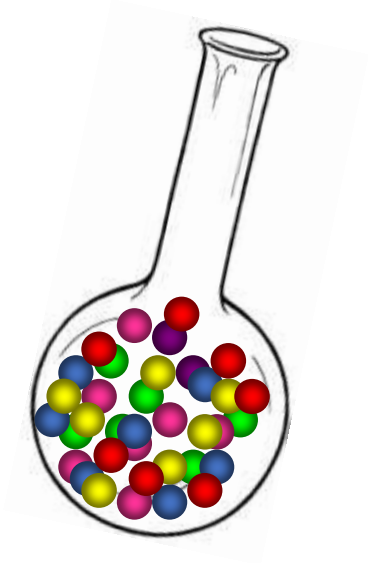
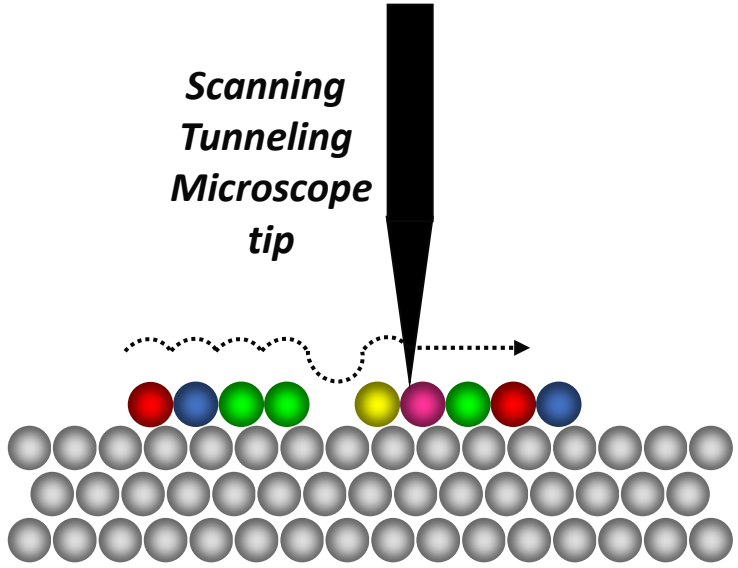
Single atom/molecule catalysis imaging

Gerhard Ertl

Ensemble averaging....versus....single molecule imaging



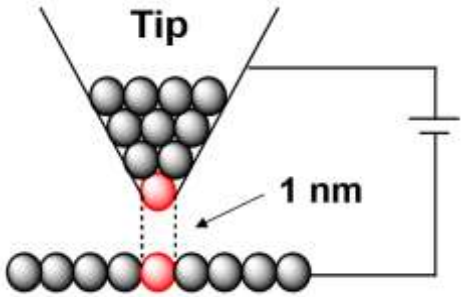


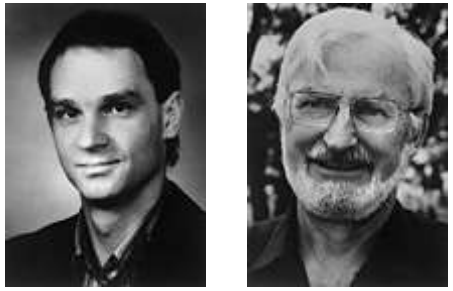
Techniques complementary to the bulk techniques

- Visualize catalyst, starting materials, products, intermediates
- Are all catalysts active, or only a fraction of them?
- What parts of a catalytic surface are active (or inert)?

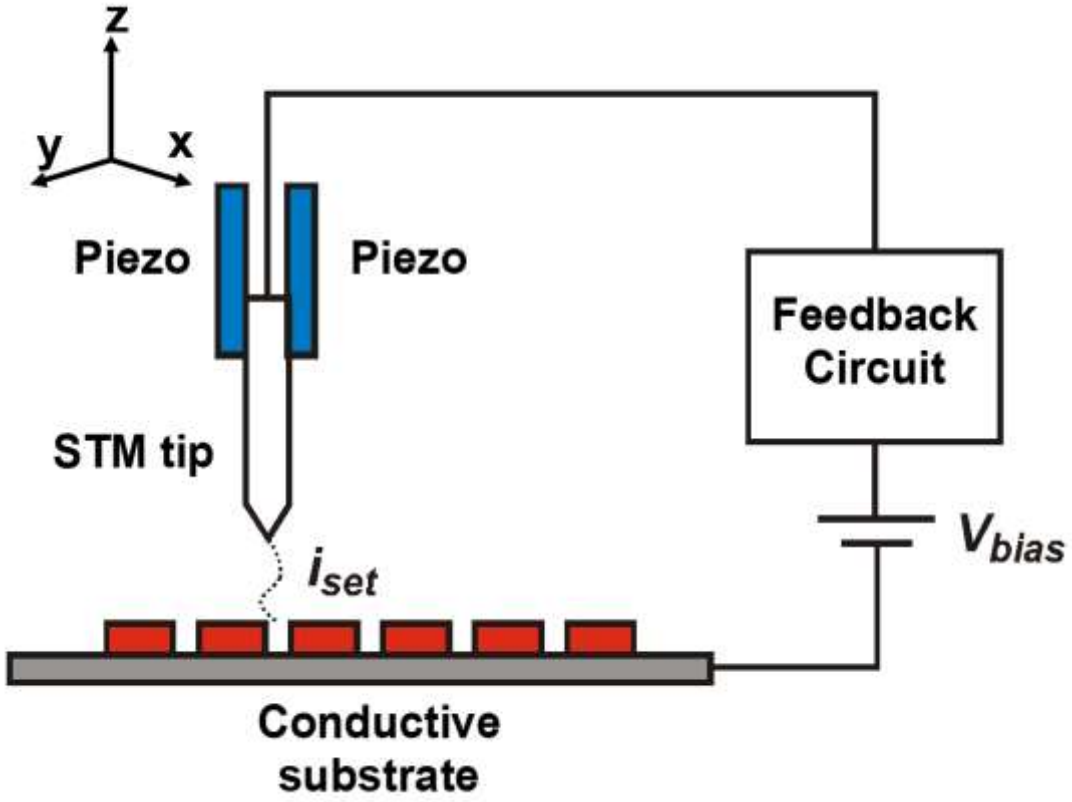
Scanning Tunneling Microscopy (STM)

