1. Introduction

The characteristics of essentially all organic electronic devices are dominated by the interfaces between their constituents. In organic electronics, such interfaces occur in different “flavors”: between organic semiconductors (OSCs) and dielectrics (e.g., in thin-film transistors), between different OSC layers in multilayer stacks of organic light-emitting devices and solar cells, between OSCs and their inorganic counterparts in hybrid devices (e.g., hybrid solar cells), and between OSCs and (often metallic) electrodes in all devices that need to interface with outside circuits. The following discussion will evolve around the electronic properties of such interfaces, where crucial parameters are the energetic alignment between the electronic states in the materials constituting the interface and adsorbate-induced variations of the work function. In particular, we will discuss how these properties are fundamentally modified by dipolar layers present at the interface.

Therefore, after briefly addressing the role of interfaces in organic (opto)electronic devices in Section 2, Section 3 will focus on the fundamental impact of regular arrangements of dipoles on the electrostatic energy of a charge carrier (at this stage mostly without referring to actual materials). This discussion will form the basis for all aspects described later in this paper. In Section 4, we will apply the developed concepts to understand the electronic properties of interfaces and how they are impacted by polar layers. Section 5 will then be dedicated to discussing the origin of polar layers at interfaces, which either arise from the adsorption of polar molecules or from interfacial charge rearrangements due to the deposition of an organic adsorbate layer. When such interfacial charge transfer occurs, one also often enters the realm of Fermi-level pinning, which results in several unusual interface properties. For example, the work function of the combined system becomes independent of the work function of the substrate. Then, the presence of dipolar layers at the interface may no longer influence its electronic properties. Conversely, changes in the adsorbate geometry at the interface may massively impact the system work function, even when the affected molecules a priori do not possess a dipole moment of their own. Section 6 will describe how dipolar layers at interfaces impact physical observables like charge-carrier injection barriers, core-level binding energies, and the electrical conductivity of monolayers. As a last aspect related to the presence of dipolar layers, we will briefly summarize how they can be used to generate new materials with unprecedented properties exploiting the concept of “electrostatic design.”

2. Interfaces in Organic Electronic Devices

Prior to an in-depth discussion of the role of dipolar layers for the electronic properties of interfaces, it is useful to briefly...
remember the diverse role interfaces play in organic electronics.[1,2] As far as the growth of organic semiconductor layers is concerned, the interaction with the substrate controls the growth mode of the organic layer, its texturing, and the size of the formed crystallites.[3–6] In many instances, interfaces even trigger the formation of surface-induced phases, which possess distinctly different structures than the corresponding bulk crystals.[7,8] In electronic devices, charge carriers can be trapped at interfaces. Historically, this significantly delayed the development of n-type organic transistors built on SiO2 dielectrics.[9] More generally, charge-carrier trapping and delayed the development of n-type organic transistors built on SiO2 dielectrics.[9] More generally, charge-carrier trapping and the resulting potential drop across the dielectric layer change parameters like the threshold voltage and can cause hysteresis effects.[10–14] In organic heterojunction solar cells, the energy-level offset at interfaces between regions consisting of electron rich (donating) and electron poor (accepting) molecules provides the driving force for overcoming the comparably large exciton binding energies.[15–17] Particularly complex organic heterostructures are found in organic light-emitting devices, where multiple interfaces between different organic semiconducting materials are exploited (often in conjunction with molecular doping).[18] to facilitate electron and hole injection, carrier transport, and minority carrier blocking.[19,20] Finally, at the interface between OSC materials and electrodes, the energetic mismatch between the respective frontier electronic states results in the formation of energy barriers[1,21–27] that hinder charge-carrier injection and give rise to (injection-limited) contact resistances.[12,28–30]

Most of the abovementioned interface properties can be controlled by dipolar layers. For example, the level offset between donor and acceptor regions in organic (as well as perovskite) solar cells can be tuned by incorporating polar interfacial layers.[31–33] A particularly intensively investigated topic is the modification of electrode work functions and, correspondingly, charge-carrier injection barriers through polar adsorbate layers. Since the seminal works of Campbell et al.,[34,35] self-assembled monolayers (SAMs) with polar groups at their periphery (so-called tail-group substituted SAMs) have been grown on various electrode materials with the intention of tuning electrode work functions and of reducing contact resistances in (opto)electronic devices.[2,36–47] Notably, when applying such SAMs, it has always been difficult to determine whether their beneficial effect resulted primarily from their impact on the growth of the OSC film,[48] or whether induced changes of the electronic properties of the interface played the decisive role. Therefore, recently also SAMs with dipoles embedded into the molecular backbones[49,50] have been successfully employed in organic devices.[49,51] These SAMs allow changing contact resistances by several orders of magnitude without impacting the growth of the OSC, thus demonstrating the crucial role of the layer’s polarity.[51]

SAMs with polar tail groups have also been grown on the dielectric layers of organic thin-film transistors in order to tune the turn-on voltages of the devices.[52,53] Originally, the SAMs’ impact on the device performance has been associated with the dipole moments of the adsorbed molecules and with the electric field inside the adsorbate layer.[52–54] However, as we will argue below, the shifts in the electrostatic energy landscape induced by realistic dipole moments are inconsistent with the observed changes of turn-on voltage, which amount to several ten volts.[51,55,56] Therefore, in the meantime it has been largely accepted that the crucial dipole at these interfaces is not the one associated with the polar substituents of the adsorbed molecules. Rather, the shift in turn-on voltage is caused by the
much larger dipole that forms across the entire dielectric due to trapping of charge carriers at the SAM and their countercharges in the gate electrodes.\textsuperscript{[11,13,14,57]}

These observations show that polar layers play a crucial role for devices. Their exact origin and their detailed properties can, however, sometimes be comparably complex. This has triggered a multitude of dedicated investigations on polar layers beyond employing them in devices and measuring the resulting changes of the device characteristics. Indeed, when aiming at a fundamental understanding of intrinsic interface properties, one typically relies on the key techniques of surface science like photoelectron spectroscopy, scanning probe techniques, and scattering approaches. Such investigations are often performed under ultrahigh-vacuum conditions, either required by the employed techniques or chosen to avoid contaminations and to realize well-defined structures. A drawback of investigating interfaces in ultrahigh vacuum is that such conditions are usually not applied when growing and operating practically relevant devices. In other words, there typically exists a “pressure gap” between surface-science investigations of interfaces and their impact on (opto)electronic devices of practical relevance. Nevertheless, the surface-science investigations are extremely useful, as well-defined and “clean” conditions are crucial for achieving a fundamental understanding of interfaces at an atomistic level. Therefore, in the following we will mostly rely on the insights generated by such experiments and related simulations. Notably, independent of the “pressure gap,” all fundamental aspects discussed below will also hold under typical device fabrication and operation conditions—only the magnitude of the encountered dipole layers might differ between atomically clean and “technical” interfaces (for the reasons discussed in Section 5.2.1).

To conclude this section, we would like to make a final note regarding the relation between the interfacial level alignment determined in surface-science investigations and the efficiency of carrier injection processes in devices: Surface-science studies typically yield the so-called nominal charge-carrier injection barriers determined by the offset of the frontier states in the OSC and the Fermi-level characterizing the electronic properties of the electrode. The effective barrier experienced by charge carriers in an operating device is, however, significantly lower due to the Schottky effect arising from a combination of the electric field at the interface caused by the externally applied bias in combination with the field due to the interaction of the injected carrier with the polarization charge it causes in the conductive substrate.\textsuperscript{[58–61]} This not only yields a massive reduction of the contact resistance, but also results in a pronounced dependence of the contact resistance on device geometry and operation conditions.\textsuperscript{[62,63]} It also renders an explicit consideration of barrier shaping fields crucial when trying to understand carrier injection for actual device structures.

3. Impact of Dipole Layers on the Electrostatic Energy of Electrons

3.1. Densely Packed Dipole Layers

The purpose of this section is to develop a fundamental understanding of the effect of ordered polar layers on the electronic properties of interfaces. For that, it is useful to compare how isolated dipoles, ordered arrays of point dipoles, and sheets of point charges impact the electrostatic energy of electrons in their surrounding (see also refs. \textsuperscript{[64,65]}).

The electrostatic energy of an electron at rest (i.e., without kinetic energy) is typically referred to as the vacuum level. When an electron comes close to a single isolated dipole, the electrostatic energy becomes strongly perturbed, as shown in Figure 1a. Naturally, the perturbation depends on whether the electron is close to the “positive” or “negative” end of the

![Figure 1](image-url)
point dipole. Hence, when the charge is close to the dipole, its energy is significantly impacted by its position. However, at increasing distances the perturbation decays rapidly, such that the exact position of the electron no longer plays a role. Consequently, there is only a single, unique energy associated with the vacuum level.

The situation is fundamentally different when considering extended assemblies of dipoles. This is shown in Figure 1b for the example of an infinitely extended 2D sheet of point dipoles (there, for the sake of simplicity, the dipole moments are arranged in z-direction). As a consequence of the superposition of all electrostatic potentials, i.e., due to so-called collective (or cooperative) electrostatic effects, a step in the electrostatic energy appears at the position of the dipole sheet, \( z_d \).\(^{[64,66–70]} \) This means that the energy of an electron changes when it is moved from left of the sheet (from \( z < z_d \)) to right of the sheet (to \( z > z_d \)). In other words, the step in electrostatic energy results in different vacuum levels left and right of the dipoles. Therefore, the infinitely extended 2D sheet of dipoles splits space into a region left and a region right of the dipole layer with a rigid shift in the relative energetics between the two regions. This has several implications:

i. From the Poisson equation it follows that the magnitude of that step, \( \Delta V_L \), is proportional to the dipole moment per area, \( \mu / \AA \)

\[
\Delta V_L = -\frac{q_e \mu}{\varepsilon_0 \AA} \tag{1}
\]

Here \( q_e \) is the charge of an electron and \( \varepsilon_0 \) is the vacuum permittivity. Only the component of the dipole moment perpendicular to the plane of dipoles determines \( \Delta V_L \), rather than its absolute value. When there are also parallel components, the situation becomes more involved, as then the electrostatic energy also varies as a function of \( x \) and \( y \). In practice, such a situation cannot occur for a dipole layer on top of a metal surface, as there the components of the dipoles parallel to the surface (and the resulting electric field) are fully screened by the conduction electrons of the metal. On semiconductors and dielectrics, the screening of the \( \mu_x \) and \( \mu_y \) components will generally be incomplete. This results in lateral gradients of the electrostatic energy, with the overall shift possible as large as the bandgap. In thermodynamic equilibrium, larger shifts are prevented by additional charge rearrangements in analogy to what has been predicted for polar multilayer films.\(^{[71,72]} \) Alternatively, lateral potential gradients can be prevented or at least mitigated by large-scale surface reconstructions. A further conceivable scenario limiting the lateral variation in electrostatic energy is the formation of domains with differently oriented polarization. To avoid such complications, for the future discussion we will assume that all dipole moments are oriented exclusively in z direction.

ii. Importantly, screening does not only impact the \( x \) and \( y \) components of the dipoles. Quite generally, when realizing dipolar layers via the assembly of polar molecules, the dipole per molecule in the assembly is different from the dipole of the isolated molecule. The reason for that is that each molecule within the layer feels an electric field originating from all other dipoles. This field, which can be calculated employing the Topping model,\(^{[73]} \) induces a polarization that reduces the net dipole moment of each molecule.\(^{[74,75]} \) Such a behavior has been observed both in experiments\(^{[69,76–80]} \) and in simulations,\(^{[64,67,76,81–86]} \) considering a variety of different substrates and adsorbate layers. The magnitude of these depolarization effects depends on the polarizability of the electrons close to the polar element, as well as on the packing density of the dipoles. In this context, it should be emphasized that the relevant polarizability is not the one of the full, isolated molecule. First, even when applying a homogeneous external field, the polarizability of a molecular monolayer significantly deviates from that of a molecule.\(^{[87]} \) Second, the field generated by an extended assembly of dipoles falls off very quickly (for tightly packed molecules, this can be within a few Å).\(^{[64]} \) Thus, the field is highly inhomogeneous and typically not the whole molecule experiences the field from the other dipoles. As a consequence, depolarization is better described by an effective dielectric constant, \( \varepsilon_{\text{eff}} \), such that Equation (1) can be expressed in terms of the dipole moment of the isolated molecule \( \mu_0 \)

\[
\Delta V_L = -\frac{q_e \mu_0}{\varepsilon_0 \varepsilon_{\text{eff}} \AA} \tag{2}
\]

