Atomic Force Microscopy and other Scanning Probes
Contents

• Atomic Force Microscopy
• Dip-pen nanolithography
• Dynamic Nanostencil
• Piezoresponse Force Microscopy
• Nanosensors (electromechanical nose)
• Scanning Near Field Optical Microscope
Atomic Force Microscope (AFM)

It also works on insulators!

Binnig, Quate, Gerber (1986)
Atomic Force Microscope
The first AFM

Atomic Force Microscopy
(a) The cytoplasmic surface of the hexagonally packed intermediate layer is an essential part of the cell envelope of *Deinococcus radiodurans*. Has protective function, acts as a molecular sieve. The pores in protruding cores are the sieve’s channels, exhibiting two dynamically changing conformations. Unit cell size: 18 nm; brightness range, 3 nm. (b) Two-dimensional crystals of bacteriophage F 29 head-tail connectors by AFM in buffer solution. The connectors are packed in up-and-down originsations. Unit cell size: 16.5 nm; brightness range, 4 nm.
AFM principle

• Principle of an atomic force microscope. A sharp tip is brought close to the sample.

• The forces acting between tip and sample lead to a deflection of the spring.

• The deflection is then measured e.g. optically.
Measuring Forces

**Force:**

\[ F = k \Delta z \]

**Harmonic oscillator:**

\[ f^2 = k/m \]

\[ F' \text{ acts like a spring in series:} \]

\[ f^2 = (k+F')/m \]

**Force gradient** \( F' \):

\[ F' = 2k \Delta f/f \]

approximation good if

\[ d^2V/dz^2 = \text{constant for } \Delta z \]

otherwise: Giessibl, APL 78, 123 (2001)
Forces between atoms

‘Back of the envelope’:

- Atomic energy scale:
  \( E_{\text{bond}} \sim 1-4 \text{ eV} \sim 2-6 \times 10^{-19} \text{ J} \)
- Typical bonding length:
  \( a \sim 0.2 \text{ nm} \)
- Typical forces:
  \( F = E/a \sim 1-3 \text{ nN} \)

Bonding forces:

- Quantum mechanical (covalent, metallic bonds): 1–3 nN
- Coulomb (dipole, ionic): 0.1–5 nN
- Polarization (induced dipoles): 0.02–0.1 nN

Comparing forces

- Comparison of the distance dependence of a short range force with the tunneling current.
Van der Waals forces

\[ F_{vdW} = \frac{AR}{6z^2} \]

A: Hamaker’s constant
R: tip radius
z: Tip–sample separation

A depends on the type of material (polarizability). For most materials and vacuum, A~1 eV (Krupp, Advances Colloidal Interface Sci. 1, 113 (1967))

R~100 nm is a typical effective radius

\[ \Rightarrow F_{vdW} \approx 10 \text{ nN at } z \approx 0.5 \text{ nm} \]
Electrostatic forces

\[ F_{\text{electrostatic}} = \pi \varepsilon_0 RU^2 / z \]

- \( U \)…Potential difference
- \( R \)…Tip radius
- \( z \)…Tip - sample separation

\( R \sim 100 \text{nm} \) typical effective radius
\( U = 1 \text{V} \)

\[ \rightarrow F_{\text{electrostatic}} \sim 5 \text{nN at } z \sim 0.5 \text{ nm} \]

Spring constants $k$ and resonant frequency $f$ of cantilevers

Spring constant $k$:

$$k = \frac{E_Y \cdot wt^3}{4 \cdot L^3}$$

typical values: 0.01 - 100 N/m

Young’s modulus $E_Y \sim 10^{12}$ N/m$^2$

Resonant frequency $f_0$:

$$f_0 = 0.162 \cdot \frac{t}{L^2} \sqrt{\frac{E_Y}{\rho}}$$

typical values: 7 - 500 kHz
Deflection sensors

A) Beam deflection
B) Interferometry
C) Piezoresisitive
D) Piezoelectric

Meyer and Amer, APL 53, 1045 (1988)

Rugar et al., APL 55, 2588 (1989)

Giessibl, APL 73, 3956 (1998)
- Laser beam deflection detection systems as often used in ambient AFMs.
- Interferometric cantilever detection system, a popular choice for low-temperature AFMs.
Feedback modes

\[ F = \text{constant} \]

\[ z = \text{constant} \]
Piezoelectric scanners

Properties:
1. Hysteresis (non-linear)
2. Creep (history dependent)
3. Aging (regular recalibration)
Creating images from the feedback signal

line scan

processed image

gray scale image
Imaging artifacts

‘High’ resolution and double tip:  

Blunt tip:
Thermal drift

Touching the microscope (e.g. sample, cantilever) will change its temperature $T$. Shining light on it too! Cantilever has a mass of $\sim 1$ ng, and thus a VERY small heat capacity.