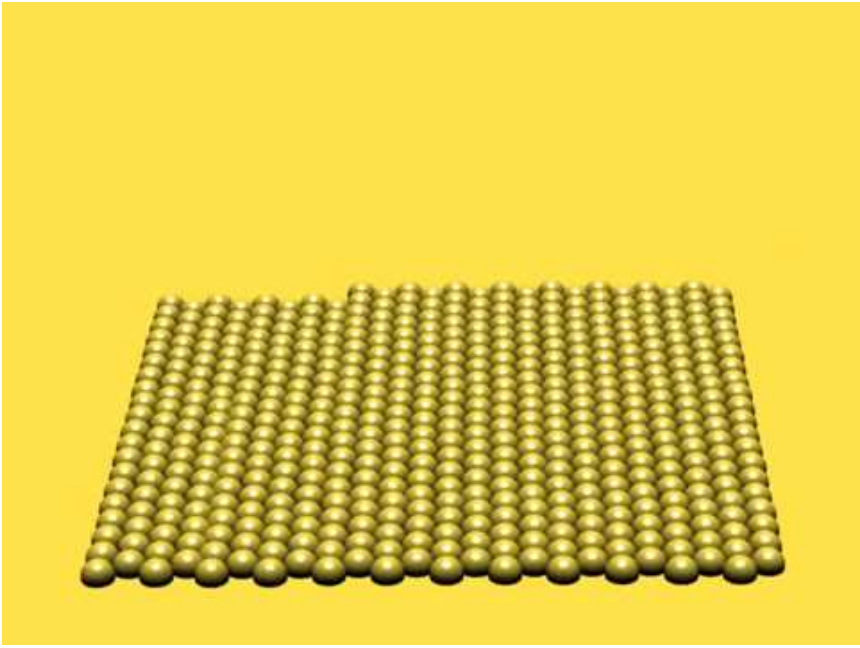
- Technique with the highest spatial resolution
- Based on tunneling current between tip and sample
- Atomic resolution on flat and conductive surfaces
- Combination of topographic and electronic information
- Disadvantage: slow technique





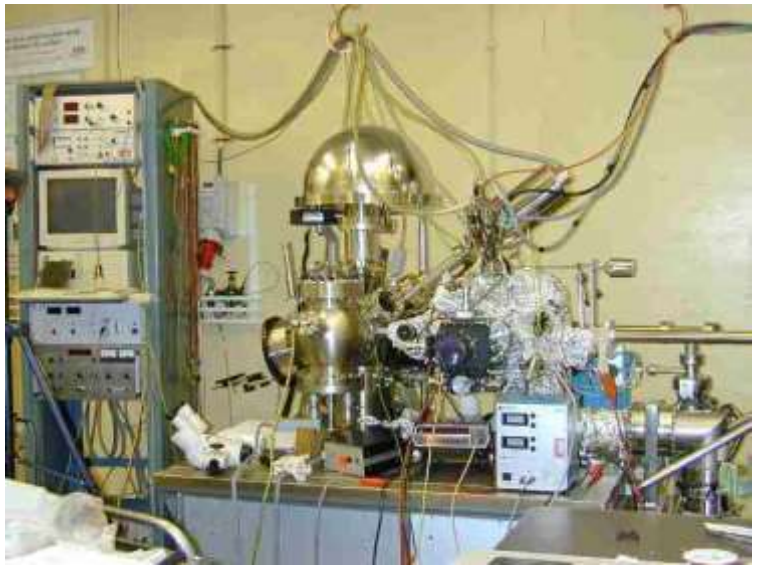
Binnig & Rohrer 1982
(Nobel prize 1986)

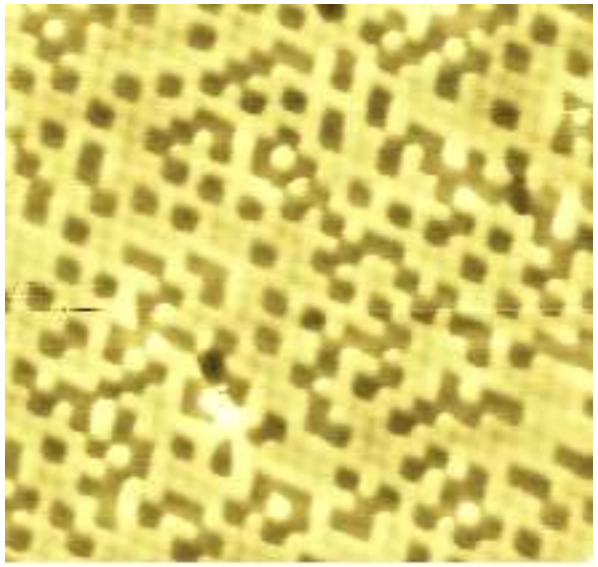




STM imaging of flat surfaces

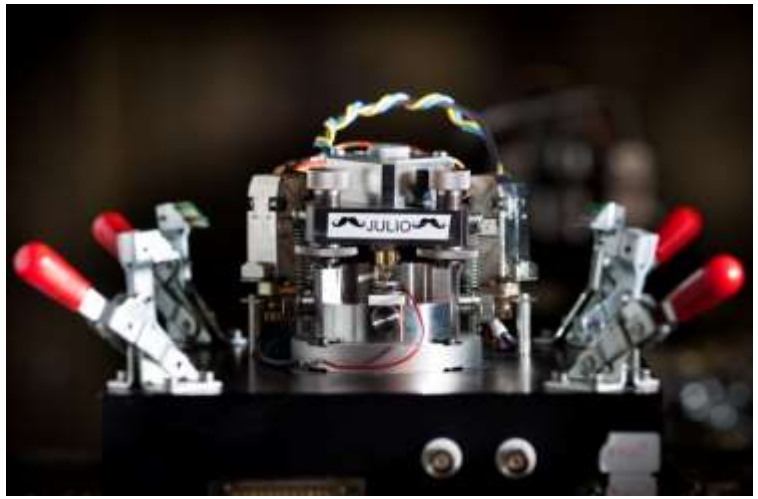
Ultrahigh Vacuum STM

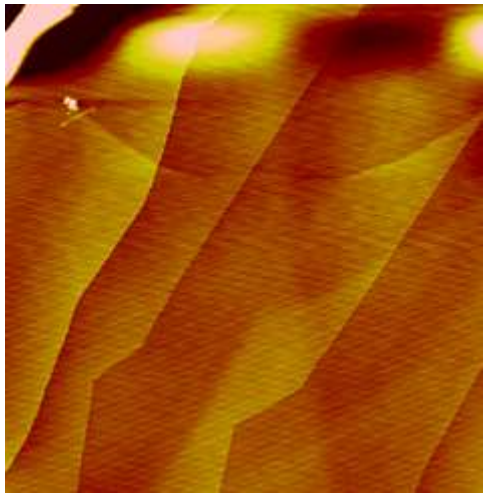




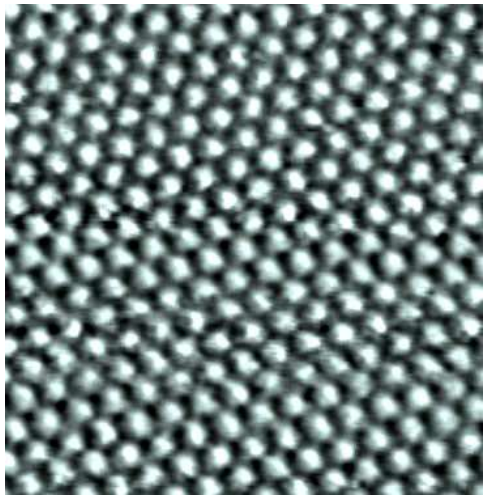
Au atoms (dark) on Fe(001)
Chemical contrast