The magnitude of depolarization effects can be sizable: For example, calculations for densely packed biphenylbenzothiol films bearing \( -\text{CN} \) and \( -\text{NH}_2 \) substituents yield values of \( \varepsilon_{\text{eff}} \) around 3.\(^{[83]} \)

iii. As indicated already above, there is virtually no electric field or potential gradient outside a densely packed assembly of dipoles, even at distances shorter than the interdipole distance.\(^{[64]} \) Consistently, the drop in electrostatic energy in Figure 1b is quite abrupt. Figure 2a shows this situation for an actual dipolar SAM consisting of cyano-biphenylthiols on a Au(111) surface: For tightly packed molecules at full coverage (left panel), the \( -\text{CN} \) groups significantly change the vacuum level, but the step in energy is confined to a very narrow region close to the substituents. Consequently, such a densely packed dipole layer will not polarize the substrate as long as it is located sufficiently far away from it. In such a case, there is also no need to invoke mirror charges or mirror dipoles in order to describe \( \Delta V_L \). Conversely, at 1/16th coverage, there is virtually no long-range shift in the electrostatic energy induced by the cyano groups. Instead, significant variations in the electrostatic energy are found in vacuum several Å right of the SAM, as well as in the empty region between the molecules, where they reach down to the metal substrate.

iv. A consequence of the abrupt potential drop for densely packed layers is that dipoles in consecutive layers do not influence each other, provided that the distance between them is sufficiently large. This is shown in Figure 1c for two consecutive dipole layers positioned at three times the distance between the dipoles in each layer. In such a situation, the net shift of the electrostatic energy is simply the sum of the shifts caused by each of the two dipole layers, an effect that has already been observed by Adam et al. in 1934.\(^{[64,89]} \) The main consequence of this aspect is that well-separated layers of dipoles neither polarize nor
depolarize each other. In practice, this allows to functionalize molecules at different positions (e.g., use different head and tail groups), with the net effect of the resulting dipoles being simply additive.\[^90\]

In the above discussion, we have considered point dipoles or dipoles associated with polar substituents of comparably small spatial extent (e.g., the $-\text{CN}$ groups in Figure 2a). The situation changes, when the dipoles are spatially extended. This occurs, for example, when they originate from the charge transfer between a substrate and an adsorbate layer several Å above the topmost substrate atoms (see Section 5.2). The simplest model representing that situation consists of two parallel sheets of point charges of opposite polarity. The field between the charged sheets is essentially homogeneous, provided that the distance between the charges within the sheets is in the same range as or smaller than the distance between the sheets, as is shown in Figure 1c. Outside the charged double layer, there is virtually no field and the electrostatic energy becomes constant. This is analogous to the situation of a charged plate capacitor. Also when the adsorbed molecules undergoing interfacial charge transfer are significantly larger than the adsorption height (i.e., the distance to the substrate), an analogous situation prevails provided that the adsorbate layer is densely packed, that all molecules are equally charged, and that the charge is rather homogeneously distributed within the adsorbed molecule (e.g., when it is transferred to a delocalized $\pi$-orbital). For the aforementioned cases, the linear drop of the electrostatic energy between the charged sheets amounts to

$$
\Delta V_L = -\frac{q_0 \sigma d}{\varepsilon_0} = -\frac{\varepsilon \sigma d}{\varepsilon_0} \quad (3)
$$

Here, $d$ is the distance between the sheets and $\sigma$ is the surface charge density. In cases in which there is a medium between the charged sheets, this can be accounted for in two ways: One can include all polarization charges already into $\sigma$ (e.g., when implicitly accounting for polarization effects in a simulation). Alternatively, one can determine $\sigma_0$, the surface charge density in the adsorbate disregarding the polarization charges in the dielectric. In a second step, one then accounts for the polarization of the dielectric medium via its dielectric constant $\varepsilon_r$. Such a description is particularly useful in more “macroscopic”

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Figure 2. a) DFT calculated electrostatic energy of a CN-substituted biphenylthiolate SAM relative to the substrate Fermi level, $E_F$, in the plane of the molecules for dense packing (left) and at reduced coverage (right). In the latter case, for the sake of the argument, the geometry has been obtained by generating a $4 \times 4$ supercell and removing all but one molecule (i.e., the geometry at reduced coverage has not been optimized). Isolines are plotted every 0.1 eV. b) Transfer characteristics (drain current, $I_D$, as a function of gate-source voltage, $V_{GS}$) of pentacene-based thin-film transistors containing acidic SAMs at the interface between the dielectric and the organic semiconductor. The drain currents are plotted on a linear (left axis) and logarithmic scale (right axis). The three panels correspond to three different thicknesses of the dielectric (100 nm for the top panel, 150 nm for the middle panel, and 250 nm for the bottom panel). The red data points have been measured for the as-fabricated devices (where the acidic SAMs generate an interfacial layer of trapped charges due to the acid residues), while blue data points have been obtained after exposing the devices to NH$_3$ gas (resulting in a compensation of the interfacial space-charge layer). The shift of the turn-on voltage between the two situations (depicted by the green arrow) is due to the dipole layer formed across the interface in the as-fabricated devices. It scales linearly with the thickness of the dielectric. For further details see ref. \[^88\] (b) Adapted with permission.\[^88\] Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA.
cases, for example, when the dipole layer originates from the accumulation of charges on two sides of the gate dielectric in an organic thin-film transistor.

There are two fundamental differences between the two limiting cases of dipole layers consisting of point dipoles and arising from charged double layers: For point dipole layers, the step in electrostatic energy is very abrupt (see above discussion), while for a charged double layer, the energy changes gradually (for a homogeneous medium linearly) between the charged sheets. Moreover, for point dipole layers, the change in electrostatic energy is determined by a single parameter, namely the dipole density. Conversely, for charged double layers, besides the charge density also the distance between the charged sheets plays an important role. This has several consequences: For electron donating or electron accepting adsorbate layers undergoing interfacial charge transfer, establishing thermodynamic equilibrium usually requires a certain system-dependent shift in electrostatic energy (see Section 5.2). In such a situation, increasing the charge transfer distance results in a reduction of the amount of transferred charge and vice versa. Conversely, when the amount of accumulated charge is fixed, changing the charge transfer distance results in an increase of the shift in electrostatic energy. This effect has, for example, been observed in organic thin-film transistors containing reactive (acidic) monolayers at the interface between the dielectric and the organic semiconductor in the transistor channel.[97] There, the proton transfer to the semiconductor generates a fixed density of trapped interfacial charges. They can be compensated by mobile charges in the organic semiconductor (due to the proton-transfer doping).[88] Alternatively, when the mobile charges are removed by depleting the channel, the trapped interface charges induce an accumulation of an equivalent amount of counter-charges in the gate-electrode on the other side of the dielectric. The resulting shift in the electrostatic energy across the dielectric linearly translates into a shift of the device characteristics (see Figure 2b).[11,88] The magnitude of the change in the turn-on voltage of the transistor is then proportional to the thickness of the dielectric, as is indicated by the green arrows in Figure 2b. The net effect can be enormous, as exemplified for the transistor with the thickest dielectric considered in ref. [88] (d = 250 nm), where the shift amounts to more than 100 V.

Finally, it should be noted that yet another type of interfacial charge distribution will become relevant for the following discussion: For extended semiconductor substrates the charge in the semiconductor does not have to be concentrated into a thin (mono)layer, but can spread over a wider region. Within the abrupt junction approximation, that is typically invoked for inorganic semiconductors,[99] this region is proportional to \( \frac{1}{\sqrt{N}} \) (where \( N \) is the amount of immobile charge carriers, e.g., due to ionized dopants). This results in a linear increase of the magnitude of the electric field from the edge of the depletion (accumulation) region toward the interface and, correspondingly, in a quadratic change of the electrostatic energy. This situation is typically encountered in semiconductor pn- or Schottky-junctions. A detailed mathematical description of this band bending can be found, for example, in solid-state physics and semiconductor (device) textbooks (e.g., ref. [91]).

3.2. Finite Extent, Defective, and Inhomogeneous Dipolar Layers

Notably, the above considerations apply only to infinitely extended, defect-free, densely packed dipolar layers. Deviations from such perfect structures have several important implications.

3.2.1. Dipolar Layers of Finite Extent

While the change in electrostatic energy due to a dipole layer of infinite extent can be described by Equations (1)–(3), for dipole sheets of finite extent these equations apply only provided that the distances to the layer are comparably short. For large distances the drop in the electrostatic energy is proportional to \( 1/z^2 \), as the situation approaches that of a point dipole.[21] This is shown in Figure 3a, where we plot the distance dependence of the electrostatic energy for square dipole clusters of varying size. At very short distances, the energy above the center of the cluster is close to the value of the infinitely extended dipole sheet. The shift, however, drops significantly at distances on the order of the lateral extent of the sheet, as can be seen in the linear-log plot in the top panel of Figure 3a. Then, the electrostatic energy displays the expected quadratic drop with \( z \), which results in a linear evolution with a slope of \( \sim 2 \) in the log-log plot (bottom panel of Figure 3a). Another important aspect to keep in mind for finite-extent dipole sheets is that at their boundaries inhomogeneous fields appear. This effect is comprehensively discussed in ref. [64].

3.2.2. Defective Dipole Layers

Conceptually similar considerations as for dipole clusters of finite extent apply to infinite sheets containing finite-size defects. Electric fields and their corresponding potential variations “leak” through the hole in the dipole layer on length-scales that are larger than the extent of the defect. This is shown for a 2D dipole sheet with a hole of \( 6 \times 6 \) dipoles in Figure 3b. Here, it should be mentioned that the plot in Figure 3b assumes all point dipoles to be of equivalent magnitude. In actual, defective polar layers this is not necessarily the case, as the described depolarization effects are weaker for dipoles close to the holes, as well as for dipoles close to the edges of island structures. A more detailed discussion of the resulting “electrostatics of nonideal polar monolayers” can be found in ref. [64].

3.2.3. Inhomogeneous Dipole Layers

Significant deviations from the idealized picture also occur when the dipoles at the interface are far apart from each other. As a hypothetical model scenario, we already described the electrostatic energy distribution for a polar low-coverage SAM in the right panel of Figure 2a. In practice, the molecules in such low-coverage SAMs do, however, not remain upright. They rather “fall over,” which qualitatively changes their electronic properties.[93] Thus, in the following we will use flat-lying molecules, for which the dipole moment originates from interfacial charge transfer, as model systems for describing inhomogeneous dipole layers. In such cases, low dipole densities are
encountered, for example, when a surface is incompletely covered and the molecules repel each other.\[94,95\] Another possibility is the adsorption of extended molecules in which the charge transfer occurs to only a small region of the adsorbate (e.g., in metal-phthalocyanines, if the interfacial charge transfer occurs to only the central metal atom). In such cases, the low dipole density causes a comparably small shift of the vacuum level. Conversely, at the position of the adsorbed molecule, the local dipole has a much larger impact on the electrostatic energy, reminiscent of the situation of an isolated point dipole. This is illustrated in Figure 3c by calculations for tetrafluorobenzoquinone on Ag(111).\[92\] For full monolayer coverage (red line), the electrostatic energy experiences the abrupt step discussed above for densely packed dipoles. It is essentially the same at the position of the molecule, $z_{TFBQ,C}$, and far from the interface. Conversely, at 25% coverage (dashed blue) the shift in electrostatic energy at the position of the molecule, $z_{TFBQ,C}$, is essentially twice as large as the shift of the vacuum level above the surface. A similar situation is obtained, when the surface coverage is complete, but only a fraction of the molecules experience interfacial charge transfer. This occurs, for example, for very weakly coupled interfaces (see the integer charge transfer scenario discussed in Section 5.2.4), or at interfaces at which a fraction of the molecules is chemically modified, e.g., through reactions with a residual gas.\[93\]

3.2.4. Practical Implications of Defective and Inhomogeneous Layers

To assess the practical impact of finite-extent, defective, or inhomogeneous dipole layers, one has to identify which processes and lengthscales are relevant for a given experiment. For example, the nominal barrier for thermionic or tunneling injection of carriers into (opto)electronic devices is determined by the electrostatic energy right above the electrode at the position where the injection occurs. In that case, one is in a “near-surface” situation that is very sensitive to the local electrostatic energy. Similar considerations apply to Kelvin-probe (KP) force

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Figure 3. a) Linear–log and log–log plot of the electrostatic energy of a 2D square cluster of finite extent consisting of point dipoles (calculated above the center of the cluster) as a function of the distance from the cluster. All dipole moments in the sheet are assumed to be oriented perpendicular to the 2D plane and of the same magnitude. The length scale is given in multiples of the interdipole distance, $a$, and the shift in electrostatic energy is plotted relative to the situation obtained for an infinitely extended dipole layer. The considered clusters consist of 10 x 10 (red), 40 x 40 (blue), 160 x 160 (yellow), and 640 x 640 (green) point dipoles. The vertical arrows denote the z-distances from the clusters that equal their $x,y$-extent. b) Spatially resolved change in the electrostatic energy induced by an infinitely extended 2D sheet of point dipoles in which the central

