



Structure and electronic configuration of tetracyanoquinodimethane layers on a Au(1 1 1) surface

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ABSTRACT

The organic molecule tetracyanoquinodimethane (TCNQ) is a strong charge acceptor with a large tendency to form metal–organic charge transfer compounds. Using a low temperature scanning tunneling microscope we characterize the self-organization of TCNQ in ultra-thin films on a Au(1 1 1) surface and its electronic structure. We find that the molecules are weakly adsorbed on the metal, forming extended networks stabilized by hydrogen bonds. Despite its strong acceptor character, we find a negligible charge transfer from the metal surface.

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1. Introduction

During the last decades TCNQ, and its family of small polynitriles, have been considered as prototype π acceptor molecules and they have been widely used in the formation of charge transfer compounds. The acceptor properties of TCNQ arise from the strong electrophilic character of their two malonodinitrilo terminations. Furthermore, TCNQ exhibits a strong tendency to bond to transition metal atoms. Interaction of the cyano groups with d atomic orbitals leads to the extraction of one electron from the metal, which is accordingly placed into a π molecular orbital, forming a radical anion molecule [1]. The unpaired electron added to TCNQ through a metal–organic bond bestows magnetism to the molecule, with promising applications in the synthesis of organic magnetic materials [2,3]. It is then of fundamental interest to explore the properties of TCNQ and related components on the surface of a metal, aiming at identifying their charge state and, eventually, their magnetic state [4–8].

During the last two decades, surface science has been intensively applied to investigate the growth of organic thin films and the electronic properties of organic–inorganic interfaces. In particular, the acceptor character of TCNQ and F_4 -TCNQ has been exploited as a p dopant in organic semiconductors [9] and as a model system for gaining understanding about fundamental aspects of energy

level alignment at the metal–organic (MO) interface. Charge transfer between TCNQ and a metal, and the concomitant formation of an interface dipole, strongly determines the pinning of the molecular levels with respect to the metal Fermi level (E_F). The study of the electronic level alignment at the MO interface is thus important for its electronic functionalization design.

Here, we study the structure and electronic properties of TCNQ molecules adsorbed isolated and in self-assembled islands on a Au(1 1 1) surface using low temperature scanning tunneling microscopy (STM) and spectroscopy (STS). Our results demonstrate that TCNQ exhibits a strong tendency to form highly ordered molecular assemblies, in a similar fashion as it was previously described on copper surfaces under electrolytic conditions [10]. The formation of ordered self-assembled structures is driven by both a weak interaction with the underlying surface and a strong tendency of TCNQ to form N···H hydrogen bonds. Contrary to the case of F_4 -TCNQ, where an integer occupation of the lowest unoccupied molecular orbital (LUMO) on various metal surfaces was found [6], TCNQ is neutral on a Au(1 1 1) surface.

2. Experimental details

The experiments have been carried out in a custom-built scanning tunneling microscope, working under ultra-high vacuum conditions and at an equilibrium temperature of 5 K. TCNQ molecules (Aldrich) were deposited in vacuum from the solid compound onto an atomically clean Au(1 1 1) surface, prepared by repetitive cycles of Ne⁺sputtering and annealing. The substrate temperature is an important parameter in the growth of molecular

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species, as in many cases it can tune the film order among several possible structural phases. In this work, we deposit TCNQ onto the Au(1 1 1) surface at room temperature. Posterior to deposition, the TCNQ covered sample is placed in the low temperature stage of our STM for its inspection.

Scanning tunneling spectroscopy measurements are performed by placing the STM tip on top of an individual molecule and, after disconnecting the feedback loop, ramping the sample bias (V_s). The junction differential conductance (dI/dV) is obtained using a lock-in amplifier as proportional to the first harmonic current component reacting to a small sinusoidal bias modulation of amplitude V_{rms} . The structure in the dI/dV vs. V_s spectra can be related to the local density of states ($LDOS(E-E_F)$) at an energy $E = eV_s$.

