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Abstract
In this short review the energy level alignment of interfaces involving solution-processed conjugated polymer (and soluble small molecules) films is described. Some general material properties of conjugated polymers and their solution-processed films are introduced, and the basic physics involved in energy level alignment at their interfaces are then discussed. An overview of energy level bending in (ultra)thin conjugated polymer films (often referred to as “band bending”) is given and the effects of ion-containing interlayers typically used in organic electronic devices such as polymer light emitting diodes and organic bulk heterojunction solar cells are explored. The review finishes by describing a few of the available computational models useful for predicting and/or modelling energy level alignment at interfaces of solution-processed polymer films and discusses their respective strengths and weaknesses.

1. Introduction

The study of organic semiconductors (OSC) goes back at least the late 1940’s,[1, 2] but has received comparatively little attention compared to the field of inorganic semiconductors. Semiconducting salts of π-conjugated organic molecules were demonstrated in the 1960’s,[3] but it wasn’t until the 1970’s demonstrations of highly conducting doped π-conjugated polymers[4] and crystals of organic charge transfer salts,[5] the later material class also showing superconducting[6] and ferromagnetic[7] properties, that a significant research community was formed. Finally, a series of papers demonstrated organic photovoltaic cells (OPV)[8] and light emitting diodes (OLED)[9] using thin films of vacuum-deposited OSC molecules as the active
layers, heralded the creation of the “modern” field of organic electronics. This ground-breaking work later led to the demonstration of similar devices made by solution-processed π-conjugated polymers and molecules as the active layers, \(^{10-13}\) paving the way for printed organic electronics. The field of organic electronics can be divided into two main areas depending on the processing (and type) of organic semiconductor: vacuum-deposited small molecules and solution-processed polymers and molecules, and these two areas have progressed in parallel with their own distinct research communities. This split also likely is partly due to the difference in materials synthesis (small molecules vs polymers). Vacuum processing and solution processing have their particular strengths and weaknesses. Vacuum deposition enables relative ease of multilayer formation, good control of individual layer thickness and morphology as well as formation of multi-component layers by co-deposition of two (or more) types of molecules. \(^{14-17}\) The drawback is mainly the cost and processing time. Solution processing enables comparatively high-speed film deposition through printing (screen, slot-die, spray, etc.) and consequently lower cost and lower energy consumption. \(^{18, 19}\) Using Langmuir-Blodgett and Langmuir-Schäfer techniques enables precise deposition of ultrathin layers (down to a monolayer) of uniform thickness which is a significant advantage in interface engineering of contacts in organic electronic devices. Drawbacks are that multilayer structures are more complex to print (orthogonal solvents are required), individual layer thicknesses are harder to control and multi-component layers require that the different polymers/molecules have a common solvent (less of an issue typically). Finally, conjugated polymer films obtained from printing techniques compatible with roll-to-roll printing typically yields more disordered films than what can be achieved by vacuum-deposition of small molecules. Choice of deposition technique, vacuum- or solution-based, thus significantly affects both film and interface formation with consequences for the (opto)electronic properties. The design of the electronic devices hence depends on the film processing technique used, though the basic concepts tend to be the same. Vacuum-deposited small molecules currently dominate in terms of market
presence (OLEDs in displays for cell phones, tablets and TV), but a wide variety of solution-processed polymer (and molecule) devices are pursued for commercialization such as polymer light emitting diodes (PLEDs), \[^{[20]}\] transistors, \[^{[21, 22]}\] bulk heterojunction solar cells (BHJSC), \[^{[23]}\] light emitting electrochemical cells, \[^{[24]}\] thermoelectric power generators \[^{[25-27]}\] and various bioelectronic components \[^{[28]}\] including electronic plants. \[^{[29, 30]}\] In the latter applications, the more porous films obtained from solution-processed polymers compared to vacuum-processed molecules is an additional advantage as it helps enable ion transport and hence makes it possible to combine ionic \textit{and} electronic currents in a system. Finally, though cost and energy advantages are often highlighted for the solution-processing of organic semiconductor films, “electronic plants” illustrate that sometimes solution-processing is the only feasible way as vacuum-deposition of organic films inside of plants are not an option.

Of particular importance to (opto)electronic devices is the interface energy level alignment and its depth-dependent variation (“band bending”), which affects e.g. charge injection/extraction, exciton dissociation and spin filtering. Energy level alignment at metal-organic and organic-organic (hetero)junctions/interfaces hence to a significant extent determine device performance in e.g. OLEDs, PLEDs and BHJSC, and are of general importance in organic electronics. As noted, the film deposition process affects interface formation, both in terms of molecular order and electronic structure, and consequently the interface energy level alignment often (but not always) differ between vacuum-processed molecular films and solution-processed polymer films. In this short introductory review, we will focus on energy level alignment at interfaces of solution-processed systems for printed organic electronics. This type of interface is characterized by weak interaction, \textit{i.e.}, physisorption, in contrast to the hybridized, more strongly-interacting interfaces typically formed upon vacuum-deposition. Readers interested in interfaces of vacuum-deposited OSC molecules are referred to e.g. these review papers. \[^{[31-35]}\]
This review is organized as follows: we first describe some general material properties of solution-processed OSC materials and films, where upon we introduce a conceptual model that describes the basic physics involved in energy level alignment at their interfaces and enables empirically-based predictions of energy level alignment. We discuss energy level bending in (ultra)thin conjugated polymer films (often referred to as “band bending”) and look at the effects of ion-containing interlayers typically used in organic electronic devices such as PLEDs and BHJSCs. We finish by describing a few of the available computational models useful for in silico prediction and/or modelling of energy level alignment at interfaces of solution-processed OSC films, and discuss the approximations used and the computational models’ relative strengths and weaknesses. [34, 36-42]

**Figure 1.** Sketch of sp\(^2\) hybridization and orbitals 2p\(_x\)-2p\(_z\) overlap forming a \(\pi\)-bond. The sp\(^2\) lobes forming the hand-shake \(\sigma\)-bonds are not shown.

