

4.1 Final Publishable Summary Report

4.1.1 Executive Report

Minotor: Modelling of Electronic Processes at Interfaces in Organic-Based Electronic Devices

Minotor is a three-year project focusing on the theoretical modelling of interfaces involving organic semiconductors for applications in the blooming field of organic electronics. The project gathers ten groups, with academic and industrial partners, including one research group in US (Georgia Institute of Technology). This project was motivated by the fact that many key electronic processes occur at interfaces in organic-based devices such as light-emitting diodes, solar cells or field-effect transistors; this is the case for charge injection, light conversion into charges or recombination of charges into light. The project was methodology oriented by looking at the most appropriate theoretical approaches to describe the interfacial electronic processes and material oriented by establishing guidelines for the choice of the interfacial components expected to improve device performance. We wanted to obtain a unified view by considering in parallel metal/organic interfaces (M/O), organic/organic interfaces (O/O), and inorganic/organic (I/O) interfaces. In the case of M/O interfaces featuring a strong coupling between the molecules and the surface, standard DFT approaches based on LDA or GGA functionals perform well. This has been applied to the study of metals covered by self-assembled monolayers, showing that the work function of electrodes can be significantly tuned by SAMs and that there is a high degree of flexibility in the design of the SAM-forming molecules (by changing the nature of the anchoring group, functional head or intermediate spacer). This also prevails for many organic semiconductors deposited on bare metal surfaces, though the inclusion of dispersion forces is recommended to best describe the contact geometry. In the case of weak coupling (for instance in presence of passivated surfaces), DFT can qualitatively reproduce the existence of Fermi level pinning effects. A quantitative estimate of the pinning levels was reached via a phenomenological model developed in the framework of the project. In the case of O/O interfaces featuring a partial charge transfer between the donor and acceptor moieties, long-range corrected DFT functionals are recommended to properly describe the interfacial charge distribution. In contrast, DFT fails in doing a good job for systems dominated by polarization effects. However, microelectrostatic (ME) models can be applied to such systems to determine the energy landscape around the interface, and for instance to examine pathways for charge separation in solar cells. The ME model was also used to unravel the mechanism of molecular doping in organic semiconductors. Our work also demonstrated that generating realistic morphologies of the organic/organic interfaces with the help of force field calculations is highly recommended to describe the actual structural disorder which strongly impacts the interfacial electronic processes. In the case of I/O interfaces, the theoretical calculations have shown that the workfunction of oxide layers (such as ITO or ZnO) can also be tuned by grafting SAM-forming molecules functionalized by carboxylic or phosphonic groups. A proper DFT description of the interfaces is challenging since one needs to properly describe at the same time the electronic gap of the materials and the alignment of their frontier electronic levels. The use of a tight-binding DFT formalism appears as an attractive approach to tackle this issue. Many theoretical results have been directly confronted to corresponding UPS / XPS measurements to validate the theoretical procedure and assist the interpretation of the experimental data. Devices have also been fabricated to connect theory and experiment: spintronic devices based on C60/Fe interfaces, diodes and transistors showing the influence of

SAMs on oxide nanorods and contact electrodes on the I/V characteristics, respectively, and solar cells demonstrating the role of the interface morphology on the device performance.

4.1.2 Summary Description of the Project Context and the Main Objectives

Project Context

The MINOTOR project took place at the crossroad between fundamental research on organic based materials science, and the need for a more efficient engineering of devices in energy gathering and conversion. The main paradigm of organic devices is their multi-layer architecture involving materials with the most suitable electronic properties to obtain maximum device efficiency. At this stage, the intrinsic properties of the constitutive materials, like molecular crystals, polymers or inorganic electrodes, are well-known and many studies, both experimental and theoretical, have unraveled the key parameters required for optimal light emission or absorption, charge and energy transport ability. The combination of materials optimizing these different aspects should lead to clear processing ways for developing new devices that reach new limits in efficiency.

However, what has been far less considered is the way to ideally combine these materials and to process them together without loss of efficiency. Building multi-layer devices imply multiple interfaces that can strongly affect the device performance. Therefore a proper control of the processes taking place at these interfaces is highly desirable. It is proven experimentally that the electronic and structural properties of two distinct materials in interaction strongly differ with respect to their bulk properties. Electronic and structural reorganizations, generating interface dipoles and band bendings, are affecting the relative position of the electronic levels which, in turns change the entire device performance. Therefore, a fundamental understanding of the factors at the origin of these electronic interface properties is critically needed. So far, only little theoretical and experimental work was performed on the comprehension and the prediction of such properties.

The MINOTOR project proposed to gather top level scientists specialized in multi-scale modeling and experimental characterization of interfaces to unravel the nature of the interactions between organic semiconductors and organic, metallic and inorganic surfaces and their impact on the entire device performance. This project also aimed at developing an efficient toolbox and assessing the efficiency of theoretical methodologies to investigate and predict the structural and electronic properties of interfaces.

General Objectives

The objectives of the project were two-fold: i) the main objective was the development and assessment of a modeling protocol for studying organic-based molecular devices that could be subsequently turned into an efficient engineering tool. This protocol should be able to provide an understanding of interfacial effects, and should have been evaluated and compared with experimental measurements, ii) the second objective of this project was to unravel and evaluate the different effects that might arise at an interface with respect to bulk material properties, and how this should affect the efficiency of these materials when processed in electronic devices. To confirm our understanding in the processes taking place at the interface, we confronted our theoretical results to UPS experiments and device fabrications.

To unravel these two issues, MINOTOR was casted down into three scientific work packages, each one corresponding to a given type of interface that is present in organic-based multi-layer devices. The first work package was devoted to the study of metal organic interfaces, and encompasses the deposition of molecular electron donor or acceptor organic molecular layers on different metal surface and the possibility to control electronic properties of metallic electrodes by using self-assembled monolayers. Deposition of organic molecules was also considered for spintronics applications using ferromagnetic metals. The objective of this work package was to understand the impact of the organic layer on the charge injection efficiency in the metal electrode. It also permits to clarify the origin of the pinning level and the influence of the type of interaction (strong vs. weak) between the organic semi-conductor and the metal surface.

The second work package treated organic/organic interfaces between donor and acceptor molecules. The main goal of this work package was to understand the nature of the interactions between the two components and their effect on the energy level alignment at the interface. A deeper knowledge on this issue and on the influence of structural disorder aimed in particular to better apprehend the complex process of charge separation taking place at interfaces in a photovoltaic device. Another goal was to assess the impact of tuning the molecular properties on key parameters like the short circuit current and open circuit voltage of photovoltaic cells. A special emphasis was focused on studying the effect of structure relaxation through the modeling of relaxed interfaces.

The third work package was treating, similarly to the first one, the interface between inorganic semi-conductor and various organic donor or acceptor molecules. The main objective was to understand the impact of the interactions between the semiconductor and the organic material on the barrier injections at the inorganic electrode. The study focused on the addition of intercalating layers, like SAMs, to tune the interfacial electronic properties and hence optimize the injection process. The work also included a more realistic description of the oxide surfaces by introducing defects and adsorbed impurities, and its influence on the electronic properties at the interface.

Finally, the entire knowledge gained during the period of the project was compiled within a cross-fertilization work package to highlight the common features and methodologies identified for an optimal description of the interfacial properties in a development and engineering process.

Achievements

The main achievement of MINOTOR was to assess and provide a modeling protocol for investigating interfaces in organic-based electronic devices and deepen our understanding of the link between the interfacial properties and the efficiency of the devices. This protocol has been widely applied and assessed in comparison to experiment on the three different types of interface that the project encompassed, and allowed the different partners to provide a clear and exhaustive overview of the different interfacial effects that are playing a role in the design of efficient materials for opto-electronic devices. In particular, and inside the three main workpackages, the achievements obtained during the Minotor project are the following:

- For metallic-organic interfaces, we have analyzed and unraveled the origin of the interfacial dipole moment at the interface between clean metal surfaces such as gold and silver, or more

reactive metals like Cu or Ca and different organic semiconductors with varying donor/acceptor character, going from tetrathiafulvalene (TTF) to tetracyanoquinodimethane (TCNQ) and the tetrafluoro-tetracyanoquinodimethane (F4-TCNQ), including also pentacene, perylene-tetracarboxylic-dianhydride (PTCDA) and naphthalene-tetracarboxylic-anhydride (NTCDA), tris(8-hydroxyquinolinato)aluminium (Alq3).

- The influence of self-assembled monolayers (SAMs) on the work function of metallic surfaces has been studied for alkane-thiol and functionalized alkane-thiol based SAMs deposited on the gold (111) and silver (111) surfaces. In particular, the project focused on the ability to tune the metal work function by changing the nature of the anchored molecules. The influence of the orientation of the molecules, the nature of the anchoring or ending groups, the rate of coverage, as well as the respective contribution of the molecular and interfacial contribution to the shift of the work function have been unraveled.

- A pinning level model has been developed for passivated surfaces that correspond to an interface in which the metal is covered by a thin layer of native oxide. The prediction of the pinning levels for these interfaces has been compared with success to experimental photoelectron spectroscopy measurements.

- Applications to spintronic based devices have also been considered by treating the case of ferromagnetic metals combined with organic semi-conductors, both theoretically and experimentally. In particular the interfaces made of Co-graphite and Fe-C60 have been characterized in view of designing performing spin selective interfaces.

- For organic-organic interfaces, we have set up a complete multi-scale modeling process aiming at defining the nature of the interactions between the two semi-conductors, mainly based on partial charge transfer or on weak polarization interactions, and the impact of the nature of this interaction on the energy profile of charges in the materials and at the interfaces. In particular, the case of the well-known and largely used bulk heterojunction pentacene-C60 device has been examined and the origin of the charge separation process in this interface has been explained. Other interfaces based on TTF, pentacene, Alq3, oligothiophenes as donor materials, and PTCDA, NTCDA, C60, TCNQ as acceptor materials, have been studied, with a good correlation with UPS measurements for the selected couples for which the experimental data have been obtained.

- The importance of the structure of these organic-organic interfaces has also been assessed by generating relaxed interfaces via force-field calculations and Monte-Carlo algorithms, either based on crystal relaxation or on deposition modeling. The influence of this structure relaxation on the electronic properties at interfaces has been evaluated with our multi-scale model. This has been performed for the pentacene-C60 interface, but also the pentacene-PTCDA, the sexithiophene-C60, and the TTF-TCNQ interfaces. The most important effect of the structural disorder on the electronic properties of O-O interfaces is the generation of new pathways for charge separation at the interface.

- An organic solar cell has been made and characterized by BASF partners, based on a heterojunction between merocyanin and C60 molecules. The whole design of this solar cell has benefited from all the knowledge and the guidelines that the project has accumulated.

- For inorganic-organic interfaces, general methodological schemes were devised for simulating the vapor deposition of organic compounds and providing reliable interface configurations for the quantum chemistry calculations.

- A multi-scale modeling approach has been developed for characterizing the electronic processes at I-O interfaces. The theoretical tools have been applied in particular to the theoretical study of SAMs (substituted benzoic acids, 4-terbutyl-pyridin) and small organic molecules (pentacene, TTF, TCNQ and F4-TCNQ) in contact with polar and non-polar ZnO surfaces, allowing us to predict the shift in the substrate work function and to identify its dependence on chemisorption, physisorption, coverage, and water contamination.
- With a bottom-up approach combining QM calculations, atomistic simulations, microelectrostatic calculations and experiments, it was possible to relate the SAM-induced threshold voltage shift in pentacene-based transistors to the chemical nature of the SAM and the variation of the electrostatic landscape with respect to the bare SiO₂ substrate.
- UPS measurements of the work function shift were carried out for ZnO and TiO₂ surfaces covered with organic semiconductors. In spite of the problems in the production of clean ZnO surfaces, the realization of working ZnO-based diodes allowed for the comparison and exploitation of results in real devices.

Partners

Minotor involved 9 partners over 7 European countries and collaboration with a group in the United States, for a total of 36 researchers during the three years of the project. Each partner is a leading group in their field of research and belongs to reputed universities and research centres. The industrial partner of the project is a major industrial player in the field of plastic electronics.

The partners involved were:

University of Mons (Belgium) (coordinators),
 IMEC research centre (Belgium),
 BASF (Germany),
 University of Twente (Netherlands),
 University of Linköping (Sweden),
 Karlsruhe Institute of Technology (Germany),
 University of Bordeaux (France),
 University of Madrid (Spain),
 University of Bologna (Italy),
 and the Georgia Institute of Technology (United States)

4.1.3 Description of the Main S &T results/foregrounds (25 pages)

Workpackage 1

Metal/organic interfaces were modeled at the Density Functional Theory (DFT) level, using different methods (SIESTA, VASP, and FIREBALL), and were investigated experimentally, mainly with photoelectron spectroscopic techniques. Several different systems were studied: donor or acceptor molecules on metals, self-assembled monolayers (SAMs) on metals, and interfaces between ferromagnetic metals and organic semiconductors. Initially, the performance of the different theoretical models was compared on a model system, tetrathiafulvalene (TTF) on Au (111). Using SIESTA, the results were very sensitive to the parameters used, and the computational cost to reach a good accuracy increased very rapidly,

the effect of which is worsened by the restriction of not being able to run the SIESTA code in parallel. Although qualitative agreement between SIESTA and VASP could be reached for SAMs (methanethiols) on gold and silver (111), the decision was made to abandon SIESTA for metal/organic systems. The results of calculations with VASP and FIREBALL (upon inclusion of 1. energy gap corrections due to the molecule charging energy, and 2. van der Waals interactions) show good agreement, also when compared to experimental data. Later in the project, a release of SIESTA allowing parallelization of the calculation and more efficient algorithms occurred that enabled it to compete in terms of speed of calculation with the VASP package. Use of SIESTA for metal-organic interfaces was thus reinstated and the studies expanded to include a significant number of additional molecules including e.g. pentacene, TCNQ and NTCDA as well as hexagonal boron-nitride. Based on those (and previous) studies, one can distinguish between different contributions to the potential step at the metal-organic interface, all that can successfully be described and modelled theoretically:

- (i) The chemical interaction between the organic material and the metal gives a charge displacement at the interface (caused the formation of chemical bonds, exchange repulsion, or any other terms contribution to the interaction).
- (ii) A transfer of electrons between the organic material and the metal. Those electrons stay close to the interface, because of the attractive electrostatic image charge potential, which then results in an interface potential step.
- (iii) Ordering of static multipoles of the molecules comprising the organic material can give rise to an interface potential step.

