Phenomenological Prediction of the Band Diagram of Organic–Organic and Inorganic–Organic Heterointerfaces

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Herein, a phenomenological rule is presented for the estimation of electronic contact properties of organic–organic and inorganic–organic heterointerfaces, which is deduced from a large number of experimentally studied heterojunctions. The data for the present study are summarized from in situ step-by-step interface experiments using photoelectron spectroscopy. Organic and inorganic (oxide) materials are investigated which are used for the manufacturing of organic based optoelectronic devices in the InnovationLab Heidelberg. It is shown that the measured values of the interface dipole as well as of the band bending linearly depend on the work function difference between substrate and adsorbate. The data suggest that the investigated materials as technologically applied films contain a prototypical concentration of electron states at the interface and in the bulk, the charge of which is adjusted to reach thermodynamic equilibrium at a contact. As a consequence, a generally applicable empirical formula to predict the energetic band alignment due to dipole formation and the contact potential distribution due to band bending can be deduced, which is given by just the work function differences between the pristine layers. This result suggests that band bending as well as interface dipole formation are both attained by redistribution of electronic charge via integer charge transfer processes.

1. Introduction

Organic optoelectronic devices offer a number of advantages compared to their inorganic counterparts. Besides organic solar cells (OPV), organic light emitting diodes (OLEDs) are the most prominent examples of this emerging device generation. Due to their outstanding properties such as deep black color, high intrinsic contrasts, and low power consumption OLEDs are on the way to dominate today’s display technology especially in the smart phone sector. As all organic devices consist of complex multilayer stacks, the energetic band energy adjustment at the internal organic and organic–inorganic interfaces crucially influences the device performance.[1,2,3] Therefore a reliable prediction of the energy band alignment and the contact potential distribution is mandatory to enable a knowledge-based material selection for further device improvement.

Some general theoretical concepts of contact formation shall be summarized. In the following two organic semiconductors (OSCs) are considered in their contact formation mechanism. As marked in Figure 1a each OSC is characterized by its work function $\phi$, its ionization potential (IP) and its electron affinity (EA). An important quantity is the concentration of active, i.e., charge exchanging states within the bulk of each material, which for semiconductors determine the position of the Fermi level in the energy gap. A high concentration of surface states is not considered. Brought into contact, charge is transferred from one to the other phase to establish thermodynamic equilibrium, i.e., alignment of the Fermi levels as shown in Figure 1b. Driving force is the work function difference $\Delta \phi$. It is well known that the simple Anderson–Model assuming vacuum level alignment fails for most systems.[4–6] Instead an additional interface dipole potential $\delta$ forms at the interface. The remaining work function difference, i.e., $\Delta \phi$ minus $\delta$ will be compensated by the formation of band bending $eV_{BB}$ in extended space charge layers until the Fermi levels in the contact phases coincide. The potential drops in the adjacent phases are marked with $eV_{BB1}$ and $eV_{BB2}$. In order to determine the magnitudes of the interface dipole and the potential drops in the space charge regions long lasting and elaborate interface experiments have to be performed using photoelectron spectroscopy of in vacuo step-by-step prepared contacts.

Up to now there is still a lack of knowledge which electron states must be considered in the prediction of the band energy diagram of organic interfaces in equilibrium. Previous studies only concentrate on the interface dipole but do not cover the contact potential distribution.[1,2] At this point we start with our work and present a formula to forecast not only the magnitude of the dipole potential drop but also the overall potential drop in the space charge regions only from the knowledge of the work...
2. Results

