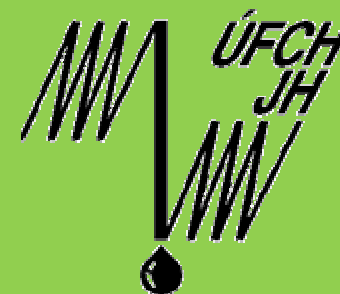


Adsorption of N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)aniline on Gold(111) Substrate

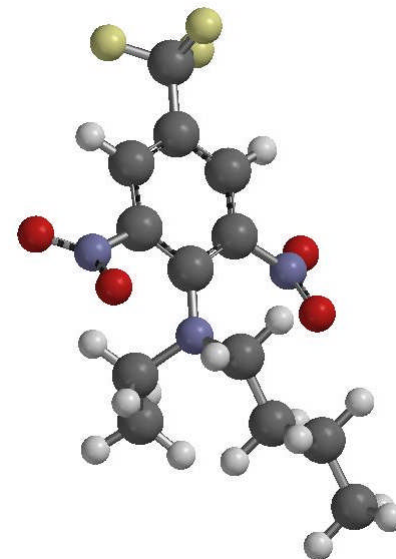
Romana Sokolová

*J. Heyrovský Institute of Physical Chemistry, v.v.i.,
Academy of Sciences of the Czech Republic*



Outline

Electrochemical and AFM/STM study



→ ADSORPTION ON DROP MERCURY ELECTRODE

- AC polarography
- **Capacitance – time** measurements on HMDE

→ ADSORPTION ON GOLD(111) ELECTRODE

- The electrochemical impedance spectroscopy **EIS**

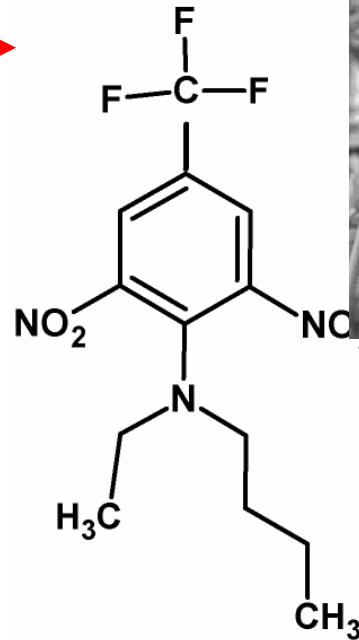
→ CHARACTERIZATION OF THE LAYER OF BENFLURALIN

- Scanning tunneling microscopy **STM**
- Atomic force microscopy **AFM**

Pesticides

→ **dinitroaniline herbicide:**

- **BENFLURALIN**
N-butyl-N-ethyl- 2,6-
dinitro-
4-(trifluoromethyl)aniline



Microtubule assembly inhibition.
It inhibits tubulin protein synthesis.

ACCUMULATION AT THE INTERFACE contamination of the environment

→ **SURFACE LAYERS OF SOIL**

exposed to - the activity of microorganisms
- photoprocesses

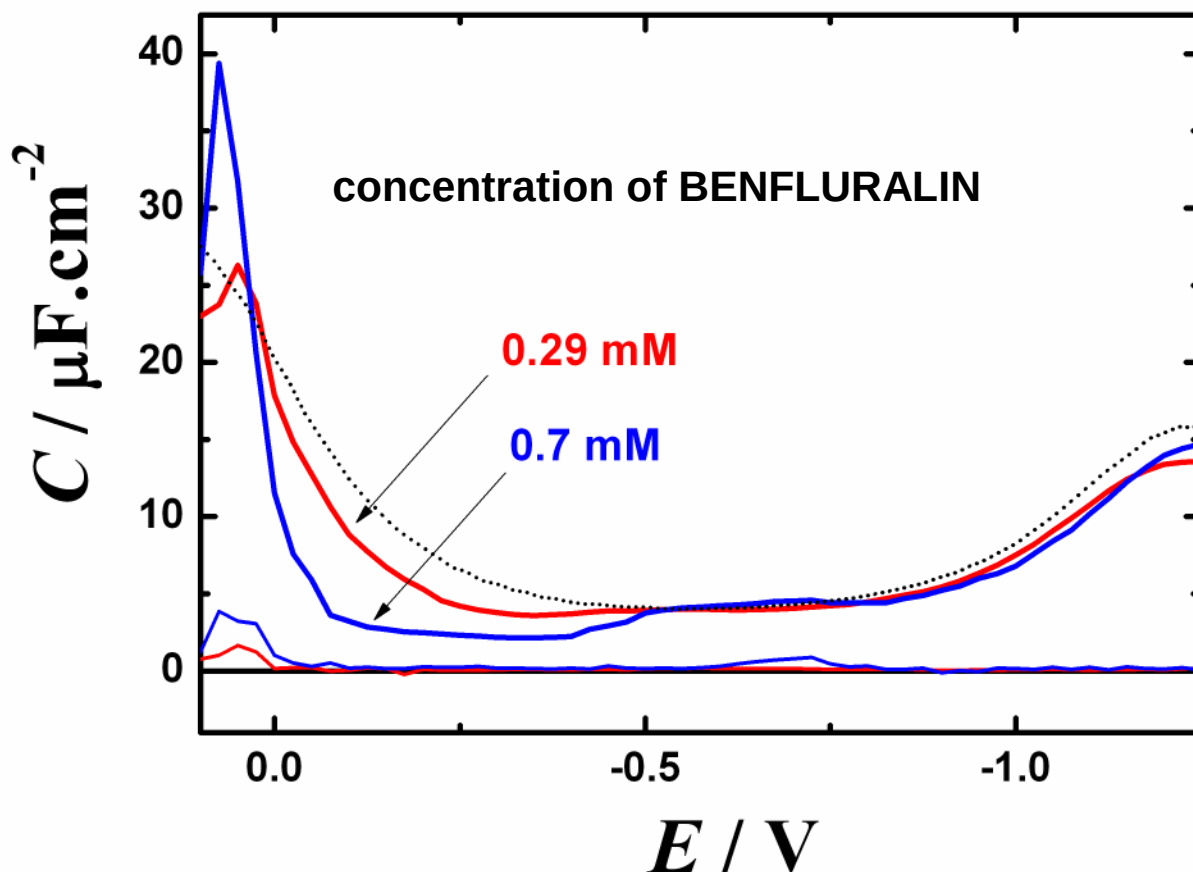
→ **GROUND WATER**

sources of drinking water

Adsorption properties of benfluralin

hanging mercury drop electrode, HMDE

AC voltammetry



Surface coverage

$$\theta = \frac{(C_0 - C)}{(C_0 - C_1)}$$

Diffusion-controlled adsorption process

$$\theta \sim t^{-1/2}$$

Compact layer

- desorption of solvent
- strong adsorbate – adsorbate interactions

0.7 mM benfluralin in 0.8 M KF and 20% ethanol (v/v), $f = 320 \text{ Hz}$.

