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Studies of Materials and Interfaces for Organic Electronics

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Abstract

Organic electronics is a rapidly evolving field with vast number of applications having high potential for commercial success. Although a great progress has been made, many organic electronic applications: organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic solar cells, *etc*; still require further optimization to fulfill the requirements for successful commercialization. For many applications, available at this time organic materials do not provide satisfactory performance and stability, which hinders the possibility of a large-scale production. Therefore, the key ingredient needed for a successful improvement in performance and stability of organic electronic devices is in-depth knowledge of physical and chemical properties of molecular and polymeric materials. Since many applications encompass several thin film layers made of organics, and often also inorganic materials, the understanding of both organic-organic and hybrid interfaces is yet another important issue necessary for the successful development of organic electronics.

The research presented in this thesis is based mainly on photoelectron spectroscopy, which is an experimental technique especially suited to study both surfaces and interfaces of materials. In the thesis, the properties of one of the most successful polymeric materials, poly(3,4-ethylenedioxythiophene), often abbreviated as PEDOT, have been extensively studied. The research was done in close cooperation with an industrial partner – AGFA Gevaert, Belgium. The study was focused on the exploration of the intrinsic properties of the material, such as stability, morphology and conductivity. In addition, however, a possibility of alternation of these properties was also explored. This thesis reports also about investigations of the properties of various organic-organic and hybrid interfaces. The energy level alignment at such interfaces plays important role in charge injection and performance of the thin film organic-based devices. The conditions for different energy level alignment regimes at the various interfaces have been studied. The studies on interfaces were performed in close collaboration with the R&D division of DuPont Corporation, USA. This work led to the significant advances in understanding of the interface energetics and properties of industry-relevant organic materials, as represented not only by published scientific papers, but also patent applications.

Sammanfattning

Organisk elektronik är ett snabbt växande område med många produkter med stora möjligheter för kommersiell framgång. Trots stora framsteg krävs fortsatt optimering för att uppnå de krav som finns för en framgångsrik kommersialisering. För många tillämpningar t.ex. organiska lysdioder, organiska fälteffekttransistor, organiska solceller, osv uppvisar de material som finns tillgängliga idag varken tillräcklig prestanda eller stabilitet, vilket förhindrar möjligheterna för storskalig produktion. Fördjupad kunskap om fysiska och kemiska egenskaper av de molekylära och polymera materialen är därför av stor vikt för att förbättra både prestanda och stabilitet inom organiska elektronik. Eftesom många applikationer omfattar flera tunna lager av både organiska och inorganiska material så är förståelsen av gränssnitten både mellan de organiska materialen och mellan organiska och inorganiska material ett område där kunskap är av stor vikt för framgångsrik utveckling av organisk elektronik.

Forskningen som presenteras i denna avhandling baseras till stor del på fotoelektron-spektroskopi, som är en teknik som särskilt lämpar sig för studier av både ytor och gränssnitt mellan material. I den här avhandlingen har egenskaperna hos ett av de mest framgångsrika polymera materialen, poly(3,4-ethylenedioxythiophene), vanligtvis förkortat som PEDOT, blivit utförligt undersökta. Arbetet utfördes i nära samarbete med en industriell partner – AGFA Gevaert, Belgien. Studien fokuserades på att undersöka materialets inre egenskaper såsom stabilitet, morfologi samt ledningsförmåga. Dessutom studerades möjligheterna till förändring av dessa egenskaper. Avhandlingen innehåller också studier av gränssnitt mellan olika organiska material samt gränssnitt mellan organiska och inorganiska material. Upplinjeringen av elektronernas energinivåer vid sådana gränssnitt spelar en viktig roll vid laddningsinjektion och prestanda hos de organiska komponenterna. Villkoren för olika fall av upplinjering av energinivåer har studerats hos ett antal olika gränssnitt. Studierna av dessa gränssnitt har skett i nära samarbete med forskningsavdelningen på DuPont Corporation, USA. Arbetet ledde till stora framsteg i förståelsen för de energiförhållanden som råder vid gränssnitten samt för de egenskaper hos organiska material som är relevanta för industrin, vilket framgår inte bara av de publicerade vetenskapliga artiklarna utan även av patent ansökningarna.

Preface

This thesis includes some of the research results that I have achieved in the Surface Physics and Chemistry group at the Department of Physics, Biology and Chemistry, Linköping University, Sweden.

The large part of the thesis is based on the projects which were carried in close cooperation with industrial partners: Agfa-Gevaert N.V. (Mortsel, Belgium) and E. I. DuPont de Nemours and Co., Inc., Dupont Displays, (research stations in Santa Barbara, CA and Wilmington, DE, USA).

The projects can be divided in three parts: First – DOTCON project, mainly focused on the study related to the properties of polymer blend: PEDOT-PSS, and was carried out in close cooperation with AGFA Gevaert. The results from this project are included in papers I and II in this thesis. The second project involved study on the other PEDOT-related materials in a collaboration with Dupont Displays' research station in Santa Barbara. The materials studied are used in buffer layers in prototype polymer light-emitting diodes PLEDs. The third project was focused on the issues related to the energy level alignment at the interfaces relevant for organic light-emitting diodes (OLEDs). Some of the results obtained are summarized in paper III. The topic of interfacial energetics is further discussed in paper IV and paper V.

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Papers included in the thesis:

- **Light Induced Damage in Poly(3,4-ethylenedioxythiophene) and its Derivatives Studied by Photoelectron Spectroscopy**

S. Marciniak*, X. Crispin, K. Uvdal, M. Trzcinski, J. Birgeron, L. Groenendaal, F. Louwet, and W. R. Salaneck

Synthetic Metals 141 (2004) 67-73

Author's contribution:

Most of the experimental work and all of the data analysis. Wrote the first draft and responsible for the iterative process to the final version.

- **Conductivity, Morphology, Interfacial Chemistry, and Stability of Poly(3,4- ethylene dioxythiophene)–Poly(styrene sulfonate): A Photoelectron Spectroscopy Study**

X. Crispin, S. Marciniak*, W. Osikowicz, G. Zotti, A. W. Denier Van Der Gon, F. Louwet, M. Fahlman, L. Groenendaal, F. De Schryver, W. R. Salaneck

Journal of Polymer Science: Part B: Polymer Physics, 41(2003) 2561-2583

Author's contribution:

Most of the experimental work and data analysis concerning: secondary doping, interfacial chemistry and light-induced degradation of PEDOT-C₁₄, PEDOT-PSS and PSS. Took part in the process of writing.

- **Energy level alignment regimes at hybrid organic–organic and inorganic–organic interfaces**

S. Braun, W. Osikowicz, Y. Wang and W. R. Salaneck

Organic Electronics 8 (2007) 14-20

Author's contribution:

All the experimental work and data analysis. Wrote the first draft and responsible for the iterative process to the final version.

*Name before marriage

- **Fermi level pinning at interfaces with tetrafluorotetracyanoquinodimethane (F4-TCNQ): The role of integer charge transfer states.**

S. Braun and W. R. Salaneck

Chemical Physics Letters 438 (2007) 259

Author's contribution:

All the experimental work, theoretical work and data analysis. Wrote the first draft and responsible for the iterative process to the final version.

- **Energy level alignment of organic interfaces under reversal of deposition sequence – the role of Fermi level pinning**

S. Braun, M. P. de Jong, and W. R. Salaneck

submitted

Author's contribution:

All the experimental work and data analysis. Wrote the first draft and responsible for the iterative process to the final version.

Related papers, not included in the thesis:

- Y. Wang¹, W. R. Salaneck², S. Braun²
US patent application No. 11/475407 - “Hole injection electrode”
 - ¹ E. I. DuPont de Nemours and Co., Inc., Dupont Displays, P.O. Box 80356, Experimental Station, Wilmington, Delaware 19880-0356 U.S.A.
 - ² Linköping University, Linköping, Sweden.
- Che-H-Hsu¹, S. Marciniak^{*2}, M. Fahlman², W. R. Salaneck²
International patent application - WO/2005/090434 - “Water dispersible polydioxythiophenes with polymeric acid colloids and a water-miscible organic liquid”
 - ¹ E. I. DuPont de Nemours and Co., Inc., Dupont Displays, Santa Barbara, CA 93117, U.S.A.
 - ² Linköping University, Linköping, Sweden.
- Ultraviolet light–ozone treatment of poly(3,4-ethylenedioxy-thiophene)-based materials resulting in increased work functions.
C. Tengstedt, A. Kanciużewska, M. P. de Jong, S. Braun, W. R. Salaneck and M. Fahlman, *Thin Solid Films*, 515 (2006) 2085.
- Structure and mechanical properties of arc evaporated Ti-Al-O-N thin films.
J. Sjölen, L. Karlsson, S. Braun, R. Murdey, A. Hörling and L. Hultman, *Surf. Coat. Tech.*, 201 (2007) 6392.
- Energetics at Au top and bottom contacts on conjugated polymers.
W. Osikowicz, M. P. de Jong, S. Braun, C. Tengstedt, M. Fahlman and W. R. Salaneck, *Appl. Phys. Lett.* 88 (2006) 193504.
- Enhancement of Iridium-based organic light-emitting diodes by spatial doping of the hole transport layer.
Y. Wang, W. Gao, S. Braun, W. R. Salaneck, F. Amy, C. Chan and A. Kahn, *Appl. Phys. Lett.* 87 (2005) 193501.
- Poly(3,4-ethylene dioxythiophen)- and Polyaniline- Poly(perfluoroethylene-sulfonic acid) a photoelectron spectroscopy study.
C. Tengstedt, S. Braun, W. R. Salaneck and M. Fahlman, *submitted*
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R. Friedlein, F. von Kieseritzky, S. Braun, Ch. Linde, W. Osikowicz, J. Hellberg, W. R. Salaneck, *Chem. Commun.* 15 (2005) 1974.

