Impact of Bidirectional Charge Transfer and Molecular Distortions on the Electronic Structure of a Metal-Organic Interface

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Interface energetics are of fundamental importance in organic and molecular electronics. By combining complementary experimental techniques and first-principles calculations, we resolve the complex interplay among several interfacial phenomena that collectively determine the electronic structure of the strong electron acceptor tetrafluoro-tetracyanoquinodimethane chemisorbed on copper. The combination of adsorption-induced geometric distortion of the molecules, metal-to-molecule charge transfer, and molecule-to-metal back transfer leads to a net increase of the metal work function.

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The development of organic electronic devices requires a thorough understanding of all physicochemical processes taking place at the metal-molecule interfaces. Adsorption of organic molecules on metal surfaces is known to result in modifications of physical and chemical properties of both molecules and metal surface [1–9]. Weakly bound (physisorbed) molecules reduce the substrate work function via Pauli repulsion (decreasing the metal surface dipole) and thus *increase* the hole-injection barrier at an organic/metal interface [1,4,10]. Efficient strategies for reducing the hole-injection barrier are much needed but rarely found [11]. One successful approach is based on the use of strong electron-accepting molecules adsorbed onto the metal electrode prior to deposition of the active organic layer [12]. Adsorption-induced charge transfer from the metal substrate to the acceptor molecules has been suggested based on photoelectron spectroscopy data [12].

The interface energetics at the metal-molecule contact is determined by a delicate balance among several mechanisms in addition to simple metal-to-molecule charge transfer. The relative contributions of these mechanisms are usually hard to assess, because experiments can often detect only their *cumulative* effects. Therefore, conclusions drawn solely on the basis of spectroscopic data can be incomplete or even misleading.

Here, we present a detailed study of the interface between Cu(111) and a layer of the strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8 tetracyanoquinodimethane (F4-TCNQ; see Fig. 1). Using complementary experimental techniques in conjunction with first-principles calculations, we are able to derive a comprehensive picture of the interfacial electronic structure. The net work-function modification is demonstrated to originate from a subtle interplay between (i) metal-to-molecule electron transfer, (ii) molecule-to-metal electron back transfer resulting from a strong hybridization of deep-lying occupied molecular orbitals (MOs), and (iii) strong geometric distortions of the molecules. Collectively, these three processes result in a net work-function *increase* of up to *ca.* 0.6 eV.

Ultraviolet photoelectron spectroscopy (UPS) measurements were performed at the end station FLIPPER II (HASYLAB, Hamburg), and x-ray standing wave (XSW)

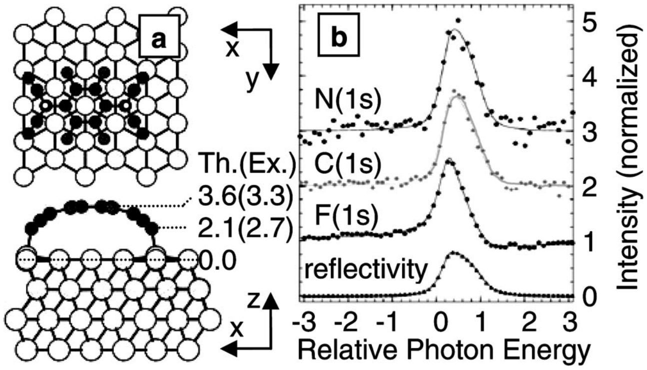

FIG. 1. (a) F4-TCNQ on Cu(111) in the $3\sqrt{3} \times 5$ surface unit cell as seen from the side (bottom) and from above (top). The calculated (experimental) atomic distances to the surface are given to the right. (b) Total photoemission and reflectivity measurements as a function of photon energy relative to the Bragg energy. The fits (solid lines) to the experimental data (symbols) yield the average coherent positions P_{eff} and coherent fraction f_{eff} [13] used to determine the bonding distances for F ($P_{\mathrm{eff}} = 0.59$, $f_{\mathrm{eff}} = 0.43$), N ($P_{\mathrm{eff}} = 0.30$, $f_{\mathrm{eff}} = 0.28$), and C ($P_{\mathrm{eff}} = 0.33$, $f_{\mathrm{eff}} = 0.15$) atoms. A coherent fraction of the C signal of roughly one-third compared to the F signal is in excellent agreement with what can be derived from the calculated positions in the bent molecule.

experiments at ID32 (ESRF, Grenoble) [13]. Ultrahigh vacuum conditions were preserved during sample preparation and measurements (base pressure $<5 \times 10^{-10}$ mbar). Cu(111) crystals were cleaned by repeated Ar-ion sputtering and annealing cycles. F4-TCNQ (Aldrich) was evaporated from resistively heated pinhole sources and the deposited mass thickness was monitored by quartz crystal microbalances.