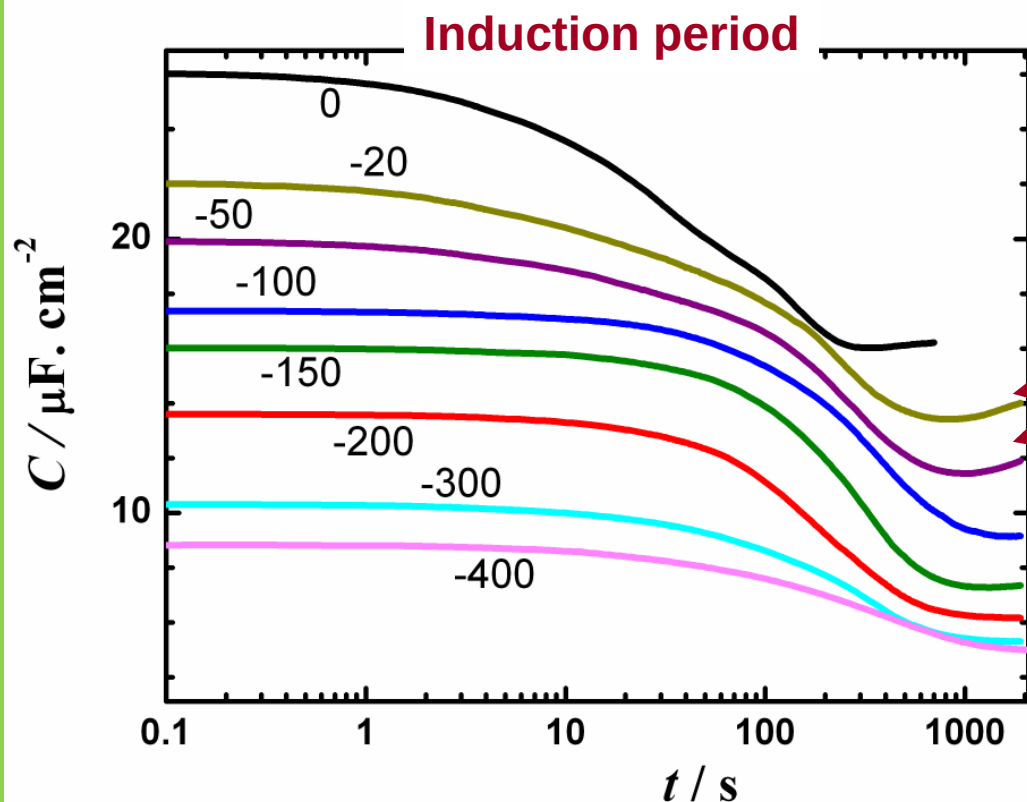
adsorbate – adsorbate interactions



adsorbate – surface interactions

Adsorption properties of benfluralin

hanging mercury drop electrode HMDE



$C \sim t$ curves

Compact film formation controlled by the nucleation and growth of a surface film

Film rearrangement

Increase of capacitance signifies partial release of the free surface.

- desorption of adsorbate
- transition of 2D to 3D film
- onset of hole nucleation
- coalescence of surface clusters

0.7 mM benfluralin in 0.8 M KF and 50% ethanol (v/v), $f = 320$ Hz.

adsorbate – adsorbate interactions



adsorbate – surface interactions

Adsorption properties of benfluralin

hanging mercury drop electrode HMDE

$$\theta = \frac{(C_0 - C)}{(C_0 - C_1)}$$

Avrami - Canac model

$$\theta = 1 - \exp[-b t^m]$$

$$\ln[-\ln(1-\theta)] = m \ln t + \ln b$$

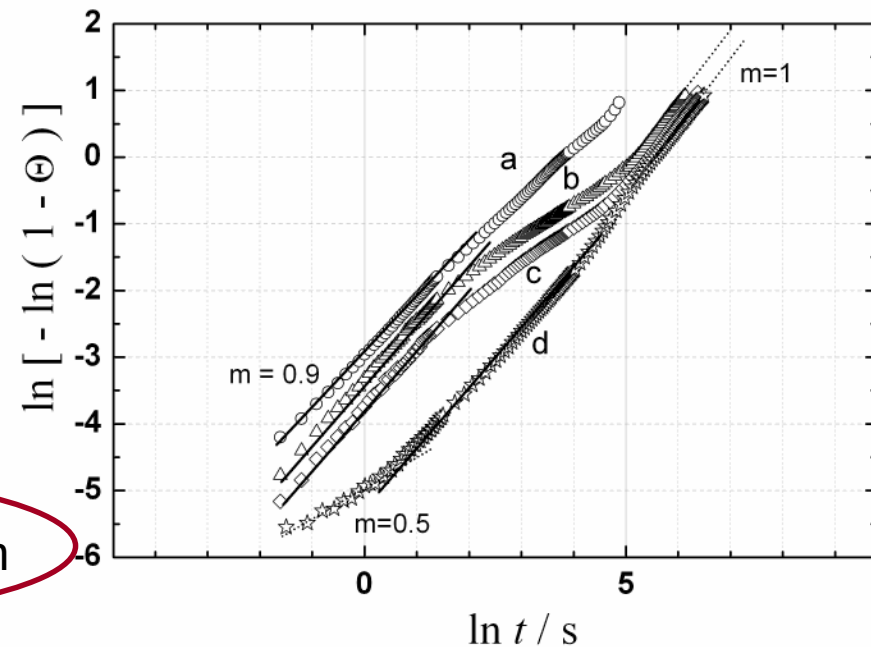
b combines the overall nucleation-and-growth rates
 m is related to the growth mechanism

- $m = 0.5$ instantaneous one-dimensional nucleation
controlled by the surface diffusion
of the adsorbate to the center of the growth
- $m = 1$ one-dimensional surface growth of fibers
- $m = 2$ instantaneous nucleation process
- $m = 3$ progressive nucleation process

controlled by the surface diffusion

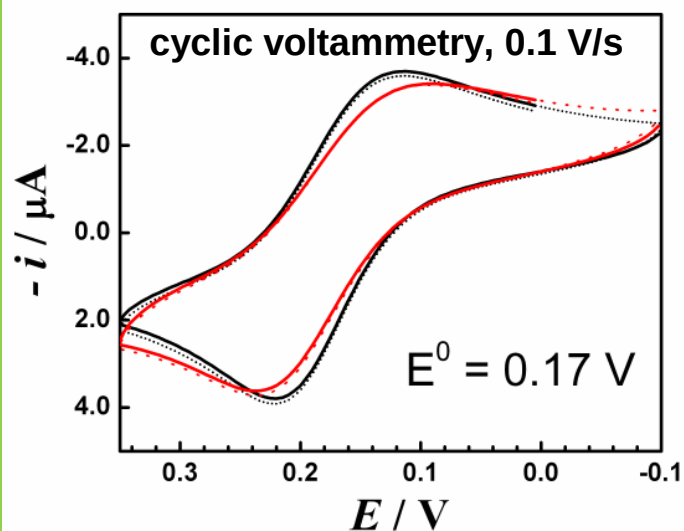
$C \sim t$ curves

Compact film formation
controlled by the nucleation
and growth of a surface film



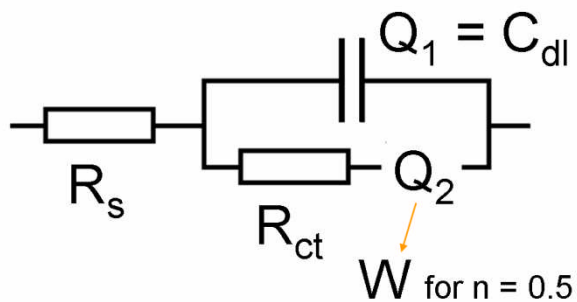
Electrochemical impedance spectroscopy

Au(111) electrode in hanging meniscus configuration

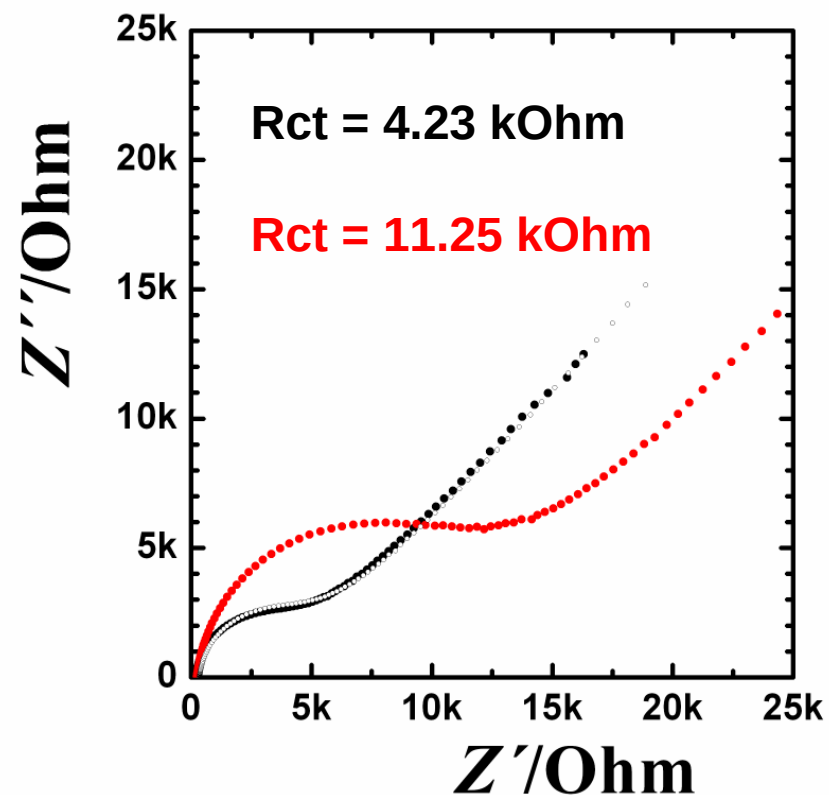


Equivalent circuit: $R_1(Q_1[R_2Q_2])$

Randles circuit



Fit and simulation FRA (Autolab)



