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#### Fermi level pinning at donor-acceptor molecular hetero-junctions

#### in multi-layered thin film stack of TTF and TCNQ

S. Braun, X. Liu, W. R. Salaneck and M. Fahlman

#### Abstract

Organic hetero-junctions in a multi-layered thin film stacks comprising alternate layers of the molecular donor - tetrathiafulvalene (TTF) and the acceptor - tetracyanoquinodimethane (TCNQ), have been studied by Ultraviolet Photoelectron Spectroscopy (UPS). We show that the energy level alignment at the organic-organic interfaces in the stacks depends only upon the relative energy structure of the donor and acceptor molecules, in particular, the molecular integer charge transfer (ICT) states. The observed interfacial dipoles, across the multi-layered organic stacks, correspond to the difference in energy between the positive and the negative charge transfer states of the molecules constituting the interface. Consequently, Fermi level across the multi-layer system is pinned to those states, since the energetic conditions for the charge transfer across the interface are fulfilled. Hence the energy level alignment at donor-acceptor interfaces studied can be rationalized on the basis of integer charge transfer model (ICT-model). Moreover, we present the photoelectron spectra where 0.85eV shift of the highest occupied molecular orbital (HOMO) of TTF during formation of TCNQ over-layer is directly observed. These studies contribute to the understanding of the nature of the offset between the frontier electronic levels of the donor and acceptor components which is of high importance in the engineering of efficient organic solar cells.

## Introduction

The understanding of electronic structure of organic materials and energy level alignment at all-organic and hybrid interfaces is the subject of many recent extensive research efforts. In particular, photoelectron spectroscopy has been a very fruitful tool for elucidation of the electronic properties of thin organic films [1]. A detailed knowledge of the electronic structure of condensed molecular solid films and even conjugated polymers has contributed significantly to emerging industrial applications in the area of organic electronics.

Organic electronic devices are usually composed of several thin film layers that facilitate various functionalities, *e.g.*, charge injection and transport, recombination/extraction of charges, as discussed elsewhere [2-4]. Within such multilayer thin film architectures are contained interfaces, the properties of which influence and control device operational characteristics. Consequently, a detailed understanding of the interfaces involved in organic electronic devices is critical for improvement of device performance. Particularly important for device operation is electronic level alignment. The significance of this topic is related to the fact that interfacial energetics determines the conditions for the injection of charges from electrodes and charge transport across the device. According to a simple model, energy level alignment at given interface can be estimated by simply lining up the separately observed electronic structures of organic layers. However, as found by Seki and co-workers, this assumption is not valid in many cases [5]. It has been shown that various phenomena, *e.g.* formation of chemical bonds, charge transfer, "push-back effect" or adsorption of molecules, result in the formation of interfacial dipoles, which result in a vacuum level offset [6]. Such vacuum level discontinuity imposes a

relative shift between the energy levels of materials constituting interface. Hence the magnitude of the interfacial dipole is an essential parameter to fully characterize interface energetics. The interfacial dipole can be used as a tool to enhance charge injection properties of an electrode. The magnitude of the dipole can be engineered through various surface modifications [7-9]. However, a complete and systematic understanding of energy level alignment has not yet been achieved. Interfacial interactions have been addressed by a large number of theoretical and experimental studies [10-14]. The concept of induced density of interface states (IDIS), based on the interaction between metals and organics has been developed to predict trends in the magnitude of interfacial dipole [15]. For a class of weakly interacting interfaces, the integer charge transfer (ICT) model was recently proposed [16,17]. This semi empirical model originates from the photoelectron spectroscopy, which reveals characteristic trends in energy level alignment of various organic semiconductors [18-20]. The model predicts that for a large-enough range of work functions, a "Z" shaped ("Mark of Zorro") type of dependence between substrate work function and the work function of the organic layer adjacent to the substrate should be obtained. Hence, for a range of substrates with different work functions, and a given organic material, a transition between vacuum level alignment and Fermi level pinning should occurs if the substrate work function enables charge transfer between the substrate and the organic overlayer. The interface will then be in equilibrium when the Fermi level of the metallic substrate is pinned at interfacial states in the organic layer, near the HOMO or LUMO levels of the molecular material. The pinning levels are determined by properties of the organic layer, defined by the nature of the charge transfer states. According to the experimental data, when the Fermi level of the metallic substrate falls within the gap (vacuum level alignment regime) any barriers for charge injection (or lack thereof) are dependent of the work function of the electrode and follow Schottky-Mott limit behavior, *i.e.*, they scale linearly with the work function of the electrode. Within the pinning regimes, when the electrode work function enables interfacial charge transfer, the barriers, if any, has a constant value determined by energy of integer charge transfer states [16-22]. In the context of device engineering, the model predicts that the charge injection barriers can be modified by changing the work function of an electrode only within certain limits [20,23-26]. Considerable interest has been also directed toward more complex systems, containing more than one organic over-layer [27-31]. Such multi-layered structures can help understanding the electronic processes in organic electronic devices.

