united nations educational, scientific and cultural organization
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the abdus salam international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 32

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE

(24 May - 11 June 2004)

NANOSCALE SURFACE PHYSICS WITH LOCAL PROBES:

(i) Two-dimensional self-assembly of supermolecules and of atomic superlattices; (ii) Insulators at the limit

PART I

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These are preliminary lecture notes, intended only for distribution to participants.

Wolf-Dieter Schneider

Institut de Physique des Nanostructures

Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland

EPFL

INSTITUT DE PHYSIQUE DES NANOSTRUCTURES

Nanoscale surface physics with local probes

Part I: Two-dimensional self-assembly of supermolecules

Part II: Two-dimensional self-assembly of atomic superlattices

Part III: Insulators at the limit

Supramolecular Self-Assembly in Two Dimensions: A Local View

<u>Experiment:</u>

M. Böhringer (Bosch, Stuttgart)

R. Berndt (Kiel)

K. Morgenstern (Berlin)

M. Wühn (Bochum)

C. Wöll (Bochum)

WDS

<u>Theory:</u>

A. De Vita (Trieste, London)

F. Mauri (Paris)

R. Car (Princeton)

M. Vladimirova (Toulouse)

M. Stengel (EPFL, IRRMA)

A. Baldereschi (EPFL, IRRMA)

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Definition

Self-assembly is the autonomous organisation
of
components
into
patterns or structures
without
human intervention

G. M. Whitesides, B. Grzybowski, Science **295**, 2418 (2002)

Fig. 1. Examples of static self-assembly. (A) Crystal structure of a ribosome. (B) Self-assembled peptide-amphiphile nanofibers. (C) An array of millimeter-sized polymeric plates assembled at a water/perfluorodecalin interface by capillary interactions. (D) Thin film of a nematic liquid crystal on an isotropic substrate. (E) Micrometer-sized metallic polyhedra folded from planar substrates. (F) A three-dimensional aggregate of micrometer plates assembled by capillary forces. [Image credits: (A) from (24); (B) from (25); (C) from (26); (D) from (27); (E) from (28); (F) from (29)]

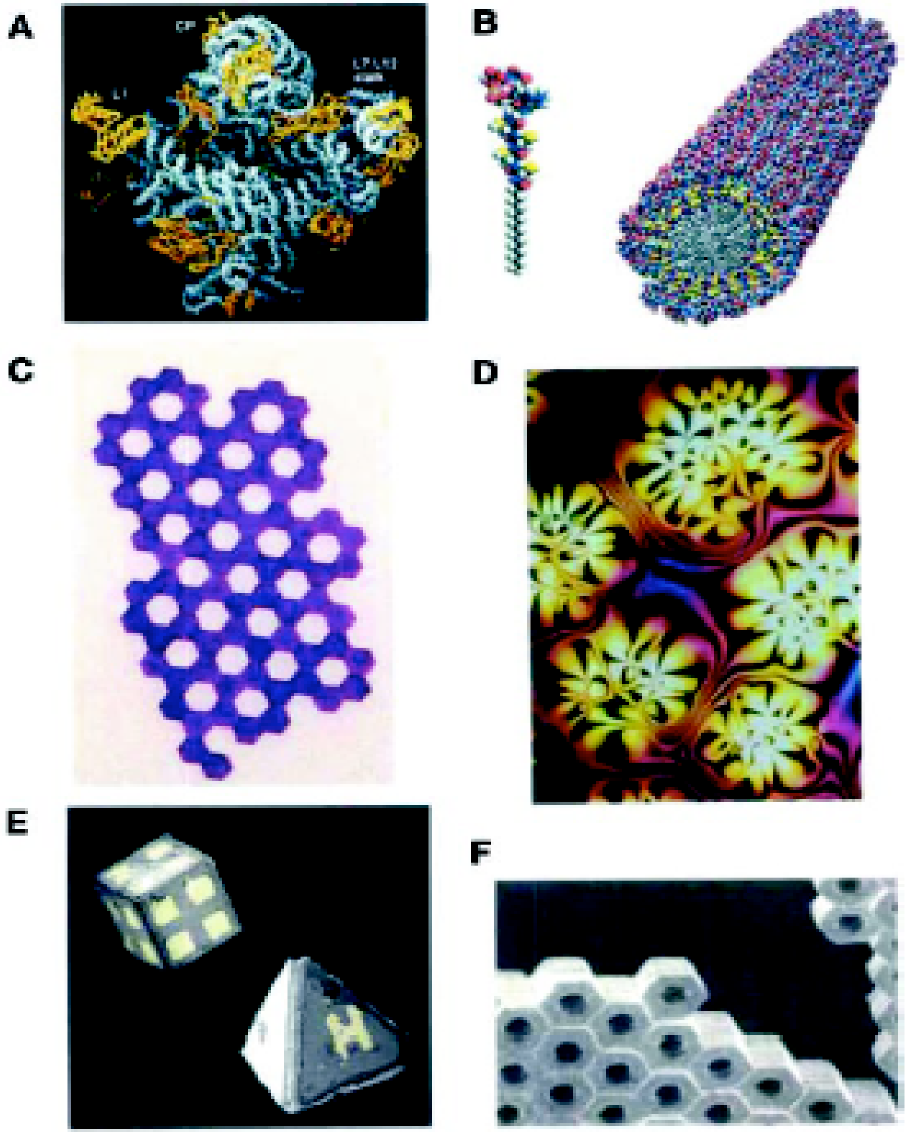
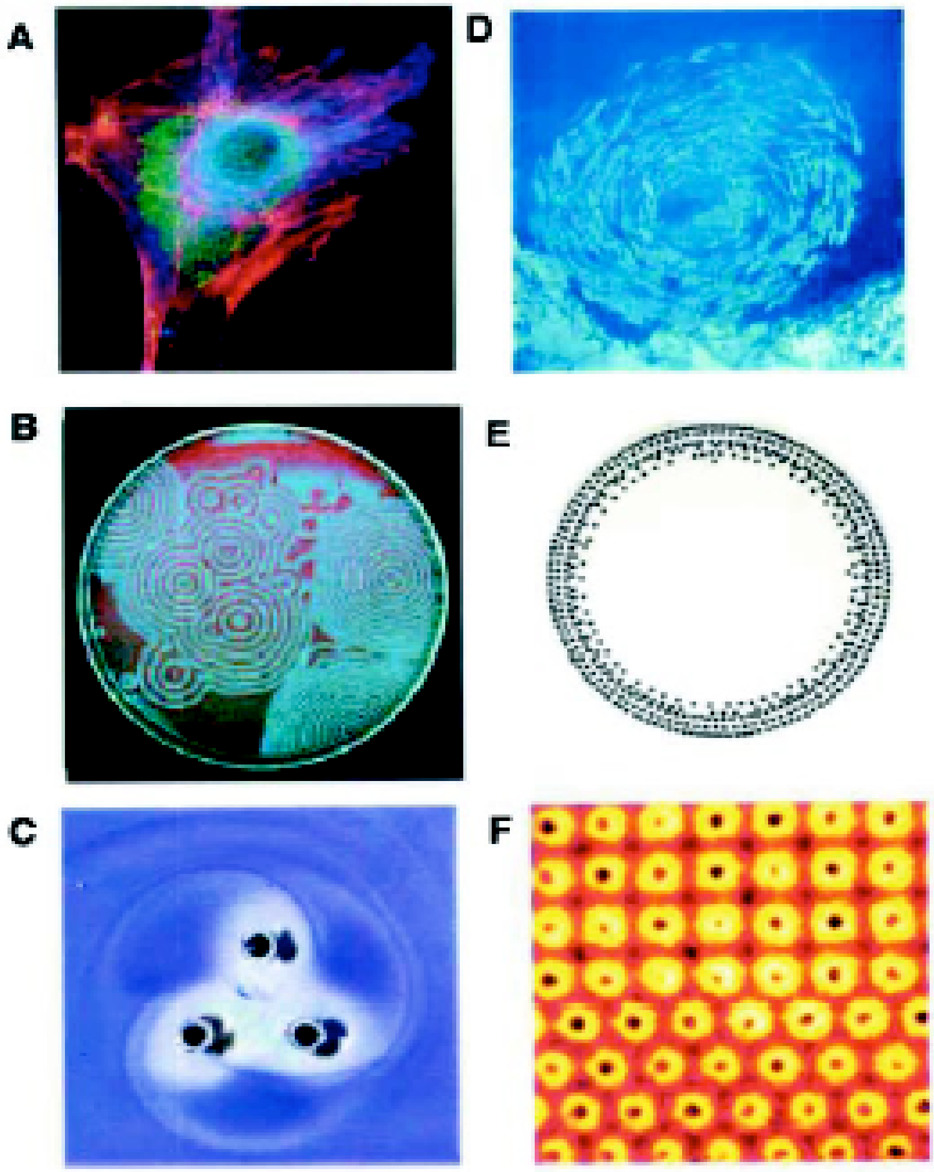


Table 1. Examples of self-assembly (S, static, D, dynamic, T, templated, B, biological).

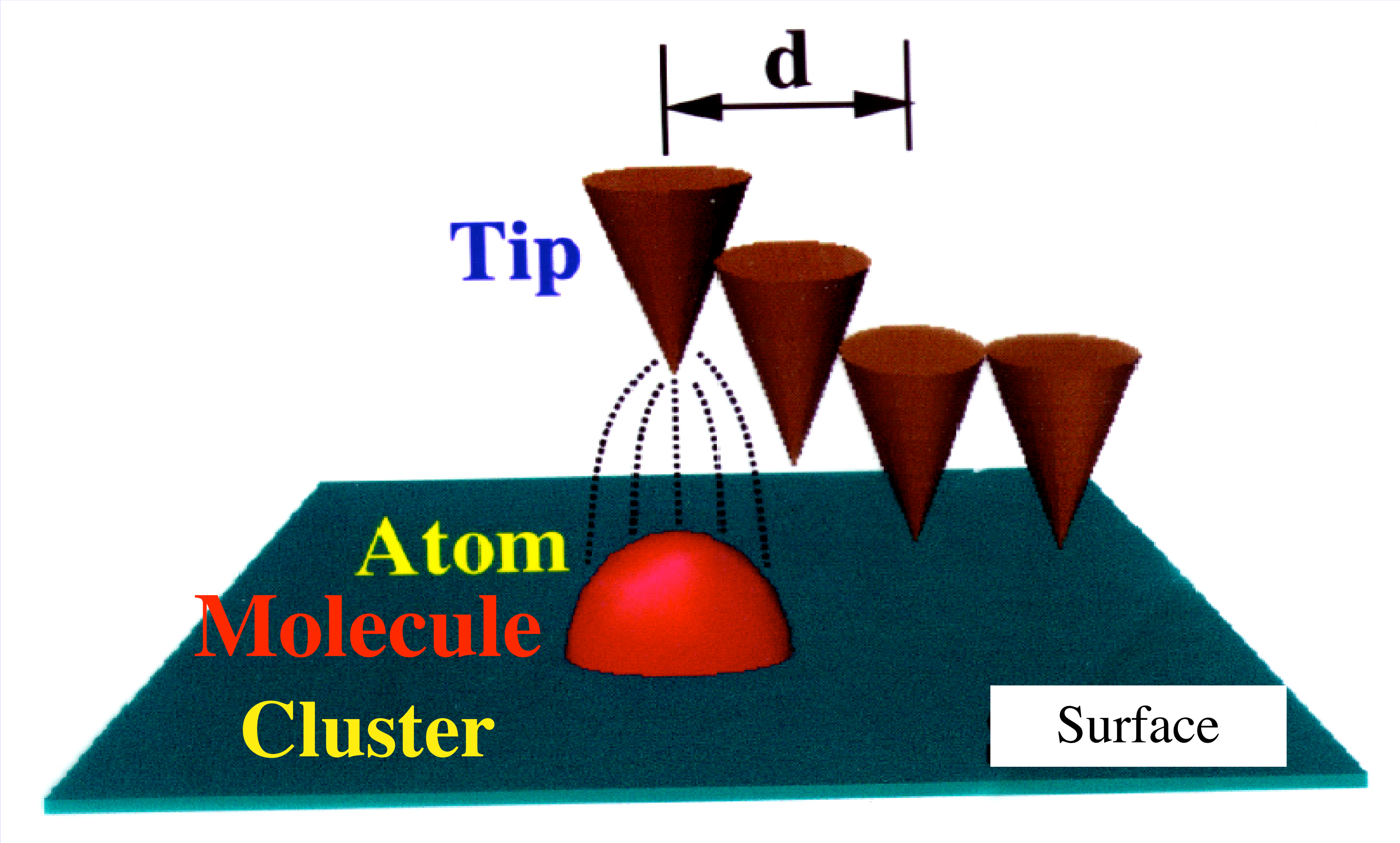
Fig. 2. Examples of dynamic self-assembly. (A) An optical micrograph of a cell with fluorescently labeled cytoskeleton and nucleus; microtubules (~24 nm in diameter) are colored red. (B) Reaction-diffusion waves in a Belousov-Zabatinski reaction in a 3.5-inch Petri dish. (C) A simple aggregate of three millimeter-sized, rotating, magnetized disks interacting with one another via vortex-vortex interactions. (D) A school of fish. (E) Concentric rings formed by charged metallic beads 1 mm in diameter rolling in circular paths on a dielectric support. (F) Convection cells formed above a micropatterned metallic support. The distance between the centers of the cells is ~2 mm. [Image credits: (A) from (*30*); (B) from (*26*); (C) from (*31*)]



Motivation for a local investigation in 2D:

- Driving Force for Self-Assembly of Supramolecular Structures
- Chirality of Single Molecules and of Supermolecules
- Enantiomeric Separation on the Nanoscale
- Chiral Phase Transition in 2D

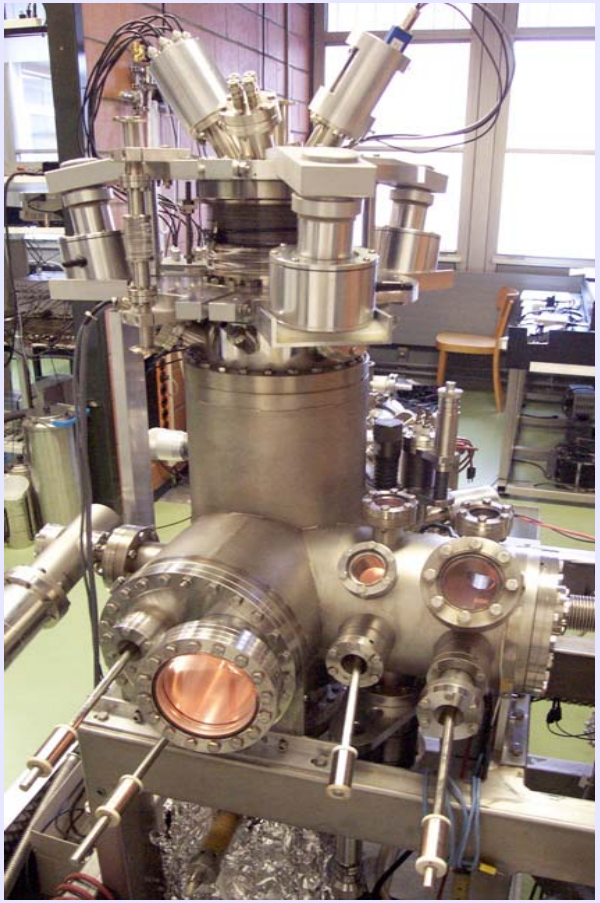
A typical « local » experiment



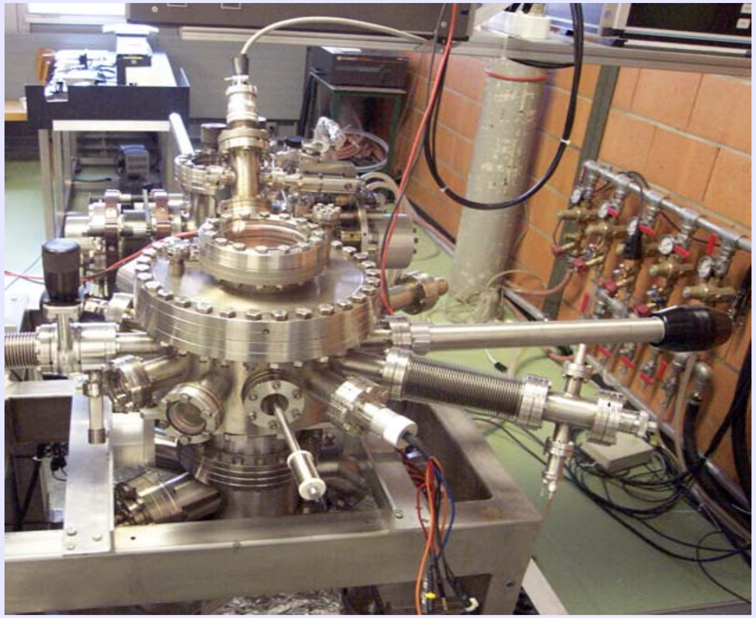
J. Li, PhD Thesis, Lausanne (1997)

Low-temperature STM
(50 K, 4.8 K, 3.9 K)

