Final Master Thesis

Large area molecular electronic devices: nanofabrication methodologies

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Abstract

Nowadays, electronic devices are a fundamental part of our daily lives and have transformed the world by implementing a huge variety of services, allowing communication and information sharing all over the world, and ultimately, improving our standard of living. All this has been possible by the development of technology, that is, scientific knowledge applied to the production of devices that can be mass-produced and purchased by anyone. However, due to the increasing miniaturization of these devices, current semiconductor technology is reaching its limit.

One of the alternatives to continue with the optimization and miniaturization of electronic devices is **molecular electronics**. This promising field uses organic compounds attached between electrodes as building blocks of the electronic devices. Single molecules or molecular assemblies can be sandwiched between the electrodes, each one oriented to a specific application. The advantage of using molecules is that they allow fabricating devices with different functionalities, which will depend on the intrinsic properties of the compound. In addition, collective effects that arise from the intermolecular interactions between molecules forming molecular assemblies are also important to take into account.

In this final master thesis, the possible use of two novel compounds in the field of molecular electronics is studied by the fabrication and characterization of monolayers. Both the Langmuir-Blodgett (LB) method and the self-assembly (SA) technique have been used to form the monolayer in terms to study the influence of the approach in the arrangement of the monolayer. However, due to the COVID19, the experimental work was interrupted, limiting the work to some preliminary results. Accordingly, a bibliographical review of the state of the art of molecular electronic devices has been carried out, to complement the work left uncomplete due to the global pandemic.

1. Objectives

1.1. Academic objectives

This final master project aims to provide the student with competences at the master level and with a high level of specialization in a chosen topic in the field of Nanotechnology. These competences include the ability to work independently in the laboratory, and apply theoretical knowledge learned in the different modules of the master as well as to interpret and extract conclusions from the experimental results aided by an adequate literature search. Communication competences are also a fundamental objective: be able to communicate ideas and present the obtained results rigorously, which is assessed through the master thesis dissertation and the presentation of the results to a panel of examiners.

1.2. Scientific objectives

The scientific objective of this final master thesis is to analyse the surface behaviour and deposition capabilities of two novel compounds onto a solid electrode for subsequent applications in the field of molecular electronics. Monolayers of the two compounds will be fabricated by different bottom-up approaches: the Langmuir-Blodgett (LB) method and the self-assembly (SA) technique. These monolayers will be characterized by spectroscopic, electrochemical and microscopic techniques for a better understanding of the organization of the molecules within the film.

However, due to the global pandemic caused by the COVID19, the experimental work had to be ended by mid-March when only some preliminary results had been obtained. For this reason, the obtained results are inconclusive and further experiments need to be done to gain further information and get consistent conclusions. Consequently, the objectives of this project were reoriented according to the University indications, and a much more comprehensive section covering a revision of the state of the art in molecular electronics has been included.

2. State of the art in molecular electronics

Our current style of life cannot be understood without the presence of electronic devices. The impact of the electronic industry in our daily work and how we interact with each other has resulted in a constant pursuit for maximizing and squeezing the properties and potential applications that these devices can offer.

The real breakthrough in the electronic industry was the creation of integrated circuits in 1959. In these devices, the electronic components (transistors, diodes, resistors…) are integrated in a single semiconductor chip, usually made of silicon. The combination of large numbers of integrated circuits allowed to achieve advances such us portable devices, more powerful computers, and digital domestic appliances.[1] In 1965, Gordon Moore, co-founder of Intel Corporation, stated that the number of transistors in an integrated circuit would double every 2 years. This prediction, which was also used as a goal to reach and to keep increasing the power of these devices, was called "Moore's Law".[2]

Since this law was stated, great effort has been made by the industry to fulfil this prediction. Consequently, the components of the integrated circuits have become smaller, following a roadmap called More Moore. However, nowadays this tendency is reaching its limits and there are some unavoidable physical limitations that the current semiconductor technology cannot overcome. For instance, the thermally-induced error generated by heat produced when several components are integrated in the same area, or the limit reached by silicon when working with gate lengths below 5 nm.[3] Another work tendency, which does not necessarily follow Moore's Law, is called More than Moore. This tendency does not focus on finding a better performance to cost ratio of the devices. Instead, its objective is to fabricate devices adding new functionalities so they can have more applications, such as sensors or optoelectronic devices.[4] With this aim, novel materials are being developed and explored, such as 2D graphene-like compounds or spintronic materials.

One of the modern investigation fields that can potentially merge More Moore and More than Moore tendencies is **molecular electronics**. In this field, organic molecules are used as building blocks to fabricate electronic components. The molecules are assembled between electrodes, and under an applied bias between the contacts, charge flows from one side to the other due to the conduction properties of the compounds. The nanometric size of the molecules allows continuing with the miniaturization of the devices. In addition, these devices could be suited to different applications, depending on customizable parameters such as the presence of functional groups, molecular length or geometry. In fact, by using a variety of compounds, diodes, capacitors, insulators, transistors or wires have been successfully demonstrated in the laboratory.[5] There are two paradigms in the field of molecular electronics: the study of a single molecule located between two (or three) electrodes, or the study of large-area devices using monolayers sandwiched between the electrodes. Both methodologies are of fundamental importance for the development of molecular electronics. Experts point out that large area devices, will probably be a mature technology before single molecule devices and, therefore, are attracting a large interest.

The phenomenon behind electron transport between the electrodes separated by a few angstroms is the tunnelling effect. This effect causes that, even in the absence of direct contact between the electrodes, electrons can flow from one electrode to the other. With molecules sandwiched between the contacts, the possibility of electron transport is enhanced.

2.1. Large area vs single molecule devices

As mentioned above, there are two paradigms in the study of molecular electronic devices. One involves using a single molecule between the electrodes, and the other uses a molecular assembly between the electrodes, forming a large area device. The study of these molecular junctions provide different information. The single molecule junction allows studying fundamental intrinsic properties of an isolated molecule, whereas in large area devices collective interactions affect the intrinsic properties of the molecules. Nevertheless, fabrication and characterization of large area devices is faster and easier, and can be potentially scaled-up and implemented in the market.

2.1.1. Single molecule:

Single-molecule electronics allows studying the molecules as isolated objects, eliminating the interaction with other molecules.[6] Therefore, we can gain insight of the intrinsic transport properties of the compounds used, and how the anchoring groups, the length of the molecule, or the temperature affect the electron transport.[7]

However, the measurement of these properties and the fabrication of the single molecule-metal junction is not straightforward, and requires advanced and sophisticated procedures. Some of the techniques for determining the electrical properties of molecular junctions include the scanning tunnelling microscope-break junction, the mechanically controlled break junction, electromigration, or matrix isolation.[8] The complexity of these techniques limits the scope of single molecule electronics to the research field, and nowadays it has no scaling-up perspectives.

The conditions for assembling the molecule between the contacts result in some limitations in the final junction. For instance, the metal-molecule binding has to be mechanically stable and strong which results in improved electronic coupling. The conduction is also sensitive to the compressive or tensile forces applied to the molecule, which can easily change between experiments.[9] All these conditions and the complexity of the fabrication of the junction, result in low reproducible measurements. Consequently, for determining the conductance, large numbers (hundreds or thousands) of measurements are needed, and afterwards, a thorough statistical analysis of the results is mandatory.[10]

2.1.2. Large area:

In large area devices, the conduction is not just due to the intrinsic conduction properties of the molecules. The collective effects caused by the interactions between the molecules, such as the packing of the monolayer, or the orientation of the molecules with respect to the plane of the electrodes, may increase or decrease the charge transport.[11]

The fabrication of monolayers sandwiched between electrodes is less demanding than that of single molecule junctions. By using the chemical affinity of the molecules with specific substrates, or the spontaneous orientation of the compounds at the air-water interfase, metal-monolayer junctions can readily be produced. These devices show higher mechanical stability than single molecule junctions as a result of both stronger molecule-electrode interactions and the lateral interactions among neighbour molecules. This increased stability has not only the advantage of easier manipulation conditions but also results in higher reproducible measurements.[10]

