Role of Adatoms for the Adsorption of F4TCNQ on Au(111)

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ABSTRACT: Organic adlayers on inorganic substrates often contain adatoms, which can be incorporated within the adsorbed molecular species, forming two-dimensional metal–organic frameworks at the substrate surface. The interplay between native adatoms and adsorbed molecules significantly changes various adlayer properties such as the adsorption geometry, the bond strength between the substrate and the adsorbed species, or the work function at the interface. Here, we use dispersion-corrected density functional theory to gain insight into the energetics that drive the incorporation of native adatoms within molecular adlayers based on the prototypical, experimentally well-characterized system of F4TCNQ on Au(111). We explain the adatom-induced modifications in the adsorption geometry and the adsorption energy based on the electronic structure and charge transfer at the interface.

1. INTRODUCTION

Metal–organic interfaces play a major role for the performance of many modern devices, especially in the context of organic electronics. Often, thin (mono)layers of organic molecules, which are sometimes referred to as charge-injection layers, are inserted between the (metallic) electrode and the active organic material in order to improve the device performance. These layers serve two purposes: first, they change the effective work function of the electrode and, as a direct consequence, the level alignment with respect to the active material. Second, they electronically decouple the electrode and the active material. Depending (inter alia) on whether the charge-injection layer itself is metallic (i.e., exhibits density of states [DOS] at the Fermi edge) or not, this can either lead to an increase in device performance or to a decrease due to a larger tunneling barrier.

It is commonly assumed that, upon the right deposition conditions, organic molecules self-assemble into ordered structures on metal surfaces. This assumption is frequently corroborated by low-energy electron diffraction or scanning tunneling microscopy experiments, which demonstrate large domains with long-range order. However, there are also recurrent reports where the organic molecules do not purely self-assemble, but rather incorporate “adatoms” originating from the substrate, forming structures that are more reminiscent of two-dimensional metal–organic frameworks. Especially adatoms of the same species as the substrate atoms are naturally present at the surface. They can be extracted from the bulk when the adsorption energetics favors the incorporation of adatoms within the adlayer. Thus, the bulk serves as a natural adatom reservoir, and adatoms can inevitably be created during the adsorption of the molecules. The situation is made more complicated by the fact that, in some cases, adatoms cannot readily be observed by STM experiments, for example, because they are sterically inaccessible to the tip or because they do not exhibit states near the Fermi energy. They are also generally invisible to most spectroscopy methods (such as core spectroscopy), because their signal is too weak compared to the signal from the bulk substrate.

Yet, recent studies, based on the determination of adsorption heights and ab initio calculations, indicate that adatom-containing structures may be more prevalent than hitherto thought, even calling previous studies explicitly into question. If this hypothesis holds true, a more detailed understanding of the role of adatoms, that is, the impact they have on metal–organic interfaces, is urgently required.

In this work, we will focus on two suites of questions: First, why are adatoms incorporated at all? That is, how do they affect the adsorption energetics at the interface, and how do they change the way a molecule binds to the surface? Second, how does the presence of adatoms affect electronic properties relevant for devices, for example, the work function and the DOS near the interface? To answer these questions, we study the adsorption of the prototypical molecule F4TCNQ (2,3,5,6-

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Tetrafluoro-7,7,8,8-tetracyanoquinodimethane adsorbed on Au(111) with and without Au adatoms by means of dispersion-corrected density functional theory. We find that the presence of adatoms significantly alters the charge-transfer between the substrate and adsorbate. While the overall charge of the molecule remains reasonably similar (approx. neutral with adatom vs 0.2 e⁻ net charge on F4TCNQ without adatoms), both the charge backdonation from the cyano groups and the charge donation into the lowest unoccupied molecular orbital (LUMO) become twice as large if adatoms are present. This goes along with a significant change in the binding energies. In particular, the contribution from the covalent bonding (the charge backdonation) is significantly larger when adatoms are present. At the same time, we find that filling the LUMO with two electrons, which would be strongly unfavorable for many molecules, has a negligible impact here. Conversely, the geometric distortions that F4TCNQ undergoes lead to increased first and second electron affinities which offset the energetic cost of the geometric change.

