Self-assembly of organic molecules on solid surfaces is nowadays a more than promising bottom-up approach to create functional nanostructures. In particular, the controlled adsorption of suitably tailored carboxylic acids offers a flexible route to the nano-scale engineering of chemically functionalized surfaces. First, the possibility of hydrogen-bond formation between complementary carboxylic groups allows fabricating highly organized 2D structures of flat-lying molecules [2]. In addition, since upright-standing adsorption geometries are also possible (depending on the substrate temperature, molecular coverage, deprotonation of the carboxylic groups...), it is also possible to prepare functionalized surfaces with a carboxylate group interacting with the metal surface and an intact acid group upright at the vacuum interface. These surfaces may have a very wide range of applications, including the immobilization of biomolecules, molecular recognition, biosensors, molecular electronics, and molecule-based magnetic materials [3].

In this work we report on a combined STM and XPS study of the self-assembly, under ultra-high vacuum conditions, of the smallest dicarboxylic acid, i.e. oxalic acid (Figure 1), onto Cu(111) and Cu(100) surfaces. Although a relatively simple molecule, the experimental results show a very rich behavior depending on the surface geometry and the annealing temperature, giving rise to different structures with, probably, very different functionalities.

After depositing 1 ML of C$_2$O$_2$H$_2$, at room temperature, on Cu(111), the molecular overlayer forms a very regular pattern, with hexagonal symmetry, based on the hydrogen bonds between the carboxylic groups of neighboring molecules (Figure 2a). Annealing at high temperatures (~100 °C) causes the decomposition of the molecule, giving rise to a different, also ordered, molecular arrangement now containing two different species (Figure 2b). On the Cu(100) surface, on the other hand, no ordered structure can be observed after room temperature deposition. Only after annealing at moderate temperatures (~50 °C) a rectangular pattern, probably involving metal-ligand coordination bonds, is formed (Figure 3a). Further annealing produces again the decomposition of the oxalic acid, creating a more disordered, labyrinth-type structure (Figure 3b). The origin of the different arrangements, and its relationship to the particular molecular state will be discussed.

References:

Figures:

![Chemical structure of the oxalic acid](image)

**Figures 1:** Chemical structure of the oxalic acid

![STM image of the Cu(111) surface](image)

**Figures 2:** STM image of the Cu(111) surface a) after adsorption of ~1 ML of oxalic acid at room temperature; and b) after annealing at 75 °C.

![STM image of the Cu(100) surface](image)

**Figures 3:** STM image of the Cu(100) surface after adsorption of ~1 ML of oxalic acid at room temperature; b) after annealing at 50 °C; y c) after annealing at 80 °C