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# **Influence of intermolecular order at the interfaces**

**Parisa Sehati**



**Linköping University**  
**INSTITUTE OF TECHNOLOGY**

**Department of Physics, Chemistry and Biology**

**Linköping University, SE-581 83 Linköping, Sweden**

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**To my family**



## ABSTRACT

The work presented in this thesis covers a range of different surfaces and interfaces of organic molecules/polymers and metallic materials. It is of vital importance to understand how charge transfer processes and other electrical interactions existing at physisorped contacts can influence the electronic structure at an interface. Hence our mission in these studies was to understand the physics happening at the aforementioned surfaces and interfaces of relevance to electronic devices, mainly solar cells.

In order to explain the observed measurements at physisorped interfaces, a model previously has been put forward. The Integer Charge Transfer (ICT) model explains why and how charge transfer can occur at an interface consisting of  $\pi$ -conjugated molecules/ polymers and a metallic/semi-conducting substrate. The main output of this model is depicted in a typical curve and considers two different regimes, namely when charge transfer occurs and when it doesn't happen. This curve is obtained through measuring work function of the organic semi-conducting material atop of different substrates covering a wide span of work functions. The measured work function of the organic-substrate is visualized as the vertical axis of a graph with the substrate work function as the horizontal axis. The ultimate curve then resembles the famous, well-known "*mark of Zorro*". The part with slope=1 is an indication of the vacuum level alignment. In plain text it means there is no charge transfer between deposited/ span material and substrate. On the other hand, part of the curve with slope=0 is a measure of Fermi-level pinning and occurrence of charge transfer. The threshold point between these two regimes is called pinning point which either implies ICT<sup>+</sup> (positive Integer Charge Transfer state) or ICT<sup>-</sup> (negative Integer Charge Transfer state). It is crucial to realize that a  $\pi$ -conjugated molecule can be both acceptor or donor depending on the substrate work function.

Our efforts were aimed toward further improving this model and understanding impacting factors on charge transfer and the pinning point.

Factors such as interface dipole and inter- and intra-molecular order are among the most important ones. Order and packing of the spin-coated and vacuum-deposited materials thus directly affect the position of the pinning point/Integer Charge Transfer states. Therefore any parameter which can influence order/packing can affect the interface dipole and resulting energy level alignment. Intra-molecular order, for example, can be tuned by annealing (twisting of the conjugated chains, crystal grain growth) while thickness of the deposited material also can modify intermolecular packing. All those factors were studied in the context of this thesis, mainly using materials common in so-called bulk heterojunction solar cells. Another way to tune the energy level alignment at interfaces is through Self-Assembled Molecules (SAMs). We have utilized such molecules to manipulate the surface of zinc oxide, a common ingredient of transparent solar cells, studying the effects on work function and therefore charge injection properties.

## POPULÄRVETENSKAPLIG SAMMANFATTNING

I dagens moderna samhälle, "Organisk Elektronik" industri har kommit i kontakt med vårt dagliga liv, mycket närmare än vi vet. Apparater och komponenter baserade på "Organisk Elektronik" kan hittas i mobiltelefoner och eller tabletter. Lysdioder (Organic Light Emitting Diodes- OLED), organiska solceller samt TV-apparater som innehåller Organiska Displayer, börjar lanseras på marknaden. Mer ambitiösa produkter såsom "Elektroniskt papper" syns i horisonten. Alla de ovan nämnda apparater och komponenter är gjorda av organiska molekyler vilka som sunt förnuft accepteras att vara elektrisk "isolerande material". Men verkligheten är helt annorlunda. Plaster kan vara halvledande och även ledande snarare liknande metaller.

Organiska halvledare kan vara antingen molekyllära fasta (som är ganska små) eller polymera material som är relativt stora molekyler som utgörs av hundratals atomer och monomerer. Dem molekyllerna hålls samman av svaga Van der Waals krafter vilket i sin tur påverkar materialegenskaper som ledningsförmåga samt hur de staplas och ordnar sig på föregående skikt. Van der Waals krafter finns både sinsemellan molekyllerna samt mellan molekyler och substrat. Slutsatsen är att morfologin kan förändra andra mätbara egenskaperna (utträdesarbete, jonisering potential, mm) och tillsammans kan de påverka funktionen hos komponenterna.

Därför är vårt mål i denna avhandling att förstå hur inter- och intramolekyllära faktorer påverkar laddningsöverföring samt anpassning av energinivåer i organiska halvledare som används främst i organiska solceller. Inter- och intramolekyllära hänvisar till saker som sker sinsemellan respektive inom molekyler/monomerer. Anpassning av energinivåer betyder modifiering och anpassning av de energinivåer som tar emot en elektron eller ett hål vid laddningsöverföring.

Intramolekyllära ordning och dess påverkan på energinivån anpassning samt laddningsöverföring undersöktes i artiklarna I & II, medan i artiklar III & V har

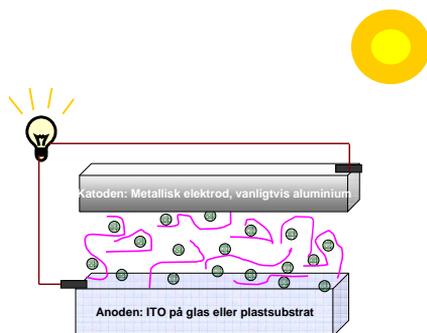
vi fokuserat på intermolekylära nyckelparametrar. Artikel IV ägnades åt att förstå hur ytor av "enkristallint" ZnO kan modifieras genom att ytbeläggning med organiska molekyler.

I första artikel belyste vi relationen mellan gränsytans dipol och elektron-hålparens sönderdelning i solcellens aktiva organiskt material och korrelerade detta med solcellens effektivitet. En organisk solcell är en apparat som omvandlar solenergi till el. Solcellen består av 2 elektroder, ofta Aluminium och Indium Tenn Oxid (ITO), samt minst 2 olika organiska halvledande material vilket en är elektron ledande och den andra överför positiv laddning. Sol fotoner träffar solcellen och om de absorberas skapas excitoner: elektron-hål-par. Dessa par binds samman av elektrostatisk attraktion (elektronen är negativ, hålet är positiv). I en solcell vill man att excitoner sönderdelas och att de fria laddningar, det vill säga elektroner och hålen, sedan leds bort mot sina respektive elektroder vilket gör att ström sedan kan gå i en extern krets (se Bild. 1). På så sätt, kan man omvandla sol strålningar till el.

Vi fann att en dipol vid gränsytan mellan de organiska materialen i en sol cell kan förekomma redan i grundtillståndet och spekulerade i att detta ökar sannolikheten för att de elektron-hål-par som skapas sönderdelas och fria laddningar når ut till elektroderna, vilket direkt skulle förbättra solcellens effektivitet.

I nästa artikel (II) expanderade vi vår undersökning och fokuserade på termiskt inducerat vridning i sidokedjorna i en halvledare polymer som kallas P3HT. Vårt mål var vidare studera inter- och intramolekylär ordning och deras effekt på energinivåupplinjerig vid gränsytor samt deras påverkan på solceller baserad på P3HT/PCBM. Värmebehandling ger ökad kristallinitet men introducerar också oordning vid gränsytorna mellan de olika kristallkorna, vilket introducerade dipoler vid dessa gränsytor då spontan laddningsöverföring kan ske från P3HT till PCBM under dessa förutsättningar.

Kombinationen av dessa två effekter leder till en förbättrad generering av fria laddningar i solcellen.



**Bild 1. Schematisk bild av en organisk solcell: små bollar liknar PCBM medan krökta linjerna representerar en polymer såsom P<sub>3</sub>HT. Organiska solceller kan baseras på andra organiska material. I detta exempel valde vi en av de rådande kombinationerna av aktivt organiskt material.**

I artiklar (III & V) har vi fokuserat på de intermolekylära egenskaperna enbart. Vi belade substrat med olika molekyler och mätte deras joniseringspotential och gränsytans dipol, vilket gjorde det möjligt att bestämma molekylernas orientering och energinivåupplinjering. Det visade sig att sättet de belagda molekylerna staplas ovanpå varandra och ovanpå substratet kan vara beroende av växelverkan mellan substrat/belagda molekyler och tjockleken av filmen.

Papper III handlade om pentacen och PTCDA. Pentacen är känd för sin höga mobilitet och PTCDA valdes eftersom den har varit "försökskanin" för ytfysiker i mycket lång tid. Vi belade kemisk rengjort guld med pentacene och senare täckte den med PTCDA. Det visade sig att dipoler skapas genom laddningsöverföring vid båda gränssytorna, Au/pentacen och pentacen/PTCDA, och att Fermi-nivån vid de två gränssytorna låses till hål-injektionsnivån i pentacen respektive elektron-injektionsnivån i PTCDA: pentacen bidrar med elektroner till både guld och PTCDA vid gränssytorna. Resultaten antyder även

att interaktionen mellan PTCDA och pentacen kan under vissa förhållanden vara stark för att ändra pentacens struktur vid beläggning av PTCDA.

I artikel V studerade vi hur intermolekylär ordning påverkar energinivåupplinjerings då molekylerna även har en intrinsisk dipol. Vi använde här Acridine Orange Base (AOB) som är en stark elektondonator och har en intrinsisk dipol. Vi beläggning av AOB på ett större antal substrat kunde vi påvisa ett starkt beroende på molekylernas ordning och den resulterande energinivåupplinjerings, där t.ex. Fermi-nivåns position vid gränssytorna kunde variera med över en elektronvolt.

Papper IV innehåller studier av en något annorlunda kategori av halvledande material: oorganiska fasta ämnen. Kisel-baserade solceller kräver mycket produktionsenergi och därför letar man efter nya material och metoder för att ersätta dessa. Zinkoxid, ZnO, är ett lovande halvledande material som är transparent, relativt energisnålt att tillverka och kan användas som elektroder i t.ex. organiska solceller eller OLED. För att kunna anpassa ZnO ytornas egenskaper till en viss komponentfunktion, kan man belägga ytorna med t.ex. organiska molekyler som ökar eller minskar utträdesarbetet. Vi undersökte hur olika zinkoxid ytor kan modifieras just på detta sätt. Zinkoxid proverna är utskurna ur enkristaller av zinkoxid och kan existera antingen i polära eller icke polära former. De polära ytorna kan antingen vara terminerade av zink eller syre, och dessa två ytor var föremålen för vår studie där en stark elektondonator användes för att minska utträdesarbetet för att förbättra ytornas funktion som elektron-injicerande elektroder.

Nu hoppas jag att läsaren har fått en inblick i den forskning som genomförts under mina doktorandstudier där energinivåupplinjerings vid organiska gränssytor har studerats med avsikt att klargöra effekter av inter- och intramolekylär ordning vid gränssytorna. Resultaten är till nytta för teoriutveckling men även för förbättrad design av organiska elektronikkomponenter.

## ACKNOWLEDGEMENT

It has been fantastic years and journey for me at the division of surface physics and chemistry, IFM department, Linköping University. When I started as PhD student, I didn't know anything about surface Physics but I had encountered problems originating from "Surfaces" during the time I worked at plastic and rubber industry in Iran where we used to have metal-rubber adhesion and plating of plastic articles. During adhesion process, metal surfaces needed to be polished; some surfaces should be cleaned by chemical solvents with different pH and for some of them solvents needed to be warm. On the other hand, another group of metal treatments required sand blasting of the metal surface. I had a vague idea that there should not be anything between metal and rubber article except adhesive material but why some metals should be sand blasted and some others should be cleaned with weak alkaline solvents? Or why for some surfaces we needed warm solvents? Another applied issue which kept me busy for long time was plating of plastics. Electroplating of plastics was a mystery to me as I knew the fundamentals of electroplating process but how come we can plate a plastic article when plastics are insulators? It never occurred to me that plastics can be semiconductors even conductors. I didn't know the answer of those questions but I wanted to know and learn more. Just following instructions without knowing "why" did not satisfy me. Couple of years later, I attended a course named "Organic Electronics I" taught by Prof. Michel P. de Jong at Linköping University which could answer some of my "old" questions. It was clear to me: I would like to learn more about these fascinating materials. So, I applied for a PhD position at the division of "surface Physics and Chemistry" which I was accepted. It was a fantastic, golden opportunity for me to know more about both surfaces and polymers.