2. METHODS

All calculations were performed using the version 210413 of the FHI-aims software package. The PBE exchange–correlation functional was used together with the zeroth order regular approximation (ZORA) to account for relativistic correlation functional was used together with the zeroth order exchange functional (ZORA). The PBE 39 exchange–correlation functional was used together with the zeroth order exchange functional (ZORA) to account for relativistic correlation. For the self-consistent field (SCF) cycles of the DFT calculations, multiple convergence thresholds were simultaneously employed, as recommended by best practices. The change in the volume-integrated root-mean-square of the density was set to $10^{-3}$ e⁻. The difference in the total energy was set to $10^{-6}$ eV. Furthermore, the threshold for the sum of the eigenvalues of the Kohn–Sham states was set to $10^{-2}$ eV and the change of the forces acting on each atom were converged to $10^{-3}$ eVÅ.

The FHI aims software package provides different levels for the numerical parameters (such as the integration density) and the numerically tabulated atom centered basis functions. In this work, we used the “tight” defaults, which were shown to yield converged results in a previous work. Going beyond these settings, we furthermore increased the onset of the basis set cutoff potential from the default of 4 to 6 Å in order to obtain adsorption energies converged within 1 meV (see Supporting Information).

The reciprocal space was sampled using a $\Gamma$-centered k-grid with a k-point density (in the directions of the reciprocal lattice vectors) of approximately 14 1/Å⁻¹, also yielding adsorption energies that are converged to 1 meV (see Supporting Information). This corresponds to $7 \times 12 \times 1$ k-points for the $(\frac{1}{3})$ unit cell (which is the experimentally determined unit cell) and $5 \times 6 \times 1$ k-points for the $(\frac{8}{3})$ which we used for comparison in the Supporting Information.

The Au substrate was modeled by slabs consisting of 5 layers of Au atoms, forming an Au(111) surface with the surface normal vector in z-direction. To describe the organic–inorganic interface using a three-dimensional periodic calculation, a repeated slab approach was applied. The slabs were separated by 40 Å of vacuum in the z-direction, avoiding quantum mechanical interaction between consecutive slabs. To compensate for the dipole potential jumps of asymmetric slabs, the built-in dipole correction of the FHI-package was applied.

All adsorption geometry optimizations were performed using the trust radius method, relaxing all atoms of the molecule, the adatom and the top two layers until the maximum remaining force fell below 0.01 eVÅ.

3. RESULTS AND DISCUSSION

3.1. Adsorption Geometry and Energy. To study the role of adatoms, we chose F4TCNQ on Au(111), since multiple independent studies have found that it readily and reproducibly forms well-ordered structures containing adatoms as part of the adlayer. The surface structure consists of only one F4TCNQ molecule and one adatom per unit cell, which reduces the computational effort and facilitates the analysis of this system (compared to larger unit cells). The strong interactions between the adsorbate and substrate lifts the herringbone reconstruction of Au(111), and the F4TCNQ molecule-Au-adatom network is arranged in a $(\frac{5}{3} \frac{2}{3})$ Au(111) surface supercell, as shown in Figure 1.

![Figure 1. Minimum energy structures of F4TCNQ adsorbed on Au(111) in the $(\frac{5}{3} \frac{2}{3})$ Au(111) surface supercell](image)

The first step in our study is to determine the impact of the adatoms on the geometry of the interface, both laterally (i.e., how the adsorption site of the molecule changes with respect to the surface) and vertically (i.e., the adsorption heights of the different atoms and the bending induced by the adsorption on the surface). The adsorption height was calculated as the vertical distance between the top layer of the substrate and the atoms of the adsorbed F4TCNQ. The top layer was defined by the average height of all Au(111) surface atoms (neglecting possible adatoms) in the reconstructed adsorption geometry. Vertical modifications in the geometry are particularly relevant, since they are experimentally accessible (e.g., via X-ray standing wave experiments) and can be used to indirectly infer the presence of adatoms. But also lateral positioning is
important, since it gives us a first insight about how adatoms change the interaction with the surface.

Therefore, the geometry of F4TCNQ in the experimentally determined unit cell was optimized including and excluding the adatom. In these calculations, the molecule, the adatom (if present), and the top two metal layers were relaxed. The optimizations with/without the adatom were started from six/four different adsorption positions, initially placing the center of the molecule in an atop, bridge, fcc, or hcp hollow position as well as placing the adatom on the fcc or hcp hollow position. The relative position of the adatom in the adlayer was kept constant. Five optimizations with adatom lead to the global minimum, while one leads to a local minimum. Two optimizations without adatom lead to the global minimum, while the other two lead to local minima. A compilation of the initial geometries is given in the Supporting Information.