So what!?!  

$\Delta L/L = \text{const} \Delta T$; $\text{const} \sim 10^{-5}$
Examples of ‘writing’ by AFM
’Dip-pen nanolithography’

Chad Mirkin (1999)
Dynamic (AFM) Nanostencil

Scheme of the experimental apparatus:

- The material is deposited from source A through series of collimating apertures
- Optical beam from source B reflects off a cantilever (D)
- Position-sensitive detector (C) used to regulate proximity of the cantilever tip with respect to substrate surface (E)
- Series of small apertures: the cantilever defines pattern of deposited material at E

Dynamic (AFM) Nanostencil

SEM images of a Si$_3$N$_4$ cantilever featuring several holes in and near pyramidal tip - milled by focused ion beam (Ga ions, 70 pA, 30 kV).

AFM images of atomically clean Cu lines grown by dynamic stenciling: (a) line, (b) circle, (c) interdigitated line, and (d) lines connecting two pads (height of the lines: 10–30 nm).

Piezoresponse Force Microscopy

Converse piezoelectric effect:
strain = (piezoelectric coefficient) × (electric field)
Detection of out-of-plane domains by PFM
Piezoresponse Force Microscopy

**Converse piezoelectric effect:** strain = (piezoelectric coefficient) \(\times\) (electric field)

- **a)** \(E \uparrow \uparrow P\) vertical expansion
- **b)** \(E \downarrow \uparrow P\) vertical contraction
- **c)** \(E \perp P\) \(\Rightarrow\) shear movement \(\Rightarrow\) torsional deformation of the cantilever
Ferroelectricity in ABO₃ type perovskites

Ferroelectrics (polar oxides) → spontaneous electric polarization → Applications

NV - FeRAMs

Spontaneous polarization (electric dipole)

Physics Today, July, 1998 - Ferroelectric Memories
Ferroelectric switching
Detection of the out-of-plane polarization

BaTiO$_3$ on 0.1\%Nb doped SrTiO$_3$ (100)

AFM topography

Piezoresponse hysteresis loop

Before switching

Ferroelectric domain structure

After switching

Applications: nanosensors

Ways to functionalize cantilevers:
- Evaporation of metal layers through shadow masks
- Self–assembly of monolayers
- Spray–coating with polymers
- Coating using a microfluidic network

IBM and the Nanomechanical Nose

Scanning Near Field Optical Microscopy

Near-field scanning optical microscopy (NSOM/SNOM): microscopy technique for nanostructure investigation that breaks the far field resolution limit by exploiting the properties of evanescent waves.

Place the detector (usually a fiber optic cable) very close ($<< \lambda$) to the specimen surface, allowing for surface inspection with high spatial, spectral and temporal resolution. Image resolution is limited by the size of the detector aperture and not by the wavelength of the illuminating light, which is the case in optical microscopy due to diffractive effects.

As in optical microscopy, the contrast mechanism can be adapted to study different properties (e.g. refractive index, chemical structure and local stress. Dynamic properties can also be studied at a sub-wavelength scale using SNOM.
Optical microscopy

The wave-like nature of light causes it to diffract – limits the spatial resolution of a microscope. Under certain assumptions, the minimum detectable separation of two light scatterers for a given optical system is the Rayleigh Criterion. This limits traditional light-microscopy to a resolution of 200-300 nm, at best (exception: cutting edge photolithographic systems whose 100 nm resolution is achieved by using vacuum ultraviolet light).
Aperture near field microscopy

Aperture scanning near-field microscopy is a technique that allows for arbitrarily small details to be resolved. It works by scanning a small aperture over the object. Light can only pass through the aperture, and this size determines the resolution of the system.

