

Enhanced charge transfer in a monolayer of the organic charge transfer complex TTF–TNAP on Au(111)

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Abstract

Electronic doping is a key concept for tuning the properties of organic materials. In bulk structures, the charge transfer between donor and acceptor is mainly given by the respective ionization potential and electron affinity. In contrast, monolayers of charge transfer complexes in contact with a metal are affected by an intriguing interplay of hybridization and screening at the metallic interface, determining the resulting charge state. Using scanning tunneling microscopy and spectroscopy, we characterize the electronic properties of the organic acceptor molecule 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP) adsorbed on a Au(111) surface. The ordered islands remain in a weakly physisorbed state with no charge transfer interaction with the substrate. When the electron donor tetrathiafulvalene (TTF) is added, ordered arrays of alternating TNAP and TTF rows are assembled. In these structures, we find the lowest unoccupied molecular orbital (LUMO) of the free TNAP molecule shifted well below the Fermi level of the substrate. The TNAP is thus charged with more than one electron.

(Some figures may appear in colour only in the online journal)

1. Introduction

Organic semiconductors are a cheap and versatile alternative to customary silicon based semiconductor technology. The tuning of the electronic band structure is crucial for the conductance or optical properties of these materials. A common design strategy is the inclusion of electron accepting or electron donating atoms or molecules, thus acting as doping centers. Organic charge transfer complexes solely consist of electron acceptor and electron donor molecules. Their structural arrangement is usually governed by π -stacking interactions. Between these stacks there is charge transfer that provides the necessary charge carriers to form (low-dimensional) electronic bands.

In a monolayer, the conditions for charge transfer are altered significantly. The π orbitals interact with the substrate giving rise to a flat adsorption geometry and an inhibition of purely organic electronic bands [1, 2]. Hence,

a comparison of the amount of charge transfer on the surface with the respective bulk material is *a priori* difficult. The stabilization of a possible charge transfer includes an intriguing interplay between hybridization with the substrate and charge screening [3, 4]. Interestingly, the charge transfer may exceed the one known in the respective bulk material. This difference may also cause intriguing new properties, such as magnetism and superconductivity [5–7].

In particular, in a monolayer of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ), one electron is transferred into the lowest unoccupied molecular orbital (LUMO) of the free molecule [5]. This localized electron thus leads to a paramagnetic ground state of the molecule, which can be probed by a Kondo resonance in tunneling spectroscopy. The precise conditions for this peculiar charge stabilization are still obscure. To get more insight into the charge transfer reactions, one approach is to vary slightly the properties of the electron acceptor.

Our choice of acceptor molecule is thus 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP). This molecule consists of two quinonoid moieties in the central molecular backbone, one more than the TCNQ parent species. The larger distance between the electrophilic parts leads to a larger electron affinity [8, 9]. Here, we explore whether the tendency for TNAP to accept electrons is comparable to that of TCNQ when adsorbed on a gold surface. We show that the surface itself is weakly interacting with the TNAP molecules, leaving their molecular orbitals largely unperturbed, and the molecules stay in their neutral ground state. Co-deposition of the charge donor TTF leads to a mixed self-assembly, whose structure resembles that of the parent complex TTF-TCNQ. In contrast to TTF-TCNQ, we find no Kondo resonance in the TTF-TNAP compound. Instead, scanning tunneling microscopy suggests that the LUMO is shifted well below the substrate's Fermi level, indicating an occupation by more than one electron.

2. Experiment

All experiments were carried out on a Au(111) single crystal surface cleaned by repeated Ne⁺ sputtering and annealing cycles in ultra-high vacuum. TNAP molecules were evaporated from a Knudsen cell onto the Au(111) surface at a temperature of 450 K. TTF molecules were sublimated from the mixed TTF-TCNQ compound at a temperature of 350 K, well below the sublimation temperature of TCNQ. The Au(111) surface was kept at room temperature during both depositions. The sample was then pre-cooled and transferred into the STM, where all data were taken at a temperature of 4.8 K. Scanning tunneling spectroscopy (STS) was performed using a lock-in amplifier in the open feedback condition.

