

# Interface Dipoles for Tuning Energy Level Alignment in Organic Thin Film Devices

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**Abstract:** One of the key features of organic optoelectronic and electronic devices resides in the multilayer architecture of the device stack. The performance of the latter strongly depends on the interface quality between organic layers or at the electrode heterojunction. Apart from interface thermodynamics governing adhesion and wetting, the electronic energy levels of the organic semiconductor are affected by the interface properties in a drastic way. This mini review gives a short overview on the possibilities to adjust frontier orbital energy levels using oriented electrical dipoles at the interfaces.

**Keywords:** Dipole · Interfaces · Optoelectronic devices · Organic semiconductors · Self-assembled monolayers

## Introduction

Organic optoelectronics and plastic electronics are booming fields in research and certain applications have already reached the market. Convincingly, smart phone display applications have swept away the apprehension that organic materials are not stable enough for reliable applications in electronics. While stability has reached a level that is sufficient for particular applications in consumer electronics,<sup>[1–4]</sup> this is still to be demonstrated for large area and large-scale applications. Device failure not only occurs due to photochemical reaction pathways such as the well-studied photo-oxidation processes, but also due to morphological changes of the thin films. Drastic morphological changes such as crystallization of the organic layer can lead to electrical short circuits between the top and bottom electrodes of the thin film device. This issue was observed at a quite early stage for triphenyl-diamine based hole conducting layers in organic light-emitting devices (OLED).<sup>[5,6]</sup> As a remedy, new functional molecules were developed with higher glass transition temperatures up to 125 °C that indeed behaved much more stably

under thermal aging.<sup>[7]</sup> Reconstruction of thin organic films also occurs in organic thin film transistors (OFET) when devices are heated above a critical temperature<sup>[8–11]</sup> or using solvent annealing.<sup>[12–16]</sup> In organic photovoltaics (OPV) too, finely tuned intermixed phase domains in the nanoscale are often achieved by thermal<sup>[17–25]</sup> or solvent annealing.<sup>[17,26–32]</sup> This so-called bulk-heterojunction geometry, however, is not necessarily at thermal equilibrium and subsequent morphological transformations<sup>[33–36]</sup> can adversely affect device performance.

Besides this rather large-scale three-dimensional reconstruction, more subtle changes can occur at the various interfaces present in the device. Similarly to inorganic devices where, for example, sodium from the soda lime glass substrate can diffuse across interfaces and alter device performance,<sup>[37,38]</sup> organic and inorganic species are also able to diffuse to the electrode surface or across organic heterojunctions.<sup>[39–41]</sup>

Frontier orbital energy alignment at interfaces is yet another important factor determining heterogeneous electron transfer processes<sup>[42–46]</sup> and, given the subtle equilibrium at interfaces, are a determining factor for device stability. Energy alignment was first studied at most common electrode interfaces, being indium tin oxide (ITO),<sup>[47]</sup> conducting polythiophenes such as PEDOT:PSS,<sup>[48]</sup> or metal electrode films consisting of aluminum silver or gold.<sup>[49–51]</sup> Organic heterojunctions have also been well studied for the most important materials systems in OLED<sup>[52]</sup> and OPV<sup>[53–55]</sup> devices. All these studies have clearly shown that in most cases, the vacuum level is far from being flat across the device interfaces and interface dipoles give rise to large energy level shifts of orbital and electrode

wave functions.<sup>[56–58]</sup> This follows immediately from a simple electrostatic argument treating the dipole layer as an infinite parallel plate capacitor (see Fig. 1):

$$\Delta\phi = \frac{N\mu}{\epsilon\epsilon_0} \quad (1)$$

where  $\epsilon_0$  is the vacuum permittivity. Relatively modest surface dipoles of  $\mu = 4$  D can readily produce a potential energy shift of  $\Delta\Phi = 0.5$  eV, if the dipoles are oriented perpendicular to the surface and have a density of  $N = 10^{18}$  m<sup>-2</sup> (corresponding to an occupied area of the surface dipole of 100 Å<sup>2</sup>). The rather low dielectric constant

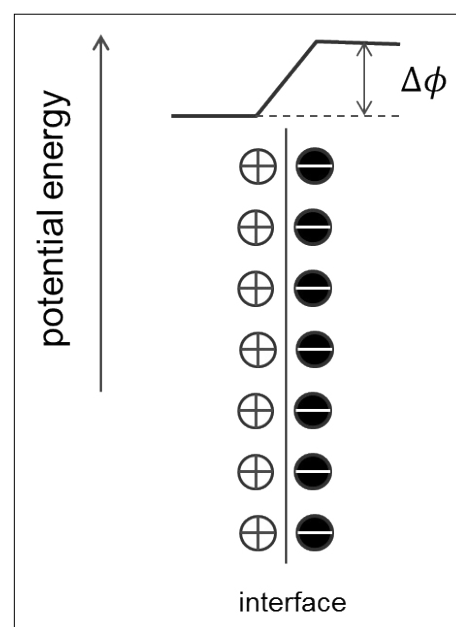


Fig. 1. Interfacial electrical dipole layer represented by positive and negative surface charges across the interface leading to a vacuum level shift  $\Delta\phi$ .

