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PHOTO-ELECTRON SPECTROSCOPY STUDY OF ENERGY LEVELS IN CONJUGATED OLIGOMERS

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ABSTRACT

We report on the valence orbital structure of poly(*para*-phenylenevinylene) (PPV)-like oligomers. We studied these molecules as isolated oligomers in the gas phase, as well as in thin films deposited on metal substrates. We use a simple model based on a previously reported Hamiltonian that accurately describes the development of the low lying electronic excitations as a function of the number of repeating units. In the study on the thin organic films we report on the energy level alignment at metal / organic and organic / organic interfaces, where the organic layer is either a PPV-like oligomer or C_{60}. The results are important for understanding organic photovoltaic devices.

INTRODUCTION

Organic semi-conducting materials have attracted a lot of attention in the scientific community, because of their interesting physics and potential applications in light emitting devices (LEDs), field effect transistors (FETs) and photovoltaic devices (PVDs). We have focussed our attention to these devices, especially the PVDs. Bulk heterojunction PVDs contain most often a conjugated polymer as donor (D) and a C_{60}-derivative as acceptor (A). After optical excitation, the charge separation occurs at the D-A interface [1]. After this exciton dissociation step the separate charges need to be transported towards the electrodes by propagation of the electron through the fullerene network to the cathode and the hole through the intercalated conjugated polymer to the anode. At the electrode / organic interfaces the charges should efficiently transfer from the organic system to the inorganic metallic electrodes.

Here we report on a combined experimental and theoretical approach to get a better understanding of the device properties of D-A based organic PVDs. A brief description is given of a theoretical model with which we obtain good estimates of the different low energy electronic excitations in conjugated oligomeric and polymeric systems. In this paper we mainly focus on the energy level alignment at the different interfaces found in bulk heterojunction organic PVDs.

EXPERIMENT

The method with which we measured the gas phase photoelectron spectra was described in previous work [2]. All spectra were obtained with He-I radiation of 21.22 eV and the binding energies were calibrated using the Xe $^2P_{3/2}$ line (gas phase measurements, typical resolution 120meV) or by the low kinetic energy onset of the

spectrum (solid state measurements) which is directly related to the vacuum level. The latter measurements were performed in another UHV system consisting of a preparation chamber (base pressure $<2\times10^{-9}$ mbar), and a measurement chamber (base pressure $<2\times10^{-10}$ mbar). Thin polycrystalline metal films were prepared by thermal deposition of the metal onto the natural oxide layer of Si-wafers, except for the reported Ag / C_{60} interface where we used a thin Ag foil. Other details may be found elsewhere [3].

RESULTS

Low energy electronic excitations in oligo-phenylenevinylenes

In order to gain more insight in the nature of the electronic structure of conjugated polymers we studied the valence orbital structure of isolated poly(para-phenylene-vinylene) like oligomers with gas phase photoelectron spectroscopy. Besides the experimental approach to learn about these systems we also used a theoretical model based on a simple tight-binding, two band Hubbard Hamiltonian. This model contains the following parameters: a transfer integral (t), an on-site Coulomb interaction (U), a next neighbour Coulomb interaction (V) and an exchange interaction (K). This model gave accurate predictions for low energy electronic excitations of thiophene based oligomeric and polymeric materials, as reported elsewhere [2]. Here we apply the same model to
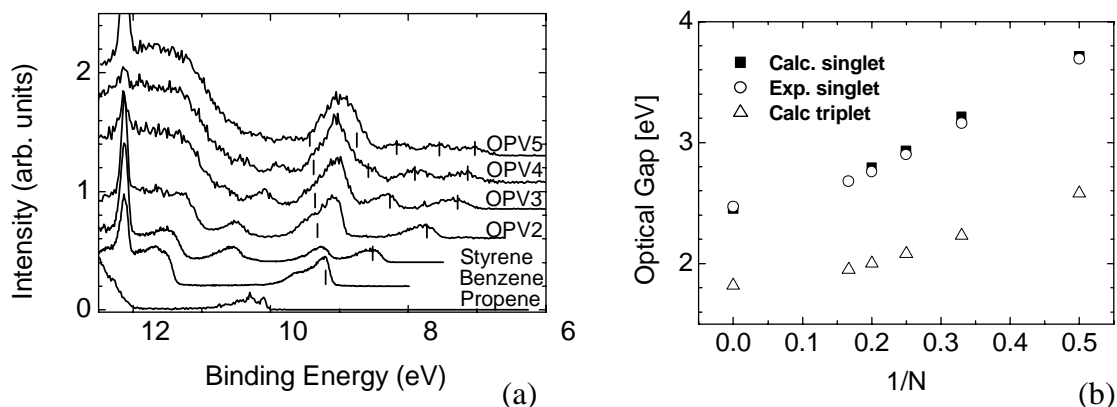
Figure 1. Gasphase photoelectron spectra of propene, benzene, styrene and oligo-phenylenevinylenes (OPVn, where n corresponds to the number of phenyl rings) (a). The lowest electronic excited states obtained from ref. 4 and from a Hubbard model Hamil-tonian calculation as a function of the reciprocal chain length (1/N) (b).

