Resolution of intramolecular dipoles and push-back effect of individual molecules on a metal surface

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Abstract

Molecules consisting of a donor and an acceptor moiety can exhibit large intrinsic dipole moments. Upon deposition on a metal surface, the dipole may be effectively screened and the charge distribution altered due to hybridization with substrate electronic states. Here, we deposit Ethyl-Diaminodicyanoquinone molecules, which exhibit a large dipole moment in gas phase, on a Au(111) surface. Employing a combination of scanning tunneling microscopy and non-contact atomic force microscopy, we find that a significant dipole moment persists in the flat-lying molecules. Density-functional theory calculations reveal that the dipole moment is even increased on the metal substrate as compared to the gas phase. We also show that the local contact potential across the molecular islands is decreased by several tens of meV with respect to the bare metal. We explain this by the induced charge-density redistribution due to the adsorbed molecules, which confine the substrate’s wavefunction at the interface. Our local measurements provide direct evidence of this so-called push-back or cushion effect at the scale of individual molecules.

Introduction

Donor-acceptor molecules exhibit two charge-separated moieties, which make them interesting for applications in molecular electronics\textsuperscript{1,2} and optoelectronic devices\textsuperscript{3}. When adsorbed on a surface, the intramolecular charge distribution may change drastically\textsuperscript{4,5}. In particular, the adsorption on metal surfaces usually leads to hybridization, charge transfer and screening, which alter the molecular properties\textsuperscript{6–8}. To reduce hybridization and screening from the substrate, thin insulating layers are often introduced at the interface to a metal substrate\textsuperscript{9–14}. However, some applications may require adsorption directly onto metal surfaces. Therefore, finding a suitable donor–acceptor molecule, which preserves its properties upon adsorption on a metal surface, is of great interest.

Another interesting aspect of molecular adsorbate layers on metals is their potential
to tune charge injection barriers at organo-metallic interfaces\textsuperscript{15,16}. Typically, a molecular adsorbate layer suppresses the decay of the metallic states into the vacuum. This results in a reduction of the spill-out of the electron charge. The induced electric dipole perpendicular to the surface leads to a lower workfunction. The reduced workfunction can be easily detected in photoelectron spectroscopy, with the phenomenon being termed push-back or cushion effect\textsuperscript{6}.

The resolution of intramolecular dipoles and the push-back effect on the single-molecule scale requires a technique, which probes the structure and charge distributions with atomic resolution. Kelvin probe force microscopy (KPFM) measures the local contact potential difference (LCPD) between a conducting tip of an atomic force microscope (AFM) and a sample\textsuperscript{17}. Since its invention, KPFM has quickly evolved as a highly versatile tool to map charge distributions and workfunction changes with nanoscale resolution, most commonly applied to metallic and semiconducting structures\textsuperscript{18}. With the development of qPlus sensors, KPFM could be combined with scanning tunneling microscopy (STM). This combination led to the seminal mapping of charge distributions at the atomic scale\textsuperscript{19} and to a number of important insights into intramolecular charge distributions\textsuperscript{4,5,14,20–23}. However, a quantitative determination of the charge distribution within molecules and molecular layers remains challenging and it is important to consider that the LCPD value is detected at a certain tip height\textsuperscript{20}.

Here, we chose Ethyl-Diaminodicyanoquinone (Ethyl-DADQ) as a potential candidate to map intramolecular charges as well as the push-back effect on a Au(111) substrate. These molecules have a large dipole moment due to their donor–acceptor units, and they have shown recently to be highly fluorescent\textsuperscript{24}. They consist of a quinone moiety with a dicyanomethylene and an imidazolidine group bound to it on opposite sites. Figure 1a (inset) shows the optimized gas-phase structure of the molecule. The two end groups have different electron affinities, which results in a large lateral dipole moment of about 17.3 Debye. Apart from two hydrogen atoms of the imidazolidine group that stick out of the molecular plane,
the molecule is flat and thus ideally suited for obtaining an in-plane dipole on a surface.

**Methods**

We have performed combined STM/AFM experiments probing Ethyl-DADQ on a Au(111) single-crystal surface. The Au surface was cleaned by repeated sputter/anneal cycles until a clean, atomically flat termination was obtained. Ethyl-DADQ molecules were evaporated at 500 K onto the clean sample held at room temperature. The experiments were carried out at a base temperature of 4.8 K. Differential-conductance spectra were taken with a lock-in amplifier at a modulation frequency of 909 Hz. A qPlus sensor\textsuperscript{25} was used for combined STM/AFM measurements.

