

Unraveling the Charge Injection Mechanism at Metal-Organic Semiconductor Interfaces

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3. Abstract

The field of organic electronics has matured to the point where several applications have been, or are about to be, commercialized. Transport of charge carriers across the interfaces between metal electrodes and the organic materials often determines the performance of these devices. Via systematic studies on the tuning of metal work functions by using self-assembled monolayers, together with the temperature dependent measurements for the injection current of organic optoelectronic devices, this proposal is aiming at establishing a comprehensive model with parameters that can be measured via independent experiments, to reveal a complete charge injection mechanism at metal-organic semiconductor interfaces. We will investigate the formation and fundamentals of metal-organic interfaces and examine how the characteristics of the interfaces and the bulky properties, such as the mobility, energy levels and width of the density-of-states of semiconducting materials affect the charge injection and consequently the device performance.

4. Duration of the Project

The project will start in September 2008 and will continue until August 2012: a regular PhD duration.

5. Personnel

The personnel working on this project are all part of the research group *Molecular Electronics: Physics of Organic Semiconductors*, part of the *Zernike Institute for Advanced Materials*:

Prof. Dr. Ir. P.W.M. Blom (Professor / Leader of the research group)

Prof. Dr. B. de Boer (Associate Professor / Project Leader)

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6. Cost Estimates

The funding is requested for the applicant, one PhD position. Furthermore, all specifically related needs such as substrates, solvents, evaporation masks and chemicals (different kinds of metals, functional polymers, and SAMs molecules) will be acquired from this budget. The equipment needed for this project is already present in the laboratory of the research group or within the *Zernike Institute for Advanced Materials* and no other support will be required for this project.

Budget summary of the funding requested:

| | 2008 | 2009 | 2010 | 2011 | 2012 | Total |
|-----------------|----------|----------|----------|----------|----------|-----------|
| PhD Students | 1 | 1 | 1 | 1 | 1 | |
| Postdocs | - | - | - | - | - | |
| Technicians | - | - | - | - | - | |
| Guests | - | - | - | - | - | |
| Personnel Costs | € 21.500 | € 43.000 | € 43.000 | € 43.000 | € 21.500 | € 172.000 |
| Running Budget | € 7.500 | € 15.000 | € 15.000 | € 15.000 | € 7.500 | € 60.000 |
| Equipment | - | - | - | - | - | - |
| Total | € 29.000 | € 58.000 | € 58.000 | € 58.000 | € 29.000 | € 232.000 |

7. Research Programme

7.1. Introduction

Recent developments in molecular electronics, where organic semiconductors constitute active layers in various electronic devices such as field-effect transistors (FETs) ^{[1],[2]}, photovoltaic (PV) cells ^[3], and light emitting-diodes (LEDs) ^{[4],[5]} are presently receiving great interests. The basic structure of most of these devices consists of one or more layers of active organic materials sandwiched between two electrodes. The different layers of the various devices are optimized for the transport of either electrons or holes, or for the efficient photo generation of charge carriers, or for efficient emission of light. The electrodes either inject or remove charge from the devices and provide electrical contact with other components. Without describing here the details of operation of all of these devices, it should be apparent that efficient charge transfer across the metal-organic interface is critical to their performance. The most important (but not the only) factor that controls the charge injection process is the energy barrier to be overcome as the charge carrier crosses the interface.

The starting point in the description of the interface between a metal and a semiconductor ^[6] is to define the energy difference between the respective Fermi energies of the isolated materials—the so-called built-in potential, V_{bi} . When the contact is made, equilibrium dictates that charge flows from one material to the other, until the Fermi levels align. There are two extreme cases to consider, depending on whether the transferred charge forms an interfacial dipole within the first molecular layer of the semiconductor, or occupies only dopant levels in the bulk. The latter case yields the Mott–Schottky rule ^[6], which states that the vacuum levels align at the interface, and then the additional charge resides in a depletion zone created by ionizing donor or acceptor dopants and causes band bending. In many applications of organic semiconductors there are no dopants intentionally incorporated. As a result, the Fermi level is not easily determined, making the analysis of experimental data liable to misinterpretation. An additional difficulty arises due to the fact that one has to take into account the image potential ^{[7], [8]}, which attracts charges back towards the interface.

In many respects the fabrication processes which are used to make organic devices are far from ‘ideal’: both metal electrodes are almost certainly polycrystalline and rough at the relevant molecular length scale; the bottom one may be coated with a layer of (native) oxide; there may be a chemical reaction between the metal and organic material, particularly when the top electrode is deposited; and the organic semiconductor may be doped either accidentally or deliberately in order to change its transport properties. All of these phenomena will affect the charge injection in some way. Even in the extremely simple case, namely that between a ‘clean’ metal surface and a ‘van der Waals’ solid, where the molecular energy levels are such that one expects no chemical reaction, the charge injection process is still complicated by the amorphous nature of the organic layer, which results in highly localized electronic states with a random distribution of energies and a low carrier mobility.