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of organic semiconductors ( $\epsilon \approx 3$ ) only modestly screens the charges and therefore allows for the important potential shifts.

Needless to say that such huge vacuum level shifts imply energy level offsets that completely determine photoinduced charge transfer processes such as charge injection or charge collection at an electrode, exciton dissociation or short range energy transfer. In many cases such interface dipoles are indeed beneficial to device performance.

As a matter of fact, these shifts are not solely due to interface dipoles such as permanent dipoles or interfacial charge redistribution following the adsorption reaction of the organic layer onto the electrode. Importantly, charge is also transferred at the interfaces leading as well to large vacuum level shifts which are commonly termed as band bending. Elaborated studies were carried out in order to understand the origin of these surface effects more deeply. Photoelectron emission (PES) spectroscopy has provided invaluable insight into band level offsets and has also been able to distinguish between pure dipole contributions and band bending effects.<sup>[59,60]</sup> Numerous reviews have extensively covered the basic concepts of energy-level alignment at organic–metal and organic–organic interfaces.<sup>[45,61–65]</sup>

In this short review, the focus is laid on work that has deliberately employed interface electrical dipole layers to offset electronic energy levels in order to tune electron transfer processes across the interface of organic optoelectronic or electronic devices.

### Measuring Molecular Energy Levels across Interfaces

Molecular valence and conduction orbital energy levels are most important since these frontier orbitals are responsible for the fundamental processes occurring in organic semiconductor devices. Energy levels are usually determined with respect to a reference Fermi level while ionization potential, electron affinity and work function are other parameters which are necessary to understand energy level alignment at electrode surfaces.

The organic semiconductor bandgap  $E_{\text{gap}}$  is defined by the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as shown in Fig. 2. While this gap is well defined, it is almost impossible to measure it and quantum calculations need to be interpreted with care.<sup>[66]</sup> This has to do with the fact that Coulombic charges are not screened effectively in organic semiconductors and that the material is polarized as soon as a charge

is taken from or added to it. Furthermore, electron–phonon interaction is particularly effective in organic solids due to charge localization.<sup>[67]</sup> Both the electronic polarization cloud around the charge in the solid as well as lattice distortion due to strong electron–phonon coupling (polaron formation  $P^+$  and  $P^-$ ) lower the potential energy of the charged system. A very nice illustration of the order of magnitude of such energy relaxation is provided by the measurement of electron affinity on anthracene derivatives and clusters thereof.<sup>[68]</sup> Clusters containing up to 100 molecules have electron affinities that are higher by 1.5 eV as compared to monomers illustrating the large difference between LUMO and  $P^-$ . The true HOMO and LUMO energy levels can therefore only be assessed by quantum chemical calculations since experimental determination requires probing by a charge. The difference between the polaron levels  $P^+$  and  $P^-$  is defined as the transport gap ( $E_{\text{transp}}$ ). Another way to probe the gap of an organic semiconductor is to measure the optical absorption spectrum of the materials. Generally, the optical gap ( $E_{\text{opt}}$ ) is again smaller than  $E_{\text{transp}}$  due to the rather large exciton binding energy in organic semiconductors.<sup>[69]</sup>

Photoelectron spectroscopy (PES) has proven to be extremely successful and appropriate to investigate interfaces between an electrode and an organic semiconductor or between two organic materials.<sup>[67,70–73]</sup> Ultraviolet (UPS) or X-ray (XPS) photons excite core and valence electrons, which can leave the substrate surface provided that their kinetic energy is larger than the work function. Although X-ray and ultraviolet photons penetrate deeply into the substrate, only those electrons close to surface (up to 1 nm for UPS) will have

enough energy to leave the substrate due to their short inelastic mean free path. While XPS is able to probe atomic core levels and provide information on chemical composition and molecular bonding, UPS is the method of choice to investigate the density of states of valence electron states, in particular also the HOMO energy level. Additionally, the ionization energy  $I$  and work function  $\Phi$  can be easily assessed (see Fig. 3). The density of empty electronic states (such as the LUMO) can be measured using the complementary inverted photoelectron spectroscopy (IPES).<sup>[69]</sup> In this method, a well-defined electron beam couples with unoccupied electronic states in the organic semiconductor and electrons decay radiatively by emitting ultraviolet light. What is very interesting in photoemission experiments is the possibility to map the electronic energy levels of the organic semiconductors as a function of distance from the interface. The excellent depth resolution makes it possible to deposit and analyze PES spectra in a layer-by-layer fashion. For example, the degree of protonation of a diamine compound as a function of distance from an acidic oxide surface could be measured by this way.<sup>[74]</sup>

