Investigation of Energy Alignment Models at Polymer Interfaces

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Investigation of Energy Alignment Models at Polymer Interfaces

by

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A dissertation submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy
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Date of Approval:
April 8, 2014

Keywords: Energy Alignment, electrospray, photoemission spectroscopy, P3HT, MEH-PPV, CNL, IDIS, ICT.

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Dedication

This dissertation is dedicated to my mother, Minjie Wang, father, Zhonghuan Wang and my girl friend, Weiwei He. Thank you for your love, support and encouragement throughout my graduate study in the United States.
Acknowledgments

I would like to express my sincere gratitude to my major professor, Dr. Rudy Schlaf, for the patient guidance, encouragement and advice he has provided throughout my time as his student. It is extremely lucky to have him as my supervisor. There is no question that this dissertation cannot be completed without his efforts.

Additionally, I would like to thank my committee members, Dr. Li, Dr. Malik and Dr. Batzill for their guidance in my research.

I would like to thank all members of the Surface Science Laboratory at the University of South Florida for their consistent helps and supports during my study.
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List of Abbreviations

BE: binding energy
CHA: concentric hemispherical analyzer
CNL: charge neutrality level
DOS: density of states
ICT: integer charge transfer
IDIS: induced density of interface states
LIXPS: low intensity X-ray photoemission spectroscopy
MEH-PPV: poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene]
MFP: mean free path
P3HT: poly(3-hexylthiophene)
PE: passing energy
PES: photoemission spectroscopy
UHV: ultra high vacuum
UPS: ultra-violet photoemission spectroscopy
XPS: X-ray photoemission spectroscopy
Abstract

The presented study investigated the Induced Density of Interface States (IDIS) model at different polymer interfaces by using photoemission spectroscopy in combination with electrospray deposition.

In recent years, organic electronics have attracted considerable attention due to their advantages of low-cost and easy-fabrication. The performance of such devices crucially depends on the energy barrier that controls the interface charge transfer. A significant effort has been made to explore the mechanisms that determine the direction and magnitude of charge transfer barriers in these devices. As a result of this effort, the IDIS model was developed to predict the energy alignment at metal/organic and organic/organic interfaces. The validity of the IDIS model on molecular interfaces was confirmed by the results of a series of experiments with small molecular materials, which are in good agreement with the theoretical calculations from the IDIS model. The charge neutrality level (CNL) and screening factor for various organic materials can be determined from the linear correlation between the hole injection barrier at metal/organic interface and the work function of its corresponding metal substrate, which stands as one of the most important features of the IDIS model.

The study presented here explores whether the IDIS model is also valid for polymer interfaces. Two prototypical polymer materials: poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) were selected for the investigation. In the first part of this study, a series of metal/polymer
interfaces were prepared using electrospray and investigated with photoemission spectroscopy. The linear relationship between the hole barriers extracted from the metal/polymer interface and the work function of its respective metal substrate suggests that the IDIS model is also valid for metal/polymer interfaces. The CNLs and the screening factors of P3HT and MEH-PPV are determined respectively. The experiment results are also discussed with regard to the Integer Charge Transfer (ICT) model. The comparison between the two models suggests that the IDIS model should be applied to interfaces prepared in vacuum while the ICT model works on interfaces with an ambient contamination layer present. The second part of the dissertation discusses the photoemission results of the MEH-PPV/P3HT heterojunction from the perspectives of the two models. The results indicate that the IDIS model is valid for polymer/polymer heterojunctions. The IDIS model more accurately predicted the measured orbital line up by using its principles for organic/organic heterojunction than the ICT model.
Chapter 1 Introduction and Fundamental

1.1 Motivation and Outline

The discovery of the implementation of organic materials in electronic device fabrication can be traced back to the early 1940s. However, due to low mobility of the organic materials and poor performance of the electronic devices made of these materials did not attract considerable attention. This situation changed in the 1980s with the first demonstration of a thin film organic light-emitting diode (OLED) by Tang and the successful application of an organic material used to fabricate organic photovoltaic devices by Heeger. These developments established a foundation for applying organic materials in device fabrication, which were at the time dominated by “conventional” semiconductor materials such as Si. These organic devices are usually prepared with a multilayer structure and the energy barriers at the interface between each layer critically affect the performance of the organic electronic devices. Since these energy barriers are extracted from the relative positions of molecular energy levels at metal/organic or organic/organic interfaces, the energy alignments at such interfaces have been extensively investigated in the past few decades.

The experimental investigation of metal/organic interfaces yielded interface energy alignments that deviate from the Shottky-Mott limit, which defines the “vacuum level alignment”. This deviation is caused by the formation of substantial interface dipoles. Figure 1 shows the comparison between the interface orbital alignments with and
without interface dipole. It is obvious to see that the presence of interface dipole alters the vacuum level alignment and changes the positions of HOMO and LUMO relative to the vacuum level. Many mechanisms were proposed to explain the formation of the interface dipole, such as charge transfer, formation of gap states and chemical reactions etc.

![Figure 1. Orbital alignments of metal/organic interface with and without interface dipole.](image)

In the past decade, the Induced Density of Interface States (IDIS) model was developed as a new framework for predicting the electronic properties at metal/organic and organic/organic interfaces. In general, this model proposed a mechanism based on the charge rearrangement at interface through the induced density of states and the tendency of Charge Neutrality Levels (CNLs) to align with the metal Fermi-level. Recently, experiments conducted on metal/small molecular interfaces demonstrated that the IDIS model is also valid for these interfaces. These experiments were accomplished by in-vacuum evaporation of small conjugated molecules on metal substrates to form intimate contacts. However, it is difficult to prepare clean metal/polymer contacts that are similar to the small molecular interfaces, since in general high-molecular mass polymer
thin films cannot be prepared in vacuum. Therefore, the validity of IDIS model for polymer interfaces had remained unknown.

In this study, the clean polymer interfaces were achieved by using the electrospray deposition technique, which allows in-vacuum deposition of high molecular weight materials with the exclusion of significant ambient contamination. The main objective of this work is the investigation of the electronic structure of these polymer interfaces. The results were discussed with regard to the IDIS model to explore its applicability on polymer interfaces. The dissertation can be divided into two parts each discussing the investigation of a polymer interface.

The first part of the dissertation discusses the results of the investigation of metal/polymer interfaces. A series of metal/polymer interfaces were prepared with two prototypical polymer materials: poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV). The experimental results were collected through photoemission spectroscopy measurements. The energy barriers obtained from the orbital line-ups of these interfaces were discussed in combination with previous publications, suggesting that the IDIS model is valid for metal/polymer interfaces. The Charge Neutrality Level (CNL) and corresponding screening parameters of both P3HT and MEH-PPV were also determined.

The second part of the dissertation focuses on the study of the electronic structure at the polymer/polymer heterojunction. The orbital line-up of the MEH-PPV/P3HT interface was compared with the prediction of the orbital alignment by the IDIS model derived from the CNLs determined from the first part. The results suggest that the IDIS model can also be applied to polymer/polymer heterojunctions. The results were also
discussed with respect to the Integer Charge Transfer (ICT) model. The deviation of the prediction based on the ICT model from the actual orbital line-up suggest that the ICT models should be used for interfaces with contamination present while the IDIS model should be applied to in-vacuum prepared clean interfaces.

1.2 The development of models for Energy Alignment at Organic interfaces

The development of modern theories for energy alignment at organic interfaces will be briefly discussed in this section. The principles and limits of the IDIS and ICT models will be explained in the following paragraphs.

1.2.1 IDIS model

In the past few decades, significant research activities were conducted in order to develop a mechanism to explain the formation of interface dipoles that cause the deviation of interface orbital alignment from the Shottky-Mott limit. One of the outcomes of these efforts is the Metal Induced Gap States (MIGS) model developed by Tersoff and Heine.\textsuperscript{29,30} The MIGS model was based on the concept of “metal induced gap states”, which form at clean metal/semiconductor contacts within the band gap of the semiconductor. These states are induced as a result of the overlap between the metal wave function and the band structure. Any state in the band gap of the semiconductor can be considered a mixture of valence/conduction band and the metal wave function. Since the MIGS are derived from bulk energy bands, they predominantly keep their donor or acceptor characteristics. By integrating these states up to an energy that is equally donor or acceptor like, the “Charge Neutrality Level” is defined.
As a subsequent derivative of the MIGS model, the IDIS model was developed in order to extend the MIGS method to metal/organic and organic/organic interfaces.\textsuperscript{22-26} The IDIS model was based on the introduction of the “Induced Density of States”. The IDIS forms as a result of the hybridization of the molecular orbitals of conjugated molecules with metal substrates. The interaction between the metal wave function and molecular orbital alters the initial “discrete” molecular states into a continuum density of states (DOS) within the band gap of the organic material. By integrating these IDIS to a state of a neutral molecule, the energy position of the CNL can be determined. It should be mentioned here that the IDIS model applies to interfaces where chemical interaction is moderate but not negligible. These interfaces are usually prepared by in-vacuum vapor deposition of conjugated molecules onto non reactive metal substrates like Au.\textsuperscript{12}

For metal/organic interfaces, the position of the CNL relative to the Fermi level of a metal substrate determines the direction and magnitude of charge transfer at the interface, hence affecting the magnitude of the interface dipole. As shown in Equation 1, the value of interface dipole is proportional to the energy offset between the work function of metal substrate and the CNL energy.

\[ eD = (1 - S)(\Phi_m - CNL) \]  \hspace{2cm} \text{Equation 1}

The value \( S \) is the “slope parameter” (referred as “screening factor” in this study), which represents the ability of screening the potential difference between CNL and metal Fermi level.\textsuperscript{24} As shown in Equation 2, the \( S \) can be determined from the density of states at the Fermi level \( (D(E_F)) \), the distance \( (d) \) between the molecule and the metal and the interface area of the molecule \( (A) \).

\[ S = 1/(1 + 4\pi e^2 D(E_F) d/A) \]  \hspace{2cm} \text{Equation 2}
The $D(E_F)$ is calculated by implementing a DFT-LACO method in combination with the modification to account for the influence from the metal wave function. The area of the interface molecule ($A$) can be estimated if the orientation of molecules on the metal substrate is in a fixed direction, i.e. flat, upright or skewed at a certain angle. The distance ($d$) between molecules and metal substrate strongly affects the value of the slope parameter but has less influence on the position of the CNL. However, $d$ cannot be accurately predicted using conventional DFT calculation methods due to the weak interaction between the metal and the organic molecule. Consequently, $d$ is usually obtained from the experimental results.

A number of experiments with small molecular interfaces have been conducted in order to test the validity of the IDIS model. These results are compared with the predictions from the IDIS model. Figure 2 shows the summary of the experimental results of different metal/organic interfaces, which were prepared by vapor deposition on clean metal substrates. The experiment data are plotted as the solid lines while the Schottky-Mott limit is plotted as the dashed lines in each chart for comparison.

The linear relationship between the interface $E_F$ position and the metal work function is in good agreement with the linear correlation assumption between energy barrier and the metal work function in the IDIS model. The energy difference between the solid line and the Schottky-Mott line corresponds to the interface dipole at an interface with a certain work function. The slope parameter $S$ varies between different organic materials and corresponds to the strength of interaction between the organic and
metal substrates

Figure 2 Summary of experiment results on different interface. The linear relationship between the interface $E_F$ position and the metal work function suggests that the IDIS model is valid for metal/small molecules interfaces.

The IDIS model can also be applied to organic/organic heterojunctions with the same CNL methodology as metal/organic interfaces. The energy alignment at the organic/organic heterojunction is determined by the relative positions of the CNLs of the two organic materials. Shown in Equation 3, the dipole at the heterojunction is proportional to the energy offset between the two CNLs. Similar to the metal/organic interface, the slope parameter $S_{oo}$ determines how the energy offset is screened at the interface.

$$eD = (1 - S_{oo})(CNL_1 - CNL_2)$$  \hspace{1cm} \text{Equation 3}
The $S_{oo}$ cannot be directly calculated in the same manner as the $S$ parameter for metal/organic interfaces, but its value can be estimated by following Tersoff’s proposal for inorganic semiconductors as shown in Equation 4. Where, $\varepsilon_1$ and $\varepsilon_2$ correspond to the dielectric constants of the two organic materials respectively.

$$S_{oo} = \frac{1}{2} \left( \frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} \right)$$  \hspace{1cm} \text{Equation 4}$$

The screening factor for metal/organic interface is usually smaller than the screening factor for organic/organic heterojunctions. The electrons at the metal interface are more delocalized than at the organic heterojunction, hence screening the energy difference at the interface more efficiently. Due to the weak interaction between organic materials in contact, the interface dipole at the organic/organic heterojunction is smaller than that of the metal/organic interface. The results from experiments performed with heterojunctions consisting of different small molecular materials have shown good consistency with the theoretical calculations from the IDIS model.

1.2.2 ICT model

A parallel effort to the IDIS model for predicting the energy alignment of organic interfaces is the “Integer Charge Transfer” (ICT) model, which is applied to weakly interacting interfaces. These interfaces are normally formed in ambient conditions, i.e. atmosphere or glove-box environments. The ICT model assumes that the energy alignment at organic interfaces is accomplished by charge transfer via tunneling between the materials in contact. The concept of the “polaron” state or the so-called ICT state was introduced as the energy that is required to remove/add one electron from/to the molecule/polymer to form a both electronically and geometrically fully-relaxed state. The energy alignment at organic interfaces is governed by the position of the polaron
state: if the metal substrate work function is within the polaron band gap, no charge transfer occurs between the materials in contact and the vacuum level alignment rule applies. If the substrate work function exceeds the polaron gap, charge transfer occurs and the metal Fermi-level is pinned to the polaron state. The principles of this mechanism are summarized in Figure 3\textsuperscript{40}.

![Diagram of energy alignment from ICT model](image)

**Figure 3** Schematic of energy alignment from ICT model. (a) Substrate work function is within the polaron gap. (b) Substrate work function exceeded the positive polaron state. (c) Substrate work function is lower than the negative polaron state.

The concept of the polaron state can also be used to predict the alignment of organic/organic heterojunctions. Recent studies on polymer/molecule and molecule/molecule interfaces\textsuperscript{41,42} have shown that the energy alignment at organic/organic heterojunctions also obey the principles discussed above when the metal/organic structure as a whole is treated as the substrate for the other organic material in contact.

The IDIS and the ICT models apply to different types of interfaces. The IDIS
model describes the direct-contact interface that is prepared in vacuum while the ICT model applies to the weakly-interacting interface that forms in ambient environment. Unlike the intimately contacted metal/organic interface prepared in vacuum, the interface prepared in ambient environment is separated by a layer of hydrocarbon contamination. The contamination layer would strongly reduce the work function of the metal substrate causing a significant interface dipole. This phenomenon is known as the “push back effect”, so named because it is caused by pushing the tailing electron back into the metal. Due to the presence of this contamination layer, the interface at the metal surface is dominated by localized charge transfer between the metal substrate and the contamination layer. The deposited organic material actually forms a “heterojunction” with the contamination layer. In the ICT model, the contaminated metal surface with this “heterojunction” structure is considered the substrate to form metal/organic interface. Consequently, a near-vacuum alignment dominates with interfaces that the ICT model describes.
Chapter 2 Experimental Methodologies

This chapter introduces the experimental methodologies involved in this study. The working principles of electrospray deposition will be explained in the first section. The second section will focus on the introduction of photoemission spectroscopy, used as the major characterization method in the study. Lastly, the instrument setup and the experiment procedure will be discussed.

2.1 Electrospray

In this study, the polymer interfaces are fabricated using a home-built electrospray deposition system. In contrast to traditional film preparation methods, electrospray allows for direct deposition of macromolecular material into vacuum without introducing significant surface contamination. In this section, the application of electrospray for the preparation of polymer thin films and the general working principle of electrospray will be discussed.

2.1.1 Electrospray in Film Preparation

The preparation of organic thin films is a problem frequently encountered in device fabrication and analytical measurement. Various preparation methods have been demonstrated in published studies, such as spin-coating, ink-jet printing, and evaporation of organic materials in vacuum environment. Although these techniques have been largely adopted in research and device manufacturing processes, limitations of these methods in preparing polymer thin films are observed. For example, solution-based
film preparation methods such as spin-coating and ink-jet printing allow for quick and easy fabrication of polymer thin films on various substrates. However, these methods can only be accomplished in an ambient environment. A significant amount of surface contamination is inevitably introduced on to the sample, which may severely interfere with experimental results when a pristine sample surface is required. High temperature evaporation of polymer materials in vacuum also cannot be utilized for polymer thin film preparation. This is because the required evaporation temperature exceeds the polymer decomposition point which would cause severe structural damage to the heated polymer\textsuperscript{49,50}. The reverse preparation, that is, the evaporation of a metal film on to a polymer thin film prepared in ambient environment, would not work either, since unwanted chemical reactions between the heated gas phase metal atoms and the polymer material would occur at the to-be-investigated interface\textsuperscript{51,52}.

Due to the drawbacks of the traditional thin film preparation methods mentioned above, a novel preparation method is desired for the fabrication of clean polymer thin film samples. In the presented study, this issue was solved by the use of electrospray deposition. The electrospray phenomenon was originally discovered by G.M. Bose\textsuperscript{53} in the eighteenth century. Around two hundreds years later, electrospray technique was developed and successfully applied in the field of painting\textsuperscript{54-56}. After several decades of development and refinement, electrospray deposition in the modern world has been largely applied in the field of mass spectroscopy in order to generate a gas phase sample plume, which can be detected by the mass spectrometer\textsuperscript{57-59}. Electrospray has also been applied in thin film preparation, allowing for polymer coatings\textsuperscript{60,61}, fabrication of ceramic layers\textsuperscript{62,63} and deposition of biomolecules\textsuperscript{59,64,65}. Samples prepared by
electrospray do not suffer inhomogeneity and poor thickness uniformity caused by edge effect, which inevitably appears in traditional polymer thin film preparation methods such as solvent casting and spin coating. In this study, the integration of the electrospray deposition system with a vacuum chamber further refines the electrospray technique by enabling in vacuum deposition of polymer materials. The electrospray technique is particularly useful in the laboratory-scale preparation of clean polymer thin film samples.

