_0$ vs V_{gs} and (b) I_{gs} vs V_{gs} for OECT using Ag (circles) and Pt (squares) gate electrodes. 0.1 M NaCl_(aq) was used as electrolyte. The surface area of the Pt gate electrode was 10.8 mm², while the surface area of the Ag gate electrodes were 1.62 mm² (small gate) and 3.3 mm² (large gate). For the data reported in (b) the gate electrode surface area is 3.3 mm² for Ag and 10.8 mm² for Pt. (c) Potential distribution between the gate electrode and the channel for Ag and Pt gate electrodes.

For instance, at $V_{gs}=0.5$ V, $\Delta I/I_0$ reaches a value of ~ 0.85 for the Ag OECTs, which is about a factor of four higher than $\Delta I/I_0$ measured for the Pt OECT (~ 0.20) [167]. The origin of the different behavior of Ag and Pt electrodes is attributable to the distinct manners these electrodes affect the electrolyte solution potential, named V_{sol} , that is the potential acting on the OECT channel, and which ultimately determines the OECT current modulation [69, 105].

An OECT can operate in two regimes as far as the interface between the electrolyte and the gate electrode is concerned [71, 105]. In the first one (capacitive, or non-Faradaic regime), the application of V_{gs} induces a transient current in the electrolyte. In the second one (Faradaic regime), a steady-state current due to reduction/oxidation (redox reactions) is sustained in the electrolyte. As a consequence, the OECT gate-source current (I_{gs}), which results from capacitive effects and/or from redox reactions at the gate electrode, can be used as a fingerprint of the regime of OECT operation [71]. Our measurements in halide-based aqueous solutions (**Figure 4.1b**) show the presence of a large steady-state gate-source current in Ag-OECTs, indicative of the presence of Faradaic processes at the gate electrode [50]. In contrast, Pt OECTs show a small gate-source current consistent with the polarizable nature of a Pt electrode [168]. A qualitatively similar behavior has been found with other halide electrolytes (e.g., CaCl_2 and cetyl trimethylammonium bromide, CTAB). The Faradaic process likely consists of the oxidation of the Ag gate electrode in the halide environment according to the reaction [169]:



The formation, through a precipitation reaction, of stable silver halide solid species (such as AgCl) renders particularly favorable Ag oxidation. In fact, the AgCl precipitation lowers the potential at which Ag oxidation takes place in absence of this precipitation ($E_{\text{AgCl}+e^- \leftrightarrow \text{Ag}+\text{Cl}^-}^0 = +0.222$ V, whereas $E_{\text{Ag}^++e^- \leftrightarrow \text{Ag}}^0 = +0.7991$ V. The equilibrium constant for the equilibrium $\text{AgCl} \leftrightarrow \text{Ag}^+ + \text{Cl}^-$ ($K_{ps, \text{AgCl}}$) is 1.7×10^{-10} from [169]).

The different responses of Ag and Pt OECTs are therefore due to the Faradaic process described in Equation 4.1, which takes place only at the Ag electrode (and not at Pt). In agreement with our hypothesis, when a non halide electrolyte is used with Ag gate, e.g., the ionic liquid 1-ethyl-3-methylimidazolium bis trifluoromethylsulfonyl imide, there is no substantial difference in I_{gs} for Pt and Ag OECTs.

The higher response of Ag OECTs can be explained by the value of V_{sol} in Ag- and Pt- OECTs (**Fig. 4.1c**). In Pt-OECTs, an electrical double layer forms at the Pt/ $\text{NaCl}_{(aq)}$ interface so that $V_{sol} < V_{gs}$. In Ag OECTs the reaction described in Equation 4.1, means that a steady-state current flows from the gate electrode to the electrolyte solution and no double layer is formed. The absence of a potential drop at this interface means that $V_{sol} \sim V_{gs}$. This hypothesis is supported by our experiments showing that the area of the Ag gate electrode does not change significantly the response of Ag-OECTs (**Figure 4.1a**). In contrast, OECTs employing Pt gate electrodes show a response that depends on the area of the gate electrode [105]. It should be noted that Pt-OECTs can also be made to operate in a Faradaic regime, and as such they have been used in enzymatic glucose sensors [68, 105]. Such devices detect H_2O_2 (an intermediate product of glucose oxidation) based on a redox reaction at the Pt gate electrode. In this case the Pt gate electrode acts as a catalyst for the oxidation of H_2O_2 . The mechanism of operation of Ag-OECTs differs in the fact that the gate electrode directly participates in a redox reaction with the ions of the electrolyte. The operation of Ag-OECTs in halide environments yields a response that depends on the concentration of Cl^- ions. The 3-Dim dimensional plot in **Figure 4.2** shows $\Delta I/I_0$ as a

function of the NaCl concentration from 10^{-6} M to 1 M at different V_{gs} .

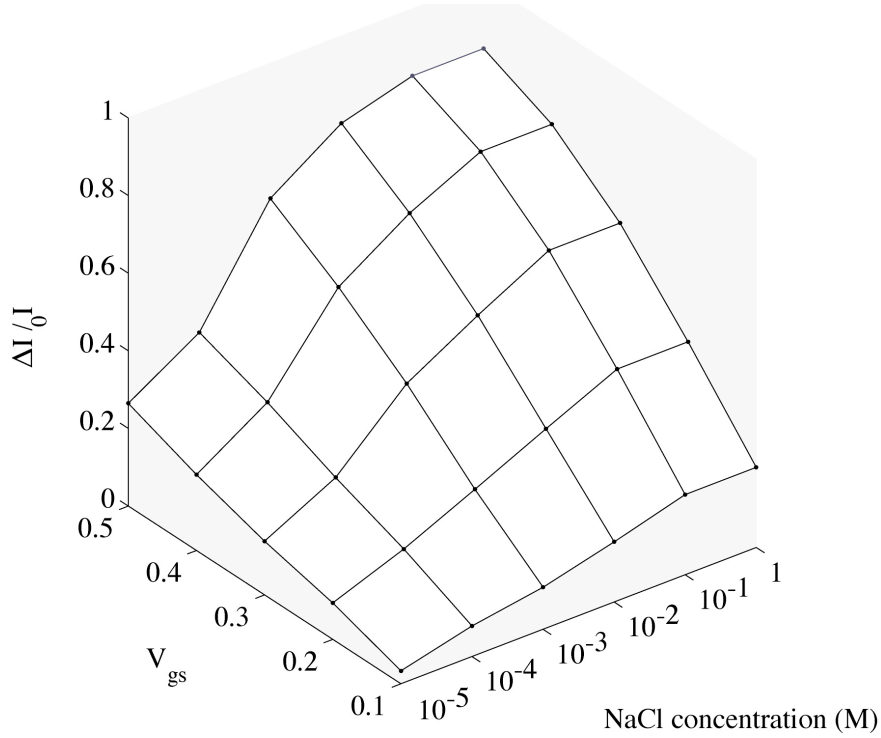


Figure 4.2. $\Delta I/I_0$ as a function of NaCl concentration and V_{gs} for Ag OECTs.

$\Delta I/I_0$ increases with both V_{gs} and NaCl concentration, which demonstrates that Ag OECTs can act as halide sensors in aqueous environment. An increase in NaCl concentration displaces reaction of **Equation 4.1** toward the right. At the same time, reaction in equation of ... is also displaced toward the right, and an increased concentration of Na^+ de-dopes the PEDOT:PSS channel, which translates in a larger $\Delta I/I_0$.

In conclusion, in this experiment the role of the gate electrode material in OECTs that utilize a halide electrolyte has been investigated. We observed that the use of Ag gate electrodes leads to high current modulation compared to OECT that utilize Pt gate electrodes. This was attributed to a redox reaction between ions in the electrolyte and the Ag gate electrode. The high modulation can be exploited for halide sensing.

4.2. OECT sensing in micellar electrolytes

In the following we demonstrate that an OECT can work as sensing devices, revealing micellar aggregation in water of Cetyl Trimethyl Ammonium Bromide (CTAB) ionic surfactant. The aim of this experiment has been to explore the role of electrolyte in the OECT response.

The use of this electrolyte results in large transistor current modulation, especially beyond the critical micellar concentration, in water (cmc_w). The current response as a function of the surfactant concentration permits the detection of micelles in solution, that is the transition phase from the dissociated to aggregate state. I have compared the current response of CTAB and NaCl, observing different behaviour, in correlation with the presence of spherical micelles, able to de-dope PEDOT:PSS more efficiently than more conventional cations. Finally, upon gate bias application, we observed electrochromic effects in PEDOT: PSS.

I have already mentioned that one of the most interesting aspects of electrochemical organic transistors is the interplay between ionic and electronics charge carriers in the conductive polymer transistor channel [1, 12]. Exploiting this property OECTs have been widely used with different kinds of electrolytes, like conventional salts [72, 73], phosphate buffer saline solution (PBS) [68, 69] and also ionic liquids [76] for chemical and biological sensing [14, 17, 170]. OECTs give different current responses with different electrolytes, as well as different gate materials [73] as shown in Section 1. Despite the progress made in recent years, the device physics of OECTs remains mostly unexplored, for example the role of electrolytes has yet to be fully understood. In this Section, we report about OECTs using CTAB ionic surfactant as the electrolyte.

CTAB is a cationic surfactant made of amphiphilic molecules with charged head group of 16-carbon tail.