PES and IPES are complementary techniques that would allow the bandgap of the semiconductor  $E_{\text{gap}}$  to be determined. However, both techniques probe final states and therefore measure the molecular orbital level of the oxidized or reduced surface species including the electronic polarization cloud and, to some extent, the deformation of its environment. Due to long-range Coulomb interaction, significant contributions are coming from a distance of up to 50 nm as measured on molecular clusters of different sizes.<sup>[68]</sup> For thin organic films deposited on a metal

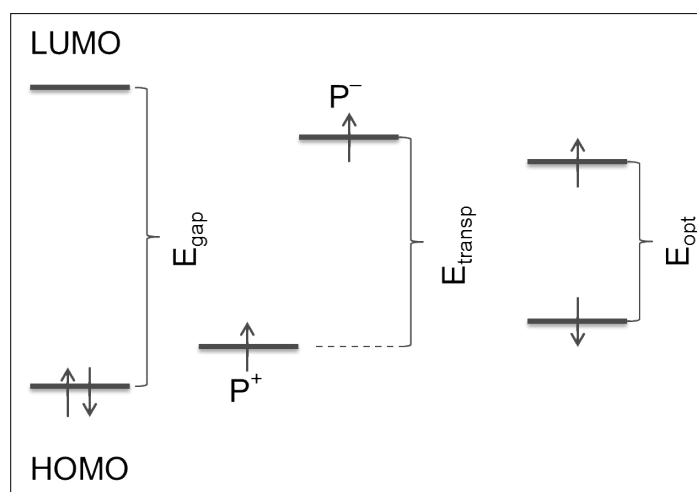


Fig. 2. The bandgap of organic semiconductors is defined in several ways. While the HOMO–LUMO gap  $E_{\text{gap}}$  represents the difference of the highest occupied molecular orbital and the lowest unoccupied molecular orbital in the ground state, the transport gap  $E_{\text{transp}}$  is defined by the energy difference between the polaron state of a single negative and positive charge,  $P^-$  and  $P^+$ , respectively. The optical gap  $E_{\text{opt}}$  corresponds to lowest photoinduced electronic transition in the organic semiconductor.

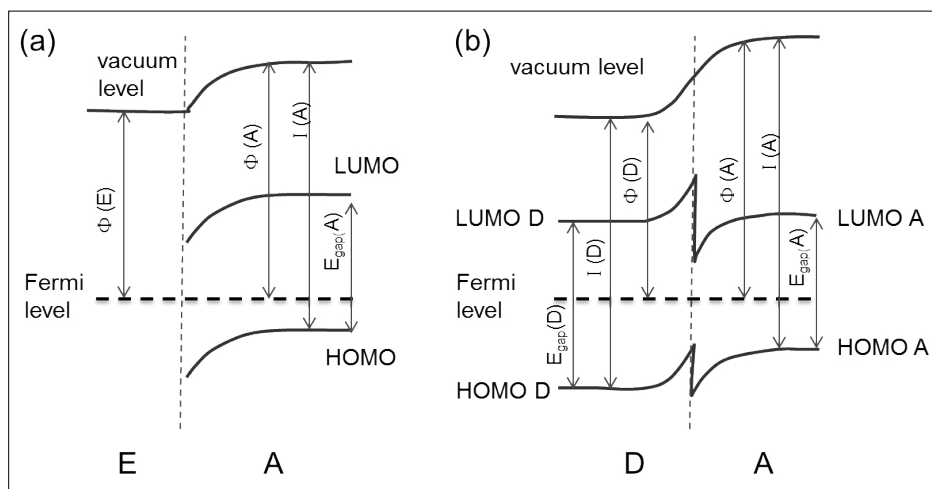


Fig. 3. Energy level diagram across the interface between an electrode E and an organic semiconductor A (a) and between a donor and acceptor organic semiconductor, D and A, respectively (b). The work function  $\Phi$  and ionization potential  $I$  as well as the HOMO-LUMO gap  $E_{\text{gap}}$  is indicated at various positions across the interface.

electrode, the electronic polarization may therefore also contain contributions from the metal substrate. Another issue requiring some attention relates to the time scale in PES measurements.<sup>[70]</sup> The extraction of an electron from a molecule by a photon occurs in about 1 fs, which is ten times slower than the electronic relaxation time of the environment. However, nuclear geometric relaxation leading to polarons  $P^+$  and  $P^-$  occurs within the frequency of phonons which is 2–3 orders of magnitude slower than the photoelectron emission process. For this reason PES usually measures charged final states including the electronic polarization cloud, but underestimates complete geometrical nuclear relaxation. In the following, we will use the terms HOMO and LUMO in band diagrams, knowing that the energy levels accessible by experiment rather correspond to the charged transport states.