2.1.2 Working Principle

Figure 4 shows the schematic of the electrospray process. The material to be deposited was dissolved in solvent and kept in a syringe with a hypodermic needle (sometimes referred to as electrospray capillary). A high voltage was applied between the needle and deposition chamber. The sample substrate was connected via the vacuum chamber transport rod to the deposition chamber, which was grounded. The high voltage applied to the needle established an electric field between the needle tip and sample substrate in the vacuum chamber.

During the electrospray process, the ions in solution within the capillary are attracted by the electric field towards the sample. At the tip of the syringe capillary, the electric field creates a conical meniscus at the surface of the solution known as a “Taylor cone”. At the tip of this meniscus the solution breaks into a number of charged, ion containing droplets forming a plume directed toward the sample substrate. In order to minimize the introduction of ambient contamination, the space between capillary tip and the inlet of the vacuum chamber is shrouded with a Pexiglass container and filled with high-purity N₂ gas. The ejected droplets contain solute ions and solvent molecules that are oppositely charged. As these droplets travel through the two differential pumping
stages, the solvent molecules evaporate causing the droplets to shrink, increasing the charge density inside the droplets. When the Coulomb force between charged particles becomes large enough to overcome the surface tension force, the droplet ejects individual charged polymer gas phase ions. As a result of this “Coulomb explosion”, the solute molecules are mostly extracted from the solution; a relatively clean beam of gas phase solute ions forms and impinges on the substrate forming a thin film.

Figure 4 Schematic of electrospray process. A high voltage is applied between the syringe and the deposition camber. The ejected droplet contains of solute ions and solvent molecules that are oppositely charged. These droplets ‘explodes’ into individual charged polymer particles as a result of the “Coulomb explosion”. Since the solvent molecules were extracted by vacuum, a relatively clean beam of solute forms and impinges the substrate.
2.2 Photoemission Spectroscopy

The major characterization method of the presented study is photoemission spectroscopy (PES). PES has been recognized as one of the most versatile analytical techniques to investigate the surface structure of solid and gas phase materials. The results of PES yield a material energy diagram that is extremely useful in the study of solid-state physics. In this section, an over view of the PES method will be given that covers the principles of common PES techniques such as XPS, UPS, and recently developed LIXPS by this group.

2.2.1 Working Principle

PES is developed based on the well-known photoelectric effect, which was discovered and demonstrated by Hertz\textsuperscript{67} and Hallwachs\textsuperscript{68} in the late 19\textsuperscript{th} century. The photoelectric effect was first explained by Einstein in 1905 by introducing the concept of the photon and the correlation between the energy of incident photon \((h\nu)\) and the maximum kinetic energy of the photo-emitted electron \(E_{\text{kin}}^{\text{max}}\),

\[
E_{\text{kin}}^{\text{max}} = h\nu - \Phi \\
\text{Equation 5}
\]

where \(\Phi\) is the work function of the exposed sample in the incident light.

Based on this theory, Siegbahn and co-workers developed the first high-resolution photoemission analyzer in the 1950’s\textsuperscript{69}. The detection limit of energy lower than 1 eV allows a subtle detection of chemical shifts and a detailed study of core-level binding energies of materials. This technique has been known as “ESCA”(Electron Spectroscopy for Chemical Analysis)\textsuperscript{70, 71}.
Figure 5 shows the principle of the PES process. Photoemission occurs in a three-steps process. First is the absorption of the energy of the incident photon by the electron in the solid sample. The absorption of energy allows the electron to transfer from its initial state to the final state. Next, the electron travels towards the sample surface. During this step, the majority of the excited electrons undergo inelastic collisions with neighboring atoms, causing a loss of kinetic energy. These electrons are known as secondary electrons. In contrast, the electrons that do not lose energy while travelling out of the material are known as primary electrons. The last step is the emission of electrons into vacuum. In this step, the electrons retain the kinetic energy imparted to them as they leave the sample surface and are detected by the electron analyzer.

![Diagram](image)

**Figure 5 Principle of PES process. Photoemission occurred in a three-steps process: absorption, excitation & travel and emission.**

Figure 6 correlates the photoemission process with a spectrum schematic. The incident photons liberate electrons with an initial energy of $h\nu$. Depending on the binding energy (BE) and work function ($\Phi$), the photoemitted electrons leave the sample surface with a kinetic energy of

$$E_{\text{kin}} = h\nu - BE - \Phi.$$  

Equation 6
Since primary electrons do not lose any energy during the travelling, these electrons preserve the information regarding the binding energy of core-levels, which are reflected as distinct sharp peaks in the spectrum. The secondary electrons show as a continuous peak with a sharp ending, which represents the electrons with zero kinetic energy. This feature will be discussed in detail in the following section.

Figure 6 Schematic of PES spectrum. The binding energy of free electrons can be determined by: \( BE = \hbar \nu - E_{kin} - \Phi \).

A schematic of a modern PES system is shown in Figure 7. The system must be operated under an ultra-high vacuum (UHV) environment with a pressure range of \( 10^{-8} \) to
10^{-12} mbar. UHV conditions are necessary to minimize the chance of absorbance of low energy electrons by gas molecules. A typical PES system consists of two basic light sources, an X-ray gun for XPS analysis and gas discharge lamp for ultra-violet photoemission spectroscopy (UPS). X-ray photons are generated by striking electrons on a metal anode such as Al and Mg. The energies of the characteristic X-ray emissions used in XPS are AlKα (1486.6 eV) and MgKα (1253.6 eV). These are the so-called ‘soft’ X-rays. These energies are selected as the photon source due to their narrow bandwidth. Both AlKα and MgKα have a bandwidth of lower than 1 eV, which guarantees a good resolution of the spectrometer. Before entering the concentric hemispherical analyzer (CHA), the electrons are focused by passing through an electromagnetic transfer lens. The CHA consists of two concentric hemispherical plates. By applying differential negative voltages to the outer and inner hemispheres, a median equipotential is generated inside the analyzer, which only allows electrons with a specific kinetic energy to pass through and reach the electron detector. The electron energy that the CHA allows to pass is called ‘Passing Energy’ (PE). Consequently, it is necessary to ‘adjust’ the kinetic energies of the injected electrons to the PE so that the electrons can be detected. The kinetic energies are reduced by an electron retardation device located in front of the entrance slit of the CHA, which generates a variable electric field to slow the passing electrons. By keeping the PE at a constant level and recording the changes of the retarding potential, the density of incoming electron with various kinetic energies can be obtained. Due to the mechanical design, the resolution of the CHA is a fixed value (0.05% of the transmission energy). Therefore, the PE is usually kept at a low level (10-
100 eV). For example, since the CHA resolution is 0.5%, a PE of 1000 eV would result in a resolution of 5 eV, while a PE of 100 eV would yield a resolution of 0.5 eV.

![Diagram of PES instrument](image)

**Figure 7 Schematic of PES instrument.** A typical PES system consists of a UV gas discharge lamp, an X-ray gun, a transfer lens, a retarding device, a CHA and a channeltron multiplier.

### 2.2.2 X-ray Photoemission Spectroscopy

Figure 8 shows an XPS spectrum of a clean Au sample. The peaks shown in the spectrum can be categorized into three types: photoemission from core levels, photoemission from valence band and Auger emissions. The core level emissions contributions are mainly from primary electrons. These peaks can be used for elemental
composition analysis, stoichiometry and quantitative analysis, which will be explained in
detail in the following paragraphs. The valence band related emissions are located at low
binding energies (0-20 eV), and are useful in determining material electronic structure.
The Auger emissions excited by the X-ray illumination are usually at higher binding
energies and also reveal information about elemental composition. Another feature of the
XPS spectrum is the step-like background. Such background is generated by the inelastic
scattering of secondary electrons generated by primary electrons passing through the
solid.

![Complete XPS spectrum of Au surface](image)

**Figure 8 Complete XPS spectrum of the pristine Au surface.**

XPS is particularly useful in distinguishing bonding shifts caused by different
chemical bonding. For example, Figure 9 shows the XPS spectrum of an Al surface. The
freshly prepared pristine Al sample exhibits a characteristic Al 2p emission at 73 eV. If
oxidized, another peak is observed at 75.6 eV, which corresponds to Al atoms bonded to
oxygen. Its binding energy is higher than the Al 2p emission of the pristine Al sample as higher energy is required to remove an electron from the 2p orbital (the location of atoms that form the covalent bond with oxygen).

![Al2p emission](image)

**Figure 9 Al 2p emissions of pristine and oxidized Al samples.**

Spin orbital splitting of core level peaks is also a common feature in an XPS spectrum. Spin orbital splitting is caused by the coupling of orbital and spin angular moment of an unpaired electron in atom sub shells introduced by photoemission. The emission of the same orbital splits into two spinning figures depending on the spinning direction of the unpaired electron, i.e. $j_1 = l + 1/2$ or $j_2 = l - 1/2$. The relative intensity of the
doublet peaks are linked to the degeneracies of the final states, given by $2j_1+1:2j_2+1$.

The state with maximum $j$ is has lowest energy, since the shell is more than half full. For example, Figure 10 shows the XPS spectrum of Au4f emission. The relative intensity of $f$ orbital doublets is $2(5/2)+1:2(7/2)+1$ (f 5/2 to f 7/2 emission), a 3:4 ratio. The f 7/2 peak is at lower binding energy than f 5/2.

![Au4f emission spectrum](image)

**Figure 10** Au 4f emission. 4f emission splits into a doublet peaks of a f 5/2 and a f 7/2

XPS can also be applied to surface stoichiometry analysis. When investigating film samples, the substrate related emission is attenuated as the sample overlayer grows thicker. The thickness of the overlayer can be estimated by Lambert-Beer’s law,
\[ d = -MFP(\ln \frac{I}{I_0}) \]  

where \( MFP \) is the mean free path of the photoemitted electron, \( I \) is the intensity of the top surface covered by film, \( I_0 \) is the original emission intensity of the uncovered substrate.

### 2.2.3 Ultra-violet Photoemission Spectroscopy

As a complimentary surface analysis method to XPS, UPS is frequently employed to determine the material electronic structure, i.e. work function, valence band etc. The working principle of UPS is similar to XPS however, many differences between the two techniques exist.

![Electron mean free path versus its kinetic energy](image)

**Figure 11** Electron mean free path versus its kinetic energy

In contrast to XPS, UPS generates free electrons by exposing the sample to ultra-violet radiation, typically HeI (21.22 eV) or HeII (40.8 eV) emission. The energy line widths of such emissions are in meV level. Because of this UPS has a higher resolution than XPS\(^{73}\). However, the low photon energy is only strong enough to ionize the outermost electrons.
located in valence band. In comparison with XPS, UPS is a far more surface sensitive technique, due to the short mean free path of the electrons released by ultra-violet light exposure. Figure 11 shows a plot of the relationship of the mean free path versus the kinetic energy of free electron. Since most of the detected free electrons originate from a depth of 0 to 3 MPF of the free electrons, the probing depth of UPS is in angstrom level in contrast to the nanometer level of XPS.

Figure 12 shows a complete UPS spectrum of the Au surface covered with [6,6]-Phenyl C$_{61}$ butyric acid methyl ester (PCBM).

![UPS spectrum of Au covered with PCBM](image)

**Figure 12** UPS spectrum of Au surface covered with PCBM. The determination of HOMO cutoff is shown in the inserted graph.
The PCBM HOMO related emissions (or valence band emission for semiconductor materials) can be directly obtained from the spectrum. By fitting a line into the spectrum onset, the HOMO cutoff of PCBM is determined. This feature and the fitted line are enlarged and shown in the inset in Figure 12. The value of the HOMO cutoff is important, since it is often used to calculate the energy barrier at the interface. Another useful feature of the UPS spectrum is the emission from the inelastically scattered electrons, recognized as the large steep peak at high binding energy. Secondary electrons have just over the minimum energy required to escape the sample surface. Because of this the electrons’ kinetic energy is assumed to be nearly zero. The cutoff binding energy of reflected secondary electrons can be used to determine the value of work function.

\[ \Phi = h\nu - BE \]  

Equation 8

One drawback of UPS is that the introduction of the ultra-violet radiation can induce potentially unwanted effects on the material. Such effects are the charging related effects and the ultra-violet light induced surface reactions. In order to investigate these phenomena, Low Intensity Photoemission Spectroscopy (LIXPS) was also adopted in the study.

### 2.2.4 Low Intensity Photoemission Spectroscopy

LIXPS was firstly used to the study of the change in work function of indium tin oxide films induced by UPS measurements by Schlaf et al.\textsuperscript{74} It was demonstrated in the study that the LIXPS can be applied as a complementary measurement technique to UPS to investigate surface reactions.\textsuperscript{75} LIXPS can also be used to detect charging related effects caused by UPS measurement. The photon flux for LIXPS measurement is several magnitudes lower than UPS allowing for measurement of these effects. This application
is especially useful for the investigation of organic interfaces, since the conductivities of organic materials are high enough to screen the local charging caused by photoemission measurements. Figure 13 shows the comparison between the LIXPS and UPS measurement of the same P3HT film prepared using the electrospray deposition system in several steps. The LIXPS measurements were performed before the UPS measurements.

Figure 13 LIXPS (left) and UPS (right) measurements of P3HT film. The stronger shift of secondary edge than LIPXS indicates the occurrence of charging artifact on sample surface.

As the P3HT grows in thickness, the shift of the secondary edge towards higher binding energy, shown in the UPS spectra, is stronger than the shift in the LIXPS measurement. The large discrepancy between the LIXPS and UPS measurements indicates a charging artifact induced by the UPS measurements.
2.3 Instruments

All the experiments were performed in a commercially available UHV multi-chamber PES system (SPECS GmbH, Berlin). The base pressure of the UHV system is approximately $2 \times 10^{-10}$ mbar. As shown in Figure 14, this system consists of one preparation chamber, one transfer chamber and an analysis chamber. The vacuum chambers are interconnected with transport rods, which enable the preparation and analysis of the samples without breaking the vacuum.

Figure 14 Schematic of the PES system. The system consists of a deposition chamber, a transfer chamber and a PES chamber.

The load-lock (LL) chamber was designed for fast loading of samples into the vacuum system, and was connected to a home-built glove box. The preparation of the investigated samples were completed in the deposition chamber, which is equipped with a tungsten coil evaporator, a quartz crystal microbalance and a home-built electrospray...
system. The analysis chamber is connected with the preparation chamber, consisting of an X-ray gun, an ultraviolet source and an electron analyzer.

2.4 Sample Preparation

The metal substrates used in the presented work were prepared in two ways: ion-sputter cleaning of high purity metal substrates and in vacuum evaporation of pristine metal materials. The sputtering method is applied to prepare inert metal substrates such as Au and Ag. The Au substrates used in the presented study are 1000-Å thick Au thin film coated on glass slides covered by 50-Å-thick Ti adhesion layer. These substrates are purchased from EMF Corp. (Ithaca, NY). For the experiment on Ag substrates, a 0.1-mm-thick Ag foil is used. The Ag foil was purchased from Alfa Aesar with a purity of 99.998%. In a typical experiment, the metal substrates are cut into 1 cm² square samples, then rinsed with acetone and isopropanol. Before loading into the vacuum system, the substrates are wiped clean with a Kimwipe soaked in methanol. Once transferred into the UHV chamber, the residual ambient contamination on the substrate surface was removed by sputtering with Ar⁺ ions. The SPECS IQE 11/35 ion source was used for the sputtering process, which produces Ar⁺ ions at a kinetic energy of 5 keV and an emission current of approximately 10 mA and Ar pressure of 5 × 10⁻⁶ mbar.

For the preparation of reactive metal substrates, the sputtering treatment was not adopted as it is a complicated and time-consuming sample preparation process in comparison with the procedure for inert metal substrates. In the presented study, the reactive metal substrate (Al) was grown by evaporating pristine metal wire wrapped with a tungsten coil onto a 1 cm² square 1000 Å thick Au film at a pressure of 1 × 10⁻⁸ mbar. The Al source wire was purchased from Strem Chemicals with a purity of 99.9995%. The
deposition rate of metal is approximately 0.1 Å/s, which is monitored by using a QCM installed in the same vacuum chamber.

Two prototypical polymer materials, poly (3-hexylthiophene) P3HT and poly [2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), were selected for the presented studies. The polymer materials were dissolved in HPLC-grade toluene at a concentration of 1 mg/mL and 0.5 mg/mL for P3HT and MEH-PPV respectively. The prepared solutions were kept in dark environment to avoid exposure to light. The polymer thin films were prepared using a home-built electrospray deposition system. The deposition system is connected to the sample preparation chamber, which allows in situ sample preparation and subsequent characterization all while maintaining vacuum. The polymer solution was injected into the electrospray system from a syringe, whose needle tip was held a distance of approximately 3 mm from the orifice of the system, which acted as an interface from atmosphere to vacuum. The space between the syringe and the inlet of vacuum chamber is shrouded with a customized Plexiglas box filled with high purity nitrogen gas to minimize the effect of ambient gas from the environment. The electrospray deposition was performed at a pressure of $5 \times 10^{-10}$ mbar. During the electrospray process, a voltage of -3 keV was applied between the syringe capillary and vacuum chamber. The injection rate of syringe pump is 4 mL/h. As the charged solution droplets travelled through the inlet orifice of the vacuum system, the solvent molecules were evaporated by two differential pumping stages at 0.1 mbar and $4 \times 10^{-3}$ mbar. For more details of sample preparation procedure please see Wang et al\textsuperscript{76,78}. 
2.5 Deposition and Analysis

The polymer thin films are grown in several steps in the vacuum preparation chamber. Between each electrospray deposition, the sample was immediately transferred into the analysis chamber for a set of sequential PES characterization measurements. The chamber was equipped with a SPECS UVS 10/35 ultraviolet source, a SPECS XR 50 X-ray gun and a SPECS Phoibos 100 hemispherical analyzer. The analyzer was calibrated to yield the standard binding energy of Cu 2p 3/2 at 932.66 eV and Cu 3p 3/2 at 75.13 eV. A -10 V bias was applied to the sample holder to in order to separate the secondary emissions of the sample and analyzer. The Mg Kα X-ray emission ($h\nu=1235.6$ eV) was used for all XPS and LIXPS measurements. Regular XPS was carried out at an emission current of 20 mA. UPS characterization was performed by using He I radiation with a photon energy of 21.22 eV. LIXPS measurements were performed by operating the X-ray gun in a mode with a low emission current of 0.1 mA.