When the adatom is present, we find two stable adsorption geometries: one where the center of the F4TCNQ is located approximately above a Au(111) bridge site and the adatom in an atop position (Figure 1a), and another where the center of the F4TCNQ molecule is above an atop position and the adatom in a bridge site (see Supporting Information). The former is by approximately 160 meV energetically more stable (see below). Incidentally, placing the center of the molecule over the bridge position is also the energetically most favorable alignment without the adatom present (see Figure 1b; other local minima are shown in the Supporting Information). We note in passing that this geometry also appears at low coverage (see Supporting Information), that is, it is not influenced by intermolecular interactions. Furthermore, no adsorption geometry can be found where the adatom is in a hollow position, which would be its most stable position in the absence of molecules (see Supporting Information). In other words, the lateral position of the adatom is now determined by the energetically ideal position of the F4TCNQ molecule it bonds to, which itself is determined by the interaction between the molecule and the surface. This indicates that upon binding to the F4TCNQ molecules, the electronic coupling between the adatom and surface is substantially weakened and the dominating interaction takes place between the adatom and the F4TCNQ molecules.

Besides the relative positioning of the molecule and metal, also the adsorption heights show significant differences with and without adatoms (see Figure 2): if no adatoms are present, DOS of the full system (with adatom) onto the F4TCNQ molecule. In Figure 3b, the DOS is projected onto the adatom and resolved for the different angular momenta of the wave function. Regions where there is significant DOS from F4TCNQ frontier orbitals are highlighted. For all frontier orbitals (i.e., the former F4TCNQ HOMO − 1, HOMO and LUMO), we find that mainly the d-orbitals of the adatom contribute to the DOS. Conversely, we find contributions of the s-orbitals of the Au adatom only in regions without significant F4TCNQ DOS. This indicates a hybridization of the former F4TCNQ HOMO − 1, HOMO, and LUMO with mainly the d-orbitals of the Au adatom (see Figure 3).

With this, we can explain why only two of the four cyano groups remain in plane and bond to the adatom, while the other two bend downwards toward the substrate, it is instructive to analyze the nature of the bonding between F4TCNQ and the adatom in more detail. Figure 3a shows the projection of the adatom on the angular momentum eigenfunctions of the Au adatom.

Conversely, if adatoms are present, they attach to the cyano groups of two of the four neighboring F4TCNQ molecules. This causes the cyano groups to be lifted from the substrate toward the F4TCNQ backbone (see Figure 1a), which further corroborates the conclusion that the electronic coupling of the adatoms to the surface is weakened. The adsorption height of the adatom (3.03 Å) and the adsorption height of the backbone (3.23 Å) differ only by 0.2 Å (see Figure 2a). Consequently, the F4TCNQ cyano groups that bond to the adatom remain almost at the same height as the F4TCNQ backbone, while the cyano groups that do not bond to the adatom bend toward the substrate just like in the adatom-free case (compare Figure 2a and 2b). Due to this, the twist of the F4TCNQ geometry, which can already be observed for the adsorption geometry without adatoms, is further amplified by the presence of the adatom. The twist of F4TCNQ and the uplift of the adatom highlight the importance of the vdW contributions, since they are only reported by groups that include the dispersion corrections. Our adsorption geometry for the case with adatoms is in good agreement with the values determined via normal-incidence x-ray standing waves (NIXSW) (3.45 ± 0.20 Å for the carbon backbone) and surface x-ray diffraction (SXRD) (3.29 ± 0.04 Å for the carbon backbone and 2.95 ± 0.08 Å for the adatom) reported by Mousley et al.

To understand why only two of the four cyano groups remain in plane and bond to the adatom, while the other two bend downwards toward the substrate, it is instructive to analyze the nature of the bonding between F4TCNQ and the adatom. Figure 3a shows the projection of the adatom on the angular momentum eigenfunctions of the Au adatom.
Au atomic orbitals must match the phase of the F4TCNQ LUMO and HOMO at the cyano groups. The HOMO and the LUMO orbital of F4TCNQ are \( \pi \)-orbitals, that is, they exhibit a nodal plane in the plane of the backbone. Hence, for an Au adatom that lies within the adsorbate plane, a 5d orbital can only match this condition when it overlaps with the cyano groups of two neighboring F4TCNQ molecules (see Supporting Information). Conversely, it is not possible to build any linear combination of 5d orbitals that could overlap with, for example, four neighboring F4TCNQ molecules and match the phase of the molecular orbitals (MOs) at the cyano groups. This also explains why the 6s orbital of the Au adatom does not contribute to the bonding to \( \pi \)-orbitals: the spherically symmetrical 6s orbital cannot interfere constructively with both phases of the MOs at the cyano groups of F4TCNQ (see Supporting Information for a visualization of the relevant orbitals).

