Work-Function Modification beyond Pinning: When Do Molecular Dipoles Count?

Oliver T. Hofmann, David A. Egger, and Egbert Zojer*

Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria

ABSTRACT Deposition of monolayers of strong electron donors or acceptors on metal surfaces in many cases results in a metal-independent work function as a consequence of Fermi-level pinning. This raises the question whether in such a situation molecular dipoles, which are also frequently used to tune the interface energetics, still can have any impact. We use density functional theory to show that the spatial position of the dipoles is the determining factor and that only dipoles outside the immediate metal–molecule interface allow work-function changes beyond the pinning limit.

KEYWORDS Work-function modification, Fermi-level pinning, molecular dipoles, interfaces, metal–organic, self-assembled monolayers, organic electronics, molecular electronics

In the field of organic electronics, controlling the work function, Φ, of metal electrodes has been named as one of the most important tasks in order to improve device performance.[1] It can, for example, be achieved by introducing a dipolar layer at the interface.[2] In this context, large work-function modifications have been demonstrated using covalently bonded self-assembled monolayers.[3−12] An alternative and particular promising method to exert influence over Φ is the application of an organic monolayer consisting of molecules that are sufficiently strong electron donors or acceptors. In that case, significant interfacial charge transfer is observed and the Fermi-level gets pinned. While there is still a debate in the community about which level of the organic is actually responsible for the pinning (e.g., the charge neutrality level,[13] a (bi)polaron level,[14] or the HOMO/LUMO itself[15]), it is commonly accepted that the alignment occurs due to the formation of an interface dipole layer, emerging from the (covalent or charge-transfer driven) bond between the metal and the monolayer. Experimentally it has been established that in the case of Fermi-level pinning the work function of the combined metal/monolayer system, Φ', is independent of the Fermi level of the underlying metal (e.g., see refs 14 and 16−21). At the same time, molecular geometries are known to become distorted in the adsorption process,[15,22−26] thereby inducing additional molecular dipoles even in otherwise flat molecules. An instructive way for analyzing the total work-function modification, $\Delta\Phi$, is then to decompose it according to the origin of the contributing dipoles.[27,28] That is, $\Delta\Phi$ can be viewed as the superposition of (i) a part arising from molecular dipoles, ΔE_{mol}, and (ii) a part resulting from charge rearrangements induced by the electronic interaction of molecule and metal, ΔE_{bond}

$$\Delta\Phi = \Delta E_{mol} + \Delta E_{bond} \qquad (1)$$

For self-assembled monolayers that are not in the Fermi-level pinning regime it could even be shown explicitly that ΔE_{mol} and ΔE_{bond} are independent of each other and can be varied separately.[29]

This gives rise to a seeming contradiction: How can the molecular dipole contribute to the work-function modification, if all that counts in the case of Fermi-level pinning[30] was the energetic position of the molecular level at which pinning occurs? Solving this puzzle is also important from a practical point of view, as it relates to the question, whether one can use molecular dipoles to go beyond work-function modifications dictated by Fermi-level pinning. That the latter can indeed be a severe limitation for the achievable $\Delta\Phi$. This has, for example, been shown recently for SAMs with dipole moments distributed along the molecular backbone.[31]