Figure 15 Deposition and measurement procedure. The deposition-measurement sequence is as follow: 1. 1. Deposition of organic material using electrospray system. 2. LIXPS measurement. 3. UPS measurement. 4. LIXPS measurement. 5. XPS measurement.
Figure 15 shows a schematic of a typical experiment. A typical deposition-measurement cycle is performed in the following order: 1. Deposition of organic material using electrospay system. 2. LIXPS measurement. 3. UPS measurement. 4. LIXPS measurement. 5. XPS measurement. The LIXPS measurement was conducted twice in order to obtain a comparison before and after the UPS measurement to detect the onset of charging artifacts. This cycle will be repeated until the desired layer thickness is reached.
Chapter 3 Investigation of Polymer/metal Interfaces

This chapter summarizes the experimental results of a series of polymer/metal interfaces. In comparison with polymer interfaces prepared using traditional methods, the interfaces were prepared in vacuum in order to exclude ambient contamination. The results are discussed with regard to the IDIS model hence yielding the CNL of the investigated polymer.

3.1 P3HT interfaces

This section summarizes the results of study on P3HT/metal interfaces. The presented work has been published in Journal of Chemical Physics. See Appendix B for more details.

3.1.1 Introduction

Organic thin-film based semiconductor heterojunctions have attracted considerable attention due to their applications in electronic devices like organic light-emitting diodes\(^4,79\) (OLEDs) and organic solar cells\(^5,80\) in the past few decades. The performance of the devices highly depends on the electronic structure of the interface. The electronic structure at an organic/metal interface is mainly determined by the formation of interface dipole. The magnitude and direction of the interface dipoles were defined by the formation of metal induced gap states\(^30\) (MIGS) theory on a series of inorganic interfaces. The MIGS are the results of interaction between a metal substrate wavefunction and the density of states of a semiconductor. As discussed by Tersoff\(^30\) and
Heine, the metal conduction band overlaps with the semiconductor band gap and the electron wavefunctions of the metal decay into the semiconductor, forming the continuous MIGS. By integrating the MIGS to a ‘charge neutrality’ state, that is, the energy of the filled MIGS in the band gap that are equally donor-like and acceptor-like, the charge neutrality level (CNL) was defined. Based on these studies, Vazquez and colleagues applied the MIGS theory in the field of metal/organic and organic/organic interfaces. The so called ‘induced density of states’ (IDIS) model was proposed by introducing the induced density of interface states, which are formed by the interaction between density of states of a metal and discrete molecular orbitals. The CNL of the organic semiconductor is also introduced in this model similar to the MIGS theory, serving as the ‘Fermi level’ of the organic semiconductor. The validity of the IDIS model has been demonstrated by Kahn and colleagues on a series of metal/organic interfaces. This chapter focuses on the exploration of the electronic structure of the metal/P3HT interface in order to determine whether the IDIS is also valid for metal/polymer interfaces. A prototypical polymer, poly(3-hexylthiophene) (P3HT) was selected due to its wide application in research and relatively large mobility value.

To prepare a contamination free polymer interface, traditional preparation methods such as UHV evaporation cannot be applied, since the heat released during the evaporation process damages the structure of polymers. Ambient preparation techniques like spin-coating cannot be used either due to the introduction of surface contamination. To address this issue, an electrospray deposition system was employed. Electrospray enables direct deposition of macromolecular materials in vacuum. The deposition process is considered a ‘gentle’ deposition method that does not cause significant decomposition
of the deposited molecule or polymer. Furthermore, electrospray facilitates multi-step deposition allowing for sequential XPS and UPS measurements of the interface between deposition steps. As a complementary measuring technique, LIXPS was utilized allowing for the detection of the onset of layer thickness dependent charging artifacts encountered during PES processes and improved measurement accuracy. In this chapter, the orbital line-ups of Ag/P3HT and Al/P3HT interfaces are discussed with regard to the IDIS model. The result shows that the IDIS model is valid at polymer/metal interfaces. A CNL for P3HT was determined to be 3.44 eV. The screening factor was calculated to be 0.48 eV.

3.1.2 Experiment

See Section 2.4 and 2.5 for the procedure of photoemission spectroscopy characterization and sample preparation.

3.1.3 Results

This section describes the results of photoemission spectroscopy measurements at the Al/P3HT and Ag/P3HT interfaces.

3.1.3.1 Al/P3HT interface

Figure 16 shows the XPS data of Al 2p, C 1s, and S 2p core levels emissions. The bottom spectrum in each panel correspond to the emissions from the freshly prepared Al surface. The C 1s peak related to P3HT is observed at 286.1 eV. The absence of a satellite peak at 290 eV indicates that the P3HT polymer did not break into small conjugated lengths. The S 2p emission originates from the sulfur atom in the thiophene ring. As the number of deposition steps progresses, the S 2p doublet grows in intensity.
and stays at a binding energy of 165.2 eV. The Al 2p emission is shown in the left panel. The characteristic Al 2p emission is shown at 72.9 eV. After the first deposition step of the P3HT polymer, the secondary emission at 75.6 eV arises. This is related to the oxidation of the Al surface caused by the residual O₂/H₂O gasses introduced during the deposition process.

**Figure 16 Al 2p (left), C 1s (center) and S 2p (right) XPS spectra.**

Figure 17 shows the corresponding UPS and LIXPS spectra. The bottom spectra show the secondary edge emission from the Al substrate. The work function of the Al substrate was determined to be 4.16 eV by subtracting the energy of the secondary edge cutoff from the photon energy. An abrupt shift was observed in both LIXPS and UPS spectra after the first deposition of the P3HT polymer. This shift is caused by the oxidation of the Al surface. Is should be noted here that this shift was solely attributed to
the oxidation reaction since a control experiment was performed ruling out the possibility of P3HT in contributing to the energy shift. In the LIXPS spectra, shown in the left panel, the secondary edge continues to shift towards lower binding energies. By measuring the energy difference between the secondary edge of the last deposition and oxidized Al surface, the interface dipole was determined to be -0.07 eV. The matching UPS spectra is shown in the right panel. UPS results show a similar shift as LIXPS results after the first few deposition steps. However, as the deposition proceed, the UPS spectra start deviating from the LIXPS spectra. The discrepancy between UPS and LIXPS develops as the P3HT film grows thicker.

Figure 17. LIXPS secondary edge spectra (left). A shift of the secondary edge was caused by the oxidation of Al surface. The interface dipole was determined to be -0.07 eV
Figure 18 shows the comparison of work function values calculated based on the LIXPS and UPS data plotted versus the injected volume of P3HT. As shown in the figure, the work function obtained from UPS measurements starts deviating from the LIXPS measurements, reaching an energy difference of 0.4 eV. This difference is related to the charging artifact encountered during UPS characterization. Since the X-ray photon flux during LIXPS measurement is several magnitudes weaker than the UV photon flux in UPS characterization, LIXPS is able to detect the onset of the charging artifact\textsuperscript{84,85}. Consequently, all work function values presented in this study are determined from the LIXPS spectra.

![Graph showing work function values vs. injected volume of P3HT](image)

**Figure 18** Comparison of work function value calculated based on LIXPS and UPS data plotted against injected volume of P3HT. The deviation of UPS from LIXPS is related to the charging artifact occurred during UPS characterization.

The left panel of Figure 19 shows the unprocessed UP spectra of each P3HT deposition. The right panel shows the same spectra enlarged at the valence bands/HOMO
emissions with the background removed for better comparison. The featureless spectrum of the Al substrate is shown at the bottom in each panel. The strong emission at around 7.5 eV occurred after the after deposition and is related to the O 2p-orbital of the Al-oxide layer. This feature attenuates as the P3HT film grows thicker. P3HT related features arise after depositing 0.08 ml at a low binding energy of 4-5 eV, which corresponding to the π-states emissions. The broad band between 5 and 12 eV is related to the σ-states in the backbone and hexyl side groups of P3HT. The HOMO energy of P3HT was determined to be 1.60 eV.

Figure 19 Raw UPS spectra (left) and HOMO/valence bands emissions with background removed (right). The P3HT related emissions are shown at 4-5 eV (π-states) and 5-12 eV (σ-states). The HOMO energy of P3HT was determined to be 1.60 eV.
The weak $\pi$-orbital related HOMO emission of P3HT is observed between 2 to 3 eV. The inset spectrum shows more details about the HOMO cutoff of P3HT. The HOMO energy of P3HT was measured at 1.60 eV by identifying the intercept point between the fitted line and the spectrum base line after the 1.88 ml deposition of P3HT.

![Figure 20 XPS spectra of Ag 3d (left), C 1s (center) and S 2p (right) core level emissions.](image)

### 3.1.3.2 Ag/P3HT interface

The Figure 20 shows the results of XPS measurements. The bottom spectrum in each graph is related to the sputter cleaned Ag substrate. The Ag 3$d$ emission (left) attenuates as the P3HT film grows in thickness. In the C 1$s$ panel (center), a weak emission is observed in the first two deposition steps of P3HT. This is related to residual hydrocarbon contamination on the Ag substrate. As the deposition proceeds, the characteristic P3HT C-C bond related emission arises at 285.2 eV. The S-C bond related
emission is shown in the S 2p panel at a binding energy of 164.3 eV.

Figure 21 Normalized LIXPS (left) and UPS (center) spectra. The stronger shift of secondary edge was related to the charging artifacts. The interface dipole was determined to be 0.45 eV by measuring the total shift of secondary edge.

The right panel of Figure 21 shows the valence bands/HOMO related emission of P3HT at the Ag/P3HT interface. The Ag d-band related emission is seen at 6-8 eV, which gradually attenuates and is replaced by the π-orbital related emissions (3-4 eV) from the thiophene rings in P3HT. The determination of the P3HT HOMO energy is shown in the inserted spectrum. The HOMO of P3HT was determined to be 0.80 eV by using the UPSpectrum after 0.88 ml deposition. The left panel and center panel of Figure 21 show the secondary edge measured using LIXPS and UPS respectively. A secondary edge shift is observed in both spectra. The shift in UPS spectra is again significantly larger than it is in the corresponding LIXPS spectra. Similar to the observation on Al/P3HT interface, this
phenomenon is also related to the occurrence of the charging artifact encountered during UPS measurement. By measuring the total energy shift of the secondary edge in the LIXPS spectra, an interface dipole of 0.45 eV was determined.

3.1.4 Discussion

The following discussion will focus on the investigation of Ag/P3HT and Al/P3HT interfaces. The orbital lineup of the two interfaces was determined. The results are discussed with respect to the IDIS model and the CNL value of P3HT was determined.

3.1.4.1 Al/P3HT orbital line-up

Although the application of electrospray avoided introducing significant contamination from the ambient environment in the sample preparation process, trace amounts of residual O₂/H₂O can still oxidize the Al substrate. However, at this moment this issue seems unavoidable while investigating the deposition of macromolecules on highly reactive metal substrates such as Al and Mg. Alternative solutions such as the evaporation of metals onto polymer thin films is not an option. This is due to the issue of inter-diffusion and/or chemical reaction encountered as the ‘hot’ metal atoms impinge on the polymer materials. In order to include the interface work function in the determination of the CNL value of P3HT, the influence of the Al oxide interlayer must be analyzed. As shown in Figure 16, the Al emission consists of the metallic and oxide peaks, which are located at 72.9 eV and 75.6 eV. In order to determine the thickness of the oxide a thickness estimation model was applied. In the equation below, \( N_m \) and \( N_o \) are the volume densities of the metal atoms in a metal oxide (cm⁻³); the ratio \( I_o/I_m \) is the intensity ratio between the metal and oxide components, determined from the fitting
results to the metal and oxide peaks; $\lambda_m$ and $\lambda_o$ are the inelastic mean free paths (IMFPs) of the appropriate photoelectrons in the metal and oxide, respectively (Å); $d$ is the oxide thickness (Å); $\theta$ is the electron take-off angle. In this study, the $N_m/N_o$ ratio of 1.5, $\lambda_m$ of 22, $\lambda_o$ of 24 and a take–off angle of 90º were used in calculating the thickness $d$.

$$d = \lambda_o \sin \theta \ln \left[ \frac{N_m \lambda_m}{N_o \lambda_o} \frac{l_o}{l_m} + 1 \right]$$

Equation 9

Figure 22 shows the calculated value of oxide thickness plotted versus the injected volume of P3HT. The final thickness of the oxide interlayer was determined to be around 15 Å. A potential issue that arises here is whether this Al-oxide layer will block the tunneling of the metal wave function into the polymer thin film; will the IDIS form on this interface?

![Graph showing oxide thickness plotted versus injected volume of P3HT.](image)

**Figure 22** The calculated value of oxide thickness plotted versus the injected volume of P3HT

Since the tailing metal wave function decays into the contacted material, the interaction strength between the metal substrate and polymer strongly depends on the thickness of the oxide interlayer. According to published results, significant tunneling can still occur between a metal and contacted material with an oxide interlayer with a
thickness up to 2 nm.\textsuperscript{91,92} This indicates that the wave function from the metal substrate can still interact with the polymer DOS to form the IDIS through charge transfer at the interface. However, the induced density of states would be less delocalized and more discrete due to the presence of the Al-oxide interlayer. The strength of interaction between the contacted materials will also be weakened by the 15 Å thick insulator. However, since the DOS on both sides should still be the same where materials are in direct contact, the number of induced states should be similar to the direct contact case. This indicates that the CNL should be at an energy position similar to the direct-contact case, since the CNL is defined as the energy level where the material is in a donor or acceptor like state.

An advantage of having this oxide interlayer is that it prevented strong chemical reaction between the two material layers. It was reported that thermo-evaporated Al reacts with the α carbons of P3HT.\textsuperscript{93} This would change the electron density of these atoms and the neighboring sulfur atoms. Another effect of the Al-oxide layer is that the work function of the Al substrate is further reduced. Since the orbital alignment is established on oxide covered Al, the work function of the oxidized surface should be used for the discussion of IDIS model. Although a direct-contact interface was not achieved in the presented experiment due to the oxidation of Al surface, the low work function at the metal/polymer interface can still be used for the CNL calculation of P3HT.

Next, the orbital line-up of the Al/P3HT interface was determined. This requires the evaluation of HOMO binding energy of P3HT. Due to the low signal to noise ratio of UPS at low binding energies, the HOMO position determined from the spectrum in Figure 19 must be confirmed by an alternative approach. The HOMO position can also be
calculated from the core level energy, since the energy differences between core level emissions and the HOMO position are constants. In this case, the S 2p core level was selected for the calculation of P3HT HOMO energy. This emission was chosen as it is the most characteristic core level emission of P3HT. The energy difference between the S 2p and the P3HT HOMO position was obtained from a previous study as 163.59 eV. The HOMO position of P3HT at this interface is calculated to be 1.61 eV by subtracting this energy difference from the binding energy of the S 2p core level in this experiment. This estimated value is in very good agreement with the graphically determined HOMO position (1.60 eV). It is interesting to note that the HOMO position of P3HT is at a higher binding energy in comparison with the previously studied P3HT interfaces. The HOMO energy of P3HT of this interface is about 1.2 eV larger than HOMO on highly oriented pyrolytic graphite (HOPG). The C1s and S 2p core levels also show similar 1.0 eV shifts in comparison with the HOPG interface. These shifts of both the HOMO and core levels are caused by oxidization of the Al surface. Oxidation of the Al surface results in a 1.0 eV reduction of the work function after the first deposition, which causes a downward shift of the entire P3HT spectrum.

Figure 23 shows the complete orbital line-up of the Al/P3HT interface. The work function reduction (Δ) is caused by the oxidation of the surface of Al substrate and this value was determined to be 1.00 eV. The 15 Å thick oxide interlayer is located between Al and the P3HT thin film. The interface dipole related to the CNL calculation was determined to be -0.07 eV. The hole injection barrier (Φ_h) was determined from the HOMO energy of P3HT, which is 1.60 eV. The corresponding electron injection barrier (Φ_e) was calculated to be 0.92 eV by subtracting the Φ_h from the P3HT transport gap
(2.52 eV) measured using inverse photoemission spectroscopy. The ionization energy of P3HT is determined to be 4.83 eV by adding \( \Phi_h \) to the work function. This result is in good agreement with previous publications.  

Figure 23 Orbital line-up at the Al/P3HT interface.

3.1.4.2 Ag/P3HT orbital line-up

The orbital alignment of the Ag/P3HT interface is shown in Figure 24. The hole injection barrier \( \Phi_h \), determined from the HOMO cutoff shown in Figure 21 is 0.80 eV. The interface dipole \( eD \) was determined to be 0.45 eV as calculated in section 3.1.3.2. The ionization energy of P3HT was determined to be 4.92 eV from the secondary edge cutoff energy in combination with the HOMO energy of P3HT. Considering the uncertainty of photoemission measurements is \( \pm 0.1 \) eV, this value is in good agreement
with the ionization energy calculated for the Al/P3HT interface.

![Diagram of Orbital line-up at the Ag/P3HT interface.]

Figure 24 Orbital line-up at the Ag/P3HT interface.