The LCPD is obtained by recording the frequency shift while the bias voltage is ramped\textsuperscript{19}. Due to the quadratic dependence of the frequency shift on the bias voltage, the frequency shift $\Delta f$ as a function of the bias voltage $V$ is an inverse parabola:

$$\Delta f = -\frac{f_0}{2k} \frac{\partial F}{\partial z}, \quad F_{el} = \frac{V^2}{2} \frac{\partial C}{\partial z}.$$ 

$f_0$ and $k$ are the resonance frequency and the spring constant of the oscillating tip, $F$ and $F_{el}$ are the total and the electrostatic contribution of the force acting on the tip, and $C$ is the capacitance of the junction. By a parabolic fit of the individual $\Delta f(V)$ curves, one can extract the voltage at the maximum of the curve, which is needed to compensate for the electrostatic forces due to charges at the interface\textsuperscript{19}.

Periodic density-functional theory (DFT) calculations were performed with the periodic plane-wave code PWscf of the Quantum Espresso software package\textsuperscript{26}, using the PBE exchange-correlation functional of Perdew, Burke and Ernzerhoff\textsuperscript{27}, Vanderbilt ultrasoft pseudopotentials\textsuperscript{28}, and a plane-wave basis set with an energy cutoff of 30 Ry. Dispersion corrections to PBE energies and forces were included by our recently introduced $D3^{surf}$ scheme. $D3^{surf}$ is an extension of the original D3 method proposed by Grimme et al.\textsuperscript{29}.
\[ \delta^+ - \delta^- + \mu \approx 17.3 \text{ D} \]

Figure 1: (a) STM topography of Ethyl-DADQ adsorbed on a Au(111) surface. The topography was recorded at 1 V, 100 pA. Inset: Structure of the Ethyl-DADQ molecule. It consists of a benzene ring (green) with a dicyanomethylene (tail, purple) and a imidazolidine (head, red) group bound to it. The different electron affinities of the head and tail group lead to a large dipole moment of about 17.3 Debye in the gas phase. (b) STM topography of a chain of Ethyl-DADQ. The superimposed structure model (optimized by DFT) indicates the proposed orientation of the molecules. The red dotted lines represent CN···HN hydrogen bonds. The topography was recorded at 2 V, 306 pA. (c) Simulated STM topography (1 V, isodensity $2 \times 10^{-4} e/\AA^3$) of a three-molecule wide chain on a Au(111) substrate, calculated for the relaxed structure shown in (d). Red and green ellipses indicate the asymmetric head-to-tail contact between rows of the chain, which is visible in STM as alternating brighter and darker dots.

which the parameter set of coordination-dependent $C_6$ coefficients is extended by additional values for atoms at higher coordination numbers\textsuperscript{30,31}.

The Au(111) surface was represented by periodically repeated slabs with a thickness of four atomic layers. The calculated PBE+D3\textsuperscript{surf} Au bulk lattice constant of 4.118 Å was used for the lateral extension of the slabs. The structure search was carried out with various surface-unit-cell sizes representing different surface coverages and adsorbate structures. Unit cells of the slabs contained up to 456 gold atoms. In the geometry optimizations, the bottom two atomic layers were kept fixed, while the upper two layers and the adsorbed molecules were relaxed. The density of the Monkhorst-Pack k-point mesh for Brillouin zone sampling was larger or equivalent to a (24,24,1) mesh for the primitive surface unit cell. STM images were simulated using the Tersoff-Hamann approximation\textsuperscript{32}.
Results and Discussion

Structure of Ethyl-DADQ on Au(111)

Ethyl-DADQ molecules deposited onto a Au(111) surface at room temperature self-assemble into straight chains across the whole surface (STM image in Fig. 1a). The chains do not affect the Au(111) reconstruction lines and do not show preferred adsorption directions with respect to the symmetry of the Au surface, indicating a rather weak chemical bonding to the surface. The widths of the chains can be tuned by varying the molecular coverage. A close-up view on one of these chains is shown in Fig. 1b. Each individual molecule is imaged with an almost oval shape with one termination being slightly wider than the other one. Across the rows of the chains, the molecules are arranged head to tail. The neighboring molecules within a row are oriented in the opposite direction and shifted with respect to each other. The suggested model is indicated by a superimposed molecular structure onto the STM image. Such an alignment is favored by the formation of CN⋯HN hydrogen bonds (indicated by red dotted lines) and electrostatic interactions due to the anti-parallel alignment of the dipoles.