Air/liquid STM



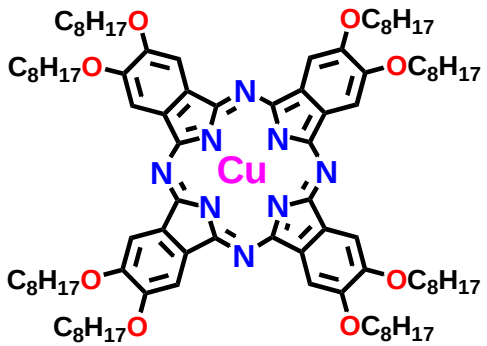


Graphite 1.5 x 1.5 μm



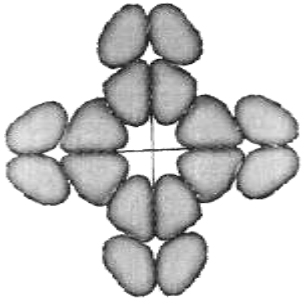
Graphite 3 x 3 nm

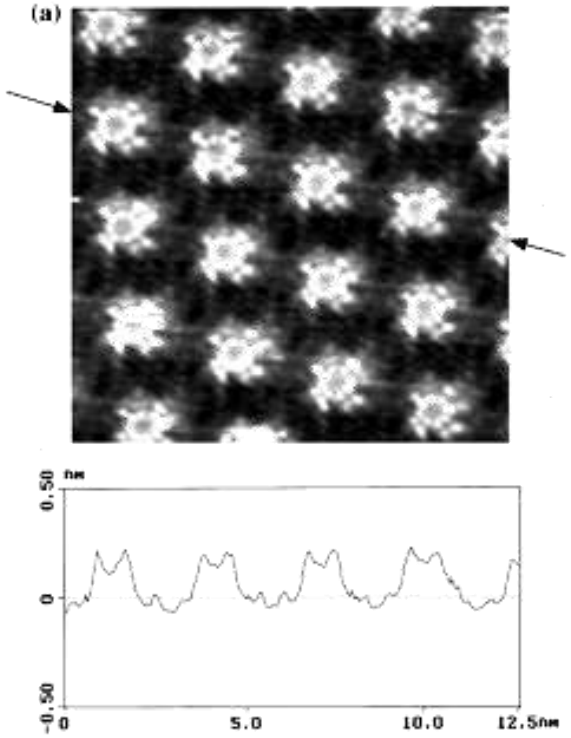
Probing of the local density of states (LDOS)



V_{bias} negative

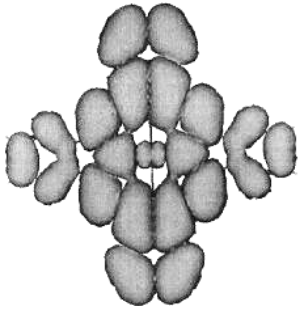
HOMO





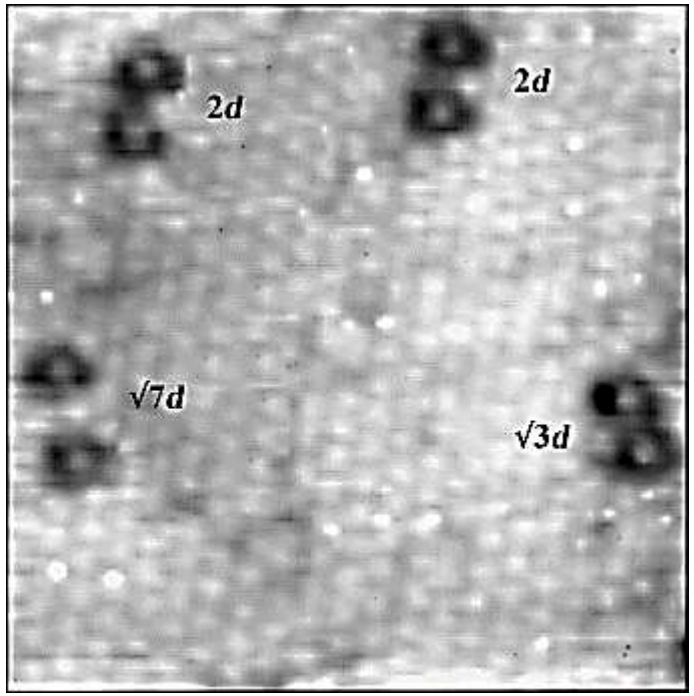
V_{bias} positive

LUMO

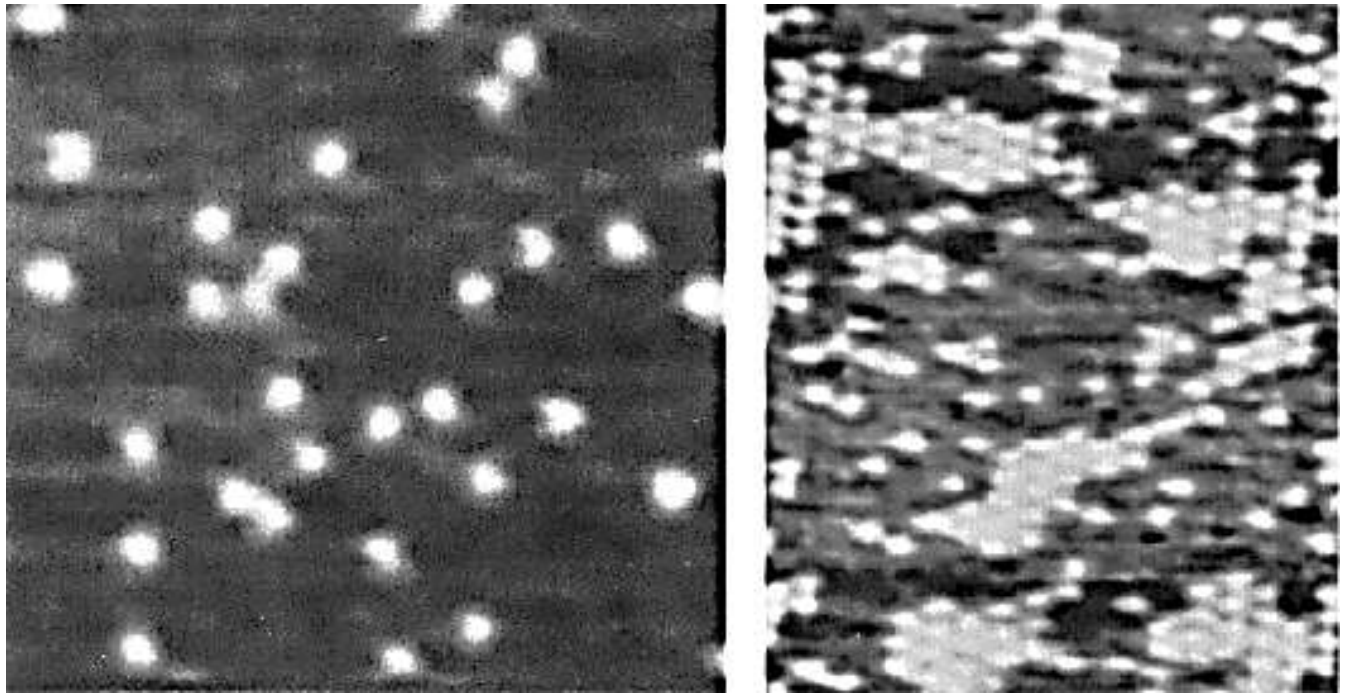


J. Am. Chem. Soc., **2000**, *122*, 5550

Heterogeneous catalysis at the atomic scale



O_2-dissociation on a Pt(111) surface
(5.3 x 5.5 nm)