When we were kids in Iran, we learned a short poem attributed to Avicenna: "my knowledge reached a level to know how much I do not know". I learned how much exists out there, that neither I nor anyone else knows....An

amazing experience, I call it! But despite all unknowns and lack of my knowledge, at least I can claim I know what a surface is!!

I have to express my deepest gratitude to my first supervisor, Prof. Michel P. de Jong, currently pursuing his research carrier at the University of Twente, The Netherlands and my present supervisor Prof. Mats Fahlman to pave my path and give me the opportunity to learn more about Organic Semi-conductors at the division of “Surface Physics and Chemistry” in Linköping University. I really appreciate that you counted on me and gave me the chance to work as PhD student at your group. Thank for all your patience, assistance and time you invested on me!

Working in a scientific environment requires collaboration, asking for help and assisting your lab fellows. In this regard, I would like to express my gratitude to all my colleagues and friends, for their precious support, for all the discussions, long hours in the lab together, coffee breaks, Friday group lunches and overall for making a friendly, cheerful place to work. I wish you, all the best!

Being admitted as a PhD student is not the easiest of all for the family members: My family members tolerated tough conditions since there was stressful and long working hours which made me apart from them. There is no doubt that their encouragement and patience is not comparable to any thing else. My deepest gratitude to Per and Tara.....for all those moments that you stepped in for me and accepted my unusual schedule.....Tara, one day I may read your thesis and attend your defense lecture since I have seen glimpses of observation and research in you, my lovely girl!

My sisters Laleh, specifically Arezu always encouraged me and tried to ease my mind and pushed me forward. Thank both of you.

I wish my mother could attend my dissertation. Unfortunately, she suddenly passed away in May 2012. It still breaks my heart and brings tears into my eyes that she will not be there. I imagine you are there, mom!



## PAPERS INCLUDED IN THIS THESIS

### ▪ Paper I

**Energy level alignment at metal-organic and organic-organic interfaces in bulk heterojunction solar cells.**

P. Sehati, S. Braun, L. Lindell, X. Liu, L. M. Andersson and M. Fahlman

*IEEE Journal of selected topics in quantum electronics*, 16(2010)1718

### ▪ Paper II

**Spontaneous charge transfer and dipole formation at the interface between P<sub>3</sub>HT and PCBM.**

H. Aarnio, P. Sehati, S. Braun, M. Nyman, M. P. de Jong, M. Fahlman and R. Österbacka

*Advanced Energy Materials*, 1 (2011)792

### ▪ Paper III

**Energy level alignment in Au/Pentacene/PTCDA trilayer stacks**

P. Sehati, S. Braun, M. Fahlman

*Manuscript*

### ▪ Paper IV

**The influence of SAM on the polar ZnO surfaces**

P. Sehati, S. Braun, M. Fahlman

*Manuscript*

### ▪ Paper V

**Tuning low work function contacts using molecular donor layers: intermolecular order effects.**

P. Sehati, D. Çakır, G. Brocks, M. Fahlman and S. Braun

*Manuscript*

### **My Contribution to the papers:**

I was responsible for all the spectroscopy and deposition experiments and wrote the manuscript/ first draft except paper V which I only was responsible for the laboratory- related works and participated in making the final draft.

### **PAPERS NOT INCLUDED IN THIS THESIS**

- 1) Determination of energy level alignment at interfaces of hybrid and organic solar cells under ambient environment

R. J. Davis, M. T. Lloyd, S. R. Ferreira, M. J. Bruzek, S. E. Watkins, L. Lindell, **P. Schati**, M. Fahlman, J. E. Anthony and J. W. P. Hsu

*Journal of Materials Chemistry*, 21(2011)1721

- 2) Solution processed ZnO nanowires/ polyfluorene heterojunctions for large area lightening

A. Wadesa, G. Tzamalís, **P. Schati**, O. Nour, M. Fahlman, M. Willander, M. Berggren and X. Crispin

*Chemical Physics Letters*, 490(2010), 200-204

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## 1. General introduction

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### 1.1 History

*To understand a science, it is necessary to know its history.*

*- Auguste Comte*

This thesis is about the physics occurring at the surfaces and interfaces featuring organic conjugated molecules/polymers. Organic Electronics, known also as polymer electronics and plastic electronics, is the scientific field & industry that applies conducting/semiconducting properties of organic conjugated materials in order to achieve a specific outcome such as light emission or electric current.

Despite the general belief that plastics and organic materials are electrically insulators, these fascinating materials provide a wide range of electrical conductivity: insulation, semi-conduction or even metal-like conduction. The first scientifically produced organic semiconductor during an early recorded polymerization reaction took place in year 1862 by Henry Letheby [1]. He produced polyaniline through anodic oxidation of aniline dissolved in sulphuric acid while he was trying to understand the fatal

poisoning effect of nitrobenzol and its reaction with stomach's hydrochloric acid which led (according to him) to aniline.

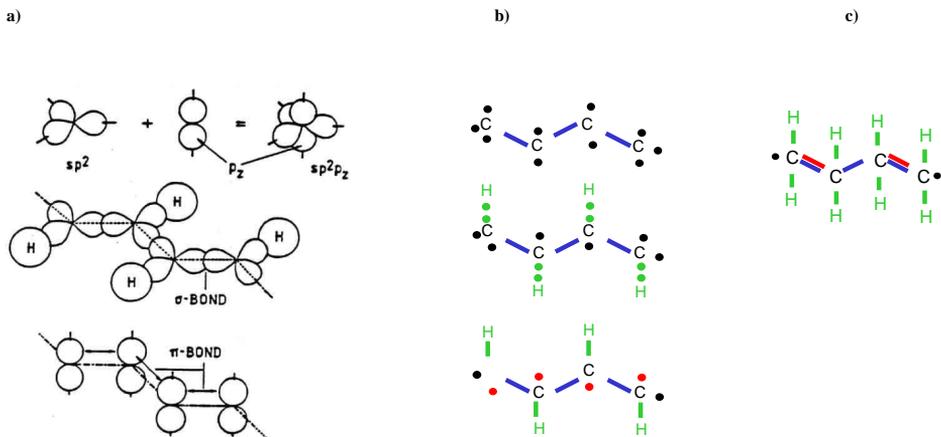
Later on, long before the official discovery of conductive organic polymers at 1970s, organic semi-conductors were used in devices such as solar cells. Already at 1950s there were organic solar cells with p-type organic semiconductors which could generate voltages up to 1V [2]. Electrical conductivity of organic materials such as anthracene was studied and reported simultaneously [3].

Almost a century after Letheby's experiment, during 1970s, an accident made by a graduate student in consuming 1000 times more Ziegler-Natta catalyst for polymerization of acetylene in Hideki Shirakawa's lab led to the discovery of ragged pieces of a silver colored compound. Shirakawa discussed the mysterious compound with MacDiarmid, professor in chemistry in University of Pennsylvania, who was visiting researcher in Japan at the time and had given a talk regarding polymeric sulfur nitride (SN)<sub>x</sub> in Tokyo Institute of Technology. Sulfur nitride polymers have metallic gold color and show electrical properties although they are not metals. MacDiarmid and A. Heeger, who was physics professor at the same time in University of Pennsylvania, had extensive experience on them. So when MacDiarmid heard about another compound having metallic appearance, he invited Shirakawa to University of Pennsylvania in order to study the new class of materials. Heeger and MacDiarmid had previously doped sulfur nitride polymers with bromine to increase their conductivity. After doping of nitride sulfur polymers, conductivity increased 10 times but when they doped the new substance, polyacetylene, with bromine, its conductivity increased as large as 10 million times![4] This breakthrough occurred at year 1976 and with that a new era began: the era of plastic electronics! Soon after that, scientists rushed to work on organic materials which are cheap and flexible, had potential for low production cost due to ease of processing, could realize devices with low power consumption and had the possibility to tune color and optical properties. Soon after, plastic conductors and semi-conductors found their way in various applications ranging from transistors

[5, 6], organic light emitting diodes [7-10], photovoltaic cells [11, 12] to more exotic applications like spin valves [13, 14] and light emitting electrochemical cells [15].

## 1.2 Conjugated materials

Conjugated materials are organic semiconductors composed mainly of carbon and hydrogen atoms and occasionally made of other low weight atoms such as oxygen, nitrogen and sulfur. Their conjugation, *i.e.*, alternative single and double bond between adjacent carbon atoms compel delocalization of the electron wave function. Delocalization of the electrons wave function means that electrons participating in  $\pi$ -bonding between C-C atoms can move rather freely along the conjugation chain. In the case of polymeric systems delocalization of  $\pi$ -electrons can extend over fairly large part of the chain. Otherwise in an organic molecular solid, delocalization typically extends over the whole molecule. Let's have a look at electronic structure and bonding in polyacetylene (see Figure 1.1).



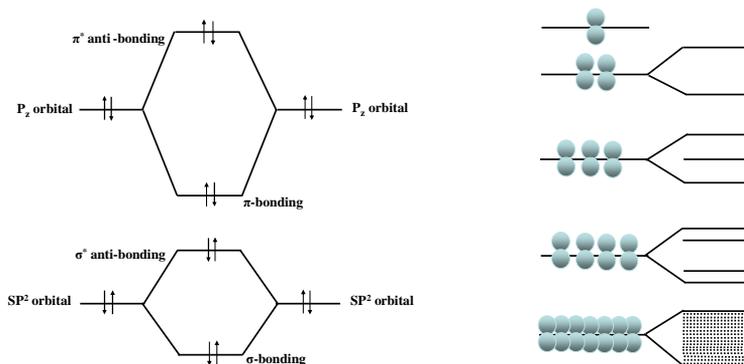
**Figure 1.1:** Schematic structure of polyacetylene showing conjugation along its chain. a) Both  $\pi$ - and  $\sigma$ - bonds along with different orbitals are visible. b) Single bonds are shown with green and blue color while red dots in the lowest part resemble electrons in  $p_z$  orbital which eventually form  $\pi$ -bond. c) Final molecular structure of polyacetylene with  $\pi$ -bonds shown with red color. The other bonds shown by blue and green color are covalent single bonds.

Covalent single bonds ( $\sigma$ -bonds) are built up upon overlap between  $sp^2$  orbitals. There are 3  $sp^2$  orbitals in each C atom. Two of those orbitals bond to their counterpart orbitals belonging to the adjacent carbon atoms and the third one forms a single bond with hydrogen atom. The fourth valence electron of carbon atom exists in  $p_z$  orbital which is perpendicular to the  $sp^2$  orbitals. Every carbon atom forms double bond ( $\pi$ -bond) with only one of its neighboring carbon atoms by overlapping between  $p_z$  orbitals. Due to the existence of  $sp^2$  hybridization, the backbone of polyacetylene, *i.e.*, its conjugation chain is absolutely planar. The planarity of the conjugation backbone is a common feature among all the members of organic semiconductors family which includes both molecules and polymers.