Density functional theory (DFT) calculations were performed using the plane wave-based VASP code [14] in the repeated slab approach with the PW91 functional [15,16]. Four layers of copper represent the Cu(111) surface and a 16 Å vacuum gap separates the slabs. A $3\sqrt{3} \times 5$ surface unit cell [see Fig. 1(a)] was considered with a $3 \times 3 \times 1$ Monkhorst-Pack grid of k points. This relatively large size of the unit cell keeps intermolecular interactions small, which allows us to address the more relevant [12] limit of isolated molecules at submonolayer coverages. We also used the atomic orbital-based SIESTA code [17] to calculate the (charge-conserving) projection of the density of states (DOS) onto the MOs [18,19] (VASP and SIESTA provide essentially identical full and molecular DOS) and the GAUSSIAN03 [20] code to obtain isodensity representations of MOs. The geometry was optimized (force cutoff of 0.01 eV/Å) starting with planar F4-TCNQ molecules 3.3 Å above the surface. The atoms in the bottom two copper layers were fixed to their bulk positions. The calculated binding energy of 2.6 eV per molecule is indicative of strong chemisorption.

The calculated and measured geometric parameters are summarized in Fig. 1. The experimental data are obtained by the XSW technique [13], which provides element-resolved adsorption distances for F4-TCNQ on Cu(111); the XSW data [photoelectron yields while scanning through the Cu(111) Bragg reflection] are shown in Fig. 1(b). The carbon XSW signal exhibits a low coherent fraction due to the various inequivalent C sites and is thus difficult to analyze in terms of positions. The N and F signals, however, allow specifying clear differences in the positions of these elements above the substrate. Theory and experiment concur in locating the F atoms at significantly larger distances from the Cu surface than the N atoms: upon adsorption, the F4-TCNQ molecules do significantly bend. The calculated curvature, with F at 3.6 Å and N at 2.1 Å above the surface, is somewhat larger than the experimental one, with F at 3.3 ± 0.1 Å and N at 2.7 ± 0.1 Å. The theoretical results are insensitive to variations in the adsorption site and rotations of the molecule in the x-y plane which is consistent with the observation [21] that the bonding of TCNQ (for which the F atoms are replaced by hydrogens) is only weakly site specific. Also, increasing the size of the unit cell in the x direction does not alter the optimized geometry, indicating that intermolecular interactions are already very small for the chosen surface unit cell.

The strong molecule-metal interaction also leads to marked changes in bond lengths within F4-TCNQ. In the gas phase or in the crystal, the molecule adopts a fully planar, quinoidlike geometry (calculated C–C bond lengths of 1.44 Å and 1.36 Å within the phenylene ring). Adsorption on the Cu(111) surface results in (i) the ring geometry becoming nearly aromatic (C–C bond lengths of 1.41 Å and 1.39 Å) and (ii) the carbon atoms carrying the nitrile groups (marked by white dots in Fig. 1) rehybridizing from sp^2 toward sp^3. The latter is responsible for the strong bending of the molecule. These geometric distortions are similar to those suggested for reduced TCNQ [22] and are consistent with populating the lowest unoccupied molecular orbital (LUMO). The UPS spectrum for F4-TCNQ on Cu(111) (Fig. 2) shows the appearance of a new peak at ~1 eV below the Fermi energy (E_F), similar to the case of F4-TCNQ on Au(111) where this peak has been assigned to the partially filled LUMO [12].

The experimental UPS spectrum can be well reproduced by the calculated DOS projected onto the molecular region (see Fig. 2). In order to assign the peaks, we further partitioned this calculated DOS into contributions from the MOs of the isolated molecule [18,19]. The projection onto selected MOs is shown in Fig. 3 and confirms that the LUMO-derived DOS is located below E_F. The degree of occupation of the individual orbitals can be obtained via integration of the projections up to the calculated E_F. We find that 1.8 e are transferred from the metal to the F4-