Another advantage for the large area approach is that characterization techniques are much more straightforward and can be directly applied to the monolayers. In contrast, the formation of single-molecule junctions is usually confirmed by conduction measurements, and other techniques like inelastic electron tunnelling spectroscopy (IETS).[12] Apart from measuring the conductance, many surface characterization techniques give additional information about the quality of the monolayer. There are many reported experiments in the literature where the homogeneity, thickness and density of the monolayer are studied by atomic force microscope (AFM), X-ray reflectivity (XRR) or X-ray photoelectron spectroscopy (XPS).[13] Additionally, AFM can provide an averaged value of the roughness of the monolayer, an important parameter that affects the charge transport as well. For assessing the chemical composition of the monolayer, XPS, infrared spectroscopy (IR) and/or surface-enhanced Raman spectroscopy (SERS) are the main techniques used. These techniques allow to resolve the bond structure between molecule and substrate, and study the orientation of the compounds and the anchoring groups.[14]

An important disadvantage of the monolayers is the effect that impurities or structural defects can have in the charge transport. These structural defects may arise from the presence of grain boundaries in the monolayer, or from the formation of unstable multilayers. These defects can also find its origin on the electrode. Although it is assumed that the electrode surface is ideally flat, usually that is not the case, and it can be the source of the named "hot conduction spots" which dominate the overall conductance of the monolayer.[15]

2.2. Assembling the molecules onto the bottom electrode

The formation of the monolayers and deposition onto the bottom electrode is usually achieved by bottom-up methods. In bottom-up fabrication methods, the molecules are used as building blocks, and its aggregation, which can even be spontaneous, results in the final device.[16] In the field of molecular electronics, the fabrication of the molecular junction is mainly focused on three techniques: self-assembly, Langmuir-Blodgett and electrografting using diazonium salts as the monolayer precursors.

2.2.1. Self-assembly (SA) technique

In the self-assembly (SA) technique the molecules interact spontaneously with the substrate and assemble forming a monolayer without any external action. The driving force that allows the formation of the monolayer is the chemical affinity between specific parts of the molecules and the substrate. This particular part of the molecules is the head group, and shows higher chemical affinity with the substrate than the rest of the molecule. Usually, the monolayer precursors in the self-assembly technique are in solution. The substrate to be covered is immersed in a solution containing the molecules of interest. After an incubation time, the molecules will adsorb spontaneously to the surface forming a monolayer.

The molecules assembled by SA are chemisorbed to the substrate. In chemisorption, the forces that tie together the molecules to the surface are of the same order of the ones involved in chemical bonds. Electrons are transferred or shared between the species, and the resulting interaction is usually two orders of magnitude stronger than physisorption. In physisorption, weak intermolecular forces are involved, such as Van der Waals, dipole-dipole, London forces… Consequently, these interactions are weak, reversible and non-specific.[17]

The formation of the self-assembled monolayers (SAMs) has several steps. First, the molecules chemisorb to the substrate by the interaction of the head groups with the substrate. Then, the molecules adjust their position until they reach their minimum free energy state. This process is possible due to the softness of the non-covalent interactions between the molecules. Due to the combination of weak and strong interactions, the molecules display a dynamic behaviour such as lateral diffusion, conformational isomerism and even reconstruction. All these phenomena explain why this technique achieves some of the most stable, highly organized (even crystalline) and defect-free monolayers.[18]

Nonetheless, the reasons that make this technique extremely useful and straightforward for the assembly at the bottom electrode, also highlight its limitations. The number of compounds, which can form monolayers by SA depends on the number of molecular groups that can specifically interact with the substrate. An example are the monolayers formed by the specific interaction of thiolate-derivatives with gold or silver substrates.[19] Besides, as mentioned before, the monolayer formation depends on several parameters: the affinity of the head groups and the substrate, the lateral interactions between molecules that affect the organization degree of the system and intramolecular interactions that affect the final structure of the lattice, like the tilt angle. Depending on the molecular characteristics, all these parameters compete in the assembly process. For instance, the tail of the molecules (part which does not chemisorb to the substrate), may experiment steric hindrance if they are long molecules or have bulky groups.[20] This will affect the packing of the monolayer and result in structural defects, like grain boundaries.

Overall, the self-assembly technique is the most used assembly method for the fabrication of monolayers in molecular electronics. This is due to its ability to form large area aggregates and assemble with little or no external influence, resulting in a very straightforward technique. These properties and its potential to be scaled-up, make the SA very appealing for the industry. More details about the experimental procedure will be explained in the experimental and results part of this master thesis report.

2.2.2. Langmuir Blodgett (LB) technique

The Langmuir-Blodgett (LB) technique is based on the transference of a monolayer formed at the air-water interface to a solid substrate. A solution containing the molecules is spread over the surface of a liquid, usually water, called the subphase. Then, the monolayer is formed by a compression process, in which the molecules go from low aggregation states (gas) to a highly packed system (solid). Finally, the monolayer is transferred to a solid substrate. Therefore, the main difference between SA and LB, is that in the first technique the molecules chemisorb to the substrate, meanwhile in LB method molecules are first assembled at the air-water interface and then transferred to the substrate. The molecules suited for the LB method are amphiphilic compounds, where one part interacts with water (hydrophilic) and the other points out to air (hydrophobic).[21]

The first step is the formation of the monolayer at the air-water interface (Langmuir monolayer). The compound that will form the monolayer is dissolved in an appropriate solvent. Then, drops of the solution are carefully deposited at the surface of the subphase. After the deposition, the solvent will evaporate and the molecules will remain in the interface. The solvent needs to be highly volatile, insoluble in the subphase, and have a positive spreading coefficient.[22] These parameters are very important. A positive spreading coefficient means that the drops will not form globule-like structures, and the molecules will disperse equivalently over the surface.[23] In addition, if the solvent were soluble in the subphase, the molecules would not accumulate at the air-water interface. Instead, the drops would sink to the bottom, and the formation of the monolayer would be impossible. Chloroform is one of the main used solvents because it matches all these conditions. The composition of the subphase can also be changed. Depending on the compounds used and in order to enhance and stabilize the assembly of the molecules, the pH can be altered or metal ions or anions can be included.[24]

Once the solvent evaporates, the compression step begins. Two hydrophobic barriers, usually made of Teflon, start to compress the molecules and reduce the available area for them. Therefore, interactions between the molecules are more likely to occur. As the compression proceeds, the molecules undergo several bi-dimensional phase transitions. First, they go from a gas state to a liquid-expanded phase, and then to a liquid-condensed phase. Finally, the compression results in the formation of a bi-dimensional solid phase or even the collapse. The mentioned phases may not take place; it depends on the nature of the molecules, the temperature and the speed of the compression.[25]

Once the monolayer is formed, it can be transferred to a solid substrate. Usually the substrate is immersed before spreading the solution, and once the monolayer is assembled, the substrate is pulled up. Since the first part of the monolayer that will make contact with the substrate is the one oriented towards the water (hydrophilic part), the monolayer will be transferred with the same orientation it had at the air-water interface. By performing several immersion-emersion cycles, multi-layered structures can be assembled; a feature that SA could not achieve. These multilayers will have different orientations depending on whether the monolayer is transferred during the immersion, the emersion or in both processes.[25] Other possibility is to introduce the substrate once the monolayer is fabricated. By this procedure, the hydrophobic part will be in contact with the substrate, and the transferred monolayer will have the opposite orientation to the monolayer formed at the air-water interface, although occasionally reorientations of the molecules within the film may occur. Another related approach is the Langmuir-Schaefer method. In this case, the substrate is pushed down parallel to the plane of the subphase until contact is made between the monolayer and the substrate. Then the substrate is withdrawn, and the monolayer is adsorbed by the hydrophobic part of the molecules.

There are several parameters that affect the monolayer formation. The concentration of the solution and volume to be spread are of paramount importance. Normally, the concentration tends to be as low as possible to minimize the interaction between the molecules prior to the compression process, so the molecules do not form three-dimensional aggregates in the solution.[26] The speed of the compression is also controlled, so that it is a quasi-equilibrium process. The pressure of the molecules (the surface pressure) exert to a detector is controlled and measured as well.

One advantage of the LB technique respect to the SA is the versatility of the technique. Depending on the nature of the molecules and the substrate, the monolayer will be chemisorbed or physisorbed; therefore, a wider number of compounds and substrates can be used. For instance, oligo(phenylene-ethynylene) (OPE) derivatives with a variety of anchoring groups such as carboxylic acids, nitriles, amines, thiols or esters have been successfully transferred to a variety of substrates, and their electrical properties have been studied in the field of molecular electronics.[27]

The main disadvantage of this technique is its limitation to the research filed. The experimental procedure is complex and time consuming, and the conditions of the technique make the LB method very difficult to be scaled up.