Due to that, the overlap between  $p_z$  orbitals is considerably smaller than the overlap between  $sp^2$  orbitals which means double bonds are weaker than single bonds. Even energetically, double bonds have higher energy and are less stable compare to single bonds which means highest filled levels/HOMO and lowest empty states/LUMO originate from  $\pi$ -bonding and  $\pi^*$ -antibonding orbitals, respectively. Breaking the  $\pi$ -bonds doesn't lead to degradation of the molecular structure since  $\sigma$ -bonds are stronger than  $\pi$ -bonds and are left even after breaking the  $\pi$ -bonds. Highest Occupied Molecular Orbital (HOMO) in organic solids is analogous to Valence Band (VB) in inorganic materials. Similarly, Lowest Unoccupied Molecular Orbital (LUMO) in an organic semiconductor is equivalent to Conduction Band (CB) in their inorganic counterparts. According to *Band theory* [16], the origin of bands in a large inorganic solid can be attributed to its large number of particles and its well-defined crystalline structure. Given a solid material with large number of constituting atoms/molecules sitting in a crystal structure, its energy levels lie closely to each other, so close that they literally build a band (Figure 1.2). The band built by highest occupied levels is known as valence band (VB) and the one constituted from the lowest unoccupied levels, as conduction band (CB). Very often, we apply "band" for HOMO and LUMO levels in polymers which is not completely true since number of particles in polymers, even very large ones, is not comparable to the number of particles in a solid material such as Fe or SiC. Furthermore, the energy discrepancy among sublevels of energy levels in

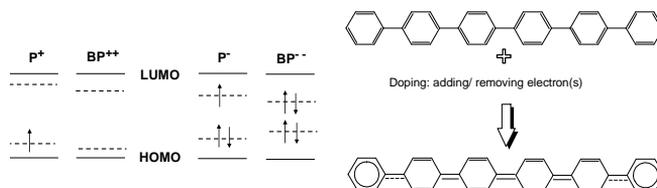
organic materials is rather large in comparison to their inorganic equivalents and finally, due to the weak van der Waals forces which hold them together, organic solids rarely exist as single crystals and even when they do exist, the wave function overlap between neighboring molecules is rather small. Hence, organic solids do not generally have bands in the sense that they exist in inorganic materials. But yet, this terminology is often accepted and practiced by the scholars of the field.

Doping *i.e.*, adding or removing an electron from a conjugated system involves population of LUMO and depopulation of HOMO. Upon adding/ removing an electron to/from the system, organic materials undergo relaxation mechanisms: electronic relaxation and nucleic relaxation. Nucleic relaxation manifests itself as alteration of the bond lengths and bond angles, *i.e.*, geometrical modifications. The newly formed particle with modified geometry is known as polaron. Geometrical modification (polaron) is delocalized over the backbone of the polymer to a certain degree. Due to the certain delocalization of the charge, nuclei have enough time to respond to the new conditions: lack/ surplus of charge. If there were complete delocalization of the charges in the system, then charges would not stay on each position long enough until nuclei react to them by translational changes. In such a case, then the energy of the doped



**Figure 1.2:** Left) Overlap between  $sp^2$  orbitals and  $P_z$  orbitals results in  $\sigma$  and  $\pi$  bonds: bonding and anti-bonding. Right) Simple illustration of formation of bands due to the overlap of many similar orbitals belonging to chemically equivalent atoms/building units. Here we depicted dumbbell-like  $p$ -orbitals.

system would have been equal to the energy of LUMO (HOMO) but in reality delocalization is confined which leads to geometrical relaxation and as a result of them, the energy of the negatively (positively) doped system is lower (higher) than LUMO (HOMO) [17]. Doping (adding or removing electron) of the cyclic conjugated compounds leads to the formation of quinoid structures (right panel Figure 1.3) which are less stable than the original aromatic rings [18]. Quinoid structures are accompanied by both geometrical changes (usually elongation of bond length of C-C bonds parallel to the chain axis direction) and modification of band gap (energy difference between highest bonding and lowest anti-bonding orbitals) [19]. Theoretical results gathered in [19] demonstrated a direct relationship between reduction of band gap and increase of



**Figure 1.3:** Left) Electronic and geometrical modifications upon doping can be seen. Right) Delocalization area (quinoid structure) is confined between dotted lines. Figure is based on a similar illustration in reference[20].

quinoid structure due to doping. These findings can easily be interpreted by polaron/bipolaron concept. Upon doping of an aromatic conjugated system, new electronic states appear in the previously forbidden gap which leads to the contraction of band gap (left panel Figure 1.3).

### 1.3 Electrical conductivity in solids

Conductivity is generally the ability of the material to conduct either electricity (electrical conductivity:  $\sigma$ ) or heat (thermal conductivity). In order to manifest conductivity, conductors *i.e.*, carriers should exist. Carriers can be ions (in that case conductivity has ionic nature) or free electrons as in the case of electrical conductivity. Conductivity is related to the number of free carriers (both negatively ( $n_n$ ) and

positively ( $n_p$ ) charged), the charge they carry ( $q_n$  and  $q_p$ ) and their mobility ( $\mu_n$  and  $\mu_p$ ) according to the following equation:

$$\sigma = n_n q_n \mu_n + n_p q_p \mu_p$$

**Equation 1**

where  $n_n$  and  $n_p$  refers to the number of negatively and positively charged carriers, respectively.

Considering electrical conductivity, there are three classes of materials: insulators, semiconductors and metals. This classification is based on the size of their band gap  $E_g$  and the way they fill their energy levels/bands (Figure 1.4). As a rule of thumb, materials with 1 eV- 2 eV even up to 3 eV [21] band gap are known as “semiconductors”.

In order to experience electronic conductivity in materials, charge carriers should be either in partially filled levels or have access to empty states. If the specimen is irradiated by the photons with proper energy, proportional to the band gap, or have enough thermal energy then electrons can be excited into the LUMO/CB. Thereafter, excited electrons staying in unoccupied levels do have access even to the empty states of neighboring molecules/atoms. Another way of having electrical conductivity in a (semiconducting) material is by enforcing it, *i.e.*, by either doping it or applying electric potential [18]. In both of them free charge carriers will be flowed into the material that will lead to electrical conductivity. Insulators have such a large band gap that at room temperature or by irradiation with optical light charge carriers/electrons of HOMO/VB can not overcome it and ascend to LUMO/CB. Metals on the other hand, have no gap as they feature a partially filled highest occupied band and as a result the electrons can easily, without any external energy, move to empty sites within the band. Electrons thus can freely move to everywhere in the metal which means high electrical and thermal conductivity.

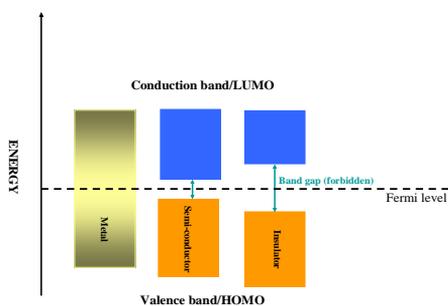


Figure 1.4: Filled and empty energy bands/levels in metals, semiconductors and insulators.

## 1.4 Fundamental concepts in surface science

*God made solids, but surfaces were the work of the devil.*

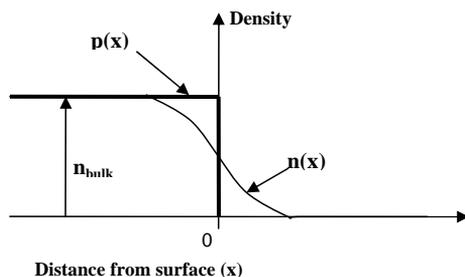
- Wolfgang Pauli

In this thesis we discuss properties of surfaces and interfaces of organic solids. Obviously, we take into account tailoring of these surfaces as well. We will employ terms such as work function, Ionization Potential (IP), surface and interface, surface dipole and etc. But what do they really mean? In this chapter, we try to briefly explain these fundamental concepts.

*Surface:* The most trivial definition of a surface is the area that has no boundary neighbors. IUPAC definition for surface is: “***the boundary between two phases***” [22]. In order to produce two surfaces from a solid, a specific amount of energy should be consumed. This energy is known as *surface energy* [23]. Energetically, all surfaces are unfavorable since they need positive energy of formation. In material physics, surface will be defined as an area consisting molecules/atoms that are not chemically bonded to any other molecules/atoms. These molecules/atoms have the so-called *dangling* bonds: a term referring to unsatisfied/unpaired/broken covalent orbitals existing at/extending out from the surface due to the lack of pairing molecules/atoms which is a consequence of surface formation. Hence, a dangling bond is nothing but the surface electrons spilling out or leaking into vacuum whenever crystal symmetry (bulk) is broken at the

surface [24]. These electrons/electronic tail extending out from the surface are denoted as  $n(x)$  in Figure 1.5. Presence of dangling bonds leads to the formation of surface states. Surface states energetically are in the band gap, namely between HOMO/valence band and LUMO/conduction band. Another very important feature of dangling bonds is the so-called *push back (pillow) effect*. Gold, a frequently used substrate in surface physics, is known for its dangling bonds and *push back (Pillow) effect*.

*Push back (Pillow) effect*: Materials that exhibit the intrinsic property of dangling bonds have their (clean) surface covered with electronic cloud which leads to the formation of a negative dipole barrier at the surface, namely (intrinsic) *surface dipole*. The negative pole of surface dipole points out and causes the *work function* of that surface to increase. Enhancing the work function is done through pushing up the (surface) *vacuum level* of the respective surface. When metal surface is deposited/coated with contaminations/adsorbates, this electronic tail will be pushed back toward metal surface which leads to reduction of the overall work function of the system [25].



**Figure 1.5:** A schematic illustration of metals electronic tail extending out into the vacuum.  $n(x)$  denotes the negative charge distribution, *i.e.*, electrons, at the clean metal's surface whilst  $p(x)$  represents the positive charge distribution, *i.e.*, image charges intended to balance out the surface electrons, inside metal structure. Original illustration can be found in reference [20].

(Surface and infinite) *Vacuum level VL*: The basic concept of vacuum level and its role as reference level in defining core parameters such as ionization potential and work function is not without complexity [26]. In the context of solids, there are two

distinctive vacuum levels: (i) surface vacuum level and (ii) vacuum level at infinity. Based on the best of author's knowledge, the term surface vacuum level was coined for the first time by Seki, et al. [26] and it refers to a point just *outside* the material at a microscopical distance where electrons are at *rest* in that point but they still feel potential field of the material. This vacuum level is known as (surface) vacuum level denoted as VL (s). As a result of correspondence between (surface) vacuum level and surface dipole, surface vacuum level of various surfaces of the same solid are different. However, an electron can be at rest at a macroscopical distance sufficiently far enough so that it will not have any type of interaction with the material it was removed from. This vacuum level is called vacuum level in infinity VL ( $\infty$ ). Cox et al. believes this sufficiently far distance is at the order of tens or hundreds of angstroms [27] while Perry et al. assess it at almost 1 $\mu$ m [28]. It is important to realize that in energy diagrams, by vacuum level, one usually refers to vacuum level at the surface, though it is almost never mentioned particularly. Surface concepts such as work function and interface dipole (which will be introduced later on in this thesis) are directly related to surface vacuum level.

*Work function*  $\Phi$ : One of the most important parameters in surface science, particularly in the field of organic electronics, is work function. It is the minimum energy for extracting an electron from *Fermi level* of a solid and putting it at rest at its (surface) vacuum level. Work function consists of two parts: surface part and bulk/ volume part [29, 30]. Bulk contribution takes into account the bulk (*chemical*) *potential* while the surface part represents surface dipole.

$$\Phi = -\mu + D$$

**Equation 2**

where  $\mu$  stands for the internal bulk chemical potential and D denotes surface dipole barrier due to the electron tails spilling out. Any surface modification, namely morphology and or adsorption, leads to modification of one of these parameters which gives rise to alteration of work function [31]. For example, in a single crystal, different planes with various packing own different work functions. In this regard, densely packed planes show higher work function than the more open planes [32]. Accordingly,

it is not possible to assign a single number as work function to a crystalline material. The corresponding crystallographic plane along which work function has been measured should always be recorded.