6 x 6 dipoles are missing. The plotting range corresponds to 40–$a$ in the direction parallel and 6–$a$ in the direction perpendicular to the dipole sheet. c) Change of the electrostatic potential energy, $\Delta U$, upon deposition of the strong electron acceptor tetrafluorobenzoquinone (TFBQ) on Ag(111), as a function of the vertical distance from the molecular adsorbate. The red line shows $\Delta U$ for the adsorption of a full monolayer of TFBQ. In that case, the vacuum level above the sample (determined by $\Delta U$ at high $z$) is almost the same as $\Delta U$ at the position of the molecule (at $z = z_{TFBQ,C} = 0$). The blue, dashed line shows $\Delta U$ for a reduced coverage of 25%. There, the potential at $z = z_{TFBQ,C} = 0$ has essentially the same value as in the full monolayer situation (indicating that the molecular levels are shifted just as much relative to the metal). However, due to the loose packing, for larger values of $z$, $\Delta U$ decays to ~50% of its maximum value. The full blue line corresponds to the adsorption of a mixed monolayer of TFBQ and para-tetrafluorobenzodiole (TFBD), a weakly physisorbed molecule. Qualitatively, the situation is equivalent to that for the neat TFBQ film at low coverage (maximum of $\Delta U$ at $z = z_{TFBQ,C} = 0$ and decay to smaller values for larger distances from the surface). A quantitative discussion is given in ref. [92]. Reproduced under the terms of the Creative Commons CC-BY license.\[93\] Copyright 2015, American Chemical Society.
microscopy measurements.\cite{96-99} Also in X-ray photoelectron spectroscopy (XPS) experiments, the relevant quantity is the local electrostatic energy around the atom at which the core electron is excited.\cite{100,101}

The “near surface” quantities are likewise relevant, when performing conventional KP measurements, or when determining the secondary cutoff (SECO) in photoelectron spectroscopy experiments. For the SECO this is because the dipoles create a potential barrier near the surface, which needs to be overcome. This barrier (rather than the electrostatic energy at the detector) determines the lowest kinetic energy electrons that are able to leave the sample. These define the energetic position of the SECO.\cite{102}

As KP and photoemission average over comparably large areas, they are, however, rather insensitive to local lateral variations in the electrostatic energy. Therefore, only a single cutoff (corresponding to the average electrostatic energy at the surface) is detected, even when lateral inhomogeneities extend over several nm.\cite{103} Only for rather extreme lateral energy variations, a second cutoff can be observed.\cite{104} For such a situation (in this case encountered for a patterned surface with a periodicity of several µm), Schultz et al. have shown recently that one of the two cutoffs corresponds to the area-averaged value of the electrostatic energy, while the second one is determined by its maximum.\cite{105}

Interestingly, in some cases defects and deviations from the perfect periodicity in polar adsorbates are even crucial for adsorbed polar layers to have an impact: For example, it has been argued that in Schottky junctions, in which the metal and the semiconductor are separated by a polar organic layer containing pinholes, the dependence of the current through the pinholes on the dipole orientation arises from stray fields in the defective SAM.\cite{64} Also the impact of adsorbed polar monolayers on the electric current in silicon devices\cite{66,106} has been associated with charge transfer triggered by residual fields.\cite{64} For further details on the role of molecular monolayers within metal/semiconductor junctions, we refer the interested reader to the recent dedicated review by Vilan and Cahn.\cite{107}

4. Electronic Structure of Inorganic/Organic Hybrid Interfaces

Prior to discussing the possible origins of dipolar layers at interfaces, it is useful to briefly review the fundamental aspects of the electronic structure of organic–inorganic heterostructures, and how they are impacted by dipolar layers. Here, as a first step, it is useful to discuss the electronic properties of the individual components that will eventually form the heterostructure.

4.1. Properties of the Sub-Systems Forming the Interface

4.1.1. Metal Substrates

The most relevant parameter describing the electronic properties of a metal in the present context is its work function, \( \Phi \) (see Figure 4a). It represents the energy to add/remove an electron to/from the metal and can be described as the energy difference between the Fermi level of the metal and the vacuum level. As discussed in Section 3, the vacuum level is defined as

the energy of an electron at rest infinitely far away from the metal. Its position is independent of the path along which the electron is removed. In contrast to the situation at infinity, the vacuum level near the metal surface does depend on the actual orientation of the surface through which the electron is ejected.\cite{21} For example, for tungsten the vacuum level measured for the (110) surface is 0.62 eV higher than that of the (100) surface.\cite{108} This is a consequence of the spill-out of electrons from the metal surface, which extends over several Å\cite{109} and creates a dipole layer that shifts the energy landscape (and with it the vacuum level) above the surface. The magnitude of that spill-out depends on the packing density of the metal atoms in the top layer and, thus, on the exposed surface. Due to the finite lateral extent of the metal substrate, upon increasing the distance from its surface the surface vacuum level gradually merges into the vacuum level at infinity, as discussed in Section 3.2.1 (see Figure 3a). Notably, the quantity relevant for the following discussion of the interface energetics is the vacuum level directly above the metal. In the following, the energy difference between this energy level and the Fermi level will be referred to as the work function of the substrate, \( \Phi_{\text{sub}} \).

4.1.2. Inorganic Semiconductor Substrates

The key quantities for semiconductors are the electron affinities (EA) and ionization energies (IE) of the material, i.e., the energies gained when adding an electron and paid when removing an electron from the semiconductor. Within a single-particle picture (and for the discussion throughout this paper), they are approximated by the positions of the valence and conduction band edges. In practice, (almost) all semiconductor substrates are doped. Therefore, they exhibit a Fermi level that will typically deviate from the mid-gap position. As for metallic substrates, the energetic distance between the Fermi level and the vacuum level defines the substrate’s work function, \( \Phi \). Notably, the positions of the Fermi level and the band edges relative to the vacuum level above the sample can again be modified by the presence of surface dipoles. Such dipoles occur, e.g., due to different surface reconstructions and terminations. A common example are hydrogen overlayers, which saturate the dangling bonds at a cleaved surface.\cite{110} Moreover, significant electric fields can be present within thin films of polar semiconducting substrates,\cite{111-115} where the field originates from the asymmetry of the unit cell. Notably, the presence of surface states due to dangling bonds at the semiconductor surface or due to (geometric) surface reconstructions can change the density of mobile carriers in the semiconductor close to the interface. The resulting net charge density (e.g., due to uncompensated ionized dopants) locally causes an electric field, which gives rise to surface band bending \( \Delta \Phi_{\text{BB}} \) (cf., discussion in Section 3).\cite{211} Therefore, akin to the role of surface dipoles for the work function of a metal, the band bending plays a crucial role for the effective work function of the substrate \( \Phi_{\text{sub}} \), also for semiconductors, as indicated in Figure 4b. Importantly, the presence of band bending leads to different energetic positions of the band edges in the bulk viz-a-viz the surface: Ionization energy and electron affinity in the bulk (defined as the energies of the band edges relative to the vacuum level outside the
Figure 4. Schematics of the electronic structure of a) a metal substrate, b) an inorganic semiconductor substrate including surface band bending, c) an isolated organic molecule, and organic monolayers consisting of molecules with d) zero or e) nonzero net dipole moments. The various indicated quantities are explained in detail in the main text. Shaded orange areas correspond to states in the metal substrate and in the semiconductor, while blue areas correspond to orbitals or bands in the organic molecules and monolayers. Dark shading refers to occupied and light shading to unoccupied states. The horizontal arrow in (b) symbolizes the dipole layer associated with band bending.
sample) are increased (in the case of upward band bending, as shown in Figure 4b) or reduced (for downward band bending) by $\Delta \Phi_{BB}$. Conversely, at the very surface the positions of the bands relative to the vacuum level remain unchanged by $\Delta \Phi_{BB}$ (as indicated by $E_{A\text{SC}}$ and $I_{E\text{SC}}$ in Figure 4b). The local shift of the bands, however, modifies their distance from the Fermi level, which is consistent with the change in the free-carrier density close to the surface.

In the present context it is important to emphasize that the semiconductors used as transparent electrodes for organic optoelectronic applications are typically highly doped wide-bandgap semiconductors, like indium-doped tin oxide (ITO), ZnO, or GaN. Due to their large ionization energies, they are often (involuntary) n-type doped. This leads to states in the bandgap close to the band edges, albeit with a very low density. Often, the actual situation in such wide-bandgap semiconductors is not well described with a single kind of dopant. Rather, a more realistic scenario is to invoke shallow donors (e.g., due to hydrogen uptake) and deep donor levels (e.g., from surface oxygen vacancies, which are prevalent in transparent conductive oxides). As a consequence, the band bending cannot assume arbitrary values (limited only by the magnitude of the bandgap), as one would expect for conventional semiconductors. Instead, band bending due to ionized shallow donors only occurs until it shifts the levels of the deep donors into resonance with the Fermi level. At this point, the deep donors become electronically active, effectively increasing the amount of available charge carriers. In practice, the result of this effect is that the observed values for band bending tend to be much smaller than one would expect in the absence of the deep donor states. Accordingly, also the band-bending region becomes much narrower than what would be predicted when only considering the density of shallow donors. Although this means that the abrupt junction approximation may often not be well justified for these semiconductor materials, in lieu of a better model it is still frequently used in simulations.

4.1.3. Organic Semiconductors

For discussing the electronic properties of molecular organic semiconductors, it is useful to start with the underlying molecular properties, like the molecular ionization energy, $I_{Emol}$, and the molecular electron affinity, $E_{Amol}$ (see Figure 4c). Their difference defines the fundamental gap, $F_{G\text{mol}}$. This quantity is not to be confused with the excitation gap measured in optical absorption experiments, which is smaller by the exciton binding energy. In molecules the exciton binding energy is sizable due to weak electrostatic screening and it remains large also in organic solids (amounting to several tenths of an eV up to ~1.6 eV).

Generally, one has to distinguish between vertical and adiabatic energies, where the latter includes the energy gained by the geometry relaxation of the charged systems. Consequently, adiabatic $I_{Emol}$'s are smaller and adiabatic $E_{Amol}$'s are larger than vertical ones. Whether one has to consider vertical or adiabatic values depends on the process of interest. For example, for quasi-instantaneous photoionization processes the relevant quantities are the vertical ones. Conversely, whether in thermodynamic equilibrium charge-transfer processes occur is determined by the adiabatic quantities.

When the molecules form a (hypothetical) free-standing monolayer (or a molecular crystal) several effects occur, which modify the quantities discussed above (see Figure 4d)

i. In addition to the geometry relaxation effects, also dielectric screening within the monolayer stabilizes the charged species. Thus, screening increases the electron affinity and reduces the ionization energy. Electrons and holes within the monolayer get dressed and form quasi-particles, which drag a polarization cloud along. The resulting changes in energy are typically on the order of 1–2 eV for OSC bulk materials, both experimentally and in simulations.

ii. Due to the interaction between neighboring molecules, bands of finite width form. As the $I_E$s and $E_A$s are defined based on band edges, this again reduces $I_E$s and increases $E_A$s. The effects described in (i) and (ii) also decrease the fundamental gap of the monolayer, $F_{G\text{ml}}$, compared to the isolated molecule.

iii. An additional aspect that is often overlooked but absolutely crucial for interfaces is that also in molecular layers, surface dipoles exist. These arise mostly from polar bonds in the molecular periphery, which can be due to polar substituents, peripheral heteroatoms, or even C–H bonds (which are also polar). When ordered molecular assemblies are formed and there is a nonvanishing dipole component perpendicular to the surface of the layer, a step in electrostatic energy occurs, which shifts the molecular states relative to the vacuum level. In the following, it will be referred to as the surface dipole of the monolayer, $S_{D\text{ml}}$ (cf., Figure 4d). Notably, this surface dipole shifts the occupied and unoccupied states in the same direction and, thus, does not change the fundamental gap of the monolayer. As $S_{D\text{ml}}$ depends on the orientation of the molecules in the monolayer, changing that orientation also changes the monolayer ionization energies and electron affinities, $I_{Emol}$ and $E_{Amol}$. In passing, we note that a finite $S_{D\text{ml}}$ also exists for disordered layers, since the surface dipoles at the periphery of organic molecules sometimes point in the same direction largely independent of the molecular orientation (e.g., for pure hydrocarbons, all C–H dipoles point outward). Thus, even after averaging over random orientations, a local net dipole at the surface of the organic layer often persists.

The impact of surface dipoles in organic molecules has been shown, for example, for the ionization energy of a $\alpha,\omega$-dihexyl-sexithiophene, which can be changed by ~0.6 eV solely by varying the orientation of the molecules in the monolayer. Furthermore, calculations by Heimel et al. on highly ordered poly(3-hexylthiophene) monolayers suggest that varying the orientation of the polymer chains changes the monolayer $I_E$s and $E_A$s by 0.4 eV, while for partially fluorinated side chains the magnitude of effect not only more than quadruples, but the shift also changes its sign. For layers consisting of equivalent molecules with different terminations, changing their ratio even allows tuning the ionization energy of the monolayers. In all examples discussed in this paragraph, the dipoles at the left and right “surface” of the monolayer are the same. Thus, the net dipole
moment of the monolayer vanishes and the vacuum level left and right of the layer has the same value (see Figure 4d).

