Phthalocyanine interfaces
- the monolayer region

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Materials Physics
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Royal Institute of Technology
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i. Abstract

Organic molecules adsorbed on inorganic substrates are the topics of interest in this thesis. Interfaces of this kind are found in dye sensitized solar cells that convert solar energy to electricity, a promising environmentally friendly energy source which might provide a route to replace fossil fuels. Another field where these interfaces play a role is in molecular electronics, an approach to solve the down scaling in the ever increasing hunt for miniaturized electronic devices. The motivation for this work lies among other in these applications and surface science is a suitable approach to investigate the electronic and morphologic properties of the interfaces as it provides detailed knowledge on an atomic level.

Phthalocyanines are the organic molecules investigated and the inorganic substrates range from wide band gap via narrow band gap semiconductors to metals. Photoelectron and X-ray spectroscopy experiments are performed to shed light on the electronic properties of the adsorbed molecules and the substrate, as well as the chemical interaction between adsorbate and substrate at the interface. The ordering of the adsorbate at the interface is important as ordered molecular thin films may have other properties than amorphous films due to the anisotropic electronic properties of the organic molecules; this is investigated using scanning tunneling microscopy.

We find that the phthalocyanines are affected by adsorption when the substrate is TiO$_2$ or Ag, where charge transfer from the molecule occurs or an interface state is formed respectively. The molecules are adsorbed flat on these surfaces giving a large contact area and a relatively strong bond. On Ag, ordered structures appear with different symmetry depending on initial coverage. The reactivity of the TiO$_2$ surface is not ideal in the solar cell application and by modifying the surface with a thin organic layer, the negative influence on the adsorbed phthalocyanine is reduced. ZnO is not as reactive as TiO$_2$, thanks maybe to the upright adsorption mode of the phthalocyanines. The semiconductor InSb is less reactive leading to self-assembled molecular structures on the (001) surface, either homogenously distributed in a one monolayer thick film or in strands along the reconstruction rows. InAs on the other hand has a larger influence on the adsorbed molecules resulting in a metallic film upon thermal treatment.
ii. List of Appended Papers


IV. P. Palmgren, S. Yu, F. Hennies, K. Nilson, B. Åkermark and M. Göthelid, ”Changing adsorption mode of FePc on TiO$_2$(110) by surface modification with bipyridine”, Manuscript

V. P. Palmgren, B.R. Priya, N.P.P. Nirmal and M. Göthelid, “Self-ordering of metal-free phthalocyanine on InAs(100) and InSb(100)”, J. Phys.: Condens. Matter 18 (2006) 10707

VI. K. Nilson, P. Palmgren, J. Åhlund, J. Schiessling, E. Göthelid, N. Mårtensson, C. Puglia and M. Göthelid, “STM and XPS characterization of Zinc Phthalocyanine on InSb(001)“, Accepted for publication in Surface Science

VII. J. Åhlund, K. Nilson, P. Palmgren, E. Göthelid, J. Schiessling, M. Göthelid, N. Mårtensson and C. Puglia, “STM investigation of FePc on InSb(001)c8×2”, Manuscript
VIII. P. Palmgren, F. Hennies, S. Yu, K. Nilson and M. Göthelid, “Thermal effects on order at organic/inorganic interfaces: TiOPc on InSb(001)c(8×2)”, Manuscript

IX. P. Palmgren, J. Åhlund, K. Nilson, E. Göthelid, J. Schiessling, C. Puglia and M. Göthelid, “Adsorption site of phthalocyanines on the InSb(001)c(8×2) surface”, Manuscript

X. M. Göthelid, P. Palmgren, S. Yu, B. Agnarsson, A. Önsten, M. Månsson and B. Brena, “Charge transfer and band alignment at the InSb(111)B-TiOPc interface”, Manuscript

iii. Work not included in this thesis

- J. Weissenrieder, P. Palmgren, T. Claesson, M. Göthelid, U.O. Karlsson, “Initial oxidation of Fe(100) and Fe(110)”, Manuscript


• A. Önsten, D. Stoltz, P. Palmgren, F. Hennies, T. Claesson, M. Göthelid, and U.O. Karlsson, “Surface chemistry of water and sulfur dioxide on Zn(0001) and ZnO(0001)”, Manuscript
iv. Contribution of the respondent

Experimental physics is a team effort and good experimental results and papers is the outcome from many persons labor. I was responsible for performing the experiments, the data analysis and writing a first version in Papers I-IV, VIII, IX and XI as well as the submission process in Papers I, II and XI. In Paper V, I performed the experiments, wrote a first version of the paper and performed parts of the data analysis. I was responsible for the experimental work in Paper X, performed parts of the experimental work in Papers VI and VII and participated in discussing the obtained results.
v. Acknowledgement

I am grateful to my supervisor Doc. Mats Göthelid; I have gained a lot of new knowledge under your supervision and it has truly been a great time working with you! I am also grateful to Prof. Ulf Karlsson who is leading a great department to which it is a pleasure to belong.

Our collaborators in Uppsala are kindly acknowledged for many interesting discussions and long, but worthwhile, hours at the beam line: Katharina Nilson, John Åhlund, Emmanuelle Göthelid, Joachim Schiessling and Doc. Carla Puglia, as well as our French collaborators in Marseille: Prof. Thierry Angot, Prof. Guy Le Lay, Eric Salomon, Nicolas Papageorgiou and Prof. Jean-Marc Layet. I would also like to thank the staff at Maxlab, especially Franz Hennies, Lisbeth Kjeldgaard and Thorsten Schmidt for their help and support.

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Finally I would like to thank my family for all support.
### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>Conduction Band</td>
<td></td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction Band Minimum</td>
<td></td>
</tr>
<tr>
<td>CL</td>
<td>Core Level</td>
<td></td>
</tr>
<tr>
<td>DOS</td>
<td>Density Of States</td>
<td></td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
<td></td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
<td></td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
<td></td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
<td></td>
</tr>
<tr>
<td>MIGS</td>
<td>Metal Induced Gap States</td>
<td></td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
<td></td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
<td></td>
</tr>
<tr>
<td>OMBD</td>
<td>Organic Molecular Beam Deposition</td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>Photoelectron Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Pc</td>
<td>Phthalocyanine</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
<td></td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
<td></td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
<td></td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
<td></td>
</tr>
<tr>
<td>VIGS</td>
<td>Virtual Induced Gap States</td>
<td></td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
<td></td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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1. Introduction

The focus of this thesis is the study of interfaces using surface science techniques, in particular interfaces between organic molecules and semiconductors or metals. The interest in these systems comes from the important role they play in as diverse applications as organic electronics and solar cells. The organic molecule phthalocyanine finds potential use in both cases due to their chemical stability and appropriate electronic properties, and here it is adsorbed on surfaces with different electronic structure: wide and narrow band gap semiconductors and a metal. The first layer of the adsorbed molecules is of great importance as its electronic properties largely determine charge transport in and across the interface. The structural properties of a film could also be influenced by the first layer as the continuing growth of higher layers may inherit the morphology of the first layer. Both electronic and structural properties are to a large extent governing device function.

In the present work, the first layer of phthalocyanines is investigated on an atomic level. The substrates onto which it is deposited largely influence the electronic properties of the molecule. On InSb the molecule – substrate interaction is weak and the molecular properties are relatively unaffected by adsorption. Several different morphologies can be obtained: an evenly distributed and homogenous first layer or molecular aggregates with high aspect ratio, depending on the central moiety of the phthalocyanine, but the molecular film remain semiconducting. On the closely related InAs substrate however, the phthalocyanine also form an evenly distributed molecular film but upon thermal treatment, the film becomes metallic. Substrates relevant in a dye-sensitized solar cell point of view have also been investigated. In this application the first layer molecules are responsible for injecting charge into the substrate and their electronic properties are hence important. To date, few studies of the phthalocyanine – oxide interface exist and the surface chemistry is not well known. The ZnO substrate allows for ordered growth of the phthalocyanine but the film rearranges upon thermal treatment leading to stronger adsorbate – substrate interaction. TiO₂ is a reactive substrate and the phthalocyanines are oxidized in the first layer, which could have detrimental consequences for the cell performance. An inter-mediate case is the silver substrate where the phthalocyanine forms ordered films with several symmetries.
depending on initial coverage and thermal treatment but the interaction with the substrate is strong enough to result in electronic interface states.

This thesis is organized in the following way: chapter 1 gives an introduction covering basic concepts about electronic and geometric properties of interfaces together with a brief description of applications in which these interfaces are found. The experimental techniques used in this work are briefly described in chapter 2. A discussion of the obtained results is given in chapter 3. A summary for each appended paper is given in chapter 4 and a future outlook presents potential next steps for continuing this work in chapter 5. In chapter 6 finally are the references found.

1.1 Surfaces and ordered interfaces

When crystals are terminated to create a surface, the periodicity normal to the surface is lost and inter-atomic bonds are broken. The surface can (in a diatomic crystal) be terminated with a stoichiometric number of both kinds of atoms or only one species of atoms. The broken bonds form dangling bonds, which represent an electric potential on the surface. This leads to polar surfaces if there is a net electrostatic dipole or nonpolar surfaces if the atomic plane is charge neutral\(^1\). Electron orbitals constitute the dangling bonds, which can be either empty or filled. In order to minimize the surface energy, the surface will reconstruct or relax. A relaxation means that the outermost atomic layers are compressed or expanded in the direction of the surface normal. A reconstruction means that the surface atoms rearrange to form a new ordered structure, which may have a different periodicity than the bulk.

A convenient way of describing the reconstructions is to use Wood’s notation\(^2\). For element X and lattice plane \(\{hkl\}\), the notation is \(X\{hkl\}(p\times q)\) or \(X\{hkl\}c(p\times q)\), where c stands for centered, i.e. an extra net point in the center of the surface mesh. The c can be exchanged with a p, which stands for primitive. It means that the surface cell is a primitive cell. An R after \((p\times q)\) means that the surface mesh is rotated relative to the substrate. The \(p\) and \(q\), in the notation above, are defined in equations 1.1 and 1.2.
In the equations above, \( \mathbf{a}_i \) is the translation vector of the bulk unit cell in the surface plane and \( \mathbf{b}_i \) is the translation vector of the surface superlattice. This is valid if \( \mathbf{b}_1 \) is parallel with \( \mathbf{a}_1 \) and \( \mathbf{b}_2 \) with \( \mathbf{a}_2 \). Wood’s notation is best used when there is a simple relationship between overlayer periodicity and the substrate periodicity.