A polymeric light-emitting diode (PLED) consists of a low work function cathode, a light-emitting polymer (active layer), a hole transporting layer (PEDOT: PSS), a transparent anode (indiumtin oxide: ITO) and a glass substrate [see Fig. 1 (left)] ^[9]. Applying a small voltage across the device results in charge carriers that drift through the light-emitting polymer under the influence of the applied field. In the emissive polymer layer, charge carriers can recombine producing photons that are emitted through the transparent anode [see Fig. 1 (right)]. The process occurs many times per second and produces the device brightness. The bandgap of the light-emitting polymer gives the color of the emitted light. Tailoring the material properties of the polymer through chemistry, light can be emitted in all colors of the spectrum. Full color displays can be made from an array of such PLEDs and the LED pixels can be accessed individually.

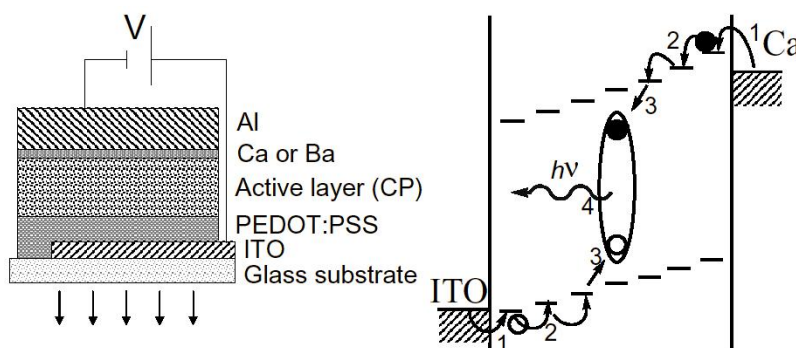


Figure 1: Left: device layout of a typical polymer light-emitting diode (PLED). Right: working principle of a PLED. Four important processes have been shown (according to the numbers in the picture): (1) Injection (2) Transport (3) Exciton formation (4) Emission. The last two steps together form the recombination process. ^[9]

Since the discovery of polymeric LEDs, it has directly been recognized ^[10] that charge injection is one of the critical processes with regard to their device performance. The charge injection process may be

hindered by the presence of an interface barrier at either the electron or hole contact. Such interface barriers result in an unbalanced charge carrier injection, which gives rise to an excess of one carrier type and consequently in a large decrease of the conversion efficiency. For a small energy barrier the contact can facilitate any required injection rate, and the performance of the device is limited by the (transport) properties of the polymer itself (bulk-limited). The metallic contacts that are readily available like Calcium (Ca), Barium (Ba), Samarium (Sm), Aluminum (Al), Silver (Ag), Palladium (Pd), and Gold (Au) have a limited range of work functions, varying from ~3 eV for Ca and Ba to ~5 eV for Au [11]. Also ITO and PEDOT: PSS have a work function of ~5 eV. PEDOT: PSS has the advantage over ITO that it maintains this high work function, whereas the ITO work function is slowly reducing with time. Consequently, with the range of available contacts, for small band gap polymers (like MEH-PPV) the interface energy barrier for both electrons and holes is small, and injection does not limit the device performance [12]. However, a large band gap polymer like the blue light-emitting poly (9, 9-dioctylfluorene, 2, 7-diyl) (PFO) has a highest occupied molecular orbital (HOMO) of 5.8-6.1 eV [13], and consequently the injection into the HOMO is expected to severely limit the device performance.

As mentioned above, for efficient electron and hole injection into polymeric LEDs, the work function of the electrode has to 'match' (within a few tenths of an eV) the energy level of the lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO) of the polymer layer, respectively [14], [15]. Furthermore, in conjugated polymer/fullerene-based solar cells, the experimental open-circuit voltage (Voc) for non-Ohmic contacts is determined by the difference in the work functions of the electrodes. For Ohmic contacts, the Voc is governed by the HOMO and LUMO levels of the donor and acceptor, respectively [16]. Similarly, for ambipolar FETs, the main difficulty is achieving injection of both electrons and holes in the organic semiconductor from the same electrode, since the work function will always result in an injection barrier of at least half of the bandgap for one of the carriers [17]. Facilitating the charge injection improves the device performance and tuning the work function of the metal to match the HOMO (or valence band) and/or LUMO (conducting band) is desirable. Obviously, the performances of all the devices mentioned above are determined by the work functions of their metal electrodes.

