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Letter

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Anticorrelation between the Evolution of Molecular Dipole Moments and Induced Work Function Modifications

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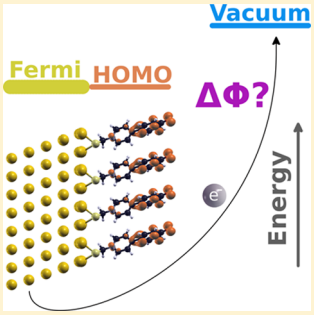
Supporting Information

ABSTRACT: We explore the limits of modifying metal work functions with large molecular dipoles by systematically increasing the dipole moment of archetype donor−acceptor molecules in self-assembled monolayers on gold. Contrary to intuition, we find that enhancing the dipoles leads to a reduction of the adsorption-induced change of the work function. Using atomistic simulations, we show that large dipoles imply electronic localization and level shifts that drive the interface into a thermodynamically unstable situation and trigger compensating charge reorganizations working against the molecular dipoles. Under certain circumstances, these are even found to overcompensate the effect that increasing the dipoles has for the work function.



SECTION: Physical Processes in Nanomaterials and Nanostructures

The work function Φ defined as the minimum energy to extract an electron from a solid material is a fundamental physical quantity. When measured by photoemission spectroscopy, it is determined as the difference between the vacuum energy just outside of the material, E_{vac}, and the Fermi Energy, E_F.[1,2] Φ can be altered easily as it is strongly influenced by the detailed atomistic structure of the surface.[1] This triggered the seminal idea of tuning Φ via the adsorption of ordered polar species, which can be exploited to improve the efficiency of charge carrier injection in electronic devices.[3] Organic molecules have been identified as ideal agents for this task as their permanent dipole moments can be efficiently adjusted through chemical substitution. Moreover, they offer the possibility to cover a substrate as a self-assembled monolayer (SAM), this way operating as ideal surface dipole layers.[4−6] While the magnitude of the monolayer dipole moment determines the amount of the work function change ΔΦ, the dipole polarity determines its sign. This correlation between the dipole moment of the SAM molecules and ΔΦ is a well-established concept and has been confirmed experimentally for a number of metal−SAM systems.[1,3,7,8] For "conventional" SAMs, it is recovered also with the methodology used here, as shown for a number of systems contained in the Supporting Information (SI).

Still, a direct correlation between the molecular dipole moment and the SAM-induced ΔΦ can be disturbed by several effects.[9] First, the chemical bonding of the SAM to the substrate is associated with substantial charge rearrangements affecting Φ[10] Their magnitude critically depends on the SAM docking chemistry.[11,12] Also, the possibility of structural reorganizations such as dimerization of the molecules (see ref 13 and references therein) can reduce the monolayer dipole moment and, thus, impede the impact of the molecular dipole onto ΔΦ. Moreover, even in a well-ordered layer, inherent depolarization of the dipoles due to the neighboring polar molecules occurs.[14−20] Such a depolarization causes the dipole moment per molecule to be significantly smaller in the monolayer than that in the gas-phase, effectively limiting the achievable work function change. A saturation of ΔΦ with the molecular dipole has actually been predicted by Vager et al. based on the dielectric breakdown of the layers.[21] For large dipoles and SAMs of low polarizability, also significant charge transfer between the substrate and the SAM has been suggested based on electrostatic total energy arguments.[14]

In this Letter, we show for deliberately chosen donor−acceptor based "push−pull" molecules bonded to Au(111) using state-of-the-art atomistic simulations that under certain circumstances, increasing the molecular dipole moment can, in fact, reduce the change of the work function. This unexpected anticorrelation, which effectively goes beyond the saturation of Φ anticipated from the aforementioned depolarization effect or dielectric breakdown, is rationalized by a dipole-induced localization and renormalization of the electronic levels in the SAM (i.e., traced back to a quantum mechanical origin). These state localization and level shifts, in fact, originate already at the molecular level but are found to prevail in the densely packed monolayer and, thus, withstand competing electrostatic effects such as depolarization. At the metal−organic interface, they lead to charge rearrangements that preserve thermodynamic equilibrium and overcompensate for the increase in dipole moment. The underlying effects are of fundamental nature and

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can be expected to apply quite generally for the adsorption of molecules with large, extended dipoles.

