Journées 3N Réseau National en Nanosciences et en Nanotechnologies 6 au 8 novembre 2006

NANO-OBJETS CONDUCTEURS OU SEMI-CONDUCTEURS PAR EMPREINTE SUPRAMOLECULAIRE

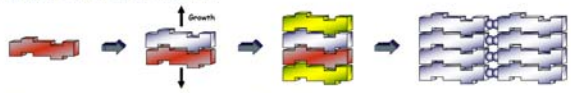
Interactions and multilevel ordering in supramolecular assemblies

F. Vonau[1], D. Suhr[2], D. Aubel[1], L. Bouteiller[2], G. Reiter[3] and L. Simon[1]

(1)Laboratoire de Physique et de Spectroscopie Electronique (LPSE) CNRS-UMR 7014, 4, rue de frères Lumière 68093 Mulhouse Cedex, France
(2)Laboratoire de Chimie des Polymères, UMR 7610, Université Pierre et Marie Curie, 4, place Jussieu, 75252 Paris Cedex 05, France
(3)Institut de Chimie des Surfaces et Interfaces CNRS, 15, rue Jean Starcky, B. P. 2488, 68057 Mulhouse Cedex, France

Introduction

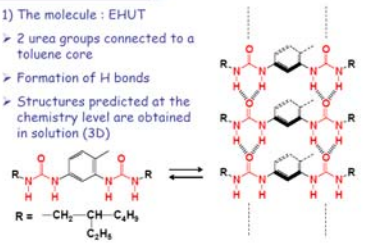
- The process of self-assembly at multiple length scales of bis-urea substituted toluene evaporated on a Au(111) surface is studied by *Low Temperature Scanning Tunneling Microscopy*.
- Two-dimensional Pattern formation is controlled by specific hydrogen bonds and weak lateral coupling, resulting in supramolecular polymers quasiepitaxially interlocked with the substrate as a function of maturation conditions.



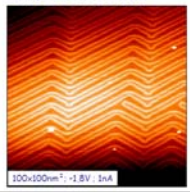
- Here, we show step by step the process of self-organization of a supramolecular assembly on a surface

The system

1) The molecule : EHUT
- 2 urea groups connected to a toluene core
- Formation of H bonds
- Structures predicted at the chemistry level are obtained in solution (3D)

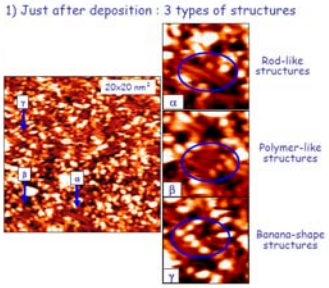


2) The substrate : Au(111) surface $22 \times \sqrt{3}$ reconstruction

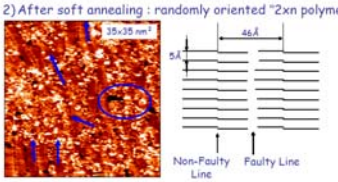


Results

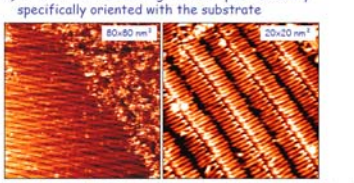
1) Just after deposition : 3 types of structures

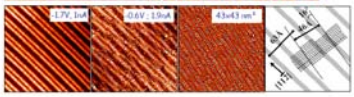


2) After soft annealing : randomly oriented "2xn polymers"

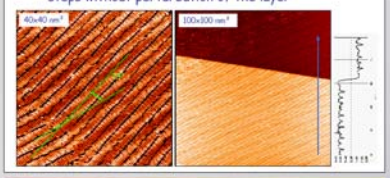


3) After further annealing : nxn compact assembly specifically oriented with the substrate





4) After many months maturation at RT under UHV
- Formation of wide domains
- Change of the orientation with the substrate from 16° to 12°
- Growth of the layer over Au(111) monoatomic steps without perturbation of the layer

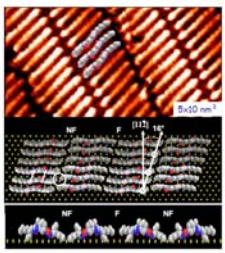


Experimental

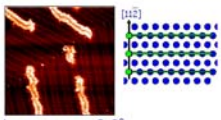
- EHUT molecules are evaporated under high vacuum onto a Au(111) surface kept at room temperature.
- The process of formation of hierarchical structures is induced by soft annealing and long maturation periods at room temperature under UHV conditions.
- Each step is followed by Scanning Tunneling Microscopy at 77K (Omicron LT-STM).

Discussion

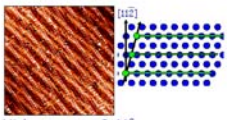
1) Molecular model :
- No spectroscopic effect in LDOS images, antiparallel H-bonds and toluene core perpendicular to the surface induce a curvature of the molecule forming a bridge over the surface
- The bridge shape induces the apparition of specific interactions between the endgroups of the molecule leading to the observed faulty and non-faulty lines as opposite to single polymer chains obtained in solution.
- The bridge shape gives rise to particular electronic behavior evidenced by Tunnel transparency
- The commensurability of every second molecule is obtained in compacts arragements when the non-faulty line shows an angle of 16° with the [1 1 -2] direction of the Au(111) herringbone reconstruction



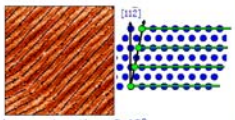
2) Evolution of the commensuration as a function of coverage and maturation time



Low coverage : θ=0°
Every molecule is commensurable with the substrate



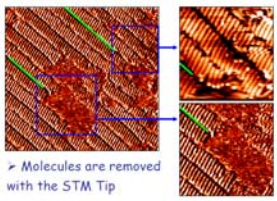
High coverage : θ=16°
Every second molecule is commensurable with the substrate



Long maturation : θ=12°
Every third molecule is commensurable with the substrate

- The strength of the interaction between the layer and the substrate decreases when the size of layer increases

- Strength of the interactions at the endgroups of the molecule



- Molecules are removed with the STM Tip

- When molecules along the non-faulty line are removed, the 2D layer becomes unstable and tries to explore the 3rd dimension, like in solution
- When molecules along the faulty line are removed, the 2D layer remaining on the surface is not affected

This behavior shows that the Van der Waals Forces at the endgroups have the same importance as the H-bonds in the formation of the 2D supramolecular layer

Conclusion and Perspectives

- Bringing supramolecular chemistry at surfaces leads to new specific interactions due to the reduction of dimensionnality from 3D to 2D.
- The ability to tailor supramolecules at surfaces appears to be different as in solution, since the combination of strong interactions with much weaker interactions is needed for large scale ordering.
- Electronic properties of the layer have to be more intensively investigated

F.Vonau *et al, Phys. Rev. Lett.* **94**, 066103(2005)

E-mail : F.Vonau@uha.fr

LPSE UMR 7014 — L.C.P. — I.C.S.I. — CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE