CHARGE-TRANSFER-INDUCED STRUCTURAL REARRANGEMENTS AT BOTH SIDES OF ORGANIC ACCEPTOR/METAL INTERFACES

C. Urban[1], J. M. Gallego[2], Y. Wang[3], T-C. Tseng[4], D. Écija[1], M. Trelka[1], R. Otero[1, 5], Steve L. Tait[4], Nian Lin[4], Mitsuharu Konuma[4], Alexei Nefedov[7], Christof Wöll[7], María Ángeles Herranz[5], U. Starke[4], M. Alcamí[3], F. Martín[3], N. Martín[5, 6], K. Kern[4] and R. Miranda[2,6]

[1] Dpto. Física de la Materia Condensada, Univ. Autónoma de Madrid. Madrid, Spain
[2] Instituto de Ciencia de Materiales de Madrid, CSIC. Madrid, Spain
[3] Dpto, Química, Univ. Autónoma de Madrid. Madrid, Spain
[4] Max Planck Institute für Festkörperforschung, Sttugart, Germany
[5] Dpto, Química Orgánica, Univ. Complutense de Madrid. Madrid, Spain
[6] IMDEA-Nanociencia, Madrid, Spain
[7] *Lehrstuhl f˙ur Physikalische Chemie,Ruhr-Universität Bochum, Germany*

Christian.Urban@uam.es

Since the discovery of the first organic conductor in the charge transfer complex TTF-TCNQ, organic heterostructures based on blends of donor and acceptor molecules have displayed exciting electrical and optical properties with promising technological applications, which requires understanding the alignment of the energy levels and the corresponding charge transfer processes at metal/organic interfaces. Charge transfer, however, leads not only to modifications in the alignment of energy levels, but also to *structural* transformations. Such charge transfer-induced structural rearrangements might have significant effects on the subsequent growth and structure of organic films and, thereby, on device performance.

Here we report on the self-assembly under UHV of the strong organic acceptor TCNQ (tetracyanoquinodimethane) on Cu(100) by STM, LEED, XPS, XAS and DFT calculations. STM images rectangular TCNQ islands whose structure is determined by LEED. DFT and STM reveal that the adsorbed molecules are strongly deformed with respect to their gas phase configuration. Furthermore, while the molecular arrangement along the shortest side of the islands can be modelled by simple direct intermolecular interactions, the DFT simulations show that the inter-adsorbate interactions along the fast-growth direction of the rectangular islands arise from stress-relief induced by TCNQ molecules sitting in neighbouring sites. This is due to the strong charge transfer (confirmed by XPS and XAS) resulting in an adsorbate-induced reconstruction of Cu (100). The mechanism might be general for strong organic-acceptor/metal interfaces.

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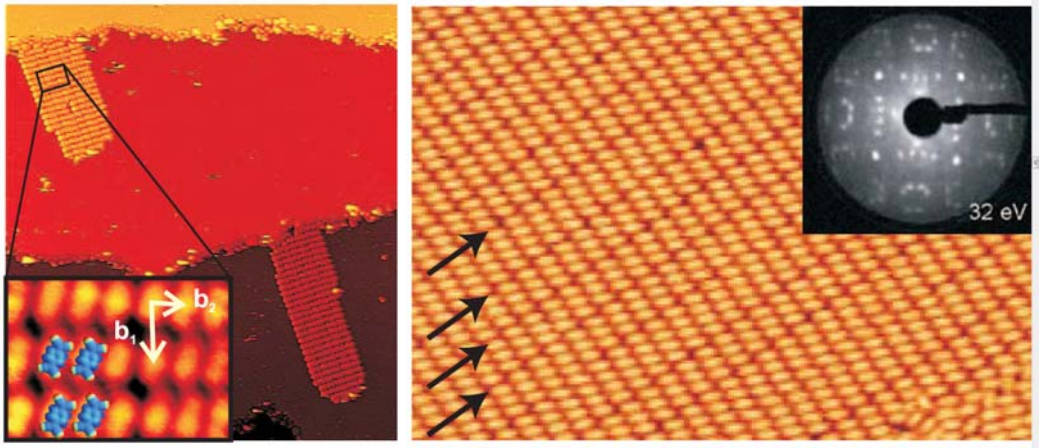
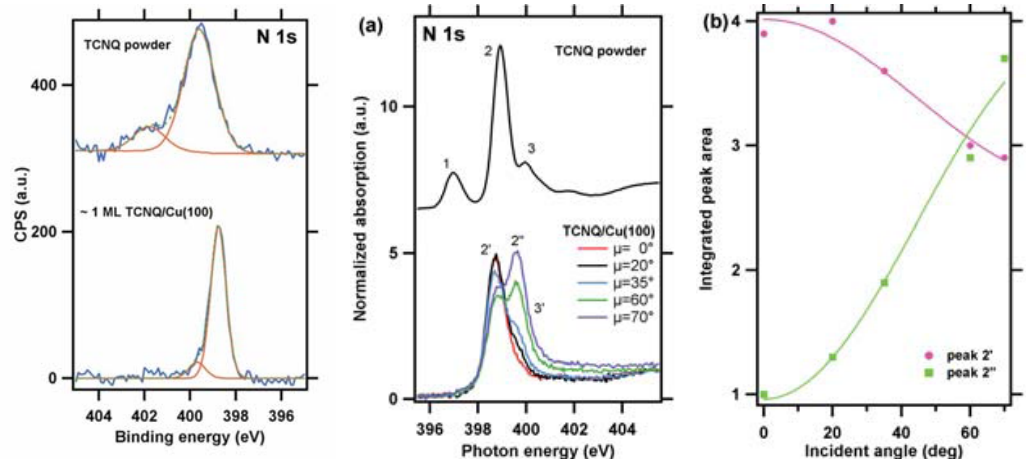
Figures:


b2
b1
32 eV


TCNQ powder
N 1s
~ 1 ML TCNQ/Cu(100)
CPS (a.u.)
Binding energy (eV)
(a)
N 1s
TCNQ powder
TCNQ/Cu(100)
μ= 0°
μ=20°
μ=35°
μ=60°
μ=70°
Normalized absorption (a.u.)
Photon energy (eV)
(b)
Integrated peak area
peak 2'
peak 2''
Incident angle (deg)