3. Results and discussion

3.1. Domain structure

Room temperature sub-monolayer deposition of TCNQ molecules onto a Au(111) surface results in the formation of

highly ordered TCNQ self-assembled domains extending for hundreds of nanometers over the surface (Fig. 1a). The STM images show, superimposed to the molecular corrugation, the unperturbed shape of the underlying herringbone reconstruction of the Au(1 1 1) surface. This is a characteristic fingerprint of a weak interaction between the molecular adlayer and the surface. Hence, TCNQ on Au(1 1 1) populates a physisorbed state, characteristic of many planar aromatic species on this surface. We may then expect that the molecule adopts a planar adsorption geometry, parallel to the metal, in contrast with the bent adsorption structure adopted by the fluorinated molecule F_4 -TCNQ on Cu(1 1 1) [8].

In spite of its physisorbed state, TCNQ exhibits a certain degree of commensuration with the gold atomic lattice. From the STM images we obtain a molecular unit cell with dimensions $a_1 = a_2 \cong 1$ nm. We find that the short vector of this unit cell, a_1 , runs along the $\{1\ 1\ \bar{2}\}$ surface directions (Fig. 1b). A structural model that accounts for this molecular lattice, and also assumes full commensuration with the underlying gold atomic lattice, is shown in Fig. 1c. According to this model, the molecules alternate adsorption on two different atomic sites. The layer is stabilized by the formation of

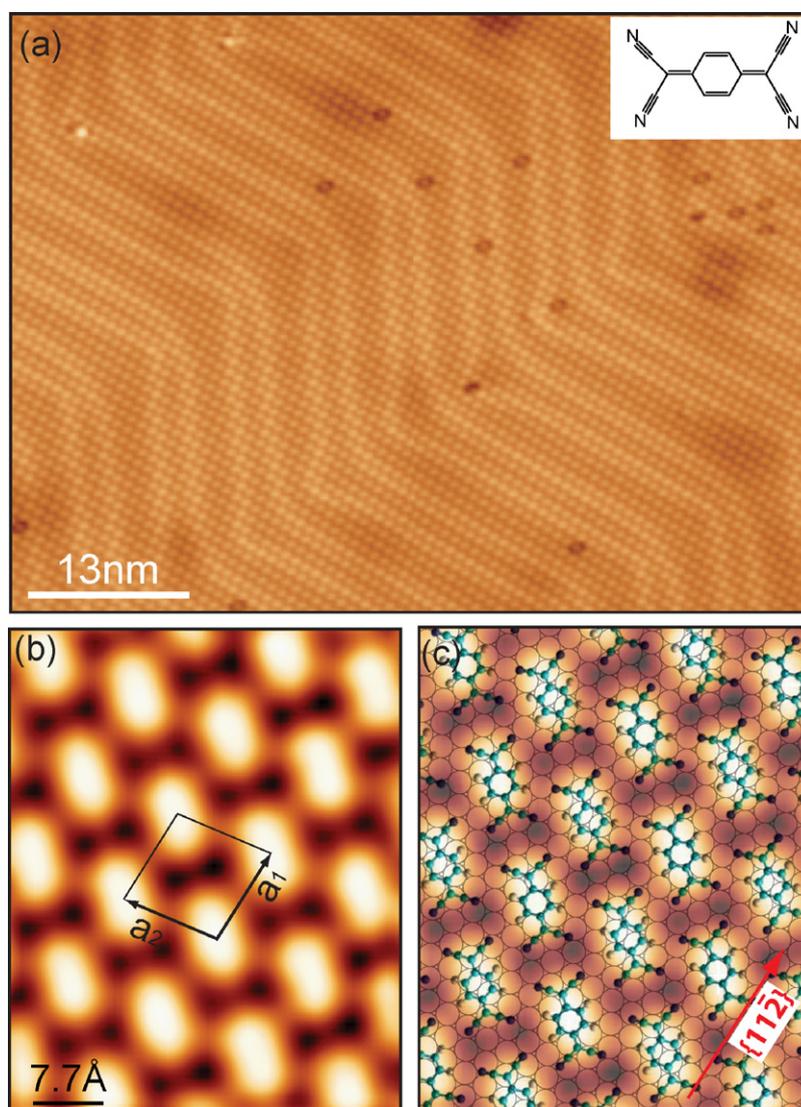


Fig. 1. (a) Large scale STM image showing the homogeneously ordered structure of a self-assembled domain of TCNQ. The reconstructed Au(1 1 1) surface with the characteristic herringbone pattern is visible through the molecular island ($V_s = 2.1$ V, $I = 1.9$ nA). The inset shows a molecular model of TCNQ. (b) Small scale STM image of a similar TCNQ island ($V_s = 3$ V, $I = 2.2$ nA). The molecular unit cell is indicated, with dimensions $a_1 = a_2 \cong 1$ nm. (c) Structural model of the self-assembled TCNQ constructed on the base that the molecular layer is commensurate with an fcc atomic lattice of Au(1 1 1). Data analysis was performed using the software WSxM [26].