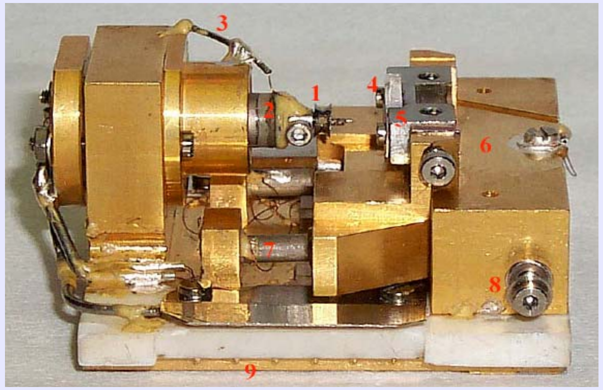
STM chamber



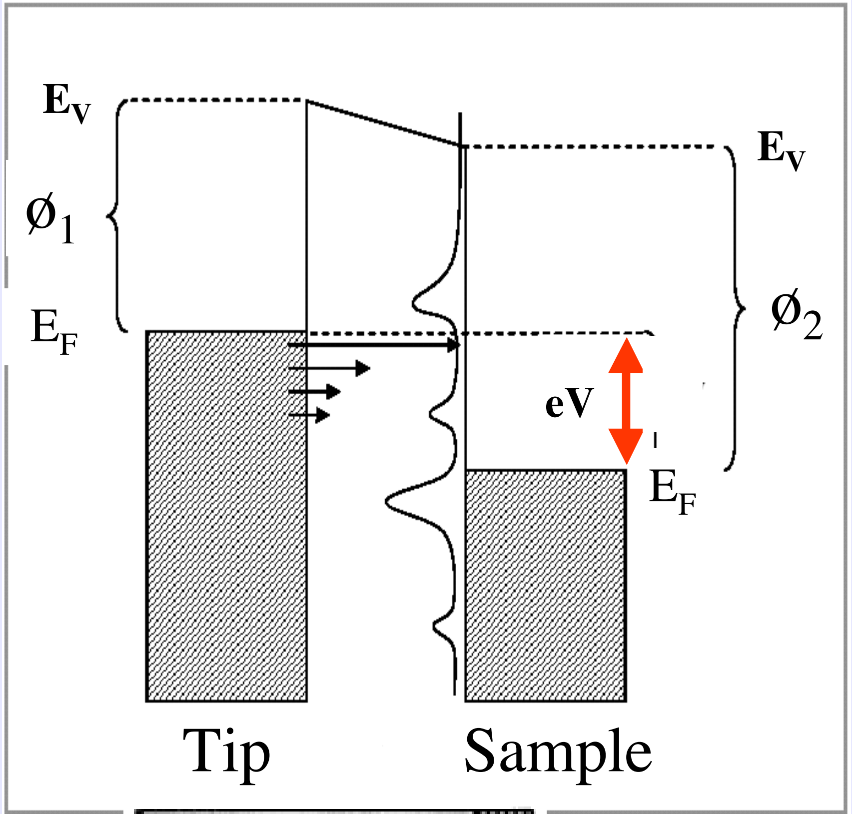
Preparation chamber

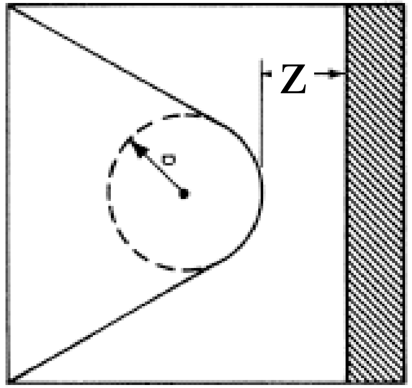


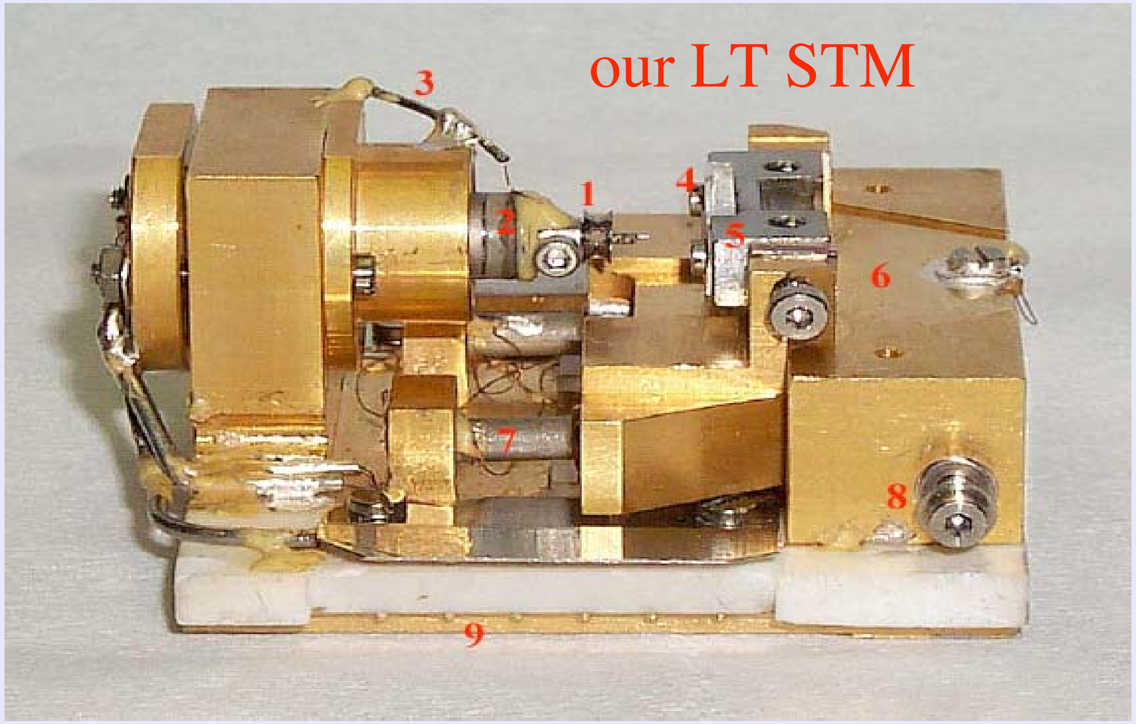
STM head



Scanning probe methods: STM, STS



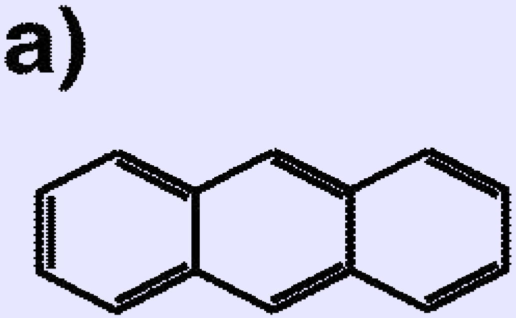




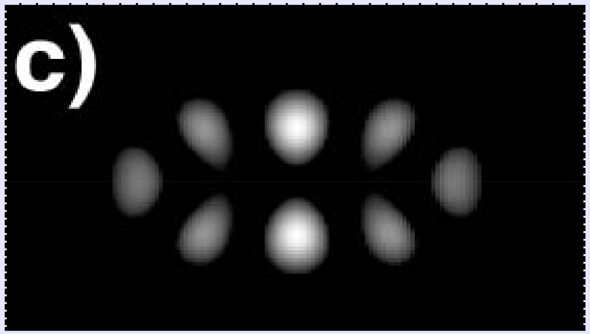
$$I(V) \propto \int_0^{eV} \rho_t(\pm eV \mp E)\, \rho_s(E)\, T(E, eV)\, dE$$

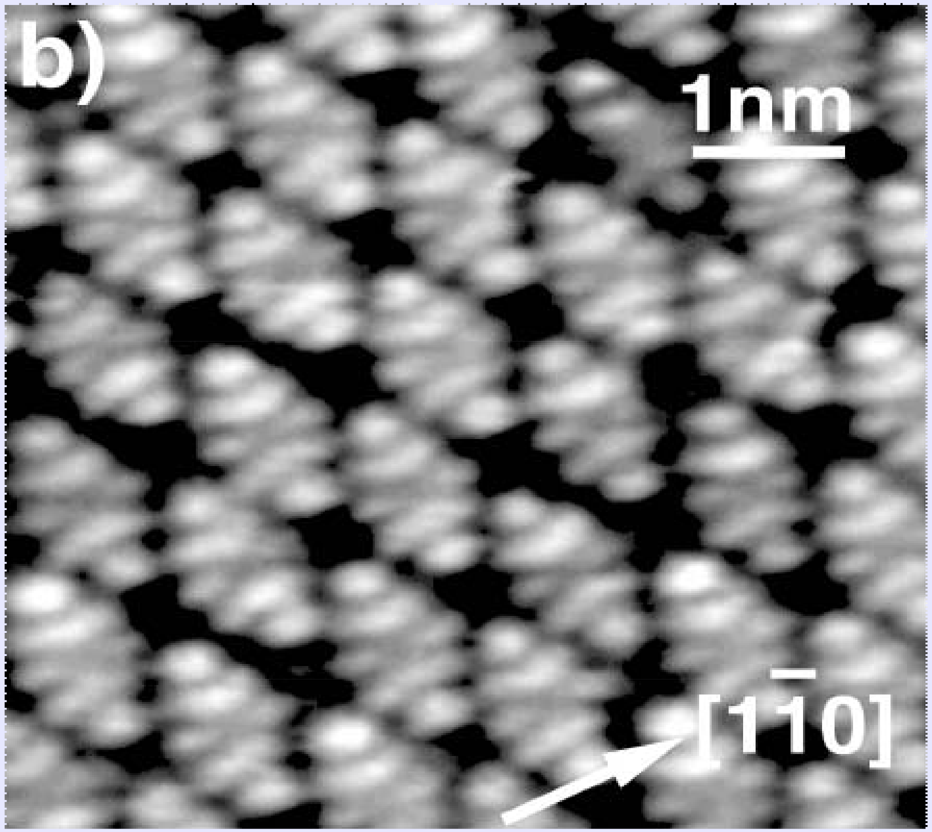
$$\frac{dI}{dV}(V) \propto e\, \rho_t(0)\, \rho_s(eV)\, T(eV, eV)$$

Anthracene on Ag(110)



LUMO at 0.3nm above molecular plane

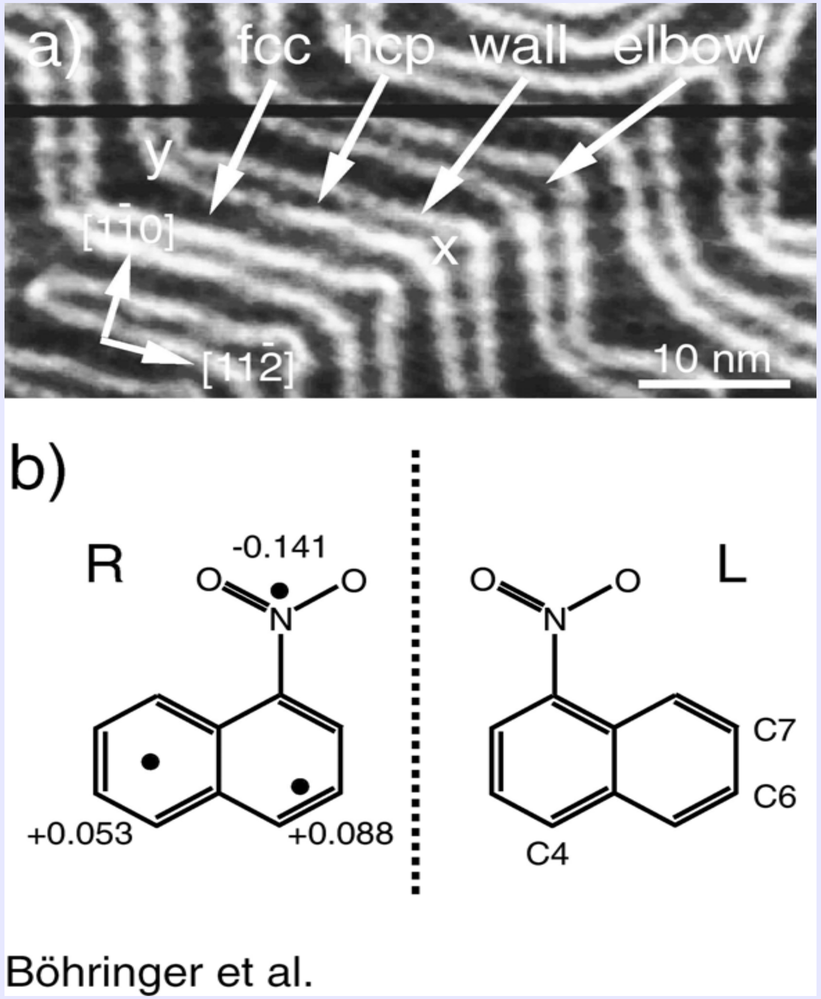




M. Böhringer, WDS, R. Berndt, Surf. Sci. **408**, 72 (1998)

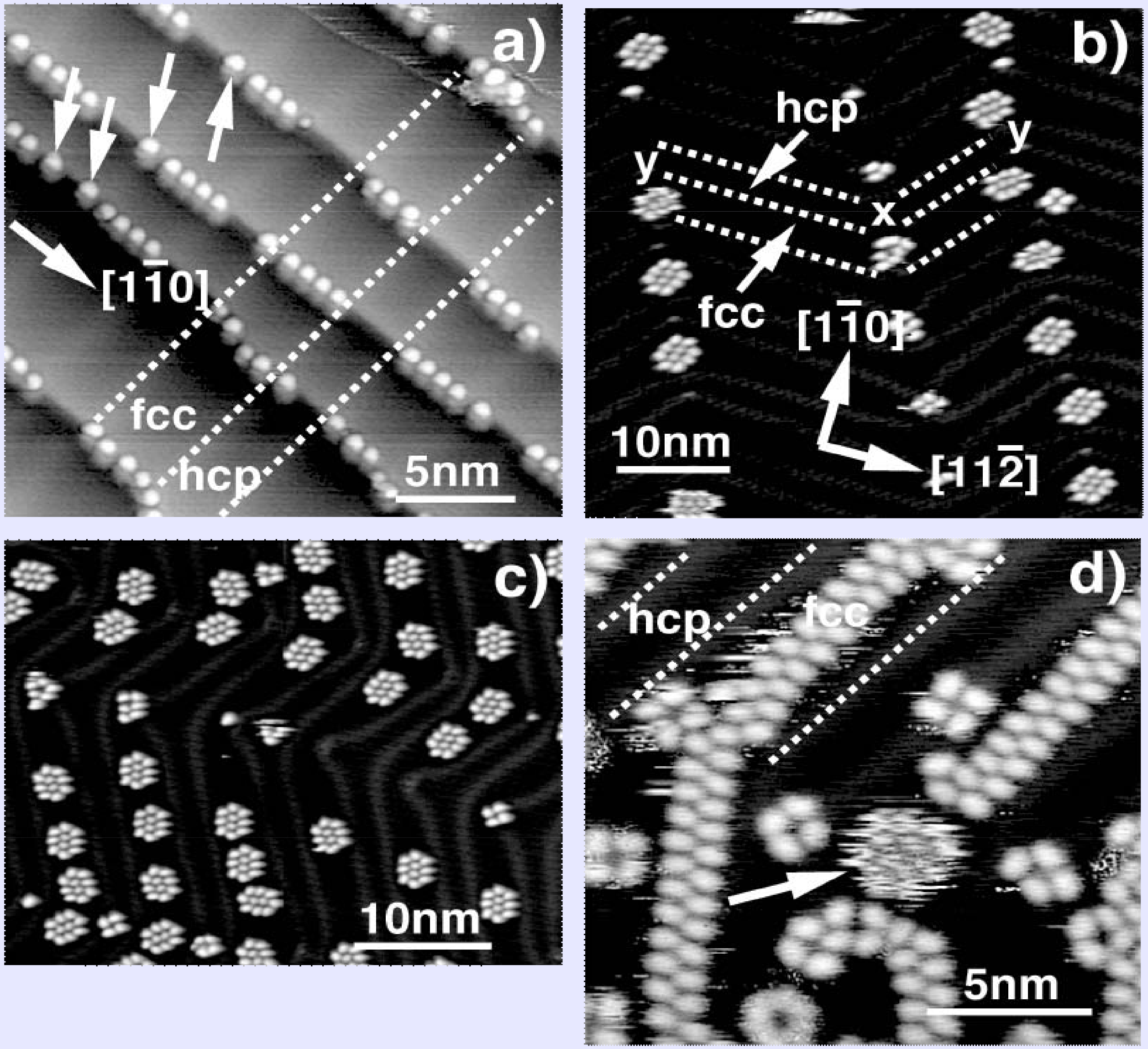
Reconstructed Au(111)

