Abstract

Organic–metal and organic–organic interfaces account for the functionality of virtually all organic optoelectronic applications and the energy-level alignment is of particular importance for device performance. Often the energy-level alignment is simply estimated by metal work functions and ionization energies and electron affinities of the organic materials. However, various interfacial effects such as push back, mirror forces (also known as screening), electronic polarization or charge transfer affect the energy-level alignment. We perform x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) measurements on copper-hexadecafluorophthalocyanine (F\textsubscript{16}CuPc) and titanyl-phthalocyanine (TiOPc) thin films on Ag(111) and use TiOPc bilayers to decouple F\textsubscript{16}CuPc layers from the metal substrate. Even for our structurally well-characterized model interfaces and by stepwise preparation of vacuum-sublimed samples, a precise assignment of vacuum-level and energy-level shifts remains challenging. Nevertheless, our results provide guidelines for the interpretation of XPS and UPS data of organic–metal and organic–organic interfaces.

1. Introduction

The functionality of virtually all organic and hybrid (opto-)electronic devices depends on interface energetics, and a thorough understanding of energy-level alignment mechanisms at organic–metal and organic–organic interfaces is indispensable for further efficiency improvements [1–5]. For example, the energy-level offset at the donor–acceptor interface in organic photovoltaic devices is crucial for exciton dissociation [6–8]; chemisorbed molecular monolayers on metals can tune the substrate work functions by an interfacial charge transfer [9, 10] and allow, consequently, to lower charge injection barriers into electrodes [11, 12]. The number of organic materials used for optoelectronic applications is virtually unlimited [13, 14] and energy-level diagrams (ELDs) are frequently used to choose the best material for a given purpose [4, 15]. The energy values such as the ionization energies (IEs) for these ELDs are often taken from ultraviolet photoelectron spectroscopy (UPS) measurements on copper-hexafluorophthalocyanine (F\textsubscript{16}CuPc) and titanyl-phthalocyanine (TiOPc) thin films on Ag(111) and use TiOPc bilayers to decouple F\textsubscript{16}CuPc layers from the metal substrate. Even for our structurally well-characterized model interfaces and by stepwise preparation of vacuum-sublimed samples, a precise assignment of vacuum-level and energy-level shifts remains challenging. Nevertheless, our results provide guidelines for the interpretation of XPS and UPS data of organic–metal and organic–organic interfaces.
gives insight into the chemical states of adsorbate atoms via so-called chemical shifts [24, 25]. Our focus issue article highlights that, in order to get a full picture of organic–metal and organic–organic interface energetics, advanced characterization by photoelectron spectroscopy—including UPS and XPS—is mandatory.

We start with a short introduction to photoelectron spectroscopy at these interfaces. UPS and XPS are both surface sensitive techniques and for organic materials (and measurements with typical lab light-sources like HeI and Al Kα) the mean free path of photoelectrons, i.e. the information depth, is around 5–10 Å for UPS and 50–100 Å for XPS [26, 27]. This applies for valence levels like the highest occupied molecular orbital (HOMO)-level (measured by UPS) and for core levels like the C 1s level (measured by XPS). Furthermore, the low kinetic secondary electron cutoff (SECO) of UPS allows to measure the surface potential of the sample, which is usually referred to as vacuum level (VL) [28, 29]. It becomes apparent that these different information depths are a challenge for the analysis of photoelectron spectra, especially for inhomogeneous samples [30, 31] and in case of energy-level bending, i.e. the parallel shift of VL, valence and core levels as function of layer thickness [32–34]. The chemical shift of the C 1s core level between carbon atoms in the conjugated backbone and in the functional groups of an organic molecule allows to assign spectral signatures to a specific layer in an organic heterostructure [9, 18]. Noteworthy, chemical shifts can be rather small [35, 36] and require high energy-resolution XPS data, i.e. measurements with a monochromatized x-ray source or at a synchrotron radiation facility. Furthermore, XPS allows to estimate the coupling strength at organic–metal interfaces as chemisorption, i.e. the re-hybridization of the molecular adsorbate in the contact layer [37, 38], leads to additional chemical shifts [10, 39].

