

# Fermi level pinning induced electrostatic fields and band bending at organic heterojunctions

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## Abstract

The energy level alignment at interfaces between organic semiconductors is of direct relevance to understand charge carrier generation and recombination in organic electronic devices. Commonly, work function changes observed upon interface formation are interpreted as interface dipoles. In this study, using ultraviolet and X-ray photoelectron spectroscopy, complemented by electrostatic calculations, we find a huge work function decrease of up to 1.4 eV at the C<sub>60</sub> (bottom layer)/zinc phthalocyanine (ZnPc, top layer) interface prepared on a molybdenum trioxide (MoO<sub>3</sub>) substrate. However, detailed measurements of the energy level shifts and electrostatic calculations reveal that no interface dipole occurs. Instead, upon ZnPc deposition, a linear electrostatic potential gradient is generated across the C<sub>60</sub> layer due to Fermi level pinning of ZnPc on the high work function C<sub>60</sub>/MoO<sub>3</sub> substrate, and associated band-bending within the ZnPc layer. This finding is generally of importance for understanding organic heterojunctions when Fermi level pinning is involved, as induced electrostatic fields alter the energy level alignment significantly.

The energy level alignment at organic and molecular semiconductor heterojunctions is generally recognized to be essential for the function and performance of organic electroluminescent<sup>1,2</sup> and photovoltaic devices.<sup>3,4</sup> Because of its direct relevance for understanding the underlying fundamental mechanisms, such as charge carrier recombination and generation,<sup>5-7</sup> the energy level alignment at these interfaces has been extensively studied by ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS, respectively).<sup>8-11</sup> Due to the weak van der Waals interaction between the organic materials, Schottky-Mott-limit like behavior is often assumed<sup>12</sup> with vacuum level alignment (VLA) across the interface, i.e., a constant electrostatic potential. Nevertheless, for numerous organic semiconductor combinations deviations from VLA were observed, e.g., bathocuproine (BCP)/3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA)<sup>13</sup> and 4,4',4''-tris[3-methyl-phenyl(phenyl)amino]-triphenylamine (m-MTDATA)/4,4'-*N,N*-dicarbazolyl-biphenyl (CBP).<sup>14</sup> The shift of the vacuum level (measured as work function change) at the interfaces is generally attributed to the formation of an interface dipole. Several explanations for this have been put forward, ranging from molecular quadrupoles,<sup>15</sup> interface charge transfer involving induced density of interface states,<sup>9</sup> to molecular polaronic levels,<sup>10</sup> or tailing of the density of states into the energy gap of the semiconductor films.<sup>16</sup>

In this contribution, we demonstrate that for the molecular heterojunction C<sub>60</sub> (bottom layer) / zinc phthalocyanine (ZnPc, top layer) formed on molybdenum trioxide (MoO<sub>3</sub>)-covered gold, the shift in the vacuum level is caused by the highest occupied

molecular orbital (HOMO) level pinning<sup>17</sup> of the top organic layer. The charges transferred to the top layer due to pinning induce an electric field across the bottom layer, which mimics - in the sequence of measurements with increasing thickness - an interface dipole. This mechanism was identified by determining the electronic structure at the C<sub>60</sub>/ZnPc interface with UPS/XPS measurements and corresponding electrostatic calculations.

The Au/MoO<sub>3</sub>/C<sub>60</sub>/ZnPc heterostructure was grown in a preparation chamber (base pressure < 5 × 10<sup>-8</sup> mbar). Prior to the deposition of the heterostructure, the Au(111) crystal was cleaned by repeated Ar ion sputtering (1 keV, ~1 μA) and annealing (~500 °C) cycles. The surface cleanliness was confirmed by the appearance of the surface state in the UPS spectrum [Fig. S1(a), supplemental material].<sup>18</sup> Then 2 nm MoO<sub>3</sub> was deposited to increase the sample work function from initially 5.4 eV to 6.7 eV (see Fig. 1a). The organic heterostructure comprised a 12 nm C<sub>60</sub> bottom layer, and was completed by evaporating ZnPc on top. The ZnPc layer was deposited in several steps, in order to determine the evolution of the energy level alignment at the organic/organic interface. UPS/XPS spectra were taken for each step in an analysis chamber (base pressure < 4 × 10<sup>-9</sup> mbar) interconnected to the evaporation chamber, with He I<sub>α</sub> (21.22 eV, UPS) and Al K<sub>α</sub> (1486.7 eV, XPS) excitation energies, respectively. He I<sub>β</sub>- and He I<sub>γ</sub> satellites are already subtracted from the UPS spectra presented here. The sample work function (Wf) was inferred from the secondary electron cutoff (SECO) spectra, recorded

with a DC sample bias of  $-10.0$  V. In the main text we focus on the valence electronic structure, while the corresponding XPS spectra can be found in the supplemental material [Fig. S1].<sup>18</sup>

