1. Introduction

Ultrathin films of dielectrics on metals constitute a fascinating class of materials, as they can exhibit unusual properties that are found in neither of the bulk phases of the two compound materials. This can be due to the stabilization of novel phases with unusual structures and stoichiometries.[1] However, even without such changes, the mere presence of the overlayer may lead to significant alteration of the substrates’ electronic properties. For instance, ultrathin MgO(100) films on Ag(100) or Mo(100) are known to promote charge transfer into adsorbates via tunneling. Beginning with Pacchioni’s seminal theoretical paper on the prediction of charge transfer,[2] several studies, in particular of adsorbed Au atoms and clusters,[3] but also for some small molecules such as NO$_2$,[4] H$_2$O,[5] and O$_2$[6] have supported this proposal. It has been realized that in addition to the thickness of the dielectric, the reduction of the work function of Ag by the MgO film in combination with a sufficiently high electron affinity of the adsorbate will be the most important parameters for charge transfer to occur, as these factors determine the energy level alignment. While charge transfer has been discussed for the MgO(100)/Ag(100) system mainly in the light of promoting catalytic activity,[6,7] conceptually similar aspects will be significant at the interfaces of hybrid inorganic/organic optoelectronic devices.

Due to its critical importance to charge injection and thus organic device performance, there have been numerous studies on the energy level alignment of organic films on different substrates with different work functions.[8] These have led to the consensus that, for any particular organic film, there are two regimes which can be related to whether there is charge transfer at the interface or not: The Fermi-level pinning and vacuum-level alignment regimes. These were inferred by simple measurements of the work function of the substrate before and after formation of the organic film. In the case of vacuum level alignment, where no charge transfer occurs, the electronic levels of the organic layer and thus the final work function (Φ$_{\text{f}}$) shift linearly with the work function of the clean substrate (Φ$_i$). In contrast, in the Fermi level pinning regime, the organic film always leads to the same final work function (pinning work function, Φ$_{\text{pin}}$) irrespective of the substrate work function and the molecular levels always appear at the same binding energy with respect to the Fermi level (E$_F$). Here, charge transfer is inferred. However, from where the charge originates (dielectric or metal), whether it is integer or fractional, and the equilibration mechanism that leads to the constant final work function are still in question.[8c-d,9]

In this study, we investigate the charge transfer into the model organic semiconductor pentacene (5A) on ultrathin MgO(100) films epitaxially grown on Ag(100). We show that the work function of MgO(100)/Ag(100) can be tuned over a large range. This allows us to decouple the parameters that govern charge transfer to 5A and to quantify the number of charged molecules both as a function of work function and oxide interlayer thickness. Identification of the frontier molecular orbitals reveals that Fermi level pinning is realized within a single monolayer by the adaptation of the portions of two molecular species—singly charged and neutral—with very distinct electronic

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Whether intentional or unintentional, thin dielectric interlayers can be found in technologies ranging from catalysis to organic electronics. While originally considered as passive decoupling layers, recently it has been shown that they can actively promote charge transfer from the underlying metal to adsorbates. This charging can have profound effects on the surface chemistry of atoms, atomic clusters, and molecules, their magnetic moments, and charge injection at the contacts of organic devices. Yet, controlled studies required to understand the charge transfer process in depth are still lacking. Here, a comprehensive analysis of the phenomenon of charge transfer using the atomically controlled system of pentacene on ultrathin MgO(100) films on Ag(100) is presented. It is shown that the charge transfer process is governed by the charged and uncharged molecular species with distinct energy levels in the first monolayer. The experimental approach applied in this work allows to observe and control their ratio through direct tuning of either the work function or the thickness of the dielectric interlayer.
surface. At positive sample bias, imaging the unoccupied states, the lowest unoccupied molecular orbital (LUMO) can be clearly identified by its nodal structure (Figure 1, corresponding to the Fermi level, in the new film all molecules again display LUMO appearance of the frontier orbitals). While above vacuum levels, rod-like molecular appearance at intermediate negative bias ($U_{\text{bias}} = -1.5$ V) and faintly visible HOMO appearance at higher negative bias ($U_{\text{bias}} = -2.0$ V). The image recorded with $U_{\text{bias}} = -3.2$ V was taken at a different spot on the surface and shows coexisting molecules with HOMO and LUMO appearance. All STM images were taken at 77 K. c) Iso surface depiction of LUMO and HOMO of 5A as obtained from DFT.