Here, we aim to give guidelines for extracting meaningful energy levels from photoelectron spectroscopy data by taking several interface phenomena into account. In particular, we focus on the push-back effect, the image-charge effect (‘screening’) and possible charge transfer at the organic–metal interface [18] and at polarization effects (induction and electrostatic), possible intermolecular interaction and dipole layers at the organic–organic interface [40, 41]. Notably, the latter effects can also occur at organic–organic homointerfaces and the complex situation is illustrated in figure 1 by schematic ELDs of molecular thin films on clean metal surfaces. In both panels, the Fermi-level (Ef) and the work function (φ) are shown for the metal substrate. For each of the molecular layers (MLs), the VL, the lowest unoccupied molecular orbital (LUMO)-level, the HOMO-level, the carbon core level (C 1s) and a core level of a heteroatom (HA) are shown. Figure 1(a) shows four layers of a chemisorbed, non-polar molecule and figure 1(b) two layers of the same molecule on a spacer comprising two layers of a polar molecule. The VL, and the binding energy (BE) positions of valence and core levels at these interfaces are affected by:

1. The push-back effect decreases the VL at both interfaces (figures 1(a) and (b)) upon deposition of the contact layer (1 ML) [5, 42].
2. The bond dipole increases the VL due to interfacial charge transfer at the chemisorptive interface (figure 1(a)) [39, 43].
3. The p_z-component of the dipole layers impacts the VL and the energy levels due to molecular dipole moments [44, 45]. In the contact layer (1 ML) of figure 1(b) only the HA of the molecule is located above this dipole layer and, consequently, only the HA energy level is affected by the dipole layer; in the second layer (2 ML) the molecular dipole moments cancel each other [40].
4. The screening effect (also called image-charge effect) affects the BE positions of unoccupied and occupied energy levels between the monolayer and the bilayer and leads to a decrease of the molecular energy gap in the contact layer at both interfaces (figures 1(a) and (b)) [46, 47].
5. Chemisorption (figure 1(a)) leads to energy-level shifts in the contact layer [38, 39]. As chemisorption often goes along with a charge transfer, these energy-level shifts are related to the VL-shifts caused by effect #2.
6. Polarization effects lead to energy-level shifts at each organic–organic interface [48–50]. For the sake of clarity, only the impact on the third ML by deposition of the fourth ML is shown in figures 1(a) and (b). The polarization can be divided into two contributions: (1) the induction contribution depends mainly on the dielectric constant of the MLs and (2) the electrostatic contribution takes also the molecular quadrupole moments into account [41].

This list and the ELDs in figure 1 are rather simplified as the interface phenomena leading to the shifts are correlated to each other. However, a detailed description of the physical mechanisms leading to shifts of VL and energy levels at these organic–metal and organic–organic interfaces is beyond the scope of this article and the reader is referred to the references, e.g. to the comprehensive review article ‘The Impact of Dipolar Layers on the Electronic Properties of Organic/Inorganic Hybrid Interfaces’ by Zojer et al [40]. Furthermore, for all layers in figure 1 (with the exception of the chemisorbed monolayer), Ef is rather at mid-gap position and energy-level and VL-shifts due to Fermi-level pinning at the frontier molecular orbitals and/or gap states.
Figure 1. Schematic ELDs of organic–metal and organic–organic interfaces. The metal substrate is characterized by its work function ($\phi$), i.e. the energetic difference between the Fermi-level ($E_F$) and the VL. For each ML the LUMO- and the HOMO-levels, the C 1s core level and the core level of a HA are shown. The arrows show VL and energy-level shifts upon deposition of the respective layer. For the sake of clarity, the polarization effects at the organic–organic interfaces are only shown for 3 ML; full bars depict the energy levels before and dotted bars after deposition of 4 ML. (a) The contact layer (1 ML) is chemisorbed involving a partial filling of the F-LUMO. (b) The contact layer is physisorbed; the $p_z$-components of the polar molecules in 1 ML and 2 ML are antiparallel.