Exact knowledge of the interface geometry (molecular orientation, adsorption distance) is generally required for the correct modelling of such interface-related processes at atomically clean metal surfaces. For passivated metal surfaces, however, i.e, where the metal surface is no longer atomically clean but has a thin layer of native oxide or hydrocarbon contamination, a DFT-based version of the so-called Integer Charge Transfer (ICT) model was developed by introducing an approximation where the interfacial charge distribution is described by a plane capacitor, which enables the $E_{\text{ICT}^{+,-}}$ levels (called $W^{+,-}$ in the DFT-based model) and interface dipole to be calculated without knowing the adsorption distance. This unification of the experimentally [1,2] and theoretically [3] derived ICT models has, with the exception of TCNQ, produced agreements between model prediction and experiment within the error of the measurement techniques used for all metal-organic (and organic-organic, inorganic-organic) interfaces studied during the project as well as for comparison with experimental values obtained from literature. An overview of some calculated values compared to experiment is given in Table 1 below.

Acceptor	W^- (eV)	Exp (eV)	E_{relax} (eV)
F ₄ TCNQ	5.7	5.6	0.10
F ₁₆ CuPc	5.2	--	0.02
TCNQ	5.4	4.8	0.10
PTCDA	4.7	4.7	0.09
C60	4.4	4.5	0.05
NTCDA	4.4	4.4	0.12
CuPc	3.3	3.3	0.02

Donor	W^+ (eV)	exp (eV)	E_{relax} (eV)
T6	3.8	--	0.10
TTF	4.2	4.2	0.10
CuPc	4.4	4.4	0.02

Table 1. The calculated pinning levels W^- for electrons in a layer of acceptor molecules and W^+ for holes in a layer of donor molecules. Most structures are obtained by cutting layers from the corresponding molecular crystal structures, with the molecules standing upright with respect to the plane of the layer. Exceptions are PTCDA and NTCDA, where we use the herringbone structure with the plane of the molecules parallel to the plane of the layer, and C60, where we use the (111) plane of the fcc structure. The second column gives the experimentally determined pinning levels. The third column gives the calculated relaxation energy upon charging the molecules with an extra electron or an extra hole.

Having demonstrated the viability of calculating energy level alignment at metal-organic interfaces for a specific adsorption geometry, the modification of energy level alignment due to a change of orientation of molecules with and without a strong intrinsic dipole deposited on metal surfaces was explored using the SIESTA, VASP and FIREBALL program packages and measured using the UPS technique, where the latter method made use of substrates of differing surface energy and roughness to provoke variations in monolayer intermolecular order. Both theory and experiments concluded that variation in molecular order can induce changes in the resulting interface dipole in excess of 1 eV in the systems studied, with good and sometimes excellent (within the error margin of the experiment) agreement between theory and measurement. The added complexity of interfaces featuring molecules with a strong intrinsic molecular can be illustrated by Alq₃. Following the plot in Fig. 1 for the data points taken at different substrate work functions it becomes clear that though the overall behavior of Alq₃ follows the ICT model, there is a displacement of ~0.3-0.4 eV of the data points away from the Schottky-Mott limit for the vacuum level alignment part of the plot. This interface dipole is attributed to ordering of Alq₃ at the substrate interface giving a net effect of the intrinsic dipole of the molecules. For substrate work functions higher than ~4.7 eV, Fermi level pinning is seen yielding an $E_{\text{ICT}^+} = 4.3$ eV, with the size of the resulting interface dipole following the ICT model's prediction ($\Delta = \Phi_{\text{SUB}} - E_{\text{ICT}^+}$). Note that the on-set of the pinning regime is modified by the intrinsic dipole of Alq₃, so that the substrate work function must overcome the extra barrier from the dipole to promote charge transfer with the Alq₃ film.

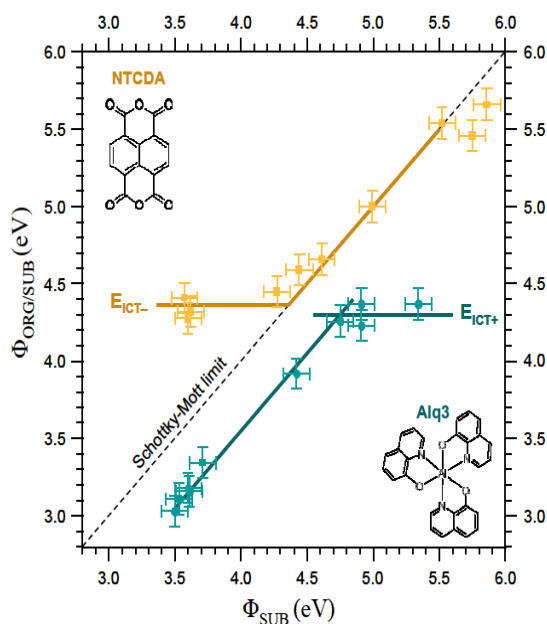


Figure 1. Pinning regimes of NTCDA and Alq₃. The lines are added as a guide for the eye and are not intended to represent the exact values for pinning energies.

SAMs (alkane thiols) on Au (111) have been modeled with SIESTA. The impact of changes in the molecular geometry at different levels was addressed, *e.g.* derivatization by butanethiol with the terminal methyl unit substituted by a series of chemical functions. The impact of such structural modifications on the gold work function was investigated, as well as the molecular *versus* interface contributions. Experimentally, alkane thiol SAMs was applied to study the impact on Fermi level pinning in Au/SAM/F4-TCNQ systems. No significant influence of the distance between metal and F4-TCNQ on the value of the pinning level was observed for the SAM chain lengths used; on the other hand different end groups do impact the pinning level, due to different polarizability or due to the formation of a different order in the F4-TCNQ overlayer. The observed effects are important for the design of SAMs to tune energy level alignment at interfaces. Much effort has been invested in modeling and designing SAMs that through the anchor- and end-unit induced dipoles modify the substrate work function in a very precise way, in theory then tuning the subsequent energy level alignment of a next layer of π -conjugated molecules. However, as our results show, as long as the SAM induced work function (Φ_{SUB}) falls within one of the three regimes of the ICT model: (a) $\Phi_{\text{SUB}} > E_{\text{ICT}+}$, (b) $E_{\text{ICT-}} < \Phi_{\text{SUB}} < E_{\text{ICT+}}$, (c) $\Phi_{\text{SUB}} < E_{\text{ICT-}}$, the exact value of the Φ_{SUB} does not influence the resulting position of the Fermi level that will be pinned to the $E_{\text{ICT}+}$ or $E_{\text{ICT-}}$ level for cases (a) and (c) respectively. Instead, precise tuning of the interface energetics can be achieved by modifying the end group so as to introduce different molecular order in, or screening of, the subsequent overlayer, as this will significantly affect the $E_{\text{ICT}+,-}$ energy of the molecules at the interface.

It has been observed experimentally and predicted by the ICT model that interface potential steps depend on the order in which the individual layers are deposited, and not only on which substrate they are deposited on. Using the basic assumptions of the ICT model, a method was developed where the interface potential steps and potential profile over the whole of a multilayer stack can be deduced from the sequential order of the layers, and the differences between their pinning levels. An example is given below in Fig. 2 (a-c) that exactly describes the situation of the AlO_x/TTF/TCNQ trilayer previously reported [4] and yields the

experimentally observed values for the vacuum level shift as well as predicts the potential gradient over the TTF film obtained in the experiment [4].

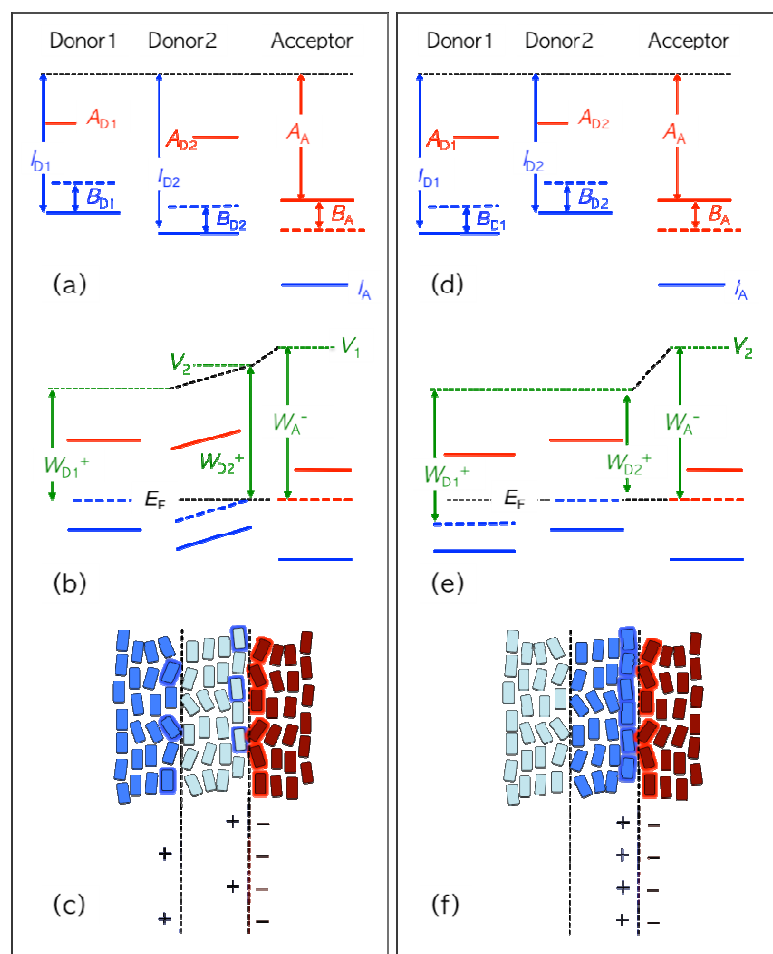


Figure 2. (a-c) Charge equilibration across a donor1\donor2\acceptor trilayer, in case donor1 is a stronger donor than donor2, as expressed by $W_{D1}^+ < W_{D2}^+$. Depositing donor2 onto the acceptor gives a potential step $V_1 - V_2 = W_A^- - W_{D2}^+$ at the interface. Subsequent deposition of donor1 onto donor2 results in a potential step $V_2 = W_{D2}^+ - W_{D1}^+$ across the whole thickness of the donor2 layer. (d-f) Charge equilibration across a donor1\donor2\acceptor trilayer, in case donor1 is a weaker donor than donor2, as expressed by $W_{D1}^+ > W_{D2}^+$. Depositing donor2 onto the acceptor gives a potential step $V_2 = W_A^- - W_{D2}^+$ at the interface. Subsequent deposition of donor1 onto donor2 does not result in any additional charge transfer.

Though most of the comparison with experiment has been made using photoelectron spectroscopy techniques, in a separate effort, accurate theoretical STM images for organic molecules on metals have been calculated, and compared with the available experimental evidence. The calculation method was used to determine the adsorption geometry of molecules on metals and to analyze the drastic improvement in intramolecular and intermolecular resolution that is observed experimentally in Scanning Tunneling Hydrogen Microscopy (STHM).

Interfaces between ferromagnetic metals (FM) and carbon-based systems (organic semiconductors, graphite) were studied experimentally using scanning tunneling microscopy (STM), (magneto) transport devices, and electron spectroscopic techniques. For example, Co/graphite interfaces were studied using XAS/XMCD measurements, demonstrating that Co-carbide formation plays a role in the nucleation of clusters during Co growth, consistent with previously described STM results. In terms of the lattice-matched spin filtering interfaces suggested by theoretical work, where FM/graphite interfaces are basic building blocks, the results obtained by the structural and magnetic characterizations suggest that such epitaxial interfaces cannot be obtained straightforwardly with conventional approaches. Consequently, epitaxial growth at $\text{Co}_{72}\text{Fe}_{20}\text{B}_8$ /graphite interfaces, prepared by e-beam evaporation of CoFeB onto graphite (HOPG) surfaces, was investigated. The surface structure was characterized with LEED and X-ray diffraction, while depth-profiles of elements were obtained using sputtering-XPS. The results obtained on these interfaces show that solid state epitaxy of initially amorphous ferromagnetic alloys can be used to obtain structurally ordered interfaces with graphite/graphene, which is a prerequisite for spin filtering.

C_{60} on Fe (100) interfaces have been studied, focusing on the spin-polarized electronic structure. Oscillatory spin polarization of C_{60} -derived states was observed from C K-edge x-ray magnetic circular dichroism (XMCD) measurements of C_{60} monolayers on Fe (001), see Fig. 3. Combined XMCD, UPS and XPS characterization of the C_{60} /Fe interfaces demonstrated that hybridization occurs between the frontier orbitals of C_{60} and continuum states of Fe, leading to the formation of an interface dipole due to charge transfer and a significant magnetic polarization of $\text{C}_{60} \pi^*$ -derived orbitals.

