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ULTIMATE
ITN NETWORK

Organic molecules on the Cu(110)-(2×1)O striped phase

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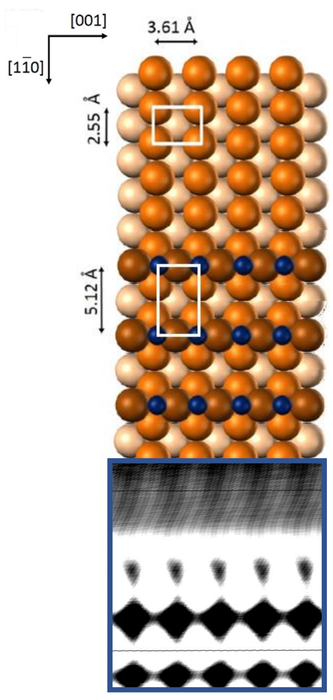
Introduction

The deposition of molecules onto single-crystal surfaces allows their investigation at the single-molecule level by scanning tunneling microscopy (STM), in particular for planar molecular structures. Here, we have studied flat 2,6-dibromoanthracene (DBA) molecules on the Cu(110)-(2×1)O stripe phase under ultra-high vacuum conditions with low-temperature STM.

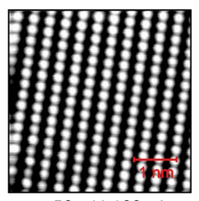
Preparation of Cu(110)-(2×1) striped phase

Cu(110)-(2×1)O is a well-known "added row" surface reconstruction which is formed as a result of the oxidation of clean Cu(110) surface and growth of the oxide strings (-Cu-O-Cu-O-) in [001] direction.
At oxygen coverages below 0,5 monolayer at certain conditions one can obtain the so-called stripe phase consisting of alternating stripes of oxide Cu(110)-(2×1)O and clean Cu(110) [1].

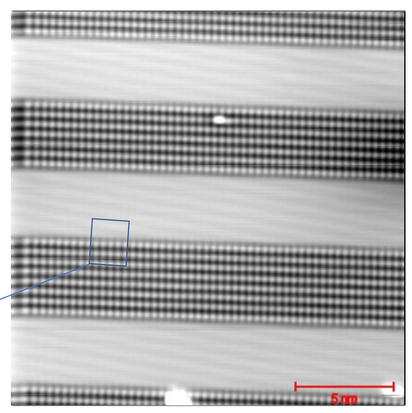
Structure of Cu(110) and Cu(110)-(2x1)O [3]



Cu(110) $\xrightarrow{O_2,\ 280\ ^\circ C}$ **Stripe phase Cu(110) / Cu(110)-(2x1)O**



+50 mV, 100 nA



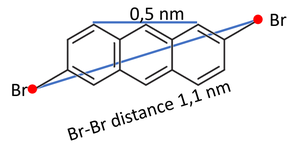
Bottom plane Cu
Top plane Cu
Adlayer Cu
O

Interpretation of STM images of the Cu(110)-(2×1)O phase is not straightforward [2]. Depending on the state of the STM tip, either copper or oxygen atoms can appear as bright protrusions in the oxide strings. At the left image both phases are atomically resolved, and bright lobes on the oxide lay on the same lines as copper atoms of bare Cu(110) seen as corrugation. Therefore, in this case we can attribute those bright lobes on the oxide to oxygen atoms.

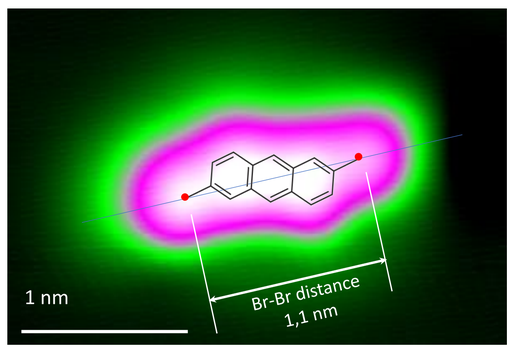
Single molecules on Cu(110)

We deposited DBA molecules on the stripe phase of the sample at room temperature by evaporation under UHV conditions.
At low coverages (<0,33 ML) only molecules on Cu(110) stripes can be found, which indicates high mobility of DBA on CuO. Single molecules are oriented mostly along [001] direction.