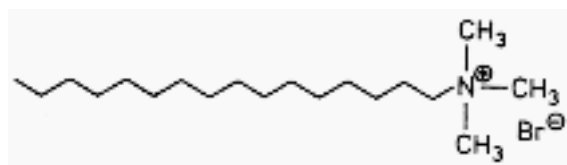


Figure 4.3 Structure of CTAB

It is widely used in biology and, as a non-conventional electrolyte for OECTs, it is promising as highly efficient electrolyte. More, cationic lipids in general open the possibility to study in-vitro biomedical application inside electronic devices, with a real-time detection of its interaction with bio-elements. The ability to form micelles of different shape and dimensions allows understanding the role of electric and charging properties of micelles in PEDOT: PSS de-doping.

The behaviour of OECTs making use of aqueous electrolytes containing CTAB was investigated for CTAB concentrations ranging between 10^{-8} M to 10^{-2} M. As gate electrode, a Pt wire was employed (surface area of 0.6 mm^2). Because of the nature of the gate electrode and the electrolyte, the OECT works in non-faradaic regime: in fact, as shown in **Figure 4.4**, we observed a small gate current for CTAB acquired at all the concentration from 10^{-8} M to 10^{-2} M. This is the fingerprint of a capacitive mode of operation, as explained in Section 1.

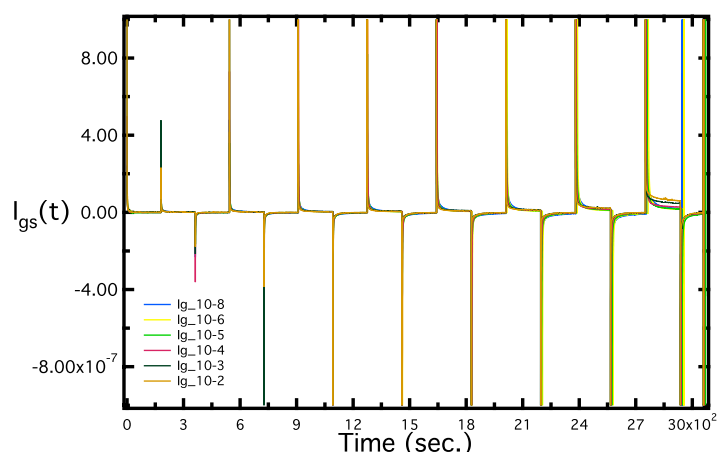


Figure 4.4 Typical gate current (I_{gs} vs. time) curves for an OECT, with a Pt-wire gate electrode, characterized in CTAB aqueous solution. All the CTAB concentrations (ranging from 10^{-8} M to 10^{-2} M) are acquired, not clearly visible in the figure due to their low and overlapped signals.

CTAB is a cationic surfactant, with a critical micellar concentrations in water (cmc_w), leading to the formation of spherical micelles from single molecules. The cmc_w occurs at the concentration of 9.5×10^{-4} M [171, 172]. Worth to note here that a few works in literature report also the presence of a second critical micellar concentration, leading from spherical to worm-like micelles, occurring at about 10^{-3} M [45, 173, 174]. It is also well known that before cmc_w pre-micellar aggregates can form in solution: recently the pre-micellar critical concentration of CTAB in water has been estimated by spectroscopic technique [45]. **Figure 4.5** shows a schematic representation of the transition phases that CTAB undergoes at increasing concentration.

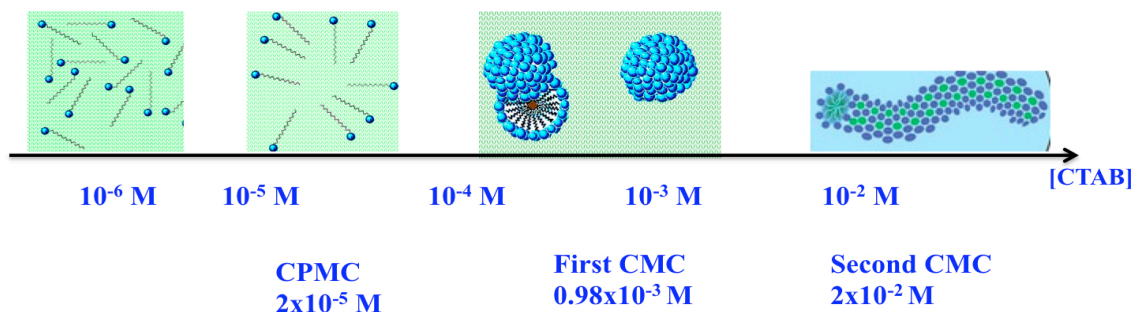


Figure 4.5 Transition phases of CTAB at different increasing concentration in water.

OECT current response *versus* V_g , obtained at increasing CTAB concentrations, shows an unexpected behaviour (**Figure 4.6**): below the cmc_w , from 10^{-8} to 10^{-5} M, the OECT response is about 0.3 modulation units for $V_g = 1$ V. Starting from the concentration value of 10^{-4} M, that is about at the cmc_w , the response increases to 0.55 modulation units, jumping to its maximum value of 0.9 for the concentrations 10^{-2} and 10^{-3} M, at $V_g = 1$ V. The difference signal between the highest (0.91 at CTAB 10^{-2} M) and lowest concentrations (0.33 at CTAB 10^{-8} M) for $V_g = 1$ V is 0.58 modulation units, corresponding to an increase of 175% of the current signal. These values of the modulation are greater than the typical errors we retrieve in organic transistors, about 0.05 modulation units, estimated by repeated acquisition in the same conditions.

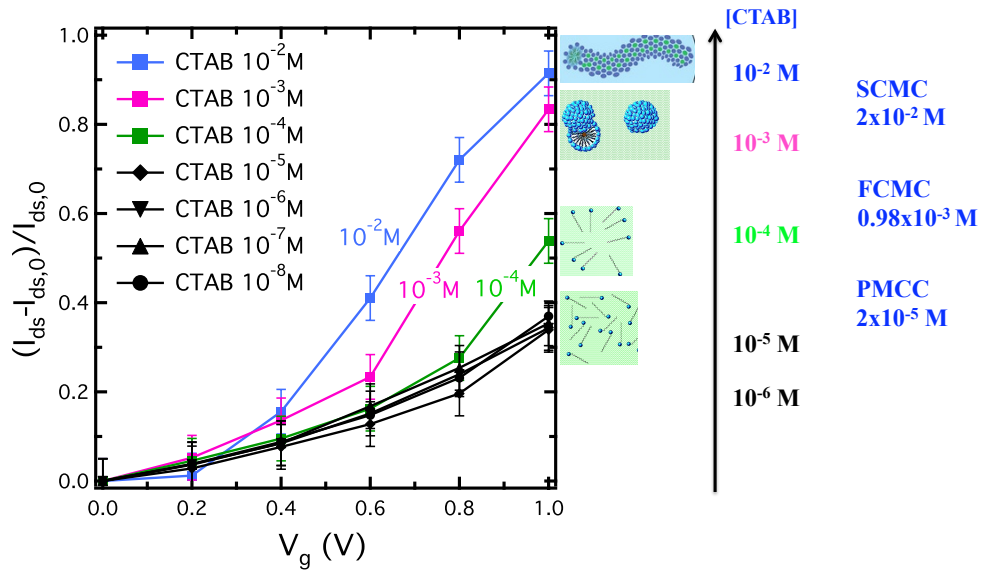


Figure 4.6 (a) Current response ($\Delta I/I_0$) of OECT at different CTAB concentrations in water. Close to the first CMC_1 (about 10^{-4} M) the response starts to increase and achieves its maximum values above the CMC_2 , at 10^{-3} M and 10^{-2} M where the CTAB micellar phase has changed from a spherical to worm-like shape.

This high repeatability in the response measurements makes OECTs a reliable sensing devices with a capability to detect variations in CTAB concentration in the range from 10^{-5} M to 10^{-2} M. In order to highlight the concentrations effects, an acquisition have been carried out applying V_g from 0 to 1.2 V. We used two different concentrations, just below (10^{-5} M, red line) and above (10^{-3} M, blue line) the cmc_w value at RT, with the drain-source voltage set at the fixed value of -0.4V. In **Figure 4.7** the lower concentration of CTAB remains below the higher one for all the gate voltage applied. At $V_g = 1.2$ V the lower concentration (red line) achieves a full saturation of the drain current. Instead at the concentration of 10^{-3} M (blue line) saturation is achieved earlier at $V_g = 1.2$ V.

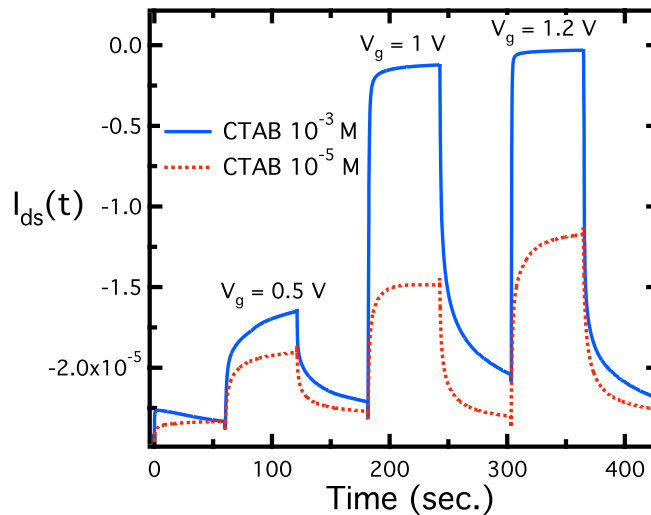


Figure 4.7 Current as a function of time for an OECT at different CTAB concentrations in water: just below (10^{-5} M, red line) and above (10^{-3} M, blue line) the cmc_w value at RT (about 10^{-4} M). Beyond the cmc_w saturation of PEDOT:PSS is achieved faster and at lower voltages ($V_g = 1$ V) while below the cmc_w saturation is not yet achieved at $V_g = 1.2$ V.