2.2.3. Electrografting

The electrografting technique involves the electrochemical reaction and consequent deposition of a monolayer into the desired substrate. The main monolayer precursors used in electrografting are diazonium salts. Since the origins of the technique,[28] several diazonium derivatives have been used, and with a larger variety of substrates. To date, grafting of amines, carboxylates, alcohols, vinyl derivatives and, of course, diazonium salts, have been reported.[29]

The steps and conditions to be used vary depending on the compounds used. In the case of the diazonium salts, the methodology is well reported. First, the salt (usually a 4-nitrobenzenediazonium salt) is dissolved in an aprotic solvent with a supporting electrolyte or in an acidic aqueous media.[30] Then, the compound is reduced using the substrate as a cathode. The reduction results in the formation of aryl radicals and nitrogen. The radicals readily react with the electrode surface in a reaction involving electron transference, producing strong and stable monolayers. Grafting can be achieved using a large variety of substrates, both conducting and non-conducting, like metals, carbon, metal oxides and even polymers.[29]

However, this method shows disadvantages not present in the previous procedures. The radicals are very unstable and reactive species, and they will interact with the substrate in an uncontrolled fashion. The resulting monolayers will have inhomogeneous thickness, varying from 1 to 50 nm, and in many cases produce disordered multilayers.[31] Under certain controlled and well-known conditions, the assembly of stable and well-packed monolayer can be achieved. These strategies to form stable and homogeneous monolayers mainly depend on the precursor used, but also on its concentration, the composition of the substrate, and the bias applied to the system. Importantly, the use of inhibitors and bulky terminal groups in the grafted material can be used to induce a 2D deposition avoiding 3D growths.

2.3. Top contact electrode deposition

The deposition of the top contact electrode in the monolayer-bottom electrode system to close the circuit is one of the most crucial and delicate steps in molecular electronics. However, there is still not an optimum method that ensures the formation of reproducible, reliable and defect-free molecular junctions. The search for overcoming this bottleneck has resulted in a high variety of methodologies and strategies.

2.3.1. Temporary contacts

The fabrication of temporary contacts is only oriented to laboratory work, to study the conductance and structural details of the monolayers. The main procedures involved in the fabrication of temporary contacts use scanning probe microscopes (SPM) and liquid metals. With the SPM, the tip of the instrument makes contact with the molecules and completes the circuit. However, due to the size of the tip, only a single or small number of molecules are contacted and measured simultaneously.[32]

An alternative is the use of liquid metals. Hg and InGa[33] alloys electrodes are the main choice for several reasons. Hg has a very high surface tension and behaves as a semi-noble metal; which are very useful properties for an electrode. However, Hg is well known for its high toxicity and it is very reactive to many substrates (forming amalgams), like Au and Ag. Therefore, it is mainly used with monolayers adsorbed on oxides or oxide-free silicon.[14] InGa alloys, also called EGaIn, are much less reactive towards the substrates, although the presence of a gallium-oxide film makes the measurements more difficult.

2.3.2. Permanent contacts

Mostly, top contact electrodes in molecular junctions have been fabricated using vapour deposition methods, especially physical vapour deposition (PVD). The metal source is heated to sufficiently high temperatures, and the metal atoms emitted condense and assemble at the surface of the monolayer. However, the thickness and deposition rate of the metal is very difficult to control, resulting in low reproducibility between the junctions. In addition, the monolayer is usually damaged due to the energetic metal atoms, and the soft nature of the molecules. One typical phenomenon that occurs is the formation of direct contact between the electrodes, called metal penetration, and it produces short-circuits during the measurements.[32, 34] Chemical vapour deposition methods (CVD) are chemical selective and have higher control in the thickness of the final monolayer. However, the energetic conditions intrinsic to CVD produce the same defects in the final device as PVD.

Other methods to prepare top contact electrodes use atomic layer deposition (ALD). This technique is used to form a thin layer of the contact electrode, covalently bounded to the monolayer. This thin layer acts as a protective layer and keeps the structural integrity of the monolayer; serving as seed to deposit a thicker contact with other methods such as

PVD or CVD.[35] The ALD technique follows several steps. First, a gas precursor is introduced in the reaction chamber, which reacts with the monolayer. Usually, the free-ends of the monolayer have chemical affinity with the precursor, to favour a selective reaction. Then, the system is purged with an inert gas like N_2 to eliminate the excess of precursors or any by-products. This process can be repeated several times with different precursors until the final layer is assembled.[36]

Another alternative to physical deposition methods is electroless deposition (ED).[37] In this case, the deposition is caused by the reduction of metal ions from solution, without applying an external potential difference. An advantage of this methodology is that it can be performed at low temperatures, eliminating the inconvenient of metal penetration of the previous techniques. Usually, a catalyst adsorbed into the monolayer is necessary to start the deposition, for instance Pd nanoparticles.[38] However, it can contaminate the final contact and affect the functionality of the junction. To control the diffusion of the catalyst in the molecular structure, some monolayers are functionalised to selectively adsorb the catalyst and limit the metallization to the functionalised areas.

Another family of deposition methods directly transfer a pre-made electrode to the monolayer. These soft techniques have the advantage of avoiding prior inconveniences, such as monolayer damage or metal penetration; and result in high yield and reliable molecular junctions. Some of these techniques involve nano-transfer printing (nTP), lift off and float on (LOFO) and polymer assisted LOFO (PALO).[39] In nTP, the metal contact is transferred to the monolayer from an elastomeric stamp. The transference is due to the surface chemistry between the metal contact and the anchoring groups of the monolayer, for instance a thiol-terminated monolayer and a gold substrate.[19] LOFO consists on the transference of a metal film floating on the surface of a liquid to the molecule-treated substrate. The metal film is detached from the original substrate by an etching solution. Then, the functionalised substrate is lifted from the solution with the film deposited on top. In addition to the affinity between monolayer and metal film, the solvent plays an important role in the adhesion of both surfaces, enhancing the interaction between them. Therefore, the solvent has to be removed carefully and in a controlled fashion.[40] Nevertheless, the methodology involved is complex, the appearance of wrinkles is not rare and the contacts are deposited one by one. To overcome this limitations, polymer assisted LOFO was developed.[41] Metal stripes, usually gold, are patterned on a sacrificial substrate. Then, a polymer layer, which is normally poly (methyl-methacrylate) (PMMA), is spin coated and the whole substrate surface is covered. The polymer and the electrodes are detached from the substrate (lift off) and transferred to the monolayer, in the same way as LOFO. Finally, the PMMA is removed with an organic solvent. However, this etching may increase the surface roughness, and therefore, can affect the underlying monolayer. One alternative is changing the PMMA by a photoresist, and selectively remove the polymer with photolithography. Although these systems have not been fully optimized yet, they open the option of mass-producing molecular devices.

In recent years, novel methods have been reported. For instance, use of an organometallic compound as precursor to form metal nanoparticles with a thermal treatment. The technique is named thermally decomposition of an organometallic compound (TIDOC).[42] The organometallic compounds, gold derivatives, were transferred and immobilized in a substrate by using the LB technique. Once the precursors were assembled, an annealing process was applied which resulted in the rupture of the metal-carbon bonds, and in the reduction of Au(I) to Au(0). This technique was demonstrated with different substrates and proved that no metal penetration took place, although coalescence of the gold nanoparticles occurred to form gold-nanoislands (GNIs). Moreover, the nanoislands could be used as seeds to induce the deposition of additional metal layers by other techniques, such as electroless deposition.

One similar method is the photoreduction of a metal-organic precursor incorporated to the LB monolayer to generate metal-nanoislands.[43]. So, for example, a gold precursor ($AuCl_4^-$) solution is used as the subphase of the Langmuir through; which is incorporated with the ionized monolayer formed at the air-water interfase during the transference process to keep the electroneutrality of the system. After that, the LB film is irradiated with UV light, at 254 nm, to convert the gold precursor in gold nanoislands. The presence of the gold nanoislands was confirmed by scanning electron microscopy and atomic force microscopy; meanwhile the absence of metal penetration, that is, short-circuits, was studied by conducting-atomic force microscopy by registering I-V curves. Both methods propose an easy and cheap assembly process, which can potentially be applied to different metal precursors such as Ag, Pt or Cu.