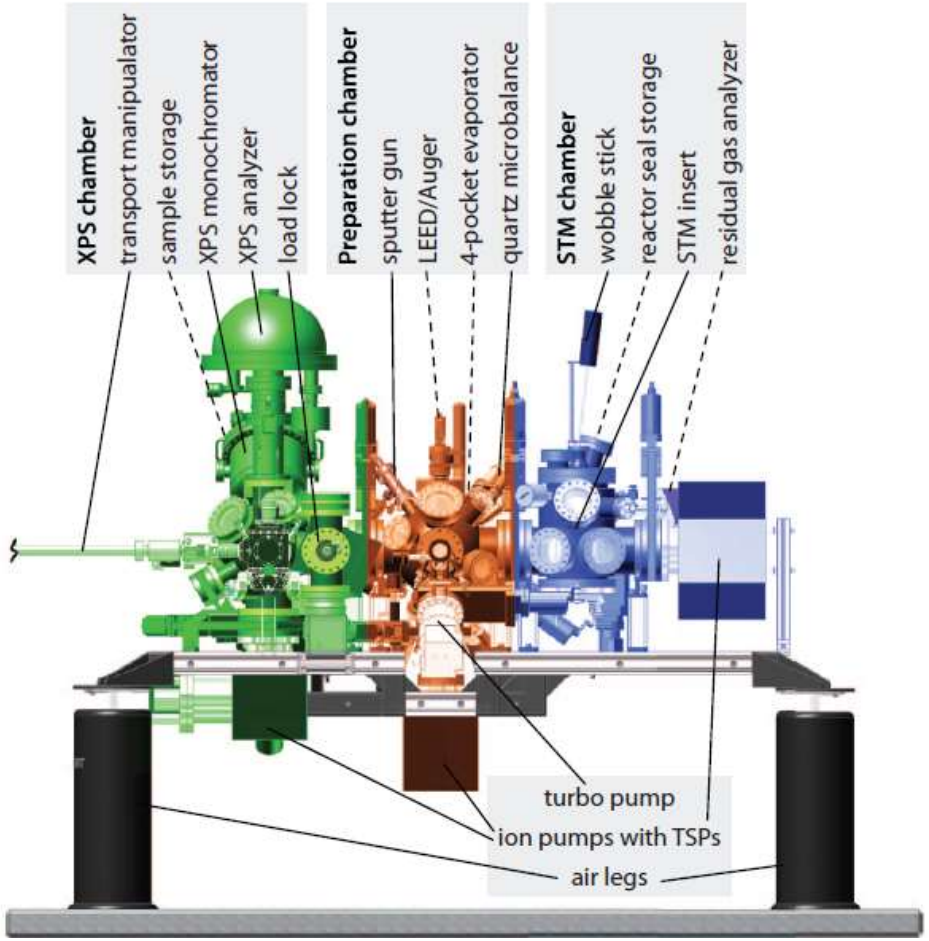


O-atoms on a Ru(100) surface

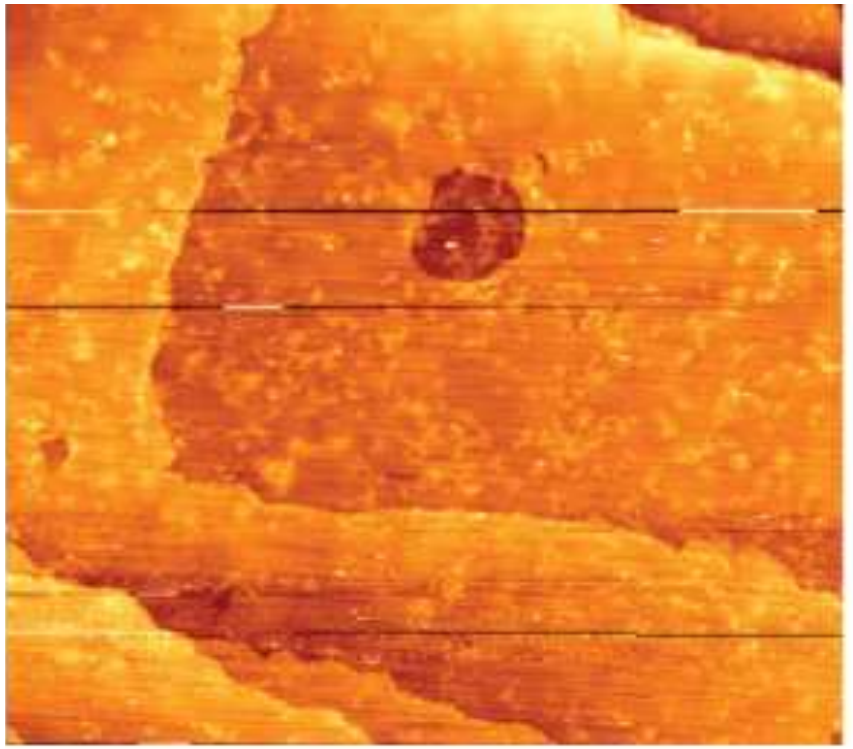
Angew. Chem. Int. Ed. **2008**, *47*, 3524