### 3.1.4.3 Charge neutrality level of P3HT

The most distinguishing feature of the IDIS model is the linear correlation between energy barriers and metal substrate work functions. By using the same method as Vazquez\textsuperscript{26}, the results of this experiment are discussed to test the validity of the IDIS model for metal/polymer interfaces.

As shown in Figure 25, the hole injection barriers obtained from the investigated interfaces are summarized and plotted against their corresponding substrate work functions. The data were fitted with a linear regression. The linear dependency between hole injection barriers and their corresponding substrate work function demonstrates that the IDIS model can be applied for polymer/metal interfaces. The Schottky-Mott limit (dashed line) is plotted on the chart for better comparison with the fitted line. The
difference between the two lines represents the value of dipole to be expected at P3HT interfaces to a substrate with a particular work function. All the data shown in Figure 25 are summarized in Table 1.

Figure 25 Hole injection barrier plotted versus the work function of corresponding metal substrate. The slope of the fitted line represents the ‘screening factor’ S. The position of the CNL of P3HT is determined from the intersection between the fitted line and Schottky-Mott limit (dashed line).
According to the IDIS model, a linear relationship is established between the interface dipole and the energy difference between substrate work function and the CNL,

\[ eD = (1 - S)(\Phi_m - CNL) \]

\[ \iff CNL = \Phi_m - \frac{eD}{1 - S} \quad \text{Equation 10} \]

From the equation above, the CNL can be directly determined from the intersection point between the regression line and the Schottky-Mott line, since this intersection represents the case of a direct alignment between the CNL and metal Fermi level. The slope of the fitted line represents to the ‘screening factor’ \( S \) which appears in the IDIS model and was determined to be 0.48. Consequently, the CNL was determined to be 3.44 eV from Figure 25.

It is interesting to compare the screening parameter determined here with the slope estimated using Mönch’s empirical model. The formula to determine the slope parameter is given by,
\[ S = \frac{A_x}{1 + 0.1(\varepsilon_\infty - 1)^2}. \]  

Equation 11

The \( \varepsilon_\infty \) term is the relative permittivity of the organic material and \( A_x \) is a constant proportional factor (0.86 eV) for the linear correlation between work function and electronegativity of the contact metals. By applying a \( \varepsilon_\infty \) value of 2.6 to Equation 11, a slope parameter of 0.69 was determined. This value is 50% larger than the experimentally obtained screening factor determined here. It is interesting to see that most organic interfaces calculated using Mönch’s model appear to have larger screening parameters than those determined by the IDIS model. This is probably due to the weak interaction between organic materials and metals compared to the covalent bonds present at inorganic interfaces.

It is interesting to compare the CNL determined here with the small molecular material pentacene, which has a similar ionization energy and band gap to P3HT (\( E_i = 5.0 \) eV, \( E_g = 2.20 \) eV).\(^{27}\) Figure 26 shows the comparison of energy diagrams of the two materials. The CNL of P3HT (3.44 eV) is in close agreement with the theoretically calculated (3.80 eV)\(^{98}\) and experimentally determined (3.69 eV)\(^{99}\) CNL of pentacene. The slope parameter at the P3HT interface (0.48) is also close to experimentally determined slope parameter of pentacene (0.39)\(^99\). This is reasonable since both materials are in \( \pi \)-conjugated structures and the interaction between organic materials and metals are mainly through Van Der Waals forces. The differences between the slope parameter values are probably related to the structural differences between the two materials and the different experimental methodologies utilized.
Figure 26 Energy diagrams of Pentacene (left) and P3HT (right). The positions of the CNLs are marked by the dashed lines.

Al/P3HT and Ag/P3HT interfaces were deposited using electrospray deposition and investigated by photoemission spectroscopy. These results are combined with a previous study on the Au/P3HT interface. A linear correlation between barrier heights and substrate work functions indicates that the IDIS model may also be valid for metal/polymer interfaces. The corresponding screening factor and charge neutrality level (CNL) of P3HT were determined to be 0.48 and 3.44 eV respectively relative to the vacuum level.
3.2 MEH-PPV interfaces

The experiments in section 3.1 demonstrated that the IDIS is valid for metal/polymer interfaces. The following section focuses on the results of a study performed on metal/MEH-PPV interfaces. The presented work has been published in Langmuir.

3.2.1 Introduction

A model developed in parallel to the IDIS model is the “integer charge transfer” (ICT) model, which was based on experiments of spin-coated polymer films deposited on evaporated metal interfaces. It was concluded that a vacuum level alignment would establish at the interface as long as the metal Fermi level was within the polaron band gap of the polymer material. If the metal Fermi level were above or below the polaron band gap, the polaron states would be pinned at the metal Fermi level. It is interesting to compare the IDIS model with the ICT model. However, it should be noted that the IDIS model was developed for interfaces prepared in vacuum in the absence of ambient contamination, while the ICT model was applied mainly to contacts “insulated” by a certain degree of contamination introduced during sample preparation. Since the experimental results presented here are obtained from in-vacuum prepared metal/polymer interfaces, this allows for a direct comparison between the ICT and IDIS models regarding their validity on metal/polymer interfaces.

In the presented work, poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) was selected as the polymer to be investigated due to its extensive applications in organic electronic devices. The results obtained from the experiment performed on Al substrates expands the data set towards the lower work function
substrate. Combined with the results of previous measurements on Au and Ag substrates, the CNL of MEH-PPV was calculated based on the hole injection energy barriers and their corresponding substrate work functions. The linear correlation between the energy barrier heights and the corresponding work function suggests the IDIS model is also valid for metal/polymer interfaces provided they are clean. The ICT model on the other hand appears to comply only with interfaces which contain a hydrocarbon contamination layer.

### 3.2.2 Experiment

See Section 2.4 and 2.5 for the procedure of photoemission spectroscopy characterization and sample preparation.

### 3.2.3 Results

Figure 27 shows the core level emissions of Al 2p, C 1s and O 1s. The initial spectrum in each picture corresponds to the emission from a freshly prepared Al substrate. The following spectra show the emission from sample surface after each deposition. The left panel reveals the Al 2p emission. The characteristic emission from metallic Al atoms is located at 72.9 eV. A side peak at 75.7 eV appears after the first deposition of MEH-PPV. This is due to the partial oxidation reaction of the Al surface caused by residual O₂/H₂O during electrospray. More details regarding the influence of this oxidation reaction will be covered in the following section. The O 1s emission at 532.4 eV shown in the right panel also corresponds the oxidation of Al surface. As the polymer film grows, the C-O related side peak develops and dominates the O emission after the last deposition step. The C 1s emission is shown in the center panel of Figure 27.
The emission at 286.2 eV is related to the residual solvent molecules (toluene) on the sample surface. It should be noted that this binding energy is in excellent agreement with a control experiment (not shown here) where pure solvent was used as the injected solution. As the electrospray deposition proceeds the residual toluene peak is gradually replaced by the emission located at 285.6 eV, corresponding to the emission of the C-C bond from the alkane chains of the MEH-PPV polymer. The side peak at 286.8 eV is related to the C-O bond in the alkoxy groups in MEH-PPV.

![XPS spectra](image)

**Figure 27 XPS spectra of Al 2p (left), C 1s (center) and O 1s (right) emissions with background removed.**

Figure 28 shows the secondary edge spectra measured using LIXPS. The reason that LIXPS was selected is to exclude the influence of the charging artifacts encountered during UPS measurements. LIXPS prevents the charging artifact as the photon flux is magnitudes lower than that of UPS\(^{84, 102}\). The bottom spectrum corresponds to emission from the clean metal substrate. After the first deposition of MEH-PPV a shift of 1.16 eV shift of the secondary edge towards higher binding energy is observed. This shift is caused by the oxidation of the Al substrate during the electrospray process. It should be
noted here that the shifted secondary cutoff generally reflects the work function of the oxidized Al surface with limited contribution from the MEH-PPV film. The work function value obtained here was consistent with the one obtained from the control experiment mentioned above. As the deposition proceeds, the secondary edge shifts to lower binding energies. A measurement of the secondary edge difference between the metal substrate and the last deposition allows for the calculation of the interface dipole related to the CNL calculation of MEH-PPV.

**Figure 28** LIXPS (left). The strong shift of secondary edge towards higher values is caused by the oxidation of Al surface. Complete UPS spectra (center). The strong emission at around 7.4 eV is related to the emission from the Al-oxide layer. MEH-PPV HOMO related emissions gradually replaced Al-oxide valence band emission at the last few depositions. Valence band/HOMO related emissions (right). The HOMO energy of MEH-PPV was determined to be 2.17 eV as shown in the inserted graph.

The center picture of Figure 28 shows the raw UPS data of all deposition steps. The right panel shows the valence band/HOMO region with background removed. The
bottom spectrum corresponds to the freshly prepared Al substrate. Due to the weak emission from Al substrate, the spectrum is magnified for better comparison. The broad peak located at around 7.4 eV is related to the O 2p emission from the chemiabsorbed O atoms in Al-oxide formed during electrospray. As more MEH-PPV is deposited, the MEH-PPV HOMO emission increases in intensity and replaces the Al oxide valence band related emission during the last few depositions. As shown in the right panel, these spectra are also magnified due to their weak emission intensities. Considering the potential influence from the charging artifact to the HOMO position at the 6.88 ml deposition step, the spectrum of the 3.88 ml deposition was chosen to determine the MEH-PPV HOMO energy, shown in the inserted graph.

### 3.2.4 Discussion

The primary objective of this study is the determination of the CNL of MEH-PPV. This result is combined with a previous study to determine the CNL of MEH-PPV. The orbital alignment of the Al/MEH-PPV interface is discussed with regard to the IDIS and ICT models.

#### 3.2.4.1 Al/MEH-PPV orbital line-up

Although electrospray significantly reduces the amount of sample surface contamination, the highly chemically reactive Al substrate can be oxidized by trace amounts of O₂/H₂O introduced during solution injection. This oxidation phenomenon is consistent with the Al/P3HT interface discussed in section 3.1.4.1. An alternative sample preparation method (evaporation of Al onto the polymer film in vacuum) was performed but excluded from the results, as interdiffusion and strong chemical reactions occurred at the direct contact between polymer and vaporized metal material. In order to evaluate
the influence of this oxide layer on the Al/MEH-PPV interface, its thickness is estimated by using Strohmeier’s thickness estimation model: 

$$d = \lambda_o \sin \theta \ln \left[ \frac{N_m \lambda_m}{N_o \lambda_o} \frac{l_o}{l_m} + 1 \right]$$

Equation 9

For details regarding the parameters shown in this equation, see section 3.1.4.1. Figure 29 shows the estimated thickness plotted versus the corresponding volume of injected solution. The final thickness of this oxide layer is determined to be 16.4 Å. Since the metal wave function exponentially decays into the band gap of the material in contact, the thickness of this oxide interlayer strongly affects the formation of IDIS. According to the published studies, significant tunneling can still occur between the materials in contact in the presence of an interlayer with a thickness of up to 2 nm. Therefore, IDIS can still form at the investigated interface as a result of hybridization of metal wave function the metal and MEH-PPV molecular orbitals. However, the strength of the interaction between the two materials is reduced due to the presence of the thin oxide interlayer. This results in a less delocalized induced density of states The induced density of states should have more discrete features than in the case where metal and polymer materials are directly in contact. However, since the band gap of Al-oxide is broad and featureless, the influence of the DOS of Al oxide to the IDIS is limited or even negligible. Because of this thin Al-oxide interlayers were usually considered as a surface modification layers instead of insulators. Since the DOS of the metal and the polymer are the same despite the presence of an interlayer, the CNL of MEH-PPV should be at a similar energy in comparison with a direct-contact case.
Figure 29 Thickness of Al-oxide plotted against the volume of injected solution. The final thickness of Al-oxide is calculated to be 16.8 Å.

Similar to the Al/P3HT interface, the Al-oxide interlayer blocked strong chemical interactions between the Al metal substrate and MEH-PPV polymer. This is supported by the absence of an emission at a binding energy located at 283 eV in the XPS measurements. This peak corresponds to the emission of carbon-metal bonds from the reaction between Al and the alkoxy groups in MEH-PPV.\textsuperscript{51, 52} It is known that the partial decomposition of the alkoxy groups could change the hole transporting abilities of the MEH-PPV in a device,\textsuperscript{106} and also reduce the Coulomb interaction and relaxation energy of exitons.\textsuperscript{107} The reaction also introduces localized trap states or distributed states.\textsuperscript{52, 108} The effects of these reactions on device performance are hard to predict. The thin oxide layer presented here appears have prevented chemical reactions between the contacted materials, yet still allows significant charge transfer between the two sides to form the induced density of states.

Figure 30 shows the orbital line-up of the Al/MEH-PPV interface, summarizing the analysis above. The thin Al oxide interlayer (light grey area) is located between the
Al substrate and the MEH-PPV film. The work function reduction (Δ) of 1.16 eV is caused by the oxidation of the Al substrate. The work function of the Al substrate covered with the oxide layer was determined to be 3.14 eV. The interface dipole (eD) for the CNL calculation was determined to be -0.43 eV. The hole injection barrier (Φ_h) was determined to be 2.17 eV, which corresponds to the energy of MEH-PPV HOMO.

The corresponding electron injection barrier (Φ_e) was calculated to be 0.28 eV, by decuting the Φ_h from the MEH-PPV band gap (2.45 eV) determined by Campbell et al. The ionization energy of MEH-PPV was determined to be 5.74 eV. This value is in good agreement with the published study.
3.2.4.2 CNL of MEH-PPV

According to the IDIS model a linear correlation exists between the charge transfer barriers and their corresponding work function values, the linearity of such correlation was defined as the ‘screening factor’ $S$. This value between organic materials depending on their screening abilities at different organic/metal interfaces.\textsuperscript{12, 24}

![Graph showing CNL of MEH-PPV](image)

**Figure 31** $\Phi_h$ plotted against the work function of metal substrates. Solid circles: Presented results. Empty triangles: Internal photoemission measurements by Campbell. Solid triangles: $I$-$V$ measurements by Parker.\textsuperscript{109} In order to determine the screening factor $S$ of MEH-PPV, the $\Phi_h$ value obtained from each interface was summarized and plotted in Figure 31 against the substrate work function. The solid circles represent the experimentally obtained data from this study combined with previously published results.\textsuperscript{28, 111} The low work function point (3.14 eV)
shown in the graph corresponds to the results obtained in the present study. The Schottky-Mott limit (vacuum level alignment) is also plotted in the graph for better comparison with the fitted line. The screening parameter $S$ was directly determined to be 0.21 from the slope of the fitted line. From Equation 10 (see section 3.1.4.3), the CNL of MEH-PPV is immediately determined to be 3.76 eV from the intersection between the fitted line and the Schottky-Mott limit. The intersection point corresponds to a direct lineup between the CNL and the metal Fermi level. The difference between the two corresponds to the interface dipole to be expected at an interface given a certain work function.

It is interesting to discuss these results with regard to the ICT model, which proposes that there is vacuum level alignment as long as the metal Fermi level is within the polaron band gap of the organic material in contact. To the best of our knowledge, no photoemission results are available which investigate the ICT model. Published results from Campbell$^{109}$ and Parker$^{110}$ obtained from electroabsorption and $I-V$ measurements, are used in this study. In their studies$^{109,110}$, the metal layers were evaporated onto polymer films that had been prepared by spin-coating. This is similar to the experiments that used in the development of the ICT model. Their results are shown as the open and the filled triangles in Figure 31. It is obvious to see that the slopes determined by Campbell and Parker are close to 1, indicating vacuum level alignment, hence proving the prediction of the ICT model. The offset between the two lines is probably due to the presence of ambient contamination and different measurement methods.

Based on the comparison to the in-vacuum interface, the ICT model appears to be valid at polymer interfaces where a contamination layer is present. This layer separates
the materials in contact and alters the orbital line-up at the interfaces. The consequence of
having a contamination layer is that there is vacuum level alignment with little to no
interface dipole. On the other hand, the in-vacuum prepared interface creates an intimate
and abrupt contact, resulting in the formation of an interface dipole. The direction and
magnitude of the interface dipole is determined by the interaction between the metal and
the polymer and the screening ability of the polymer.112 These conclusions are similar to
the results of recent studies on small molecular material/metal interfaces with and without
ambient contamination layers.112,113 It was reported that the contamination layer can
cause the reduction of the metal substrate work function, and the formation of a
significant interface dipole at the metal surface. The subsequently deposited molecules
have little contribution to the magnitude of this dipole. This indicates that the deposited
molecular film actually forms a secondary “heterojunction” on top of the contamination
covered metal surface, while the dipole formed at this surface is a result of the localized
charge transfer between the contamination film and the metal substrate. The ICT model
applies to metal/polymer interfaces, that is, a vacuum level alignment at with the
molecular film contact, if the metal surface with contamination is treated as the substrate
for the polymer/metal interface formation.

To sum up, the orbital line-up at Al/MEH-PPV interface was determined using
electrospray deposition and photoemission spectroscopy. The CNL of MEH-PPV was
determined to be 3.76 eV relative to vacuum level. The screening factor $S$ was calculated
to be 0.21. The results indicate that conjugated polymer interfaces conform to the IDIS
model as long as they are contamination free. The results were also discussed with regard
to the ICT model. The comparison between the in-vacuum prepared interfaces to those
with ambient contamination present suggests that surface contamination separates the materials in contact and alters the orbital line-up at the interfaces, resulting a vacuum level alignment between the contacted metal and polymer.
Chapter 4 Investigation of Polymer/polymer Heterojunction

4.1 Introduction

In the past few years, the concepts of CNL and induced density of interface states (IDIS) have been extended to the organic/organic heterojunction interface. The magnitude and direction of charge transfer are determined by the relative energies the two CNLs of the contacted organic materials. Similar to the model for metal/organic interfaces, the interface dipole at heterojunctions can be calculated using the materials CNLs and “screening factors”, which describe the strength of the interactions between the organic materials in contact.