Finally, recent studies have tested the use of graphene as a protective layer between the monolayer and the top contact electrode. The use of protective layers is not new; several devices have been made with conducting polymers as PEDOT:PSS[44] to protect the monolayer. Although the metal penetration is avoided, the PEDOT:PSS layer produces other problems like poor interfacial contact with the monolayer and phase segregation between the components. Consequently, graphene arises as a promising alternative due to its atypical characteristics. Graphene is a bi-dimensional material made by covalently bonded carbon atoms, producing a honeycomb lattice due to the sp^2 hybridization of the atoms.[5] The inter-layers interactions are caused by σ-bonds. This structure results in outstanding electrical conductivity, chemical stability and mechanical material properties.[45] The deposition of graphene multilayers, could allow using aggressive deposition methods like PVD to produce top contacts without damaging the underlying monolayer.

2.4. Patterns

The presence of patterning methods in the literature applied to molecular junctions is scarce. From the previously mentioned deposition techniques, few can be used for producing quality patterns or applied without damaging the monolayer. Lithography methods were the first option used. By irradiating specific areas of self-assembled monolayers (SAMs) with UV light projected through a mask, these areas became functionalized.[46] With an appropriate solvent, the irradiated areas were removed, and a second SAM of different composition was assembled in the vacant spaces. Finally, by physical vapour methods, the metal contacts were deposited. By choosing SAMs with different end groups, different metals can be used to form the contacts. However as mentioned in previous sections, physical methods can damage the structure of the monolayer and in this case, affect the lateral resolution of the pattern.

Soft deposition methods like polymer assisted lift off and float on (PALO) and nano transfer printing (nTP) have been used to transfer patterned contacts. Nano printing has received special attention due to its ability to produce and transfer large area patterns. First, the patterned metal contacts are defined with photolithography or shadow-mask methods.[47] Then, the contact is transferred to the monolayer from a polymeric stamp. The patterns can be transferred to a large variety of substrates, including flexible and non-planar surfaces. However, it still has some limitations that prevent it from producing patterns suited for molecular electronics. For instance, the resolution of the technique is limited to that of the polymeric stamp, which is usually around 50 nm.[48] In addition, specific treatments are needed occasionally to transfer the contact to the monolayer, as thermal treatments. This process can affect both the resolution of the pattern and the structure of the molecules. Some recent developments of the technique have reached sub-

50 nm resolution by using more rigid stamps, which avoided the transfer of material between structures.[49] However, the patterning was only tested with silicon substrates, and no experiments on monolayers were performed.

An alternative is the use of constructive lithography. This technique produces patterns on monolayers by electrochemical processes to selectively deposit metal contacts.[50] Typically, the precursors are octadecyltrichlorosilane derivatives (OTS) and the pattern is generated by conductive-atomic force microscopy (c-AFM). The OTS monolayer and substrate act as anode and the c-AFM tip acts as cathode. The electrolyte is a thin water layer from ambient humidity, and produces the patterning oxidizing the CH_3 end groups to COOH. In the method cited in ref. 49, the patterned monolayer is used as a stamp to replicate the features on other substrates. Once the monolayer is treated, metal contacts can be deposited using other techniques as electroless deposition. A different approach, is to create a pattern of deposited OTS which act as resists, so the metal ions are only deposited in exposed substrate areas.[51]

2.5. Three-terminal devices

All the devices and assembling systems described above are oriented to the fabrication of 2-terminal devices. A 2-terminal device references the use of two electrodes, a bottom electrode and a top electrode, between which the molecules are adsorbed. A 3-terminal device displays both electrodes and one additional contact, which incorporates the possibility of fabricating molecular transistors.[5] A transistor is a 3-terminal device, where 2 of the electrodes act as the source and the drain, and the third terminal as the gate. The source and the drain control the potential difference applied between the electrodes, whilst the gate changes the electrostatic potential of the molecular components of the junction. Under these conditions, the energy of the molecular orbitals can be altered and aligned to the fermi levels of the electrodes. With this system, additional information from the molecules can be obtained, such as vibrational modes, excited states as well as measuring the magnetic behaviour of single molecule magnets.[52] Transistors are the most important components of an integrated circuit, so the fabrication of reliable and efficient molecular transistors will represent an important step forward in the field of molecular electronics.

To date, the fabrication of molecular transistors is limited to single molecule devices. The field lines of the gating electrode can only affect the perimeter of the monolayer in large area junctions. However, in single molecule transistors, the gate electrode can interact with the isolated molecules and change the conductance of the molecule from high conduction (ON state) to low conduction (OFF state). Rotaxanes have been used for these devices. Under an applied voltage, the molecule changes its structure and therefore its conductivity.[53] Another alternative is the use of electrochemical gating with redox-active molecules. For example, for pyrrolo-tetrathiafulvalene (pTTF) molecules, ON/OFF ratios of ca. 4 were achieved using electrochemical gating with scanning tunnelling microscope break junction (STMBJ) and mechanically controllable break junction (MCBJ) methods.[54]

Recently, a novelty method has been reported for fabricating transistors using SAMs as the molecular components.[55] The system is formed by gate/graphene/SAM/gold cross-plane vertical heterostructures. A gold film was deposited in an exposed area of a Si/SiO_2 chip and connected to a source electrode placed at the corner of the chip. The molecules tested were pseudo-p-bis((4-(acetylthio)phenyl)ethynyl)-p-[2,2,]cyclophane (PCP) and 1,4-bis(((4-acethylthio)phenyl)ethynyl)benzene (OPE3); immobilized on the gold surface. Then, a graphene layer was deposited on top of the SAM and connected to a drain electrode. Finally, the heterostructure was covered by an ionic liquid, DEME-TFSI. The encapsulation of the SAMs by the graphene layer and the strong binding by the S-Au bonds prevented direct contact between molecules and the ionic liquid.

The gating effect is generated by the electrical double layer of the ionic liquid. The field lines of the liquid, controlled by a gate electrode, penetrate through the graphene layer and tune the energy levels of the SAM. The results showed that the devices worked effectively even at room temperature.

2.6. Main challenges

Although in recent years the field of molecular electronics has experienced a large development, there are many issues concerning the molecular properties that are not fully understood. These uncertainties render the fabrication of molecular devices far from being optimized.

Some of these problems arise from the poorly known effects that molecule-contact interactions have on the electron transport.[14] Briefly explained, the interaction between contacts and molecules can be defined by two main concepts: the coupling parameter (Γ) and the addition energy (U). Γ is the broadening of the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

(LUMO). Usually the energy distribution of both orbitals is narrow, but due to the coupling between the orbitals of the molecules and the electrode, the energy broadens. Whilst U is the energy difference between the HOMO and the LUMO.[56] Conditions such as molecular length, adsorption and orientation of the molecules, will affect both U and Γ, and therefore the performance of the junction.

For instance, in case of chemisorbed molecules, typically a strong Γ is obtained. However, strong bonding of the end groups with the electrode may lead to electron localization at those orbitals, which could limit the electron transport. Therefore, the coupling between the frontier molecular orbitals and the fermi levels of the electrodes will depend on the composition of the end groups and the type of chemical bonding, making it fundamental to understand the nature of this coupling to control the transport through the junction. In addition, the same can occur to physisorbed molecules. Γ tends to be weak, but depending on the system, the opposite can happen. As can be expected, the length of the compounds will also determine the electron transport[57] and the characteristics of the monolayer, like the U factor, or the packing parameter. The orientation of the monolayer is also an important factor, because the energy coupling depends on the symmetry of the involved orbitals. The packing and tilt angles will also be affected by the chosen substrate, producing different structures and therefore having different electronic characteristics.[58]

One of the next trends in molecular electronics is oriented to the fabrication of all carbon and biocompatible molecular devices. The objective is to eliminate the use of metals and materials that can be toxic and produce residues, which are difficult to eliminate. There are works based on fabricating all carbon devices, using carbon-based and highly oriented pyrolytic graphite (HOPG) electrodes.[59] Other experiments use graphene or single-walled carbon nanotubes (SWCNTs) as contacts between the molecules.[60]

Nevertheless, newly one of the main limitations in this field is to deposit a top contact in the monolayer without damaging its structure and producing short cuts, as explained in previous sections. Ideally, apart from solving the drawbacks of current deposition methods, this technology should be able to mass-produce molecular devices in a cheap way, in order for the process to be scaled-up and incorporated to the market. Nowadays, there are no molecular junctions present in the market. However, a device with tested applications as an active component in audio distortion circuits has been developed.[61] The molecular junction integrated in the circuit produces unique sounds that have not been achieved by typical devices that use semiconductors.