Other methods such as cyclic voltammetry also infer the relevant frontier orbitals involved in optoelectronic processes, but the electrochemical method probes reduced and oxidized isolated molecules in an electrolyte under equilibrium conditions, meaning that the system has always sufficient time to relax to its lowest energy state. In photoelectron spectroscopy, the polarization of the bulk material may differ quite strongly from the polarization in an electrolyte and therefore caution has to be applied when relating frontier orbital energy levels.<sup>[69,75]</sup> Contrary to PES, however, cyclic voltammetry requires a reference potential to assign absolute values for the molecular orbital energy levels.

The Kelvin probe technique was also used to determine work function shifts at electrode interfaces coated with organic semiconductors.<sup>[76–78]</sup> This method, too, is a relative one and absolute values can only be obtained in conjunction with a

reference electrode. For inhomogeneous surfaces, the Kelvin probe technique may provide an average value of the work function, while PES tends to emphasize those sites with lower work function. In general, some care has to be applied when relating the two methods.<sup>[79]</sup>

Yet another technique has been employed using electron tunneling spectroscopy to infer the transport gap  $E_{\text{transp}}$  of organic semiconductors.<sup>[80,81]</sup> This technique needs rather elaborate sample preparation and can reveal the relative energy positions of frontier molecular orbitals and neighbors thereof.

Finally, there are several indirect electrical measurements such as current-voltage,<sup>[82–85]</sup> photovoltage<sup>[82,86–88]</sup> and surface photovoltage techniques<sup>[89]</sup> or impedance spectroscopy<sup>[90–92]</sup> where interface properties can be investigated. For example, interface states and dipoles could be inferred from capacitance–voltage analysis.<sup>[93]</sup>

### Potential Shifts at Electrode Interface Layers

Electrode surfaces are the most convenient interfaces to study. First of all they can be easily prepared or cleaned using well-established methods such as solvent and surfactant cleaning, mechanical cleaning, as well as various other treatments such as ozone or plasma treatments. It is clear that such treatments *per se* will modify the surfaces. For conductive indium tin oxide, for example, oxygen treatments lead to intercalation of oxygen atoms at partially coordinated Sn sites.<sup>[94]</sup> This results in a higher negative partial charge distribution at the surface which gives rise to the increase in work function. At the same time, doping due to oxygen deficiency is compensated and the electrode interface

becomes insulating at its outer layer. Metal electrodes such as gold can be cleaned with little influence on its surface composition and work function. Surface modification due to the cleaning procedure is not necessarily a drawback for tailoring the interface of a conductor. What is more important is the fact that the surface can be prepared in a reproducible way before constructing the interface.

Various effects have been identified to produce important vacuum level shifts upon depositing a surface layer onto the electrode (Fig. 4) and have been investigated both theoretically<sup>[95–99]</sup> and experimentally.<sup>[61–64,100–102]</sup> Any electrode overlayer, even a noble gas, limits the full spatial deployment of the conductive electron wave function at the electrode surface by Pauli repulsion and therefore induces less electron density just outside the surface of metals (also called ‘pillow’ or ‘push-back’ effect).<sup>[103,104]</sup> This leads to a decrease of the effective work function of the electrode. If the electrode overlayer is doped, charge transfer may occur at the interface (Schottky junction).<sup>[105–108]</sup> Such transfer also occurs for undoped organic semiconductors, if the electrode work function is quite large or if it is rather low as for gold and alkali or alkaline earth metals, respectively.<sup>[103]</sup> The driving force for the latter partial charge transfer reaction can be understood in terms of the energy difference between the metal electrode work function and the so-called charge neutrality level of the organic semiconductor (corresponding to the energy level reached by filling all electrons into the density of states of the organic semiconductor).<sup>[109]</sup> There may also be a chemical reaction involving bonding to surface states. Very often, the reaction has reductive or oxidative character and therefore gives rise to a surface dipole contribution.<sup>[110–112]</sup> If ions are present in the add-layer, similar phenomenon occurs as with an electrolyte at the electrode–liquid interface (build-up of a Helmholtz layer).<sup>[113,114]</sup>

Very often, various surface interaction effects cooperate and contribute to the resulting energy level shifts observed. It is therefore challenging to tune interface energy levels with precision. In the following, we will discuss more particularly energy level shifts that have been induced deliberately by using permanent electrical dipoles.