Therefore, we performed density functional theory (DFT) based band-structure calculations on carefully chosen test systems with strong charge-transfer character, where molecular dipoles with different magnitude and at different spatial locations are introduced either via modification of the geometry or systematic chemical derivatization. Employing periodic boundary conditions in the framework of the repeated-slab approach allows the study of the two-dimensional (2D) infinitely periodic interface. In these fully self-consistent calculations, important effects like depolarization[32,33] and interfacial charge transfer are taken into account. We have used the VASP code and the results have been visualized using XCrysden.[35] The employed methodology is well tested and has been successfully applied to reproduce experimental data, in particular, for donor and acceptor systems closely related to those studied below.[15,26,41] It is explained in more detail in the Supporting Information, along with further
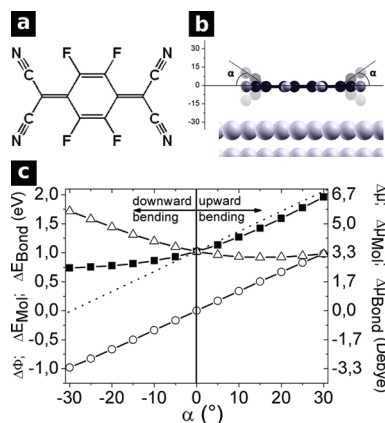
FIGURE 1. (a) Chemical structure of 2-(4-dicyanomethyl-2,3,5,6-tetrafluoro-cyclohexa-2,5-dienyl)-malononitrile (F4TCNQ). (b) Structure of planar F4TCNQ on Ag(111) with the bending illustrated by the semitransparent atoms. (c) Evolution of $\Delta\Phi$ (closed squares), ΔE_{Mol} (open circles), and ΔE_{Bond} (open triangles) as a function of the bending of the cyano-groups in F4TCNQ. The left y-axis gives these quantities in eV, while the right y-axis lists the corresponding dipole moments per adsorbate molecule. The vertical solid line indicates the planar structure and the dotted line indicates the evolution of $\Delta\Phi$ in the hypothetical case of ΔE_{Bond} being unaffected by the bend (details see text).

information on the approach to calculate $\Delta\Phi$, ΔE_{mol}, and ΔE_{bond}, as well as the employed unit cells and adsorbate structures.

Results and Discussion. A set of prototypical systems, where large contributions from ΔE_{Bond} and ΔE_{Mol} occur simultaneously, are monolayers of the strong acceptor 2-(4-dicyanomethylene-2,3,5,6-tetrafluoro-cyclohexa-2,5-dienylidene)-malononitrile F4TCNQ (see Figure 1a) on coinage metals.[15,26] F4TCNQ covered Cu(111), Ag(111), and Au(111) surfaces display virtually the same work functions determined by pinning.[26] Ultraviolet photoelectron spectroscopy (UPS) and corroborating DFT calculations indicate a strong net charge transfer from the metal to the molecular monolayer giving rise to a substantial charge-transfer induced ΔE_{Bond}.[26] Additionally, X-ray standing wave measurements on Cu(111) reveal that the cyano-groups at the periphery of the molecule are located 1.2 Å closer to the surface than the central ring.[15] DFT calculations show that a similar bending occurs on all coinage metals.[26] These observations have been confirmed for the related molecule TCNQ on Cu(100).[36] The bending down of the polar −CN groups causes a substantial value of ΔE_{Mol}, which is of the same order of magnitude as ΔE_{Bond}. Both have opposite signs and, consequently, partly cancel each other. Thus, despite the observed Fermi-level pinning, the actual work-function modification appears to arise from a subtle interplay between charge-transfer and bending-induced dipoles.[15]

To analyze the actual influence of the molecular bend and hence ΔE_{Mol}, DFT calculations for a densely packed monolayer (1 molecule per 115 Å^2) of F4TCNQ on Ag(111) in an experimentally motivated unit cell (see Supporting

