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The geometric and electronic structure of TCNQ and TCNQ+Mn on Ag(0 0 1) and Cu(0 0 1) surfaces

V. Feyer[a,*], M. Graus[b,c], P. Nigge[b,c], G. Zamborlini[a], R.G. Acres[d,1], A. Schöll[b,c], F. Reinert[b,c], C.M. Schneider[a,e]

[a] Peter Grünberg Institute (PGI-6) and JARA-FIT, Research Center Jülich, 52425 Jülich, Germany
[b] Universität Würzburg, Experimentelle Physik VII & Röntgen Research Center for Complex Material Systems RCCM, 97074 Würzburg, Germany
[c] Karlsruher Institut für Technologie KIT, Gemeinschaftslabor für Nanoanalytik, 76021 Karlsruhe, Germany
[d] Sincrotrone Trieste S.C.p.A., 34149 Basovizza, Trieste, Italy
[e] Fakultät f. Physik and Center for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, 47048 Duisburg, Germany

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ABSTRACT

Copper and silver surfaces can be used as model systems to study structure formation and interfacial bonding upon adsorption of organic molecules. We have investigated the geometric and electronic structure of ordered monolayers of TCNQ on Cu(0 0 1) and Ag(0 0 1) and of TCNQ+Mn on Ag(0 0 1) surfaces by LEED and photoelectron momentum microscopy. While TCNQ forms an incommensurable superstructure on Cu(0 0 1), two coverage-dependant, commensurable superstructures are established on Ag(0 0 1). Subsequent adsorption of Mn on top of TCNQ/Ag(0 0 1) results in the formation of a long-range ordered mixed metal–organic superstructure, which is also commensurable with the Ag(0 0 1) substrate. The photoelectron spectroscopy (PES) data shows a filling of the TCNQ LUMO by charge transfer from the substrate for all investigated interfaces and the coadsorption of Mn leads to an energy shift of the TCNQ HOMO and LUMO of 230 meV with respect to TCNQ/Ag(0 0 1). The characteristic angle-dependent intensity pattern of the TCNQ LUMO in PES was utilized to investigate the azimuthal orientation of the molecules in the respective unit cells. The angle-resolved PES data was further analyzed to identify lateral band dispersion effects in the adsorbate layers, but no significant dispersion was observed.

1. Introduction

Tetracyanoquinodimethane (TCNQ, see molecular structure in Fig. 1) is a well-known strong electron acceptor that forms a rich variety of charge-transfer materials. For example, a combination of TCNQ and tetrathiafulvalene (TTF) results in a strong charge-transfer complex [1]. The discovery of metallic electrical conductivity in molecular-based materials such as TTF-TCNQ [2] has led to the development of a new field of research with huge potential for technological applications, e.g. in molecular electronics.

Recently it was shown that organic semiconductors can possibly also be applied in the fast growing field of spintronics, where active manipulation and control of the electronic spin degree of freedom are of interest [3–5]. TCNQ is particularly suited since it tends to form coordination networks with transition metals (TM) [6–8], exhibiting intriguing magnetic properties which can be controlled by employing different combinations of TM atoms.

It has been demonstrated that formation of such TCNQ+TM networks goes along with a charge transfer of two valence electrons from each TM-atom to the TCNQ moiety. Among these compounds, TCNQ+Cr, TCNQ+Mn, and TCNQ+Fe exhibited long-range antiferromagnetic coupling while TCNQ+Co was found to be paramagnetic. This tuneable magnetic behaviour may provide a route for the development of novel materials for magnetic storage and spintronics [9].

Creating organic–organic and metal–organic coordination networks involving TCNQ molecules with such promising functionalities, however, requires a comprehensive understanding of the adsorption behaviour of the individual molecules on the underlying substrate and the electronic interaction with the substrate. In particular, this organic–metal interface plays a crucial role for the structure formation and the electronic properties of the adsorbed complexes.

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[*] Corresponding author.
E-mail address: v.feyer@fz-juelich.de (V. Feyer).
[1] Present address: Australian Synchrotron, Imaging and Medical Beamline, 3168 Clayton, Victoria, Australia.

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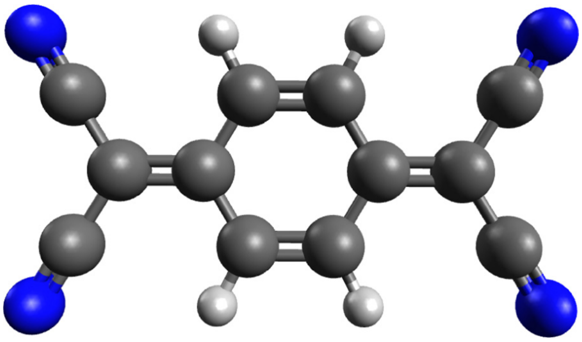

Fig. 1. Molecular structure of TCNQ. Colours represent: dark blue – nitrogen; dark grey – carbon; light grey – hydrogen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Copper and silver crystals are widely used as model systems to study this adsorption behaviour, providing different chemical environments and reactivities during the absorption process. Indeed, recent studies have shown that TCNQ molecules strongly bond on Cu(0 0 1) surfaces involving bending of the C═C bonds on the functional groups and a significant lift-up of copper atoms out of the surface to attain energy equilibrium. Near edge X-ray absorption fine structure experiments furthermore suggest strong interaction of the C≡N groups with the Cu(0 0 1) substrate [6]. Scanning tunnelling microscopy (STM) data have shown that TCNQ adsorption on Cu(0 0 1) leads to substantial structural and electronic rearrangements on both the organic and metallic sides of the interface. On Ag(0 0 1), however, the interfacial bonding was found to be less pronounced leading to a higher lateral mobility of the TCNQ molecules [7].