The higher signals obtained at the concentrations above the CMC_w , means that OECTs are able to detect the presence of CTAB micelles, which make a more efficient doping/dedoping process in the

PEDOT: PSS polymer channel, respect to other standard electrolytes, such as ion salts. In order to confirm our hypothesis, a sensing experiment has been performed with an OECT working in non-faradaic regime using Sodium Chloride (NaCl) salt as electrolyte. OECT characterization has been performed using the same concentrations used for CTAB (**Figure 4.8**).

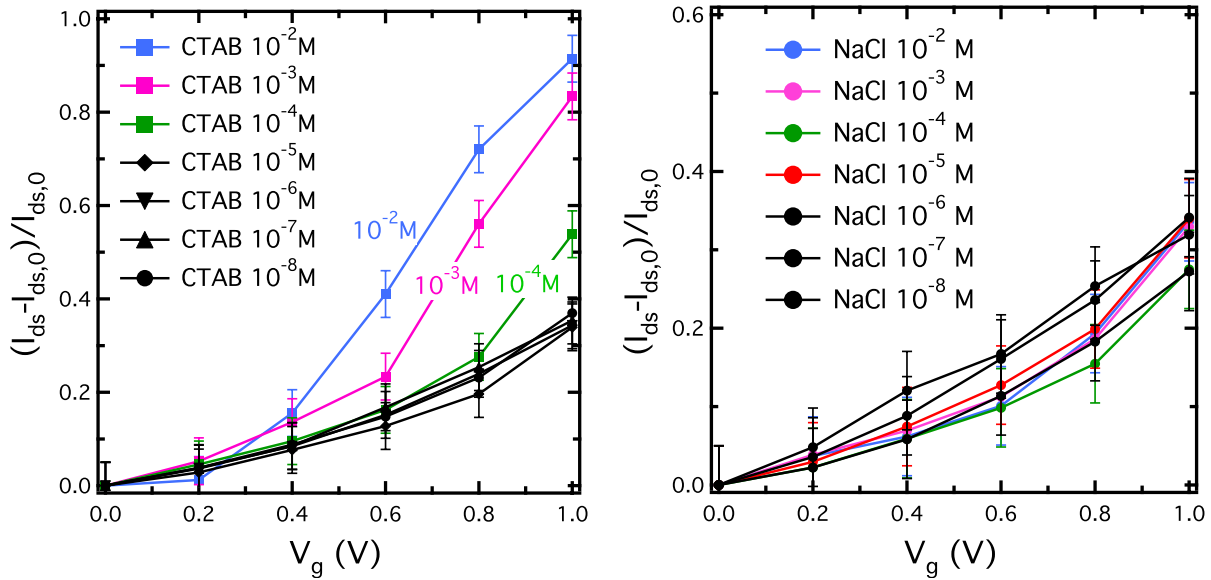


Figure 4.8 OECT response $(\Delta I/I_0)$ vs V_g for different NaCl concentrations, in water, ranging from 10^{-8} M to 10^{-2} M. The OECT response is almost the same for each salt concentration that is about 0.3 modulation units.

Sodium Chloride is completely dissociated in solution for all the concentrations that is it doesn't aggregate in any kind of micelles, as well as any other common salts. The modulation curves of NaCl present no effective changes in modulation signal for all the concentrations for every voltage applied. The response is about 0.3 modulation units for all the concentrations and the differences in the detection curves remains in 0.1 in modulation range. The effect of the micelles on the response is highlighted for the CTAB electrolyte (**Figure 4.6**). Once the transition phase has completed, after the cmc_w , the phase aggregation of CTAB micelles is fully spherical and the signal response achieves its maximum value (about 0.9 times of normalized response). The differences in signals are more pronounced at high voltages where in NaCl remains constant for all the voltages applied. In CTAB the maximum difference signal from the lowest and highest concentration is 0.58 modulation units, with respect to 0.1 in NaCl. The curve at the concentration of 10^{-4} M, when micellation starts, is placed among the full spherical micellar phase and the dissociated phase: this shows that OECT sensor is highly sensitive to ionic electrolyte modifications. This comparison between CTAB and NaCl probe the validity of our hypothesis regarding the primary role played by the micelles in the interaction with the PEDOT:PSS. Micelles present a more efficient doping/dedoping process of the PEDOT:PSS polymer channel, leading to the higher modulation signal acquired at the highest concentrations.

Dynamic Light Scattering and Zeta Potential

In order to characterize the size of the CTAB micelles, Light Scattering measurements on CTAB 10^{-3} M in aqueous solution have been performed. I found a mean size of micelles of about 3-4 nm. This value is much higher than classical electrolytes like NaCl or KCl, where the cations size is in the order of one hundreds pm (for example the size of 127pm for Na^+). The higher dimension of CTAB micelles results in an efficient de-doping process in PEDOT: PSS. This is consistent with the estimated internal structure of PEDOT:PSS, made of pancake-like particles of about 5-6 nm height, [175] which is larger

but comparable respect to the micelle size. Surface charge of the micelles has been measured by the Zeta Potential technique, using a Zeta Potential Analyser (Brookhaven Instr. Corp.) for different concentration of the surfactant, below and above the cmc_w . For the concentration of CTAB at 10^{-5} M, the Z-potential is zero, as expected for the fully dissociated surfactant, below the cmc_w . At the concentration of CTAB 10^{-4} M the surface charge resulted +35.1 mV, while the resulting charge, carried by the micelles at the concentration of CTAB 10^{-2} M, reaches the highest value at +87.10 mV, that is a reasonable value in agreement with previous calculated values [176-178] as well as with the change of shape that CTAB micelles undergoes in that range of concentration. Figure 4.9 represents the zeta potential values at the crossing of cmc_w .

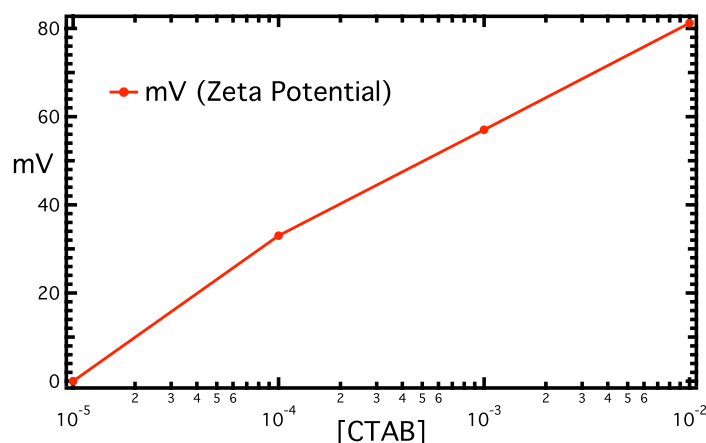


Figure 4.9 Zeta potential of the CTAB micelles as a function of the surfactant concentration.

Chromic effect

In order to confirm the injection of micelles into the polymer film, a spectroscopy study of the polymer, upon bias applied, has been realized. Conducting polymers such as PEDOT:PSS are known to exhibit electrochromism with ionic electrolyte as doping elements [179, 180]. Upon the application of a gate bias to OECT device, the film colour can be switched from light to dark blue. The colour changes is due to the electrochemical reduction of PEDOT:PSS [181], which is accompanied with an increased absorption in the visible part of the spectrum. When no V_g is applied, PEDOT: PSS is in its pristine, oxidized (PEDOT^+) state with a transparent and slightly blue colour (**Figure 4.10a**). The oxidized PEDOT:PSS can be switched from transparent state to its deep blue, neutral state in accordance with the reaction given in Eq. 1. The number of bipolarons decreases upon reduction, PEDOT^0 in the PEDOT: PSS film starts to absorb more light in the visible region, resulting in an opaque deep blue colour. In our case the chromic effect of PEDOT: PSS has been realized applying a continuous gate voltage in a CTAB solution of 10^{-2} M, as shown in **Figure 4.10a,b**.