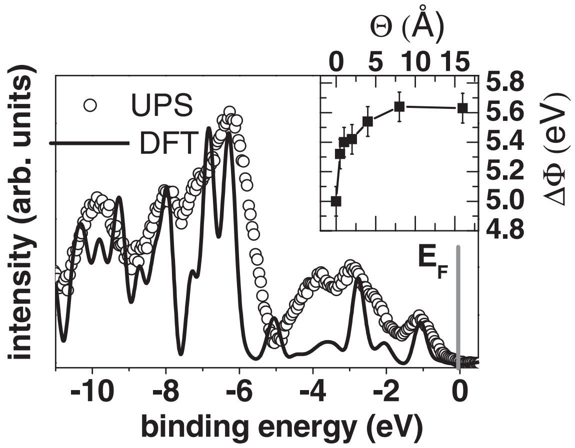

FIG. 2. UPS spectrum (circles) and DFT calculated DOS (solid line) of the organic layer. The experimental spectrum is obtained by subtracting the UPS signal of the bare Cu(111) surface from that of a covered surface with a nominal layer thickness of 4 Å (*ca.* 1 monolayer) F4-TCNQ/Cu(111). Spectra at nominally 2 Å and 1 Å layer thickness look virtually identical. In the calculations, photoemission cross sections are not taken into account and the energy scale has been shifted (−0.2 eV) after expanding it (by a factor of 1.34), which is common practice when comparing DFT data within the generalized gradient approximation to UPS data [28]. The inset illustrates the measured work-function modification, ΔΦ, as a function of film thickness Θ.

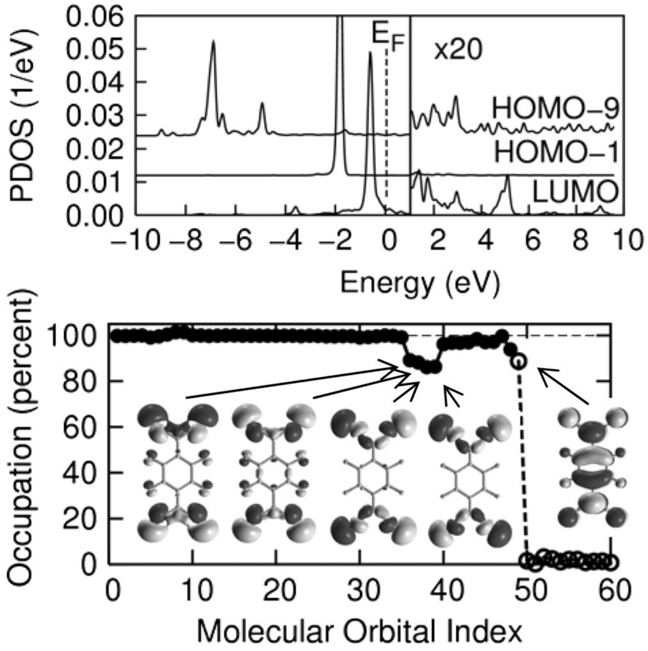

FIG. 3. Top: DOS projected onto selected MOs. For clarity, the curves have been displaced on the vertical axis and the y scale has been multiplied by a factor of 20 for energies greater than 1 eV above E_F. Bottom: Occupation (in percent) of the lowest 60 MOs. The full (open) circles and solid (dashed) lines correspond to the orbitals which are occupied (unoccupied) in the isolated molecule.

TCNQ LUMO (the formerly empty LUMO is 90% occupied in the adsorbed molecule). This is a very large metal-to-molecule charge transfer; e.g., it is markedly larger than the 0.6 e transfer reported for another prototypical system, 3,4,9,10-perylene-tetracarboxylic acid dianhydride chemisorbed on Ag(111) [5].

If we were to estimate the impact of that charge transfer from the metal to each molecule on purely electrostatic grounds, such a transfer of nearly two electrons would result in a work-function (Φ) increase for a F4-TCNQ covered Cu(111) surface by (an unreasonably large amount of) ~5 eV [23]. Actually, UPS shows a Φ increase by up to 0.6 eV. Clearly, this indicates that other mechanisms must be operational in addition to simply filling the LUMO. Such issues have been discussed for smaller molecules such as carbon monoxide [18,24–26] or benzene [8–10], where electronic polarization of metal and molecule and/or electron donation and backdonation change the occupations of the MOs.

The key to a complete understanding of the Cu/F4-TCNQ interface resides in the bottom part of Fig. 3, which illustrates that, besides filling of the LUMO, the molecule transfers ~1.0 e back to the metal essentially from the HOMO-9 to HOMO-12 levels (i.e., those four levels are each only 80% to 90% occupied after adsorption). They correspond to σ levels localized on the four nitrile groups of the molecule, which participate most strongly in the chemical bonding with the Cu atoms; the strong interaction of these levels with the Cu surface is underlined by the broadening of the corresponding projected DOS (i.e., significant PDOS also at energies away from the main peak, as shown in Fig. 3 for the HOMO-9; for the sake of comparison, Fig. 3 also shows the DOS projected onto the noninteracting HOMO-1). Summing over *all* MOs gives a net negative charge of ~0.6 e per F4-TCNQ molecule. Thus, the charge on the molecule is determined by a delicate balance of electron loss and gain, also involving deep-lying orbitals. We note that this finding helps in the understanding of related systems [27], where F4-TCNQ is adsorbed onto a variety of substrates (some covered with a thin insulating layer) and for which integer charge transfer states have been proposed.