Recently we have shown that the energetics across a multi-layered structure depends on the interplay between electrode work function and the charge transfer states in organic overlayers [32]. Consequently, the magnitude of the dipole may be dependent on the sequence in which adjacent layers are present in the stack of thin film layers. Those points out the complexity of the interfacial energetics that must be addressed in the consideration of real organic- based devices.

In this report, we focus on the energy level alignment at interfaces in a multi-layer donoracceptor organic stack. Organic donors and acceptors are commonly used in various applications where their unique properties associated with high electron affinity alternatively low ionization potential are exploited. They are often utilized to form charge-transfer complexes that are used to enhance electronic properties or they serve as the active entity to facilitate charge separation in photovoltaic cells [33,34]. In the present case, the molecular donor-acceptor pair of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) (see Fig.2), has been studied [35,36]. The stacks of up to four layers have been prepared in different deposition sequences. In addition, particular attention has been paid to whether TTF or TCNQ is adjacent to the substrate, as shown in Fig. 3. The results obtained on such stacks revealed that the influence of the substrate on the organic-organic interfaces is confined to the first two organic layers, and that subsequent layers exhibit exactly the same interfacial off-sets, independent of the substrate. Moreover by a careful choice of the substrate work function the position of HOMO level of the molecular donor (TTF) at the interface with the acceptor (TCNQ) could be directly observed by photoelectron spectroscopy.

#### **Experimental**

The multilayer stacks comprising thin films of TTF and TCNQ were prepared in situ under ultra high vacuum (UHV) conditions by physical vapor deposition (PVD). The molecules: TTF and TCNQ were purchased from Sigma-Aldrich. The deposition rate was set to approximately: 5Å/min, as calibrated from the attenuation of the Au(4f) core level line of a gold substrate, measured by X-ray photoelectron spectroscopy (XPS). The aluminium substrate with a native oxide has been used. During the film growth and measurement, the substrates were cooled to - 100°C.

Ultraviolet photoelectron spectroscopy (UPS) was used to examine the correlation between the substrate work function and the energy level alignment at the organic-organic interfaces formed upon deposition of the donor and acceptor molecules. This technique is especially suited for such studies, since it enables direct probing of the occupied valence electronic levels as well as the vacuum levels, and therefore also of vacuum level shifts, upon forming the interface. The value of the vertical ionization potential (IP) is measured as the onset of the HOMO edge versus the vacuum level. UPS measurements were performed using monochromatized HeI radiation (hv = 21.2 eV) in a spectrometer of our own design and construction [37]. The measurement sequence involved characterization of the bare substrates followed by stepwise deposition and characterization of molecular add-layers.

#### **Results and Discussions**

Thin films of the molecular donor- TTF and the acceptor- TCNQ, have been subsequently deposited onto AlOx substrate. As shown in Figure 2, the deposition sequence has been varied so either TTF or TCNQ has been put in direct contact with AlOx. In both cases there are four molecular layers deposited on the substrate in order to study the energy level alignment across the multi-layered organic stack.

As shown in Figure 3, upon deposition of TCNQ onto AlOx, the dipole of 1.2eV is present at the interface. Consequently, this dipole shifts the vacuum level from 3.6eV, as observed for AlOx, to the value of 4.8eV. This shift sets the substrate Fermi level in the vicinity of LUMO of TCNQ that is located at 4.5eV [R. Murdey private commun.]. The obtained result is in line with the previously reported energy level alignment of TCNQ on the various substrates [38]. In those cases, the interfacial dipole scales with substrate work function in such a manner that the substrate Fermi level stayed pinned at about 4.8eV. In the case reported here, the low work function of the AlOx (3.6eV) also enables charge transfer between the substrate and the TCNQ molecules. In this process, it is expected that charges are transferred to the LUMO-derived states and the substrate Fermi level is pinned in the vicinity to LUMO.[39]