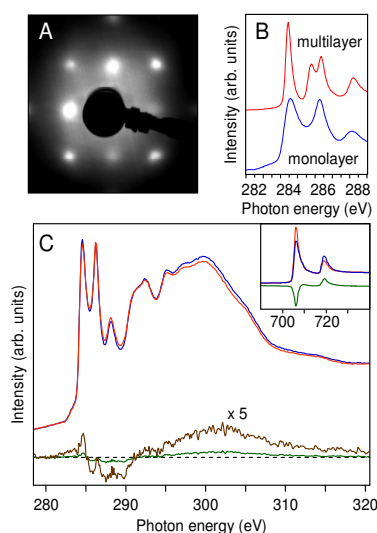


Figure 3. (A) LEED pattern of an epitaxial *bcc*-Fe (001) film on MgO(001); (B) XAS spectra of a multilayer (red) and monolayer (blue) of C_{60} on Fe (001); (C) C K-edge and Fe L-edge (inset) XAS and XMCD spectra of a ML C_{60} /Fe(001) sample. The XMCD spectra (green) were obtained by taking the difference between the XAS data recorded with parallel (red) and antiparallel (blue) alignment of the magnetization and photon helicity [5].

Continuing the study, the effect of C_{60} chemisorption on Fe surface magnetic properties was explored as well, as this too likely will affect spin-injection properties in a hybrid organic spin-valve device. Ultrathin Fe films (several monolayers) on W(001) were prepared in situ and the evolution of the magnetic properties upon C_{60} deposition was followed using XAS/XMCD spectroscopy. Fig. 4 shows the results of these XAS/XMCD measurements for a 0.5 nm Fe film, before (A) and after (B) growing the C_{60} overlayer. Significant effects on the

XMCD signal, and thus the surface magnetic moments, are observed and the integrated XMCD spectra can be used to determine quantitative information on the spin- and orbital moments using the XMCD sum rules.

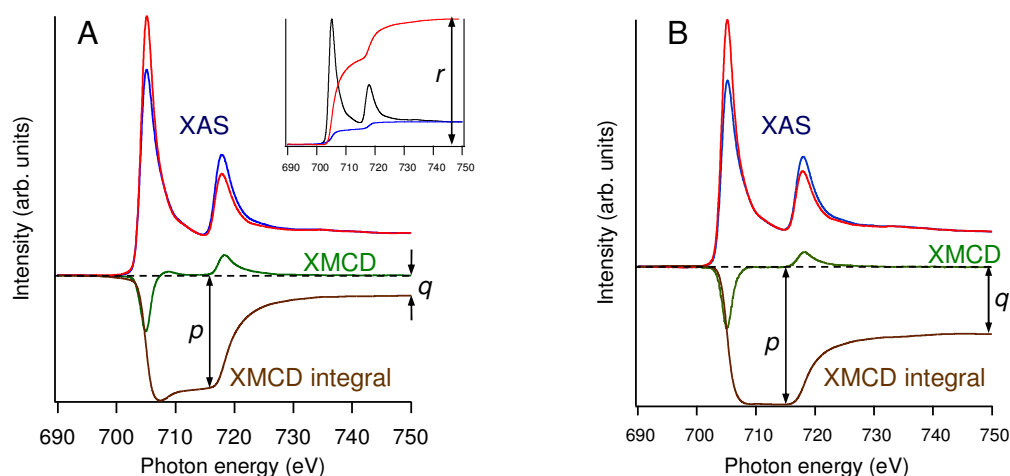


Figure 4. XAS and XMCD measurements of 0.5 nm Fe on W(001), before (A) and after (B) C₆₀ deposition. XAS spectra were recorded with parallel (red) and anti-parallel (blue) orientation of the in-plane magnetization and the photon helicity. The XMCD spectra were obtained by subtracting the red from the blue spectra. The inset in (A) shows the sum spectrum (red plus blue), and the background used to determine the integrated intensity over both edges.

The spin moments of the Fe surface atoms are, on average (i.e. averaged over all surface atoms), reduced by 6%, while the orbital moments are increased by a factor of three according to such analysis, demonstrating the importance to consider the effect of interface formation not only on the organic semiconductor molecule, but also on the ferromagnetic electrode itself.

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Workpackage 2

Organic photovoltaic cells (OPVs) have numerous advantageous features for solar energy conversion compared to silicon-based cells, which include environment friendly and low-cost production, flexibility, tunability and lightness. However, their power conversion efficiencies are still relatively low compared to their inorganic counterparts (10% versus 20-25%), due to a more complex photoelectric conversion process. While the light absorption leads to the direct creation of free charge carriers in inorganic semiconductors, this leads in organic semiconductors to the formation of a localized electron-hole pair, electrically neutral, which is referred to as an exciton. Obtaining a photocurrent requires prior dissociation of this

exciton into a pair of free positive and negative charges. This is achieved through an heterojunction combining electron-donor (D) and acceptor (A) semiconducting materials. Thus, the photoconversion mechanism is usually described via five main steps, as schematized on Figure 1: (i) the optical absorption and exciton formation, (ii) the exciton migration to the (D/A) interface, (iii) the exciton dissociation into charges that results in a Coulomb bound electron-hole pair, referred to as a charge-transfer (CT) state, (iv) the separation of the positive and negative charges and their migration toward the electrodes, and (v) the charge collection at the electrodes. The electronic structure, geometric structure, and electric field at the D/A interface all play a critical role in the efficiency of the exciton-dissociation and charge-separation processes, and thus in the efficiency of the organic solar cell. In the simplest picture, the relative energies of the exciton states, charge-transfer states (where an electron [hole] has jumped from the excited donor [acceptor] to a neighboring acceptor [donor]), and charge-separated states (where the electron and hole are far away and completely screened from one another) determine the rates at which charge dissociation or recombination occurs.

As reviewed by some of the MINOTOR partners (i) characterizing the geometric and electronic structures at the interface between organic conjugated materials remains a formidable task that has been the object of the second Work Package of the project (WP2). Interfacial properties cannot be easily accessed at the experimental level since most spectroscopic techniques provide a signal dominated by the bulk of the materials, and surface techniques like X-ray photoelectron spectroscopy (XPS) are not often sensitive enough to probe accurately the electronic properties of interfaces (for instance the exact amount of charge transfer between the two components); another disadvantage of XPS or ultraviolet photoelectron spectroscopy (UPS) is that the signal is averaged over the probed zone, thus missing the actual events occurring at the molecular scale. The theoretical description of the morphology of organic D/A interfaces under given thermodynamic conditions (including temperature and composition), can also be viewed as one of the most challenging tasks to be tackled by computational physical chemists. In contrast to inorganic:inorganic p-n interfaces (and to some extent to inorganic:organic hybrid junctions) where strong covalent and ionic forces are in play, the nature of the organic:organic (O/O) interfaces is dominated by a combination of weak van der Waals dispersion forces, electrostatic interactions, and steric repulsions acting between the often flexible small molecules or macromolecules composing the system. Consequently, not only in the bulk crystalline phase of organic compounds, but even more so at their interfaces, the free energy landscape becomes a very complex function of the atomic positions, characterized by the presence of several local minima with very similar energy. While several experimental studies have demonstrated the crucial role of the interface morphology on the energy landscape in organic:organic heterostructures (i) standard quantum chemical techniques based on a formalism using periodic boundary conditions are not adapted to the description of such highly disordered interfaces. In this context, we have developed a multiscale modeling approach that combines molecular dynamics simulations, which give insight into the intimate morphology of the interfaces, to quantum-chemical and classical microelectrostatic (ME) (ii) calculations, which provide a picture of the energetic landscape for charge carriers at these interfaces. While a quantum-chemical description provides a quantitative picture of the electronic structure at the interface without adjustable parameters, the parametrized ME approach, in which molecules are coarse-grained into electrical multipoles, allows to study larger-scale clusters by accounting for long-range electrostatic interactions. These theoretical calculations were supported by UPS experiments carried out on the most representative systems.

Various types of O/O interfaces have been investigated by means of complementary modeling and experimental techniques. As a first working horse, we considered the

pentacene/C60 interface, which is archetypal of bulk heterojunctions involving electron-acceptor fullerene-type molecules that exhibit quantitative conversion of photogenerated singlet excitons into free charge carriers (iii) Then, as described below, other interfaces classified into three categories were investigated: i) interfaces featuring a negligible charge transfer in the ground state between the donor and acceptor materials, ii) interfaces featuring a sizeable charge transfer, and iii) interfaces including donor or acceptor molecules featuring an intrinsic dipole. Finally, an industrial relevant target system was examined, in order to provide a practical application example of the methodological framework developed within MINOTOR WP2.

Pentacene/C60 interfaces

Atomistic simulations of the pentacene/C60 interface morphology were performed in parallel to electronic calculations on model molecular aggregates, with for objective to get a deep understanding on the impact of the interfacial structure on the efficiency of the free charges generation process. The growth of pentacene on C60 was simulated by mimicking the vapour phase deposition process, in order to identify the most stable arrangement of pentacene on C60. These simulations evidenced two regimes depending on the coverage rate of the C60 (001) surface: at low coverage, pentacene molecules lay flat on the C60 free surface, gradually changing their orientation. When coverage reaches the value of about 2.5 molecules per nm², a collective reorientation phenomenon takes place, and pentacene molecules change their orientation with respect to the surface, going from an almost planar to an almost perpendicular alignment (Figure 2) (i). This spontaneous transition from planar to parallel alignment indicates that the thermodynamically favored arrangement of pentacene on C60 (001) is the (001) one.

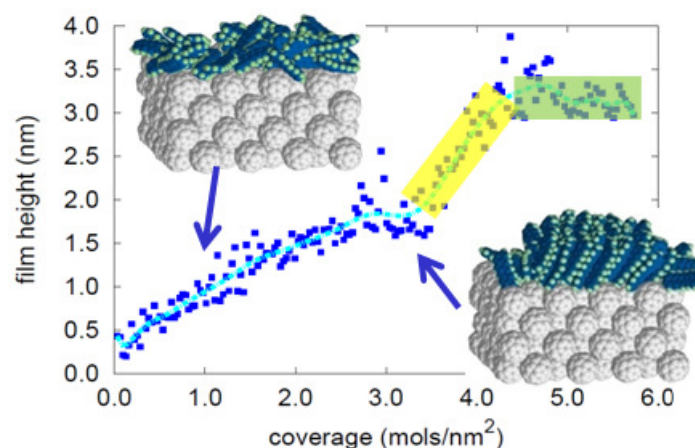


Figure 1: Maximum film height measured during the first monolayer growth. Two regimes are apparent: at low coverage, pentacene molecules lay flat on the C60 free surface, gradually superimposing and increasing their orientation with respect to the surface.

Quantum chemical calculations have been carried out on molecular clusters of increasing complexity to address the origin of the interfacial dipole moment in these heterojunctions, starting with cofacial arrangements of pentacene/C60 dimers. Results demonstrated that for intermolecular distances larger than 3 Å, the charge transfer between the two molecules is very weak, and the interface dipole mostly results from polarization effects. It was also shown that the orientation of the interfacial dipoles depends on whether the C60 center-of-mass is located on top of the pentacene molecular backbone, or at the edge

of the pentacene molecule, as illustrated Figure 2 (ii). This effect can be traced back to the uncompensated quadrupolar field at the interface. The pentacene quadrupole can be viewed as the result of a collection of 14 CH units that are polarized with negative partial charges on the inner carbon atoms and positive partial charges on the outer hydrogen atoms. When the C₆₀ molecule mainly interacts with the π -electronic density of the carbon atoms of pentacene, the reorganization of the electronic cloud over the fullerene molecule promotes a sizable intramolecular charge transfer away from pentacene. Interactions with the hydrogens atoms of pentacene generate the opposite polarization of C₆₀.

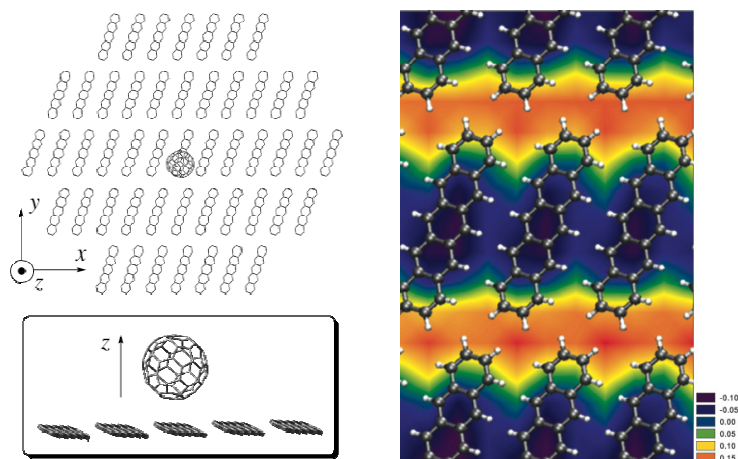


Figure 2: (left) C₆₀ molecule above a plane of pentacene units. (right) amplitude of the z-component of the induced dipole on the C₆₀ molecule as a function of its position on the (x, y) plane.

Our investigations have also demonstrated that the asymmetry in the electrostatic potential at the interface reshuffles the energy landscape explored by the charges as they move from the interface to the bulk [i]. Fragment orbital calculations (IV) on model 1D arrays stacked cofacially along the direction normal to the interface show that the ionization potential (IP) of the pentacene units is reduced while the electron affinity (EA) of the C₆₀ balls increases when going away from the interface (Figure 3, left). In contrast, the IP and EA show much weaker deviations from their bulk values in an edge-to-edge arrangement, owing to the weaker overlap between the electronic clouds of neighboring molecules (Figure 3, right).

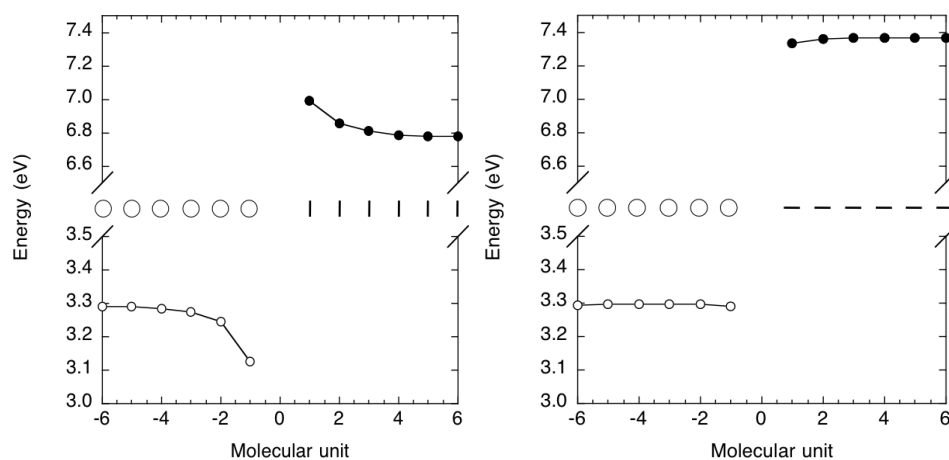


Figure 3: Ionization potential of pentacene and electronic affinity of C₆₀ in one-dimensional stacks in which the pentacene molecules are stacked parallel (left) or perpendicular (right) to the interface.

