

Strongly Reshaped Organic-Metal Interfaces: Tetracyanoethylene on Cu(100)

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The interaction of the strong electron-acceptor tetracyanoethylene with the Cu(100) surface is studied with scanning tunneling microscopy experiments and first-principles density functional theory calculations. We compare two different adsorption models with the experimental results and show that the molecular self-assembly is caused by a strong structural modification of the Cu(100) surface rather than the formation of a coordination network by diffusing Cu adatoms. Surface atoms become highly buckled, and the chemisorption of tetracyanoethylene is accompanied by a partial charge transfer.

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Molecules containing multiple cyano (CN) groups such as tetracyanoethylene (TCNE) [1], 7,7,8,8-tetracyanoquinodimethane (TCNQ) [2], or 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) [3,4] represent the archetype of strong electron acceptors. Furthermore, there is a promising development in the design of molecule-based magnets with high Curie temperatures that are based on strongly charged ligands anchored to paramagnetic transition metal atoms [5–8]. However, a significant amount of structural characterization still needs to be carried out in order to understand and describe the interaction of such strong acceptor ligands with metallic substrates. Recent studies on the adsorption of TCNE and F4-TCNQ on single crystal surfaces such as Cu(111) [3,9] and Au(111) [4,10] reveal the existence of strongly bound species where a large variation in charge density is invariably observed near the interface. In a comparative study of TCNE adsorption on various metal surfaces, it was found that TCNE strongly self-assembles into chains on the Cu(100) surface. Moreover, scanning tunneling microscopy (STM) images contain additional bright protrusions and dark trench features that have been interpreted as consequences of a strongly reconstructed surface with buckled surface Cu atoms [10].

In this Letter, we present results of first-principles density functional theory (DFT) calculations and STM simulations as well as STM experiments of the structural and electronic properties of adsorbed TCNE on Cu(100). We found that TCNE is strongly adsorbed on the surface, and the adsorption gives rise to a reconstruction of the surface where the topmost Cu atoms bonded to TCNE are highly buckled with respect to the remaining surface Cu atoms. We have identified the presence of resonance peaks below the Fermi level that are associated to the highest occupied molecular orbital (HOMO) and to the lowest unoccupied molecular orbital (LUMO) of TCNE.

Electronic structure calculations were carried out using the DFT within a local density approximation (LDA) [11]

included in the SIESTA package [12]. For core electrons, norm-conserving pseudopotentials following a Troullier and Martins scheme [13] were used with relativistic corrections for Cu atoms. For the representation of valence electrons, we used an extended atomic basis set of polarized double- ζ type. The one-dimensional TCNE chain was built periodically from a supercell containing one molecule and a Cu(100) slab of three atomic layers with about 3×8 Cu atoms in each layer. All atoms were allowed to relax except for Cu atoms in the bottom layer. Geometries were fully optimized using a Broyden scheme until a tolerance of 10^{-3} Ry/Bohr was reached for each system under study along with their deformation and adsorption energy, total density of states (DOS), projected DOS (PDOS), Mulliken population analysis, and charge density. STM simulations were performed with our SPAGS-STM (strongly parallel adaptive grid solvers-STM) software to evaluate topographic mode images and scanning tunneling spectra. The software includes several algorithmic strategies such as parallel computation of the tunnel currents [14] and

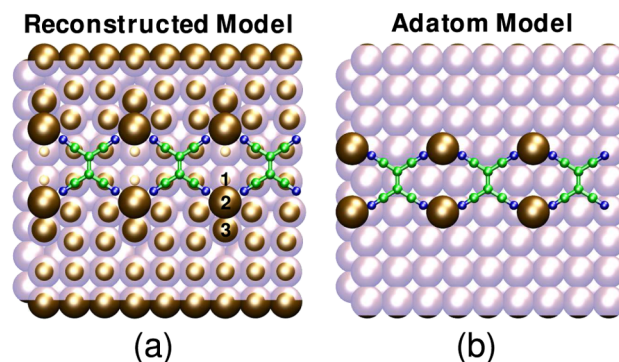


FIG. 1 (color online). DFT-LDA optimized structural geometry for the one-dimensional chain arrangement of TCNE on the Cu(100) surface (a) for the reconstructed model and (b) for the adatom model. A transparent plane is used to emphasize the magnitude of reconstruction of the topmost Cu layer.

adaptive grids that minimize the probing sites needed to obtain a high resolution image [15]. In STM simulations, the tunnel current was computed within a scattering approach based on the Landauer-Büttiker formalism [16] along with an extended Hückel theory Hamiltonian [14,17]. The sample preparation of TCNE/Cu(100) and STM experiments (using a Pt/Ir tip) were performed as described in Ref. [10].

