Molecules containing multiple cyano (CN) groups such as tetracyanoethylene (TCNE) or 7,7,8,8-tetracyanoquinodimethane (TCNQ) or 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) 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. 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) and Au(111) 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.

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 DFT within a local density approximation (LDA) included in the SIESTA package. For core electrons, norm-conserving pseudopotentials following a Troullier and Martins scheme were used with relativistic corrections for Cu atoms. For the representation of valence electrons, we used an extended atomic basis set of polarized double-$\zeta$ 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 3x8 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 (STS). The software includes several algorithmic strategies such as parallel computation of the tunnel currents and adaptive grids that minimize the probing sites needed to obtain a high resolution image. In STM simulations, the tunnel current was computed within a scattering approach based on the Landauer-Büttiker formalism along with an extended Hückel theory (EHT) Hamiltonian. The sample preparation of TCNE/Cu(100) and STM experiments (using a Pt/Ir tip) were performed as described in Ref.

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 an 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...
FIG. 1: 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.

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 C_{90}H_{98} at the step edge of a Cu(110) surface was used to build a molecule-sized electrode [19]. In another case, the removal of C_{60}H_{66} self-assembly from a Cu(110) surface left imprinted trenches underneath [20]. Metal surfaces roughening with C_{60} were also reported [21, 22, 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 eV + 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 GGA functionals and basis set superposition error (BSSE) [24], the comparison of relative values obtained at LDA level should give an appropriate description. In addition, the deformation of isolated TCNE contributes to reduce its HOMO/LUMO gap from 2.61 eV 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 four-fold 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 four-fold 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. (iii) Dark trenches surround the buckled atoms or adatoms above and below the TCNE chain.

The STM simulation of the reconstructed model...
probed with a Pt(111) tip is displayed in Fig. 2(b) [31]. 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 adatoms (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±0.1 Å along the chain and 7.3±0.3 Å across. Both theoretical models show a distance of 7.7±0.2 Å along the chain (i.e., three 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±0.2 Å, 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±0.2 Å across the chain, similar to the actual adatom distance across the TCNE chain. This is in strong disagreement to 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 TCNE—metal donation but also on the metal—TCNE backdonation [2]. Hence, a fractional net charge on TCNE would reflect that a charge transferred to the metal (donation) is significantly returned back to the molecule (backdonation).

Fig. 3(a) shows the total DOS and various PDOS for a buckled Cu surface without TCNE and (b) after adsorption of TCNE, and total DOS of an isolated TCNE one-dimensional chain. (c) Wavefunction contours of the molecular orbitals located at −8.9 eV and −5.5 eV in (b) and HOMO and LUMO of isolated TCNE.

FIG. 3: (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) Wavefunction contours of the molecular orbitals located at −8.9 eV and −5.5 eV in (b) and HOMO and LUMO of isolated TCNE.
TCNE/Cu(100) system gives a net charge of 0.30 |e| on TCNE, which indicates that Cu receives \(\sim\)HOMO and HOMO-charge transfer of 0.55 |e| from a polycrystalline Cu surface to TCNE has been deduced from surface-enhanced Raman scattering experiments \[23\]. 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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1 Electronic address: stephane.bedwan@polymtl.ca
2 Electronic address: crommie@berkeley.edu
3 Electronic address: alain.rochefort@polymtl.ca

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