3. Results and discussion

3.1. TNAP on Au(111)

Deposition of TNAP on the Au(111) surface at room temperature leads to the formation of extended ordered molecular islands like those shown in figure 1(a). Closer inspection of the TNAP molecular lattice reveals a rhombic unit cell with lattice parameters $a = 1.0 \pm 0.1$ nm, $b = 1.0 \pm 0.1$ nm, enclosed by an angle $\alpha = 85^\circ$. This allows the molecules to lie flat on the surface, which is common to two-dimensional organic molecules on metal surfaces [10]. The corresponding structural model shows that all terminal nitrogen atoms point to hydrogen atoms of the neighboring TNAP molecules (figure 1(c)). The average distance between the electronegative N atoms and the H atoms amounts to ≈ 2 Å, typical for electrostatic intermolecular bonding. Since the lattice structure does not allow for any commensuration with the substrate, the stabilization of the TNAP islands is solely driven by these electrostatic intermolecular interactions. A second indication that the molecular layer is weakly interacting with the substrate, is the observation of the soliton lines of the herringbone reconstruction of the underlying surface. This

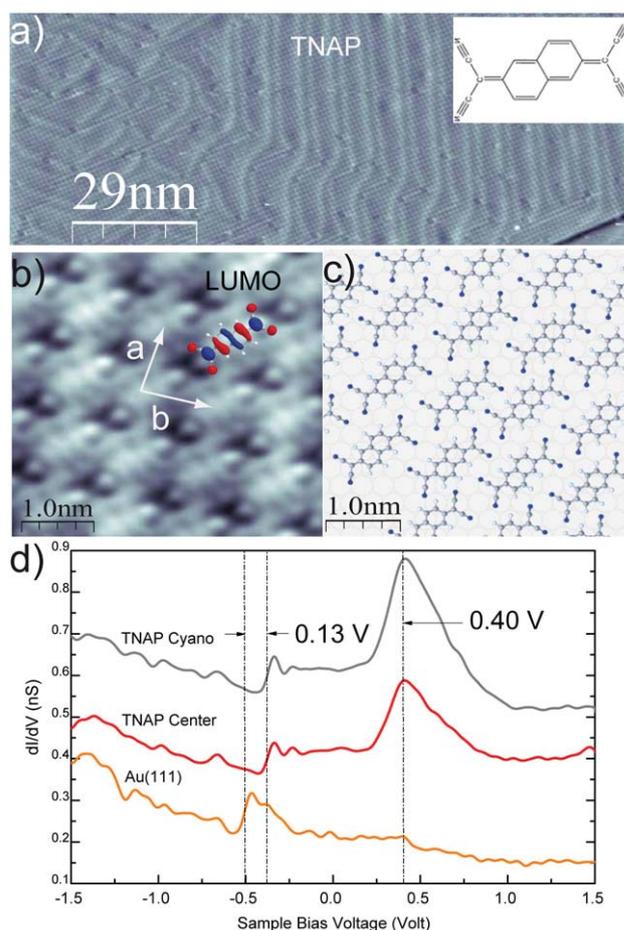


Figure 1. (a) STM topography image of a large ordered TNAP island (scanning parameters: sample bias voltage $V_S = 1.3$ V, tunneling current $I_T = 0.07$ nA). (b) Zoom of the ordered structure (scanning parameters: $V_S = 0.4$ V, $I_T = 0.50$ nA). (c) Structural model of the self-assembled TNAP layer. (d) dI/dV spectra obtained at different locations on the TNAP layer and on the clean Au(111) surface. The spectra taken on a TNAP molecule reveal a molecular resonance at 0.4 V and a shift of 0.13 V of the onset of the Au(111) surface state (feedback opened at $V_S = 1.5$ V, $I_T = 0.4$ nA, lock-in modulation 10 mV rms at 933.1 Hz). The STM images were processed by the freeware WSxM [24].

surface reconstruction can only be retained when the surface is unperturbed by the adsorbates [11].