Information) were performed with the molecular backbone fixed to the optimized adsorption distance of 3.57 Å.[26] Then, the CN-groups were systematically flexed as shown in Figure 1b. This bending reflects a somewhat hypothetical situation, but, as will become clear below, serves as an excellent test-bed to explain the effects determining the interface energetics. The contributions of ΔE_{Mol} and ΔE_{Bond} to $\Delta\Phi$ were calculated and are shown together with $\Delta\Phi$ in Figure 1c. For ΔE_{Mol}, a linear dependence on the −CN out-of-plane bent is found with values ranging from −0.98 to +0.98 eV. The dotted line in Figure 1c represents the (hyptothetical) situation of a constant ΔE_{Bond}, that is, the situation one would encounter, if $\Delta\Phi$ was determined by ΔE_{Mol} plus the value of ΔE_{Bond} of the planar geometry. The calculated $\Delta\Phi$ (solid squares in Figure 1c), however, displays a markedly different evolution: When the cyano-groups are located between the backbone and the metal, i.e., when the cyano groups are bent downwards, as in the actual adsorption geometry found in experiment, we observe only a very weak dependence of $\Delta\Phi$ on the position of the −CN groups. The evolution of ΔE_{Bond} with the −CN bending largely compensates the change of ΔE_{Mol}. In this case, the work-function of the F4TCNQ covered surface is determined by Fermi-level pinning. The fact that $\Delta\Phi$ does not remain absolutely constant will be explained below.

In sharp contrast to the situation described above, upward bending of the −CN groups hardly affects ΔE_{Bond}. Hence, in this region the actual evolution of $\Delta\Phi$ closely matches the hypothetical situation described by the dotted line, and work-function modifications beyond the "pinning-limit" can be observed. This asymmetric dependence of $\Delta\Phi$ on the bending does not arise from interactions between the −CN groups and the Ag(111) surface, as it is also observed when F4TCNQ is located 10 Å above the metal surface and is also not limited to the F4TCNQ/Ag interface (see Supporting Information). At this point, it should be emphasized that this is also not a consequence of molecule−molecule interaction or depolarization effects. In fact, one arrives at the same conclusions when studying the F4TCNQ/Ag interface in a different packing motif and packing density (also shown in the Supporting Information).

The origin of this observation rather lies in the spatial location of the molecular dipoles (here the −CN groups) relative to the region in which the charge rearrangements between metal and molecule occur: Fermi-level pinning, by definition, requires the pinned molecular state at energy ε to align with the substrate's Fermi energy, E_F. This leads to a relative shift of the potential landscapes of the metal and the monolayer by an energy ΔE that equals the difference between ε and E_F (cf., Figure 2a). It can be achieved by charge rearrangements between the metal and the molecular layer giving rise to ΔE_{bond}. Introducing a dipole layer between the metal and the adsorbate, as schematically shown by the vacuum energy discontinuity in Figure 2b
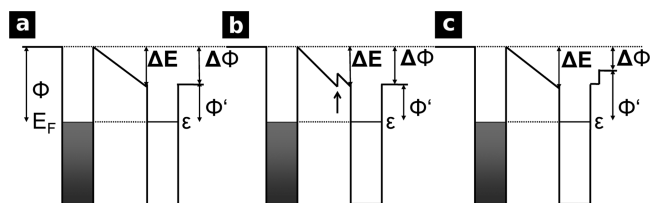
FIGURE 2. Schematic representation of the interface energetics in Fermi-level pinned metal/monolayer interface. The left potential well represents the metal, the right well corresponds to the molecular monolayer. E_F denotes the Fermi energy, and ε the energy of the pinned level. Φ and Φ' are the work-function of the pristine metal and the work function of the joint system, respectively, and $\Delta\Phi$ denotes the work function change. ΔE is the potential drop required to align ε and E_F. In (a), the situation without any molecular dipole is shown and (b) depicts the interface energetic with a molecular dipole induced potential step (indicated by the arrow) between metal and molecule. In (c), the situation for the potential step being located above the metal/monolayer junction is shown.

(highlighted by an arrow and, here, representing a ΔE_{mol}), must not change the relative alignment between ε and E_F. That is, ΔE needs to remain the same and the impact of the additional dipole layer has to be compensated by a larger (or smaller) ΔE_{bond}. To a first approximation (vide infra), also the sample work function Φ' would not be affected by the additional dipole layer.