Fischer Tropsch process in a high pressure STM

$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \quad n = 10\text{-}20$



- *T* up to 600°C
- *p* between UHV and 6 bar

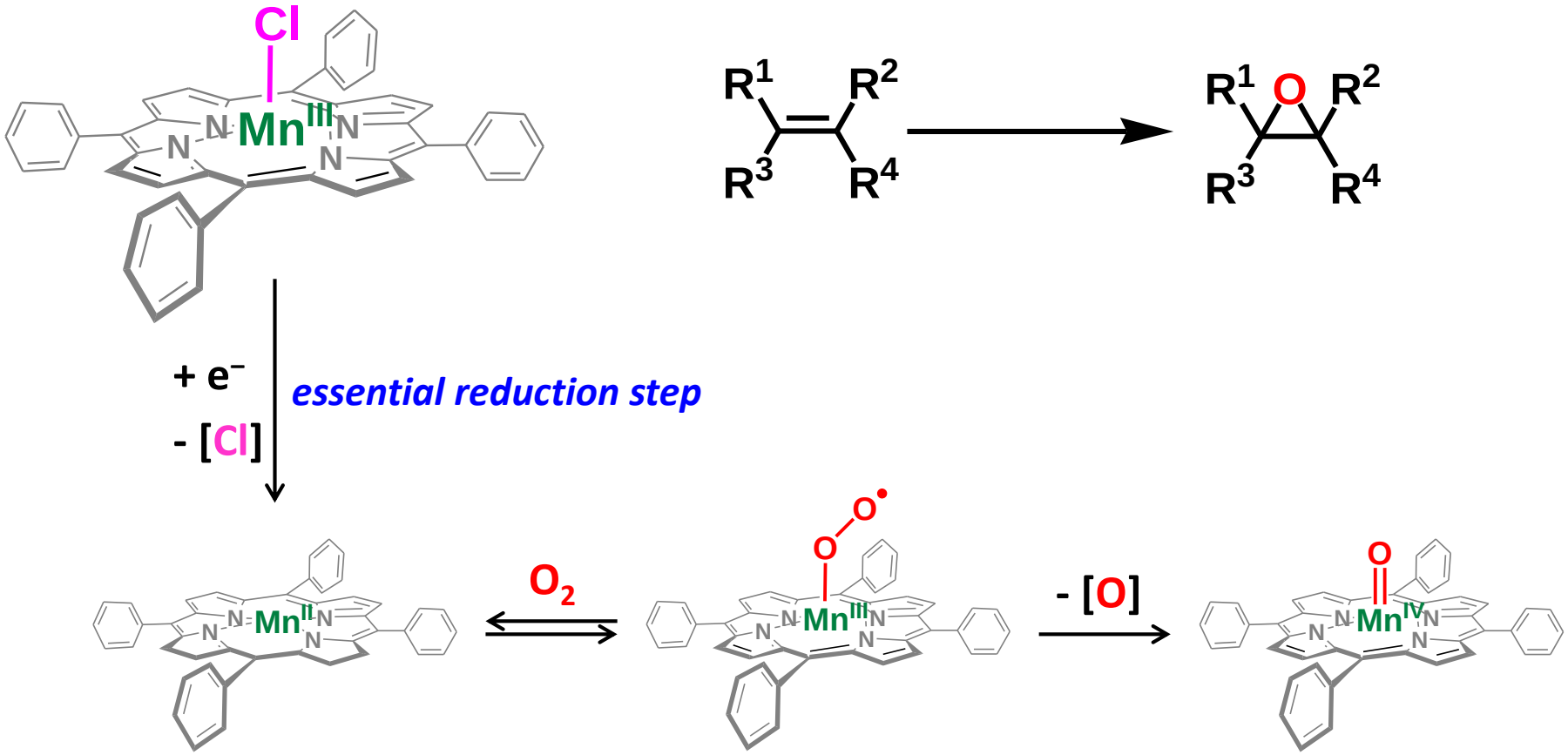


Co(0001) surface + CO + H_2
(320 x 280 nm)

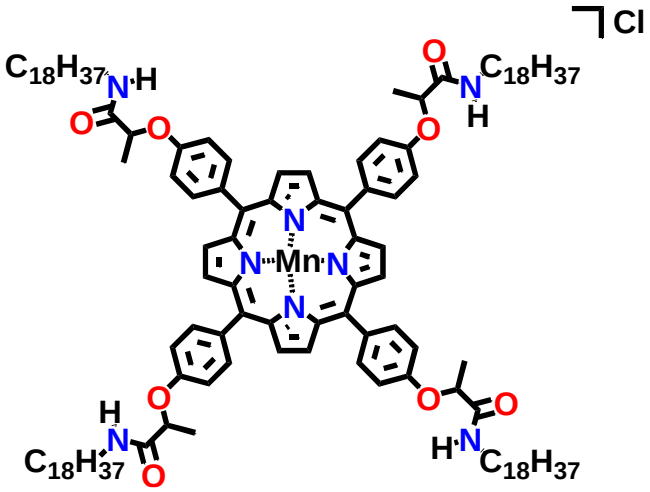
Rev. Sci. Instr. **2014**, *85*, 083703

Liquid STM on manganese porphyrin catalysts

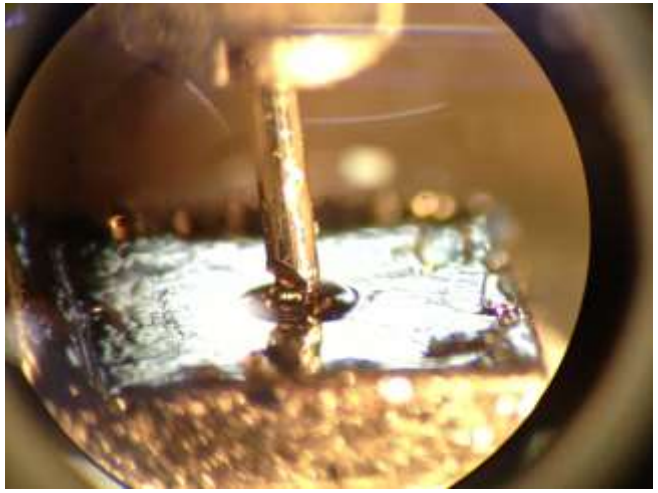
Efficient homogenous catalysts for the epoxidation of alkenes