Organic semiconductors differ from inorganic ones as they are composed of molecules and their intermolecular forces are relatively weak. In a bulk material this increases the importance of electron-phonon and electron-electron interactions [18]. At a metal-organic interface the energy barrier for charge carrier injection into the organic material is often determined by the formation of an interface dipole localized at the first molecular layer. The interface dipole can be extracted by monitoring the change in the metal surface work function after deposition of an organic layer [19], [20]. Atoms and molecules that are physisorbed on a metal surface usually decrease the work function, because the Pauli repulsion between the molecular and surface electrons decreases the surface dipole [21], [22]. Meanwhile, chemisorption can give an increase or a decrease of the work function, and can even lead to counterintuitive results [23], [24]. Self-assembled monolayers (SAMs) are exemplary systems to study the effect of chemisorbed organic molecules on metal work functions [25]. More specifically, alkylthiolate ($C_nH_{2n+1}S$) SAMs on a gold (111) surface are among the most extensively studied systems [26]-[30]. The sulphur atoms of the thiolate molecules form stable bonds to the gold surface and their alkyl tails are close packed, which results in a well-ordered monolayer. SAMs with similar structures are formed by alkylthiolates on a range of other (noble) metal surfaces [26], [30], [31]. Often the change in work function upon adsorption of a SAM is interpreted mainly in terms of the dipole moments of the individual thiolate molecules, whereas only a minor role is attributed to the change induced by chemisorption [25], [27], [28], [32]. This assumption turns out to be reasonable for adsorption of methyl thiolate (CH_3S) on Au (111) [29], but for CH_3S on Cu (111) it is not [30]. In recent years, self-assembled monolayers (SAMs) have also become an important subject in the field of molecular electronics [33], [34], [43], in which SAMs offer a promising route to the fabrication of reliable devices, and charge transport through SAMs of alkanethiols is well understood, with non-resonant tunnelling dominating the transport mechanism [35]. In device geometry, a wide variety of molecular junctions based on SAMs has been reported [36]-[39], [43].

At the *Zernike Institute for Advanced Materials* of the University of Groningen, tuning of metal work functions with self-assembled monolayers derived from hexadecanethiol and 1H, 1H, 2H, 2H-perfluorinated alkanethiols was initially investigated [28] and B. de Boer et al. have demonstrated that the work function of Ag electrode ($\Phi_{\text{Ag}} \sim 4.4$ eV) can be tuned from 3.8 to 5.5 eV using these two SAMs, respectively. Meanwhile, on Au electrode, the SAM of 1H,1H,2H,2H-perfluorinated alkanethiols raised Φ_{Au} (~ 4.9 eV) by 0.6 eV to 5.5 eV, whereas hexadecanethiol decreased Φ_{Au} by 0.8 eV. These chemically modified electrodes were used in polymeric LEDs and hole injection into MEH-PPV was studied. An Ohmic contact for hole injection between a silver electrode functionalized with the perfluorinated SAMs and MEH-PPV (with a HOMO of 5.3 eV) was established. Conversely, a SAM of hexadecanethiol lowered Φ_{Ag} of a silver electrode to 3.8 eV, and blocked hole injection into PPV [see Fig. 2 (A)], which enabled studying the electron transport in composite devices. The electron-only current was measured in a polymer/polymer blend PV cell based on MDMO-PPV and PCNEPV [see Fig. 2 (B)]. These results demonstrate a simple and attractive approach to modify and improve metal/organic contacts in organic electronic devices like LEDs, Solar Cells, and FETs.

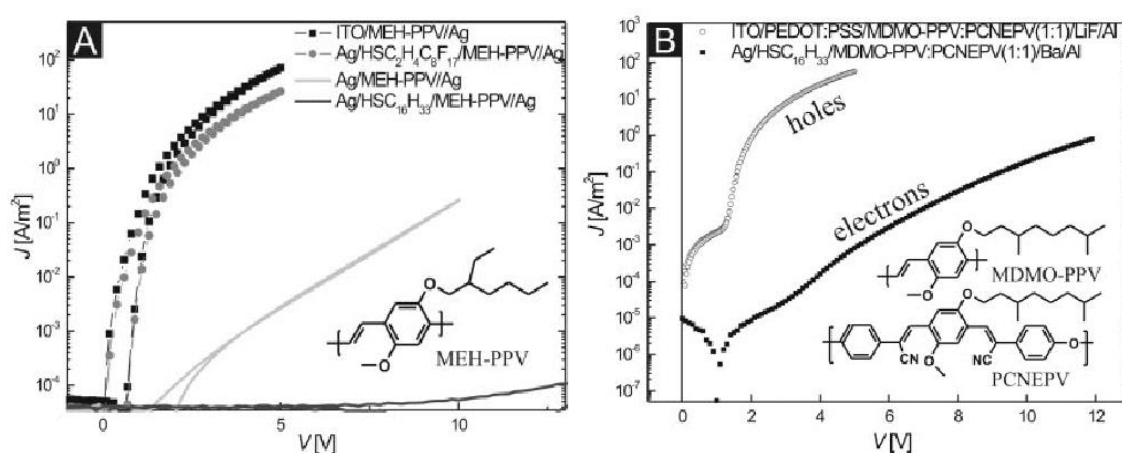


Figure 2: A) Current density-voltage characteristics of diodes based on MEH-PPV. The hole-injection electrode was modified to be: ITO, Ag with 1H, 1H, 2H, 2H-perfluorodecanethiol, unmodified Ag, and Ag with hexadecanethiol. B) Current density-voltage characteristics under dark conditions for a solar cell based on MDMO-PPV and PCNEPV (1:1) with PEDOT:PSS and LiF/Al electrodes, and with Ag/HSC₁₆H₃₃ and Ba/Al electrodes. [28]

The study so far was merely a proof of concept and no quantitative analysis or modeling was performed on the injection of charge carrier across such metal-organic interfaces. The truly understanding of the charge injection mechanism at metal-organic interfaces and its consequences for the performance of organic opto-electronic devices is one of the major motivations for this proposal.

