# Nucleation and growth in action: BDA on Cu(100) studied by LEEM

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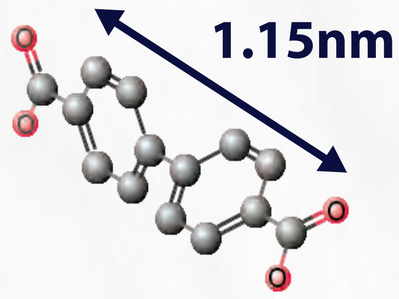
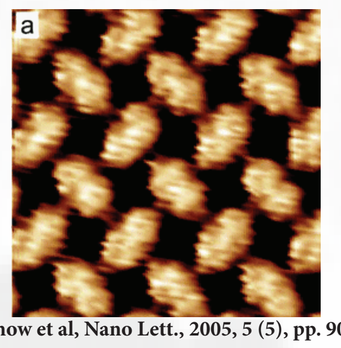
## Introduction

The self assembly of organic molecules into large supramolecular structures is a promising method for the fabrication of novel nanoscaled structures. Since the choice of organic molecules with different functionality is practically infinite, potential applications of such structures cover a wide range including: molecular electronics, biosensors, materials science or host–guest chemistry. The resulting nanostructures are formed by the molecule-substrate, the molecule-molecule interaction and simple thermaldynamics. Usually molecules interact through hydrogen bonds which are weak compared to the molecule-substrate interaction. Understanding the exact nucleation mechanisms of such systems is crucial to effectively applying this form of supramolecular chemistry.

4,4' Biphenyldicarboxyclic acid (**BDA**) is built out of two phenyl rings each with a carboxyclic acid group at opposite ends. The two phenyl rings are twisted along the long axis of the molecule due to steric effects.
From O to O it is 1.15nm long.



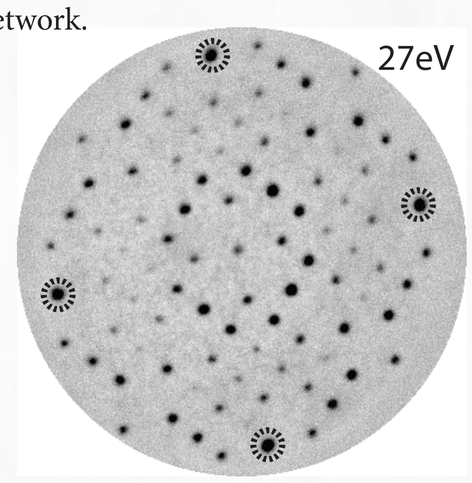




S. Stepanow et al, Nano Lett., 2005, 5 (5), pp. 901-904

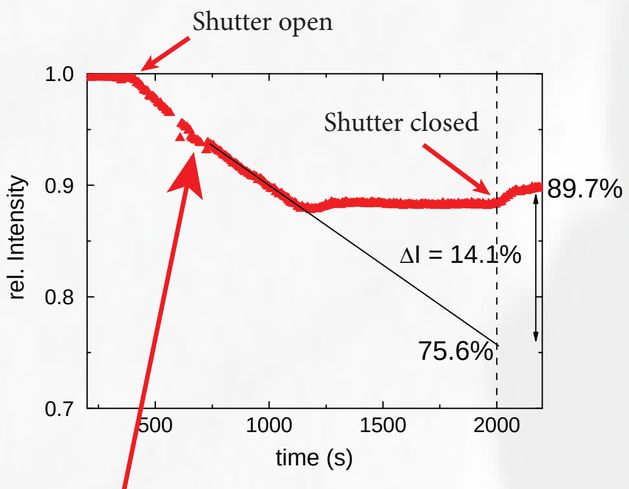
BDA, as a powder, is evaporated from a Knudsen cell onto a clean Cu(100) surface. There it adsorbs lying down flat, rather tightly bound through the π-electrons of the phenyl rings (approx. 1.38eV).
However, the molecules are free to diffuse on the surface, where they form a 2D gas.
Under the right conditions molecules will find each other and self assemble into stable, hydrogen bonded, networks.
On the left there is a STM image of such a network.