2.1. The Interface MoO₃-CBP

We show the evaluation of one interface experiment in detail to illustrate the typical behavior in the contact formation in a step-by-step interface experiment. As prototype example the MoO₃-4,4'-bis(9-carbazolyl)-1,1'-biphenyl (CBP) interface is chosen: CBP is deposited in seven steps up to a thickness of around 210 Å onto a 40 nm thick MoO₃ layer which was deposited before in the same UHV set-up. After each step the evaporation time of CBP is doubled. The spectra of the secondary electron edge, the valence region, and the MoO₃ core level spectra are depicted in Figure 2a. As expected, the intensity of the MoO₃ core level lines gradually decrease, but the emission lines do not show any binding energy changes with increasing CBP coverage. This is a clear indication for a flat band situation in MoO₃ evidently due to its high n-doping level. In contrast the highest occupied molecular orbital (HOMO)-onset of CBP as well as the secondary electron edge shift to higher binding energies the more CBP is evaporated on top of the MoO₃ layer. Figure 2b summarizes the energetic positions of these three emission lines in dependence of the adsorbate layer thickness. The secondary edge represents the work function of the sample and indicates a fast initial work function reduction which is saturated after the first CBP monolayer deposition. The energetic shift of 0.85 eV of the HOMO onset indicates band bending in CBP. At higher thicknesses both the HOMO onset and the secondary electron edge shift in parallel. For the very low CBP thicknesses the secondary electron edge shows a 1.15 eV stronger shift than the HOMO onset corresponding to the formation of an interface dipole. The complete information on the contact formation across the interface is summarized in a band diagram in Figure 2c. The results shown here for the MoO₃/CBP heterointerface is a prototypical experimental outcome as found for nearly all heterointerfaces we have studied in the last years. The initial work function difference of 1.35 eV of the two phases is shared between an interface dipole potential drop and the band bending due to extended space charge layer formation in the space charge regions of the bulk semiconductors in contact. For nondegenerate doped semiconductors the dipolar potential difference develops after the deposition of the first monolayer as well but space charge layers are found in both semiconductors in contrast to the case shown in Figure 2 (see also results given in Table S1 of the Supporting Information). A summary of the experimental results of our studies, which will be used for the further data analysis is given in Table S1 in the Supporting Information of this paper.

2.2. The Experimentally Deduced Dependence of Formed Interface Dipoles on φ₁ − IP₂

Recently Li et al. published a “universal map for interface dipole” formation.[3] They investigated the alignment of a monolayer of an organic semiconductor on top of several other organic semiconductor substrates and found a correlation of the dipole potential (corresponding to a double layer potential across the hetero interface) with the energy difference φ₁ − IP₂ between work function of the substrate material φ₁ and ionization potential IP₂ of the adsorbate material. If the work function of the substrate φ₁ is smaller than the ionization potential of the adsorbate IP₂, but still larger than its electron affinity the dipole δ changes linearly with φ₁ − IP₂ with a slope of −0.15. (Outside this linear elastic range the Fermi level is pinned to either the HOMO or the lowest unoccupied molecular orbital (LUMO) of the overlayer molecules. In order to establish a Fermi level equilibration in case of pinning, only an integer charge transfer double layer potential difference can form. Therefore, the slope in the plot of dipole δ versus φ₁ − IP₂ is one. With our own data on a different set of semiconductor junctions, which are summarized in Table S1 in the Supporting Information, we could confirm the results by Li et al.[3] In Figure 3 the interface dipole (double layer potential difference) is shown in dependence of φ₁ − IP₂. In very good agreement to Li et al. we determined a slope of −0.17 in the linear elastic range and we also observe the
pining regions with a much larger interface dipole of around 1, if \( \phi_1 \) exceeds the bandgap region. Figure 3 also includes our interface data using inorganic substrates. With these data we refer to a study presented by Greiner et al. in which the energy-level alignment of organic molecules on metal oxides has been investigated\[7–9\]. They also report about pinning of the Fermi level if the work function of the oxide exceeds the ionization energy of the organic material. If the substrate Fermi level is situated within the energy gap of the organic material a linear dependence with a slope smaller than one has been observed.