Another way to describe the periodicity at the surface for more complex cases is to use the overlayer matrix, \( \mathbf{M} \). It relates the adsorbate or overlayer periodicity defined by the translation vectors \( \mathbf{b}_i \) to that of the substrate lattice vectors \( \mathbf{a}_i \) via the integer \( m_{ij} \) according to equation 1.3:

\[
\begin{pmatrix}
\mathbf{b}_1 \\
\mathbf{b}_2
\end{pmatrix} =
\begin{pmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{pmatrix}
\begin{pmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2
\end{pmatrix} =
\mathbf{M}
\begin{pmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2
\end{pmatrix}
\tag{1.3}
\]

The superlattice is said to be a commensurate lattice if the matrix determinant is an integer; a coincidence lattice if it is a rational number or an incommensurate lattice if it is an irrational number. The incommensurate lattice is commonly found where the substrate is weakly interacting with the adsorbate and the forces between the molecules in the overlayer are dominating.

### 1.2 Adsorption and Interface morphology

When atoms or molecules are deposited onto a surface and adhere to form an adsorbate, two typical cases of substrate–adsorbate interaction are identified: physisorption and chemisorption. Physisorption is the weaker form of interaction and van der Waals forces are responsible for coupling the adsorbate to the substrate. Chemisorption is governed by stronger forces between them and a chemical bond is formed. Adhesion energies are up to a few hundred meV for physisorption and the energies involved in chemisorption are on the order of eV. The division between the two is floating and intermediate cases occur.

The growth of a film can in a simple picture proceed in three different ways. In the first case, the atoms build up complete layers on
the substrate and the next layer does not begin to grow until the former is completed. This mode is known as Frank – van der Merve growth or layer by layer growth. The second case is the formation of islands, consisting of the deposited adsorbate, on the substrate. This is known as Volmer – Weber growth or island growth. The third case is a combination of the two previously mentioned modes. The first monolayer (ML) or several layers are formed and after it’s (their) completion, islands start to grow. This growth mode is called Stranski – Krastanov growth or layer plus island growth. An explanatory figure is presented below in Figure 1. One of the determining factors to which growth mode is prevailing is the affinity between the adsorbed species and substrate; if the interaction between the atoms/molecules in the adsorbate is stronger, islands will form and if the interaction is stronger between adsorbate and substrate, layers will form. Layer plus island growth occurs when the influence from the substrate is negligible in the second layer and adsorbate – adsorbate interaction becomes dominant.

Figure 1: a shows Frank – van der Merve growth, b shows Stranski – Krastanov growth and c shows Volmer – Weber growth mode. Θ is the coverage in monolayer. After Ref. [2].

1.3 Energy level alignment at the interface

In an isolated atom the electrons occupy discrete energy levels but when a huge number of atoms are put together to form a solid crystal,
energy bands of allowed electron states emerge. The band can be populated by electrons, known as a Valence Band (VB) or void of electrons and known as a Conduction Band (CB). Three cases are recognized: a) in a metal the VB and CB overlap or the band is half filled and electrons can easily change their energy leading to good electric conductivity, b) in a semiconductor a small gap (~1 eV) exists between the VB and CB and electron transfer over the energy gap ($E_g$) is scarce giving poor conductivity, c) the distance between VB and CB is large (several eV) and the material does not conduct electricity, it is an insulator. The highest occupied energy level in a metal is known as the Fermi level ($E_F$). In the last two cases $E_F$ is found in the energy gap.

The Schottky model offers a simplistic view of how the electronic bands of two solids are aligned when they are put into contact with each other. Maybe the simplest interface is that of an ideal (no intermixing) metal-metal contact, depicted in Figure 2a, where the lower row shows the materials in contact with each other and the upper row is before contact. In this case the Fermi levels of the two materials will align, i.e. charge will flow from the metal with a low work function ($e\varphi_1$) to the one with higher work function ($e\varphi_2$) until equilibrium is attained. The difference in work function, referenced to the vacuum level, results in the formation of a contact potential ($\Delta V$). This creates a space charge layer in each metal and hence a dipole layer at the interface which is screened by the conduction electrons. The size of this layer is given by the Thomas-Fermi screening length, estimated by Equation 1.4 below.

$$r_{TF} \approx 0.5\left(\frac{n}{a_0^3}\right)^{1/6}$$

(1.4)

The Thomas-Fermi screening length is in the order of Å ($10^{-10}$ m) assuming an electron density $n$ of $10^{23}$ cm$^{-3}$ and with $a_0$ as the Bohr radius. This means that the interface region is only a few Å wide.

Things get a bit more complicated when one of the metals is exchanged for a semiconductor as in Figure 2b and c. The chemical potential will be equal in both metal and semiconductor after contact is established but the space charge layers are different. The metal has conduction electrons that efficiently screen the charged region but the semiconductor does not; the free carrier concentration is much lower
and hence the space charge layer is larger, extending up to several hundred \( \text{Å} \) inside the crystal.

Two cases of metal-semiconductor interfaces are depicted in Figure 2. In Figure 2b the metal work function compared to the vacuum level is significantly larger than the electron affinity (\( \chi_{sc} \)) of the semiconductor; upon contact the alignment of the Fermi levels causes the bands to bend in such a way that a potential barrier is formed. This barrier is known as the Schottky barrier (\( e\phi_{SB} \) in Figure 2b) and the space charge layer is a depletion region. Electrons crossing the interface need to overcome this potential (\( \varphi_{SB} \)), leading to nonlinear I-V characteristics. When the metal work function is smaller than the electron affinity of the semiconductor, the situation depicted in Figure 2c arises. In this case the semiconductor bands bend and cross the Fermi level, thereby populating the conduction band states closest to the interface and forming an accumulation layer. This leads to a smooth electronic transit from the metal to the semiconductor resulting in a linear I-V behavior following Ohm’s law, i.e. an ohmic contact forms. In a more refined picture, metal deposition onto a semiconductor leads to the formation of
interface states (known as Metal Induced Gap States (MIGS)) which pins the Fermi level at the interface. Another perspective is that of Virtual Induced Gap States (VIGS) where Bloch states are pictured to spill out from the bulk into the forbidden gap and decay exponentially outside the metal due to the lost periodicity at the surface. The VIGS are derived from semiconductor bulk states and thus states both from the conduction and the valence band contribute. The point of overlap is known as the branching point energy (E_{BP}) and here the electron states have equal valence and conduction band character. The density of states (DOS) gives weight to the participating donor/acceptor states of the VIGS and thus determines the position of E_{BP} in the gap, so that charge neutrality is set up in the acceptor and donor derived VIGS. Upon contact between metal and semiconductor, the E_{BP} will align with E_{F}.

An even more complicated case is the ideal semiconductor-semiconductor interface in Figure 3a. The Fermi levels strive to align upon contact as they must at thermal equilibrium and the band bending situation becomes complex.

![Diagram of semiconductor-semiconductor interface and Virtual Induced Gap States (VIGS)](image)

*Figure 3: a) a semiconductor-semiconductor interface before and after contact and b) VIGS for the semiconductor-semiconductor interface.*
Within the refined VIGS model the branching point energies of the two semiconductors will become equal at the interface. An energy gap exists as they are derived from bulk semiconductor states. In Figure 3b is a schematic picture of the VIGS for the semiconductor-semiconductor case, $E_{\text{BP}}$ is at the position of DOS-weighted amount of acceptor states (solid line) and donor states (dotted line) for each semiconductor and they align upon contact. The VIGS are shown for semiconductor 2 but omitted for clarity in the semiconductor 1 schematic.

In the figures only n-type semiconductors are shown but a similar situation occurs for p-type semiconductors but here the position of the Fermi level in the semiconductor is close to the valence band resulting in different band bending. This is still a simple model and neglects to account for several important factors such as intermixing of the elements, geometrical aspects (e.g. lattice mismatch) or the creation of chemical bonds between the atoms in the two materials.

The Schottky model works fine for systems involving metals and inorganic semiconductors in which the Fermi level is well defined. It is however not sufficient to describe the energy level situation when large organic molecules, such as phthalocyanines, are deposited on semiconductor surfaces. A single molecule is not big enough to have developed bands and the Fermi level is thus not defined. Instead they are somewhere in between small molecules with hybridized but discrete energy levels and solids with wide bands. When this type of molecules forms solids, crystals with a narrow bandwidth develop.

Several explanations have been given to account for the energy level alignment in these systems. Maybe the simplest one is that the vacuum levels of the two materials align at the interface, also know as the Schottky-Mott limit, but it has been disproved and interface dipoles can form. At reactive surfaces charge transfer between adsorbate and substrate, rehybridization of molecular orbitals as well as chemical reactions may occur which often leads to Fermi level pinning and the formation of interface dipoles. Other models (see e.g. Ref [4] and references therein) foremost intended to account for the energy level alignment at weakly interacting organic-metal interfaces have been put forth. In analogy with the VIGS and branching point energy defined for metal/inorganic interfaces a Charge Neutrality Level (CNL) is defined in the Induced Density of Interface States (IDIS) model. These
interface states are quasi-continuous in similarity with the DOS in the solid state. Upon contact between the organic adsorbate and the substrate, the CNL will align with $E_F$ at the interface. An alternative explanation is offered by the Integer Charge Transfer (ICT) model, where discrete energy levels instead of a continuous DOS are formed at the interface. The ICT model predicts the existence of two regions: Fermi level pinning or vacuum level alignment depending on the relationship between substrate work function and, in the case of small organic molecules the energy levels HOMO and LUMO (Highest Occupied Molecular Orbital, Lowest Unoccupied Molecular Orbital). If $E_F$ is located in the molecular energy gap, vacuum level alignment results whereas it is pinned if it coincides with or is above/below the LUMO/HOMO. The significant parameter is the substrate work function, but it may be unreliable for prediction. The work function change with different faces of the same material, e.g. the (111) face may not have the same work function as a (110) face or a polycrystalline sample, different reconstructions on the same surface plane or with step density. It is also very sensitive to contamination of foreign species on the surface. Neither of these proposed models takes chemisorption, physisorption, adsorbed molecular dipoles at the surface or orbital rehybridization into account.