### Surface Potential Shifts at the Electrode Induced by Oriented Permanent Electrical Dipoles in OLEDs

Adapting electrode work functions for more efficient injection into organic semiconductor devices is probably the first implication of oriented molecular

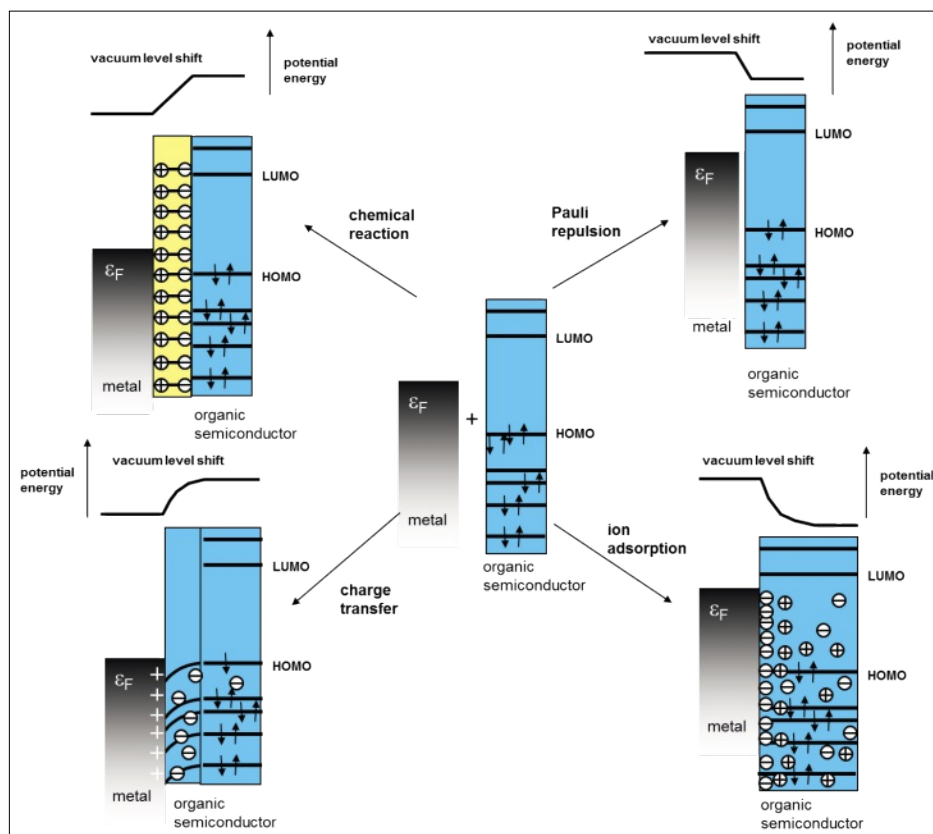


Fig. 4. Schematic drawing of possible spontaneous interface formation scenarios when adding an organic layer onto a conductive electrode. A number of basic electrode-semiconductor interactions give rise to vacuum level shifts at the interface: Pauli repulsion ('push-back' effect), specific ion adsorption in the case of ionic semiconductors, charge transfer to doped organic semiconductor, chemical reaction upon adsorption of the semiconductor onto the electrode. The Fermi level of the electrode  $\epsilon_F$  and the vacuum level shift are also indicated in the figure. Ions or localized charges are indicated by encircled plus and minus signs while electrons in a specific energy orbital state are represented by an arrow and straight line, respectively.

surface layers with permanent electrical dipole moments.<sup>[115,116]</sup> Numerous studies followed and have revealed the merit of this approach, which consists of matching the Fermi level of the electrode with the frontier orbital energy level of the organic semiconductor (Fig. 5). The prime interest in these developments has been to improve charge carrier injection and hence luminous efficiency in OLEDs. Very interesting is the possibility to anchor these molecules both on rough and planar surfaces using specific functional groups.

On conductive oxide surfaces, carboxylates,<sup>[117,118]</sup> acid chlorides,<sup>[119,120]</sup> phosphates<sup>[85,121–124]</sup> or silanes<sup>[121,125,126]</sup> have been employed as anchoring groups. Shifts to larger work functions are obtained with molecules where the negative pole of the dipole looks away from the surface, while the positive pole is closer to it. Typical electron attractive moieties can therefore be used as functional tail groups of the dipole molecules to be grafted on the electrode surface. Among others, these include halide, nitrile, carbonyl or nitro. Surface modifiers with electron-donating tail groups such as amine, alcohol or alkoxy can be used to lower the work function. A few works

have demonstrated zwitterionic molecules to provide large dipole shifts.<sup>[127,128]</sup> Mineral acids or bases can also be used for effective work function shifts on oxides. Thiol anchoring groups are mostly used on gold<sup>[129–131]</sup> and silver.<sup>[132]</sup> Monolayers can be adsorbed either from solution or from the gas phase, but also offer the possibility to be deposited by microcontact printing.<sup>[133,134]</sup>