7.2. Research Questions and Goal

The theory of charge injection from a metal into an insulator or semiconductor has a long and illustrious history. Thus there are many arguments in the literature, which were used for the analysis of their experimental data, respectively. Unfortunately none of all these analyses so far has been performed with a proper understanding of the relevance of a complete theory to the experimental conditions under given consideration. The injection current follows neither standard thermionic emission theory, nor obeys tunneling through a simple potential barrier. Rather it is a hybrid process, where the crucial first injection event is thermally assisted tunneling into a distribution of localized

states. Consequently, there is no complete analytic theory with parameters that can be measured through independent experiments.

7.2.1 Models on Charge Injection

The earliest theoretical approach to the charge injection from a metal into an insulator or semiconductor dates back to the calculations of Richardson^[44] and Dushman^[45], who considered the thermionic emission of electrons from a metal surface into the vacuum, which is inherently a quantum mechanical calculation^[45] because in vacuum the electrons are freely propagating and are considered to be wavelike. Based on this initial model, Bethe^[46] assumed that the electrons move ballistically and that the metal acts as an almost perfect sink. Because of doping in the semiconductor, the applied voltage is dropped across the depletion depth, through which the electrons move without scattering. Meanwhile, Schottky considered the effect of scattering and diffusion^[47], and later Crowell and Sze^[48] developed their model of charge injection across metal/ (crystalline or inorganic) semiconductor interface by solving the drift-diffusion equation in the potential across the depletion zone. Their result does not include the explicitly quantum mechanical nature of freely propagating electrons in the limit of small electric field.

Another frequently cited paper describing charge injection is that of Fowler and Nordheim (FN)^[49] who considered a case appropriate for extremely high field. In the context of the present discussion, this would correspond to the situation where tunneling occurs from states at the metal Fermi level, directly into states beyond the maximum in the barrier. The FN calculation is intrinsically quantum mechanical, with free carrier propagation on the far side of the (triangular) barrier. In the application of FN theory, little consideration seems to have been given as to whether the final states are localized (i.e., the lowest unoccupied molecular orbital or LUMO as in organic semiconductors) or propagating as may be the case for electrons emitted directly into 'hot' states of higher energy. However, to extend this work to metal/organic (polymer) interface, we must take into account that polymers are highly disordered/amorphous materials in which the charge transport can no longer be described as free propagation in extended states, but rather as a hopping mechanism between highly localized electronic states. Emtage and O' Dwyer^[50] gave one early treatment of carrier transport across metal/polymer interface based on a solution of the drift-diffusion equation of electrons in a potential which includes the image charge potential due to electrons leaving the metal (Schottky effect). Their main result includes a steady-state current across the metal/polymer interface which is proportional to the carrier mobility. Koehler and Hummelgen^[51] developed an injection model in which tunneling is heavily emphasized. In their model, the barrier at the metal/polymer interface is assumed to be triangular in shape and the Wentzel-Kramers-Brillouin-Jeffreys (WKBJ) approximation is used to calculate the tunneling probability through the barrier. The model gives a temperature dependence of the tunneling current which seems to fit some experimental data on metal/MEH-PPV interface, where MEH-PPV is a well known and commonly used amorphous semiconducting polymer. However, the agreement with experiments requires an adjustment of potential barrier height at the metal/polymer interface. This approach may be well suited to obtain an estimate of the barrier height but fails to include the importance of image charge potential at the interface.

Davids et al.^[52] developed a model of charge injection in single layer OLEDs which includes charge injection, transport and space charge effects in the organic semiconductor. Their model includes both thermionic and tunneling injection of carriers and also a backwards flowing interface recombination current, which shows that for a Schottky barrier height at the metal/polymer interface equal to a few tenths of an electron volt, the current flow through the OLED is space-charge limited and the electric field from anode to cathode is highly non-uniform. On the other hand, for larger Schottky barrier height (around 1eV), the current through the device is injection limited, i.e., charge injection into the organic material is controlled by thermionic emission and tunneling. In this limit, the net charge from the metallic contact is relatively small resulting in a spatially uniform electric field across the organic

thin film. The steady state current is dominated by thermionic emission at relatively small bias and by tunneling emission at larger bias due to image force lowering of the injection barrier. The analysis of Davids et al. ^[52] is based on a numerical solution of the time dependent continuity equations with a description of the electron and hole current densities using a drift-diffusion model.