Thus, these calculations show that an intrinsic band bending can be settled at organic/organic interfaces and help in the charge separation process, provided a favorable interface morphology. Accordingly, we have estimated the energy landscape for charge separation in more extended C₆₀/pentacene interfaces, by gluing different facets of the pentacene molecular crystal with the (011) crystalline facet of C₆₀. So, the profile of the hole and electron energy landscape in the vicinity of the two interfaces calculated at the microelectrostatic level showed that an energy difference of ≈ 0.4 eV needs to be overcome to split the geminate pairs into separate charges in the case of the pentacene(001)/C₆₀ interface, while the charge separation process is quasi barrierless in the pentacene(01-1)/C₆₀ interface [ii]. These results thus offer a nice explanation for the highest performance typically obtained in solar cells including C₆₀ derivatives.

Similar ME calculations were performed on more realistic structures extracted from the MD simulations, featuring a certain amount of structural disorder. As a striking consequence, it was shown that a very modest interfacial disorder can give rise to a dispersion of the site energies by several hundreds of meV. This broadening of the energy levels at the interface creates new pathways for the geminate pair recombination/dissociation and further affects the dynamics of these processes. Moreover, the presence of several geminate pairs at the interface can also participate to the energetic disorder, in particular when the pair density is sufficiently high that coulombic potentials induced by the individual pairs start to overlap. ME calculations assuming the random dispersion of the excess pairs at the interface have demonstrated that the average destabilization energy experienced by a hole in the first pentacene monolayer steadily increases with the charge pair density. This destabilization partially counterbalances the stabilization of the hole by its counter charge on C₆₀, and thus favors the dissociation. Thus, after reaching a threshold density, every additional charge pair has a 100% chance to dissociate. Below the threshold, dissociation process is statistically governed by the thermal vibration of the IE, and only a certain fraction of the pairs can overcome the dissociation barrier. Finally, a complete picture of the dynamics of charge separation process in pentacene/C₆₀ interfaces is about to be obtained by means of master equation simulations, accounting for energetic disorder both arising from thermally-induced structural fluctuations and dispersion of excess geminate electron/hole pairs at the interface.

D/A interfaces featuring a negligible charge transfer in the ground state

Following the modeling strategy developed for pentacene/C₆₀ interfaces, we have then extended our investigations to other donors and acceptors, where the out-of-plane component of the quadrupole moment can either be enhanced or decreased with respect to pentacene. Donor molecules such as cyano-pentacene, oligothiophenes and dicyanovinyl-substituted oligothiophenes were thus combined to either C₆₀ or PTCDA as acceptors. In all these interfaces, quantum chemical calculations performed on model systems evidenced a negligible ground-state charge transfer between the donor and acceptor, accompanied by a significant interfacial dipole arising exclusively from polarization effects. Moreover, calculations similar to those reported Figure 3 for pentacene/C₆₀ interfaces allowed to draw general trends regarding the relationships between the chemical nature of the donor and acceptor molecules and the efficiency of free charge separation. As a general conclusion, imparting a quadrupolar moment polarized in opposite directions for the donor (with local

dipoles having their positive poles lying outwards with respect to the center of the molecule, e.g. C-H in pentacene) and the acceptor (with local dipoles having their positive poles lying inwards with respect to the center of the molecule, e.g. C=O in PTCDA) appears as an attractive strategy to bias the energy landscape in favor of full separation of the charge transfer pairs^(vi).

Electronic structure calculations were eventually carried out on realistic interfaces provided by atomistic simulations. Sexithiophene/C60 interfaces with different morphologies, either obtained from vapor deposition (VD) or liquid crystal (LC) annealing techniques (Figure 4, left), were first investigated by means of a hybrid quantum chemical/molecular mechanics (QM/MM) scheme. This method allows partitioning large chemical systems into an electronically important region that requires a quantum mechanical treatment and a perturbative region that permits a classical MM description (see Figure 4, right). The first objective was here to disentangle the various contributions to the interface dipole, possibly arising from a partial charge transfer from T₆ to C60, electronic polarization effects or structural distortions of the molecules at the interface. From these calculations, the vacuum level shift (VLS), which is directly connected to the dipole component normal to the interface and accessible experimentally via UPS measurements, has been evaluated. The theoretical results show a qualitative agreement with reported experimental data, indicating that the method developed is suitable for the calculation of the interface dipole at amorphous interfaces.

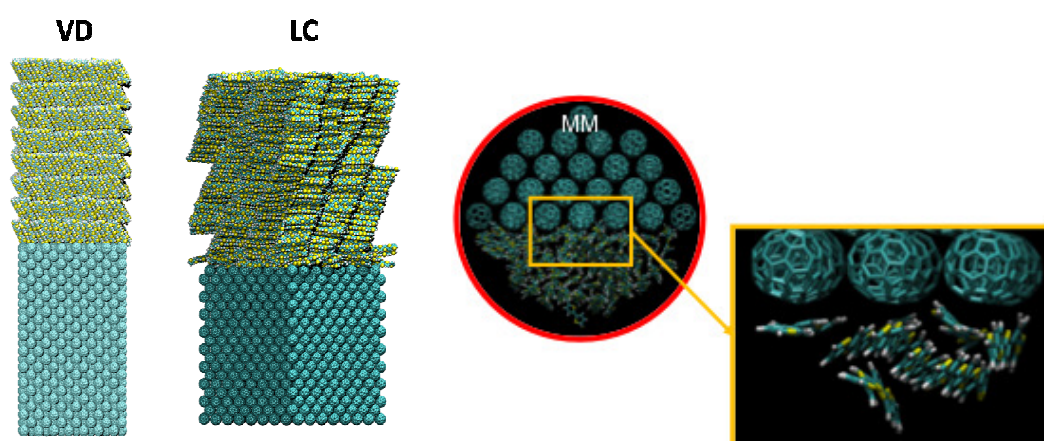


Figure 4: (left) Large T6/C60 interfaces obtained from vapor deposition (VD, left) and liquid crystal annealing (LC, right). In the VD interface, the T6 molecules (layers) are parallel (perpendicular) to the interface, while the opposite is observed for the LC system. (right) Partition of a T6/C60 aggregate into QM and MM regions.

The morphology as well as the electronic structure of PTCDA/pentacene interfaces were also characterized by means of joint theoretical and experimental investigations. UPS measurements revealed that an interface dipole of ~ 0.25 - 0.3 eV is observed upon deposition of PTCDA onto pentacene. Moreover, the presence of additional peaks on the UPS spectra (see Figure 5, left) indicate that pentacene molecules can either adopt a standing or a lying-down orientation relative to the PTCDA interface. These findings suggested that the roughness of the PTCDA/pentacene interface controls the local order of the pentacene molecules. For a rough surface featuring small pentacene grains (island growth or layer-by-layer growth in the initial stage of a new layer), the face-down PTCDA molecules initiate a face down reorientation of the pentacene molecules at the surface. For larger grains of

pentacene, the energy required is too huge to overcome and the pentacene molecules remain standing at the interface.

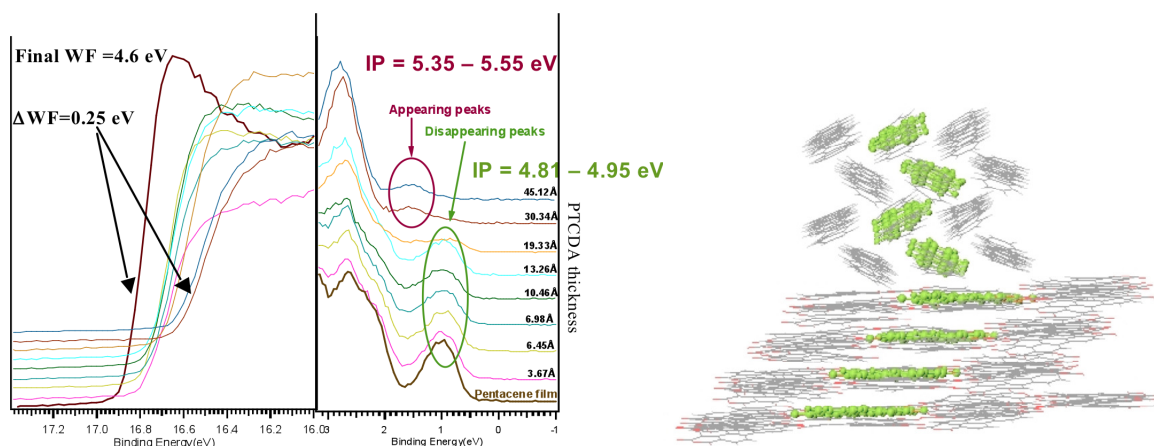


Figure 5: (left) UPS spectra of PTCDA films deposited on pentacene. The additional peak appearing at about 1.6eV is attributed to pentacene molecules in the vicinity of the interface. (right) pentacene/PTCDA aggregate extracted from atomistic simulations. The charge injection channel is highlighted at the center of the cluster.

The electronic structure of pentacene/PTCDA interface was also addressed theoretically using various aggregates issued from atomistic simulations. Calculations performed at the DFT level confirm that no charge transfer occurs between the pentacene and the PTCDA layers, and that the origin of the level alignment in this interface is purely of electrostatic polarization nature. Larger scale fragment orbital calculations evidence a bending of the electronic levels detrimental to the conversion of bound charges into fully separated charges in the case of a lying-down orientation of the pentacene molecules (Figure 4, right), while the opposite is found in the case of a standing orientation.

D/A interfaces featuring a significant partial charge transfer in the ground state

The formation of an interface dipole at O:O interfaces can be triggered by polarization effects (i.e., reorganization of the electronic density within the molecules across the interface), as discussed above, as well as by (partial) charge transfer between the donor and acceptor units. A charge transfer requires the overlap between the molecular orbitals of the two molecules in contrast to the long-range polarization effects. As representative examples of this kind of heterojunctions, TTF-TCNQ, TTF-F4TCNQ and AOB-F4TCNQ interfaces have been investigated through collaborative theoretical and experimental (UPS and XPS) studies. The later have demonstrated that the strength of interface dipole is dependent on the relative strength of the donor and acceptor molecules that constitute the interface. As can be deduced from the case of AOB/F4TCNQ, different deposition order is also a factor that impacts the strength of an interface dipole.

On the theoretical side, we have assessed the reliability of the Density Functional Method (DFT) for modeling these charge-transfer organic/organic interfaces, since DFT is presently the most efficient method to study medium-size systems including electron correlation at a reasonable cost. Comparison to high level *ab initio* calculations demonstrated that the use of a long-range corrected exchange-correlation (XC) functional is prerequisite to

study the interfacial charge transfer in TTF-TCNQ cofacial stacks, and that the wB97x functional is the best compromise to obtain a reliable description of the interfacial electronic structure. Various morphologies of the TTF-TCNQ interface were then simulated using force-field molecular dynamics, by connecting different crystalline blocks of the two materials as starting structures. The energy level alignment and charge transfer properties at two relaxed interfaces extracted from these MD simulations (showing either strong or weak π - π interactions between the donor and acceptor molecules), were eventually investigated by means of the density of interfacial states (IDIS) model (iii). The key feature of this model is to associate to a given organic semiconductor a quantity referred to as the charge neutrality level (CNL), which can be experimentally determined by depositing the molecular semiconductor on a nonreactive surface. The CNL has to be seen as equivalent to a “Fermi level” of the molecule that will govern the direction and amplitude of the charge transfer at the organic/organic interface: The charge transfer should occur in such a way as to equalize the CNLs of the two molecules. DFT calculations (iv) show that the TTF-TCNQ interface is metallic, as predicted by recent experiments (v) due to the overlap (and charge transfer) between the TTF-HOMO and TCNQ-LUMO levels, indicating that the main mechanism controlling the TTF-TCNQ energy level alignment is the charge transfer between the two materials. In these calculations it was also analyzed the effect on the interface electronic properties of applying a bias voltage between the two materials finding that for a bias larger than ~ 0.5 eV (shifting TTF towards higher binding energies w.r.t. TCNQ) the system becomes an insulator.

D/A interfaces including molecules featuring an intrinsic dipole

In the systems presented so far, the interface dipole either originates from a partial charge transfer or from electrostatic polarization. We have investigated another category of interfaces, in which the molecules of one of the organic semiconductor materials possess an intrinsic dipole moment. Indeed, the presence of a permanent dipole is expected to have a large impact on the energetic landscape at the interface, as it represents a direct potential barrier for positive or negative charges. In order to investigate this parameter, we have conducted joint theoretical and experimental investigations on the interface combining the Alq3 donor molecule, which is characterized by an intrinsic dipole between the oxygen and the nitrogen atoms of the ligands, and the electrophilic NTCDA molecule.