In order to understand the relative contributions of these effects to the F4-TCNQ induced work-function modification, $\Delta\Phi$, it is useful to partition $\Delta\Phi$ into two components: $\Delta\Phi = \Delta E_{\mathrm{vac}} + \mathrm{BD}$ [15,16]. ΔE_{vac} represents the change in potential energy of the electrons between the left and right sides of the F4-TCNQ molecular layer *without* considering charge transfer between the molecules and the metal; the molecules are assumed to be already in the geometry they adopt upon adsorption. BD represents the bond dipole (*vide infra*). ΔE_{vac} is proportional to the molecular dipole moment perpendicular to the surface, which is nonzero as a result of the bent molecular conformation. Thus, ΔE_{vac} represents the *geometry-induced contribution* to the work-function modification; it amounts to *decreasing* Φ by 0.8 eV (see Fig. 4).

The charge rearrangements upon adsorption (i.e., the net transfer between molecule and metal) *counteract* ΔE_{vac}. Their role is quantified by the bond dipole, BD, which can

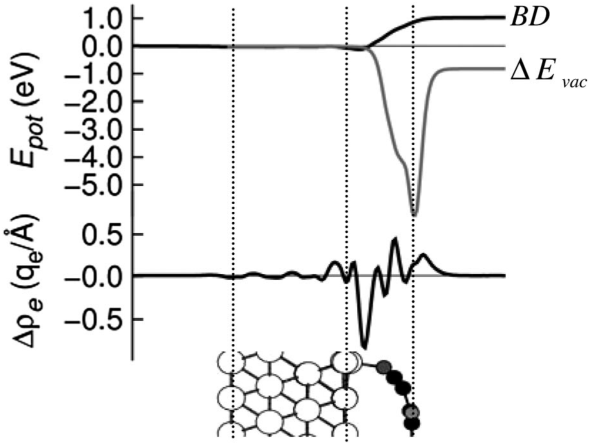

FIG. 4. Charge rearrangement $\Delta\rho_e$ and related potential energy of an electron (black lines). q_e is the charge of an electron. $\Delta\rho_e$ is calculated by subtracting the noninteracting electron density from the electron density of the interacting system and averaging in the x-y plane. The gray curve represents the xy-averaged potential energy of an electron for the noninteracting F4-TCNQ monolayer (see the text).

be obtained by solving the Poisson equation [15,16] for the xy-averaged charge rearrangements $\Delta\rho_e(z)$ (see Fig. 4). The $\Delta\rho_e$ curve shows a pronounced minimum between the topmost Cu layer and the N atoms; there, electron density is removed in agreement with the loss of electrons from the HOMO-12 to HOMO-9 levels and the Pauli pushback effect. Furthermore, electrons flow to regions between the C and N atoms of the nitrile docking groups and onto the aromatic ring, consistent with the filling of the LUMO. As shown in the top part of Fig. 4, the resulting BD amounts to 1.0 eV. This results in a total calculated $\Delta\Phi$ of $+0.20$ eV, i.e., a net *work-function increase*, which is in qualitative agreement with the experimental UPS value of $+0.6$ eV. That the calculated value is somewhat smaller can be rationalized (i) by an overestimation of the molecular bend in the theoretical geometry optimizations: ΔE_{vac} is highly sensitive to the curvature of the molecule; when performing a calculation with the N and F atoms fixed at their experimental distances from the Cu layer, ΔE_{vac} reduces from -0.8 eV to -0.3 eV. As BD stays nearly the same, this would result in $\Delta\Phi = +0.70$ eV. (ii) By the assumed nondense (lateral) packing. The detailed structure of a densely packed layer of F4-TCNQ on Cu(111) is not experimentally known; the theoretical results reported here are thus based on a relatively low coverage describing the limiting (but highly relevant [12]) case of virtually noninteracting F4-TCNQ molecules; as shown in the inset of Fig. 2, in the submonolayer region, $\Delta\Phi$ scales roughly linearly with the coverage, which is consistent with limited intermolecular electronic interactions.

To summarize, band-structure calculations and XSW measurements reveal major geometric distortions of F4-TCNQ upon adsorption onto Cu(111). The aromatic stabilization as well as the π-acceptor nature of the nitrile groups drive a charge transfer of nearly 2 e from the metal into the F4-TCNQ LUMO. However, the Cu-N chemical bonding induces a significant charge transfer back to the metal. This is consistent with both calculated and measured work-function changes indicating a much smaller ($\sim$0.6 e) net charge transfer between metal and molecule. Interestingly, the back transfer does not involve frontier molecular π orbitals, but rather deep-lying σ orbitals localized on the nitrile docking groups, which experience a particularly strong hybridization with the metal states. Our analysis of the individual contributions to the observed increase in work function also underlines the critical role played by molecular distortions (bending of the molecules upon adsorption) in addition to the impact of charge transfer.

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