[51–54] are not considered. Noteworthy, the density of gap or tailing states is usually too low to be detected with conventional UPS-setups [55, 56]. Nevertheless, they provide a charge reservoir for electronic-equilibrium-driven interfacial charge transfer, which typically leads to energy-level bending over a few organic layers [51, 52]. In contrast, a charge transfer by chemisorption leads to an interface dipole, i.e. an abrupt change of VL at the organic–metal interface [9, 18]. Noteworthy, the effects mentioned above impact the position of energy levels and further effects impact the line shape and intensities of UPS and XPS spectra, they include energy dispersion [27, 57, 58], orbital delocalization [59, 60], hole–phonon coupling [61, 62], photoelectron angular distribution [63–65], photoelectron diffraction [66, 67], core-hole screening [68–70] and shake-up excitations [71, 72]. Several tutorial-like review articles give guidelines how to analyze XPS data [73–75]; for UPS the reader is referred to these books [76, 77].

To model the organic–metal and organic–organic interfaces of figure 1, phthalocyanine-derivatives are chosen because they allow simple replacement of central atoms and further functionalization by molecular side groups [78, 79]. We use titanyl-phthalocyanine (TiOPc) as the bottom layer of the heterostructure: the intrinsic dipole moments of TiOPc have an antiparallel orientation in the first and second layer on Ag(111) with layer-by-layer growth and thereby provide a stable, weakly interacting contact layer [80–83]. Furthermore, homogeneous and well-ordered bilayers can be prepared by thermal desorption of multilayers and bilayer formation can be evidenced by XPS [84]. The TiOPc bilayer thickness of $\sim$6.3 Å [80] should be sufficient to shield the metal substrate from the second organic layer (i.e. the one above the TiOPc bilayer) and to facilitate a true organic–organic interface. We use copper-hexadecafluorophthalocyanine (F$_{16}$CuPc) as the second layer: fluorine functionalization adds an additional core level for XPS investigation and prevents undesired molecular diffusion [85]. Furthermore, fluorination of conjugated molecules leads to interesting and partially unexplained thickness-dependent energy-level shifts [86–89]. Overall, we perform thickness-dependent UPS and XPS measurements of TiOPc and F$_{16}$CuPc (chemical structures in figure 2) deposited on Ag(111) and compare the results with F$_{16}$CuPc/bilayer TiOPc/Ag(111) heterostructures. Our photoelectron spectroscopy data show that all the effects mentioned above and highlighted in figure 1 occur at these structurally well-defined interfaces. Therefore, they serve as model systems for the advanced characterization of organic–metal and organic–organic interfaces by UPS and XPS using lab-based monochromatized UV and x-ray light sources.
2. Experimental methods

Thickness-dependent UPS and XPS measurements were carried out in an ultra-high vacuum system consisting of three interconnected chambers: an evaporation chamber (base pressure: $3 \times 10^{-10}$ mbar), an annealing and sputtering chamber ($3 \times 10^{-10}$ mbar) and an analysis chamber (base pressure: $2 \times 10^{-10}$ mbar). Ag(111) was cleaned by several cycles of Ar$^+$ ion bombardment and annealing ($400$ °C–$500$ °C). F$_{16}$CuPc and TiOPc were sublimated by physical vapor deposition from resistively heated cells with deposition rates of $\sim 0.2$ Å min$^{-1}$. The mass-related thickness was monitored by a quartz-crystal microbalance (QCM) positioned near the sample. In general, for phthalocyanines with a lying adsorption geometry a mass thickness of around 4 Å corresponds to nominal monolayer coverage [18]. UPS experiments were performed using monochromatized He I radiation (21.22 eV) and a SPECS PHOIBOS 150 analyzer. The energy resolution was 80 meV. The angle between the incident beam and the sample was fixed to 40°. The spectra were collected at photoelectron take-off angles of 45° with an acceptance angle of ±12° along the <11–2> azimuthal direction of Ag(111). A sketch of the measurement geometry can be found in [90]. The SECO (to determine the VL) was measured in normal emission with a bias potential of $-3$ V. XPS was performed using a monochromatized Al Kα source (1486.6 eV). The data analysis was carried out by a nonlinear least-square fitting routine, using Gaussian/Lorentzian peak shapes and a Shirley background. The error bar for the BEs is estimated to be ±0.05 eV. All measurements have been performed at room temperature (295 K).