The situation changes qualitatively when the SD$_{ml}$ to the left and to the right of the monolayer are no longer identical. This is, for example, the case for “classical” self-assembled monolayers, in which the docking group (on the left side of the schematic monolayer in Figure 4e) is chemically different from a structural group substituent (on the right side). Then the adsorbate layer corresponds to two successive dipole layers, whose effects no longer cancel and, thus, induce a shift in the vacuum level, $\Delta V L_{int}$ between the left ($VL_{left}$) and right ($VL_{right}$) side of the monolayer (Figure 4e). Importantly, in such a situation the monolayer ionization energies and electron affinities are no longer unambiguously defined. One now needs to differentiate between left- and right-sided quantities, as removing an electron from the monolayer to the left and to the right costs different amounts of energy. The same rationale applies to the gain in energy upon adding an electron (see Figure 4e).

Finally, the role of the Fermi level of the organic semiconductor layer shall be discussed briefly. For an (admittedly hypothetical) intrinsic OSC layer it is in the middle of the fundamental gap also at finite temperatures, due to the very narrow valence and conduction bands. Because of the large bandgaps typically encountered in OSC materials, the position of the Fermi level will, however, vary significantly, even when only minute amounts of charge are transferred or when the layer is only weakly contaminated by electrically active impurities. Therefore, we will refrain from basing the following considerations on the Fermi level of the OSC and its equilibration with the substrate Fermi level. Nevertheless, it should be mentioned that the related charge-neutrality level has been employed successfully for understanding interfacial level alignment in the framework of the induced density of interface states (IDIS) model. This works because in the IDIS model, one does not rely on the density of states (DOS) of the undisturbed semiconductor, but considers the formation of hybrid states due to the interaction between substrate and adsorbate.

### 4.2. Electronic Structure of Interfaces

#### 4.2.1. Metal–Organic Interfaces

A useful gedankenexperiment for understanding the properties of a metal–organic interface is to start from the individual components discussed above (the metal substrate and the free-standing monolayer). As a first step, one then aligns their vacuum levels, where for polar monolayers like the one depicted in Figure 4e, the vacuum level facing the substrate (i.e., the “left” vacuum level) is the one to be used. Assuming that the two constituents do not otherwise influence each other (i.e., in the Schottky–Mott limit, SM, see Figure 5a,b), the level alignment expressed by the electron- and the hole-injection barriers, $E I B_{SM}$ and $H I B_{SM}$ is simply given by

$$E I B_{SM} = \Phi_{sub} - E A_{ml} \quad \text{and} \quad H I B_{SM} = I P_{ml} - \Phi_{sub}$$

The net work function of the combined system in the Schottky–Mott limit, $\Phi_{SM}$, becomes

$$\Phi_{SM} = \Phi_{sub} + \Delta V L_{ml}$$

Consequently, for the adsorption of a layer with no net dipole moment (cf., Figure 5a), $\Phi_{SM}$ and $\Phi_{sub}$ are identical, i.e., the work function change $\Delta \Phi$ is zero.

When switching on the interaction between substrate and adsorbate,

i. Screening effects are massively increased. This results in a sizable bandgap renormalization for adsorption on metals as well as on insulators. Consequently, the electronic parameters of the adsorbate layer are again modified, leading to the interface-specific quantities $E A_{int}$ and $I P_{int}$. Note that the bandgap renormalization decreases roughly with one over the distance of the adsorbate layer from the mirror-image plane of the metal substrate, as can be shown by electrostatic image-charge self-energy corrections assuming perfect screening by the metal surface.

ii. Eventual chemical interaction between substrate and adsorbate results in the formation of hybrid bands, which increases the effective bandwidths of the states derived from the organic semiconductor. The magnitude of that effect strongly depends on the type of interaction, as will be discussed below.

iii. Changes in the geometry of the adsorbate (e.g., due to interfacial charge rearrangements or due to molecular distortions triggered by the formation of bonds between substrate and reactive groups in the adsorbate—see below) can also modify the ionization energies and electron affinities of the adsorbate layer as well as the step in electrostatic energy across the layer, $\Delta V L_{int}$.

iv. Most importantly, there will always be interfacial charge rearrangements, whose origin will be discussed in the following section. While the effects described in (i)–(iii) are usually directly attributed to the molecule (thus replacing $\Delta V L_{ml}$ with the corresponding quantity at the interface, $\Delta V L_{int}$), the consequences of interfacial charge rearrangements for the energetic level alignment are often collected into the so-called bond dipole (BD). Strictly speaking, for the present considerations, BD also contains changes in electrostatic energy associated with geometric rearrangements of the metal substrate. Here, mere relaxations of the substrate geometry typically have only a comparably minor impact. Conversely, surface reconstructions, such as the appearance of adatoms can play a more dominant role.

Note that BD, by definition, includes all image-charge and image-dipole effects, both due to the bonding as well as, in principle, due to molecular dipole moments. We, however, emphasize that provided that $\Delta V L_{int}$ arises from densely packed dipoles at sufficient distance from the substrate surface (e.g., dipoles due to polar tail-group substituents in self-assembled monolayers), there is no such dielectric screening of the molecular dipoles by the metal substrate (cf., Section 2).

The key consequence of the bond dipole is that it causes a shift in the energy landscape, as discussed in Section 2. This is schematically shown in Figure 5c,d. Thus, the work function of the combined interfaces is given as

$$\Phi = \Phi_{sub} + \Delta \Phi = \Phi_{sub} + BD + \Delta V L_{int}$$
where we adopt the sign convention that a bond dipole that reduces $\Phi$ is counted as negative.$^{[21]}$ Note that Equation (6) assumes that the bond dipole drops essentially between the substrate and the adsorbate, i.e., it is spatially separated from $\Delta V_{\text{int}}$. In practice, Equation (6) can also be used as the equation defining the bond dipole. This is, e.g., done in density-functional theory simulations.$^{[65,70,90]}$ The situation becomes more complex, when there is no clear spatial

Figure 5. Energy level alignment at interfaces between an organic semiconductor and a–d) a metal or e) an inorganic semiconductor. The situations depicted in panels (a) and (b) correspond to the Schottky–Mott limit (vacuum-level alignment), while panels (c)–(e) show the equilibrium situation including the bond dipole, BD, and in the case of the semiconductor substrate also a possible change in the band bending $\Delta BB$. Notably, for the metal substrate (panels (c) and (d)), we here assume a situation in which no electrons are transferred into the unoccupied states of the adsorbate layer (i.e., in which the electron affinity of the adsorbate layer is not sufficiently large). The case including charge transfer and the resulting Fermi-level pinning situation will be discussed in detail for the adsorption on metals in Section 5.4. Conversely, for the semiconductor substrate (panel (e)) such charge transfer is assumed as a prerequisite for the discussed (significant) increase of the band bending in the inorganic semiconductor. To obtain that charge transfer, we consider the adsorption of a strongly electron accepting layer with a large electron affinity achieved in part by inverted surface dipoles of the monolayer compared to the situation depicted in Figure 4d (and assumed in Figure 5a,c). In all schematics, the adsorption of organic monolayers is considered, such that band-bending effects within the adsorbate layer can be neglected. The various indicated quantities are explained in detail in the main text. Shaded orange areas correspond to states in the metal substrate and in the semiconductor, while blue areas correspond to states or bands in the organic monolayers. Dark shading refers to occupied and light shading to unoccupied states.
separation between the charge rearrangements causing BD and the groups bearing the molecular dipoles. This might occur, for example, for the adsorption of flat-lying polar molecules. In such cases the two dipoles from Equation (7) will couple and influence each other. This can massively change the adsorbate-induced work-function modification, as will be discussed in detail below in the context of Fermi-level pinning.

Overall, this yields the following expressions for electron- and hole-injection barriers at metal–organic interfaces\(^{[65,70,90]}\)

\[
E_{\text{IB}} = \Phi_{\text{sub}} - E_{\text{A inf}} + \text{BD} \quad \text{and} \quad H_{\text{IB}} = E_{\text{B inf}} - \Phi_{\text{sub}} - \text{BD}
\]

(7)

Importantly, for the adsorption of polar molecules, again the electron affinity and ionization energy on the side of the monolayer facing the interface (i.e., the “left” quantities) are the relevant ones.

### 4.2.2. Interfaces between Organic and Inorganic Semiconductors

For such interfaces, the situation is complicated by the band bending within the inorganic semiconductor discussed in Section 4.1.2. Notably, as sketched in Figure 5e, neither the original surface band bending nor its modification through an adsorbate change the alignment between the frontier states in the organic semiconductor and the band edges of the inorganic semiconductor right at the interface. Moreover, the adsorption of physisorbed or covalently bonded molecules causes only very local charge rearrangements, which do not notably affect the surface band bending\(^{[85,154]}\), unless the surface chemistry is substantially altered (e.g., by the removal of hydroxyl groups).\(^{[135]}\) For the adsorption of organic electron acceptors on n-type or electron donors on p-type materials, however, the semiconducting nature of the substrate can have a tremendous impact. Provided that the adsorbate depletes charge carriers (i.e., electrons or holes) at the surface and in the bulk, this results in an additional band bending, \(\Delta \text{BB}\), within the semiconductor substrate, can be found in ref. \([115]\). [135] Importantly, the physics that leads to the formation of the BD (between the substrate and the adsorbate) and the band bending \(\Delta \text{BB}\) (within the substrate) are related, as both occur due to charge transfer and the ensuing shift in the electrostatic energy. Hence, both terms must have the same sign. Moreover, in a combined system there is no clear definition where the substrate ends and the adsorbate beings. Hence, there is some ambiguity as to how to partition the total interface dipole between these two terms.\(^{[123]}\) For the present discussion, and as shown in Figure 5e, it is most useful to define \(\Delta \text{BB}\) as the change of the substrate bands relative to the Fermi level (implicitly assuming that there is no hybridization between the molecular and the substrate states, which would make this distinction impossible).

The adsorbate-related change of the semiconductor work function then arises from the modification of the band bending due to the interfacial charge transfer, \(\Delta \text{BB}\), the bond dipole at the interface, BD, and potentially a shift in the vacuum energy due to intrinsic dipoles of the adsorbate layer in the configuration it assumes at the interface, \(\Delta V_{\text{Lint}}\). The resulting equation reads

\[
\Delta \Phi = \Delta \text{BB} + \text{BD} + \Delta V_{\text{Lint}}
\]

(8)

If one was rather interested in the work-function change due to the interface as a whole (i.e., relative to a semiconductor with flat bands), \(\Delta \Phi’\), one also needs to consider the band bending prior to deposition of the adsorbate, \(\Delta \Phi_{\text{BB}}\), and Equation (8) becomes

\[
\Delta \Phi’ = \Delta \Phi_{\text{BB}} + \Delta \text{BB} + \text{BD} + \Delta V_{\text{Lint}}
\]

(9)

The overall situation (here assuming a strongly electron accepting adsorbate layer without an intrinsic dipole) is depicted in Figure 5e. A more in-depth discussion of the electronic structure of the interfaces between organic semiconductors and ZnO, as a prototypical example for an inorganic semiconductor substrate, can be found in ref. \([115]\).

### 4.2.3. Organic Monolayers versus Multilayers and Doped Films

The above considerations focus on adsorbing a single organic monolayer. Therefore, band bending within the OSC has so far not been considered for establishing the energetics of the interface. In order to understand (potential) band bending in organic multilayers, it is useful to first consider the situation for Schottky contacts between metals and inorganic semiconductors.\(^{[91]}\) There, one finds that the width of the depletion layer, over which the band bending occurs, is proportional to \(1/\sqrt{N}\) (where \(N\) is the space charge density in the depletion layer, which, within the abrupt junction approximation and in the saturation regime of doping, corresponds to the doping density). This implies that for very small doping concentrations the band bending occurs over comparably large distances. Consequently, for thin films that are smaller than the depletion layer, the band bending is essentially “cut off,” i.e., only the part of the band bending that fits into the spatial extent of the thin film is realized. Following these arguments, also for nominally undoped organic thin films, which are not excessively defective or where the defects are not electronically active, the shift of the electronic states that occurs within a few ten nm from the electrode (as the typical thickness of OSC layers in devices) becomes negligibly small.