On a freshly prepared  $\text{MoO}_3$  substrate, with a Wf of  $6.7$  eV, a  $12$  nm thick  $\text{C}_{60}$  layer was deposited. As a result, the sample Wf decreased to  $6.0$  eV [see Fig. 1(a)]. As previously reported,<sup>19</sup> this is rationalized in terms of Fermi level pinning of the  $\text{C}_{60}$  HOMO levels (ionization potential =  $6.4$  eV<sup>17</sup>). Due to this pinning of the occupied states, electrons are transferred from  $\text{C}_{60}$  to the substrate to establish thermodynamic equilibrium.<sup>20</sup> The occupied levels, as measured with UPS, are shown in Fig. 1(b), where only the spectral signature of  $\text{C}_{60}$  is visible (at the bottom), indicating that the surface of  $\text{MoO}_3$  is fully covered. For the  $12$  nm thick  $\text{C}_{60}$  film the density of charged molecules at the surface is too low to be visible in the UPS spectrum.<sup>21</sup>

The organic heterostructure was then built by evaporating ZnPc onto the  $\text{C}_{60}$  layer. In Fig. 1(a) a further reduction of the Wf upon ZnPc deposition to a final value of  $4.6$  eV is apparent. In the valence region [Fig. 1(b)], a continuous change from the spectral signature of  $\text{C}_{60}$  towards ZnPc can be observed. Additionally, Fig. 1(b) shows that the ZnPc HOMO level is close to zero binding energy (BE) and gradually shifts towards higher BE as a function of increasing thickness. This is highlighted in Fig. 1(c), where only the region close to the Fermi level is depicted. Up to a thickness of  $1$  nm ZnPc, where the  $\text{C}_{60}$  spectral signature can still be distinguished, a gradual shift of also the  $\text{C}_{60}$

features towards higher BE by up to  $\sim 0.9$  eV is evident. The continuous reduction of the Wf, together with the shift of the ZnPc levels towards higher BE, is again a clear signature of HOMO level pinning. As the ionization potential of ZnPc (4.8 eV) is lower than the Wf of the C<sub>60</sub>-covered MoO<sub>3</sub>/Au substrate and therefore, as in the case of C<sub>60</sub> on MoO<sub>3</sub>, electrons are removed from the ZnPc layer. In principle two scenarios are plausible, either the charges are transferred to the C<sub>60</sub> layer, producing an interface dipole, or the charges are transferred all the way through the film to the metal substrate. If we assume an interface dipole to be formed, 25 % of the molecules have to be charged to produce the full Wf shift observed (for the calculation, see the supplemental materials).<sup>18</sup> In this case, in the UPS spectrum clearly charged and neutral molecules should be both visible.<sup>21-23</sup> On the other hand, if we assume the charges to be located in the metal substrate, only as little as 1 % of the molecules have to be charged to account for the Wf shift. This is because the individual dipole moments are way bigger due to the increased distance of the charges forming them. This fraction of charged molecules is too small to be seen in the UPS spectrum [Fig. 1(b)].

Complementary XPS measurements are fully in line with the UPS results and are discussed in detail in the supplemental materials [Fig. S2].<sup>18</sup> Also in the XPS spectra no signs of charged molecules are visible at the heterojunction interface. A summary of all core level peak position shifts is shown in Fig. 1(d). Gradual shifts towards higher BE are observed for the ZnPc levels starting from 0.5 nm, where peak positions could be reliably determined (all peaks shift in parallel). The full range of the shift caused by

ZnPc cannot be measured because the reference position is that without ZnPc. Therefore, at a layer thickness of 0.5 nm, the ZnPc already experiences the shifted Wf (cause by ZnPc itself) of  $\sim 0.9$  eV. Alas, to the measured shift, the Wf reduction has to be added. Nevertheless, the subsequent shifts follow, as expected, the general trend of the Wf reduction. Noteworthy, the apparent shift of the  $C_{60}$  core level (max.  $\sim 0.9$  eV) appears significantly larger, because the  $C_{60}$  shifts can be followed already from the very first ZnPc deposition, but the overall shift is still smaller than the final Wf reduction of 1.4 eV. Analogous arguments explain the difference in the maximum shifts of the HOMO levels of  $C_{60}$  and ZnPc in Figs. 1(b) and (c).