The important questions, at this point, are (i) whether the structure with a Au-adatom is indeed energetically more favorable, and (ii) if so, why that is the case, that is, what drives the incorporation of adatoms into the F4TCNQ layer? To answer the first question, the adsorption energy (\( \Delta E_{\text{ads}} \)) of F4TCNQ on the Au(111) surface both with and without adatom was calculated according to eq 1.

\[
\Delta E_{\text{ads}} = E_{\text{fin}} - E_{\text{init}} \tag{1}
\]

Equation 1 describes the adsorption energy as the difference between the energy of the final geometry-optimized structure after the adsorption process (\( E_{\text{fin}} \)) and the energy of all components in their initial geometry before the adsorption took place (\( E_{\text{init}} \)). Without adatoms, \( E_{\text{init}} \) consists of the Au(111) slab energy of the \( \left( \frac{5}{1} \frac{2}{3} \right) \) supercell and the energy of the free F4TCNQ molecule in vacuum. With adatoms, the situation is more ambiguous, as three different cases could be made: one for assuming that the adatom is already initially there, one for taking Au-atoms from kinks or step-edges, or one for taking the atom out of the bulk. Here, we opt for the third. It is, on the one hand, the most conservative assumption in terms of the adatom formation energy because a bulk atom has the highest coordination number of all possibilities. On the other hand, it is also the necessary choice if the bulk is to be seen as reservoir for the Au atoms, that is, if a whole F4TCNQ layer forms rather than just a few molecules. Based on these assumptions, we find \( \Delta E_{\text{ads}} = -1.81 \) eV in the adatom-free case and \( \Delta E_{\text{ads}} = -2.41 \) eV when adatoms are present, that is, the adsorption is by \(-0.60 \) eV more favorable when adatoms are involved. This clearly shows that the phase with adatoms incorporated within the adlayer is not only kinetically trapped but, in fact, the thermodynamically stable phase.

At this point, one may ask what makes the adatom-containing structure so much more beneficial despite the additional cost of extracting an adatom. To shed light onto this question, we separate the adsorption process into three hypothetical steps: (1) The “preparation” of the substrate, that is, the energy required for the substrate atoms to rearrange into the geometry it has after adsorption. In the case of the adatom-containing structure, this includes the energy required to extract an adatom from the bulk and place it in the atop position. (2) The “preparation” of F4TCNQ, that is, the energetic cost for a gas-phase F4TCNQ molecule to deform into the geometry it assumes on the surface. (3) The adsorption, that is, the combination of the “prepared” geometries into the final, joint geometry. Figure 4 compares the evolution of the energy for the situation with the adatom (right side of Figure 4a) and without the adatom (Figure 4b).

In both cases, the energy of the initial state, \( E_{\text{init}} \), consists of the unreconstructed Au(111) slab and the energy of the free F4TCNQ molecule in vacuum \( E_{\text{gas phase}} \) at infinite separation (see eq 2). For the case with the adatom, one has to add the energy of a single Au bulk atom to the initial state energy.

\[
E_{\text{init}} = E_{\text{slab}} + E_{\text{gas phase}} \tag{2}
\]

As a next step, the slab is set into the geometry it assumes on the surface. Without the adatom, this entails only small movements of a few atoms, costing approx. \( \Delta E_{\text{prep-slab}} = 0.08 \) eV (see eq 4). For the situation with the adatom, conceptually,
first an additional Au-atom has to be taken from the bulk overcoming the cohesive energy of Au ($\Delta E_{\text{coh}} = 3.39$ eV); then, it is adsorbed in the position it would assume on its own\(^{22}\) (i.e., the hollow position, $\Delta E_{\text{ads}}^{\text{bulk}} = -2.65$ eV, see Supporting Information). Thus, the formation of an adatom (at the hollow position) from the bulk amounts to an energetic cost of $\Delta E_{\text{prep-slab}} = 1.98$ eV, according to eq 3.