A combination of low energy electron diffraction (LEED) and photoelectron momentum mapping (PMM) is used in the present work to analyze the electronic and geometric structure of TCNQ monolayers [10–12]. For this purpose, energy resolved two-dimensional photoelectron momentum distributions were collected systematically using synchrotron radiation excitation. In particular, the characteristic angle-dependent photoelectron intensity distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of TCNQ upon adsorption on Cu(0 0 1) and on Ag(0 0 1) and after coadsorption of TCNQ and Mn on Ag(0 0 1) were investigated. The data allows statements on the structural arrangement of TCNQ in the respective interfacial layers and on the possible formation of a lateral band structure of molecule-derived states.

2. Experimental details

Experiments were performed at the NanoESCA beamline of the Elettra synchrotron in Trieste, Italy [13]. All PMM experiments were performed in an ultrahigh vacuum system with a base pressure of 8×10^{-11} mbar using a NanoESCA photoemission spectrometer. The setup includes an electrostatic photoelectron emission microscope (PEEM) and a double-pass hemispherical analyzer. This instrument is equipped with a transfer lens behind the immersion lens objective to map the angular distribution of the photoelectrons by imaging the Fourier plane. It can collect energy resolved photoemission intensities in the whole hemisphere above the sample surface with very high efficiency [14]. Energy and momentum resolution were estimated to be 150 meV and ±0.05 Å^{-1} respectively. Momentum images were recorded with a photon excitation energy of 26 eV using linear p-polarized synchrotron light. All photoemission measurements were performed at room temperature. For LEED measurements, a SPECS LEED system was used.

Clean surfaces of Ag(0 0 1) and Cu(0 0 1) were prepared by cycles of Ar$^+$ ion sputtering (kinetic energy 2.0 keV), followed by annealing at 800 K. The surface order and cleanliness were monitored by LEED and photoelectron spectroscopy (PES).

A few mg of TCNQ were loaded into a crucible of a home-made Knudsen cell type evaporator in an attached preparation chamber, and thermally evaporated at a temperature of 380 K onto the clean silver and copper substrates, which were held at room temperature.

In a subsequent step Mn was deposited from a molybdenum crucible in an electron-beam heated evaporator (also in the preparation chamber) onto the TCNQ layer. Also in this case the sample was held at room temperature during deposition, followed by subsequent annealing at 500 K to optimize lateral order.

The quantum-chemical calculations were performed using Perdew–Burke–Ernzerhof pseudopotentials in the GGA approximation with the Abinit code [15,16]. The cut-off energy was set to 10 Hartrees. For computation of the TCNQ HOMO and LUMO, the planar geometry of an isolated molecule was considered and momentum patterns (k-space) were generated using a procedure described previously [10–12,17,18]. As shown for similar molecules on metal surfaces, the geometrical deformation of the molecule upon adsorption induces only minor changes in the characteristic momentum maps of the molecular orbitals which justifies the isolated molecule approach.

3. Adsorption structures

Despite many existing studies of the adsorption of TCNQ on copper surfaces, some confusion remains in the literature concerning the structure of monolayers on Cu(0 0 1). In STM images, two superstructure matrixes (4, 3/−2, 2) and (4, 3/−2, 3), both commensurate with the Cu(0 0 1) lattice, were suggested [6]. Recently, Fladisher et al. simulated the LEED pattern reported in Ref. [19] and showed that the commensurate structures do not correctly describe the observed LEED image [3]. Based on helium atom scattering and LEED a new superstructure matrix (3.86, 2.86/−2, 2.2) was proposed that appropriately described the TCNQ monolayer on Cu(0 0 1), but was – unlike in the previous studies – incommensurate with the substrate. It is noteworthy that the authors followed a different preparation route to obtain long-range ordered overlayers by deposition of TCNQ molecules onto Cu(0 0 1) at a substrate temperature of 110 K, followed by annealing at 315 K [19].

In the present study, the growth of the TCNQ films was monitored and optimized by LEED. For TCNQ/Cu(0 0 1), sharp LEED patterns indicating large ordered domains were obtained by molecular beam deposition at a rate of ≈1 ML per 5 min onto the substrate kept at room temperature. For the films on the Cu(0 0 1) substrate a post-deposition annealing temperature of ≈530 K turned out to be ideal to achieve further sharpening of the diffraction spots. This can be straightforwardly explained by supplying additional thermal energy to increase the TCNQ mobility and therefore lateral order, while at the same time the temperature is too low to induce thermal desorption or degradation of individual molecules.

In addition, a dependence of lateral order on coverage was observed. When increasing the coverage in the sub-monolayer regime the corresponding LEED patterns got sharper until a full monolayer was established. Further TCNQ deposition led to a blurring of the diffraction spots which we interpret as the onset of bilayer growth. Consequently, the coverage leading to the sharpest LEED pattern was taken as a reference for the first full layer and will be denoted as “one monolayer (1 ML)” in the following.

The LEED pattern of 1 ML TCNQ/Cu(0 0 1) is shown in Fig. 2a. In order to determine the proper superstructure matrix, a LEED pattern simulation was fitted to the experimental data. We found the best match between simulation and experiment for an

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