0.4 mM $K_3[Fe(CN)_6]$ in 0.1 M KF
30 kHz – 0.1 Hz, 0.1 Hz – 30 kHz

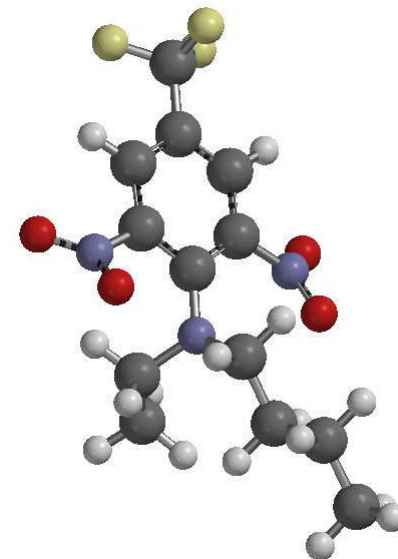
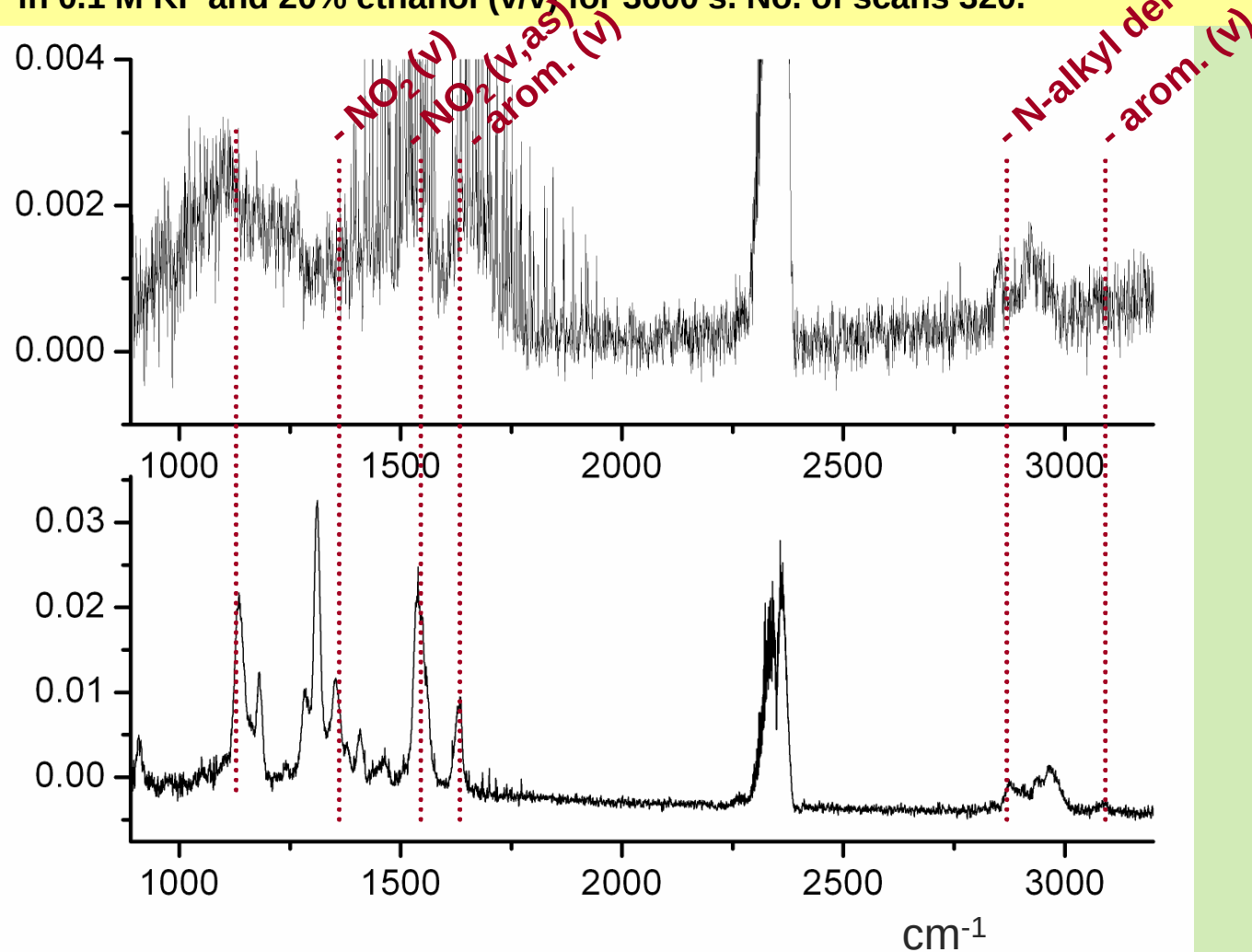
after electrochemical deposition of benfluralin for 2000 s

Adsorption properties of benfluralin

ATR-FTIR

Glass/Au(111) substrate

The layer deposited at - 0.1 V from the solution of 0.13 mM benfluralin in 0.1 M KF and 20% ethanol (v/v) for 3600 s. No. of scans 320.



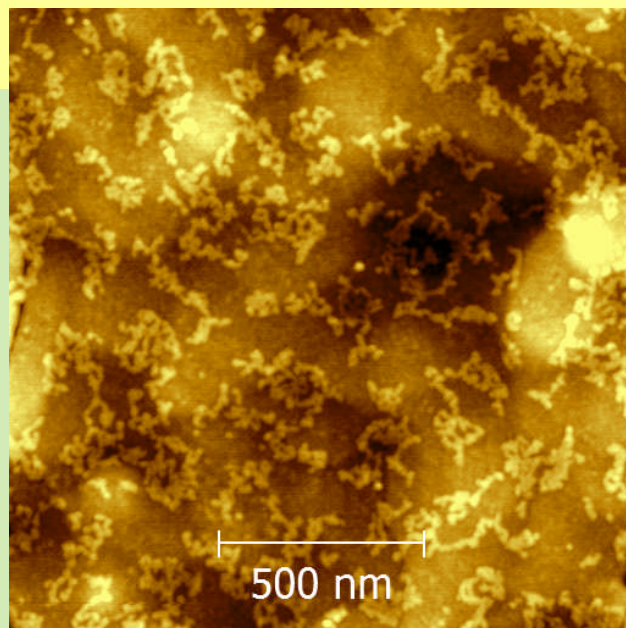
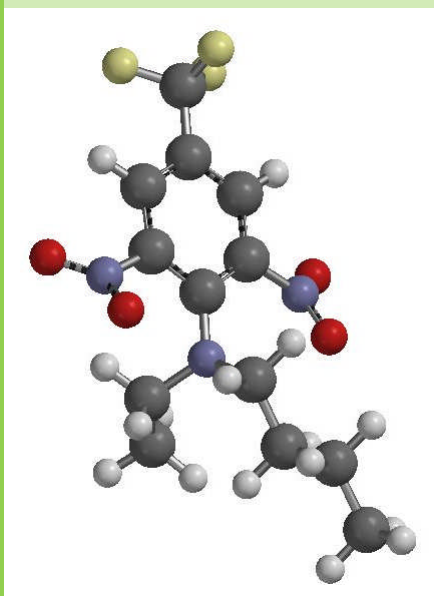
Adsorption properties of benfluralin

Atomic force microscopy AFM

Glass/Au(111) substrate

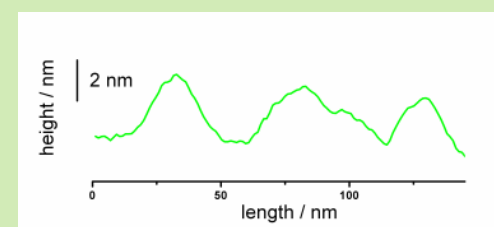
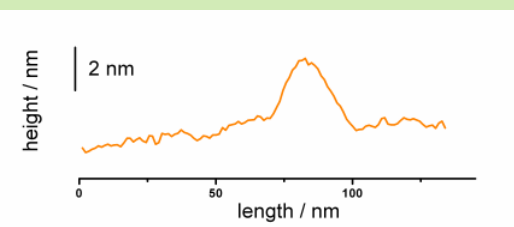
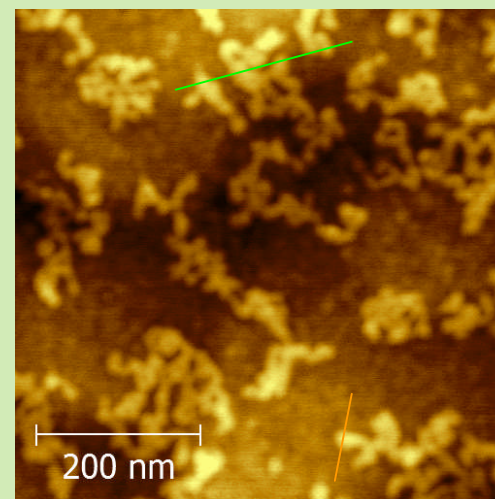
TOP-MAC-AFM

200 s



topography

11.7 Å



The electrochemical deposition on the gold surface at - 0.1 V from the solution of 0.5 mM benfluralin in 0.8 M KF and 20% ethanol (v/v). Ex-situ micrographs.