2.3. The Experimentally Deduced Prediction of the Band Diagram in Dependence of \( \phi_1–\phi_2 \)

Li et al. (and also Greiner et al.) only concentrated on the alignment of a monolayer of the organic material on top of several substrate materials\[1,7\]. As we are interested in the prediction of the whole band energy diagram with dipole and band bending, we go one step further and focus on the driving force determining the entire interface formation process. As explained above in Figure 1, the Fermi level alignment in thermodynamic (electronic) equilibrium is governed by the work function difference of the two neighboring phases \( \phi_1–\phi_2 \), if enough charge...
carriers and electron states are available on both sides of the contact. Therefore, the question arises, if the work function difference is also related to the magnitude of the interface dipole. To test for such a correlation the 40 interfaces already presented in Figure 3 are plotted in Figure 4 versus $\phi_1 - \phi_2$. In this plot one can observe a, at first, surprising change in the dependence. Instead of the three regimes (pinning and linear elastic regime) the dipole now shows a single linear dependency on the work function difference for all samples. Applying a linear fit routine a slope of $-0.57$ is determined. Thus around 60% of the original work function difference drops across the short range interface dipole layer. The remaining 40% of the work function difference are compensated by the potential drops (band bending) due to the extended space charge regions of the two phases. We also screened the data presented in Figure 4 according to the geometrical structure of the organic molecules (1D, 2D planar, 3D isotropic, 3D anisotropic). No trend or change of dependence could be observed. Independent of the molecular geometry, all interface dipoles of organic–organic and inorganic–organic semiconductor hetero junctions in Table S1 of the Supporting Information fit well to the 60% rule. As a consequence, the dipolar potential drop $\delta$ and sum of band bending $eV_{BB1} + eV_{BB2}$ in dependence of the work function difference $\Delta \phi$ can mathematically be written as

$$\delta = a \Delta \phi$$

$$eV_{BB1} + eV_{BB2} = (1-a) \Delta \phi$$

Here the parameter $a$ is 0.57 as determined from the linear fit to the data in Figure 4. It should be mentioned already at this stage that we do not claim that this dependence is a universal rule, which is not modified by material’s and experimental parameters as, e.g., the doping or defect concentrations of the used materials. However, the influence of such extrinsic materials related parameters seem to be weak and is evidently very similar for very many practically used materials. Therefore, we do expect that very many hetero interfaces investigated for device manufacturing will follow the dependence shown above. We suggest that Equations (1) and (2) with $a = 0.6$ will provide an improved first estimate of the energy band diagram of organic devices including interface dipole (60% of $\Delta \phi$) and band bending (40% of $\Delta \phi$).

3. Discussion

Many physical concepts have been developed in literature to explain and determine the magnitude of the interface dipole. Vazquez propose that the interface dipole is triggered by the difference of the charge neutrality levels weighted with a dielectric screening factor.$^{[10]}$ Oezelt et al. instead suggested an electrostatic double layer model on the basis of Fermi–Dirac occupation of the electronic states at the very interface using Poisson equation.$^{[11]}$ It is important to note that all these concepts need intense theoretical calculations. In contrast, our experimental approach is only based on the thermodynamic (electronic) equilibrium of electron charge redistribution to equilibrate the Fermi level position of the contact materials. At this point of the discussion the question arises how can we interpret or what do we learn from the fact that in the studied cases always around 60% of the work function difference drops across the interface dipole. Here two aspects should be further discussed. The dipole formation (double layer potential difference) takes place across and within the first monolayer of the organic material(s) in contact to each other. As the dipole depends on the work function difference, apparently the molecules directly at the interface react in response to the differences of the Fermi level positions of the two contact phases. In the redistribution of interfacial electron charge, the adjustment of the space charge layer may occur in parallel but is less evident as equilibrium is reached and can be measured only after several nm of material growth. The relative contributions to the short range double layer dipole and the long range space charge potential step depend on the number and energetic availability of the possibly rechargeable electron states. The 60% rule, as determined in our experiments, may also provide an idea on the dominant mechanism governing the dipole formation.

For further discussion several possible dipole formation processes summarized in Figure 5 shall be considered. Classically an interface dipole can be induced by charge rearrangement due to rearrangement of the orbital geometry arising from molecular adsorption (see Figure 5a). Here only a structural deformation of the molecular orbitals and related intramolecular charge redistribution takes place. Another mechanism explaining the dipole formation can be a partial charge transfer between the interacting molecules directly at the interface due to bond formation. For this purpose, e.g., the HOMO of substrate molecule (phase 1) and the LUMO of the overlayer molecule (phase 2) form a charge transfer complex at the interface (see Figure 5b$^{[12]}$). For this model the wave function of the substrate and the adsorbate molecules must show sufficient hybridization which may not be the case for most hetero interfaces. A generalized mechanism is the integer charge transfer
model assuming a donor acceptor electron transfer between the surface species at the very interface. In cases, where the charges are only exchanged directly at the interface, local interface dipoles (double layers) form. Additionally, a long range charge transfer leads to the formation of space charge regions as indicated in Figure 5c.