poly(para-phenylenevinylene) and the related oligomers. In figure 1a we show the development of the valence orbital structure from fragments (represented by propene, benzene and styrene) of the parent PPV polymer up to the five ring oligomer (OPV5). From the UPS spectra one can identify the development of a broad band in which an extra occupied energy level is created each time the polymer fragment is extended by a benzene ring. The spacing between these energy levels (indicated by short lines in figure 1a) are related to the transfer integral (t) [2]. This band originates from one of the degenerate HOMO-orbitals of benzene. The other degenerate HOMO orbital on benzene

forms a narrow band in the polymer limit, centred around 9 eV. Orbitals contributing to this narrow band are localised on the benzene rings since they have no electron density on the two *para* carbon atoms that connect to the neighbouring phenyl-rings through the vinylene-bridges.

The energy levels that contribute to the broad band together with energy levels that constitute to a similar developed *unoccupied* band mainly determine the low lying electronic excited states in PPV-based oligomers and the polymer. The other parameters for the model are obtained from optical data of these oligomers: the exchange interaction (K) is taken from the known singlet-triplet splitting of stilbene [5]. U is determined from the ratio of U/t. This ratio determines the curvature of the line through the experimental determined optical gaps, see figure 1b. V is used as a fitting parameter. One way to improve the efficiencies of organic PVDs is to find new conjugated polymers that absorb a larger part of the solar spectrum. This model may help to develop new conjugated polymers with low optical bandgaps that better match the solar spectrum.

Interfaces in bulk heterojuction based organic PVDs

In the remainder of this paper we will focus our attention to another important aspect of organic PVDs, namely the interfaces between the different components constituting these devices. Recently, interface dipole layers have been reported at numerous metal/organic interfaces by comparing the low kinetic energy cut-off, or secondary electron cut-off in the UPS spectra of the substrate and the absorbent [5]. A misalignment between these cut-off's indicates the existence of an electric field at the interface. Several mechanisms have been proposed to explain the observations for example: electron transfer from a donor to an acceptor, image effects, modifications of the diffuse, asymmetric electron clouds of the metal at the interface, metal induced gap states and covalent chemical interactions [5].

In a previous paper we discussed the energy level alignment between poly-crystalline noble metals and two conjugated PPV-like oligomers OPV5 and MEH-OPV5). Since this interface represents the electrode/electron donor interface as found in organic PVDs, we summarise those results in Table 1. Although the exact mechanism causing these dipoles is not known yet, we note that similar results are obtained at other metal /organic interfaces [5].

Table I. UPS measurements (eV) on OPV5 and MEH-OPV5 deposited on polycrystalline Au and Ag (Φ_{Au} = 5.1±0.1eV; (Φ_{Ag} = 4.4±0.1eV).

Interface	Δ	I_s	ε_V^F	$\varepsilon_V^F{}_{(\Delta=0)}$
Au/OPV5	-1.0	5.6	1.4	0.4
Ag/OPV5	-0.4	5.6	1.7	1.3
Au/MEH-OPV5	-1.2	5.2	1.2	0.0
Ag/MEH-OPV5	-0.5	5.3	1.3	0.8

Δ represents the vacuum level shift (± 0.1eV), a negative dipole corresponds to a downward shift in an energy diagram; I_s, the ionization energy (±0.1 eV); ε_V^F, measured hole injection barrier; $\varepsilon_V^F{}_{(\Delta=0)}$, calculated hole injection barrier for Δ=0 (±0.1 eV).

The presented UPS results of interfaces formed by evaporating PPV-type oligomers onto metals (Ag and Au) reveal a misalignment between the vacuum levels of the metal substrate and the organic overlayer. This shift of levels, presumably caused by an interfacial dipole layer, strongly influences the hole injection barriers in such a way as to keep this barrier nearly constant and therefore at most weakly sensitive to the workfunction of the electrode. Knowledge of this interfacial dipole layer is therefore crucial for understanding the electrical characteristics of devices made of this type of organic semiconductor.