The Fermi level, which is pinned at 4.8eV upon deposition of TCNQ, is the reference level for TTF over-layer. As TTF is deposited onto TCNQ to form TTF/TCNQ/AlOx stack, the interfacial dipole appears but in the reverse direction with respect to the TCNQ/AlOx interface. This can be rationalized on the basis of integer charge transfer model. Since the charge transfer state of TTF is at 4.2eV it is then 0.6eV lower than the position of Fermi level (4.8eV). In order to reach equilibrium, the Fermi level aligns with the TTF pinning level and the interfacial dipole is formed. The magnitude of the dipole corresponds directly to the difference between the Fermi level and the positive pinning level of TTF. As revealed by UPS and shown in Fig.3, the same mechanism is observed when the next molecular layers are deposited. The Fermi level stays aligned to the positive integer charge transfer state (ICT+) of TTF and the negative charge transfer state (ICT-) of TCNQ. Consequently the vacuum level shift is equal to the energy difference of those charge transfer states. There are alternating positive and negative dipoles of the same magnitude equal 0.6eV at each consecutive interface.

The stack of TTF and TCNQ layers has been also studied in the configuration where TTF layer has been deposited first onto AlOx. As shown in Fig. 3 the deposition of the first layer does not change vacuum level and there is no dipole at the interface. This situation is apparently different from the cases studied by Murdey et al. when TTF was deposited on the substrates with work function ranging from 4.3 to 5.1eV. As depicted in Figure 4, within this range of work functions, the magnitude of the dipole scales with the substrate work function in such a way that the substrate Fermi level is pinned at the constant distance from HOMO level of TTF. The lack of interfacial dipole in the case of TTF/AlOx indicates that there is no charge transfer between TTF and AlOx. This can be rationalized on the basis of the ICT model. Since the work function of AlOx substrate (3.6eV) is lower than the positive pinning level of TTF (4.2eV), there is no favorable condition for charge transfer between organic layer and the substrate. Consequently, the lack of interaction does not alter the electronic conditions at the interface and leads to the observed vacuum level alignment. In the next step, a thin layer of TCNQ has been deposited onto TTF/AlOx. As shown in Figure 3, this leads to a large work function shift of 1.2eV (the vacuum level is lifted upward to the value of 4.8eV). The observed energy level alignment at this organicorganic interface is attributed to the favorable energetic conditions for charge transfer between those two organic materials. Even though TTF does not alter the vacuum level position set by AlOx, the Fermi level, which is set at 3.6eV versus vacuum level, enables charge transfer between TTF and TCNQ. Consequently, upon deposition of TCNQ, the vacuum level observed for TTF is shifted to the value of the pinning level of TCNQ (4.8eV). Note that the work function shift (1.2eV) is larger than the interface dipole of 0.6eV obtained at the TTF/TCNQ and TCNQ/TTF interfaces (0.6eV being the difference between the ICT+ (TTF) and ICT- (TCNQ) energies). Hence additional charge must be transferred across the interface to bring the system into equilibrium. This may be facilitated by transferring charge from the AlOx substrate through the TTF layer to the TCNQ at the TCNQ/TTF interface, which would lead to a linear potential gradient over the TTF layer, as schematically pictured in Fig. 3. More charges could be transferred from the TTF layer extending further away from the interface, creating a "bandbending-like" potential gradient over that region. Alternatively, some contribution to the observed work function shift may originate from the polarization effect, as suggested in the recent work of Avilov et al [40].

On such TCNQ/TTF/AlOx structure the third and fourth organic layer was deposited to finally form the stack in the following configuration: TCNQ/TTF/TCNQ/TTF/AlOx. As revealed by the photoelectron spectra the two top most interfaces follow the path of alternating vacuum level shifts that correspond to the 0.6eV difference between the pinning levels of TTF and TCNQ. Hence the energy level alignment of those top interfaces is invariant versus the deposition sequence. This, in turn, leads to the conclusion that the influence of the substrate work function on the energy level alignment at organic ad-layers is confined to the first two layers in a multi-layered stack *e.g.* where the first layer is adjacent to the substrate.

The direct observation of HOMO level of a molecular layer, while building the interface with another organic material, is often obscured by the similarity in the binding energies of those levels. The overlapping contributions in photoelectron signal introduce apparent ambiguity in interpretation of the spectra. This problem is circumvented in the present studies: when TCNQ layer is deposited on TTF/AIOx the onset of HOMO level of TCNQ is present at 2.75 eV. In the case of the TTF layer, when deposited on AIOx, the HOMO onset is at 1.2eV. Hence, the large difference in the binding energy of HOMO peaks gives a unique opportunity for a direct observation of the position of HOMO level of the molecular donor – TTF versus Fermi level, upon building the interface with TCNQ.