We here rely on donor−acceptor (push−pull-type) merocyanine derivatives (MCs), as shown in Figure 1a, because of

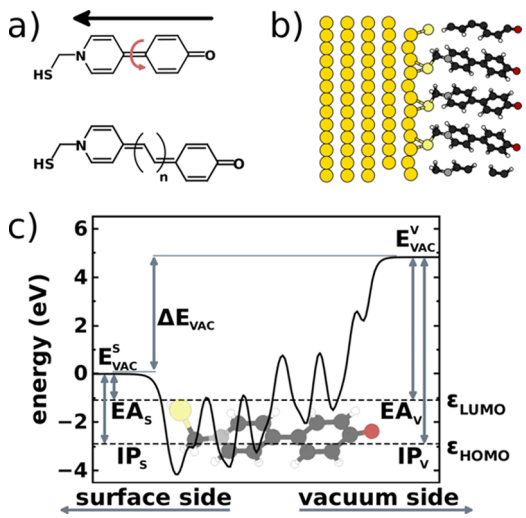

Figure 1. (a) Chemical structures of the investigated MCs. To increase dipole moments, the molecules can be twisted (top) and the separation between the donor and acceptor parts can be increased (bottom). (b) Side view of the Au(111)/MC-SAM interface. (c) Plane-averaged electron electrostatic energy of the planar, free-standing MC-SAM. The vacuum levels (E_{vac}), ionization potentials (IPs), and electron affinities (EAs) are indicated for the side oriented toward the metal surface (s) and toward the vacuum (v). (Structural representations produced using XCrySDen.[22])

their very large molecular dipole moments (ca. −13 D) with the charge separation extending over the molecular backbones. Such systems have been successfully synthesized and employed in the field of nonlinear optics.[23−26] MCs offer exceptionally convenient ways to systematically explore the impact of increasing dipoles as the latter can be tuned by twisting the molecule along the central inter-ring carbon−carbon bond (Figure 1a, top), which drives the molecule into a zwitterionic ground state.[25] Note that such twisting has been achieved experimentally[26] by attaching substituents to the center of the molecule (for a discussion of the possible existence of a biradical state as suggested in ref 27, see the SI). As an alternative strategy for increasing the dipole of MCs, one can elongate the molecules by inserting $-C_2H_2-$ spacers between the donor and acceptor parts (see Figure 1a, bottom).

Experimentally, the assembly of zwitterionic molecules with large dipole moments on inorganic substrates has been realized for several systems.[28,29] For the case of donor−acceptor molecules, it was shown that using chemical linkers to bind the molecules to the substrate results in stable SAMs on Au.[30] Therefore, we functionalized MCs with thiol (−SH) docking groups (cf. Figure 1a and b), allowing for a strong gold−molecule bond, and modeled these MC-SAMs on Au(111) in a ($\sqrt{3} \times 3$) surface unit cell (Figure 1b). Our simulations and optimizations (for details, see the SI) rely on state-of-the-art density functional theory (DFT) calculations conducted with the electronic structure program VASP[31] and the optimizer GADGET.[32] To obtain the final electronic structure, we performed computationally demanding HSE06 hybrid DFT band structure calculations.[33] This is necessary as it has been shown that hybrid DFT functionals correct some of the errors inherent to standard (semi)local xc functionals,[34] especially for differently localized electronic states.[35]