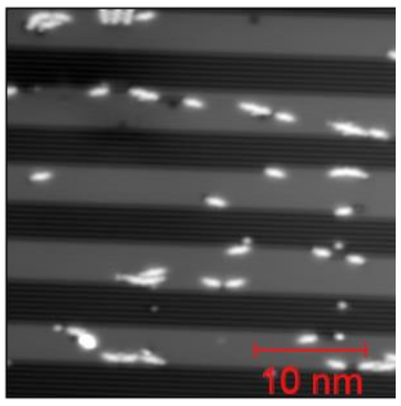
DBA molecule



STM image of the DBA molecule adsorbed on Cu(110)

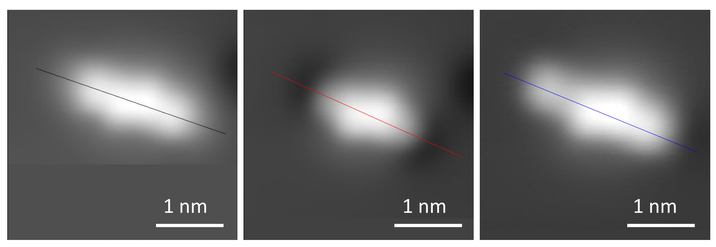


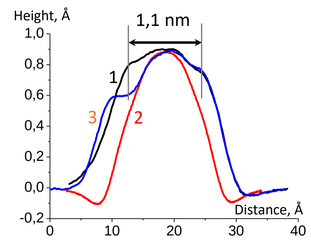
DBA molecules on copper (0,03 ML)



Most single molecules have four lobes.
According to the theoretical atomic coordinates the distance between two bromine atoms is 1,1 nm. The same distance is measured between two end lobes in the four-lobe molecule image, which indicates that this molecule is intact.
During scan of the intact molecule (1) at bias +2,5 V it was doubly debrominated (2).
Some adsorbed single molecules are already debrominated, like (3).

Intact molecule (1) **Debrominated molecules (2, 3)** **Height profiles**

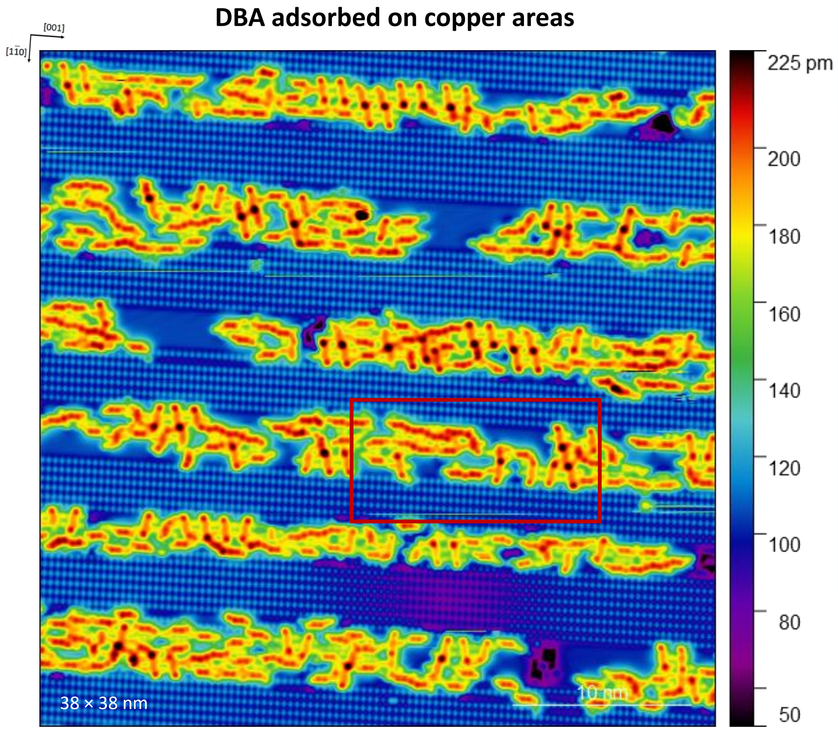




1 – Intact molecule; 2 – The same doubly debrominated molecule; 3 – Other mono- debrominated molecule with the adsorbed Br atom.
All images are taken at +0,1 V and 0,1 nA

Organometallic chains

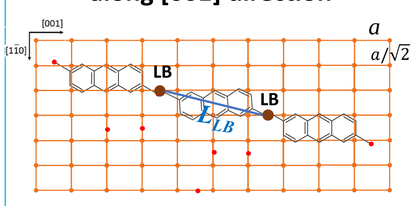
DBA adsorbed on copper areas



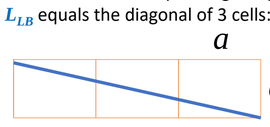
At coverage 0,33 ML all molecules are adsorbed on Cu areas due to high mobility on Cu-O areas caused by slight decoupling. Molecules form linear structures with bright protrusions.