Implemented by tapering a fiber optic to a narrow point and coating all but the tip with metal. By this method, images with resolution far beyond what is possible with traditional microscopy can be recorded.
McGill University, Montreal, Jan. 8th 2009

Scanning Tunneling Microscopy at the NFL

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Properties of large organic molecules on metal surfaces

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Scanning Tunneling Microscopy
Manipulation of Complex Organic Molecules on Solid Surfaces

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and Flemming Besenbacher2

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Key Words organic adsorbates, nanotechnology, single-molecule studies

Abstract Organic molecules adsorbed on solid surfaces display a fascinating
variety of new physical and chemical phenomena ranging from self-assembly and
molecular recognition to nonlinear optical properties and current rectification. Both
the fundamental interest in these systems and the promise of technological applica-
tions have motivated a strong research effort in understanding and controlling these
properties. Scanning tunneling microscopy (STM) and, in particular, its ability to ma-
nipulate individual adsorbed molecules, has become a powerful tool for studying the
adsorption geometry and the conformation and dynamics of single molecules and
molecular aggregates. Here we review selected case studies demonstrating the enor-
mous capabilities of STM manipulations to explore basic physicochemical properties
of adsorbed molecules. In particular, we emphasize the role of STM manipulations in
studying the coupling between the multiple degrees of freedom of adsorbed molecules,
the phenomenon of molecular molding, and the possibility of creating and breaking
individual chemical bonds in a controlled manner, i.e., the concept of single-molecule
chemistry.
Objective

**understanding how molecules assemble**

Our Approach (reductionist!):

I. Molecule–molecule interactions. Solid-liquid interface: weak coupling to the surface; physisorption (e.g. graphite)

II. Ultra High Vacuum: more flexibility in choice of substrate, allows to play with surface chemistry.

*Intermolecular forces & surface–mediated interactions intermediate coupling; creating and exploiting surface templates (e.g. on copper)*
Studies in Ultra High Vacuum: good control of surface chemistry, choice of substrate
Surface Diffusion
Surface diffusion

hopping rate: \( h = h_0 \exp(-E_D/kT) \)

random walk: \( \langle (\Delta x)^2 \rangle = \lambda^2 ht \)
\( \lambda \) - RMS jump length

tracer diffusion coefficient:
\[
D = \frac{\langle (\Delta x)^2 \rangle}{2t}
\]
\[
D = D_0 \exp\left(-\frac{E_D}{kT}\right)
\]
with \( D_0 = h_0 \lambda^2/2 \)
Molecular structure: model systems

**Decacyclene, DC**

C_{36}H_{18}

spacer groups => separation of \( \pi \) – system from substrate

**Hexa–(tert–butyl)decacyclene, HtBDC**

C_{60}H_{66}

50×50 Å²
DC Movies

- 1 D Diffusion along the close packed direction [110] of Cu(110)

HtBDC Movies

1 D Diffusion along the close packed direction [110] of Cu(110)

500x500 Å²
T = 194 K

~15 seconds per image

500x500 Å²
T = 203 K

Arrhenius analysis: D

$E_D = 0.71 \pm 0.05 \text{ eV}$

$D_0 = 10^{-1.0 \pm 1.0} \text{ cm}^2\text{s}^{-1}$

$E_D = 0.62 \pm 0.04 \text{ eV}$

$D_0 = 10^{0.9 \pm 1.0} \text{ cm}^2\text{s}^{-1}$

=> Arrhenius parameters are related to molecular structure
Arrhenius analysis: $h$

$E_D = 0.71 \pm 0.05 \text{ eV}$

$h_0 = 10^{13.9 \pm 0.7} \text{ s}^{-1}$

In general, $E_D$ is a fraction of the adsorption energy
Displacement distribution: HtBDC

Temperature: 185 K
Time per image: 13.5 sec

Temperature: 194 K
Time per image: 13.7 sec
Jump lengths – results

\[ \langle (\Delta x)^2 \rangle = \lambda^2 \, ht \]

HtBDC/Cu(110) \( \lambda = 6.8 \pm 0.3 \)

DC/Cu(110) \( \lambda = 3.9 \pm 0.2 \)

Pt/Pt(110) \( \lambda = 1.11 \pm 0.01 \)

(10% of jumps are non-nearest neighbor)