2. **Conjugated polymer films**

The concept of \(\pi\)-conjugation is important for understanding the properties of OSC materials. The ground state electronic configuration of a carbon atom has six electrons: 1s\(^2\)2s\(^2\)2p\(^2\). When interacting with nearby atoms the electrons in the occupied valence \((n = 2)\) atomic orbitals can reorganize themselves to minimize the overall energy by promoting one of the two 2s electrons into the empty 2p orbital, subsequently forming linear combinations of the original \(n = 2\) orbitals. The \(\pi\)-conjugated polymers have sp\(^2\) hybridized carbon atoms forming the “backbone”, i.e. a linear combination between the 2s and the 2p\(_x\) and 2p\(_y\) orbitals, with the
2p\textsubscript{z} orbital unchanged, see Figure 1. As atomic orbitals are connected to the electron density around an atom, the electron density then is distributed in “lobes” extending out from the carbon atom specific to the sp\textsuperscript{2} hybridization. The location/direction of the lobes determines the bonding structure of the carbon as the lobes of neighboring atoms form bonds through a sort of hand shake. The high electron density in the intersecting lobes will screen the positive charge on the nuclei, decreasing the Coulomb repulsion and allowing them to move closer to each other compared to a case where the approach is along an axis lacking lobes and hence features less screening of the nuclei charge. From Figure 1 we see that sp\textsuperscript{2} hybridized carbon forms chemical bonds with three neighbors in plane at an angle of 120°. This type of bond is called covalent, as the two atoms forming the bonds share (valence) electrons. Bonds formed as a hand-shake between two lobes of neighboring atoms are called σ bonds as they are circularly symmetrical in cross section when viewed along the axis of the bond (the lobe hand-shake). The 2p\textsubscript{z} orbitals also can form bonds, so called π-bonds, see Figure 1, where two overlapping 2p\textsubscript{z} orbitals don’t contribute with electron density in the plane of the σ-bonds (not in the direct line drawn along the bond of the two carbon atoms), but they still contribute additional screening of the nuclei and hence produce slightly shorter bond lengths as compared to the simple σ-bonding case (sp\textsuperscript{3} hybridize or so-called saturated carbon). This is a so-called double bond (a σ- and a π-bond working together) and alternating single and double bonds due to sp\textsuperscript{2}-hybridized carbons and the so-called Peierls transition is a defining feature of π-conjugated materials. As noted, when σ- and π-bonds are formed, they form by overlap between atomic orbitals on adjacent atoms. When these electron clouds coincide in space, both the energy and the shape of the interacting orbitals change. The resulting shared orbitals are called molecular orbitals, and the electronic structure of a molecule can be described as a linear combination of its molecular orbitals, in analogy how the electronic structure of an atom can be described as a linear combination of its atomic orbitals.\textsuperscript{[43, 44]}
Figure 2. Top: Illustration of a monomer, oligomer, polymer, copolymer and ordered polymer chains vs. bent/folded chains. Bottom: Evolution of the electronic structure near the HOMO-LUMO gap going from a monomer to a polymer.

The electronic structure of a conjugated polymer chain is defined by the choice of molecular repeat unit (monomer), number of repeat units and the relative concentration and repeat order in the case of several repeat units (copolymers). The molecular orbitals of each conjugated repeat unit overlap and create new hybridized orbitals, where the resulting polymer highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are typically of $\pi$ and $\pi^*$ type. For sufficiently long linear polymer chains, energy bands are
eventually formed in the ideal case, with the polymer HOMO becoming the valence band edge
and the polymer LUMO the conduction band edge. The band gap defined as the HOMO-LUMO
energy difference can be tuned by introducing intermolecular torsion (decreasing the \( \pi \)-orbital
overlap between the repeat units) or as noted above using two or more different OSC molecules
as repeat units, in different relative concentrations and either in a specific pattern or randomly
mixed along the linear chain. Sometimes non-conjugated segments are added in the polymer
chain to break conjugation and localize the orbitals over segments, basically creating a set of
linked oligomers. Kinks or twist in the polymer chain can do the same thing and a bent/folded
polymer chain is thus electronically and optically ~equivalent to a set of oligomers of varying
length, each of which have distinct HOMO/LUMO orbitals and optical band gap, see Figure 2.
[43, 44]

OSC, polymers and molecules, are “soft” materials, not only from a mechanical
standpoint but also in terms of the electronic structure. In general, adding charge to (reducing)
or subtracting charge from (oxidizing) conjugated molecules causes both electronic and bond
distortions as the molecule first reorganizes its electronic density in response to the charge,
where after the nuclei react to the new electron density. Increased electron density between the
nuclei causes decreased bond length as the positive charge of the nuclei are better screened.
Decreased electron density between the nuclei correspondingly yields increased bond length.
The combination of a charge with an accompanying distortion of the polymer/molecule lattice
is called a polaron, and they are then inherently localized in space, typically on a single
molecule or part of a polymer chain. Note that the cost in energy of removing an electron from
the HOMO, called the ionization potential (IP), is thus less than the HOMO energy versus the
vacuum level, as the polymer re-optimizes both its electronic and bond-structure in response to
the created hole. Similarly, the energy gained from adding an electron to the LUMO, called
electron affinity (EA), is greater than the LUMO energy vs vacuum level difference for the
analogous reason. The IP/EA are thus the positive/negative polaron formation energies.
Figure 3. Change in IP and EA going from gas phase to a solid.

A single polymer chain (or molecule) in gas phase is not what is used in organic electronic devices. Instead we have e.g. polymer films, films of polymers blended with other organic semiconductors or with (poly)electrolytes. This has an effect on the electronic (and optical) properties. If we remove an electron from the HOMO of a polymer chain, the polymer reorganizes its electron density as described above and additionally the electron density on the nearby polymer chains in the film will also be slightly modified, further screening the charge on the ionized polymer. \[45\] The local medium is polarized in response to the charge on the polymer and both the gas phase IP and EA will be modified:

\[
IP_s = IP_g - P_+ \quad \text{and} \quad EA_s = EA_g + P. \tag{1}
\]

