

# Chapter 8

## Outlook: Beyond the TTF-TCNQ monolayer

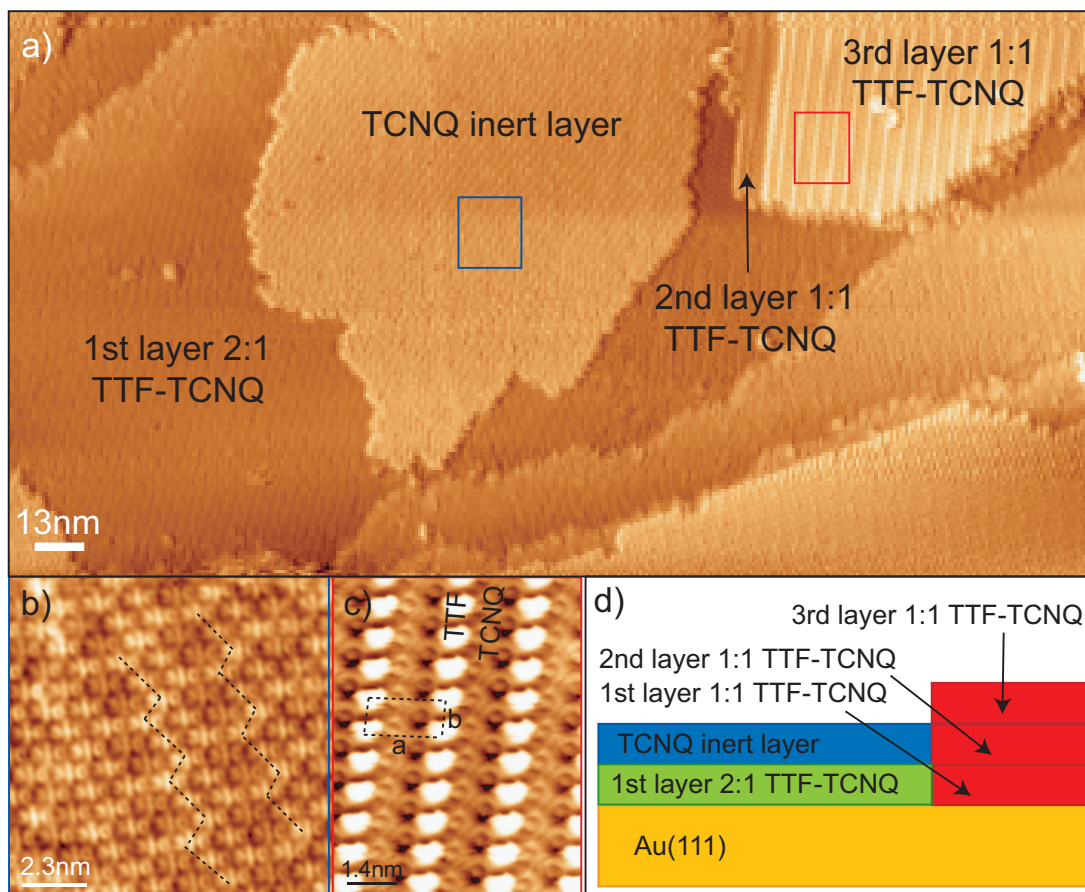
A monolayer of TTF-TCNQ on Au(111) has evidenced many fascinating properties of the organic-metal interface. We have shown that the metal surface plays a crucial role in the evolution of electronic bands. The next goal is to understand the evolution of the structural and electronic properties in the transition from the monolayer to the multilayer regime and, eventually, to the bulk structure of the charge transfer salt.

Experimentally, the adsorption of more than one TTF-TCNQ ML turns out to be extremely dependent on the surface temperature. Co-deposition at room temperature leads to a preferential formation of the stoichiometric 2:1 phase in the first adlayer. The stronger interaction of TTF with the Au(111) surface favors its adsorption as opposed to TCNQ, which is pushed into the second layer. The second layer is formed entirely by self-assembled TCNQ (Fig. 8.1(a) and scheme on (d)). Once formed, this TCNQ layer is inert towards further adsorption of organic material at room temperature. This TCNQ wetting layer exhibits a hexagonal-like Moiré pattern caused by the interference with the periodic structure of the underlying TTF-TCNQ (Fig. 8.1(b)).

Nevertheless, the formation of a first 2:1 TTF-TCNQ layer can be suppressed by co-deposition at lower surface temperatures. The lower mobility of the adsorbates hinders the segregation of TCNQ into the second layer. On the other hand, the formation of self-assembled 1:1 TTF-TCNQ structures needs to be thermally activated at a threshold temperature of  $T_s \sim 150$  K. Hence, the adsorption temperature should exceed this value.

Co-deposition at  $T_s \sim 200$  K leads to the formation of small patches of the 1:1 phase. These areas act as nucleation centers for further adsorption of the 1:1 TTF-TCNQ structure (Fig. 8.1(a)). The second and third layers of TTF-TCNQ show a preferential adsorption parallel to the homomolecular chains formed in the first layer. TTF binds preferentially onto TTF chains and a correspondent behavior is exhibited by TCNQ.

High resolution STM images of the third layer structure show a unit cell of the mixed structure similar to that one of the first layer (Fig. 8.1(c)). The dimensions indicate that molecules still lay parallel to the surface and no sign of intermolecular  $\pi$ -stacking within the rows is observed. Hence, in order to approach the bulk crystal structure, either adsorption of more than three layers is needed, or the adsorption on a less reactive surface, for example, Bi(111).



**Figure 8.1:** (a) Large STM image (0.9 V, 0.3 nA) exhibiting the possible structures built upon TTF-TCNQ deposition at a surface temperature of 200 K. Small patches of TTF-TCNQ 1:1 phase adsorbs in the 1st layer and act as nucleation centers for further TTF-TCNQ adsorption. (b) Zoom in the TCNQ inert layer (0.66 V, 0.07 nA). The dashed lines indicates the Moiré motif produced by interference with the underlying 2:1 TTF-TCNQ layer. (c) Zoom in the 3rd layer TTF-TCNQ with stoichiometry 1:1 (0.87 V, 0.3 nA). The dashed lines mark the TTF-TCNQ unit cell. It has the same dimensions as its homologous in the 1st layer. (d) Scheme of the adsorption of 2:1 and 1:1 TTF-TCNQ layers up to the third layer.

Nevertheless, with a view in the future growth of multilayer TTF-TCNQ, a good control of the surface temperature during co-deposition is crucial for the formation of larger patches of 1:1 TTF-TCNQ phase that leads to higher layer growth of this structure.