3. Experimental results

The C 1s XPS data of the single-component systems and the heterostructure are shown in figure 2. The spectrum of TiOPc in multilayers (QCM thickness: 64 Å) on Ag(111) (top panel of figure 2(a)) is in accordance with literature data [84]. The three distinct peaks can be assigned to carbon atoms bound to another carbon atom (C–C), centered at 284.90 eV BE, carbon atoms bound to a nitrogen atom (C–N), centered at 286.45 eV BE, and a shake-up satellite, centered at 288.35 eV BE. In the spectrum of the nominal TiOPc bilayer (QCM thickness: 8 Å) (figure 2(b), middle panel) the C–C and C–N peaks are substantially broadened, which is due to monolayer contributions to the spectrum (the information depth of XPS is much larger than the overall film thickness). To fit this spectrum, the BEs of the C–C and C–N peaks are fixed at their multilayer positions and the four additional peaks, which are necessary to get a good fit, stem from...
Figure 3. UPS data of stepwise deposited thin films of (a) TiOPc, (b) F₁₆CuPc on Ag(111) and (c) F₁₆CuPc on a nominal bilayer TiOPc on Ag(111). The spectra with a nominal monolayer, bilayer and multilayer coverage are highlighted by darker lines. (d) Thickness-dependent evolution of the VL w.r.t. the Fermi-level for all investigated thin films on Ag(111).

TiOPc in the contact layer. The C 1s spectrum of the nominal TiOPc bilayer prepared by stepwise deposition is rather similar to that of TiOPc prepared by multilayer desorption (figure S1), which shows that a thickness of 8 Å corresponds, indeed, to bilayer coverage. Furthermore, the multilayer contribution to the spectrum of the nominal monolayer (QCM thickness: 4 Å) (figure 2(a), bottom panel) is rather weak, which shows that the first two layers of vacuum-sublimed TiOPc on Ag(111) grow almost layer-by-layer. Before discussing the reasons for the doubled monolayer contributions, we turn to F₁₆CuPc on Ag(111). In the spectrum with multilayer coverage (top panel of figure 2(b)), in addition to C–C and C–N, C–F is apparent and the spectrum is almost identical to the multilayer spectra on other substrates [91]. The spectrum of nominal F₁₆CuPc bilayer coverage (middle panel of figure 2(b)) exhibits multilayer and monolayer features and the latter features are dominating the spectrum with nominal monolayer coverage (bottom panel of figure 2(b)).

The C 1s spectrum of the nominal F₁₆CuPc monolayer on Ag(111) is virtually identical to a previously published spectrum of the same sample [68]. In this publication, Borghetti et al used near-edge x-ray absorption spectroscopy and UPS to show that the doubled core levels are due to a lifted degeneracy of the LUMO-level upon partial charging in combination with core-hole screening effects. Following these arguments, we used two sets of monolayer peaks with the same intensity to get the fitting results in figure 2(b). Furthermore, also our UPS results show a partially filled former LUMO (F-LUMO) for the F₁₆CuPc monolayer on Ag(111) (figure 3(b)). Likewise, also the LUMO of TiOPc gets partially filled in the monolayer (figure 3(a)) and the C 1s core level spectrum of the TiOPc monolayer (figure 2(a)) can be fitted in an analogous way to the F₁₆CuPc monolayer. All shifts of the C 1s components as well as N 1s and F 1s (figure S2) are summarized in table S1 and will be discussed further below. In the heterostructures (figure 2(c)), the C–F component of F₁₆CuPc is well separated from the TiOPc features and shifts by ~0.1 eV to lower BE by increasing the F₁₆CuPc coverage from monolayer (bottom panel) to multilayer (top panel).
The C–C component shifts in parallel, while the C–N component shifts slightly to higher BE. However, as these components overlap with the TiOPc features, their BE positions are not as reliable as those of C–F.

The valence UPS data of TiOPc on Ag(111) (figure 3(a)) are virtually identical to previous data [80, 84]: for nominal monolayer coverage, the HOMO-derived peak is centered at 1.27 eV BE, and a peak near the Fermi edge is assigned to the F-LUMO, which becomes partially populated by charge transfer from the substrate. For nominal bilayer coverage, the intensities of the F-LUMO and the HOMO peaks decrease while a peak centered at 1.62 eV BE emerges, which is attributed to the second layer and shows a further shift by increasing the coverage to multilayers. The VL (as derived from the SECOs, figure S3) decreases by 0.32 eV until bilayer coverage is reached and stays constant upon further increase of the coverage (figure 3(d)).