J. V. Barth et al., Phys. Rev. B 42, 9307 (1990)



1-Nitronaphthalene:
2D Chiral

M. Böhringer, K. Morgenstern, WDS, M. Wühn, Ch. Wöll, R. Berndt, Surf. Sci. **444**, 199 (2000)

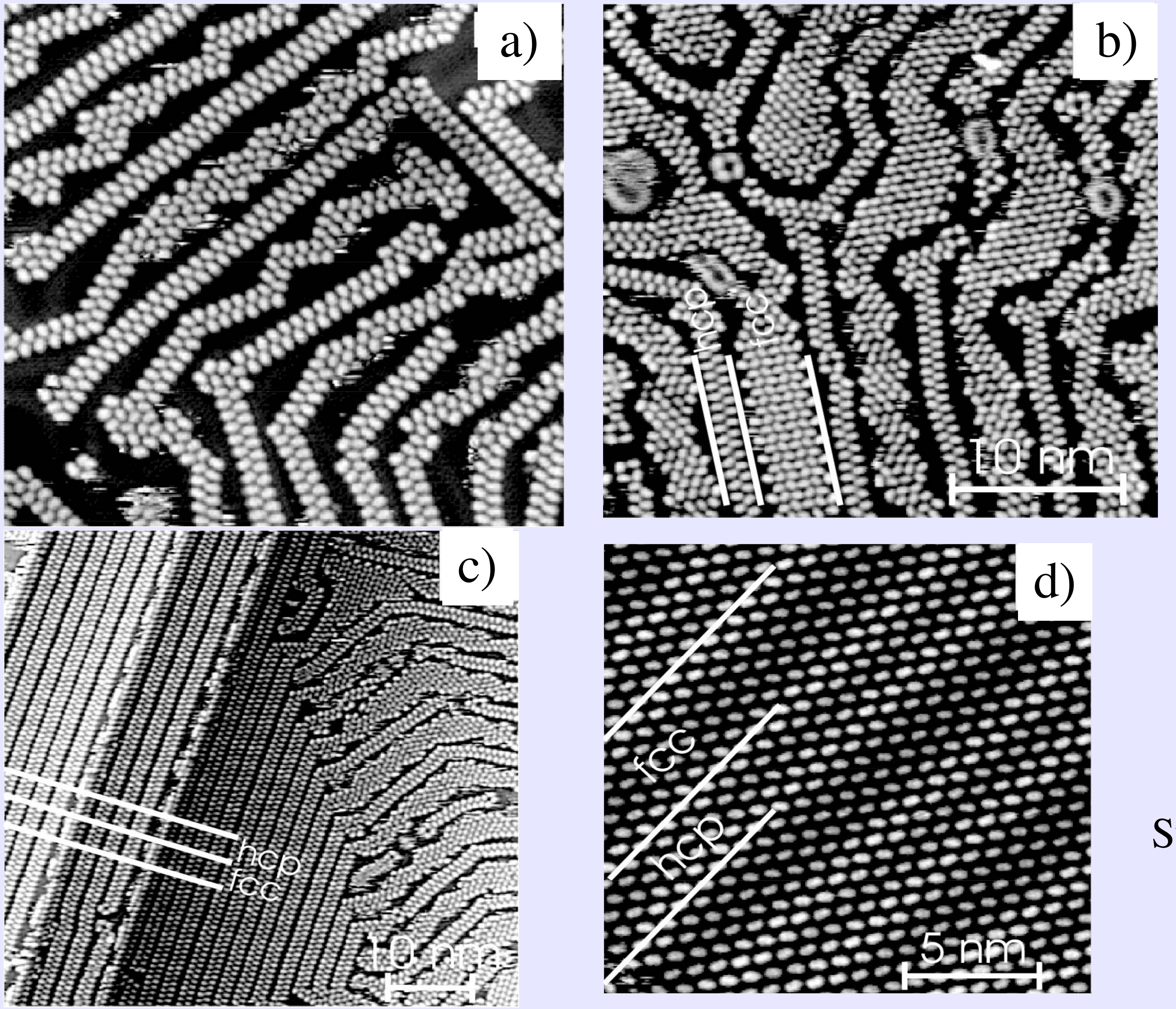


One- and two-dimensional self-assembly of 1-Nitronaphthalene

towards

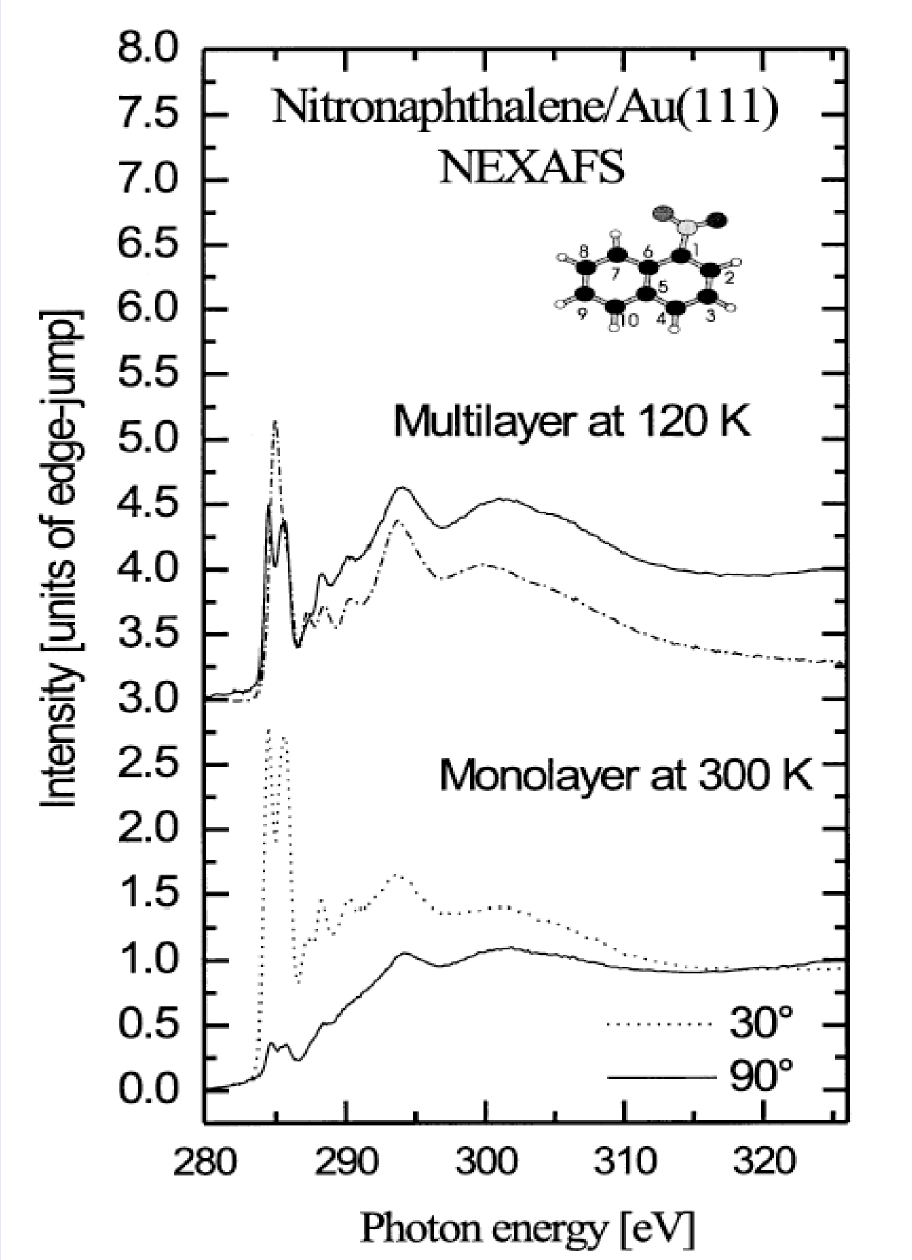
supramolecular chains & clusters

M. Böhringer et al., Surf. Sci. **444**, 199 (2000)



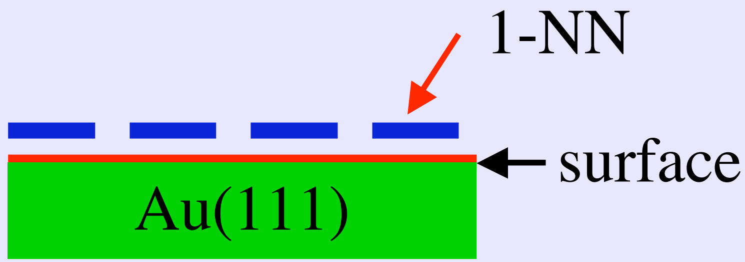
1-NN: Coverage-dependent patterns

M. Böhringer et al.,
Surf. Sci. **444**, 199 (2000)



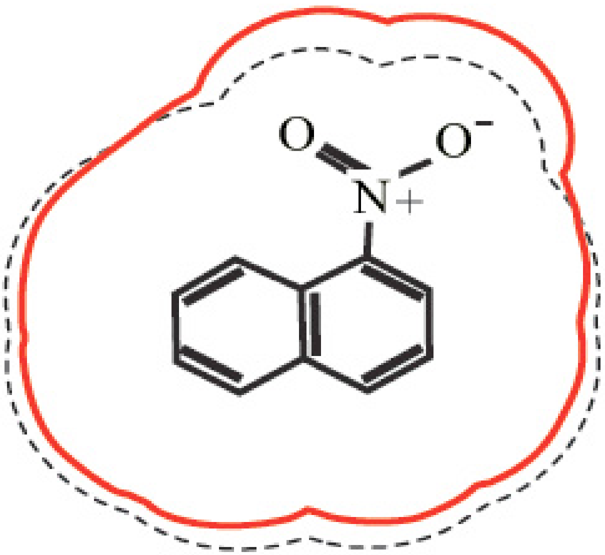
Polarisation dependence:

Molecules are positioned with their π - system parallel to the surface



M. Böhringer et al., Surf. Sci. **444**, 199 (2000)

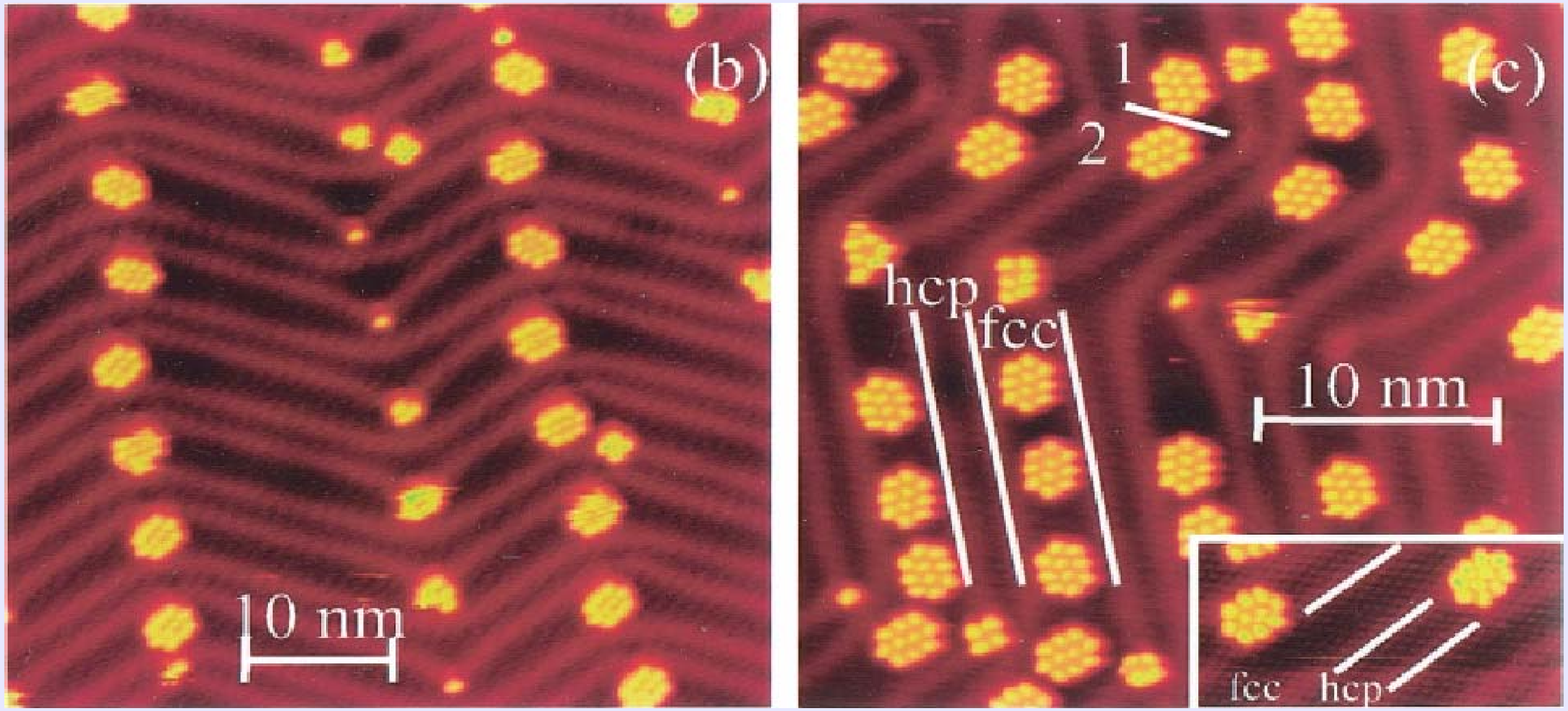
Theory



1-NitroNaphthalene (1-NN)

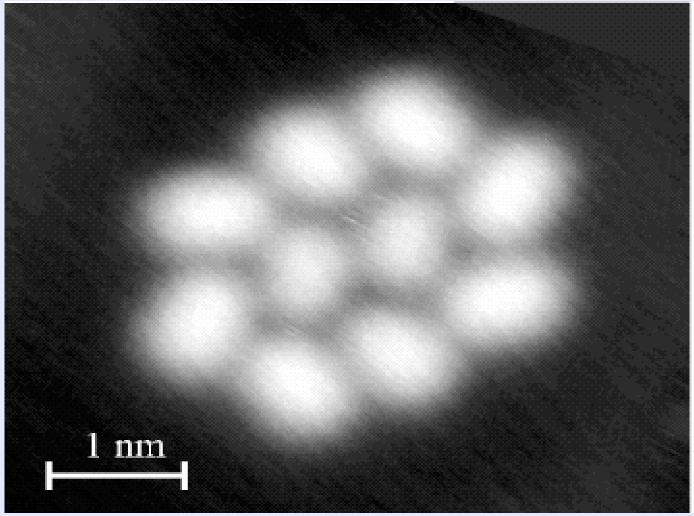
- ❑ Assumptions:
  - ✓ molecules are planar rigid units
  - ✓ physisorbed at 0.35 nm parallel to surface
  - ✓ steric repulsion
  - ✓ electrostatic interaction screened by metallic substrate
  - ✓ neglect atomistic detail of the substrate
- ❑ ab-initio electrostatic potential from Density Functional Calculation
  - ✓ atomic point charges which best fit potential outside exclusion area
- ❑ Molecular Dynamics

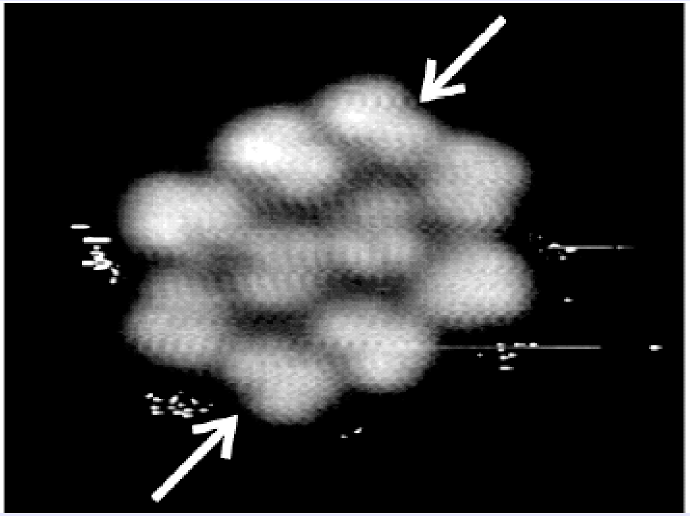
Two-dimensional self-assembly of supramolecular clusters
(1-Nitronaphthalene)

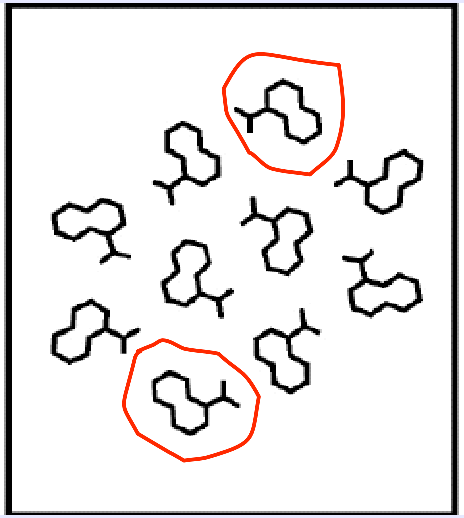


M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

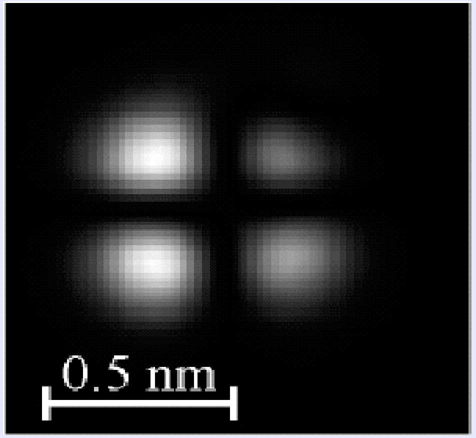
A supramolecular cluster at submolecular resolution

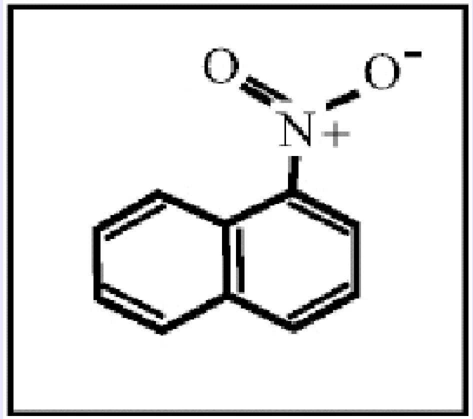






Comparison with theory

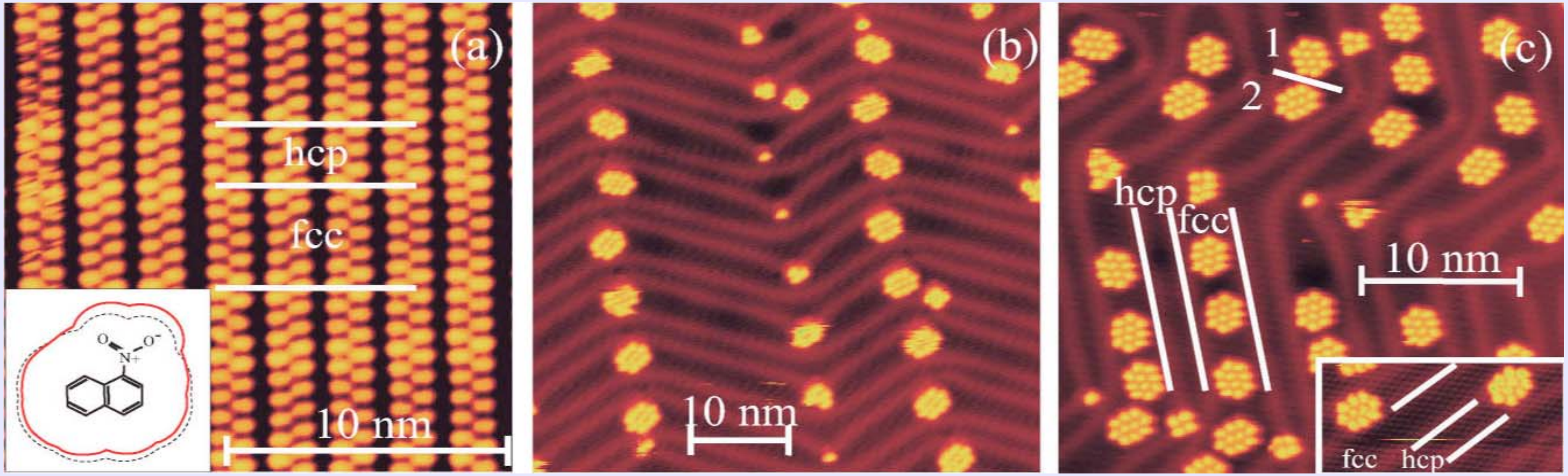




M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

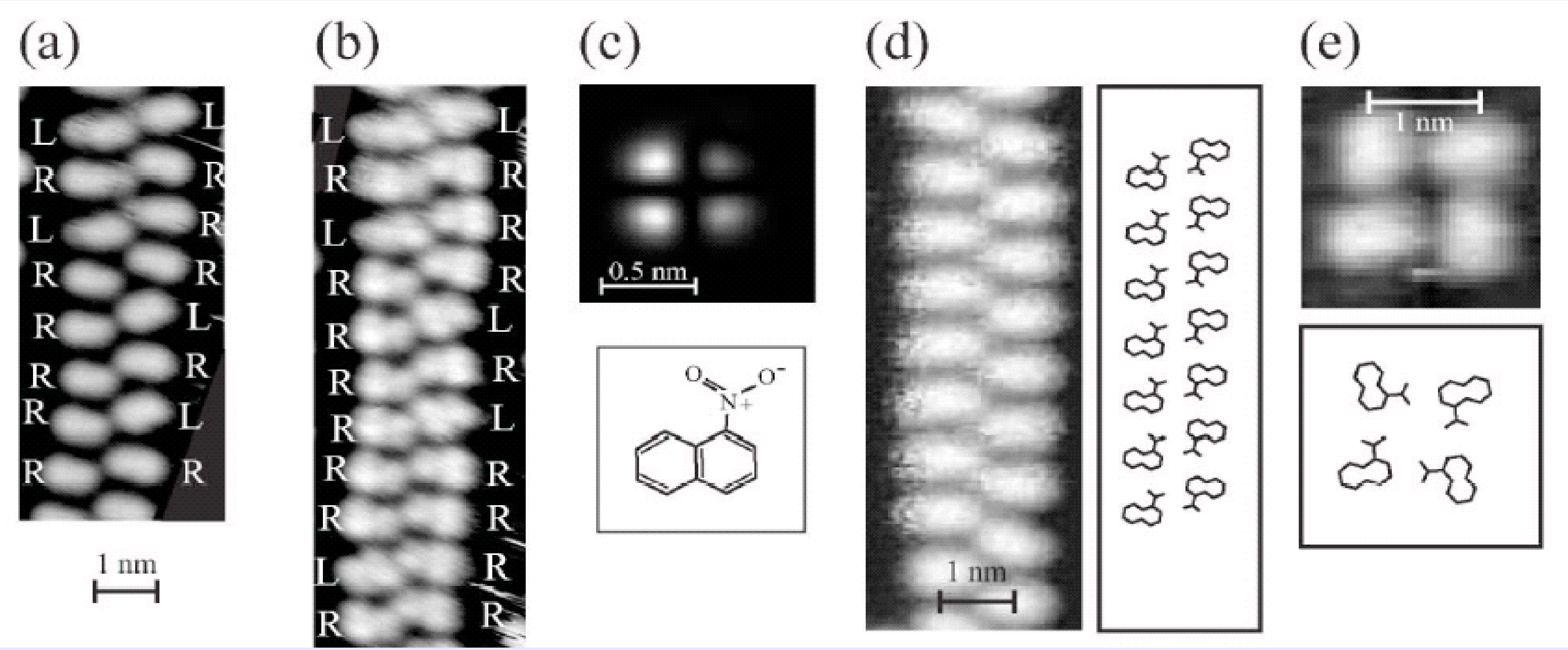
Two-dimensional self-assembly of supramolecular chains & clusters