To rationalize this model, we performed a systematic structure search using density-functional theory (DFT) calculations. To arrive at a realistic structure, we first determined the preferred adsorption site and molecular orientation of a single Ethyl-DADQ molecule in a large surface unit cell. We find that the preference of the adsorption site and molecular orientation is not very pronounced, as the energy cost to shift and tilt the molecule out of the preferred site and orientation is rather small. Such a shallow adsorption energy landscape indicates that the adsorption is mainly driven by isotropic van-der-Waals forces and electrostatic interactions. Nonetheless, the adsorption energy of 1.96 eV is quite large (see Table 1).

Next, we constructed molecular dimers and trimers on the surface to determine the preferred alignment and the equilibrium distances of the molecules. Interestingly, we find a
huge energy gain of 0.51 eV per molecule for an antiparallel orientation of the Ethyl-DADQs on the surface (see Table 1). This structure is mainly stabilized by CN⋯HN hydrogen bonds, which leads to the characteristic parallel displacement of the cyano and the imidazolidine groups between neighboring molecules. As the antiparallel alignment entails the largest contribution to the bonding energy, extended molecular structures are expected to be quasi one-dimensional, in agreement with the observation of long chains in experiment.

To capture the structure of extended chains on the Au(111) surface, we constructed commensurate models of chains with increasing width. In doing so, we made sure that the molecular distances of the dimers and trimers as well as their orientation and relative position with respect to the substrate is maintained as closely as possible. This was fulfilled by orienting rows of molecules along the crystallographic [235]–direction (with periodicity of \( \frac{1}{2}[235] \)) and by stacking them asymmetrically together. Consecutive rows are slightly shifted so that in the head-to-tail alignment of molecules between neighboring rows, the imidazolidine group is closer to one of the two CN groups than the other. This is shown in Fig. 1d for the case of a three-molecule wide chain. The symmetry breaking is rooted in optimizing the molecular head-to-tail contact and the relative position of the molecules with respect to the substrate. Finally, two-dimensional commensurate models for describing

| Structure   | \( E_{\text{ads}} \) (eV) | \( \Delta E_{\text{ads}} \) (eV) |
|-------------|----------------|----------------------------|
| Monomer     | -1.96          | –                          |
| Dimer       | -2.47          | -0.51                      |
| Trimer      | -2.57          | -0.10                      |
| Single chain| -2.77          | -0.20                      |
| Double chain| -2.81          | -0.04                      |
| Triple chain| -2.83          | -0.02                      |
| Monolayer   | -2.87          | -0.04                      |
inner parts of wider chains were built by connecting the sides of a two-molecule wide chain by a corresponding unit-cell vector. This was done again in such a way that all structural elements and the asymmetric head-to-tail contacts between rows are reproduced as found for the chains with finite width.

The structure obtained by this systematic search is in very good agreement with the experimental results. Direct evidence of the match can be obtained from a simulated STM image shown in Fig. 1c. This captures very well the experimentally observed asymmetry of the individual molecules. In addition, fine details such as the alternating distance between imidazolidine head and CN groups of molecules in neighboring rows are resolved that can equally be found in experiment and are reflected in a periodic line of brighter and darker dots between the molecules, see Fig. 1b-d.

**Charge distribution within Ethyl-DADQ on Au(111)**

To learn about the electronic properties of the molecules in this structure, we performed dI/dV spectroscopy. Figure 2 shows a constant height (left) and a constant-current (right) dI/dV spectrum recorded on a molecule. Two resonances can be observed, one located at around \(-1\) V and the other at around \(2.5\) V. We attribute these resonances to tunneling into the ionization and from the affinity level of the molecules, respectively. The large noise

![Figure 2: dI/dV spectra recorded on a molecule. Resonances can be seen around \(-1\) V (left side, attributed to the ionization level) and \(2.5\) V (right side, attributed to the affinity level). The left spectrum was recorded at a setpoint of \(1\) V, \(100\) pA, the right spectrum was recorded in the constant current mode at \(100\) pA. The modulation amplitude was \(5\) mV (left) and \(10\) mV (right).]
signal in the spectra at positive bias voltages indicates an instability of the molecules at these bias voltages. The width of the positive ion resonance amounts to $\sim 160$ meV, which is narrower than resonances from other extended organic molecules on Au(111). The narrow linewidth points to a weaker coupling to the surface than typically observed$^8$. The negative ion resonance appears broader, which probably results from excitation of vibronic states$^{10}$ and vibration-assisted tunneling processes$^{34,35}$.