- Surface-induced vertical alignment of self-assembled supramolecular columns of large polycyclic aromatic hydrocarbons and porphyrins.
R. Friedlein, X. Crispin, W. Osikowicz, S. Braun, M. P. de Jong, C. D. Simpson, M. D. Watson, F. von Kieseritzky, P. Samorí, S. K. M. Jönsson, M. Fahlman, F. Jäckel, J. P. Rabe, J. Hellberg, K. Müllen, W. R. Salaneck, *Synth. Met.* 147 (2004) 79.
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Minkov, F. Gel'mukhanov, R. Friedlein, W. Osikowicz, C. Suess, G. Öhrwall, S. L. Sorensen, S. Braun, R. Murday, W. R. Salaneck, H. Ågren, *J. Chem. Phys.* 121 (2004) 5733.
- Stability of indium tin oxide/polymer interfaces.
Crispin, X. Crispin, A.; de Jong, M.P.; Marciniak,* S.; Osikowicz, W.; Jonsson, S.; Fahlman, M.; Kugler, T.; van Ijzendoorn, L.J.; de Voigt, M.J.A.; Salaneck, W.R. *Mater. Res. Soc. Symposium Proceedings*, Vol.747 (2003) 315.
- Electronic structure of highly ordered films of self-assembled graphitic nanocolumns.
R. Friedlein, X. Crispin, C. D. Simpson, M.D. Watson, F. Jäckel, W. Osikowicz, S. Marciniak*, M. P. de Jong, P. Samorí, S. K. M. Jönsson, M. Fahlman, K. Müllen, J. P. Rabe, and W. R. Salaneck. *Phys. Rev. B* 68 (2003) 195414.

*Name before marriage

Content

1. Introduction	3
2. Organic materials	7
2.1 Background	7
2.2 The electronic structure of some conjugated polymers	10
2.3 Charge carriers: solitons, polarons, bipolarons	12
2.4 Doping of organic materials	14
2.5 Poly(3,4-ethylenedioxythiophene) – PEDOT	16
3. Interfaces in organic electronics	19
3.1 An example of organic electronic device: organic light-emitting diode (OLED)	20
3.2 Operational principles of OLEDs	21
3.3 The role of interfaces for charge injection	24
4. Quantum chemical calculations	27
5. Experimental technique	29
5.1 Background information	30
5.2 The theory of photoelectron emission	33
5.3 XPS – core level spectroscopy	35
5.4 UPS – spectroscopy of valence levels	36
5.5 The reference level	38
6. Experimental Equipment	41
7. References	43
Paper I	51
Paper II	69
Paper III	111
Paper IV	127
Paper V	139

1

Introduction

Organic electronics is now a rapidly evolving research field with vast number of applications having high potential for commercial success. Research in this field is conducted on a largely multidisciplinary level, involving: theoretical physics and chemistry, synthetic chemistry, various material and device characterization methods, device engineering. In order to fulfill the demand for the expertise necessary to appropriately address the organic electronics-related scientific topics, the research projects are often conducted in co-operations between various research groups. Since organic electronics has a potential to provide substantial revenues in the near future, electronic and chemical industries also show increasing interest in this field. As an outcome of this interest a significant research effort is also undertaken by industrial research and development (R&D) laboratories. It is worth noting that a significant part of this thesis is based on the research conducted with close collaboration with the industrial partners.

For the development of new organic electronic applications and improvement of performance of the already existing prototype devices, materials with desired properties play an instrumental role. They are the key ingredients, which provide competing functionalities (e.g. flexibility, lightweight) to the electronic devices. One of the most advantageous features, associated however mostly with soluble organic materials, is their good processing ability. The various organic-based devices can be made by

printing methods, *e.g.* inkjet, roll-to-roll, which simplifies and speeds up the production process. Consequently, it also greatly lowers the manufacturing costs, which are often regarded as the deciding factors for successful commercialization of the devices.

Some of the developed organic materials already exhibit properties enabling their use in the electronic devices. Though for many applications, available at this time materials, do not provide satisfactory device performance and operational stability. Nowadays these shortcomings definitely hinder the progress in commercialization of organic-based electronic devices. For the sustainable development of organic electronics in-depth knowledge and understanding of physical and chemical properties of organic materials is necessary. One of the biggest drawbacks of organics is its tendency for alternation of properties not only during operation of devices but even under ambient conditions (often referred to as ageing). This in-turn constitutes a significant problem that limits both shelf and operational lifetime of the devices. In this thesis, papers: I and II contain research results related to the stability of organic materials. Since many organic electronic applications encompass several thin film layers made of organics, and often also inorganic materials, the understanding of interfaces is another important issue for the development of organic electronics. The energy level alignment at various organic-organic and hybrid interfaces has been studied in papers: III, IV and V.

Research presented in this thesis is based predominantly on photoelectron spectroscopy. This material characterization technique is a very fruitful method for studying physical and chemical properties of organic materials. The possibility of high-resolution x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements allow for studying electronic and chemical properties of the materials.¹⁻⁵ Since photoelectron spectroscopy is a surface sensitive technique, physical and chemical interactions at surfaces and interfaces can be studied in details. Ultraviolet photoelectron spectroscopy is also very useful for studies of interfaces since it enables direct probing of the occupied valence electronic levels as well as vacuum level shifts upon forming the interface.

The thesis comprises of an introductory part, which is expected to provide a short description of the concepts involved in the presented papers. In the chapter 2 the basic information concerning conjugated organic materials is given. Since the first two papers included in the thesis, relate to the properties of the conjugated polymer

poly(3,4-ethylenedioxythiophene) (PEDOT), some background information related to this polymer is included in the chapter 2. In chapter 3, a general description of interfaces and their role for operational conditions in organic electronic devices, is presented. The next chapter contains short description of quantum chemical calculations of electronic structures. Some theoretical aspects of photoelectron spectroscopy are included in chapter 5. Chapter 6 presents the equipment on which experimental work has been performed. In the next part of the thesis the scientific publications are presented.

2

Organic materials

2.1 Background

The discovery of the dramatic increase in electrical conductivity, upon doping of semiconducting polymers, established the foundation to the field of organic electronics.^{6,7} Since then, the doped conjugated polymers, as well as molecules, have been extensively studied in the context of their possible application in organic electronic devices. Organic materials found their way in many applications like: light-emitting diodes,²⁷ transistors,¹⁵ photovoltaic devices,⁸ photo-detectors,⁹ polymer-based memories,^{10,11} chemical vapor sensors,¹² *etc.* Hence, to a large extent the prospects for a new organic electronic industry has been the driving force for the research and engineering efforts concerning this class of materials for already many years. It should be realized that organic materials provide a combination of properties that are not found for inorganics. This combination includes lightweight, flexibility, relatively easy processing as well as controllable in a wide range electrical conductivity. Though there exist significant drawbacks that must be overcome in order to make devices that fulfill commercial requirements. The development of new molecules and polymers has enabled continuous progress of the knowledge in the field. The number of possible applications has grown as materials with desired properties became available.

Organic materials are composed mainly of carbon atoms. Other low atomic number atoms, like: oxygen, sulfur, are also common building elements. The electronic configuration of carbon atom allows it to form different hybridized orbitals, namely sp , sp^2 and sp^3 , as the chemical bonding configuration. The electronic configuration of carbon atom consists of 2 electrons in core $1s$ level denoted as $1s^2$ and 4 valence electrons residing in $2s$ and $2p$ levels, which can be denoted as $2s^2$ and $2p^2$, respectively. In order to explain electronic configuration in different compounds involving carbon, the concept of hybridized orbitals is used. Hybridized orbitals are assumed to be mixtures of atomic orbitals. The wave functions of the s and p atomic orbitals combine to form a new set of equivalent hybrid orbitals. New orbitals are linear combinations of atomic orbitals and the reason they form is to minimize the total energy of the formed compound.¹³ When one s orbital mixes with three p orbitals it yields four sp^3 type hybrid orbitals. Each of them consists of two lobes of different size. Four larger lobes are oriented towards the corners of a tetrahedron at angles of 109.5° . When carbon atoms are bonded in such a scheme each of them has four neighbors. This configuration can be found in diamond. Another type of hybridization is the one that involves only one s and two p atomic orbitals. The three hybrids are span in the plane and are oriented at angles of 120° to one another and contain one electron each. The remaining electron resides in unhybridized p orbital oriented perpendicular to the plane of sp^2 orbitals. This type of hybridization will be discussed in more details in the context of conjugated polymers. Here, for completeness the remaining sp configuration will be presented. In that case only one s and one p electrons form hybrid orbital. The remaining two p electrons are unhybridized and reside in orbitals oriented at 90° to the sp hybrids. Such hybridization scheme accounts for linear geometries.

When two atoms are bond through hybridized orbitals, two different types of bond exist, depending on their alignment with respect to the bonding direction. Sigma bonds, denoted as σ , are symmetrical about the axis joining the two nuclei. This type of bond allows for rotation of atoms along the bonding direction. Most often such rotation is prevented by existence of π bonding. This bonding is constructed from electrons in unhybridized p orbitals and geometrically is perpendicular to the axis joining two nuclei. Hence, when two carbon atoms are bonded through σ and π bonds, the later prevent rotation of these two atoms. These two types of bonds differ significantly by means of their strength. Since the spatial overlap of orbitals is larger for σ type of bonding than π type, the later is significantly weaker. This invokes consequences for the

energy associated with σ or π electronic levels in a molecule (or bands in a polymer). The general picture in both cases is such that σ states are always lower in energy than π states (and *vice versa* for the occupied states).

The existence of a single, double or triple bonds corresponds directly to the type of hybridization occurring when a molecule or polymer is formed. Another consequence of different hybridization schemes is the geometry of a compound.

Polymers can be formed through sp^3 or sp^2 hybridization, which determines their electronic properties. Polymers with a backbone build from sp^3 hybridized carbon atoms have large band gap (above 3eV), which implies optical transparency and insulating properties. Units in such polymers are connected only through σ bonds. Another class of polymers often referred as conjugated polymers have their backbone build through sp^2 hybridization. In such configuration both σ and π bonds are present. The later are responsible for unique electronic properties of such systems. Since there is interaction between π bonds of

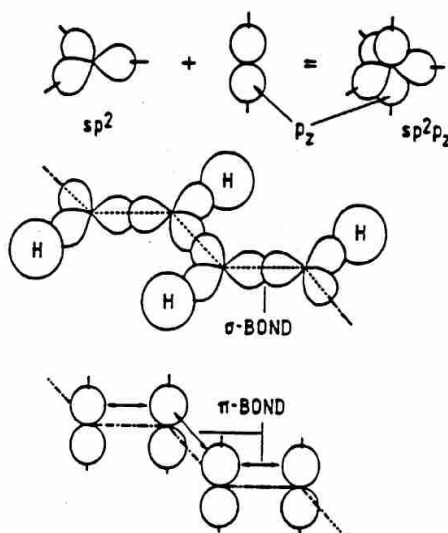


Figure 2.1 Formation of the conjugated backbone exemplified by polyacetylene. The sp^2 -hybridized carbon orbitals form in plane σ -bonds, whereas perpendicular p_z orbitals form the overlapping π -bonds.

carbon atoms, the electronic wave function is delocalized along the polymer chain.¹⁴ This delocalization enables fast movement of charge-carrying species (polarons/bipolarons) along the backbone.

