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Supramolecular Assembly on Curved Surfaces: the Case of Nanoparticles

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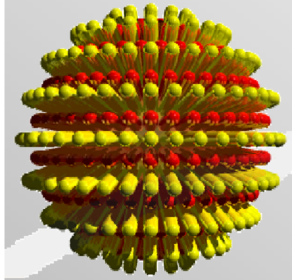

SuNMaG

The Supramolecular Nano-Materials Group

Supramolecular Assembly on Curved Surfaces: the Case of Nanoparticles

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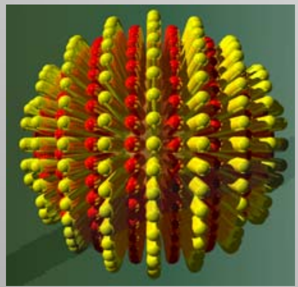
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

DMSE

SuNMaG Research Efforts

S u N M a G

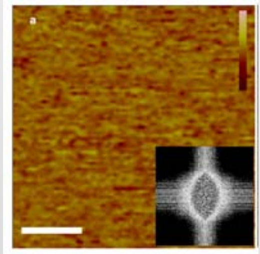
Monolayer Protected Metal Nanoparticles



*Jackson, Myerson, Stellacci, **Nat. Mat.**, 3, 330, 2004*

*Jackson, Silva, Hu, Stellacci, **JACS.**, in press*
Brunnbauer, Stellacci, manuscript in prep.

Akthakul, Hochbaum, Stellacci, Mayes,. ***Adv. Mat.***, 17, 532, 2005



*Halik, M. et al. **Nature**, 431, 963, 2004*

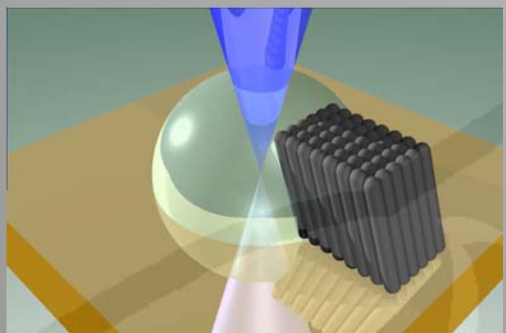
NANO-MATERIALS

Sidewall Functionalized Carbon Nanotubes

Wunsch, Stellacci, Prato, manuscript in prep.

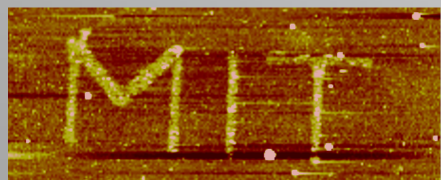
Supramolecular Materials Science

Supramolecular Lithography

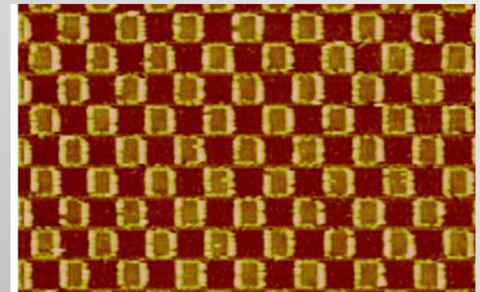


*Barsotti, O'Connell, Stellacci, **Langmuir**, 20, 4795, 2004*
Barsotti, Stellacci, J. Mat. Chem., 16, 962, 2006

LITHOGRAPHY

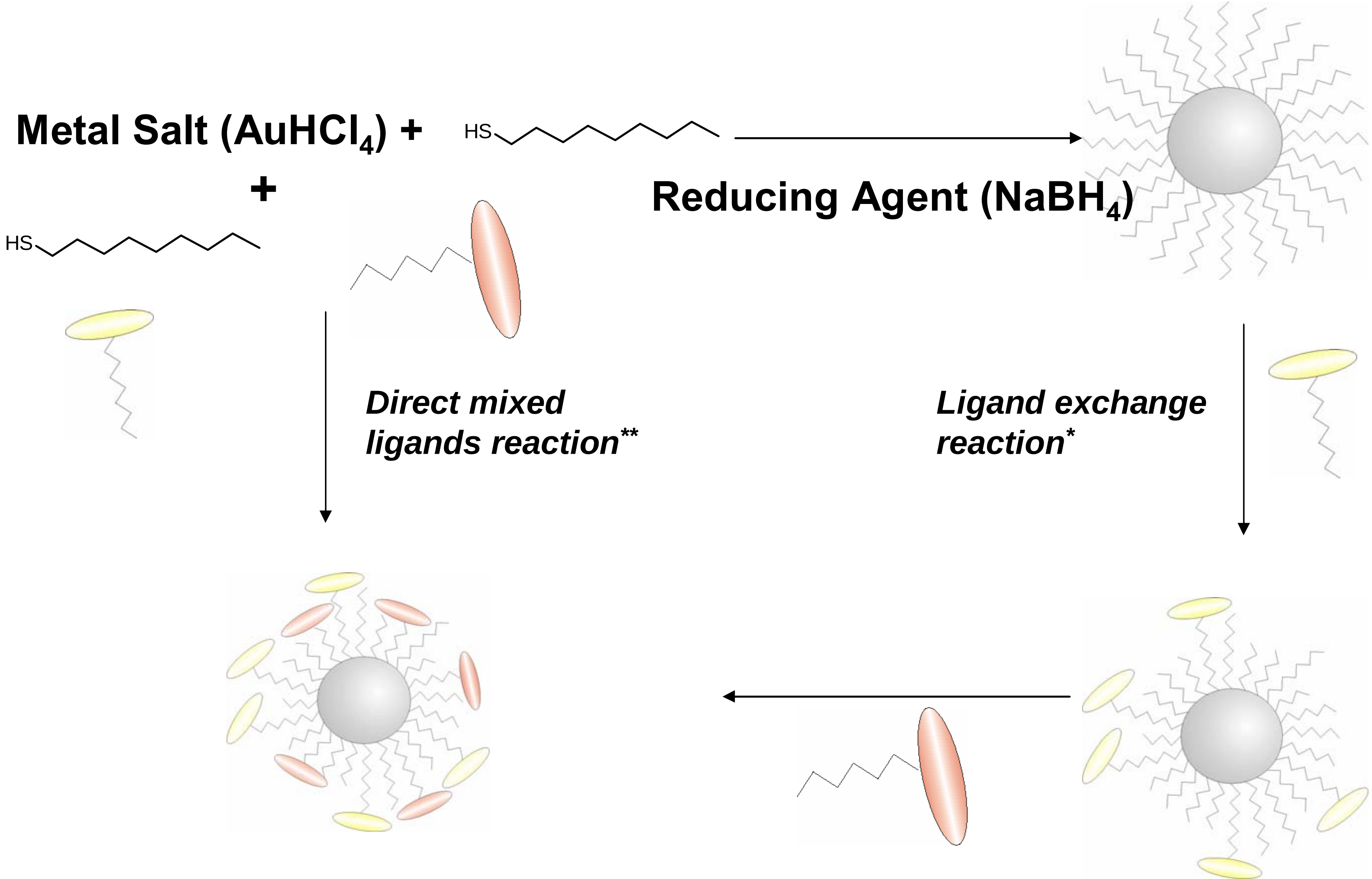


Supramolecular Nano Stamping



*Yu, Stellacci, **Nano Letters**, 5, 1061, 2005*
*Yu, Stellacci, **JACS**, 127, 16774, 2005*
*Yu, Stellacci, **J. Mat. Chem.**, accepted*

Metal Nanoparticles Synthesis

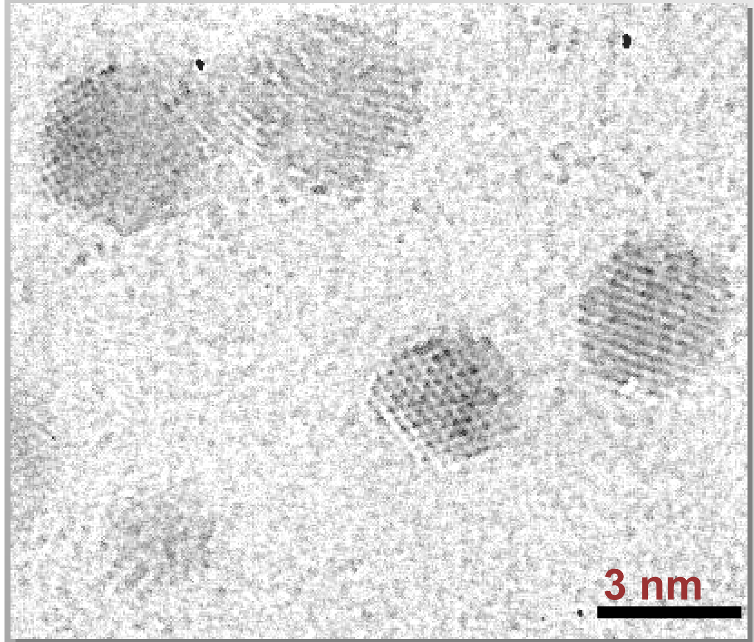


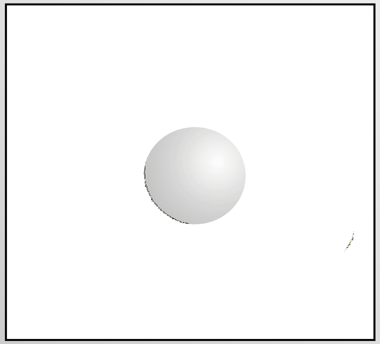
F. Stellacci, et al. *Adv. Mat.* **2002**, 14, 194

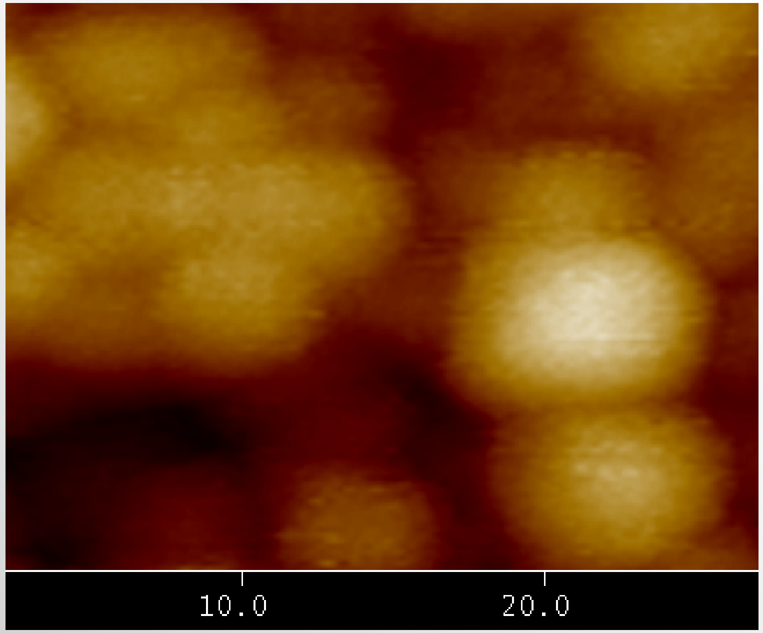
A. C. Templeton, M. P. Wuelfing and R. W. Murray, *Accounts Chem. Res.* **2000**, 33, 27

Characterizing Metal Nanoparticles

S u N M a G

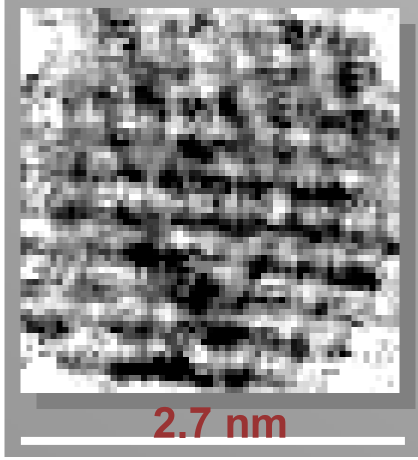


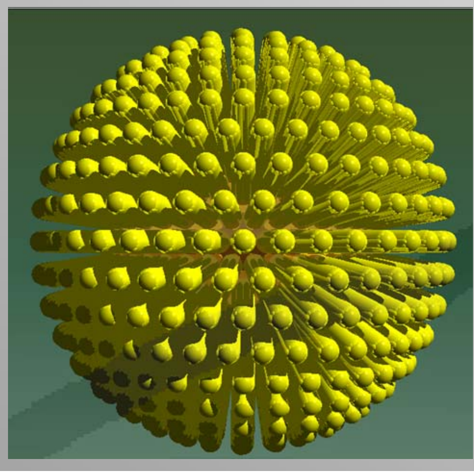


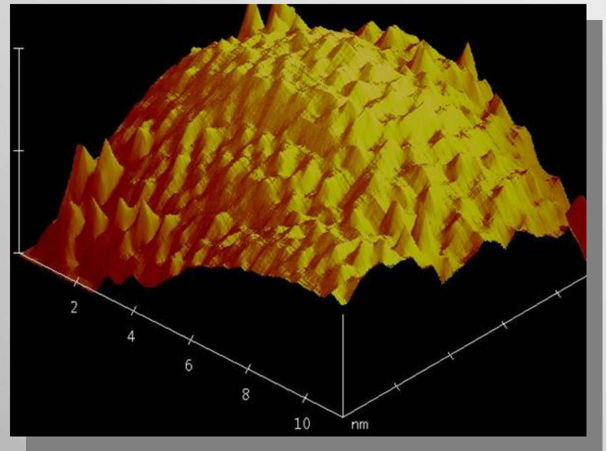


TEM shows atoms in the core

STM shows ligands in the shell

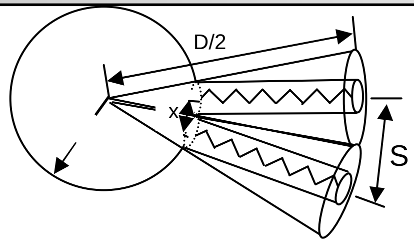






Homoligand particle's ligand structure

S u N M a G



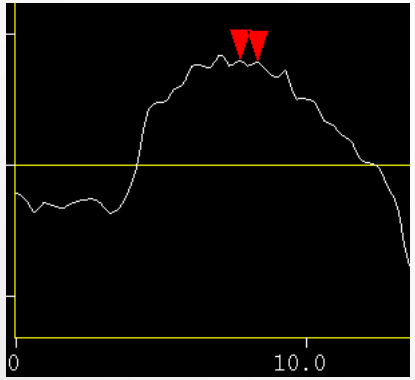
S = STM observed spacing
x = ligand spacing at core surface (adjacent Sulfur-Sulfur distance)
D = STM observed np dimater (core + ligand shell)
d = diameter of np core

S/D = x/d

Assumptions:
The nanoparticle can be approximated as a sphere
Ligand length (L) is constant around the shell i.e. (D/2) = Constant

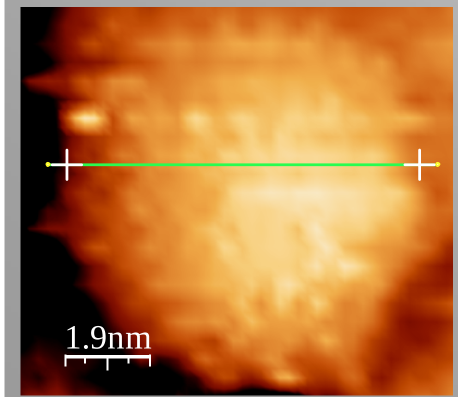
For a fully extended ligand chain of length L, with n carbon atoms, Use L = 0.12 (n+1) nm

Based on Luedtke and Landman Faraday Discussions 2004, 125, 1-22



W. D. Luedtke and Uzi Landman
J. Phys. Chem. B, *102 (34), 6566,, 1998*

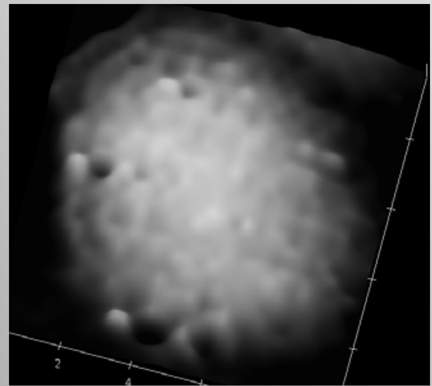
Octanethiol (C8) homoligand np



Diameter =7.422nm
Ligand length= 1.08 nm
Average STM observed headgroup spacing
<S> = 0.5

Average S-S spacing
<X>=.409

Dodecanethiol (C12) homoligand np



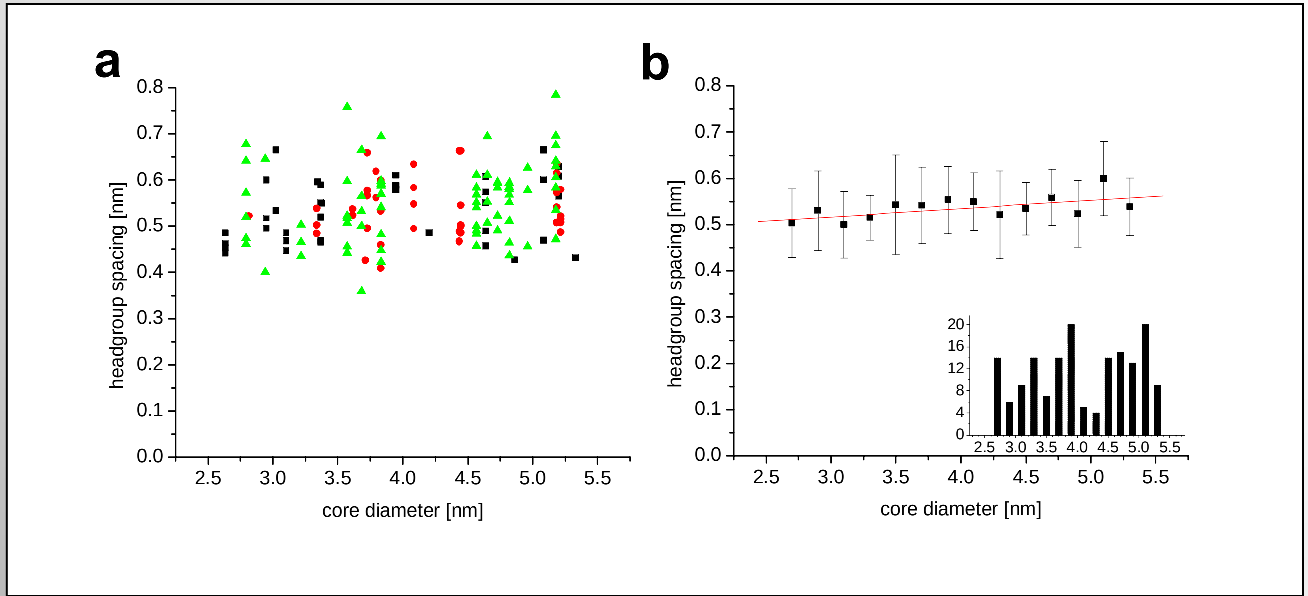
Diameter=7.418
Ligand length=1.56 nm
Average STM observed headgroup spacing
<S>= 0.6305

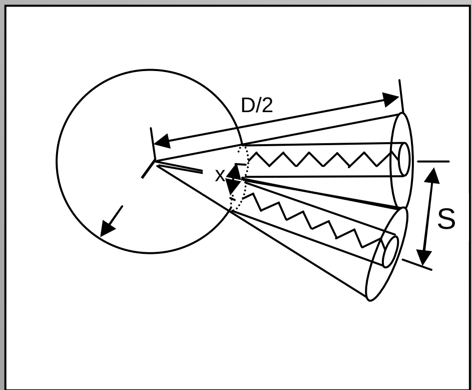
Average S-S spacing
<X>=0.3646

How do molecules assemble?