To find out if the dipole is preserved upon adsorption, we measured the LCPD signal along a three-molecule wide chain as shown by STM in Fig. 3a. We find an overall decrease of the LCPD values on the molecules as compared to the bare substrate (Fig. 3b). Additionally, the signal is modulated within the molecular island. The superimposed structural model obtained from the simultaneously recorded STM image shows that the regions of lowest LCPD correspond to the imidazolidine group of the Ethyl-DADQ.

A better perception of the modulation along the molecules can be gained from a line profile of the LCPD signal across a three-molecule wide island (see Fig. 4, blue curve). In agreement with the map, we observe the overall reduction of the LCPD above the molecular layer as well as the additional oscillation on the molecular scale. As illustrated by the comparison of the LCPD line and the topographic image, the oscillation can be directly
Figure 4: Plot of the LCPD value (blue solid line) measured across a molecular chain as indicated by the blue dashed line in the STM topography below the graph. The spectra were recorded at a setpoint of 2 V, 300 pA and the STM topography was recorded at a setpoint of 1 V, 172 pA. The calculated electrostatic potential across the molecular chain at a height of 9.3 Å above the surface is shown in red. The planar averaged potential is set to zero. The vertical black dashed lines indicate the position of the imidazolidine group of each individual molecule in the chain.

linked to the locations along the individual molecules. The lowest LCPD value is found at the imidazolidine group of the Ethyl-DADQ, whereas the largest value is found toward the dicyanomethylene group, but not exactly on top of it as may be expected from the dipolar charge distribution of the gas-phase molecule with positive charge at the imidazolidine group and negative charge at the dicyanomethylene group. This is due the fact that the measured LCPD value corresponds to the electrostatic potential at the tip height above the island. Furthermore, we note that the values at the edges of the chain are affected by the overall decrease of the LCPD and, additionally on the right side, by the neighboring molecules sticking out of the chain structure. However, from the LCPD modulations, we can conclude that the Ethyl-DADQ molecule preserves a finite dipole moment even on the metallic Au(111) surface.

To corroborate this interpretation, we calculated the charge distribution of the surface-adsorbed Ethyl-DADQ molecules. We started with a simple Bader charge analysis which we
benchmark against the gas-phase molecule. As a test to see how well Bader charges reproduce the dipolar properties of a molecule, we used the atomic Bader charges of the gas-phase Ethyl-DADQ molecule and calculated the molecular dipole moment. We obtain a value of 25.5 Debye, which is in reasonably good agreement with the true dipole moment of 17.3 Debye as determined from the full charge distribution within the molecule. We can therefore expect that Bader charges capture well changes in intramolecular charge distributions and molecular dipole moments if molecules are transferred into a different environment.

For analyzing the variation in charge distribution upon adsorption on the surface and within different arrangements, we divided the Ethyl-DADQ molecule into three units: the dicyanomethylene tail, the central benzene ring, and the imidazolidine head. The Bader charges of the atoms within each unit are added and the total Bader charges of the three units are reported in Table 2. As expected, the results show an accumulation of electrons on the cyano groups and an electron depletion on the benzene ring and the imidazolidine unit. Interestingly, upon adsorption on the Au(111) surface, the dipolar character is not reduced but even enhanced, with a small net transfer of electrons to the Au substrate.

For better comparison with experiment, we calculated the electrostatic potential above

| Structure          | cyano unit | benzene unit | imid unit | \(\Delta q\) |
|-------------------|------------|--------------|-----------|-------------|
| Gas phase         | -0.51      | +0.31        | +0.20     | -           |
| Monomer           | -0.54      | +0.29        | +0.40     | +0.15       |
| Single chain      | -0.64      | +0.24        | +0.48     | +0.08       |
| Triple chain (1)  | -0.64      | +0.23        | +0.47     | +0.06       |
| (2)               | -0.67      | +0.24        | +0.47     | +0.04       |
| (3)               | -0.67      | +0.24        | +0.48     | +0.05       |
| Monolayer         | -0.67      | +0.24        | +0.47     | +0.04       |

\(\Delta q\) is the charge transfer from the molecules to the Au substrate.