For a zero external electric field (due to the applied bias between anode and cathode), Scott and Malliaras ^[53] used the principle of detailed balance between the injected current (modeled as a Richardson thermionic current) and the surface recombination current to determine the effective Richardson constant in the injection current expression. In their study, charge recombination near the metal/polymer interface is treated as a hopping process in the image charge potential of electrons outside the metal. Scott and Malliaras derived an exact expression for the surface recombination rate which is a major improvement to the model of Davids et al. ^[52] in which the surface recombination velocity is treated as an adjustable parameter. The total current flowing through the device is then obtained as the difference between the Richardson injection current and the surface recombination current. This approach yields an effective Richardson constant for carrier injection which is proportional to the density of trapping sites and carrier mobility in the polymer. This simple analytical approach provides a mean to derive the electric field-dependence of thermionic injection.

Up to this point, none of the theories of injection takes into account the energetic disorder which is inherent in organic semiconductors (especially polymers). Various approaches to do so are based on the Gaussian disorder model ^[54], in which the distribution of energies follows a Gaussian density of states (DOS). In a series of papers the group of Bäessler and Arkhipov et al. describes injection as a two step process, using both an analytic approximation ^{[55], [56]} to the calculation and a Monte Carlo simulation ^[57]. The first step is the tunneling from the metal into one of the localized states of the organic semiconductor; the second is the escape from that state into the bulk of the organic film. Thus the calculation gives the injection current in terms of the tunneling rate across the interface, summed (or integrated) over all initial (thermally occupied) states in the metal and the final, disorder-induced density of molecular states. This rate is then multiplied by the probability of escape, given in the analytic version of the theory, by the one-dimensional Onsager probability ^[58], as calculated by Blossey ^[59]. This approach has the merit that it explicitly considers the effects of energetic disorder on the injection rate, and indeed shows that disorder enhances the injection current because of tunneling into, and hopping among states deep in the tail of the DOS. There is one undefined parameter of the theory (and equivalently in the Monte Carlo approach of Gartstein and Conwell ^[60]), the hopping attempt frequency, which is taken to be the same for the initial tunneling event as for subsequent hops within the organic material. The parameter can be estimated by comparing simulations with experimental data and plays a similar role in connecting Monte Carlo transport calculations with mobility measurements ^[54]. Diffusive currents enter this model implicitly through the stochastic nature of the Monte Carlo approach, or by inclusion of the Onsager result. The energetic disorder creates a tail of low lying energy states which are more likely to be thermally occupied and provide preferred sites for the initial hop across the interface. As we will discuss in more detail in the next section, this has significant consequences for the temperature dependence of the injection current. In summary, up to now charge injection is best described as field-assisted thermionic injection (or alternatively thermally assisted tunneling) into a random distribution of localized states. As a result, the standard theoretical predictions of neither Richardson–Schottky nor Fowler–Nordheim are totally applicable. The crux of the problem lies in accounting for the all-important first tunneling event. One approach is to use the principle of detailed balance to connect the injection rate to a macroscopic material parameter, namely the carrier mobility ^{[50], [53]}, but this ignores the important effects of energetic disorder and assumes that the charge distribution remains in thermal equilibrium. The other approach is to calculate a charge distribution on the organic side of the interface based on one or more adjustable parameters^{[56],[57],[60],[61]}.

7.2.2 Goal of the proposed research

This proposal is aiming at establishing a comprehensive model in which its parameters can be measured via independent experiments, to reveal a complete charge injection mechanism at metal-organic semiconductor interfaces.

The first step towards implementing our idea is to design an experimental scheme which will allow us to investigate and understand the formation and fundamentals of metal-organic interfaces and examine how the characteristics of the interface and the bulky properties of functional materials affect the charge injection and consequently the device performance. Section 7.3 will describe such a design in which all the technologies required are accessible to the current laboratory level.

7.3. Methods of Proposed Research

Since the injection of charge carriers into organic semiconductors is dominated by both a) the energy barrier offsets between the metal's Fermi energy and the HOMO/LUMO levels of the organic semiconductors, and b) the temperature dependence, the methodology of our proposal will be synthesized from two experimental lines: the systematically tuning of metal work functions by using self-assembled monolayers and the temperature dependent measurements for the injection current of organic opto-electronic devices. Firstly, we will give a brief description of the key elements of tuning the metal work functions by using self-assembled monolayers. Then we will move on to analyze the field and temperature dependences of the injection current for organic opto-electronic devices, followed by an analysis of the advantage and innovation of this proposed scheme. Finally, we give an experimental plan which combines these two research lines above.

7.3.1 Tuning of Metal Work functions using Self-Assembled Monolayers

Self-assembled monolayers (SAMs) of organo-thiolate molecules on gold are studied for a wide range of applications, such as supramolecular assembly, biosensors, molecular electronics and microelectronic devices [62]-[65]. We have shown that chemisorption of a SAM on the surface of the metal electrode can alter its work function substantially [see Fig. 3 and Ref. 28]. By tailoring the SAM's chemical structure this effect can be used advantageously to lower the energy barrier for charge injection and increase the device performance [25], [28], [66].