This suggests that band bending in organic semiconductors beyond the first monolayer is primarily relevant for less ideal situations, e.g., for (intentionally or unintentionally) doped organic semiconductors\(^{[156,157]}\) or when dealing with materials having defect- or disorder-induced states in the gap.\(^{[158]}\) For example, Ishii et al.\(^{[159]}\) observed depletion-layer widths of ~100 nm for C_{60}/metal interfaces, while they found flat bands when using N,N’-bis(3-methylphenyl)-N,N’-diphenyl-1,1’-biphenyl-4,4’-diamine (TPD) as semiconductor. These flat bands they attributed to the high purity of the used TPD. Band bending for nominally pristine organic semiconductors has also been observed, when studying various interfaces with conjugated polymers\(^{[160-165]}\) and when separating the metal from the organic semiconductor using an insulating alkali-halide layer.\(^{[166]}\) In such cases, this is typically explained by the filling of electronic states in molecules at some distance from the interface.\(^{[161,162,166,167]}\) Energetically, these states are found “tailing” into the nominal gap and they are typically attributed
to structural imperfections and defects.\[^{161,168-171}\] Notably, this band bending due to the accumulation of additional carriers in the OSC beyond the first monolayer is fundamentally different from the “conventional” band bending described above for (doped) inorganic semiconductors. There, the necessary space-charge region typically does not arise from accumulating additional carriers but is rather the result of a depletion of mobile carriers leaving behind uncompensated charged dopants.

An instructive semi-quantitative analysis of the origin and implication of the accumulation-triggered band bending at interfaces has been presented by Oehzelt et al.\[^{172}\] They self-consistently modeled the formation of an accumulation-generated space-charge layer and the resulting band bending for different shapes and widths of the density of states in the OSC material. Consistent with the band bending arising from charge transfer into states tailing into the nominal gap, the extent of the band bending in their model crucially depended on the assumed shape of the DOS. For actual interfaces the latter is determined by the prevalence of defects and the degree of interaction between substrate and adsorbate. Overall, this suggests that for multilayer organic films band bending (with a spatially extended region of electrostatic energy variation) is favored for weakly interacting systems and when there is a small but non-negligible density of states in the nominally forbidden gap.\[^{172}\] Conversely, for highly pure, defect-free organic semiconductors and for strongly coupled interfaces at which the density of states is broadened significantly,\[^{138-140}\] the interfacial potential change is restricted essentially to the first adsorbate layer.\[^{172}\] In passing we note that an effect not considered in the model by Oehzelt et al. that might modify the actual situation is that charge transfer beyond the first monolayer goes into molecules, for which the larger distance from the substrate results in a reduced screening. This gives rise to smaller electron affinities and larger ionization energies, which increases the energetic cost for charge transfer beyond the first monolayer. Notably, such distance-dependent polarization effects have also been suggested as an alternative explanation for the dependence of the ionization energy on the thickness of the adsorbate.\[^{173}\]

When band bending in an OSC layer occurs, the total interface dipole can be decomposed into a bond dipole at the immediate metal–organic interface and the energetic shift caused by the band bending.\[^{167}\] This situation is analogous to that discussed above for inorganic semiconductor substrates. Like there, one needs to distinguish between the energetic offsets between electronic states directly at the interface and those far away from it. Again, the former offset remains unaffected by band bending, while the latter is significantly modified.\[^{172}\]

An interesting special case here are organic/organic heterojunctions. It has been argued\[^{177}\] that there, the level alignment may not be determined directly by interfacial charge rearrangements. Rather, the heterojunction is in thermodynamic equilibrium with a substrate that acts as charge reservoir. In appropriate material combinations (e.g., when first an inert material and then a strong electron acceptor is deposited on a metal), charge flows from the substrate—across the “first” organic material—into the second organic material. As a result, there is a homogenous potential drop in the first organic material, and a charge accumulation with the corresponding band bending in the second organic layer (see Figure 6).\[^{117}\] Notably, in these cases, the evolution of the electrostatic potential depends strongly on which of the organic materials is in direct contact with the substrate surface, which is a possible explanation, why the level alignment in organic heterojunctions changes if the order in which the organic materials are deposited is changed.\[^{26,174-177}\]

Finally, it should be noted that “conventional” band bending can be realized via intentional redox-doping of the organic

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Figure 6. Charge accumulation (bottom panel) and level alignment (top panel) of an organic/organic heterojunction in contact with a low work-function electrode (\(E_F = 2\) eV). The substrate ends at \(z = 0\), the first organic material extends from 0–10 nm, and the second organic material from 10–20 nm. In the top panel, the orange boxes denote the valence bands, the blue boxes the conduction bands, and the solid black line the evolution of the vacuum level linked to the electrostatic potential. Both organic materials are electron acceptors. The second organic material is a stronger electron acceptor, indicated by its lower conduction band. In thermodynamic equilibrium, little charge is transferred to the weak acceptor, while a larger amount of charge is transferred to the strong acceptor. This gives rise to the more extended space charge region in that material (see blue regions in the bottom panel). The corresponding potential evolution (top panel) shows a quasi-linear increase within the weak acceptor and levels off with a strong parabolic evolution in the strong acceptor. Reproduced under the terms of a Creative Commons Attribution 4.0 International License. Copyright 2015, The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science.
semiconductor,[18,178,179] which results in a sharply reduced depletion-layer widths.[180,181] An in-depth discussion of doped adsorbate layers, however, goes beyond the scope of the present review and we refer the reader to recent, more specialized papers.[182–185]

5. Dipole Layers and Interfacial Charge-Rearrangements

The next aspects that need to be discussed are the possible origins of the interfacial dipole layers, which cause the shift of the electrostatic energy. So far, we have described primarily the two sources of more macroscopic origin, band bending and charge trapping.

In the present section we will focus on the origins of much more local, microscopic dipoles with an extent of at the most a few Å. As summarized in Figure 7, such dipoles can originate from polar functional groups that are part of the adsorbed molecules, or they arise from interfacial charge transfer processes like the omnipresent Pauli pushback, charge rearrangements due to the formation of covalent bonds, or because of the adsorption of strongly electron donating or accepting molecules. In the latter case one has to distinguish between so-called fractional and integer charge transfer, both of which commonly result in Fermi-level pinning.

5.1. Adsorption of Polar Molecules

One possible source of dipolar layers at interfaces is the adsorption of molecules containing polar bonds and/or polar functional groups. To align them in an ordered fashion in configurations with a net dipole moment, typically self-assembly processes in combination with anisotropic bonding to the substrate are employed. The latter is needed to overcome the repulsion between neighboring parallel dipoles and often relies on the formation of strong (covalent) bonds between the substrate and functional docking groups attached to the adsorbed molecules.[33,47,49,50,133–136,186,187] Covalently bonded SAMs complicate, for example, thiolute[186,189–194] and selenolate-docked molecules[195–198] on noble metals, or phosphonates[186,188,199–201] and silanes on oxides.[13,14,52,53,57,188,201] A review of the properties of such layers also beyond the aspects discussed here can, for example, be found in refs. [36,202–204].

For cleverly designed structures, also weaker interactions, e.g., arising from van der Waals, vdW, forces can be sufficient to align molecules such that their intrinsic dipoles are parallel.[78–80,205–207] This requires a molecular shape, where one particular molecular orientation has a larger adsorption energy than all others. Such a situation can, for example, be realized for shuttle-cock shaped phthalocyanine-based systems or for porphyrins and phthalocyanines bearing axial polar substituents.[78–80,205–207] An example for such a situation is shown in Figure 8, where for the Cl-up orientation of GaCl-phthalocyanine (GaCl-Pc) the vdW-contact area between substrate and adsorbate is maximized. For the less favorable Cl-down orientation, the vdW attraction to the surface results in a significant distortion of the molecular backbone. Due to the larger average distance between the atoms in the substrate and those constituting the adsorbate it also causes a significantly reduced interaction energy.[208] In spite of the small van der Waals energy per atom, this effect is significant due to the resulting large van der Waals contact areas comprising a sizable number of atoms per molecule. In passing we note that for a priori less planar sub-phthalocyanines bearing polar Cl–B groups, the van der Waals attraction to the surface is even strong enough to essentially planarize the molecules with profound consequences also for the electronic properties of the adsorbate.[209] Interestingly, besides polar molecular systems, also polymers bearing polar groups have been successfully applied as surface modifiers to produce a variety of low work function electrodes.[210]

A particularly intriguing example of polar, van der Waals aligned adsorbate layers is encountered at the interface between polar phthalocyanines and graphite. Upon depositing OTi-phthalocyanine (OTi-Pc), CIAL-phthalocyanine (CIAL-Pc), or OV-phthalocyanine (OV-Pc), Fukagawa et al. observed the buildup of a sizable surface dipole during the formation of the first molecular monolayer. An equivalent observation has been made by Blumenfeld et al. for the adsorption of OV-naphthalocyanine on the same substrate.[206] The dipole arises from a parallel alignment of the polar OTi/CIAL/OV groups in the molecules in direct contact with the graphite surface.[206] As shown in Figure 9, this results in a linear shift of the vacuum level to higher energies relative to the Fermi level with increasing CIAL-Pc coverage (up to an effective coverage of ≈0.36 nm; see white ellipse). When continuing the growth, the net dipole moment of the adsorbate disappears due to the antiparallel alignment of the molecules in the second layer (up to a nominal coverage of 0.7 nm).

Figure 7. Overview of the origins of interfacial dipole layers at inorganic–organic interface.
An aspect to keep in mind when molecules are deposited on comparably reactive surfaces is that their chemical integrity on the surface is not necessarily guaranteed. For example, tris(8-hydroxyquinolino)aluminum (Alq₃) has been reported to decompose on Ca[211] and partial decyanation has been observed for tetracyanoquinodimethane (TCNQ) derived molecules on Cu(100).[212] For the adsorption of polar molecules a partial decomposition upon adsorption might then result in the loss of the polar group. This has been observed, e.g., for phthalocyanine-derived molecules bearing chlorine-containing polar groups on Cu(111) surfaces: A final adsorption state of the abovementioned GaCl-Pc/Cu(111) interface is a system in which the Cl atom has been separated from the molecule (see Figure 8c), which results in a significant reduction of the molecular dipole. This also modifies the adsorption-induced work-function change (albeit in a more complex way than expected based solely on the molecular dipoles, as will be discussed in Section 5.4).[208] Dechlorination processes have also been observed for chloro-boron-subphthalocyanine (ClB-subPc) on Cu(111), although there it has been argued that only the molecules landing in Cl-down orientation undergo the dechlorination.[213]

5.2. Interfacial Charge Transfer

A further possible origin of interfacial polar layers besides intrinsic molecular dipoles are charge rearrangements upon interface formation.[21,27] In this context, it should be mentioned that describing these charge rearrangements as dipoles is a coarse simplification, as intramolecular charge distributions as well as interfacial charge rearrangements are typically more complex than a simple separation of positive and negative charges. Thus, when quantitatively deriving shifts in the interface energetics, it might not be sufficient to apply Equation (1), but one will typically have to solve Poisson's equation with the actual (plane-averaged) charge redistributions as source term.

Figure 8. DFT-simulated structures of GaCl-Pc on the Cu(111) surface for a) the Cl-up and b) the Cl-down configuration, as well as c) for the dechlorinated molecule. In the Cl-up case, the vdW-contact between substrate and adsorbate is maximized. The vdW attraction to the surface results in a significant distortion of the molecular backbone. Reproduced under the terms of the Creative Commons CC-BY license.[208] Copyright 2015, American Chemical Society.

Figure 9. Map of the HeI UPS spectral intensities for CIAL-Pc deposited onto graphite as a function of coverage. The feature found around −1.2 eV at low coverage corresponds to the HOMO-derived band, while the dotted line starting at 4.5 eV represents the vacuum level. As the energy scale is aligned to the Fermi level, the latter also represents the work function of the system. Adapted with permission.[79] Copyright 2011, American Physical Society.
Nevertheless, for more qualitative arguments, approximating the actual situation as a dipole layer typically eases the discussion without introducing serious artefacts.

Charge rearrangements involving a direct coupling between the substrate and the adsorbate go hand in hand with the formation of hybrid states, where one can distinguish between three different processes, which often occur simultaneously.

5.2.1. Pauli Pushback (Cushion Effect)

When the bonding and antibonding of these hybrid states are simultaneously occupied, this results in a repulsion of the electron clouds of substrate and adsorbate. In other words, due to the Pauli principle, the electron clouds are pushed back into the respective sub-systems. This is shown in Figure 10 for benzene on a Au(111) surface. Pauli pushback is particularly pronounced for metal substrates, as its magnitude depends on the (relative) polarizability of substrate and adsorbate. As far as the electronic properties of the interface are concerned, the pushback of the electron cloud spilling out of a metal results in a significant reduction of the metal work function. Strictly speaking, this effect is not the consequence of forming a new dipolar layer at the surface, but rather results from reducing the already existing metal surface dipole discussed in Section 3.