$$\Delta E_{\text{form}} = \Delta E_{\text{coh}} + \Delta E_{\text{ads}}^{\text{bulk}}$$  \hspace{1cm} (3)

Finally, all atoms of the slab are moved into the position they assume in the combined system, including moving the adatom to the atop position ($\Delta E_{\text{surf reorder}}^{\text{with adatom}} = 1.24$ eV), see eq 4. Overall, for the adatom system, this results in a quite significant preparation energy of the slab of $\Delta E_{\text{prep-slab}} = 1.98$ eV.

$$\Delta E_{\text{prep-slab}} = E_{\text{slab}}^{\text{reconstructed}} - E_{\text{init}}$$

It is important to notice that $E_{\text{slab}}^{\text{reconstructed}}$ is the energy of the initial slab that includes the energy of one single bulk Au atom.

The F4TCNQ deformation energy ($\Delta E_{\text{df}}$) must be overcome regardless of the presence of adatoms. The deformation energy can be obtained from the energy difference between the F4TCNQ molecule in the gas phase geometry and the bent geometry it assumes on the surface (both calculated non-periodic), as defined in eq 5.

$$\Delta E_{\text{df}} = E_{\text{F4TCNQ}}^{\text{gas phase}} - E_{\text{F4TCNQ}}^{\text{planar}}$$  \hspace{1cm} (5)

Naively, one could expect that the deformation without adatoms is energetically more costly, as all four CN-groups bend downward, while otherwise two remain approximately planar. Surprisingly, we find that for the free molecule, the geometry of the adsorbed state without adatoms is the more favorable one. The deformation energy per molecule, $\Delta E_{\text{df}}$, increases from 212 meV for the adsorption geometry without adatoms to 334 meV for the adsorption geometry with adatoms (see Figures 4 and 5a). Therefore, the deformation energy change of F4TCNQ due to different adsorption geometries can be excluded as the driving force for the energetical preference of the adatom-incorporating structure.

This leaves, as a last step, the combination and interaction of the two prepared subsystems. Since both the preparation of the substrate and the preparation of the molecule are energetically less favorable when an adatom is included, but the overall adsorption is more beneficial, it is immediately clear that a much more favorable interaction between the molecule and the substrate occurs when the adatom is present: to quantify this interaction, we introduce the molecule–substrate interaction energy $\Delta E_{\text{mol–sub}}^{\text{intct}}$ (eq 6). It is defined as the energy difference between the final structure after the adsorption and the structure made of the F4TCNQ molecule in the adsorbed adlayer geometry and the slab with the adatom at the atop position.

$$\Delta E_{\text{mol–sub}}^{\text{intct}} = E_{\text{fin slab}} - (E_{\text{slab}}^{\text{unreconstructed}} + \Delta E_{\text{df}})$$  \hspace{1cm} (6)

As Figure 4 shows, without the adatom, the interaction between the molecule and the substrate is approximately $\Delta E_{\text{mol–sub}}^{\text{intct}} = -2.10$ eV, while with the adatom, it is as large as $\Delta E_{\text{mol–sub}}^{\text{intct}} = -4.72$ eV. It is interesting to note at this point that almost the whole interaction energy without the adatom is due to vdW interactions ($\Delta E_{\text{vdW}} = -1.74$ eV), that is, there is almost no net energy gain due to “chemical” interaction such as charge transfer and covalent bonding. Conversely, since with the adatom the vdW energy is similarly large ($\Delta E_{\text{vdW}} = -1.74$ eV), an energy gain of almost -2.98 eV due to charge transfer and covalent bonding is realized.

To understand to what extent the different interaction originates from the interaction of F4TCNQ with the adatom itself, it is useful to also look at the adsorption process in a slightly different way: the left side of Figure 4a shows a hypothetical reaction pathway where first a free Au atom is created ($\Delta E_{\text{coh}} = 3.39$ eV), which then forms a 2D-MOF with F4TCNQ ($\Delta E_{\text{2DMOF}} = -3.83$ eV) and is subsequently deformed into the geometry on the surface, before it interacts with the Au slab. Notably, the interaction energy of the 2D-MOF with the surface is about the same ($\Delta E_{\text{2DMOF-sub}} = -2.13$ eV) as the interaction of F4TCNQ alone with the surface and is also mostly driven by vdW interactions ($\Delta E_{\text{mol–sub}} = -2.10$ eV). This is further corroborated by the fact that the vdW interaction energy gain of the 2D-MOF when adsorbing on the Au(111) surface is only marginally smaller $\Delta E_{\text{vdWMOF}} = -1.82$ eV.