1.4 Solar cells

Several approaches have been tried in order to collect the energy from the sun. Among these are photovoltaic cells based on polymers, elemental or compound semiconductors such as silicon or III-V materials or other advanced alloys such as e.g. CuInGaSe$_2$ (CIGS). In these cells photons excite electrons over the semiconductor bandgap into the conduction band and establish a photocurrent. Another way of converting sunlight to useful electricity is to use organic dyes, which are efficient photon absorbers, and combine them with transparent semiconductors. This concept is known as dye-sensitized solar cells and has several advantages such as low manufacturing costs and flexibility but they suffer from low energy conversion efficiencies. The dye-sensitized solar cell is a quite recent concept which shows promising capability to convert sunlight into electrical energy, the
maximum efficiency reached with this type of cell is about 10%\textsuperscript{16}, having the possibility of competing with Si cells which so far show 25% efficiencies for crystalline cells\textsuperscript{17}.

The basic working principle of the dye-sensitized solar cell, schematically depicted in Figure 4, is the excitation of an electron in the dye molecule by a photon in the impinging sunlight. This electron transits the molecule’s HOMO-LUMO gap, is injected into and subsequently conducted away in the substrate conduction band. Regeneration of the dye is done by an electrolyte, usually containing an iodine-based redox couple, thus closing the circuit.

![Figure 4: The dye-sensitized solar cell.](image)

Transition metal oxides play an important role as substrates in the dye-sensitized solar cell application as they frequently are optically transparent semiconductors with a relatively large bandgap. The most commonly used substrate material is nanocrystalline TiO\textsubscript{2} that show low optical absorption in the visible region but other oxides can also be used such as e.g. ZnO\textsuperscript{18}, preferably ones with a large band gap so that the incoming photons are not absorbed by the substrate. Some substrates are not suitable as their bandgap is too small, e.g. 1.1 eV for Si or 0.18 eV for InSb, and they are hence opaque in the visible region. The dye molecules are usually organometallic complexes which are efficient absorbers of light. A variety of compounds have been tried in the dye-sensitized solar cell, among other porphyrin\textsuperscript{19} or phthalocyanine based organometallic complexes\textsuperscript{20-23}, for which conversion efficiencies
of about 4% for monochromatic illumination has been reported\textsuperscript{21}, but the most efficient so far is Ru-based complex with bipyridine-based chelating ligands\textsuperscript{16}. The phthalocyanines are in this context suitable and show potential for use in a solar cell as they are thermally and chemically stable and their band gap is around 2 eV, a good match for the sunlight spectrum.

Of utmost importance is how the energy levels align in the cell. It is imperative that the LUMO of the dye molecule is above the Conduction Band Minimum (CBM) of the oxide electrode, otherwise electron injection is impossible. The electron injection into the substrate is competing with recombination within the molecule or CB-HOMO charge transfer. Spatial separation of the HOMO of the dye with the semiconductor substrate is believed to slow down the recombination\textsuperscript{24}. A bonding configuration where the phthalocyanine molecules are upright on the surface ought to favor electronic transfer into the CB while a configuration with flat lying molecules may have the opposite effect, with the HOMO spatially close to the substrate. The efficiency of the cell is highest when the dye has ML coverage on the electrode. Agglomeration into thicker layers gives rise to unwanted side effects such as intra-molecular charge transfer and recombination or shielding\textsuperscript{25,26}. One way to achieve this separation is to add ligands to the center or periphery of the molecules. These ligands function as spacers both to the substrate surface and adjacent molecules, preventing close contact with the surface as well as agglomeration.

Injection of the electrons from the excited state into the TiO\textsubscript{2} CB are for phthalocyanines a rapid process (order of 100 fs) while the recombination takes place over longer times (order of 100 ps to \textgreater;1 ns). This is to be compared with the more efficient dyes such as the Ru complexes, (e.g. Ru(dcbpy)\textsubscript{2}(NCS)\textsubscript{2}, dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) having similar injection rates but even slower recombination\textsuperscript{27}. The time window for injecting the excited electron is short; therefore coupling of the molecule to the semiconductor substrate is important and the bonding geometry and electronic properties of the interface plays an important role in cell performance.

In this thesis, the dye-semiconductor interface is investigated for metal-free and iron phthalocyanine adsorbed on single crystal TiO\textsubscript{2}(110) as well as titanyl phthalocyanine adsorbed on a ZnO(0001) single crystal. Despite their frequent use in various applications, it is not
well understood how the phthalocyanines bond to oxide surfaces, how adsorption affects the molecules electronic properties or if they form any ordered superstructures. The titanium dioxide is reactive and the phthalocyanine is strongly coupled to the substrate. By modifying the surface with a small organic molecule, 4-4′-bipyridine, the surface is passivated and the effect of adsorption on the molecules is less severe.

1.5 Organic molecular electronics

Down scaling in microelectronics have continued to produce smaller and smaller devices and semiconductor structures, but in order to reach the smallest possible structures, i.e. of atomic or molecular sizes, something new is needed and here the “bottom up” approach comes into play. By means of self-organization it is possible to assemble nanometer sized or 1-D structures on a substrate. One approach to achieve self-assembled structures is to deposit the organic film in vacuum by means of Organic Molecular Beam Deposition (OMBD) in which a beam of highly purified organic material is impinging on the surface and the molecules organize themselves upon landing or after thermal treatment. This method has the advantage of incorporating very few defects and contaminants in the molecular film as the deposition can be controlled to a high degree. The phthalocyanines can be sublimed from a crucible without breaking up into fragments. They also have interesting anisotropic electronic properties due to the delocalized π-electron system. More complex structures can be formed as several different molecules can be deposited simultaneously giving multiple possibilities to tune the properties of the interface²⁸.

The substrates are however of crucial importance as they need to supply a suitable template to achieve ordered and self-assembled molecular films. The low index surfaces of the noble metals are frequently used as well as HOPG and they provide the possibility for the molecules to order either in a tightly packed ML or in an arrangement set by the substrate surface²⁹-³³. The III-V semiconductors have a high electron mobility and are in a mature state gained from years of microelectronics related research; the (100) surface is a suitable substrate for growth of ordered molecular layers as it consists of atomic rows spaced about 2 nm apart. Phthalocyanines self-assemble
on many of these surfaces, making it possible to obtain highly ordered and well defined interfaces. On the surfaces of interest to this thesis, InSb(100) and InAs(100), e.g. PbPc and SnPc have been shown to form ordered structures consisting of 1-D chains after prolonged thermal treatment. The molecules investigated here, H2Pc, ZnPc, FePc and TiOPc follow the same trend. We show that this ordering appear in the as-deposited molecules. In addition, FePc adsorb pairwise along the [110] direction and patches of molecules correlated in the perpendicular direction forms, whereas TiOPc forms long (up to several hundred nm) molecular stripes in the [110] direction after thermal treatment. In the InSb(1 1 1)-TiOPc system we find charge transfer from the Sb related dangling bonds to the phthalocyanine and the interaction is therefore stronger. Some substrates are unsuitable as templates for self-organizing phthalocyanine molecules; they are too reactive and bind the molecule too tight with their dangling bonds. Two examples that have been tried with limited success are Si(111) and GaAs(100)2×1 surface) and GaAs. On these substrates it would of course be interesting to achieve ordered molecular growth as they are commonly used substrates in the semiconductor industry. One approach to resolve this issue is to terminate the dangling bonds with H in the case of Si and S or Se in the case of GaAs, leading to weakly interacting surfaces.

Examples of electronic components with organic materials (not necessarily by self-assembly) are the Field Effect Transistor, gas-sensor, rectifier, and Organic Light Emitting Diode (OLED). The scale of these devices is not yet in the bottom-up “regime”, and many obstacles are still to be overcome in order to enter. To illustrate the importance of interfaces, the OLED is chosen as an example. An ordinary LED consists of a p-n junction and its basic working principle is to inject minority carriers, i.e. injection of holes into the n-type semiconductor and electrons into the p-type semiconductor. The minority carriers recombine with the holes/electrons in the respective layer. If the semiconductor is a direct band gap material a photon will emerge from this process whereas in an indirect semiconductor the generation of heat will severely compete with the production of photons. The OLED is built up in a slightly different way; it is usually a hetero-structure (with many interfaces) with multiple organic layers on a conducting glass substrate serving as window but the operation
principle is similar: injection of minority carriers for radiant recombination. Phthalocyanines are commonly found as hole conductors closest to the substrate since they are p-type semiconductors with a relatively large band gap giving less absorption of the generated photons. The emitting material is also an organic, e.g. Alq3 (or aluminum tris(8-hydroxyquinoline)) and it also serves as the electron transport layer. The electrons injected into the Alq3 layer recombines here with holes conducted by the phthalocyanine layer and photons emerge.

The coupling between molecules and substrate is important as charge transfer should not be impeded over the interface nor should it be too easy as in a short circuited interface layer. Therefore, defects such as pinholes need to be avoided when creating multilayered structures. This can be done if epitaxial or self-assembled layers are utilized as they can supply an abrupt and well-ordered molecule-semiconductor interface. How the molecules are ordered at the interface is also an important factor as organic molecules have anisotropic conductance. The electronic properties of the interface largely dictate the function of the device and how the energy levels align at the interface is, as in the solar cell application previously described, also important in molecular electronics as energy barrier formation may have negative influence on device performance.
2. Experimental techniques

Atomic scale studies require a well controlled and clean environment to avoid contamination of the sample which would interfere with the measurements. Therefore the experiments are performed in vacuum chambers with a base pressure of about $1 \cdot 10^{-10}$ Torr, 12-13 orders of magnitude lower than atmospheric pressure. Under these conditions, the sample can be used for several hours before a new film needs to be prepared. To get a detailed picture of the geometric and electronic properties of the interface, several experimental techniques are utilized and also necessary; each method provides different information about the system under study and contributes only a part to the puzzle. The following section briefly describes the techniques with which the experiments in this thesis were performed.