These networks are well ordered and form a square superstructure on the Cu(100) lattice.

With the LEEM it is possible to take a μ-LEED pattern of these domains, showing a (4√2x4√2)-R45° superstructure.



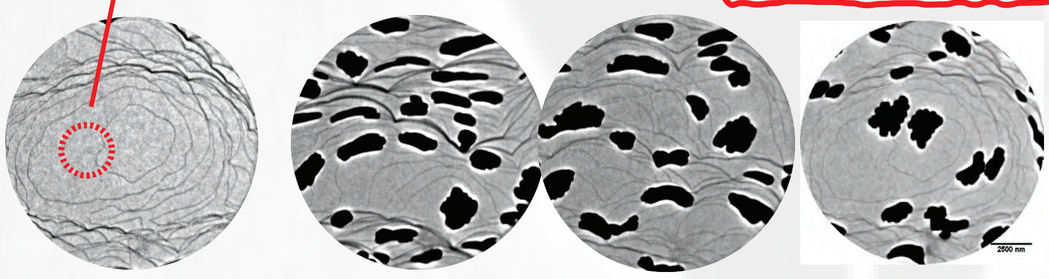

## Calibrating the BDA gas phase cross section



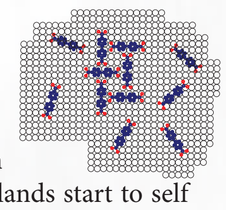

While the BDA in the 2D gas phase can not be seen directly in the LEEM, its effect on the image intensity can be. For the densities used in the experiments it is lowering the intensity linearly with density.

By averaging the BDA island size of several (>10) images and taking into account the BDA still in the gas phase, it is possible to give a calibration factor:

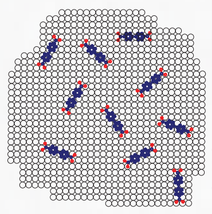
$$1.1 \times \frac{I(0) - I(t)}{I(0)} ML$$

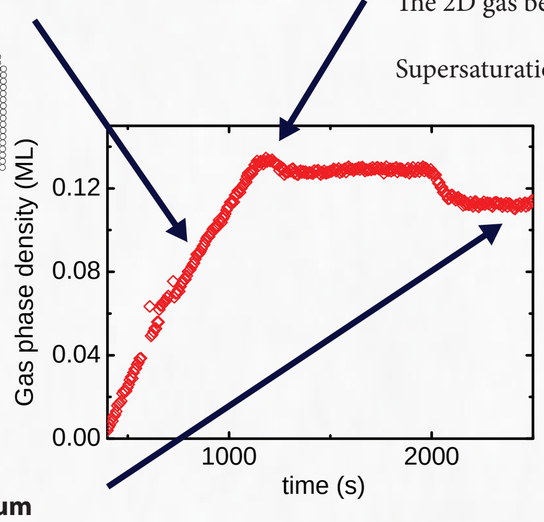


## Steps in the BDA island growth



**1. Build up of gas density:**
Molecules are deposited at a constant rate and form a 2D gas with increasing density.



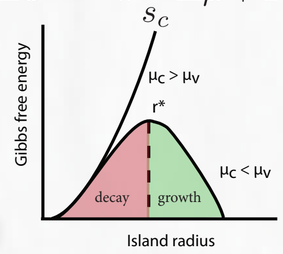



**2. Fluctuations & Nucleation**
Close to the critical pressure islands start to self assemble into small islands.
These are unstable due to the energy cost to form a small island creating a nucleation barrier.
The 2D gas becomes supersaturated.

Supersaturation: $\Delta\mu = kT \ln\left(\frac{n}{n_{eq}}\right)$

The Gibbs free energy has a volume term, which gains energy and an interface term, which costs energy for the system:

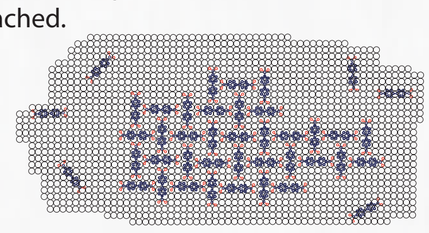
$$\Delta G = -\pi \frac{r^2}{s_c} \Delta\mu + 2\pi r \chi$$




For a critical island size r* the barrier has a maximum. Smaller islands have a higher propability to decay, larger to grow.