2.2 The electronic structure of some conjugated polymers

The simplest conjugated polymer: polyacetylene contains only sp^2 hybridized carbon atoms with one hydrogen atom, attached via σ bond to each carbon atom, as shown in Fig. 2.2. The

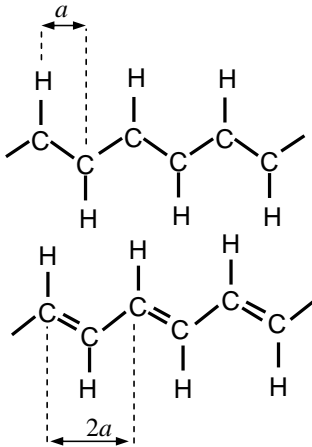


Figure 2.2 Polyacetylene (a) with homogeneous delocalisation of π electrons (b) dimerized by Peierls distortion

interacting π orbitals constitute a one-dimensional delocalized electronic system. The electronic properties of polyacetylene are dependent on the spacing between carbon atoms or in other words on the carbon-carbon bond lengths. In the case when all the C-C bonds have the same length, the size of repeat unit is a , as shown in Fig. 2.2. The dimension of corresponding first Brillouin zone is then π/a . When each of the carbon atom adds one electron to the π band and each allowed state can be occupied by two electrons (of different spin) the result is a half-filled valence band. Such a band corresponds to a one-dimensional metal. However, as showed already by Peierls in 1930, the equidistant spacing of atom nuclei is unstable configuration in the systems with degenerate ground state.¹⁵ Therefore for trans-polyacetylene, in the ground state, the bonds connecting carbon atoms have alternating length of 1.36\AA and 1.44\AA . The requirement of degeneration is fulfilled since the bond alternation order does not change the total energy of the polymer. Regardless to the alternation order, the minimum total energy of the system is preserved. In this case, the imposed mechanical strain is compensated by the gain in electronic energy. This in turn, has important consequences for electronic

atoms with one hydrogen atom, attached via σ bond to each carbon atom, as shown in Fig. 2.2. The interacting π orbitals constitute a one-dimensional delocalized electronic system. The electronic properties of polyacetylene are dependent on the spacing between carbon atoms or in other words on the carbon-carbon bond lengths. In the case when all the C-C bonds have the same length, the size of repeat unit is a , as shown in Fig. 2.2. The dimension of corresponding first Brillouin zone is then π/a . When each of the carbon atom adds one electron to the π band and each allowed state can be occupied by two electrons (of different

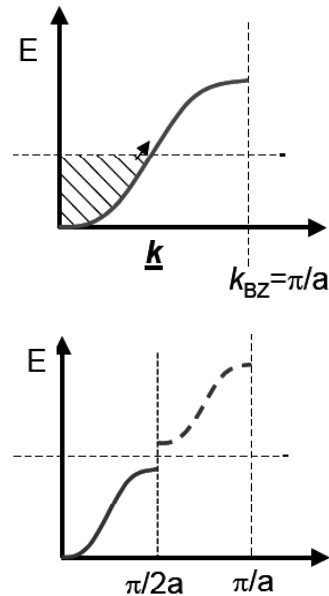


Figure 2.3 The band structure of polyacetylene (a) with homogeneous delocalisation of π electrons (b) dimerized by Peierls distortion

properties of the polymer. Even though the length of the bonds differs only by 0.08 Å, the electronic properties are changed dramatically.¹⁶ Due to the bond alternation, the repeat unit along the dimerized chain doubles the size. Since the dimension of the Brillouin zone is inverse distance of the unit cell, the first Brillouin zone moves into the position of $\pi/2a$ (Fig. 2.3). Consequently, the zone edge of the dimerized chain meets the band structure just at the Fermi energy. The energetic gap opens up at the Fermi level, which is manifested by semiconducting properties of trans polyacetylene.^{17,18}

The examples of other, more complex polymers, are depicted in Fig 2.4. In contrast to trans-polyacetylene, they have non-degenerate ground state structures. The bond alternation order is associated with the change of the total energy of polymer. When the polymer structure involves rings, the ground state geometry has aromatic form (Fig. 2.5 a). The other possible bond alternation configuration corresponds to the quinoid form (Fig. 2.5 b), which is energetically less favorable. Hence there is only one bond alternation scheme that corresponds to the minimum energy.

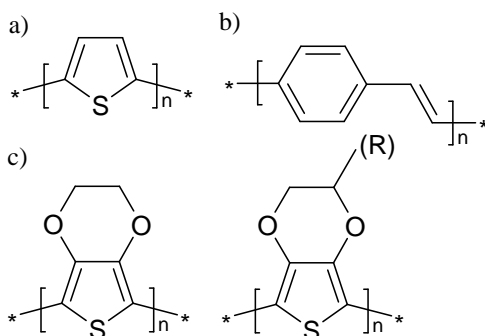


Figure 2.4 The chemical structures of
 (a) polythiophen, (PT);
 (b) poly(paraphenylenevinylene), (PPV);
 (c) poly(3,4-ethylenedioxythiophene)(PEDOT).

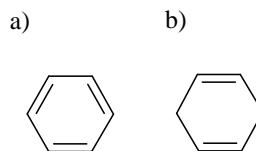


Figure 2.5 Schematic structure of
 benzene ring in (a) aromatic and (b)
 quinoid form. The aromatic form
 corresponds to ground state
 geometry

2.3 Charge carriers: solitons, polarons, bipolarons

The bond alternation scheme in any conjugated polymer can be locally (several units) distorted. Such distortion perturbs the electronic structure so that new available states are created. These states appear in the previously forbidden energy gap, therefore their presence changes properties of the material. The short description of possible new states will be now presented.

As mentioned in the previous paragraph, polymers may have degenerate or non-degenerate ground state geometry. In the first case, the local bond alternation disruption may be introduced and leads to a new state called soliton. Interestingly the new state has no charge but has a spin. The charge can be added or withdrawn from such a state, which leads to positively or negatively, charged solitons.

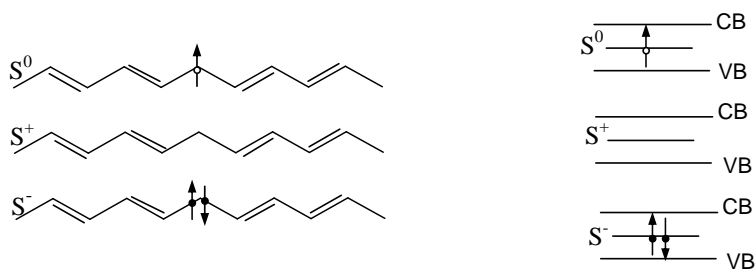


Figure 2.6 Schematic representation of solitons in *trans*-acetylene.

Since the neutral soliton has a spin, addition or extraction of an electron cancels the net spin. In the case of negatively charged solitons the resulting electronic structure of polymer includes half-filled states (bands) at Fermi level. Therefore presence of these states invokes electrical conductivity increase of the polymer. The soliton states may be induced by absorption of light, or by "doping", when charge-exchange process occurs between the polymer chain and a dopant (*e.g.* atom, molecule). From the chemical point of view such doped system can be viewed as salt.¹⁹

The majority of conjugated polymers have non-degenerate ground state. Therefore, in such systems, formation of soliton would convert the polymer geometry to a more quinoid like structure. This, in turn, would raise the total energy, since there is

only one ground state configuration for such polymers. The energy rise would then be proportional to the extension of the bond alternation distortion. In other words, the longer the polymer with quinoid-like structure, the higher the total energy. Since it is the extension of perturbation that defines energy rise of the system, it is then energetically favorable to confine the distortion within short distance. Therefore the stable configuration comprises of two defects. Such a quasi-particle is called polaron. This configuration corresponds to the two new states in the previously forbidden energy gap. These new states can accommodate up to 2 charges. The possible configurations are depicted in figure 2.7. In certain material systems, the combination of two polarons into one bipolaron leads to a lower total energy.²⁰

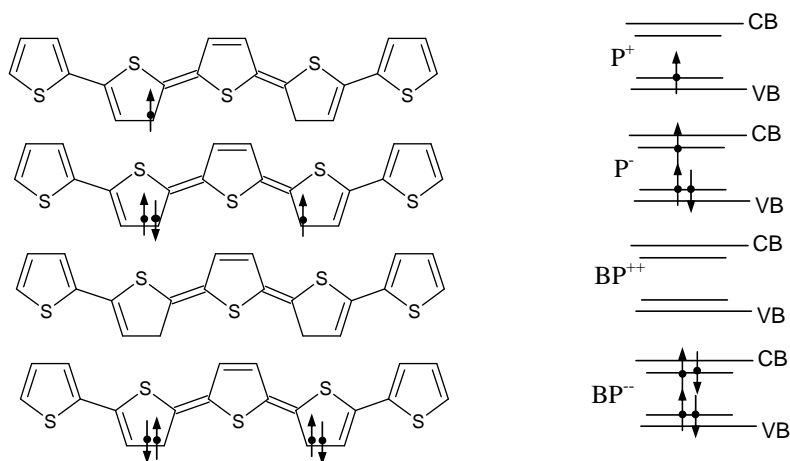


Figure 2.7 Schematic representation of quasi particles: polarons and bipolarons for polythiophene.