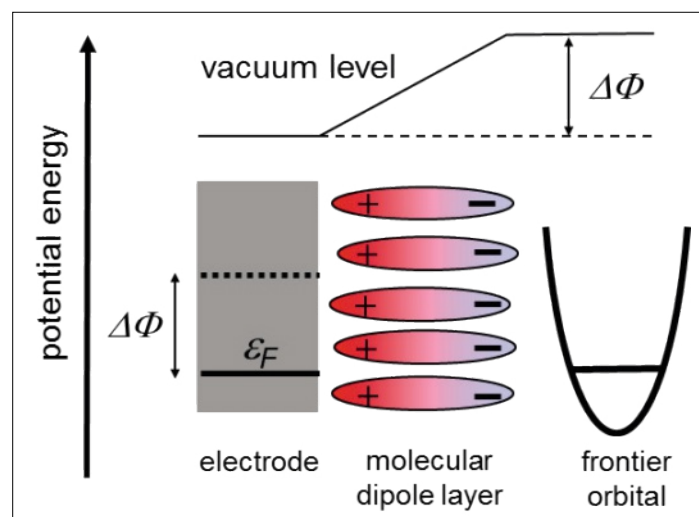


Fig. 5. Schematic drawing of energy level alignment between the Fermi level  $\epsilon_F$  of the metal electrode and the frontier orbital level of the organic semiconductor, which is induced by a monomolecular oriented dipole layer at the electrode surface.

However, it is much more difficult to employ the same principle on the top electrode, which is usually the cathode. The reason is that the top electrode is very often deposited by evaporation and therefore it is difficult to self-assemble molecules on the electrode side facing the organic semiconductor by an equilibrium process. One possibility is to deposit alkali metal salts such as LiF,<sup>[135]</sup> CsF,<sup>[136]</sup> Cs<sub>2</sub>CO<sub>3</sub><sup>[137]</sup> or other Li composites<sup>[138]</sup> first, before depositing the metal cathode on top of the layers. The introduction of the thin salt film leads to lower work function and hence more efficient electron injection. One of the reasons is that a favorable dipole moment is created at the electrode interface.<sup>[83,139–143]</sup> Only few studies report on the possibility of spontaneous orientation of dipolar molecules between the organic semiconductor and the cathode, once the cathode metal has been deposited on top of the thin interfacial film.<sup>[127]</sup> Other techniques use lamination or laser transfer techniques to deposit the top electrode, which allows for monolayer functionalization as described above.<sup>[144,145]</sup>

#### Interface Electrical Dipole Layers in OPVs

Following the same concepts as for OLED devices, the basic idea of energy level matching between the effective electrode work function and the frontier molecular orbital of the organic semiconductor can be applied the same way in OPV.<sup>[57,130,146,147]</sup> While for OLED devices interface layers reduce the operation voltage onset thereby increasing the luminous efficiency, dipole layers in OPVs can improve power conversion efficiency by improving open circuit voltage and fill factor. Benzoic acids with different functional groups have been used to tune the effective electron work function and to drastically alter charge collection in organic solar cells.<sup>[147,148]</sup> Grafting dipolar molecules onto oxide electrode surfaces has become particularly interesting for

the so-called inverted solar cell architecture, where electrons are collected at the transparent oxide cathode.<sup>[149]</sup> For normal cell architecture, another method has been demonstrated, where the dipole layer is deposited between a ZnO layer and the metal electrode, again optimizing open circuit voltage and fill factor.<sup>[150]</sup> Bases and in particular NaOH have shown to decrease the work function of oxides and to stabilize the performance of OPV devices.<sup>[151]</sup>

Thiols were used on Au anodes to replace PEDOT:PSS as interface layer.<sup>[152]</sup> Thiol-modified oligothiophenes<sup>[153]</sup> or sulfonated compounds such as sulfonated poly(diphenylamine) reduce the extraction barrier for positive charge carriers at Au electrodes and can be used in device configurations where Au is the top electrode. Other research has functionalized and improved the PEDOT:PSS surface using ambipolar molecules that orient with their ethoxysilane head pointing to the conductive polymer and their fluoroalkyl chains sticking out of the surface.<sup>[154]</sup>

Acridine orange base was shown to produce large decreases of the effective Au work function when deposited onto the latter.<sup>[155]</sup> From OPV device studies, the same work provides evidence that the thin molecular interlayer also has the same effect when Au is deposited on top of a thin acridine orange base layer. Another approach where the metal electrode is deposited on top of the interface layer utilizes diblock copolymers incorporating a fluoroalkyl and polythiophene block. The block copolymer orients spontaneously at the interface, providing a favorable dipole moment for increased open-circuit voltage and fill factor.<sup>[156]</sup>