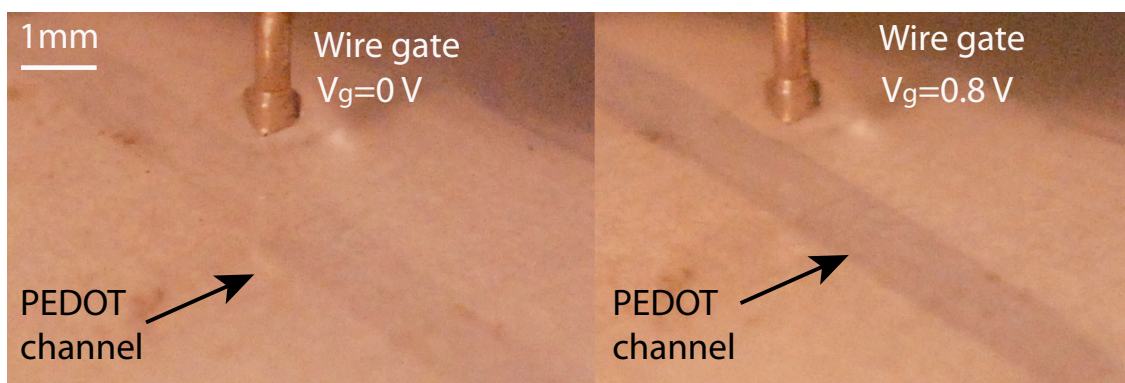


Figure 4.10a,b. Electrochromic effect in the PEDOT:PSS channel with CTAB 10^{-2} M as electrolyte. Photo on the left shows PEDOT:PSS channel when no bias is applied, with a transparent and light blue colour. Photo on the right shows PEDOT:PSS channel upon bias application, with a dark blue.

At the concentration of 10^{-2} M, CTAB is completely aggregated in a micellar phase. The chromatic effect in this case probes that micelles are acting as a doping element inside PEDOT: PSS. Then we measure the UV-Visible spectra of PEDOT:PSS in situ, using a working OECT and acquiring the current response simultaneously. An OECT device has been realized on this purpose, sealed with another glass slide as shown in **Figure 4.11**. The electrolyte solution has been injected into between the two slides.

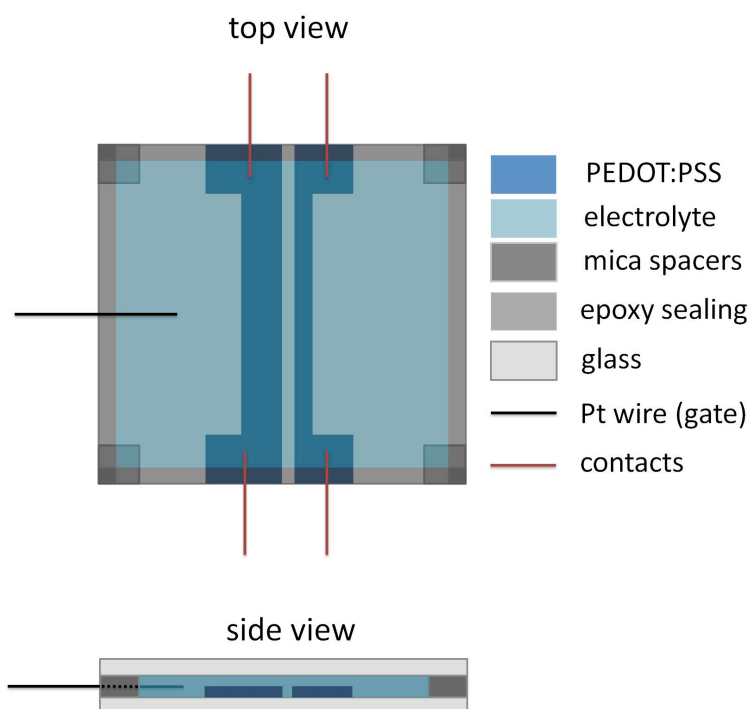


Figure 4.11. Device realized for the VIS-absorption measurements, performed during the OECT current acquisition.

The presence of the electrochromic effect strongly suggest that micelles are being incorporated in the PEDOT: PSS channel. The UV-Visible spectra of PEDOT: PSS measured in situ on a working OECT exposed to 10^{-2} M CTAB_(aq), is reported in **Fig. 4.12**. The baseline has been acquired through glass and CTAB electrolyte in water, then a first optical measurement on PEDOT:PSS with no bias applied has been acquired (Fig. 4, dotted black line). After that, a constant source-drain current has been set to -

0.4V and only a weak different absorption spectra is visible (line-points blue line), meaning that the source-drain current doesn't affect significantly the optical absorption of PEDOT:PSS.

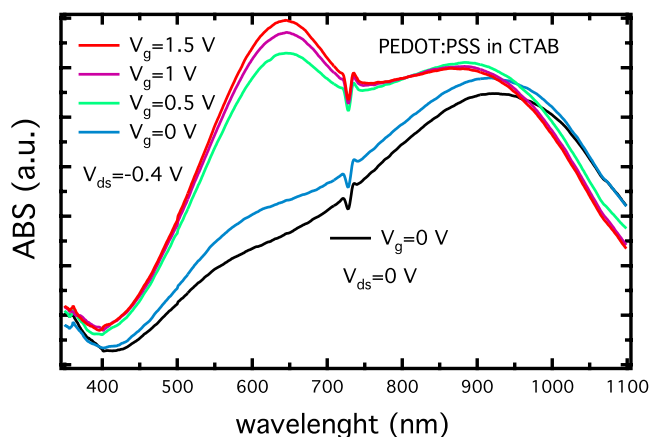


Figure 4.12. Absorption spectra of PEDOT:PSS channel upon bias application, with CTAB in water 10^{-2} M as electrolyte.

Upon application of a gate voltage of 0.8V the absorption of the PEDOT:PSS changes, revealing an absorption peak at about 630nm. The intensity of the peak increases at the increasing of the gate voltage. The spectra reveals that the PEDOT:PSS absorption power changes with the gate voltage applied. The peak at about 630nm corresponds to a typical absorption peak of PEDOT:PSS under reduction [182-184]. Vis-spectra confirm the role played by micelles on the dedoping of PEDOT:PSS.

Micelles definitely enter in the conductive polymer acting as an effective dedopant elements, such as common ions. The increasing of modulation signal, due to the doping of micelles, could be explained referring to the electrical conduction of conjugated polymers. Ions from the electrolyte neutralize electrons injected from the contacts. A micelle, carrying an higher surface charge, could create a local excess of positive charge in the polymer, entrapping more electrons than a simple ion can do.

In summary, a cationic surfactant has been used as electrolyte in an organic electrochemical transistor. The current response is different respect to common electrolytes, like salts, especially above the cmc_w concentration. The ionic surfactant is able to give significantly higher modulation signals. This is due to the ability of spherical micelles to dedope PEDOT:PSS more efficiently than the dissociated ions. The role of micelles has been confirmed through a comparison with the modulation response with a common salt (NaCl). Electrochromic effect and visible spectra of the PEDOT:PSS have been acquired during at different voltages applied. The quantitative analyses of the optical spectra show a peak of absorption for the PEDOT:PSS with CTAB electrolyte at 10^{-2} M at the increasing of the gate voltage, confirming a higher electrochromic effect due to PEDOT:PSS reduction by micelles in the electrolyte. Since micelles play a primary role in biological processes and drug-delivery systems, the use for micellar electrolytes opens new exciting opportunities for the use of OECTs in bioelectronics.

4.3. From mono to bi-layers: liposomes sensing in OECT.

With the previous experiment the role of monolayer micelles has been investigated as electrolyte inside an organic electrochemical transistor. The passage from mono to bi-layer is quite natural, and among the bilayers structure, the lipids bilayers are well known and easy to make. In the following an experiment regarding the use of liposomes in phosphate buffer solution is reported.

Micelles formed by a double layer are called vesicles. Phospholipids vesicles are referred as liposomes, discovered for the first time in 1965 by Bangham *et al.* [185]. Because of phospholipids are composed by a hydrophilic head, attracted by water, and a hydrophobic tail, that is repelled, in water solution liposomes spontaneously self-assemble in closed structures entrapping the solvent.

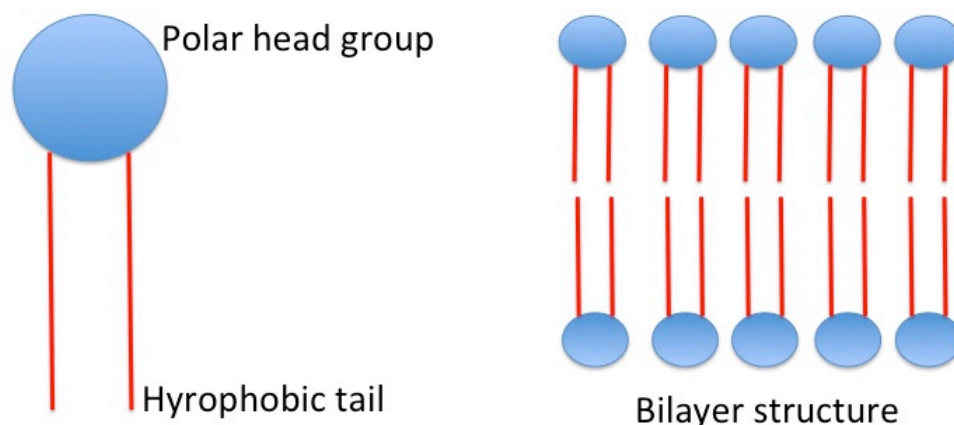


Figure 4.13 Phospholipids structure with the polar hydrophilic head and the non-polar hydrophobic tail.

The head group in phospholipid can have or not a net charge on their surface: some polar head are charged, for example, phosphatidyl serine (PS), phosphatidyl inositol (PI), and phosphatidyl glycerol (PG); other are dipolar charges (separate positively and negatively charged regions), for example, phosphatidyl choline (PC), and phosphatidyl ethanolamine (PE). If drugs are dissolved in the solvent, it will be entrapped into the liposome, which can be used as a container.