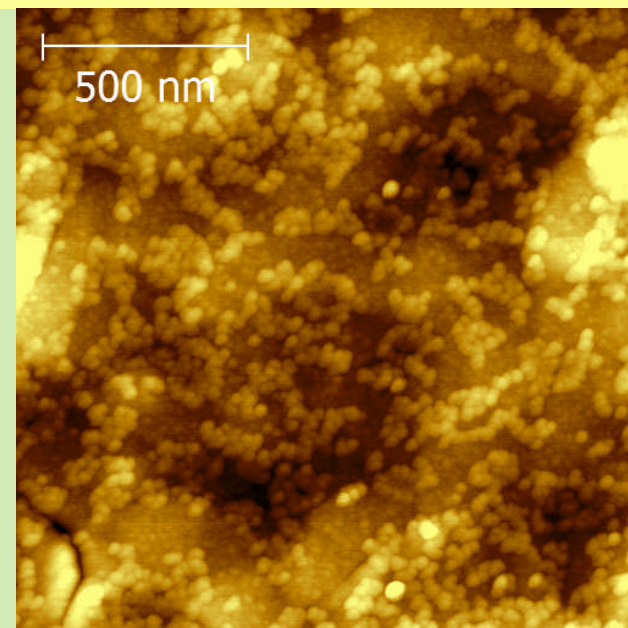
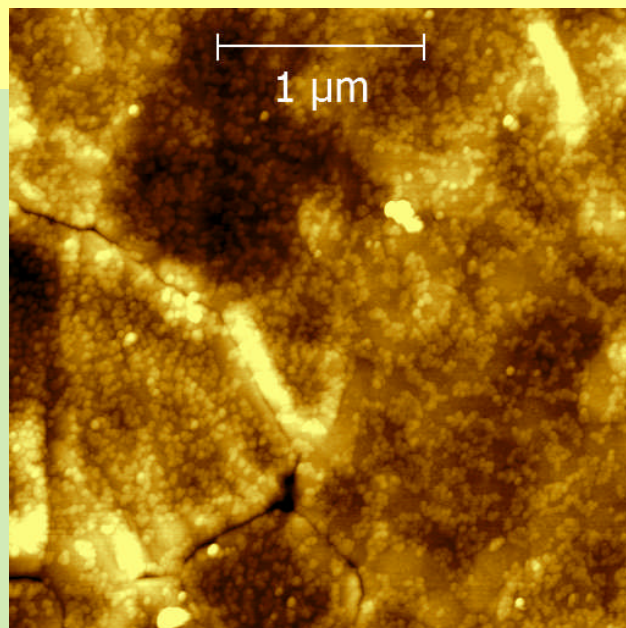
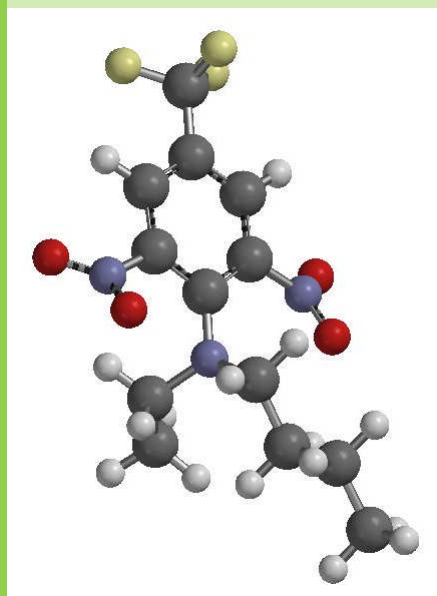
Adsorption properties of benfluralin

Atomic force microscopy AFM

Glass/Au(111) substrate

TOP-MAC-AFM

200 s



topography

11.7 Å

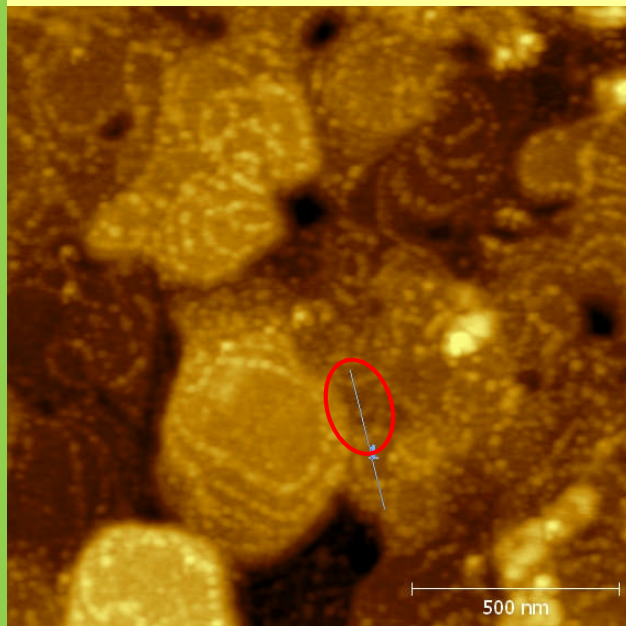
The electrochemical deposition on the gold surface at - 0.1 V from the solution of 0.5 mM benfluralin in 0.8 M KF and 20% ethanol (v/v). Ex-situ micrographs.

Adsorption properties of benfluralin

Atomic force microscopy AFM

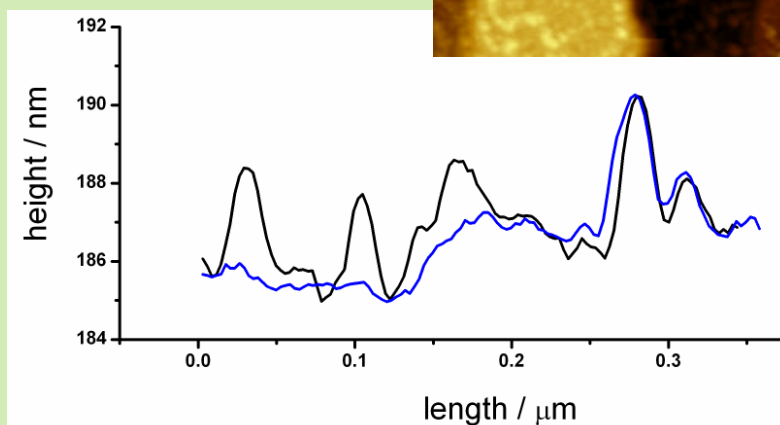
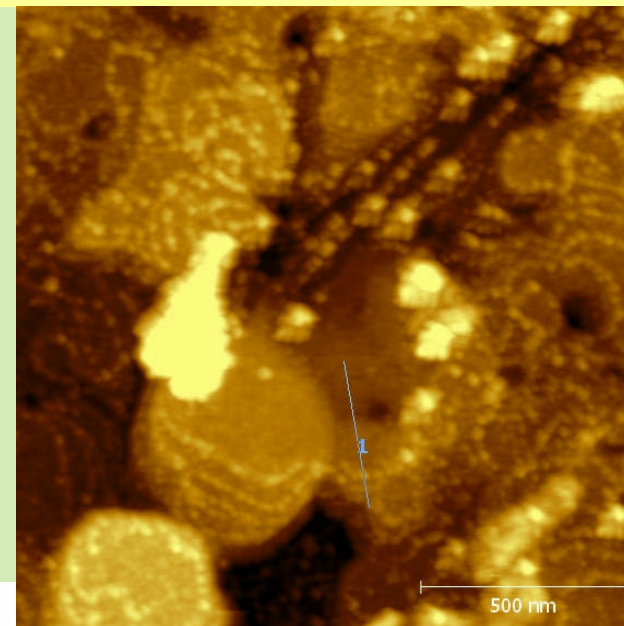
Mica/Au(111) substrate

TOP-MAC-AFM



topography

200 s



The electrochemical deposition on the gold surface at - 0.1 V from the solution of 0.13 mM benfluralin in 0.08 M KF and 20% ethanol (v/v). Ex-situ micrographs.