## Diffusion conclusions

<table>
<thead>
<tr>
<th></th>
<th>DC</th>
<th>HtBDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_D$ (eV)</td>
<td>0.71 ± 0.05</td>
<td>0.62 ± 0.04</td>
</tr>
<tr>
<td>$\lambda$ (nn dist)</td>
<td>3.9 ± 0.2</td>
<td>6.8 ± 0.3</td>
</tr>
</tbody>
</table>

1. Long jumps may be predominant in surface diffusion of large organic molecules

2. Tailoring diffusion properties (using specially designed molecules)
Diffusion coupled to rotation

with high resolution we observed the rotation of single molecules, coupled to diffusion: the molecules behave like nano-disks

Diffusion of DC on Cu(110), high resolution movie

200 x 200 Å²
Conformations, adsorption sites and diffusion of a ‘molecular’ switch
Model System: azobenzene

- Considered as a model-system for molecular switches

- Undergoes light induced reversible trans-cis isomerizations
Molecule adsorbs on top of a [1-10] copper row with the N=N at a bridge site

\[ T \sim 140 \text{ K}, \ (70 \times 70 \text{ Å}^2), \ -0.12 \text{ V}, \ 0.850 \text{ nA} \]

J.A. Miwa et al., *J. Am. Chem. Soc.* 2006; 128; 3164-3165
RT Adsorption

- Molecules do not show tendency to cluster
- Near half saturation molecules are stacked in columns in the [001] direction
- Molecular head-to-head interactions ([1-10]) appear to be weak or even repulsive
- Distances: $a = 7.9 \pm 0.8 \, \text{Å}$, $b = 14.3 \pm 1.4 \, \text{Å}$

$T = 120-170 \, \text{K}$, (70x70 Å²)

- Limited long range order at saturation - columns are often shifted by one lattice spacing along the [001] direction

J.A. Miwa et al., *J. Am. Chem. Soc.* 2006; 128; 3164-3165
Chirality of azobenzene

- Chirality = a molecule that is not superimposable on its mirror image
- Only the *trans* isomer is imaged; the *cis* conformer may be too diffusive

*trans* enantiomers

Clean Cu(110) imaged at \(\sim 120 \text{ K}
\)
-2.0 V, 0.350 nA (50x30 Å²)

J.A. Miwa et al., *J. Am. Chem. Soc.* 2006; 128; 3164-3165
LT Adsorption

T ~ 150 K, (70x70 Å²), -2.0 V, 0.350 nA

- At LT, two distinct adsorption configurations are observed: parallel and perpendicular
- At RT the perpendicular species is not observed (metastable?)

J.A. Miwa et al., *J. Am. Chem. Soc.* 2006; 128; 3164-3165
Surface Diffusion of Large Molecules

1 D Diffusion along the close packed direction [1-10] of Cu(110)

DC HtBDC

Jump length

Comparative diffusion of DC and HtBDC on Cu(110):

Diffusion of azobenzene

- Both species are mobile along the closed-packed direction of the surface
- Molecules become immobilized at step edges

STM movie acquired at $T = 168$ K

J.A. Miwa et al., J. Am. Chem. Soc. 2006; 128; 3164-3165
Diffusion: Quantitative

\[ D = \frac{1}{2} \lambda^2 h \]

\[ D = D_0 e^{-E/k_B T} \]

\[ D_{\parallel} = 0.2 \times 10^{-16} \text{ cm}^2/\text{s} \]

\[ D_{\perp} = 1.3 \times 10^{-16} \text{ cm}^2/\text{s} \]

\[ E_{\parallel} = 0.44 \text{ eV} \]

\[ E_{\perp} = 0.41 \text{ eV} \]
Surface Templates
Nanoscale Grating


Nanopatterning

100x100 nm²

Template width: 2 nm; periodicity: ~5 nm

\( \alpha \)-quinquethiophene (\( \alpha \)-T5) on Cu(110)

Model studies of adsorption of T5 on Cu(110) in the early stages of growth

T5 is used for organic devices (e.g. organic transistors)

F. Cicoira et al., Small 2, 1366 (2006)
α-T5 on the (2x1)O-Cu(110) nanotemplate

O-Cu nanotemplate, created by controlled oxidation of the Cu(110) surface

T5 initially adsorbs only on bare Cu stripes

Increasing the coverage, after saturation of the Cu stripes T5 adsorbs also on oxigenated stripes

F. Cicoira et al., Small 2, 1366 (2006)
α-T5 on (2x1) O-Cu(110)

T5 also adsorbs on a completely oxidized Cu surface, forming a regular pattern.