As shown in Fig. 5, the HOMO level of TTF deposited on AlOx moves towards Fermi level as the coverage of TCNQ increases. At the same time, the gradual shift of vacuum level at this interface, from 3.6eV to 4.2eV, has been observed. The total shift of HOMO level of TTF, measured between the neat TTF film and the TTF film with 8 nm thick over-layer of TCNQ is 0.85eV. With the increasing thickness of TCNQ the HOMO peak of TTF becomes less intense, as shown in Fig.5. This is the effect of the gradually prevailing contribution to the photoelectron signal from TCNQ. The leading edge of the highest molecular orbital of TTF is finally observed at 0.35eV from Fermi level. As shown in Fig. 6, this value is already reached for the less than 8nm thick TCNQ. This new position of HOMO edge (0.35eV) is similar to the position observed when the TCNQ layer obeys the Fermi level pinning regime. Note that the HOMO leading edge of TTF does not reach the Fermi level which could be an expected result in the scenario of charge transfer. However, for a very small molecule strong localization of transferred charges could lead to Coulomb gap that would prevent appearance of the density of states at the Fermi level.

Recently, Duhm *et al.* reported that for the ordered film of  $\alpha,\omega$ -dihexyl-sexithiophene (DH6T), energy level alignment can be dependent on the orientation of the molecules due to the collective electrostatic effect of the highly anisotropic intramolecular charge distribution [41]. This dependence is manifested by the changes in ionization potential of the molecular film that for DH6T riches value of 0.6eV. In the case of TTF/TCNQ interface, we do observe a difference

between vacuum level shift (0.6eV) and TTF HOMO shift of (0.85eV) which points out that the ionization potential of TTF molecules in vicinity of TCNQ overlayer is changed by 0.25eV. This, in turn, would suggest reorientation of some TTF molecules as the effect of changes in electrostatic field caused by charge transfer at the interface. To clarify this issue, however, the further research including assessment of the molecular orientation of the TTF and TCNQ films is needed.

In theory, the evolution of the TTF HOMO edge upon TCNQ deposition could be used to differentiate between the linear potential drop or "band-bending-like" potential gradient over the TTF layer (discussed in connection with Fig. 3) as the UPS signal is attenuated by the TCNQ overlayer and we are hence probing more and more shallow into the TTF layer as the TCNQ thickness increases. However, as we do not believe that the TCNQ overlayer grows uniformly, we refrain from attempting such an analysis, leaving the question open until more reliable techniques such as energy dependent depth probing at a synchrotron radiation light facility has been performed.

#### Summary

The interfaces between thin films of donor- TTF and acceptor-TCNQ have been studied by means of ultraviolet photoelectron spectroscopy. We demonstrated that the energy level alignment across the multilayer stack of thin films of molecular donor and acceptor is interdependent on the molecular integer charge transfer states and the sequence in which the layers are deposited on the substrate. These results are reminiscent to the previously studied interfaces of CBP and m-MTDATA deposited on the high work function polymer: PEDOT-PFESA [32]. Since the studied structures include four organic layers, we have verified that across the stack of those layers, the observed interfacial dipoles (0.6eV) are such that the Fermi level stays pinned to either positive or negative charge transfer state of TTF and TCNQ, respectively. There is however an exception to this scenario. When TTF layer is adjacent to the aluminum substrate, the work function increase upon TCNQ deposition has the magnitude of 1.2eV. This result is rationalized on the basis of integer charge transfer model with an additional potential gradient over the TTF layer, supported by the experimental results on the TTF HOMO evolution.

These studies contribute to the understanding of the nature of the offset between the frontier electronic levels of the donor and acceptor components which is of high importance in the engineering of efficient organic solar cells.

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# **Figure captions**

# FIG.1

The molecular structures of the organic molecules studied: (a)Tetrathiafulvalene (TTF), (b) Tetracyanoquinodimethane (TCNQ).

# FIG.2

Schematic drawing illustrating the molecular stacks studied.

# FIG.3

UPS spectra and the corresponding diagrams of energy level alignment of interfaces at multilayer stacks of TTF and TCNQ.

## FIG.4

Schematic drawing presenting energy level alignment regimes for TTF and TCNQ as a function of substrate work function.

FIG.5

UPS spectra of HOMO of TTF for different thickness of TCNQ overlayer.

FIG.6

Binding energy shift of HOMO edge versus thickness of TCNQ overlayer.









Figure 3



Figure 4



Figure 5