If we now consider all processes which may lead to dipole formation, the integer charge transfer is the only process that is triggered by the Fermi level difference. As the 60% rule is valid for all interfaces we have investigated and does not assume specific structural or electronic bonding interactions, it can be concluded that the contacts in organic electronics as described by the interface band energy diagram including the local and extended dipole are mainly formed due to an integer charge transfer. As not all data points perfectly lie on the regression line presented in Figure 4 it may well be that the small deviations result from the also still possible contributions of other dipole formation mechanisms as presented above in Figure 5.

4. Conclusion

In this paper, we have investigated the energetic band alignment and contact potential distribution at organic–organic and inorganic–organic hetero interfaces. Using our data sets, we could confirm results by Li et al. who found a correlation between the magnitude of the interface dipole and the energy difference of the work function of the substrate and the ionization potential of the adsorbate material. In this correlation three different regimes have been observed: a linear regime and two pinning regimes. Having in mind that the Fermi level alignment is triggered by the work function difference of the two phases, we could show that the dipole (dipolar double layer potential difference) linearly depends on the work function difference for all investigated interfaces. With this knowledge it is possible to predict the interface band diagram: around 60% of the work function difference drops across the interface dipole while the remaining 40% leads to the formation of band bending in extended space charge regions in the neighboring phases. These predictions are probably valid for most organic semiconductors which show a prototypical concentration of rechargeable electron states at the interface and within the bulk of the materials. These are expected for the typical sequences and efforts in material synthesis and cleaning procedures. Furthermore, from the 60% rule we came to the conclusion that the interface dipole is mainly formed due to an integer charge transfer process involving donor acceptor couples across the very interface.

5. Experimental Section

In this work the energy band diagrams of 40 organic interfaces were determined (for a detailed listing of the obtained results compare Table S1 of the Supporting Information). Somewhat more than half of the investigated interfaces were organic–organic heterointerfaces, while in case of the remaining ones an inorganic substrate material was used. The inorganic materials cover transition metal oxides (MoO3, WO3), transparent conductive oxides like indium tin oxide (ITO), as well as inorganic semiconductors (ZnSe, TiO2, Si). Concerning the organic semiconductors of this study a broad variety of materials was studied. These are linear materials like α,α-diethylhexylsexithiophene (DHET) as well as 2D planar ones like perylenetetracarboxylic diimide (PTCDI) and the phthalocyanines (CuPc, ZnPc, F4CuPc). C60 is a typical example for a 3D isotropic molecule, while materials like N,N′-Bis(naphthalene-1-yl)-N,N′-bis(phenyl)benzidine (NPB) or Spiro-2,2′,7,7′-Tetrakis[N,N-di(4-methoxyphenyl) amino]9,9′-spirobifluorene (MeoTAD) belong to the group of 3D anisotropic ones. These materials were used within the InnovationLab in Heidelberg to cover a wide range of applications spanning from organic photovoltaic cells and organic light emitting diodes to organic transistors.

All organic layers and some of the inorganic ones were deposited by thermal evaporation of the powder materials under UHV conditions (base pressure 10−9 mbar) using homemade effusion cells. The evaporation rate was in the range of 10–30 Å min−1. For the interface experiments a thick layer of the substrate material was prepared or cleaned with well documented procedures. Subsequently, the adsorbate material was evaporated onto the substrate layer. Starting with 2 s, the deposition time was doubled each step. After each preparation step X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed. The samples were transferred to the photoemission unit without breaking the vacuum. Survey and core level spectra as well as spectra of the secondary electron edge and the valence band region were recorded. The evaporation of the adsorbate material was continued until no further changes in binding energy position could be observed. Typically, the spectral changes were observed to saturate after a layer thickness of 50–100 nm. Further information on the interface experiments can be found, for example, in refs. [15–17].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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contact potential distribution, energy band alignment, interface experiments, photoelectron spectroscopy, space charge layers, surface dipole

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