4 $C \equiv N \cdots H-C$ hydrogen bonds per molecule. All terminal N and H atoms are directly involved in the formation of intermolecular bonds. The model in Fig. 1c allows us to also extract an intermolecular spacing (distance between the N and H atoms) of ~ 3 Å. This is a large separation compared to the typical interatomic distance in hydrogen bonds in liquid and gas phase complexes [11]. It reflects the non-negligible role of the surface atomic corrugation, in spite of the physisorptive character of the interaction. The molecules adopt a structure and separation that maximize their mutual interaction while maintaining the commensuration with surface.

The formation of this ordered structure on a metal surface contrasts with the behavior found for other molecules with a strong tendency to donate/accept charge. For instance, the donor species TTF becomes positively charged at the gold surface by electron donation to the metal. The resulting repulsive electrostatic interaction between molecules hinders the formation of a self-assembled layer at low molecular coverage [12]. The strong tendency of TCNQ to assemble in compact structure layers thus poses the question of its charge state on the metal. We expect that either this species is essentially neutral on the gold surface, or the strong attractive nature of $N \cdots H$ hydrogen bonds annihilates the effect of electrostatic repulsion between negatively charged molecules. To solve this question, we have performed scanning tunneling spectroscopy measurements on the TCNQ layer.

3.2. Tunneling spectroscopy on the TCNQ layer

Fig. 2b shows the differential conductance spectrum measured on top of a TCNQ molecule located in an ordered layer, compared to the spectrum taken with the same conditions on the nearby bare Au(111) surface, as indicated in Fig. 2a. The spectrum on the molecule shows a broad peak located at $V_s = 700$ mV, which is not observed on the spectrum of the metal. Its origin is the presence of an unoccupied molecular resonance at the corresponding energy position (eV_s) above the Fermi level.

To identify the electronic state that causes this feature, we relate this energy value to the intramolecular structure observed in the STM images. As shown in Fig. 2c and d, TCNQ molecules are imaged as elliptical and featureless protrusions at negative sample bias values (hence tunneling from occupied states of the metal + molecule system) and at low positive bias values. However, for sample bias corresponding to the unoccupied molecular resonance (Fig. 2e) the molecular shape changes, now appearing with four arm-like features connecting each molecule to its neighbors. For the case of planar organic adsorbates weakly distorted by the surface, the intramolecular structure resolved by STM can be usually correlated to the unperturbed shape of molecular frontier orbitals [13], thus providing a hint about its origin.

Fig. 3a shows the molecular surfaces of the frontier orbitals for a free TCNQ molecule. We observe that the four-arm struc-