With minor deposition of F16CuPc (1 Å and 2 Å) on Ag(111), shown in figure 3(b), the HOMO-derived peak is centered at 1.30 eV BE and the HOMO peak at higher BE are visible. The fine structure in the rather sharp HOMO peak can be assigned to stem from hole-vibration coupling [61] and confirms that the F16CuPc monolayer on Ag(111) is well ordered, as was shown previously by means of scanning tunneling microscopy (STM) [92–94]. With more F16CuPc deposition the intensity of the HOMO peak increases and a small peak near the Fermi edge (0.11 eV), which can be assigned to the HOMO, gains intensity and submerges beyond nominal monolayer coverage. Strikingly, for monolayer coverage the formerly faint peak centered at 1.77 eV BE has almost the same intensity as the HOMO-derived peak (at 1.30 eV BE). For multilayer coverage, only one broad peak at 1.94 eV BE is apparent, which is in accordance with previous multilayer F16CuPc/Ag(111) UPS data [95]. Overall, the thickness-dependent evolution of the valence band spectra is similar to F16CuPc/Au(111) [88] and to perfluorinated pentacene/Ag(111) [87] but different to CuPc/Ag(111) [96]. This demonstrates the decisive impact of the intramolecular polar C–F bonds on the electronic structure as will be discussed in more detail further below.

For the heterostructures, TiOPc bilayers on Ag(111) have been prepared by thermal desorption of multilayers (figure S1). The valance band spectra of F16CuPc/TiOPc/Ag(111) are shown in figure 3(c): upon stepwise deposition of F16CuPc the intensity of the TiOPc HOMO-derived peak attenuates gradually and still remains clearly visible for nominal F16CuPc multilayer coverage. The F16CuPc HOMO-derived peak on bilayer TiOPc/Ag(111) is centered at approximately 2.00 eV BE for all thicknesses (from 1 Å to 4 Å). By initial F16CuPc deposition the VL (figure 3(d)) stays constant at 4.32 eV up to a thickness of 4 Å and shifts gradually to 4.51 eV by further F16CuPc deposition.

4. Discussion

In order to discuss the electronic structure of the interfaces according to effects #1 to #6 mentioned in the introduction, we show growth models based on literature data in the top panel of figure 4. In the TiOPc monolayer on Ag(111) the molecules show a TiO-up orientation and form a highly ordered checkerboard structure [11, 97]. The second layer shows a TiO-down orientation [80], which leads to antiparallel molecular dipole moments as shown in figure 4(a); in multilayers also two-dimensional TiO-up and down layer-by-layer formation takes place [81, 83]. For F16CuPc on Ag(111) (figure 4(b)) the molecules adopt a bent conformation in the monolayer, with the central copper atom being located at a lower position and the fluorine atoms being adsorbed at a higher vertical position, as experimentally determined [88, 98] and shown by density functional theory (DFT)-modeling [92]. It is reasonable to believe that the molecules remain in their planar gas phase conformation from the second layer onwards. Furthermore, STM studies indicate a well-ordered monolayer structure with the molecules in the second layer being located at the bridge positions of the first layers and a 45° rotation between the molecular axes [92–94] and STM also indicates layer-by-layer growth of the first and second layers [93]. For the heterostructures, it was shown that fluorinated hexazatrinaphthylene and perylenetetracarboxylic dianhydride show both an ordered growth on CuPc monolayer on Ag(111) is well ordered, as was shown previously by means of scanning tunneling microscopy (STM) [92–94]. With more F16CuPc deposition the intensity of the HOMO peak increases and a small peak near the Fermi edge (0.11 eV), which can be assigned to the HOMO, gains intensity and submerges beyond nominal monolayer coverage. Strikingly, for monolayer coverage the formerly faint peak centered at 1.77 eV BE has almost the same intensity as the HOMO-derived peak (at 1.30 eV BE). For multilayer coverage, only one broad peak at 1.94 eV BE is apparent, which is in accordance with previous multilayer F16CuPc/Ag(111) UPS data [95]. Overall, the thickness-dependent evolution of the valence band spectra is similar to F16CuPc/Au(111) [88] and to perfluorinated pentacene/Ag(111) [87] but different to CuPc/Ag(111) [96]. This demonstrates the decisive impact of the intramolecular polar C–F bonds on the electronic structure as will be discussed in more detail further below.