2.4 Doping of organic materials

In the ground state, conjugated polymers are semiconductors with the band gap mostly confined within 1-3.5eV range. However, as it was discussed in the previous paragraph, the change in bond alternation scheme influences the electronic structure so that new states (polarons or bipolaron) are created. In the presence of electric field, these charge carriers can move along the polymer backbone since there is conjugation of π orbitals. The distortion of bond alternation can be imposed by addition or extraction of charge often called - doping. When the doping level is sufficiently high, the electronic structure evolves to that of a metal.⁶ Consequently, the modification of the physical properties (conductivity, optical response) of a doped material is observed.

There are various methods which allow for doping of organic materials:

- charge-transfer redox chemistry – chemical doping
- electrochemical doping
- photo-doping
- interfacial doping

The first type of doping involves oxidation (p-type doping), or reduction (n-type doping) by interaction of polymer chain with atomic or molecular charge donors (or acceptors). Upon interaction the new states are created in polymer chain while the dopant maintains charge neutrality thus acting as counter ion. The chemical doping can be maintained both on molecular or polymeric systems, and is rather efficient though difficult to control. The later issue is strongly related to the fact that amount of dopant introduced in the material often does not correspond to the achieved doping ratio. Chemical doping was the mechanism involved in the discovery of conducting polymers. Performed on trans-polyacetylene yielded metallic material with conductivity close to that of copper.²¹

In electrochemical doping the polymer is reduced or oxidized by the redox charge, provided by electrode. Results presented in paper I and II in this thesis involves PEDOT samples prepared by this method. The role of electrolyte is to compensate the electronic charge. Practically, doping at any level can be achieved by controlling the

voltage and time of the reaction. When the system is at electrochemical equilibrium, the doping level is determined by voltage between the conducting polymer and the counter electrode. For some materials this process can be reversed. Since doping is associated with change of conductivity or sometimes other properties, this can be utilized in a practical way. This property makes such materials promising for applications like electrochromic windows,^{22,23} transistors,²⁴ *etc.*

So far, the types of doping discussed provide changes in a polymer that are relatively stable in time. In these cases the induced electrical conductivity is permanent as long as the charge carriers are not chemically compensated or removed by undoping. In the case of photo-doping the induced effect can be transient and exists only until the excitations decay back to the ground state. Similarly, the interfacial-doping rely on the applied voltage. It is worth noting that the doping can be performed not only on polymers but also on small molecules. The doping can be realized via charge exchange with “guest” molecules or with atoms like Na or Li and leads to the new electrical properties of a molecular layer.²⁵⁻²⁸ In paper IV, the doping with sodium atoms of vacuum deposited molecular films of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) was performed. The studies have revealed that the doping significantly alters the electronic structure of the molecules. Moreover, it was shown that the observed doped-induced changes are reminiscent of the interfacial states observed for a submonolayer deposited on Aluminum oxide substrate.

There is also a certain type of doping that significantly increases conductivity of polymeric films but is not associated with a process of charge exchange. Such a doping is called: *secondary doping* and relates to the inclusion of an inert substance that enhances conductivity of already (primarily) doped system. Such a substance, usually organic solvent, introduces various changes to the polymeric system: changes in a chain conformation, changes in the interaction strength between the polymer and counterions or changes in morphology. The inclusion of a secondary dopant may also promote better chain stacking which in turn enables better charge hopping between polymer chains. Consequently, a better pathway for charges to travel in the polymeric film (via inter-chain hopping) is available.

2.5 Poly(3,4-ethylenedioxythiophene) (PEDOT) – a conjugated polymer

Conjugated polymer - PEDOT has a unique combination of properties which makes it extremely attractive for organic electronics applications.²⁹ It is utilized in organic-based optoelectronic devices: as a charge injecting layer in light-emitting devices;^{30,31} as a component in electrochromic displays²² and even as electrodes in field-effect transistors³² and photovoltaic cells.³³

PEDOT is an intrinsically insoluble polymer, which can be chemically or electrochemically doped (doping processes are discussed in paragraph 2.4). Doping transforms PEDOT from an opaque insulator to a quasi-transparent material with high electrical conductivity.^{34,35}

The most common form, in which PEDOT is used, comprises poly(styrene sulfonate)

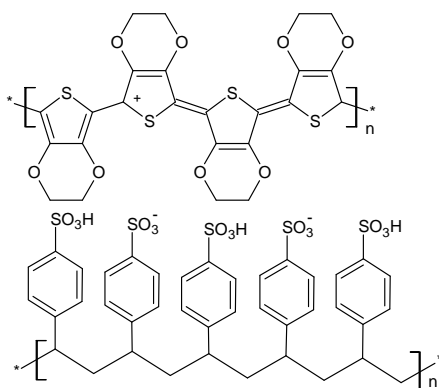


Figure 2.8 The chemical structure of PEDOT-PSS

abbreviated often as PSS. Such complex is known as PEDOT-PSS. The synthesis of PEDOT-PSS involves polymerization of EDOT monomers in a polyelectrolyte solution of PSS. Polymerization is initiated by removal of charges from EDOT monomers. Formed in this way radicals inhibit polymerization of EDOT units while PSS acts as counter ion balancing positive charge residing on PEDOT. The final product comprises of aqueous dispersion of PEDOT-PSS, which chemical structure is shown in figure 2.8.

PEDOT chain stores charges in the form of polarons/bipolarons. As discussed earlier, these quasi-particles are associated with the geometrical distortion, which can be

delocalized over several monomer units. The charges are balanced by presence of SO_3^- groups of PSS. Films formed from PEDOT-PSS dispersion have conductivity of about 0.01-0.05 [S/cm]. The substantial increase in conductivity of the films can be achieved through the process called: secondary doping. (in paper II, a three orders of magnitude increase of conductivity is reported as the effect of secondary doping). The mechanism of the secondary doping is discussed in chapter 2.4.

The distinct property of PEDOT-PSS is its ability to form aqueous dispersion. This is possible because of the long chains of polystyrene sulfonates. In the form of dispersion this polymeric complex is ideal for making thin conducting films by spin coating. This method of film preparation enables large-scale and low-cost production of the devices.

PEDOT-PSS has also been used as a buffer layer in organic-light emitting diodes (OLEDs) sandwiched between inorganic electrode indium tin oxide (ITO) and an active layer of an electroluminescent polymer or a layer of evaporated small-molecules. The presence of PEDOT-PSS smoothes rough surface of ITO and increases the work function of the electrode. Interfacial chemistry between PEDOT-PSS and ITO is important in the context of device operational stability and lifetime. This issue is of the main focus in paper II. PEDOT-PSS films have intrinsically high work function of about 5.2eV that facilitates good conditions for hole injection.²⁶ Thanks to the recent achievements in development of this material it is also possible to obtain PEDOT-based films with different work functions.³⁶ The exceptionally high work function (up to 6.1 eV), can be obtained from the other PEDOT-based system: PEDOT-PFESA [or poly(3,4-ethylenedioxythiophene) poly(per- fluoroethylene sulfonic acid)]. The work function of PEDOT-PFESA films can be tuned by exposure to UV radiation or by a chemical modification of the dispersion. Both methods however, alter conductivity of the films.³⁷ A dispersion of PEDOT-PFESA has been used to prepare high work function films in order to study energy-level alignment with various molecular materials (see papers: III, IV and V).

3

Interfaces in organic electronics

In this chapter the motivation for studying the interfaces relevant for organic electronics is described. In the further part, the example of an organic device: organic light-emitting diode (OLED) is given. Finally the role of interfaces in organic-based devices like OLEDs is discussed.

Since applications like organic light-emitting diodes (OLED), organic field-effect transistors (OFET) or photovoltaic cells, encompass several thin film layers, the understanding of interfaces is a central issue for the further development of these devices. The particularly important seems to be the electronic level alignment at the interfaces of various organic materials. The importance of this topic is related to the fact that the interfacial energetics sets the condition for the injection of charges in a device, which has a profound influence on the device operational characteristics, i.e. current-voltage characteristic. Interfaces have been studied by various research groups and a great progress in their understanding has been made.^{5,26,38-60} However, despite all these efforts, the energetics of organic-organic and hybrid interfaces is still not completely understood. The attempt of finding a model that would be capable to predict the energy level alignment of broad range of interfaces has been made by Vázquez and co-workers. A model of energy level alignment at the “atomically clean” metal–organic and organic–organic interfaces was proposed, where the interfacial electronic structure was interpreted in terms of induced density of interface states (IDIS).⁶¹⁻⁶³ In the recent

studies, however, it was shown that various type of interfaces do not comply with this model.⁶⁴⁻⁶⁶

3.1 An example of organic electronic device: organic light-emitting diode (OLED)

Organic light-emitting diode is one of the main applications in which novel properties of organic materials are utilized. The study by Tang and Van Slyke, showing reasonably efficient electro-luminescence from molecular thin films, opened the route for utilization of organic materials as light emitters. The early prototype device was build of inorganic electrodes (ITO and Mg/Ag alloy) and two subsequently deposited molecular layers. The first layer comprised of aromatic diamine, which served as hole-transporting layer (HTL), while the second included 8-hydroxyquinoline-aluminium,

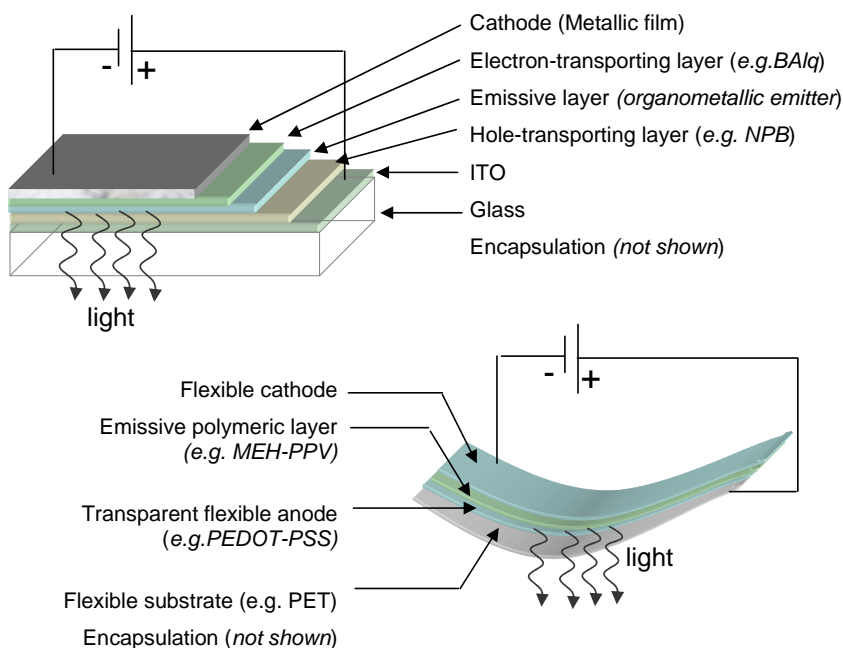


Figure 3.1 Schematic picture of some organic light-emitting diodes (OLEDs): (a) small molecule-based OLED, (b) all-polymer flexible PLED.