Table 2: Bader charges of the three subunits of Ethyl-DADQ molecules (see inset of Fig. 1a) in the gas phase and adsorbed on the Au(111) surface for different coverages and structures. For the 3-molecule wide chain, the Bader charges of the three nonequivalent molecules (1) to (3) as indicated in Fig. 1d are given separately.
Figure 5: Molecular electrostatic potential drawn on an isosurface of the electron density with isovalue of 0.002 a.u. for (a) an Ethyl-DADQ molecule in the gas phase and (b) for an adsorbed monomer on Au(111). The color-coded potential values are given in eV with respect to the vacuum level. Red areas are attractive for electrons, blue areas are repulsive.

The surface which can be directly compared to the LCPD measurements. We first note that the distribution of the electrostatic potential supports the conclusion from the Bader charge analysis. Figure 5a shows the molecular electrostatic potential on the van der Waals surface of a gas-phase Ethyl-DADQ molecule. As expected, the potential is repulsive for electrons above the negatively charged cyano groups, whereas the positive charge on the imidazolidine unit creates an attractive potential. After adsorption on the Au(111) surface, this characteristic distribution of the molecular electrostatic potential is maintained, see Fig. 5b, which indicates that the intramolecular charge transfer and thus the molecular dipole moment are preserved.

Within a densely packed molecular layer, the charge distribution within the individual molecules may be influenced by the local environment and deviate from an isolated molecule. Furthermore, it is important to note that the measurements probe the LCPD at a certain tip height above the molecular layer. To account for these effects and for direct comparison with experiment, we plot the two-dimensional map of the electrostatic potential (Fig. 3c) and a corresponding line profile (Fig. 4, red line) across a three-molecule wide chain. While the main character of the variation of the electrostatic potential is preserved along the individual molecules, it is notable that the largest LCPD is not located precisely at the dicyanomethylene group, but affected by the imidazolidine group of the neighboring molecule and thus slightly shifted toward the molecule’s center. These details are in very good agreement with
Figure 6: Electron density difference plot for a Ethyl-DADQ monomer on Au(111) in (a) a plane 1 Å above the surface atoms ($\Delta n = 1.5 \cdot 10^{-2} e/Å^3$) and (b) a plane perpendicular to the surface through the central axis of the molecule ($\Delta n = 1.5 \cdot 10^{-3} e/Å^3$). The positions of the planes are indicated by cyan lines. The orientation of the molecules is the same as in Fig. 5. Blue areas show electron accumulation, red areas electron depletion.

the variation of the LCPD signal. The calculations thus corroborate the dipolar character of the Ethyl-DADQ molecules on the Au(111) surface and their persistence in the densely-packed islands.

In agreement with experiment, the calculations also show the overall reduction of the electrostatic potential above the molecules compared to the plain Au(111) surface. To unravel the origin of this, we analyzed the induced charge density redistributions. They are calculated by subtracting the electron density of the molecule and the surface determined by separate calculations for the two fragments from the electron density of the combined structure. Fig. 6a shows the electron density difference in a plane 1 Å above the surface. We find a significant electron accumulation underneath the imidazolidine unit whereas electron depletion is observed underneath the cyano groups. This is direct evidence that the dipole of the adsorbed molecule induces a compensating mirror dipole in the metal substrate. A cut through the electron density difference perpendicular to the surface through the central axis of the molecule (see Fig. 6b) visualizes the induced electron density redistribution due to the presence of the molecules. Close to the imidazolidine group a zone of electron depletion is visible, which is in agreement with the more positive Bader charge upon adsorption, see above. However, in a large area between the molecule and the surface, the electron density is increased, which demonstrates the compression (push-back) of the electron density of
the metal surface leaking into the vacuum, which is also termed “cushion effect” or “pillow effect”6,15,36–38. A consequence of this is the reduction on the local work function.

Conclusions

We investigated Ethyl-Diaminodicyanoquinone molecules adsorbed on a Au(111) surface. By measuring the local contact potential using a nc-AFM we observed that the intramolecular dipole is preserved upon adsorption on the surface. Interestingly, our calculations indicate that the dipole is even increased upon adsorption on the metal surface. We also showed that the local work function is generally lower on the molecular sites as compared to the bare metal substrate. This effect originates from a local-scale push-back effect, where the molecules repel the wave function of the substrate electrons, leaking out into the vacuum. Both observations could be equally interesting for application in single-molecule electronics and the energy alignment at metal–organic interfaces.

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