Similarly to OLED devices, LiF and other metal fluorides have been proven to enhance charge carrier collection at the cathode side especially when evaporated aluminum forms the top cathode.<sup>[139]</sup> As an alternative to fluoride salts, pyridinium salts were also used as cathode interlayer in conjunction with an aluminum cathode.<sup>[157]</sup> Polymers containing simple aliphatic amine groups were applied as thin films on various electrodes to lower the effective work function and improve electron collection.<sup>[158]</sup>

### Self-assembled Electrical Dipole Layers in OFETs

Contrary to the two organic optoelectronic devices discussed above, there is one prominent self-assembled monolayer that has been successfully employed in OFETs; octadecylsilanes (OTS).<sup>[159]</sup> This comes from the fact that most OFETs employ a silicon oxide dielectric layer where silanes have a passivating effect. Most impor-

tantly, they improve the crystalline growth of the overlaying organic semiconductor and reduce the interfacial trap states. It was then recognized that electrical dipoles could be introduced to the surface grafting layer using fluoroalkyl chains, amine groups and other polar moieties. This allows the threshold voltage and the charge carrier density in the channel to be tuned at a given gate voltage.<sup>[160–165]</sup> Using the same effect it was possible to fabricate p-channel inverters that use two transistor elements that differ only by the dipole layer grafted to the silicon oxide gate dielectrics.<sup>[166]</sup> Interestingly, derivatization of the glass substrate with dipolar molecules also has drastic effects on the threshold voltage in top gate OFETs.<sup>[167]</sup> Only few works have investigated dipolar layers on dielectrics other than silicon oxide. For example, self-assembled monolayers on aluminum oxide gate surfaces have been investigated using carboxylic acid and phosphonic acid derivatives.<sup>[168]</sup> Crosslinkable resins as dielectric oxide overlayers have also been shown to induce dipole effects that influence the threshold voltage.<sup>[169]</sup>

Disperse red molecules were also grafted to gate oxide dielectrics. These layers can be polarized by photoinduced electron transfer and induce threshold voltage shifts of up to 100 V.<sup>[169]</sup>

Several research groups report on controlling charge injection from source and drain contacts by using thiol functionalized self-assembled polar molecular layers grafted to Au contacts.<sup>[130,170–174]</sup> For n-type transistors, amino-functionalized polymer layers at source and drain electrodes were shown to improve electron injection into the channel.<sup>[158]</sup>

### Chemical Potential Shifts at Organic–Organic Interfaces

Energy barriers at organic–organic interfaces are crucial for exciton dissociation and subsequent charge carrier generation in organic photovoltaic devices. They are as important for charge recombination in light emitting devices where excitons are formed at well-defined locations within the device. As in the case of charge injection at an electrode, energy offsets are driving electron transfer processes. Very often, however, it is difficult to predict the type of interface that will be formed. Different types of organic–organic heterointerface formation scenarios have been assessed both theoretically<sup>[175,176]</sup> and experimentally<sup>[1177–179]</sup> (see Fig. 6).