Depending on the method of preparation and on the lipid molecule, different kinds of liposomes are possible to make up with different sizes: the main types are the Multi Lamellar Vesicles (MLV), with the Small Unilamellar Vesicles (SUV) and the Large Unilamellar Vesicles (LUV) (Table...).

	MLV	SUV	LUV
Range Size (μm)	0.1 – 5	0.02 – 0.05	> 0.06

Table 4.3.1 Types of Liposomes at the varying of their size

Liposomes filled with a specific drug, are extensively studied as nanovectors for drug-delivery in cancer treatments of other diseases. Some liposomes-based drugs are already commercially available (Ref.) and found applications in many areas, from genetic engineering, chemotherapy, and diagnostic to cosmetics. This wide range of application comes from the possibility to exploit liposomes as cell membrane model, vaccine vehicles, or non-viral vector of genetic material. Literature about liposomes is already huge and many reviews report the most recent advances in research [186, 187]; here the only objective of this section is showing that an OETC can be used as a sensor to detect charged liposomes. The availability of a liposomes-based electrochemical sensor could yield the opportunity to have a device for in-vitro studies of lipid membrane dynamics and geometries [188] as well as the drug release dynamics. More generally, a platform for nanomedicine [189] research and for the development of protocell-based devices [190].

Liposomes as Drug delivery vectors.

Respects to other colloidal systems, liposomes offer many advantages, mainly due to their high encapsulation ability. Drugs can be entrapped into liposomes in three ways: encapsulation,

partitioning and reverse loading. The encapsulation method is useful for water-soluble drug and consists in exploiting the self-assembly property of liposomes: the lipid molecules injected in a water solution of drug, form the liposomes, which entrap passively the drug. Reverse loading is a smart way exploiting the property of some drugs to be charged or uncharged in depending on the pH of the solvent. In the uncharged phase, the drugs can enter the liposomes through the lipids bilayer; inside the liposome they found a pH to charge their surface: after charging the drug molecule cannot further move through the lipids bilayer and remain entrapped.

Lecithin liposomes

Liposomes have been prepared with egg lecithin using a protocol already reported [191]. Two Lecithin liposomes solution has been prepared with a concentration of 2mg/ml and $2 \times 10^{-2} \text{mg/ml}$, both in phosphate buffer solution (PBS). **Figure 4.14** represents the lecithin structure used to make the liposomes used in the OECT sensing experiment.

In order to verify the size of liposomes, Dynamic Light Scattering (DLS) measurements have been performed with a Brookhaven Zeta Potential Analyzer with a laser source at 632nm.

We found the liposomes size is **97,8 nm**. Zeta potential measurements gives information about the surface charge that is estimated about **-18mV**. The calculated polydispersity index is 0,181. A tampon phosphate solution has been used as electrolyte, in order to control the pH solution. A Platinum wire, with 2mm^2 of size, acts as gate electrode in order to work under a non-faradaic regime.

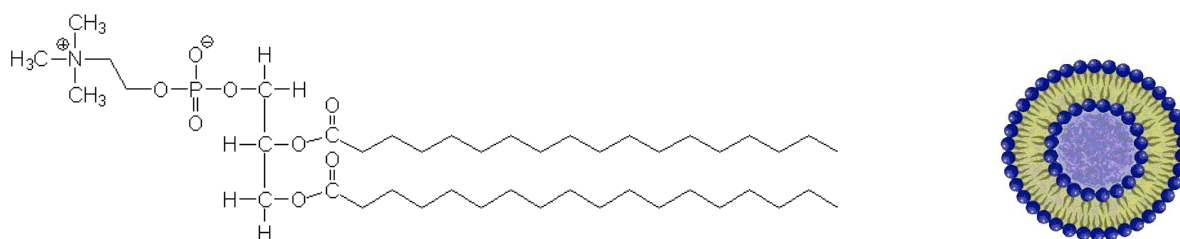


Figure 4.14 Lecithin liposomes used for the sensing experiment in OECT.

The setting for current measurements have been used as in other experiments: the gate voltage ranging from 0 V to 1 V, with 0.2 V steps, has been applied, with a fixed drain-source voltage of -0.4 V. In this experiment the drain current has been acquired as a function of time for 120 sec. at each step, that is the time in which OECT can achieve a stable saturation signal. Gate voltage has been applied from 0 V to 1 V with steps of 0.2 V. Between each step, a gate bias step is added at $V_g = 0$ V, in such a way the doping process of PEDOT:PSS occurs by ions diffusion from the polymer to the electrolyte. The OECT has been characterized by acquiring the OECT current response expressed as $\Delta I/I_0 = |I_{\text{ds,off}} - I_{\text{ds,0}}|/I_{\text{ds,0}}$ as a function of V_{gs} , as previously reported.

Current response: in situ detection.

In order to monitor the response of the OECT upon addition of liposomes, a real-time acquisition has been performed at fixed gate voltage applied ($V_g = 0.6$ V) and the source-drain bias keeps constant at $V_{\text{ds}} = -0.4$ V. **Figure 4.15** shows the drain current $I_{\text{ds}}(t)$ vs. time of the OECT with the addition of $25\mu\text{L}$ of liposomes solution during acquisition. The real-time measurement is more intuitive and gives a direct idea of the sensor ability of the OECT.

The plot represents the drain current $I_{\text{ds}}(t)$ as a function of time of the OECT acquired for 900 sec. In the first step (180 sec.) only the tampon phosphate solution has been inserted into the PDSM reservoir of the OECT, and $V_g = 0$ V. The $I_{\text{ds}}(t)$ current has a stable signal (-18 μA). At the time of 180 sec. the gate voltage has been set at 0.6 V for 300 sec (second step). The signal start to increase to due the ions in

solution forced to move towards the PEDOT:PSS channel ($-13 \mu\text{A}$). Finally at the time of 300 sec., at the end of the second step, 2 drops of liposomes have been injected into the reservoir, for a total amount of about $25 \mu\text{L}$. Under the presence of liposomes, the $I_{ds}(t)$ current increase ($-7.92 \mu\text{A}$) of about $5 \mu\text{A}$, that is the same order of the current increased by the gate voltage effect. The device exhibits a good response and the relative change of I_{ds} reaches $5 \mu\text{A}$ instantly after addition of liposomes. The I_{ds} vs. time curve is a more efficient way to demonstrate the real-time response of the sensor to additions of liposomes.

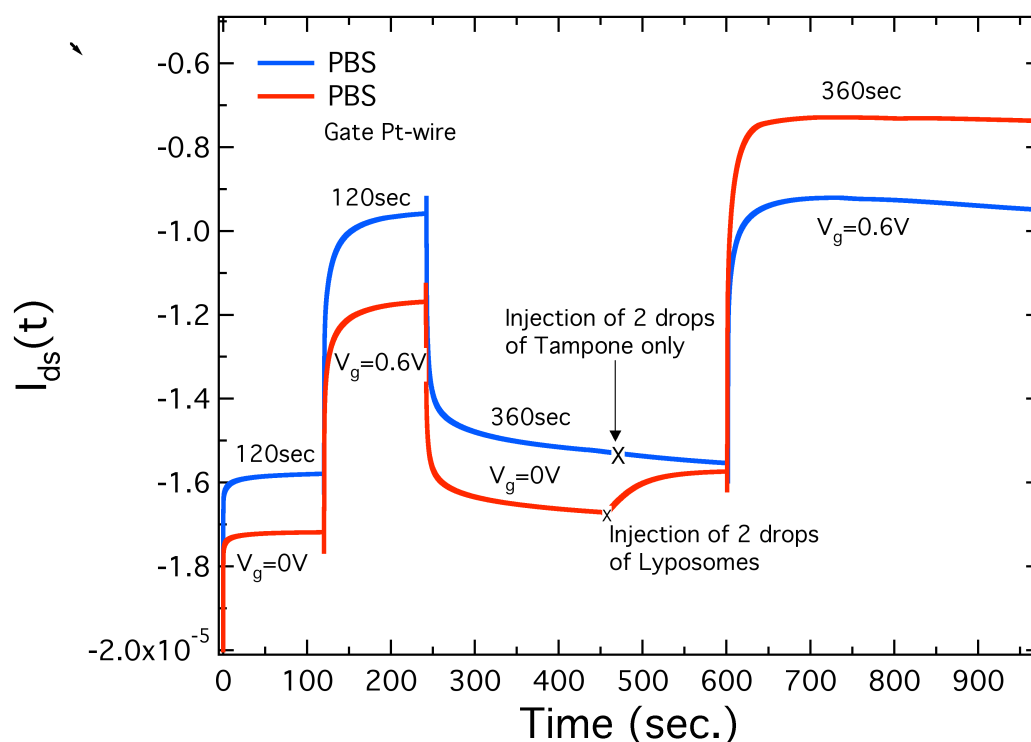


Figure 4.15 Real-time detection of lecithin liposomes in OECT

Current response: modulation.

In **Figure 4.16** the OECT current response is represented before the addition of liposomes, and for two different liposomes concentrations.

First, the acquisition of the OECT current response with the electrolyte solution, without liposomes, has been done: the OECT response shows the lowest signal of 0.34 units in current modulation. The response signal start to increase with the lower concentration of liposomes ($2 \times 10^{-2} \text{ mg/m}$), reporting the value 0.45 unit in modulation, and reaches the highest value for the higher concentration (2 mg/ml) at 0.56. The difference in the signal response is of 0.22 units in modulation, representing an increasing of 65% of the sensing response. Repeated measurement reported the same result, showing the reproducibility capability of the device. An important point to note here is that the signals are different in all the gate potential range applied.