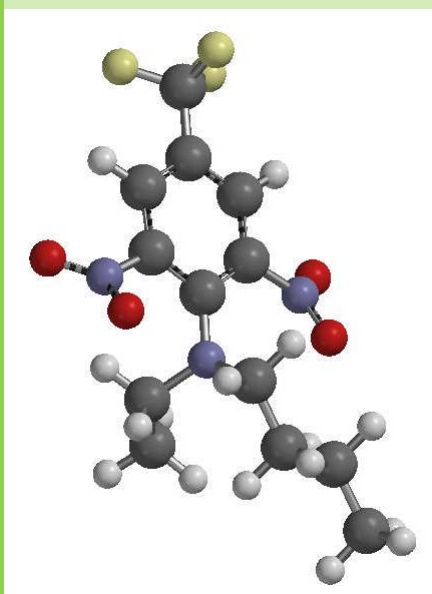
Adsorption properties of benfluralin

Atomic force microscopy AFM

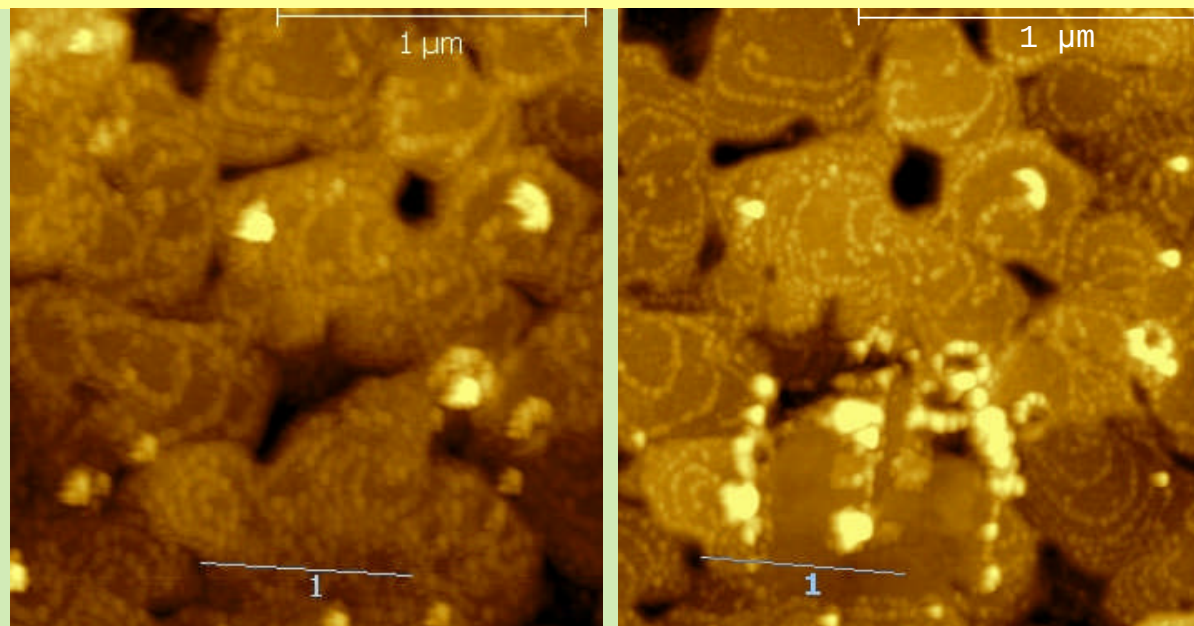
Mica/Au(111) substrate

TOP-MAC-AFM

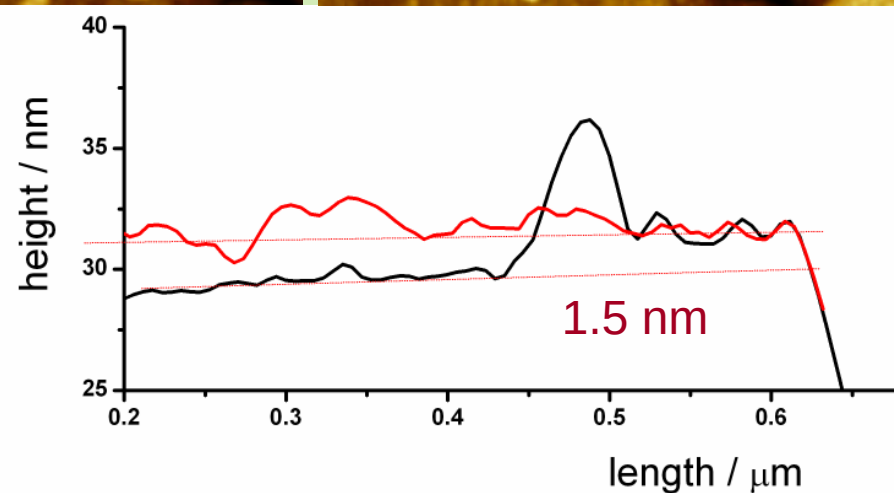
200 s



11.7 Å



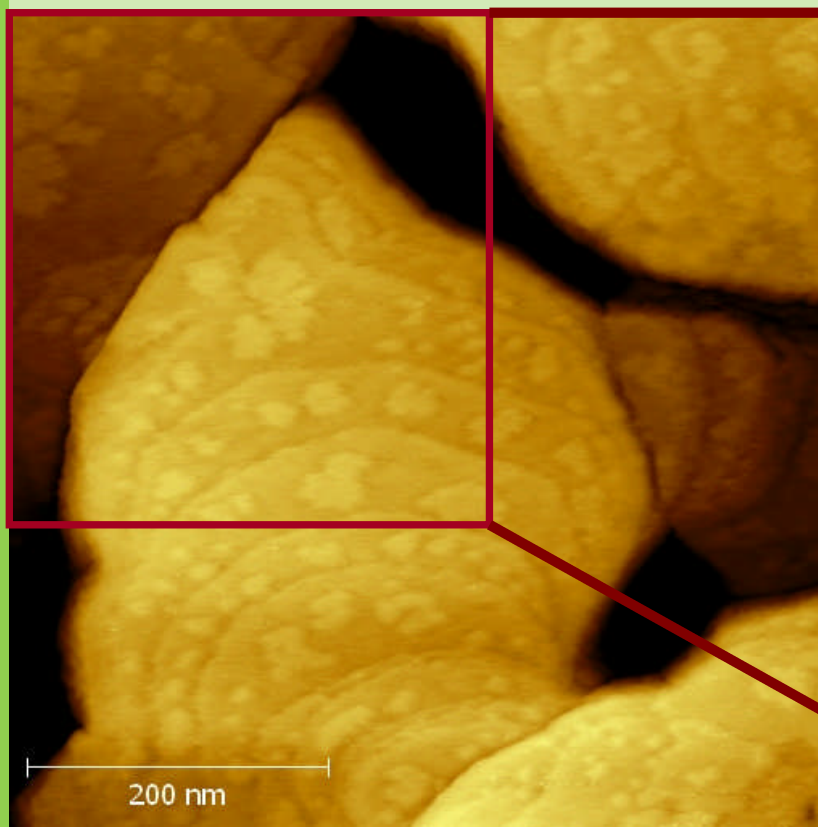
topography



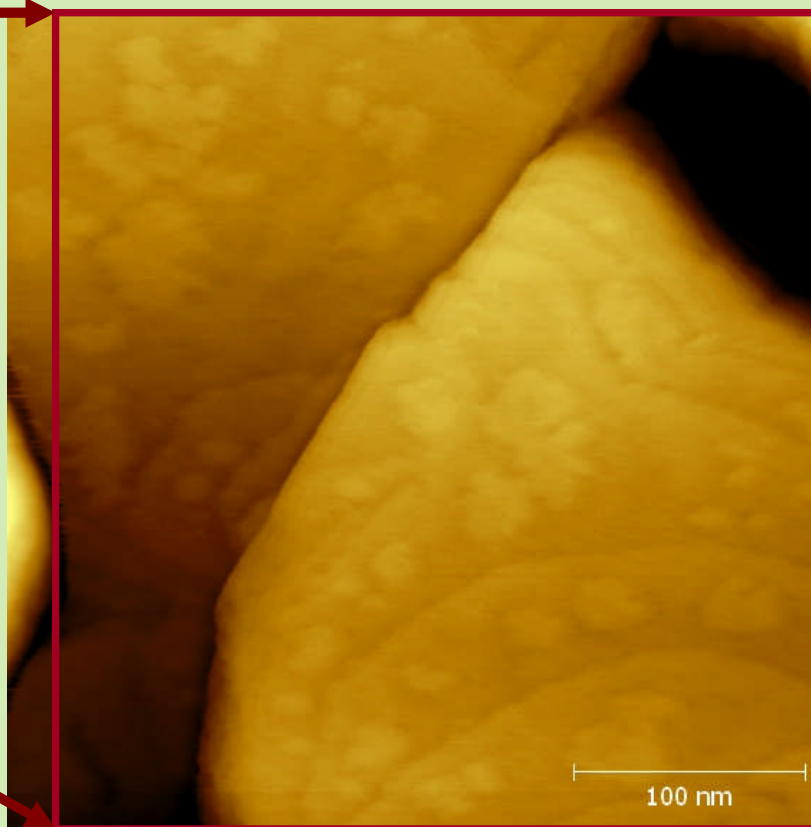
Adsorption properties of benfluralin

Scanning tunneling microscopy STM

Mica/Au(111) substrate



topography



topography

6 min

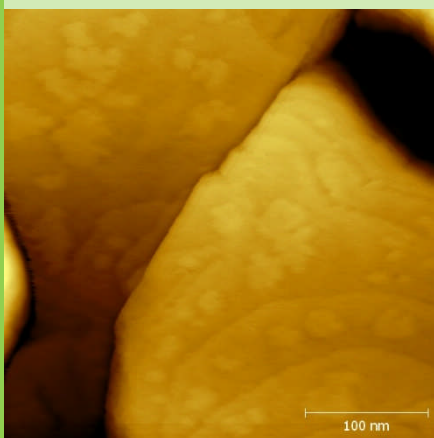
adsorbate – adsorbate interactions