First, we investigate the unbound molecular layer of MC molecules. In Figure 1c, we show the plane-averaged electron electrostatic energy of the hypothetical, "free-standing", H-saturated MC-SAM (i.e., the system in the absence of the gold substrate; the corresponding plot for the bonded SAM is contained in the SI). The strongly polar MC molecules modify the electrostatic potential energy in a profound way.[10] Arranged in an ordered fashion, they "split space" into two regions with different vacuum levels, E^s_{vac} on the side eventually oriented toward the metallic surface and E^v_{vac} toward the vacuum (see Figure 1c). Due to the strong dipoles, the associated potential energy jump (ΔE_{vac}) is particularly large (ca. 5 eV). Consequently, the monolayer ionization potential IP obtained from the maximum of the band derived from the highest-occupied molecular orbital (HOMO) is largely different for removing an electron to one or the other of the two sides of the monolayer (IP_s versus IP_v; see Figure 1c).[10] Importantly, we find that IP_s is small (ca. −3 eV) compared to the work function of pristine Au(111) calculated to be −5.1 eV. This comparably small IP_s (and large IP_v; cf. Figure 1c) is a direct consequence of the huge ΔE_{vac} as the latter results in a reduction of IP_s and increase of IP_v compared to the molecular situation. Thus, the peculiar alignment of the molecular relative to the metallic levels discussed in detail below, naturally arises from the large molecular dipole moments.

Increasing the dipole moment of the MC molecules in the free-standing SAM by increasing the inter-ring twist angle (see Figure 1a) further amplifies ΔE_{vac} by up to ∼0.7 eV (stars in Figure 2a). Traditionally, one would expect that this tuning of the conformation should boost the SAM-induced change in $\Delta\Phi$ in a similar manner.

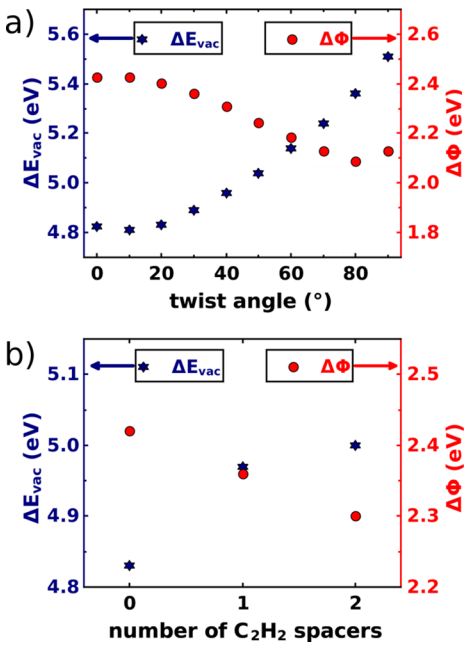

Figure 2. Calculated step in the electrostatic energy for the free-standing SAM, ΔE_{vac}, and induced work function modification, $\Delta\Phi$, for the same SAM adsorbed on gold. Data are plotted both as a function of the inter-ring twist angle (a) and the number of inserted $-C_2H_2-$ spacers (b). Note that for the chosen packing density, 1 eV in energy translates to a dipole moment of −1.2 D per molecule.

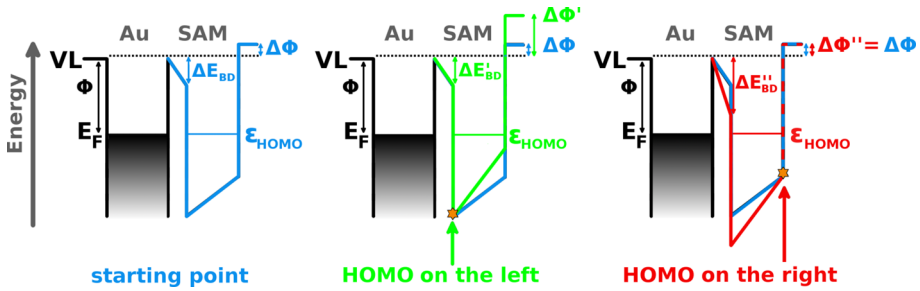

Figure 3. Schematic showing the impact of orbital localization on $\Delta\Phi$ when increasing ΔE_{vac} in the pinning regime. Starting from Fermi-level alignment (left panel and all blue plots), a continuous increase in ΔE_{vac} maps onto an increase in $\Delta\Phi$ when the pinning level is localized close to the metal (green line, center panel) and is diminished by a decrease of ΔE_{BD} when the state is localized toward the vacuum (red line, right panel).