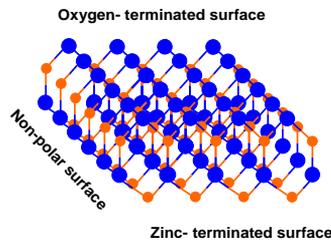
*Fermi level:* The most prevalent definition of Fermi level is the energy of the highest occupied states at  $T=0$ . The other common definition of Fermi level considers it as the *Chemical potential* ( $\mu$ ) of a free electron gas. This definition suits very well to our needs and aims of defining Fermi level. To refresh our mind, chemical potential is defined as the changes of enthalpy upon modifications of particle number in the system. By particles, one means literally any type of particles even electrons and holes. Therefore, one can deduce that chemical potential of electrons is their *Fermi energy*. Very often, *Fermi energy* and Fermi level are used as the same. In metals valence electrons are almost behaving as free electrons, therefore, the highest energy level of valence electrons is attributed as Fermi level but in an intrinsic semiconductor which experiences electron-hole symmetry (*i.e.*, is undoped), Fermi level locates in the middle of the gap. This means that highest occupied state, *i.e.*, HOMO is located  $\frac{1}{2} E_g$  below Fermi level. Traditionally, the way to calculate ionization potential in organic semiconductors is to add up the difference between HOMO (namely HOMO onset) and Fermi level to its corresponding work function. Therefore, ionization potential of semiconductors is somewhat analogous to work function in metals since both of them represent the lowest energy needed to oxidize the sample.

## 1.5 ZnO: an inorganic semiconductor

Zinc oxide, a material still known as the “future material”, has extensively been studied for nearly a century with the first investigation recorded to happen at 1935 [33]. It crystallizes in wurtzite structure in a way that every  $Zn^{2+}$  cation is surrounded by a tetrahedra of  $O^{2-}$  anions and vice versa [34]. Zinc oxide is a direct band gap material, transparent in visible spectral region but shows strong absorption in near ultraviolet region [35]. Zinc oxide has gained attention due to its remarkable characteristics which has made it suitable for various applications such as: white pigment (zincwhite) used

for coloring papers and even generally as white color [36], due to its antiseptic properties is applied in medicine for wound care, as hydrogen sensor [37] and many more interesting applications. As zinc oxide is transparent, not toxic, is photochemically stable [38], largely available in single crystal form [39] and has low price in comparison to Si-based applications therefore it is not surprising that zinc oxide has gained much attention for its application in the organic photovoltaic devices [38]. In addition to the previously mentioned applications of zinc oxide, it can be utilized as a semiconductor as well. Zinc oxide is a wide band gap semiconductor and its band gap in crystalline form has been a subject of debate with various numbers reported in different scientific publications ranging from 3.1 eV to 3.3 eV [40]. Investigation of zinc oxide's semiconducting properties has been rather challenging since it is not a trivial task to control its electrical conductivity. Originally known to be an intrinsic n-type semiconductor with Fermi level located 0.2 eV under conduction band minimum [41] is still being investigated to clarify the origin of its n-conductivity [42].

Single crystals of ZnO can be truncated along different planes which results in both polar and non-polar surfaces (Figure 1.6): polar Zn-terminated ( $0001$ ) and O-terminated ( $000\bar{1}$ ) and the non-polar faces of  $(11\bar{2}0)$  &  $(10\bar{1}0)$ .



**Figure 1.6:**  $(0001)$ ,  $(000\bar{1})$  and  $(10\bar{1}0)$  surfaces in truncated ZnO. If single crystal of ZnO is imagined as a standing hexagonal, then surfaces at the top and bottom are polar  $(0001)$  &  $(000\bar{1})$  faces whilst the side surface is not polar due to the alternated existence of both zinc and oxygen at the same surface. Zinc and oxygen atoms are shown in orange and blue, respectively.

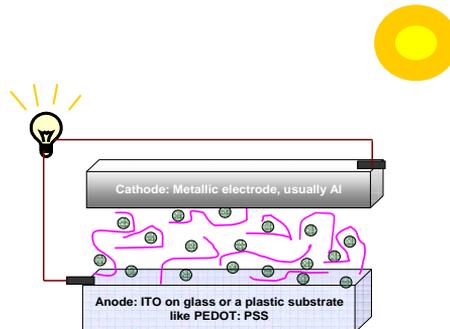
Atomically clean polar surfaces of ZnO undergo different stabilization process such as reconstruction (changing the geometry of the surface) and or charge transfer between

the two polar surfaces [36]. In order to apply ZnO as electrode in diodes and photovoltaic cells, one needs to understand the charge transfer process at the different surfaces of ZnO and the surfaces interaction with other materials (the later a topic in paper IV).

## 1.6 Fundamentals of organic solar cells

A solar cell is a device (more precisely a diode) that turns the solar energy directly into the electricity. Conversion of light into electrical power is known as photovoltaic effect and was discovered by Becquerel during his research on liquid electrolytes in 1839 [43]. By an organic solar cell, one refers to the active material which is organic based. The first organic solar cells were based on pigments but later on organic semiconductors incorporated into solar cells in a very simplified structure consisting of organic layer(s) sandwiched between two electrodes [44]. The most recent development of the field is the concept of bulk heterojunction (BHJ) solar cells using blend of donor and acceptor organic molecules and polymers. They can be fabricated either through co-deposition of two molecular solids [12] or *e.g.* blending two semiconducting polymers (one is donor and the other one is acceptor) in solution [45, 46]. As a general rule, a conjugated polymer is used as the electron donor while a derivative of the C<sub>60</sub> Buckminster fullerene molecules is utilized as acceptor. One of the most common and promising blends is P<sub>3</sub>HT/PCBM. An organic solar cell (Figure 1.7) consists of cathode (a low work function metal such as aluminum), anode (a transparent high work function electrode often ITO or an organic polymer such as PEDOT: PSS) and the active semiconducting material. Active semiconducting material, *i.e.*, the bulk heterojunction blend, is the central reactor of the device: it is where the most important steps of solar energy conversion into electrical energy take place: (i) *absorption* of photons with proper energy, namely appropriate to excite electron(s) into LUMO energy states which leads to the formation of exciton, attached electron-hole pair, then (ii) *diffusion of excitons* to the interface of donor- acceptor polymer blend in order to go through (iii) *charge dissociation* and finally the last step which is (iv) *charge transfer* toward relative electrodes that is holes (cations) toward anode and

electrons (anions) toward cathode. If charge dissociation doesn't happen at the proper time and at the proper location (exciton diffusion length is known to be 5-15 nm) [47] then exciton will collapse/recombine and as a result, light will be produced. Recombination of exciton brings about severe reduction of the cell's power conversion efficiency. There are various loss/ recombination processes: (i) geminate recombination [48] occurs when electron-hole are not allowed to drift away and are kept together due to the Coulombic interaction which eventually leads to recombination; (ii) bimolecular free carrier recombination [47] occurs due to low mobility of the dissociated free carriers (after charge separation) and different mobility of electrons and holes; (iii) trap recombination [47] happens at the energetic defects which are made due to impurities brought to the system during processing; and (iv) interface recombination [47] that takes place at the vicinity of electrodes.



**Figure 1.7:** A schematic picture of an organic solar cell. Small balls resemble PCBM while curved lines represent a polymer such as P<sub>3</sub>HT. There can be organic solar cells based on other organic materials, as well. In this example we chose one of the prevalent combinations of active organic material.

Loss processes are not the only limiting parameters in a BHJ solar cell. There are other limiting criteria as well that can be classified in two main strategies of maximizing efficiency of BHJ solar cells [49]: (i) harvesting more sunlight which is done through reducing the polymers' optical absorption gap. This strategy brings about maximization of short-circuit current density ( $J_{SC}$ ) and is not the most desired, optimum solution since it trades-off open circuit voltage ( $V_{OC}$ ) [43] (ii) Maximizing  $V_{OC}$ . Open circuit voltage ( $V_{OC}$ ) can be defined as the existing voltage in the cell under no load and no

illumination. Despite extensive investigation its origin is not settled yet [43, 50, 51]. Some scholars showed that its origin is not correlated to the energy difference between donor's HOMO and acceptor's LUMO [50, 51] whilst others found that the open-circuit voltage depends on the work function difference of the applied electrodes [52, 53]. As open circuit voltage is a limiting factor in designing BHJ solar cell it is vital to be able to understand it and realize parameters influencing it. Open- circuit voltage is found to be influenced by electrode interface dipoles and dipoles at the donor/acceptor interface with the negative side pointing toward the acceptor, which in turn can assist exciton dissociation [54, 55].



## 2. Photoelectron spectroscopy in theory and practice

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*So free we seem, so fettered fast we are.*

*- Robert Browning*

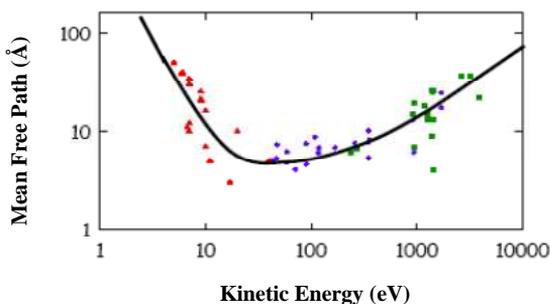
One of the main methods of studying surfaces and interfaces is spectroscopy and among many different techniques of spectroscopy, Photoelectron Spectroscopy (PES) possesses a well-earned place due to its remarkable surface sensitivity (which will be revisited in more detail in chapter 2.1). Light atoms such as carbon, nitrogen and oxygen (the main constituents of organic solids) can easily be detected and studied by these non-destructive techniques. The very important underlying principle of PES methods is photoelectric effect, known even as “Hertz effect” to honor Heinrich Hertz who discovered it for the first time and published it in 1887 in “*annalen der physik*, 1887, 267(8), S. 983-1000”. Later on Einstein explained photoelectric effect mathematically using Planck’s quantization of energy concept in 1905 and was awarded Nobel price in Physics in 1921 “*for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect*” [taken from Nobel price homepage].

Generally speaking, Photoelectron Spectroscopy refers to irradiating of the specimen with photons of light with specific energy. Upon absorption of photons with proper energy (photo) electrons will be emitted from the surface of the irradiated sample. Irradiation of material(s) with photons can lead to many different processes such as ionization, excitation and relaxation. Before initiation of the irradiation, the specimen is in its “initial state” but after being irradiated and absorbing energy it will ended up in its “final state”. Depending on the incident radiation’s energy and also the leaving particles, final states can be quite diverse: (i) core-hole final state which is the result of direct photoemission process. One electron from occupied levels is emitted during the photoemission process; (ii) shake- off final state which is a core-ionized state. Photoemitted electron *e.g.* kicks-out another loosely bound electron on its way toward the surface and as a result the final state lacks 2 electrons; (iii) Shake-up final state refers to a situation when a photoemitted electron “collides” with another electron on its way toward vacuum and excites it to an unoccupied level. As a result, this final state is an ionized- excited state. For both X-ray Photoelectron Spectroscopy; XPS, and Ultraviolet Photoelectron Spectroscopy, UPS, the final state always is an ionized final state.

## **2.1 Surface sensitivity of PES**

As it was mentioned before, during the photoemission process photons with known and appropriate energy will be shone on to the specimen. Upon absorption of radiated photon(s) electrons are emitted and propagate toward the surface and vacuum. During propagation, photoemitted electrons may collide with each other. If they loose kinetic energy during collisions then the corresponding collision is called inelastic collision. Mean free path,  $\lambda$ , a measure of the attenuation length, is the distance traveled by the electron between successive collisions with modification of its energy. Seah, et al. [56] gathered experimentally measured inelastic- mean free path of most of the elements (in solid form) in a curve similar to Figure 2.1. Inelastic collisions can lead to the so-called secondary electrons which either show themselves as background in the spectra or

never reach the surface (due to the loss of energy). Universal curve (Figure 2.1) shows the correspondence of  $\lambda$  to the kinetic energy of the photoemitted electrons.