where \(P_+\) and \(P_-\), are the polarization energies in response to a positive and negative charge, respectively, and subscript \(s\) (\(g\)) indicates solid (gas) phase, see Figure 3. Hence, less energy is required to oxidize a polymer chain in the solid state (film) and more energy is gained
when reducing the polymer chain, $\langle \text{IP}_g \rangle$ and $\langle \text{EA}_g \rangle$ (EA and IP are defined as positive). This effect is significant, typically well over 1 eV. There are additional structural effects appearing going from gas phase to solid phase. Most conjugated polymer films are amorphous or a mixture of well ordered (polycrystalline) regions and disordered (amorphous) regions. Hence, the concept of energy bands does not hold, and the electronic structure of a conjugated polymer films is defined by localized states (molecular orbitals). As the local environment varies in the films, the $P_+$ and $P_-$ contributions will vary as well. This means that we have a distribution of ionization energies for each orbital, resulting in a much broader density of such states as compared to the discrete states (neglecting vibrational broadening) in gas phase, see Figure 3. The film disorder may also introduce kinks, varying degrees of intrachain torsion and different interpolymer orientations, further contributing to the energetic disorder. So, in a polymer film, we will have a distribution of polaron formation energies localized on specific segments on the polymer chains, and the film IP will then be defined as the smallest individual positive polaron formation energy and the film EA as the largest individual negative polaron formation energy, both connected to polymer segments that can be found somewhere in the film. The distributions of polaron formation energies will hereafter be referred to as polaron density of states (DOS). Note that there are per definition no gap states in absence of doping or impurities as the frontier IP/EA energies created by variations in molecular order, etc., define the actual gap. (In practice, one typically selects a point, i.e. the edge, of the respective polaron DOS obtained from experiments, and the remaining tail states are unfortunately often referred to as gap states in literature). Note that this is fundamentally different from a single crystal where we have a well-defined crystal structure, energy bands derived from that crystal structure and thus a well-defined gap between the upper edge of the valence band and the lower edge of conduction band. The polaron DOS is not necessarily the same in the bulk compared to the interface region(s), as the interface may affect the local film order and hence the polarization energy. Additionally, the screening from the substrate/contact material can play an important
role as e.g. for a metal substrate where the Coulomb interaction with the image charge formed upon ionization of a polymer segment will have a significant distance-dependent contribution to the overall polarization energy.\footnote{49-52} Hence, the center of the polaron DOS at an interface is typically shifted compared to the corresponding polaron DOS in the bulk of the film and the width/shape of the polaron DOS may differ as well. These are important points for device design, as we will discuss further in the review.

3. **Energy level alignment at solution-processed interfaces**

Ultraviolet photoelectron spectroscopy (UPS) is a technique commonly used to study energy level alignment at interfaces as it is surface sensitive and can track both the vacuum level (\textit{i.e.} work function) shifts and the occupied electronic structure of both the substrate and the organic overlayer at an interface (though the latter sometimes overlap),\footnote{31,32} unlike Kelvin probe measurements that only track the vacuum level shift upon interface formation. The UPS measurement uses monochromatized light (typically HeI with $\nu =21.2$ eV) to ionize a material and the subsequently photoemitted electrons and their kinetic energies are then detected, yielding the ionization energies, including the ionization potential (the energy needed to ionize the HOMO, typically defined as the low binding energy edge of the UPS spectrum). The work function is obtained from the so-called secondary electron cutoff, \textit{i.e.}, the binding energy versus vacuum level of the electrons that are photoemitted from the sample with a zero kinetic energy (the high binding energy edge of the UPS spectrum).\footnote{31,32}

Interfaces created by solution-processed deposition of polymer films onto a substrate (organic or inorganic) differ from vacuum-processed deposition of organic molecules onto e.g. atomically clean metal substrates. In the latter case, chemisorption typically occurs with resulting hybridization between the molecular orbitals and the surface states of the metal and partial (non-integer) charge transfer between the adsorbed molecules and the substrate. The energy level alignment at such interfaces will then depend on the specific chemical interactions
and hence the substrate material, its surface crystal orientation (if any) and the organic molecule. The hybridization between the substrate and the molecules at the interface that almost always features a net charge transfer, together with the so-called “push-back” effect, ensure that there will be a shift in the vacuum level at such interfaces.\cite{32} For the solution-processed films, the substrate surface is “pre-passivated” by interaction with atmosphere (or solvent), often modifying the substrate work function in case of metals, and the polymer films are physisorbed.\cite{32, 49} There is no significant hybridization of the molecular orbitals at such interfaces and hence no partial charge transfer across the interface.\cite{32, 49} Hence, as we shall show in the following paragraphs, energy level alignment at such interfaces display a much more regular behavior and quite often feature no vacuum level shift. The situation is less clear-cut for vacuum-processed organic films on organic (semi)conductor substrates that in fact typically feature physisorption (unless involving e.g. organic radicals), and for metal and inorganic semiconductor substrates with native oxides or surface hydrocarbon contaminates present, there can be a mixture of chemisorption and physisorption or just physisorption depending on the completeness of coverage of the oxide/hydrocarbon surface layer. In general, substrates handled in air prior to vacuum deposition and not cleaned in situ are expected to yield physisorbed interfaces.

The energy level alignment of such interfaces involving solution-processed conjugated polymer films (and weakly-interacting physisorbed OSC interfaces in general) follows the general trend described in the so-called Integer Charge Transfer (ICT) model \cite{32, 49, 53} and obtained in experiments \cite{32, 38, 39, 49, 53-62}; three distinct energy level alignment regions are observed when tracking the resulting work function ($\Phi_{\text{ORG/SUB}}$) upon coating of a substrate (i) $\Phi_{\text{SUB}} < E_{\text{ICT}}$: Fermi level pinning and substrate-independent work function, slope = 0; (ii) $E_{\text{ICT}} < \Phi_{\text{SUB}} < E_{\text{ICT}+}$ vacuum level alignment and a substrate-dependent work function, slope = 1; (iii) $\Phi_{\text{SUB}} > E_{\text{ICT}+}$ Fermi level pinning and a substrate-independent work function, slope = 0,
see Figure 4, where $\Phi_{\text{SUB}}$ is the work function of the (surface-passivated) substrate and $E_{\text{ICT}^{+/-}}$ are called the positive/negative pinning energies. This behavior is in sharp contrast to the case of chemisorbed molecular OSC layers $^{[31, 33]}$ and thus serves as a marker for physisorbed interfaces.