The prediction of the IDIS model with organic/organic heterojunction is consistent with the experimental results for small molecular organic interfaces. However, the validity of the IDIS model on polymer/polymer heterojunctions remains unknown since no related study has been performed on these types of interfaces. The experimental results in Chapter 3 have demonstrated that the model is valid for metal/polymer interfaces. The CNL of two prototypical polymers, poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) were determined previously. In light of these results, it is hypothesized that the IDIS model can also be applied to polymer/polymer heterojunctions. Another interesting aspect is to investigate the heterojunction electronic structure with regard to the ICT model. It was reported that the ICT model
can be applied in determining the orbital line-up of organic/organic heterojunctions by using the same principles applied when calculating the metal/organic interface\textsuperscript{36,41}. Predictions of both models were investigated to determine which of the two, if either, accurately predicted the measured orbital line up.

An integrated electrospray deposition apparatus and an XPS and Ultraviolet photoemission spectroscopy system allowed \textit{in situ} sample preparation and characterization. Based on the results of this experiment, the orbital line-up of the MEH-PPV/P3HT heterojunction was determined. Combined with previous studies, the experimental results are discussed with regard to the IDIS model. The results indicate that the IDIS model is also valid for polymer/polymer heterojunction interfaces. The comparison between predictions based on the IDIS model with the ICT model suggests that IDIS can more accurately predict the orbital line-up of contamination free interfaces.

4.2 Experiment

The MEH-PPV/P3HT heterojunction structure was fabricated on top of a gold substrate and characterized with photoemission spectroscopy. For more details regarding the sample preparation and characterization procedures, see section 2.4 and section 2.5.

4.3 Results

Figure 32 shows the XPS measurements of the Au 4\textit{f} (left), O 1\textit{s} (center) and C 1\textit{s} (right) core levels before and after the deposition of MEH-PPV and P3HT. The bottom spectrum in each panel (colored black) correspond to the measurements of the pristine Au substrate. The sequential measurement spectra following the deposition of MEH-PPV and P3HT are distinguished by their green and blue color respectively. The left panel
shows typical Au 4f emissions, whose intensity attenuates during the polymer deposition process. The O 1s emission is shown in the center panel. The emission from oxygen is attributed to the C-O bond in the side chains of MEH-PPV polymer. As expected, the intensity of the emission at 533 eV binding energy gradually strengthens as a result of the growth of MEH-PPV film. This peak’s intensity decreases as the MEH-PPV is subsequently covered by the P3HT deposited on its surface. A weak emission at lower energy (532.6 eV) is observed after the first deposition.

Figure 32 Au 4f (left), O 1s (center) and C 1s (right) background removed XP spectra during the polymer deposition. The green spectra show the MEH-PPV deposition sequence. The blue spectra correspond to the P3HT depositions. This is most likely due to the residual atmospheric O₂/H₂O, which contaminated the film during the electrospray deposition process. The C 1s spectra shown in the right panel show a faint peak (284.6 eV) after the initial deposition of MEH-PPV. This peak is most likely related to the absorption of a small amount of residual toluene on the Au surface.
This solvent related emission is suppressed later by deposited MEH-PPV and P3HT characteristic emissions. The major emission near 285 eV corresponds to the C-C bonds in both MEH-PPV and P3HT. The emission that appeared as a shoulder peak (286.2 eV) in the deposition of MEH-PPV is related to the C-O bonds in MEH-PPV side chains.

The right panel of Figure 33 shows the background-removed UP-spectra of the deposition sequence. The bottom spectrum corresponds to the sputtered cleaned Au substrate. In order to better compare results, the Au spectrum shown is scaled to one tenth of its original intensity. The typical d-band related emissions (2-7 eV) of the Au substrate are gradually suppressed by the characteristic emissions from the MEH-PPV HOMO, which is later replaced by the emerging P3HT HOMO related emissions. The insets show how the HOMO energy was determined for each polymer. The left panel shows the LIXPS measurements of the secondary edge of the sample. The reason that LIXPS was selected for the secondary edge measurements was due to charging artifacts observed during the UPS measurements (not shown here), which strongly affect the measurement accuracy when determining the secondary edge. Charging artifacts occur much less when using LIXPS than with UPS. This is due to the photon intensity of X-ray flux of LIXPS, which is several magnitudes lower than that of the UV source. For more details about LIXPS, see Ref.84, 102. After the first two depositions of MEH-PPV, the sample secondary edge shifts significantly (1.09 eV) towards higher binding energy. The abrupt shift of the secondary edge corresponds to the formation of a surface dipole. The secondary edge shifts minimally in the following MEH-PPV and P3HT deposition steps. The slight energy difference between the secondary edges of the sample surface deposited with
MEH-PPV (0.15 ml) and P3HT (0.75 ml) yielded a small interface dipole (0.04 eV).

Figure 33 The LIXPS spectra (left) show the positions of secondary edges. The background-removed UP-spectra (right) show the valence band emission of deposition sequence. HOMO energies of P3HT and MEH-PPV are determined to be 0.50 eV and 1.53 eV respectively.

4.4 Discussion

The main focus of this study was the investigation of the orbital line-up at the MEH-PPV/P3HT heterojunction. The obtained results were compared with predictions made using the IDIS model in order to test its validity of the model on polymer heterojunctions. Figure 34 a. (left) shows the orbital line-up, summarizing the experimental results. Figure 34 b. (center) and Figure 34 c. (right) show the predicted
orbital line-up at the MEH-PPV/P3HT interface based on the IDIS and ICT models respectively. All orbital line-ups have the same scale and are aligned with their respective Fermi-levels for better comparison. The orbital line-up determined from the experimental data presented here will be discussed in Section 3.4.1 while Section 3.4.2 will focus on the comparison between the two orbital line-ups predicted from the IDIS and ICT models.

Figure 34 a. (left) The orbital line-up of MEH-PPV/P3HT heterojunction determined from the presented data. b. (center) The orbital line-up predicted based on IDIS model. c. (right) The orbital line-up predicted based on ICT model. The comparison among the three orbital line-ups shows that the IDIS model appears to be more accurate in predicting the orbital line-up of polymer heterojunction than the ICT model.

4.4.1 MEH-PPV/P3HT Orbital Line-up

Figure 34 a shows the orbital line-up at the MEH-PPV/P3HT heterojunction determined from experimental data. The initial surface dipole (Δ) of 1.09 eV was calculated from the work function difference between the sputter-cleaned Au substrate and the 0.15 ml MEH-PPV deposition step. This value is in perfect agreement with published results\(^\text{111}\). It is interesting to note that this result is in direct contrast with the interface prepared in ambient environment, where almost no surface dipole is formed.
between the metal substrate and polymer material\textsuperscript{115}. This difference can be explained by the “push-back effect\textsuperscript{8}” caused by the ambient contamination on clean metal surface. Since it is known that an ambient contamination layer will push tailing electrons back into a metal substrate, the work function value of a contaminated surface is greatly reduced. Consequently, vacuum level alignment applies when no dipole forms at the contaminated interface\textsuperscript{115}. However, in the data presented here, the absence of significant contamination from ambient environment allows an intimate contact between the metal substrate and MEH-PPV polymer. The formation of a significant interface dipole is caused by charge transfer occurring at the contact interface.

The dipole at the MEH-PPV/P3HT heterojunction was determined to be 0.04 eV from the difference between the work function of the sample surface covered with the MEH-PPV (0.15 ml deposition step) and the final work function of the sample covered with the P3HT (0.75 ml) thin film. By subtracting the HOMO energy of P3HT from the HOMO energy of MEH-PPV, the hole injection barrier ($\Phi_h$) was determined to be 1.03 eV. The band gap energy of MEH-PPV and P3HT used in this work are 2.45 eV\textsuperscript{109} and 2.52 eV\textsuperscript{96} respectively. The corresponding electron injection barrier was calculated by adding the band gap difference and the HOMO energy difference between each polymer, i.e. (2.52-2.45)+(1.53-0.50)=1.10 eV.

**4.4.2 IDIS and ICT Models**

The primary objective of this study is to determine the validity of IDIS model at polymer/polymer heterojunctions. According to the IDIS model, the alignment of an organic/organic heterojunction is determined by the tendency of CNLs to align. The energy difference between the two CNLs determines the direction and magnitude of
charge transfer between the two sides. This is slightly different than the model for metal/organic interfaces where the CNL of an organic material aligns with the CNL of the contacted organic material to reach equilibrium instead of aligning with the Fermi-level of the contacted material.\(^{23}\) The formula to calculate the interface dipole for organic/organic heterojunction is given by:\(^ {23}\)

\[ S_{oo} = \frac{1}{2} \left( \frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} \right) \]

Equation 4

and

\[ eD = (1 - S_{oo})(CNL_1 - CNL_2) \]

Equation 3

where \( S_{oo} \) is the screening factor for the O/O heterojunction, \( \varepsilon_1, \varepsilon_2 \) are the dielectric constants of the two materials respectively. The value of \( S_{oo} \) is proportional to the inverse of the static dielectric functions, assuming the potential drop occurs half the distance between both materials. The dipole at O/O heterojunctions, \( eD \), is determined by the energy offset of the two CNLs, which is screened by the factor \( S_{oo} \) estimated above. See Section 1.2.1 for more details regarding the IDIS model for organic/organic heterojunctions.

Based on the prediction of the IDIS model, the MEH-PPV/P3HT orbital alignment is plotted and shown in Figure 34 b (center). The orbital alignments of the Au/MEH-PPV and MEH-PPV/P3HT interfaces were predicted using the corresponding metal/organic model and organic/organic model in the IDIS theory respectively. Since the Au/MEH-PPV interface was already extensively discussed in a previous study\(^ {111}\), the following discussion will focus on the study of the electronic structure of MEH-PPV/P3HT heterojunction. The work function of the Au substrate was determined to be 5.53 eV by LIXPS measurement. This value was used as the substrate work function in generating the IDIS and ICT (see below) orbital alignments in this discussion. The
screening factor and CNL for MEH-PPV were extracted from our recent study. By applying a screening factor $S$ of 0.21 and a CNL of 3.76 eV for MEH-PPV, the initial dipole $\Delta$ at the metal/polymer interface was determined to be 1.40 eV. The relative permittivity values of 2.6 for P3HT and 3.61 for MEH-PPV were used for the determination of the screening factor at the polymer heterojunction. By inserting these numbers into Equation 4, a screening factor for the heterojunction, $S_{oo}$ was calculated to be 0.33. The CNL of P3HT (3.44 eV) relative to the vacuum level was determined in previous studies. Using the $S_{oo}$ and CNLs of both polymers in Equation 3, the dipole at the polymer/polymer heterojunction was determined to be 0.21 eV.

Figure 34 c (right) shows the orbital-line-up predicted by the ICT model. For better comparison with the IDIS model, the same substrate work function of 5.53 eV was used in the orbital line-up. According to the principles of the ICT model, if the metal Fermi-level exceeds the band gap of polaron (or the so called “ICT”) states, the Fermi-level is pinned at the polaron state. In this case, since the substrate work function exceeded the ICT$^+$ state of METH-PPV (5.4 eV), the Au Fermi level is pinned to the ICT$^+$ state yielding a small interface dipole of 0.13 eV at the Au/MEH-PPV interface.

The orbital alignment at the heterojunction can also be predicted if the Au substrate covered with MEH-PPV is considered a “new” substrate from the perspective of the P3HT. This estimation method is similar to experiments on polymer/molecule and molecule/molecule interfaces where the metal substrate is first covered with an organic material and is treated as the substrate for the deposition of a second molecular material in. In this case, the work function of the “new” substrate exceeded the ICT$^+$ state (4.0 eV) of P3HT by 1.40 eV. This potential difference would trigger a charge transfer
between the two side and results in a large dipole of 1.40 eV at the MEH-PPV/P3HT heterojunction.

When predicting the orbital lineups, the ICT and IDIS models produced different results. The dipole (0.21 eV) at the P3HT/MEH-PPV heterojunction predicted by the IDIS model is significantly smaller than the dipole predicted by the ICT model (1.40 eV). This dipole is also relatively closer to the experimental value (0.04 eV). This is most likely due to the fact the ICT model was developed based on experimental results where the organic interfaces were prepared in ambient environment, resulting in a layer of ambient contamination located between the metal substrates and the organic materials in contact. This contamination layer can strongly reduce the work function of metal substrates, resulting in a significant interface dipole. Because of this, values of metal work function presented in the experiments related to the study of the ICT model are usually smaller than those of pristine metals without ambient contamination. If the work function of a naturally passivated Au substrate (4.4-4.5 eV) were used for the prediction by the ICT model, the Fermi level of the substrate would be located within the polaron band gap of MEH-PPV, leading to a near vacuum level alignment orbital line-up between the metal and the MEH-PPV film. Consequently, a dipole of 0.4-0.5 eV would be anticipated at the MEH-PPV/P3HT heterojunction when treating the Au/contamination/MEH-PPV sandwich-like structure as the substrate for the P3HT polymer thin film. This value is more reasonable than the significant heterojunction dipole predicted based on the in-vacuum prepared interface from this study. This deviation also demonstrated that the ICT should not be applied to interfaces prepared in vacuum, since little to no contamination exists between the materials in contact at such
interfaces. The contamination layer alters the interface orbital alignment and plays an important role in the ICT model.

In comparison with the ICT model, the orbital line-up predicted by the IDIS model is much closer to that calculated from the experimentally obtained results. This is not surprising, since the IDIS model was developed in order to predict orbital alignments of interfaces prepared in vacuum conditions without significant surface contamination. These results also demonstrate that the IDIS model is also valid at polymer/polymer heterojunction interfaces. It is interesting to note that the calculated dipole (0.2 eV) at the polymer heterojunction is much smaller than the dipoles at metal/polymer interfaces. This suggests only limited interaction occurred at the polymer heterojunction interface. This difference can most likely be explained by the differences in weights of participation of the metal induced density of states at different interfaces. At the metal/polymer interfaces, the contact between polymer and metal is intimate. The induced density of interface states results in the redistribution and delocalization of the electrons between the two sides and the formation of an interface dipole. However, at the polymer heterojunction presented here, the metal substrate and the P3HT layer are separated by the MEH-PPV interlayer with a thickness of 44.5 Å (the thickness is estimated by using an exponential decay function, see Dam et al. for more details). The possibility of the wave function of the metal tailing into the P3HT layer would be significantly reduced or even eliminated due to the separation caused by the MEH-PPV film. Consequently, the metal wave function may have a very limited contribution on the electron delocalization at the polymer heterojunction. It is more likely that the polymers are only physically attached to each other through Van Der Waals force, a much weaker bond in comparison
to the interactions experienced at the metal/polymer interface. To summarize, the potential difference can be screened better at metal/polymer interfaces than at polymer/polymer interfaces due to the presence of more delocalized electrons at metal/polymer interfaces than at polymer/polymer interfaces. This results in a much smaller dipole at polymer heterojunctions than at metal/polymer interface. The 0.16 eV discrepancy between the dipoles of IDIS scenario and experimental result is close to the ±0.1 eV measurement uncertainty.

In conclusion, the IDIS model is valid at polymer/polymer heterojunctions. This model appears to be more accurate in predicting the orbital line-up of polymer heterojunctions than the ICT model. This is most likely due to the fact that the interfaces presented here are prepared in vacuum, therefore excluding significant ambient contamination. The intimate contact between the metal and polymer and the contact between polymer and polymer allows for more intense interaction between contacted materials without interference from an environmental contamination interlayer. The ICT model may be applied to interfaces with ambient contamination present. However, the explanations on the mechanism of charge transfer and energy alignment are general and intuitive. Considering the present study combined data from different experimental methodologies in the analysis, further experiments with well controlled interfaces are required to explore the effect of the polymer structure and contamination on the formation of interface energy structures.
Conclusion

The dissertation presented here investigated the energy alignments at different polymer interfaces with regard to the IDIS model. The first part of the dissertation explained the results of metal/P3HT and metal/MEH-PPV interfaces. These interfaces were prepared by electrospray deposition in order to avoid surface contamination. The orbital line-up of each respective interface was determined from the data collected through photoemission spectroscopy measurements. The energy barriers obtained from these orbital line-ups were discussed in combination with previous publications. The linear correlation between the hole injection barrier and the work function of its corresponding metal substrate suggests that the IDIS model is valid for metal/polymer interface. The CNL of each polymer and the corresponding screening parameters were determined from the experimental data.

The electronic structure of a polymer/polymer heterojunction was studied in the second part of this dissertation. The orbital line-up of the MEH-PPV/P3HT interface was determined from the photoemission characterization of the in-vacuum prepared polymer heterojunction. The prediction of the orbital alignment is derived from the IDIS model by using the CNLs of P3HT and MEH-PPV determined in part one. The results suggest that the IDIS model can be applied to polymer/polymer heterojunctions. The experimental results were also compared with the Integer Charge Transfer (ICT) model. The deviation of the prediction based on the ICT model from the actual orbital line-up suggests that the ICT models should be applied to interfaces prepared in ambient environment with surface
contamination present rather than the interfaces prepared in vacuum with intimate direct contact between materials.
References


   299-300, 928-944.

   909-927.

   Miyazaki, T.; Harima, Y.; Yamashita, K., The electronic structure and energy level 
   alignment of porphyrin/metal interfaces studied by ultraviolet photoelectron 

20. Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M., Large On-Off Ratios and 
   1550-1552.

   Self-Assembled Monolayers on Metals. *Accounts of Chemical Research* **2008**, 41, 721- 
   729.