**Figure 2.1: Universal curve of the inelastic mean free path versus kinetic energy of the photoemitted electrons. Figure has been extracted from reference [56].**

Beer- Lambert law provides a clear correspondence between the intensity  $I_0$  of an electron being attenuated at a depth  $d$  below the surface with its mean free path  $\lambda$  and its intensity when it reaches the surface [57]:

$$I = I_0 \exp(-d/\lambda) \quad \text{Equation 3}$$

A simple math shows that 95% of the collected signal (*i.e.*, the intensity of those photoemitted electrons reaching surface) comes from a depth as high as  $3\lambda$  which typically is in the order of several nm(s).

## 2.2 X-ray Photoelectron Spectroscopy

The photoelectric effect was further developed by K. Siegbahn who incorporated it in a spectrometer. Those developments during 1950's- 60's led to the first spectrometer based on photoelectric effect which brought its inventor, K. Siegbahn, Nobel price in Physics in 1981 "*for his contribution to the development of high-resolution electron spectroscopy*" [taken from Nobel price homepage]. Siegbahn baptized the fruit of his efforts as Electron Spectroscopy for Chemical Application (ESCA) but later on this spectroscopy method adopted the generally-accepted term of X-ray Photoelectron

Spectroscopy (XPS) [58] which utilizes soft x-ray as radiation source. The XPS method can be used for both solid and gaseous samples but the scope of this study considers only solid species. The radiation source in laboratory-scale spectrometers typically is either Al ( $k_{\alpha}$ ) (1486.6 eV) or Mg ( $k_{\alpha}$ ) (1253.6eV).

As it mentioned previously, the final state in XPS and UPS is an ionized state. Photoionization of the specimen with incident photons of known energy can be described by [17]:



where  $M_0$  denotes the initial state of the system in its ground state and  $M_+^*$  stands for the final state in the form of a positive excited molecular ion (cation) and  $e^-$  is the photoelectron leaving the system with kinetic energy  $E_k$ . If  $E_k$  is large enough, then the photoelectron and the original molecule are not bonded together any more, *i.e.*, photoelectron has left the system which is ionized now. Equation above can be re-written in terms of the energy of the related species:

$$E_0 + h\nu \rightarrow E_+^* + E_k \quad \text{Equation 5}$$

with  $E_0$  as the energy of the initial ground state of the material and  $E_+^*$  for the final state of it. Einstein equation relates binding energy of the electron before excitation relative to vacuum level to photon energy and kinetic energy of the photoelectron (given energy conservation principle):

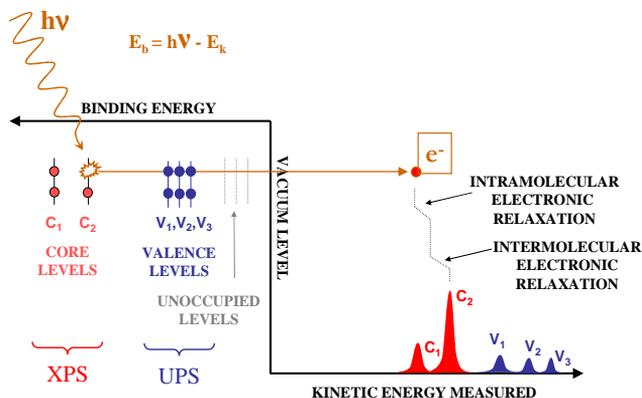
$$E_B^V = E_+^* - E_0 = h\nu - E_k \quad \text{Equation 6}$$

In this equation, binding energy is equal to the energy difference between initial ground state  $E_0$  and final state.

This equation looks like an absolute perfect fit with the photoelectron spectroscopy experiment, but one important fact/parameter deviates: the photoelectron-induced final

state is not the fully relaxed final state. The electron emission in the PES experiment occurs in the time scale of  $10^{-15}$  sec while electronic relaxation takes place in about  $10^{-16}$  sec and is thus included. Given the larger mass of the nuclei, however, it needs longer time to relax and the nuclear relaxation response happens in the time scale of  $10^{-13}$  sec [17, 20, 59]. Therefore, after an electron is being taken away from the system, hole (spatial lack of electron) is electronically fully relaxed but the lattice (bond structure) is frozen in the original ground state configuration, which leads to a higher energy of the PES final state and as a result of that, overestimation of the binding energy!

Usually, there will be a main line in the XPS spectrum with the highest intensity in the spectrum, which represents direct removal of one electron from the initial state (core-level) leading to the photoionized final state of the specimen. Irradiation of the specimen during XPS measurement gives rise to other types of photoemission processes as well but their corresponding intensity is typically smaller. These small intensity satellites correspond to variations in the screening of the core-hole, shake-up and/or shake-off processes. The final photoemission spectrum of a material thus incorporates various final states (generated by different photoemission processes) and can be recognized by different peaks at different binding energies with different intensities. A schematic illustration of those peaks can be seen in Figure 2.2. It is noteworthy to understand that core-level lines of any element are specific to that element. This means different elements have different core-level spectral line with binding energies absolutely characteristics of that specific element. This makes XPS a perfect tool for differentiating between various elements existing on a surface. Due to this capability of X-ray Photoelectron Spectroscopy in identifying different elements, it is often being referred as a *finger print* technique. Another important feature of XPS technique is the so-called chemical shift or change of binding energy. This simply refers to the alteration of the core level binding energy due to modifications of its chemical environment. That is to say, if the oxidation state of an element changes or



**Figure 2.2:** A schematic representation of a spectrum exhibiting photoemission process occurring during a single presumable XPS event. Regions corresponding to UPS and XPS are marked distinctively. Figure is based on a similar illustration in references [17, 58].

neighboring atoms have different electronegativity and/or number and type of the atoms in vicinity are different, then the measured binding energy of the atom being studied is different. Finally, intensity of each core-level line is proportional to the concentration of that specific element in the sampled region.

### 2.3 Ultraviolet Photoelectron Spectroscopy

Ultraviolet Photoelectron Spectroscopy, UPS, is originally another variant of photoelectron spectroscopy specialized to map out valence electrons. Since cross-section of photoionization of valence electrons with XPS photon energies are considerably lower than core electrons [60] (couple of orders of magnitude) and that results in considerable increased scanning time, it is not practical to use X-ray to study valence electrons. Therefore, ultraviolet radiation, UV, is an alternative energy source to investigate valence electrons. Properties of organic-metal or organic-organic interfaces such as charge injection barriers (caused *e.g.* by the mismatch of a metal's Fermi level and the polaronic states of organic layer) are well described and mapped out by UPS. Direct probing of the most important surface parameters like work function ( $\Phi$ ) (difference between Fermi level and surface vacuum level) and ionization



The probed sample was gold and PFO-coated gold. Information obtained by UPS is highly valuable in determining electronic levels of the polymers/molecules engaged in generating surfaces and interfaces. This information is of vital importance when attempting to assess fundamental parameters such as charge injection barrier. Without these inputs, designing any new devices and or organic polymers/molecules is severely complicated.

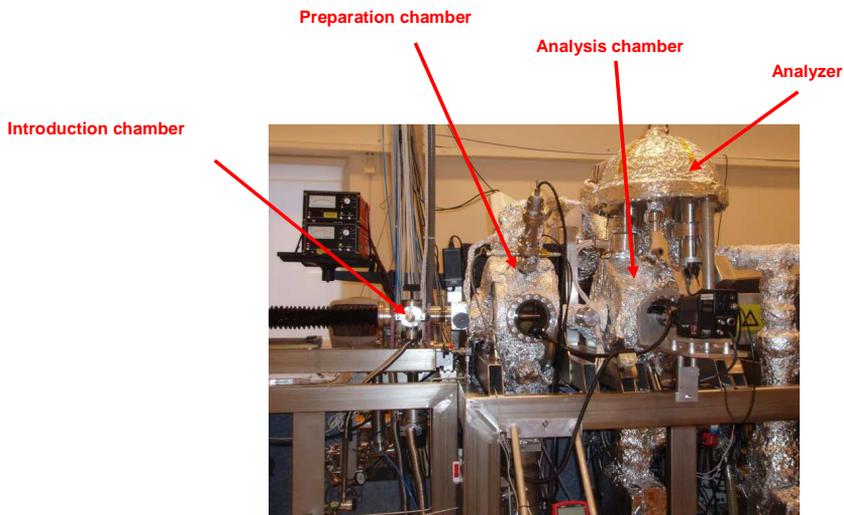
## 2.4 Instrumentation

All of the measurements presented in this thesis have been carried out in a spectrometer of our own design and construction, named MOSES. It is possible to perform both XPS and UPS measurements with this machine. A monochromatic Helium discharge lamp generates radiations with 21.2 eV (HeI) and 40.8 eV (HeII) energy. An x-ray gun produces unfiltered Al( $k_{\alpha}$ ) radiation with 1486.6 eV energy utilized in XPS. This spectrometer has three distinctive chambers which are interconnected to each other horizontally. A photo of the main chambers of the instrument is depicted in Figure 2.4. These chambers are (i) introduction, (ii) preparation and (iii) analysis chamber.

*Introduction chamber:* A specimen is loaded through introduction chamber which is equipped with a roughing and a turbomolecular pump. Since a turbo pump can not have a direct exhaust to the atmospheric pressure it should have an exhaust into the subatmospheric pressures therefore a backing pump, namely roughing pump is used for it. When pressure in the introduction chamber reaches  $10^{-6}$  mbar then it is possible to move the sample to the preparation chamber.

*Preparation chamber:* This chamber is equipped with three pumps: roughing pump, turbo pump and cryo pump. To maintain UHV in the preparation chamber locally around the sample during film growth, which is prerequisite condition for many experiments, other types of pumps are needed besides the roughing pump and turbo pump. Entrapment pumps provide a surface cooled by various methods (liquid nitrogen or helium) to very low temperatures and then adsorb gas molecules on that cooled

surface. The trapped gas molecules will be adsorbed on that surface as long as the very low temperature is maintained. If the temperature of the surface increases to for example room temperature, then all those trapped molecules will be released. As a matter of fact, that is the way to clean and rejuvenate the cryo pump. (After a period of successive using of the cryo pumps, they will be saturated and need to be cleaned). Cryo pumps utilizing helium refrigerators (which is used in our spectrometer) can work only under UHV ( $P < 10^{-7}$  mbar) conditions. In our system, a Cu-cylinder around the sample is cryo-cooled and molecular/atomic particle beams can impact on the sample surface through holes drilled in the cylinder sides. The preparation chamber is equipped to  $\text{Ar}^+$  ion-sputter gun and can accommodate (i) a vacuum sublimation source (resistively heated source known as Knudssen cell) for evaporating organic molecules; (ii) Physical Vapor Deposition (PVD) source; (iii) another resistively heated source mounted vertically which is applied for alkali metal doping.



**Figure 2.4:** Photo of our home made spectrometer, MOSES, with its different chambers.

*Analysis chamber:* The analysis chamber is equipped with a roughing pump, a turbo pump, a cryo pump and finally an ion pump. By the help of the ion pump and cryo-pump, it is possible to achieve pressures as low as  $10^{-10}$  mbar (locally) in the analysis

chamber. The ion pump falls in the getter pumps category: their main concept is having a reactive surface which gas molecules can react with it and therefore leave the vacuum environment. In the case of ion pumps, first the gas molecules get ionized and then adsorbed on the reactive surface of the ion pump. This pump can survive both HV and UHV conditions but higher pressures can kill the pump by poisoning its reactive surface. The analysis chamber is equipped with concentric hemispherical electron-kinetic-energy analyzer (the most common type of electrostatic deflection-type analyzer). Concentric analyzer consists of two electrodes with a gap between them. A negative voltage which determines the so called pass energy is applied between the two electrodes. In this way, only a fraction of photoelectrons emitted from the sample which have the appropriate energy will make it to the analyzer. The rest of the photoelectrons with kinetic energies higher or less than pass energy will hit the walls and never reach analyzer.