If, however, the dipole layer was introduced above the region where the states responsible for pinning are localized (Figure 2c), this would not interfere with Fermi-level pinning and, thus, it would have no impact on the energetics in the region between the metal and the molecular layer. In this case, ΔE_{bond} would remain constant and ΔE_{mol} would change the vacuum energy (E_{VL}) above the system. This results in a modified sample work function Φ' in spite of pinning. The situation outlined in Figure 2b(c) is strongly reminiscent of what is shown in Figure 1c for downward (upward) bending of the $-$CN groups. Indeed, when plotting the electron potential energy for a hypothetical free-standing F4TCNQ layer perpendicular to the long molecular axis (Figure 3a,b) or the plane-averaged electron potential energy (Figure 3c), one sees that the vacuum energy changes significantly only above that side of the layer toward which the $-$CN groups are bent.

At this point the question arises to what extent other parameters like the adsorption distance play a role and whether effects like the distance dependent Pauli push-back[37] are of any relevance. Following the above considerations, one might come to the conclusion that neither of them counts, as Pauli push-back is an intrinsic part of ΔE_{Bond} and changing the charge-transfer distance will be compensated by a different amount of transferred charge in a straightforward manner. In this context, one, however, must not forget that charging the molecular layer per se affects the energetic position of molecular levels[38] and hence also the position of the pinning level ε. This, naturally, changes ΔE in Figure 2a$-$c and consequently also the system work function Φ'. The dependence of the
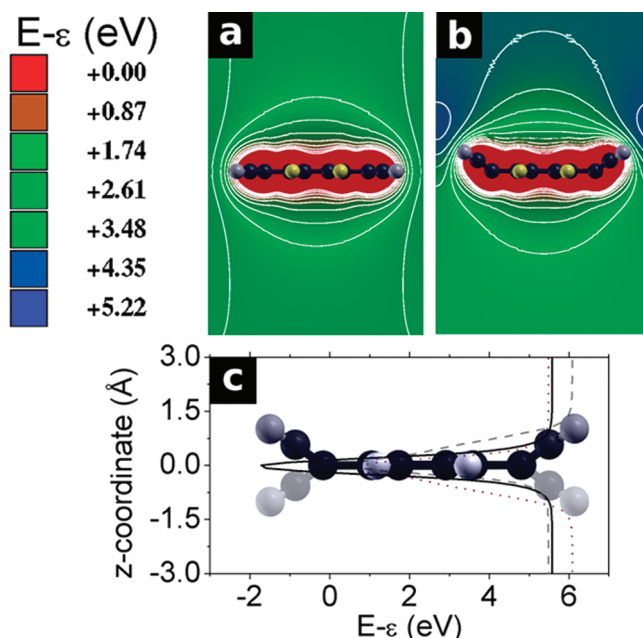

FIGURE 3. Electron potential energy (relative to $\varepsilon = 0$) for a hypothetical free-standing F4TCNQ monolayer in a plane perpendicular to the plane of the central ring and coincident with the long molecular axis for the planar (a) and bent (b) geometry. White lines are isodensities representing a step of ca. 0.3 eV. (c) The electron potential energy averaged over the plane parallel to the surface for the planar (solid black line), downward bent (dashed light gray), and upward bent (dotted dark gray) geometry.

work-function change on the adsorption distance has indeed been documented in a computational study on 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) adsorbed on coinage metals.[39] Another effect is that geometric distortions also change the molecular eigenstates, thus affecting the position of the pinning level (cf. Supporting Information). A combination of the above-described aspects is responsible for $\Delta\Phi$ being not exactly constant for the downward bent $-$CN groups as shown in Figure 1c. In this context it should be mentioned that varying the packing density (surface coverage) of the adsorbate layer necessarily also modifies the amount of transferred charge per molecule to realize a certain ΔE, which in turn changes ε and, thus, somewhat impacts the work-function modification. A second consequence of electrostatic intermolecular interactions is that at higher packing densities depolarization effects reduce in particular the molecular dipole moments in the situation depicted in Figure 2c.[40] Independent of all these effects, the pronounced asymmetry in the evolution of $\Delta\Phi$ with the out-of-plane bend, α, is clearly a consequence of the different location of the molecular dipole relative to the charge-transfer region.