As a starting point, we intuitively placed the TCNE molecule in a highly symmetric adsorption site on a flat Cu(100) surface. As shown in Fig. 1(a), the DFT-LDA geometry optimization reveals that a TCNE chain assembly induces a strong reconstruction of the topmost Cu(100) surface layer, most dramatically where the Cu-N bonds are formed. Within the one-dimensional chain structure, we can identify three different Cu atoms that are involved in the surface reshaping process: One Cu atom underneath the molecule chain is pushed below the surface plane by 0.3 Å (marked as “1”), another surface atom (marked as “2”) is highly buckled by 1.3 Å out of the surface plane, and finally a third surface atom outside the chain (“3”) opens a trench by sliding laterally by 1.0 Å toward the chain and 0.3 Å out of the surface plane. The distance between highly buckled Cu atoms is 7.7 Å along the chain direction and 6.6 Å in the perpendicular direction. The energy difference between the buckled and a flat Cu(100) surface is 3.55 eV, which gives a deformation energy of 1.78 eV per buckling. Strong interaction of adsorbates with substrates can induce nanoscale surface reshaping [18]. For example, a single molecule C₉₀H₉₈ at the step edge of a Cu(110) surface was used to build a molecule-sized electrode [19]. In another case, the removal of C₆₀H₆₆ self-assembly from a Cu(110) surface left imprinted trenches underneath [20]. Metal surfaces roughening with C₆₀ were also reported [21–23].

On this reconstructed surface, TCNE is strongly bonded to Cu atoms. The energy needed to dissociate the TCNE/Cu(100) complex into individual but unrelaxed components is 6.60 eV. Adsorbed TCNE is significantly deformed with respect to the gas phase structure; the relaxation of the molecule gives a deformation energy of 0.71 eV. Hence, the formation of this strongly buckled structure would necessitate a minimal energy amount of $(3.55 + 0.71)$ eV = 4.26 eV, which is still 2.34 eV lower than the calculated dissociation energy for the TCNE/Cu(100) complex. Although energies can be more accurately obtained by considering generalized gradient approximation functionals and a basis set superposition error [24], the comparison of relative values obtained at the LDA level should give an appropriate description. In addition, the deformation of isolated TCNE contributes to reduce its HOMO/LUMO gap from 2.61 to 1.98 eV.

While the DFT-LDA optimization of the TCNE chain on Cu(100) suggests the described strong surface reconstruction, an entirely different self-assembly mechanism of molecules on Cu(100) is known to exist due to the fact

that Cu adatoms from step edges can easily diffuse along the Cu(100) terraces [25]. These Cu adatoms can connect to molecules and promote ordered molecular structures via formation of a coordination network [26,27]. In order to consider such a self-assembly process for the TCNE chains on Cu(100), we also performed DFT-LDA calculations on the adsorption of TCNE with four Cu adatoms located in fourfold sites of the Cu(100) surface. The calculated optimized geometry is shown in Fig. 1(b). In this case, the surface layer remains unreconstructed, and the adatoms have left their fourfold positions to establish covalent bonding with CN groups. The surface structure of this adatom model shows a distance between Cu adatoms of 7.7 Å along and 5.4 Å across the chain, the latter being significantly shorter (by 1.2 Å) than in the reconstructed model. In addition, the dissociation energy for this complex is 7.67 eV, which makes the TCNE more tightly bound to the surface than in the reconstructed model.

Although the exclusion of one of the two mechanisms remains a difficult task without investigating the dynamics of the processes, we can try to discriminate between them by comparing how well simulated STM images of both models resemble the experimental STM images of the TCNE chains, which show three characteristic features [Fig. 2(a)]: (i) The TCNE molecules appear as a bright, elongated protrusion centered around the C = C bond and four faint lobes close to the CN groups (referred to as *short legs* in Ref. [10]); (ii) additional protrusions next to CN groups of neighboring molecules above and below the TCNE chain (*extended legs*) are presumably caused either by buckled Cu surface atoms or by bound Cu adatoms [28]; (iii) dark trenches surround the buckled atoms or adatoms above and below the TCNE chain.