22. Vázquez, H.; Dappe, Y. J.; Ortega, J.; Flores, F., A unified model for 
   **2007**, *126*, 144703.

23. Vázquez, H.; Flores, F.; Kahn, A., Induced Density of States model for weakly-


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Author: Wenfeng Wang, Jan H. Almeier, and Rudy Schaf

Publication: Langmuir
Publisher: American Chemical Society
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Appendix B: Publication 1: Determination of the charge neutrality level of poly(3-hexylthiophene)

Note to Reader

Determination of the charge neutrality level of poly(3-hexylthiophene)

Wenfeng Wang,1 Jan H. Almeida,2 Matthäus Wolak,2 and Rudy Schlab2,4*
1Department of Chemistry, University of South Florida, Tampa, Florida 33620, USA
2Department of Electrical Engineering, University of South Florida, Tampa, Florida 33620, USA
(Received 25 October 2012; accepted 9 January 2013; published online 4 February 2013)

The Al/poly(3-hexylthiophene) (P3HT) and Ag/P3HT interfaces were investigated using photoinjection spectroscopy in combination with in situ thin-film deposition. The P3HT thin films were deposited directly into high vacuum from solution on the two metal substrates using an electrospary system and characterized via photoinjection spectroscopy. The electronic structure and charge injection barriers at these interfaces were determined from the evaluation of the resulting spectra sequences. A linear correlation between barrier heights and substrate work functions was observed from the collected data in combination with previously published results, suggesting that the “Induced Density of Interfaces States” model for small molecular materials is also valid for conjugated polymer interfaces. The corresponding P3HT “screening factor” as well as its charge neutrality level was determined to be 0.48 and 3.44 eV, respectively. © 2013 American Institute of Physics.

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I. INTRODUCTION

In the last two decades, organic interfaces have attracted considerable attention due to their importance for the performance of devices like organic light-emitting diodes (OLEDs) or organic solar cells (OSCs). A significant research effort ensued to elucidate the mechanisms that determine the magnitude of the charge injection barriers at such interfaces. For small molecular materials it was concluded that the formation of organic/metal contacts follows a similar process like that encountered for inorganic Schottky barriers. The orbital line-up is mainly determined by the formation of an interface dipole, which shifts the frontier orbitals of the organic material relative to the Fermi level of the metal contact. The magnitude of this dipole is defined by the formation of metal induced gap states (MIGS) at the interface. As discussed by Tersoff4 and Heine5 for the case of inorganic junctions, the electron wave functions of the metal overlap with those of the semiconductor, forming a continuous band of MIGS within the semiconductor bandgap. Since the MIGS are derived from bulk energy bands, they predominantly keep their respective donor- or acceptor character. This allows the definition of a “charge neutrality level” (CNL), which identifies the energy of those MIGS in the bandgap that are equally donor-like and acceptor-like. Based on these studies, Vazquez and co-workers6,7 subsequently applied the MIGS approach to metal/organic and organic/organic interfaces. This effort yielded the “Induced Density of Interface States” model (IDIS),8,9 which is based on the introduction of an induced density of interface states formed by the interaction between the metal bands and the discrete molecular orbitals of the organic molecules in contact. This model also introduces a CNL similar to the MIGS theory, which allows a first-order prediction of the orbital line-up between organic materials and metals based on a linear relationship governed by a screening factor.

Kahn et al.10 experimentally demonstrated the validity of the IDIS through measurements on a series of metal/molecular organic interfaces. The experiments presented here explore whether the IDIS also holds for conjugated polymeric materials. As prototypical semiconducting polymer poly(3-hexylthiophene) (P3HT) was selected. This material is in wide use in device related research due to its relatively large mobility values.11,12 The aim was to determine the CNL value for P3HT, and to determine whether there is a linear relationship between hole injection barriers and the work function of the metals in contact, as predicted by the IDIS. To achieve this goal measurements on Al and Ag substrates were performed and the results combined with previously published results on the P3HT/Au interface.13 A major issue with regard to photoinjection spectroscopy measurements on polymer interfaces is to achieve clean and direct interfaces through in vacuum preparation under exclusion of ambient contamination. Since high-molecular mass polymer thin films can generally not be prepared through evaporation, electrospray deposition was used.14 This method enables the deposition of macromolecular materials in vacuum directly from solution. Similar to the approach utilized for electrospray mass spectrometry, a solution of the polymer material in question is sprayed from a fine capillary under a high voltage potential within a nitrogen filled chamber onto a transfer orifice to the vacuum chamber. Differential pumping stages remove most of the solvent and the nitrogen enabling the deposition of thin films with little contamination (in comparison to deposition methods under atmospheric pressure like spin coating or spraying). Another advantage of this technique is that it enables the fabrication of multi-material, multilayer thin-film stacks without resolution and intermixing issues. Furthermore, the electrospray process is considered “gentle,” i.e., there is no significant fractioning of the injected...
macro-molecular materials. This enabled the performance of multi-step deposition sequences of P3HT on Ag and Al surfaces, with X-ray and ultraviolet photoemission (XPS, UPS) measurements carried out in between deposition steps. The resulting data give detailed information about the formation of the interface electronic structure. Using low intensity x-ray photoemission spectroscopy (LIXPS) the onset of layer thickness dependent charging artifacts was pinpointed, which further enhanced the measurement accuracy. The results of these experiments indicate that the IDIS model may be valid for polymer interfaces. A CNI value of 3.44 for P3HT was determined. The corresponding IDIS “screening factor” was calculated to be 0.48.

II. EXPERIMENTAL SETUP

The experiments were carried out in a commercial multichamber ultra-high vacuum system (SPECS GmbH, Berlin), which has a base pressure of $2 \times 10^{-10}$ mbar. This system consists of three sample preparation chambers and one analysis chamber interconnected with each other via in situ UHV sample transport mechanisms. The analysis chamber used for sample characterization is equipped with an X-ray gun, an ultraviolet source and an electron analyzer. One of the preparation chambers features a home-built electrospray system, which enables the in situ deposition of macroscopic molecular materials from solution.

Pristine Al films were grown by evaporating Al from a tungsten coil wrapped with Al wire onto a $1 \times 1 \text{ cm}^2$ 100 Å-thick Au film. The Al wire used as the evaporation source was purchased from Alfa Aesar. The purity of the Al film was measured with a quartz crystal microbalance. For the experiments on Ag substrates, a 0.1-nm-thick Ag film of 99.998% purity (purchased from Alfa Aesar) was cut into $1 \times 1 \text{ cm}^2$ samples, then rinsed with acetone and isopropanol, and wiped with a KimWipe soaked in methanol before being mounted on the sample holder. Once loaded into the UHV system, residual ambient contamination was removed by sputtering (SPECS IQE135 ion source) with Ar$^+$ ions at a kinetic energy of 5 keV and an emission current of approx. 10 mA.

The P3HT (regioregular, purchased from Sigma-Aldrich, 4450703) was dissolved in toluene at a concentration of 1 mg/ml and kept in a dark environment to avoid exposure to light. The deposition of the polymer thin film was performed using a homebuilt electrospray injection system. This system is attached to the sample preparation chamber and enables in situ thin-film deposition and subsequent PES analysis without breaking the vacuum. The P3HT solution was injected from a syringe pump onto the transfer orifice of the system from within a nitrogen filled shroud. Two differential pumping stages at 0.1 mbar and $4 \times 10^{-9}$ mbar extract solvent molecules and nitrogen molecules, thereby separating the polymer molecules from the solution. This results in a P3HT “beam” directly into the vacuum environment. For more details on the electrospray system, see Dam et al. The injection rate of the syringe pump was 4 ml/hr. A voltage of $-3.5$ kV was applied to the syringe capillary, which was held at a distance of about 3 mm to the transfer orifice of the electrospray chamber.

The polymer thin-films were grown in several steps without breaking the vacuum. Between each deposition, the sample was transferred in situ into the analysis chamber and characterized with photoluminescence spectroscopy using a SPECS UNI 10/05 ultraviolet source and a SPECS XR 80 x-ray gun. All UPS measurements were performed using He I radiation ($h \nu = 21.22$ eV). Mg Kα X-ray emission ($h \nu = 1253.6$ eV) was used for all XPS and LIXPS measurements. Regular XPS core level characterization was performed at an emission current of 20 mA. The LIXPS measurements were carried out by operating the X-ray gun in stand-by mode at 0.1 mA emission current. The resulting low flux of photons (several magnitudes lower than during UPS measurements) enables the detection and quantification of charging or photochemical reaction artifacts during UPS measurements that potentially occurred.

A $-10$ V bias was applied to the sample holder for all UPS and LIXPS measurements in order to separate the work functions of sample and analyzer. Analysis of the photoelectrons was performed using a SPECS Phoibos 100 hemispherical analyzer. The spectrometer was calibrated to yield the standard Cu Kα line at 932.66 eV and the Cu Lα line at 75.13 eV.

The collected data were analyzed using JOCR PRO (Wavemetrics, Inc.). Work function and highest occupied molecular orbital (HOMO) binding energy values were determined by fitting lines into the respective spectral onset. The intersection points with the spectra base lines were used for the work function and HOMO determination. In order to correct for the analyzer-related spectral broadening, 0.1 eV was added to all presented values.

III. RESULTS

A. Al/P3HT orbital alignment

Figure 1 shows the XPS spectra of the Al 2p, C 1s, and S 2p core level emissions. The bottom spectra in each panel correspond to the emissions of the Al surface as prepared by evaporation. The C 1s sequence shows that the emission feature related to the P3HT layer stays steady at 286.1 eV during the deposition sequence. The absence of shake-up satellite peaks at a binding energy of 290 eV indicates that the polymer did not break into smaller conjugation lengths during the electrospray process. The S 2p emission features for the first two deposition steps overlap with Al related emissions, which results in a broadened peak at lower binding energies. As more P3HT is deposited, the S 2p emissions become more distinguishable and show a doublet that stays at a constant binding energy value (165.2 eV). In the left panel, the characteristic metallic Al 2p emission arises at 72.9 eV. The secondary peak at 75.6 eV is related to the oxidation of the Al surface, which is caused by residual atmospheric O$_2$/H$_2$O partial pressure during the electrospray deposition process.

The matching set of secondary edge spectra is shown in Fig. 2. The left panel shows the secondary cutoff as measured by LIXPS (prior to the UPS measurement of each deposition
step), The bottom spectrum corresponds to the clean Al surface with a cutoff at 17.16 eV. This corresponds to a work function of the Al substrate of 4.16 eV. After the first deposition of 0.01 ml of PSHT solution, an abrupt shift of the secondary edge of 1 eV is observed, caused by the formation of a thin surface oxide layer during the deposition process. The corresponding work function was determined to be 3.16 eV. It should be noted here that this work function value corresponds exclusively to the oxidized Al surface with no significant contribution from the PSHT film. This was confirmed through a control experiment (not shown here) where pure solvent was electrospray deposited onto a freshly cleaned Al surface. During the subsequent PSHT depositions, the secondary edge continues to slightly shift to lower binding energies. By measuring the difference between the secondary edge of the oxidized metal substrate and the last deposition, a small interface dipole of ~0.07 eV was determined. The right graph in Fig. 2 shows the corresponding UPS sequence. In contrast to the LXPS sequence, a relatively large continuous shift of the secondary cutoff towards higher binding energies is observed. For better comparison, the calculated work function values, based on the binding energies of the secondary edge cutoff, are plotted against the injected volume of PSHT in Fig. 3. As shown in this chart, the work function measured by UPS starts deviating from the LXPS values after the 0.18 ml deposition. The discrepancy increases as the PSHT film grows thicker, resulting in a difference of over 0.4 eV after the final deposition. This difference is related to charging artifacts occurring during the UPS measurements, which increase in strength as the film grows thicker. Charging effects affect UPS measurements much more strongly than LXPS due to the several magnitudes higher photon intensity of the UV source relative to the X-ray flux during LXPS measurements. This allows the use of LXPS measurements to detect the onset of charging phenomena. Charging artifacts usually become more intense as the poorly conductive polymer layer increases in thickness. Since LXPS is not significantly affected by charging artifacts at the layer thicknesses investigated in this experiment (this was demonstrated earlier through direct comparison with in situ Kelvin probe measurements), all work function values given in this paper were derived from LXPS data.

The complete set of raw UPS spectra as measured during the deposition sequence is shown on the left in Fig. 4. On the right, the valence bands/HOMO region is shown with the background removed for better comparison. The bottom

FIG. 1. Al 2p (left), C 1s (center), and S 2p (right) XP spectra before and during the seven-step PSHT deposition series. A secondary peak located at 75.6 eV appears in the Al 2p, indicating the oxidation of Al surface during the electrospray process.

FIG. 2. Normalized LXPS secondary edge spectra (left). The oxidation of Al surface causes the abrupt shift of secondary edge of 1.0 eV at the initial electrospray deposition. A small interface dipole of ~0.07 eV between the oxidized surface and the PSHT overlay was determined by measuring the difference between the secondary edge of the oxidized metal substrate and the last PSHT deposition. The matching UPS secondary edge spectra are shown on the right. The stronger shift of the UPS secondary edge spectra at higher PSHT coverage in comparison to the LXPS spectra indicates the onset of charging artifacts.

FIG. 3. Comparison of work function values extracted from both LXPS and UPS measurements in relation to the amount of deposited PSHT. The difference at higher coverages (injected volume) is related to the onset of sample charging.
C–C bond related emission at about 285.2 eV. In the S 2p spectra, the peak at 164.3 eV is attributed to the S–C bonds in the polythiophene.

The right panel of Fig. 6 shows the HOMO UP spectra (0–10 eV) magnified after background removal. The characteristic δ-band emissions (6–8 eV) of the Ag substrate are gradually attenuated by the thiophene ring π-orbitals of the PSHT layer (3–4 eV) during the deposition process. After the deposition of 0.08 ml of the PSHT solution, the Ag emissions are completely suppressed by the emissions of the PSHT layer. The inserted graph shows the determination of the HOMO onset in the 0.88 ml spectrum. A HOMO value of 0.80 eV was obtained after the 0.88 ml PSHT deposition. The center panel shows the secondary edge cutoff of the UP spectra. The left panel shows the same feature, but the spectra were obtained using LIXP S prior to the UPS measurements. A shift of the secondary edge can be observed in both panels. However, this shift is again larger in the UP spectra, which indicates the occurrence of charging artifacts, similar to what was seen at the AIP/PSHT interface.

Figure 7 shows the work function value measured with LIXP S and UPS plotted against the injected volume of PSHT. The work function measured by LIXP S gradually shifts to lower values and remains constant in the last two steps. The UPS measurements show similar shifts up to 0.08 ml, after which the secondary edge significantly deviates from LIXP S towards higher binding energies. This deviation is related to charging artifacts caused by the high photon flux used during the UPS measurements. The total reduction of the sample work function calculated from the LIXP S secondary edge energies is about 0.45 eV, which is related to the formation of a dipole at the interface.

IV. DISCUSSION

A main objective of this work was the investigation of the electronic structure of AIP/PSHT and Ag/PSHT interfaces. In the following the orbital alignment at the AIP/PSHT and Ag/PSHT interfaces will be determined, and the CNL value of PSHT determined.
A. Orbital alignment

1. Al/P3HT interface

Although electrospray provides a fairly clean in situ deposition environment, which avoids significant surface contamination in comparison with sample preparation methods under ambient condition, an inevitably introduced small residual O₂/H₂O partial pressure during injection of the solution can still cause the formation of a thin oxide layer on highly reactive surfaces like pure Al. Unfortunately, this issue appears inevitable at this point for experiments on low work function materials since currently there is no cleaner in situ preparation method for large (i.e., not evaporable) molecules available.

Reverse deposition, i.e., evaporation of a low work function metal onto a polymer film is also not a good option, since usually inter-diffusion and/or chemical reactions result. Hence, in order to be able to include a well-defined low work function interface into the evaluation, the influence of the oxide layer needs to be considered for analyzing the electronic structure of the investigated Al/P3HT interface. As shown in Fig. 1, the Al 2p peak splits into a metallic and oxide peaks, located at 72.9 eV and 75.6 eV, respectively, after the first deposition step. By using the thickness estimation model developed by Strohmeier, the thickness of this Al-oxide layer can be approximated from the intensities of these peaks. As prescribed in the model, a Gaussian-Lorenz curve was fit to the metallic and oxide peaks and the independent intensity of each peak was determined. By measuring the intensity ratio between the oxide related and metallic components \( I_0 / I_\text{metal} \), the thickness \( d \) of the oxide film can be estimated using the following equation:

\[
    d = \lambda_0 \sin(\theta) \ln \left( \frac{N_\text{ox}}{N_\text{metal}} \frac{I_0}{I_\text{metal}} \frac{1}{N_\text{ox} / N_\text{metal}} \right) \, .
\]  

In the equation, \( N_\text{ox} \) and \( N_\text{metal} \) are the volume densities of the metal atoms in the metal and oxide (cm⁻³); \( \lambda_0 \) and \( \lambda_\text{metal} \) are the inelastic mean free paths of the appropriate photoelectrons in the metal and oxide (Å); \( d \) is the oxide thickness (Å); and \( \theta \) is the electron take-off angle. A \( N_\text{ox} / N_\text{metal} \) ratio of 1.5, \( \lambda_0 \) of 22, \( \lambda_\text{metal} \) of 24 and a take-off angle of 90° were used for calculating the thickness \( d \). The graph in Fig. 8 plots the oxide film thickness against the injected volume of P3HT. The final thickness of the Al-oxide layer is estimated from this graph to be around 15 Å. The question that arises here is whether these 15 Å of Al-oxide will prevent the formation of metal induced gap states or not, and whether this data can be used together.
with the noble (high work function) metal interfaces to Ag and Au to determine the CNL value of P3HT.

Since the wave function of the metal decays exponentially into the contact material, the strength of interaction between metal substrate and polymer is sensitive to the thickness of this layer. It was established earlier that an interlayer of oxide with thickness up to 2 nm sandwiched between metal and semiconductor still allows significant tunneling between the two sides.28,29 This suggests that the densities of states of the metal substrate and the polymer are still interacting at the investigated Al/P3HT interface, and it can be expected that an induced density of states is developing at the interface, and also that Fermi level alignment can occur through charge exchange. However, the 15 Å insulator layer will result in less delocalization of the induced density of states due to the reduced overlap between the states on either side. This will result in a more discrete character of the induced gap states compared to the case without oxide layer. However, the number of induced states should still be similar to the direct-contact case, since the density of states on both sides outside the oxide layer should be the same as for the direct-contact case. This suggests that the resulting CNL should be at a similar energy as for the case of the direct contact, since it is defined by the tipping point between acceptor and donor like states among the induced states in the organic semiconductor.