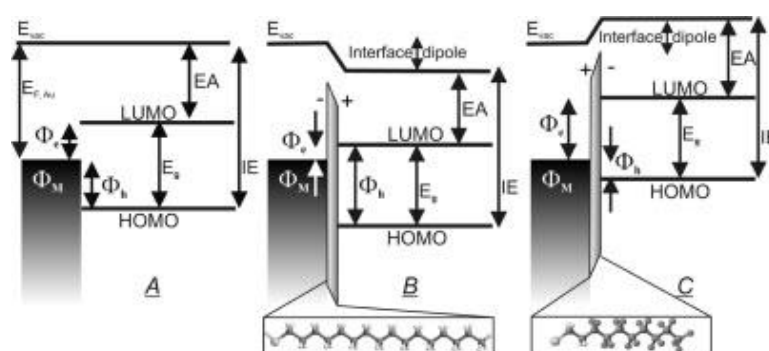


Figure 3: Schematic energy-level diagrams of metal/organic interfaces with metal work function Φ_M , located within the HOMO-LUMO gap (E_g) of the organic semiconductor. A) Electron injection barrier (Φ_e) and hole-injection barrier (Φ_h) for an untreated interface (without SAM). B) Alkanethiols impose an interface dipole that decreases Φ_e and increases Φ_h . C) 1H, 1H, 2H, 2H-perfluorodecanethiols impose an interface dipole that increases Φ_e and decreases Φ_h . [28]

According to classical electrostatics, the work function change of the surface is directly proportional to the change in the surface electric dipole caused by the adsorption of SAMs and a linear correlation was suggested to exist [67]. However, there are also reports that a linear correlation may not exist [68]. In particular, when one tries to correlate the charge injection efficiency with the injection barrier, more effects need to be considered. One of these is the additional interface formed when an organic layer is deposited on the SAM-modified metal surface [27], [35], [69]–[71], i.e., another interfacial dipole, depending on the character of the organic layer and the surface monolayer, may complicate the energy alignment. Another factor is the tunneling barrier introduced by different adsorbates. For molecules of similar dipolar nature, different tunneling barriers may be imposed because of different molecular shapes, lengths, electronic structures, and so on [35], [70], [72].

Therefore, in order to understand the relation between the work function change and the SAM's chemical structure one has to focus on the dipoles formed in the SAM-metal interface region. One obvious contribution to the surface dipole stems from the permanent dipoles of the molecules within the SAM. It has been demonstrated experimentally that a strong correlation exists between the molecular dipole moments and the work function changes induced by SAMs on gold and silver surfaces [25], [27], [28], [66]. The dense packing of molecular dipoles in a SAM, however, causes a sizable depolarizing electric field, which polarizes the molecules such as to effectively reduce their dipole. This effect is often modeled empirically by using an effective dielectric constant for the molecular layer.

A second major contribution to the surface dipole results from the charge reordering associated with the formation of the chemical bonds between the metal surface and the adsorbate molecules. This contribution is foremost determined by the nature of the chemical bonds, but can also be modified by the packing density of the molecules. Thiolate molecules on gold surfaces are among the best studied systems, but it is still debated whether there is a sizable charge transfer between the surface and the molecules upon chemisorption.

7.3.2 Temperature Dependence of Injection Current

Experimentally, the major features of the theory of injection are qualitatively confirmed; however, the quantitative details are less well established, due to the difficulty of fabricating samples for transport measurement with well characterized interfaces. Clearly, the dominant parameter that controls the injection current is the height of the Schottky barrier, and there is ample evidence that injection decreases dramatically as the barrier height increases. The first work that discusses this from the point of view of OLEDs is that of Parker [73], who examined the currents and luminous efficiency of a series of OLEDs fabricated using the same polymer emitter, but with various metals for the cathode. Parker's work revealed a weak temperature dependence and a strong field dependence, which he interpreted in terms of Fowler–Nordheim tunneling. In retrospect, this may have been over simplistic, but nevertheless the correlation of electron injection with metal work function was clear. Many authors since then have confirmed the role of the barrier height [55], [61], [15], [74]–[76].

Unfortunately, there is a major complication in the examination of the other aspects of the injection theory—the field dependence of the Schottky effect and of the simplified model for carrier mobility (which enters the pre-exponential) are identical ($\exp \sqrt{E}$), and moreover, both injection and hopping mobility are thermally activated processes. Therefore it is not clear how to interpret the field and temperature dependences of the injection current. Indeed, there are many instances in the literature where the temperature dependence of the current is analyzed to extract the barrier height, ignoring the role of mobility.