### 3. ENERGY LEVEL ALIGNMENT IN ORGANIC CONJUGATED MATERIALS

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*What we experience of nature is in models, and all of nature's models are so beautiful.*

*- Buckminster Fuller*

This chapter is the heart of the thesis in front of you: energy level alignment at organic/organic and or metallic/organic interfaces. All of the papers included try to shed light on energy level alignment at interfaces and its influence on the visible/measurable properties of organic electronic devices. Understanding of energy level alignment and the mechanisms by which it affects device function has profound importance. Consequently, efforts have been put into elucidating this chapter as detailed as possible.

The term energy level alignment essentially refers to the modification of energy levels at the interfaces generated upon contact between two materials. In this thesis we only consider the case of organic materials deposited on either another organic solid or on a metallic/inorganic substrate. The case of metals deposited on organic solids is out of the scope of this study.

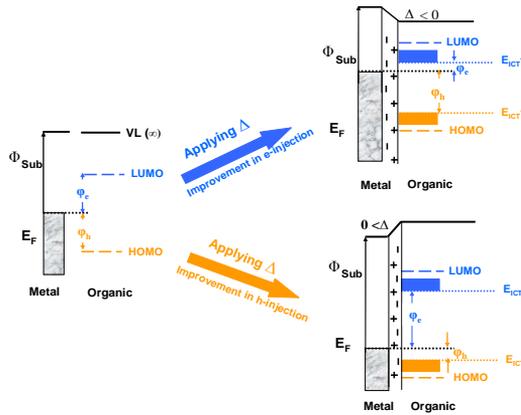
### 3.1 Determining reference level

All of the samples and species studied in this thesis are in the solid state form, with majority of them falling in the semi-conducting class of solids. The natural reference level for photoelectron spectroscopy of gaseous samples is the vacuum level at infinity VL ( $\infty$ ) but studies of solid samples typically use the Fermi level (*i.e.*, binding energy of the electron with respect to the Fermi level;  $E_B^F$ ) as standard reference level. If the solid samples are in electrical contact with the spectrometer through sample holder, their Fermi levels will be aligned and equilibrated [59]. The binding energies referenced to vacuum level then can be obtained (if needed) by adding the work function to the binding energies referenced to the Fermi level.

### 3.2 Interface dipole: Influence of adsorbate

Upon contact between (metallic, inorganic or organic) substrate and an organic semiconductor which is done through *e.g.* coating or vacuum-deposition of an adsorbate, some phenomena may occur: the electronic structure of both of them is modified, their surface dipole barrier is changed which means their work function alters and that eventually leads to the appearance of *interface dipole shift* denoted as  $\Delta$ . Modification of the work function after coating or deposition is due to the shift of (surface) vacuum level and is the best measure of appearance of interface dipole. As it was discussed earlier in this thesis, work function is composed of two contributions: bulk and surface. Therefore, coating or deposition of an atomically cleaned surface by an adsorbate directly regulates surface contribution of the work function which demonstrates itself as modification of work function. The connection between adsorption and work function is a key concept in designing organic electronics devices. A central parameter in designing an electronic device is charge injection barrier, known as Schottky-Mott barrier. Charge injection barrier is a measure of amount of energy that is needed to inject a charge (either electron or hole) in the corresponding orbital. Electron (hole) injection barrier is generally understood in the scientific literature to be

the energy difference between metal's Fermi level and LUMO (HOMO) of the organic material which it is not completely true. The exact definition is the energy difference between the electrode's Fermi level and the negative polaron (positive polaron) of the organic material. Since existence of interface dipole directly influences work function, then it automatically carries an impact on charge injection barrier as well. Figure 3.1 illustrates impact of interface dipole on charge injection barrier schematically.



**Figure 3.1: Illustration of electron/hole injection barrier being manipulated by interface dipole considering  $E_{ICT+} / E_{ICT-}$ .**

An interface dipole has various origins [62, 63]: it can be formed due to (i) compression of the electronic tail/dangling bonds of a metallic surface, *i.e.*, surface dipole, toward inside the metal surface, namely push back (pillow) effect (ii) presence of permanent (intrinsic) dipole moment in (usually) organic adsorbate which is perpendicular to the surface and (iii) existence of dipole due to chemisorption and partial/integer electron transfer [64, 65]. Lindell et al. classified all the aforementioned origins in the following equation [66]:

$$\Delta W = eD_{int} = f(e\Delta D_{met}, eD_{mol}, eD_{chem}) \quad \text{Equation 8}$$

where  $\Delta W$  is the alteration of work function upon introducing interface dipole. Among them, modification and compression of metals surface states occurs when an organic adsorbate is physisorbed on the metallic surfaces. Push back effect always reduces the

work function of metal substrate and is always present at metallic surfaces while the two other contributions (dipole due to chemisorption and intrinsic permanent dipole moment) might not exist always. In addition to that, their impact on the total, net interface dipole is absolutely individual. Every single case can be different from the similar cases.

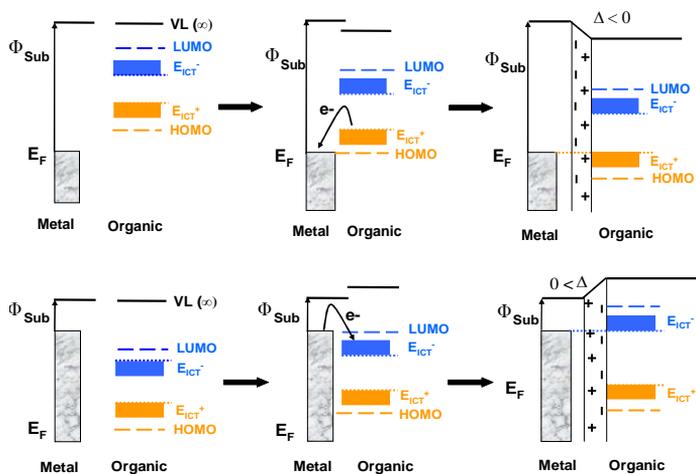
### **3.3 Integer Charge Transfer (ICT) model**

Given an organic interface, generated through either contact or deposition, energy levels of both adsorbate and substrate will be modified. In contrary to well-understood inorganic semiconductor models, no current single model can explain all the possible adsorbate induced interactions at organic heterojunction interfaces. Type and strength of the existing interactions at the interface is a determining factor. Interactions can be classified as follows [20]:

- Physisorption with lack of charge transfer. An example is: Nobel gas atoms on clean metal surfaces [67]
- Physisorption with possible through-tunneling integer charge transfer like: Conjugated solids on passivated metal surfaces [68, 69]
- Weak chemisorption with possible partial charge transfer: Conjugated solids on non-reactive clean metal surfaces [70, 71]
- Strong chemisorption with covalent bonding and partial charge transfer: Conjugated molecules/polymers on reactive clean metal surfaces [62]
- Strong chemisorption with covalent bonding at specific sites, partial charge transfer and surface dipole: Conjugated molecules with intrinsic dipole and anchoring groups on clean metal surfaces [72]

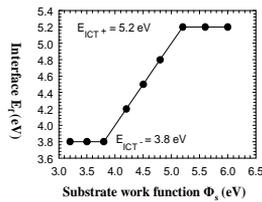
The most prevalent interface between a metallic substrate/electrode and an organic adsorbate and organic–organic heterojunctions in organic electronic applications

consist of physisorption *i.e.*, weak interaction. An interface prepared at ambient condition is an example of such weakly interacting interface. In an interface prepared at ambient atmosphere, hydrocarbon contaminants and oxides exist at the surface of *e.g.* metal substrate, preventing it from having direct coupling with the organic layer. Lack of coupling means lack of through-bond charge transfer between the metal substrate and organic adsorbate although charge transfer can occur through tunneling as long as the hydrocarbon contamination/native oxides are thin enough. The Integer Charge Transfer (ICT) model explains how charge transfer through tunneling can influence energy level alignment at such weakly interacting organic interfaces [20]. The main roots of this model go back to theoretical articles published by Davids, et al. [73, 74] where they calculated the bipolaron formation energy. They argued that charge transfer occurs if the Fermi level of metal electrode is higher than the negative bipolaron formation energy. ICT model contains similar statement [20, 68, 69]: if the Fermi level is lower (higher) than the formation energy of positively (negatively) charged state namely polaron, then there will be charge transfer from (into) the organic adsorbate.



**Figure 3.2:** Upper row: Fermi level pinning to positive charge state energy which is accompanied by charge transfer from organic solid into the metallic electrode. Lower row: charge transfer from electrode into the organic adsorbate with pinning of Fermi level to the negative polaronic level.

By positively (negatively) charged state, one refers to the fully relaxed polaron species after removing (adding) one electron from (to) the organic system. Charge transfer occurs across the interface in packages of one electron at the time and as a result of charge transfer, the metal's Fermi level will be aligned to the positively (negatively) charged state. This positively (negatively) charged state is denoted as:  $E_{ICT+}$  ( $E_{ICT-}$ ). Alignment of Fermi level with  $E_{ICT-}$  or  $E_{ICT+}$  is called pinning, *i.e.*, Fermi level of metal is being pinned to the positive /negative integer charged state. In the case where the substrate Fermi level is positioned in between the  $E_{ICT+}$ , - there will not be charge transfer since there are barriers for both hole- and electron injection. This case is categorized as “vacuum level alignment” and has been known for inorganic semiconductors as the Schottky- Mott regime. Figure 3.2 shows the interface energetics of both regimes (pinning, vacuum level alignment) schematically. It is possible to demonstrate these two different regimes of energy level alignment in another way: to draw the curve showing the work function of different substrate against the work function of those substrates with a single case of organic adsorbate. It is of crucial importance to choose many different substrates with wide span of work functions: both very low and very high work functions.



**Figure 3.3: Mark of Zorro: Vacuum level alignment with slope = 1 and Fermi level pinning regime with slope = 0 is visible. In this hypothetical case, can one see two pinning points: the first one corresponds to the case when Fermi level of electrode is higher than the negative charge state which leads to electron transfer from electrode into the organic adsorbate. The second threshold manifests the opposite case when organic positive polaronic energy is lower than the electrodes Fermi level and that brings about flow of charges from organic solid into the electrode.**

The resulting curve, given sweeping a large enough range of substrate work function, will resemble somewhat the famous “*mark of Zorro*” as shown in Figure 3.3. In that graph, part of the curve with slope=1 represents vacuum level alignment whereas slope =0 manifests Fermi level pinning. Threshold point between these two regimes is

basically pinning point where the organic solid switches from one regime to the other one.



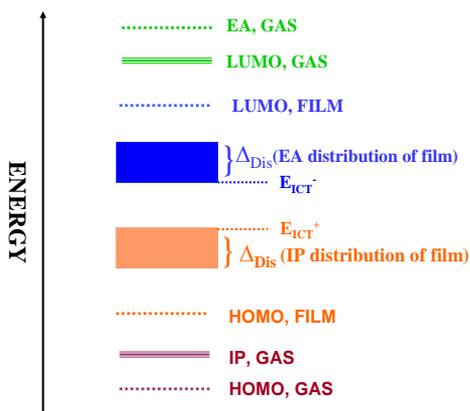
## 4. SUMMARY OF THE THESIS

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The essence of Integer Charge Transfer (ICT) model is the relevance of formation energy of polaronic species to the pinning energy of the investigated material, not the corresponding HOMO and LUMO energies of it. The actors existing at the interface can influence the polaronic energy states and as a result, the pinning energy. Ordering of the adsorbate at the interface and screening by the substrate (impact of image charges) are among the key grounds affecting polaronic formation energy [68]. Ordering of the organic solid at the interface can simultaneously act upon intrinsic dipole which is yet another way to manipulate pinning energy. Therefore, it is of crucial interest to investigate the correlation between order and even screening with polaronic formation energies and eventually pinning energy.