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The UPS and XPS results are schematically summarized with ELDs in the bottom panel of figure 4. In each case, the work function of the Ag(111) substrate as well as the HOMO and F-LUMO level position and the respective core levels (including the different components due to chemical shifts) of the organic layers are displayed. For the single-component systems, the values are taken from the spectra of organic layers with nominal monolayer coverage (QCM thickness: 4 Å), nominal bilayer coverage (QCM thickness: 8 Å) and multilayer coverage (QCM thickness: 64 Å). For the heterostructure, the energy levels of the annealed TiOPc bilayer and these of subsequently deposited F16CuPc layers with QCM thicknesses of 4 Å and 48 Å are shown. In our ELDs we use the peak maxima for valence and core levels, although in literature ELDs often the onset of the HOMO-level is used, as it is the relevant parameter for charge transport and injection [101–103].
Figure 4. Schematic growth models (top panel) and energy level diagrams (bottom panel) of the investigated thin films. The growth models show side views of the thin films and are based on literature data as described in the text. The energy values of the ELDs are based on the respective peak maxima of our UPS and XPS measurements. In each ELD on the left the Ag(111) substrate with its work function and Fermi-level ($E_F$) is displayed. For the molecular thin films, the position of the HOMO, the F-LUMO and the core levels are shown. For the single-component systems, monolayer (1 ML), bilayer (2 ML) and multilayer coverage are shown and for the heterostructure monolayer and multilayer $F_{16}CuPc$ on a bilayer TiOPc is shown.

However, the determination of the onset can be ambiguous, in particular if spectral signatures from different layers overlap, e.g. in the spectrum of the 8 Å thick $F_{16}CuPc$ film on Ag(111) in figure 3(b).

The electronic structure of TiOPc deposited on Ag(111) indicates a clear chemisorption behavior (effect #5): the chemical shift between C–C and C–N decreases from 1.55 eV in the multilayer to 1.30 eV in the monolayer, which is a tell-tale sign for chemisorption [18, 38]. Furthermore, the LUMO-derived feature in the monolayer is clearly visible and well below the Fermi-level of the metal substrate. This is due to electron transfer from the substrate into the LUMO. Such a directed charge transfer leads to an interface dipole, which should increase the VL (effect #2) and the dipole layer of the monolayer with TiO-up orientation should additionally increase VL (effect #3). However, the VL decreases by 0.18 eV and it can be concluded that the push-back (effect #1) dominates the position of the VL for monolayer coverage. The subsequent decrease of the VL upon bilayer formation is due to the dipole layer of TiOPc in the TiO-down orientation (effect #3). Notably, this VL-shift does not affect the position of the HOMO-level and the core levels: for the TiO-up orientation the molecular dipole moments are located above the main molecular plane comprising all of the carbon and nitrogen atoms. Consequently, the C 1s and N 1s core levels (and likewise the HOMO-level) are not significantly affected by the molecular dipole layer [40]. For the bilayer system the dipole layers are located between the two molecular main planes and cancel each other. Further deposition of TiOPc leads to a shift to higher BE of both, the valence band and core levels, due to the screening (effect #4) at the organic–metal interface. Overall, even for this structurally well-characterized system [80, 81, 83, 84, 100, 104], a quantitative assignment of the shifts remains challenging, since too many contributions occur concomitantly: the shift of the HOMO between mono- and bilayer has a screening, a chemisorption and a molecular dipole contribution; the VL-shift is affected by the push-back effect, charge transfer and the molecular dipole moments, which first increase (TiO-up) and then decrease (TiO-down) the VL. Furthermore, adsorption induced bond-length changes can alter the molecular dipole moment in the contact layer to a metal substrate [105, 106].