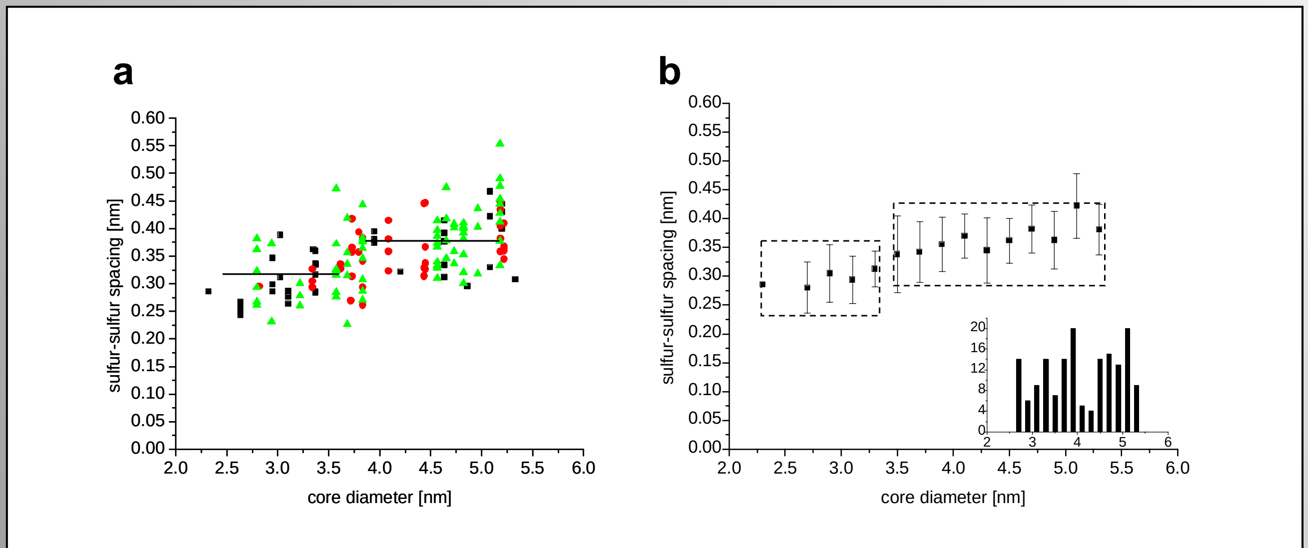
S u N M a G

Headgroup Spacing S →



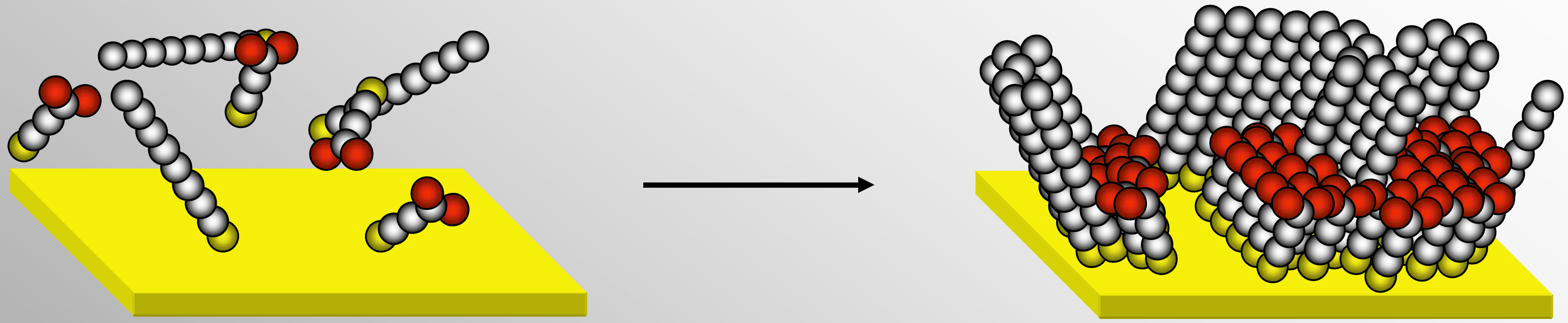


Sulfur-Sulfur Spacing at the Gold Plane x →

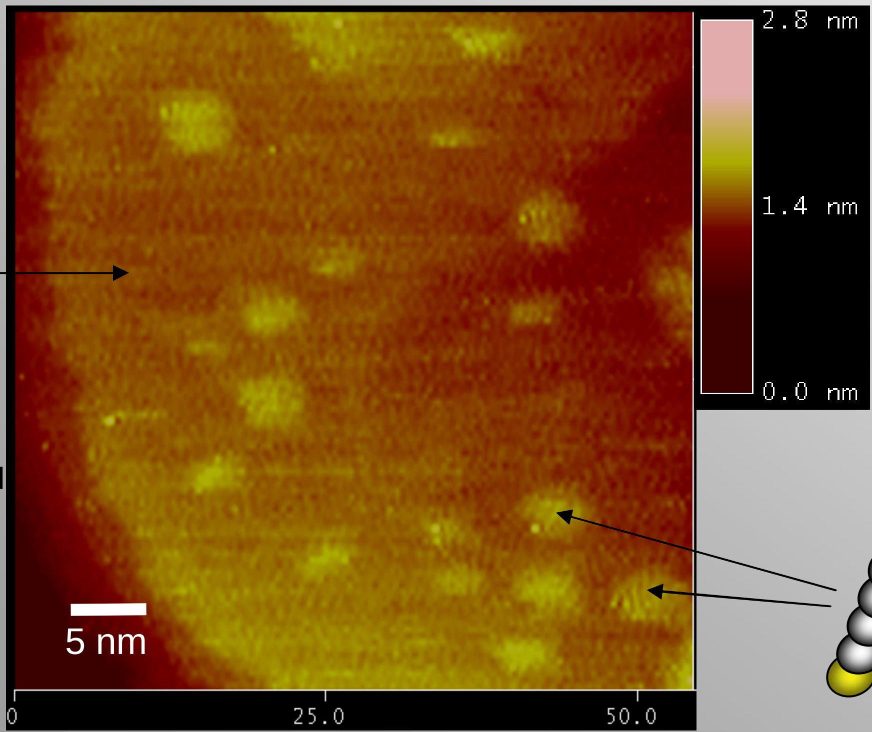


Mixed Self-Assembled Monolayers

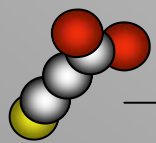
S u N M a G



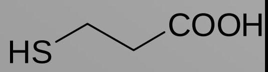
Au (111)

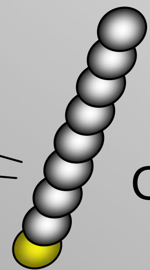


STM Height Image of OT/MPA Mixed Monolayer on Au(111)

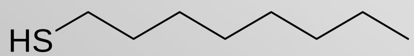


MPA





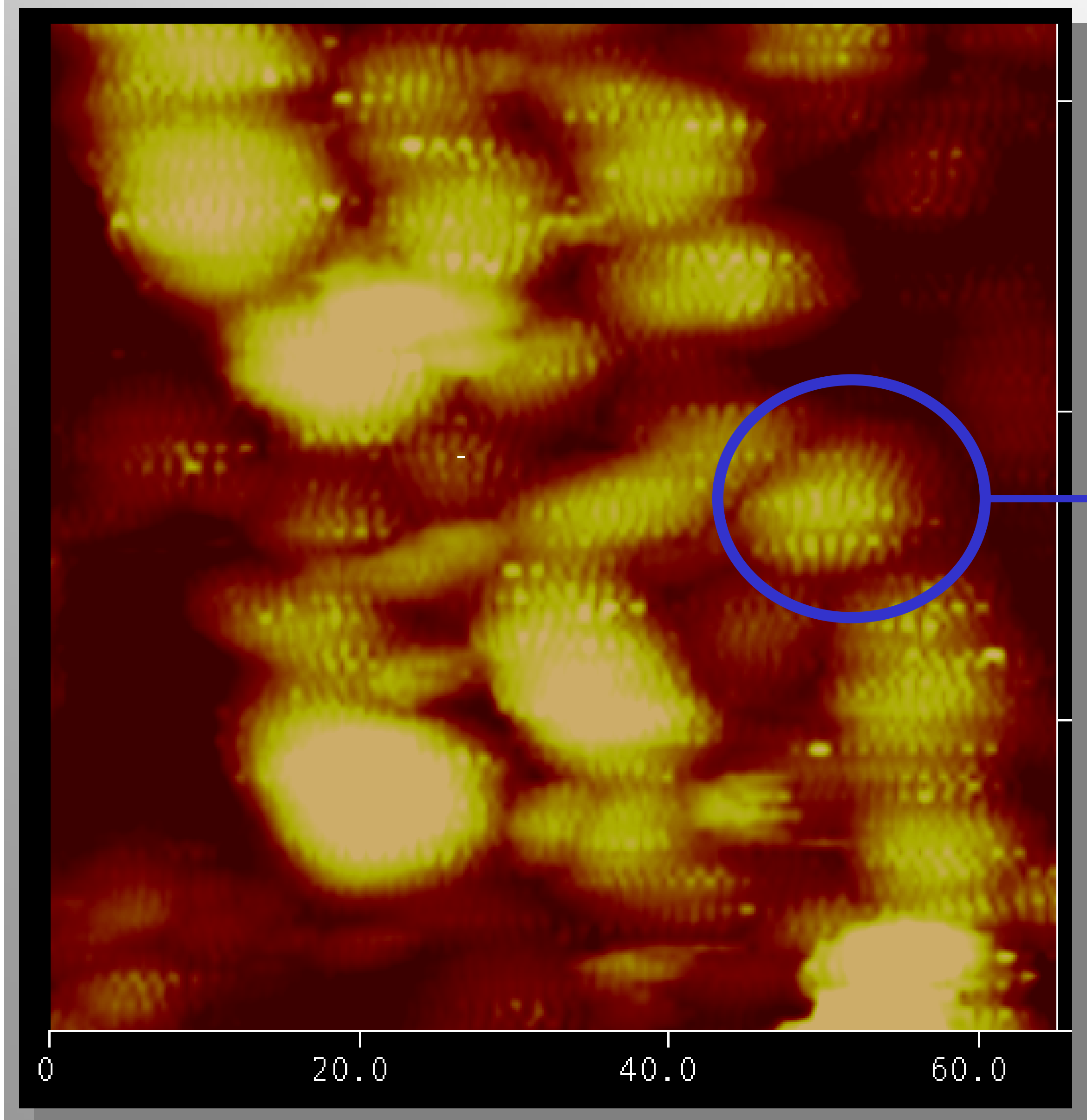
OT



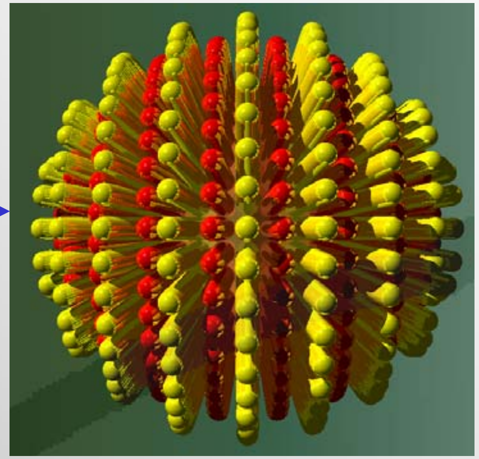
Randomly distributed domains of OT form in a surrounding matrix of MPA

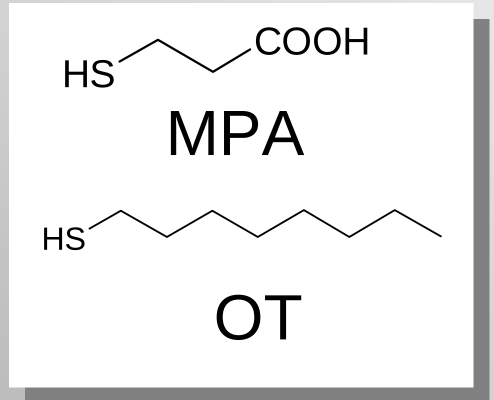
R. Smith, S. Reed, P. Lewis, J. Monnell, R. Clegg, K. Kelly, L. Bumm, J. Huthison, P. Weiss. *J. Phys. Chem. B* **2001**, 105, 1119-1122.

Ordered Domains on NPs



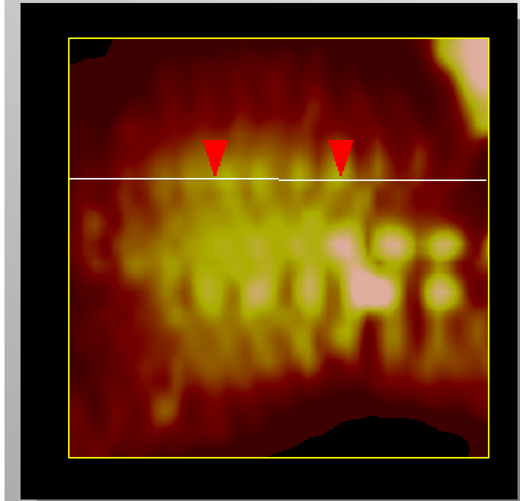
Hydrophobic/ Hydrophilic Ripples Form by Spontaneous Self-Assembly