After desorbing 5A and increasing the work function of the same 2 ML MgO(100)/Ag(100) film and therefore shifting it toward the vacuum-level alignment regime (high $\Phi_i$), newly adsorbed 5A molecules have the same orientation as on the low-$\Phi_i$ film. However, there is a distinct change in the appearance of the frontier orbitals (Figure 2b). While above the Fermi level, in the new film all molecules again display the nodal structure of the LUMO (Figure 2b, $U_{\text{bias}} = +1.5$ V), below $E_F$ ($U_{\text{bias}} = -1.5$ V) the molecules show no orbital structure. Instead, at higher negative bias voltages ($U_{\text{bias}} = -2.0$ V), the nodal structure of the highest occupied molecular orbital (HOMO) becomes faintly visible. This reflects the behavior of neutral (uncharged) 5A molecules. Significantly, as can be seen in the STM image taken with $U_{\text{bias}} = -3.2$ V (Figure 2b, on a different area on the surface), among the molecules some also have a LUMO appearance. This suggests that on the high-$\Phi_i$ films, the majority of molecules is neutral and coexists with a minority of singly charged molecules.

2. Results and Discussion

By altering the composition at the buried MgO(100)/Ag(100) interface, we can control the work function of the MgO(100)/Ag(100) substrate from 2.3 to 4.4 eV (see Experimental Section and Supporting Information S1). Being able to tune the work function of MgO(100)/Ag(100), without changing its surface structure or composition, opens the possibility to study the phenomenon of charge transfer to adsorbed molecules across dielectric films in detail. Figure 1 displays the measured final work function ($\Phi_f$) of 5A monolayer (ML) films deposited on MgO(100)/Ag(100) of different initial work function ($\Phi_i$) for MgO(100)/Ag(100) of different initial work function ($\Phi_i$) for MgO(100)/Ag(100).

Molecular-scale insight into the morphology and electronic details of interfacial 5A molecules can be gained with scanning tunneling microscopy (STM) by imaging of their frontier orbitals. STM images of 5A deposited on a 2 ML MgO(100)/Ag(100) film with low $\Phi_i$, corresponding to the Fermi-level pinning and vacuum-level alignment regimes, giving rise to the $\Phi_f$ versus $\Phi_i$ relationship often observed for organic semiconductor films. [8c]

Figure 1. Fermi level pinning and vacuum level alignment regimes of 5A/MgO(100)/Ag(100). Final work function after 5A deposition ($\Phi_f$) as a function of the initial work function of the clean MgO(100)/Ag(100) substrate ($\Phi_i$). The line with a slope of unity expresses the Schottky–Mott limit of vacuum level alignment ($\Phi_f = \Phi_i$). The horizontal lines correspond to different pinning work functions of MgO films with different thicknesses. 2 ML MgO corresponds to a thickness of 4.21 Å.
Together, the STM results indicate that, depending on $\Phi_i$, both singly charged and neutral molecules can exist on MgO films with identical thickness. This already suggests that it is the balance of integer charged and uncharged molecules that controls the potential equilibration in the Fermi-level pinning regime. To confirm this hypothesis, to quantify the charge transfer processes, and to show that it can be ultimately controlled, we move to angle-resolved ultraviolet photoemission spectroscopy (ARUPS). Here, we take advantage of the fact that the photoemission intensity distributions of the HOMO and LUMO of 5A are very distinct and understood within photoemission tomography (see Supporting Information S2), which allows to assign the emissions to particular molecular states, selectively probe them and quantify the amount of transferred charge.\[11]\n
### 2.1. Controlling the Number of Charged Molecules via Work Function