To illustrate that the above-described mechanism does not depend on the specific system, we next discuss a conceptually different example. Doubly reduced methylviologen (MV0) is a potent electron donor, which has been
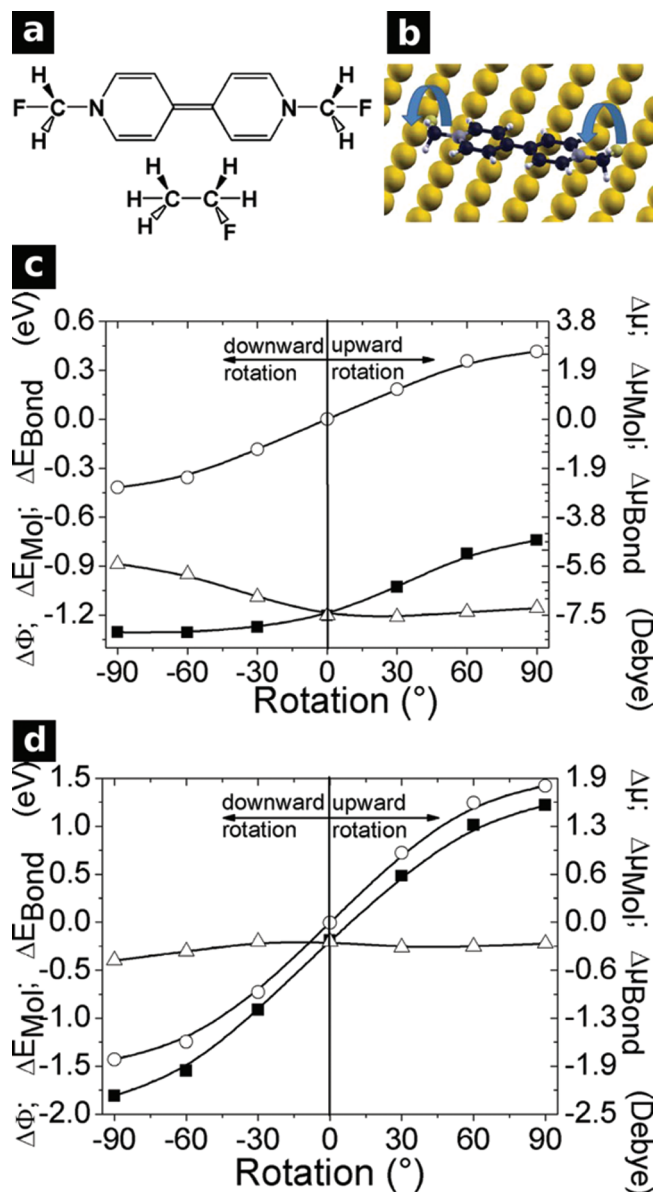
FIGURE 4. (a) Chemical structure of 1,1′-bis-fluoromethyl-1H,1′H-[4,4′]bipyridinylidene (FMV0) and fluorethane. (b) Structure of FMV0 adsorbed on Au(111). The arrows indicate the rotation of the CH$_2$F-groups. (c) Evolution of $\Delta\Phi$ (closed squares), ΔE_{Mol} (open circles), and ΔE_{Bond} (open triangles) as function of the rotation of the CH$_2$F substitutent of FMV0. The left y-axis gives these quantities in eV, while the right y-axis lists the corresponding dipole moments per adsorbate molecule. Lines are b-spline interpolations to the calculated values and intended as guide to the eye. (d) Similar to (c) for the rotation for fluorethane along its C−C bond.