A similar experiment with water electrolyte has been performed, and similar results have been found.

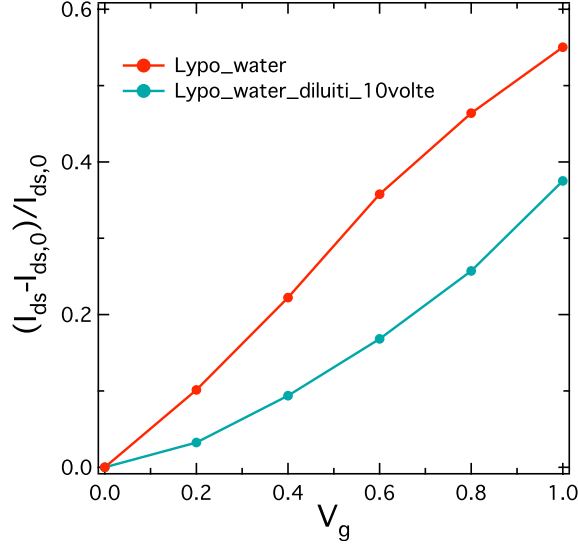


Figure 4.16 Liposomes with water electrolyte.

Currently other experiments with drug-loaded liposomes are under investigation. The opening of liposomes can be forced by the injection of an enzyme. The dynamics of lecithin liposomes have been already investigated and we know the opening can be induced in 2 hours by the enzyme pancreatine [192-194]. In order to monitor the drug release dynamics of liposomes in OECT, the pancreatin has been injected into the PDMS well during current acquisition with chitosan-loaded lecithin liposomes. The work is in progress and the preliminary results are not reported here.

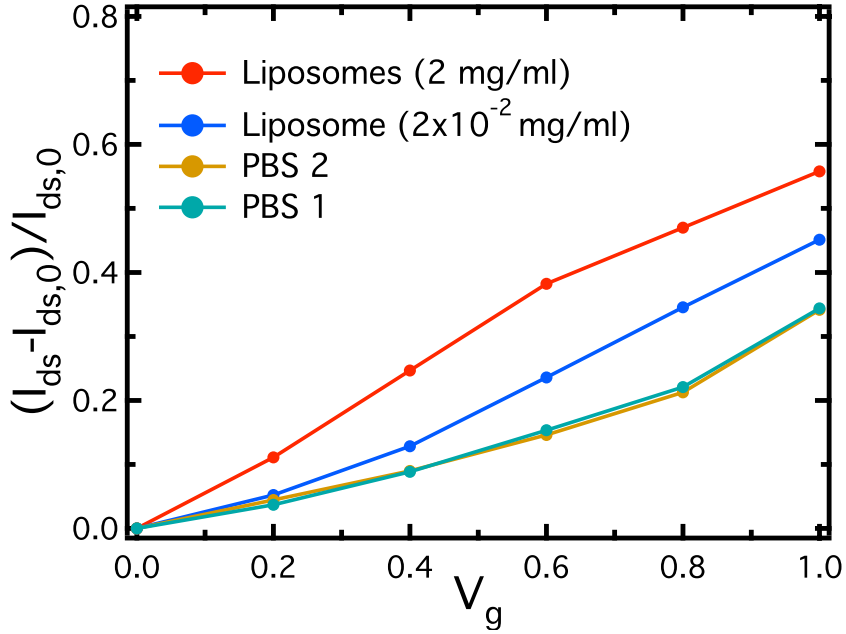


Figure 4.17 Normalized current response of OECT as a function of the gate voltage applied, for different liposomes concentration in PBS solution.

4.4. OECT monitoring functionalised magnetic nanoparticles for biomedical applications

In this section Organic Electrochemical Transistors (OECTs) have been used for the detection of polymer coated magnetic nanoparticles in electrolyte solution. The core size and crystalline structure of iron oxide nanoparticles have been observed by Transmission Electron Microscope (TEM). The hydrodynamic size of the coated nanoparticles has been measured by Dynamic Light Scattering (DLS). The normalized current $I_{ds}(t)$ resolved in time of OECT, and the I_{ds} current response at different gate voltages, with nanoparticles in solution respect to the pure electrolyte, have been analyzed. We find a different dynamics in the saturation signals and a significant shift in the effective applied gate voltage in presence of nanoparticles, that is coherent with an electrostatic interaction between nanoparticles and PEDOT:PSS channel of the OECT. The measurements show that a detection of Iron Oxide Polymer-Coated Nanoparticles has been realized by OECT, which results as a candidate for low cost and sensitive biosensors of drug-carriers nanoparticles. I have already written about the different applications of OECT in sensing and biosensing, Another crucial topic in biological and biomedical application is the use of coated nanoparticles in local drug release. Nanoparticles have been extensively used to improve pharmacokinetics and pharmacodynamics properties of drugs [195-197] and various polymers have been used as nanoparticles coating to increase therapeutic benefit. Polymer-coated nanoparticles offer many advantages: size and surface manipulation, control and sustaining release of drug during transport, site-specific targeting, different routes of drug administration [198-200]. A critical topic to perform a clinical use of magnetic nanoparticles is their local detection in biological systems by “lab-on-a-chip” microdevices [75, 201] in order to monitor the presence of nanoparticles charged with drugs and control their effects in biological systems. A local and low cost materials device, to detect and possible quantify the number of nanoparticles, which are effective as drug carriers, could be highly desirable. The possibility to locally reveal by OECT the presence of coated nanoparticles paves the way to biomedical microdevices able to monitor drug delivery with nanoparticles therapy. Such devices open new opportunities in nanomedicine [17, 86].

Nanoparticles synthesis and preparation of solutions

Iron-oxide magnetic nanoparticles of with a crystalline core have been synthesized and covered with PEG-modified phospholipid coating (PEG-NPs). The phospholipids coating of PEG has been prepared by a standard protocol already reported elsewhere [202].

PEG-NPs with a density of 0.1 mg/ml have been diluted in Ammonium Chloride NH_4Cl 0.1M, used as electrolyte in a concentration value already used for OECT before [73, 105]. The number of nanoparticles in solution can be estimated by the approximation that the mass of a single nanoparticle is mainly due to the iron core mass: $M_{NP} \approx M_{iron}$. Then $M_{iron} \approx 231.537$ (in fact $M_{Fe} \approx 55.847$ and $M_O \approx 15.999$) = $384.351 \cdot 10^{-24}$ gr. The density of nanoparticles injected is 0.1 mg/ml and we use 1 ml in volume of nanoparticles. $N_{NPs} \approx 2.5 \cdot 10^{17}$ is the number of nanoparticles in solution injected that is an average number of nanoparticles of 10^{16} in cm^3 .

Device characterization

The OECT has been characterized by acquiring the normalized I_{ds} current in function of time, at different V_{gs} modulation values, and the OECT response, expressed as $\Delta I = |I_{ds,off} - I_{ds,0}|$, as a function of V_{gs} values. The normalized I_{ds} current in function of time has been reported calculating the values of $(I_{ds}(t) - I_{ds,0}) / (I_{ds,off} - I_{ds,0})$ for every V_g applied, where $I_{ds,0}$ is the current at the beginning of the period when V_g is applied, and $I_{ds,off}$ is the current at the end of the period of 120 s when V_g is still applied. An

amount of 180 μL of the final solution has been injected into the PDMS-well reservoir of the OECT for each measurement, using a Pt-wire as gate electrode.

TEM and DLS

The core of nanoparticles have been analysed by Transmission Electron Microscope (TEM). Samples for TEM analyses were prepared by sonication and drop-casting of the nanoparticles solution onto a carbon coated copper grid. Images were acquired in a 200 kV JEOL 2200FS field-emission microscope, working both in high resolution TEM mode (HRTEM) and in High Angle Annular Dark Field scanning TEM mode (HAADF-STEM), the latter with a nominal probe size of 0.5 nm. In order to get information about the hydrodynamic size of the polymer-coated nanoparticles in solution, they have been characterized by Dynamic Light Scattering (DLS). The measurements have been performed with a Brookhaven Zeta Potential Analyser 3.3 with a laser source at 632nm. In order to minimize the effect of aggregation, nanoparticles have been treated for 30 minutes with ultra sonication just before DLS measurements in order to check their size and aggregation status. Current measurements with the OECT transistor have been carried out immediately after DLS, to maintain the solution dispersion of the particulate.

Results

In **Figure 4.18** the core size and crystalline structure of the NPs, as studied by TEM, have shown. Since the HAADF intensity depends on the atomic number, Z , as Z^α (with $\alpha \sim 2$) [203] the NPs cores are clearly identified in HAADF-STEM imaging as bright objects on a dark background corresponding to the carbon support film (Fig. 3a). Statistical analyses of the core size give a quite narrow diameter distribution centred around 10 nm. Atomic resolution structural studies (**Figure 4.18b**) confirm that each iron oxide core has a single-crystalline cubic structure, which can be imaged in HRTEM along different zone axes (e.g. found experimentally $\langle 114 \rangle$, $\langle 111 \rangle$ and $\langle 112 \rangle$ -type viewing directions). Selected-area electron diffraction patterns (SAEDP, see Fig. 3c) turn out to be ring patterns, since they stem from many NPs randomly oriented with respect to each other. Each ring corresponds to a set of lattice planes and can be indexed according to the scheme in **Figure 4.18c** on the right. The cubic symmetry and the experimental d values, as found both by HRTEM analysis of single NP and by SAEDP, are consistent with a Fe_3O_4 (magnetite) or $\text{g-Fe}_2\text{O}_3$ (maghemite) structure of the core.