Interestingly, when examining the MC-SAMs bonded to gold via the thiolate group (i.e., when considering $\Delta\Phi$), we find the exact opposite trend (circles in Figure 2a). The twisted MC molecules result in significantly smaller $\Delta\Phi$ values (by ca. 0.3 eV) than their planar (i.e., zero degree twisted) analogues. Note that the slight increase seen for $\Delta\Phi$ when increasing the twist from 80 to 90° is a consequence of a vanishing HOMO−LUMO gap in the MC-SAM. When elongating the MC molecule through inserting $-C_2H_2-$ spacers, thus enlarging the molecular dipoles by increasing the charge-transfer distance between the donor and acceptor groups (cf., Figure 1a), the same trends are found (Figure 2b); ΔE_{vac} increases by 0.2 eV (stars in Figure 2b), while $\Delta\Phi$ decreases by −0.1 eV (circles in Figure 2b). As discussed above, this anticorrelation between trends in ΔE_{vac} and $\Delta\Phi$ (i.e., between the dipolar layer in vacuum and adsorbed on a surface) is entirely unexpected from a purely electrostatic perspective and somehow reminiscent of the anomalous work function shifts reported for atomic species adsorbed on metal surfaces, where negatively charged atoms were shown to result in an unexpected adsorption-induced work function decrease.[36,37]

The origin of this unusual behavior must be rooted in the metal−organic interaction and the potential energy shift arising from the charge rearrangements upon SAM−gold bond formation. This "bond dipole", ΔE_{BD}, electrostatically shifts all molecular states with respect to E_F; with ΔE_{vac}, it adds up to $\Delta\Phi$ ($\Delta\Phi = \Delta E_{vac} + \Delta E_{BD}$).[10] For thiol-bonded SAMs on Au(111), the expected ΔE_{BD} is, however, only on the order of ∼−1 eV,[10] which is much smaller than the relatively large ΔE_{BD} = −2.4 eV calculated from $\Delta\Phi$ and ΔE_{vac} for the planar MC-SAMs on Au(111). Remarkably, we obtain a pronounced amplification of ΔE_{BD} by ∼−1 eV from the planar to the perpendicular configuration, with ΔE_{BD} eventually reaching a value of −3.4 eV (see Figure S4 in the SI). As a consequence, ΔE_{BD} not only counteracts the twisting-induced effect of 0.7 eV in ΔE_{vac}, it even overshoots it in magnitude by 0.3 eV. To appreciate the general relevance of this behavior, it is necessary to understand its microscopic origin. Interfacial charge rearrangements comparable in magnitude to the present ones have previously been shown to occur as a consequence of Fermi level pinning.[38] This mechanism manifests itself in a strong response in the interfacial charge density, which ensures that equilibrium is maintained by preventing occupied states in the organic from lying above (or unoccupied below) the Fermi level.[39,40] Typically, the energy of the frontier electronic states in the organic is then found to be close to E_F of the substrate.[41−44] Recalling that IP_s of the planar free-standing MC-SAM is only ∼−3 eV (see Figure 1c) and Φ of the bare Au(111) substrate is −5.1 eV in the calculations, Fermi level pinning is to be expected here (and also for less noble substrates such as the Ag(111) surface). Indeed, our calculations confirm that the highest-occupied band aligns with E_F for all studied systems.