2.1 Probing Real Space – Scanning Tunneling Microscopy

With Scanning Tunneling Microscopy (STM) it is possible to create images of solid surfaces with atomic resolution. The microscope was developed in the early 1980’s by Binnig and Rohrer and rendered them the Nobel Prize in Physics in 1986. The STM image is depicting the electron orbitals protruding from the surface and in the case of e.g. III-V semiconductors the orbitals can also be localized at the atoms as dangling bonds. The image obtained in a STM experiment is thus related to the positions in real space of the electronic orbitals. For metals the corrugation of the surface is smaller, due to the delocalized conduction electrons.

Tunneling of electrons through a vacuum barrier is a quantum mechanical phenomenon and the principle used in STM. The wave functions of the electrons in the sample and in the tip have a small extension out into the vacuum and a tunneling current is possible when they overlap. The wave functions decrease exponentially with distance from tip and from the sample, hence the exponential behavior of the tunneling current, as is seen in equation 2.1.
In equation 2.1 (based on the Fowler-Nordheim relation), $U$ is the bias between sample and tip, $K$ is a constant equal to $1.025 \text{Å}^{-1}\text{eV}^{-1/2}$, $d$ is the distance from sample to tip and $\bar{\phi}$ is the average work function of the tip and the sample$^2$. The exponential behavior also implies that the distance between tip and sample cannot be too large, a separation of $\sim 5 - 10 \text{Å}$ is necessary to achieve a tunneling current.

Since the tunneling current is highly sensitive to the separation of tip and sample, the distance must be controlled with high accuracy. This is accomplished with piezoelectric elements, both for the distance to the surface and the in-plane movement. The piezoelectric elements stretch or contract when a positive or negative bias is applied to it. The change in length is on the order of Å when the bias is on the order of tenths of Volts$^2$.

The basic principles of STM is displayed in Figure 5a, where $I_t$ is the tunneling current and $V_{\text{bias}}$ is the voltage applied between sample and tip. $V_{x,y,z}$ are the voltages applied to the piezoelectric elements, controlling the motion of the tip, and $s$ is the separation between tip and sample. In the work done for this thesis, a VT-STM (variable temperature-STM) manufactured by Omicron in Germany was used. In this model, a piezoelectric tube scanner is moving the tip over the sample surface instead of the tripod depicted in Figure 5. Depending on the sign of the bias, it is possible to tunnel electrons into the sample or out of it. In the VT-STM, positive bias is defined so that the electrons tunnel to the sample (probing empty states) and the opposite occurs at negative bias (probing occupied states).

In Figure 5b, the potentials for the tip – vacuum – sample surface are displayed. The tip, in the figure ‘metal’, is made from W wire and electrochemically etched in a KOH or NaOH aqueous solution, biased with roughly 10 V. The sample, in the figure denoted ‘semiconductor’, does not necessarily have to be a semiconductor; the only requirement is that it conducts electricity so a metal will also work. In the figure, $\phi_m$ represent the work function of the tip and $\chi_{\text{sc}}$ is the sample electron affinity. $E_F$ is the Fermi level and $V_{\text{bias}}$ is the tunnel voltage.
On a scanning tunneling microscope, a feedback loop correlates the tunneling current with the voltage over the piezoelectric element normal to the surface, $V_z$. Usually the STM measurements are in constant current mode, i.e. the tunneling current is kept constant, and at a fixed bias. The feedback loop causes $V_z$ to change in order to keep $I_t$ constant. This implies that the tip moves according to the surface topography. The STM image is a recording of the voltages over the
piezoelectric elements; V_x and V_y give the coordinates in the surface plane while V_z gives the topography.

2.2 Probing Reciprocal Space – Low Energy Electron Diffraction

The purpose of a Low Energy Electron Diffraction (LEED) experiment is to determine whether the surface of the crystal is ordered or not. It is a diffraction technique, which utilizes the elastic scattering of electrons from the surface. According to de Broglie, the electron has an associated wavelength, given by Equation 2.2:

\[ \lambda = \frac{h}{\sqrt{2mE}} \]  

(2.2)

This expression is valid for free electrons. In the equation, h is Planck’s constant, m the electron mass and E their energy. For low energy electrons e.g. E = 50 eV, the de Broglie wavelength is 1.7 Å. This makes them useful for investigating atomic structures, which are on the Å scale. When low energy electrons irradiate single crystal surfaces, they are diffracted by the periodic atomic structure. The electrons interfere constructively in certain directions, both for the bulk periodicity and the periodicity of the surface superlattice. The diffracted electrons are seen as spots on a fluorescent screen. LEED is a surface sensitive method due to the small escape depth of low energy electrons.

The diffraction condition for the LEED situation is the same as for x-ray diffraction:

\[ \mathbf{k} = \mathbf{k}' + \mathbf{G} \]  

(2.3)

Here k is the wave vector of the incident beam, k’ is the wave vector of the diffracted beam and G is a reciprocal lattice vector.

In brief, the experiment is done by accelerating electrons from an electron gun in the center of the diffractometer; the setup is shown in the schematic in Figure 6. Electrons emitted from a heated filament are accelerated by a variable voltage and impinge upon the sample, where they are diffracted and traverse the vacuum to a series of grids. This variable voltage determines the kinetic energy of the emitted electrons,
ranging from about 10 to several hundred eV. The first grid is grounded in order to obtain a field-free region. The second and third has a variable voltage, the suppress voltage, so that the background of inelastically scattered electrons can be filtered out. Between the fourth grid and the fluorescent screen is a high voltage, which accelerates the electrons so that they gain enough energy to light up the screen and a diffraction pattern can be seen.

Figure 6: Experimental setup in LEED.

2.2.1 The Ewald construction

One way to determine which directions that fulfill the diffraction conditions is known as the Ewald construction\textsuperscript{62}. It is shown in Figure 7 below, where the dots correspond to reciprocal lattice points.

In the 2-dimensional case, as for surfaces, a circle is drawn with a radius of $|\mathbf{k}| = 2\pi/\lambda$ and the point of the vector at an arbitrary reciprocal lattice site. If the circle intersects two lattice points, a contribution to the diffracted beam is given.
The angle of diffraction ($\theta$) is given by the difference in directions between the incoming and diffracted beam, shown as the angle $2\theta$ in Figure 7. The dots on the fluorescent screen image the reciprocal space. Not only determination of the surface symmetry, but also the lattice parameter of the crystal is possible to calculate from the dots on the fluorescent screen.

2.3 Photoelectron Spectroscopy

In Photoelectron Spectroscopy (PES), the photoelectric effect described by Einstein in 1905 is used. The basic principle is to irradiate the sample with photons of well-defined energy, $\hbar\omega$, which will be absorbed by the electrons in the sample. This excitation causes the electrons to gain enough energy to leave the crystal. The transferred photon energy has to exceed the electrons binding energy, $E_b$, and the work function, $\phi$. Otherwise the electrons will not be emitted from the crystal. The rest of the photon energy is converted into kinetic energy of the photoelectrons, according to equation 2.4:

$$E_{\text{kin}} = \hbar\omega - E_b - \phi$$  \hspace{1cm} (2.4)
Several acronyms are used in the field of photoemission; traditionally XPS (X-ray Photoelectron Spectroscopy) or equivalently ESCA (Electron Spectroscopy for Chemical Analysis) and UPS (Ultra-violet Photoelectron Spectroscopy) are used stemming from the excitation source used but with the advent of synchrotron radiation the terms are overlapping.

![Figure 8: Some photoemission processes. Open or filled circles represents empty or filled states respectively.](image)

The basic process involved in the two are schematically shown in Figure 8 above, XPS probes the Core Level (CL) and UPS the VB of the atom, of course XPS also probes the VB but the cross-section for photo-ionization is low and the signal is therefore weak. An open circle is an empty state and the filled circle is an occupied state and \( \gamma \) symbolizes the photon. The third part of Figure 8 is mentioned later in the text. All elements have specific binding energies of the core electrons; it is therefore possible to determine the composition of a sample with XPS.

A simple picture of the photoelectron emission process is provided by the three step model; Figure 9 below is a schematic drawing of the process. In step 1, the photoelectron is excited from the initial energy level \( E_i \) to a final state with energy \( E_f \) by a photon with energy \( \hbar \omega \). In step 2 the electron travels to the surface and finally in step 3 the photoelectron traverses the surface and finds its way to the detector.
During the second step the electron can be scattered by phonons or plasmons causing the photoelectron to loose energy. Herein is the benefit to surface science, only those electrons within a few mean free paths from the surface will contribute to the useful signal. This phenomenon causes PES to be very surface sensitive, the mean free path is about 5-20 Å for electrons with kinetic energies in the range of 20-1000 eV, typical for electrons excited by commonly used photon sources such as X-ray tubes or synchrotron light.

It is possible that the photoelectron on its way to the surface interacts with the valence electrons, and excites them to higher energy levels. The photoelectron is only slightly affected by this and looses typically a few eV, this phenomenon is called shake-up and is schematically shown in Figure 8. Normally in semiconductors the VB is about 5-10 eV wide and the energy gap is a few eV, this means that the shake-up related intensity is seen with a few eV higher binding energy than the main peak in the spectra. This loss feature is commonly seen in photoelectron experiments. In the case of phthalocyanines, the shake-up mirror the energy gap (i.e. the HOMO – LUMO distance) of the organic material and if the molecular energy levels are altered e.g. by adsorption, the shake-up may change. How the shake-ups are distributed in the spectrum for this type of molecule has been calculated by Brenna et al.\textsuperscript{63}, and it is found that the distance to the main line correspond well with the energy gap.
How the mean free path varies with kinetic energy is shown in Figure 10. The various symbols represent different elements (the legend is omitted) and the calculated (assuming free electrons) dashed line follows the data points.