**Figure 4.** Top left panel: Typical energy level alignment behavior for weakly-interacting organic semiconductor interfaces that follow the ICT model, where the resulting work function ($\Phi_{\text{ORG/SUB}}$) is either independent (i, iii) or linearly dependent with a slope of ~1 (ii) of the substrate work function ($\Phi_{\text{SUB}}$). Top right panel: Diagram showing energy level alignment including pinning energies and the interface distance dependence of the polaron DOS. Here the Fermi level is pinned to the $E_{\text{ICT}^{+}}$ (oxidation of polymer segments at the interface causing Fermi level equilibrium). Bottom left, center and right panel: interface energy level diagrams illustrating regions (i), (ii) and (iii) of the ICT model, respectively.
What then is the origin of this regular behavior? In general, when two surfaces are brought into contact, the chemical potential must be equilibrated across both films including their interface. This is typically referred to as Fermi level equilibration, a terminology we will use in this review as well. This occurs through the flow of charge across the interface, which builds up a potential step (Δ) shifting the vacuum level, the more charge transferred, the larger the potential step. Conceptually, this is similar to water flowing between two bodies of water that are connected, equilibrating the water level in both. The regions (i) and (iii) of the ICT model feature Fermi-level pinning and slope=0, i.e. a vacuum level potential step Δ that scales with the difference between the substrate work function and polymer film-dependent pinning energies (E_{ICT+/}). The observed potential step originates from spontaneous integer charge transfer across the interface via tunneling to equilibrate the chemical potential (Fermi level). This occurs when the substrate work function is higher than the energy required to take away one electron (lower than the energy gained from adding one electron) from (to) the polymers at an interface, i.e. the positive (negative) polaron formation energies. The most easily oxidized/reduced segments of the polymers hence will be “used up” until enough charge has been transferred across the interface to create a potential step that equilibrates the chemical potential (Fermi level). The energy where the Fermi level is subsequently pinned is referred to as E_{ICT+/} depending on if it is positive or negative polarons that are being created. Now, for region (ii) of the ICT model we have vacuum level alignment, slope = 1 and hence no potential step at the interface. Conceptually, this is the case of where one of the connected water reservoirs has a comparatively very small volume, and then only a negligible volume of water need to be transferred to equilibrate the respective water levels, see Figure 5. Analogous, if the substrate Fermi level is positioned where the density of states (DOS) available for charge transfer in the polymer films is very low, i.e., in the IP-EA gap, the chemical potential is equilibrated without creating a significant potential step and the vacuum levels thus align. The DOS in the film IP-EA gap is not zero, but for typical conjugated polymer films it is low enough
so that no potential step is observed even for micrometer thick films.[63] Note that the analogy in Figure 5 is over-simplified. The charge transfer is affected by the electrostatic force and hence rather than drawing an equal amount of charge from each layer of the film, most of the charge is obtained from the region close to the interface (see e.g. “depletion region” in semiconductor physics) unlike the water reservoirs where the gravitational force ensures an equal amount of water drawn from across the whole reservoir.

Figure 5 Chemical potential (Fermi level) equilibration in region (ii) of the ICT model illustrated by water levels in two containers before and after connection. As the smaller container has negligible volume of water (DOS) compared to the large container, the water (charge) transferred to equilibrate the water (Fermi) level is negligible and the common post-connection water (Fermi) level is ~unchanged from the large container’s pre-connection water (Fermi) level ($E_F = E_{1F}$).

Unless a crystalline film, the interface polarons will be localized on one or more polymer segments (depending on local order, orbital overlap etc.). Note, the ICT states formed in this process are not pre-existing polarons (nor are they photogenerated), they are created upon interface formation if equilibration of the Fermi level demands it. Furthermore, as noted, they generally do not have the same formation energy as the bulk polarons do, mainly due to strong Coulombic interaction with the opposite charge across the interface (and sometimes different film order at the interface compared to the bulk, also affecting the polarization contribution to the polaron formation energy as noted). There is thus a distribution of these
energies connected to specific polymer segments of varying size, orientation, local environment and distance to the substrate, and this interface polaron DOS (sometimes referred to as ICT DOS to highlight the contribution to the polarization energy from the transferred integer charge) typically will differ from the bulk polaron DOS.\textsuperscript{[49, 64, 65]} Hence it is not enough to use the bulk polaron formation energies (IP/EA) to estimate interface energy level alignment, measured (or calculated) values for the interface polaron formation energies are needed as well. In fact, the energy level alignment for polymer (or molecular) films can be understood as a series of individual polymer layers, each with their own polaron DOS and their respective interface energy level alignments described by the ICT model, in analogy with what has been demonstrated for hetero-multilayer films.\textsuperscript{[37, 66]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Experimentally derived $\Phi_{\text{ORG}}$ vs $\Phi_{\text{ORG/SUB}}$ for a series of solution-processed OSC films where the substrates include metals, metal oxides, semiconductors and conducting polymers. Data taken from Bao, \textit{et al.}~\textsuperscript{[60]}}
\end{figure}
Despite the dependence on local order, solution-processed small molecules such as fullerenes and conjugated polymers typically display $E_{\text{ICT}^+, -}$ values independent on the substrate they are combined with.\cite{32, 38, 39, 49, 53-62} This may at first glance appear counterintuitive, yet is a direct consequence of the non-single-crystalline nature of such films. Unless the surface energies of the substrates are radically different, the same types of local molecular order at the interface will be present upon film formation (to greater or lesser degree) and so are then the “most easily oxidized / reduced” sites that participate in the equilibration of the Fermi level. Hence, the $E_{\text{ICT}^+, -}$ values obtained typically deviate very little ($\pm 0.1$ eV) as can be seen from \textit{e.g.} Figure 6, even though both organic and inorganic substrates featuring different surface roughness, surface energy and potential for solvent-induced interface intermixing are used. However, if ordered films are formed and the orientation can be controlled by \textit{e.g.} roughness or widely differing surface energy of the substrates, the expected corresponding order dependence in $E_{\text{ICT}^+, -}$ values, which can be as large as $\sim$1eV, is indeed obtained,\cite{67} a consequence of the demonstrated effects of intermolecular order on ionization energies.\cite{45, 46, 48}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Energy level alignment diagram illustrating (a) abrupt potential step and (b) extended energy level bending in region (iii).}
\end{figure}