This provides a first indication that the reason for the incorporation of Au atoms into the molecular network is not driven by charge transfer with the surface, but rather due to the fact that in this geometry, a stronger covalent bond between the molecule and Au can be formed.

A summary of the several energies used to describe the adsorption process and bond structure with and without adatoms (see Figures 4 and 5) is provided in Table 1.

### 3.2. Electronic Structure and Electrostatic Potential.

Overall, we have seen that most aspects (the reconstruction of the substrate, the deformation of the molecule, and even the vdW interaction between the molecule and metal) are energetically worse for the situation with the adatom. The only energetic contribution making the structure with the adatom more favorable than the one without is the electronic...
adatom, the LUMO is in direct resonance with the Fermi level. Consistent with earlier reports, we assume a strongly metallic character; the presence of adatoms determining how the MOs align energetically with respect to the Fermi level. Figure 6 compares the situation without the adatom, approximately a single electron is added to the negatively charged molecule must be overcome. Since without the adatom, the Coulomb-repulsion from the substrate (including adatoms). Thus, we will now shine a light on the adatom-induced changes in the electronic structure.

A useful way to determine the impact of adsorption on the electronic structure is the projection of the DOS onto the MO, particularly the cyano groups. The charge donation to F4TCNQ (i.e., forward donation) can be quantified by summing the occupation numbers, $N_i$ of all formerly unoccupied orbitals of the F4TCNQ molecule (see eq 7).

$$Q_{\text{forward}} = \sum_{i=LUMO}^{\infty} N_i$$

We find a forward donation of 2.2 and 1.3 electrons per adsorbed F4TCNQ molecule, with and without adatoms, respectively. Hence, the adatom causes a significant increase in the charge transferred from the Au substrate to the initially unoccupied MOs of F4TCNQ. These results are in accordance with previous works dealing with isolated F4TCNQ molecules without adatoms as well as dense packed layers including adatoms.

In passing, we note that previous theoretical studies, which did not utilize any dispersion correction methods, came to different conclusions regarding the electronic structure of F4TCNQ with as well as without adatoms. Those contradicting results can most likely be attributed to the differences in adsorption geometry when neglecting vdW contributions, especially the larger adsorption distance (compare Section 3.1 for details).

The vastly different occupation of the LUMO, with and without adatoms, raises an important issue: for many molecules, even when the insertion of one electron into the LUMO is exothermic (i.e., the first electron affinity is negative), adding another electron to the same orbital is endothermic (i.e., the second electron affinity is positive), since for the second electron, the Coulomb-repulsion of the negatively charged molecule must be overcome. Since without the adatom, approximately a single electron is added to the LUMO, while in the presence of an adatom, the LUMO gets doubly occupied (see Figure 6); it is worthwhile discussing the electron affinity of F4TCNQ. Figure 7 shows the change of the energy upon charging (i.e., the electron affinity) for a free F4TCNQ molecule in the gas phase for (a) the gas-phase optimized geometry and (b) the geometry it assumes on the surface with the adatom. Qualitatively, as expected, for all geometries, we see that the first electron affinity is strongly negative, while the second electron affinity is positive. However, the second electron affinity is already quite small for the gas phase molecule (only 402 meV), showing that the quantum-mechanical gain of adding an electron to the LUMO and the Coulomb-repulsion from the first electron approximately compensate. Moreover, when the molecule is calculated in its final geometry on the surface, the second electron affinity notably decreases. Qualitatively, this is to be expected, as a system out of equilibrium becomes more reactive and exhibits a smaller gap (and, thus, an energetically lower LUMO).

Quantitatively, it is still interesting to notice that both the first and the second electron affinities become

| Interaction | with adatom | no adatom |
|-------------|-------------|-----------|
| $\Delta E_{coh}$ [eV] | 3.39 | 2.13 |
| $\Delta E_{surf}$ [eV] | 2.65 | 3.39 |
| $\Delta E_{adatom}$ [eV] | 1.24 | 0.74 |
| $\Delta E_{total}$ [eV] | 4.72 | 2.65 |

Table 1. Summary of All Adsorption Process Energies Introduced in the Text

*For a definition of the different energies, see Figure 4.*

interaction between the (distorted) molecules and the substrate (including adatoms). Thus, we will now shine a light on the adatom-induced changes in the electronic structure.