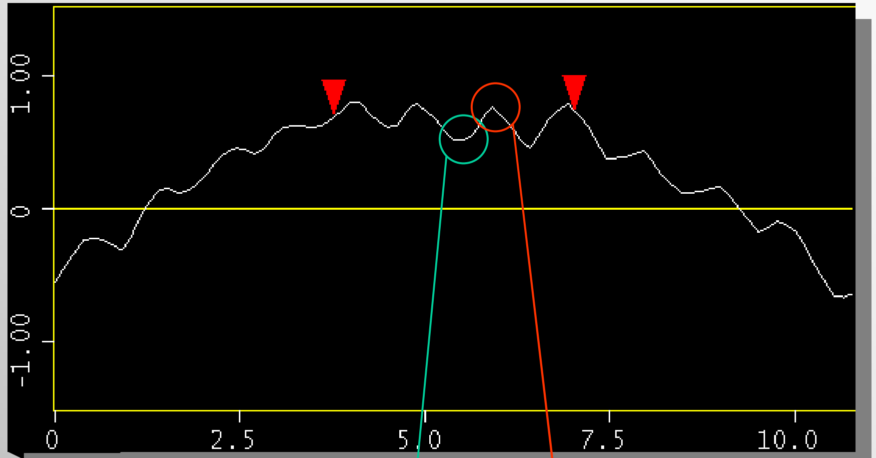


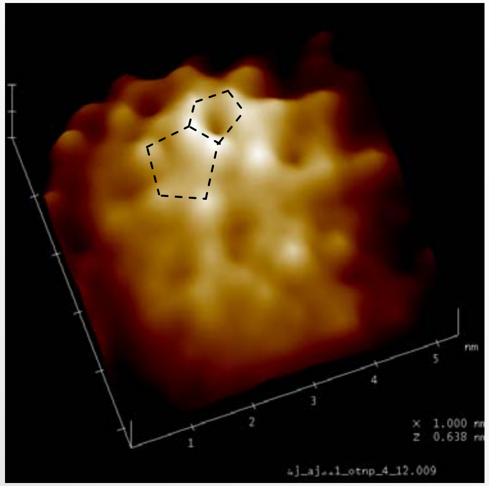


Hydrophobic/Hydrophilic Ripples

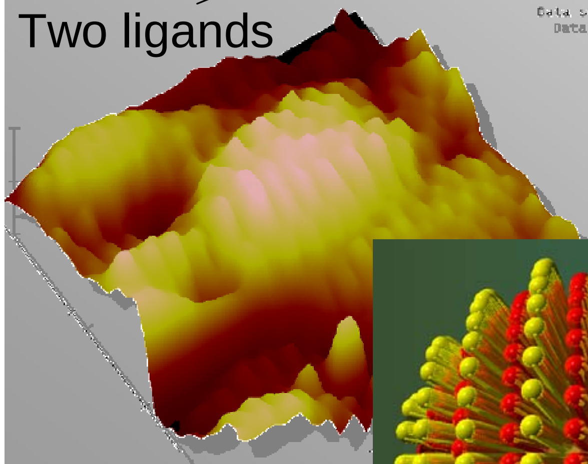
S u N M a G





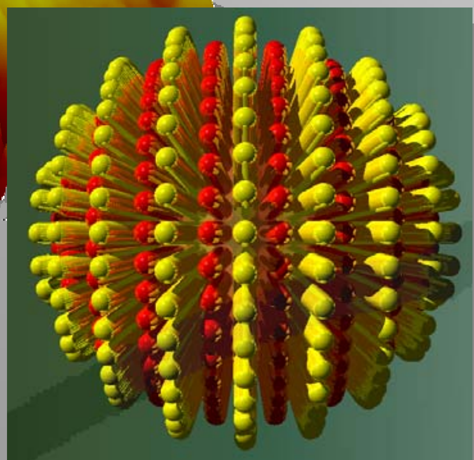


Two ligands

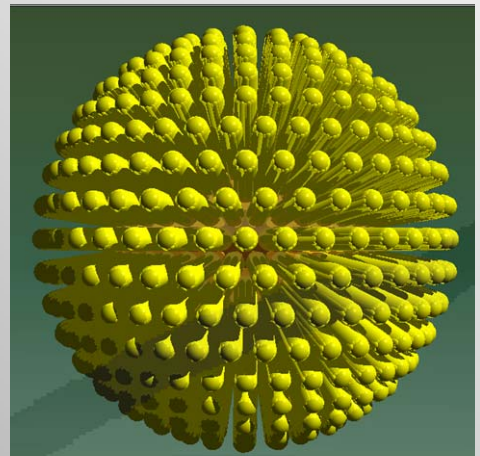


Hydrophilic Region:
Carboxylic Acid Terminated Molecules

One Ligand

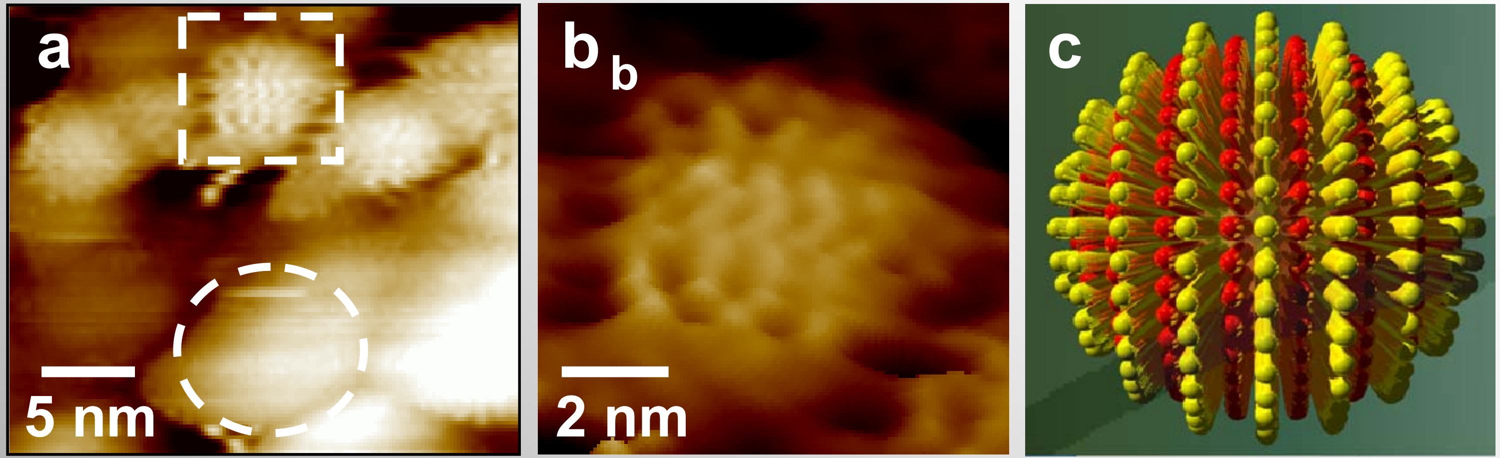


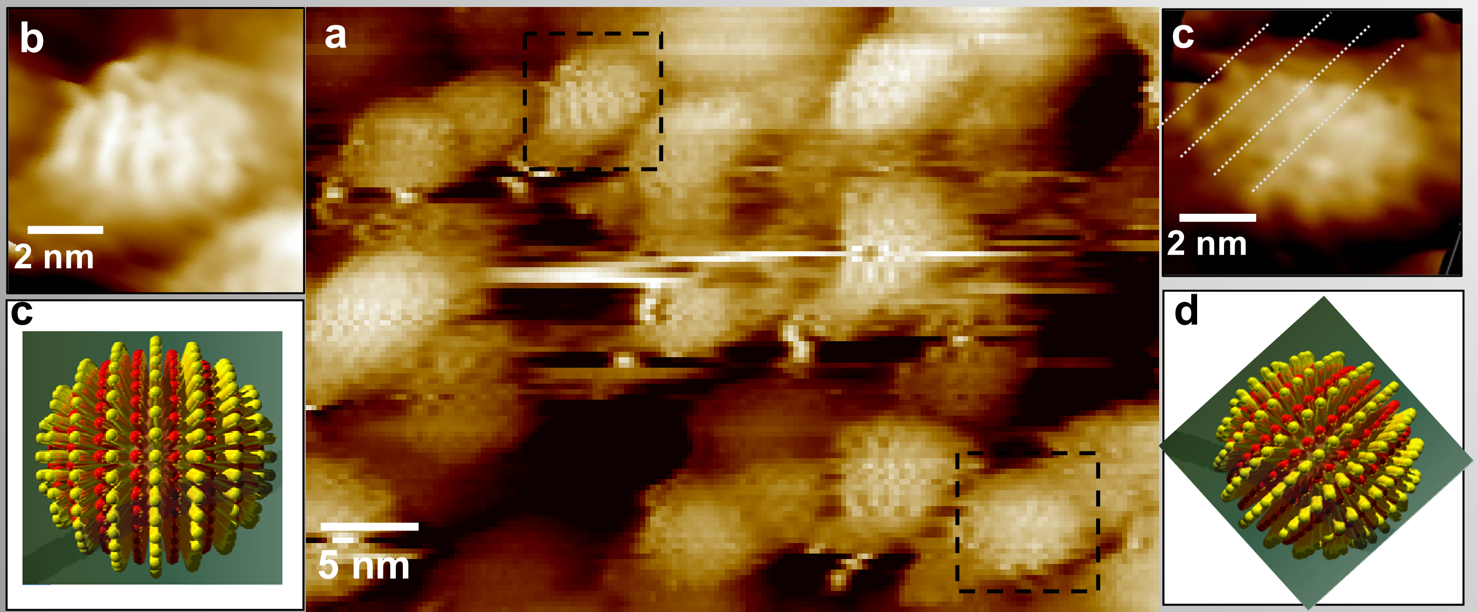
Hydrophobic Region:
Methyl Terminated Molecules



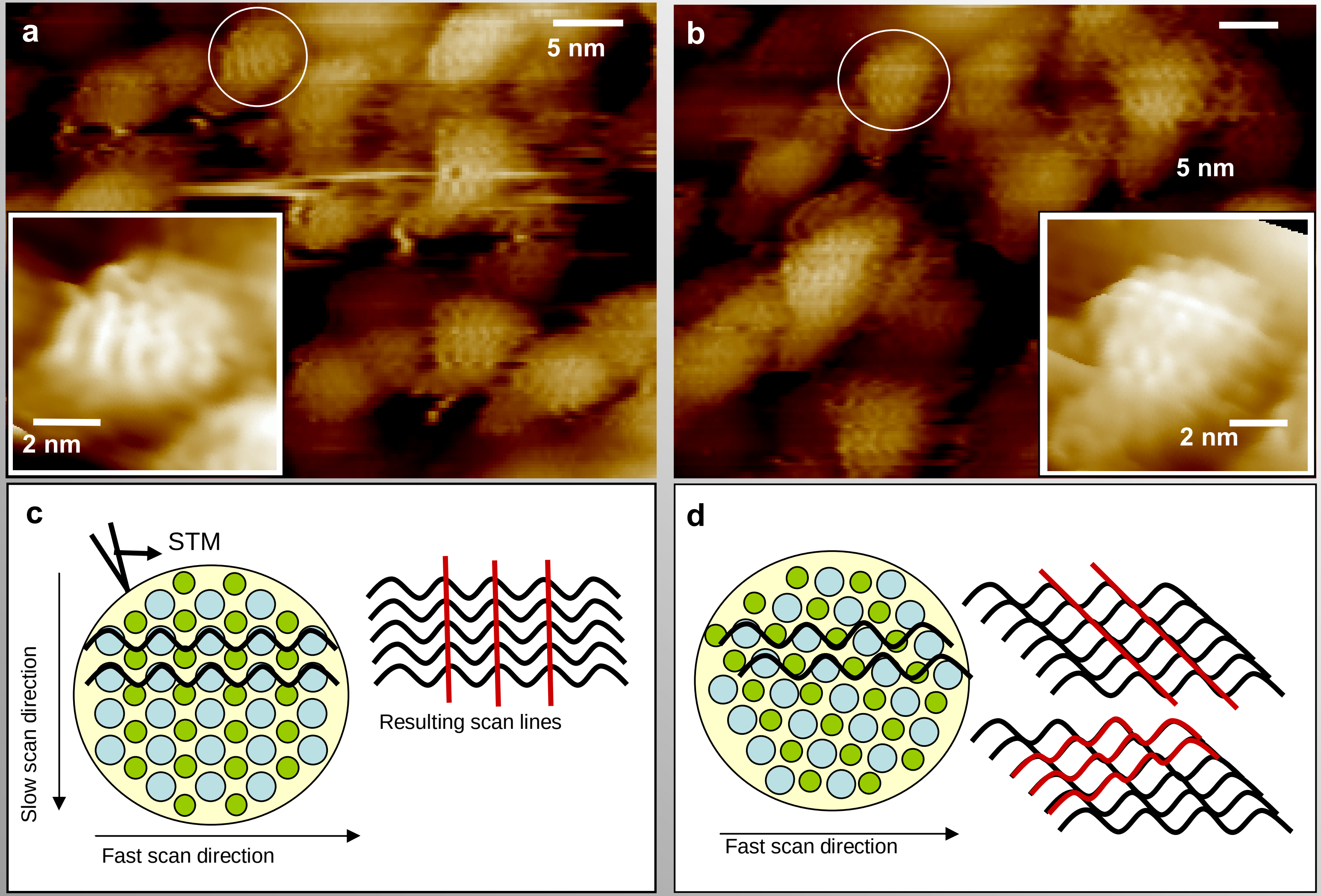
STM Imaging

S u N M a G





Rotation of Ripples



Artifacts and Real Features

S u N M a G

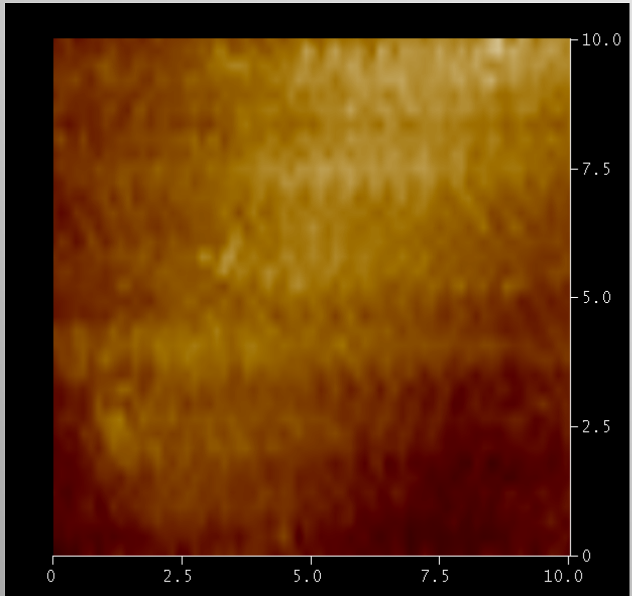


Image taken at 0.49 μm/s

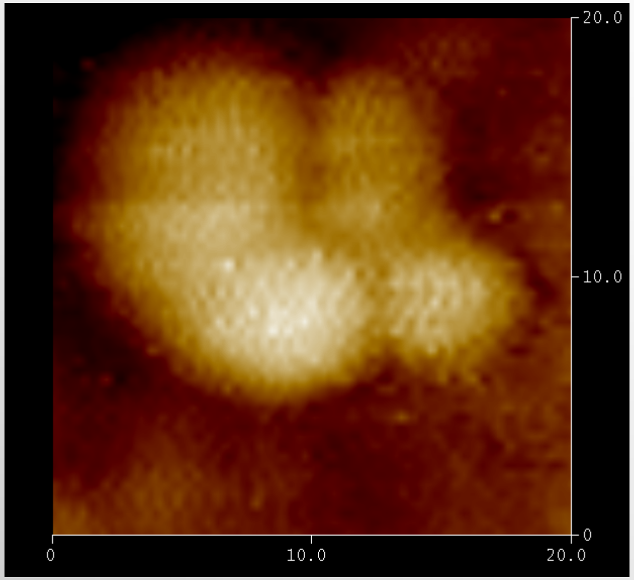


Image taken at 0.681 μm/s

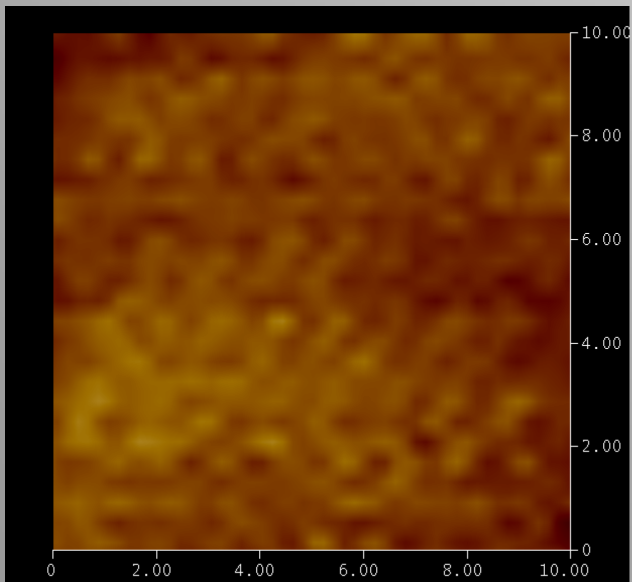


Image taken at 1.01 μm/s

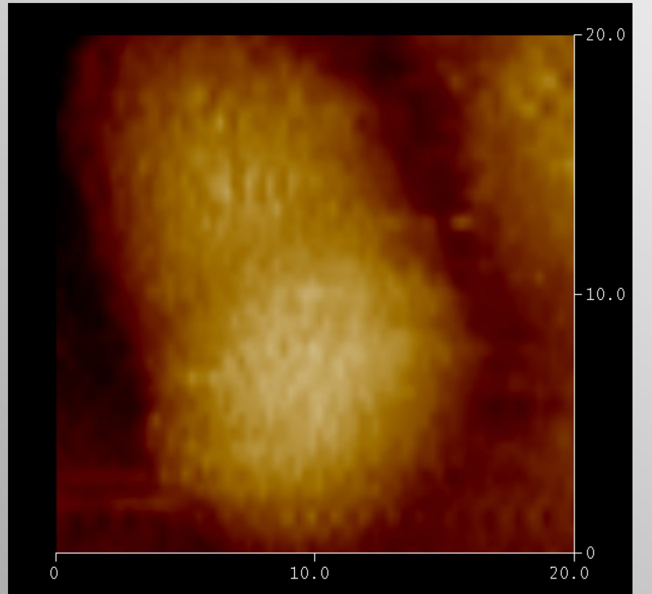


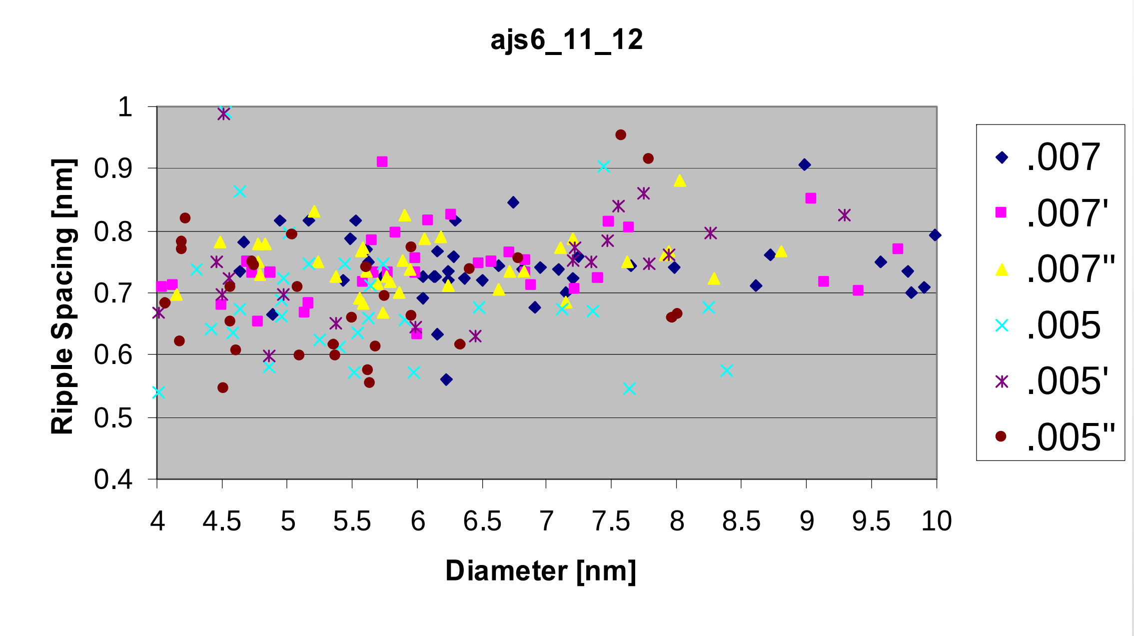
Image taken at 1.13 μm/s

Ripple Spacing and Imaging Speed

S u N M a G

005 image taken at 0.57 μm/s

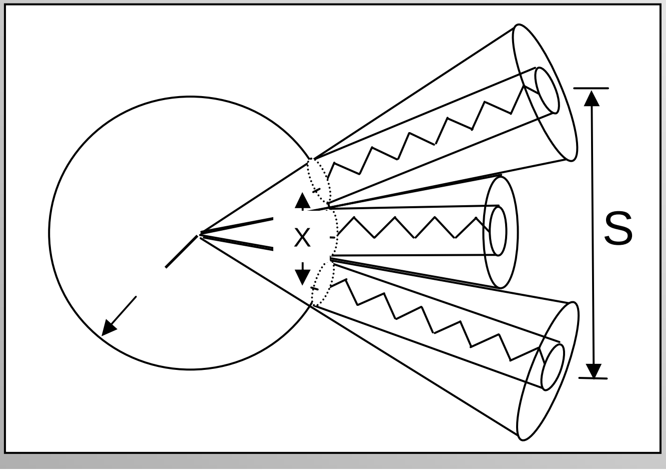
Shows average ripple spacing of 0.699 nm ±0.098 nm