Ex-situ micrographs of the adsorbed benfluralin on the gold surface from the solution of 0.2 mM benfluralin in 0.1 M KF and 20% ethanol (v/v). Freshly adsorbed for 6 min. $I = 20$ pA.

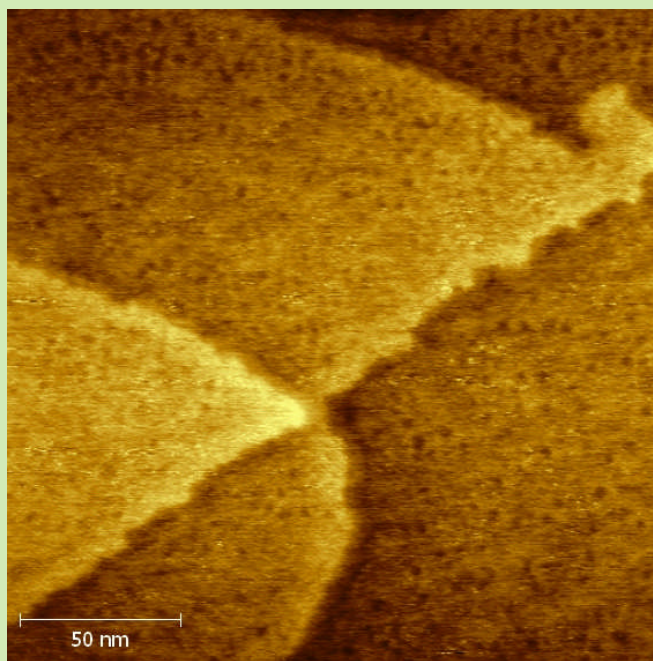
Adsorption properties of benfluralin

Scanning tunneling microscopy STM

Mica/Au(111) substrate

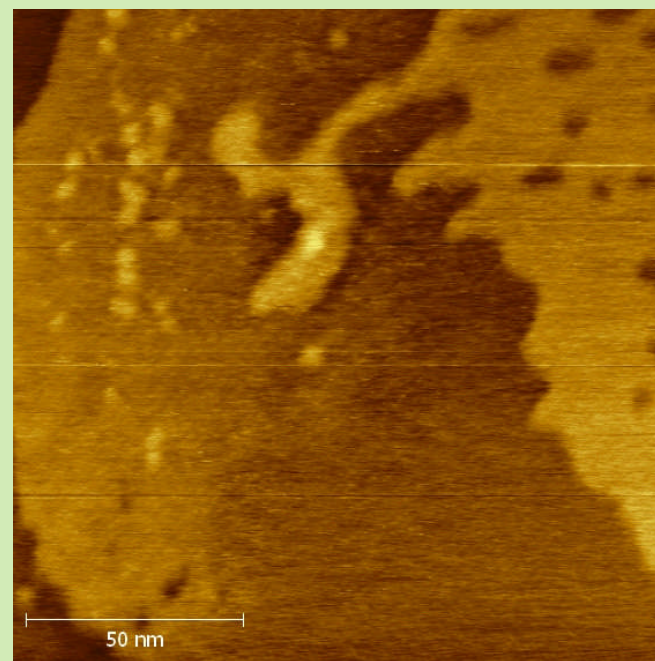


6 min



topography

2 h



topography

9 h

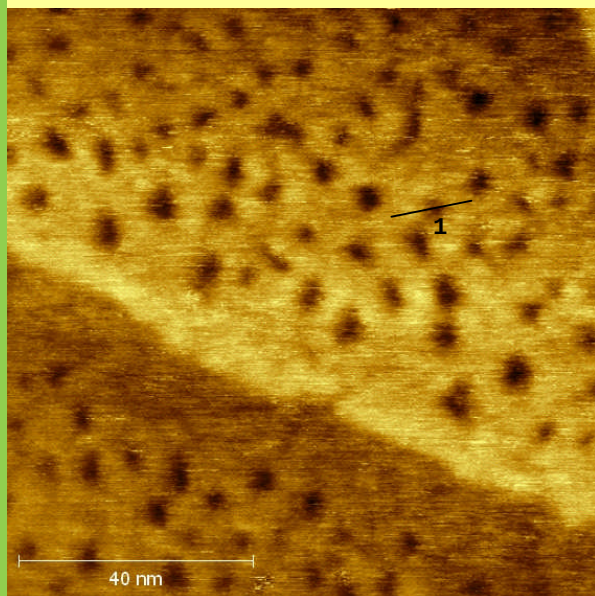
compact layer

Ex-situ micrographs of the adsorbed benfluralin on the gold surface from the solution of 0.2 mM benfluralin in 0.1 M KF and 20% ethanol (v/v). Freshly adsorbed for 6 min, 2h and 9h.