![Figure 10. Visualization of Pauli pushback for a benzene molecule lying flat on a Au(111) surface calculated employing dispersion-corrected density-functional theory. Panel (a) shows the electron density of the metal (ρ_{\text{slab}}) plus the charge rearrangements Δρ induced by the adsorption of benzene, due to wave function orthogonalization (see main text: isovalue: 0.00025 e^- bohr^-3). Δρ is calculated as the density of the isolated subsystem minus the density of the isolated subsystem, i.e., Δρ = ρ_{\text{combined}} - ρ_{\text{slab}} - ρ_{\text{benzene}}. The displayed quantity ρ_{\text{sub}} + Δρ is, thus, equal to ρ_{\text{combined}} - ρ_{\text{benzene}}; hence, in contrast to the commonly employed plots, like the one in Figure 11, the charge density of the pristine metal slab is not subtracted. Blue regions correspond to positive and pink regions to negative values. To better visualize the situation for the metal, in panel (b) only the positive values less than 2.95 Å above the topmost Au layer are shown.](image)

The magnitude of the pushback can be sizable. Using n-tetrayctetracontane on Au(111) as a prototypical physisorbed system, Mizushima et al. observed a work-function reduction due to pushback in excess of 1 eV. They also provided a more detailed description of the interaction, involving, e.g., an adsorbate-induced modification of the Shockley surface state of the metal in combination with system-specific interfacial charge rearrangements.

These are rationalized through electron sharing between substrate and adsorbate involving bonding and antibonding C=H states in the metal–molecule bond and by including the hybridization between metal d-bands and unoccupied molecular orbitals.

In the context of Pauli pushback, one also has to keep in mind that it is massively reduced, when the metal substrate is not clean (e.g., covered by a thin hydrocarbon layer) or when it is intentionally or unintentionally covered with a thin non-metallic layer (e.g., an oxide). In that case, the majority of the pushback already happens when the original contamination occurs and no further significant work-function reduction due to OSC growth is to be expected. On more practical grounds, such considerations also apply when growing OSC layers under high vacuum instead of ultrahigh vacuum conditions or when depositing the OSC from solution. There, the processing conditions result in electrode contamination already prior to the OSC growth. The resulting "technical" electrodes have a significantly reduced work function to start with, but when growing OSC layers on top of them also the work-function reduction due to pushback will be much smaller. The situation is fundamentally different when growing OSC molecules that strongly bind to the substrate (like thiolates on Au), where it is possible that contaminants are displaced as a result of bond formation between substrate and docking groups. In that case an atomically clean metal substrate will be the ideal reference system for analyzing the situation, even if the films have not been grown under ultrahigh vacuum conditions.

5.2.2. Chemical Bonding to the Substrate

When, in contrast to the above situation, more bonding than antibonding hybrid orbitals are occupied, a chemical bond is formed between the substrate and the adsorbate. This is typically associated with pronounced charge rearrangements, which, as discussed above, give rise to a shift in the electrostatic energy landscape in analogy to the formation of a dipole layer. Such chemical bonds are, for example, formed when thiolates bond to coarsage metal surfaces during the formation of a self-assembled monolayer comprised of upright-standing molecules. Similar considerations apply to selenolate-, phosphoryl-, and silane-docked molecules. Local charge rearrangements influencing the interface dipole also occur when flat-lying molecules bearing reactive substituents adsorb on metals. Examples for such reactive substituents are the –CN groups in 2,3,5,6-tetrafluoro-7,8,8-tetracyanoquinodimethane (F4TCNQ) adsorbing on coinage metals or on graphene/Ir(111), or the carboxyl groups in 5,7,12,14-pentacenetetrone (P4O) bonded to Cu(111) and Ag(111) or the carboxylic groups upon interface formation between perylenetetracarboxylic dianhydride (PTCDA) and Ag(111).
5.2.3. Fractional Charge Transfer to Electron Donating or Electron Accepting Molecules

When the molecules adsorbing on a substrate have strongly electron donating or electron accepting character, the hybrid orbitals formed at the interface are highly polarized, i.e., they are quite strongly localized on one subsystem (the substrate or the adsorbate). By filling, e.g., primarily the orbitals with a dominant weight on the adsorbate, a net transfer of a fractional number of electrons per molecule is realized. In passing we note that the actual amount of transferred charge cannot be uniquely quantified, as a “molecular charge” is no physical observable in an extended system (just like an atomic charge in a molecule). Nevertheless, approximate values can be determined employing various partitioning schemes.[230]

The main difference between charge transfer to adsorbed donors and acceptors and the formation of covalent bonds discussed in the previous paragraph is that here charge is not rearranged only locally but is typically transferred to/from the extended $\pi$-system of the adsorbate molecules. For donors, the above-described fractional charge transfer (FCT) leads to work-function reductions with the magnitude of the effect significantly exceeding Pauli pushback. Typical examples are the interfaces between tetrathiafulvalene[94,231–233] or viologen (derivatives)[232,234] and a Au(111) substrate. For the methylviologen-modified Au substrate, a work-function decrease as large as 2.2 eV has been observed. This resulted in a reduction of the electron-injection barrier into a subsequently deposited OSC layer by 0.6–0.8 eV[230] compared to an interface where only Pauli pushback is active. For strong acceptors, the electron transfer to the adsorbate can surpass the inevitable pushback, such that the net effect is a work-function increase due to molecular adsorption. Such a behavior has been observed for many interfaces comprising adsorbate layers consisting, e.g., of F4TCNQ, P40, or PTCDA[220–223,236] The adsorption of (comparably weaker) acceptors can lead to the observation that electron transfer to the adsorbate exactly cancels Pauli pushback with the consequence that the work function remains almost unaffected by the adsorbate. This, for example, happens at the interface between hexaazatriphenylene-hexacarbonitrile (HATCN) and Ag(111) up to monolayer coverage.[238] Notably, even the deposition of such comparably weak acceptors as an interfacial layer significantly reduces the hole injection barrier into subsequently deposited OSC layers[230] The reason for that is that in the absence of the interfacial layer, only pushback would occur at the interface, which would significantly reduce the substrate work function.

Whether a molecular adsorbate is a sufficiently strong donor or acceptor to trigger the above-described electron transfer mostly depends on its adiabatic ionization energy or electron affinity. These quantities sometimes are also associated with so-called “polaronic” levels.[240] Particularly large IEs/EAs are realized, when the charge transfer triggers the conversion of an antiaromatic or quinoidal structure into an aromatic one,[225] as such an aromatic stabilization is known to energetically stabilize the charged species.[241]

For a detailed discussion of the charge-transfer mechanisms in the focus of this section, it is useful to take a closer look at the situation encountered for F4TCNQ on flat coinage metal substrates.[220–223,236] In this context, it should be mentioned that it has been suggested recently that for TCNQ on Ag(111) adatoms might be present on the surface, which fundamentally changes the adsorption geometry.[152] However, even in

![Figure 11. a,b): Isodensity plots of the DFT-calculated charge density rearrangements upon adsorbing an F4TCNQ layer on the Ag(111) surface. Electrons flow from the dark grey to the light grey areas. c) Molecular orbital population analysis[242,243] (obtained by integrating the orbital-projected density of states up to the Fermi level) for F4TCNQ adsorbed on Ag(111). The bands derived from the isolated molecular monolayer were taken as reference for the projection. The full (open) circles correspond to molecular orbitals occupied (unoccupied) prior to adsorption. Adapted with permission.[221] Copyright 2009, American Physical Society.](image-url)
that case, the simulations on the flat substrate are particularly instructive for illustrating the fundamental aspects of the charge-transfer mechanisms present at strongly coupled metal–organic interfaces.

The isodensity plots of the charge-rearrangements occurring for F4TCNQ on Ag(111) are shown in Figure 11a,b. They reveal several interesting aspects: There is clear charge-density accumulation in the π-system of the molecule (areas shaded in light gray), with the nodal pattern of the charge rearrangements strongly reminiscent of the lowest unoccupied orbital (LUMO) of F4TCNQ. This means that hybrid orbitals formed between the molecular LUMO and the sp-band of Ag become occupied. These hybrid orbitals are mostly localized on the F4TCNQ molecule (cf., above discussion). The filling of LUMO-derived states in F4TCNQ upon adsorption is also supported by the molecular orbital population analysis, which testifies to a nearly 90% effective filling of the LUMO upon adsorption (see red circle in Figure 11c).

At the same time, there is charge density depletion (areas shaded in dark grey) in the region of the σ-system, which can be associated with a relaxation of the electronic states within the molecule in reaction to the filling of the LUMO. Notably, in the same spatial region also Pauli pushback due to the overlap between the σ-electrons of F4TCNQ and the electron density tail from the Ag surface occurs. Considering, however, that in similar plots for the adsorption of strong donors, one observes electron accumulation in the σ-region, we deem the relaxation effect to dominate. Particularly strong electron depletion is observed locally in the region of the σ-states associated with the −CN groups. This transfer of electrons from the molecule to the substrate occurs from deeper lying σ-states localized on the −CN groups, as can be concluded from the reduced effective occupation of these states in the adsorbate (see blue ellipse and rectangle in Figure 11c). Due to the vicinity of the −CN groups to the Ag surface, these states hybridize so strongly with the metal d-bands that a significant fraction of the resulting hybrid states come to lie above the Fermi level. As a consequence of this superposition of charge forward and backward donation, in spite of the LUMO-derived band being nearly completely filled, the net charge transfer between the metal substrate and the F4TCNQ layer amounts to only ~0.56 e− per molecule (as estimated from the cumulative charge rearrangements between the sub-systems, as described in detail in ref. [221]).

Finally, it should be mentioned that in recent years also mixed donor/acceptor adsorbates on metal surfaces have been investigated. In such cases the question arises, whether intermolecular or molecule-to-substrate charge transfer dominates. Answering that question is tightly linked to the issue, whether the mixed adsorbate layers phase segregate or mix homogeneously. A detailed discussion of the properties of mixed donor/acceptor adsorbate layers, however, goes beyond the scope of the present manuscript. Therefore, we refer the interested reader, for example, to the discussion of this issue in the review by Otero et al.

5.2.4. The Integer Charge-Transfer (ICT) Situation

Establishing thermodynamic equilibrium typically requires a noninteger number of electrons per molecule to be transferred between substrate and adsorbate. This can be described by the model discussed in the previous section for interfaces at which substrate and adsorbate states hybridize. In the case of weakly coupled interfaces, there are no polarized hybrid states, whose filling would result in a fractional net transfer of charge. Therefore, in such situations instead of fractionally charging every molecule (FCT), a fraction of the molecules receives an integer charge, i.e., one observes integer charge transfer (ICT).

Depending on the intermolecular coupling, the charge might also be delocalized over a few molecules. The FCT and ICT scenarios are schematically compared in Figure 12a, where in the case of FCT translational periodicity is preserved, while it is broken in the ICT case. Notably, the ICT charge distribution should not be viewed as static, but the additional integer charges can tunnel between adsorbate molecules, unless they are stabilized on certain sites due to defects or by lattice relaxations of the substrate.

Traditionally, ICT dominates i) for interfaces formed under ambient conditions by solution-processing of the organic adsorbates, ii) when using metal substrates passivated by a native oxide layer (e.g., Al) or by an organic interlayer, iii) when depositing molecules on conductive oxides, or iv) when using a conducting polymer like poly(3,4-ethylenedioxythiophene) poly(oxythiophene) polystyrene sulfonate (PEDOT/PSS) as a substrate. More recently, ICT has also been observed in simulations (see Figure 12b) and experiments, when intentionally separating a metallic substrate from an electron accepting adsorbate layer by a dielectric layer with a thickness of only a few monolayers (provided it does not prevent charge transfer altogether). A particularly interesting situation has been computationally predicted for F4TCNQ on the 1010 surface of ZnO. There, ICT due to the bonding of the −CN groups to the Zn atoms at the surface (affecting all molecules in Figure 12d) coexists with ICT into the π-system of only a fraction of the adsorbed molecules (molecule 1 in Figure 12d). Whether charge transfer occurs at all for a specific material combination, again depends on the adiabatic ionization energies or electron affinities of the adsorbate layer, but also on the structure and density of the molecular overlayer, as well as on the thickness of the dielectric layer. Whether the charge localizes or not (i.e., whether ICT or FCT occurs) depends on the degree of hybridization and the strength of the lattice relaxation.

The consequences of an ICT situation are manifold: For instance, the coverage-dependence of the adsorbate-induced work-function change distinctly differs between ICT and FCT scenarios (see Figure 12c). Notably, in the ICT case the maximum adsorbate-induced work-function change is observed at comparably low coverages (0.4 monolayers in the example shown in Figure 12c). This can be explained by the fact that a charged molecule raises the electrostatic potential in its vicinity. Consequently, the LUMOs of neighboring molecules are often shifted above the substrate’s Fermi level, removing the driving force for further charge transfer. Therefore, in the case of ICT one must not associate the maximum in the work-function change with the closure of the monolayer.