Figure 3a shows the evolution of the photoemission spectrum in the MgO bandgap with increasing 5A dose on an 8 ML MgO(100)/Ag(100) film with $\Phi_i = 2.7$ eV. The most intense molecular feature can be identified as the former LUMO by its photoemission intensity distribution. This orbital is singly occupied and will thus be referred to as the SOMO henceforth.\[11]\n
Its intensity grows with the 5A dose, while its binding energy (BE) with respect to $E_F$ decreases slightly. Saturation is reached at a dose of about 2 Å at a BE of 0.7 eV on this specific MgO film. As shown in Figure 3b, the work function rises with increasing 5A dose, reaches 3.5 eV at 2–2.5 Å, corresponding to 1 ML coverage, and stays constant above 1 ML. The corresponding work function change is approximated by a homogenous 2D negative charge density ($-\sigma$) within the molecular monolayer and a corresponding dielectric constant $\varepsilon_r$ and charge transfer distance $d_{cs}$ in the capacitor model. (From left to right: metal, dielectric, molecules.)

Having established that $I_{SOMO}$ reflects the number of singly charged 5A molecules, we can then determine how this number changes as $\Phi_f$ is varied across the Fermi level pinning regime. Figure 3d shows a set of ARUPS spectra taken from the same 8 ML MgO film but with different $\Phi_f$, after adsorption of a 5A monolayer. For all these spectra, the BE of the SOMO is the same, so Fermi level pinning is directly observed. Notably, this pinning relative to $E_F$ occurs even though the SOMO is measured not at $E_F$, but 0.7 eV below it. As $\Phi_f$ is increased, the intensity of the SOMO peak decreases (Figure 3d). This implies that the number of charged (uncharged) molecules decreases (increases) when the transition point from Fermi-level pinning to vacuum-level alignment is approached. Our results suggest a gradual variation in the ratio of charged and uncharged molecules, which is proportional to the potential difference across the oxide thin film induced by the charged molecules, expressed by $\Delta \Phi = \Phi_f - \Phi_i$ (Figure 3e).

On a macroscopic level, this behavior can be described with a simple capacitor model illustrated in Figure 3f. Assuming that for the 5A/MgO(100)/Ag(100) system the transferred charge originates from the metal/oxide interface, the charge distribution is approximated by a homogeneous 2D negative charge density ($-\sigma$) within the molecular monolayer and a corresponding final work function is the pinning work function ($\Phi_{pin}$) and is the same irrespective of the initial work function, if $\Phi_f < \Phi_{pin}$ (Figure 3b). The work function rise is a result of the dipole created through charge transfer and can be expected to be proportional to the number of charged molecules.\[9a,13\] Hence, we expect the integrated SOMO intensity ($I_{SOMO}$, from Figure 3a) to be linearly proportional to the induced work function change ($\Delta \Phi = \Phi_f - \Phi_i$, Figure 3b), and this is indeed the case as shown in Figure 3c.e.

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positive charge density at the metal/oxide interface ($+\sigma$). From simple electrostatic relations, it follows that (Equation (1))

$$\Delta \Phi = \frac{\sigma (d_{\text{dil}} + d_0)}{\varepsilon_0 \varepsilon_r} - \frac{\sigma d_s}{\varepsilon_0 \varepsilon_r},$$

where $\Delta \Phi$ is in eV and $\sigma$ is in C m$^{-2}$. $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the dielectric constant of the dielectric thin film, and $d_s$ is the charge separation distance, which is given by the dielectric thickness $d_{\text{dil}}$ and $d_0$, the height of the transferred charge (and its mirror) above (below) the dielectric. From theoretical considerations, $d_0$ is estimated to be around 2 Å (see Supporting Information S3).

### 2.2. Controlling the Number of Charged Molecules via Dielectric Film Thickness

So far we have kept the dielectric thickness constant and have not considered its role in charge transfer. According to the capacitor model (Equation (1)), if the charge originates from the metal support, the same charge density $\sigma$ will produce a larger $\Delta \Phi$ when the dielectric thickness increases. Given there is a pin that cannot be exceeded, the number of integer-charged molecules must decrease with increasing dielectric thickness.