![Figure 10: Mean free path of electrons at various kinetic energies](image)

In the photoelectron experiments done in this thesis, the core levels of the atoms are probed. The core levels are electron states that are localized to each atom and remain essentially atomic like. A change in the atoms geometrical or chemical surroundings might also affect the CL. This is the origin of the surface or chemical shift in the measured photoelectron energy. The surface shift is due to the different arrangement of atoms that occur when a surface is created and the chemical shift comes from the difference in electronic structure when the atoms form new chemical bonds, e.g. to adsorbed atoms or molecules.

2.3.1 Analysis of photoelectron spectra

The spectra obtained in a PES measurement are plots of intensity versus binding energy. The analysis of the recorded spectra is not straightforward. In order to resolve surface and chemical shifts, the spectra usually need to be fitted numerically because the shift might be small.
This is done by fitting several Voigt functions (a combination of Gaussian and Lorentzian functions) so that the sum of the introduced functions equals the experimental data. The Voigt functions are symmetric and are commonly used when the substrate is a semiconductor. If the substrate is a metal the DOS close to the Fermi level may be high and the photoelectron is affected by this on its way out and the result is an asymmetric line profile. Therefore a parameter accounting for this asymmetry needs to be introduced and the core levels are best fit with a so called Doniach-Sunjic line shape.

There are several parameters that need to be adjusted. The position on the energy axis of the Voigt function gives the binding energy of the core level; the intensity in the peak is related to how many atoms that contributes. The spin-orbit (S-O) interaction results in an energy split between the $d_{3/2}$ state and the $d_{5/2}$ state in e.g. a d-level. The branching ratio is the intensity ratio of the two peaks in the spin-orbit split Voigt function. The width of the core level peak has two principal contributions. The first has Gaussian shape coming from the change of potential (due to the charged final state), which creates phonons due to the different bonding situation, inhomogeneities in the surface and an instrumental contribution. The second has Lorentzian shape and it comes from the limited lifetime of the core hole. The core hole is filled by another electron in Auger decay; if it is a rapid Coster-Kronig process the energy broadening is larger. The asymmetry parameter is introduced to account for the small energy losses photoelectrons suffer by scattering from the electrons close to the Fermi level. It is not applicable in the analysis of semiconductors as they do not have a high density of states close to $E_F$. To account for the background of inelastically scattered electrons in the spectra, a Shirley background (i.e. integrating the background) is chosen.

The curve fitting is done in a computer and as a measure of the goodness of fit between the sum of the fitted curves and the experimental spectrum, besides the visual alikeness, the program calculates $\chi^2$ for the fitting procedure according to equation 2.5:

$$\chi^2 = \frac{\sum_n \left( I_n^M - I_n^E \right)^2}{N}$$

(2.5)
In the equation above, \( n \) corresponds to one data point i.e. a value of the binding energy, \( I^M \) is the measured intensity in the point \( n \), \( I^F \) is the calculated intensity for the sum of the fitted curves in the point \( n \) and \( N \) is the total number of points.

### 2.3.2 Synchrotron radiation

A suitable light source for photoelectron spectroscopy experiments is synchrotron radiation. From the beginning it was a byproduct from storage rings used for accelerator experiments but as it proved to be a powerful tool for scientific analysis, the modern electron storage rings are used solely to produce synchrotron radiation.

![Figure 11: Spectrum for synchrotron radiation and some other light sources](image)

*Figure 11: Spectrum for synchrotron radiation and some other light sources.*
In the ring the electrons travel with near the speed of light. When the electrons are deflected, they will emit light with a wide spectral range and high intensity. The light is linearly polarized with the E-vector in the horizontal plane. The spectrum begins with X-rays and stretches into the ultraviolet region, as is seen in Figure 11 above.

In Sweden there are three storage rings; MAX 1, 2 and 3, all found at MAX-lab in Lund. The electrons travel in bunches in the ring, one bunch is \( \sim 20 \) ps long, and in the MAX 2 case the total current is about 200 mA and the electron energy is 1.5 GeV. The ring is actually a polyhedron with a circumference of about 90 m. In the storage ring, magnetic and electric fields control the path of the electrons. The straight parts of the polyhedron hold devices, such as quadrupoles for focusing the beam, undulators and wigglers, which makes it possible to extract light with enhanced intensity. These devices are basically periodic magnetic arrays, which deflect the electron beam, thus causing the electrons to emit radiation. The corners of the polyhedron hold bending magnets to guide the electrons.

In Figure 12 is a schematic of the layout of the I511 beam line presented. The role of the undulator has briefly been mentioned above and the monochromator is used to get well defined photon energy. With the beam splitter it is possible to switch between two end-stations. Before the synchrotron radiation illuminates the sample it is focused so that the spot size is about a 50 µm wide and due to the grazing incidence it is about 1 mm long on the sample. The synchrotron light is so intense that it is necessary to continuously move the sample in the beam to avoid damage of the organic matter.

![Figure 12: Schematic layout of the I511 beam line at MAX-lab.](image)
2.4 X-ray Absorption Spectroscopy

In the beginning of the last century, de Broglie pioneered work on X-ray Absorption Spectroscopy (XAS); the first absorption spectrum was published in 1913\textsuperscript{68} and W. Kossel explained the structure at the edge\textsuperscript{69}. Synchrotron radiation plays an important part in XAS as it together with the monochromator provides photons with well defined energy over a wide range, a prerequisite to obtain high quality absorption spectra. The high photon flux allows for measuring low concentrations of species present on a surface. The basic principle is to scan the photon energy irradiating the sample and when it matches the binding energy of the core electron the photon is absorbed and a core electron is excited into either an unoccupied bound state or to continuum states above the Ionization Potential (IP). XAS is element specific due to the unique binding energy of the core electron. Furthermore is XAS a local probe, the excitation from the CL to unoccupied bound states occurs in the same atom but the unoccupied states are probed in the presence of a core hole. Only certain transitions are allowed: the dipole selection rule dictates that there must be a change in the orbital quantum number $\Delta l = \pm 1$. In Figure 13 is a schematic of the principle behind XAS presented.

![Diagram of X-ray absorption process]

*Figure 13: Principle of the x-ray absorption process; the selection rule $\Delta l = \pm 1$ must be obeyed.*

XAS can be measured in several modes: partial yield in which the Auger electrons in a specific kinetic energy interval are counted, fluorescent yield where the photons from the radiant relaxation of the
core hole is measured and total yield where the current to the sample is recorded with an electrometer. Partial yield is the most surface sensitive as the Auger electrons have the same short mean free path as photoelectrons. A reference signal is also measured on a gold grid situated in front of the sample to keep track of the varying intensity of the synchrotron light and provide means for normalization of the absorption spectra.

XAS is usually divided into two regimes providing different information: Near Edge X-ray Absorption Fine Structure (NEXAFS) which covers the spectral region before the edge and about 50 eV after the edge and Extended Edge X-ray Absorption Fine Structure (EXAFS) which covers the region from 50 eV to several hundred eV after the edge. NEXAFS gives information about the systems electronic properties in the unoccupied states and how they are affected by e.g. chemisorption. The photoelectron is scattered by its nearest surroundings on its way out from the crystal which is detected as oscillations in the spectrum at higher energies after the edge; this is analyzed in EXAFS to give information about bond lengths and coordination. This thesis concerns the NEXAFS part and the absorption spectra are only recorded about 30 eV above the edge.

Synchrotron light is polarized with the E-vector in the horizontal plane and this provides means of determining the orientation of the adsorbate on a surface.\textsuperscript{69} The main idea is to measure absorption spectra in two geometries with the E vector either parallel or orthogonal to the sample surface. When the E vector coincides with the direction of the $\pi$ and $\sigma$ orbitals in the molecule, the signal strength from that particular orbital is increased which in turn indicates the orientation of the molecule as the sample geometry is known. A schematic is shown in Figure 14 in which the example is for molecules adsorbed standing upright on the surface. The bound unoccupied states at the absorption edge would be strongest in the spectrum when the E vector is parallel with the surface plane and the continuum states above the IP would be strongest in the geometry where E is orthogonal to the surface plane. The two geometries are complementary; what is not in pi is in sigma and vice versa in the respective spectrum. To make an accurate determination of the angle the molecules have with respect to the surface, several geometries needs to be measured.
The phthalocyanines studied in this work are suitable objects as they are planar molecules with a delocalized \( \pi \)-electron system. Absorption of a photon by the 1s core electron in e.g. nitrogen is possible in both geometries as it is spherically symmetric. The unoccupied final states have both p and s symmetry as the orbitals are hybridized but it must have some degree of p-character to fulfill the dipole selection rule. The \( \pi \)-electrons are directed perpendicular to the molecular plane and XAS provides a powerful tool to determine their orientation on a surface.

Figure 14: the signal strength is depending on the orientation of the molecule relative to the E-vector of the synchrotron light. The black “orbitals” symbolizes \( \pi \)-symmetry and white symbolizes \( \sigma \)-symmetry.
3. Results and Discussion

The substrates investigated in this work all have different effects on the adsorbed phthalocyanines; ranging from the weakly interacting InSb via InAs, ZnO, Ag, to the relatively strongly interacting TiO$_2$. Weakly and strongly are in a sense relative; by weakly one would mean that the influence on the adsorbate from the substrate is negligible or very small and by strongly one would mean an interaction between adsorbate and substrate that border to a chemical bond. Thus weak interaction means that the adsorbate retain the molecular properties or they are only slightly affected by adsorption whereas strong would mean that the electronic properties are altered by the substrate interaction. The interaction is however not strong enough to dissociate the phthalocyanines upon adsorption, due to their chemical stability.