To rationalize the energy level alignment at this heterointerface and the underlying mechanism, and, in particular, where the charges from ZnPc are transferred to, electrostatic calculations were carried out within a recently reported framework.<sup>20</sup> Briefly, in this model, the metal substrate is regarded as an infinite electron reservoir with a constant chemical potential.  $MoO_3$  is treated as an insulator with a dielectric constant of  $\epsilon_r = 14$ .<sup>24</sup> The density of states (DOS) of the organic layers are approximated by Gaussian peaks (representing their frontier orbital levels) and, initially assuming VLA, are occupied according to Fermi-Dirac-statistics. The resulting charge density is then used to solve the one-dimensional Poisson-equation, which yields the electrostatic potential across the  $MoO_3/C_{60}/ZnPc$  heterostructure. Then, the charge density is calculated again with the molecular DOS shifted in each layer according to the new electrostatic potential. These calculations are repeated self-consistently until a stationary

solution is obtained. A detailed list of the material parameters used here can be found in the supplemental material.<sup>18</sup>

The calculated electron potential across the heterostructure Au(111)/MoO<sub>3</sub>/C<sub>60</sub> and a series of ZnPc thicknesses (0 – 4 nm) are shown in Fig. 2(a) (black curves, and green dots) together with the measured changes of the Wf (red crosses). The agreement between simulation and experiment is remarkable. We note that the calculation (black lines) shows the electron potential within the C<sub>60</sub> film, while with UPS, due to its surface sensitivity, only the electrostatic potential of the surface region can be measured. Therefore, only the end-points of the calculated electrostatic potential curves (green dots) should be directly compared with experiment. The topmost black curve shows the situation before the organic heterostructure is formed, i.e., of only the C<sub>60</sub> film on Au(111)/MoO<sub>3</sub>. Also here, the measured MoO<sub>3</sub> Wf reduction by -0.7 eV upon C<sub>60</sub> deposition is reproduced. With increasing ZnPc thickness [following the blue arrow in Fig. 2(a)], the Wf is further reduced, as discussed before, and again perfectly agrees with the measurements [Fig. 1(a)]. The shape of the electrostatic potential within the heterostructure (black lines) reveals that the largest fraction of the potential drops across the C<sub>60</sub> layer, even though the reason for the overall Wf change is the pinning of the ZnPc layer on top. This perfectly agrees with the appreciable shift of C<sub>60</sub> (cf. Fig. 1) of ~0.9 eV, compared to the overall 1.4 eV Wf reduction. The smaller apparent shifts of the ZnPc [Fig. 1 (c) and (d)] can be now also understood by following the potential curve, starting from 0.5 nm ZnPc thickness (the 4th measurement point), the thickness from

which on the peak positions could be reliably determined. At this thickness the potential is already shifted by  $\sim 0.9$  eV. Fig. 2(b) summarizes the measured (XPS - blue, UPS - red) as well as the calculated (black and green) changes of  $C_{60}$  level BEs and potentials upon ZnPc deposition. Note that the calculated shift of the topmost layer of  $C_{60}$  is slightly overestimated compared to the measurement, even though the overall shape reproduces the experimental data. This discrepancy is most likely caused by the assumed perfect layer-by-layer growth mode in the model.<sup>20</sup> In reality, the heterointerface will have a certain roughness. Taking this into account, by comparing the experimental data to a  $C_{60}$  layer below the interface, e.g. the third one as shown in Fig. 2(b) (black curve), results in perfect agreement between measurement and calculation.

In addition to the electrostatic potential, also the charge density distribution within the heterostructure is readily available from the calculations. In Fig. 2(c) the situation before (red dots) and after ZnPc deposition (blue squares) is compared. The charge density distribution can be understood as follows:  $MoO_3$  is free of charges (an insulator was assumed), in  $C_{60}$  at the interface to  $MoO_3$  holes are accumulated due to HOMO level pinning, followed by an approximately exponential decay of the hole density away from the interface due to band-bending.<sup>20</sup> Qualitatively the same can be seen at the  $C_{60}/ZnPc$  interface. Holes are accumulated within ZnPc due to HOMO level pinning, and the density decays with increasing distance from the interface. Additionally, the electric field across the  $C_{60}$  layer shifts all  $C_{60}$  levels further away from the Fermi level



and therefore reduces the pinning at the  $\text{MoO}_3/\text{C}_{60}$  interface. This reduced pinning results in a lower hole density in the  $\text{C}_{60}$  film when ZnPc is deposited. It is noted that electrons from both ZnPc and  $\text{C}_{60}$  are transferred to the metal substrate.