DFT calculations using the long-range corrected wB97X XC potential validated for the TTF/TCNQ interfaces were first performed on model stacks of increasing size, in order to unravel the influence of the orientation of the permanent molecular dipoles on the energy level alignment at the interface. Various model 1D stacks, in which the permanent dipoles are either aligned or alternate, were considered (Figure 6). As expected, the absolute value of the interfacial dipole increases linearly with the number of molecules for parallel stackings, while it oscillates for antiparallel ones, with exact cancellation for an even number of Alq3 molecules. In all cases, the Alq3/NTCDA interface dipole is mostly dominated by polarization effects, with a negligible contribution of the charge transfer between the donor and acceptor moieties. The energy landscape for charge separation determined from fragment orbital calculations is dominated by the electrostatic interactions between the permanent dipoles of Alq3 and the quadrupoles of NTCDA. The resulting band bending strongly depends on the orientation of the dipoles, demonstrating that controlling the orientation of the permanent dipoles at the interface could be a possible strategy to bias the electrostatic potential to favor charge separation.

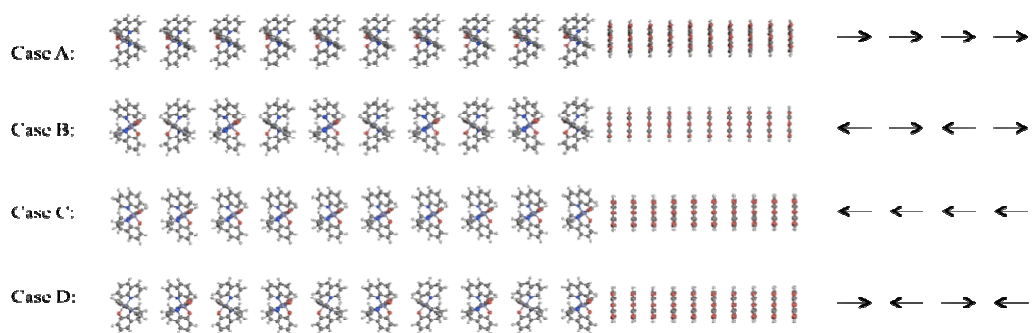


Figure 6: Different Alq3/NTCDA stacks considered in the calculations.

UPS measurements carried out on Alq3/NTCDA bilayers further confirmed that the strong intrinsic molecular dipoles in Alq3 introduce a vacuum level shift in the absence of charge transfer across the interface. Results on the sequentially formed AlO_x/Alq3/NTCDA and Alq3/NTCDA/AlO_x systems are depicted in Figure 7. Depositing an Alq₃ overlayer onto NTCDA (and waiting for equilibrium) yields an interface dipole of 0.19 eV, slightly smaller than the expected 0.4 eV obtained for Alq₃ deposition on inorganic substrates. This was attributed to a comparatively less well ordered Alq₃ film at the rougher NTCDA surface, decreasing the net collective dipole of the molecules. By changing the deposition order, a dramatically different interface dipole is achieved (1.06 eV) for the same two interface materials.

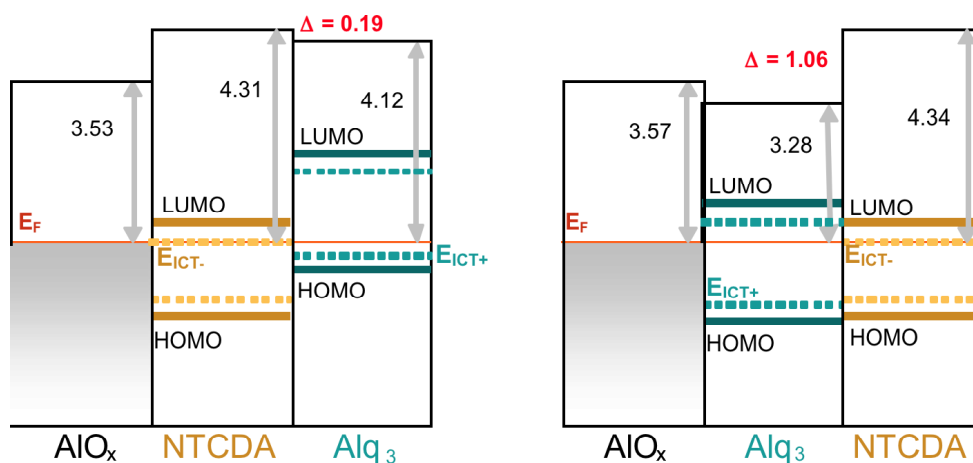


Figure 7: Interface energetics of AIO_x/NTCDA/Alq₃ (left diagram) compared to inverted sequence of the films: AIO_x/Alq₃/NTCDA (right diagram)

Demonstration of the proof of concept through fabrication of solar cells

In order to provide a practical application example of the methodological framework developed within MINOTOR WP2, an industrial relevant target system was examined. The study included an experimental characterization of interface morphologies and a detailed characterization of the corresponding solar cells. Specifically, the charge dissociation at the donor/acceptor heterointerface of thermally evaporated planar heterojunction merocyanine(ID583)/C60 organic solar cells was investigated. Deposition of the donor

material on a heated substrate as well as post-annealing of the complete devices at temperatures above the glass transition temperature of the donor material resulted in a twofold increase of the fill factor. The current-voltage characteristics of bulk heterojunction devices with different ID583:C60 layer thicknesses are shown Figure 8. An analytical model employing an electric-field-dependent exciton dissociation mechanism revealed that geminate recombination is limiting the performance of as-deposited cells. Fourier-transform infrared ellipsometry showed that, at temperatures above the glass transition temperature of the donor material, the orientation of the dye molecules in the donor films undergoes changes upon annealing. Based on this finding, the influence of the dye molecules' orientations on the charge-transfer state energies was calculated by quantum mechanical/molecular mechanics methods. The results of these detailed studies provide new insight into the exciton dissociation process in organic photovoltaic devices, and thus valuable guidelines for designing new donor materials.

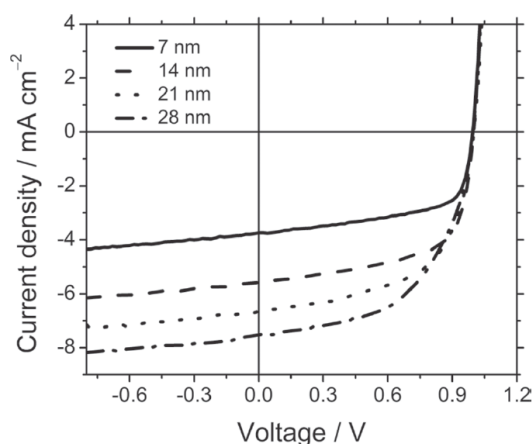


Figure 8: Illuminated J–V characteristics of bulk heterojunction devices with different ID583:C60 layer thicknesses.

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Workpackage 3

Introduction

Among the materials selected for overcoming the limitations of silicon-based electronics and allowing for the development of high performance electronic devices, inorganic oxides are now playing a predominant role in research and envisaged applications: they are in fact rather cheap and easy to produce, non-toxic and non-polluting, often transparent and have suitable and rather tunable charge transport properties. Depending on the nature of the inorganic atoms linked to oxygen, these materials can be either insulators (e. g. SiO₂, Al₂O₃) [Ponce Ortiz 2010], or semiconductors (e. g. TiO₂) [Harin 2012] and conductors (e. g. ZnO, In₂O₃/ SnO₂) [Armstrong 2009]. Additional levels of tunability are provided by the possible occurrence of several crystal structures for the same oxide, with rather different electric properties, by the presence of impurities, and by recurring to nanostructures, which again are different from bulk materials as a consequence of their enormous surface area.

More specifically, *transparent conducting metal oxides*, in particular indium-tin and zinc oxides, are used as electrode materials in organic electronics applications such as light emitting diodes and solar cells. *Transparent nanostructured semiconducting metal oxides* constitute the inorganic counterpart in hybrid inorganic/organic solar cells, i.e. cheap photovoltaics systems aimed at exploiting the advantages of inorganic and organic semiconductors [Bouclé 2012]. In this context TiO₂ constitutes the established material as electron transporter [Harin 2012], while ZnO is considered as a future promising alternative because of its higher charge carrier mobility (200 vs 0.1 cm² V⁻¹ s⁻¹), albeit for the moment ZnO-based devices do not show the expected performances [Sessolo 2011]. *Inorganic dielectrics*, and in particular silicon oxide wafers, are a standard material employed in the construction of organic transistors, where they serve both as rigid support and as dielectric layer to modulate the electric current flow [Ponce Ortiz 2010].

In all of these applications, inorganic oxides are interfaced with organic functional materials, where the organic layer is either active part of the devices (*physisorbed and chemisorbed molecules and polymers* playing the role of semiconductor, light emitter or light harvester) or consists in covalently linked coating molecules (*self-assembled monolayers, SAM*) employed for modifying the oxide surface properties [Hotchkiss 2012] or even provide new ones, for instance biocompatibility and sensing capabilities [Haensch 2010].

With the notable exception of TiO₂ in contact with organic dyes, driven by the success of dye-sensitized solar cells [Harin 2012], the nature of the electronic interactions between these functional molecules and inorganic substrates has hardly been addressed so far, despite the huge fundamental and technological interest. In the case of (semi) conducting oxides, where the key process is the transfer of one electron from/to the organic material to/from the inorganic one, the critical quantity is the *work function* of the oxide (the energy required to

extract one electron from the surface of the oxide to an infinite distance), and how it is modified by the interaction with the organic substrate. For insulating oxides instead the fundamental quantity is the dielectric constant and its local modification at the surface – the “*electrostatic landscape*”, which has a direct influence on the velocity of the charge transport happening in the adjacent organic semiconductor. In both cases, the surface energy and topography are important as well, as they do influence the morphology of the organic substrate and consequently the electronic properties of the interface.

As detailed in the following, during the three years of Minotor the WP3 team faced both the *morphological and electronic aspects* of the investigation with the help of *theory and experiments*, focussing on the most important materials in the field: Silicon, Titanium, and Zinc oxides, with a particular attention for the latter.

Overview of WP3 activity

The WP activity was devoted to the understanding of well defined inorganic surface/small molecule and /self-assembled monolayer interfaces: ZnO [I1], TiO₂ (rutile) [I2] and SiO₂ [I3] surfaces on the **inorganic** side; on the organic side, a few **small molecules** (pentacene [O1], tetrathiafulvalene [O2], tetracyanoquinodimethane [O3], tetrafluoro-tetracyanoquinodimethane [O4]), and finally as **self-assembled monolayers** (SAM), three benzoic acids [S1] with -OCH₃, -H and -CN end groups, 4-tertbutylpyridine [S2], octadecyltrichlorosilane [S3] and heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane [S4]. The detailed list of the interfaces of which the investigation was carried out in the first (I) and/or second (II) reporting period is summarized in the table below. It is worth noting that, even if no new completely new interfaces were added during the second period, also triple I3/S3/O1 and I3/S4/O1 interfaces (*), and linear 1-6 oligoacenes and heteroacenes on ZnO were studied from a theoretical standpoint (+). Finally, a strong experimental effort has been towards the studying of WP3 systems and to building devices from them (■). The joint theoretical/experimental work witnesses an efficient coordination of the WP and a remarkable number of collaboration established during the period.

Summary of the systems studied in WP3

	O1	O2	O3	O4	S1	S2	S3	S4
ZnO I1	I/II+	I/II	-	-	I/II	I/II	-	-
TiO ₂ I2	-	II	I	I/II	-	-	-	-
SiO ₂ I3	II	-	-	-	-	-	I/II*	I/II*

Thanks to the careful testing of experimental and theoretical methodologies performed in the first part of the project, in the second period the consortium activity proceeded smoothly to the achievement of scientific results, summarized below per task.

3.1 Modelling of the morphology at I/O interfaces by means of force-field calculations and coarse-grained approaches: while providing reliable interface configurations for the quantum chemistry calculations carried out in WP3.2 and 3.3, general methodological schemes were devised for simulating the vapor deposition of organic compounds via Monte Carlo and Molecular Dynamics (MD) techniques, with broader applications to any type of organic-solid interface.

3.2 Multiscale modelling of the electronic processes at I/O interfaces: regarding the methodological aspects, thorough tests were carried out to ensure the quality of the quantum mechanical calculations and the good advancement of the WP. From a theoretical point of view, measuring the extent and the importance of surface reconstruction, establishing if a

molecule undergoes chemisorption or physisorption, and describing correctly surface-induced polarization and charge transfer require on one hand a wise choice of the method used in the calculations, and on the other a careful interpretation of the results- which in the worst case could reflect the limitation of the chosen approach rather than the true nature of the inorganic/organic interaction.

The scientific activity was directed to the theoretical study of SAMs and small organic molecules in contact with polar and non-polar ZnO surfaces, allowing to predict the ensuing shift in the substrate work function and to identify its dependence on chemisorption, physisorption, coverage, and water contamination.

3.3 Extension to silicon-based interfaces: with a bottom-up approach combining QM calculations, atomistic simulations, microelectrostatic calculations and experiments, it was possible to relate the SAM-induced threshold voltage shift in pentacene-based transistors to the chemical nature of the SAM and the variation of the electrostatic landscape with respect to the bare SiO₂ substrate.

3.4 Experimental measurements and device fabrication with engineered interfaces: with a perfect parallelism with WP 3.1 and 3.2, ultraviolet photoelectron spectroscopy (UPS) measurements of the work function shift were carried out for organic-treated ZnO and TiO₂ surfaces. In addition, even facing problems in the production of clean ZnO surfaces, the realization of working ZnO-based diodes and light-emitting diodes allowed for the comparison and exploitation of WP3.2 results in real devices.