Relaxation mechanisms in solids and gaseous species are rather different although there are similarities as well: both solid and gaseous samples exhibit nuclear relaxation which takes longer time than the electronic relaxation but they behave differently when it comes to electronic relaxation. Electrons react to the photo-generated core-hole through (i) intramolecular and (ii) intermolecular relaxation mechanisms [17]. The former mechanism, which is shared by both gaseous and solid samples, is nothing but

the relaxation of electrons inside each molecule/polymer chain to response to new electronic states of the sample. It is a very fast process (in the order of  $10^{-16}$  sec as mentioned previously), compared to the photoemission process (happening in a time scale of  $10^{-15}$  sec as mentioned previously), but the latter relaxation process (intermolecular) occurs only in solid samples since it is the response of the environment/neighbors to the photo-generated core-hole. Already in the late 1970s, Salaneck could experimentally prove the presence of local screening due to intermolecular order/intermolecular relaxation effects which brings about peak broadening and distribution in ionization potential as there are local variations in the intermolecular order in organic films [75]. Ionization potential (IP) and electron affinity (EA) can be equivalent to the HOMO and LUMO energy, respectively, only if there are absolutely no electric and nucleic relaxation effects. Distribution of IP (EA) corresponds to diverse positive (negative) polaronic energies (Figure 4.4). Given that IP (EA) is the energy to take away (add) an electron from (to) the MOST easily oxidized (reduced) state, one can establish a one-to-one correlation between the measured IP (EA) and positive (negative) polaronic states.



**Figure 4.4: Comparison between various orbital energies of solid (film) phase vs gas phase. Orbital energies in solid samples are lower than their gaseous counterparts due to the extra relaxation mechanism, namely intermolecular relaxation process, which exists in the solid species.**

All the papers of this thesis use the ICT model to explain energy level alignment at interfaces and parameters influencing the alignment such as inter- and intramolecular

order. Two of the papers of this thesis (**Paper I, II**) addressed energy level alignment issues in an organic solar cells and tried to explain how the proper matching of the energy levels of the solar cell's constituents, can lead to enhancement of the cell's efficiency. We specifically focused on the charge transfer dipoles and related them to the reduced recombination losses, which in turn leads to increased cell efficiency. **Paper III, V** were devoted mainly to further develop the Integer Charge Transfer model from intermolecular point of view. Gladly, recent Density Functional Theory (DFT) studies applying ICT model could calculate the experimentally observed work functions (**Paper V**). Finally, Paper **IV** deals with another type of semiconductor: inorganic semiconductor. We mapped out interfaces of zinc oxide polar faces with a Self Assembled Molecule (SAM) named 4-tertbutylpyridine (4-TBP) which is a derivative of pyridine.

- **Paper I:**

In the first article, we highlighted the relationship between the interfacial dipole and the exciton (electron-hole pair which is held together by Coulomb interaction) dissociation and correlated that with the solar cell efficiency. An organic solar cell is a device that converts solar energy into electricity. Upon absorption of light photons with the appropriate energy by the active organic material excitons will be created. For a solar cell to be efficient excitons should be dissociated at the interface of the active organic materials and the resulting free charges, namely electrons and holes, will then be directed toward their respective electrodes so that they can flow into an external circuit. In this way, the solar rays convert into electricity.

Already theoretical studies [54, 55] had found that an interface dipole at the organic heterojunction with the negative pole pointing toward the acceptor facilitates exciton dissociation. We found that a charge transfer dipole already exists in the ground state under no illumination condition at the interface between donor organic material (P3HT) and acceptor organic molecule (60 PCBM) and speculated that this increases the likelihood of the electron-hole pair to be created and dissociated and free charges reach the electrodes, which would directly improve the solar cell's efficiency. The existence

of this dipole already at (dark) conditions also means that the most easily oxidized polymer chains and most easily reduced PCBM molecules are consumed. Consequently, the most tightly bound charge transfer states are not available for population upon absorption of light, and less tightly bound charge transfer states are thus created at the bulk heterojunction which should facilitate improved separation into free charges.

▪ **Paper II:**

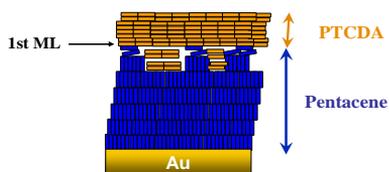
In the next article, we expanded our investigation and focused on thermally induced torsions in the side chains of a semiconductor polymer known as P3HT. Our aim was also to study inter- and intramolecular order and their effect on energy level alignment at the interfaces and their impact on solar cells based on P3HT/PCBM. Heat treatment provides increased crystallinity but also introduces disorder at the interfaces between various crystal domains, introducing dipoles at these interfaces where spontaneous charge transfer can occur from P3HT to PCBM in these circumstances. The combination of these two effects leads to an enhanced generation of free charges and enhanced efficiency of the solar cell, as discussed in article I.

At articles (III & V), we focused on the intermolecular properties alone. We coated substrates with different molecules and by measuring the ionization potentials and interfacial dipoles; we could deduce both the molecular orientation and the energy level alignment.

**Paper III:**

Paper III focused on pentacene and PTCDA. Pentacene is known for its high mobility and PTCDA was chosen because it has been the "guinea pig" for surface physicist for a very long time. We coated the chemically cleaned gold with pentacene and later covered it with PTCDA. It showed that dipoles are created due to charge transfer at both the Au/pentacene and the pentacene/PTCDA interfaces, and that the Fermi level at the two interfaces is locked to the hole-injection level of pentacene and electron

injection level of PTCDA, respectively: pentacene donates electrons to both gold and PTCDA at the interfaces. The UPS results of the valence region also suggest that the interaction between PTCDA and pentacene may under certain conditions be strong enough to modify pentacene's surface structure upon coating by PTCDA. Finally, we speculate that ultimate configuration of Au/pentacene/PTCDA is likely to look like Figure 4.5.



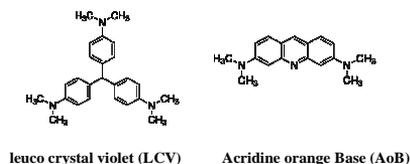
**Figure 4.5: Most probable scenario exhibiting ordering of Pentacene and PTCDA molecules. Figure adopted from Paper III (manuscript).**

- **Paper IV:**

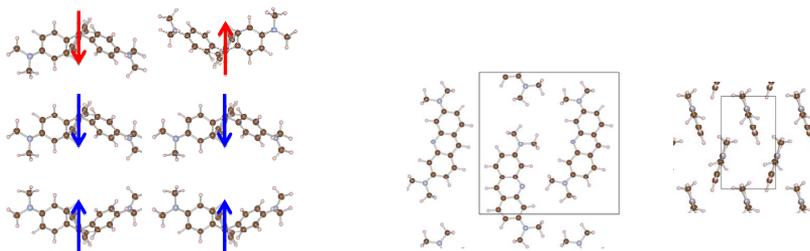
Paper IV contains a study of a different category of semi-conductive material: inorganic solids. Silicon-based solar cells require huge amount of production energy and are not cheap. Therefore we should find new materials and methods to replace silicon-based solar cells. Zinc oxide, ZnO, is a promising semiconductor material which is transparent, relatively energy efficient to manufacture, and can be used as electrodes in organic solar cells and OLEDs. In order to adopt ZnO surfaces properties to a certain component function, one can coat its (single crystal) surfaces with for example organic molecules that increase or decrease the resulting work function compared to the neat ZnO surfaces. We investigated how polar surfaces of zinc oxide can be modified in this particular way. Zinc oxide samples are cut from single crystals of zinc oxide and can exist in either polar or non-polar forms. The polar surfaces may be either zinc-terminated or oxygen-terminated. The two polar surfaces were studied using a strong electron donor in order to enhance the polar surfaces function as electron-injecting electrodes.

## ▪ Paper V:

In Article V, we performed a joint experimental/theoretical study on how the intermolecular order affects energy level alignment and the resulting work function at the interface when molecules also have an intrinsic dipole. The ultimate goal of the study was to investigate fabrication of low work function cathodes.



We used Acridine Orange Base (AOB) and leuco crystal violet (LCV) which are strong electron donors. Theoretical calculations were based on ICT model at DFT level of theory. Experimentally by measuring  $E_{\text{ICT}^+}$  of AOB and LCV on various substrates, we were able to infer a strong dependency of the molecular ordering and the resulting work function of the coated substrates ranged between 3.95 eV – 4.3 eV (LCV) and 3.2 eV – 4.43 eV (AOB).



**Figure 4.6:** Left panel) Three different intrinsic dipole moments used to calculate the positive Integer Charge Transfer State ( $E_{\text{ICT}^+}$ ). Right panel) Two inter-molecular orientations of AOB: first one denotes face-on orientation while the one at right part of the picture illustrates the so-called standing orientation. Illustration is adopted from paper V (manuscript).

LCV features a large intrinsic dipole moment along the symmetry axis of the molecule in the form of three types of inter-molecular orientations (as it can be seen in the left panel of Figure 4.6) which were used to calculate the  $E_{\text{ICT}^+}$ . Due to the planar structure of AOB, it can adopt two different orientations: face-on and standing (Figure 4.6, right

panel). These 2 orientations were used to calculate the relative polaronic energies at each of these two geometries. The theoretical calculations predict  $E_{\text{ICT}^+}$  of LCV to be in the range of 4.03 eV - 4.38 eV and 3.06 eV- 4.55 eV for AOB: both in excellent agreement with the experimental data. The large variations in resulting work function suggest that care has to be taken when using molecular modification of electrodes in the physisorbed regime.



## 5. References

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1. Letheby, H., *On the production of a blue substance by the electrolysis of sulphate of aniline*. Journal of the Chemical Society, 1862. **15**: p. 161.
2. Chamberlain, G.A., *Organic solar cells: A review*. Solar Cells, 1983. **8**(1): p. 47-83.
3. Kepler, R.G., *Charge Carrier Production and Mobility in Anthracene Crystals*. Physical Review, 1960. **119**(4): p. 1226-1229.
4. Chiang, C.K., et al.,, *Electrical Conductivity in Doped Polyacetylene*. Physical Review Letters, 1977. **39**(17): p. 1098-1101.
5. Koezuka, H., A. Tsumura, and T. Ando, *Field-effect transistor with polythiophene thin film*. Synthetic Metals, 1987. **18**(1-3): p. 699-704.
6. Horowitz, G., *Organic thin film transistors: From theory to real devices*. Journal of materials research, 2004. **19**(07): p. 1946-1962.
7. Roberts, G.G., et al.,, *Electroluminescence, photoluminescence and electroabsorption of a lightly substituted anthracene langmuir film*. Solid State Communications, 1979. **32**(8): p. 683-686.
8. Vincett, P.S., et al.,, *Electrical conduction and low voltage blue electroluminescence in vacuum-deposited organic films*. Thin Solid Films, 1982. **94**(2): p. 171-183.
9. Partridge, R.H., *Electroluminescence from polyvinylcarbazole films: Electroluminescence using higher work function cathodes*. Polymer, 1983. **24**(6): p. 755-762.
10. Tang, C.W. and S.A. Vanslyke, *Organic electroluminescent diodes*. Applied Physics Letters, 1987. **51**(12): p. 913-915.
11. Tang, C.W., *Two-layer organic photovoltaic cell*. Applied Physics Letters, 1986. **48**(2): p. 183-185.
12. Hiramoto, M., H. Fujiwara, and M. Yokoyama, *Three-layered organic solar cell with a photoactive interlayer of codeposited pigments*. Applied Physics Letters, 1991. **58**(10): p. 1062-1064.