In regions (i) and (iii) of the ICT model we see that a potential step is introduced at the interface in order to equilibrate the Fermi level. An additional factor of importance is over what
distance from the interface the potential step extends, an abrupt potential step (1-2 polymer layers) or a more long-range potential gradient (e.g. 10 or more layers), see Figure 7. Experimental results from literature give a conflicting picture as there are examples of abrupt potential steps and extended energy level bending both for vacuum-deposited conjugated molecules and solution-processed polymers.\cite{38, 64, 65, 68-76} In fact, there are examples in literature of both abrupt potential step \cite{64, 68, 72} and extended energy level bending \cite{64, 71} even for the same material, regioregular poly(3-hexylthiophene) (rr-P3HT). A general observation is that when the film is free from impurities, i.e., when well-purified molecules and polymers are used, an abrupt potential step is observed, whereas when impurities are present (due to synthetic procedure and/or deposition conditions) sufficient free charge density may be present inside the energy gap to drive extended energy level bending.\cite{73} (For such high levels of impurity concentrations in the polymer films, the vacuum level alignment of region (ii) will fail and extended energy level bending will occur also here.) Impurity-driven energy level bending however is not the only explanation to the experimentally observed cases in literature, and we will now discuss abrupt potential step vs extended energy level bending where impurities and dopants do not play a significant role.

Assuming an absence of (significant) impurities, i.e. high-quality material, we will have vacuum level alignment in region (ii) and a potential step in regions (i) and (iii), where for (i) electrons are transferred from the substrate to the polymer film and for (iii) electrons are transferred from the polymer film to the substrate, with the most easily reduced (i) or oxidized (iii) polymer segments used up until sufficient charge has been transferred to equilibrate the Fermi level. As the proximity to the interface affects the polarization energy contribution to the polaron formation energy, the polaron DOS of polymer segments located in the first layer at the interface will then on average be pushed into the gap compared to the polaron DOS of polymer segments located in layers further away from the interface. If the difference in polarization energy is sufficiently large in comparison with the polaron DOS width, the Fermi
level will be pinned to the interface layer polaron DOS and the potential step will only extend over one to two layers, \cite{64, 68, 72, 73, 75} see Figure 7a, as the polaron DOS of the subsequent polymer layers now resides deeper than the Fermi level of the “new” effective substrate and hence we are in region (ii), vacuum level alignment. If, however, the interface-distance-dependent polarization energy variation is sufficiently small in comparison with the polaron DOS width, see Figure 7b, an extended energy level bending region will be obtained.\cite{64, 69, 70}

To explain this scenario in more detail, we use the layer-by-layer application of the ICT model. First assume a polymer layer deposited on a substrate, conforming to region (i) or (iii). Then charge will flow from the polaron DOS of the polymer monolayer, breaking the vacuum level alignment by introducing a potential step at the interface that grows until Fermi level equilibrium is reached, see Figure 7b. Formation of an additional polymer layer on top of the first will cause electron transfer from the upper part of the polaron DOS tail extending above the new Fermi level position. The amount of charge transferred to the substrate will now be smaller, however, compared with the first layer, as less charge is needed to force Fermi level equilibrium at the interface between the first and second layer (Figure 7b), thus resulting in a smaller potential step. Additional layers formed will behave in the same way, but with progressively smaller amounts of charge transfer and correspondingly smaller potential steps, as less and less of the DOS tails extends above the Fermi level for the initial vacuum level alignment at formation.\cite{64, 69, 70} This will create a significant space charge region and consequently an extended energy level bending.\cite{38, 69, 70} Another reason for experimentally observed extended energy level bending is found in problems with the experimental methodology. As each polymer layer is on the order of 2-2.5 nm in thickness, to properly track the energy level bending, a series of uniform films spanning the range from 2 nm to 10-20 nm are needed, which is difficult to produce through solution processing (also the case for vacuum processing). We will further illustrate the energy level bending phenomena in (ultra)thin solution-processed polymer films using the aforementioned case of rr-P3HT.
Figure 8. Film thickness dependence for TQ1, rr-P3HT and (annealed) rr-P3HT Langmuir-Schäfer deposited films. Data taken from Bao, et al. [64] Note that annealing cause ring-torsion induced disorder in the rr-P3HT films and a decreased E_{ICT}. [64, 104]

Figure 9. Comparison of film thickness dependence for annealed rr-P3HT Langmuir-Schäfer (LS) films and spin-coated (SC) films. The film thickness for the SC films are “nominal” in that the films are non-uniform in the ultrathin region (<10 nm). The non-uniform coverage of the substrate causes the error in the SC film experimental series yielding an extended energy level bending region where there is in fact none. Data taken from Bao, et al. [64]
The literature on rr-P3HT displays contradicting energy level bending scenarios in region (iii) though their final work functions of the rr-P3HT coated substrates (\(\Phi_{\text{org/sub}}\)) are in agreement with the typical \(E_{\text{ICT+}}\) of rr-P3HT.\(^{[53, 59]}\) Schneider, et al, obtained a 40 nm energy level bending region for ITO (\(\Phi_{\text{sub}} = 4.8\) eV) substrates and virtually no potential drop at the interface, which was explained assuming a Schottky-Mott type model where the film is slightly p-doped by atmosphere and the extended energy level bending is impurity driven (depletion of impurity-induced gap states).\(^{[71]}\) Frisch, et al, on the other hand, found almost all of the potential drop occurring over the first rr-P3HT layer at a PEDOT:PSS (\(\Phi_{\text{sub}} = 4.9\) eV) interface and essentially no energy level bending extending beyond the first monolayer.\(^{[68]}\) Finally, Zhao and co-workers found that rr-P3HT (and PBTTT) films on gold (\(\Phi_{\text{sub}} = 5.3\) eV) and PEDOT:PSS (\(\Phi_{\text{sub}} = 5.2\) eV) substrates show no energy level bending beyond 5 nm and almost all of the potential drop occurs over the first monolayer at the interface (~2.5 nm), which they attributed to image charge polarization strongly affecting the polaron DOS of the interface layer\(^{[72]}\) as discussed above. All of those studies used spin-coated rr-P3HT films, which can be a source of experimental error due to the problems of making uniform ultrathin films with this deposition technique. To circumvent that problem, Bao, et al, used Langmuir-Schäfer (LS) deposition of mono- and multilayer rr-P3HT (and TQ1) films on gold to precisely track the thickness-dependent evolution of the energy level alignment and compared the results with spin-coated films of similar estimated thicknesses on the same type of gold substrates.\(^{[64]}\) The inter-polymer order (inter-chain \(\pi-\pi\) stacking) was further manipulated by annealing to probe the effect of localized versus delocalized polarons in the polymer (multi)layers. The LS films featuring more localized polarons, annealed rr-P3HT (and TQ1), showed an abrupt potential step (~1-2 layers), as expected from a strong interaction with the substrate image charge, whereas the well-ordered rr-P3HT films featuring more delocalized polarons showed a more extended energy level bending (>20 nm), again as expected from the ICT model due to weaker interaction with the
image charge, see Figure 8. Interestingly, the annealed rr-P3HT spin-coated films show extended energy level bending in the experiments due to non-uniform coverage in the ultrathin thickness range, illustrating the spurious results that can be obtained due to non-uniform ultrathin films, see Figure 9.[64]