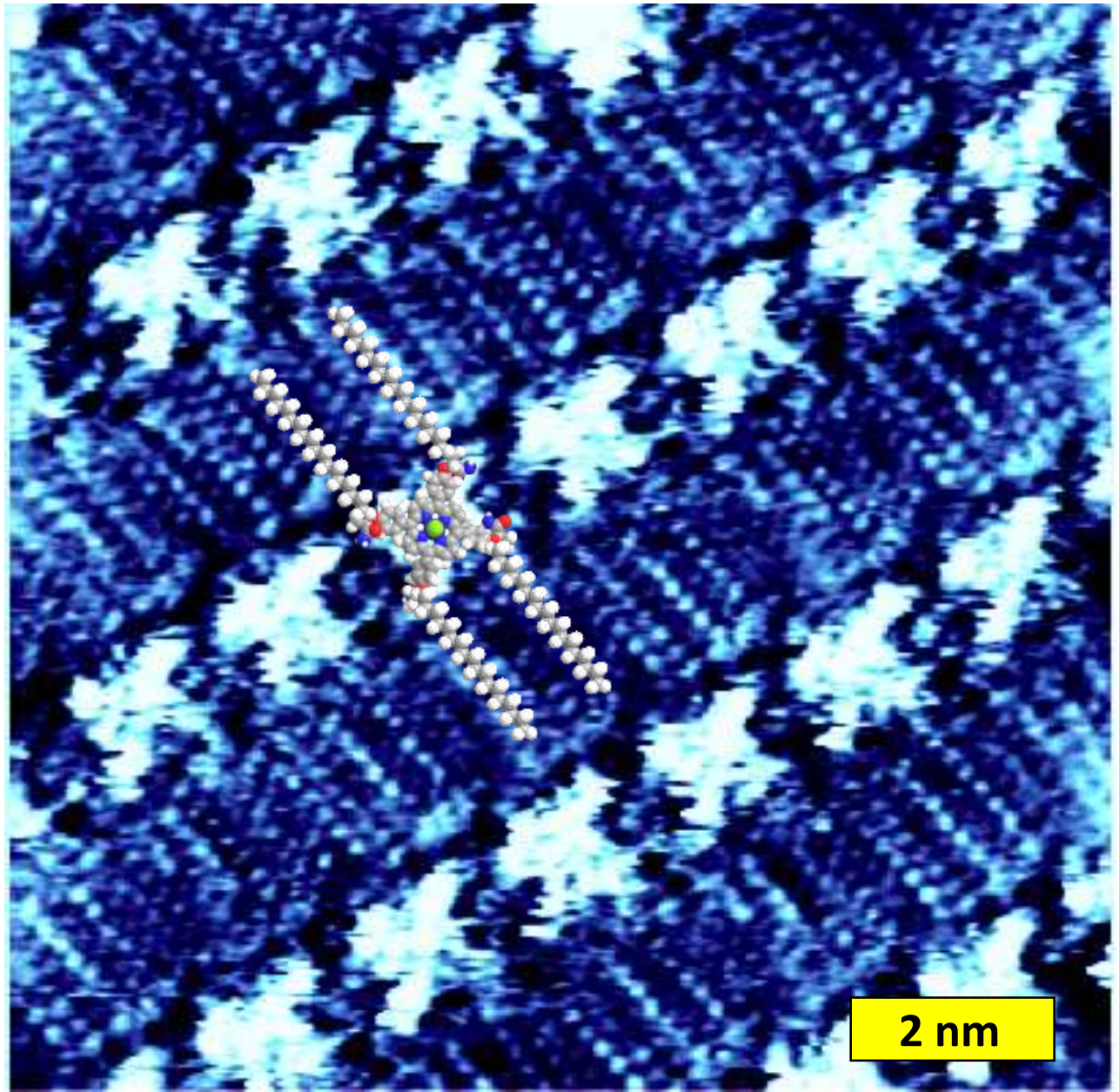
Liquid STM on manganese porphyrin catalysts



