

# Adsorption of tetrathifulvalene (TTF) on Cu(100): can $\pi$ -stacked 1-D aggregates be formed at low temperature?

Ane Sarasola\*,<sup>1,2</sup> Serge Monturet,<sup>3</sup> Sara Barja,<sup>4</sup> Amadeo L. Vázquez de Parga,<sup>4</sup> and Andrés Arnau<sup>1,5</sup>

<sup>1</sup> Departamento de Física Aplicada I, UPV/EHU, Bilbao

<sup>2</sup> Donostia International Physics Center, San Sebastián

<sup>3</sup> CEMES-CNRS, 29 rue Jeanne Marvig, BP 94347, 31055 Toulouse Cedex 4, France

<sup>4</sup> Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia) and Dep. Física de la Materia Condensada, UAM, Cantoblanco 28048, Madrid

<sup>5</sup> Departamento de Física de Materiales, Facultad de Química UPV/EHU and Centro de Física de Materiales CFM Centro Mixto CSIC-UPV, San Sebastián

[ane.sarasola@ehu.es](mailto:ane.sarasola@ehu.es)

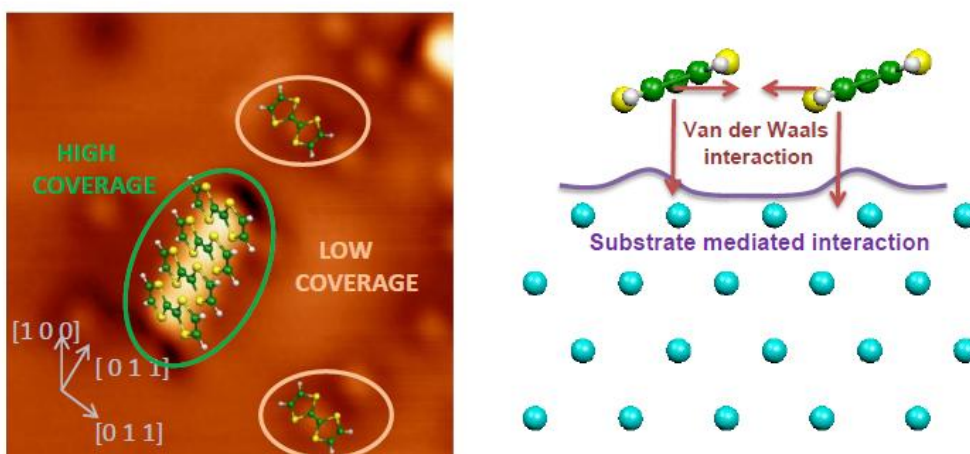
The possibility of growing one-dimensional (1-D) chains of  $\pi$ -stacked molecules, like TTF, on surfaces represents a challenge that would permit the study of fundamental electronic properties in conducting 1-D systems as an alternative to, for example, those formed by 1-D rows of Au atoms on Si vicinal surfaces [1]. Usually, the adsorption geometry of planar organic molecules, like polyarenes, on single crystal surfaces is essentially parallel to the surface [2], as the bonding is typically due to the interaction between the  $\pi$  electron cloud and the surface electrons. As a consequence of this adsorption geometry, there is no  $\pi$ -stacking between the molecules, as in the molecular crystals. However, there are exceptional cases in which the molecules are adsorbed vertically on the surface, no matter whether it is a single crystal surface, due to the formation of a particular molecule-surface bond [3] or the existence of an unusual intermolecular bonding [4]. So far, its practical realization using semiconductor or insulating surfaces does not seem to be an easy task but metal surfaces represent a first alternative to explore although, in principle, it is unclear which type surface is better: a highly anisotropic quasi-1-D surface, like O(2x1)/Cu(110) [5], or a more isotropic 2-D Cu(100) surface.

In this work we use first principles calculations to study the adsorption energy of TTF molecules on Cu(100) and explore the reasons why at low temperature STM topographical images seem to show the formation of one dimensional aggregates of  $\pi$ -stacked molecules. At low coverages, the energetically favoured adsorption geometry corresponds to planar TTF molecules parallel to the Cu(100) surface, while at high coverages a metastable phase with a tilted adsorption geometry appears to be stabilized by intermolecular van der Waals forces. Furthermore, our energetic analysis suggests the existence of a weakly attractive substrate mediated interaction. However, both the adsorption energy and the intermolecular attraction are rather weak (a few hundred meV) and, therefore, the existence of these particular TTF aggregates is restricted to low temperatures.

## References

- [1] D. Sánchez-Portal, S. Riikonen, and R. M. Martín, Phys. Rev. Lett. **93**, (2004) 146803.
- [2] N. Gonzalez-Lakunza, I. Fernández-Torrente, K. J. Franke, N. Lorente, A. Arnau, and J. I. Pascual, Phys. Rev. Lett. **100** (2008) 156805.
- [3] M.-L. Bocquet, H. Lesnard, and N. Lorente, Phys. Rev. Lett. **96** (2006) 096101.
- [4] M. Trelka, Ch. Urban, C. Rogero, P. de Mendoza, E. Mateo-Martin, Y. Wang, I. Silanes, D. Écija, M. Alcami, F. Yndurain, A. Arnau, F. Martín, A. M. Echevarren, J. A. Martín-Gago, J. M. Gallego, R. Otero, and R. Miranda, CrystEngComm **13** (2011) 5591.
- [5] M. Feng, P. Cabrera-Sanfelix, Chungwei Lin, A. Arnau, D. Sánchez-Portal, Jin Zhao, P. M. Echenique, and H. Petek, ACS Nano vol. 5, No. 11 (2011) pp. 8877-8883.

## Figure



(Left) Low temperature ( $T=4.6$  K) STM image ( $7 \times 7$  nm) of the Cu(100) surface at low TTF coverage. The green curve encloses a TTF tetramer that appears with brighter contrast in the image, as compared to the TTF monomer. (Right) Schematic representation of the adsorption geometry. Our DFT-vdW calculations suggest a planar adsorption geometry for the TTF monomer, while a tilted adsorption geometry in the one-dimensional TTF aggregate. This different adsorption geometry is due to intermolecular van der Waals attraction and the existence of a weak substrate mediated attractive interaction between TTFs.