which was the emissive layer.^{67,68} The discovery led to extensive research devoted to the improvement of OLEDs operational conditions and performance.⁶⁹ The simple structure of the early OLEDs has gradually evolved to the multi-layered devices as shown in figure 3.1.^{70,71} The incorporation of the HTL and electron-transporting layers (ETL) provides balancing of charges entering the emissive layer.⁷²

The possibility of using polymers as an electroluminescent material in a diode has been reported by the group of Prof. R. H. Friend from University of Cambridge. Electroluminescence from conjugated polymers was first reported in 1990, using poly(p-phenylene vinylene), PPV, as the single semiconductor layer inserted between metallic electrodes. PPV has an energy gap of about 2.5 eV, and produces yellow-green luminescence.⁷³ After this discovery many other polymers like polyfluorenes (PFO) and polyspiro materials have been synthesized and utilized as emitters.⁷⁴⁻⁷⁶ Unlike small molecules, polymers can be processed by wet chemistry methods like spin coating or ink jet printing. The common configuration for polymer-based diodes is very similar to those comprising small molecules. ITO is used as transparent anode,⁷⁷⁻⁷⁹ which allows the light generated within the diode to leave the device. Then the layer of electroluminescent polymer is deposited followed by deposition of top electrode. The later is obtained by thermal evaporation of a low work function metal or a metallic alloy.

The apparent advantage of polymer light-emitting diodes (PLEDs) is the possibility of fast and cheap manufacturing. Some of the polymers are soluble in water or organic solvents, which enables convenient preparation of thin layers by spin coating. In contrast, organic layers in small molecule-based devices are prepared at least under high vacuum conditions. Therefore the process is more expensive and time consuming with respect to their polymer-based counter parts. Substitution of inorganic electrodes into flexible and conducting polymer layers (*e.g.*, PEDOT-PSS) gives opportunity for all-polymer flexible devices.⁸⁰ Such devices can be utilized in applications where flexibility and large surface is desired.

3.2 Operational principles of OLEDs

In OLED devices, light is produced through the process of electroluminescence. In this process excitons (hole–electron pairs or oppositely charged pairs of polarons) are formed within emissive layer. In order to form excitons positive and negative charges must be injected into electroluminescent layer in the device. Charge supply is maintained either directly by the electrodes or what is more often the case, through the hole- and electron- transporting layers. The injected charges migrate and form excitons via coulombic interaction. De-excitation occurs through recombination process, which may be radiative or not, depending on spin configuration. In an emissive layer comprising of entirely fluorescent material, according to spin statistics, only the minority of states formed are singlets (25%) while the rest have triplet character. Since only singlets may decay radiatively, the internal quantum efficiency of the recombination process is dramatically reduced with respect to the total number of created excitonic pairs. In small-molecules based OLEDs, significant increase in efficiency was achieved by biasing singlet-triplet statistics. This can be done by using so-called triplet emitters. In such molecules singlet and triplet states are mixed through strong spin-orbit coupling induced by a heavy atom. Such molecules are referred as organo-metallic molecules since they include atoms like Ir or Pt.⁸¹⁻⁸³ The presence of heavy atoms influences electronic properties of the molecules in such way that the excited states are not entirely of singlet or triplet character. In organo-metallic compounds the time scale for (forbidden) triplet de-excitation is much shorter than in fluorescent dyes and leads to emissive decay. Recently, research effort is also focused on biasing spin statistics in polymers.^{84,85}

The extraction of photons produced is also important issue since upon de-excitation, photons propagate in every direction from the recombination site. Therefore, only some of them propagate in the direction of a semi-transparent electrode comprised of e.g. glass

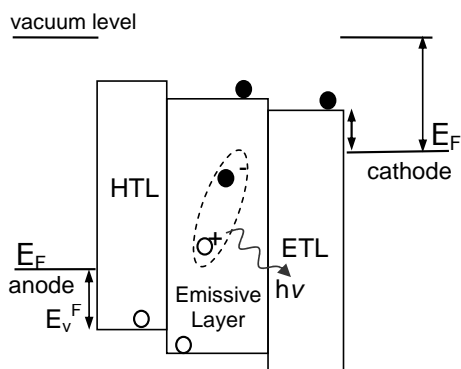


Figure 3.2 Schematic picture of energy levels in an OLED.

and ITO, and escape from the device.

Another issue, which strongly influences operational conditions of the device, is injection of charges. In order to inject charges potential barriers must be overcome by applied bias. These barriers arise from the mismatch between energy levels of materials used in the device. On the anode side, the injection may occur when Fermi level of the anode (E_F) is equal to the highest occupied molecular orbital – HOMO of hole-transporting layer.³⁸ In the case of polymeric devices, the highest occupied band is considered. Another barrier may exist at the HTL/emissive layer interface. Similar situation exists on the cathode side. Injection of electrons requires some threshold voltage that eliminates potential barrier between the Fermi level of the cathode and the lowest unoccupied molecular orbital (LUMO) of electron-transporting material (ETL). In polymer-based devices this barrier is measured versus conducting band of a polymer.⁴ When the applied voltage and the injection barrier at the interface determine current density, it is referred as contact limited injection. Such injection is characterized by the formula:

$$J \approx qN_e \mu E(0) e^{\left(\frac{q\phi_b}{k_B T} \right)},$$

where: ϕ_b is the injection barrier at the interface, N_e stands for density of states available for injection in organic film, and μ is the electron mobility. When the parameters refer to holes the equation holds also for hole mobility. It is clear that a significant increase in injection current can be achieved by reduction in the magnitude of the injection barrier ϕ_b . Another regime of charge injection that can occur during operation of a device is space charge limited injection. In this case, when near an ohmic contact provides almost a barrierless flow of charges through the interface, the limiting factor is the mobility of charges in the organic layer. At some point the flow of charges saturates due to finite mobility, which causes an increase of charge density at the interface. This, in turn builds up potential that acts as injection barrier opposing further inflow of charges.⁸⁶ Space-charge-limited current depends strongly on applied field as described below:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{V^2}{L^3} \exp\left(0.89 \sqrt{\frac{V}{E(0)L}} \right).$$

3.3 The role of interfaces for charge injection

As can be deduced from Fig. 3.2 the electronic level alignment at the interfaces sets the conditions for the injection of charges in a device like e.g. OLED. Often, in organic diodes there are electronic level misalignments at the interfaces, which lead to the contact-limited injection regime. There are mainly two reasons for this situation. First of them is the mismatch between work function of the electrode and ionization potential (electron affinity) of the material in organic film, as shown in figure 3.3. Another is the presence of additional barriers between organic layers e.g. HTL and active layer.

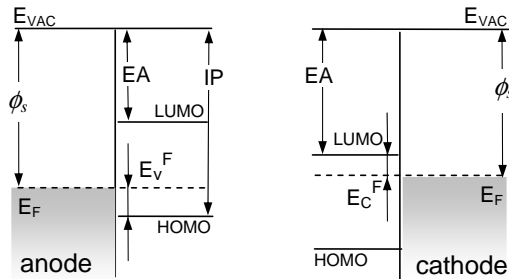


Figure 3.3 The schematic picture showing the energy level alignment at the interface of an electrode and organic layer. In these cases vacuum level alignment is assumed.

In both cases presented in figure 3.3, a common vacuum level is assumed. The position of Fermi level versus vacuum level is given by the work function ϕ_s of anode (cathode). Work function can be easily obtained by photoelectron spectroscopy as well as the threshold ionization potential (IP) of a molecule. In this way the hole-injection barrier can be estimated. In the case of electron injection barrier information of un-occupied states is needed, which can be provided by inverse photoemission spectroscopy. On this example, one can deduce that in order to obtain possibly barrier-less injection across the interface, the magnitude of the work function of an electrode should be (if possible) equal IP of organic material (or EA in the case electron injection). However, as shown by Seki *et al.* this simple picture often does not hold.³⁸

In the case of many heterojunctions, which involve inorganic electrode and organic materials, the assumption of common vacuum level is often not valid. Due to formation of chemical bonds, charge transfer or a “push-back effect”, the interfacial dipole is formed, which manifests itself as a vacuum level offset (denoted as Δ).^{3,39,41,48,49,53,87-89} As shown in figure 3.4, such offset influences the magnitude of the barrier. In some cases, even when the work function of the substrate ϕ_s equals IP or EA of organic material, there is still a barrier at the interface as the result of the vacuum level shift.

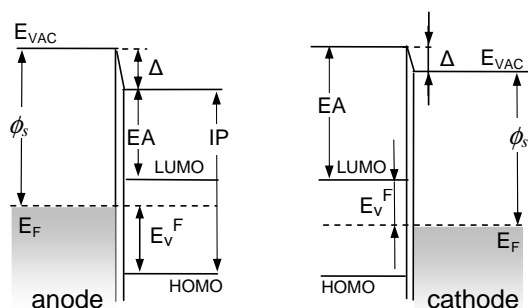


Figure 3.4 Schematic picture showing the energy level alignment at the interface of an electrode and organic layer. In these cases vacuum level shift is present, which increases injection barriers.

Therefore, the benefit of a good match between electrode work function ϕ_s and the IP of an HTL, may be reduced by a negative vacuum level shift that occurs at the corresponding interface. Such shift pushes molecular (or polymeric) electronic levels away from the substrate Fermi level. This effect seems to occur mostly for the interfaces with reactive or high work function metal surfaces, *i.e.*, metals with large surface dipole contribution to the work function. The existence of the barrier at the interface has its impact on device characteristics. In general the large magnitude of the barrier implies smaller injection current at the given voltage. This, in turn requires higher voltage applied to the device in order to achieve the desired intensity of light. These reasons are the main factors determining large interest within science and industry to understand and possibly control energy level alignment at the interfaces.