The evolution of Φ in the case of Fermi level pinning has been shown to depend on the spatial localization of the molecular pinning level.[45] We illustrate this in a *Gedankenexperiment*, where we start from a pinned situation representative of the MC-SAM on gold (Figure 3, blue curves) and then gradually increase ΔE_{vac} across the monolayer (green and red curves in Figure 3, central and right panels). When the pinning level, which for the present situation is the HOMO, is spatially close to the interface region (Figure 3, green curve in central panel), a change in ΔE_{vac} will hardly affect their relative energetic distance to E_F. Then, no further charge rearrangements are needed to maintain equilibrium at the interface (i.e., to align the pinning level with E_F), ΔE_{BD} will remain essentially constant, and an increase of ΔE_{vac} (and the molecular dipoles) directly maps onto a further increase of $\Delta\Phi$. When, however, the HOMO is localized close to the vacuum side (red curve in right panel), increasing ΔE_{vac} would shift it up in energy with respect to E_F and, consequently, trigger further charge rearrangements, keeping the HOMO and E_F aligned, which results in a larger ΔE_{BD}. In that case, an increase in ΔE_{vac} will be diminished by the amplified ΔE_{BD}, and $\Delta\Phi$ remains constant. This saturation of $\Delta\Phi$ due to orbital localization holds for layers with opposite dipole polarity as well. Large molecular dipoles pointing away from the metal surface decrease Φ until pinning of the lowest-unoccupied molecular orbital (LUMO) at E_F occurs. Then, the localization of the LUMO determines the further evolution of Φ.

The localization of the pinned states can be determined by the plane-averaged charge density corresponding to the HOMO-derived band best shown for the free-standing (i.e., nonbonded) MC monolayer (see Figure 4a). It is found to be localized toward the vacuum side of the SAM already at 0° twist (see the SI for the full real space representation of the associated electronic bands). This notion is supported by the center of the HOMO-related charge being shifted relative to that of the (positive) nuclear charge by 2 Å toward the vacuum (vertical lines in Figure 4a). Upon twisting the SAM (and thereby increasing the dipole), the localization of the HOMO even slightly increases. This (partial) localization of the HOMO on the donor side is exactly what one expects for a push−pull molecule, while the LUMO tends to be localized more on the acceptor side (molecular orbital localization). In the densely packed MC-SAM, the "molecular" situation is modified by two collective effects. As mentioned above, a parallel alignment of polar molecules results in a reduction of the individual

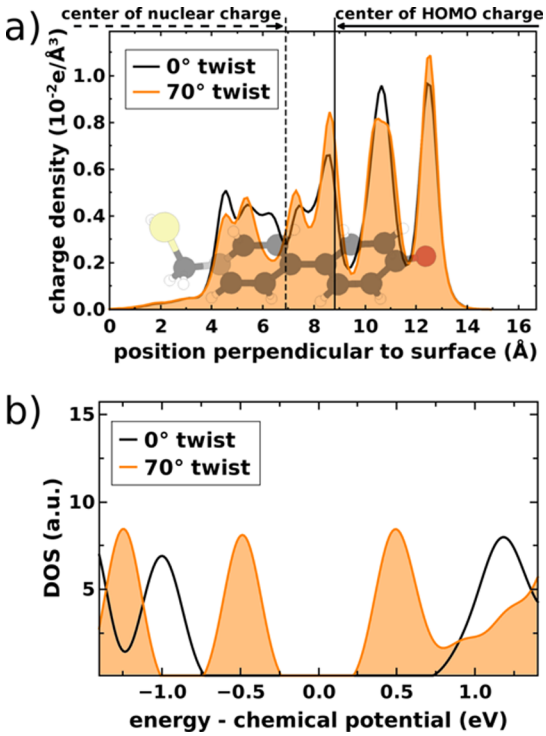

Figure 4. (a) Plane-averaged charge density corresponding to the HOMO-derived band for 0 and 70° twists; (b) corresponding densities of states for the free-standing MC-SAM. In (a), the vertical lines denote the center of the (positive) molecular nuclear charge (dashed) and the center of the charge corresponding to the HOMO (solid) for the planar MC.

molecular dipole due to depolarization effects,[9,14−21] which generally decreases the degree of the aforementioned charge localization (collective orbital delocalization).[35] Concomitantly, the extended dipole moments in the SAM cause a spatially continuous modification of the electrostatic potential along the monolayer (see Figure 1c), which results in a collective orbital localization.[35,46] We, however, do not observe profound changes in the localization of the frontier levels due to these collective effects.