The mobility dependence of the injection in organic materials was shown clearly in the experiments of Shen et al. [77] who varied the hole mobility by changing the concentration of the hole transport molecule, TPD, in polycarbonate. The mobility was measured in each sample by the standard

photoinduced time-of-flight technique with the light incident through a semitransparent blocking (Al) electrode, and then compared, reversing the voltage, with the dark injection current from the other (ITO) electrode. The data confirm the linear relationship between injection and mobility for this simple system, and moreover, the field dependence is in agreement with the previous prediction which ignores energetic disorder and may be a good approximation only when the barrier is relatively large.

Explicitly accounting for disorder, Bäessler and Arkhipov et al. have made extensive comparisons of the field and temperature dependence of the injection current from Mg: Ag into aluminum-triquinolate (Alq₃)^[78] with the predictions of the Monte Carlo simulations^[57]. The agreement is quite reasonable, and shows clearly that neither FN field dependence, nor Richardson–Schottky (RS) temperature dependence provides a good description of the data. Using the same theoretical concepts, van Woudenberg et al.^[15] in our group *Molecular Electronics: Physics of Organic Semiconductors* at Zernike Institute for Advanced Materials (RUG) conclude that injection is dominated by a few sites deep in the tail of the distribution especially at low temperature, resulting in a much weaker temperature dependence than expected for a unique barrier height. For their model system, the injection limited hole currents from Ag and Al into PPV exhibit a very weak temperature dependence, in spite of the presence of a large injection barrier energy of 1.0 eV. Such a behavior is in contradiction with classical thermionic injection models in which the temperature dependence of the injection process is dominated by the injection barrier, but consistent with the models proposed by Arkhipov et al.. The reduced temperature dependence of the injection limited current (ILC) is explained by their model which is based on thermally assisted hopping from the electrode into a due to disorder broadened density of localized states of the PPV. Furthermore it has been found that the injection as well as the transport in organic semiconductors is strongly influenced by the energetic disorder; for smaller disorder the temperature dependence of the charge injection is enhanced, whereas the absolute injection yield is reduced. This is in accordance with injection into tail states, which becomes easier for smaller disorder.

7.3.3 Innovations and Advantages

The advantages and innovations of the proposed scheme for our project are as follows:

- The charge carrier mobility in organic semiconductors is strongly affected by energetic disorder, with a charge carrier density dependence at room temperature and a field dependence at lower temperatures as recently shown^[79]. This effect was omitted by all models on charge carrier injection into organic semiconductors. In order to find a complete description of the dependence of charge injection on applied field, carrier density and temperature, all effects have to be taken into account that acts simultaneously. To overcome this discrepancy with previously proposed models, we propose to investigate these effects systematically by using both experiments and advanced modeling as was developed in our group.
- There has been one preliminary study on tuning the hole injection and charge recombination with self-assembled monolayers on silver anode in small molecules (NPB and Alq₃) OLED devices fabricated using Organic Molecular Beam Deposition (OMBD) method in which the crystallized molecular layer was thermally deposited in high vacuum chambers^[80]. Nevertheless, the charge injection from the metal into the crystallized molecular layer cannot really reflect the intrinsic property of their interface, since the local crystal structure at the interface is unknown. On the contrary, polymeric LEDs in which the luminescent or functional polymer is spincoated to form an amorphous layer on top of the metal cathode, will give us the truly intrinsic properties of their interface, which is the superiority of our proposal compared with the others' ongoing work.

- As mentioned above, the temperature dependence of the injection current is one of the key parameters in distinguishing between the classical models based on thermionic emission and the modern model that describes hopping injection in an energetic disordered medium. In the proposed scheme, this feature of the injection current will be examined in details in combination with tuning the metal work functions using self-assembled monolayers. Using different metal electrodes (Au, Ag, Pt, or etc.) whose work functions are chemically modified through the formation of chemisorbed SAMs, via systematically varying the types and lengths of different SAM molecules as well as their directions of dipole moment and their packing density, together with tuning the HOMO or LUMO levels and charge mobilities of the functional polymers adopted for device fabrication, the charge injection mechanism from a metal electrode into the polymer layer will be thoroughly investigated by measuring the current-voltage characteristics for a wide range of metal work functions, with all measurements as a function of the operating temperature.
- We also propose a systematical investigation on the interfaces formed by π -conjugated SAM molecules adsorbed on close-packed metal surfaces of Ca, Mg, Al, Ag and Au, etc. Such molecules do not have a permanent dipole moment. By studying a range of metal surfaces and using different molecules, the position of the metal Fermi level and the positions of the molecular levels can be varied, respectively. Thus, their effect on the dipole layer formation at metal-organic interfaces could be analyzed afterwards.
- Another advantage to use Au, Ag or Pt as an electrode for the device fabrication, apart from the large interface barrier, is the fact that noble metals form abrupt unreacted interfaces with the polymer ^[81]. Therefore, measurements on the injection current at such an interface directly reflect the properties of an 'ideal' metal-polymer contact (noble metals/PPVs), unnecessarily to take into account the possible chemical interactions that change the electronic properties of the polymer at the contact and therefore mask the injection process.