(1-Nitronaphthalene)



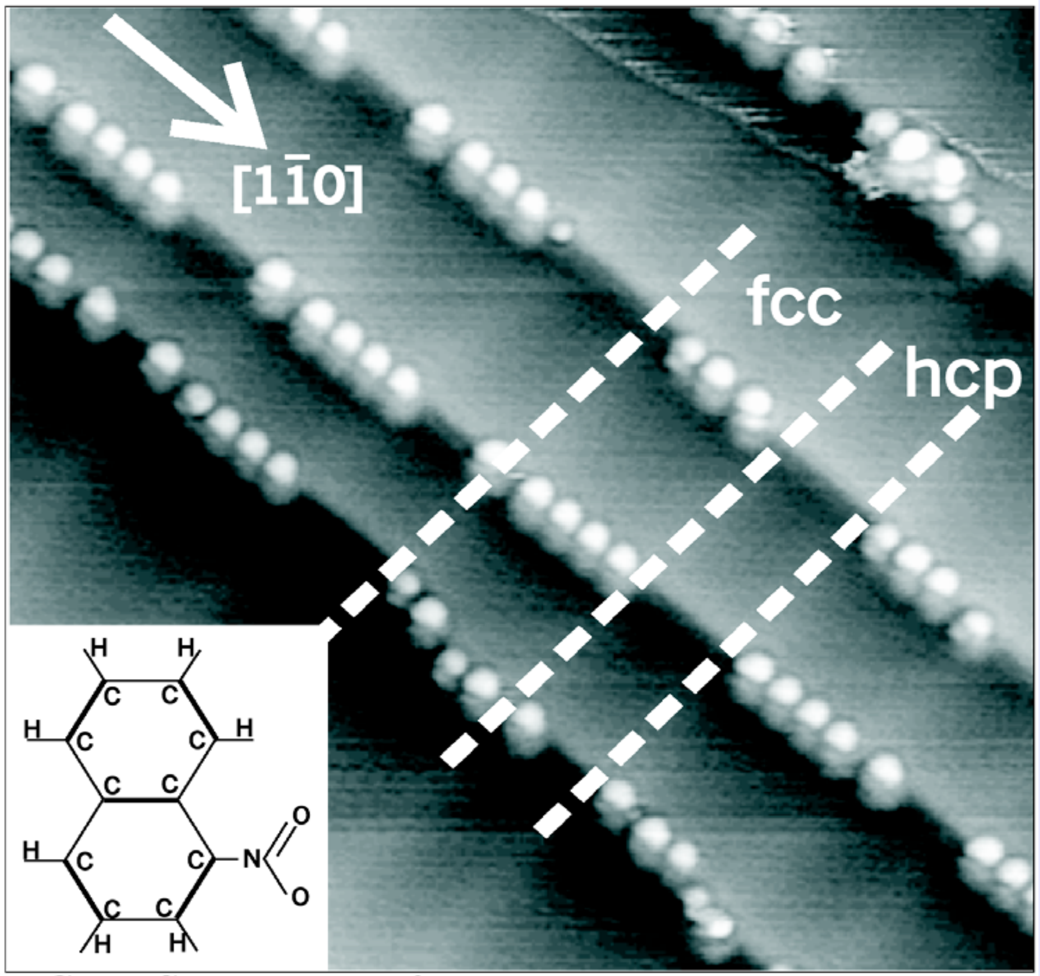
M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

Submolecular resolution of supramolecular chains: Comparison with theory

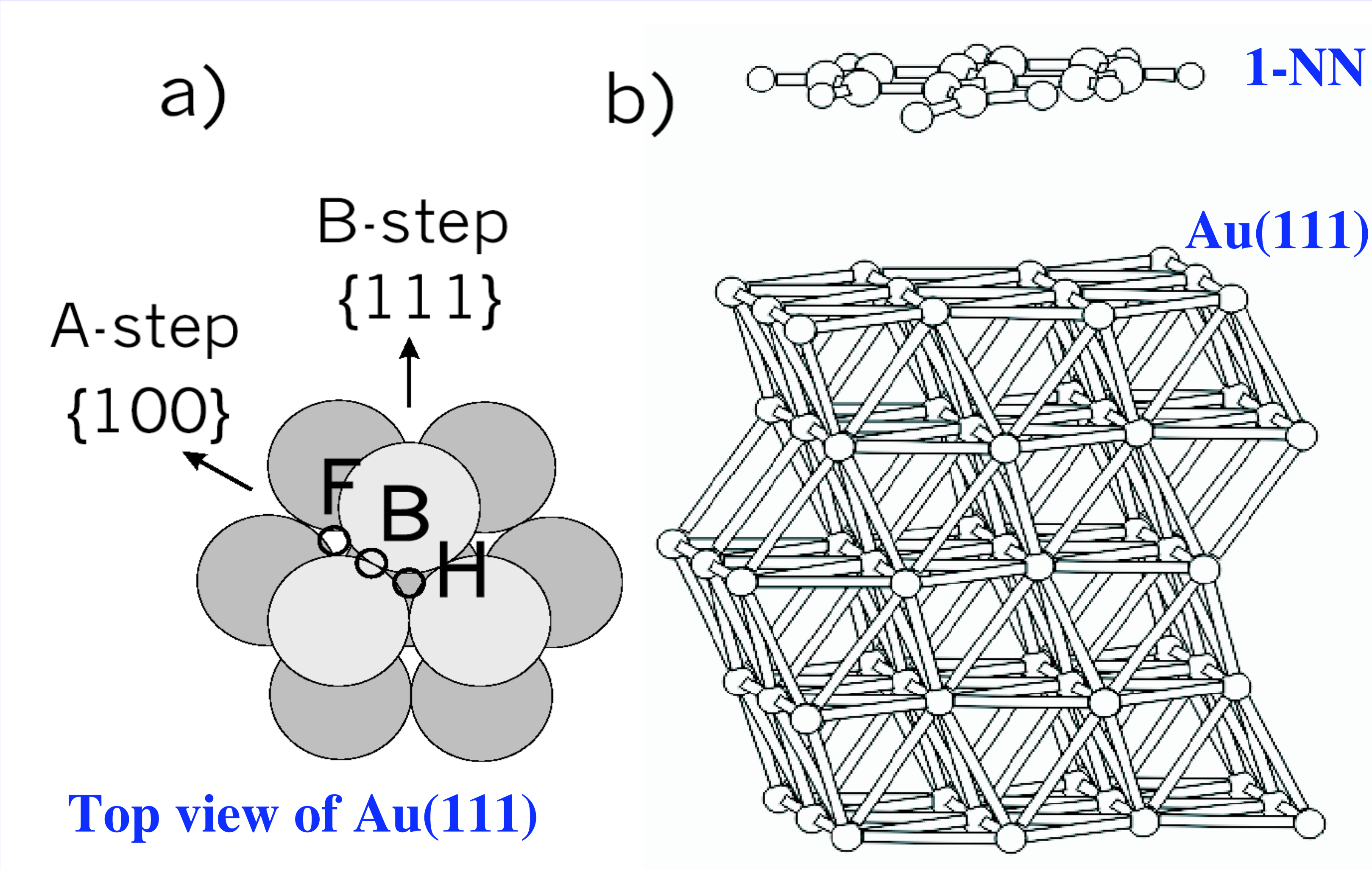


M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

Selective step decoration on Au(111)

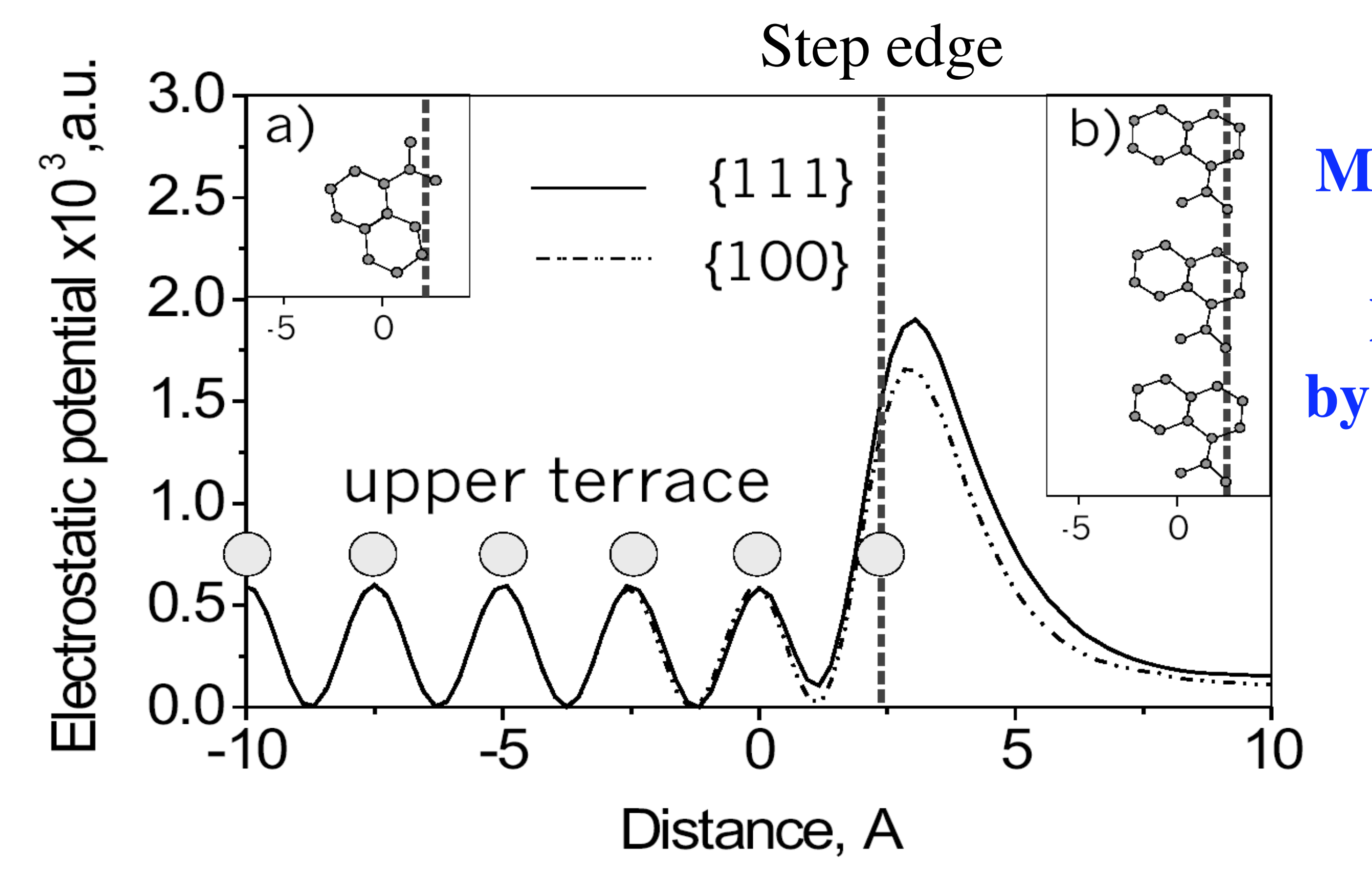


M. Vladimirova, M. Stengel, A. De Vita, A. Baldereschi, M. Böhringer, K. Morgenstern, R. Berndt, WDS, Europhys. Lett. **56**, 254 (2001)



M. Vladimirova, M. Stengel, A. De Vita, A. Baldereschi, M. Böhringer, K. Morgenstern, R. Berndt, WDS, Europhys. Lett. **56**, 254 (2001)

Electrostatic potential of the step at Au(111)



Molecular chain linked by H-bonds

M. Vladimirova, M. Stengel, A. De Vita, A. Baldereschi, M. Böhringer, K. Morgenstern, R. Berndt, WDS, Europhys. Lett. **56**, 254 (2001)

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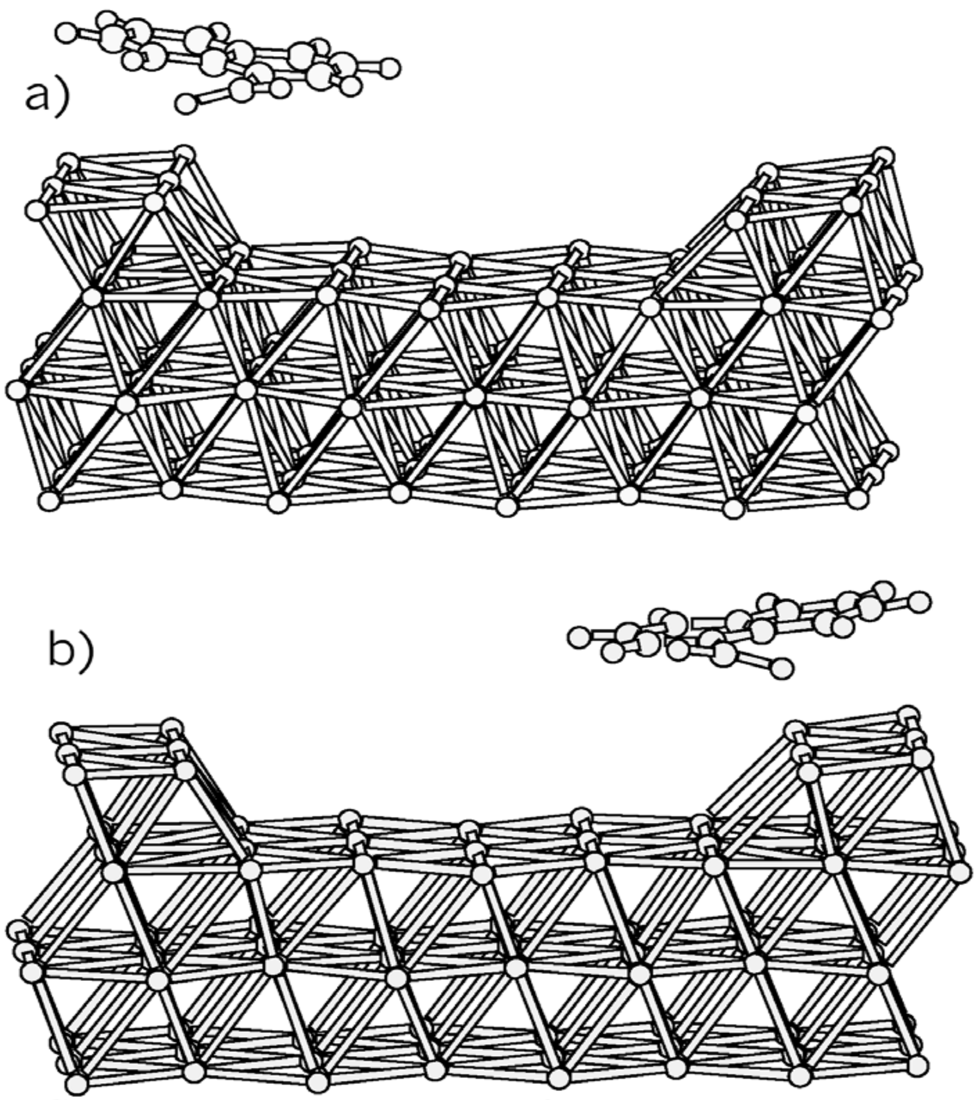
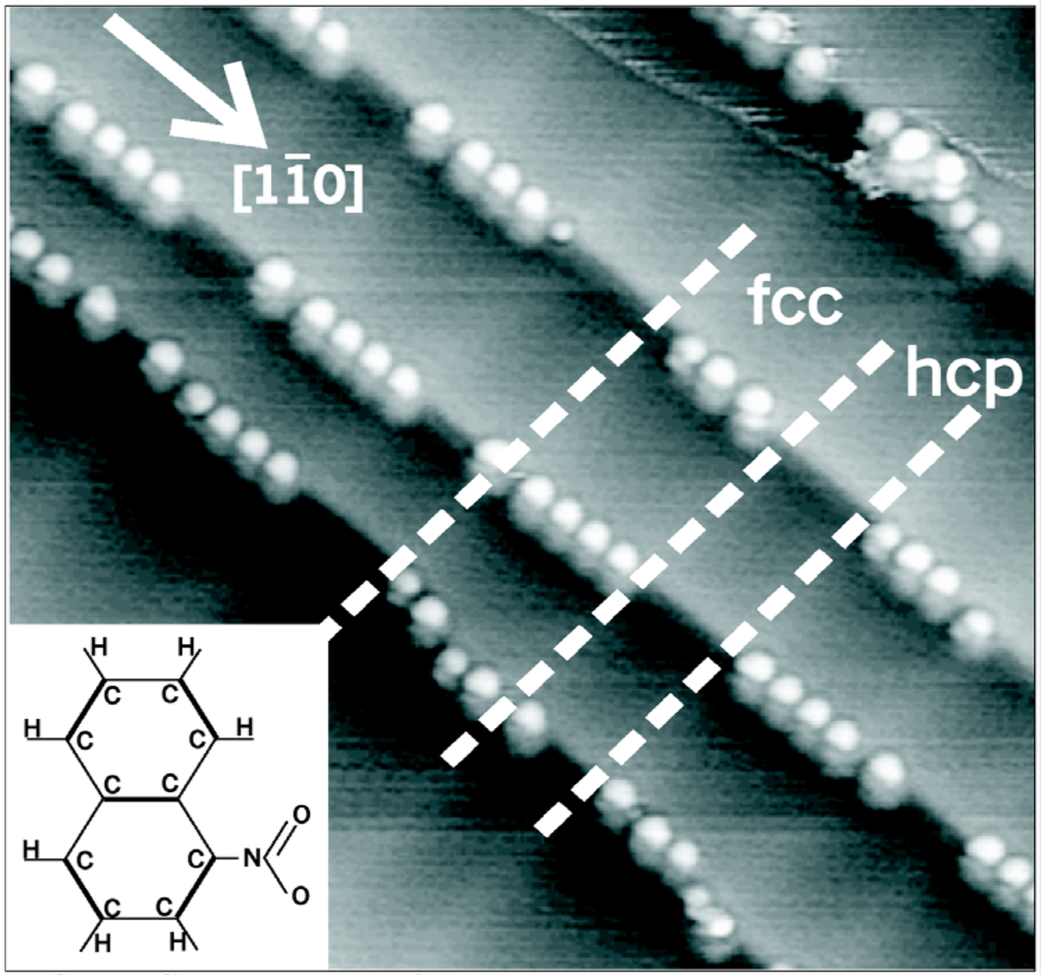
(111) microfacet
step



(100) microfacet
step

M. Vladimirova, M. Stengel, A. De Vita, A. Baldereschi, M. Böhringer, K. Morgenstern, R. Berndt, WDS, Europhys. Lett. **56**, 254 (2001)

Selective step decoration on Au(111)



Adsorption is predicted to be more stable at fcc steps:

Consistent with experimental findings!