Similarly to inorganic devices, p-n junctions incorporating a depletion

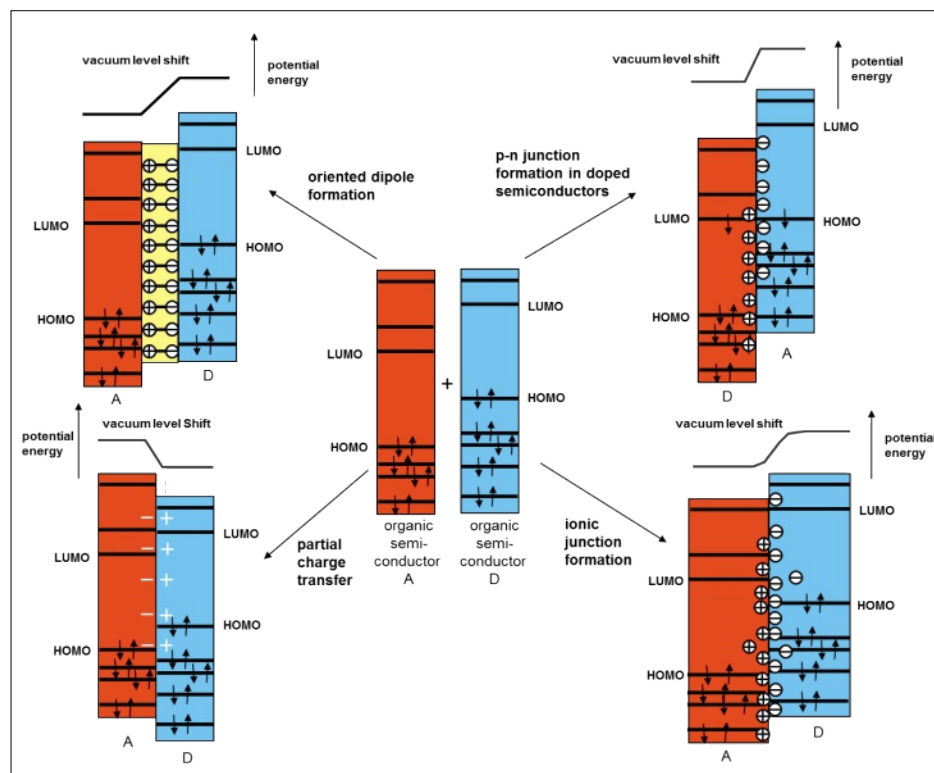


Fig. 6. Schematic drawing of interface reactions occurring at the interface between two organic semiconductors A and D, which lead to vacuum level shifts; p-n junction formation for doped A and D layers, partial interfacial charge transfer at the donor (D) – acceptor (A) interface, formation of a dipole layer due to interfacial molecular orientation, ionic junction formation. Free ions or localized charges are indicated by encircled plus and minus signs while electrons in a specific energy orbital state are represented by an arrow and straight line, respectively. Partial charge transfer is designated by white plus and minus signs.



layer can also be formed with p- and n-type doped organic semiconductors.<sup>[180]</sup> Additionally, charge carrier transfer at the heterointerface can also occur in undoped organic layers with donor–acceptor character.<sup>[181,182]</sup> This occurs not only for very strong donor–acceptor materials which are well known in charge-transfer salts,<sup>[183]</sup> but also for donors and acceptors with smaller frontier orbital offsets. In analogy to electrode–organic film interfaces, this phenomenon can be explained by invoking the energy difference between the respective charge neutrality layers.<sup>[184]</sup> Accumulation of oppositely charged carriers at the organic heterojunction can also be induced by light irradiation and produces a dipole at the interface that increases the open-circuit voltage.<sup>[185]</sup> Also, organic molecules at the organic–organic interface can orient and thereby induce an interface dipole layer, which governs energy barriers in OLEDs and open-circuit voltage in OPVs.<sup>[186–190]</sup> Finally organic–organic interface dipoles can be created with ionic semiconductors or by blending salts in organic semiconductors.<sup>[191–193]</sup>

### Deliberate Energy Level Shifts Induced by Oriented Molecular Dipoles at Organic–Organic Interfaces

The precise functionalization of organic–organic interfaces is much more difficult than the derivatization of electrode surfaces. One way that this issue may be addressed is by utilizing surface segregated monolayers.<sup>[54]</sup> Typically, organic semiconducting molecules functionalized with fluoroalkyl chains tend to segregate at the air organic–air interface where they form a low energy surface. Thereby, an interface dipole is formed at the surface. By contact film transfer, solar cells could be realized that incorporate an interfacial dipole layer between donor and acceptor.<sup>[194]</sup> Zwitterionic polyelectrolytes at the donor–acceptor interface of bilayer devices were also used to reduce the electron-hole recombination at the donor–acceptor interface.<sup>[195]</sup> Furthermore it was suggested that ferroelectric dipoles enhance exciton separation and reduce electron-hole recombination when dispersed throughout the active organic film.<sup>[196]</sup>

Tailoring the organic–organic interface is even more difficult in bulk-heterojunction solar cells, since there is almost no possibility to build the donor-interfacial layer-acceptor interface in subsequent steps. Ternary blends using surface specific molecules with intermediate surface energy between those of the donor and acceptor have been used to modify the organic–organic interface in bulk heterojunction solar cells.<sup>[197]</sup>

### Conclusion

The great success of organic optoelectronic and electronic devices is certainly due to the steady improvement of the active organic semiconductor materials. To a large part, however, this achievement is also due to the design of optimized device architectures and in particular to the control of interfaces between electrodes and organic films or at organic–organic heterojunctions. A wealth of understanding has come from elaborated experimental investigations with a strong contribution from photoemission spectroscopy technique as well as theoretical modeling. Despite the fact that organic semiconductors very often are amorphous or nanocrystalline solid films, well-defined interfaces are ordered to a large extent. This ordering manifests most intriguingly by the phenomenon of oriented interfacial electrical dipoles. The latter are very influential in governing device performance due to their strong impact on electron transfer processes. Mastering this handle provides a wonderful tool for further optimization of device performance and stability as has been demonstrated by monomolecular derivatization of electrode surfaces. In the future one may expect that interface engineering at organic–organic interfaces will become even more important in order to optimize performance and stability of organic multilayer optoelectronic devices.

### Acknowledgements

Generous support of Empa, the Swiss Federal Laboratories for Materials Science and Technology, is gratefully acknowledged.

Received: July 23, 2013

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