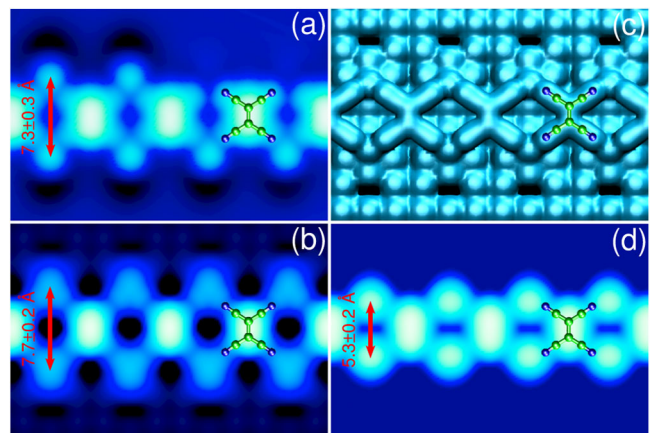


FIG. 2 (color online). Topographic STM images of a TCNE chain (a) obtained experimentally with a Pt/Ir tip ($V = 1$ mV, $I = 5$ nA) from Ref. [10] and (b) calculated on a reconstructed Cu(100) surface with a Pt(111) tip ($V = 1$ mV, $I = 15$ nA). (c) Calculated charge density of the valence electrons for the reconstructed model (a black plane is used to highlight the density drop). (d) Calculated STM image of a TCNE chain for the adatom model. All image domains are 31×18 Å².

The STM simulation of the reconstructed model probed with a Pt(111) tip is displayed in Fig. 2(b) [29]. The theoretical STM image can reproduce the first two features, although the short and extended legs appear more blurred. The third feature, the dark trench, is faint but visible in the STM simulation. Moreover, we observe a clear drop in the calculated charge density map close to the buckled atoms [Fig. 2(c)], which can be associated to the dark trench area. Overall, the characteristic experimental features are reproduced fairly well. In comparison, the simulated STM image of the adatom model is shown in Fig. 2(d). While also this model qualitatively reproduces the bright TCNE center as well as the short and extended leg features (that also appear blurred), no dark trench can be reproduced at all. Hence, a main characteristic feature of the experimental images is missing in this model.

Finally, we quantitatively compare the features related to the extended legs in experimental and simulated STM images (see arrows in Fig. 2). From the experiments we find distances of $7.7 \pm 0.1 \text{ \AA}$ along the chain and $7.3 \pm 0.3 \text{ \AA}$ across. Both theoretical models show a distance of $7.7 \pm 0.2 \text{ \AA}$ along the chain (i.e., 3 times the Cu nearest-neighbor distance), which is in very good agreement with the experiment. Across the TCNE chain, the situation changes: For the reconstructed model, the simulated STM image shows a distance of $7.7 \pm 0.2 \text{ \AA}$, which is slightly larger than the actual distance of the highly buckled atoms, because the Cu atom “3” next to the trench has a significant contribution to the apparent height in the STM image. The simulated STM image of the adatom model exhibits a distance of only $5.3 \pm 0.2 \text{ \AA}$ across the chain, similar to the actual adatom distance across the TCNE chain. This is in strong disagreement with the experiment. Consequently, the reconstructed model reproduces the experimental observations far better, and thus we conclude that the strong buckling of the Cu(100) surface is most likely the driving mechanism for the observed self-assembly of TCNE molecules into chains. In addition, the DFT and STM calculations agree to support that mobile adatoms do not apparently participate in the formation of the one-dimensional TCNE chain: The most stable geometry is not experimentally observed by STM, and the STM simulations on the reconstructed model are accurately reproducing the experimental STM results.

Another important aspect of the interaction of TCNE with surfaces is the magnitude of charge transfer. The formation of TCNE^{1-} or TCNE^{2-} species is generally assumed when low work function metals such as Na or Ca are used [1]. The situation is slightly different with transition metals for which the accumulation of net charge on TCNE depends on the magnitude of $\text{TCNE} \rightarrow \text{metal}$ donation but also on the $\text{metal} \rightarrow \text{TCNE}$ back donation [3]. Hence, a fractional net charge on TCNE would reflect that a charge transferred to the metal (donation) is significantly returned back to the molecule (back donation).