As mentioned at the beginning of this section, molecular electronics is still far from being implemented in our daily lives. The scarce knowledge about intrinsic transport properties and the effects that interactions with other species may produce in the molecules, render the fabrication of molecular devices an uncertain process, where minimal alterations between experiments produce remarkably different results. Nevertheless, the fabrication of hybrid devices, combining molecular junctions and classic semiconductor technology is a more feasible possibility, and will probably be the future trend of electronic devices. The process until molecular electronic becomes a reality will not just affect the field of electronics, but will also develop the knowledge of fundamental molecular processes which will have applications in a large variety of fields, like biochemistry, materials science or molecular computing.

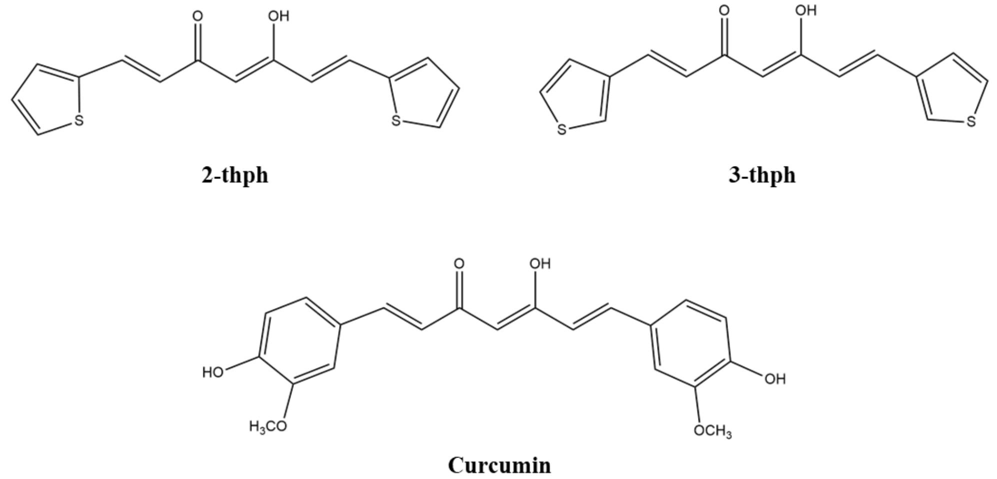
In the following sections of the final master thesis the experimental work done in the laboratory and the main conclusions obtained are presented.

3. Materials and methods

3.1 Materials

3.1.1. Compounds studied

In this final master thesis, two compounds were studied. Both of them were synthetized in the Department of Chemical Engineering, Biotechnology and Materials of the Faculty of Physical and Mathematical Sciences at the University of Chile. The compounds are curcumin derivatives, linear diarylheptanoids with thiophene rings connected by a seven-carbon chain with two α,β-unsaturated carbonyl groups. The structure of the compounds and the curcumin is shown in figure 1. The compounds were named **2-thph** and **3-thph** due to the position of the sulphur atom in the aromatic ring. In solid, both have a dark yellow colour with a molecular weight of 288.03 u.



2-thph

3-thph

Curcumin

Figure 1: *Structures of the compounds used and the curcumin.*

Several reasons make these compounds useful for molecular electronics. First, the thiophene groups in both ends favour the anchoring of the molecules to metal substrates, especially to gold due to the strong interaction S-Au.[62] The curcumin derivatives are highly conjugated molecules, so the electrons are delocalized throughout the structure and the molecule can effectively be used as molecular wire for charge transport. Finally, curcumin is a natural compound, the most abundant polyphenol found in turmeric, with several tested health benefits mainly associated to its antioxidant and anti-inflammatory effects.[63] This compound is easily isolated and used as a starting point for chemical modifications in order to enhance its properties aiming for different applications, for instance, molecular electronics.

3.1.2. Substrates and reactants used

Table 1: *Substrates used in this master thesis.*

Substrate	**Technique used**	**Cleaning process**	**Commercial data**
Gold	XPS	Washing with acetone and burnt	Arrandee™
QCM	Quartz crystal microbalance	Left in EtOH/H_2O (24 hours), then washed with $CHCl_3$ (1 hour), dried with N_2.	QCM 25, Stanford research systems

Table 2: *Reactants used in this master thesis.*

Reactant	**Use**	**Commercial data**	**CAS**
Chloroform	Cleaning, solvent	Sigma-Aldrich 99%, stabilized with EtOH 1%	67-66-3
Acetone	Cleaning	Panreac, QP, 99.5%	67-64-1
Ethanol	Cleaning	Panreac, absolute, 99.5%	64-17-5
Nitrogen	Drying	Linde, 99.999%	7727-37-9

3.2. Fabrication and characterization techniques

To characterize solutions of 3-thph and 2-thph in chloroform, Ultraviolet-visible (UV-Vis) spectroscopy was used. The spectra of the solutions can be compared with that of monolayers to study the different orientation the molecules may adquire.[64] The instrument used was a Varian Cary 50 Bio UV-VIS spectrophotometer and quartz cuvettes with a path length of 1 mm.

For fabricating the monolayers, self-assembly (SA) and the Langmuir-Blodgett (LB) method were used and have been already described previously in this master thesis. The subphase for the LB experiments was prepared with Millipore Milli-Q water, with a resistivity of 18.2 MΩ·cm. Surface pressure vs area per molecule isotherms were used to assess the reproducibility of the monolayer formed at the air-water interphase between experiments and to gain insight about the different phases occurring during the compression process. The surface pressure was measured by the Wilhelmy plate method and filter paper as the plate was used.[65] For our measurements, a Langmuir-Blodgett trough by NIMA (100 x 720 mm^2) was used. The Brewster angle microscopy (BAM) was applied to observe "in situ" the formation of the monolayer at the air-water interface during the compression process. A micro-BAM from the KSV-NIMA was used. This BAM uses a red laser (659 nm) of 50 mW and measures the reflected beam with a CCD camera, with a resolution of 640 x 480 pixels. The lateral resolution of the microscope is 12 µm.

The quartz crystal microbalance (QCM) allows to estimate the surface coverage. The working principle behind this technique is the piezoelectric effect. The frequency of the oscillation of the QCM depends on parameters of the phases adjacent to the crystal, for instance the mass of a monolayer deposited on top of the substrate.[66] A Stanford Research Systems microbalance, model QCM200 with a QCM25 sensor was used. This sensor is composed by a thin quartz disk, with circular gold electrodes in both faces of the disk and has a fundamental oscillation frequency of 5 MHz.

The XPS was used for surface characterization of the self-assembled monolayers (SAMs). The technique uses X-ray radiation to emit core-electrons from the sample and measure its binding energy.[67] The chemical environment affects the binding energies of the electrons, causing chemical shifts which allow to resolve the bond structure of the molecules adsorbed on the substrate as well as to determine the thickness of the deposited film.[68] A Kratos AXIS Ultra DLD spectrophotometer with a monochromatic Al X-ray source [AL Kα (1486.6 eV)] at the Institute of Nanoscience of Aragón was used. To correct the charge accumulation in the binding energies, the peak of C1s at 284.6 eV was used for calibration.

4. Results and discussion

As indicated previously, the experimental work was abruptly ended due to the global pandemic. Therefore, the experimental work is incomplete and some of the techniques were only applied to one compound. More experiments need to be performed in order to extract valid conclusions about both compounds and their possible use in molecular electronic devices

4.1. Characterization of 3-thph in solution

This study was necessary to determine at which concentration range we could work without having three-dimensional aggregates in the solution. Since these aggregates affect the fabrication of monolayers at the air-water interfase (Langmuir monolayers) and result in low reproducible measurements. The reason is that of the total molecules deposited only a fraction could potentially form monolayers. The rest, the three-dimensional aggregates, will not disassemble, and many of them will sink to the bottom. For this study, we measured the absorbance of the 3-thph in chloroform at different concentrations as shown in Figure 2.