Proposed adsorption geometry for T5

F. Cicoira et al., Small 2, 1366 (2006)
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SNOM RESOLUTION

Aperture-limited resolution: the amount of light that can be transmitted by a small aperture poses a limit on how small it can be made before no light passes though. The cut-off is so severe that it cannot be made smaller. As the figure illustrates, this is not a subtle extinction.

When the aperture is 100 nm, the cut-off is down four orders of magnitude, and when it reaches 50 nm, only one part in $10^8$ makes it through. The input power cannot be increased arbitrarily because $1/3$ of the power is absorbed in the coating. Increasing the input power above approximately 10 mW destroys the coating; this severely limits the signal-to-noise ratio of small apertures.

Instead of using a small aperture, it is possible to use a metal tip to provide a local excitation. If a sharp metal tip is placed in the focus of a laser beam, an effect called local field enhancement will cause the electric field to become roughly 1000 times stronger. This enhancement is localized to the tip, which has a typical diameter of 10 nm. As this tip is scanned over the surface, an image can be formed with a resolution as fine as the tip.

L. Novotny et al., Ultramicroscopy 71, 21, 1998
Molecular molding
the Lander molecule

Model of a molecular wire

C$_{90}$H$_{98}$

Ball model

di-tert-butylphenyl spacer legs

aromatic board (wire)

F. Rosei et al., Science 296, 328 (2002)
Molecular conformations: isolated molecules at low T

rhomboidal shape

rectangular shape

4 lobes = 4 spacer legs

STM

theory

Deposition @ RT
Imaging @ 200 K

linescan across two lobes

Theory: elastic scattering quantum chemistry (ESQC) + molecular mechanics (MM2)

F. Rosei et al., Science 296, 328 (2002)
Nano-molding Cu step edges

Deposition @ RT

Imaging and manipulation @ 200 K

Low temperature manipulations:

molecules are anchored to the step edge

Structures are not pulled out by STM tip

150 × 150 Å²

F. Rosei et al., Science 296, 328 (2002)
Zoom in on the nanostructures

width of the nanostructure: 2 rows of Cu atoms

7.5 ± 0.5 Å

The step restructuring is directly related to the shape and size of the molecule

F. Rosei et al., Science 296, 328 (2002)
Surface Engineering by “smart” molecular design

Violet Lander

Single Lander

Violet Lander restructuring

235 × 195 Å²,
$I_t = -0.13$ nA, $V_t = -1.25$ V

3–row structure: observed in 30 % of cases

50 × 50 Å²,
$I_t = -0.81$ nA, $V_t = -0.44$ V

Assembly of Lander molecules on Cu(110)

High coverages of Lander molecules: **partial ordering** at RT after annealing to 500 K

Typical (disordered) situation:

(a) domain of rhomboidally shaped molecules.

(b) domains of rhomboidally shaped and rectangularly shaped molecules.

(c) ball model of the double row structure.

Forced assembly: formation of 1D molecular rows

- Lander adsorbs on Cu areas, at edge of Cu / Cu–O interface
- by controlling template width, we form long molecular rows

R. Otero, Y. Naitoh, F. Rosei et al., Angew. Chem. 43, 2092 (2004)
S–Lander adsorption on nanotemplate

Molecular chain on nanopatterned Cu

The center board orientations are now parallel to the Lander row direction

molecular wire (hopefully 😊)

In reality, this is a 1 D molecular nanostructure, or molecular chain

Molecule–molecule interactions – STM studies at the solid–liquid interface: physisorption on graphite
Assembly, Self–Assembly, Forced Assembly

Molecular self–assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well defined aggregates joined by non–covalent bonds. Whitesides et al. Science 254, 1312 (1991)

Useful interactions (Non–covalent) for self–assembly:
- Hydrogen bonds
- Van der Waals interactions
- Metal–organic coordination

Self–assembly of 15–hydroxypentadecanoic acid (HO(CH₂)₁₄COOH) on graphite (HOPG)
J.A. Miwa et al., unpublished
Molecule–molecule interactions – STM studies at the solid–liquid interface: physisorption on graphite
Molecule–Molecule Interactions