graphite / 1-octanoic acid interface, argon atmosphere



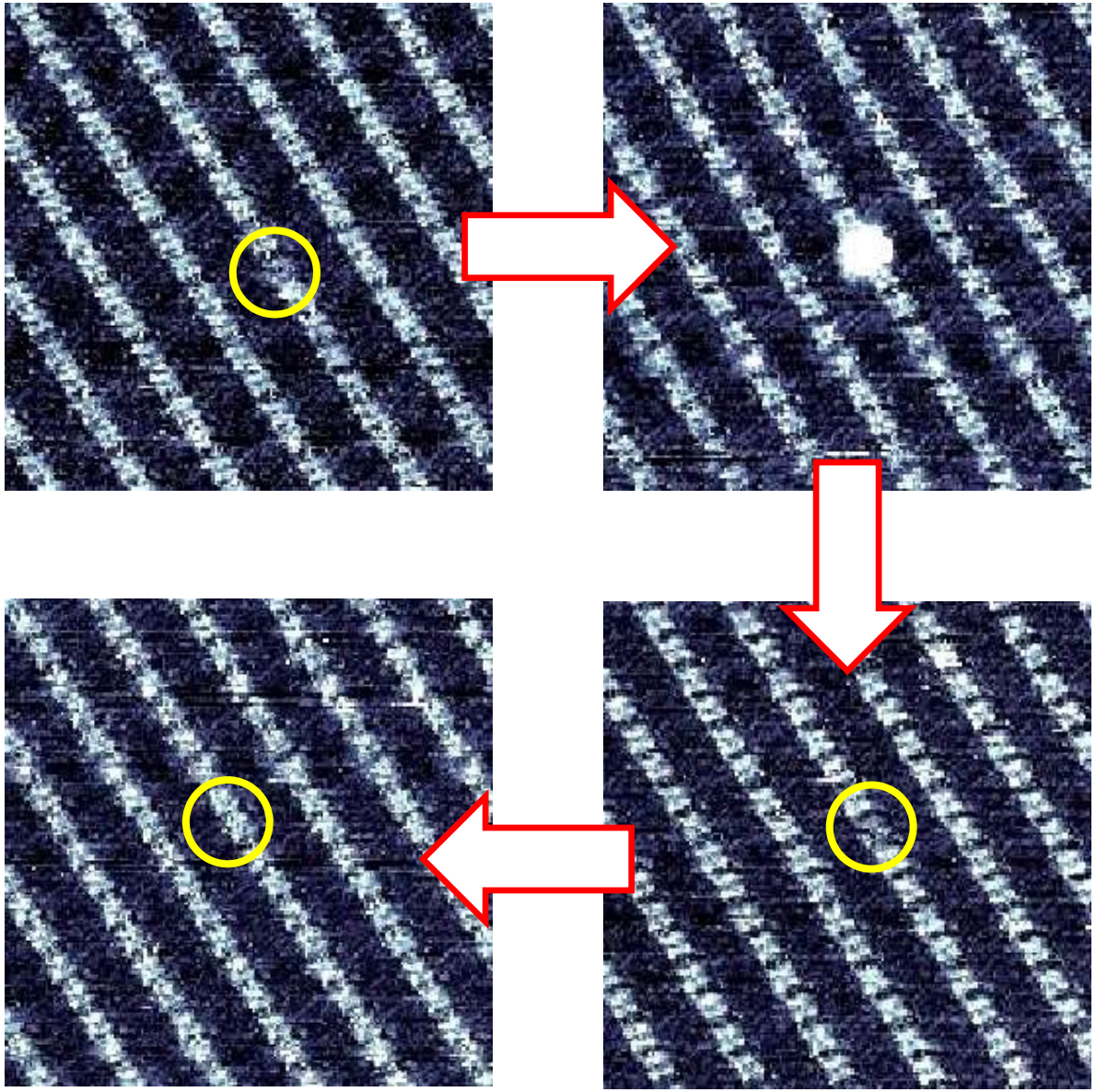
Nature Chemistry **2013**, *5*, 621




80
70
60
50
40
30
20
y (nm)
Line
Tim
Con
SPM

Visualization of an active site

Mn(II)
active site

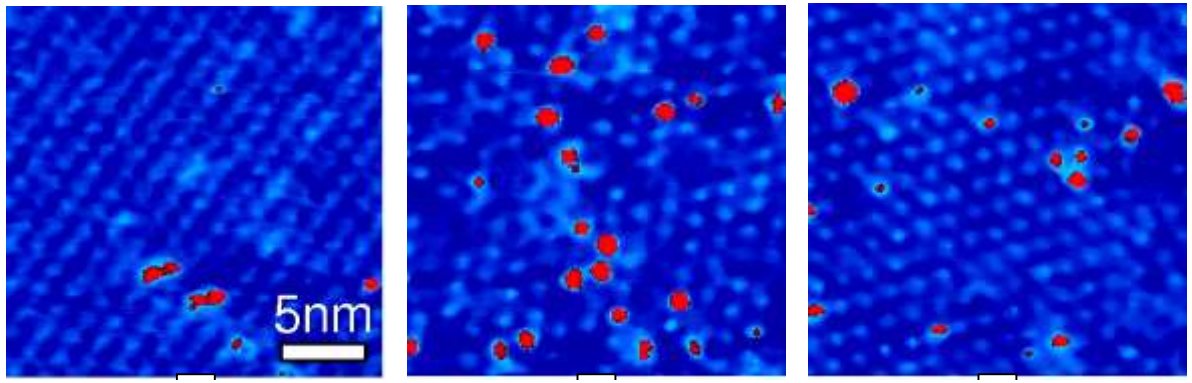


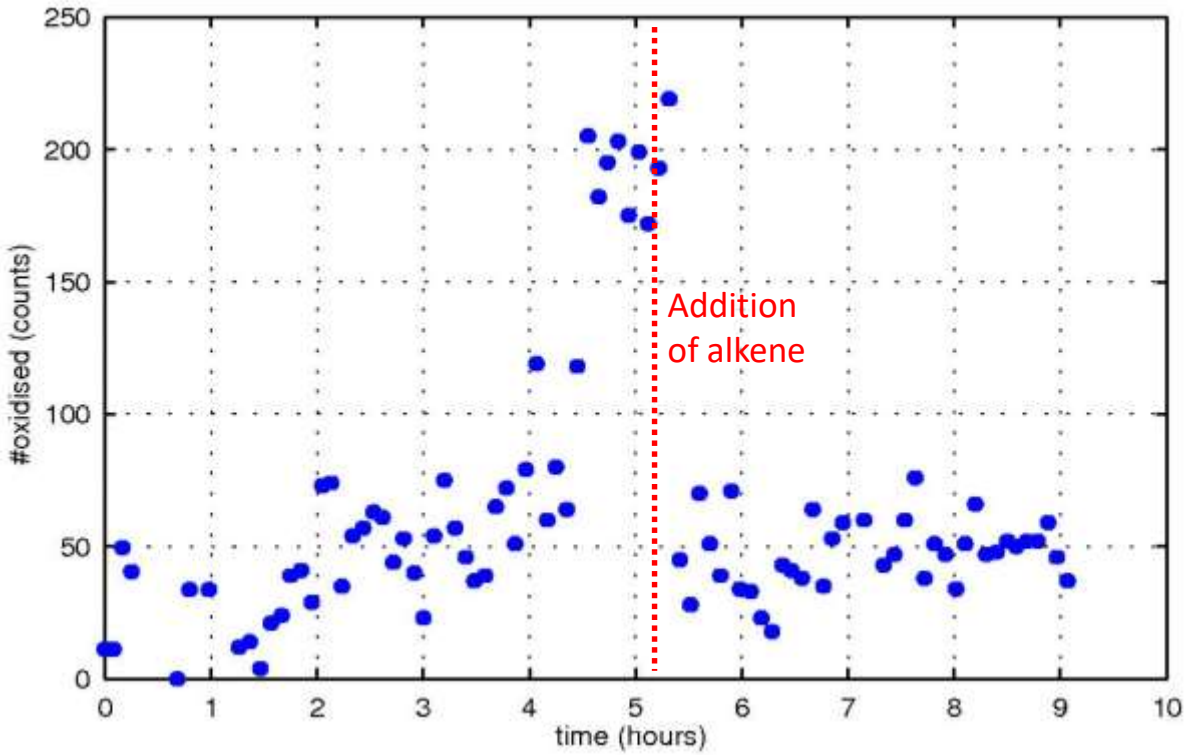
Mn(IV)=O
species

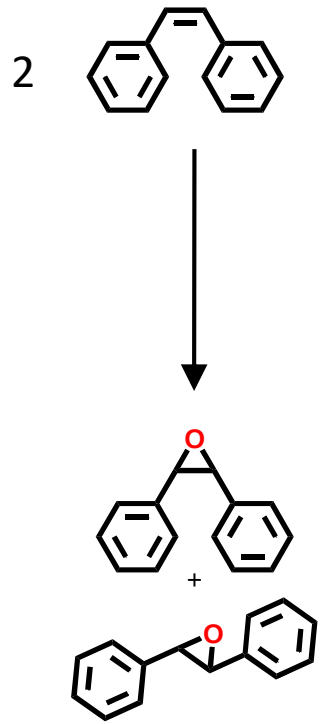
Mn(III)
inert site

Mn(II)
active site

Catalysis visualized at single catalyst level



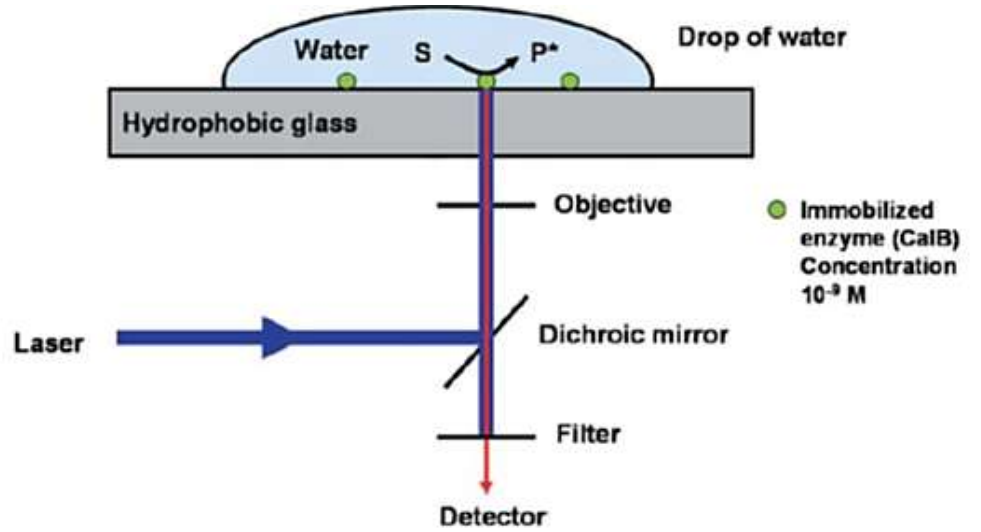


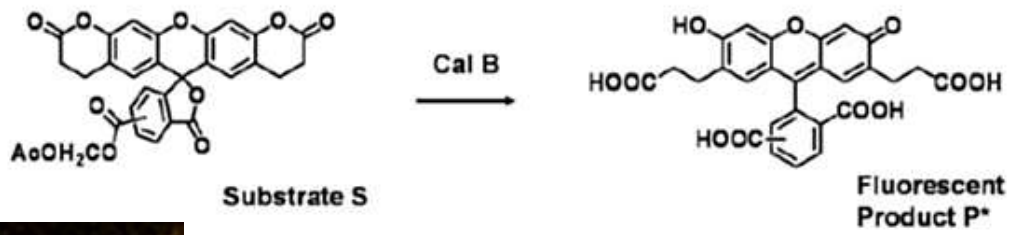


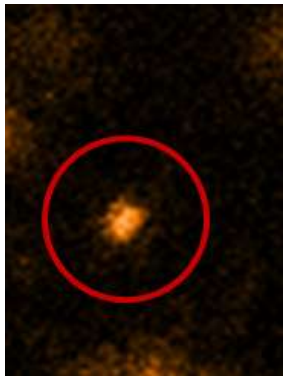
- `Turnovers` for > 1 week
- Gaschromatographic analysis after 4 days: *cis*-epoxide is formed