In the spectra, there are absorption peaks at 250, 285 and 397 nm with shoulders at 375 and 425 nm. Molecules absorb UV-Vis radiation as a result of electronic transitions from ground to excited states between molecular orbitals. These processes usually involve transitions of non-bonding electrons (n) and π orbitals to π* states.[69] According to the literature, the curcumin molecules produce characteristic bands at 265 nm and 425 nm.[70] The thiophene groups also produce peaks at low wavelengths, 250 nm.[71]

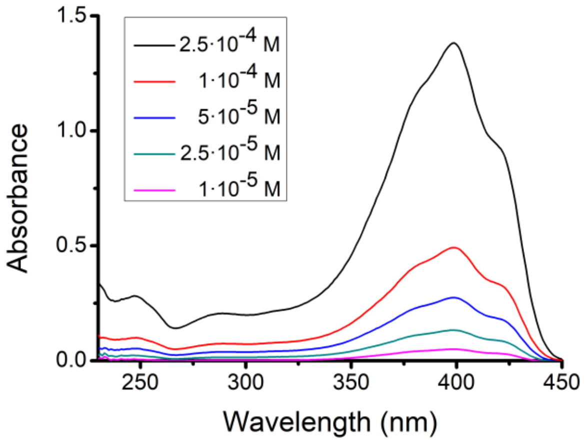
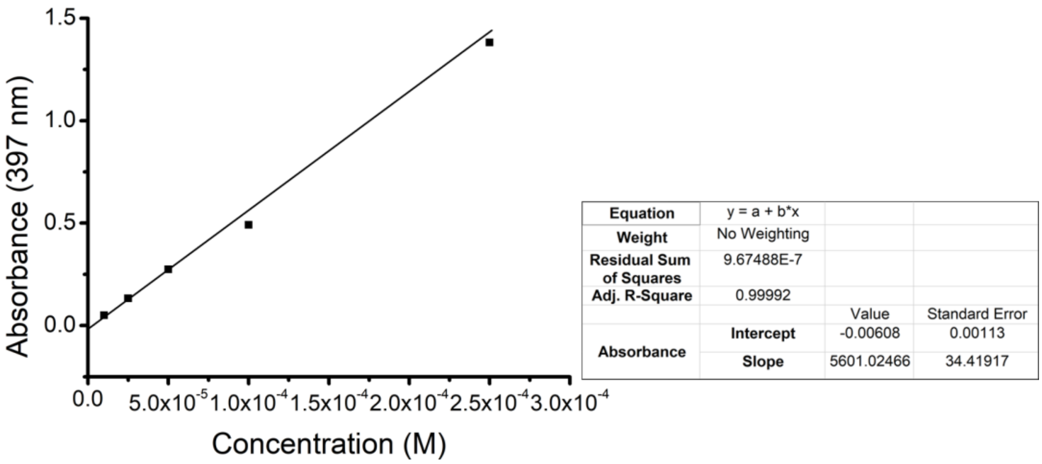


Figure 2. *UV-Vis spectra of 3-thph measured at different concentrations in chloroform.*

Once the spectra were obtained, the absorbance at 397 nm is plotted vs concentration. According to the Beer-Lambert law, the absorbance is directly proportional to the concentration of the analyte. However, this empirical law has some limitations. The presence of three-dimensional aggregates will produce higher light scattering than the isolated molecules, so the linear correlation will not comply. As shown in Figure 3, there is a decrease in the linearity at concentrations above $5 \cdot 10^{-5}$ M. This result suggests that solutions with concentrations beyond $5 \cdot 10^{-5}$ M have three-dimensional aggregates. From the slope of the absorbance vs. concentration plot, a value of 56010 $L \cdot mol^{-1} \cdot cm^{-1}$ for the molar absorptivity coefficient is obtained.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	9.67488E-7		
Adj. R-Square	0.99992		
		Value	Standard Error
Absorbance	Intercept	-0.00608	0.00113
	Slope	5601.02466	34.41917

Figure 3. *Absorbance vs concentration at 397 nm.*

4.2. Fabrication and characterization of Langmuir monolayers

4.2.1. Surface pressure vs area per molecule isotherms

Surface pressure vs area per molecule isotherms is one of the main techniques to characterize Langmuir monolayers (at air-water interface). We can gain insight about the aggregation phases of the molecules and at which area per molecule they occur upon the compression process. For both compounds, 3-thph and 2-thph, several conditions were used in terms to get reproducible isotherms, although without obtaining the desired results. The isotherms and the conditions at which these were registered for compound 3-thph are described in Table 3. The conditions considered were the concentration of the used solution, the volume spread over the subphase, if the solution was sonicated prior the deposition to eliminate potential three-dimensional aggregates, and if the solution was fresh or not. Each set of conditions was tested at least three times in terms to obtain reproducible isotherms. For compound 2-thph, the conditions are shown in Table 4. In both tables, experiments performed using different concentrations are highlighted with different color ranges. Darker colours indicate a change in the parameters between experiments with the same concentration.

Table 3. *Conditions used for registering surface pressure-area per molecule isotherms for compound 3-thph.*

Concentration (M)	**Volume (mL)**	**Sonication**	**Fresh solution**
$2.5\cdot10^{-5}$	2	No	Yes
$2.5\cdot10^{-5}$	2	No	No
$2.5\cdot10^{-5}$	4	No	No
$2\cdot10^{-5}$	5	No	Yes
$1\cdot10^{-5}$	4	No	No
$1\cdot10^{-5}$	6	No	No
$1\cdot10^{-5}$	6	Yes	No
$1\cdot10^{-5}$	6	Yes	Yes
$1\cdot10^{-5}$	6	No	Yes
$1\cdot10^{-5}$	8	Yes	No

Table 4. *Conditions used for registering surface pressure-area per molecule isotherms for compound 2-thph.*

Concentration (M)	Volume (mL)	Sonication	Fresh solution
$2.5\cdot10^{-5}$	4	Yes	Yes
$1\cdot10^{-5}$	4	Yes	Yes
$1\cdot10^{-5}$	6	Yes	No
$1\cdot10^{-5}$	6	No	No
$1\cdot10^{-5}$	6	No	Yes

In Figure 4 and 5 the most representative isotherms obtained for both compounds are showed. In addition, the theoretical values of area per molecule considering different interactions between interphase and molecules were calculated using the Spartan program. If the molecules interact with the air-water interfase using both thiophene rings or by the α, β unsaturated-carbonyl group, a theoretical area of 0.34 nm^2/molecule is obtained. Meanwhile, if the molecules interact using only one thiophene ring, the area would be 0.21 nm^2/molecule. The isotherms for 3-thph show different values of lift off area and different surface pressure values at the same area per molecule depending on the conditions used, and even between experiments performed using the same parameters. In addition, the lift off areas do not match the theoretical values that would be obtained if the molecules adsorbed by both thiophene groups or by the α, β unsaturated-carbonyl group, which would be higher. These results are obtained regardless of the conditions used, and suggest that the molecules adopt a configuration in which they adsorb just by one thiophene ring. However, three-dimensional aggregates are probably affecting the measurements and be the cause of low collapse pressure and lift off area of many isotherms.

For 2-thph, similar results are obtained. Most isotherms exhibit very low collapse pressures and lift off areas. However, some isotherms had lift off areas in agreement with molecules adsorbed by both thiophenes or by the α, β unsaturated-carbonyl group, and show larger collapse pressures than the remaining isotherms. The overall irreproducibility of the isotherms indicates that these experiments were affected by aggregates as well.

From the experiments is difficult to deduce the interaction of the molecules with the subphase, because the results do not match those calculated theoretically. To test if the prepared solutions had degraded as well as its concentration, UV-Vis spectra were recorded and compared with Beer-Lambert law. However, according to the intensity of the peaks and the wavelength at which these appeared, the solutions had not suffered degradation and had the desired concentration. To present conclusive results, more experiments have to be carried out.