![Energy Level Alignment Diagram](image)

**Figure 10.** Schematic energy level alignment and polaron DOS of (a) an interface where the Fermi level becomes pinned to the E_{ICT+}, (b) an interface with a thin interlayer (purple) inserted between the conjugated polymer (red) and electrode and (c) an interface where the Fermi level is pinned to the interlayer E_{ICT+} and the effective interlayer/electrode work function is too low to efficiently inject into the polaron DOS of the conjugated polymer film.

The generally abrupt potential step (1-2 layers) at interfaces involving solution-processed conjugated polymers has important consequences for devices such as PLEDs, BHJSC and transistors. Consider a metal/polymer contact in region (iii), Figure 10a. A hole
injected from the metal electrode into the first polymer layer will then experience a barrier moving into the second layer and beyond as the bulk polaron DOS are located below the Fermi level. The analogous situation occurs for electron injection at region (i) contacts, where the interface polaron DOS is located deeper into the gap as compared to the bulk polaron DOS. Hence, even for pinned contacts, regions (i) and (iii), there will be a barrier towards charge injection, which also is experimentally observed.\cite{65,77} By modifying the distance between the electrode surface and the polymer (or molecule), we however can decrease the image charge interaction and shift the polaron DOS of the first layer closer to that of the bulk polaron DOS, see Figure 10(b). This has been demonstrated using solution-processed non-conjugated self-assembled interlayer spacers on gold substrates and OSC molecules, where an 0.3 eV shift of the interface polaron DOS was observed going from the case of intimate contact to a ∼2 nm spacer layer.\cite{52} Kotadiya, et al, recently made use of this effect to address the problem of achieving Ohmic hole-injection into organic electronic devices.\cite{77} They demonstrated that the injected hole current from various high work function electrodes improves by more than an order of magnitude by using an organic semiconductor interlayer/spacer-layer that prevents intimate contact between the organic semiconductor and the electrode and thus reduce the polarization effect on the interface polaron DOS.\cite{77} The experimental rule of thumb was to use an interlayer with a significantly larger IP than the organic semiconductor of the main layer (>0.3 eV),\cite{77} which likely has its origin in the need to prevent the scenario where the Fermi level pinned to the interlayer polaron DOS is too shallow to effectively inject holes into the main layer, see Fig 10c.

Modification of electrodes with interlayers are thus an important tool in designing organic electronic devices, and a wide variety of vacuum-processed alkali halides and metal oxides have been used to good effect,\cite{78-80} forming either spacer-layer as above or introducing potential steps at the interface either by intrinsic dipoles of the interlayer itself or through doping of the organic semiconductors at the interface. More recently, solution-processed
interlayers for printed organic electronic devices such as BHJSC and PLEDs have achieved widespread use,\textsuperscript{[81-87]} where again intrinsic dipoles\textsuperscript{[88]} or doping\textsuperscript{[89, 90]} can play a role besides the spacer-layer effect. However, using scanning Kelvin probe microscopy van Reenen and co-workers observed that disordered ion-containing conjugated and non-conjugated polymers (polyelectrolytes) introduced significant potential steps at electrodes when used as interlayers, and furthermore, the potential steps were abrupt and independent of interlayer thickness, suggesting additional mechanisms involved.\textsuperscript{[91]} In a series of experiments using poly[(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), poly(4-styrenesulfonic acid) (PSSH) and Nafion they also tracked the substrate material dependence on the size of the potential step, see Table 1, finding that polyelectrolytes produced larger shifts in the vacuum level for interfaces with conducting substrates compared to semiconducting substrates, and virtually no shift (vacuum level alignment) for non-conducting substrates.\textsuperscript{[91]} By varying the ions and hence ion radius further information was gained in that small ions produced larger potential steps compared to large ions.\textsuperscript{[91]} Based on these observations, the effect of polyelectrolytes as interlayers was explained as follows. The polyelectrolyte interlayers contain both positively and negatively charged species. When in contact with a metallic (or highly-doped semiconductor) substrate, the substrate surface is polarized by these charged species, forming image charges. The image charges formed in the substrate have the opposite charge to their respective charged species in the interlayer and attract those species towards the substrate surface, see Figure 11a. How close the charged species in the interlayer can come to the substrate surface depends on the size of the species and their ability to move in the interlayer. A significant difference in size and/or ability to move leads to a significant difference in the final (equilibrium) positions at the substrate surface and hence induces a dipole and related potential step between the interlayer charge species, see Figure 11a. This dipole in the interlayer then induces a dipole in the substrate, creating a “double dipole step” in the vacuum level at the substrate/interlayer interface.\textsuperscript{[91]} If the anion is the
smaller/more mobile of the two charged species in the interlayer, see Figure 11b, the work function is decreased, whereas if the cation is smaller/more mobile than the anion, the work function is increased by the interlayer, see Figure 11c. (Note that the charged species do not necessarily have to be ions. In PFN, the relevant charged species are the amine nitrogen atom and its lone pair electrons in the sp³ orbital). The attracting (Coulomb) force from the image charges are significant only close to the substrate surface, which is why interlayer thickness does not significantly affect the work function shift. The strength of the polarization of the substrate by the charged species in the interlayer, significantly depends on the permittivity of the substrate material, so that for metals and to lesser extent (highly-doped) semiconductors there is a large effect, whereas for insulators, the effect will be small/negligible.