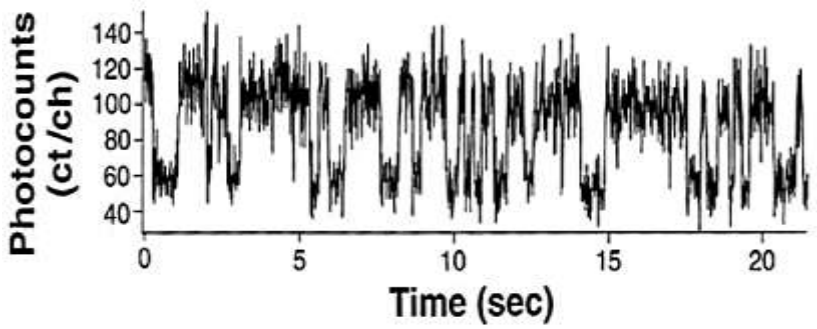
Nature Nanotechnology **2007**, *2*, 285

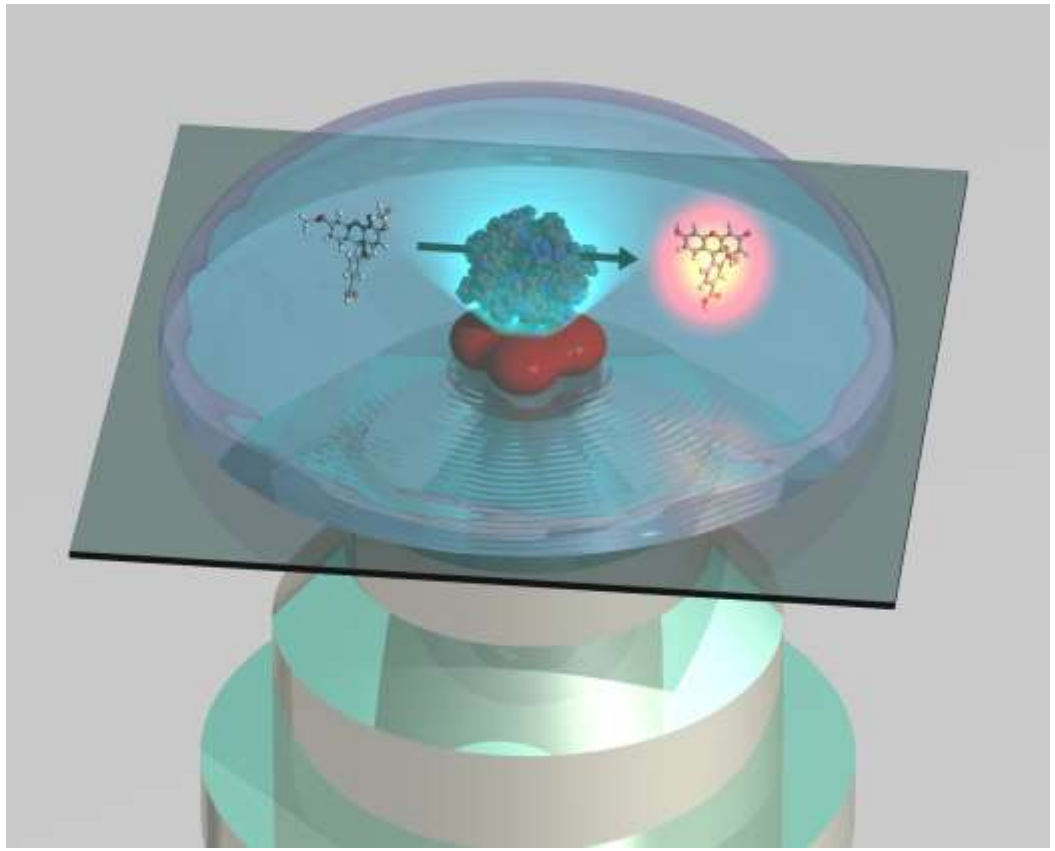
Single molecule fluorescence microscopy











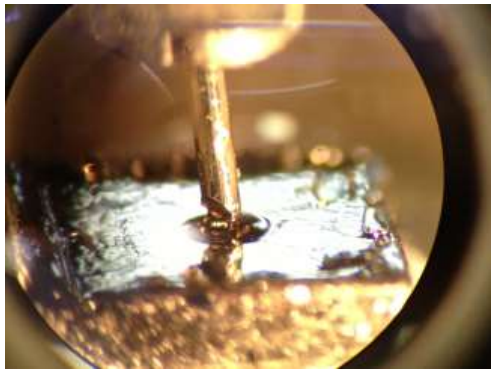
- Visualization of single catalytic turnovers
- Information about activity and stability of catalysts

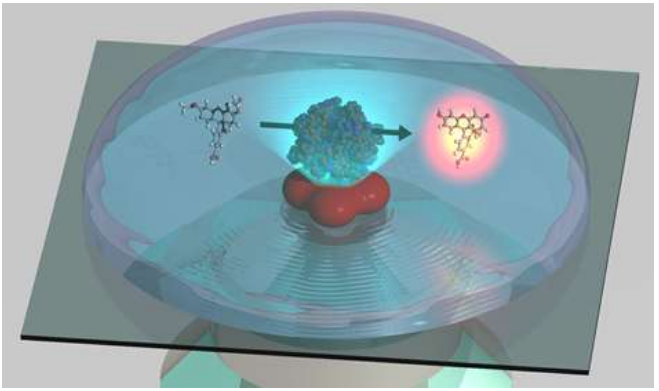
Limitation

- Fluorescent substrate or product needed

Angew. Chem. Int. Ed. **2005**, *44*, 560

Comparison of microscopies





Electron microscopy	STM	Fluorescence
Micrometer-nanometer resolution	Nanometer-atomic resolution	Micrometer-nanometer resolution
Vacuum needed	All environments	All environments
Molecules of all sizes	Small molecules (enzymes too large)	Molecules of all sizes
All surfaces	Flat & conductive surfaces	All surfaces
(Non)fluorescent molecules	(Non)fluorescent molecules	Fluorescent molecules
Fast technique	Slow technique	Fast technique

Study material

Learning goals

- You know the various techniques to characterize catalysts and their working mechanisms
- You are aware of the scopes and limitations of these techniques (e.g. of spatial and temporal resolution)

Study material

- These lecture slides
- Catalysis: An Integrated Textbook for Students (U. Hanefeld & L. Lefferts, Eds): Sections: 7.1, 7.3, 7.5