2-D Confined Hydrogen Bonded Networks of Polychlorotriphenylmethyl Radicals on Au(111) Surfaces

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Functionalization of surfaces with multifunctional molecules assembled into multidimensional networks is nowadays one of the challenges of nanotechnology, towards the preparation of devices.[1] In the frame of this stimulating research field, of great interest is the family of multifunctional open-shell molecules, namely polychlorinated triphenylmethyl (PTM) radicals, whose paramagnetic character can be switched off by electrochemical reduction to the anionic species.[2] These molecules have been successfully grafted onto surfaces by chemisorption [3] and coordination chemistry,[4] demonstrating in all cases the preservation of their open-shell electronic configuration.

Recently, we successfully achieved the deposition of the tri-carboxy PTM derivative **1** (Fig.1) on Au(111) under UHV conditions. As shown by room temperature scanning tunnelling microscopy images (Fig. 2), these non-planar molecules self-assemble into a two-dimensional surface confined network driven by the formation of hydrogen bonding between the carboxylic functions.

Nevertheless, due to the electro activity of **1**, its low reduction potential value, and to its close contact to the gold metallic surface, its radical character could be lost after deposition forming the corresponding anionic derivative of **1**, with the obtaining of a diamagnetic surface. To characterize the functionalized Au(111) and assess its robustness, we made use of many different techniques, such as EPR, XPS and Ellipsometry. The obtained results, that will be the object of this contribution, evidence the persistent paramagnetic character of the PTM derivative **1** after UHV deposition onto gold. These results pave the way towards the preparation of multifunctional hybrid surface confined open frameworks using PTM radicals as ligands of transition metal ions.

References:

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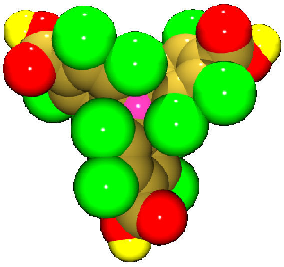
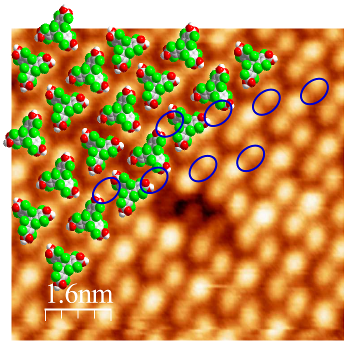
Figure 1.



Molecular structure of the tri-carboxy PTM derivative **1**.
In green the chlorine atoms; in red the oxygen atoms. In pink the carbon center bearing the unpaired electron.

Figure 2.



Room Temperature STM image of derivative 1 on Au(111). The molecule is modeled on top of the image. The circles indicate the H-bond formation.