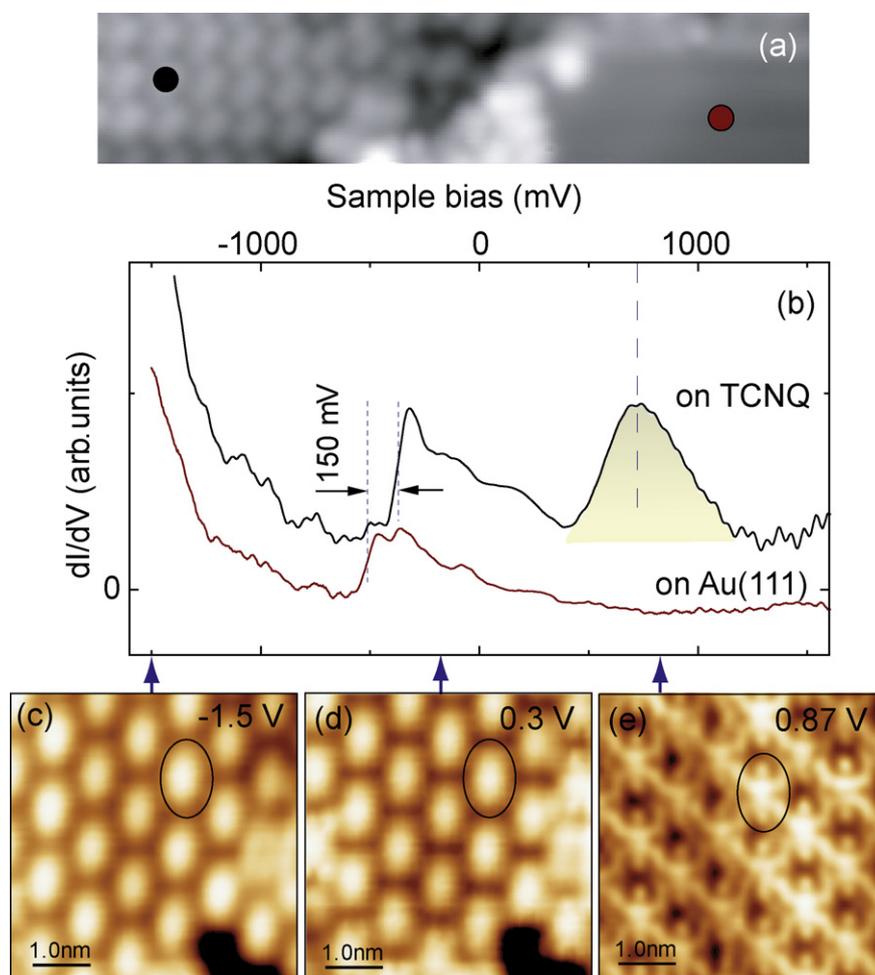


Fig. 2. (a) STM image of a region with TCNQ layer and clean Au(111) surface. Spectra in (b) were obtained in the indicated locations ($V_s = 2$ V, $I = 1.4$ nA, $V_{rms} = 20$ mV). The spectrum on the molecular layer shows an additional peak (shaded) and a shift of 150 mV of the onset of the Au(111) surface state (indicated by lines). (c–e) Topography STM images of the molecular layer in (a) obtained at different sample bias voltages. A sharp intramolecular resolution is obtained for bias voltages around the position of the molecular resonance in (a). An ellipse is used to highlight the position of a single molecule.