Figure 3(a) shows the total DOS and various PDOS for a buckled surface without the TCNE molecule. The total DOS and PDOS over most Cu atoms of the buckled surface are similar to the DOS diagram usually observed for this Cu surface [30], except for highly buckled Cu atoms for which the states are more strongly localized (sharp and intense) and more weakly bonded than other Cu surface states. The adsorption of TCNE is considered in Fig. 3(b): The sharp peak of highly buckled Cu atoms at -6.0 eV is now smeared out within the broad PDOS peaks at higher binding energy. The disappearance of the localized surface states into the higher binding energy manifold suggests an electron depletion of buckled Cu atoms and a strong mixing of states with TCNE orbitals. In Fig. 3(b), the DOS of an isolated chain shows quite narrow peaks, while the PDOS of adsorbed TCNE is much broader. Therefore, such broadening results from the important mixing between TCNE and Cu(100) states rather than from the coupling between TCNE molecules in the chain.

The nature of two TCNE-related molecular orbitals near the Fermi level are shown in Fig. 3(c). We can easily attribute the peaks at -8.9 and -5.5 eV of adsorbed TCNE to the HOMO (-8.1 eV) and LUMO (-6.1 eV) of isolated TCNE, respectively. The shifts with respect to the isolated TCNE chain can be explained in terms of charge transfer: The HOMO moves toward high binding energies (electron donation to Cu), and the LUMO moves toward low binding energies (electron back donation to TCNE). The contribution from TCNE to the wave function of the TCNE/Cu(100) complex centered at -5.5 eV is $\sim 90\%$; i.e., TCNE accepts at least $1.8|e|$ from Cu(100). Mulliken population analysis of the TCNE/Cu(100) system gives a net charge of $0.30|e|$ on TCNE, which indicates that Cu receives $\sim 1.5|e|$ from HOMO and HOMO- n states

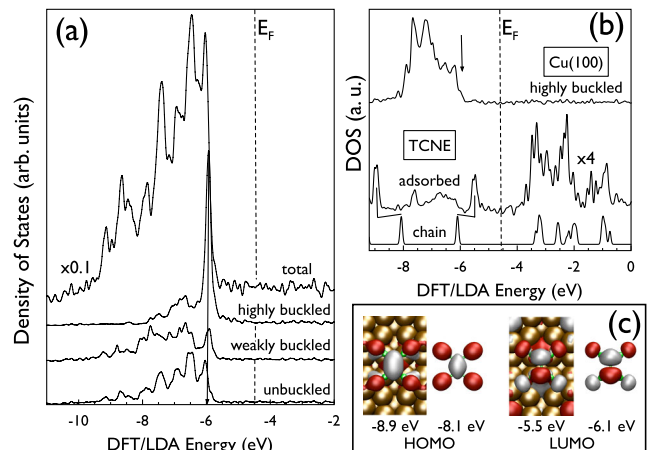


FIG. 3 (color online). (a) Total DOS and projected DOS for a buckled Cu surface without TCNE and (b) after adsorption of TCNE, and total DOS of an isolated TCNE one-dimensional chain. (c) Wave function contours of the molecular orbitals located at -8.9 and -5.5 eV in (b) and HOMO and LUMO of isolated TCNE.

of TCNE. A comparable charge transfer of $0.55|e|$ from a polycrystalline Cu surface to TCNE has been deduced from surface-enhanced Raman scattering experiments [31]. The adsorption of the electron acceptor F4-TCNQ on the Cu(111) surface also leaves a net charge on the molecule of approximately $0.6|e|$ [3].

In summary, slab DFT-LDA calculations, STM experiments, and simulations reveal that the adsorption of TCNE molecules on Cu(100) is accompanied by a reconstruction on the topmost Cu surface layer. By comparison, we exclude the possibility of an alternative self-assembly mechanism based on diffusing Cu adatoms. Reconstructing Cu atoms that bind directly to the CN groups of TCNE are strongly buckled out of the surface plane by 1.3 Å. The presence of dark trenches in STM experiments and simulations is attributed to a drop in the surface charge density that is caused by the concerted lateral displacement of Cu atoms contributing to the buckling process. TCNE interacts strongly with the Cu(100) surface leading to a large adsorption energy. However, the net charge transfer onto the TCNE moiety is relatively weak due to a significant amount of charge that is backdonated to the molecule.

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