Moreover, as bond lengths and charge distributions vary between neutral and charged molecules, X-ray photoelectron or infrared spectra of monolayers experiencing an ICT situation
should correspond to the superposition of the spectra of neutral and charged species. As in the FCT case only one (fractionally charged) species prevails, the distinction between FCT and ICT scenarios should be comparably straightforward in experimental studies, provided that the spectral resolution is sufficient. Complications might arise from the timescales of the specific experiments due to the dynamic nature of the ICT situation with transferred charges hopping between adsorbed molecules.

Alternatively, the coexistence of neutral and charged molecules on the surface in the ICT case should be detectable by scanning tunneling spectroscopy. This is frequently the case for metal atoms separated from a metal substrate by a thin dielectric layer, e.g., Au on Cu/NaCl. Recently, this was also observed for organic adsorbates, specifically pentacene on a Cu/NaCl and on a Ag/MgO substrate (although in the former case, the pentacene was deliberately charged with the scanning tunnelling microscope tip). In simulations, such an unambiguous distinction between the FCT and ICT situations is a priori not possible. This is a consequence of charge over(delocalization resulting from the many-electron self-interaction error, respectively its overcompensation, as discussed in detail in ref. [262].

5.3. Characterizing the Charge-Transfer Situation

A parameter that is commonly used in literature to characterize the implications of charge-transfer for the electronic properties of the interface is the “slope parameter,” $S$. It originates from Schottky–Mott theory and for a given (organic) semiconductor connects the work function of the bare substrate, $\Phi_{\text{sub}}$, with the work function after adsorbate deposition, $\Phi_{\text{ad}}$.

$$S = \frac{\mathrm{d}\Phi}{\mathrm{d}\Phi_{\text{ad}}}$$

For the case of vacuum-level alignment (the Schottky–Mott limit), $S$ becomes 1. This also applies, when the same bond dipole forms on different substrates. A possible scenario for the latter could be the prevalence of substrate-independent Pauli pushback. Conversely, as soon as the adiabatic ionization energy of the adsorbate layer drops below the substrate work function (or the adiabatic electron affinity rises above), additional charge has to be transferred between substrate and adsorbate. The resulting additional dipole layer then reestablishes thermodynamic equilibrium. Provided that the electron transfer to (from) the adsorbate layer does not appreciably

Figure 12. a) Schematic comparison between the ICT and FCT scenarios for charge transfer at organic/inorganic interfaces. b) Calculated electron-density difference upon adsorption of tetracyanoethene (TCNE) on Cu/NaCl. For the sake of clarity, only positive values are shown for molecules within the unit cell and the substrate atoms are omitted. c) Evolution of the TCNE-induced work-function modification as a function of coverage for the ICT (red) and FCT scenarios (black). The FCT scenario is realized by performing the simulations using a GGA functional suffering from a many-electron self-interaction error, which overdelocalizes charges. [250] d) Charge rearrangements within a surface supercell containing four F4TCNQ molecules on n-doped ZnO, averaged along the line of sight. Charge flows from the red to the blue areas. (b,c) Adapted with permission. [250] Copyright 2015, American Chemical Society. (d) Adapted with permission. [251] Copyright 2019, American Chemical Society.
change its electron affinity (ionization energy), this results in $S = 0$, i.e., the system work function becomes independent of the substrate work function. This process is typically termed Fermi-level pinning (and will be described in more detail in the following section).

Abrupt transitions between $S = 0 \rightarrow S = 1 \rightarrow S = 0$ are, indeed, commonly observed in ICT situations,[24,158,240,252–254,265,266] which is shown in Figure 13 for a series of solution-processed organic semiconductors on metals, metal oxides, semiconductors, and conducting polymers.[267] Also in the FCT case $S = 0$ is expected as soon as Fermi-level pinning sets in, as exemplified by PTCD on various substrates including coinage metals,[227,266,268] and F4TCNQ on Ag and Au.[221,236] Nevertheless, for a variety of material combinations, slope parameters between 0 and 1 have been observed experimentally.[22] Also in self-consistent electrostatic models, $S$-values between 0 and 1 have been calculated upon gradually changing the shape of the density of states of the adsorbate from Gaussian to Lorentzian.[172] This suggests that the degree of hybridization as well as the presence of defect states at the interface (both impacting the interfacial DOS) can influence Fermi-level pinning, calling for a more in-depth discussion of this effect.

5.4. Fermi-Level Pinning

As mentioned above, Fermi-level pinning typically comes into play when charges are transferred between substrate and adsorbate in order to establish thermodynamic equilibrium. To discuss its fundamental aspects and its implications, it is again useful to consider a gedankenexperiment analogous to that performed in Section 4. We start from the electronic structure of the isolated metal substrate, described by its work function, and the isolated molecular monolayer, characterized by the monolayer ionization energy and electron affinity (see Figure 14(a)). Upon contact formation, screening by the metal substrate reduces the fundamental gap; moreover, the energy levels of substrate and adsorbate are shifted relative to each other due to Pauli pushback. Provided that the resulting screened adiabatic ionization energy is smaller (or the adiabatic electron affinity larger) than the work function of the metal including pushback, charges are transferred. The resulting dipole layer triggers a shift of the energy levels such that, in a single-particle picture, the Fermi level of the substrate aligns with the partially filled band of the adsorbate layer (Figure 14b). Then, the work function of the combined substrate/adsorbate system is essentially determined by the electronic structure of the adsorbate and, thus, becomes independent of the substrate work function ($S = 0$, see above).

When analyzing the properties of charge-transfer interfaces in the context of Fermi-level pinning it is worthwhile considering the following aspects:

i. The nature of the electronic state at which pinning occurs has been somewhat controversially discussed in literature. As mentioned already above, it is undoubtedly not determined by the vertical ionization energy (electron affinity) of the adsorbed monolayer that would, e.g., be measured by (invers) photoelectron spectroscopy (UPS and IPES). Rather, electronic and geometric relaxation effects have to be taken into account.[24,240] For ICT cases, this has been described by pinning at so-called integer-charge-transfer or polaronic states.[24] Beyond the relevance of relaxation effects, it has been shown that in many cases pinning already occurs at defect or metal-related intragap states,[162,168,170,266,269] that are found in the tails of the respective densities of states reaching deeply into the gap. Moreover, for specific shapes of the density of states, band bending has been suggested (see above).[162,172] which modifies the pinning situation.

ii. The amount of transferred charge depends on the magnitude of the energy offset (prior to equilibration) between the metal Fermi level and the OSC state at which pinning occurs. The larger that offset, the larger the interface dipole has to be to align the levels. For a given charge-transfer distance (i.e., adsorbate geometry), a larger offset, thus, means that more charge needs to be transferred to establish thermodynamic equilibrium. Additionally, the geometric structure of the interface plays a role: The (average) amount of transferred charge per molecule decreases with increasing molecular coverage and with increasing adsorption distance. In both instances less charge per molecule needs to be transferred to induce the step in the electrostatic energy between substrate and adsorbate that is necessary to establish thermodynamic equilibrium.

iii. Even if the final work function in the case of Fermi-level pinning depends only on the electronic structure of the adsorbate layer, one has to keep in mind that the IE and EA of that layer will change with charge transfer. In a single-particle picture, this can be understood from a partial filling of the frontier
Figure 14. a–d) Schematics of the interfacial level alignment for a substrate/adsorbate combination for which in thermodynamic equilibrium Fermi-level pinning occurs. a) and c) display the vacuum-level alignment case, where the lowest unoccupied level lies below the Fermi level of the substrate. In (a), the surface dipoles of the adsorbed layer are symmetric and oriented such that the electron affinity and ionization energy of the adsorbate are increased. In (c), a much larger surface dipole is assumed at the side of the adsorbate facing the substrate (green arrow). b) and d) show the situation after establishing thermodynamic equilibrium, where the asymmetric dipole in (d) causes a larger amount of charge transfer, which results in a massively increased bond dipole (see red ellipse and red arrow), such that the final adsorbate-induced work-function change is the same as in (b). e) Calculated adsorption-induced work-function change for a Fermi-level pinned, terpyrimidine-based self-assembled monolayer (chemical structure shown on the left) upon changing the docking group (black squares) and upon adding polar tail-group substituents (red circles). (e) Reproduced with permission. [153] Copyright 2010, American Chemical Society.
for intact molecules with upward-pointing Cl atoms.\textsuperscript{[208]} Consequently, the measured work function allowed ruling out the latter configuration, but could not distinguish between the two former ones. This was possible only by an in-depth comparison between calculated\textsuperscript{[208]} and measured\textsuperscript{[270]} adsorption distances (which supported the existence of dechlorinated molecules). In view of the recent discussion about ad-atoms at the F4TCNQ/Ag(111) interface,\textsuperscript{[152]} we note that due to the compensation discussed in this paragraph, the presence of surface adatoms will substantially affect the molecular geometry, but will likely have a surprisingly small and often almost vanishing effect on the total work function of the system.

v. Another practically highly relevant aspect to consider in the context of Fermi-level pinning is that the ionization energies and electron affinities of adsorbate layers depend strongly on the molecular orientation due to surface dipoles (cf., Section 4.1.3).\textsuperscript{[130–132]} This is schematically shown in the central panel of Figure 15a. In particular, electron withdrawing substituents in the periphery of the molecule (due to the associated local dipoles) will typically increase IE and EA, while electron donating substituents will decrease them. Therefore, the work function of the combined metal/adsorbate system in the case of Fermi-level pinning strongly depends on molecular orientation. As depicted in the right panel of Figure 15a, one might even encounter the situation that for one of the molecular orientations Fermi-level pinning prevails (here, for the upright standing molecules), while in the other there is vacuum-level alignment (together with push-back; here, for the flat lying molecules). As a general consequence of this effect, the reorientation of molecules during film growth (e.g., as a consequence of increasing coverage) can massively change the measured sample work function,

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure15.png}
  \caption{a) Electronic structure of an interface between a metal substrate and an upright-standing (top panels) and a flat-lying (bottom panels) adsorbate layer consisting of molecules bearing polar substituents, but no net dipole moment. The central panel shows the electronic structure of the hypothetical free-standing monolayers highlighting the dependence of the monolayer IEs and EAs on the molecular orientation. Upon forming the contact with the metal (right panels), for the displayed example, Fermi-level pinning is found for the standing monolayer, while the smaller electron affinity of the lying monolayer results in vacuum-level alignment. For the sake of clarity, pushback, bandgap renormalization, screening, and relaxation effects (discussed in the main text) are not accounted for in the right graphs. b) Coverage-dependent work function of HATCN deposited onto a Ag(111) substrate. c) Coverage-dependent work function of COHON on Ag, Cu and Au surfaces. (b) Reproduced with permission.\textsuperscript{[238]} Copyright 2010, American Physical Society. The data in panel (c) are the same as in ref. \textsuperscript{[271]}.}
\end{figure}
even when the molecules themselves do not possess a net dipole moment. As, to the best of our knowledge, this effect has not been comprehensively described in literature, it shall be discussed in more detail in the following paragraph.

As an example for a reorientation-triggered work-function modification, the coverage-dependent work-function of HATCN on Ag(111) is shown in Figure 15b. For nominal coverages up to 3 Å, a flat-lying (Fermi-level pinned) monolayer is formed. For larger coverages, a variety of experiments suggest that the molecules rearrange. This results in an essentially upright-standing layer with a significantly increased monolayer electron affinity due to the polar –CN substituents. As Fermi-level pinning prevails, the resulting sample work function is increased by nearly 1 eV. For molecules with a particularly high dipole density in their periphery, such effects can even be larger, as has been observed for doubly NO$_2$-substituted pyrenetetraeno on Ag(111). There, for upright-standing molecular layers, work functions in excess of 6.1 eV have been measured. A particularly interesting situation is encountered for 1,2,5,6,9,10-coronenehexone (COHON) on coinage metals (see Figure 15c). While the work functions of the pristine substrates and at very low coverages of COHON on Au, Cu, and Ag are significantly different, at a nominal coverage of ~6 Å (which is attributed to roughly a closed monolayer of lying molecules) the work functions of COHON/Au and COHON/Cu become virtually identical. This suggests Fermi-level pinning at those two interfaces, while on Au pinning apparently does not occur yet and the electronic structure of the interface is dominated by Pauli pushback. The situation changes for even higher coverages. For nominal thicknesses exceeding 20 Å, the work functions of all three interfaces are essentially identical and, at the same time, larger than for the pinned case at 6 Å. This would be fully consistent with Fermi-level pinning for all three substrates at an essentially upright standing COHON layer with a significantly increased electron affinity due to the polar carbonyl groups in the molecular periphery. Interestingly, at least for the COHON/Cu interface there is indeed further spectroscopic evidence for such a coverage-dependent reorientation. All these examples indicate that coverage-dependent rearrangements of organic molecules on metal surfaces have massive consequences for their electronic properties. At this stage we speculate that such rearrangements might occur much more often than usually assumed.

vi. The above discussion deals with the impact of coverage beyond a (flat-lying) monolayer. Coverage, however, impacts Fermi-level pinning also in the sub-monolayer case. It has already been discussed in Section 3.2.3 (Figure 3c) that for charge-transfer layers with comparably large dipole to dipole distances, the electrostatic energy at the position of the molecule undergoing charge transfer and the energy far away from the interface differ considerably. The former, however, determines the IE and EA of the adsorbate, while the latter is relevant for the work function. As pinning still aligns the Fermi level of the substrate with the states in the molecule, this results in an adsorbate-induced work-function change that is smaller than in the full coverage case. The difference in the two electrostatic energies diminishes with decreasing dipole to dipole distance, i.e., for more tightly packed layers (see Figure 3c). This is consistent with the common experimental observation that even at interfaces at which Fermi-level pinning occurs, the adsorbate-induced work-function change displays a pronounced coverage dependence at very low nominal layer thicknesses.