The overall energy level diagram across the  $\text{MoO}_3/\text{C}_{60}/\text{ZnPc}$  heterostructure is summarized in Fig. 3. The Fermi level pinning of the ZnPc layer (due to the high Wf of the  $\text{C}_{60}$  layer) induces an electrostatic potential drop across  $\text{C}_{60}$ , and no localized interface dipole occurs at this interface, even though a huge shift of the vacuum level is measured.

In summary, the interface of  $\text{C}_{60}/\text{ZnPc}$  on a high work function substrate (6.7 eV) was studied by UPS/XPS and modelled by electrostatic calculations. The  $\text{C}_{60}$  molecules in the bottom layer of this heterostructure are HOMO level pinned due to their ionization potential of 6.4 eV, which reduces the work function to 6.0 eV. This pinning situation causes a fraction of the molecules to be charged with the majority of holes accumulated close to the interface to  $\text{MoO}_3$ . These charges are the origin of the electric field that causes the band-bending within  $\text{C}_{60}$ . Depositing ZnPc onto the  $\text{C}_{60}$  film leads to a further reduction of the work function to a final value of 4.6 eV. Also in this case, due to the ionization potential of ZnPc (4.8 eV) being lower than the underlying film work function (6.0 eV), ZnPc is HOMO level pinned and a fraction of molecules is positively charged. In this case, the electric field due to excess charges not only causes band-bending within the ZnPc layer, but extends (linearly) across the  $\text{C}_{60}$  layer below. Consequently, not only the ZnPc states are shifted upon heterojunction formation, but

also the ones of C<sub>60</sub>. Therefore, no abrupt interface dipole for the C<sub>60</sub>/ZnPc heterostructure is involved. It appears thus necessary to evaluate whether previously postulated interface dipoles at different organic and molecular heterointerfaces can be reinterpreted by Fermi level pinning and concurrent electrostatic fields.

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<sup>18</sup>See supplemental material at [URL will be inserted by AIP] for UPS and XPS spectra of the Au(111) substrate, the MoO<sub>3</sub> film and the ZnPc/C<sub>60</sub> interface, calculated fraction

of charged molecules at the organic heterojunction and the methods of electrostatic potential calculations.

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## Figure captions

Figure number	caption
Figure 1	<p>(a) Measured work function (secondary electron cutoffs, SECO) for Au(111) (green), Au(111)/2 nm MoO<sub>3</sub> (blue), Au (111)/2 nm MoO<sub>3</sub>/12 nm C<sub>60</sub> (red), as well as a series of ZnPc thicknesses on top (black). (b) Valence spectra for C<sub>60</sub> and a series of ZnPc thicknesses [colors correspond to (a)]. (c) Zoom-in on the region close to the Fermi level from (b). A magnification for the lowest ZnPc coverages is shown in the inset. (d) Summary of the peak shifts measured with XPS. C 1s for C<sub>60</sub>, and C 1s, N 1s and Zn 2p<sub>3/2</sub> for ZnPc. The measured shifts for ZnPc are offset by 0.94 eV to take the work function shift at 0.5 nm into account. See text for details.</p>
Figure 2	<p>(a) Measured (red crosses) and calculated (green dots) work function values. Black lines correspond to the shift in the electron potential energy within the respective layer. (b) Comparison of the C<sub>60</sub> HOMO level shift measured by UPS (red), the C<sub>60</sub> C 1s shift measured by XPS (blue), and the calculated electron potential shift of the topmost layer (green) and the 3<sup>rd</sup> C<sub>60</sub> layer below the interface (black). (c) Calculated charge density distribution before (red) and after (blue) completion of the heterostructure.</p>
Figure 3	<p>Schematic energy level diagram (<math>E</math> in eV) for the heterostructure 2 nm MoO<sub>3</sub>/12 nm C<sub>60</sub>/4 nm ZnPc <i>within</i> the layers. <math>E_F</math> is the Fermi level of the substrate [Au(111) / 2 nm MoO<sub>3</sub>, assuming a perfect insulator]. Energy gaps of C<sub>60</sub> and ZnPc are taken from Refs. 25 and 26, respectively.</p>