Main scientific and technological results

1) Multiscale model of pentacene/SAM interfaces on SiO₂

In organic field effect transistors, self-assembled monolayers chemically bound to the dielectric oxide and in direct contact with the electrical channel of the transistor can be used for reproducible control of the essential device characteristics, such as charge carrier mobility, threshold voltage and on/off current ratio [Di Benedetto 2009]. When assisted by high charge carrier mobility, a controllable threshold could become helpful in many particular cases to overcome common limitations of the organic circuits, for instance in speed, power consumption and yield. However, complementary theoretical understanding and fundamental origins of the threshold voltage shift are still under discussion. Several effects, including charge trapping on the SAM molecules or/and the gate dielectric, electrostatic impact of molecular dipoles confined in the SAM and charge transfer from the SAM to the transistor channel, have been proposed in literature to rationalize experimental observations [Gholamrezaie 2012]. Here we developed a multi-scale theoretical model for interfaces between inorganic substrates and SAM layers, as well as interfaces between the SAM and organic semiconductor. First, zooming up to the nanoscale, we used Molecular Dynamics simulations on a few hundreds of molecules of two chemically-bound SAM molecules (OTS and FDTS, see Figure 1) to cover a dielectric surface (SiO₂) with a smooth and uniform film. After that, we zoomed out to the sub-micrometric scale typical a transistor channel. There, we applied molecular micro-electrostatics to investigate how the surface charge distribution changes the transistor channel electrostatic landscape and address possible impacts of these changes on the charge carrier density and mobility. Finally, we validate the predictions of the theoretical model by fabricating and measuring the corresponding OTFT structures with different surface treatments. Both SAMs introduce similar amount of energetic disorder and assuming the semiconductor growth to be unchanged, comparable charge carrier mobilities are expected from our calculations, in a good agreement with experiments. The stabilization

of charged pentacene molecules generated by the SAM electric field is however much larger for the FDTS layer, suggesting that the threshold voltage shift can be explained in terms of local dipoles at the SAM termination, as suggested by Battlog and coworkers [Pernstich 2004], without the need of hypothesizing the presence of trapped charges.

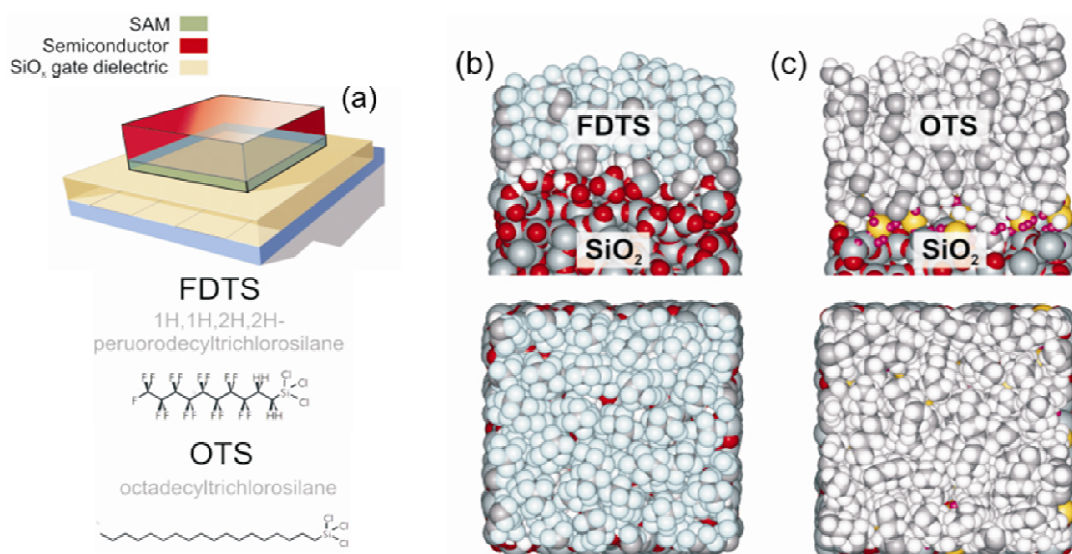


Figure 1: a) schematics of a typical SAM organic thin film field effect transistor, with chemical structures of the SAM molecules studied. Side and top snapshots of (b) FDTS/SiO₂ and (c) OTS/SiO₂ interfaces.

2) Small molecule on inorganic oxides

This section combines molecular dynamics simulations, quantum chemical calculations and UPS measurements to address the morphology and electronic processes accompanying the deposition of organic molecules on top of inorganic substrates.

a) Pentacene on ZnO

The structure of pentacene on the stable, non polar ZnO(10-10) surface, has been reproduced with a technique developed for simulating the deposition of organic molecules from the vapor phase. With Monte Carlo algorithm we sample the surrounding of the depositing molecule with a pre-defined number of trial steps of translation and rotation. Repeating trial step movement with a pre-defined step size leads to the deposition of the molecule at a local energy minimum position on the substrate surface. Then a new molecule is added to the system, iterating the scheme until a monolayer or a thin organic film is formed.

For this system, we observe a strong structural disorder of the pentacene morphology at the direct contact region between ZnO and pentacene. In this region, most of the molecules are lying flat. With increasing height, the molecules grow perpendicular to the substrate surface, lowering the amount of disorder. On the top most layer the pentacene molecules finally take the exact positions and orientations of the pentacene single crystal. The adsorption energy and geometry of pentacene has been investigated with semiempirical quantum chemistry calculations, finding that the molecule lies flat on the surface with a strong physisorption energy of 2.4 eV, confirming the Monte Carlo simulation results.

Both the highest unoccupied molecular orbital (HOMO) and lowest unoccupied (LUMO) levels of pentacene on ZnO experience a large shift to lower energies with respect to the

corresponding energies for the isolated molecule, while the energy of the valence and conduction bands of the oxide surface are barely affected by the presence of the organic layer (figure 2). As expected from their electron donor character, the surface deposition of pentacene induces a lowering of the ZnO work function, which can be evaluated from the amount of charge transferred per pentacene molecule and by the surface area occupied by pentacene. In this case, we predict a charge transfer of about 0.6 electrons per molecule, hence the organic layer is positively charged at this interface, corresponding to a work function shift $\Delta\Phi$ of -0.5 eV. Actually, increasing the molecular density at the metal-oxide surface will induce significant depolarization effects that will lower the induced dipole per surface unit. Such cooperative effects should be considered in further studies for a quantitative evaluation of the work function shift.

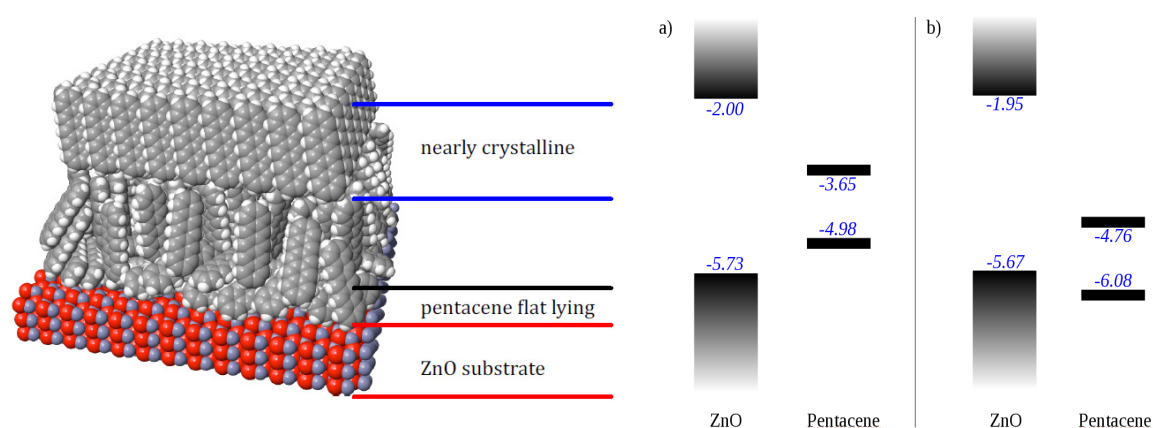


Figure 2. Left: simulated pentacene/ZnO interface morphology indicating regions of different strength of disorder. Right: electronic energy levels (eV) of ZnO and pentacene isolated (a), and interacting (b).

b) TTF on ZnO

The study of pentacene on the non polar ZnO (10-10) surface was extended to tetrathiafulvalene, another n-type organic semiconductor, but with a higher tendency to donate electrons. With respect to the previous case, a more idealized interface structure was produced, by replicating the experimental crystal structure of TTF and depositing in on top of ZnO(10-10), and equilibrating with MD simulations. The adsorption of a single TTF molecule onto the ZnO(10-10) surface has been studied by means of two different quantum-chemical methods. In the most stable structure (Figure 3a), TTF features a significant distortion compared to its planar gas-phase configuration, typical of chemisorption, while it remains flat in physisorbed structures b) and c), which however are less stable with respect to a). The calculations indicate a strong hybridization of the HOMO level of TTF with the band states of ZnO in configuration a), which determines the pinning (i.e. equalization of the relative energies) of the corresponding orbitals. For all TTF/ZnO configurations we predict a significant charge transfer from the TTF molecule to the ZnO surface, resulting in the appearance of a significant interfacial dipole. As such, the deposition of TTF molecules on the ZnO(10-10) surface reduces the work function of ZnO up to 0.7 eV and might help modulating the barrier for charge injection in hybrid opto-electronic devices. [Nenon 2012]

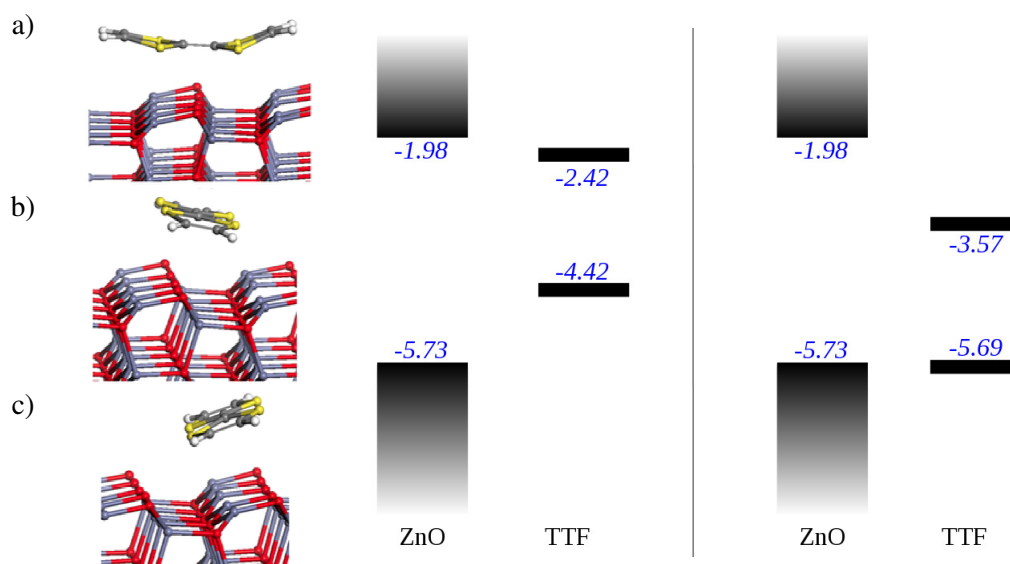


Figure 3: a-c): geometric structures of the three most stable TTF/ZnO complexes. Middle and right panels: electronic energy levels (eV) of either isolated (left) or interacting ZnO and TTF (right).

c) F4TCNQ on TiO₂

F4-TCNQ is a strong electron acceptor known to form charge-transfer complexes with organic semiconductors and to enhance their conductivity via p-doping; moreover, it can be effectively used for modifying the work function of metal surfaces. However, the nature of the electronic interactions between the molecule and inorganic surfaces / nanoparticles and the possible formation of an interface dipole was not investigated so far and here we tackled this problem from the structural point of view with MD simulations, using a deposition technique developed in WP2 [Muccioli 2011], and addressing the very common and stable TiO₂ rutile (110) surface. In short, four F4-TCNQ molecules are added to the system every 1 ns, endowed with variable initial orientation and position, and an initial velocity directed towards the surface. About 300 F4-TCNQ molecules were deposited at room temperature, to form an amorphous organic film with a thickness of about 40 Å (figure 4). Not taking into account the possibility of chemisorption or charge transfer, we found that only the first layer of F4-TCNQ molecules on rutile (110) is likely to organize in a well structured film, with molecules having their long axis parallel to the [001] direction and the medium axis tilted of 50 degrees with respect to the [110] surface normal. Quantum chemistry calculations on the same system indicate also the possibility of chemisorption. The two possible absorption modes are substantiated by the UPS measurements performed at different conditions: depositing F4-TCNQ at room temperature, a sub monolayer chemisorbed film forms, showing a work function of 5.3 eV, to be compared with $\Phi=4.3$ for clean rutile, hence a strong electron transfer from rutile to F4-TCNQ. Physisorbed, thicker films can be obtained by depositing at 100 °C, showing an even higher work function value (5.6 eV). Finally, angular dependent X-ray absorption spectroscopy measurements showed that F4-TCNQ is not flat on the surface, in qualitative accord with MD simulation results.

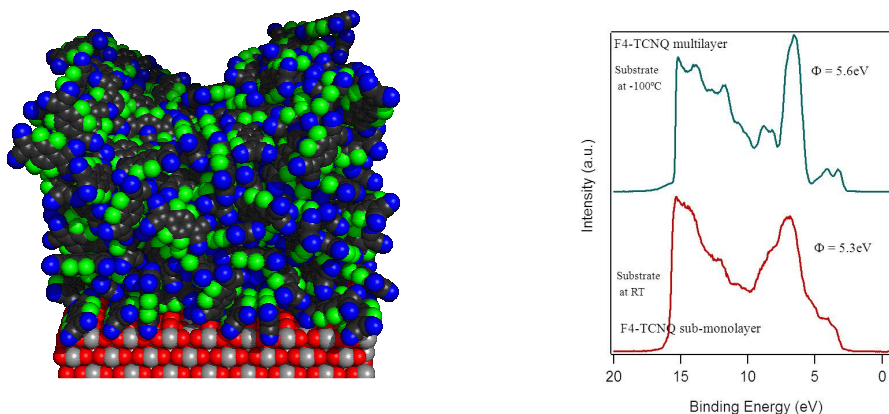


Figure 4: Left: snapshots of the structure of F4-TCNQ film on TiO₂ rutile. Right: comparison between the UPS spectra of a F4-TCNQ physisorbed multilayer film and a chemisorbed monolayer film. Note the strong modification of the frontier features (3-5 eV) of the chemisorbed sub-monolayer spectrum compared to the multilayer film.