TMA + Heptanoic Acid on HOPG

Graphite HOPG: fairly inert, so that coupling to the substrate is weak

Trimesic acid (TMA)

Hydrogen bonding: physisorption; geometry & functionality

\[ V_s = -0.95 \text{ V}, \quad I_t = 250 \text{ pA} \]

\[ V_s = -0.95 \text{ V}, \quad I_t = 200 \text{ pA} \]

\[ a = b = 1.66 \text{ nm} \]

\[ a = b = 2.63 \text{ nm} \]
Mixing TMA and undecanol

TMA co-adsorbs with undecanol on HOPG

The alcohol ‘breaks’ the 3-fold symmetry of the substrate and the H-bonding unit, forming 1-dimensional tapes spaced by the alcohol itself

spacing: 3.5 nm

C_{11}H_{23}OH,
D = 1.85 nm, P = 3.5 nm

Linear TMA patterns formed through cooperative adsorption

- When alcohols co-adsorb with TMA, a linear pattern forms, made of dimerized TMA separated by alcohol lamellae

$\text{TMA/C_{17}H_{35}OH (heptanoic acid)}$

$5.5 \times 5.5 \text{ nm}^2, V_s = -800 \text{ mV}, I_t = 20 \text{ pA}$

$\text{Alcohols}$
Fatty alcohols with the general formula

$C_nH_{2n+1}OH$

Undecanol
$(n = 11)$

where $7 \leq n \leq 30$

Modulation induced by alcohol chains

\[ \text{C}_{16}\text{H}_{33}\text{OH}, \quad D = 1.7 \text{ nm}, \quad P = 3.4 \text{ nm} \]

\[ \text{C}_{17}\text{H}_{35}\text{OH}, \quad D = 2.4 \text{ nm}, \quad P = 4.1 \text{ nm} \]

60° Tilted orientation (zigzag plane II to HOPG)

Orthogonal orientation (zigzag plane \( \perp \) to HOPG)

Rational modulation & Odd-even effect

- All odd alcohols assemble with $\sim 90^\circ$ tilt vs lamellas direction
- All even alcohols assemble with $\sim 60^\circ$ tilt vs lamellas direction

Parity effect

- Geometry of the TMA/alcohol bond depends on the parity of carbon count in the alcohol
  - Odd alcohols prefer to orient at ~90° to the TMA dimer tape
  - Even alcohols prefer to orient at ~60° to the TMA dimer tape

### Rational modulation

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>L (nm)[a]</th>
<th>P (nm)[b]</th>
<th>α (°)[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{7}H\textsubscript{15}OH</td>
<td>1.06</td>
<td>2.74±0.16</td>
<td>83±2</td>
</tr>
<tr>
<td>C\textsubscript{8}H\textsubscript{17}OH</td>
<td>1.19</td>
<td>2.69±0.12</td>
<td>64±2</td>
</tr>
<tr>
<td>C\textsubscript{10}H\textsubscript{21}OH</td>
<td>1.44</td>
<td>2.91±0.07</td>
<td>64±2</td>
</tr>
<tr>
<td>C\textsubscript{11}H\textsubscript{23}OH</td>
<td>1.57</td>
<td>3.36±0.09</td>
<td>86±2</td>
</tr>
<tr>
<td>C\textsubscript{16}H\textsubscript{33}OH</td>
<td>2.21</td>
<td>3.57±0.10</td>
<td>66±2</td>
</tr>
<tr>
<td>C\textsubscript{17}H\textsubscript{35}OH</td>
<td>2.34</td>
<td>4.10±0.09</td>
<td>83±2</td>
</tr>
<tr>
<td>C\textsubscript{22}H\textsubscript{45}OH</td>
<td>2.99</td>
<td>4.29±0.07</td>
<td>64±3</td>
</tr>
<tr>
<td>C\textsubscript{27}H\textsubscript{55}OH</td>
<td>3.63</td>
<td>5.32±0.15</td>
<td>82±3</td>
</tr>
<tr>
<td>C\textsubscript{30}H\textsubscript{61}OH</td>
<td>4.02</td>
<td>5.08±0.11</td>
<td>66±2</td>
</tr>
</tbody>
</table>

Shortest alcohol chains: C7, C8 (C6 does not work)