For a complete understanding of charge transport in devices based on electron donor and acceptor materials, the organic-organic interface needs to be characterized as well. Therefore we will now discuss the interface formation between OPV5 and C_{60} which represents the above mentioned donor acceptor interface in organic PVDs. Hill et al. [6] found that at most organic / organic interfaces the vacuum levels align, with few exceptions. Most interestingly, we found clear evidence of an interfacial dipole layer between the electron donor-acceptor system formed by OPV5 and C_{60}. We present our results in table 2

**Table 2**. UPS measurements (eV) on interfaces formed by OPV5 and $C_{60.}$

Interface	Δ (eV)	I_s, C_{60} (in eV $\pm$ 0.1eV)	$I_s,$ OPV5 (in eV$\pm$ 0.1eV)
C_{60}/OPV5	-0.25	6.7	5.8
OPV5/C_{60}	0.25	6.7	5.8

Δ represents the vacuum level shift ($\pm$ 0.1eV); I_s, the ionization energy.

From table 2 we infer that although no complete electron transfer occurs in the ground state between conjugated polymers and C_{60} derivatives as known from ESR and optical spectroscopy, at least a dipole layer exists at this interface. In addition, we note that the direction of the field is independent of the deposition order and is oriented from C_{60} (δ-) towards OPV5 (δ+). This is in correspondence with the nature of these materials with C_{60} as electron acceptor and OPV5 as electron donor. The presence of this field influences the mutual alignment of energy levels at the interface. Furthermore, it may facilitate the electron transfer from the electron donor to the acceptor.

Finally we will discuss the interface between the electrodes and the electron acceptor by presenting UPS measurements on the interfaces formed by Ag / C_{60} (figures 2) and Au / C_{60} (figure 3). UPS spectra of *monolayers* of C_{60} on Ag and Au show an increased density of states at the Fermi level of the metal substrate (see for example figure 3). These spectra are carefully corrected for the contribution of the photoelectrons from the metal substrate [7]. This spectral feature disappears when the film thickness increases. It is shown that during the formation of the first monolayer, an interface state is formed by an electron transfer from the metal to the lowest unoccupied molecular orbital (LUMO) of C_{60} [7]. Obviously such an interface charge transfer causes an electric field at the interface. As expected, the UPS spectra of C_{60} on the metal substrates show a shift in the low kinetic energy cut-off, or secondary electron cut-off. This shift is completed after the deposition of 1 to 2 C_{60} monolayers on the metal substrate. This is expected since only the LUMO of the C_{60} layer next to the metal is partially filled, as a consequence the subsequent deposited layers behave like the 'bulk' material.