In order to test this prediction, we prepared MgO films with different thicknesses (2, 4, and 8 ML), and tuned their work functions to values that would result in similar $\Delta \Phi$ upon 5A deposition and then compared the SOMO intensities of 5A monolayers on them. Corresponding ultraviolet photoelectron spectroscopy (UPS) spectra in the geometry of the SOMO maximum are shown in Figure 4a.

Indeed, the intensity of the SOMO and therefore the number of charged molecules decreases proportionally to the increasing MgO thickness. A reasonably large data set for the three different thicknesses with a range of initial work functions and 5A doses is summarized in Figure 4b. This plots the SOMO peak intensity ($I_{\text{SOMO}}$), which is directly proportional to the number of charged molecules, against the induced work function change. Each dielectric thickness yields a linear relationship with the slope ($I_{\text{SOMO}}/\Delta \Phi$) inversely proportional to the charge transfer distance $d_{\text{CS}}$, as expected from the capacitor model (Equation (1)). Note that the results presented in Figure 4b suggest that $\Delta \Phi = -0.15$ eV in the limit of zero charged molecules on the surface. This offset results from a small work function decrease, caused by a weak Pauli repulsion (push-back effect) between uncharged 5A molecules and the MgO surface.

As on MgO films grown under standard conditions, all molecules appear charged in STM, it is reasonable to assume that on 2 ML MgO(100)/Ag(100) with low $\Phi_i$, all molecules are charged ($I_{\text{SOMO, max}}$ in Figure 4b). With the knowledge of the molecular density of 1 ML 5A from STM (inset to Figure 4a), which is 0.68 nm$^{-2}$, we are now able to evaluate the results in a more quantitative way. Rearranging Equation (1) and inserting the values for $\sigma$ and $d_{\text{CS}}$ for the different film thicknesses gives an $\varepsilon_r = 5.4$ (2 ML MgO), 5.4 (4 ML MgO), and 6.0 (8 ML MgO) for our 5A/MgO(100)/Ag(100) system (another approach to calculate $\varepsilon_r$ from 5A uptake curves is presented in the Supporting Information S4). With the average $\varepsilon_r$ value, we calculate and plot in Figure 4c the $1/d_{\text{CS}}$-dependence of the number of charged molecules (expressed as the fraction of charged molecules in a 5A monolayer) for a set of $\Delta \Phi$ values. Note that under the inverse relationship between charge transfer distance and transferred charge, it would take very large dielectric thicknesses in order to effectively stop charge transfer. We have been able to grow 16 ML MgO films of reasonable quality and charged molecules could still be observed in UPS. This means the tunneling probability is still high enough, so that a thermodynamic equilibrium can be reached within the timescale of the experiment. Once an equilibrium is reached, it is purely electrostatics that determines the density of charged molecules.

We have thus shown that the simple capacitor model is well-suited to describe the number of charged molecules and that the origin of the transferred charge indeed lies at the Ag–MgO interface. DFT, using a generalized gradient approximation (GGA) employed for the exchange correlation, arrives

![Figure 4. Relation between MgO thickness and charge transfer. a) ARUPS spectra in the SOMO geometry for 1 ML 5A on MgO films with thicknesses of 2, 4, and 8 ML (from top to bottom) on Ag(100) with $\Phi_i$ leading to similar $\Delta \Phi$ (inset: STM image of a full monolayer 5A on 2 ML MgO(100)/Ag(100), 10 nm × 10 nm). b) Plot of SOMO intensity versus $\Delta \Phi$ for MgO films of 2, 4, and 8 ML thickness (different 5A doses and initial work functions) extracted from ARUPS data. Linear fits represent $I_{\text{SOMO}}/\Delta \Phi \sim \varepsilon_r/d_{\text{CS}}$. $I_{\text{SOMO, max}}$ corresponds to 100% charged molecules in the 5A monolayer. c) Graphical representation of the fraction of charged molecules in the 5A monolayer as function of $d_{\text{CS}}$ and $\Delta \Phi$ according to the capacitor model.](image-url)
at a pinning work function in agreement with the experimental values (Supporting Information S3). However, it does not get there through the correct mechanism. Instead of integer charge transfer to some molecules, DFT invokes a net fractional charge transfer to all molecules. This is due to the tendency of semilocal approximation for exchange-correlation to overly delocalize electrons. A way to overcome this problem and arrive at a situation with coexistence of integer charged and uncharged molecules has recently been suggested.[13]