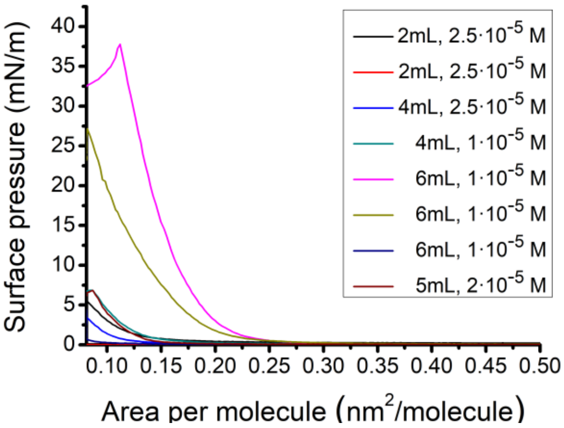


Figure 4. *Surface pressure vs area per molecule isotherms for compound 3-thph.*

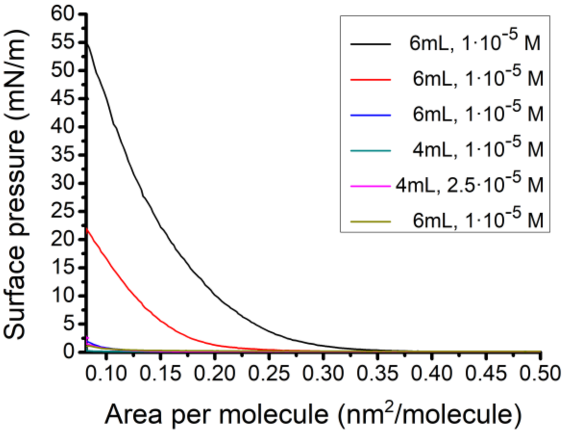


Figure 5. *Surface pressure vs area per molecule isotherms for compound 2-thph.*

4.2.2. Brewster angle microscopy (BAM)

The BAM allows observing “in situ” the formation of the monolayer upon the compression process and, therefore, the formation of aggregates and its evolution from isolated domains to more compacted states. The experiments were carried out using 6 mL of a non-fresh solution of 2-thph, $1 \cdot 10^{-5}$ M, which was not sonicated prior deposition upon the subphase. As depicted in Figure 6, at low pressures, the presence of domains is negligible and therefore, the image is almost black because no light is reflected from the interfase.

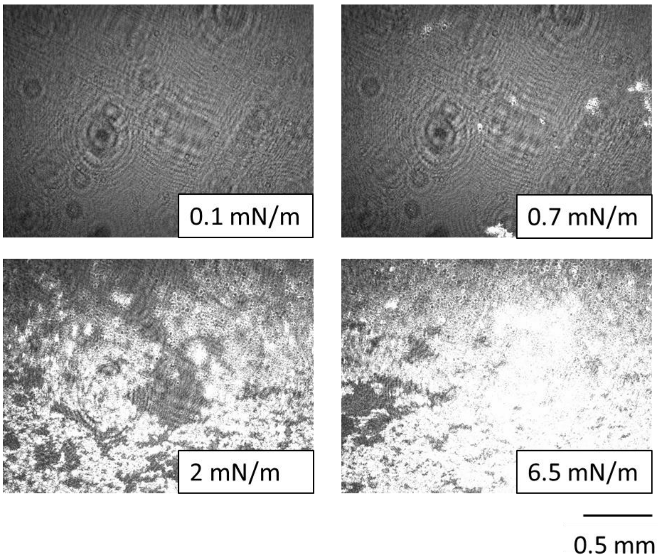


Figure 6. *BAM images recorded at several surface pressures.*

Upon the compression process, domains of molecules appear and to coalesce, which is evidenced by the appearance of white regions in the images. The interaction of the molecules produces a change in the refraction index of the water surface, and the value of the Brewster angle for that interface will not be the same as that of the air-water interface (53º).[72] Even at low pressures, the coalescence of the domains to more condensed structures can be observed, as the brightness of the images increases. However, the domains do not form homogenous structures and there are areas with different bright intensity. The difference in brightness is possibly indicating the presence of three-dimensional aggregates.

4.3. Fabrication and characterization of self-assembled monolayers (SAMs)

In parallel with the fabrication of Langmuir films, self-assembled monolayers were prepared as well. These experiments were performed in order to assess the effects that different fabrication techniques could produce in the interactions between molecules and substrates, and the molecular orientation in the monolayer.

4.3.1. Quartz crystal microbalance (QCM)

The QCM was applied to self-assembled monolayers (SAMs) of both compounds. As explained in the experimental part, the QCM is used to the surface coverage. To prepare the monolayers, two QCM substrates were incubated in solutions $5\cdot10^{-5}$ M of 3-thph and 2-thph in chloroform. With the Saurbrey equation, the frequency changes can be related with the mass variation caused by the ongoing deposition of the molecules on the substrate: (equation 1):

$$\Delta m = -C_F\cdot\Delta f \qquad \text{Equation 1}$$

where Δm is the mass change per unit area (g/cm^2), C_F is the sensitivity constant for the crystal (56.6 Hz·cm^2/µg) and Δf is the oscillation frequency variation. To assess if the deposition was completed, the changes of frequency were measured as a function of time until not variation was observed.

After 20 hours of incubation, no further changes in the frequency were observed for both compounds, which indicated that the assembly of the molecules was completed. The total variation of the frequency (after 20 hours of incubation) was -11 Hz for 3-thph. According to the Saurbrey equation; the surface coverage could be estimated:

$$\Delta m = -C_F/\Delta F = \frac{-11\ \text{Hz}}{-56.6\ \text{Hz·cm2/µg}} = 0.194\ \text{µg/cm}^2$$

$$\frac{0.194\ \text{µg/cm}^2}{288.4\ \text{g/mol}}\cdot\frac{1\text{g}}{1\cdot10^6\text{µg}}\cdot\frac{1}{2}\cdot 6.022\ 10^{23}\ \text{molecules/mol} =$$
$$= 2.03\cdot10^{14}\ \text{molecules/cm}^2$$

For 2-thph, the total variation of the frequency was -6 Hz. Repeating the calculations:

$$\Delta m = -C_F/\Delta F = \frac{-6\ \text{Hz}}{-56.6\ \text{Hz·cm2/µg}} = 0.106\ \text{µg/cm}^2$$

$$\frac{0.106\ \text{µg/cm}^2}{288.4\ \text{g/mol}}\cdot\frac{1\text{g}}{1\cdot10^6\text{µg}}\cdot\frac{1}{2}\cdot 6.022\ 10^{23}\ \text{molecules/mol} =$$
$$= 1.11\cdot10^{14}\ \text{molecules/cm}^2$$

In the experiments we obtain roughly the double of molecules deposited for 3-thph than for 2-thph. The result indicates that the position of the sulphur atom in the thiophene groups has an effect in the adsorption of the compounds. The position 3 favours the adsorption of the molecules to the gold substrate better than the position 2. In addition, the result for 3-thph is in perfect agreement with the value calculated with the Spartan program, $2.18\cdot10^{14}$ molecules/cm^2.

4.3.2. X-ray photoelectron spectroscopy (XPS)

SAMs of 3-thph and 2-thph were studied by XPS. The XPS gives information about the molecular orientation of the deposited monolayer, and about which molecular groups interact with the substrate. The SAMs were prepared by incubating gold substrates for 24 hours in solutions of $5\cdot10^{-5}$ M of both compounds in chloroform. To compare the peaks obtained and assess the changes in the spectra caused by the interactions of the compounds with the substrate, XPS spectra of 3-thph powder was also registered. The region measured was S 2p. The spectra are depicted in Figure 7.

For the 3-thph powder, three peaks are observed. The peaks at 164 and 165.15 eV are due to the emissions from the orbitals 2p 3/2 and 2p 1/2 of the sulphur atom. This doublet is characteristic of the S, and the peaks show an intensity ratio of 2:1 respectively, and a separation of ca. 1.2 eV. Meanwhile the peak at 166.6 eV is attributed to oxidized sulphur;[73] which could influence in the formation of the monolayer.