For $F_{16}CuPc$ on Ag(111), as shown in figure 4(b), the VL at the organic–metal interface is affected by the contributions of push-back (effect #1), charge transfer (effect #2) and adsorption induced molecular dipole...
moment (effect #3) (the fluorine atoms are 0.20 Å above the carbon atoms [98]). The absence of a notable interface dipole is, most likely, due to a larger net electron transfer from the substrate compared with the TiOpc/Ag(111) system. The monolayer to bilayer BE-shifts of the HOMO-level and the C 1s components (C–C, C–N and C–F) are between 0.4 eV and 0.6 eV and these non-rigid shifts are, again, mainly due to chemisorption (effect #5). Interestingly, the F 1s core level shifts only by 0.1 eV to higher BE, which might be related to the 45° rotation between the molecules in 1 ML and 2 ML [92–94], which affects the electrostatic contribution to polarization (effect #6) in the respective layers. From bilayer to multilayer, the VL stays almost constant and the core levels shift rigidly by 0.1 eV to higher BE while the HOMO-level shift amounts to almost 0.2 eV. These shifts might still have a screening (effect #4) contribution and, furthermore, the molecular packing structure in bilayer and multilayer might be different, which affects the intermolecular polarization (effect #6). The disparity of energy-level shifts measured by UPS and XPS is related to the different information depths: by UPS only the topmost layer is probed while XPS probes almost the entire organic thin film.

For the heterostructure, figure 4(c), the TiOpc layer is obtained by a desorption process, which leads to a well-ordered bilayer [82, 83], which explains the slight difference to the bilayer in figure 4(b). With deposition of F_{16}CuPc molecules the HOMO-level of TiOpc shifts to lower BE, which is due to intermolecular polarization (effect #6). The HOMO-level of F_{16}CuPc is centered at 2.04 eV BE and does not show a thickness-dependent shift. The VL shifts upwards with increasing F_{16}CuPc coverage, which is, most likely, due to pinning of the F_{16}CuPc LUMO-level at E_F [51–54]. Interestingly, despite the absence of charge carriers, Fermi-level pinning can take place at organic–organic interfaces and leads to a potential drop over the contact layer and direct charge transfer from the second layer to the (metal) substrate [32]. The constant HOMO-position and the shifting VL highlight an important difference in VL and valence energy-level determination by UPS for laterally inhomogeneous samples (i.e. F_{16}CuPc islands on the TiOpc layer): for common experimental setups, the VL is the area-averaged mean of local surface potentials (i.e. the covered and uncovered TiOpc-patches), while all valence electron features (i.e. HOMO-levels of F_{16}CuPc and TiOpc) of the probed sample area appear in the spectra [31]. Consequently, great care has to be taken for IE determination and in general thin films with multilayer coverage give the most reliable IEs: the F_{16}CuPc multilayer IEs in the single-component systems (6.56 eV) and the heterostructure (6.55 eV) are virtually identical and in particular the IE in the contact layer to the metal substrate (5.88 eV) is far too low, which is due to the screening effect and the chemisorptive behavior. Notably, F_{16}CuPc does not show such chemisorptive behavior on the TiOpc buffer layer, i.e. this layer actually decouples F_{16}CuPc from Ag(111), and the organic TiOpc layer can be regarded as a dielectric layer. Such spacers change chemisorption-driven fractional charge transfer (partially filled F-LUMO) at the organic–metal interface into electrostatically-driven integer charge transfer across the dielectric layer as was also previously shown using inorganic spacer layers [107, 108].

5. Conclusion

Virtually all optoelectronic applications rely on well-matched energy levels throughout the device structure and ELDs are central to explain device performance. Often literature values are used for ELDs and vacuum-level alignment across all layers is assumed, which, however, is rather the exception than the rule. Consequently, experimental energy-level alignment determination is indispensable for organic device design and our results give guidelines how to interpret XPS and UPS data of organic–metal and organic–organic interfaces. In particular, usually more than one spectrum is necessary to obtain a full picture of interface energetics. For example, at first glance the UPS data of the F_{16}CuPc monolayer on Ag(111) points to weak interaction (due to the constant VL). However, in fact chemisorption involving an organic–metal charge transfer and adsorption induced conformational changes takes place, which is unraveled by additional UPS data and, in particular, by the core-level shifts measured by XPS. In case extensive photoelectron spectroscopy measurements are not possible or literature values are used, multilayer IEs are most suitable for ELDs of device structures.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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