To identify them we use atomic resolution of the oxide layer to draw the Cu(110) grid corresponding to the upper layer of Cu atoms in Cu stripes

OM chain oriented along [001] direction

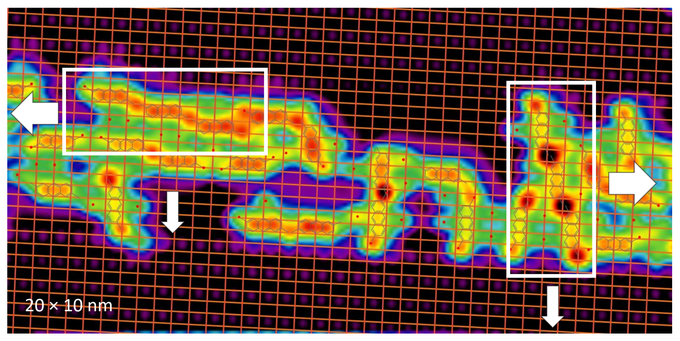


Cu atoms in the OM chains occupy the **long-bridge** sites (**LB**) of the substrate. The distance between the coresponding long-bridge sites L_{LB} equals the diagonal of 3 cells:

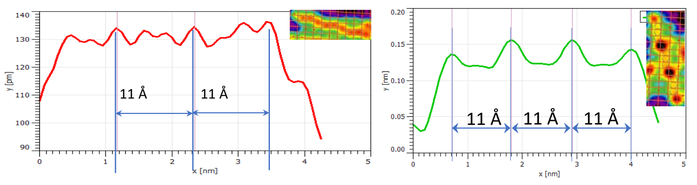


$$L_{LB} = \sqrt{\frac{19}{2}}\,a \quad (= 11{,}1\ Å)$$

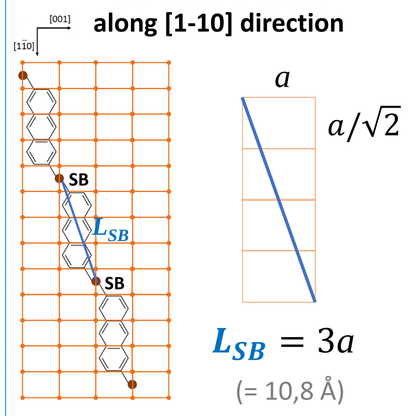
Organometallic (OM) chains with overlaid Cu(110) grid



Height profiles along the OM chains



OM chain oriented along [1-10] direction

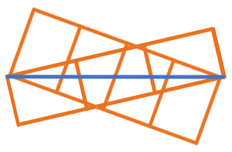


$$L_{SB} = 3a \quad (= 10{,}8\ Å)$$

Cu atoms in the OM chains occupy the **short-bridge** sites (**SB**). The distance between the corresponding short-bridge sites L_{SB} equals the diagonal of 4 cells L_v as drawn above.

$$\frac{L_{LB}}{L_{SB}} = \sqrt{\frac{19}{18}} \approx 1$$

Almost equal distances between the corresponding long-bridge sites and between the coresponding short-bridge sites makes possible the coexistence of two types of OM chains oriented along the [001] and the [1-10] directions respectively.



Take-home messages

- After deposition on the Cu(110)-(2×1)O striped phase at room temperature DBA molecules adsorb primarily on copper stripes
- Three kinds of molecular species are found on the surface: intact molecules, partially or fully debrominated molecules and organometallic chains
- DBA molecules form two types of organometallic chains oriented along the [001] and the [1-10] directions respectively, with different adsorption sites for Cu atoms of the chains
- The coexistance of the two types of OM chains is possible due to almost equal distances between the coresponding adsorption sites, and at the same time due to commensurability of DBA OM chain unit with this distance.

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References

1. K. Kern et al., Phys. Rev. Lett., **67**, 855 (1991)
2. H. Mönig et al., ACS Nano, **10**, 1201 (2016)
3. Z. Budinska, PhD dissertation, L'Université Pierre et Marie Curie (Paris, 2015)

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