There are several different approaches to engineer an interface of desired properties. First of all for anode side of the device, the electrode used is almost always ITO, which has relatively high work function but still lower than IP of the most of the HTLs.⁴⁰ Therefore various HTLs materials have been studied in order to provide the best match between energy levels.⁷² On the other hand, by the modification of the surface of ITO, the work function can be significantly increased.^{42,90-95} In paper III, it is shown however, that the hole-injection barriers can be reduced by increasing the work function of a substrate only to certain point. As the work function of the substrate exceeds the energy of integer charge transfer state (ICTS), the interfacial dipole is formed. The magnitude of the dipole scales linearly with ϕ_s , while at the same time the barriers for hole-injection remain constant. Any further increase in ϕ_s has little (if any) effect on the charge injection barrier, but results instead in an interfacial dipole layer. The conclusions presented in paper III are based on UPS results obtained on various molecular semiconductors: CBP (4,4'-*N,N'*-dicarbazolyl-biphenyl), NPB (*N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1-biphenyl-4,4-diamine), and *m*-MTDATA (4,4,4''-tris[3-methyl-phenyl(phenyl)amino]-triphenylamine). The observed alignment regimes find correspondence to the charge injection characteristics.⁹⁶ The nature of ICTS is further studied in paper IV with the aid of photoelectron spectroscopy. In order to interpret the experimental data the theoretical calculations have been also performed. In paper V, photoelectron studies of multi-layered systems comprising of two organic materials and the substrate are reported. One of the important conclusions is that the alignment of energy levels depends on the equilibration of the chemical potential throughout the entire layer stack, while any specific electronic coupling between the individual layers is of lesser importance. The results presented show also that the equality of interface energetics under reversal of deposition sequence is not always a valid assumption. These findings should be helpful in designing of multilayer structures in organic-based charge injection/extraction devices (e.g. OLEDs).

4

Quantum chemical calculations

In this chapter a very brief description of Density Functional Theory (DFT) is given. The quantum chemical calculations, based on DFT, have been performed for the sake of interpretation of photoelectron spectra in paper IV.

4.1 Density Functional Theory (DFT)

Calculations based on Density Functional Theory can provide in-depth information about electronic and chemical structure of an organic system.⁹⁷ The theory focuses on electron density $\rho(r)$ as the most important quantity from which the ground state wavefunction and the expectation value of any electronic property of the system can be obtained. DFT is based on Hohenberg-Kohn theorems,⁹⁸ which say that: (i) there is a correspondence between the ground state electron density and the ground state wavefunction of a many-particle system; (ii) the ground state electronic density minimizes the total energy of the system. The DFT became really useful for computational chemistry when Kohn and Sham introduced the formalism incorporating orbitals.⁹⁹

The important feature of DFT method is that it incorporates electron correlation effects: (i) coulombic correlation, which is associated with the coulombic repulsion force

between electrons and (ii) exchange correlation, which is related to the Fermionic nature of electrons and originates from Pauli exclusion principle. The DFT concepts can be also extended to the time-dependent description of an electronic system, which is useful in the study of various excitation processes.

4.2 Theoretical results versus photoelectron spectra

As shown in figures 4.1 and 4.2, quantum chemical calculations can provide valuable information about a molecular system. The calculated electronic structure can be used to generate a density of valence states (DOVS). Usually, in the calculations only a single molecule or (a polymer chain) is considered. The obtained on such basis theoretical results can be used to interpret photoemission data. However it should be remembered that the theoretical results do not account for some physical phenomena that occur in a real sample, like: solid-state effect or relaxation effect.

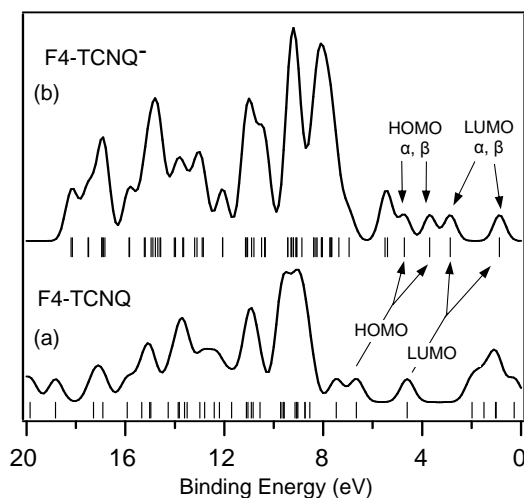


Figure 4.1 The density of valence states (DOVS) curves and the (DFT-based) eigen-energies of the molecular orbitals (vertical lines) of: (a) neutral F4-TCNQ and (b) F4-TCNQ anion.

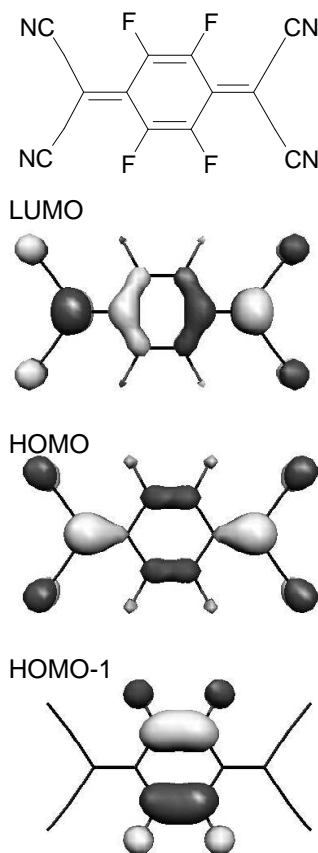


Figure 4.2 (a) Chemical structure of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ), (b) a visualization of electronic orbitals based on DFT calculations.

5

Experimental technique

Photoelectron spectroscopy is one of the most powerful experimental techniques used in the studies of materials. As the name already suggests, this technique is based on photoelectric effect observed by Hertz in 1887 and then theoretically explained by Einstein in 1905. Since the first observation of the core level lines, the technique has evolved together with development of instrumentation and advances in science. During 1960s a high-resolution spectrometer has been developed by Kai Siegbahn and co-workers.¹⁰⁰ Since then, the details of electron binding energy could be studied with the aid of well-resolved spectra. This achievement has led to the new application of photoelectron spectroscopy: chemical analysis, often called ESCA (Electron Spectroscopy for Chemical Analysis). Due to the good resolution of photoemission spectra the technique can provide wide range of useful information not only concerning atomic composition of the samples but also their physical and chemical properties. Over the years, the scope of the photoelectron studies has significantly broadened. Many different scientific topics have been studied, to mention a few: electronic structure of organic molecular materials in solid and gas phase, surfaces and interfaces of thin molecular and polymeric films, polymer blends, doped molecular and polymeric systems, adsorbates and many more.^{1,2,51,101-113}

5.1 Background information

Photoionization occurs upon interaction of light (photons) with electrons. In this process the law of conservation energy imposes conditions that govern generation of photoelectrons. The magnitude of kinetic energy of the electrons that are ejected from the sample upon photoionization process, carries information about studied sample *e.g.* atoms, molecules, polymers, *etc.* In order to extract this information the kinetic energy distribution of photoelectrons is acquired in the form of spectrum. The kinetic energy of emitted electrons is dependent on photon energy and the energy change induced in the system (*e.g.* atom, molecule). This relation has the form as follows:

$$h\nu + E_G = E_K + E_+^*, \quad (5.1.1)$$

where: $h\nu$ is the photon energy, E_G stands for the total energy of the neutral atom (molecule) in its ground state, E_K accounts for the kinetic energy of the photoelectron and E_+^* is the total energy of the ionized specie (atom, molecule) that is left after electron emission.

In the equation 5.1.1, two parameters describe the energetic states of the system namely E_G and E_+ . The first relates to the state before the photionization event while the second corresponds to the final state of the system that is without electron. Consequently the difference between these two quantities directly relates to the energy “consumed” to photoionize the system. This energy is often denoted as the binding energy of an electron:

$$E_B = E_+ - E_G. \quad (5.1.2)$$

Hence the equation 5.1.2 can be written in the form as follows:

$$E_B = h\nu - E_K. \quad (5.1.3)$$

When the incident photon energy is known, the binding energy of a certain photoelectron can be obtained by measuring its kinetic energy. The spectrum representing the kinetic energy distribution of the photoelectrons is measured, which is

complete information obtained in photoelectron spectroscopy. For a given energy of photons, the lower binding energy of the electron in the system the higher kinetic energy has this electron upon photoionization. For a particular excitation energy (photon energy) a photoelectron spectrum can be referred either to the kinetic or binding energy of electrons.

The obtained photoemission spectrum is correlated to the distribution of the final states of the system, *e.g.* molecule, polymer. Various final states are possible and derive from the electronic structure of an atom, molecule, polymer etc. In figure 5.1 the final states configurations are schematically shown.

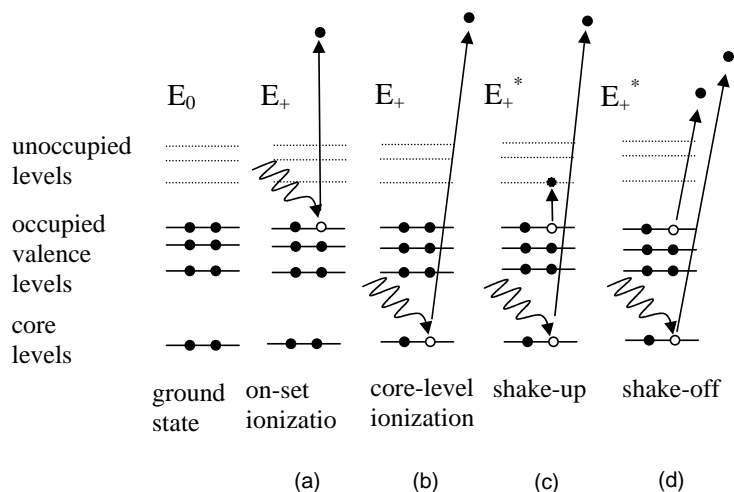


Figure 5.1 A schematic representation of various final states created in a system upon photoionization.