007 image taken at 0.814 μm/s

Shows average ripple spacing of 0.743 nm ± 0.052 nm

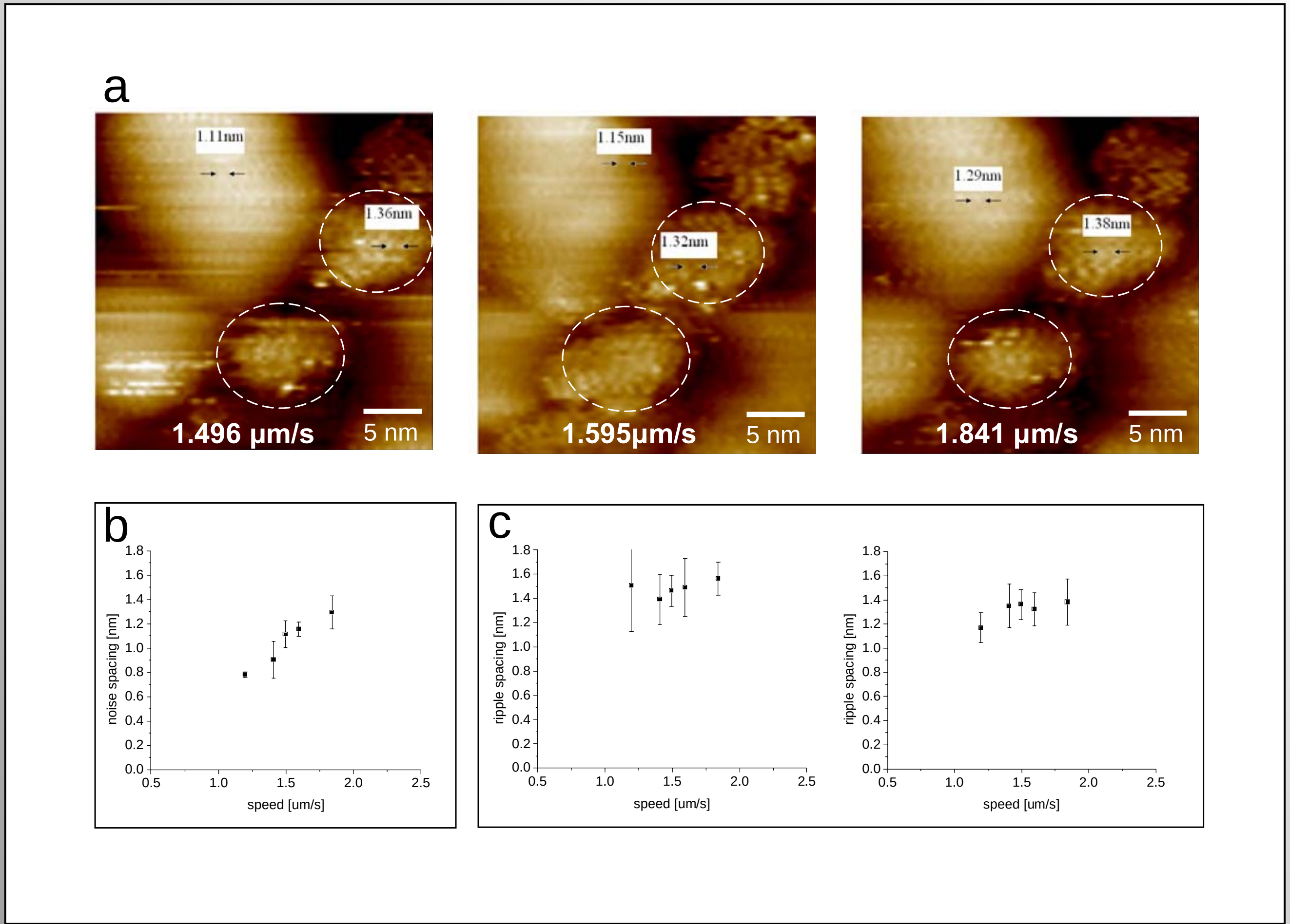
Average S-S spacing of 4.6 Å is too large to be adjacent sulfurs—suggest a 'hidden ligand'



2nm <d< 6nm S-S =0.6-0.7 nm

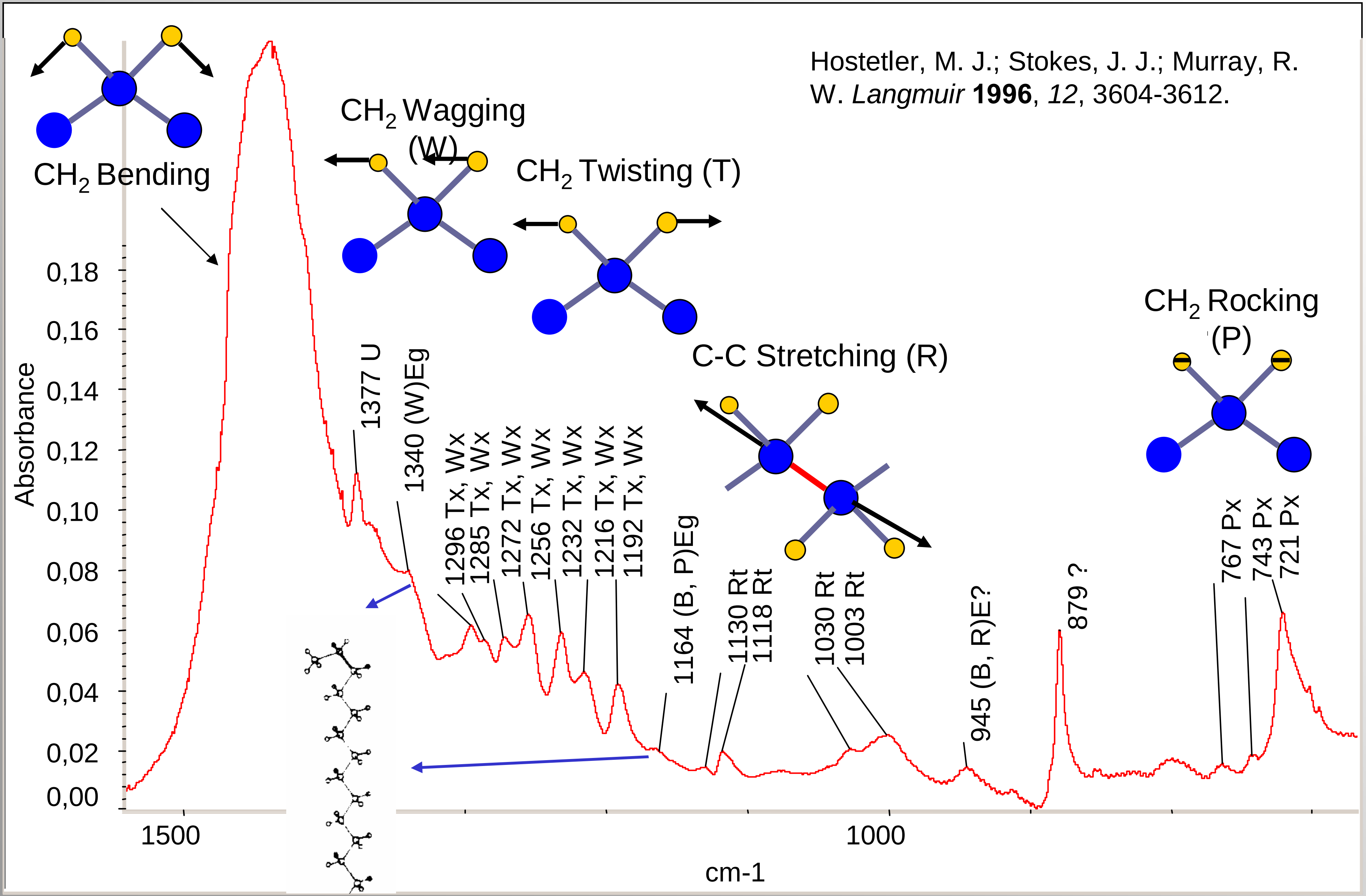
Noise and Ripples

S u N M a G



IR Spectrum of OT Nanoparticles

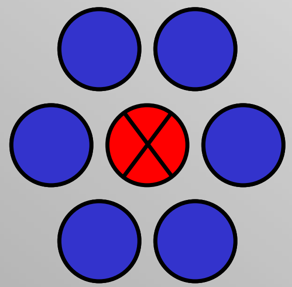
S u N M a G



Perfect Mixing vs Phase Separation

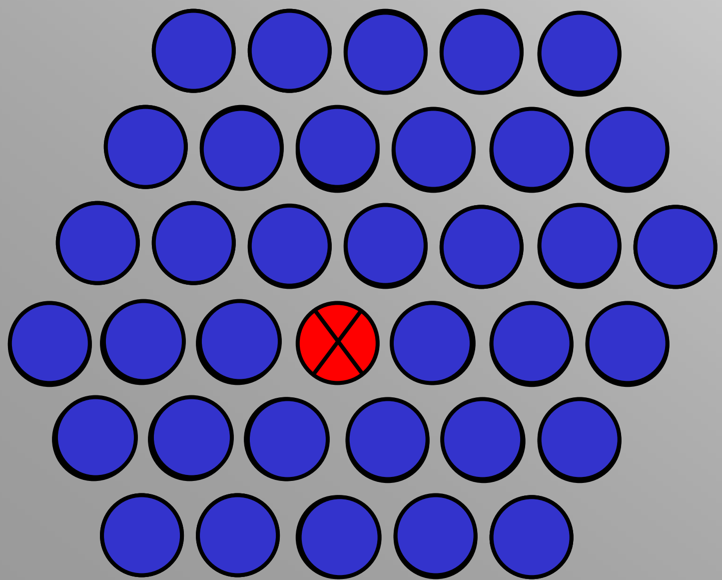
S u N M a G

PERFECT MIXING model

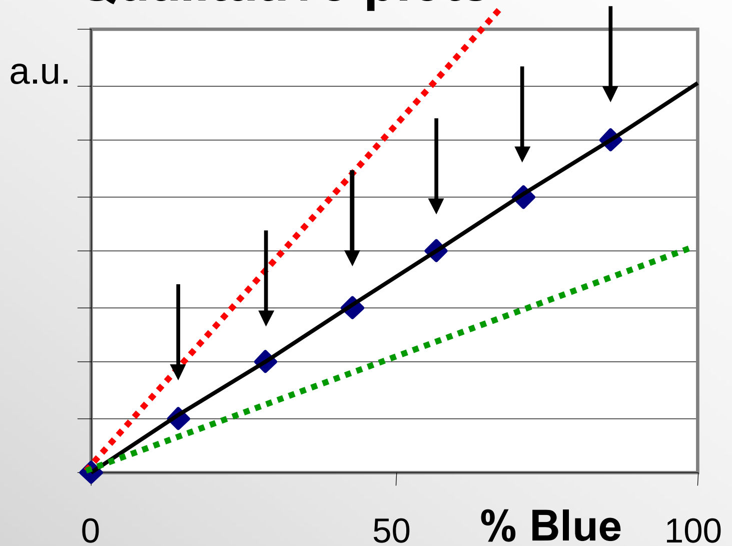


The **intermolecular coupling** between similar molecules **decreases** with dilution

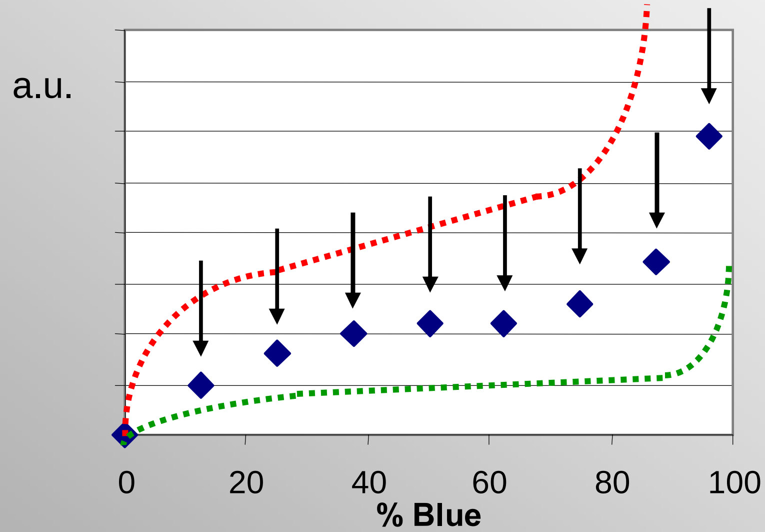
PHASE SEPARATION model



Qualitative plots



Kodati, V. R. et al. *J. Phys. Chem.* **1994**, *98*, 12191-12197.



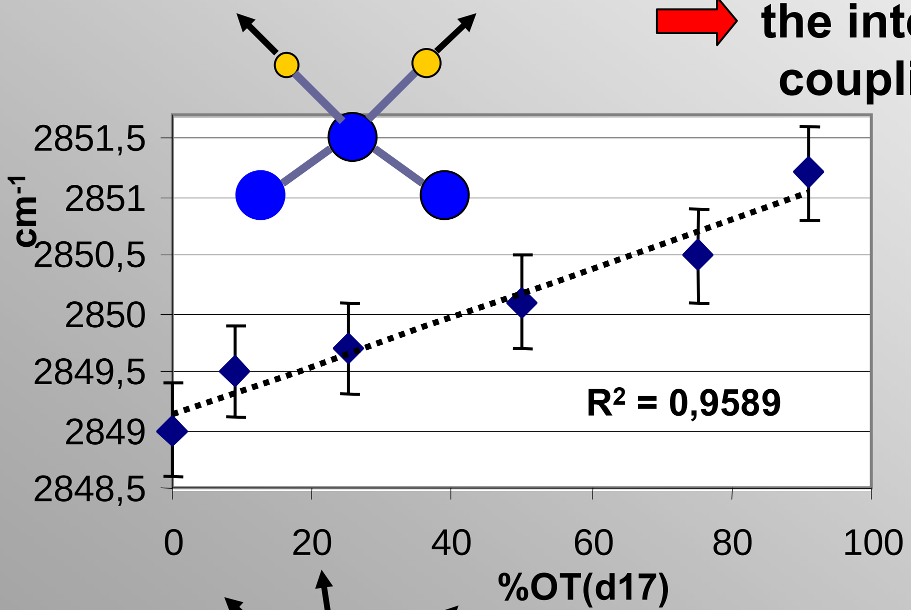
An Example of Perfect Mixing

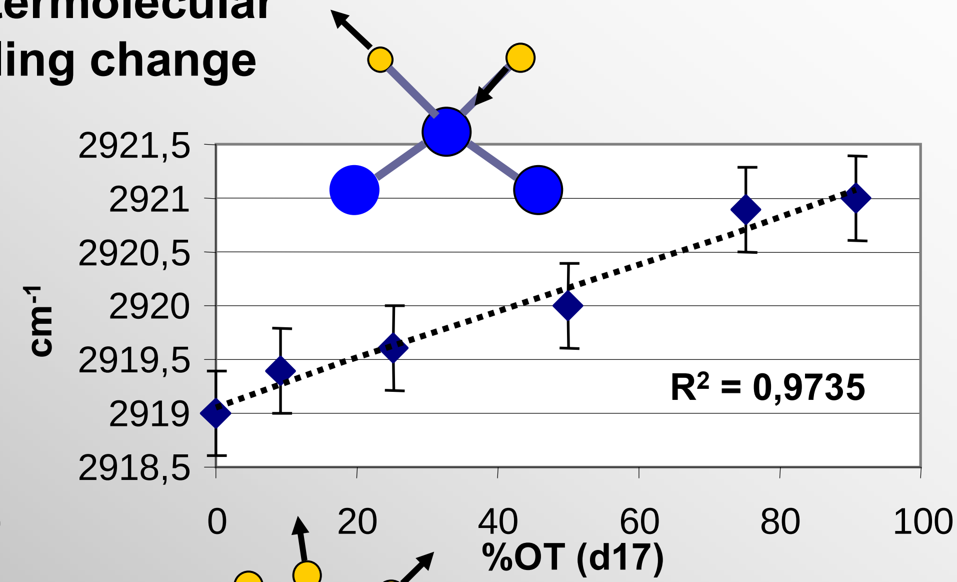
S u N M a G

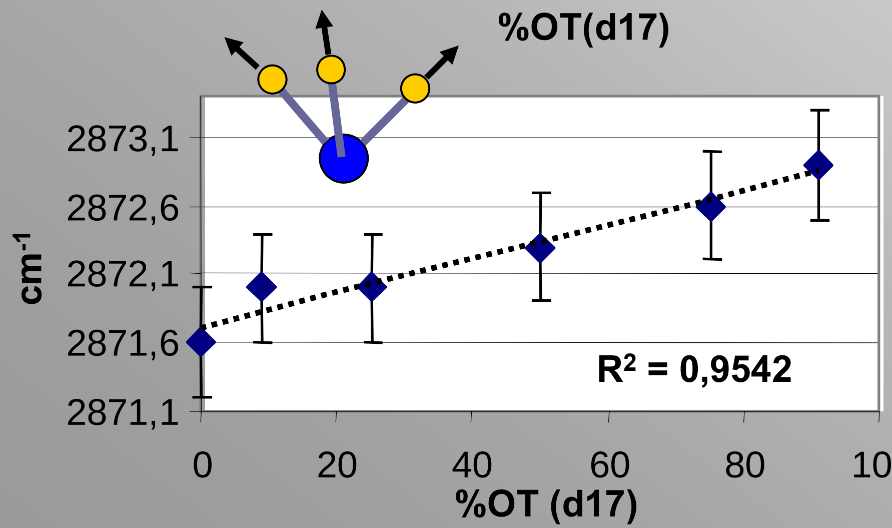
OT(d17)/OT MPMN's

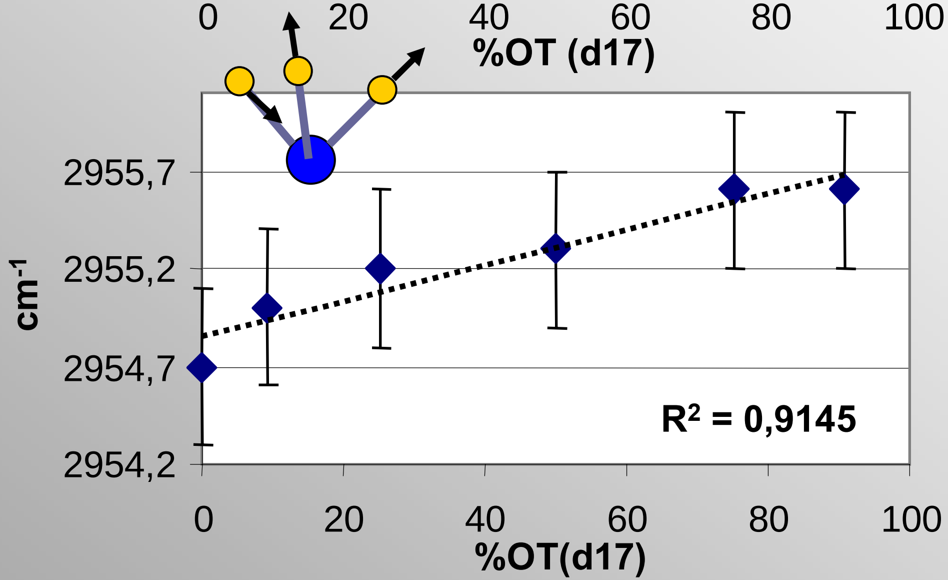
CH Stretching

the intermolecular coupling change





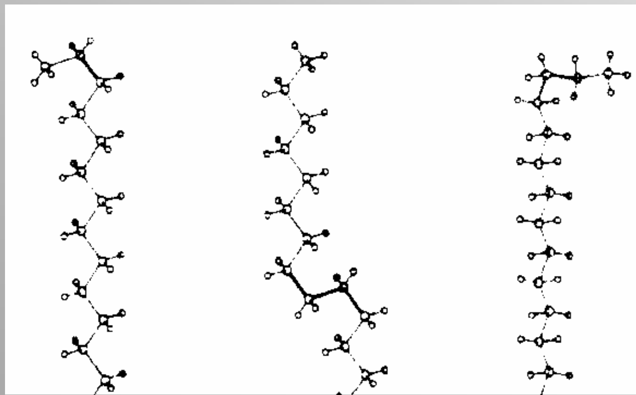




The C-H stretching region

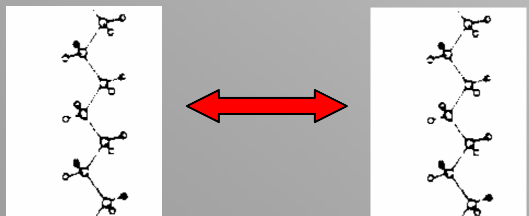
The CH_2 Stretching frequencies are influenced by:

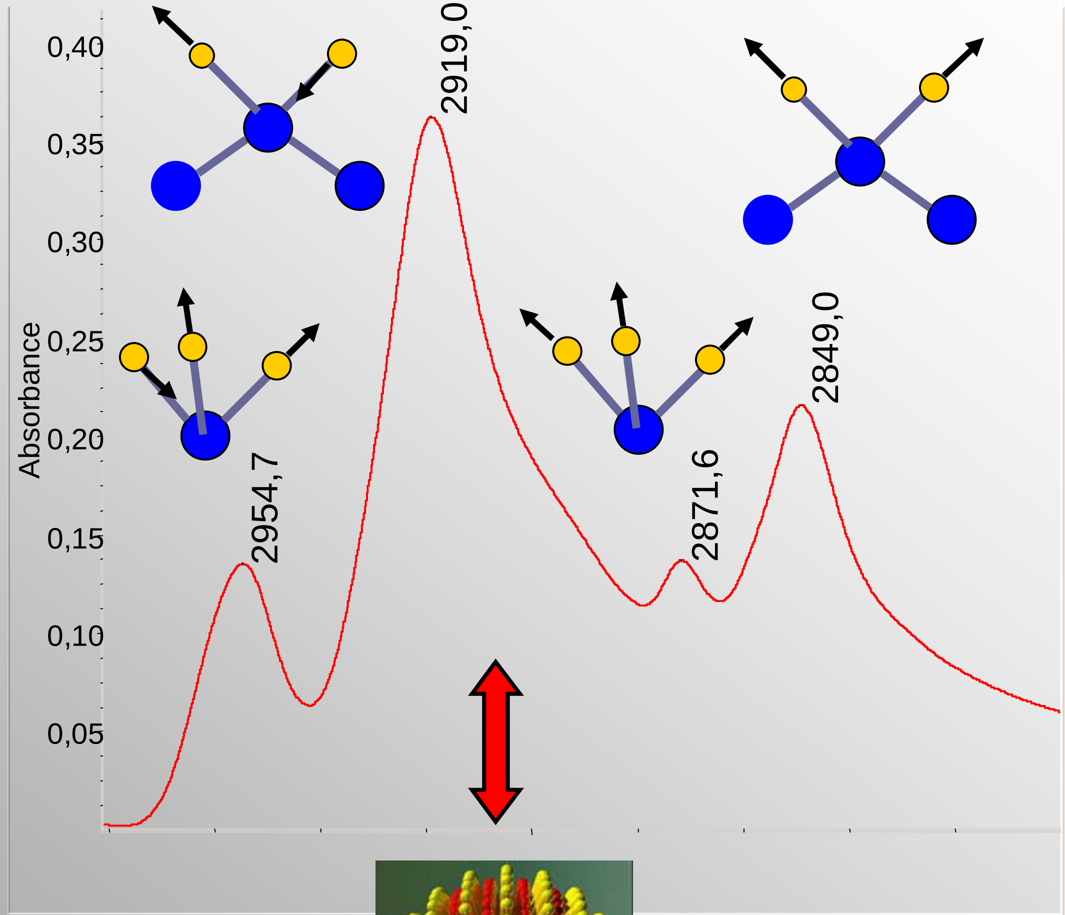
- **Intramolecular conformational defects (v↑)**

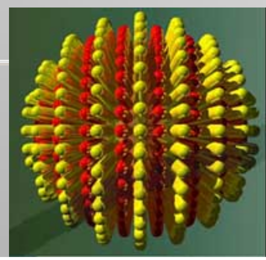


End gauche gtg' "kink" gg' double gauche

- **Intermolecular coupling (v↓)**







Snyder, R. G. et al. *Biochimica Et Biophysica Acta* **1980**, *601*, 47-53.

Kodati, V. R. et al. *J. Phys. Chem.* **1994**, *98*, 12191-12197.

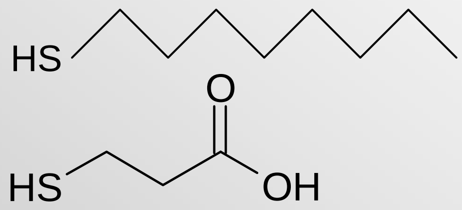
Gaber, B. P.; Peticolas, W. L. *Biochimica Et Biophysica Acta* **1977**, *465*, 260-274.

