Preferential nucleation, molecular distortion, charge transfer, and elastic effects in the self-assembly of TCNQ on Cu(100)

Christian Urban [1], Marta Trelka [1], David Écija [1], Roberto Otero [1,2], Rodolfo Miranda [1,2],
Luis Sánchez [3], Nazario Martín [2,3],
Yang Wang [4], Manuel Alcamí [4], Fernando Martín [4],
José M. Gallego [5]
[1] Dpto. de Física de la Materia Condensada, Universidad Autónoma de Madrid, Cantonblanco, 28049-Madrid, Spain
[2] Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco, 28049-Madrid, Spain
[3] Departamento de Química. Universidad Autónoma de Madrid. Cantoblanco, 28049 - Madrid. Spain
[4] Departamento de Química Orgánica. Universidad Complutense de Madrid. Cantoblanco, 28040 - Madrid. Spain
[5] Instituto de Ciencia de Materiales de Madrid - CSIC, Cantoblanco, 28049-Madrid, Spain
josemaria.gallego@uam.es

It is well known that the 2D self-assembly of organic molecules on solid surfaces is the result of a combination of molecule-molecule and molecule-substrate interactions. However, due to the large number of factors involved (which can include charge transfer between the molecule and the substrate, changes in the molecular conformation, the combination of weak noncovalent forces, like van der Waals or dispersive forces, with stronger ones, like hydrogen bonding or even covalent bonding), there are few cases where the surface arrangement of the molecule is completely understood. In this work we report on the self-assembly of TCNQ when vapour-deposited in UHV conditions on Cu(100), as studied with a combination of STM experiments and DFT calculations, which has allowed us to get a complete picture of the system, even although TCNQ is a strong electron acceptor, and then it is expected to interact strongly with the Cu surface.

The STM results show that submonolayer amounts of TCNQ grow epitaxially on Cu(100), with an almost rectangular lattice, although forming four different domains on the surface (Fig. 1). Taking into account the size of the molecule, and the angular orientation of the molecular main axis with respect to the substrate, these domains can be explained by assuming that the molecule rotates on the surface until the four N atoms are on bridge positions of the Cu atomic lattice (Fig 2). In addition, the theoretical calculations show that the Cu-N bonding changes the molecular conformation: the N atoms are closer to the Cu surface than the rest of the molecule (Fig. 3), while at the same time the Cu surface is noticeably distorted.

The self-assembly of the molecule is also the result of a combination of forces. Along one direction of the overlayer unit cell, the molecular arrangement comes dictated mainly by dispersive and van der Waals forces, in combination with elastic effects that produce the dislocations visible on the STM images. Along the other direction, on the other hand, the intermolecular interaction is mediated through the substrate, involving charge transfer and surface distortion.

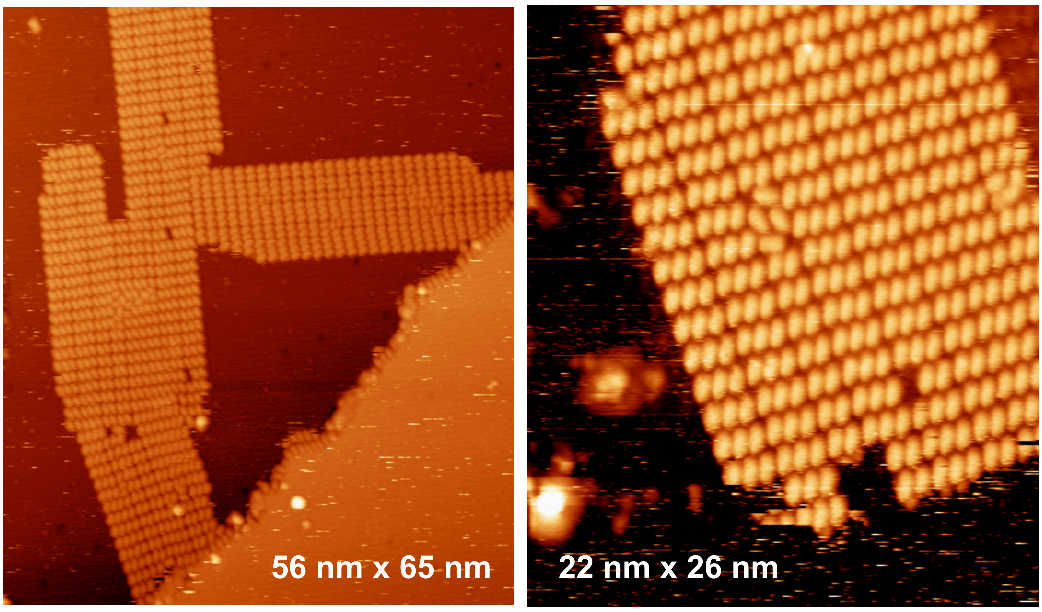

Figure 1: STM image of the Cu(100) surface after depositing ~0.4 ML of TCNQ.

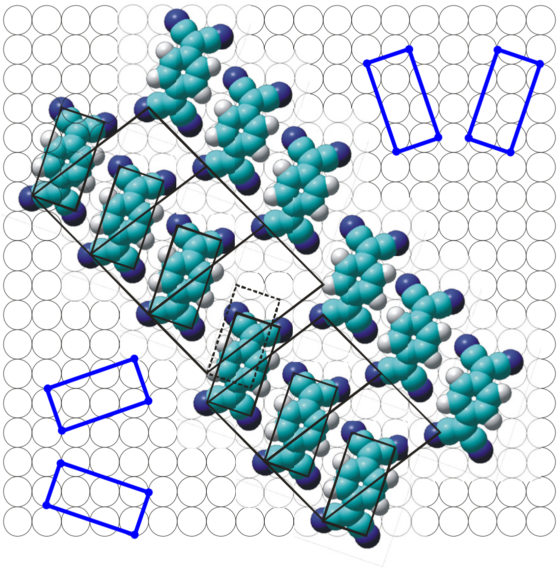

Figure 2: Proposed model of the TCNQ lattice on Cu(100), showing the surface unit cell and the molecular orientation. The blue rectangles show the four different orientations of the molecule with respect to the substrate.

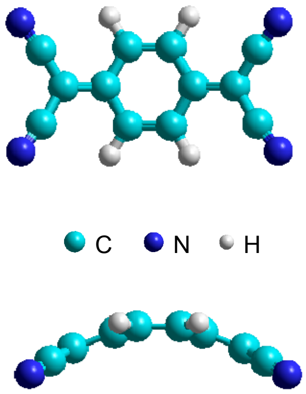

Figure 3: Top and lateral view of the calculated conformation of TCNQ when adsorbed on the Cu(100) surface.

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