Phthalocyanines are generally known to be weakly interacting with substrates such as Au, HOPG and III-V semiconductors$^{42,70,71}$, and the interface layer molecules more or less retain their properties as in the molecular solid. Whether this weak interaction actually is weak is under current debate as adsorption of phthalocyanines can cause a change in the periodicity of the Au(110) surface, lifting the 1×2 missing row reconstruction in favor of a surface with 1×3 periodicity, matching molecular dimensions$^{72,73}$. The imprint of this interaction is small in PES; the shake-up transition in C1s remains the same as in the bulk film and the highest molecular energy levels in the interface layer molecules are very close to the one in higher layers. The (001) surfaces of the III-V semiconductors are suitable templates due to their appropriate dimensions, the c(8×2) reconstruction obtained after sputter and annealing consist of atomic rows spaced about 18 Å apart, and there is no need for the substrate to rearrange in order for the phthalocyanines to be accommodated. However, even though the dimensions of the surface match the molecule size wise, no ordered adsorption occur on e.g. InSb(111)B which consist of hexamer units (each unit is build up by either 3 In and 3 Sb atoms or 2 Sb and 4 In atoms) spaced about 14 Å apart$^{74}$. On other (111) type surfaces such as e.g. InSb(111)A and InAs(111)A, both H$_2$Pc and CuPc form ordered layers resulting in a $(\sqrt{12} \times \sqrt{12})$R$30^\circ$ superstructure for the first ML on both surfaces$^{34,75}$. The dangling bonds are more numerous on a (111) type surface than on
a (100) surface, thus a potentially higher chance for charge transfer is present and the substrate – adsorbate interaction is stronger.

There is a delicate balance between the two dominating interactions at the interface, adsorbate – adsorbate and adsorbate – substrate interaction. When the former is prevailing a homogenous layer is formed and when the substrate – adsorbate interaction dominates, adsorption is governed by the surface reconstruction.

*Figure 15: STM images of the evenly distributed films of H₂Pc, ZnPc and FePc (70 K) and the strands of TiOPc on InSb(001). The even layer of H₂Pc on InAs(001) is also shown. Further details are given in Papers V-VIII.*
Take Au(111) as an example where a homogenous phthalocyanine film is formed at a full ML, but below 1 ML coverage, the molecules follow the herringbone reconstruction$^{29,76}$, all aspects of this interaction and interplay are thus not completely understood. In the present work, we find something similar for the phthalocyanines deposited on the III-V semiconductors. The STM images showing this are presented in Figure 15. The coverage in the images is just above 1 ML for H$_2$Pc on InSb and on InAs, just below 1 ML for FePc and for both ZnPc and TiOPc, the coverage is close to 1 ML. FePc (measured at 70 K but deposited at RT), H$_2$Pc and ZnPc are evenly distributed on the surface to form a homogenous molecular layer either as-deposited or after thermal treatment. TiOPc on the other hand rearranges along $[110]$ and builds up layers on top of molecules adsorbed on the In-rows instead of spreading out. The molecules in the first group are planar molecules whereas TiOPc is not and it also has an electric dipole due to the partly ionic Ti – O bond in the center, and the cancellation of the dipole might be the explanation for this behavior. However, PbPc and SnPc are also non-planar phthalocyanines but with a relatively small electric dipole and they form evenly distributed films after thermal treatment$^{40,43}$. Ordered growth of phthalocyanines is less common on relatively strongly interacting substrates such as e.g. Si$^{77}$.

Very few STM investigations of phthalocyanines deposited on oxides exist. In Figure 16, a collection of the experiments we have performed on two oxide surfaces TiO$_2$(110) and ZnO(0001), are presented. On TiO$_2$, we have deposited H$_2$Pc, ZnPc and FePc as indicated in the figure. In neither case do any ordered superstructures appear, and molecules are barely possible to image. The FePc are imaged at 110 K and are resolved to a slightly higher degree. Ordering may occur if the substrate is a suitable template, such as e.g. the 1×2 reconstruction of TiO$_2$(110)$^{78}$, which consists of small pits for the molecules to occupy. ZnO seems to be an exception as a 2×1 pattern appears upon deposition instead of the 1×1 pattern of the clean surface; the surface consist of triangular terraces, terminated by Zn-atoms in a hexagonal lattice. The ordering in this case is suggested to be due to a tilted adsorption with a TiOPc on every other Zn row. All phthalocyanines measured here on oxide substrates resulted in rather poorly resolved STM images. When the oxide substrate was covered by the small organic molecule bipyridine that passivates the surface,
images of the phthalocyanine improved; clearly the image quality in STM depends on the interaction between adsorbate and substrate.

Figure 16: The phthalocyanine-oxide interfaces. In each case is the coverage less than 1 ML, the substrate is imaged but sub-molecular resolution is difficult to obtain. In part e, the co-adsorbed bipyridine FePc system is shown

Silver, as well as Cu, are members of the noble metals but the interaction with organic molecules is not particularly weak and represents an intermediate case; the molecular electronic structure are disturbed by the adsorption seen as an interface state in PES but still ordered phthalocyanines are generally nicely imaged on both Cu and
Ag substrates. The influence from the substrate does not extend far up into thicker films, upon thermal treatment the second layer is desorbed leaving only one layer left.

A lot of information about the degree of interaction between adsorbate and substrate in the interface as well as the electronic and chemical properties of the organic-inorganic interface can be estimated or predicted by analyzing the C1s core level line shape. It has different shape depending on how tightly the molecules are bound to the surface and how much the electronic structure in the molecule is perturbed. A line shape similar to the bulk line profile is indicating a weakly interacting interface and an altered or perturbed line profile signals the opposite. The shake-up is an intrinsic property of the molecule as it exists also in spectra from molecules in the gas phase, in the case of phthalocyanines it is located about 2 eV from the main line due to the HOMO-LUMO distance in the molecule. A change in the shake-up occurs if the electronic properties of these levels are changed by adsorption on a surface; the influence of the substrate is thus mirrored by a change in the shake-up.

Spectra from various phthalocyanines deposited on the present III-V semiconductors are presented in Figure 17, in which the coverage is chosen in the 1 ML range. The C1s binding energy varies within 0.5 eV between the different phthalocyanines and in all cases the line profile is bulk like with the shake-up present at about 2 eV higher binding energy than the main line, thus both InSb(001) and InSb(111)B are weakly interacting substrates. The line profile is severely broadened in the TiOPc-InSb(001) spectrum, explained by the many adsorption possibilities of the highly mobile and diffusing molecules; after thermal treatment the line width decrease as order at the interface increase.

The situation for InAs(001) is a bit contradictory, on one hand H$_2$Pc has the same adsorption mode at low coverage as on InSb(001), evidenced by the STM images, and a thick annealed film also form a homogenously distributed first layer but InSb(001) remains semiconducting while InAs becomes metallic upon annealing as emission from the Fermi level is seen in the VB spectrum. Thus, despite their many similarities, InSb is a weakly interacting substrate and InAs seems to be more reactive.
Figure 17: C1s photoelectron spectra for sub-ML to ML coverage for different III-V semiconductor related systems. InSb show weak interaction whereas InAs seems more reactive.
In Figure 18, spectra from phthalocyanines deposited on oxide and metal substrates relevant to this thesis are presented. The TiO$_2$(110) is a reactive surface as both H$_2$Pc and FePc have an altered line profile. The shake-up is quenched leading to the conclusion of a relatively strongly interacting surface. The molecules are not dissociated as can be seen in STM images from the respective system, presented in Figure 16.
ZnO on the other hand shows a bulk like C1s line profile and a normal shake-up which can be attributed to the adsorption mode. The molecules are adsorbed tilted and the contact area with the surface is reduced leading to a weaker interaction. Having the dye-sensitized solar cell application in mind, the TiO2 is a reactive substrate. Adsorption of phthalocyanines on this surface leads to oxidation of the molecules, which ought to have a detrimental effect on solar cell performance as these electrons are supposed to be excited across the molecules energy gap. For FePc as well as H2Pc the shake-up is lost for the first molecule layer, strongly indicating the change of the energy levels in the phthalocyanines closest to the substrate, but for thicker films it emerge. The influence of the substrate does not stretch far up into the film, already the second layer is bulk like with a distinguishable shake-up. In the ZnO case, TiOPc retains the molecular properties also at the interface, evidenced by the bulk like line profile. This system shows two HOMO states depending on the orientation of the molecules; one of them has the LUMO located at the Fermi level which ought to be an unfavorable situation as charge transfer to the molecule has occurred leading to a partial filling of the LUMO. The implications for solar cell performance may be indicated in the C1s line shape; if the shake-up is not visible then the substrate-molecule interaction is large leading to affected molecular energy levels which in turn has consequences for the HOMO-LUMO electronic transition in the molecule.

For FePc on Ag(110) the C1s CL exhibits for metallic systems a characteristic asymmetric line shape. However, the spectrum can not be fitted with just a Doniach-Sunjic line shape for two chemical states; one for pyrrole type and one for benzene type carbon atoms. The molecules are affected by adsorption and the shake-up is now found at 0.5 eV above the main line caused by a transition from the interface state to the first unoccupied state. The interfaces in the present study are almost exclusively reacted leading to Fermi level pinning, either of the molecular HOMO or LUMO, and the energy level alignment thus becomes unpredictable. 
4. Summary of Papers

The central topic in this thesis is the initial stages of interface formation between phthalocyanines and different substrates such as wide band gap semiconductors (TiO₂ in Papers I, III, IV and ZnO in Paper II); narrow band gap semiconductors (InAs in Paper V and InSb in Papers V-X) and a metal (Ag in Paper XI). The phthalocyanines have a rather simple core: a metal ion (Zn or Fe), an oxymetal group (TiO) or two hydrogen (H₂) but no peripheral or central ligands are attached to the molecules. The work focuses on the chemical and electronic properties of the interfaces from a low coverage less than 1 ML to a few ML in which case the effect of the interface is no longer substantial and the organic films starts to become bulk like.