3) Self-assembled monolayers on ZnO surfaces

In principle the work function of ZnO can be efficiently controlled through surface modification using SAMs based on dipolar molecules, resulting in the enhancement of the charge injection efficiencies in hybrid organic-inorganic LEDs. ZnO nanocrystals can feature stable polar and non-polar surfaces [Dulub 2003]. Here we focus on two types: polar surfaces entirely terminated with either zinc positively charged atoms (0001) or negatively charged oxygen atoms (000-1), and a non polar one (10-10) with an equal amount of Zn and O atoms (Figure 5).

Quantum chemistry calculations on the (10-10) ZnO surface indicate a considerable geometric reconstruction upon cleaving (c.f. figure 4 a-c), resulting in a tilt of the surface Zn-O dimers. Modeling of the polar surface is more challenging as it requires partial addition of -H and -OH group (“wetting”) to avoid metallization.

Here we have considered SAMs based on molecules with two different anchoring groups: carboxylic acid (benzoic acid BA with three different head groups: -H, -CN and -OCH₃) and pyridine (PY). With this choice, it is possible to single out the contribution in the work function shift from the molecular permanent dipole. In fact, by changing the head group on the BA, the molecular dipole changes of sign. In addition, BA and PY bind differently with the ZnO surface (BA with the carboxylic group, PY with the aromatic nitrogen), the former SAM being electron withdrawing and the latter electron releasing.

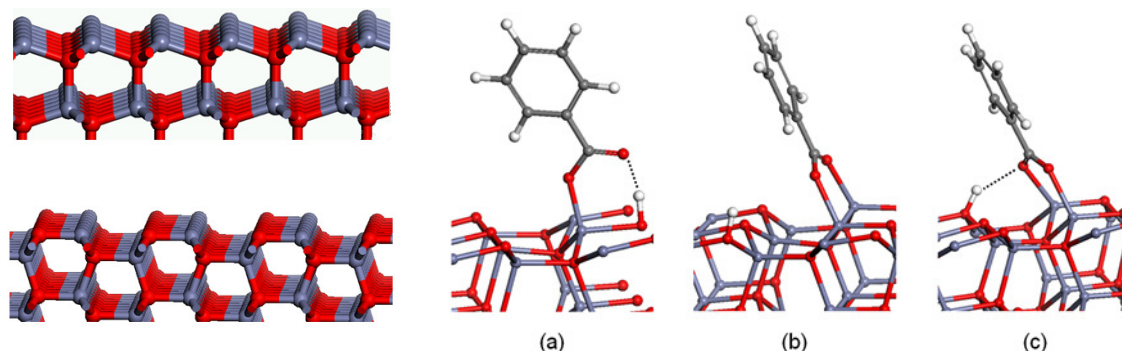


Figure 5: Left: representations of polar Zn-terminated (0001) and non polar (10-10) ZnO surfaces. Right: binding modes of benzoic acid on the non-polar ZnO surface. (a) monodentate, where only one oxygen atom (red) is connected to a surface Zn atom (light

blue). In that case, a hydrogen bond is also formed (dotted line). b,c) bidentate with two oxygen atoms bonded to two different surface Zn atoms. In this case, two main configurations can be envisaged: b) either the adsorbed hydrogen atom is not interacting with the BA molecule or c) the hydrogen is attached to the surface oxygen facing the BA molecule so that a stabilizing interaction can occur.

a) Non polar (10-10) ZnO surface

Both 4TBP and BA are chemisorbed on this surface, with binding energies of about 1.4 and 2 eV, respectively. However while 4TBP features a unique binding mode due to the formation of a Zn-N bond, for BA three different possibilities are given by the formation of one or two Zn-O bonds and a hydrogen bond (figure 5). BA SAMs produce the expected correlation between work function shift and molecular dipole: $\Delta\Phi$ can reach values of -0.3 eV for BA-H, -0.7 eV for BA-CH₃, and +1.3 eV for BA-CN, due to its strong dipole. Also 4TBP induces a strong and negative shift of Φ (-1.34 eV), generated in equal amount by the molecule permanent dipole (-0.69 eV) and by the nature of the Zn-N bond (-0.66 eV). Interestingly, the work function shift can be reduced by the presence of water molecules on the surface.

b) 4TBP on polar (0001) and (000-1) ZnO surfaces

With respect to the non polar surface, the absorption energies are lower: 0.7 eV for the Zn-terminated and 0.8 eV for the O-terminated polar surface. In the latter case also the binding mode appears different and consists in the formation of a -N-H..O- hydrogen bond. The predicted work function shifts are -0.88 eV and -1.15 eV, in qualitative agreement with the UPS measurements, which indicate shifts of -0.5 and -0.8 eV for a final work function of 3.5 eV – the clean surfaces having $\Phi=4.0$ eV (Zn-terminated) and 4.3 eV (O-terminated).

4) ZnO nanorods-based light emitting devices

a) Fabrication of ZnO nanorods films

Crystalline ZnO layers with few vacancy defects are transparent and can be used to fabricate efficient hybrid polymer LEDs [Walzer 2007]. However their manufacturing requires expensive deposition techniques that are difficult to combine with low-cost large area lightening applications. An alternative approach used here is the cheaper aqueous chemical growth process, that can easily be scaled up for large area productions. However, this process yields ZnO in the form of nanorods possessing a relatively large number of intrinsic defects and facets. These defect optical transitions results in light emission ranging from 400 nm to around 700 nm; in addition they introduce n-doping, conferring electron semiconducting properties to the nanostructures.

Here ZnO nanowires were grown vertically in situ on metal (electrode) and polymer (semiconductor) substrates, and then spin coated with an insulating polymer (polystyrene or PMMA) to fill the gaps between the rods and form an uniform and compact film. Finally, the insulating coating on top of the rods is removed by oxygen plasma etching, for a final film thickness of a few microns (Figure 6).

b) Hybrid ZnO-polymer electron-only diodes

Several electron-only hybrid diodes were fabricated as benchmark devices to study the electron transport between the ZnO and the electron transporting semiconducting polymer

Polyera Activink N2200[®]. The electrodes were chosen such that the hybrid device behaves as a rectifying diode: Au/ZnO/N2200/Al. The electric I/V measurement revealed that one of the major difficulties when fabricating a well-defined ZnO-organic heterojunction via solution processes is the presence of ZnO nanorod short circuit currents. For thick semiconducting polymer layers, most of the ZnO leakage current is eliminated and a true ZnO-polymer hybrid diode is obtained, with a rectification ratio of 300 at 1V. In the ZnO-polymer heterojunction, ZnO nanorods act as an electron injecting layer such that even a high workfunction metal can be used as cathode in a light emitting diode.

c) ZnO-diodes modified with self-assembled monolayers

In the attempt of improving the reliability of ZnO/organic hybrid devices and to investigate the impact of SAMS on the electrical characteristics, new diodes were built by growing ZnO nanorods on indium-tin oxide and burying them in a PMMA matrix. The self-assembled molecules (BA-H and BA-CN benzoic acids) were then deposited onto the ZnO surface by spin-coating, followed by the spin coating of the conducting polymer electrode PEDOT-PSS. The current-voltage characteristics indicate an impact of the SAMs mostly when trying to inject electron from PEDOT-PSS into ZnO. BA-CN facilitates the injection of electron compared to BA since a higher current level is measured at positive bias. BA-CN SAM introduces a rectification of the device, suggesting an impact of the molecular dipole on the electron injection from PEDOT to ZnO. Unfortunately due to the formation of impurity deposits on top of the ZnO nanorods during the device fabrication, the level of reproducibility of these diodes is still quite low, hampering a reliable comparison with the theoretical calculations.

d) Hybrid ZnO-polymer light emitting diodes

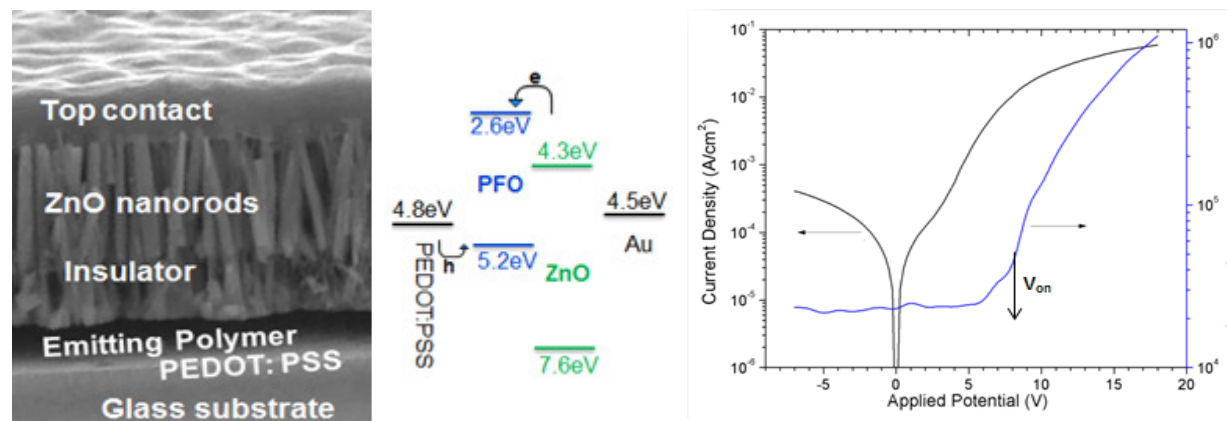


Figure 6: Left: SEM image of the cross section of the ZnO-polyfluorene LED (PFO). Middle: energy band diagram of the LED obtained from UPS measurements. Right: current and electroluminescence-voltage characteristics [Wadeasa 2010].

In these devices, ZnO nanowires are grown directly onto a thin film of the polymer semiconductor poly(9,9'-dioctylfluorene) (PFO), thus forming a hybrid semiconductor heterojunction that is produced through a low-cost solution-based process. The scanning electron microscope image in Figure 6 shows a cross section of the device clearly evidencing the alignment of the ZnO nanowires normal to the emitting polymer surface. The hybrid semiconductor junction exhibits white (blueish) light emission with CIE color coordinates: C_x= 0.238 and C_y= 0.309 [Wadeasa 2010].

In order to understand the electroluminescence mechanism, UPS measurements were performed on several relevant interfaces in order to extract the energy band diagram across

the diode (figure 6). Despite the relatively large barriers for hole and electron injection (up to 2.4 eV for a hole injected from PFO to ZnO) the device still operates at low voltages (7 V) because the accumulation of holes in PFO at the PFO/ZnO interface and electrons in the ZnO close to the PFO, lowers the barriers. Surprisingly, the analysis of the photoluminescence of isolated ZnO and PFO layers and of their interface revealed that in these LEDs most of the light comes from the emitting polymer. The proposed diode architecture is attractive for large area lightening because of it is fabricated from a solution process and allows using an air stable, high work function, electrode to inject the electrons.

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Workpackage 4

The cross-fertilization work-package aimed at gathering the knowledge and understanding of the different interfacial effects studied along the whole 36 months of the project, in order to propose a global modeling scheme and a general picture of the different effects taking place at each interface, and the influence of these effects on the global efficiency of the aimed devices.

In particular, the aim of the work-package was double: first, it should collect the different conclusions that have been drawn on the modeling of the individual types of interfaces (metal-organic, organic-organic, and inorganic-organic), and give a more general picture of the impact of the different choices that have to be done when establishing a modeling protocol: Will we use realistic interface structures or ideal ones? Which method will we use? Are these methods comparing well to experiment? Which kind of material do we want to study?

Even though in the study of the different individual interfaces, specific methods have been used that in first sight cannot be compared directly or used unilaterally to describe all kinds of interface, it was possible to establish the relationship between the reliability of the method used for a particular type of materials, and the intrinsic way the materials composing the interface are interacting, through the description of the strength of this interaction. We have therefore distinguished two main categories of interfaces, ones for which material interact in a weak regime, and ones for which there is a strong interaction, and consequently, two main protocols pathways to go from a molecular to a large scale study of interfaces.

The protocol that has been defined can therefore be followed by a newcomer in the field of interface modeling for electro-optic applications, and will help to define or refine the modeling tools in this very active field of research.

4.1.4 Potential Impact, exploitation of results and main dissemination activities

Summary of MINOTOR potential impact and exploitation of results

The field of organic electronics is about to revolutionize the way we produce light and electricity, to cite just two examples. Compared to the traditional Silicon Electronics, Organic Electronics enables production, at lower cost and requiring lower energy, of light, thin, flexible devices: transistors, solar cells, new lighting solutions and extremely sensitive sensors. If a large body of knowledge has been accumulated over the last decade on the bulk properties of conjugated organic materials, the lack of a fundamental understanding of the electronic processes going at interfaces, ubiquitous in organic electronics, has so far prevented a full optimization of the material combinations and device architectures.

The MINOTOR project contributed to the Organic Electronics field by developing a new theoretical paradigm for the modeling of organic heterojunctions, as well as metal-organic and organic-inorganic interfaces. MINOTOR results impact on socio-economy, environment, European and multisectorial collaborations and human potential, as the fundamental theoretical investigations performed on these interfaces, backed-up by experimental studies, aim at identifying engineering strategies for new applications related to energy production, energy saving, health, environmental monitoring, security, safety and welfare of citizen. These studies are thus expected to open new markets fostering industrialization, economic growth and generation of jobs in Europe. Though the fundamental nature of the project is unlikely to result in short-term economical impact, it should be stressed that the scientific work performed within MINOTOR should guide future device and materials development activity, thus reducing development costs and shortening the time-to-market of new innovations.

In terms of collaboration: 8 universities, 1 research center and 1 industrial partner have been involved in MINOTOR. This consortium of about 45 researchers has helped to form a cohesive European research area in the field of interface modeling and paved the way for the participation of several partners in follow up projects in the same area and several bilateral collaborations and business relations between partners from the consortium as well as recruitment of excellent young researchers to sustain research on a high scientific level also in industry.