shown experimentally to reduce the work function of a Au surface by 2.2 eV.[41] For this compound, we find an almost perfectly planar adsorption geometry. To endow the molecule with an intrinsic dipole moment, we have replaced one hydrogen atom in each of the methyl groups by fluorine (FMV0; see Figure 4a, top). In a monolayer of FMV0, the magnitude and spatial position of the intrinsic dipole can be tuned by a rotation of the peripheral −CH$_2$F

groups (see Figure 4b). Here we study FMV0 on a Au(111) surface in a 5 × 3√3 unit cell, corresponding to (sub)-monolayer coverage (1 molecule per 226 Å^2) in analogy to the investigation of doubly reduced viologen in ref 41. A study at full coverage is prevented by the fact that the structure of a densely packed monolayer consisting of MV0 or its derivatives is not known.

Because of symmetry reasons, an upward and a downward rotation of the terminal groups affect ΔE_{Mol} in the same way (open circles in Figure 4c). Moreover, in perfect analogy to F4TCNQ on Ag(111) and in agreement with the above reasoning, it is found that when the C−F dipole is located between the metal and the plane of the molecule (negative angles in Figure 4c), ΔE_{bond} almost perfectly counteracts the evolution of ΔE_{mol}. This results in a hardly changing $\Delta\Phi$ determined solely by pinning. For positive angles, the C−F dipole is found outside of the immediate interface (i.e., outside the charge-transfer region). Therefore, ΔE_{bond} remains constant regardless of ΔE_{mol}, and $\Delta\Phi$ strongly depends on the rotation angle.

To demonstrate that Fermi-level pinning is a necessary requirement for the asymmetry, we studied also fluorethane (Figure 4a, bottom), a wide-gap insulator that does not undergo charge-transfer with an Au(111) surface but still bears an intrinsic dipole moment, whose orientation can be easily tuned. For the sake of consistency, we assumed the same adsorption distance (3.53 Å between the top metal layer and the carbon atoms) as for FMV0. To account for the smaller size of the molecule, a 3 × √3 unit cell was chosen (1 molecule per 45 Å^2), again representing the case of a loosely packed monolayer (this results in a higher dipole density than for FMV0 discussed above resulting also in a larger ΔE_{mol}). Figure 4d shows the evolution of $\Delta\Phi$, ΔE_{Bond}, and ΔE_{mol} with respect of the rotation of fluorethane along its C−C bond. Since no significant charge transfer occurs at the interface, ΔE_{Bond} is generally small (−0.2 to −0.3 eV), and varies only as the individual atoms change their distance to the surface, thereby slightly modulating Pauli push-back. Note that in the absence of Fermi-level pinning, changes in the push-back will not be compensated by interfacial charge-transfer as described for the above cases. The variations in ΔE_{mol} are much larger (between −1.4 and +1.4 eV) and therefore determine the trend for $\Delta\Phi$ for positive and negative angles. This is because they are no longer compensated by ΔE_{Bond} for molecular dipoles between the monolayer and the metal. The larger absolute magnitude for ΔE_{mol} compared to FMV0 is simply a consequence of the higher packing density.

At this point, the question arises whether the above-described effect is only valid for flat lying molecules that undergo changes in their geometry, or whether the same trends can also be reproduced for Fermi-level pinned self-assembled monolayers. These bear the advantage that they can be derivatized in a relatively straightforward manner. A suitable example is substituted [2,5′;2′,5″]-
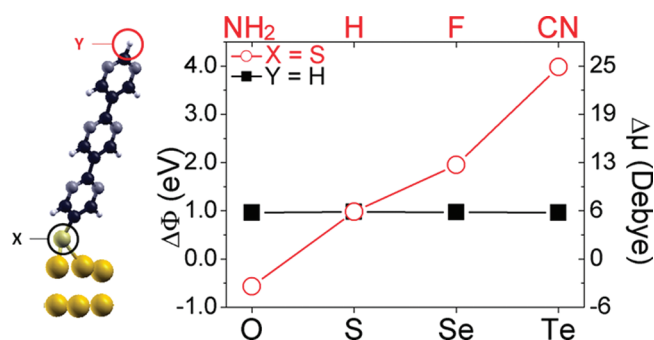
FIGURE 5. (Left) Chemical structure of the terpyrimidine SAM. Black balls represent carbon atoms, gray denote nitrogen, white balls are hydrogen atoms, golden atoms represent Au. The black circle indicates the location of the docking group, while the red circle shows the location of the tail group. (Right) Modification of the work function of a Au(111) surface by a densely packed terpyrimidine SAM with different docking groups (closed black squares head group = H) and with different tail groups (open red circles, docking group = S). The left y-axis gives the work-function change in eV, while the right y-axis lists the corresponding dipole moment per unit cell (containing two molecules).