The densely packed islands and weak interaction with the substrate suggest a neutral state of the molecular species despite their strong electron affinity [12]. To sustain this assumption, we perform tunneling spectroscopy on the individual molecules. The differential conductance (dI/dV) spectra measured at the center and the cyano group of the TNAP molecules inside the self-assembled TNAP islands, shown in figure 1(d), reveal a pronounced resonance at 0.4 eV. To trace the origin of this resonance we recorded a high resolution STM image at that particular energy. The TNAP molecules appear with four pronounced nodal planes separating circular protrusions at the ends of the molecules and three elongated ellipsoidal shapes at the molecular backbone (figure 1(b)). The LUMO of the free TNAP molecule reveals the same characteristic nodal planes, thus evidencing a largely unperturbed molecular electronic

structure on the Au(111) surface. Importantly, the finding of the LUMO well above the Fermi level reveals a negligible charge transfer with the substrate. The TNAP thus lies in a neutral state on the Au(111) surface despite its strong electron affinity. This observation resembles the findings for its smaller parent species TCNQ on the Au(111) surface [12, 13]. The slight increase in electron accepting character [8, 9] thus does not suffice to induce a charge transfer from the metal surface.

Despite this indication of no charge transfer with the surface, we note an energy shift of the Shockley type surface state of the Au(111) surface underneath the TNAP layer. While the clean Au(111) surface exhibits the surface state as a step-wise increase in the conductance located at -0.49 eV, it is found shifted by 0.13 eV towards the Fermi level on the TNAP monolayer. At first sight, this could indicate depopulation of the surface state by charge transfer from the surface to the molecular layer [14, 15]. The corresponding charge transfer per molecule would then correspond to $0.13e$. As a consequence, the LUMO level would be partially filled and should be located with a considerable overlap with the Fermi level. This is clearly not the case for the TNAP layer. Instead, we attribute the shifting surface state to changes in the work function and/or image potential, like is known for F4-TCNQ on noble metal surfaces [16]. Therefore, we conclude that the TNAP is in a neutral charged state on the Au(111) surface, in agreement with the spectroscopic data for TNAP on thin Au films [8].

3.2. TTF–TNAP on Au(111)

TTF is a prominent electron donor in the bulk and at the interface of molecular charge transfer complexes [17–19]. Also on the surface, its low ionization potential leads to the loss of electron charge into a Au(111) substrate [20]. Therefore, this potential electron donor is a promising choice to modify the charge state of TNAP on the Au(111) surface. At room temperature, the mixture of molecules self-assembles into highly ordered islands (figure 2(a)) with 1:1 stoichiometry, which co-exist with pure islands of excessive TNAP molecules. In contrast to the pure TNAP monolayer, the mixed layer removes the herringbone reconstruction of the surface, indicating a strong interaction with the gold substrate. Closer inspection of the mixed phase reveals alternating rows of TTF and TNAP (figures 2(b) and (c)), similar to the parent compound TTF–TCNQ on the Au(111) surface [5]. The individual molecules are identified by their characteristic orbital shapes. In contrast to the respective bulk phase [18] both molecular species lie parallel to the Au(111) surface. Neighboring TTF molecules are tilted by $\approx 25^\circ$ with respect to each other. The resulting lattice parameters are $a = 2.0 \pm 0.1$ nm, $b = 0.8 \pm 0.1$ nm and the angle between them $\alpha = 118^\circ$.