The expanding activity in Organic electronics in Europe and worldwide, both academic and industrial, has heightened the need for trained personnel in this area. This project contributed to the training of significant numbers of PhD students and the development of the careers of postdoctoral researchers in this important interdisciplinary area through partners collaborative work, project meetings, exchange of students as well as specific dedicated actions organized within the MINOTOR project such as the workshop "Electronic processes at interfaces to organic semi-conductors: From modeling to devices" which took place from the 29th to the 31st of May, 2012, at the University of Mons bringing together 85 participants.

The impacts of MINOTOR touched more specifically three main applications: organic OLEDs, transistors, and photovoltaic cells that are considerably funded by ICT projects in FP6 and FP7. The sustainability of the European competitiveness in this field requires in parallel to device applications a continuous increase in the understanding of fundamentals and in the design of knowledge-based materials. This is what MINOTOR aimed at.

- OLEDs for displays are a mature technology, with a market that is expected to grow to 15Bn \$/year by 2015. That expansion will increase the need for materials with improved performances (with a market around 5Bn \$/year in 2015). The need for designed functional materials simplifying the fabrication processes by reducing the number of organic layers is even clearer for future applications of OLEDs in lighting.

- Organic-based transistors for organic logic and memory devices are an emerging technology, in which European companies (Plastic Logic, Polymer Vision, PolyIC) are the leaders. The use of those transistors as back-planes for active matrix displays, circuits for RFID, volatile memory devices, or detection elements for sensors is expected to generate a 8Bn \$ market by 2015. Such growth also relies on optimized materials and improved device design aimed primarily at optimizing the charge injection processes.

- As for photovoltaic applications, devices based on organic materials will constitute a major progress with respect to the main existing technology (i.e., silicon-based systems), both economically (~ 1\$/Wp vs. ~3.5\$/Wp) and environmentally (the amount of CO₂ released to fabricate 1 m² of photovoltaic cells is about 100 times lower when using organic materials). The application of organic photovoltaic systems towards broad markets is still limited by modest efficiency and moderate lifetime. A central issue is to maximize the yield of free carrier generation in the organic blends, thus requiring a deep knowledge of the interfacial properties and hence guidelines to choose the best matching partners.

As described in length in the scientific reports and summarized above, MINOTOR largely succeeded in bringing to completion the main objectives associated to these three different applications, namely by: (i) developing a general modelling scheme for the energy level alignment at metal-organic interfaces, thereby allowing to design strategies for the tuning of electron injection to metallic electrodes; (ii) providing a molecular picture of the charge separation process at organic heterojunctions that takes into account the detailed rearrangement of the electronic density at these interfaces; and (iii) assessing the electronic processes at organic-inorganic interfaces and how one can take advantage of these to fabricate stable low workfunction metal-oxide electrodes, e.g. through the formation of self-assembled monolayers. It is worth pointing out that these results obtained from modelling studies have been largely confirmed by experimental investigations performed within MINOTOR and exploited in the fabrication of a new generation of OLEDs, FETs and OPVs, namely by the industrial partner BASF but also the research center IMEC and the academic partner LIN.

Other European companies active in the production of materials (be they polymers or inorganics) for organic electronics (Degussa, Solvay, Bayer, Ciba, Merck, HC Starck, AGFA,...) or in device fabrication (Plastic Logic, PolymerVision, Cambridge Display Technology, Philips, Siemens, OSRAM, Novald, Konarka,..) will also likely benefit from the output of MINOTOR, since the modelling protocols for interface design and the main findings of the project are applicable to all possible type of interfaces encountered in organic-based electronic devices. In the value chain for organic electronics, MINOTOR is therefore likely to impact on both upstream (the selection and synthesis of new semiconductors and electrode materials) and downstream (the optimization of device design and the improvement of their performances) R&D activities.

Summary of MINOTOR main dissemination activities

The scientific work has been widely disseminated through publications in international journals, posters and conference talks. In particular 47 articles have been published and some others are in the pipeline. The list of all articles abstracts and references is available on the public web site. In addition Minotor PIs, PHDs and Postdocs have contributed to dissemination of minotor activities via invited or contributed talks and posters (more than 120), see Final Periodic Report Month36.

Other dissemination activities include:

1) Success story Project: 228424 MINOTOR (2009 June 01 till 2012 May 31)

Modelling of electronic processes at interfaces in organic-based electronic devices (FP7)

The Minotor project was targeted as a ‘Success Story’ by the European Commission. The following summary was provided by the coordinators.

➤ *What did the project achieve?*

MINOTOR aimed at developing a multi-scale modelling approach ranging from the atomistic to the mesoscopic scale to model the processes taking place at the interfaces in electronic devices based on organic semiconductors, namely solar cells, field-effect transistors, and light-emitting diodes. These devices rely on the use of multi-layered structures and the main challenge is to understand how key parameters at the interfaces between each layer combine with the bulk of the individual materials to define the device performances. MINOTOR integrates the know-how from leading research groups in Europe and the USA in the field of plastic electronics for a better understanding of this challenging thematic. We have developed in MINOTOR new modelling approaches to investigate electronic and structural properties at organic-organic, organic-metal, and organic-inorganic interfaces, in close conjunction with corresponding experimental measurements.

In practice, MINOTOR has unravelled the various interfacial effects that can affect the intrinsic performance of a device; the electronic structure at the interface differs significantly from the bulk material, and the modelling work has highlighted the different contributions to this discontinuity. We have for instance disentangled the origin of the electronic level alignments at organic/organic interfaces that impact the short-circuit current and the open circuit voltage of solar cell devices, two key quantities that directly impact the efficiency of those cells. We have also shown that by modifying the surface of electrodes, we can tune the charge or spin injection barriers in devices such as OLEDs. Finally, the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties was also quantified.

➤ *How?*

MINOTOR brought together expertise from European academic laboratories and one industry which are leaders in their research field. Multi-scale chemistry and physics research approaches, based on both modelling and experimental techniques to identify each key point in the research challenges, were used to understand the modification of the electronic properties of materials at an interface and the impact of the different types of interfaces (interface between an electrode and a semiconductor, between two semiconductors,...) on the final characteristics of the device.

➤ *Why does this matter?*

The challenge of producing cheap and efficient electronic devices based on organic (plastic) materials is a very attractive alternative to get reliable, economic, and sustainable sources of energy. Plastic solar cells are promising systems to replace conventional silicon based solar cells, in particular due to their low production cost, their sustainability and the recycling possibilities; however, their efficiency is still too low (below 10%) for being a really affordable replacement solution to conventional devices. Due to the multi-layered structure of such devices composed of thin films or nano-particles, the control of the surface properties becomes crucial to optimize the device efficiency. In addition, interfaces are at the junction of two worlds: the world of materials of the physicists and the world of molecules of the chemists. This merging implies the definition of a new paradigm and hence the development of new computational methods to take into accounts the specificities of the two fields.

➤ *Who is involved?*

MINOTOR involved 9 partners from 7 European countries and 1 in the United States, for a total of 40 persons, including principal investigators, dedicated researchers (funded by MINOTOR) and one part-time administrative assistant. The partners are leading groups in their field of research and belong to reputed universities and research centres, and the industrial partner of the project is a major industrial player in the field of plastic electronics.

The partners involved were:

University of Mons (Belgium) (coordinators), IMEC research centre (Belgium), BASF (Germany), University of Twente (Netherlands), University of Linköping (Sweden), Karlsruhe Institute of Technology (Germany), University of Bordeaux (France), University of Madrid (Spain), University of Bologna (Italy), and Georgia Institute of Technology (United States) as associate partner.

➤ *What is the European Added Value? (Criterion added by the Cabinet)*

The MINOTOR project, through the support of the European Union, gathered expertise from different groups in different countries as well as a very large European Industrial actor in the field of plastic electronics.

Globally, this project took place in the context of a world-level challenge, which is the quest for sustainable and recyclable sources of energy at a reasonable cost. This is one of the objectives of plastic-based electronics. To this extent, the MINOTOR project is in the core of the most challenging research endeavours for the European countries. This project contributed to spur world-class research in Europe through the investigation of a central aspect (i.e., interfaces) in the development of efficient organic electronic devices. It brought together high-level researchers who contributed to the development of the research field with 42 international scientific publications. In addition, within the framework of the project, an international workshop will be organized in May 2012 to bring together world-leading scientists in the field of interfaces for the further development of interdisciplinary and international collaborations.

➤ *How much money has the EU invested in this?*

The EU invested 3 million Euros in this project, which has run over three years, from June 1st 2009 to May 31st 2012.

➤ *For more information*

<http://www.materianova.be/minotor/>

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2) Jérôme Cornil (the coordinator) has been invited for an **oral talk to Industrial Technologies 2012** (in the context of the Industrial Application Aarhus integrating Nano, materials and productions, June 19-21, Aarhus, Denmark). All information for this conference are detailed via the following Link: <http://industrialtechnologies2012.eu>

3) The basic concepts of organic electronic and the interactions between light and matter have been presented to secondary school students to stimulate their curiosity and, hopefully, encourage them to choose scientific studies.

4) An article explaining the project MINOTOR “**Electronic goes organic**” has been published by Insight Publishers Ltd., ISSN 2040-7335, edited by William Davis (Projects Issue 28, published May 2012). Summary: ‘Organic electronics is a rapidly developing new field that involves using organic/carbon-based) materials to build electronic circuitry complementary to microelectronics based on mineral semiconductors such as silicon. David Beljonne, Jérôme Cornil and Roberto Lazzaroni explain how a new project called Minotor is helping to advance our understanding of the topic.’

5) The project has been promoted by an **international Workshop on “Electronic Processes at Interfaces to Organic Semiconductors: from modelling to Devices”** that has been organized at the University of Mons (Belgium), May 29-31, 2012. For this occasion, the conference, and hence the project, was advertised to several academic laboratories and research centres at international level. A short video to promote the conference and the project was also performed and will be available soon.

The program was organized as follows:

- There were 10 oral presentations of the work realised during the three years of Minotor presented by the PI of each group (talk of 30 minutes).
- We have also invited 7 speakers outside Minotor (talk of 30 minutes).
The invited speakers were:

Richard Friend (England)

Norbert Koch (Germany)

Egbert Zojer (Austria)

Troy Van Voorhis (USA)

Maria Chiara Pastore (Italy)

Paolo Samori (France)

Jean Manca (Belgium)

- There were 8 external contributed talks (talk of 20 minutes).
- A poster session has been organised with a total of 31 posters.

- The information for logistics and registration to the workshop has been provided on the Minotor Web Site.
- A booklet with the agenda, the abstract of all talks and the list of participants has been distributed to all participants.
- The total number of participants was 85.

The List of Foregrounds is detailed below:

Type of Exploitable Foreground	Description of Exploitable Foreground	Exploitable Products or Measures	Sectors of Application	Explain of the Exploitable Foreground
BASF Basic understanding/Principles	Nature of CT-states at OPV-cell interfaces	Efficient OPV cells	OPV	rational design of specific interface morphologies
BOL Computational method and code	Simulation protocol for organic crystal growth from vapor phase	Optimization of materials and devices preparation processes	Computational Chemistry, Organic electronics and photovoltaics	Innovative computational protocol for realistic simulations of organic vapor growth based on atomistic molecular dynamics
BOL Computational method and code	Software for MicroElectrostatic Calculation in organic solids (MESCal)	Multi-scale modelling of organic semiconductors and devices	Computational Chemistry, Organic electronics and photovoltaics	Development and implementation of a novel microelectrostatic model based on point charge description of molecular charge distribution for accurate determination of charge transport levels in organic semiconductors and interfaces
LIN, UAM, UT Basic understanding/Principles	Quantitative prediction of energy level alignment at organic-organic and hybrid organic interfaces	Efficient devices	Organic electronics	Rational design of charge injecting and exciton dissociating interfaces
LIN Basic understanding/Principles	Fine-tuning of energy level alignment using SAMs	Efficient charge-injecting devices	Organic electronics	Tailoring injection levels at interface by modifying electrostatic interactions and intermolecular order of organic semiconductors at electrode interface through SAMs
IMEC Basic understanding/Principles	Mechanism of molecular doping in organic semiconductors and its efficiency (imec)	Organic electronic devices utilizing doped layers	Organic electronics	Rational design and selection of efficient host-doping combinations
Umons Methodology to model electronic properties at interfaces	Identification of the most suitable methods for M/O, O/O, and I/O interfaces and their limitations.	Fundamental understanding of other type of interfaces using the developed methodology	Computational Chemistry	Computational toolkit to model electronic structure at interfaces for organic electronics
KIT SIMONA Software Package	Monte Carlo Based Software Package for Simulation of Organic Systems	Efficient OLED/OPV simulation workflows	OPV/OLED	Testing of material and interface parameters
LIN Device Fabrication	Electron injection from high workfunction electrodes	Air stable OLEDs	OLED	ZnO nanorods grown on high workfunction electrodes (Au, ITO, PEDOT) allows easy electron injection in organic semiconductors

LIN Device Fabrication	Surface modification of ZnO nanorods with SAMS	Schottky diodes	RF to DC conversion	The rectification of a Schottky diode Electrode/ZnO nanorods/SAMS/Electrode can be controlled by the SAMS to achieve better conversion of RF signal to DC current through an antenna.
LIN Basic understanding/ Principles	Quantitative prediction of energy level alignment at organic-organic donor-acceptor and hybrid organic interfaces	Devices	Organic electronics	Rational design of charge injecting and exciton dissociating interfaces
UAM Basic understanding/ Principles	Understanding energy level alignment at metal/organic interfaces	Devices	Computational chemistry	Design of organic devices with optimal carrier injection barriers
UT Basic understanding/ Principles	Quantitative description of spin polarization at metal/organic interfaces	Devices	Spintronics	Rational design of optimal spin injection interfaces

4.1.5 Address of the public Website and relevant contact details

<http://www.materianova.be/minotor/>

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