M. Vladimirova, M. Stengel, A. De Vita, A. Baldereschi, M. Böhringer, K. Morgenstern, R. Berndt, WDS, Europhys. Lett. **56**, 254 (2001)

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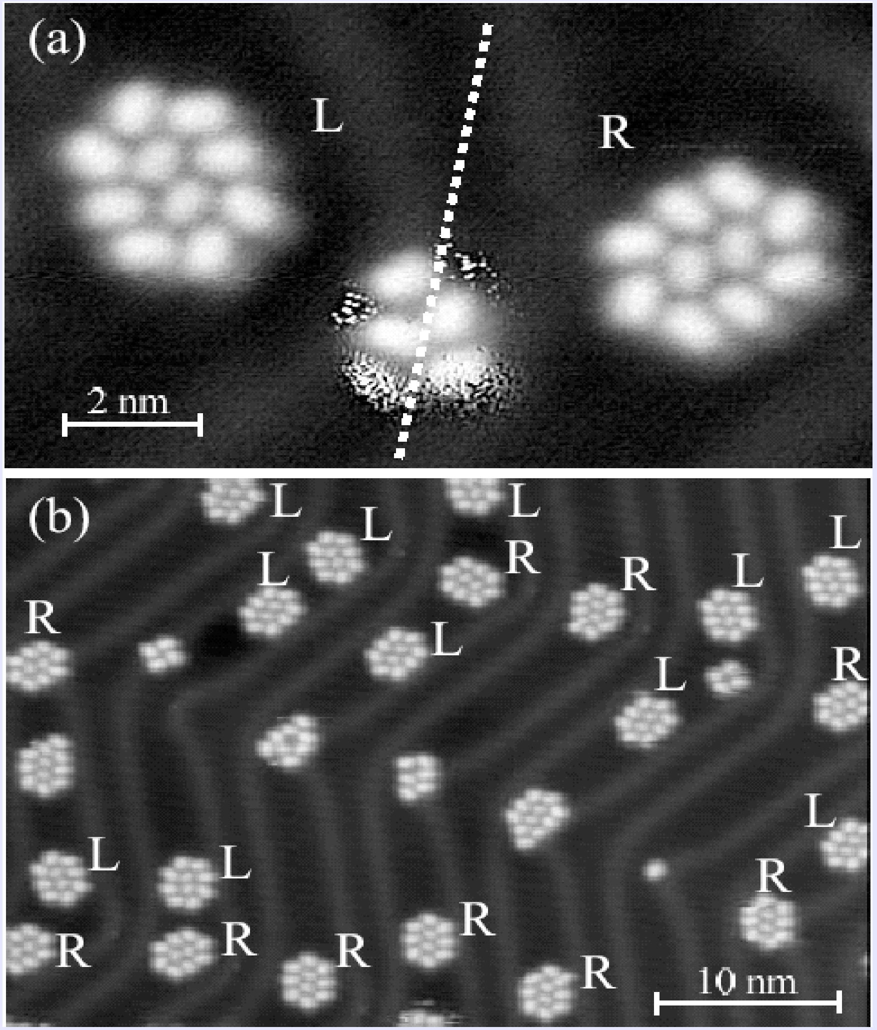
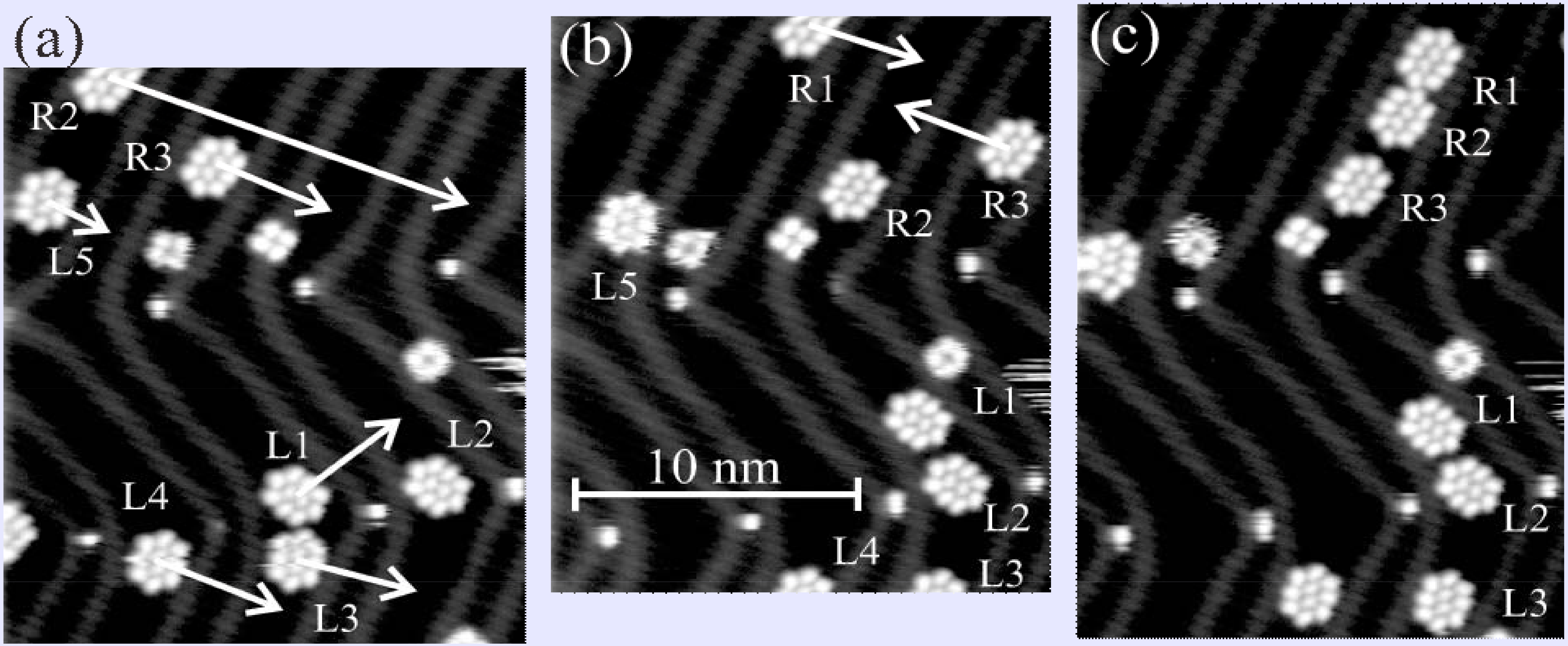
Manipulation of individual supermolecules

Two-dimensional chiral 1-NN decamers



M. Böhringer, K. Morgenstern, WDS, R. Berndt,
Angew. Chem. Int. Ed. **38**, 821 (1999)

Separation of a racemic mixture: Pasteur's experiment on the nanoscale



M. Böhringer, K. Morgenstern, WDS, R. Berndt,
Angew. Chem. Int. Ed. **38**, 821 (1999)

STM tweezes chiral clusters apart

- Just as Louis Pasteur used a light microscope to guide his tweezers to separate sodium ammonium tartrate crystals in 1848, an STM is used both to image and separate chiral decameric clusters of 1-nitronaphthalene.

- This achievement adds separation of enantiomers to the previously developed SPM techniques of atomic-scale manipulation, selective dissociation, conformal analysis, and chiral recognition, as part of the practice of nanochemistry.

Real space observation of a chiral phase transition in a two-dimensional organic layer

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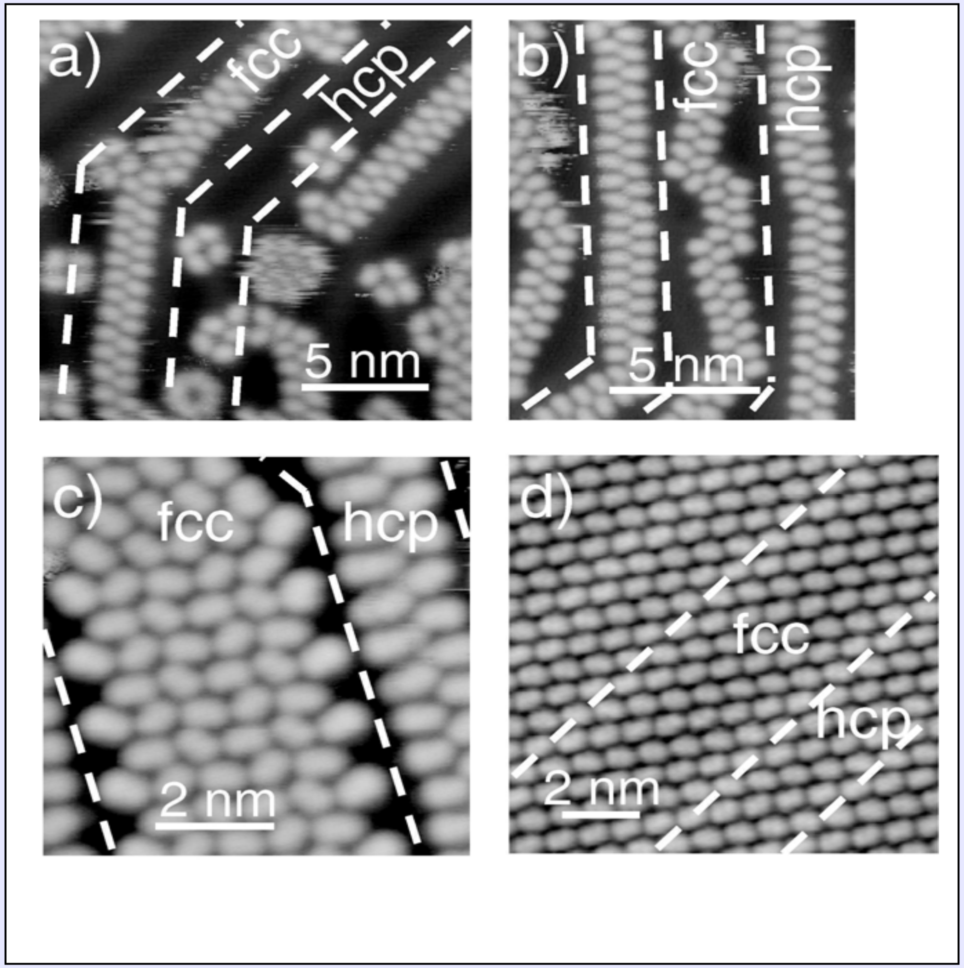
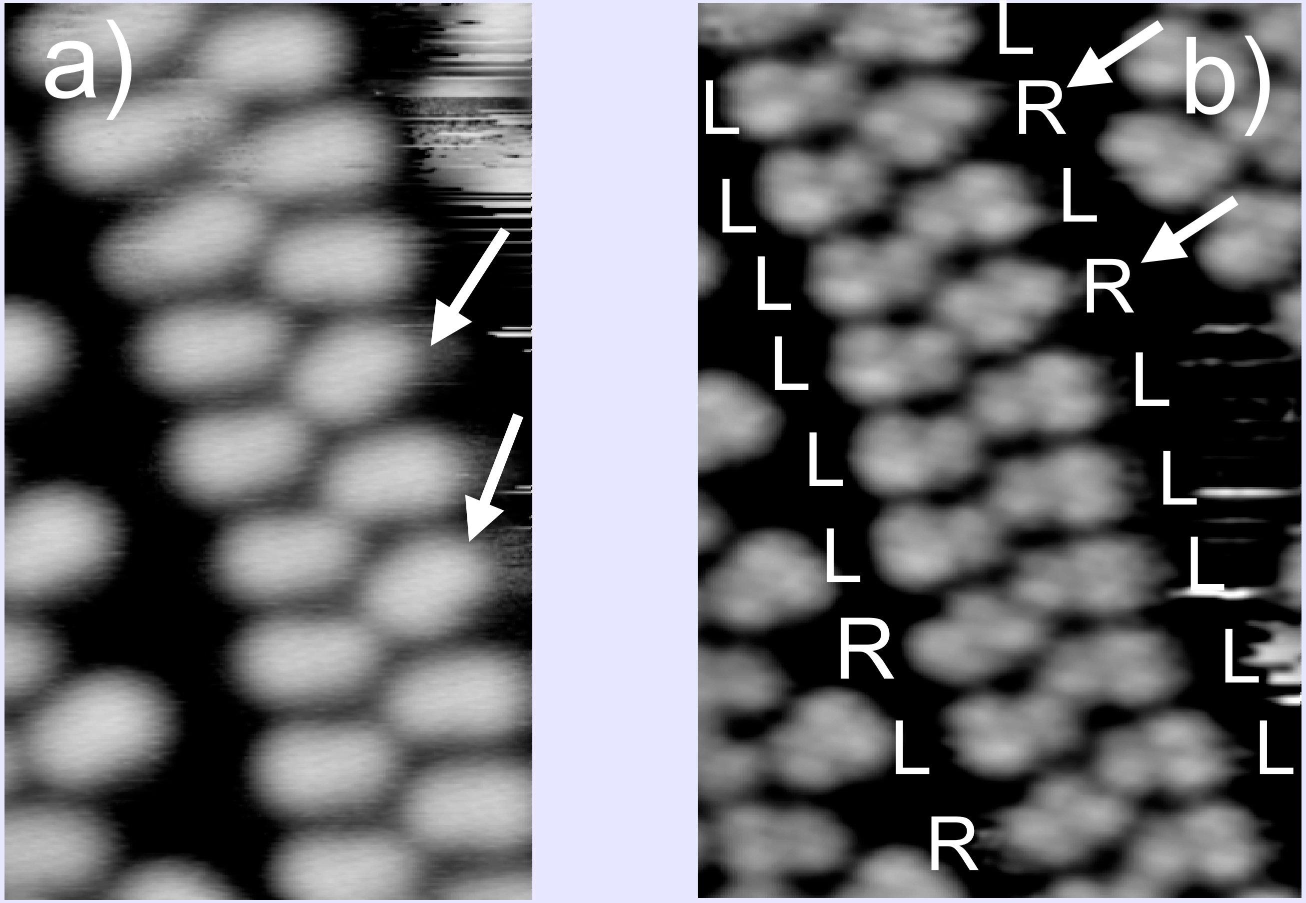
1-NN at 0.3, 0.4 and 1ML



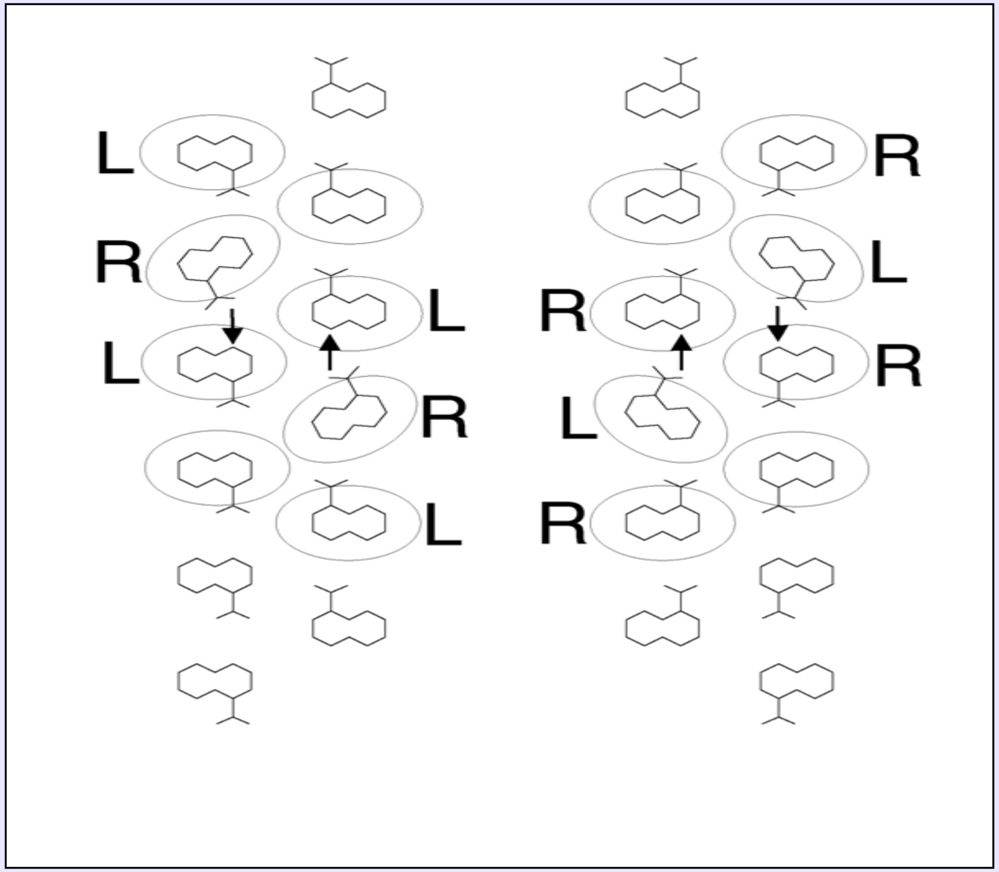
M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

