2D organic layers on surfaces: self-assembly, on-surface chemistry and electronic structure

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Understanding the basic mechanisms leading to the formation of 2D organic layers on surfaces, either via Van der Waals, ionic or covalent interactions, is a necessary step toward the development of controlled and ordered organic layers, for technological applications such as homogeneous doping of graphene or 2D organic topological insulators. Using a combination of scanning tunnel microscopy, various electron spectroscopy techniques and ab-initio calculations, we have studied several aspects of the self-assembly and reactivity of particularly interesting model systems: Zinc tetraphenylporphyrins (ZnTPP) and their derivatives, on single crystal surfaces.

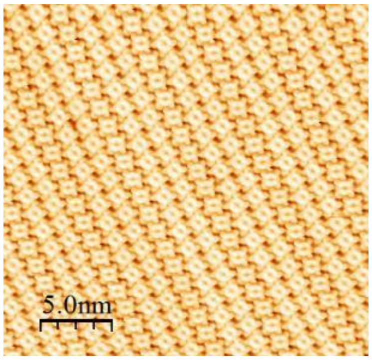

Figure 1. A highly ordered kinetically trapped system: ZnTPP on Ag(100).

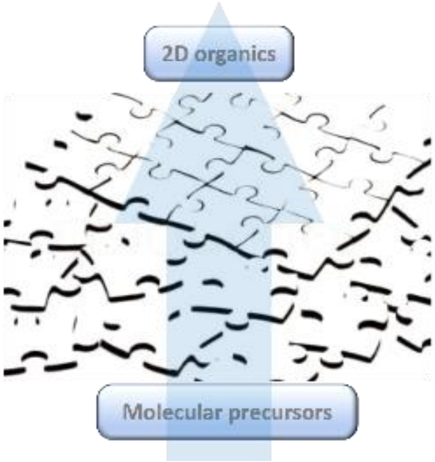

Figure 2. A strategy for 2D organic growth.

First, we have explored the delicate balance of forces during the molecular self-assembly process on metal single crystal surfaces. It is shown that molecule/molecule and molecule/surface interactions, as well as accumulated surface stress, all play an important role in determining self-assembly. In particular, self-assembly can be kinetically trapped into metastable phases different from typical equilibrium outcomes (Figure 1).

Recently, in order to develop and expand a synthesis toolbox necessary for the directed growth of highly ordered 2D covalent structures (Figure 2), we have studied novel mechanisms of surface-mediated chemistry to form intra- and inter-molecular covalent bonds between ZnTPPs (and fluorinated ZnTPPs) on metal surfaces. In particular, dehydrofluorination reactions render C-C bond formation chemo-selective as well as potentially regio-selective, if employed with a properly designed molecular precursor.