A benefit of the presence of the oxide layer is that it prevents chemical reactions between the P3HT molecules and the Al surface often caused by the oxidizing nature of pure Al. This buffering effect is suggested by the absence of lower binding energy spectral components at the 162 eV (S 2p) and 202 eV (C 1s) lines. This is also supported by a study by Dunnet et al., where it was concluded that vapor-deposited Al interacts with the α carbon atoms of P3HT, and that this modifies the electron density on these atoms and on the neighboring sulfur atoms in the polythiophene.

Another effect of the presence of the oxide layer is that the work function of the surface is further reduced (compared to the pristine Al surface), in effect producing a metal surface with a lower work function. Since the work function of the surface before P3HT deposition defines the starting point for the establishment of the orbital alignment via the exchange of charges across the interface, the work function of the oxidized surface needs to be used as the substrate work function considered during the discussion of the IDIS model below.

In summary, while the electrospray deposition of P3HT on Al may not result in a perfect direct interface, it comes close to an abrupt interface between a low work function metal/polymer interface, which can be used for the purpose of the CNL determination.

The next step of the evaluation is the determination of the HOMO binding energy. Due to the low signal-to-noise ratio of the UPS-spectrum at low binding energies, the graphically determined HOMO (see inset in Fig. 4) energy was confirmed using an alternative approach. Because the energy differences between core levels and the HOMO position can be regarded as material specific constants, the HOMO energy at an interface can also be determined from the binding energies of XPS core level peaks if the energy difference to the HOMO is known. Here, the S 2p core level was chosen for this calculation, since it is the most characteristic core level peak of P3HT. The energy difference between the S 2p and the HOMO position was previously established to be 163.59 eV.33 Using this approach, the HOMO energy of P3HT at the interface was determined to be 1.61 eV by subtracting 163.59 eV from the measured binding energy of the S 2p core level. This value is in solid agreement with the HOMO energy (1.60 eV) determined directly from the UPS spectral onset. It is interesting to see that the HOMO energy of P3HT in contact with the Al surface is at a position of higher binding energy in comparison with other P3HT interfaces studied by this group.33,34 The HOMO energy of P3HT at this interface is about 1.2 eV larger than the one measured on highly oriented pyrolytic graphite (HOPG).3 Furthermore, the C 1s and S 2p core levels exhibit similar 1.0 eV shifts in comparison with the HOPG interface. These shifts of both HOMO and core levels can be explained by the work function reduction caused by oxidation of the Al surface, which caused the electronic system of the P3HT to align at higher binding energy relative to the Fermi level of the Al substrate. This observation matches the secondary edge spectra shown in Fig. 2 where a 1.0 eV work function reduction of the Al surface is evident after the first deposition results in a strong shift of the P3HT spectrum.

Figure 9 shows the complete electronic structure of the Al/P3HT interface as determined from the analysis above. The thin Al-oxide layer is located at the interface between the Al and P3HT layer. The interface dipole between Al and Al oxide (Δ) is caused by the oxidation of the Al and was
determined to be 1.00 eV. The relevant dipole for the CNL determination (eD) is between the oxide layer and the P3HT film and was determined to be -0.07 eV. The hole injection barrier \( \Phi_0 \) relative to the Fermi level was determined to be 1.60 eV corresponding to the P3HT HOMO binding energy. The corresponding electron injection barrier \( \Phi_0 \) was estimated to be 0.52 eV by using the P3HT transport gap of 2.52 eV as determined by Guan,\(^{23}\) using inverse photoemission spectroscopy. By adding the HOMO cutoff to the work function values, the ionization energy of P3HT is determined to be 4.83 eV,\(^{21}\) which is in good agreement with previously published values.\(^{31,32}\)

2. Ag/P3HT Interface

The determination of the orbital line-up at the Ag/P3HT interface is straightforward. Figure 10 summarizes the result for this interface. The hole injection barrier \( \Phi_0 \) was determined to be 0.80 eV from the spectral onset of the UP-spectra. This value is in good agreement with the one determined using the S 2p core level-to-HOMO energy difference, which yielded 0.81 eV. The electron injection barrier \( \Phi_0 \) was estimated to be 1.72 eV using the bandgap value determined by Guan.\(^{32}\) The secondary cutoff of the 0.88 ml spectrum was determined to be 17.10 eV (after analyzer broadening correction), yielding an ionization energy of 4.92 eV. The interface dipole of eD = 0.45 eV was calculated from the difference between the initial work function of Ag and the work function after the last deposition of P3HT. It should be noted here that the ionization energy of P3HT is 0.09 eV larger than the ionization energy obtained for the Au/P3HT interface, but is in good agreement with the one measured for the Au/P3HT interface.\(^ {31}\) This difference is acceptable, considering the uncertainty of the measurement being approximately \( \pm 0.1 \) eV.

B. Charge neutrality level

A factor that both, MIGS and IDIS, have in common is the assumption of a linear correlation between the energy barrier height and the metal work function.\(^ {8,33}\) This is related to the fact that the size of the charge injection barriers between the materials is a major factor determining the quantity of charge that changes sides, while the magnitude of the barriers is directly determined by the interface dipole. Indeed, both the theoretical calculations by Vazquez et al.\(^ {11,12} \) and the experimental demonstration by Kahn et al.\(^ {5} \) show that the values of both, the hole injection barrier and interface dipole, linearly depend on the work function of the metal substrate in a first order approximation.

The experiments discussed here can be used to explore the validity of the IDIS for conjugated polymers at the example of P3HT. Using the same approach as used by Vazquez et al.,\(^ {11,12} \) the hole injection barriers of the P3HT interfaces were plotted against the substrate work functions in Fig. 11. The low work function point (3.16 eV) in the graph corresponds to the oxidized Al surface, the actual surface interacting with the P3HT film in this experiment. The data point for Au/P3HT comes from Lyon et al.\(^ {13}\) where a work function value of 5.31 eV and a hole injection barrier of 0.59 eV were determined. The data shown in Fig. 11 are summarized in Table I.

The data points were fitted with a linear function (shown in Fig. 11). The error bar (\( \pm 0.1 \) eV) of each point reflects the uncertainty of the measurement technique. The Schottky-Mott limit (dashed line; representing direct vacuum level line-up without interface dipole) is also plotted in the chart allowing the comparison with the fitted line. The difference between the two lines essentially corresponds to the interface dipole to be expected at P3HT interfaces to substrates with a particular work function. The negative slope of the fitted line corresponds to the “screening factor” \( \tau \), which was determined to be 0.48. According to the IDIS model, this dipole (eD) is also proportional to the potential offset between the

<table>
<thead>
<tr>
<th>Substrates</th>
<th>( \Phi ) (eV)</th>
<th>( \Theta ) (eV)</th>
<th>( E_\alpha ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.16(^ {11,12} )</td>
<td>1.60</td>
<td>4.83</td>
</tr>
<tr>
<td>Ag</td>
<td>4.57</td>
<td>0.80</td>
<td>4.92</td>
</tr>
<tr>
<td>Au</td>
<td>5.51</td>
<td>0.59</td>
<td>4.89</td>
</tr>
</tbody>
</table>

*Work function of oxidized Al.
metal work function and the CNI,
\[
e D = (1 - S) \Phi_m - \text{CNI}
\]
\[
\Rightarrow \text{CNI} = \Phi_m - \frac{e D}{1 - S}
\]  \hspace{1cm} (2)

From this equation it follows that the intersection between the fitted line and the Schottky-Mott line represents the case where there is no dipole at the interface, which corresponds to the case of a direct line-up between the CNI of the polymer and the Fermi level of the metal. In this case, the metal would have a work function that is equal to the CNI energy of the polymer. Hence, a graphical evaluation of the graph yields a CNI of 3.44 eV for P3HT.

It is interesting to discuss the determined slope parameter within Monch’s considerations in Ref. 35. According to Monch the slope parameter S and the relative permittivity \( \varepsilon_r \) are related through
\[
S = \frac{A_s}{1 + 0.1(\varepsilon_r - 1)^2}
\]  \hspace{1cm} (3)

where \( \varepsilon_r \) is the relative permittivity and \( A_s \) is a proportionality factor \( A_s = 0.86 \text{ eV} \) accounting for the linear relationship between work function and electronegativity of the contact metals. Using a relative permittivity of 2.6 for P3HT as determined by Estrada et al.\(^{37}\) from C-V measurements, a slope parameter of 0.69 would result for P3HT. This value is about 50% larger than the here experimentally determined value of \( S = 0.48 \). This result needs to be regarded in the larger context of the correlation between experimental data and the predictions of the model as investigated in Ref. 35. Considering Fig. 1 in Ref. 35, it is evident that there is significant scatter between calculated values and experimental validation. In fact, it appears that most organic materials considered in Monch’s work appear to have slope parameters exceeding the values predicted by Eq. (3). This may have to do with the weak interaction between organic materials and metals compared to the covalent bonds mostly present in inorganic interfaces, which account for most of the presented data.

The above determined CNI of 3.44 eV relative to the vacuum level positions the CNI well within the bandgap of P3HT, which is reasonable since the induced density of states is formed in the bandgap of organic molecules.\(^7\) It is interesting to compare this result with the well-studied small molecular material pentacene, which has a similar ionization energy and gap like P3HT (\( E_I = 5.0 \text{ eV}, E_G = 2.20 \text{ eV} \)). Figure 12 shows the energy diagrams of the two materials. The CNI of pentacene was both theoretically calculated and empirically determined to be 5.80 eV\(^{27}\) and 3.69 eV\(^{28,29}\) respectively. These are in close agreement with the value of 3.44 eV determined for P3HT. Finally, an examination of the experimentally determined pentacene slope parameter of 0.39\(^{30}\) with the P3HT value of 0.48 suggests a similar level of interaction between the organic material and the contact metal. This makes sense since both materials are \( \pi \)-conjugated and interact mostly via van-der Waals forces with metal surfaces. The approximately 20% difference between the S values between the two materials is most likely related primarily to the structural differences between the molecules, as well as the different methodological considerations in the experimental approaches and resulting limitations of the accuracy of this comparison. Further experiments on well-controlled interfaces would be required to fully delineate the effects of molecular structure and spatial molecular arrangement on the interface formation.

V. CONCLUSION

Au/P3HT and Ag/P3HT interfaces were prepared in situ using multi-step electrospray deposition. Characterization with photomission specroscopy before and in-between the deposition steps enabled the determination of the orbital line-up at these interfaces. The results of these two experiments were combined with the earlier published result on the Au/P3HT interface. The linear correlation between barrier heights and substrate work functions at these three interfaces suggests that the IDS model is also valid for conjugated polymer/metal interfaces. The corresponding screening factor S and CNI of P3HT were determined to be 0.48 and 3.44 eV relative to the vacuum level.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding by the National Science Foundation (NSF DMR 0906922).


Appendix C: Publication 2: Experimental Determination of the Charge Neutrality Level of Poly [2-methoxy-5-(2’-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV)

Note to Reader

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Experimental Determination of the Charge Neutrality Level of Poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV)

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ABSTRACT: The charge neutrality level (CNL) of poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) was determined. This was achieved by measuring the hole injection barrier at the MEH-PPV/AI interface with X-ray and ultraviolet photoelectron spectroscopies in combination with in situ multistep electrospay-based thin film deposition. This deposition technique allows the deposition of polymers into a vacuum environment from solution, preventing significant contamination of the interface. Hence, the hole injection barrier energy at the interface between MEH-PPV and AI could be determined without the presence of significant amounts of ambient contamination. The result of this measurement was combined with published barrier energies for Au and Ag measured with the same technique. This enabled the correlation between barrier heights and substrate work functions as predicted by the "induced density of states" (IDIS) model. This yielded a CNL of MEH-PPV of 3.76 eV relative to the vacuum level. The corresponding "screening factor" was calculated to be 0.21. The results are discussed in light of the IDIS, which was initially developed for small molecular materials, as well as the integer charge transfer model (ICT). The ICT model was determined for contaminated polymer interfaces featuring only weak interaction.

INTRODUCTION

In the last two decades, conjugated organic materials attracted considerable interest due to their potential applications in organic electronic devices. The performance of these devices crucially depends on the energy barriers that govern the electron or hole injection. Significant efforts have been made to understand the mechanisms that determine the magnitude of the charge injection barriers in such devices. A series of experiments on small molecular organic materials interfaces in conjunction with theoretical calculations resulted in the development of the "induced density states" (IDIS) model, which predicts a predominantly linear relationship between the hole injection barrier formed at a metal/organic interface and the work function of the respective substrate. The slope (the "screening factor") of this linear function is defined by the strength of the interaction between the metal and the organic material. This model is based on the "metal induced gap states" (MIGS) model initially introduced by Tersoff. In this model, the formation of MIGS is the result of the overlap between exponentially decaying electron wave functions from the metal with the density of states on the semiconductor side. This results in a "layer" of interface states within the semiconductor that spans across the band gap. A "charge neutrality level" (CNL) can be defined, which corresponds to the energy that is equally donor or acceptor like in the band gap of semiconductor.

This model was adopted by Vasquez and colleagues for the description of metal/organic interfaces. The resulting "induced density of states" (IDIS) model assumes the formation of interface states due to the overlap between metal states with the discrete molecular orbital system of small molecular organic materials. The IDIS model also defines a CNL allowing a first order prediction of the orbital line-up between organic materials and metals. Kahn et al. successfully demonstrated the validity of IDIS on a series of metal/organic interfaces.

A parallel effort to describe the orbital alignment at conjugated polymer interfaces resulted in the "integer charge transfer" (ICT) model. This model is based on experimental results on interfaces between spin-cast polymer films and evaporated metal contacts. Work function measurements before and after metal deposition suggested that the orbital line-up at such interfaces is governed by a vacuum level alignment between the electronic systems of the metal and the polymer in contact, as long as the Fermi level of the contact metal is located within the polaron gap of the polymer material. In cases where the Fermi level is above or below the gap (i.e., in cases of sufficiently low or high work function contact materials), the polaron levels are pinned at the Fermi level, that is, an interface dipole forms.

When comparing the ICT and the IDIS models, it is crucial to keep in mind that the IDIS was shown to be valid for interfaces fabricated in vacuum under absence of ambient conditions.
contamination, while the ICT describes experimental results at interfaces "insulated" by some degree of contamination (hydrocarbons) during the vacuum process. The results presented in this paper focus on the electronic structure of conjugated polymer/metal interfaces without the presence of significant amounts of ambient contamination, that is, a situation similar to that found in in-vacuum prepared small molecular interfaces. This allows the direct comparison between IDIS and ICT models with regard to their applicability to polymer interfaces. Poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) was chosen as prototypical conjugated polymer material for this investigation due to its applications in organic photovoltaic and light-emitting devices. The determination of the CNL of MEH-PPV requires the measurement of hole injection barriers for a range of metals with different work functions. Previous measurements already provided barriers for high work function materials such as Ag and Au. This paper describes measurements on the interface to Al to expand the data set to low work function substrates. The result of this effort is that the combination of the Au, Ag, and Al barriers suggests that there indeed is a linear relationship between hole injection barriers and the work function of the metals. At the same time it is also established that significant interface dipole forms at these interfaces. This suggests that the IDIS is also valid for conjugated polymer/metal interfaces as long as the interfaces are clean. The ICT on the other hand appears to be a good description of polymer interfaces formed in the presence of a hydrocarbon layer.

**EXPERIMENTAL SETUP**

The experiments were carried out in a commercial multichamber ultra-high vacuum system (SPECS GmbH, Berlin). The analysis chamber is equipped with an X-ray gun, an ultraviolet source and an electron analyzer, with a base pressure of $2 \times 10^{-10}$ mbar. Samples were prepared in a dedicated chamber containing an evaporator and an electrospray system. The analysis and preparation chambers are connected via transport rods, enabling preparation and PIXE analysis without breaking the vacuum. A pristine Al surface was created by evaporating a thick Al film onto a $1 \times 1 \text{ cm}^2$ glass substrate coated with a 1000 A-thick Au film under UHV conditions. The MEH-PPV (Aladdin, 27037-7, lot L0491962) was dissolved in toluene (HPLC grade) at a concentration of 0.5 mg/mL and kept in a dark environment to protect against photoinduced degeneration.

The polymer thin film was deposited in situ in multiple steps onto a freshly prepared Al film using the electrospray system, which is attached to the sample preparation chamber. The electrospray system includes two differential pumping stages at 0.1 mbar and 4 $\times$ 10$^{-5}$ mbar to separate the ionized polymers from the solvent and allow the direct injection of MEH-PPV into the vacuum chamber (see Dam et al. for details). A total amount of 6.98 mL MEH-PPV solution was injected into the electrospray chamber by a syringe pump at a rate of 4 mL/h by three deposition steps. A step of 3.5 keV was applied to the syringe capillary, which was held at a distance of about 3 mm to the orifice of the electrospray chamber. The region between injection needle and intake orifice was encased with a plastic shaft shielded with pure N2 to minimize the presence of ambient gas species. The MEH-PPV thin films were grown in several steps without breaking the vacuum. After substrate preparation and in between each deposition step, the sample was transferred to the analysis chamber and analyzed with UPS and XPS. A $-10$ V bias was applied to the sample holder to separate the work functions of sample and analyzer and increase the intensity of secondary edge measured with UPS and LIXPS. The UPS measurements were performed using He I radiation ($h\nu = 21.22$ eV). The XPS measurements were performed at an emission current of 20 mA using Mg Kα X-ray emission ($h\nu = 1253.6$ eV). The LIXPS measurements were carried out by operating the X-ray gun in stand-by mode at 0.1 mA emission current. Due to the several magnitudes lowered photon flux in comparison with UPS, LIXPS is able to detect and quantify occurrence of charging- and photochemical artifacts, which can influence the outcomes of photoemission spectroscopic measurements.