4.1 Paper I

Phthalocyanines can be used as dyes in dye-sensitized solar cells but the surface chemistry of this type of molecule is not well known on oxide substrates. In the present work, we investigate the initial stages of metal-free phthalocyanine (H₂Pc) interface formation on rutile TiO₂(110) using STM and synchrotron based PES. For weakly interacting substrates, the C1s line shape is bulk like, i.e. the two main lines (coming from benzene type and pyrrole type carbon atoms) have their respective shake-up at a distance of about 2 eV. The photoelectron spectroscopy experiment reveals a strongly modified line shape at coverage below 1 ML which indicates a strong interaction between the H₂Pc and the substrate. At higher coverage, a shoulder develops on the low energy side; a difference spectrum between the second layer and the first monolayer is created. This spectrum is representative of the C1s core-level from molecules in the second layer and has a bulk-like line shape, confirmed by a numerical fit, giving that the effect of bonding to the surface is only significant in the first layer. Upon thermal treatment the line width is reduced, indicative of increased order at the interface. This also affects the composition of the H₂Pc: changes in the N1s core level line profile points to dehydrogenation of the center of the molecule. STM results from room temperature measurements show that molecules adsorb flat on the surface, centered
on and aligned with the substrate oxygen rows. The adsorption does not lead to ordered superstructures on the surface evidenced in LEED as the 1×1 pattern remains after deposition although the pattern is attenuated due to the organic layer covering the oxide substrate.

4.2 Paper II

Alternative electrode materials in the dye-sensitized solar cell might enhance cell output if the energy level alignment is more favorable. In this application TiO$_2$ is normally used as substrate but ZnO is a possible candidate to increase cell performance as it has a slightly larger band gap. Titanyl phthalocyanine (TiOPc) has a tendency to form a bi-layer on weakly interacting substrates such as HOPG and MoS$_2$. Molecules adsorb with the molecular plane parallel to the substrate and with the oxygen atom facing inward. This affects the electronic properties and is seen in PES as a split in the TiOPc HOMO. We have investigated the initial stages of TiOPc growth on single crystalline ZnO(0001). This organic-semiconductor interface is self-organizing in a 2×1 structure upon deposition at RT. To achieve this, the TiOPc is suggested to adsorb standing or tilted with the edge of the molecule along the substrate atomic rows. Molecules lying down could not be accommodated on the surface with this periodicity; the edge of the molecules are roughly 10 Å and the Zn-row distance on the (0001) surface is 2.8 Å. Photoelectron spectroscopy is used to further analyze the electronic properties of the interface and a relatively large upwards band bending amounting to 0.5 eV is found. A splitting of HOMO occurs after thermal treatment, indicating that there is a change in the adsorption mode, leading to molecules lying down. The LEED pattern is also attenuated with increased coverage and exposure to the electron beam. The chemical properties of the interfaces are indicated by the C1s CL. For all film thicknesses investigated, ranging from less than 1 to several ML, the line shape resembles the bulk case with distinguishable shake-ups, pointing towards a moderately interacting substrate. Upon thermal treatment, the C1s line shape is severely broadened caused by the many adsorption modes. The energy level alignment at the interface is determined and it is found that the LUMO
coincides with the Fermi level or is lying in the CB depending on the adsorption of the molecule.

4.3 Paper III

Of special interest in a dye-sensitized solar cell is the energy level alignment as well as how the molecules are adsorbed on the surface as this influence the output of the cell. Charge injection into the electrode conduction band is predominately from the molecules closest to the substrate, making the interface region important. We have investigated the iron phthalocyanine (FePc) - TiO$_2$(110) interface using scanning tunneling microscopy, synchrotron based photoelectron spectroscopy and x-ray absorption spectroscopy. We find a strong coupling of the first layer FePc to the substrate resulting in an alteration of the electronic structure of the molecules, both in the occupied and unoccupied states. The molecules in the first layer are oxidized, seen as a chemical shift to higher binding energy of both the C1s and N1s core levels and weak emission from the FePc HOMO. The shake-ups in the core levels are quenched in the first layer due to the charge transfer from the molecule. The FePc in the second layer and higher have bulk like electronic properties, the shake-ups becomes visible in the core levels, the HOMO develops at a binding energy of 1.6 eV and the unoccupied states becomes similar to what is found in thicker films. Imaging conditions in the STM is poor due to the strong interaction with the substrate but we find that the growth of FePc thin films proceeds in a layer plus island mode. In both the first layer as well as in the higher layers, the molecules have their plane parallel with the surface although the first layer contains many defects and varying adsorption sites. This reacted interface layer ought to be disadvantageous in the dye-sensitized solar cell application.

4.4 Paper IV

Surface modification of reactive oxide substrates with small organic molecules to obtain a less interacting surface for dye adsorption may be a way to enhance performance in dye-sensitized solar cells. The new
template should offer a route for electron transfer into the oxide and the energy level alignment is crucial as both two molecular materials must have their lowest unoccupied states above the conduction band minimum of the oxide substrate, otherwise the cell will not deliver any energy. In this work, we have investigated the electronic and structural properties of 4,4’-bipyridine (bipy) as modifier, adsorbed on the TiO$_2$(110) surface. This modified surface is then coated with a dye molecule, in the present case iron phthalocyanine (FePc), and the properties of this heterostructure are investigated with synchrotron based electron spectroscopy and STM. We find that a saturated monolayer consisting of standing bipy molecules with one nitrogen atom pointing outwards is formed on the oxide surface; the other nitrogen atom is bonded to the Ti rows of the substrate. The FePc change adsorption mode from flat lying molecules found on the bare substrate to a tilted arrangement; the FePc are adsorbed in rows aligned with the [001] direction on the substrate and the tilt angle is due to the partial overlap between neighboring molecules along the row. The electronic properties of the FePc film resemble those of thin films on weakly interacting substrates or thicker films even in the first FePc layer. Thus with the bipy as modifier the reacted FePc-TiO$_2$ layer can be avoided. The energy level line up at the interface is clarified and we find that the LUMO of bipy as well as FePc both are above the conduction band minimum of the TiO$_2$ substrate. In the solar cell point of view, this co-adsorbed system could be favorable because the reacted first layer FePc is avoided and the energy levels in the heterostructure allow electron transfer from the dye via the bipy into the electrode.

4.5 Paper V

Self-ordering of organic molecules on inorganic semiconductors is an interesting topic due to their importance in e.g. opto-electronic devices. Phthalocyanines are in this context commonly used as hole transport layer. The interface formation for this class of molecules is of significance as the current conducting properties of the thin film in and across the interface layer largely depend on the interface quality. Smooth and well defined layers are preferred and energy barriers due to the mismatch of the energy levels at the interface should be avoided.
The adsorption and surface order of metal-free phthalocyanine (H$_2$Pc) on InAs(001)(4×2)/c(8×2) and InSb(001)c(8×2) surfaces is investigated using LEED, STM and synchrotron based PES. The two systems show structural similarities; at sub-monolayer coverage the preferred adsorption site of H$_2$Pc is on top of the In rows, and above 1 monolayer and after thermal treatment the first molecular layer is ordered in a homogenously distributed and densely packed ‘×3’ structure observed with both LEED and STM. This means that molecules arrange along the In rows in a close-packed fashion, the molecule–molecule distance in the row correspond to 3 substrate lattice parameters but there is no or only weak correlation between adjacent rows. The electronic properties and the surface bonds of the two systems are quite different: the InAs–H$_2$Pc interface is semiconducting after room temperature deposition but becomes metallic upon thermal treatment whereas InSb(001)–H$_2$Pc is semiconducting at all preparations. These differences are reflected in the C 1s line shape between the two systems; on the semiconducting InSb is the line shape, although broadened by adsorption, bulk like with distinguishable shake-ups for all coverages and after thermal treatment. On the metallic InAs is the line shape modified by adsorption at low coverage, becomes bulk like for thicker films (a few ML) and reverts to the modified line shape after thermal treatment. The N1s core level spectra recorded from both systems reveal deprotonation of the molecular center, i.e. the central hydrogen atoms are lost upon thermal treatment.

### 4.6 Paper VI

Self-organization of organic molecules on inorganic substrates and the influence thermal treatment has on the electronic and structural properties of the organic thin film are the topics in this work. Zinc phthalocyanine (ZnPc) adsorbed on the InSb(001)c(8×2) surface has been studied by LEED, STM and XPS (Al K$_\alpha$ radiation). The coverage ranges from sub-monolayer to monolayer and the molecules are found to form ordered structures on the reconstructed rows of the surface with the molecular plane parallel to the surface. A small change in the electronic structure between the sub-ML and higher coverage has been observed for the as-deposited system; the C1s peak is broadened by the
substrate interaction but the line profile becomes bulk like in the thicker films as the influence of the surface is less pronounced. Moreover, in order to study the influence of annealing on the electronic and geometric structure, the samples have been heated to about 640 K. The sub-ML films do not show a significant change as STM measurements show the usual four leaf clover shaped objects associated with the ZnPc. At coverage close to 1 ML, and after thermal treatment the ‘×3’ structure is found also for the ZnPc – InSb interface, thus a well defined and homogenously distributed first ZnPc layer is formed on this surface. The electronic properties in the annealed films differ from those of the as-deposited film, both at low and high coverage; the C1s line shape is altered and becomes much broader and featureless and the shake-ups are no longer separated from the spectral shape. The molecules have neither changed adsorption mode nor decomposed as evidenced by the STM measurements. Whether the molecular thin film is metallic could not be determined as the cross-section of the electrons close to the Fermi level is low.

4.7 Paper VII

The achievable resolution in STM is limited by the high mobility of the molecules on weakly interacting substrates. FePc on InSb(001)c(8×2) is no exception but despite suffering from rather poor imaging quality the interface can be imaged and we find that the molecules are adsorbed in evenly distributed patches or islands one layer thick. To improve imaging conditions the FePc films are prepared at room temperature and subsequently cooled to 70 K. This has a profound effect on the molecular layer; FePc are to a relatively large degree adsorbed in pair or pair wise in chains along [110], but the largest difference compared with the room temperature images is that they are now ordered along the [ ̅1 1 0 ] direction. It is visible from low coverage up to just below 1 ML. The reason for this ordering ought to be the phase transition the substrate goes through at 180 K upon cooling the sample. This leads to domain boundaries at which the molecules are hindered as they diffuse on the surface. As the coverage approaches 1 ML, a full and evenly distributed molecular layer is formed, but no LEED investigation was performed on this interface close to 1 ML coverage to see whether the
'×3' structure is also formed for FePc due to the cryogenic temperatures during the STM measurements. The molecules appearance in STM also changes with temperature; in the cooled system, FePc is almost exclusively imaged with a bright center because the HOMO is located at the molecules center as it is to a large degree derived from Fe3d related orbitals. In the room temperature images FePc are depicted with many more appearances, such as filled or void center which most likely is caused by the interaction with the substrate.