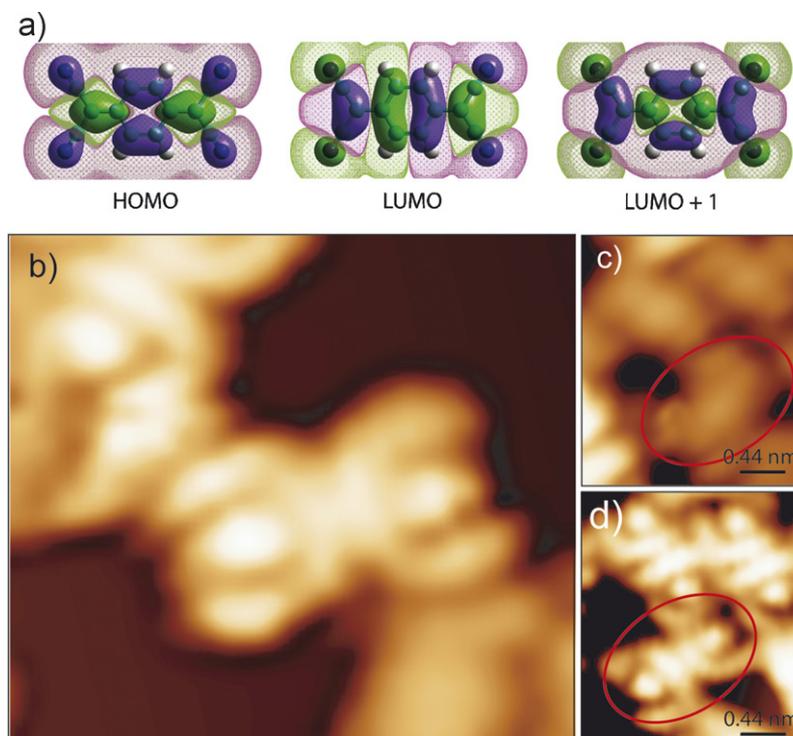


Fig. 3. (a) Molecular surfaces of free TCNQ. The plots combine two different cuts (solid 200 times larger than mesh) in order to simulate the extended shape of these orbitals. (b) TCNQ molecule imaged at positive bias voltage ($V = 0.8$ V, $I = 0.32$ nA). The intramolecular structure resembles the LUMO shape of the free molecule, as can be observed by direct comparison with the corresponding isosurface presented in (a). Panels (c) and (d) show STM images of a TCNQ group taken at negative ((c) $V = -1$ V, $I = 0.33$ nA) and positive ((d) $V = 1$ V, $I = 0.33$ nA) bias voltages. At negative bias voltages TCNQ is imaged by STM without internal contrast.

ture of TCNQ molecules in the layer resembles the spatial shape of the LUMO resonance. This correspondence becomes more clear when inspecting the shape of isolated molecules *extracted* from the ordered domains by lateral manipulation using the tip of the STM (Fig. 3b). In this case, the single molecule still appears with the distinctive four-arm structure observed in the layer. More precisely, the structure depicts 3 nodal planes perpendicular to the large axis of the molecule, thus allowing us to directly correlate the intramolecular structure with the shape of the free-molecule LUMO, shown in (a). We therefore identify the spectral feature observed in the dI/dV plot in Fig. 2b as the LUMO-derived resonance. The intramolecular shape exhibited by individual TCNQ molecules is only observed for positive sample bias values (Fig. 3c and d). This similarity to the thin film case confirms that the isolated molecules, after tip manipulation, remain in a similar chemical state as in the TCNQ film.

The alignment of this resonance well above the metal Fermi level suggests that this state does not become partially occupied. Additional charge donation patterns, as those found for F_4 -TCNQ on Cu(111) [8] are unlikely to occur here, because of the weak interaction of TCNQ molecules with the gold surface and the fairly unperturbed LUMO fingerprint in the intramolecular structure. Thus, our results indicate that the acceptor character of the TCNQ molecule does not suffice to form a charge transfer complex with the Au(111) surface.

A second spectroscopic fingerprint observed in the TCNQ spectrum of Fig. 2b is related to the Au(111) surface state. On clean Au(111), the surface state appears in the tunneling spectra as a step-like onset at 490 meV below the Fermi level [14]. This step is also observed in the spectra taken on the molecular layer, confirming the weak molecule–metal interaction, but slightly shifted 150 meV to higher energy values. Shifts of the metal surface state have been reported for different types of adsorbates on noble metal

surfaces, like noble gases [15–17], insulating thin films [18], and molecular layers [19]. Its origin is attributed to either modifications of the image potential and/or surface work functions by the dielectric medium placed above the metal surface [18,20], or to electron depopulation [21] due to charge transfer processes between the surface and the molecular overlayer. As we cannot discard the latter, we note that such depopulation would correspond to an average extra charge per molecule of $0.2e$ [22]. This value, comparable to the charge donated by TTF monomers on the same surface [12], should be reflected either by a lower energy alignment of the LUMO resonance, partially crossing E_F , or in the creation of molecular interface states as a response to charge accumulation in the molecule [6]. None of these effects is compatible with the spectra in Fig. 2b nor with the free-molecule like orbital structure observed in STM images. We may then tentatively assume here that the surface state shift observed is a consequence of the changes on work-function and/or image potential shape induced by the molecular layer. In this case, the upward shift should be accompanied by an increase in its electronic effective mass m_e . Measurement of m_e using scanning tunneling spectroscopy [23] or angle resolved photoemission spectroscopy could provide the definitive proof for this argument.

In summary, our study of ultra-thin films of TCNQ molecules on a Au(111) surface provides evidence that these molecules interact weakly with the metal underneath and are neutral. A neutral TCNQ molecule on a metal is in contrast to the anionic state usually found for this specie and its related fluorinated compound on various other surfaces [6,8,24]. TCNQ molecules show an unusual free-molecule like behavior in its orbital fingerprint. We presume that such unperturbed state on a metal also helps to maintain the strong acceptor character of this molecule in the adsorbed state, thus representing an ideal workbench to investigate charge transfer processes with other co-adsorbates directly at the surface [23,25].

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