terpyrimidine[31,42] on Au(111) shown in the left part of Figure 5. Here, X denotes the functional group that binds the monolayer covalently to the gold surface, and Y is the headgroup to be functionalized by dipolar substituents. The pinned level is located in the polar backbone of the monolayer. The right part of Figure 5 (filled squares) shows the induced work-function modification for X = O, S, Se, and Te (Y = H). Despite the different bonding chemistries, $\Delta\Phi$ does not change at all for the whole series. This is in sharp contrast to what one observes for a nonpinned terphenyl-backbone, where varying X results in $\Delta\Phi$ values differing by up to 1.4 eV (details see Supporting Information). Note that for the sake of comparability, the geometries were kept fixed at the structure of the sulfur-substituted compound at a packing density of 2 molecules per 45 Å. Figure 5 also displays the effect of varying the tail group in the thiolate-bonded terpyrimidine (Y = H, NH_2, F, and CN). Since the dipole layer created by the −Y substituents is outside the "charge-transfer" region, that is, "above" the pinning level, a work-function modification beyond pining can be observed as expected from the above considerations. For Y=CN, results in an exceptionally large value of +3.98 eV for $\Delta\Phi$ and, thus, in a work function of the SAM-covered Au(111) surface as high as 9.20 eV. To what extent such "super-dipole layers" will actually be observed in practice, only time can tell and will greatly depend on whether the necessary molecules can be made and whether they form well-ordered and densely packed monolayers.

Conclusion. To summarize, we have shown that whether molecular dipole layers play a role for the work function of Fermi-level pinned metal/monolayer systems is crucially determined by the position of that dipole layer. When the molecular dipoles are within the region affected

by the pinning-induced charge rearrangements, they have virtually no effect on the final work function of the system. This is because in that case the molecular dipoles are compensated by variations in the charge-transfer dipoles arising from the metal−molecule interaction. The finding holds true independent of the type of the adsorbed system (flat-lying donor or acceptor layer, or SAM), the charge transfer distance, and the origin of the molecular dipole (bending and rotation of substituents or change in docking groups). When, however, the molecular dipoles are located above the metal−molecule charge-transfer complex, their effect will be additive to that resulting from the pinning itself. We are optimistic that keeping that in mind will allow the design of novel systems that give rise to work-function modifications of unprecedented magnitude.

Supporting Information Available. Extensive description of the employed methodology and the used geometries, data for F4TCNQ on Ag at 10 Å distance to the surface, for FMV0 at 5 Å distance to the surface, and information on the work-function modifications for differently substituted terphenyl-monolayers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) For the situation sketched in Figure 2b, the reduction of the molecular dipoles due to depolarization again has to be largely compensated by a modification of ΔE_{Bond}.

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(42) While Fermi-level pinning has been observed experimentally for MV0 and also F4TCNQ, such molecules to the best of our knowledge have not yet been investigated experimentally. As a consequence, bearing in mind the well known band-gap problem of DFT, it cannot be guaranteed that Fermi level pinning actually occurs in this SAM. This does, however, in no way affect the fundamental conclusions drawn here.