4.8 Paper VIII

The effects of thermal treatment on the interface formed by an organic molecule with an intrinsic electric dipole adsorbed on a weakly interacting inorganic substrate are investigated in this work. Titanyl phthalocyanine (TiOPc) forms a bilayer on HOPG and MoS2 with the apical oxygen facing inwards, annealing of these interfaces causes the molecules to spread out into a single molecular layer with the oxygen pointing out from the surface. Here the interface formation and ordering in the TiOPc – InSb(001)c(8×2) system using STM and synchrotron based PES is studied. Instead of an evenly distributed interface layer which is formed upon thermal treatment in the case of H2Pc and ZnPc on InSb(001), TiOPc behaves differently. Annealing up to 475 K leads to a agglomeration of molecules and further annealing up to 565 K, leads to mesoscopic ordering into strands along the [110] direction. These strands are comprised of molecules adsorbed on the In rows as well as in a second layer and can extend hundreds of nanometers in length. As-deposited molecules are highly mobile on the surface but the last annealing step causes an increase in the adsorbate – substrate interaction leading to reduced mobility. The tendency to form a bilayer, driven by the cancellation of the intrinsic electric dipole might be the reason for this ordering upon thermal treatment. The electronic properties of the interface is measured with PES; the C1s line shape is broadened by the adsorption and substrate interaction at low coverage, thermal treatment results in significant decrease of the C1s line width interpreted as an increase of order at the interface. The energy level alignment at the interface is determined and the TiOPc lowest
unoccupied molecular orbital is found to coincide with the conduction band minimum of the substrate.

4.9 Paper IX

A detailed knowledge of the interface enables growth of epitaxial organic thin films on inorganic semiconductors depends on the geometry of the first monolayer and thus the adsorption mode of the molecule. Organic molecules are known to form ordered layers on III-V semiconductors, and in this paper we determine the adsorption site for some phthalocyanines on the InSb(001)c(8×2) surface using STM. The molecules investigated are H$_2$Pc, FePc, ZnPc and TiOPc. Normally phthalocyanines are imaged in STM as four lobes, each corresponding to one isoindole group (the benzene and pyrrole groups linked together), resembling a four leaf clover. Under some tunneling conditions, molecules are depicted with hexagonal shape. This effect is due to an enhanced local density of states at the substrate In atoms in the vicinity of the adsorbed molecules and caused by the adsorbate-substrate interaction. All phthalocyanines investigated here behave in this way but it is most pronounced for H$_2$Pc and ZnPc; TiOPc only exhibit a few of this kind and FePc, which is normally depicted with a bright center, are almost exclusively depicted with a void center if the hexagonal shape is present. This effect is also seen in STM images found in literature for PbPc. In order to extract information about the adsorption site from this observation, analysis was made by placing line profiles over the hexagonally shaped phthalocyanines. The molecule is centered between the two substrate-related protrusions and if the distance between them correspond to either a even or odd number of substrate lattice parameters, the adsorption site can be determined to be either on top or bridging respectively. The FePc shows highly mobile molecules at room temperature rendering this method useless, therefore measurements are performed at 70 K where molecular mobility is inhibited and the substrate is resolved to a high degree. Thus we find that the adsorption site for phthalocyanine molecules is centered on top of In atoms in the In-rows with a pair of isoindole groups on each side of the atomic row.
4.10 Paper X

Ordered adsorbate structures are highly dependent on the symmetry and also on the surface chemistry of the substrate. There is a close interplay between adsorbate – adsorbate and adsorbate – substrate interaction that determines the structural properties of the interface; if the molecular bond to the surface is too strong, ordered structures might not form. Results from a STM and synchrotron based PES study of TiOPc thin films on InSb(111)B (3×3) are presented in this work. This surface consists of two types of building blocks: hexamers built up from three In and Sb atoms or two Sb and four In atoms respectively, leading to a six-fold symmetry of the surface. At room temperature the first adsorbed layer includes a mobile state and a stable state with molecules in hollow sites in the middle of three surface hexamers, coordinating to antimony rest atoms in the second layer of the substrate. The energy level alignment at the interfaces is determined and the two adsorption modes at low coverage results in two separate HOMO positions; either 1.0 eV or 1.7 eV below the Fermi level. The one closer to the Fermi level corresponds to the mode with singly adsorbed molecules; the LUMO of this mode lies in the conduction band while the LUMO in the other case coincides with the Fermi level. At higher coverage a structure with molecular islands appear with several adsorption modes but this system is not self-assembling in ordered structures. The electronic properties of the molecular layer are bulk like also at low coverage indicating a rather weak interaction with the substrate, but thermal treatment causes the width of the adsorbate line shape to increase. Both substrate and C1s core levels indicate charge transfer from the Sb-lone pairs to LUMO. This effect is enhanced upon thermal treatment as the interface layer fills more sites.

4.11 Paper XI

Organic-metal interfaces, in particular self-assembling systems, are interesting in the field of molecular electronics. The noble metals have been thoroughly investigated in this context and are generally considered to be weakly interacting although this view has recently been questioned. In this study, we have investigated the formation of
the FePc – Ag(110) interface in a coverage range of less than 1 ML and up to 2 ML using synchrotron based PES and LEED and indeed we find a strong modification of the electronic properties of the organic molecule. Upon deposition, FePc forms a densely packed first layer exhibiting a $3\times2/c(6\times2)$ symmetry. Thermal treatment of this film at 550 K causes a modified interface order depending on the initial FePc coverage, resulting in less densely packed but still ordered superstructures. If the coverage is around 1 ML an interface structure with $5\times2/c(10\times4)$ symmetry mixed with a structure represented by a $(5 -1, 4 3)$ overlayer matrix results. An initial coverage of about 2 ML results in a structure having a $(4 -1, 0 4)$ symmetry, mixed with a structure having $(4 -1, 0 2)$ symmetry. These ordered structures can be considered to consist of rows of FePc in the [0 0 1] and [4 4 3] directions and the distance between rows differ in the two annealed structures. The electronic properties of the FePc are modified by the adsorption due to the relatively strong interaction with the Ag substrate, leading to the formation of an interface state just below the Fermi level derived from the molecular orbitals of the first layer FePc. Evidence of the strong adsorption is also seen in the C1s spectra where the shake-ups are found much closer to the main line. The FePc in the second layer is not as severely affected by adsorption and show bulk like properties with the usual (~2 eV) shake-up distance to the main line and the HOMO appear at 1.3 eV below the Fermi level for a film thickness of 1.25 ML and above.
5. Outlook

The results presented in this thesis are the first we have obtained in the organic – inorganic interface topic. Several things in the experiments could therefore be improved, modified or expanded.

In order to gain more information about the investigated systems it would be advantageous to combine experiment with theoretical calculations; individually theory and experiment may not be enough to provide the complete picture and the predictive power increases when they are combined. One example where this combination could be useful is in the interpretation of VB spectra from photoemission experiments; electronic orbitals in the molecule may change when the system e.g. is annealed but it is difficult to experimentally gain information about their origin (one way would be resonant photoelectron spectroscopy) and calculations could assist in pointing out the orbitals involved in the change and the location of these in the molecule. However, large systems such as phthalocyanines are difficult and time consuming to calculate and it becomes much more complex when a surface to which the molecules are adsorbed is added.

Optical excitation of electrons over the energy gap is basic in the solar cell, but the orbitals in the dye-molecule may be influenced by adsorption and bonding to the substrate surface, hence influencing the band gap. A change in this property would be of fundamental importance to the function and energy output of the cell. The electronic properties of the molecule in the occupied state are thoroughly mapped using PES and the unoccupied states with XAS. The band gap can be estimated with these experimental techniques by putting the PES and XAS spectra on the same energy scale by determining the ionization potential for the VB and the core level with PES and measure the absorption edge of that core level\(^9\). A more direct approach to measure the band gap of the adsorbed molecules would be to use UV-Vis spectroscopy. The energy of the impinging photons is scanned by a monochromator and when it is enough to excite an electron over the band gap an increase in absorption is detected. Unfortunately we have no access to this kind of instrument and most commercially available systems are made for measurements under ambient conditions.

It would also be interesting to prepare a phthalocyanine film under vacuum conditions, characterize it in STM so that it is well
defined and of known composition in an attempt to link the interface properties with the performance of an actual cell. This would require either assembly of the cell in vacuum or transfer of the film to the ambient. Vacuum preparation of the cell would be difficult as it involves a liquid electrolyte which is not compatible with vacuum conditions. The interface may not survive transfer to the ambient; a first step would be to test whether the atmosphere damages the film and if so, it would be possible to assemble a cell with a dye-layer manufactured in vacuum. Another issue is the single crystal versus nanocrystalline sample problem: characterization with STM in vacuum requires single crystalline samples but it is necessary with nanocrystalline samples to achieve a large enough surface area for the dye to attach on, in order to have a sufficiently strong signal from the solar cell.

The co-adsorption of bipyridine and phthalocyanine showed some interesting results; the dye-molecules interaction with the substrate was reduced but still a well defined heterostructure was obtained. Other molecules for modifying the titanium dioxide surface could be tested, for example variations of bipyridine, such as 2,2’-bipyridine or tert-butyl pyridine which could adsorb in another fashion and thus present other bonding possibilities for the dye molecule. Other options include pivalic acid which has been tested in connection with a Ru-based dye and the passive layer was found to survive transfer to the ambient; acetonitrile which is commonly found as solvent in the dye-molecule containing liquid the substrate is immersed in when coating it; as well as larger molecules such as e.g. alkanes (C_{34}H_{70}) to modify the surface and thus controlling the order at the interface.
6. References