For conjugated polyelectrolytes, there is an additional effect besides the image-charge-induced double dipole step, described by Bao, et al. [61] Considering regions (i), (ii) and (iii) of the ICT model, we readily see that the effect of the ion-induced interface double dipole step always will be present for all cases (assuming conducting or semiconducting substrates) as the ion-containing-interlayer-induced polarization of the substrate does not depend on the substrate work function. If the double dipole step induced modification of the work function places the Fermi level in region (i) or (iii) we will get an additional effect, as (i) negative or (iii) positive polarons then are formed in the conjugated polyelectrolyte interlayer, pinning the Fermi level and setting the lower and upper limit for the electrode work function that can be achieved, see Figure 12a. [61] In this manner, the ICT curve is shifted downwards (or upwards) by the double dipole step, see Figure 12b, depending on if it is the negative (or positive) charged species of the conjugated polyelectrolyte that is smaller/more mobile. [61] The solution-processed conjugated polymer interlayer technology thus offers tremendous design freedom as the both choice of conjugated backbone and choice of charged species can be used to tune the work function of an electrode as well as introduce selective charge blocking functionality.
4. Computational methods for energy level alignment modelling and screening of materials

The ICT model attempts to conceptually describe the physics involved in energy level alignment at interfaces involving physisorbed organic semiconductors, but it does not provide a framework for calculating charge transfer, vacuum level shifts, etc., but relies on experimentally derived parameters to make predictions and/or explain energy level alignment behavior. Hence, it does not by itself enable computational design or modelling of interfaces or interface materials which is a significant drawback. Density Functional Theory (DFT)\cite{92,93} has, to a degree, revolutionized materials research and development as its modern versions enable computational design and screening of materials.\cite{94,95} Though determining the ground state electronic structure of OSC molecules and polymers through DFT calculations are routinely done, the actual electronic (and optical) properties of their films and interfaces are in fact controlled by their ionized (or excited) states, that in turn are dependent on the intermolecular order that rarely, if ever, is single-crystalline in printed organic electronic devices. Fully transferring the ICT model into a working computational-based method hence is a difficult task. Promising efforts using multiscale modeling to obtain e.g. film morphology and corresponding optoelectronic properties starting from calculated properties of the individual molecules are under way, \cite{96,97} and through this approach, the polymer/molecular order can be modeled and knowing the local order, distance to substrate, etc., the polaron DOS hence also could be obtained and the energy level alignment determined. This multiscale approach is quite demanding in terms of computational effort, so simpler ways of dealing with film disorder and related effects are often used, e.g., by assuming a Gaussian distribution of the polaron DOS induced by the disorder. \cite{98,99} This is also the case for a number of useful computational methods, all featuring different ways to deal with the film (and particularly interface) order effects in the ICT model. The chosen approximations that have their own strengths and
limitations and also affect the predictive power (materials screening) contra the usefulness for modeling.

A paper by Bokdam, *et al.*, introduced a simple yet powerful approach to calculate the energy level alignment based on the individual molecular structure and either a known or assumed preferential order of the interface layer (the first polymer/molecular layer covering the substrate).\[40\] It is assumed that no significant hybridization of the orbitals occurs through interaction with the substrate and that integer charge transfer by oxidizing or reducing the polymer segments (or molecules) at the interface equilibrates the Fermi level when in regions (i) and (iii) and vacuum level alignment in region (ii). The Coulomb interaction between the transferred charges and their image charges locates the charge transfer mainly to the first layer at the interface (see discussion on energy level bending and the implicit assumptions on polarization strengths vs polaron DOS width) so that a “double layer” is formed. The authors thus approximate the actual interface as a plane capacitor and from this basic assumption the following expressions for the pinning energies ($E_{ICT^-}$) are derived:

$$E_{ICT^-} = EA + B^- , \quad E_{ICT^+} = IP - B^+$$

(2)

where $B^{-^+}$ is the Coulomb energy associated with charging a polymer segment / molecule in the organic layer of the plane capacitor. The authors further make the assumption that though the impact of the substrate-induced screening on EA, IP, B^- and B^+ of the organic layer can be large, they approximately cancel each other out so that $E_{ICT^-}$ (EA + B^-) and $E_{ICT^+}$ (IP - B^+) become substrate (and interface capacitance) independent. Hence the EA, IP and B^{-^+} all can be obtained through DFT calculations on the 2D polymer interface layer only, i.e., due to the approximations used, the screening from the substrate material and hence substrate – interface layer distance does not need to be included.\[40\] This computational model thus is highly suitable for screening of materials and interface designs and indeed has proven successful in generating energy level alignment estimates within ± 0.1 eV of experimental results for both simple interfaces and multilayer stacks (metal/organic, metal/organic/metal, metal/organicA/organicB,
The drawback of the model is that it excludes energy level bending beyond the first layer, having a priori limited the charge transfer to the first layer. As discussed in the energy level bending part of the review, this is typically but not always the case in solution-processed films. Note also, since the polaron formation energies (EA/IP) depend on the film order, if an incorrect film order is assumed in the DFT calculations, the E_{ICT+/} values obtained suffer in accuracy accordingly. Furthermore, by not modeling the full interface polaron DOS, a “fat tail” scenario could cause the estimated pinning energies to deviate significantly (>0.1 eV) from the experimental values.

Ley, et al, proposed a different approach focusing on metal oxide/organic interfaces (expanding upon earlier work by Greiner, et al), though the approach is applicable to other substrates typical in solution-processing such as e.g. hydrocarbon-passivated metals. Again, weakly interacting interfaces described by the ICT model is assumed and the authors also assume a plane capacitor approximation of the interface like Bokdam and co-workers. Unlike that approach, Ley, et al, keeps the interface capacitance C as a parameter, as well as the area density of charged molecules in the interface layer, n, in their calculations. From this they derive the following expression for the interface vacuum level shift $\Delta$ in region (iii):

$$\Delta = \left( e^2 n/C \right) \left[ 1 + g \exp((\text{IP} - \Phi_{\text{sub}} + \Delta)/kT) \right]^{-1}$$  \hspace{1cm} (3)