Figure 6. MADOS projected on the MOs of F4TCNQ adsorbed on Au(111) with (a) and without adatoms. (b) Occupation numbers of the MOs of F4TCNQ in the adsorbed state with and without adatoms.

Figure 6b shows the increased occupation of the former F4TCNQ LUMO in case adatoms are present in the adlayer (orange dots) compared to the adatom-free case (blue crosses).

F4TCNQ is known to undergo a Blyholder-like charge transfer with coinage metals, with a (mostly ionic) charge donation into the LUMO and a covalently driven charge backdonation originating from the molecular $\sigma$-system (particularly the cyano groups). The charge donation to F4TCNQ (i.e., forward donation) can be quantified by summing the occupation numbers, $N_i$ of all formerly unoccupied orbitals of the F4TCNQ molecule (see eq 7).

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approx. 300 meV per electron more favorable, which is in the same order of magnitude (but of opposite sign) than the energetic cost of the deformation. In other words, adding a second electron into the F4TCNQ LUMO is, per se, associated with very little energetic cost. More importantly, however, the energetic deformation makes adding the second electron less unfavorable, and, on top of this, enhances the electron affinity by an amount that completely offsets, and even overcompensates, the energetic cost of deformation (compare Figure 5).

Besides the charge donation into the molecule, F4TCNQ simultaneously donates charge back into the substrate. This is reflected in a slight decrease in the occupation numbers of all MOs that are energetically below the F4TCNQ LUMO. According to eq 8, the amount of charge shifted due to backdonation can be quantified by summing the occupation numbers of all initially occupied orbitals up to the HOMO and subsequent subtraction of the original number of electrons of the free F4TCNQ molecule (136 electrons).

\[
Q_{\text{back}} = \sum_{i=1}^{\text{HOMO}} N_i - 136
\]

Calculating the backdonation from the occupation numbers in Figure 6a according to eq 8 yields a total charge of 2.2 and 1.1 electrons shifted toward the substrate, with and without adatoms, respectively. Overall, this means that when an adatom is present (a) the charge rearrangement in both directions is significantly larger, and (b) the F4TCNQ molecule is effectively charge-neutral (i.e., donation and backdonation cancel each other). In the case without adatoms, forward donation dominates over back donation, yielding a net charge transfer of 0.2 electrons per F4TCNQ molecule. A point worth noting is the difference in the magnitude of charge transfer in both directions. We attribute this observation to the fact that in the presence of adatoms, a much stronger covalent bond between the molecule and the metal is possible (see above). Since this bond mainly results in charge backdonation, it must be compensated by a similarly large charge donation, resulting in a more strongly filled LUMO. This corroborates the above indication why adatoms are incorporated in the first place: the ability to form stronger covalent bonds leads to an energy gain that offsets the costs of generating the adatom from the bulk.

The geometry and the different charge transfer with and without the adatom also have a direct impact on interface properties that are directly relevant to applications, such as the adsorption-induced work function modification, \(\Delta \Phi\). \(\Delta \Phi\) is a direct consequence of the change of the electrostatic potential above the interface due to the formation of dipoles that form at the interface (and their density).\(^{1,5}\) To illustrate the impact of adatoms on this quantity, we apply the common approach of splitting \(\Delta \Phi\) into a contribution from the molecule, \(\Delta E_{\text{mol}}\), the contribution from the slab, \(\Delta E_{\text{slab}}\), and the bond dipole due to interfacial charge transfer, \(\text{BD}^{27,56}\) The bond dipole is caused by the total rearrangement of electron density due to the chemical interaction of the molecules with the substrate.

\[
\Delta \Phi = \Delta E_{\text{mol}} + \Delta E_{\text{slab}} + \text{BD}
\]

As all our calculations employ a dipole correction counteracting the potential difference between top and bottom of a geometry, the total interface dipole, as well as the geometric dipoles (\(\Delta E_{\text{mol}}\) and \(\Delta E_{\text{slab}}\)), can be obtained directly from calculations of the respective subsystems. As the last constituent, the bond dipole is simply obtained via subtracting the geometric contributions from \(\Delta \Phi\).