Longest chains: C27, C30

The adsorption properties of the alcohol are related to the length of the chain and to the parity of C atoms in the chain

X-ray crystallography of 3D crystals

The in-plane structure of TMA/alcohol SAMN is mimicked in 3D crystals

<table>
<thead>
<tr>
<th>Plan view</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Even</strong> TMA/C₆H₁₃OH crystal</td>
<td>TMA/C₅H₁₁OH crystal</td>
</tr>
</tbody>
</table>

- TMA bonding/alcohol lamellae are analogous to SAMN
- Parity effect is suppressed by additional freedom for bond rotation

Chirality in TMA/alcohol SAMNs

- TMA dimer tapes are prochiral
- In STM images, chirality is communicated through the alcohol tilt
- TMA/alcohol SAMN forms chiral domains

TMA (half) dimer enantiomers

<table>
<thead>
<tr>
<th>Enantiomer</th>
<th>Image Size</th>
<th>Voltage (V)</th>
<th>Current (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>13.5 × 13.5 nm²</td>
<td>Vₛ = -0.87 V, Iᵣ = 250 pA</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>13.5 × 13.5 nm²</td>
<td>Vₛ = -0.93 V, Iᵣ = 278 pA</td>
<td></td>
</tr>
</tbody>
</table>

New polymorphs at domain boundaries

- Unusual TMA bonding geometries can be stabilized at domain boundaries in the TMA/alcohol SAMN

TMA/C\textsubscript{16}H\textsubscript{33}OH (octanoic acid)
15 × 15 nm\textsuperscript{2}, \(V_s = -1.0\) V, \(I_t = 300\) pA

- Boundaries of three domains can contain a fully-trimerically bonded TMA region
- The “superflower” structure, predicted by Lackinger et al. (Langmuir 2005)

TMA/C\textsubscript{16}H\textsubscript{33}OH (octanoic acid)
20 × 20 nm\textsuperscript{2}, \(V_s = -1.0\) V, \(I_t = 300\) pA

The incomplete structure has the features of a next-generation polymorph related to chicken-wire and flower structure.

Homologic order of TMA polymorphs

- Together with the known chicken-wire and flower structures, these new polymorphs imply a homologic order of TMA phases comprising trimeric and dimeric associations

<table>
<thead>
<tr>
<th>Name</th>
<th>Chicken wire</th>
<th>Flower</th>
<th>Second-generation</th>
<th>...</th>
<th>Super flower</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td><img src="Image1" alt="Chicken wire" /></td>
<td><img src="Image2" alt="Flower" /></td>
<td><img src="Image3" alt="Second-generation" /></td>
<td>...</td>
<td><img src="Image4" alt="Super flower" /></td>
</tr>
<tr>
<td>Association</td>
<td>Dimeric</td>
<td>Dimeric + Trimeric</td>
<td>Trimeric</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Order</td>
<td>0th generation</td>
<td>1st generation</td>
<td>2nd generation</td>
<td>...</td>
<td>∞ generation</td>
</tr>
</tbody>
</table>

The open pores of the TMA chicken wire network can host C\textsubscript{60} molecules.


J.M. MacLeod, O. Ivasenko, D.F. Perepichka, F. Rosei, Nanotechnology 18, 424031 (2007)
TMA networks host other molecules

New molecule: sulflower (d ~ 0.79 nm)
Chernichenko et al, Angew Chem Int Ed Engl. 2006 45:7367

TMA/C\textsubscript{22}H\textsubscript{45}OH chicken wire + sulflower (heptanoic acid)

60 × 60 nm\textsuperscript{2}, V\textsubscript{s} = -0.8 V, I\textsubscript{t} = 75 pA

TMA chicken wire + sulflower (heptanoic acid)

29 × 29 nm\textsuperscript{2}, V\textsubscript{s} = -1.2 V, I\textsubscript{t} = 200 pA
Self-assembly of ‘sulflower’ molecules

Heterocirculenes: Sulflower, Selenosulflower – immobilized in a H-bonded matrix of TMA at the solid-liquid interface, imaged by STM


(a), (b) STM images with models (c), (d) of sulflower-TMA and selenosulflower-TMA SAMNs, respectively. 2.0×2.2 nm² zoom of TMA/sulflower image next to model in (c).