To get an insight into the electronic structure of the mixed layer, we record dI/dV spectra at different locations of the charge transfer complex. The spectra in figure 3(a) show a strong increase in differential conductance at ≈ 0.55 eV, while the original surface state of Au(111) is not present underneath the layer. A differential conductance map at this energy

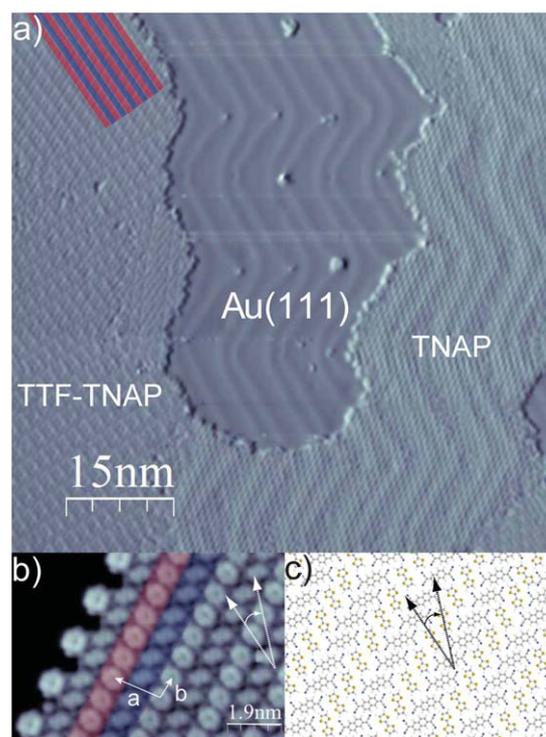


Figure 2. (a) STM topography image of an ordered mixed TTF–TNAP and a pristine TNAP island on the Au(111) surface (scanning parameters: $I_T = 0.2$ nA, $V_S = 1.0$ V). The Au(111) reconstruction is visible under the TNAP island but not under the mixed TTF–TNAP domain indicating a stronger surface–molecule interaction in the case of the TTF–TNAP layer. (b) Zoom of the ordered TTF–TNAP islands showing the parallel molecular rows of TTF and TNAP (scanning parameters: $V_S = -0.1$ V, $I_T = 0.4$ nA). (c) Structural model of the ordered self-assembled TTF–TNAP layer. The TTF molecules exhibit two different adsorption sites, which are rotated by about 25° with respect to each other.

reveals that the corresponding state is mostly delocalized along the mixed monolayer, notably having strong weight on both TTF and TNAP, despite their very different electron affinities. Hence, we can exclude this resonance being simply the LUMO of TNAP. Instead, a similarly extended state has been observed in the parent compound TTF–TCNQ on Au(111) [1]. Density functional theory simulations of that system have evidenced that the corresponding state is the surface state with some additional molecular character due mostly to the hybridization of TTF and Au states. Due to the strong structural and electronic similarities of the two monolayers of the charge transfer complex, we tentatively assign the state at 0.55 eV as the modified surface state.

Hence, our data do not provide any hint of the TNAP LUMO resonance at positive bias voltage, which was clearly resolved on the pure monolayer. The data rather suggest a strong modification of the TNAP’s electronic structure. In the case of the parent compound TTF–TCNQ the LUMO is singly occupied due to charge transfer from the TTF. A fingerprint of the single electron is the appearance of a Kondo resonance in the dI/dV spectra at the Fermi level [5]. In the present case, high resolution spectra in this energy range are essentially flat. Thus, we assume that the LUMO of the TNAP is not singly occupied.