Analysis of the photoelectrons was performed using a SPECS Phoibos 100 hemispherical analyser. The spectrometer was calibrated to yield the standard Cu 2$p$/2 line at 932.6 eV and the Cu 3$p$/2 line at 931.3 eV. The collected data was analyzed using IGOR PRO (WaveMetrics, Inc.). Work function and highest occupied molecular orbital (HOMO) binding energy values were determined by fitting a line into the respective spectral onset. In order to correct the analyzer-related spectral broadening, 0.1 eV was added to all the determined work function and HOMO values.

**RESULTS**

Figure 1 shows the background-removed XPS spectra of the Al 2p, C 1s and O 1s core level emissions. The bottom spectrum of each panel corresponds to the Al substrate surface as prepared by evaporation. The subsequent sequences of spectra reflect the surface after each deposition of MEH-PPV. The parameter gives the respective amount of solution that was injected during each step. The left panel shows the Al 2p

![Al 2p](image1.png)

![C 1s](image2.png)

![O 1s](image3.png)
emission originating from the metal substrate. The characteristic emission of Al located at 72.9 eV is observed through the entire sequence, which corresponds to metallic Al atoms. A second peak at 75.7 eV arises after the first deposition of MEH-PPV as a result of a partial oxidation of the Al surface due to traces of ambient oxygen and water introduced during the electrospray process. The influence of this oxidation on the orbital alignment will be discussed in the Discussion section. The O 1s line shown in the right panel of Figure 1 confirms the oxidation on the Al surface. The peak located at 532.4 eV arises after the first deposition of MEH-PPV, which corresponds to the emission of O atoms in Al oxide. As the polymeric film grows thicker during the electrospray deposition process, a second C–O related peak emerges at about 534 eV. It dominates the O emission by the end of the deposition sequence as the substrate becomes fully covered. The C 1s emission (central panel of Figure 1) initially appears at 286.2 eV after the first deposition of MEH-PPV and stays at the same binding energy until the deposition of 0.18 mL. This initial peak is mainly caused by the deposition of residual toluene molecules on the sample surface during the electrospray process. The binding energy of this peak is in good agreement with the results of a control experiment (not shown here) in which only toluene was sprayed onto a freshly prepared Al substrate. During the electrospray deposition sequence, this peak is gradually replaced by a peak at lower binding energy as the formation of the MEH-PPV layer displaces the weakly bound toluene from the surface. At least two C 1s spectral components are observed in the spectra corresponding to higher coverages of MEH-PPV. The peak at 285.6 eV corresponds to the emission from C–C bonds of the backbone and alkane side chains of the polymer, while the shoulder at 286.8 eV is related to the C–O bonds in the alkoxy side chains in MEH-PPV.

The secondary edge spectra are shown in Figure 2. The left panel shows the secondary cutoff as measured by LIEDPS prior to the UPS characterization of each deposition step. The right graph shows the corresponding secondary edge feature as measured by UPS. The reason that LIEDPS measurements were chosen for the work function calculation is due to the appearance of charging artifacts in the UPS secondary edges at higher coverage. Generally, LIEDPS prevents significant charging artifacts during work function measurements due to its several magnitudes reduced photon flux,16,17 which strongly reduces sample conductivity requirements for successful measurements. The bottom spectrum corresponds to the clean Al substrate with a secondary cutoff at 16.92 eV, corresponding to a work function value of 4.30 eV. After the first deposition of MEH-PPV an abrupt shift of the secondary cutoff by 1.16 eV occurred toward higher binding energy. This is related to the formation of a thin oxide layer on the Al surface during the electrospray process. The corresponding work function of the oxide layer was determined to be 3.14 eV. At this point in the experiment there is only insignificant contribution by the MEH-PPV film to the work function since the film is still marginal. This conclusion is supported by the fact that the work function value is in excellent agreement with the work function measured in the control experiment with pure toluene mentioned above. During the subsequent depositions of MEH-PPV, the secondary cutoff continues shifting to higher binding energies until the deposition of 0.18 mL, which is most likely still related to the oxidation of Al substrate.

The central panel of Figure 2 shows the complete set of UPS spectra as measured during the deposition sequence. The valence band/HOMO region is shown in the right panel after inelastic background removal. The bottom spectrum corresponds to the clean Al substrate as prepared by in situ evaporation. In order to provide a better comparison, the substrate spectrum is shown at 20% magnification due to the comparably weak emissions from the clean Al substrate. After the first deposition of MEH-PPV, a broad peak appears around 7.4 eV, which mainly corresponds to the O 2p emission from the thin Al-oxide layer that formed during the deposition.19 The MEH-PPV HOMO emissions subsequently attenuate the
Al-oxide valence band as the MEH-PPV film grows thicker. Due to the relatively weak intensity, the spectra of the last three deposition steps are shown at 6× magnification for better comparison. Considering the strong shift of the secondary edge due to charging artifacts after the 6.68 mL deposition step, the 3.88 mL spectrum was used instead for the determination of the HOMO binding energy of MEH-PPV (inserted graph). The HOMO was determined to be 2.17 eV including a 0.1 eV correction to account for spectral broadening.

**DISCUSSION**

The primary focus was the determination of the hole injection barrier of the Al/MEH-PPV interface and using it for the determination of the CNL of MEH-PPV, and the discussion of the orbital line-up at conjugated polymer interfaces prepared in vacuum in light of the IDIS and the ICT models. The following sections discuss the measurement results and the determination of the CNL.

(a) **Orbital Alignment at the Al/MEH-PPV Interface.**

Although the electrospray technique prevents the introduction of significant amounts of ambient contamination to the sample surface in comparison with ambient sample preparation techniques (spin-coating, etc.), the trace amounts of air entering the system despite purging the intake end of the high purity N2 is sufficient to form a thin native oxide layer on the highly reactive Al substrate during the deposition sequence. These results are in consistent with the recent study of the Al/P3HT interface.20 Being aware of this issue, alternative deposition methods (i.e., in vacuum evaporation of Al on polymer film) were tried but excluded from the evaluation. This is due to the fact that chemical reaction and interdiffusion effects at the interface as results of direct contact between the polymer material and the "hot" impinging Al atoms.31,32 This significantly alters the structures of both polymer and interface. Therefore, in absence of a more perfect in situ deposition technique, the influence of the oxide interlayer on the electronic structure of the investigated Al/MEH-PPV interface must be evaluated in order to be able to include a low-work function interface into the determination of the CNL value. As shown in Figure 1, the Al 2p lines show metallic and oxidic emissions at 72.9 and 75.7 eV, respectively. The thickness of the Al-oxide after each deposition was obtained by applying the thickness estimation model developed by Strohmeier.33

\[
d = \frac{3}{N_0/2N_e} \left( \ln \left( \frac{N_e/2N_0}{I_e/I_o} + 1 \right) \right)
\]

In the equation above, \(d\) is the oxide thickness (Å), \(N_0\) and \(N_e\) are the volume densities of the metal atoms in the metal and oxide (cm\(^{-3}\)), \(I_o\) and \(I_e\) are the inelastic mean free paths of the appropriate photoelectrons in the metal and oxide (Å), and \(\theta\) is the electron takeoff angle. According to Strohmeier's study, a \(N_e/2N_0\) ratio of 1.5, \(I_o/2I_e\) of 22, \(I_e/24\) and a take-off angle of 90° are suitable choices for the thickness calculation. The intensity of the oxidic and metallic components (\(I_o\) and \(I_e\)) were determined by applying a Gaussian–Lorentzian curve fit to the metallic and oxide peaks in each Al 2p spectrum. The estimated thickness of the Al-oxide layer is plotted against the volume of the injected solution in Figure 3. According to the plot, the maximum thickness of the Al-oxide is 16.4 Å. The critical question arising here is whether the presence of this 16.4 Å oxide layer will sufficiently impede the overlap of the wave function of both sides to prevent the formation of the induced interface states or not.

Since the metal wave functions exponentially decay into the gap of the contact material,24 the possibility of formation of IDIS at the interface crucially depends on the thickness of the oxidic interlayer. It was demonstrated that the presence of oxide interlayer with a thickness up to 2 nm still allows significant tunneling between the materials in contact.25,26 This suggests that a significant wave function overlap between metal and MEH-PPV can be expected at the investigated interface, and the induced states would form. However, the overlap of states between polymer and metal will be weaker due to the interlayer. Consequently, this would result in less delocalization of the induced states, that is, more discrete states would arise than in the direct-contact case. However, considering the Al-oxide interlayer is extremely thin with a large featureless band gap, the contribution of Al-oxide interlayer to the formation of interface states is minor or even negligible. Hence, the thin oxide layer is often treated as a modification layer instead as an insulating layer.27-29 More importantly, since the density of states of both metal and polymer are the same regardless of the presence of the oxide layer, a similar number of induced states to form are expected. This suggests that the CNL should form at a similar energy with oxide present compared to the direct contact scenario, since the CNL represents the neutral energy level between donor- and acceptor-like states among the induced states in the organic material.

An interesting aspect of this discussion is, that the presence of Al-oxide interlayer actually prevented a chemical interaction between the polymer material and Al substrate due to the inertness of the oxide. This is supported by the comparison of the XPS results presented in this work (Figure 1) with published studies,30-33 where Al was evaporated in several steps on a MEH-PPV film prepared by spin-coating. It is evident that the MEH-PPV prepared by electrospray did not undergo a strong interaction with Al atoms, since no C 1s emissions were observed at lower binding energies at around 283 eV, which is usually attributed to formation of carbon–metal bonds due to the chemical reaction between Al with alkoy groups in MEH-PPV.31-33 Hence, it appears that the thin Al-oxide layer formed during the initial deposition steps protects the MEH-PPV film from the reactive Al surface. This suggests the investigated interface can be regarded as abrupt transition between MEH-PPV and the oxide covered Al surface.31-33 In contrast, the studies based on evaporated Al resulted in partial decom-
position of the alkoxy groups due to the chemical reaction between Al and MEH-PPV. This could potentially alter the hole transporting properties of MEH-PPV in devices, since the alkoxy side chains in MEH-PPV are known to act as electron donors, and reduce the Coulomb interaction and relaxation energy of excitons. Furthermore, the reacted complexes can cause localized trap states and/or broadened and distributed energy states, which make it hard to predict the effect on devices. In summary, it appears that the thin oxide layer created an abrupt physiosorbed interface at the cost of a less delocalized induced density of states. This still allows sufficient charge transfer across the interface to form an orbital line-up defined by the interaction between the metal Fermi level and the MEH-PPV CNL.

Since the charging artifact, which occurred during the UP measurement after the 6.88 mL deposition step, could potentially cause a shift of the HOMO position of MEH-PPV toward higher binding energies, the HOMO value of MEH-PPV was determined from the 3.88 mL deposition sequence instead, as shown in Figure 2. An alternative approach to confirm the determined HOMO position can be used to confirm the HOMO energy. Since the energy differences between core level peaks and HOMO-related features are material constants, the HOMO position can also be calculated from a XPS core level peak if this energy difference is known from previous measurements. Since the emissions originating from the alkoxy groups of MEH-PPV partially overlap with the emission of Al-oxide, a calculation of the HOMO position based on the O 1s peak would not be reliable. Therefore, the C 1s peak which is located at 285.6 eV was chosen for the HOMO position determination. In previous experiment, the energy difference between the C 1s and the HOMO binding energy was determined to be 283.37 eV. Consequently, the HOMO energy was determined to be 2.23 eV by subtracting 283.37 eV from 285.6 eV, which is in good agreement with the fit-determined position from the UPS measurement.

Figure 4 shows the orbital alignment of the Al/MEH-PPV interface as a summary of the analysis above. The thin Al-oxide layer between the Al substrate and MEH-PPV film is schematically displayed as the light gray area. The schematic shows the work function reduction (Δφ) of 1.16 eV caused by the oxide layer. This reduces the work function of the substrate to 3.14 eV. The interface dipole between the oxidized surface and the MEH-PPV film was found to be −0.43 eV. The hole injection barrier between Al and MEH-PPV HOMO was determined to be 2.17 eV, corresponding to the MEH-PPV HOMO binding energy. By subtracting the hole injection barrier from the HOMO–LUMO transport gap (2.45 eV) as determined by Campbell et al., the electron injection barrier was estimated to be 0.28 eV. The addition of the HOMO energy to the work function of the polymer thin film resulted in an ionization energy of MEH-PPV of 5.74 eV, which is in good agreement with the previously published value. It is interesting to note that the here presented hole injection barrier is about 1 eV larger than the barrier values determined by Parker and Broeve et al. based on I–V measurements. This difference is likely related to the sample preparation method involving spin-cast MEH-PPV films and on-top evaporated Al films. Such interfaces typically contain an ambient contamination layer in between the metal and the polymer decoupling the electronic system, which alters the orbital line up (see discussion of the ICT model below).

(b) CNL of MEH-PPV. Similar to the MIGS theory, the IDIS model assumes a linear correlation between charge injection barriers and metal work functions. The slope of the hole injection barrier vs substrate work function graph defines the 'screening factor' S in the IDIS model, which varies between organic molecules depending on their particular screening related interface properties.

In order to determine the value of the parameter S of MEH-PPV, the hole injection barrier was plotted against the metal substrate work function (Figure 5), similar to the approach
used by Vangavan et al.10 The line with solid circle represents the presented data and the previous results published by this group.1,3 The error bar (51.3 eV) for each point in this study reflects the uncertainty of the photoemission measurement.

The low work function point (3.14 eV) in the graph corresponds to the results discussed above. The slope parameter S ("screening factor") was determined to be 0.21 from the slope of the fitted line. According to the IDIS model,6 the interface dipole (ed) is proportional to the energy difference between the CNL and metal work function:

\[
ed = (1 - S) (\Phi_m - \text{CNL})
\]

\[
\Phi_m = \frac{ed}{1 - S}
\]

(2)

From this equation, the CNL level can be immediately determined as the intersection between the fitted line and the Schottky-Mott line, which corresponds to vacuum alignment without interface dipole. This yields a CNL of MEH-PPV of 3.76 eV (see Figure 5). This point corresponds to the case of a direct line-up between metal the Fermi edge and the CNL. It is interesting to note that in Figure 5 the difference between the Schottky-Mott limit and the fitted line essentially corresponds to the interface dipole to be expected at MEH-PPV interfaces to substrates with a particular work function (see arrows in Figure 5).

It is interesting to also discuss these findings in light of the ICT model, which predicts vacuum alignment for conjugated polymer interfaces where the Fermi level is located within the transfer gap of the polymer in contact. Unfortunately, to the knowledge of the authors, there are no published photoemission data on MEH-PPV interfaces vs the ICT model for a direct comparison with the here presented data. However, results published by Campbell and Parker,6 which were obtained from internal photoemission and I-V measurements, respectively are available. In these experiments MEH-PPV interfaces were prepared using spin coating and metal evaporation similar to the technique used for the experiments leading to the ICT model.6 The data sets by Campbell and Parker are included in Figure 5 for direct comparison with the data presented here. Their results, marked as empty triangles and filled triangles, indicate vacuum alignment confirming the prediction of the ICT model. The vacuum alignment (Schottky-Mott) limit (dashed line) is plotted as dashed line for comparison with the measurement results. It is obvious that the data by Campbell and Parker essentially follows this line (i.e., their curves have a slope close to unity), albeit at an offset. This offset is probably related to the presence of the contamination layer, but also possibly related to the different measurement methods.

Comparison to the in-vacuum prepared interfaces discussed here suggests that the ICT gives a good description of polymer interfaces where a contamination layer separates the materials in contact, thereby altering the energy alignment at interface. This has the consequence that no or only small interface dipoles form, resulting in ‘vacuum level alignment’ between the contaminated surface and the polymer. In contrast, the in-vacuum prepared interfaces show a similar behavior like small molecular materials interfaces, which are usually prepared via in-vacuum evaporation of the organic material, which creates a direct and abrupt interface. This results in the formation of interfaces whose magnitude is defined by the interplay between energy difference between metal Fermi level and polymer CNL and the screening ability of the polymer material.

These conclusions are supported by recent investigations where the orbital line-ups at small molecule/metal interfaces with and without contamination layer were directly compared.13,14 These experiments clearly show that the contamination layer causes significant dipoles at the metal surface, strongly reducing its work function. In these experiments subsequently deposited molecular layers only had a small additional effect on the dipole magnitude. This suggests that the interface at contaminated metal surface is dominated by localized charge transfer between the contamination film and the metal surface, while the deposited molecular film forms a secondary molecular ‘hetero-interface’ with the contamination layer, which only results in small dipole due to the typically weaker charge transfer between organic materials. If the contaminated metal surface is considered the starting point for the interface formation (for example in experiments where the work function before and after ex-situ molecular material deposition is considered), then it is obvious that such effects result in a near-vacuum alignment with the molecular film in contact, that is, the ICT rule properly describes the orbital line-up.

■ CONCLUSION

The orbital line-up at the Al/MEH-PPV interface was determined using in situ multistep electrospay thin film deposition in combination with photoemission spectroscopy. The influence of the presence of a thin oxide layer on the interface energy structure was discussed. In conjunction with earlier results on high work function Au and Ag interfaces, the results on the low work function interface allowed the determination of the charge neutrality level (CNL) of MEH-PPV (3.76 eV). The corresponding screening factor S was calculated to be 0.21. A consideration of this result in light of the IDIS and ICT models suggests that conjugated polymer interfaces form in accordance with the ICT model similarly to small molecular materials interfaces as long as the interfaces are contamination free. Comparison with interface data measured at MEH-PPV interfaces with ambient contamination present indicates that contamination modifies the metal substrate surfaces, resulting in ‘vacuum level alignment’, between the contaminated metal surface and the polymer.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Science Foundation (NSF DMR 0906922).

■ REFERENCES