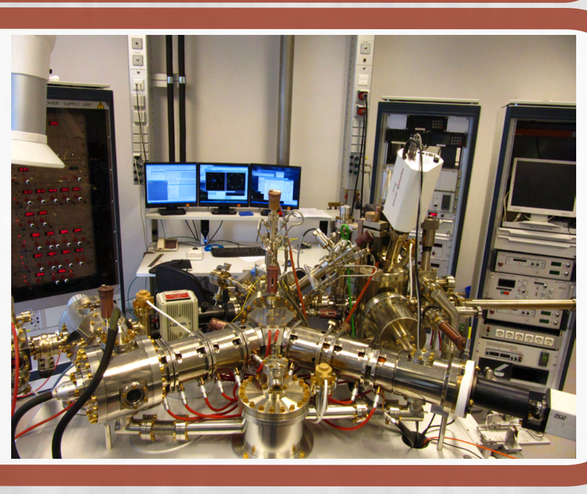
$$r^* = \frac{\chi\, s_c}{\Delta\mu}$$

**3. Equilibrium**
The shutter is closed and the equilibrium pressure at T is reached.



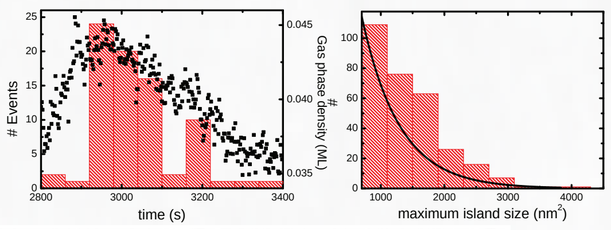
Low Energy Electron Microscopy (LEEM) allows the real time observation of processes on surfaces with nanometer spatial resolution. At the same time structural information is accessable by μ-LEED.

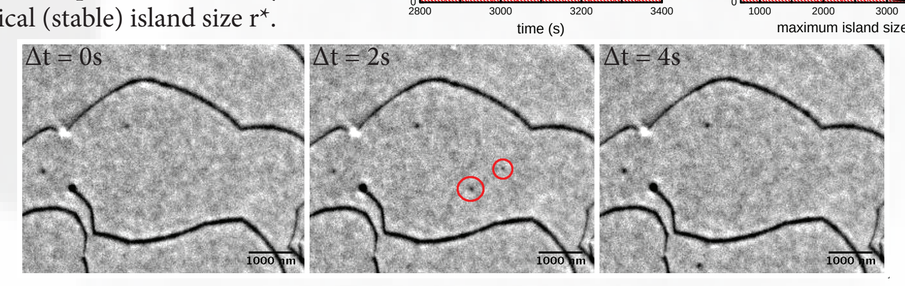
Possible imaging modes in our instrument:
- LEEM
- PEEM
- Mirror mode (MEEM)
- spin polarized LEEM
- μ-LEED



## Visualizing the nucleation process

**Low Temperature:**
At low temperature (23°C-70°C) the nucleation process is slow enough to observe island fluctuations live and to determine the gas phase density (supersaturation) at the same time. This makes it possible to directly determine the critical (stable) island size r*.




**High Temperature:**
At high temperature (100°C-150°C) the nucleation process is much faster and the island size is only limited by Cu terraces. This leads to an interesting effect: The BDA gas density is not homogeneous anymore and can change locally by as much as 0.03ML. This causes a supersaturation and new nuclei to form in areas surrounded by BDA islands which are blocked to grow further by Cu steps. The new nuclei reduce the supersaturation as they grow.
Surprisingly a similar supersaturation of 0.01ML as in the low temperature range is needed for nucleation.