However, the shift in the spectra of the C_{60} / Au interface is in the other direction originates from an overall electric field pointing from C_{60} towards Au. This seems to contradict the mechanism of a partial occupation of the LUMO by an electron transfer from Au to C_{60}.
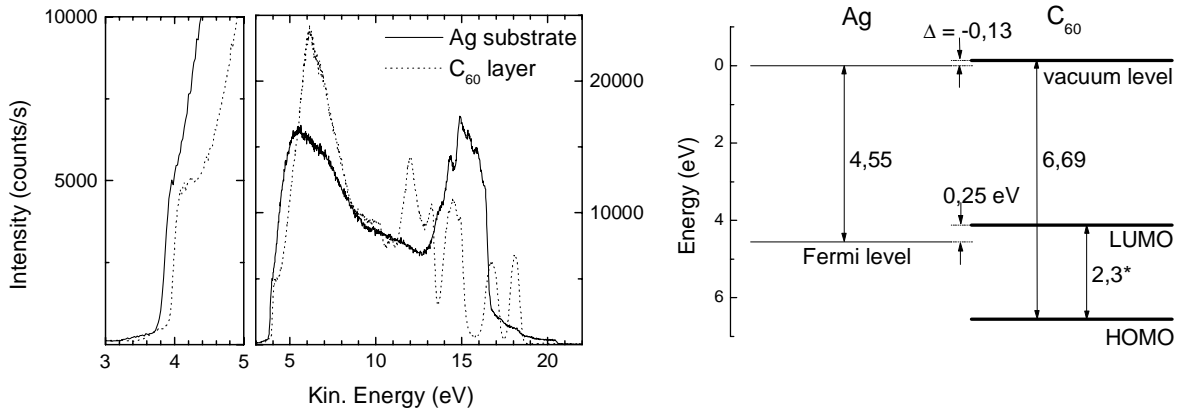
Figure 2. UPS spectra of polycrystalline Ag (line) and of a several nanometer thick layer of C_{60} deposited on polycrystalline Ag (square symbols). Energy level diagram of the alignment of energy levels between polycrystal-line Ag and bulk C_{60} deduced from both UPS spectra shown in the left panel. The HOMO-LUMO gap is taken from ref. 8.
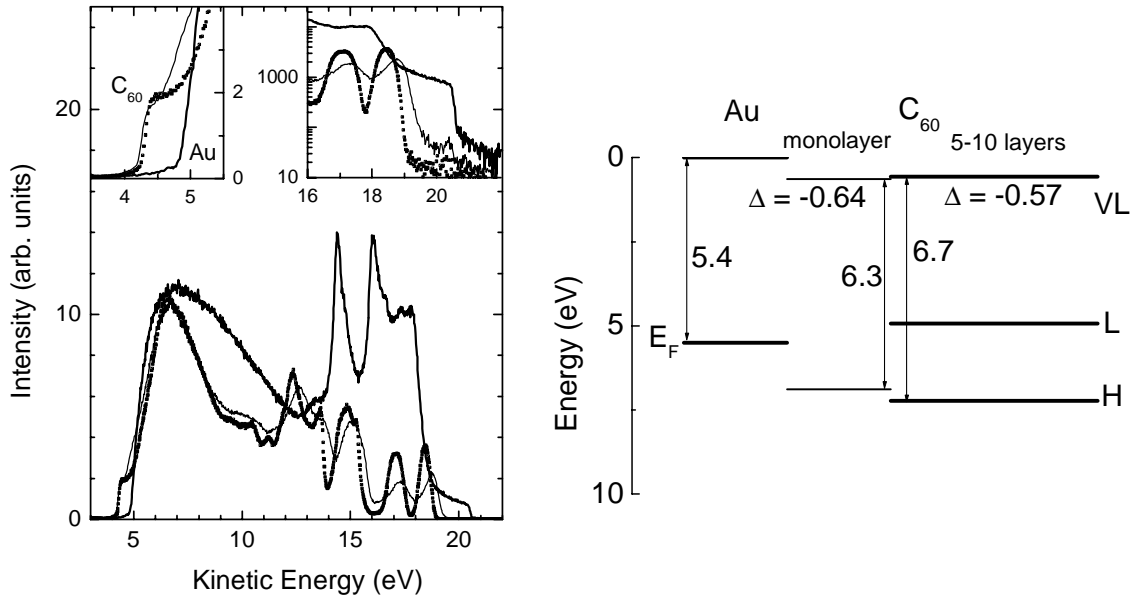
Figure 3. UPS spectra of a polycrystalline Au substrate (thick continuous line), a monolayer of C_{60} on the Au substrate (thin continuous line) and layer of C_{60}, several nanometer thick (square symbols) (a). Energy level diagram (in binding energy) of the inter-face between Au and C_{60} deduced from the UPS spectra shown in the left panel. H represents HOMO; L, LUMO; VL, vacuum level; E_F, Fermi level, Δ interfacial dipole.

Many metal / C_{60} interfaces have been studied and substantial workfunction changes have been observed [9]. The authors explain their observations by the supposed

metallic nature of the C_{60} overlayer, making the workfunction of the C_{60} overlayer independent of the metal substrate. However, this does not explain the observed differences in workfunction of the C_{60} overlayer of 4.7 for C_{60} on Au(111) and 5.25 for C_{60} monolayer on Al(110) and 5.4 for a C_{60} overlayer on Ta, since it is supposed to be a material property, independent of the substrate.

We propose an explanation for the experimental findings on the polycrystalline Au / C_{60} interface by describing three interacting effects. First, a screening effect of the metal substrate reducing of the on-site Coulomb interaction leading to a reduction of the energy gap between occupied and unoccupied levels. Secondly, broadening of the spectral features due to hybridization between the Au 6sp-band and the occupied π and unoccupied π^* orbitals of C_{60}. The combination of the reduced gap and the spectral broadening results in an electron transfer from the metal substrate to the C_{60} LUMO. Thirdly, an induced dipole field at the Au / C_{60} interface caused by the deposition of C_{60} onto the clean Au surface. The adsorbed C_{60} molecules redistribute the Au 6sp electrons whose wavefuctions extend far into the vacuum (known as 'spill-out') prior to the adsorption of C_{60} to the substrate. This redistribution causes a dipole layer in the first Au layer. This field opposes the electric field caused by the electron transfer from the metal substrate to C_{60}. We think that the same processes occur at the polycrystalline Ag / C_{60} interface however, in that system the magnitudes of the different contributions to the total field lead to a dipole pointing from C_{60} to Ag.

CONCLUSIONS

This study shows that the low-lying electronic excitations of PPV-based oligomers can be accurately described by a model we previously formulated for thiophene based oligomers. Further we show that at interfaces found in bulk heterojunction organic photovoltaic devices dipole layer exists significantly influencing the alignment of energy levels at the metal / organic and the organic donor / acceptor interfaces.

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