Adsorption properties of benfluralin

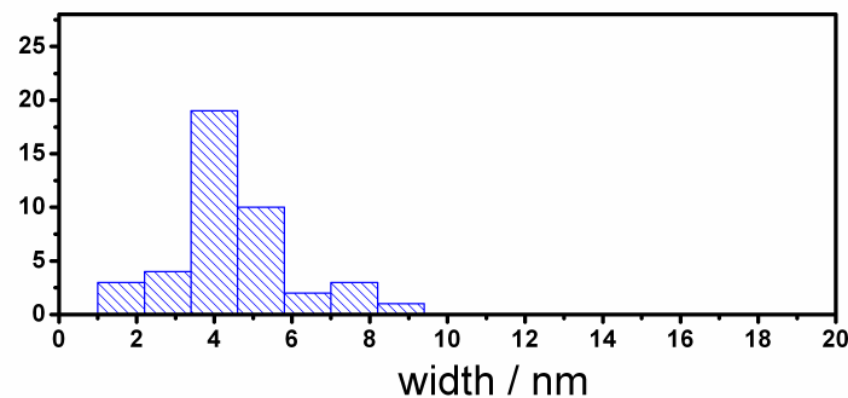
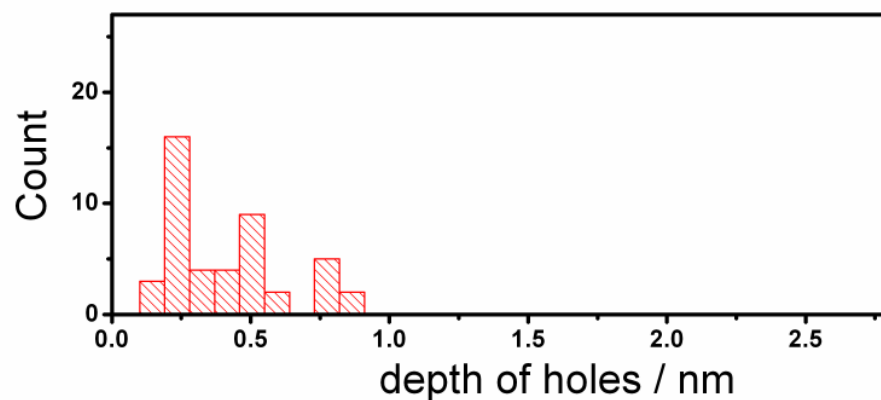
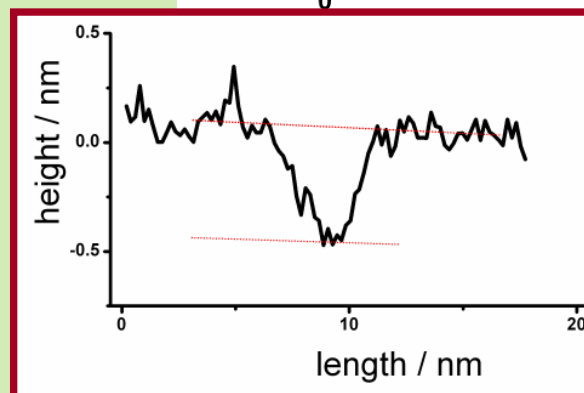
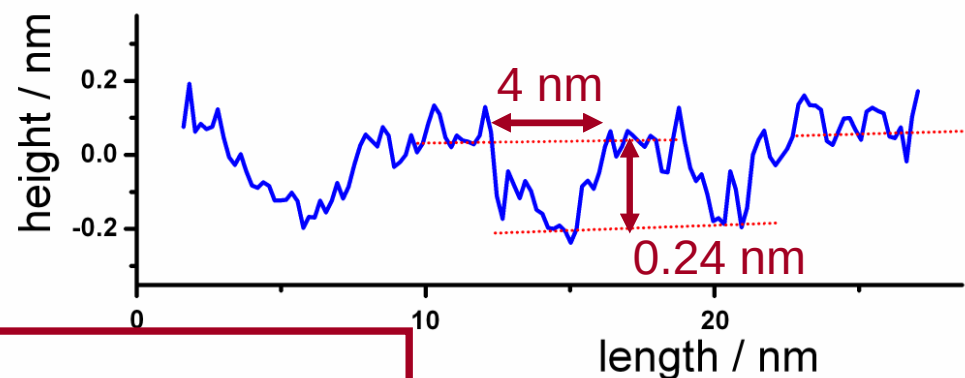
Scanning tunneling microscopy STM