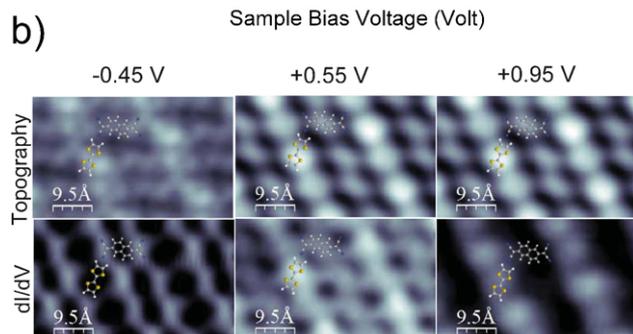
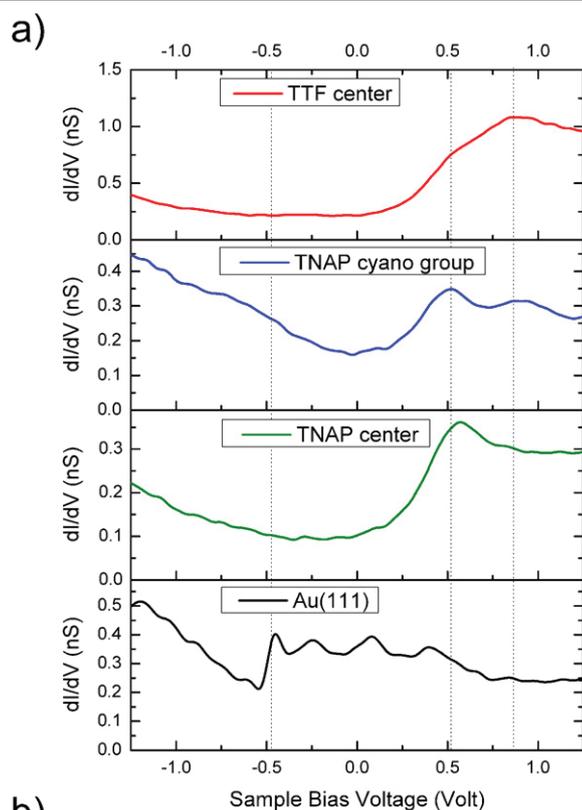


Figure 3. (a) Electronic structure of the mixed TTF–TNAP charge transfer complex. The spectra show a pronounced increase in differential conductance at 0.55 eV (feedback opened at $V_S = 1.5$ V, $I_T = 0.4$ nA, lock-in modulation 10 mV rms at 921.1 Hz). (b) Topography and constant current dI/dV maps at different sample bias voltages of the TTF–TNAP mixed island ($I_T = 0.4$ nA, lock-in modulation 10 mV rms at 923.3 Hz). The same absolute color scale is used for all dI/dV conductance maps in order to improve comparability. At -0.45 V the dI/dV signal is mainly located at the cyano groups of the TNAP species. At the positive voltage $+0.55$ V the dI/dV signal is evenly spread over the whole molecular layer including TTF and TNAP. At higher positive bias of $+0.95$ V the dI/dV signal is localized at the TTF sites of the TTF–TNAP island.

The larger electron affinity of TNAP compared to TCNQ suggests a larger charge transfer in this otherwise similar overlayer. This would imply the alignment of the former LUMO at negative sample bias. A fingerprint of its existence can be found in conductance maps of the occupied states. These resolve an increased differential conductance localized at the cyano groups of TNAP (figure 3(b)). The corresponding dI/dV spectra do not show any pronounced resonance. Only a slight change in the background slope of the conductance at the CN terminations as compared to other sites in the charge

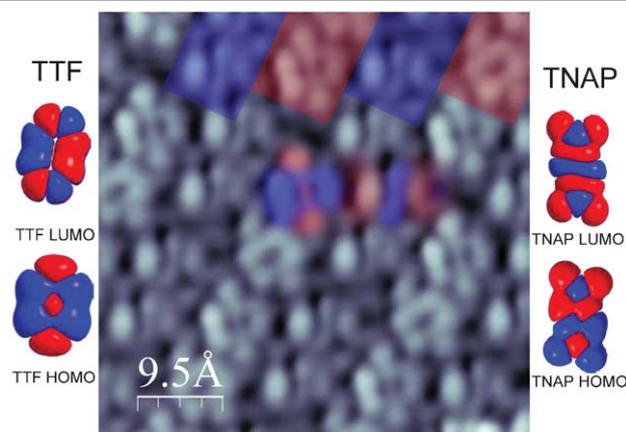


Figure 4. The HOMOs and LUMOs of the free TTF and TNAP molecules calculated by density functional theory as implemented in the Gaussian code, using the B3LYP functional. Constant current topography of the mixed TTF–TNAP island was taken at a sample bias voltage of $V_S = -0.5$ V with a functionalized STM tip. The intramolecular resolution of the TNAP molecules resolves the LUMO shape of the neutral molecule, thus indicating its charging by more than one electron.

transfer complex suggests the presence of states which are drastically broadened, presumably by the interaction with the surface.