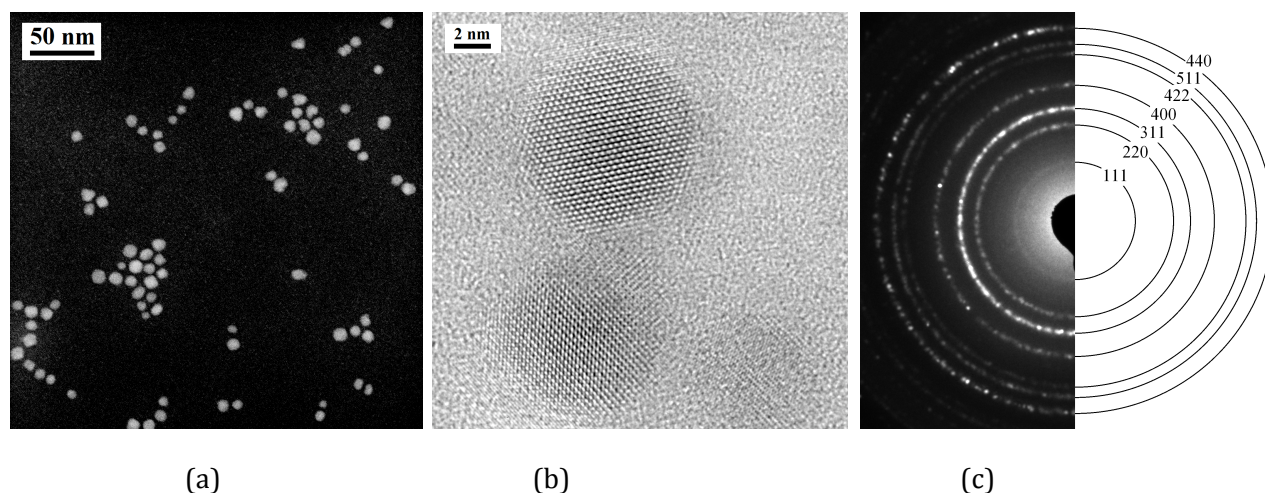


Figure 4.18 (a) HAADF-STEM image. The NPs have a quite narrow size distribution centred around 10

nm. (b) HRTEM image of two neighbour NPs, showing each NP is single-crystalline. (c) SAEDP, with indexing scheme, taken in a region of the TEM grid containing about a hundred NPs.

In **Figure 4.19** the average hydrodynamic size distribution of the polymer-coated nanoparticles obtained by DLS measurement is reported. About 57% of nanoparticles have a size between 45 nm and 55 nm, representing the estimated radius of isolated coated nanoparticles, about 38% fall between 63 nm and 98 nm, representing a estimated degree of aggregation of about 2 coated nanoparticles, while the other 5% have a size above 100 nm. A minor percentage of particles have a mean size greater that 100 nm, so that the overall size-distribution represents an good degree of dispersion and separation.

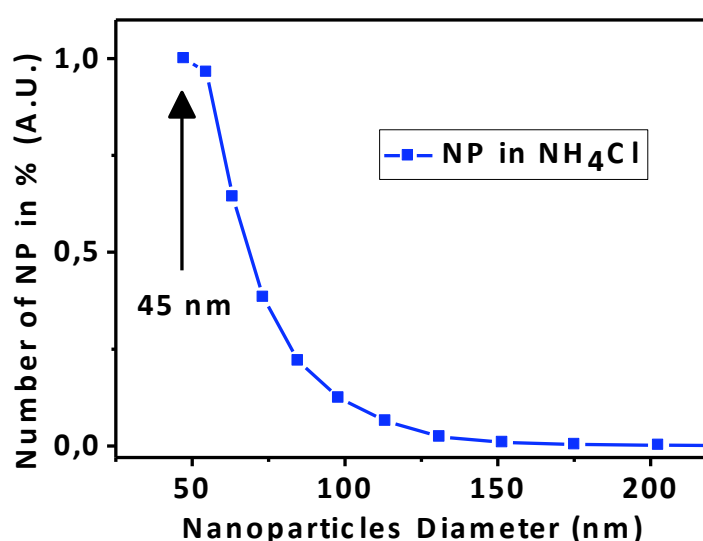


Figure 4.19 Average size distribution of nanoparticles as retrieved by Dynamic Light Scattering measurement performed on the PEG-coated magnetite nanoparticles just before the measurements with electrochemical transistors. The hydrodynamics diameter is about 45nm for almost 50% of particles.

Current measurements

We compared the measurements of the ($I_{ds}(t)$) current and the OECT response (expressed as ΔI vs. V_g) of the NH_4Cl electrolyte, with and without nanoparticles diluted.

In **Figure 4.20** the normalized $I_{ds}(t)$ current as a function of time of the NH_4Cl electrolyte has reported, without (**Figure 4.20a**) and with (**Figure 4.20b**) the presence of coated nanoparticles in solution. The calculation has been done to refer every current value, during the OECT acquisition, in the (0,1) range. In the case of the pure electrolyte (**Figure 4.20a**) the normalized current $I_{ds}(t)$ achieves a complete saturation in less than 120 sec. for the V_g value from 0.6 to 1 V. With the presence of nanoparticles in the electrolyte, the normalized current $I_{ds}(t)$ results in a slower response and a not complete saturation (**Figure 4.20b**) for all the V_g values. The I_{ds} current dynamic in function of time results sensitive to the presence of nanoparticles in solution.

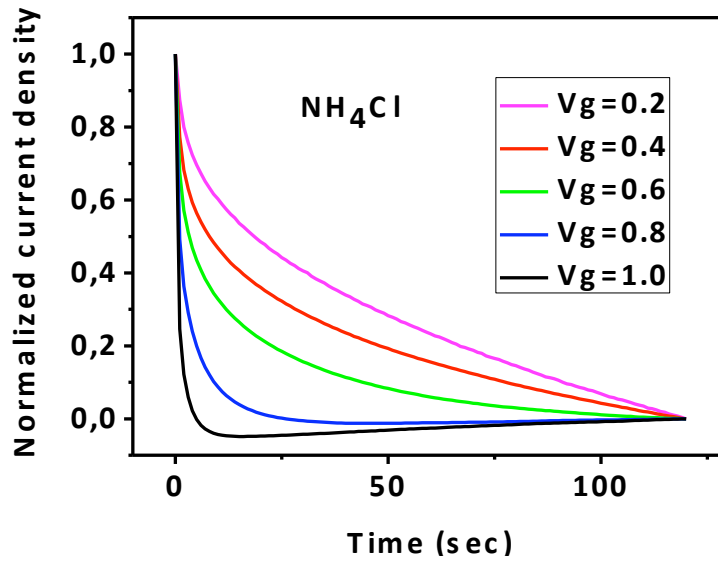


Figure 4.20a Normalized I_{ds} current as a function of time for the NH_4Cl electrolyte at different applied gate voltages.

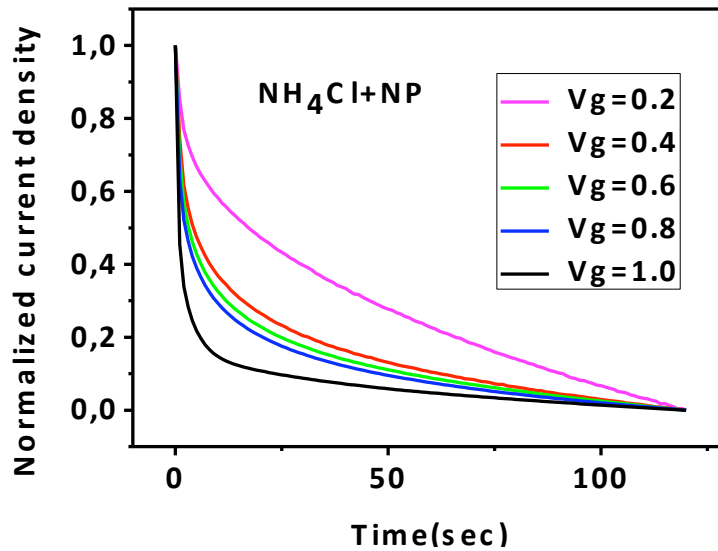


Figure 4.20b Normalized I_{ds} current density as a function of time for the NH_4Cl electrolyte with the nanoparticles injected at different applied gate voltages.

Gate Voltage Shift

Next, **Figure 4.21** shows the transfer characteristic of the device. The ΔI_{ds} current is reported in function of V_g in NH_4Cl solution with and without Nanoparticles.

The OECTs current response displays a different value throughout all the investigated V_{gs} range. The transfer characteristic shifts toward an higher gate voltage for an amount of about +250mV for all the ΔI current response, after the addition of nanoparticles in solution.