Segment of a 1-NN double chain



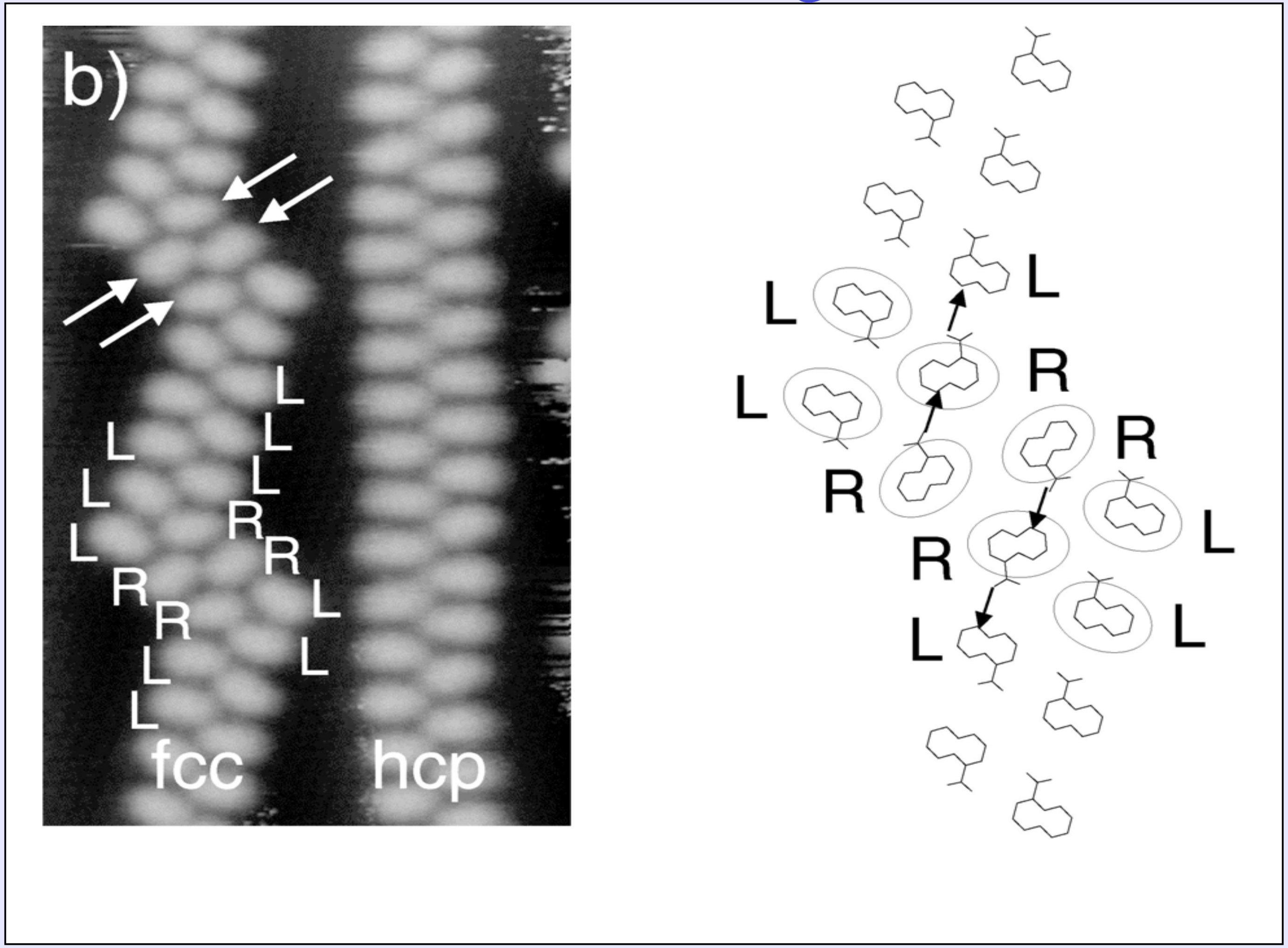
M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

Double chain with chiral defects



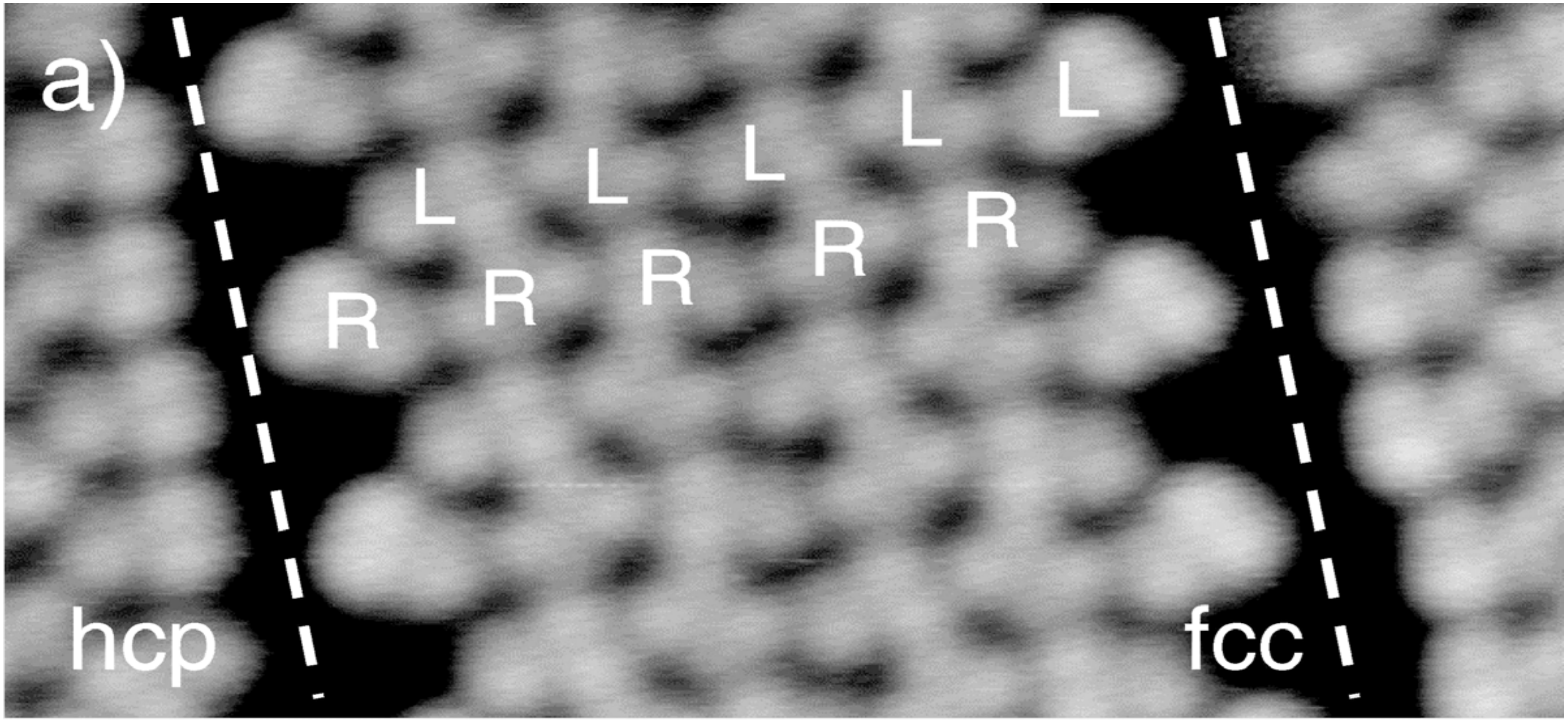
M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

Zig-zag structure within fcc domains (0.4 ML coverage)



M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

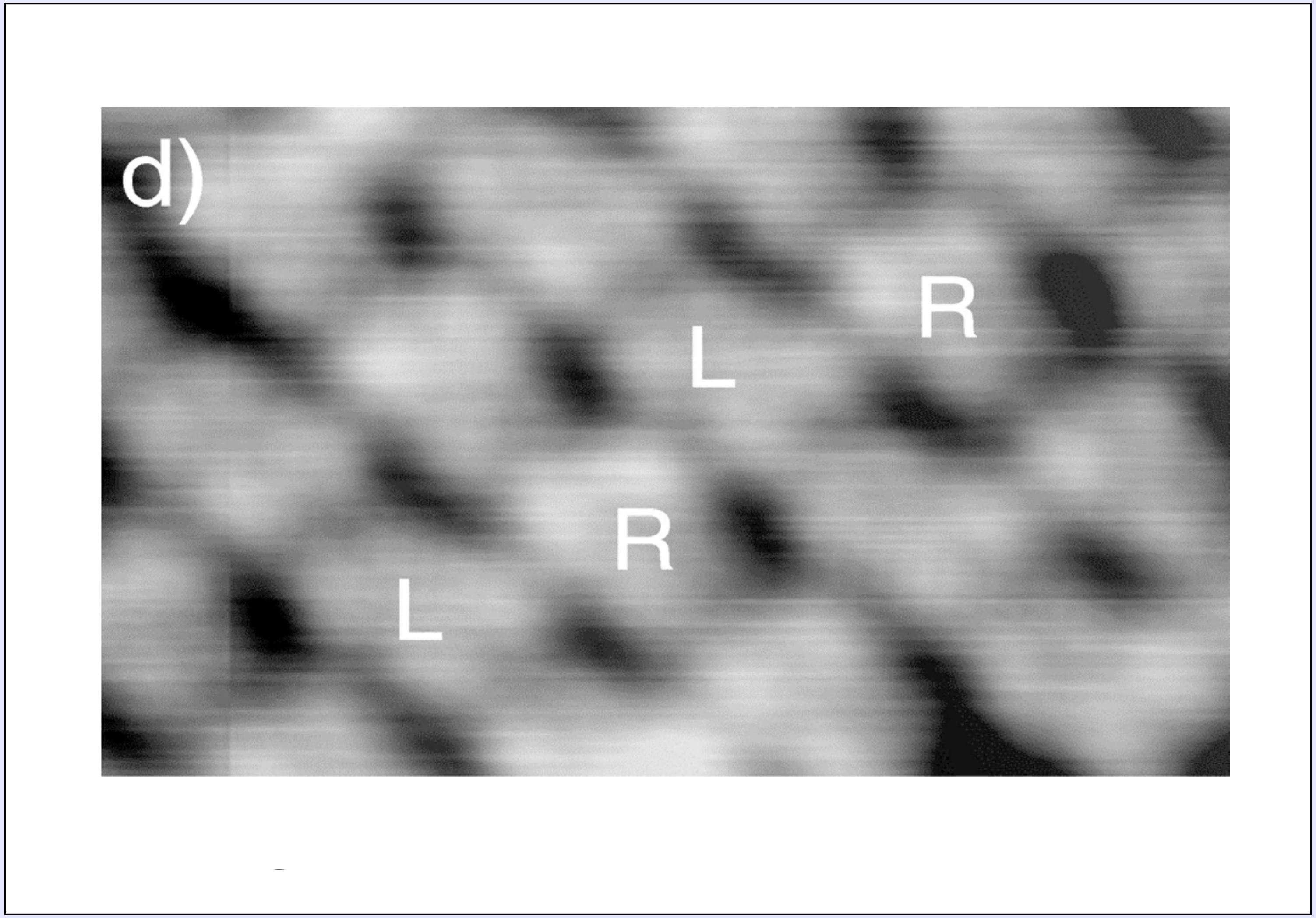
Quasi-1D racemate in fcc domains



Böhringer et al. Angew. Chem. Int. Ed. **39**, 792 (2000)

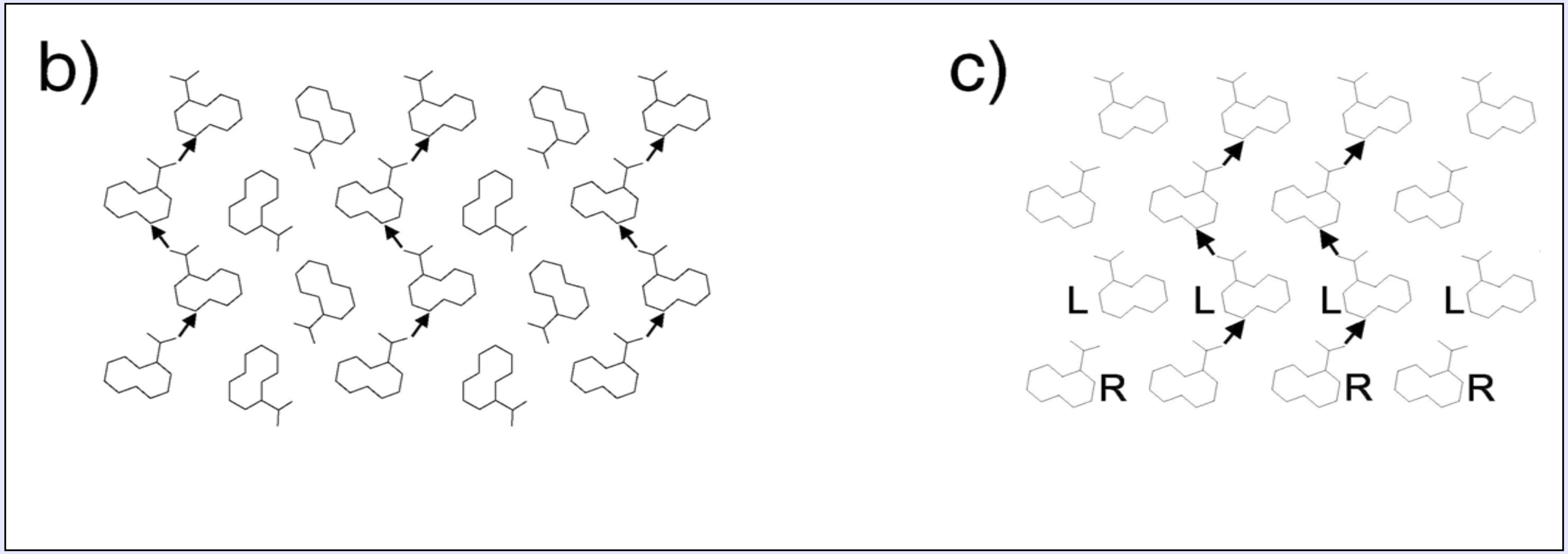
Monolayer Coverage

2D-racemate at monolayer coverage



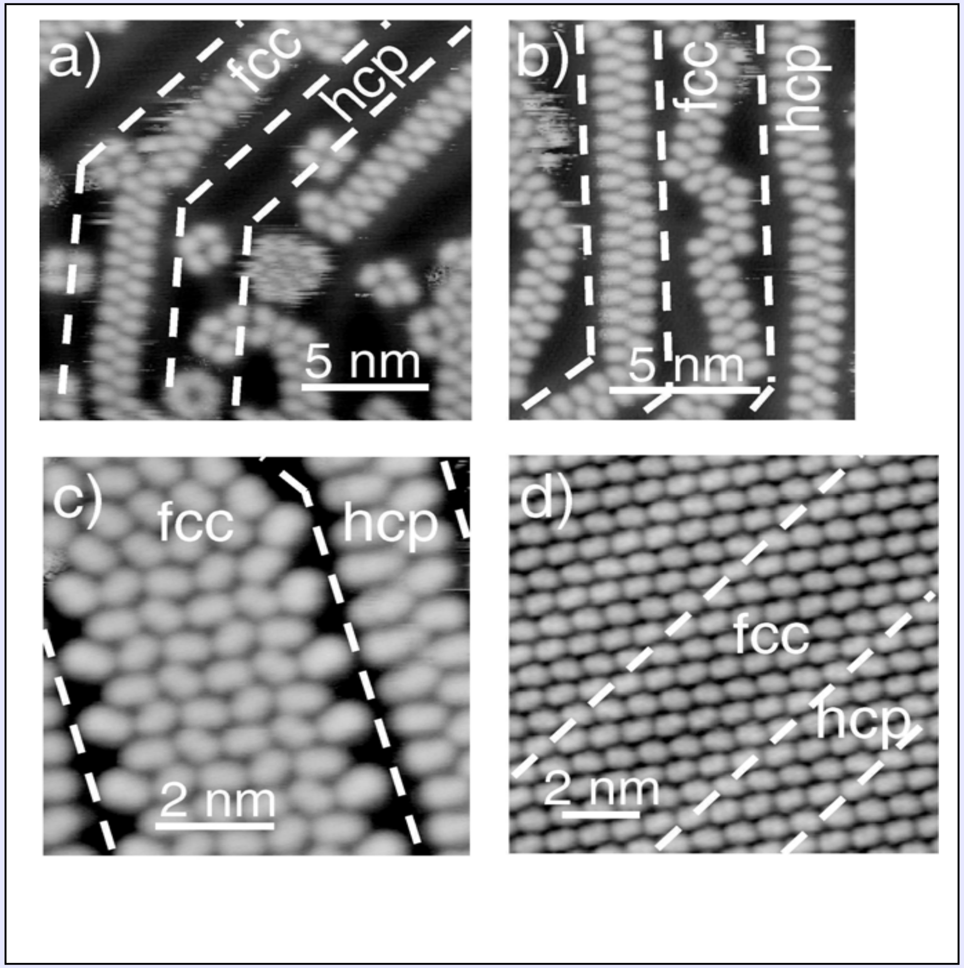
M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

2D periodic racemic structure at monolayer coverage



M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

1-NN at 0.3, 0.4 and 1ML



M. Böhringer, WDS, R. Berndt, Angew. Chem. Int. Ed. **39**, 792 (2000)

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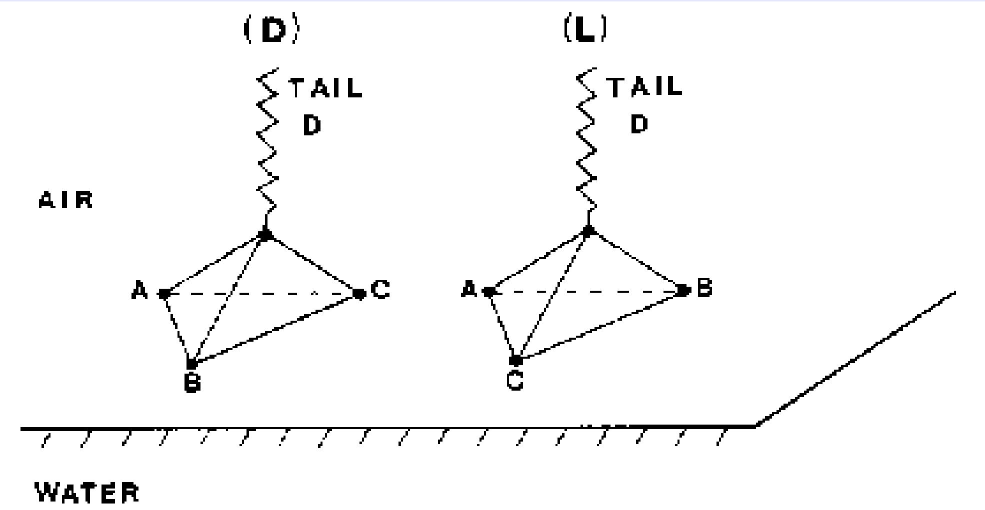
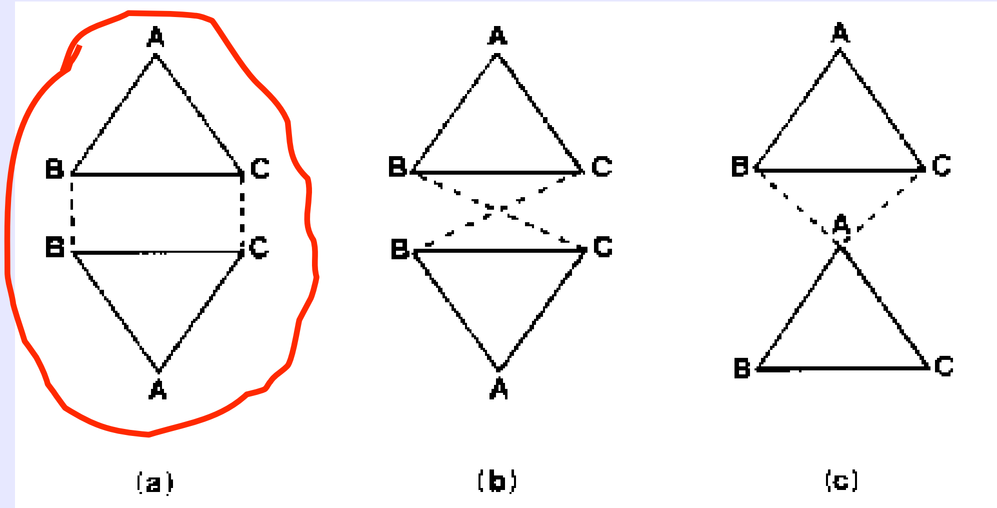
Chiral discrimination and phase transitions in Langmuir monolayers