Mica/Au(111) substrate



topography

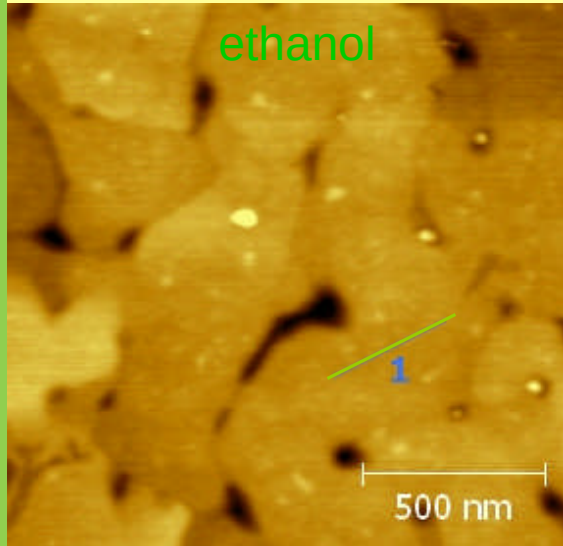
200 s



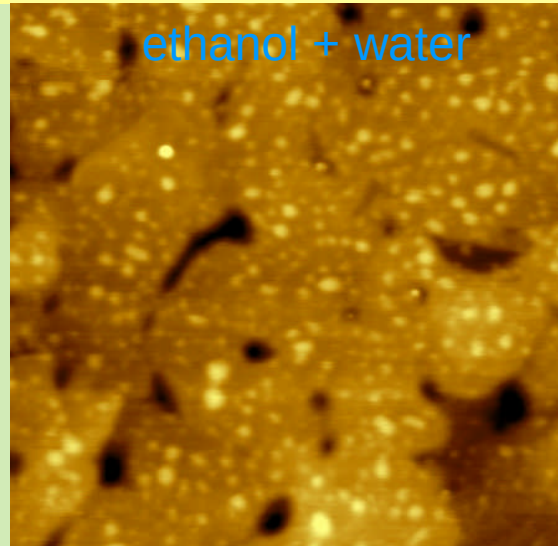
Adsorption properties of benfluralin

Atomic force microscopy AFM

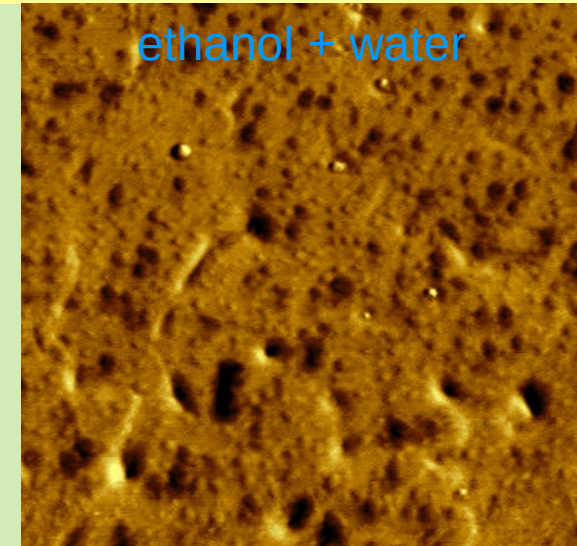
Mica/Au(111) substrate



topography

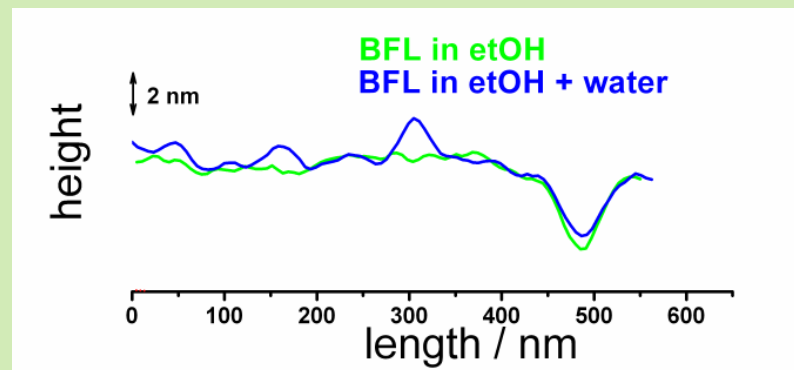


topography



phase

the presence of nanobubbles
in water

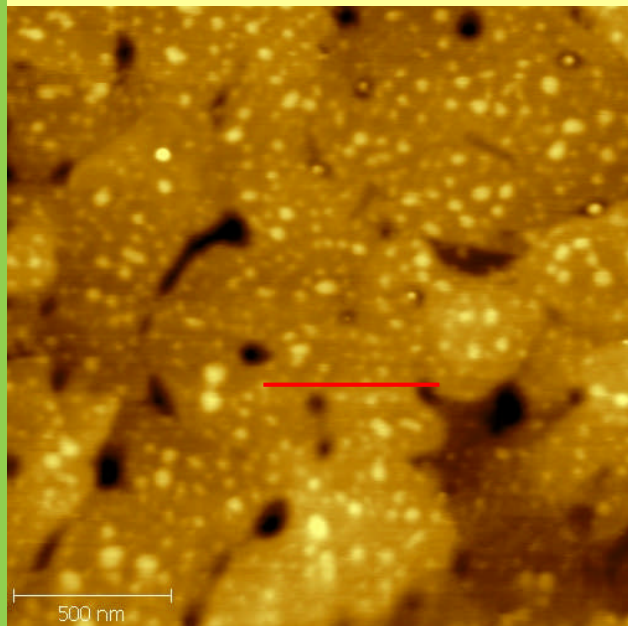


IN-SITU TOP-MAC-AFM

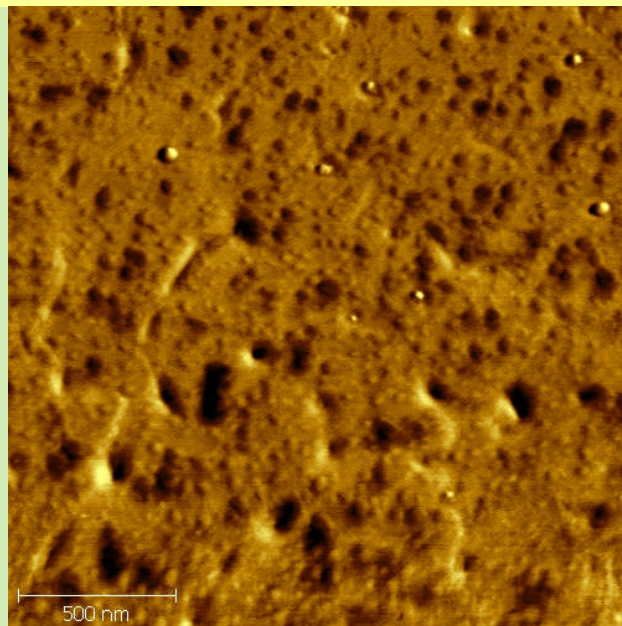
Adsorption properties of benfluralin

Atomic force microscopy AFM

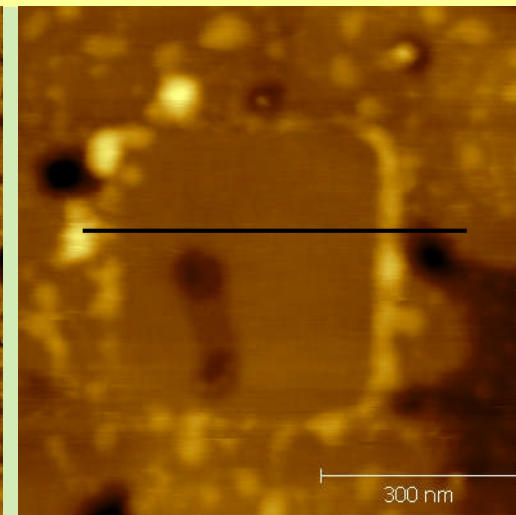
Mica/Au(111) substrate



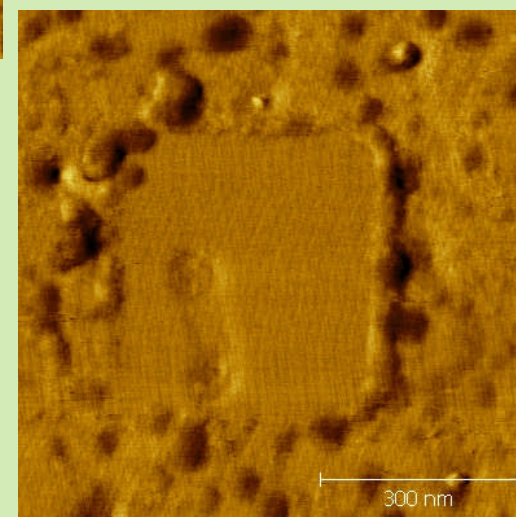
topography



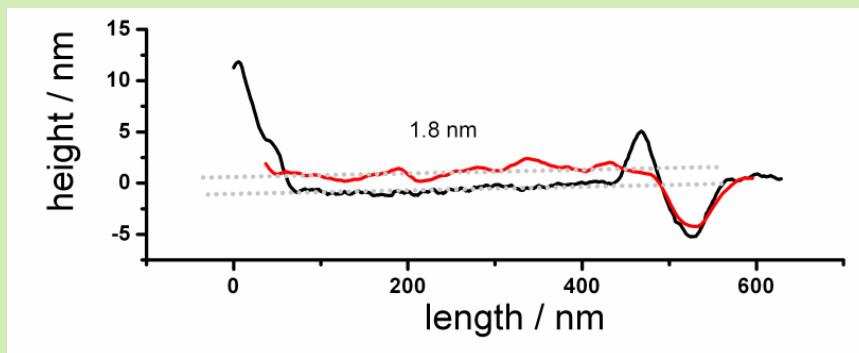
phase



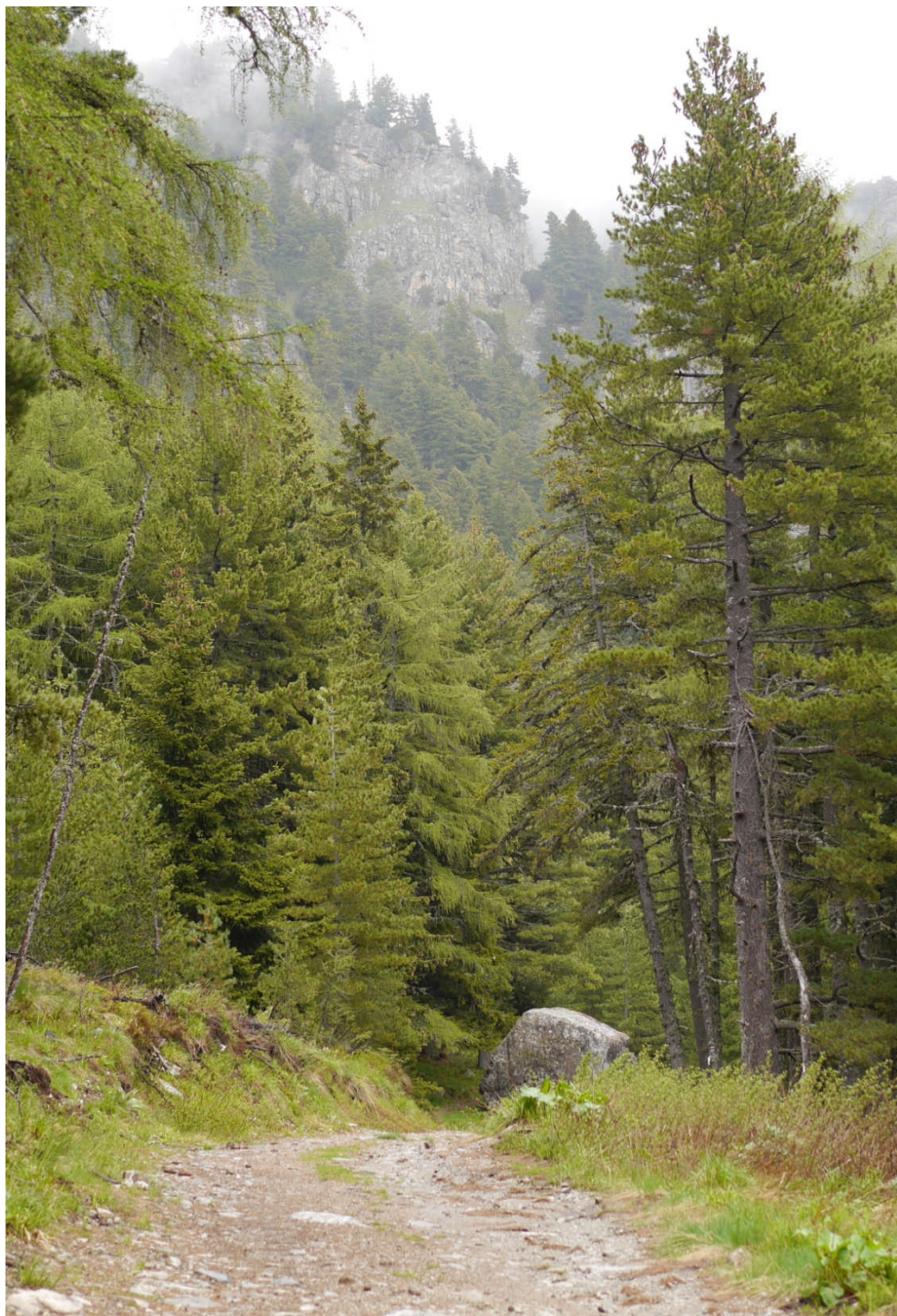
topography



phase



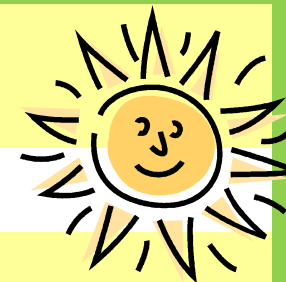
IN-SITU TOP-MAC-AFM



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Lubomír Pospíšil

→ Fruitful discussion



Viliam Kolivoška

Miroslav Gál

Magdaléna Hromadová

→ AFM and STM imaging

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**Thank you
for your attention**