The localization of the relevant states has two important consequences for Φ: (i) Monolayers with particularly large, delocalized dipoles will typically comprise pinning levels more localized toward the vacuum, which in itself poses a natural obstacle for increasing Φ, and for strong localization, even a natural limit for ΔΦ achievable with ordered dipolar layers (see Figure 3, right panel). This rationale prevails when reversing the dipole direction as the change in sign of ΔE_{vac} entails pinning to occur at the LUMO, which then, due to the change in dipole polarity, is again localized close to the vacuum side. (ii) The localization of the frontier states together with the potential gradient within the SAM (see Figure 1c) results in a particularly small IP_s for dipoles pointing toward the surface and particularly large EA_s for dipoles pointing away from it, creating a situation prone to Fermi level pinning independent of the specific nature of the molecules in the SAM. Of course, whether Fermi level pinning is ultimately observed depends on the electronic structure of the substrate (Φ in particular), the electronic levels within the adsorbate, and the amplitude of the molecular dipole moment.

The remaining question is why in the case of the MC-based SAMs on gold one goes beyond the above described saturation of Φ, that is, why does increasing the dipoles result in a decrease of ΔΦ. Indeed, a saturation of ΔΦ can also be inferred from electrostatic models, as explicitly shown in ref 21. To explain the anticorrelation observed here, one however needs to dig deeper and analyze how strategies for increasing dipoles typically affect the molecular electronic structure. Comparing the density of states (DOS) of the MC-SAM at planar and twisted geometries (Figure 4b; see the SI for the complete data set), we find that increasing the dipole by twisting the molecular segments leads to a strong energetic upshift (destabilization) of the HOMO and a downshift (stabilization) of the LUMO; the band gap is reduced significantly (see Figure 4b). For the MC-SAM on the Au(111) substrate (see Figure S7 in the SI), we find a comparable band gap reduction. As the HOMO is aligned with E_F due to Fermi level pinning, this results in a reduced energetic difference between E_F and the vacuum level (i.e., the work function is decreased). This eventually causes the observed anticorrelation between the molecular dipole and ΔΦ. Similar effects are observed when increasing the charge-transfer distance by inserting $-C_2H_2-$ spacers. As the conjugation length of the molecules in the SAM is extended, its band gap is reduced, and thus, Fermi level pinning involving the HOMO-related band becomes more effective. The net effect can also be explained through the impact of the reduced gap on interfacial charge rearrangements. To maintain equilibrium and retain the alignment of the HOMO with E_F, the destabilization of the HOMO that occurs already in the free-standing SAM has to be compensated for by additional charge rearrangements when the layer is brought into contact with the metal, which further boosts ΔE_{BD}. Consequently, the total ΔE_{BD} not only compensates for increases in ΔE_{vac}, it even overshoots it in magnitude and causes the observed anticorrelation (see Figures 2a and b).

In summary, we have shown that, in sharp contrast to intuition, increasing the dipole of SAM-forming molecules attached to a metal substrate does not necessarily result in an increase of ΔΦ. As soon as the dipole moments surpass a certain limit, Fermi level pinning becomes inevitable, which can pose a natural limit to achievable work function modifications, in line with earlier electrostatic considerations.[21] To what extent the charge rearrangements can fully compensate for the dipole increase, however, depends on the localization of the pinned states, that is, their quantum nature. The latter becomes even more relevant for explaining our most unexpected finding, namely, an anticorrelation between the evolutions of the dipole moment and induced work function changes observed here for MC-type SAMs on Au(111). It is found to arise from an energetic shift of the HOMO occurring as a consequence of increasing the dipoles.

■ ASSOCIATED CONTENT

Supporting Information

Additional data, including the calculated step in the electrostatic energy for free-standing tail-group substituted biphenylthiol SAMs, ΔE_{vac}, the induced work function modification for the same SAMs bonded to the Au(111) surface, the plane-averaged electron electrostatic energy of the planar Au(111)/MC-SAM, the bond dipole ΔE_{BD} for the MC-SAMs on Au(111), real-space representations of the electronic states, density of states plots, details of the system setup, additional methodological details, and a discussion of the possible existence of a biradical state for the twisted merocyanine molecule. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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