13. Dediu, V., et al.,, *Room temperature spin polarized injection in organic semiconductors*. Solid State Communications, 2002. **122**(3–4): p. 181-184.
14. Xiong, Z.H., et al.,, *Giant magnetoresistance in organic spin-valves*. Nature, 2004. **427**(6977): p. 821-824.
15. Matyba, P., et al.,, *Flexible and Metal-Free Light-Emitting Electrochemical Cells Based on Graphene and PEDOT-PSS as the Electrode Materials*. ACS Nano, 2010. **5**(1): p. 574-580.
16. Ashcroft, N.W. and N.D. Mermin, *Solid State Physics*1976: W. B. Saunders Company.
17. *Semiconducting Polymers*. 2nd Edition ed, ed. G. Hadziioannou, Malliaras, G. G. Vol. 1. 2005: Wiley-VCH Verlag GmbH & Co. KGaA.
18. Roncali, J., *Molecular Engineering of the Band Gap of  $\pi$ -Conjugated Systems: Facing Technological Applications*. Macromolecular Rapid Communications, 2007. **28**(17): p. 1761-1775.
19. Bredas, J.L., *Relationship between band gap and bond length alternation in organic conjugated polymers*. The journal of chemical physics, 1985. **82**(8): p. 3808-3811.
20. Braun, S., W.R. Salaneck, and M. Fahlman, *Energy-Level Alignment at Organic/Metal and Organic/Organic Interfaces*. Advanced Materials, 2009. **21**(14-15): p. 1450-1472.
21. Levinshstein, M. and G. Simin, *Transistors from crystals to integrated circuits*1998: World Scientific Publishing Co. Pte. Ltd.
22. *IUPAC. Compendium of Chemical Terminology*, A.D. McNaught and A. Wilkinson, Editors. 1997, Blackwell Scientific Publications, Oxford.
23. Desjonqueres, M.C. and D. Spanjaard, *Concepts in surface physics*. 2 ed1995: Springer.
24. Gutmann, F. and E.L. Lawrence, *Organic semiconductors*1967, United States of America: John Wiley & Sons, Inc.
25. Osikowicz, W., et al.,, *Energetics at Au top and bottom contacts on conjugated polymers*. Applied Physics Letters, 2006. **88**(19): p. 193504.
26. Ishii, H., et al.,, *Energy Level Alignment and Interfacial Electronic Structures at Organic/Metal and Organic/Organic Interfaces*. Advanced Materials, 1999. **11**(8): p. 605-625.
27. Henrich, V.E. and P.A. Cox, *The surface science of metal oxides*1994: Cambridge University press.
28. Broughton, J.Q. and D.L. Perry, *Electron binding energies in the study of adsorption by photoelectron spectroscopy: The reference level problem*. Surface Science, 1978. **74**(1): p. 307-317.
29. Rhoderick, E.H. and R.H. Williams, *Metal- semiconductor contacts*. 2 ed, ed. P. Hammon and R.L. Grimsdale1988: Oxford science publications.
30. Leung, T.C., et al.,, *Relationship between surface dipole, work function and charge transfer: Some exceptions to an established rule*. Physical Review B, 2003. **68**(19): p. 195408.
31. *Physical structure*. Handbook of surface science, ed. N.V. Richardson and S. Holloway. Vol. 1. 1996.
32. Besocke, K., B. Krahl-Urban, and H. Wagner, *Dipole moments associated with edge atoms; A comparative study on stepped Pt, Au and W surfaces*. Surface Science, 1977. **68**(0): p. 39-46.
33. Finch, G.I. and S. Fordham, *The effect of crystal-size on lattice-dimensions*. Proceedings of the Physical Society, 1936. **48**(1): p. 85.
34. *Zinc oxide bulk, thin films and nanostructures : processing, properties and applications*, ed. C.C. Jagadish and S.J. Pearton2006: Elsevier.
35. Thomas, D.G., *The exciton spectrum of zinc oxide*. Journal of Physics and Chemistry of Solids, 1960. **15**(1–2): p. 86-96.

36. Wöll, C., *The chemistry and physics of zinc oxide surfaces*. Progress in Surface Science, 2007. **82**(2–3): p. 55-120.
37. Krummel, C., et al.,, *Induced zinc desorption from zinc oxide during exposure to a reducing agent*. Fresenius' Journal of Analytical Chemistry, 1995. **353**(5): p. 521-523.
38. Hosono, E., S. Fujihara, and T. Kimura, *Fabrication of Nanocrystalline ZnO Thick Films for Solar Cells*. Key Engineering Materials, 2002. **216**.
39. Reynolds, D.C., D.C. Look, and B. Jogai, *Optically pumped ultraviolet lasing from ZnO*. Solid State Communications, 1996. **99**(12): p. 873-875.
40. Srikant, V. and D.R. Clarke, *On the optical band gap of zinc oxide*. Journal of applied physics, 1998. **83**(10): p. 5447-5451.
41. Jacobi, K., G. Zwicker, and A. Gutmann, *Work function, electron affinity and band bending of zinc oxide surfaces*. Surface Science, 1984. **141**(1): p. 109-125.
42. Anderson, J. and C.G. Van de Walle, *Fundamentals of zinc oxide as a semiconductor*. Reports on progress in physics, 2009. **72**(12).
43. Kippelen, B. and J.-L. Bredas, *Organic photovoltaics*. Energy & Environmental Science, 2009. **2**(3): p. 251-261.
44. Hoppe, H. and N.S. Sariciftci, *Organic solar cells: an overview*. Journal of materials research, 2004. **19**(7).
45. Yu, G., et al.,, *Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions*. Science, 1995. **270**(5243): p. 1789-1791.
46. Halls, J.J.M., et al.,, *Efficient photodiodes from interpenetrating polymer networks*. Nature, 1995. **376**(6540): p. 498-500.
47. Tvingstedt, K., *Light trapping and alternative electrodes for organic photovoltaic devices*, in *Biomolecular and organic electronics, Applied Physics, IFM2008*, Linköping University: Linköping.
48. Müller, J.G., et al.,, *Ultrafast dynamics of charge carrier photogeneration and geminate recombination in conjugated polymer:fullerene solar cells*. Physical Review B, 2005. **72**(19): p. 195208.
49. Chen, H.-Y., et al.,, *Polymer solar cells with enhanced open-circuit voltage and efficiency*. Nat Photon, 2009. **3**(11): p. 649-653.
50. Vandewal, K., et al.,, *On the origin of the open-circuit voltage of polymer-fullerene solar cells*. Nat Mater, 2009. **8**(11): p. 904-909.
51. Perez, M.D., et al.,, *Molecular and Morphological Influences on the Open Circuit Voltages of Organic Photovoltaic Devices*. Journal of the American Chemical Society, 2009. **131**(26): p. 9281-9286.
52. Frohne, H., et al.,, *Influence of the Anodic Work Function on the Performance of Organic Solar Cells*. ChemPhysChem, 2002. **3**(9): p. 795-799.
53. Mihailetchi, V.D., et al.,, *Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells*. Journal of applied physics, 2003. **94**(10): p. 6849-6854.
54. Arkhipov, V.I., P. Heremans, and H. Bässler, *Why is exciton dissociation so efficient at the interface between a conjugated polymer and an electron acceptor?* Applied Physics Letters, 2003. **82**(25): p. 4605-4607.
55. Verlaak, S., et al.,, *Electronic Structure and Geminate Pair Energetics at Organic–Organic Interfaces: The Case of Pentacene/C60 Heterojunctions*. Advanced Functional Materials, 2009. **19**(23): p. 3809-3814.
56. Seah, M.P. and W.A. Dench, *Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids*. Surface and Interface Analysis, 1979. **1**(1): p. 2-11.

57. Briggs, D. and M.P. Seah, *Practical surface analysis*. 2 ed. Auger and X-ray photoelectron spectroscopy. Vol. 1. 1996: John Wiley & sons.
58. Salaneck, W.R., S. Stafström, and J.L. Brédas, *Conjugated polymer surfaces and interfaces :Electronic and chemical structure of interfaces for polymer light emitting devices*1996: University Press: Cambridge.
59. Brucker, C.F., *Electron spectroscopy: Theory, techniques and applications, vol. 4. C. R. Brundle and A. D. Baker (Editors)*. Academic Press London, 1982. Surface and Interface Analysis, 1982. **4**(6): p. i-ii.
60. Yeh, J.J. and I. Lindau, *Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters:  $1 < Z < 103$* . Atomic data and nuclear data tables, 1985. **32**(1).
61. Salaneck, W.R., et al.,, *Conjugated Polymer And Molecular Interfaces:Science And Technology For Photonic And Optoelectronic Application*2002: New York : Marcel Dekker, cop.
62. Crispin, X., et al.,, *Characterization of the Interface Dipole at Organic/ Metal Interfaces*. Journal of the American Chemical Society, 2002. **124**(27): p. 8131-8141.
63. Yan, L., et al.,, *Thermodynamic equilibrium and metal-organic interface dipole*. Applied Physics Letters, 2002. **81**(15): p. 2752.
64. Crispin, X., et al.,, *Understanding the initial stages of polymer grafting on metals: a photoelectron spectroscopy study of acrylonitrile adsorption on transition metal surfaces*. Journal of Electron Spectroscopy and Related Phenomena, 2001. **121**(1–3): p. 57-74.
65. Crispin, X., et al.,, *Chemisorption of acrylonitrile on the Cu(100) surface: A local density functional study*. Journal of Chemical Physics, 1999. **111**(7): p. 3237.
66. Lindell, L., et al.,, *Characterization of the interface dipole at the paraphenylenediamine-nickel interface: A joint theoretical and experimental study*. Journal of Chemical Physics, 2005. **122**(8): p. 084712.
67. Lang, N.D., *Interaction between Closed-Shell Systems and Metal Surfaces*. Physical Review Letters, 1981. **46**(13): p. 842-845.
68. Fahlman, M., et al.,, *Electronic structure of hybrid interfaces for polymer-based electronics*. Journal of Physics: Condensed Matter, 2007. **19**(18): p. 183202.
69. Tengstedt, C., et al.,, *Fermi-level pinning at conjugated polymer interfaces*. Applied Physics Letters, 2006. **88**(5): p. 053502.
70. Vázquez, H., F. Flores, and A. Kahn, *Induced Density of States model for weakly-interacting organic semiconductor interfaces*. Organic Electronics, 2007. **8**(2–3): p. 241-248.
71. Braun, S., et al.,, *Influence of the electrode work function on the energy level alignment at organic-organic interfaces*. Applied Physics Letters, 2007. **91**(20): p. 202108.
72. Heimel, G., et al.,, *The Interface Energetics of Self-Assembled Monolayers on Metals*. Accounts of Chemical Research, 2008. **41**(6): p. 721-729.
73. Davids, P.S., A. Saxena, and D.L. Smith, *Bipolaron lattice formation at metal-polymer interfaces*. Physical Review B, 1996. **53**(8): p. 4823-4833.
74. Davids, P.S., A. Saxena, and D.L. Smith, *Nondegenerate continuum model for polymer light-emitting diodes*. Journal of applied physics, 1995. **78**(6): p. 4244.
75. Salaneck, W.R., *Intermolecular Relaxation Energies in Anthracene*. Physical Review Letters, 1978. **40**(1): p. 60-63.