where g is the degeneracy factor for the molecular orbital associated with the IP. For region (i), Equation 3 is reproduced by replacing IP with EA, and g becomes the degeneracy factor for the molecular orbital associated with EA. The IP/EA values of the polymer segments / molecules in the interface layer can be calculated using DFT, which also gives the respective g. This computational model reproduces the typical ICT-curve ($\Phi_{\text{ORG/SUB}}$ vs $\Phi_{\text{SUB}}$) but with slightly “round” shoulders rather than sharp angles at the transition points between regions (i) and (ii) and regions (ii) and (iii), sometimes also observed experimentally. The advantage of this model is that the effects of the passivating layer on a metal surface (carbohydrates, native
oxides, alkali-halides etc.) can be modeled and Ley and co-workers also show how defect densities in the substrate surface layers (often important for metal oxides\textsuperscript{[101, 102]} and alkali-halides\textsuperscript{[103]}) can be treated by an extension of this approach. The drawbacks with the model are again that the plane capacitor approximation does not explicitly enable the treatment of energy level bending (charge is assumed to reside in the first layer only) and that the added freedom of having C and n as parameters in modeling also means that they must be known, measured or correctly guessed in order to be used for predictive purposes (materials / interface design). Finally, this model also does not treat the full interface polaron DOS, which as mentioned can introduce significant errors.

A computational approach that does include a treatment of disorder-induced polaron DOS has been introduced by Oehzelt, et al.\textsuperscript{[34]} Their model makes use of multilayer stacks of organic molecules where the number of molecules, layer thickness and polaron DOS can be introduced individually for each layer, so that both the center energies and widths of the polaron DOS can be varied depending on layer distance to substrate \(z\) to simulate effects of image-charge polarization, different intralayer order and hence intralayer polarization, etc. The polaron DOS is however not calculated, but the IP/EA are broadened using e.g. a Gaussian function of a chosen width for weakly interacting interfaces (or a Lorentizan function when simulating chemisorbed layers). The charge density of each layer \(\rho(z)\) is then calculated and the generalized one-dimensional Poisson equation is solved in an iterative fashion, yielding the potential \(V(z)\) at each distance \(z\) from the substrate \((\varepsilon(z)\) is the permittivity of the layer located a \(z\) distance from the substrate):

\[
\nabla[\varepsilon(z)\nabla V(z)] = -\frac{\rho(z)}{\varepsilon_0}
\]

This approach essentially enables a layer-by-layer application of the ICT model, starting with the substrate/monolayer interface that then forms the new effective substrate for the second layer, and so on, obtaining the potential step for each interface/layer! The main strength of this
detailed computational model is that it gives a huge degree of freedom for modeling experimental data on energy level alignment and can also explicitly treat energy level bending. The model also can model energy level alignment in multilayer stacks.\textsuperscript{[41]} The drawback, if any, is the same huge degree of freedom – if the model is to be used for material screening purposes, the many input parameters all need to be calculated, guessed or obtained from measurement, which is a significantly larger task than what is involved in e.g. the simpler model by Bokdam, \textit{et al.}\textsuperscript{[40]}

5. Summary and outlook

We have described the basic model for energy level alignment at the weakly-interacting interfaces obtained from solution-processing of organic semiconductors, such as conjugated polymers. We also have discussed energy level bending in ultrathin polymer layers, describing why in the majority of cases, the energy level bending is abrupt (1-2 layers) and also how more extended energy level bending can be obtained. The effect of thin electrode interlayers was explained including the “spacer” effect (decreasing coupling between the interface polaron and the substrate image charge) and the charged-species-induced double dipole steps (polyelectrolytes). We introduced a few computational models, described the approximations made and their respective strength and weaknesses in terms of predictive power vs. modelling power. Existing models were found to be capable of well-reproducing experimental data and even provide predictive estimates of energy level alignment within the experimental error of typical measurement techniques (ultraviolet photoelectron spectroscopy, Kelvin probe). Long term, further development of multiscale modelling should enable complete realization of \textit{in silico} design of materials and interfaces for solution-processed organic electronics and bioelectronics.

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References


Figure 11. Schematic illustration of (a) a polyelectrolyte interlayer on a conducting substrate, where the negative-charged species are more mobile than the positive-charged species in the polyelectrolyte; (b) a polyelectrolyte/substrate interface where the negative-charged species are more mobile than the positive charged species and the dipoles and the image dipoles hence form two potential steps ($\Delta_1$, $\Delta_2$) that downshift the vacuum level (VL) vs the Fermi level and thereby decrease the work function; (c) polyelectrolyte/substrate interface where the positive-charged species are more mobile than the negative-charged species, and the dipoles and the image dipoles hence form two potential steps that upshift the VL versus the Fermi level and thus increase the work function.
Figure 12. (a) Experimentally derived $\Phi_{\text{ORG}}$ vs $\Phi_{\text{ORGSUB}}$ for a series of solution-processed conjugated polymer interlayer films where the substrates include metals, metal oxides, semiconductors and conducting polymers. Data taken from Bao, et al. $[61]$ The typical ICT model behavior is observed but with an additional shift due to the double dipole observed for both the pinned and unpinned regions. The direction of the shifts follows the prediction of van Reenen, et al.$[91]$ upshift when the positive-charged species are more mobile, downshift when the negative-charged species are more mobile. The Schottky-Mott limit (slope = 1) is depicted as a dashed line. (b) Shift of the standard ICT curve (solid black line) by the double dipole step $\Delta_{dd}$ caused by inclusion of charged species in the film for when the positive-charged species are more mobile (blue dashed line) and for when the negative-charged species are more mobile (red dashed line).
Table 1. Work function, in eV, of a series of substrates before (pristine) and after coating by PFN, PSSH and Nafion. PSSH and Nafion are good ion-conductors but electrical insulators. Both PSSH and Nafion have a positive ion as the more mobile charged species, in contrast to PFN. PFO is a conjugated polymer, whereas the polymers PS and PMMA are electrical insulators. Data taken from van Reenen, et al.\textsuperscript{[91]}

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In this short review we describe the energy level alignment of interfaces involving solution-processed organic semiconductor films. We introduce the general material properties of such films and discuss the basic physics involved in energy level alignment as well as describe a few computational models in terms of approximations made and strengths/weaknesses.

Keywords: Organic electronics, energy level alignment, interfaces, interlayers, polymers

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Interfaces of (ultra)thin polymer films in organic electronics