The measurements have been repeated without nanoparticles, and the current values are confirmed with a variability of $\pm 10mV$ due to a non-complete doping/dedoping process during modulation steps. The shift of +250mV results hence compatible with an effective measurement of a nanoparticles sensing.

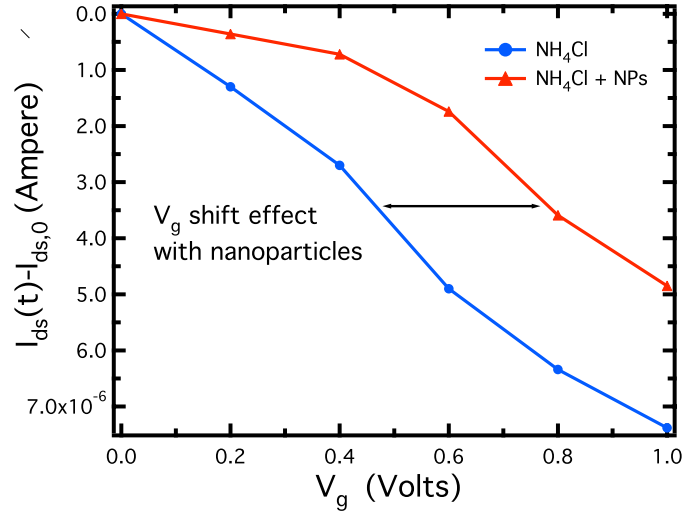


Figure 4.21 Transfer characteristic of the OEET. The curve shift toward an higher gate voltage for an amount of +250mV after addition of the nanoparticles in solution.

In OEETs the variation of the drain current is related to the number of NH_4^+ ions that interact with the polymer film, forced by the gate bias applied. The drain current decreases after ions make a dedoping of the PEDOT:PSS, because the number of holes carrier suitable for conduction reduces.

When no gate voltage is applied, the drain current has its highest value. At the increasing of the gate voltage, ions are forced to enter the polymer and the drain current decreases as much as higher gate voltage is applied. According to the **Figure 4.21**, nanoparticles have the overall effect to hinder the positive ions of electrolyte during the dedoping process. The slowing of the saturation process and the inhibition of the dedoping process, could be due to the formation of an electrostatic and physical obstacle, realized by the coated nanoparticles in the electrolyte, probably in the form of an electrostatic layer on the PEDOT:PSS surface. The presence of nanoparticles reduces the ions able to perform the de-doping process and affect the effective gate voltage in the transistor.

Next, we will discuss the mechanism of the shift transfer characteristic of the device.

Consider in the following the equations representing the channel current of an OEET, as reported by the Bernards' model [50, 204]:

$$I_{ds} = \frac{q\mu p_0 t W}{L V_p} \left(V_p - V_g^{eff} + \frac{V_{ds}}{2} \right) V_{ds}$$

$$V_p = \frac{q p_0 t}{c_i}$$

$$V_g^{eff} = V_G + V_{offset}$$

where q is electronic charge, μ is the hole mobility, p_0 is the initial hole density in the organic semiconductor before the application of a gate voltage, t is the thickness of the organic semiconductor film, W and L are the width and length of the OEET device, respectively, V_p is the pinch-off voltage, V_g^{eff} is the effective gate voltage applied, and V_{offset} is an offset voltage related to the potential drop at the two interfaces: gate/ electrolyte and electrolyte/channel. It is worth noting that c_i is the effective capacitance per unit area of the transistor, which is not only related to the capacitance of the interface between the electrolyte and organic semiconductor channel (C_d) but also that of the interface between

the electrolyte and the gate electrode (C_g). In our case the presence of nanoparticles could induce a capacitive effect, with a formation of a capacitive layer at the PEDOT surface, due to accumulation of the nanoparticles under electrostatic potential in the electrolyte. The origin of the different behaviour of OECT in presence of nanoparticles can be attributed to the way nanoparticles affect the electrolyte solution potential V_{sol} (corresponding to V_g^{eff} in the equations), that is the potential acting of the OECT channel and which ultimately determines the OECT current modulation. In OECTs-based sensors the V_g^{eff} is sensitive to the potential drops of electrolyte/semiconductor and electrolyte/gate interfaces. As shown in Fig. 6, the OECT gate voltage shifts of +250mV in presence of nanoparticles. This means that V_g^{eff} of OECT changes with nanoparticles on the PEDOT:PSS. That could be explained considering that nanoparticles could make an capacitive adhesion layer on the PEDOT:PSS, causing a potential dropping at the electrolyte/semiconductor interface. The contribution could be due to electrostatic property of the layer or to a mechanical effects that could hinders ammonium cations to enter the polymer channel. At this stage of our experiment, the full mechanism is not well understood, more experiments are in progress. But the results show that OECT can be used as an effective nanoparticles sensor.

Next, another example of application of OECT as nanoparticles-sensor, is reported, using magnetic nanoparticles coated with poly acrylic acid (PAA-NPs) in DI-Water as electrolyte. Three concentration of nanoparticles have been prepared in water solution: with of 0.1, 1 and 10 mg/ml. An Ag wire has been used as gate electrode (**Figure 4.22**). Using a Silver (Ag) gate electrode the OECT response increases dramatically: the signals are 0.44 for 0.1 mg/ml and 0.61 mg/ml, with an increased response of 0.17, which is higher than the experimental error.

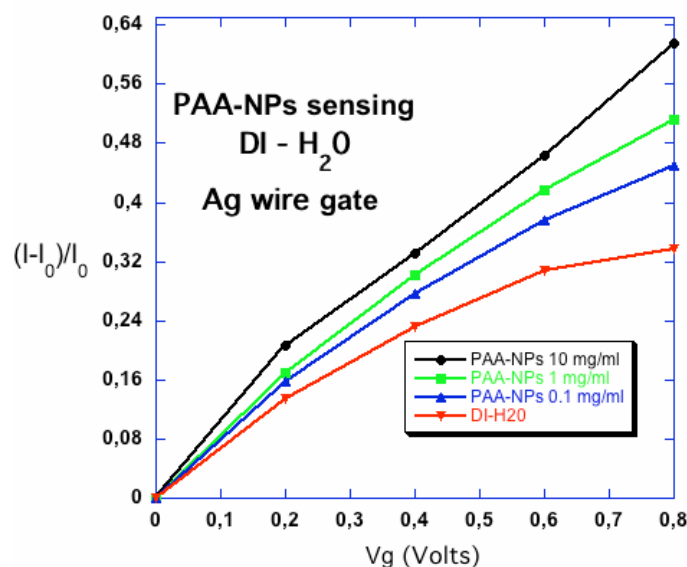


Figure 4.22. detection of PAA-NPs by OECT with PEDOT:PSS (a) and Ag wire (b) as gate electrode.

In conclusion we demonstrated the possibility to detect magnetic nanoparticles by electrochemical organic transistors. The iron core size of the nanoparticles has been studied by TEM and the hydrodynamic size of the polymer-coated nanoparticles in solution have been analysed by DLS. An organic electrochemical transistors based on PEDOT:PSS conductive polymer has been used as a nanoparticles-sensor with ammonium chloride as electrolyte. The normalized drain current presents different behaviour when nanoparticles are present in solution, and the OECT signal $I_{ds}(t)$ shows a reduced saturation effect respect to the pure electrolyte. The transfer characteristic of OECT show a gate voltage shift of +250mV, which is imputable to the electrostatic interaction of nanoparticles with the PEDOT: PSS polymer.

5. Conclusions and Outlook

In the last years tremendous advanced has been done in organic bioelectronic and especially in the applications of organic electrochemical transistors: enzymes, cells, DNA, neurotransmitters and nanoparticles have been successfully analyzed and detected through their interaction with the PEDOT:PSS conductive polymer.

The work carried out under the present PhD thesis is only the beginning of a long-term project where paramount goals wait to be achieved.

Some properties of conjugated polymers have been investigated and advanced modeling tools have been used to get insights into the structural properties of organic thin films. The working mechanism of electrochemical transistors has been studied and the OECT device has been exploited for application in sensing and biosensing experiments.

In particular the role of the gate material in OECT response has been investigated, leading to the exploiting of OECT as halide sensor. The experiment highlighted the two working mechanism an OECT can operate: the faradaic regime – where the OECT response is governed by the Nerst-like equation - and the non-faradaic regime – where a capacitance is formed at the gate/electrolyte interface and the transistor response doesn't depend directly on the concentration of electrolyte. After, the role of electrolyte has been extended to include micellar structures as candidates for a new class of electrolyte, able to open new and unexplored opportunities for application in nanomedicine: OECTs could be an advanced-platform where to investigate, inside an electrochemical environment, the ability of micelles and liposomes to trap and release drugs at the varying of different geometrical membranes. The nanoparticles-based sensor we have developed, is another opportunity to exploit OECTs to face one of the main task of today nanotechnology: that is the role of nanoparticles in toxicology and as drugs nanovectors. The interest in electrochemical transistors is growing, and it is becoming a more and more competitive filed, as probed by the new groups of research, which started with their own research just in the last two years.

In conclusion, this research work shed light on some peculiar properties of organic thin films by which high-performance OFETs have been realized and extended the sensor capabilities of OECT, acting on the gate materials, the electrolyte, but also on the organic polymer active layer.

Very interesting questions related to polymer doping, gating modulation and organic functionalization are to be fully understand yet, in order to improve and tailoring the OECT-based sensors.

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