2.3. Level Alignment of Uncharged Molecules

We finally turn our attention to the spectroscopic signature and level alignment of uncharged 5A molecules. Their presence can be inferred from the suppression of the MgO substrate emissions and the offsets in the plots in Figures 3e and 4b. However, it is difficult to identify emissions from uncharged molecules in ARUPS a priori, when charged molecules are also present. Therefore, we focus on the transition region around $\Phi_{\text{pin}}$ (Figure 5a), in this case for 2 ML MgO(100)/Ag(100) with $\Phi_{\text{pin}} = 3.75$ eV. UPS spectra of 5A films grown on these films are shown in Figure 5b. The measurement geometry corresponds to the HOMO maximum for flat lying molecules. For the spectra at $\Phi_i < \Phi_{\text{pin}}$, the HOMO of the charged molecules (HOMO*) is seen at 1.8 eV BE and the HOMO-1* at about 3.0 eV BE. With increasing $\Phi_i$, the emission intensity from the HOMO* decreases until it is extinguished at $\Phi_i > \Phi_{\text{pin}}$, while the emission in the region of HOMO-1* remains. This emission now has the angular distribution of the HOMO, which is slightly different from HOMO-1*[14] and is thus identified as the HOMO of the uncharged species. For $\Phi_i > \Phi_{\text{pin}}$, the HOMO emission shifts rigidly with $\Phi_i$ (Figure 5b), as expected for vacuum-level alignment of uncharged molecules. For $\Phi_i < \Phi_{\text{pin}}$, the levels of the uncharged 5A molecules present on the surface also appear to be aligned with $E_F$. This is a natural consequence of the constant (global) surface potential in the pinning regime.

It is worth noting that X-ray photoelectron spectroscopy, generally considered the technique of choice for recognizing and quantifying charged species, could not differentiate between charged and uncharged pentacene. This is reasonable as one electron in the LUMO is shared by 22 carbon atoms and little chemical shift would be expected.

3. Conclusion

The molecular level behavior observed for adsorbates on thin dielectric interlayers is schematically summarized in Figure 6. Quantum mechanical tunneling results in integer charge transfer with the number of adsorbates charged being controlled by the dielectric thickness and the work function of the dielectric on the metal substrate. The latter could be tuned over a large range by changing the composition at the dielectric–metal interface, allowing a detailed investigation of the transition from vacuum level alignment to Fermi level pinning.

In the vacuum level alignment regime, where $\Phi_i$ is greater than $\Phi_{\text{pin}}$, the adsorbed molecules remain uncharged and the work function is not affected apart from a small reduction through push-back. In the Fermi level pinning regime, where...
\( \Phi \) is smaller than \( \Phi_{\text{pin}} \), charge transfer to the molecules occurs. A work function increase proportional to the amount of transferred charge is induced. This process continues until \( \Phi_{\text{pin}} \) is reached, where upon no further charge transfer can occur. As the frontier molecular orbitals could be identified and quantified, this equilibration process could be shown to be facilitated by the proportions of singly charged and neutral molecules in the first adsorbate layer and does not require the often invoked band bending in the molecular film to be taken into account.\(^{[8,9]} \)

The magnitude of \( \Phi_{\text{pin}} \) will be directly related to the electron affinity (EA) of the adsorbate. However, EA is not a material constant as it is increased by the polarization response of the adsorbates’ environment. The EA in the gas phase of SA is 1.4 eV, while the pinning work function on MgO/Ag is considerably higher (3.45–3.75 eV). As dielectric thickness decreases, the polarization response is expected to increase, leading to a higher EA and \( \Phi_{\text{pin}} \) as evident in Figure 1 due to the proximity of the underlying metal and a higher ionic polarizability of the MgO film.