Case (a) corresponds to the photoionization of the least bound electron. The lowest photon energy, which is sufficient for this process to occur, is referred as the on-set ionization energy. In the case (b), an electron from a deeper level, hence having larger binding energy, is ejected. So far discussed cases correspond to the final states represented by a single hole created in the direct photoelectron emission. However, more complicated scenarios are possible and give contribution observed in photoelectron spectra as well. In shake-up processes (c), photoionization is

accompanied by promotion of another electron to a previously unoccupied electronic level. To satisfy energy conservation rule, the kinetic energy of the photoelectron escaping from the sample is reduced by ΔE^* :

$$E_K = h\nu - E_B - \Delta E^* \quad (5.1.4)$$

In shake-up the final state constitutes of core-hole and excited electron in valence level. Photoionization can lead also to promotion of another electron to the continuum of unbound states. Such a process is called shake-off (d) and corresponds to a doubly ionized system as the final state.

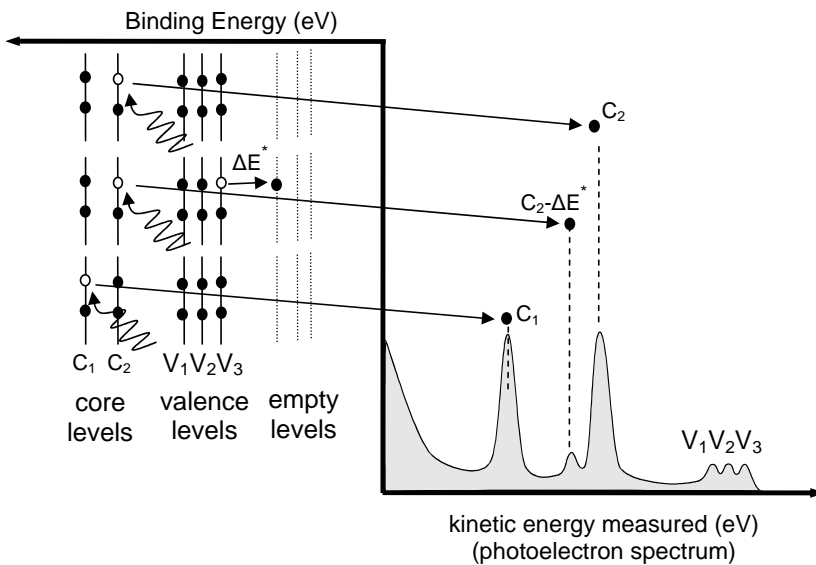


Figure 5.2 The schematic picture of the photoelectron spectra and its correspondence to the electronic structure.

The features observed in the photoelectron spectrum (figure 5.2) correspond to the previously discussed final states. The most intense peaks originate from photoelectrons corresponding to the final state with a single core hole only. The small peak observed on the lower kinetic energy side of C₂ derives from shake-up. The shake-off process contributes to the background observed on the lower kinetic energy side of the main line. The probability of additional electronic excitation that leads to shake-up or shake-

off depends on the electronic structure of an investigated system. Nevertheless the most probable final state is a single hole final state, which gives the strongest contribution to PES spectrum. Apart of shake-off, there are other contributions that lead to the observed background. After an electron is emitted upon excitation from electromagnetic field of incoming photon, it propagates in the solid. On its way to the surface it can experience inelastic and elastic scattering. This, in turn, leads to the decrease in the initial kinetic energy. The probability of scattering rises as photoelectron path to the surface increases. As a result of scattering an emitted photoelectron may never approach the surface and its kinetic energy may be totally dissipated. This implies certain limitations to the photoelectron technique.¹¹⁴

The mean free path of electrons propagating in the sample determines the depth from which photoelectrons can escape from the sample undisturbed. The inelastic scattering leads to the so-called secondary electrons, which either contribute to the spectrum in the form of background or are not detected since they remain in the sample. The mean free path in a solid sample depends on the kinetic energy of photoelectrons. Since the kinetic energy of the emitted electrons depends on the excitation energy, the probing depth also varies significantly for different excitation energies. Even for high kinetic energy electrons ($E_k > 1 \text{ keV}$) the mean free path does not exceeds 100 \AA , which makes photoelectron spectroscopy a very surface sensitive method.

5.2 The theory of photoelectron emission

The photoelectron emission in a solid sample is often considered as a three-step process. First step includes the interaction between photon and a bound electron, which leads to photoexcitation of the electron. This process is followed by perturbed (dissipation of kinetic energy) or unperturbed propagation of electron in the solid. Relevant to this work, however, are only electrons traveling towards the surface, since they take part in the final step, which is penetration through the surface into the vacuum.

Photoexcitation can be described by transition probability σ . For a perturbation Δ , the transition probability σ between initial states i is characterized by the wave function ψ_i and final states f with the wave function ψ_f , is given by Fermi's Golden Rule:

$$\sigma \propto \frac{2\pi}{\hbar} |\langle f | \Delta | i \rangle|^2 \delta(E_f - E_i - \hbar\omega). \quad (5.2.1)$$

The operator Δ can be expressed in terms of the vector potential \mathbf{A} and the momentum operator \mathbf{p} through the formula:

$$\Delta = \frac{e}{mc} \mathbf{A} \circ \mathbf{p}. \quad (5.2.2)$$

In the simplest picture, the assumption of one-electron wavefunction in initial and final state is made with free electron characterized by kinetic energy E_K . The initial-state and the final-state wavefunctions: $\psi_i(N)$ and $\psi_f(N)$, can be expressed as the product of orbital ϕ_k from which the electron is excited and the wavefunction of remaining electrons is $\psi_{i,R}^k$:

$$\psi_i(N) = C \phi_{i,k} \psi_{i,R}^k(N-1). \quad (5.2.3)$$

Similar expression describes the final-state wavefunction:

$$\psi_f(N) = C \phi_{f,Ekin} \psi_{f,R}^k(N-1), \quad (5.2.4)$$

where in both cases C is the operator that antisymmetrizes the wave functions.

Hence the transition matrix element from equation 5.2.1 is obtained as:

$$\langle \psi_f | r | \psi_i \rangle = \langle \phi_{f,Ekin} | r | \phi_{i,k} \rangle \langle \psi_{f,R}^k(N-1) | \psi_{i,R}^k(N-1) \rangle. \quad (5.2.5)$$

Under the assumption that the orbitals are the same before and after the photoionization, the electron overlap integral would be unity. In such a case the transition matrix element consists only of one-electron contributions. This approximation neglects however relaxation effect, which occurs upon release of an electron. The remaining (N-1) electrons rearrange in order to screen the hole created in photoionization process, which minimizes the total energy of the system. In order to express the photoemission intensity I , equations 5.2.1 and 5.2.5, are combined to give the formula:

$$I \propto \sum_{f,i,k} \left| \langle \phi_{f,Ekin} | r | \phi_{i,k} \rangle \right|^2 \sum_{f,j,n} \left| \langle \psi_{f,n}^k(N-1) | \psi_{i,R}^k(N-1) \rangle \right|^2 \times \delta(E_{f,kin} + E_n(N-1) - E_0(N) - \hbar\omega) \quad (5.2.6)$$

Photoionization from a particular orbital k gives rise to the line in kinetic energy photoelectron spectrum. If there is more than one possible final state it is manifested by set of satellites according to the probability distribution of these states.¹¹⁴

5.3 XPS - core level spectroscopy

The value of the binding energy of a particular core level in an atom is a unique quantity which can be used to obtain information of the atomic composition of a sample. This can be visualized by observing the example of XPS spectrum in figure 5.3. The 1s core level of carbon atom has a far lower binding energy than the corresponding 1s level of the nitrogen atom, even though their atomic numbers differ only by 1. Significant differences in binding energies of the peaks deriving from different atoms make photoelectron spectroscopy ideal technique for obtaining the qualitative information of the composition of the investigated sample. Therefore photoelectron spectroscopy is often regarded as a finger-print method.

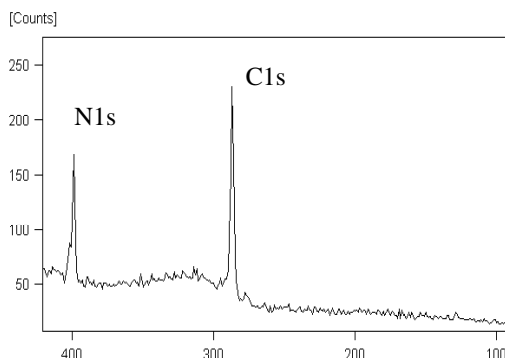


Figure 5.3 The example of XPS spectrum.

Additional information about a sample can be obtained when intensities of the observed peaks are properly interpreted. The intensity of a given peak depends on the excitation probability (cross-section), which was discussed in the previous section of this chapter. The probability varies significantly among specific orbitals and atoms. Another complexity derives from the transmission function of the spectrometer, since number of the detected electrons is a function of their kinetic energy. Therefore in order to obtain a meaningful correspondence between number of detected photoelectrons and

the actual chemical composition of a sample, the sensitivity factor that provides appropriate scaling for the photoelectron peaks intensities, are used.

Binding energy of the observed photoelectrons depends also on chemical environment of their origin atom.¹¹⁵ When an atom is a part of a molecule or polymer, the binding energy of its particular core level is affected by the density of valence electrons localized close to the atom. This local density of charge is called “an effective charge”. Even for the same atoms, an effective electronic charge can be different due to the different chemical environment. This effect is often pronounced in the photoelectron spectra and is called a chemical shift. In molecular or polymeric systems, strongly electronegative atoms withdraw electronic density from the less electronegative ones. This, in turn is manifested by a change in the effective charge. Therefore the described effect can be seen as the one that influences the initial state of an atom in terms of its charge. The simple hypothesis, that the binding energy should be a function of such an effective charge, has been shown to be a very good model to explain the differences observed in binding energy of photoelectrons. On the other hand, binding energy of electron is referred to as the energy difference between the ground and a final state. Hence the chemical shift can be also discussed in terms of the different conditions for creation of core hole. Intuitively, the higher electronic charge density on the atom should correspond to a decrease of the required energy to create a core-hole.

5.4 UPS - spectroscopy of valence levels

In ultra-violet photoelectron spectroscopy (UPS) the often used source of photons is HeI radiation of energy $h\nu=21.2\text{eV}$ or HeII radiation ($h\nu=40.8\text{eV}$). These photon energies allow for mapping out the valence electronic states of a molecular or polymeric sample. The UPS spectra can provide valuable information not only about details of the electronic structure of the studied material but also about its work function ϕ , and also the ionization potential (IP).