The full \(\Delta \Phi\) amounts to +0.23 eV without adatoms and −0.20 eV with adatoms. Its components are visualized in Figure 8. In both cases, the molecular dipole opposes the bond dipole, but due to the stronger bending of the molecule geometry without the adatom, also its dipole component is stronger (−0.55 vs −0.36 eV). In the structure with the adatom, this dipole is further decreased by the substrate dipole opposing the molecular dipole (0.13 eV). For the case without adatoms, the substrate dipole can be neglected (0.01 eV).

The last contribution is the bond dipole. For the system without the adatom, the charge transfer from the substrate to the adlayer leads to a dipole of roughly 0.8 eV. With adatoms in the adlayer, this is reduced to only 0.03 eV due to the small net charge transfer. The bond dipole can also be calculated via the charge rearrangements of the electron density. This approach leads to slightly different results, but allows for some qualitative arguments about the origin of the dipole. Therefore, a discussion of this approach is presented in the Supporting Information.
4. CONCLUSIONS

In this work, we discuss how surface adatoms influence the adsorption of F4TCNQ on Au(111). We find strong indications that the incorporation of adatoms is driven by the fact that the molecule, specifically its cyano groups, can form more efficient covalent bonds with adatoms than with Au atoms in the first layer. This finding is supported by the observation that the adatom is moved away from its initial equilibrium position at the Au(111) hollow site toward an Au(111) atop site (also in agreement with literature\textsuperscript{44,46}) while being lifted up to the adsorption height of the F4TCNQ adlayer.\textsuperscript{46} The finding is furthermore corroborated by the observation that the interaction between the surface and F4TCNQ alone, as well as with a hypothetical F4TCNQ–Au network, is driven mostly by vdW forces. The energy gain from the improved (covalent) bonding is so large that it readily offsets the energetic cost of extracting an Au atom from the bulk metal.

Interestingly, despite the fact that the adatoms allow two of the four cyano groups to remain approximately in the molecular plane, the different adsorption-induced distortion of the molecule plays a minor role for the energetics. In fact, in contrast to the naive expectation, in the presence of adatoms, F4TCNQ even experiences an increased twist, which is in agreement with other reports.\textsuperscript{46} The geometry optimization shows that the adatom only bonds to two of four neighboring F4TCNQ molecules, which can be explained by the hybridization between the atomic orbitals of the adatom and the MOs of the F4TCNQ molecule. By projecting the DOS on both the orbitals of the adatom and the molecule, we find that mainly the d orbitals of the adatom hybridize with the F4TCNQ frontier MOs, allowing for a coordination of the adatom to only two of four neighboring F4TCNQ molecules.

The presence of an adatom and the ensuing stronger covalent bonding leads to a marked increase in charge backdonation, that is, from the molecular σ-orbitals to Au, from ca. one electron without an adatom to two electrons with an adatom. To maintain Fermi-level pinning, this increased backdonation is compensated by a larger donation, that is, filling of the molecular LUMO (also here from ca. 1 electron to approx. 2 electrons). Filling the LUMO twice is energetically relatively favorable for F4TCNQ. Here, this is due to the fact that neutral F4TCNQ is a quinoid molecule (with 4 electrons in the π-system), and filling the LUMO twice thus fulfills the Hückel rule (i.e., creates a π-system with 4π + 2 electrons in the π-system), that is, makes the molecule aromatic and thus particularly stable. This is a classic example for surface-induced aromatic stabilization.\textsuperscript{55}

As a tentative synopsis of these observations, we expect systems that easily sustain significantly increased charge transfer, that is, that show a particularly low second electron affinity, to be particularly likely to extract adatoms from the bulk and include them into the molecular framework.

The presence of adatoms also directly affect various interface properties. A direct consequence of the charge transfer is that without adatoms, the LUMO is in direct resonance with the Fermi-energy, that is, the adsorbed molecule shows a large DOS at $E_F$ ("metallicity"), while with adatoms, only the high-energy flank of the LUMO crosses $E_F$, that is, the metallicity of the adlayer is, counterintuitively, small. Furthermore, we find that due to the modified charge transfer and molecular distortion, the adsorption-induced work function modification is significantly smaller (by ca. −0.4 eV) when adatoms are present.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c00994.

Convergence tests for the basis function cutoff radius, integration grid, explanations, and visualizations of stable F4TCNQ adsorption geometries with and without adatoms, bond dipoles calculated via electron densities, visualizations of the frontier orbitals of F4TCNQ, and a gold atom (PDF)

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