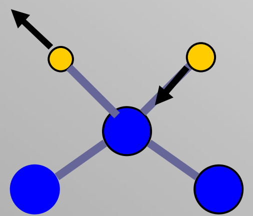
OT/MPA NPs: a case of phase separation

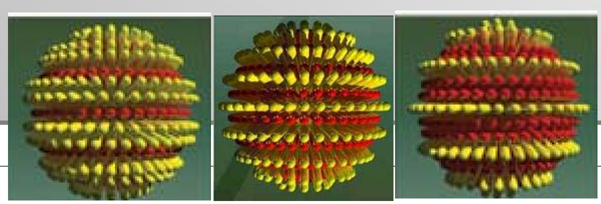
S u N M a G

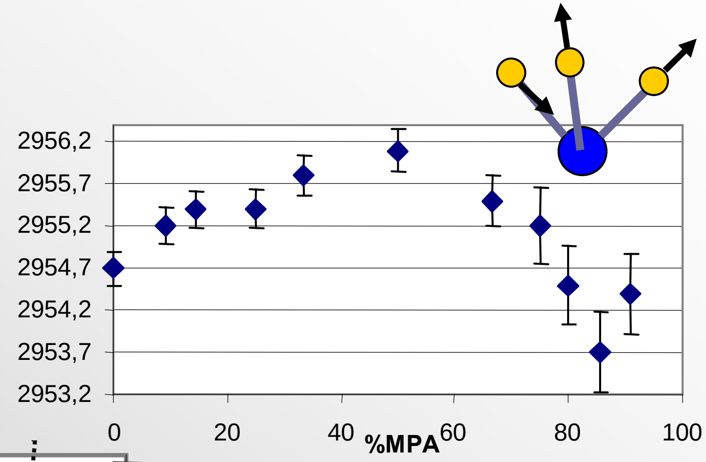
OT

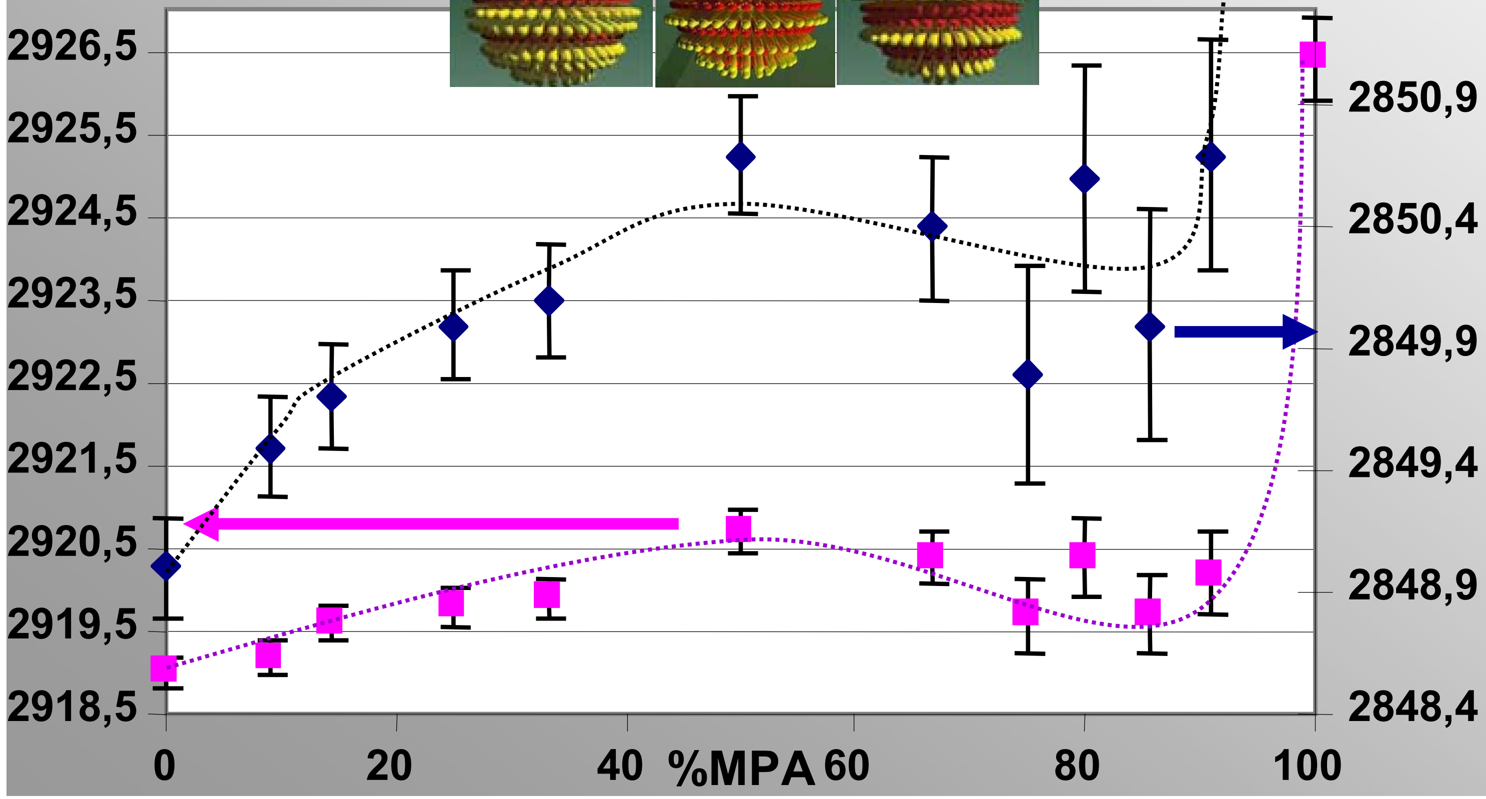
MPA

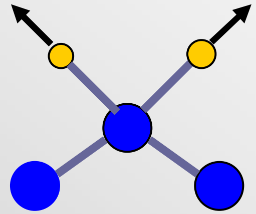






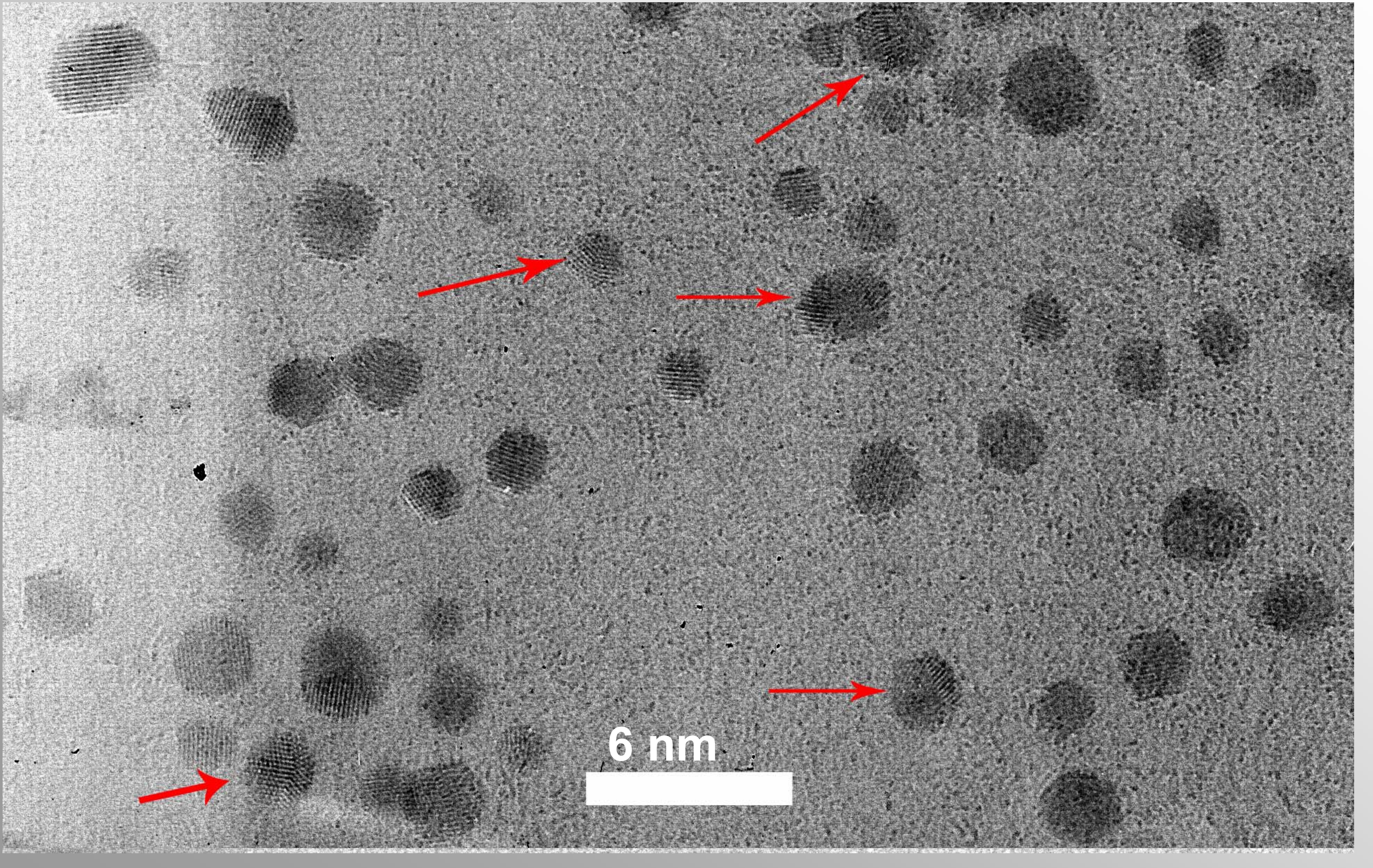






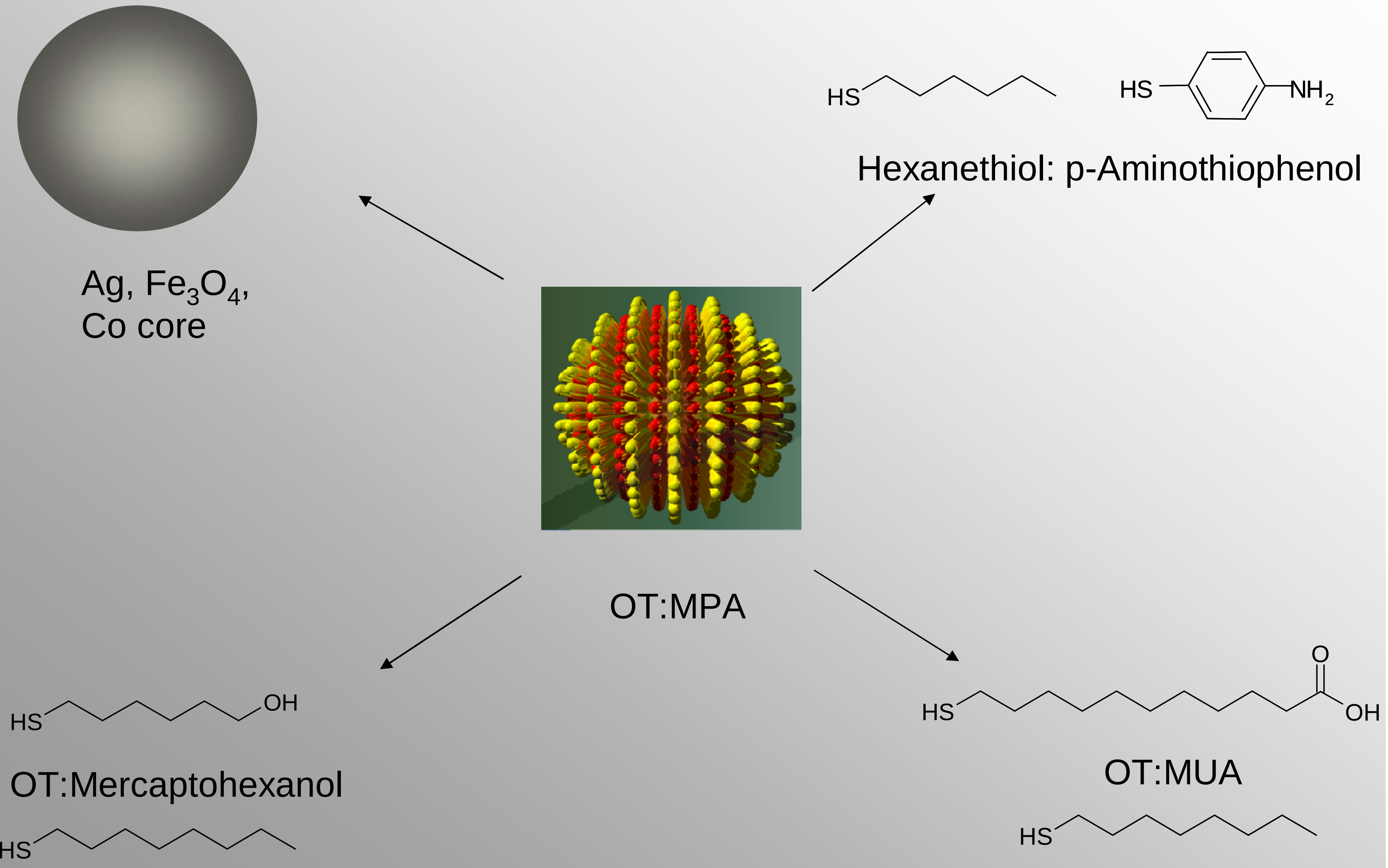
Lines only to guide the eye

Core Effect



Phase Separation on Nanoparticles

S u N M a G

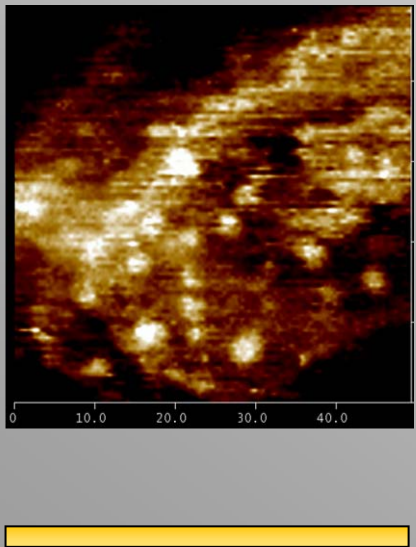


Curvature Effects

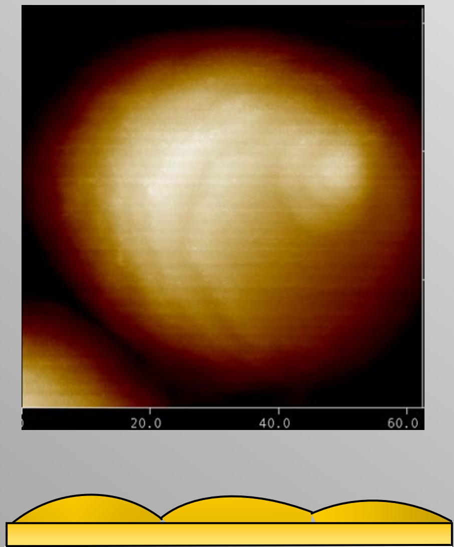
S u N M a G

OT:MPA Mixed Monolayers formed on surfaces of varying curvatures

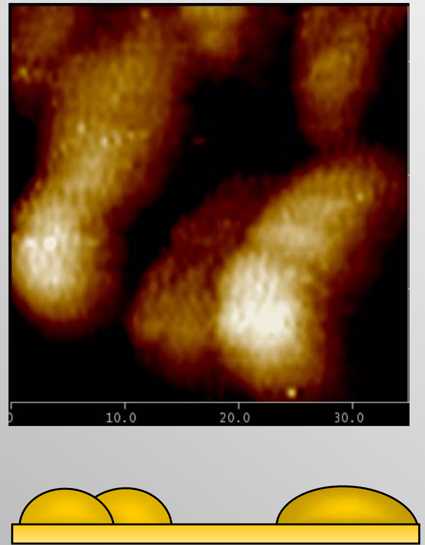
Increasing Curvature



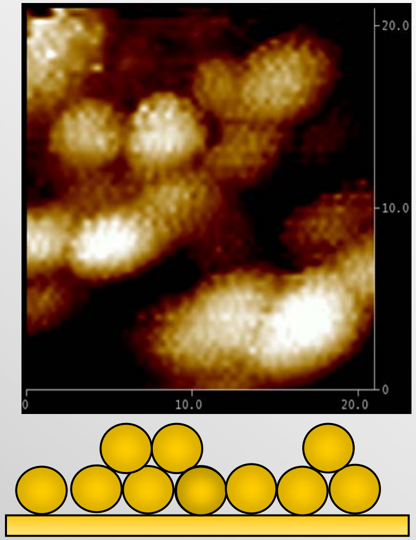
Flat Au (111) on Mica



Au on Si, with 20 nm hemispheres



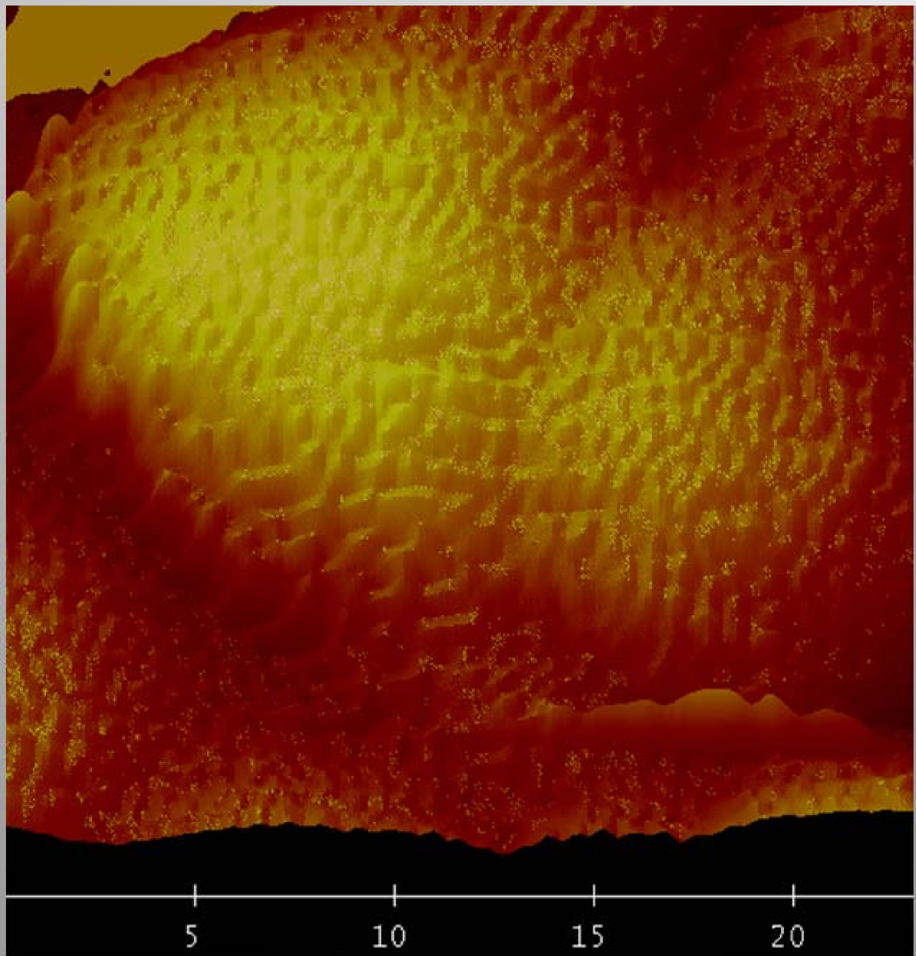
Au film with Au crystals ~ 10 nm



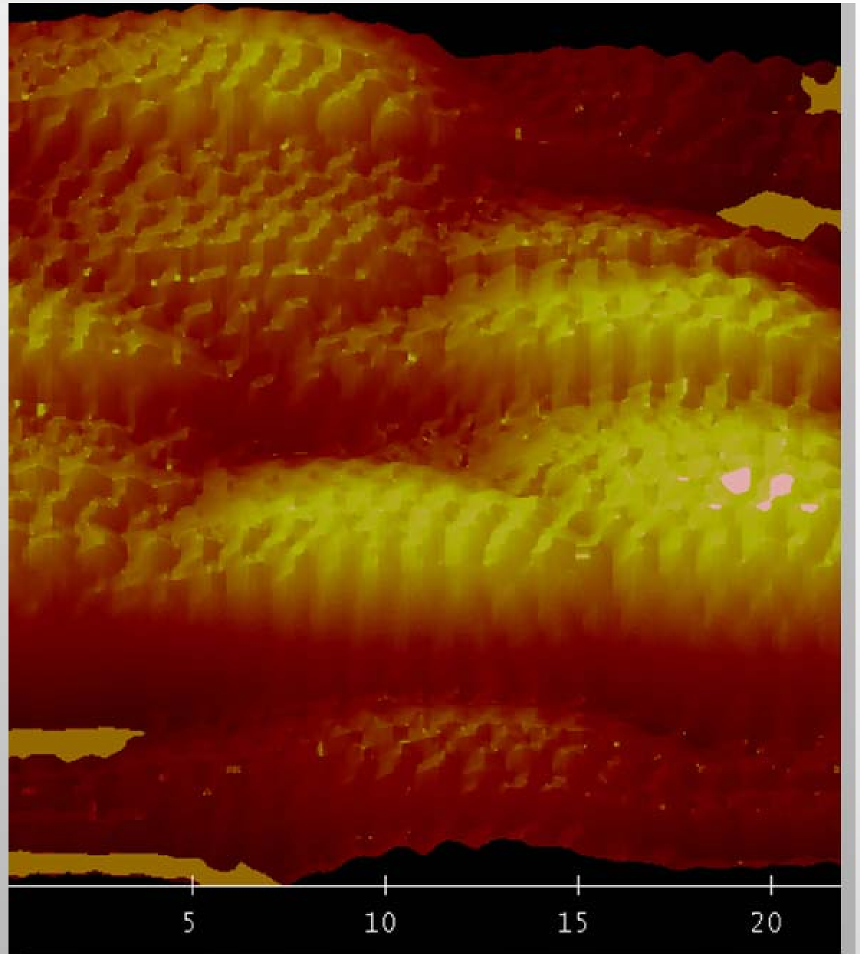
Au film with Au crystals ~ 4 nm

Synthesis and Conformation

S u N M a G



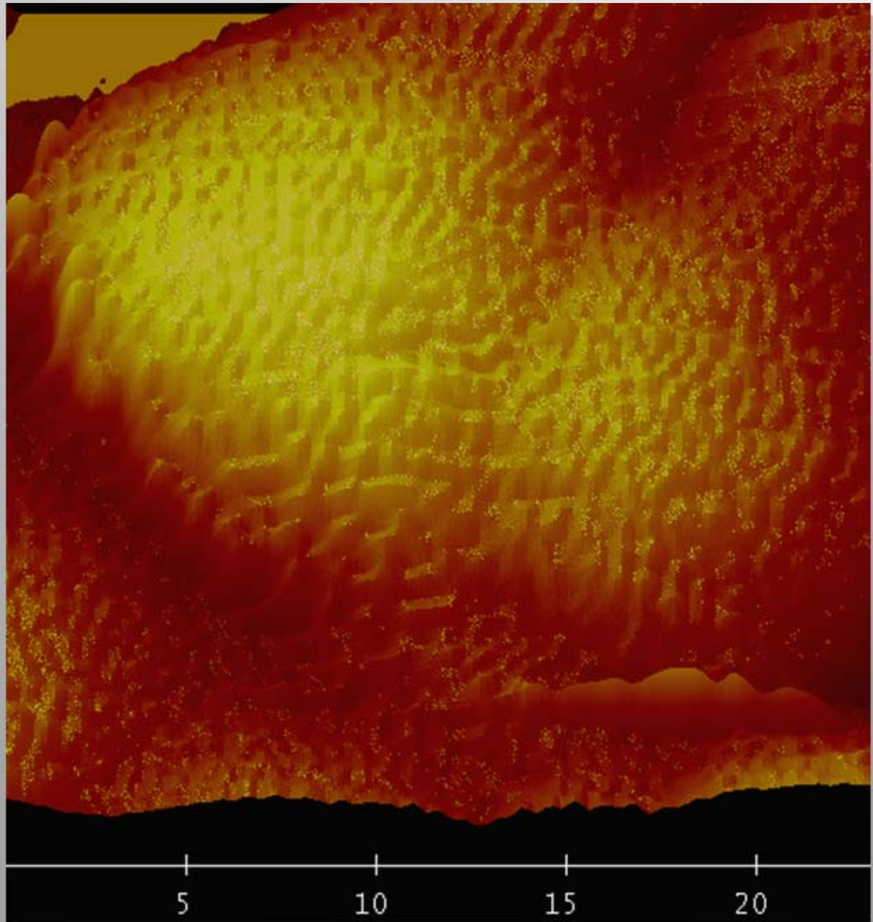
Nanoparticles obtained via the **two-step** method