As the dielectric thickness increases, the number of charged molecules decreases. This behavior is a natural consequence of the increase in the local potential, as the dipole length of charged molecules and their image charges in the underlying metal increase. Having understood the controlling parameters of the charge transfer process at the molecular level, it is worth considering it at a macroscopic level. The simple relationship observed between the number of integer-charged molecules, the dielectric thickness and the change in the work function can be described very well in terms of a simple capacitor model. The results show that our model system follows closely the ideal behavior, where the charge originates solely from the underlying metal, as opposed to defects or gap states in a dielectric that have been invoked for many systems.\(^{[13]} \)

The understanding gained here applies likewise for electron and hole transfer and is applicable to other dielectric and semiconductor thin films, supported 2D van der Waals layers, and adsorbates including atoms, clusters, molecules, and polymers. It demonstrates, how the charge transfer and level alignment is controlled and opens the way to tune the chemical and electronic properties of adsorbates in desired directions.

4. Experimental Section

**Experimental Details:** Experiments were performed under UHV conditions with a base pressure of about 3 \( \times \) 10\(^{-10} \) mbar. The Ag(100) crystal was cleaned by three to four cycles of Ar\(^+\) sputtering and annealing at 800 K. MgO films were grown by Mg evaporation in an oxygen environment. Mg fluxes used were of the order of 1 Å min\(^{-1} \) as monitored by a quartz microbalance. The MgO deposition was done at a temperature of 540 K and in an O\(_2\) pressure of 10\(^{-7} \) mbar. MgO deposition was followed by slow cooling (roughly 2.5 K min\(^{-1} \)), the accepted procedure for the growth of epitaxial MgO(100) films.\(^{[10-16]} \)

One monolayer of MgO is defined as a single atomic layer, i.e., half a bulk unit cell or 2.105 Å. Work functions, measured from the secondary electron cutoff in photoemission, could be reduced by annealing in UHV or further Mg exposure while annealing. The work function could be increased by O\(_2\) exposure (5 \( \times \) 10\(^{-7} \) to 2 \( \times \) 10\(^{-4} \) mbar) at moderate temperatures. Monitoring the work function during this post-preparation allowed a close control of this parameter. As the work function tuning happened at the buried interface, it was more difficult to modify the work function of thicker films over a large range. Pentacene (5A) was deposited at a rate of 0.8–3 Å min\(^{-1} \) at room temperature. When the 5A thickness was described in Angstroms, a density of 1 g cm\(^{-3} \) was assumed. After 5A deposition, clean MgO(100)/Ag(100) could be reobtained by flashing to 640 K. This allowed the experiments to be performed on the exact same thickness MgO film with different work functions.

Details of the ARUPS setup and identification of molecular orbitals can be found in Hollerer et al.\(^{[11]} \) Binding energies (BE) were defined relative to the Fermi level (\( E_F \)). Spectra were taken at room temperature in experimental geometries that yielded the maximum photoemission intensity of either the HOMO or the LUMO (occupied by charge transfer). For the HOMO, this geometry was corresponded to a polar angle of 48° along \([001]\), the LUMO had its maximum emission at about 44° along \([001]\). Intensities of molecular photoemission features were determined by subtracting the background measured prior to the adsorption of the molecules and determining the area of the peak.

STM measurements were performed at 77 K with a low-temperature STM attached to a ultrahigh-vacuum preparation chamber (base pressure 2 \( \times \) 10\(^{-10} \) mbar) using electrochemically etched tungsten tips. The bias was applied to the sample, and during scanning on SA surfaces, the tips were never intentionally functionalized.

**Computational Details:** The electronic structure calculations for 5A monolayers adsorbed on MgO(100)/Ag(100) were carried out using a repeated slab approach. The substrate was modeled by five metallic layers and MgO films ranging between 2, 4, or 8 MLs. Using the 5A azimuthal orientation and adsorption site as described in ref. \([11]\), and a vacuum layer of 15 Å, the structures were fully relaxed, fixing only the bottom three Ag layers, by employing a CGA\(^{[17]} \) for exchange-correlation combined with the vdW-surf method\(^{[18]} \) to account for van der Waals interactions. Further computational details are identical to those used in ref. \([11]\).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

dielectric constants, integer charge transfer, tunneling, ultrathin films, work function

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