Notably, also the aggregation of molecules into islands can result in an apparent coverage dependence of the measured work-function change. This is in particular the case, when sections of the substrate remain uncovered (e.g., for Volmer–Weber type film growth) and when area averaging experimental techniques are employed in the experiments (e.g., SECO-measurements in photoelectron spectroscopy experiments or Kelvin probe; see discussion in Section 4).

vii. As discussed above, in the case of Fermi-level pinning, the final work function is only determined by the adsorbate properties. This implies that, for adsorption on (inert) semiconductors, the doping concentration (which is a substrate property) does not influence the final work function. Since the initial work function of the substrate is typically only weakly dependent on the doping concentration (particularly for highly doped semiconductors, which are commonly used as electrodes), also $\Delta \Phi$ hardly depends on it. Nevertheless, the relative contributions of the BD and the adsorption-induced band bending, $\Delta BB$, (cf. Equation (9)) do depend on the doping concentration: The smaller the amount of free charge-carriers, the larger the relative contribution of $\Delta BB$ to $\Delta \Phi$ (and the smaller that of BD). In other words, in the case of Fermi-level pinning the overall potential shift between substrate and adsorbate is a fixed quantity. However, the larger the amount of free carriers (i.e., the larger the doping concentration) is, the smaller the fraction of the potential drop that occurs within the substrate (i.e., the smaller $\Delta BB$ and the larger BD). Since, as discussed in Section 4.2.2, only BD affects the relative offset of the substrate bands and the adsorbate states directly at the interface, the doping concentration indirectly affects the level alignment. This is indeed corroborated by quantum-mechanical simulations.

For practical applications, however, two words of caveat are required: First, as discussed above, in realistic wide-bandgap semiconductors, the maximum band bending that can be obtained is often limited by surface states (acting as deep donors). Due to the high concentration of deep donor states, the corresponding charge-rearrangements are usually very short ranged and, hence, are usually factored into BD (rather than $\Delta BB$). In practice, this means that the relative contributions of BD and $\Delta BB$, and hence the level alignment, is less doping-dependent than one might initially assume.

Second, the strong doping dependence occurs only for the adsorption on inert semiconductors, where the charge-transfer is driven by the difference of the electron affinity (or ionization energy) of the organic adsorbate and the Fermi level of the substrate. The situation changes fundamentally for strong hybridization between adsorbate and the substrate valence or conduction bands. There, the situation is more reminiscent of the FCT scenario on a metal (including very short-ranged charge rearrangements, that lead to an absence of band bending).
6. Impact of Dipolar Layers on Physical Observables—Contact Resistance, Core-Level Excitation, and Monolayer Transport

To comprehensively discuss the impact of dipolar layers on physical observables typically measured at hybrid interfaces, in Figure 16 we show the (comparably complex) situation of an upright-standing adsorbate layer consisting of i) an embedded dipolar (ED) element as part of the molecular backbone and ii) a polar tail-group dipole (TD). iii) Moreover, the molecules are covalently bonded to the substrate, giving rise to yet another dipole layer, the bond dipole (BD). Upright standing molecules are chosen for the present discussion, as in them the BD-, ED-, and TD-dipole layers can typically be identified unambiguously. To understand how quantities like the work function, the energetic positions of the frontier states, and core-level binding energies in this system are influenced by the three dipole layers, in the following a (hypothetical) photoelectron spectroscopy experiment performed at this interface shall be discussed. What will be crucial for each of the energies is, how many of the dipole layers the photoelectron has to cross, before it can leave the sample, respectively, before it reaches the detector:

i. The work function, \( \Phi \), is determined by measuring the SECO, i.e., by the photoelectrons with vanishingly small energies that barely make it out of the sample (see green arrow to the left). Consequently, \( \Phi \) is shifted by the steps in the electrostatic energies due to all three dipole layers (BD, ED, and TD). This has motivated the application of polar SAMs in (optoelectronic) devices for tuning electrode work functions and carrier-injection barriers (see Section 2).

ii. The situation is different for the core-level binding energies. They are measured relative to the Fermi level of the substrate. Thus, they are affected by the dipole layers between the respective atom and the surface of the substrate. Consequently, for the atoms in region (1) of the adsorbate (see Figure 16), only the bond dipole BD matters, while for those in section (2) also the embedded dipole layer ED is relevant. The tail-group dipole TD, due to the locality of collective electrostatic effects (see Section 3), has no impact. Consequently, the inclusion of dipoles into adsorbate layers results in electrostatically induced shifts in the kinetic energies of the photoelectrons, as is shown in the right part of Figure 16a. These “electrostatic” XPS shifts are superimposed on the commonly observed chemical shifts due to differences in the atomic charge densities resulting from neighboring atoms. The electrostatic shifts can easily be in the range of one eV, as it is shown for ester-containing alkylthiolates in Figure 16b.[116,276,277] Both, in the simulated and measured spectra contained in that plot, one observes a double-peak structure for the main C1s features between \(-284\) and \(-286\) eV binding energy. Based on the density functional theory (DFT) simulations contained in the left panel of Figure 16b, these features can be unambiguously assigned to the chemically identical CH_{2} groups left and right of the ester moiety. Consequently, the difference in the associated binding-energies is of purely electrostatic origin and is caused by the dipoles of the embedded ester groups. This can be shown, for example, by diluting the dipole density in a hypothetical low-coverage SAM, in which the molecules are

![Figure 16](image-url)
kept in their upright-standing orientation. Similar observations have been made also for aromatic SAMs containing embedded pyrimidine dipoles.

In that spirit, XPS can be used as a probe for shifts in the local electrostatic energy within an adsorbate layer. Due to the sensitivity of core-level binding energies to the local electrostatic energy, XPS measurements can also be used to probe inhomogeneities of the potential at the immediate surface of the sample. In a similar spirit, they can be applied to probe the uniformity of mixed adsorbate layers, provided that the different constituents contain chemically identical atoms, but at the same time shift the electrostatic energy differently (e.g., via embedded dipoles incorporated in different orientations). When associating core-level binding energies with the local electrostatic energy, care has to be taken for atoms close to the interface. There, the electrostatic shifts can be masked by chemical shifts due to interfacial charge rearrangements, by lateral potential inhomogeneities, or by shifts resulting from the adsorption-height dependence of screening by the metal or semiconductor substrate.

iii. As far as the frontier levels are concerned, their energetic positions relative to the Fermi level are shifted by the bond dipoles, as discussed already in Section 4.2. Concomitantly, the bond dipoles also modify electron- and hole-injection barriers for carriers into the SAMs. Conversely, the tail-group dipoles do not impact the level alignment, due to the locality of the dipole-induced step in the energy. The situation for embedded dipoles is somewhat more involved: Provided that the valence states are fully localized either left or right of the embedded dipole layer, e.g., by breaking the conjugation or by using extended semiconducting segments minimizing the localization energy (see ref. [278]), a situation analogous to that discussed for the core-levels is encountered (see “red valence states” in Figure 16a). In that case, all states are shifted relative to the Fermi level by BD and the states right of the embedded dipoles are additionally shifted by ED.

Such a situation is shown in Figure 17. For the energetic positions of the frontier states relative to the vacuum level, the relevant dipole layers are TD and ED. Notably, an analogous rigid connection between core-level and frontier-level energies has also been observed for the adsorption of mixed donor/acceptor layers.

When the electronic states are only partially localized by the embedded dipoles, BD and TD still play the same role as above. Also ED still either stabilizes or destabilizes the states relative to $E_F$ (depending on the dipole orientation). The magnitude of that shift is, however, smaller than ED. It is intermediate between the shifts in electrostatic energy in the region left of the dipoles (unaffected by ED) and right of the dipoles (fully shift by ED) with the exact magnitude of the shift depending on the localization of the state in the respective regions (see blue states in the valence region indicated in Figure 16a).

To probe the positions of the occupied (unoccupied) frontier levels one can, for example, perform UV-photoelectron spectroscopy (and inverse photoelectron spectroscopy) experiments. Alternatively, the interfacial level alignment can be determined by scanning tunneling spectroscopy experiments and monolayer transport measurements on molecules or monolayers sandwiched between two electrodes. Here, fundamental differences between molecular and monolayer junctions are to be expected, as collective electrostatic shifts occur only for densely packed monolayers (due to the BD and TD layers), while they are essentially absent for isolated molecules. The situation becomes even more complex for charge transport through molecular clusters, for which also significant edge effects occur.
originating from the surrounding dipoles, while the effect diminishes toward the periphery.\cite{285} Transport measurements have also been used to probe the role of ED in embedded-dipole SAMs, where distinct shifts of the so-called transition voltage have been observed depending on the orientation of the embedded dipole\cite{280} fully consistent with the considerations in the previous paragraph.

7. Electrostatic Design

The omnipresence of collective electrostatic effects at interfaces raises the question, whether one could intentionally integrate dipolar layers into materials to locally manipulate their electronic structure, thereby creating materials with unprecedented properties. Building on density-functional theory calculations, this led us to suggest the concept of electrostatic design, which could, for example, be used to develop an electronic LEGO approach with monolayers consisting of semiconducting, polar, or even radical building blocks.\cite{278} The simulated electronic structure of such a layer consisting of a docking functionality (thiolate), one electrostatic shifting functionality (a methyl-substituted bipyrimidine segment), and two semiconducting regions (two tolane sections) is shown in Figure 17. More complex structures following the same design strategy could, for example, serve as interfacial quantum-wells.\cite{278} Similarly, the inclusion of polar layers between 2D semiconductors in van der Waals stacks can pave the way for novel quantum-cascade structures,\cite{286} which, for example, facilitate exciton dissociation (see simulated data in Figure 18). Employing electrostatic design in covalent organic or metal–organic frameworks with properly arranged dipolar linkers can also be used to create quantum-checkerboards with electrostatic potential distributions localizing electrons and holes in spatially separated regions consisting of identical semiconducting entities.\cite{287} Interestingly, such electrostatically tuned covalent networks have in the meantime also been realized in practice, albeit not in the bulk, but on surfaces.\cite{288}

8. Conclusions

For interfaces, it is safe to state that “dipoles are always and everywhere.” As periodic assemblies of dipoles cause a step in the electrostatic energy, they profoundly impact the electronic properties of interfaces. In the present paper, we provide an in-depth discussion of the underlying effects and their consequences starting with a description of collective electrostatic effects caused by periodic dipole assemblies. We also review how the properties of hypothetical, infinitely extended interfaces...
differ from realistic samples with a finite spatial extent containing defects and structural imperfections. This is followed by a discussion of how dipolar layers impact the electronic properties of the isolated subsystems eventually constituting an interface (e.g., metal or semiconductor substrates and thin organic layers) and how new dipole layers originating from the interface formation further modify the alignment of electronic states and the sample work function. The multiple possible origins of interfacial dipoles are reviewed, discussing the properties of aligned polar functional groups contained in the adsorbate, metal surface dipoles due to the tailing of the electron cloud out of the surface, band bending in doped inorganic semiconductors, charge rearrangements due to the formation of strong chemical bonds between the substrate and the adsorbate layer, and charge transfer to/from monolayers consisting of electron accepting or electron donating molecules. In this context, especially interfacial charge transfer processes display particularly rich physics, as one has to distinguish between situations in which each of the adsorbed molecules is fractionally charged and cases in which a fraction of the molecules carries an integer charge. Moreover, Fermi-level pinning due to interfacial charge transfer renders the system work function independent of that of the substrate and negates the impact of ordered dipole layers spatially arranged between substrate and adsorbate. It can also give rise to massive changes in the electronic structure of the interface upon molecular reorientation processes, even if the adsorbed molecules do not possess a net dipole moment. Notably, interfacial dipole layers not only change electrode work functions and, concomitantly, carrier-injection barriers (which makes them interesting for applications in (opto)electronic devices). They also modify core-level binding energies and transport properties of monolayer junctions. All the aspects mentioned above raise the question, whether polar layers could not be used for manipulating the electronic properties of materials in order to realize systems with unprecedented properties in the framework of an “electrostatic” design approach.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords
collective electrostatic effects, energy-level alignment, Fermi-level pinning, interfacial charge transfer, organic/inorganic interfaces

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