In summary, we expect such a 'marriage' between the organic opto-electronic device physics and self-assembled monolayers could foster plenty of fruitful insights into the mechanism of charge carrier injection into polymeric and organic semiconductors.

7.3.4 Experimental Scheme

To carry on the proposed research, the following experiments will be performed:

1. Experimental investigations on the dipole formation at interfaces formed by self-assembled monolayers (for example the $-\text{CH}_3$ and $-\text{CF}_3$ terminated alkylthiolate monolayers) on close-packed metal surfaces such as Au (111).

In particular, we will monitor the relative changes in metal work functions upon chemisorption of SAMs using Kelvin Probe measurements or Scanning Kelvin Probe Microscopy (SKPM) technique, via systematically varying the following parameters:

- Different kinds of noble metals with their intrinsic work functions;
- Different SAMs (alkylthiolate or π -conjugated monolayers):
 - a) different types of molecules
 - b) dipole direction of the molecules
 - c) length of the molecular chains
 - d) with different packing density of molecules

All the results acquired from this part will serve as the crucial enlightenment and inspiration for the next step of our scheme.

2. Fabrications of polymeric LEDs (double carrier), hole-only and electron-only devices with different charge injection barriers:
 - a) Standard procedure for cleaning the glass substrates;
 - b) Bottom contact evaporation of noble metals onto glass substrates using high vacuum deposition system under N₂ in glove box: Glass/Cr/Au, Ag, Pt, or etc;
 - c) Tuning of the hole injection barrier by modifying the work functions of bottom electrode using chemisorbed SAMs on the metal anodes;
 - d) On top of the electrodes chemisorbed by SAMs, spincoating the functional polymers with:
 - various HOMO and LUMO levels (to fine tune the charge injection barrier)
 - different charge carrier mobilities (by structural modifications in the polymer chains)
 - e) Top contact evaporation of metal cathodes:
 - PLEDs (double carrier): Glass/Cr/noble metal/(SAMs)/functional polymers/Ba/Al
 - Hole-only devices: Glass/Cr/noble metal/SAMs/functional polymers/noble metal
 - Electron-only devices: Glass/Cr/noble metal/SAMs/functional polymers/Ba/Al
3. Temperature dependence measurements of the PLEDs, hole-only and electron-only devices using cryoprobe stations down to 8K: measure the current density vs applied voltage characteristics as a function of the operation temperature.

Through the numerical and analytical modelling of all the experimental data acquired, we will modify the existing models and then come up with a complete description/model of charge injection mechanism at metal-organic semiconductor interfaces to finalize this research.

8. Infrastructure

All research equipment needed for this project is present within the research group *Molecular Electronics: Physics of Organic Semiconductors* or the *Zernike Institute for Advanced Materials* (RUG).

9. Application Perspective

For at least the last 40 years, research into the electrical and optical properties of organic materials has been strongly motivated by their potential application in opto-electronic devices. Nevertheless, it is only in the past 10 years that serious efforts have been made to bring devices based on organics to commercialization. Leading this trend is the novel flat-panel display technology based on organic/polymeric light-emitting diodes (OLED/PLED) as now sold by Sony and others^[82]. Within the Netherlands, Philips research, TNO, Holst Centre, and others are pursuing the fabrication of PLEDs for lighting applications. More recently, breakthroughs have been made in the performance of organic field-effect transistors (OFET), where a primary motivation lies in the possibility of inexpensive solution processing^[83]. Patterning may be accomplished by simple printing techniques such as stamping, ink-jet, and screen printing. Of course, the performance of the electronic circuits fabricated in this manner is not expected to compete with that of silicon, but the low cost and the possibility of printing circuits on various kinds of substrates suggest applications that are ubiquitous: frequently mentioned are radio-frequency identification tags, attached to virtually every commodity. Organic

photovoltaics (OPV) are also being investigated for use in solar energy conversion and even more recently, crosspoint memory elements have been fabricated and shown to have promising bistable behaviour that would make them ideal components in non-volatile data storage arrays [84].

Although many aspects of organic devices mentioned above are already well understood and have been thoroughly documented in scientific and technical literatures, other properties, including charge injection at the interface between metal electrodes and organic semiconductors, which is the objective of this proposal, remain as topics of research. Part of the reason for the lack of complete understanding arises from the complexity of the interface, and the large number of chemical, structural, and morphological factors which affect the charge injection process. Another reason is the experimental difficulty of characterizing a buried interface, and the relatively small ratio of molecules at the interface to molecules in the bulk.

The commercial success of organic electronics will depend on continuing scientific progress in our understanding of charge injection mechanism. The proposed work is oriented to attack and eliminate the scientific and technical obstacles of this issue, aiming at unraveling a complete charge injection mechanism at metal-organic semiconductor interfaces. Such a critical and promising study will not only benefit the fundamental research but also bring us potential profits in the rapid-growing electronics industry.

10. References

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