The data for a SAM of 3-thph shows three peaks at 161.85, 163.0 and 164.8 eV. These peaks are assigned to the same transitions observed in the powder. The 2:1 intensity ratio and the displacement of 1.16 eV between the peaks allows to determine that at 161.85 and 163.0 eV, the transition from S 2p 3/2 and S 2p 1/2 take place. The peak at 164.8 is associated to a S 2p emission from oxidized sulphur. The displacements to lower binding energies are due to the S-Au binding.[74] In addition, since there are no peaks at the binding energies obtained for the powder, it indicates that all the S atoms are interacting with the gold substrate. For the SAM of 2-thph the peaks appear at 161.85, 163.05 and 164.8 eV. Due to the binding energies and the intensity ratios, the peaks correspond to the same transitions as those of 3-thph. Therefore, the peaks at 161.85 and 163.05 are assigned to S 2p 3/2 and S 2p 1/2 respectively. The peak of oxidized sulphur appears at 164.8 eV. Accordingly, from the XPS results, it is deduced that both 3-thph and 2-thph bind to the Au substrates through both thiophene groups.

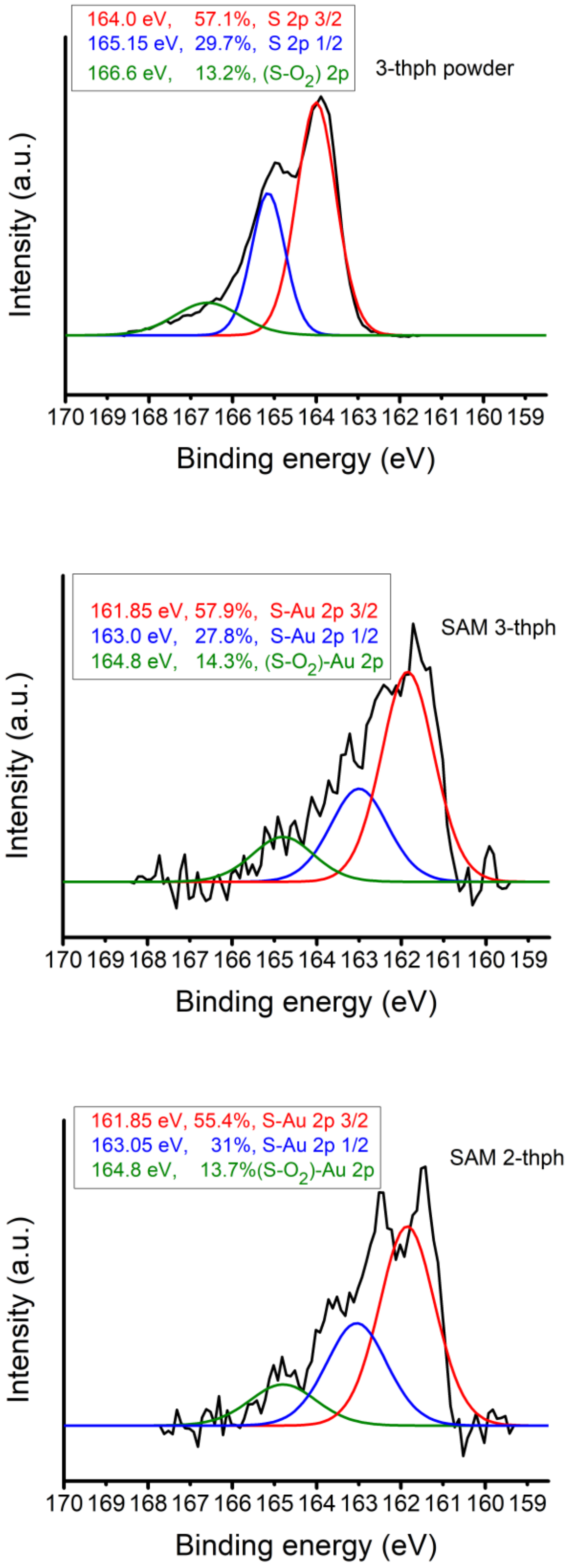


Figure 7. *XPS spectra in the S 2p region for SAMs of 3-thph and 2-thph, and for the 3-thph powder.*

The thickness of both SAMs was also determined. For that purpose, the intensity of Au 4f signals for a bare Au substrate are measured and compared with the signals of Au 4f for substrates covered with SAMs of 3-thph and 2-thph. The attenuation of the signal is related to the thickness of the deposited monolayer as expressed by equation 2:

$$d = \lambda \cdot \text{sen}\theta \cdot \ln (I_{Au}/I) \qquad \text{Equation 2}$$

where d is the monolayer thickness, λ is the inelastic mean free path of the photoelectrons (4.2 ± 0.1 nm), θ is the emission angle of the photoelectrons (90º) and I_{Au} and I are the intensities of the substrate without film and with deposited film, respectively.

By applying the equation 2, values of 0.85 nm for 3-thph and 0.81 nm for 2-thph are obtained. Both values match the calculations obtained by the Spartan program, which gives a height of 0.8 nm for a molecule adsorbed by both thiophenes. The spectra are provided in Figure 8.

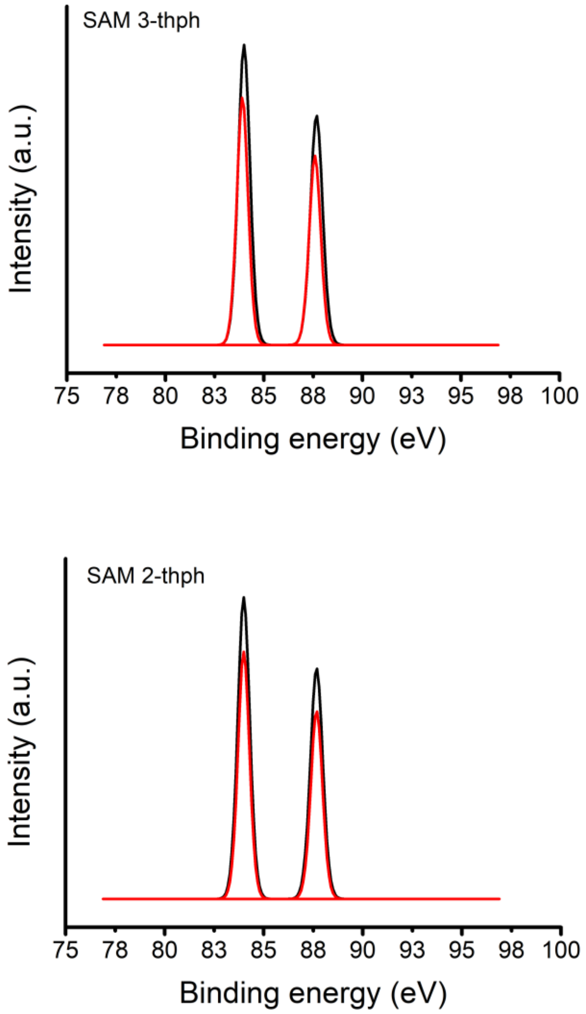


Figure 8: *XPS spectra in the Au 4f region for bare gold (black) and for SAMs of 3-thph and 2-thph (red).*

5. Conclusions

In this final master project, the state of the art in the field of molecular electronics, with particular emphasis on the fabrication techniques of electrode | monolayer | electrode, has been presented. Accordingly, to the most relevant bottom-up techniques used in the field of molecular electronics, namely the self-assembly and the Langmuir-Blodgett methodologies, in this project the surface behaviour and assembly capabilities of two curcumin derivatives have been studied. As mentioned before, only preliminary results and conclusions have been obtained due to the confinement imposed by the COVID-19 and closure of the laboratories. Among the most relevant conclusions so far obtained we can mention:

- Monolayers of 3-thph and 2-thph can be fabricated using the self-assembly technique.
- QCM measurements of SA monolayers reveal that the adsorption of 3-thph is favoured compared to that of 2-thph, therefore the position of the S atom affects the deposition and the packing of the molecules in the molecular assembly.
- XPS data indicate that both 3-thph and 2-thph are chemisorbed onto the gold substrate by interacting with both S atoms of the thiophene groups.
- The characterization of 3-thph in solution indicated that according to the Beer-Lambert law, solutions with concentrations above $5 \cdot 10^{-5}$ M contain three-dimensional aggregates.
- Further experiments are needed to optimize the conditions for the fabrication of Langmuir-Blodgett films since the information obtained from the characterization of the monolayers at the air-water interphase (by surface pressure vs area per molecule isotherms and BAM) is not conclusive.

In the near future, further experiments will be done including not only the optimization of the conditions (if possible) for the fabrication of LB films, but also a comprehensive the characterization of the monolayers deposited onto the bottom-electrode as well as the measurement of the electrical properties of these nascent junctions.

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