To further analyze the charge state of the TNAP molecules, we aim at an increased energy resolution of the molecular orbitals. Typically, this can be achieved by functionalizing the tip with a small molecule. We attach an (unknown) impurity molecule to the tip apex and image the TTF–TNAP layer at negative sample bias as in figure 4. While care has to be taken in the interpretation of the obtained images, the mixed layer allows us to get a certain insight into the imaging properties. The TTF molecules are essentially imaged with their free HOMO shapes despite some minor distortions depending on the molecular orientation. This appearance is expected for negative bias voltages [20] and, hence, we conclude that the functionalized tip is capable of imaging filled orbitals of the molecular layer at negative bias. It simply shows an enhancement of contrast at the nodal planes [21]. We can now turn to the investigation of the TNAP orbital shapes. We clearly resolve a central protrusion of the molecule adjacent to two nodal planes separating two U-like protrusions. Despite some asymmetry, possibly arising from a slightly tilted adsorption geometry, this shape closely resembles the LUMO of the free molecules (color masked in figure 4). Importantly, the odd number of protrusions in TNAP can clearly not account for the shape of the HOMO, which has a nodal plane in the center of the molecule. This observation implies that the observed TNAP state has a strong LUMO character. Its alignment in the occupied region of sample states suggests a charge transfer of more than one electron into this orbital.

In comparison to the very similar self-assembled TTF–TCNQ monolayer on Au(111), where the TCNQ LUMO is charged with one electron [5], the acceptance of more than one electron of TNAP follows the tendency of larger electron affinity than TCNQ (TNAP: $E_A = 4.7$ eV; TCNQ:

$E_A = 4.23$ eV [8]). Recently, it was shown that extensive doping of TNAP multilayers by potassium can lead to dianionic TNAP states [9]. However, we note that in 1:1 stoichiometric structures of charge transfer complexes, the charge transfer amounts to only at most one electron per molecule. Nonetheless, we find fingerprints of a larger charge transfer into the TNAP when it is mixed with TTF on the gold surface. We ascribe its stabilization to the interplay with the metallic substrate: the metal substrate serves as a reservoir for charges and can thus provide additional charge to the TTF–TNAP mixture. The lifting of the herringbone reconstruction underneath the TTF–TNAP layer in fact indicates a charge transfer process [11]. Furthermore, the conduction electrons can effectively screen excess charges. The Coulomb charging energy of the molecule is thus reduced [22, 23] and larger charge states can be stabilized.

4. Summary

Adsorption of the organic electron acceptor TNAP on a Au(111) surface leads to a weakly physisorbed state, in which the molecules retain their neutral state and the self-assembled structure is solely governed by electrostatic intermolecular interactions. Mixing the organic electron donor TTF with TNAP leads to the assembly of highly ordered structures of alternating TTF and TNAP rows. This molecular layer strongly interacts with the surface as revealed by the lifting of the herringbone reconstruction and the presumable hybridization of the surface state with molecular states. Interestingly, the TNAP molecules exhibit their LUMO resonance at negative bias voltage, indicating its occupation by more than one electron. The tendency of TNAP to accept more electrons than TCNQ in similar self-assembled structures on Au(111) agrees with the larger electron affinity of the free molecules. However, this large charging is surprising in comparison to the bulk charge transfer complexes [18]. We suggest that the stabilization of this large charge accumulation in the LUMO is due to the effective screening of the underlying metal, which significantly reduces the Coulomb charging energy.

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