Tripod amphiphiles



Pair interactions

D. Andelman, P.-G. de Gennes, C. R. Acad. Sci.(Paris) **307(II)**, 233 (1988)
D. Andelman, J. Am. Chem. Soc. **111,** 6536 (1989)

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Partition function:

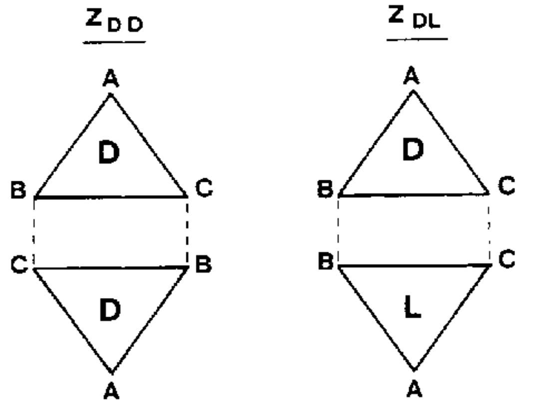


Figure 7. One of the nine orientations used to calculate Z_{DD} and Z_{DL}.

$$Z_{DD} = Z_{LL} = f_{BC}^2 + f_{AB}^2 + f_{CA}^2 + 2f_{CC}f_{AB} + 2f_{BB}f_{CA} + 2f_{AA}f_{BC} \quad (1)$$

where $f_{ij} = \exp(-V_{ij}/k_B T)$, and V_{ij} is the interaction between the two groups i, j (i, j = A, B, or C) of the two molecules; T is the temperature and k_B the Boltzmann constant. Similarly, for a pair of different enantiomers, D and L

$$Z_{DL} = Z_{LD} = f_{AA}f_{BB} + f_{BB}f_{CC} + f_{CC}f_{AA} + 2f_{AB}f_{BC} + 2f_{BC}f_{CA} + 2f_{CA}f_{AB} \quad (2)$$

The chiral discrimination parameter is conveniently defined as $\Delta = Z_{DD} - Z_{DL}$. From (1) and (2)

$$\Delta = f_{BC}^2 + f_{AB}^2 + f_{CA}^2 - f_{AA}f_{BB} - f_{BB}f_{CC} - f_{CC}f_{AA} + 2f_{CC}f_{AB} + 2f_{BB}f_{CA} + 2f_{AA}f_{BC} - 2f_{AB}f_{BC} - 2f_{BC}f_{CA} - 2f_{CA}f_{AB} \quad (3)$$

Depending on the sign of Δ, two cases are distinguished: if $\Delta > 0$, the homochiral interactions, D–D and L–L, are larger than the heterochiral one, D–L, and there is a tendency for chiral segregation. This is the homochiral case (HOC). On the other hand, $\Delta < 0$ is the heterochiral case (HEC), where chiral segregation is disfavored. We discuss now some specific examples

$\Delta > 0$ HOC

$\Delta < 0$ HEC

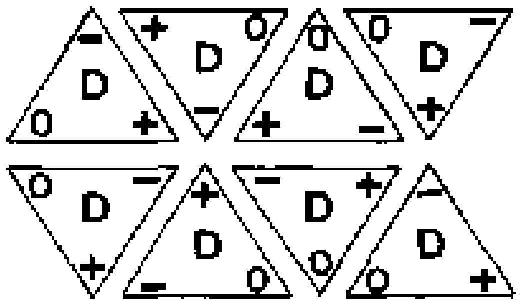
D. Andelman, P.-G. de Gennes, C. R. Acad. Sci.(Paris) **307(II)**, 233 (1988)

D. Andelman, J. Am. Chem. Soc. **111,** 6536 (1989)

Chiral discrimination and phase transitions in Langmuir monolayers

Chiral Discrimination in Langmuir Monolayers

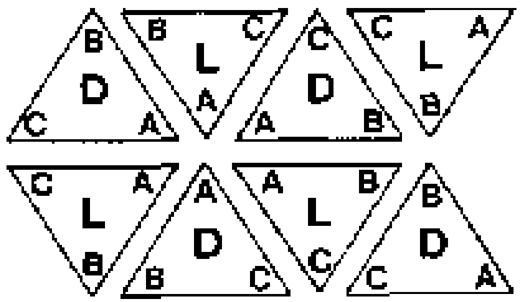
Homochiral



Pure electrostatic interactions

Figure 8. HOC ground-state arrangement for case 4 of section V.

Heterochiral



Intermolecular interactions between the same group

Figure 9. HEC ground-state arrangement for case 5 of section V. Nearest-neighbor groups are always the same.

D. Andelman, P.-G. de Gennes, C. R. Acad. Sci. (Paris) **307(II)**, 233 (1988)

D. Andelman, J. Am. Chem. Soc. **111,** 6536 (1989)

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Chiral Phase Transition in 2D

From conglomerate (pure enantiomer) at low coverage:

(homochiral chains → zig-zag segments of opposite chirality in fcc

→ homochiral in hcp domains)

towards a racemate (1:1 (L, R)) at high coverage:

(at 1 ML a 2D periodic racemic structure unstable with respect

to decay into a 2D racemate in fcc

and a 1D conglomerate in hcp)

Driving force : electrostatic

adsorption strength

Andelman & De Gennes:

For tripod amphiphiles: purely electrostatic interaction

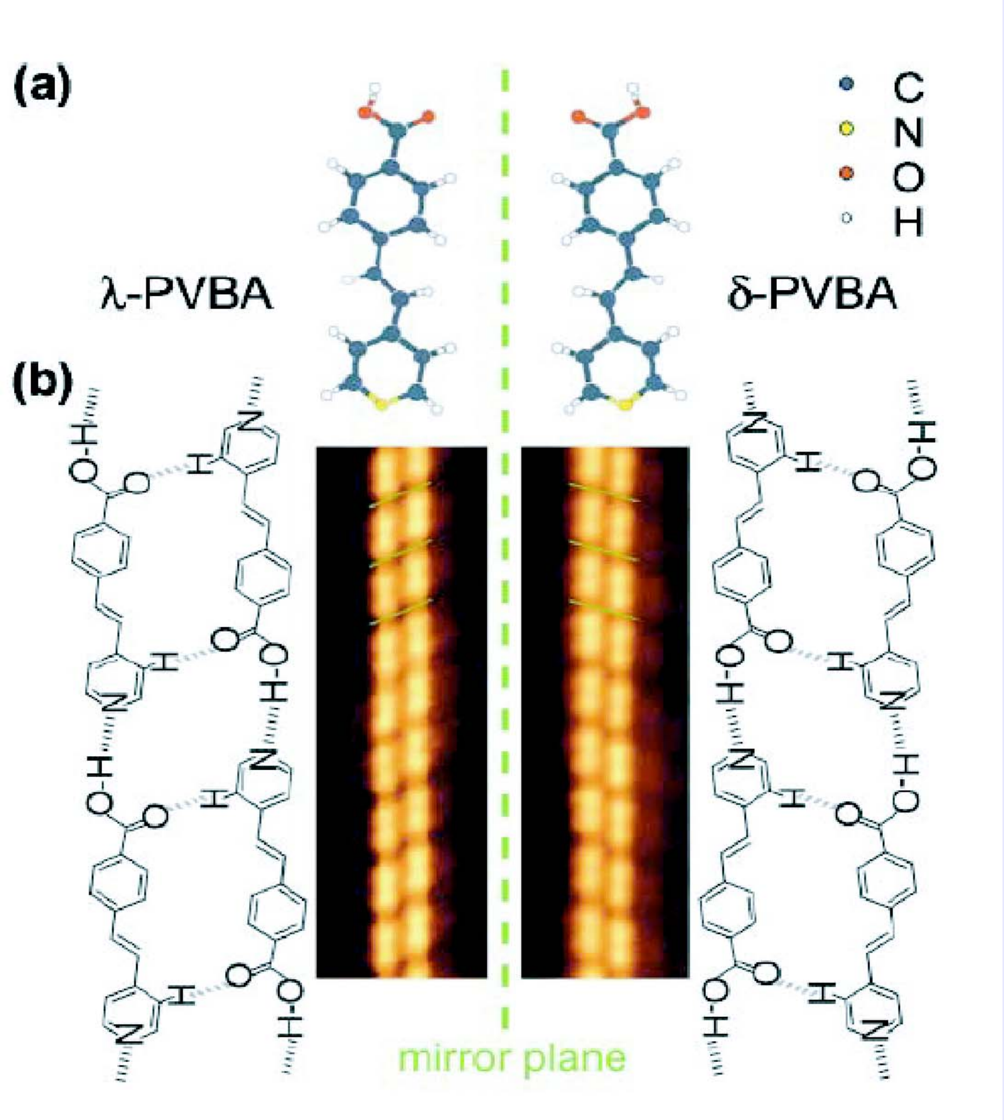
favours pure enantiomers

Conclusions

STM observations and modeling ⇨

- Stability, chirality, and arrangement of 2D self-assembled supramolecular structures
- Chirality of single molecules and decamers
- Chiral phase transition in 2D

Chirality upon confinement to two dimensions: Two possible supramolecular chiral twin chains from self-assembly of PVBA on Ag(111)



J. Weckesser, A. DeVita, J. V. Barth, C. Cai, K. Kern, PRL **87**, 096101 (2001)

Selective assembly on a surface of supramolecular aggregates with controlled size and shape

Takashi Yokoyama*, Shiyoshi Yokoyama†, Toshiya Kamikado†, Yoshishige Okuno† & Shinro Mashiko†

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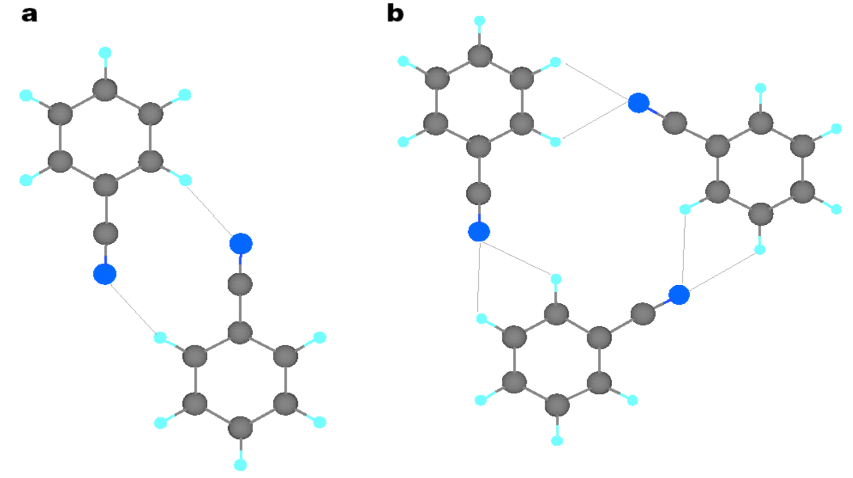


Figure 1 Calculated molecular aggregations. **a**, Cyanobenzene dimer; **b**, trimer. Colours correspond to the elements: H, light blue; C, black; N, dark blue.

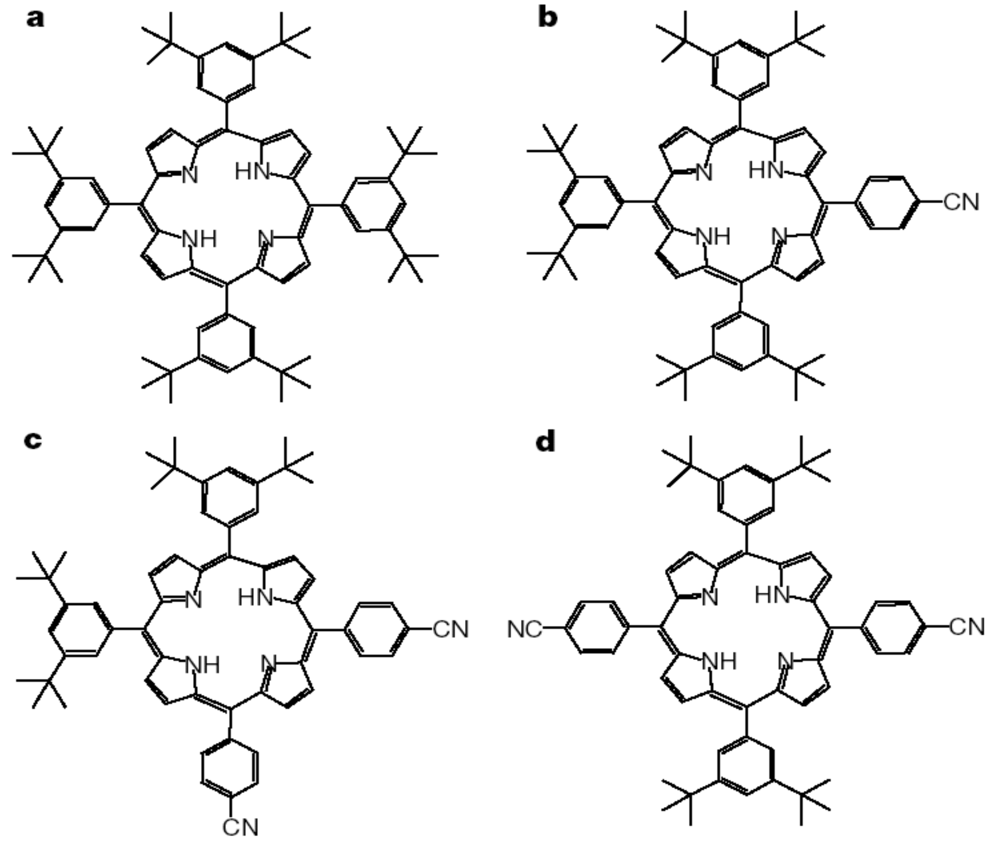


Figure 2 Structural formula of the porphyrins. **a**, H_2-TBPP, which is composed of a free-base porphyrin and four tBP substituents. In the ideal conformation, the phenyl rings are rotated by about 90° with respect to the porphyrin blane. **b**, CTBPP, where a tBP substituent of H_2-TBPP is replaced with a cyanophenyl substituent. **c**, *cis*-BCTBPP, where two cyanophenyl groups were substituted at the *cis* position. **d**, *trans*-BCTBPP, where two cyanophenyl groups were substituted at the *trans* position.

T. Yokoyama et al., Nature **413**, 619 (2001)

Selective assembly on a surface of supramolecular aggregates with controlled size and shape

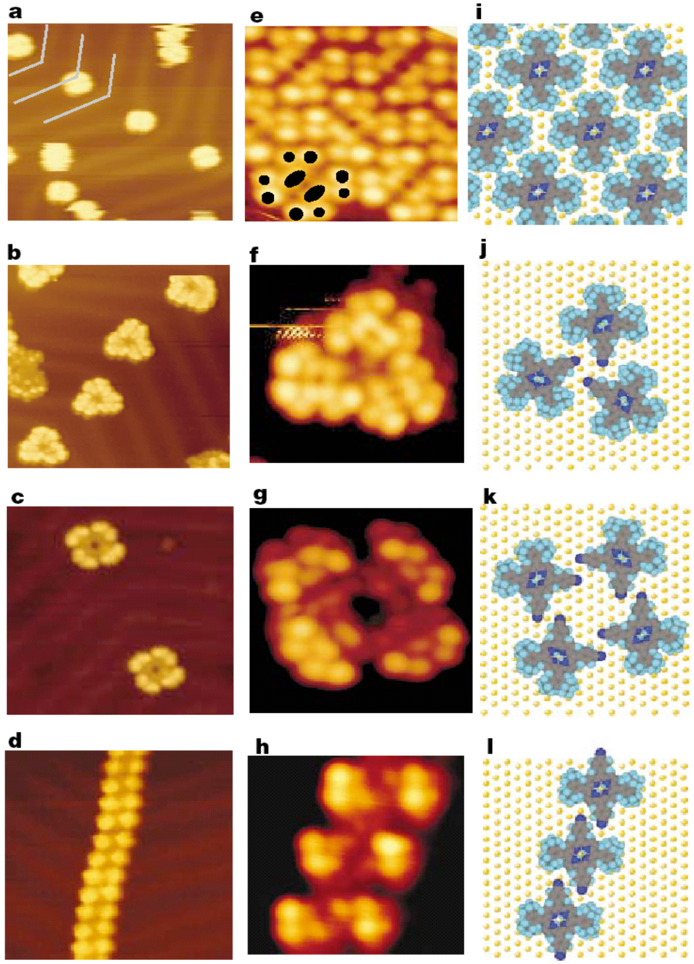


Figure 3 Scanning tunnelling microscope images at 63 K of supramolecular aggregations induced by the cyano groups. At small coverage, individual molecules or clusters are preferentially positioned at the elbows of the herringbone patterns of the Au(111) surface (imaged area, 20 × 20 nm): **a**, H_2-TBPP; **b**, CTBPP; **c**, *cis*-BCTBPP; **d**, *trans*-BCTBPP. High-resolution STM image (imaged area, 5.3 × 5.3 nm) and the molecular model: **e**, **i**, H_2-TBPP island; **f**, **j**, CTBPP trimer; **g**, **k**, *cis*-BCTBPP tetramer; **h**, **l**, *trans*-BCTBPP wire. As indicated by black dots in **e**, the STM image of the single H_2-TBPP molecule is composed of four paired lobes surrounding two oblong protrusions, corresponding to the tertiarybutyl substituents and the central porphyrin.