Work function is a very important parameter, which determines the minimum energy necessary to remove an electron from the material. When the energy of photons $h\nu$ is known (for HeI source - 21.2eV), the work function can be obtained from the measured energy of the secondary electron cutoff (E_{cutoff}) (see Fig. 5.4). The simple formula for obtaining work function has a form as follows: $\phi = h\nu - E_{\text{cutoff}}$.

The ionization potential (IP) of a material can be easily determined from its valence photoemission spectrum. It corresponds to the energetic distance between the highest occupied molecular orbital - HOMO (the highest occupied band in the case of polymers) and the vacuum level. Such a determination of IP is based on certain assumptions. It is assumed that the energy of the electronic levels is not affected by the photoionization process. Consequently, the orbitals can be regarded as frozen when an electron is ejected from the sample. This, in turn means that all the relaxation effects following ionization process are neglected. Under this assumption, according to the Koopman's theorem: the binding energy of the ejected electron corresponds to the energy of the orbital (with a negative sign) from which the electron was removed.¹¹⁶ On the basis of this theory we can consider the binding energy of the ejected electrons from the highest occupied orbital (band for polymers) as the threshold ionization potential of the studied material.

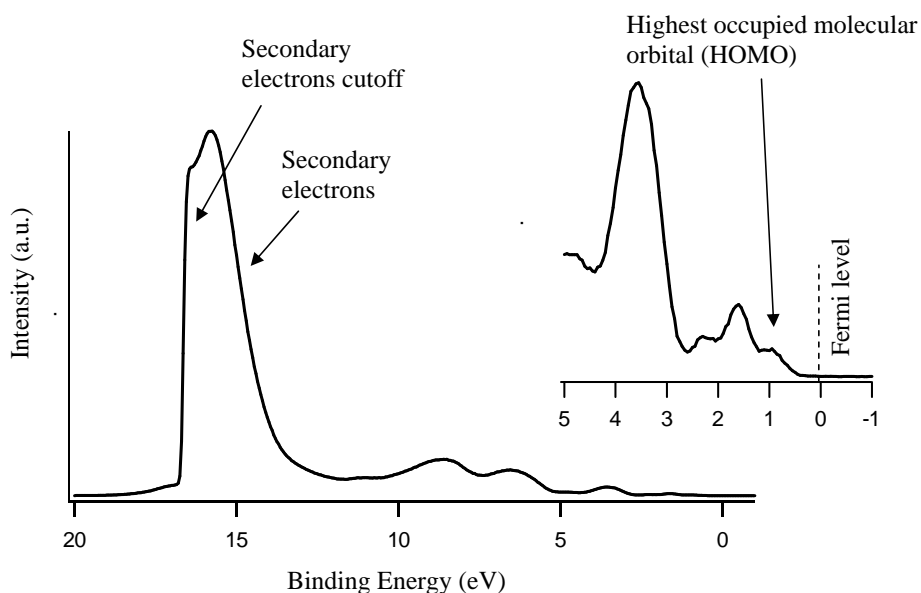


Figure 5.4 UPS spectrum of a molecular film of m-MTDATA, (4,4,4''-tris[3-methyl-phenyl(phenyl)amino]-triphenylamine).

UPS can be also applied for probing the vacuum level shifts upon forming the interface. In such studies the measurement sequence involves characterization of the bare substrate followed by deposition and characterization of molecular or polymeric add-

layers. The studies presented in paper III, IV and V were based on the above described measurement scheme.

5.5 The reference level

In order to obtain absolute values of the measured binding energies of the photoelectron lines a non ambitious reference is required. In the case of good conductors the alignment between Fermi level of the sample and spectrometer is maintained by charge transfer. Therefore the Fermi level can be regarded as the reference level. When the equilibrium is established the photoelectron that propagates from the sample, has a kinetic energy E_k' . The photoelectron is either accelerated or retarded while propagating to the entrance slit of the analyzer. The magnitude of the change in kinetic energy on the way to analyzer equals the difference between the work function of the sample ϕ and the work function of the spectrometer

ϕ_{sp} . The kinetic energy E_K of photoelectrons reaching the analyzer is expressed as follows:

$$E_K = E_K' - e(\phi_{sp} - \phi).$$

(5.5.1)

In order to fulfill conservation energy rule the photoelectron emitted from a core level with binding energy, (referred to the Fermi level), has kinetic energy, which is equal to:

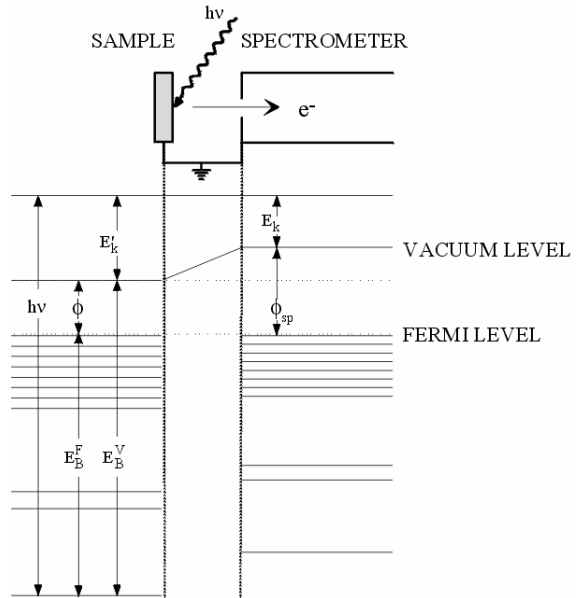


Figure 5.5 Schematic representation of energy level alignment between a conducting sample and spectrometer. Since the sample is in good electrical contact with the spectrometer, the sample Fermi level is aligned to the Fermi level of the spectrometer. Therefore the Fermi level of the spectrometer constitutes an unambiguous reference level.

$$E'_K = h\nu - e\phi - E_B^F. \quad (5.5.2)$$

By combining equations (5.5.1) and (5.5.2) the formula for kinetic energy of photoelectron reaching the analyzer is expressed through the photoelectron's binding energy, referred to the Fermi level, as follows:

$$E_K = h\nu - E_B^F - e\phi_{sp}. \quad (5.5.3)$$

Hence, when the photon energy and the spectrometer work function are known, the measurement of photoelectrons kinetic energy can be related to the binding energy of the emitted electrons relative to the Fermi level. The photoelectrons originating from given core level will always appear in the spectrometer with the same kinetic energy regardless to the work function of the sample (under assumption that the photon energy is kept constant).

In the case when the sample is poorly conductive the positive charges created upon photoionization process cannot be neutralized. In such a case the assumption of common Fermi level of the sample and the spectrometer is not valid. During the measurement uncompensated positive charges accumulate in the sample, which is often referred as charging. In this situation Fermi level of the sample is shifted versus that of the spectrometer in such a way that the measured binding energy is always higher than in the case when the charge flow is sufficient to maintain sample neutrality. Enhancing compensation rate of positive charges might solve the problem of charging. This can be done by using an external source of electrons, such as an electron flood gun.

6

Experimental equipment

Most of the work included in this thesis has been carried out in the laboratory of the Surface Physics and Chemistry group at Linköping University. The main instrumentation comprises of two photoelectron spectrometers used for characterization of polymeric and molecular thin films.

The Scienta ESCA 200 is a commercially available system for X-ray and Ultraviolet Photoelectron Spectroscopy (XPS, UPS), but modified for special sample handling. The system is based on three vacuum chambers. The base pressure in the preparation and analysis chambers is on the order of $1 \cdot 10^{-10}$ mbar. Ultra high vacuum (UHV) conditions are maintained by a combination of ion, sublimation and turbo molecular pumps. The spectrometer is equipped

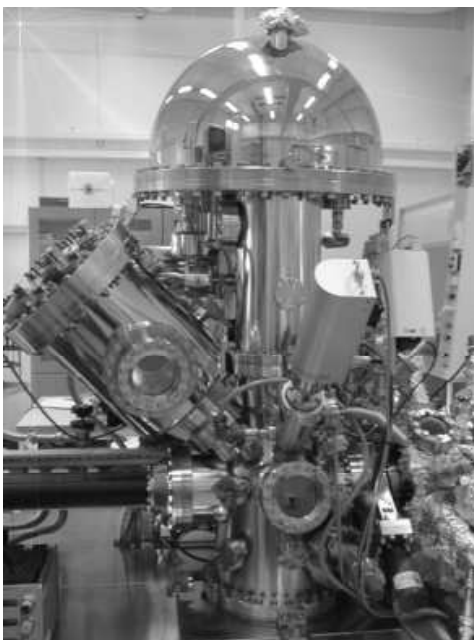


Figure 6.1 The photoelectron spectrometer "Scienta"

with a monochromatized Al-K α X-rays source (1486.6 eV) and HeI and HeII source (21.2, 40.8 eV). A high transmission electron lens system combined with the SES 200 electron energy analyzer and a multi-channel plate detector facilitate high resolution for XPS and UPS measurements. Additional instrumentation for *in situ* sample preparation is present in the spectrometer: The triple head evaporator allows for well-controlled deposition of thin molecular and solid films. Alternatively, evaporation of molecules can be done from resistively heated Knudsen cell. The spectrometer is equipped with electron gun that allows for compensating charging on poorly conducting samples. Preparation of atomic clean surfaces can be performed with ion gun mounted to the port of preparation chamber.



Figure 6.2 The photoelectron spectrometer "Moses"

The custom-build spectrometer¹¹⁷ (Moses) is designed for XPS and UPS measurements. The instrument is composed of three separate chambers. The UHV condition ($p < 10^{-9}$ mbar) is maintained by a combination of turbo molecular, ion and cryogenic pumps. Two types of photon sources are available: (i) X-ray gun that provides Al K α radiation (1486.6 eV), (ii) helium discharge lamp that gives characteristic helium radiation (HeI=21.2 and HeII=40.8 eV). The ultra violet radiation is monochromatized in order to reduce the background counts and thus provide much cleaner spectra. Additional instrumentation for *in situ* sample preparation is present in the spectrometer.

7

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