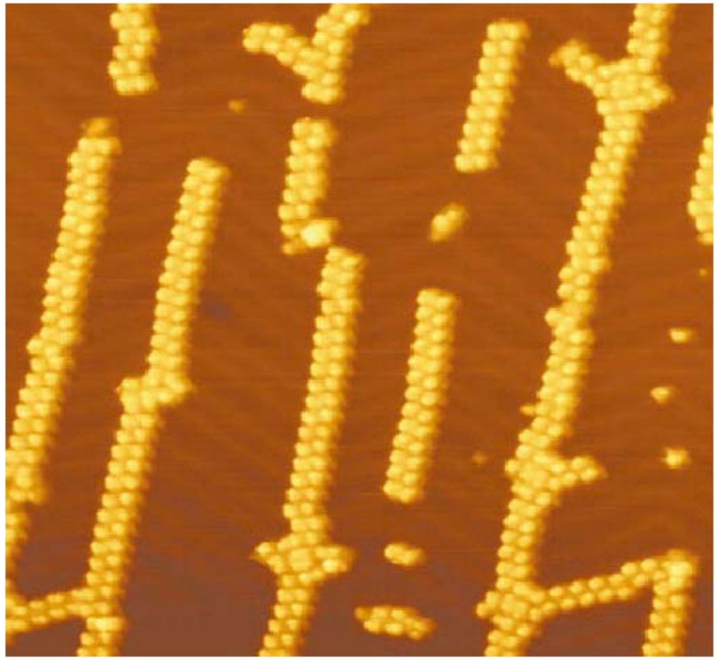
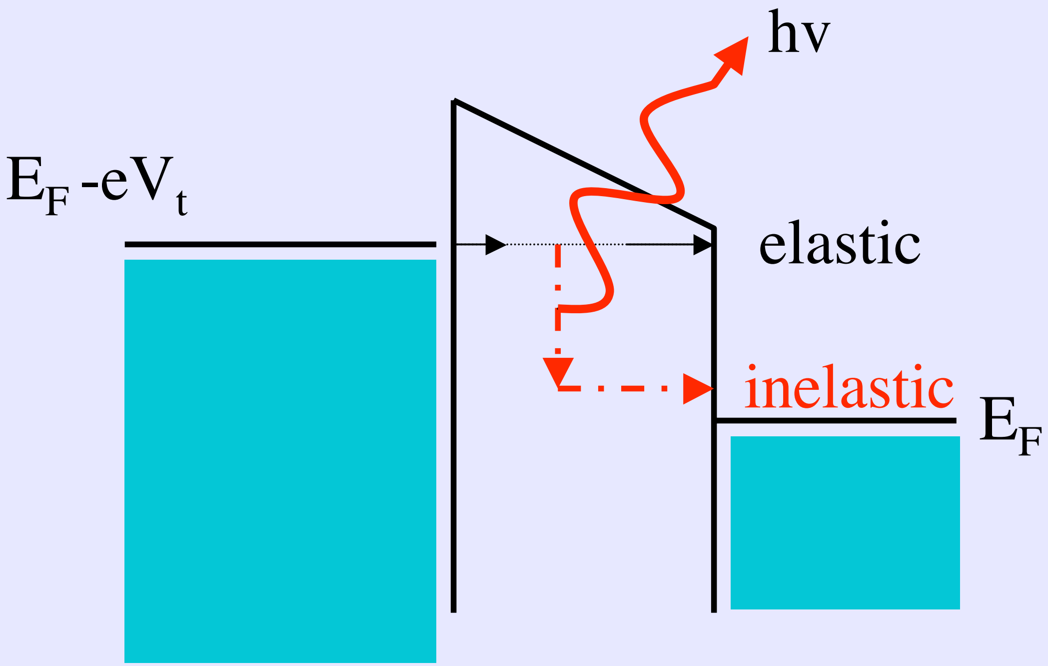


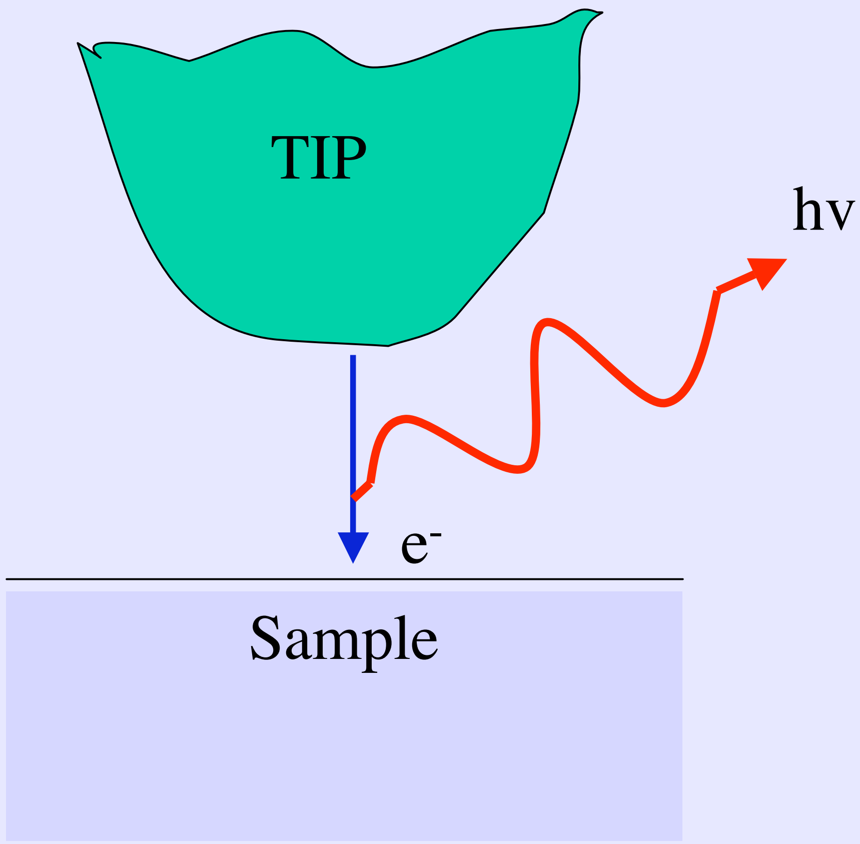
Figure 4 STM image at 63 K of *trans*-BCTBPP wires formed on the Au(111) surface (imaged area, 70 × 70 nm). The supramolecular wires extended across the elbows of the herringbone patterns, and the observed maximum length is above 100 nm, which depends on the terrace width.

T. Yokoyama et al.,
Nature **413**, 619 (2001)

Photonemission induced by an STM-tip

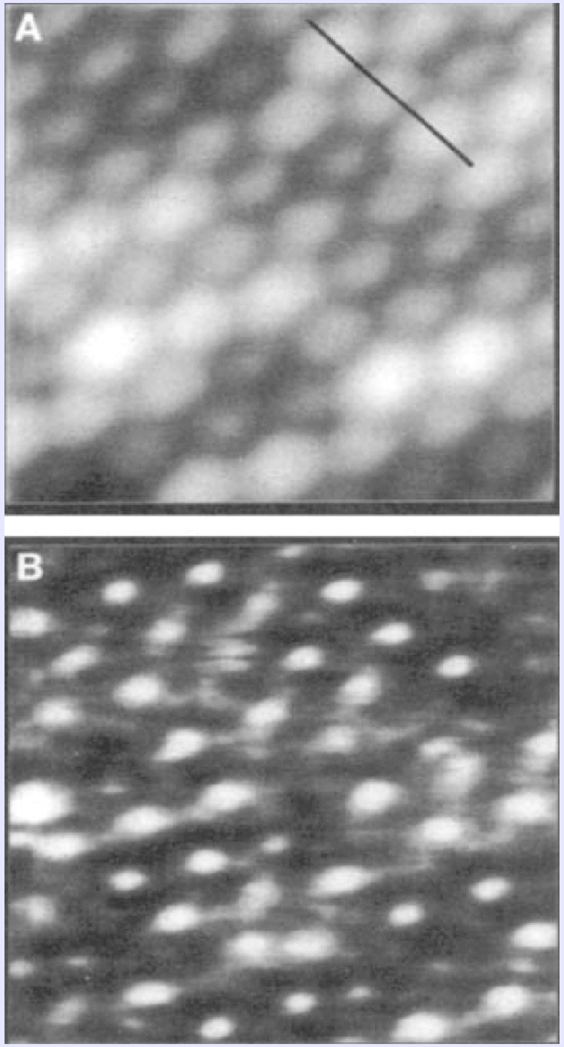
J. K. Gimzewski et al., Z. Phys. B 72, 497 (1988)

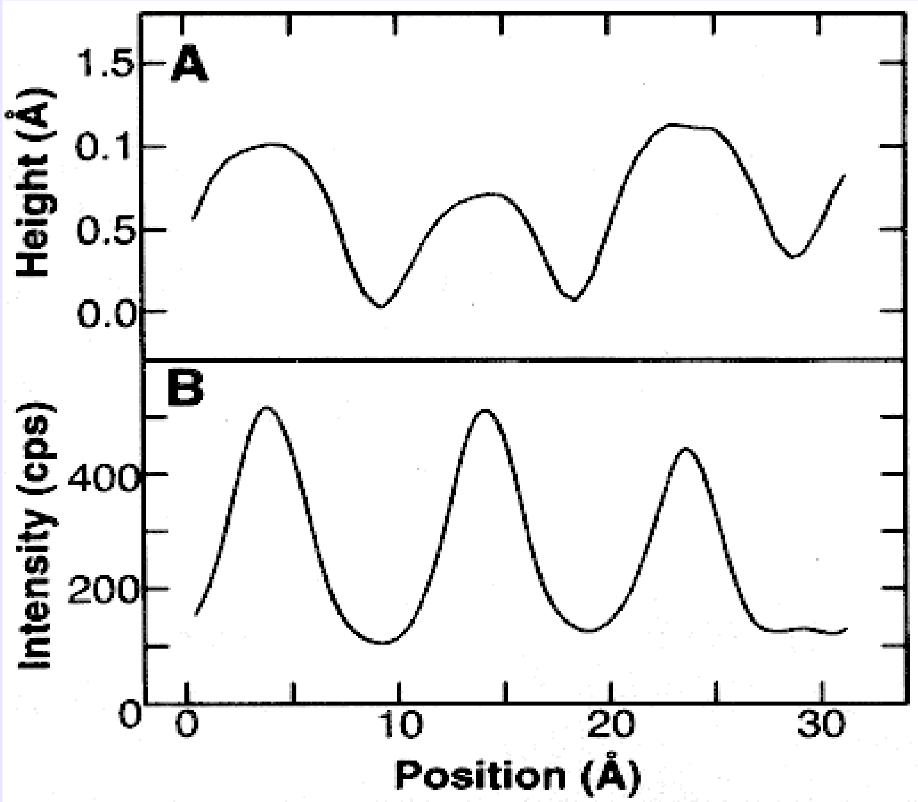




- Inelastic process
- P ≈ 10^{-4} photons/electron

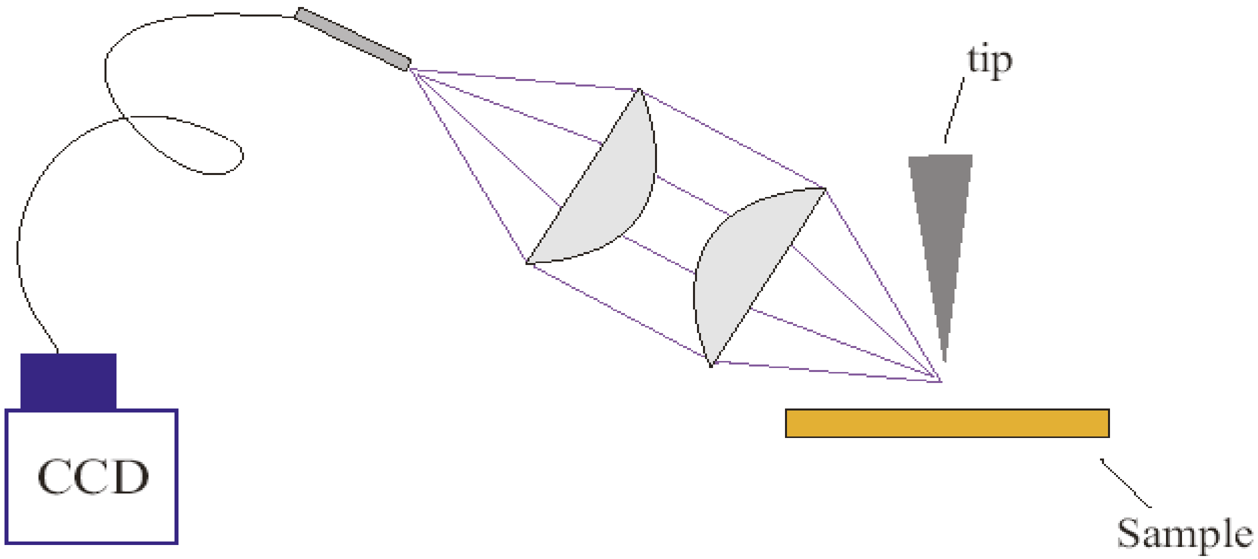
Photon emission from C_{60} on Au(110)





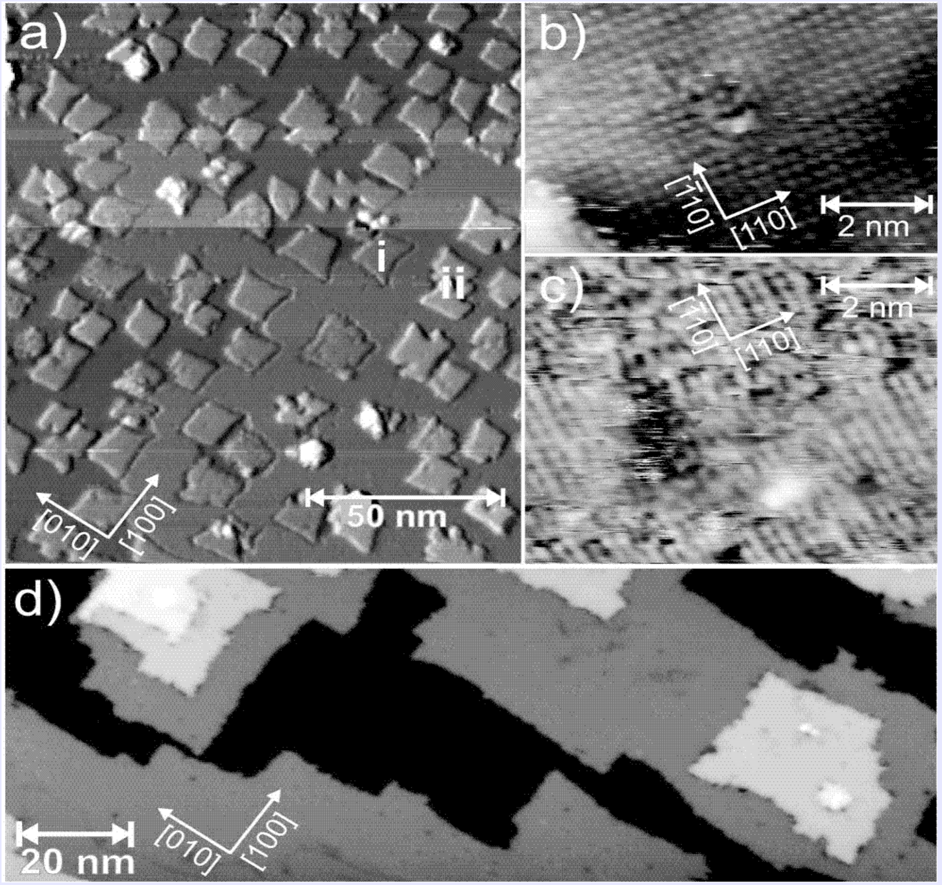
R. Berndt, R. Gaisch, J. K. Gimzewski, B. Reihl, R. R. Schlittler, WDS, M. Tschudy, Science **262**, 1425 (1993)

Experimental setup



E. Cavar et al.

MgO(100)/Ag(100) @ 50 K



S. Schintke et al., PRL **87**, 276801 (2001)

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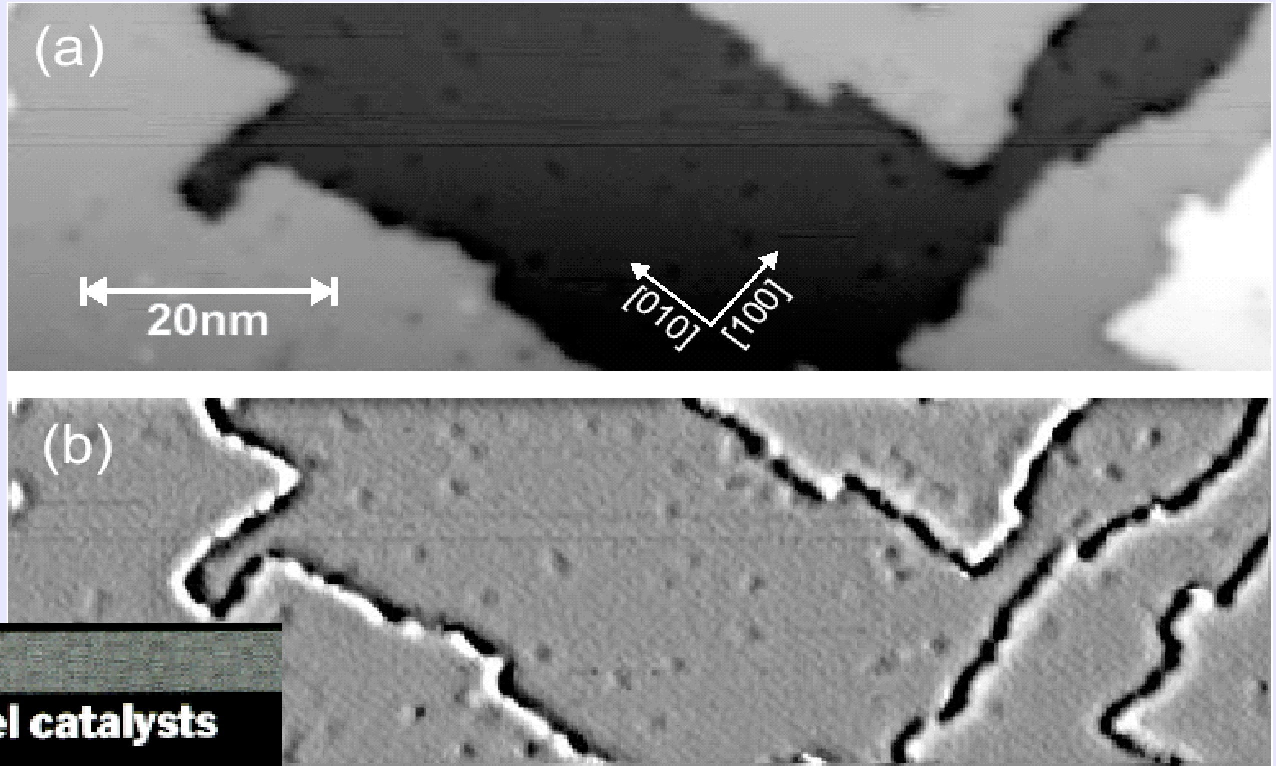

Volume 33 Number 11 7 June 2000

Review article: Nanoassembled model catalysts

U Heiz and W-D Schneider

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Thank you
for your attention!