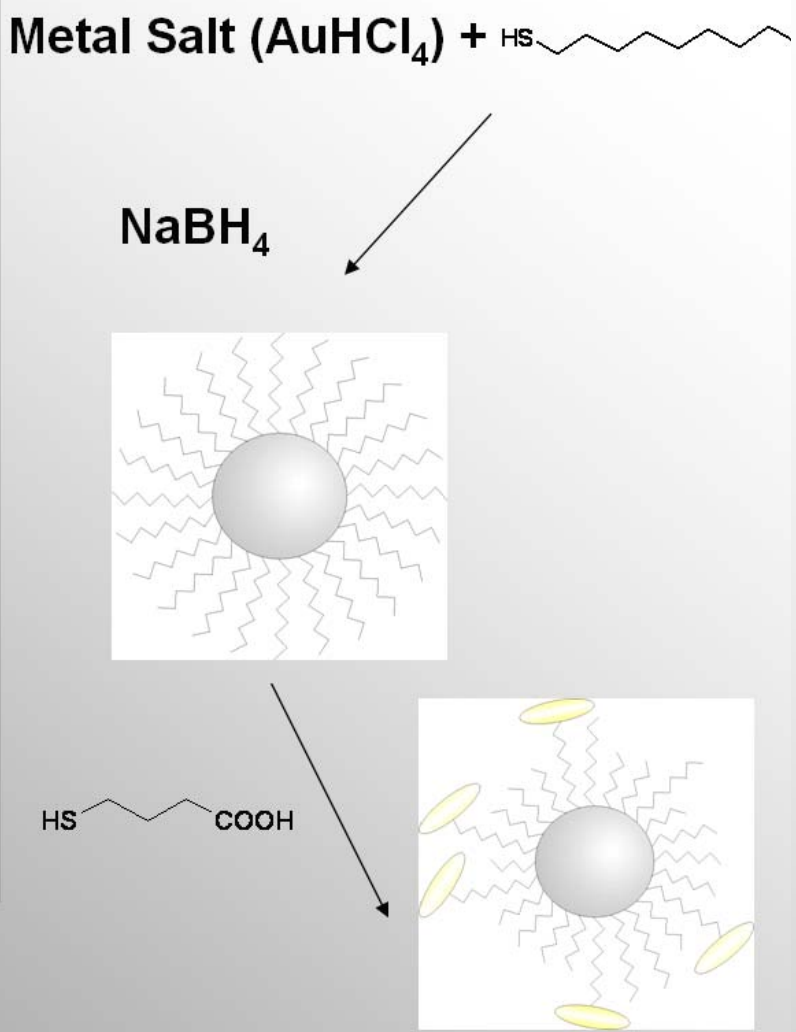


Nanoparticles obtained via the **one-step** method

Synthesis and Conformation

S u N M a G

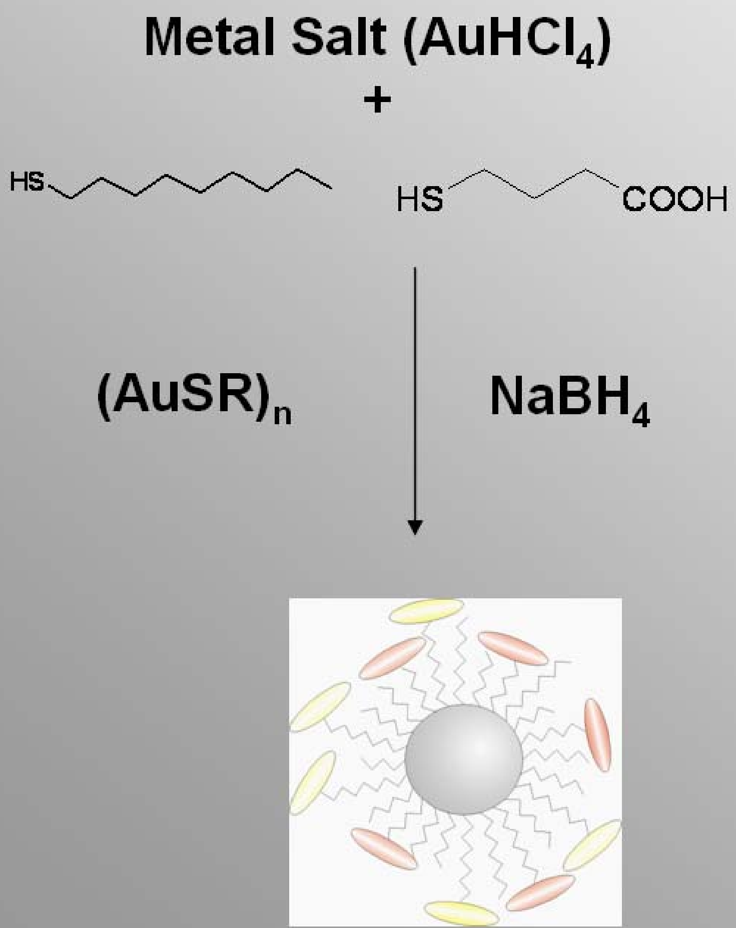


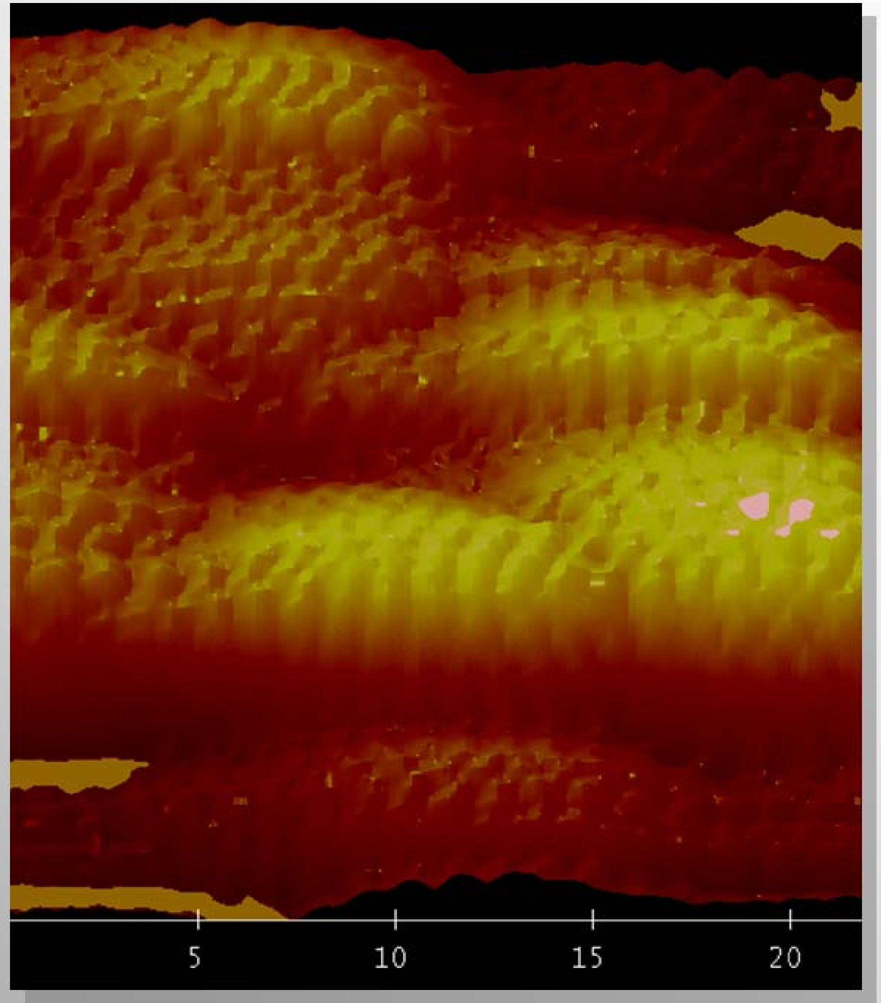


Nanoparticles obtained via the **two-step** method

Synthesis and Conformation

S u N M a G

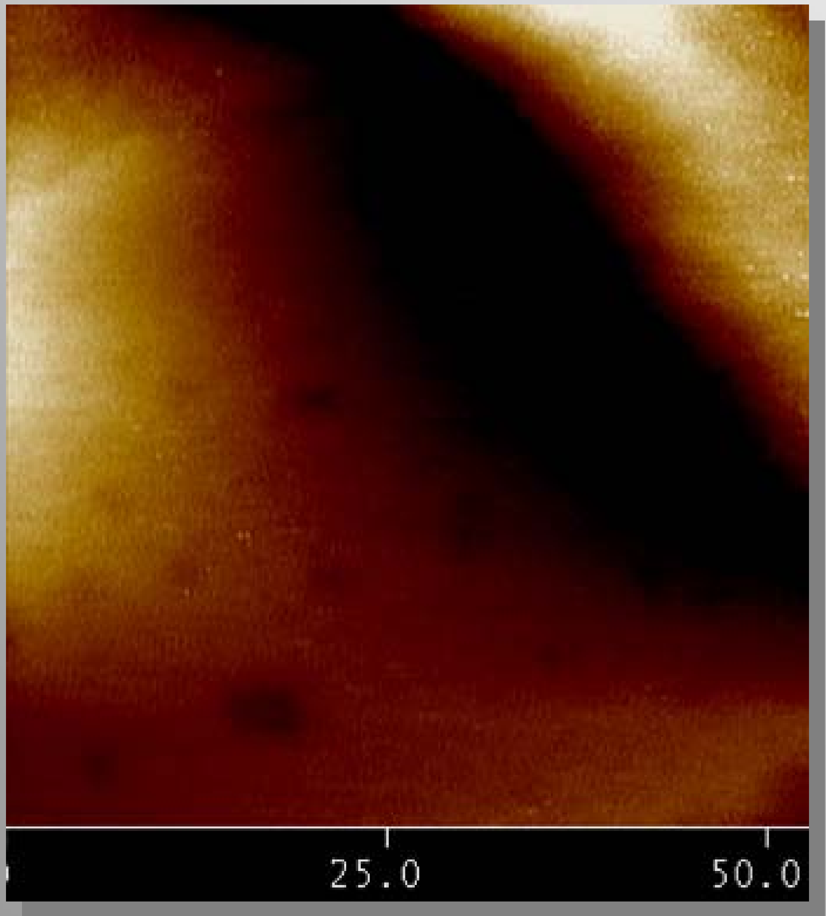




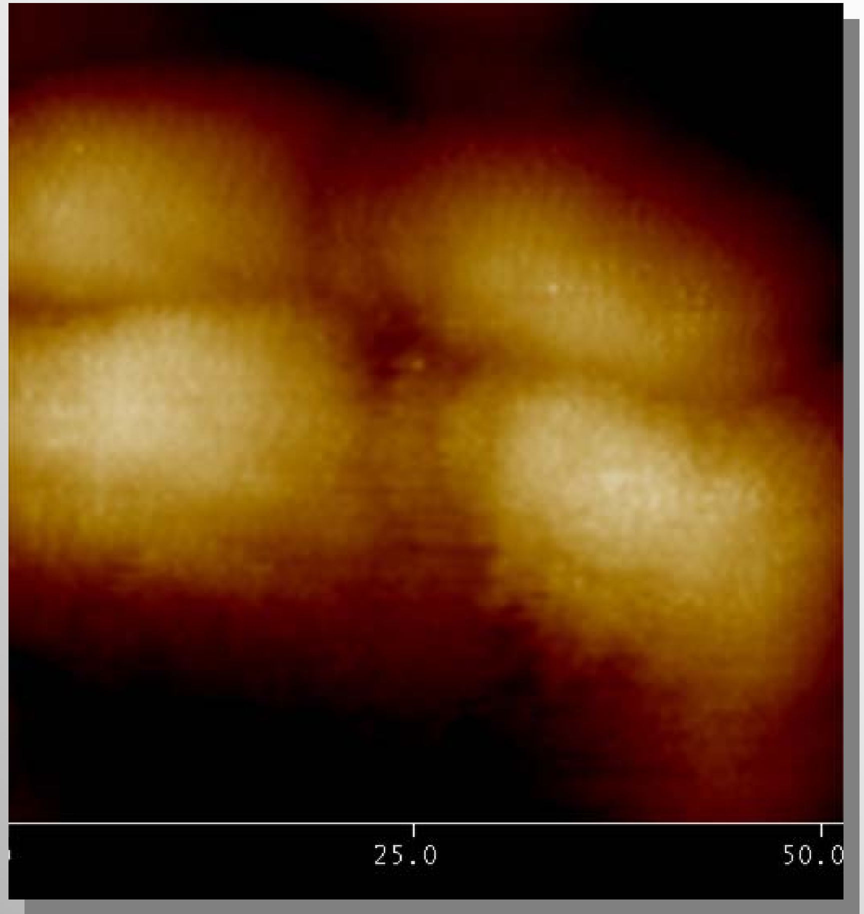
Kinetic Effect

S u N M a G

Au thermally evaporated on Si



SAM formed in the absence of $(AuSR)_n$

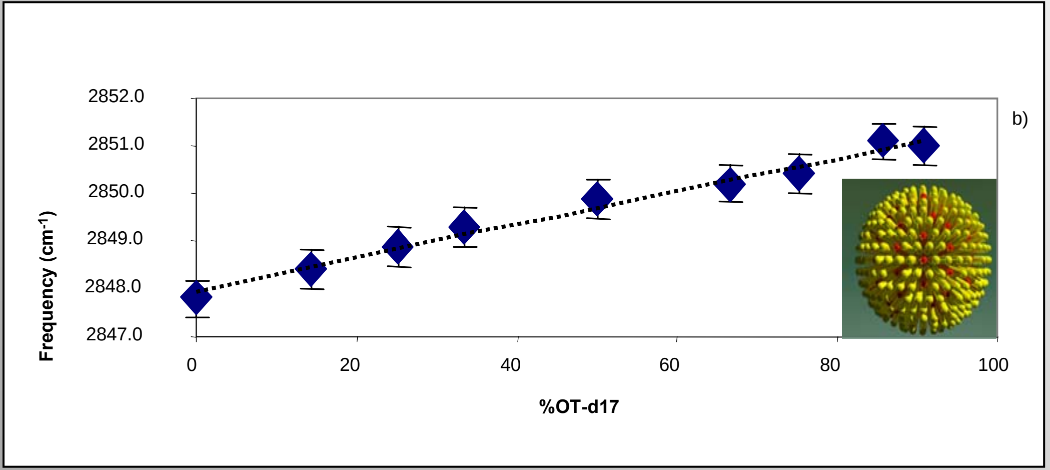


SAM formed in the presence of $(AuSR)_n$

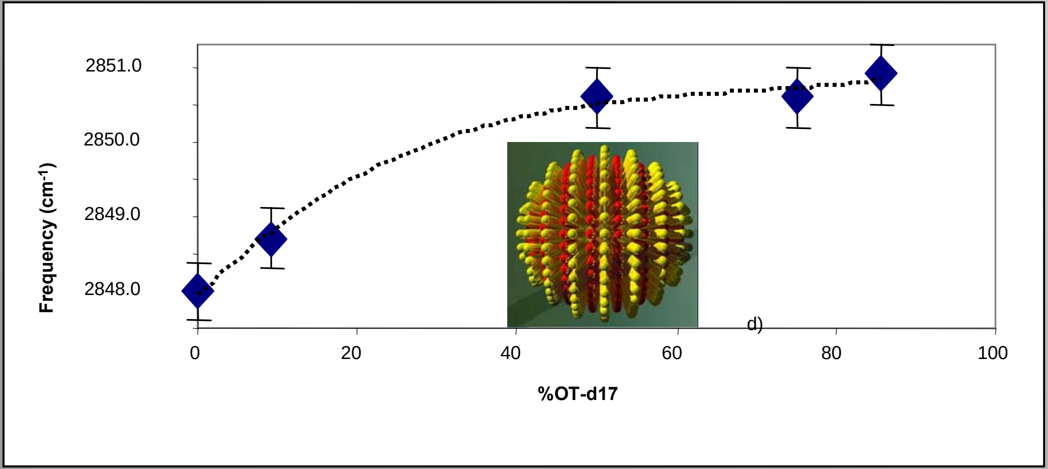
Ripple Development Over Time

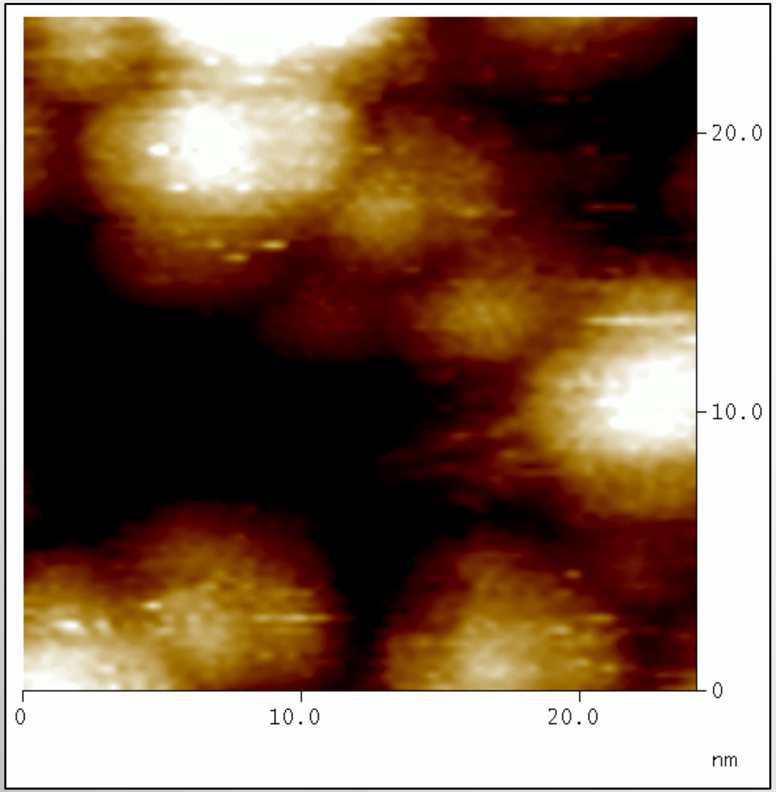
S u N M a G

As Synthesized



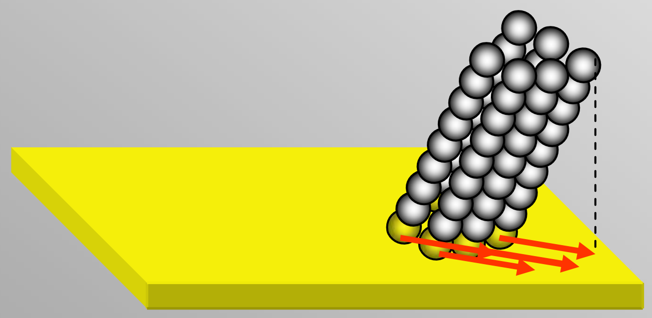
Two Weeks Later





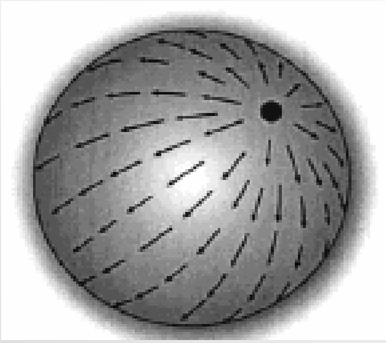
The hairy Ball Theorem and SAMs

Vectorial Order in SAMs



Molecules in SAMs form a 2D crystal.

The hairy ball theorem

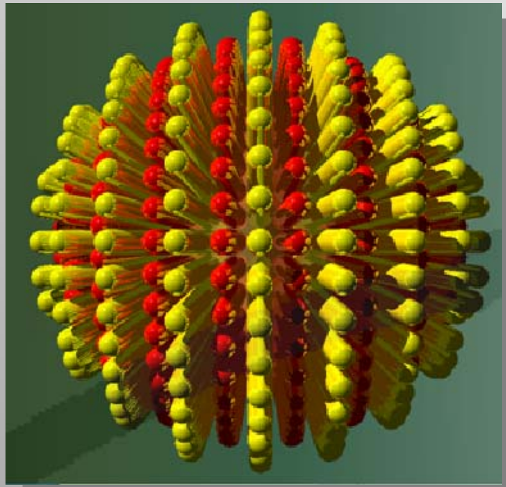
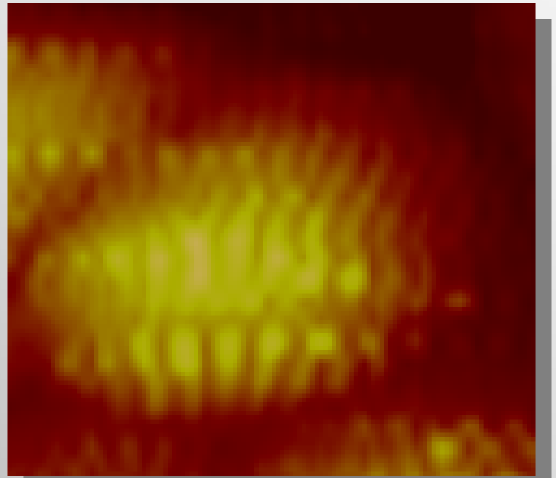


The hairy ball theorem states that a vectorial order cannot propagate on a topological sphere unless the vector assumes a zero value in at least two points, called poles.

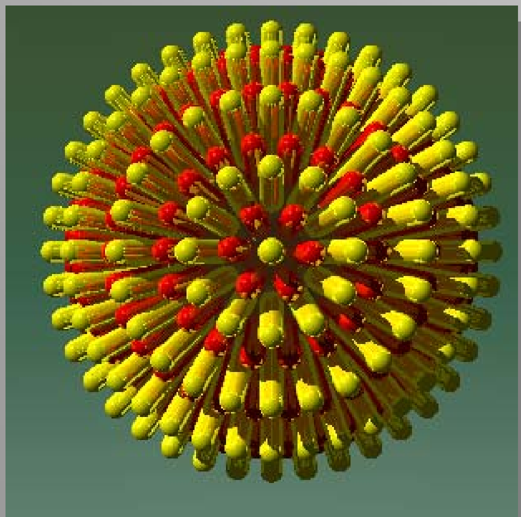
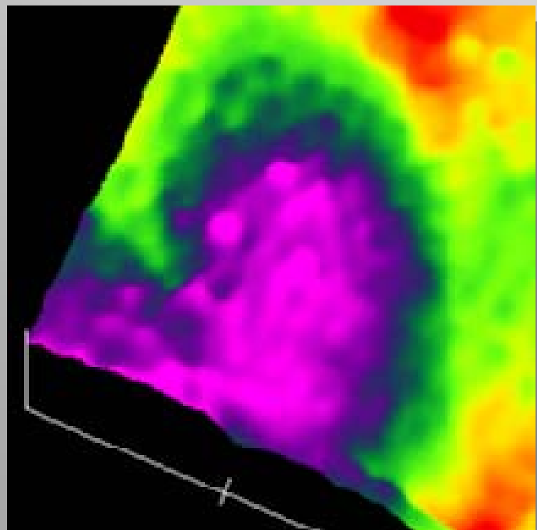
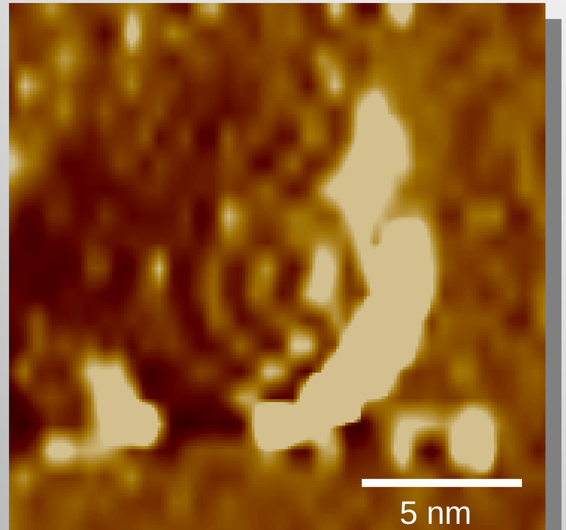
Poles on Domained NPs

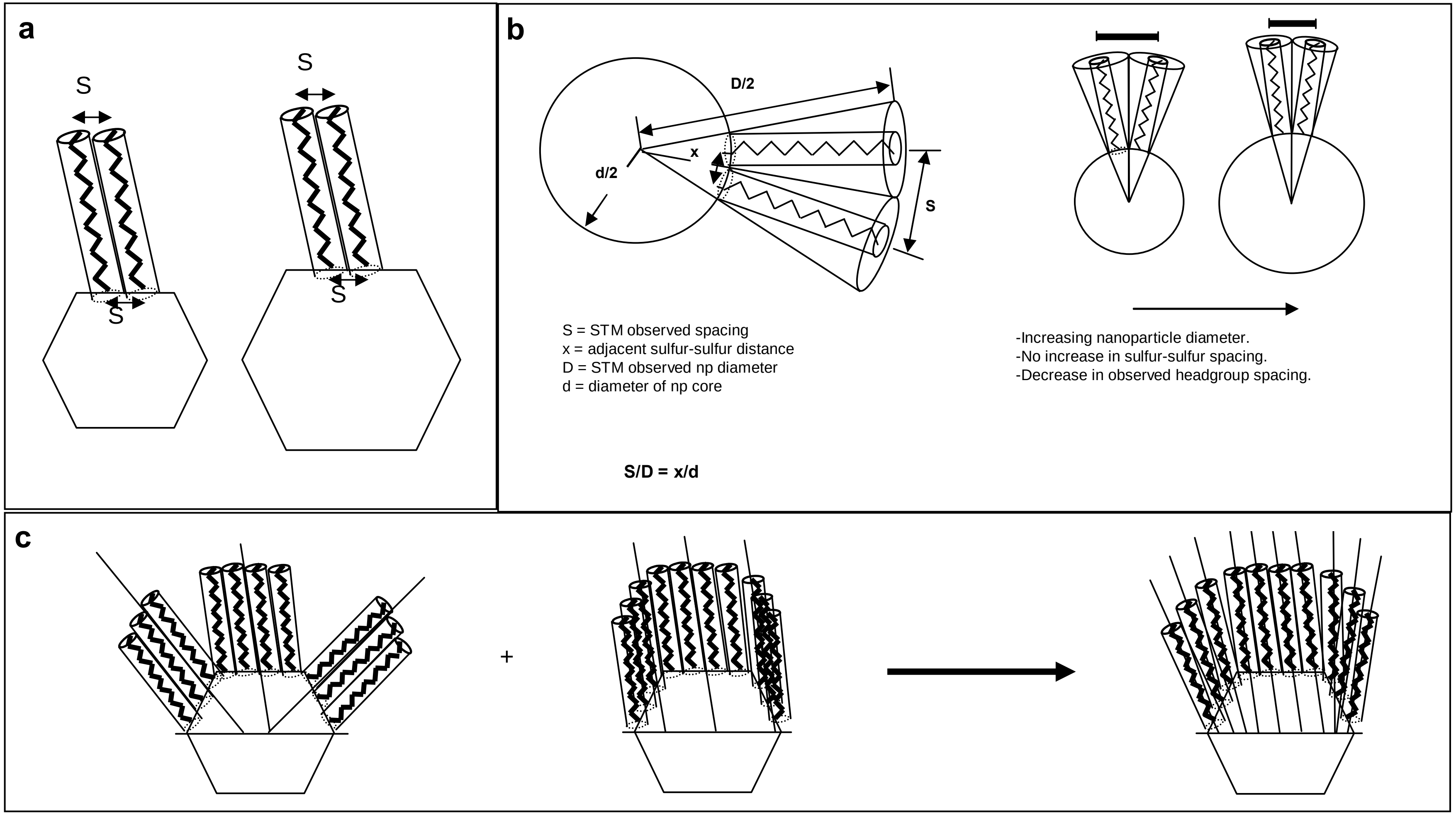
S u N M a G

To have order on a nanoparticle:

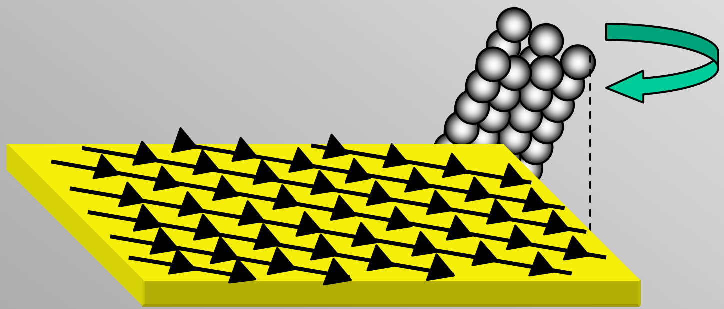

Poles are needed:


a
S
S
S
S
b
D/2
x
d/2
S
S = STM observed spacing
x = adjacent sulfur-sulfur distance
D = STM observed np diameter
d = diameter of np core
S/D = x/d
-Increasing nanoparticle diameter.
-No increase in sulfur-sulfur spacing.
-Decrease in observed headgroup spacing.
c
+

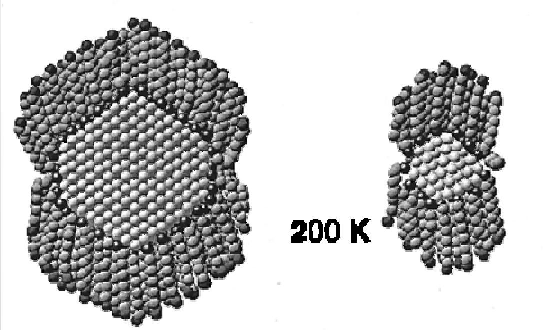
Thermodynamic interpretation

What is the Vectorial Order in SAMs?

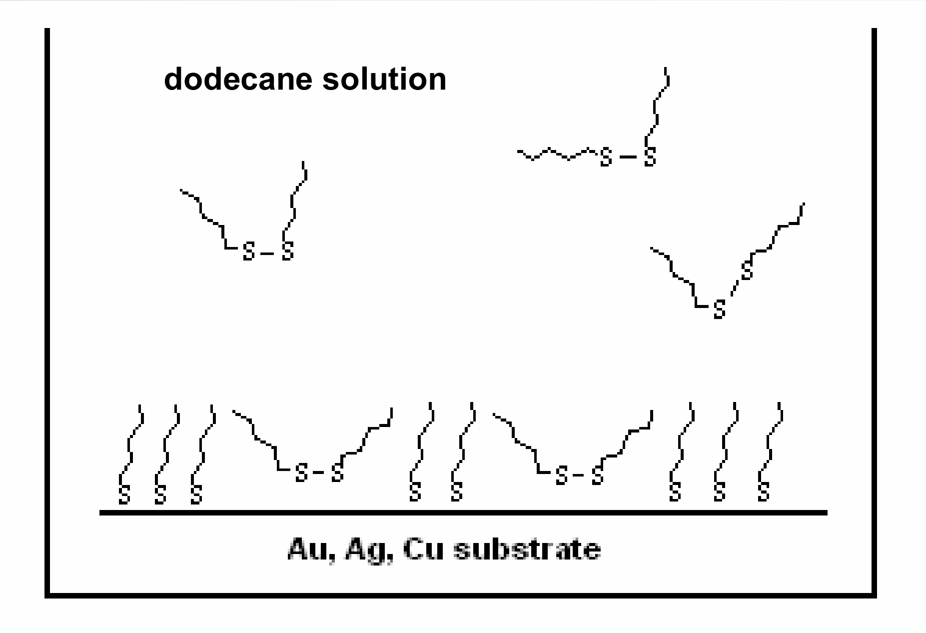


- Molecules in SAMs form a **specific angle** with the surface normal in order to maximize van derWaals interactions.
- One can define a vector (from the attachment point to the projection of the molecular head group) to describe the molecular position.

What is a topological sphere?



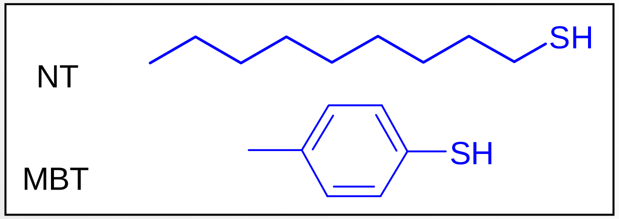
W. D. Luedtke and Uzi Landman ***J. Phys. Chem. B,*** *102 (34), 6566,, 1998*



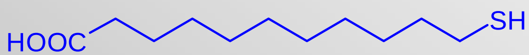
Chemistry of chain formation

S u N M a G

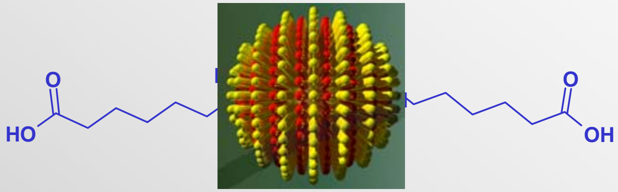
Gold nanoparticles with mixed ligand shell:
Nonanethiol (NT) : Methylbenzenethiol (MBT)



1. Pole functionalization with 11-Mercaptoundecanoic acid (MUA)



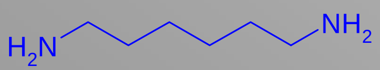
Short reaction times allow functionalization *only* at the polar singularities

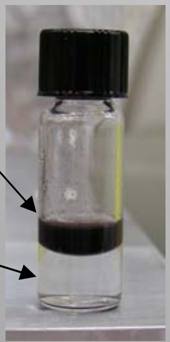


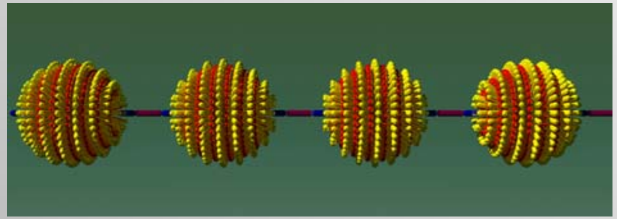
2. Two-phase reaction system: interface-controlled stoichiometry

Nanoparticles in toluene (organic phase)

1,6-Diaminohexane
in water phase







"Nano-nylon"

Nano-Nylon Two-Phase TEM images

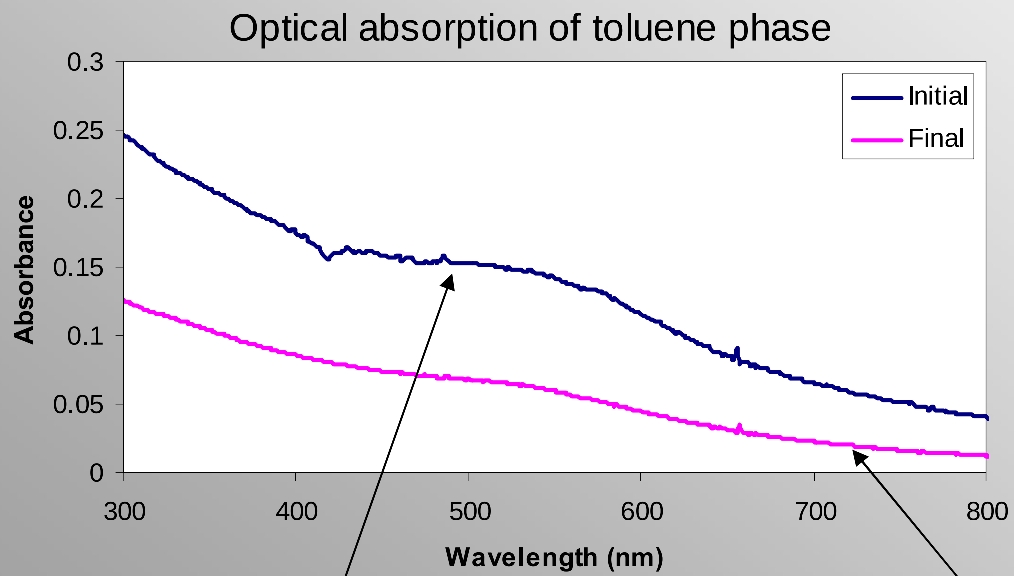
S u N M a G

Precipitation from solution

S u N M a G

Precipitate immediately begins to form at the toluene-water interface, indicating the formation of insoluble material.

After a few hours, the reaction has completed: the toluene phase is nearly colorless and almost all the nanoparticle material is in precipitate form.



The absorption cross section of a solution is directly related to its concentration

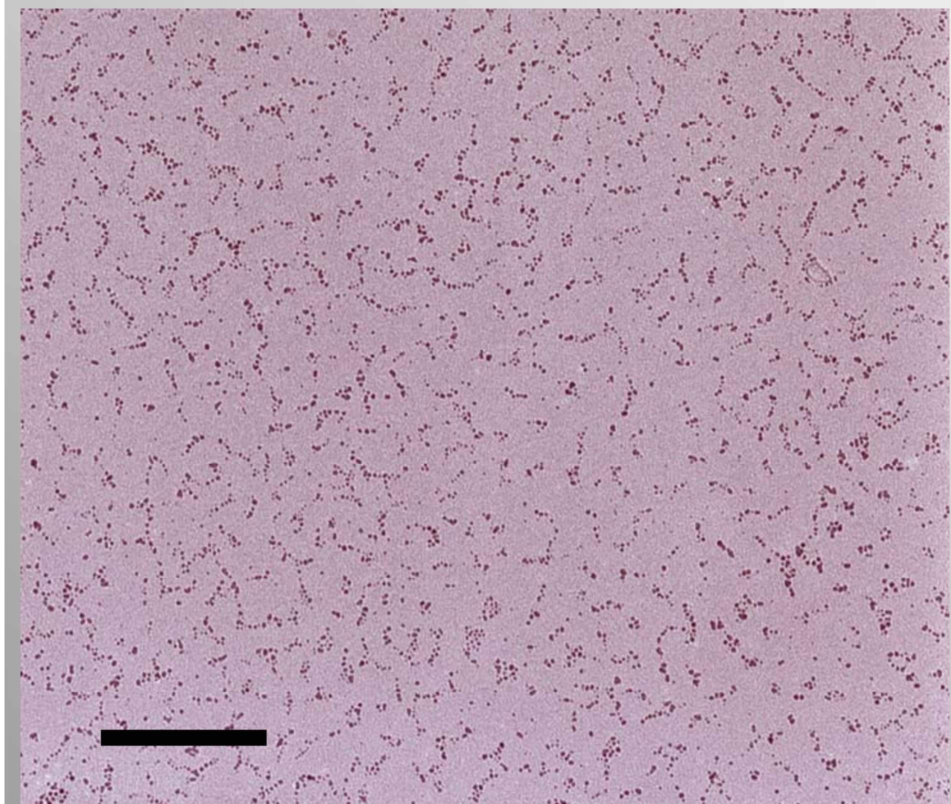
Initial

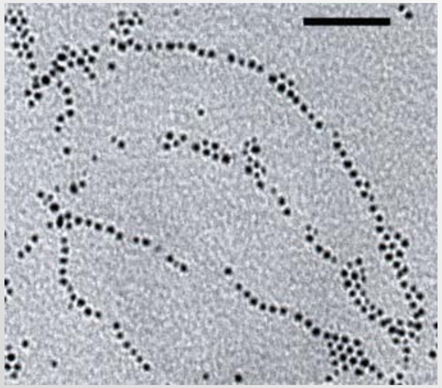
Precipitate

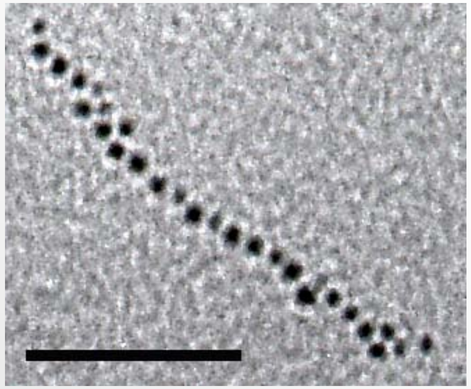
Final

Place Exchange Rate at the Poles

S u N M a G







Length range: 3 – 20 particles

Most common lengths are 6-8 particles

Infrequent branching confirms pole functionalization theory of placing only two molecules in diametrically opposed positions

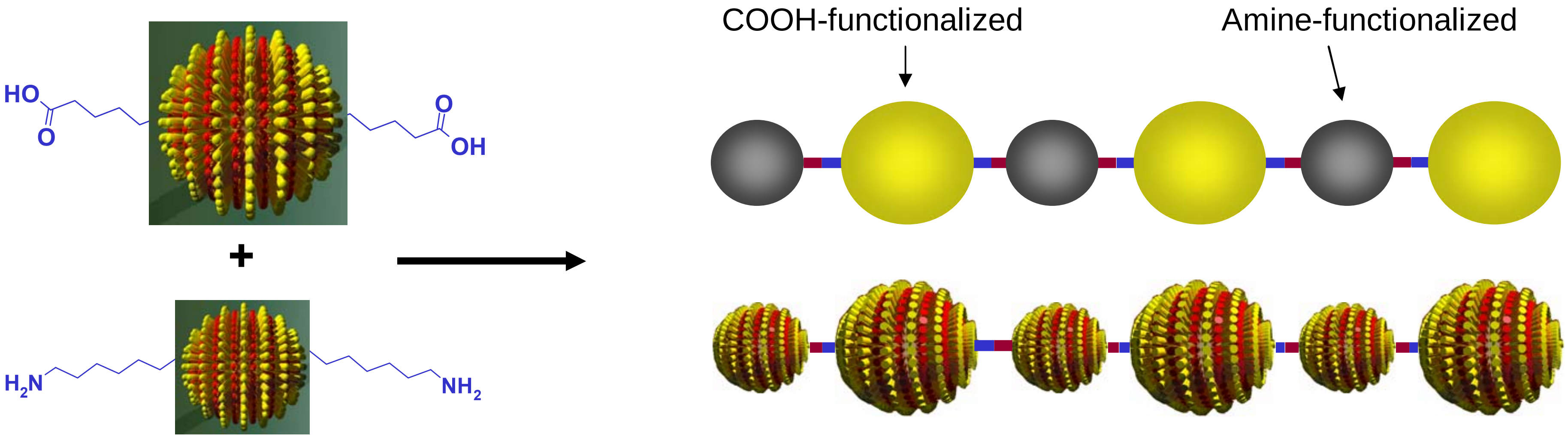
Second Order Rate for 'Pole' Place Exchange: **2.8 M^{-1} s^{-1}**

Second Order Rate for 'Defect' Place Exchange [1]: **3 10^{-2} M^{-1} s^{-1}**

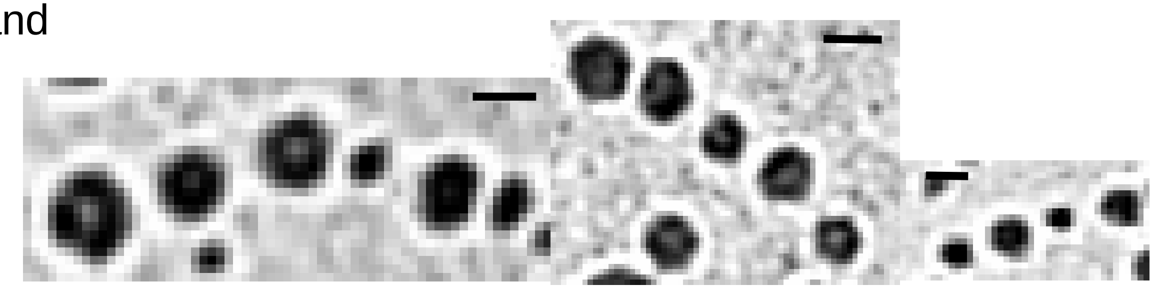
[1] Hostetler, M. J., Templeton, A. C. & Murray, R. W. **Langmuir** *15*, 3782-3789 (1999)

Controlling chain composition

Choose pole functionality so that only silver-gold bonds are allowed



Peptide bond formation only between COOH-functionalized Au particles and NH_2-functionalized Ag particles

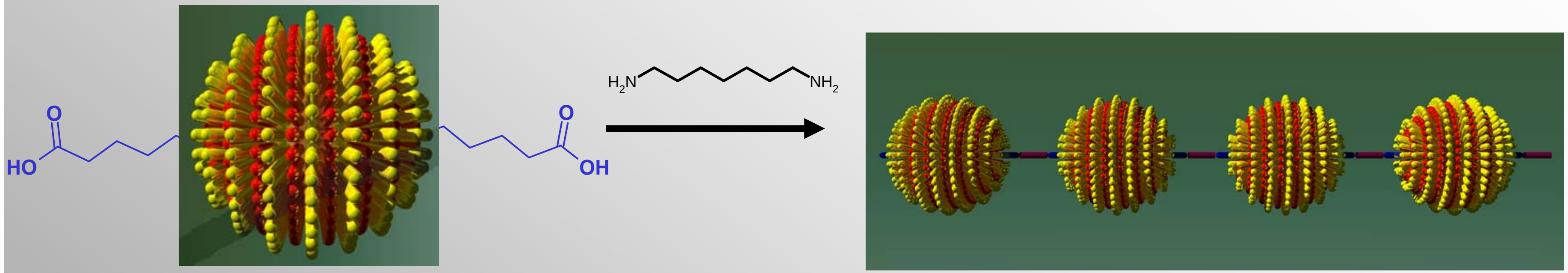


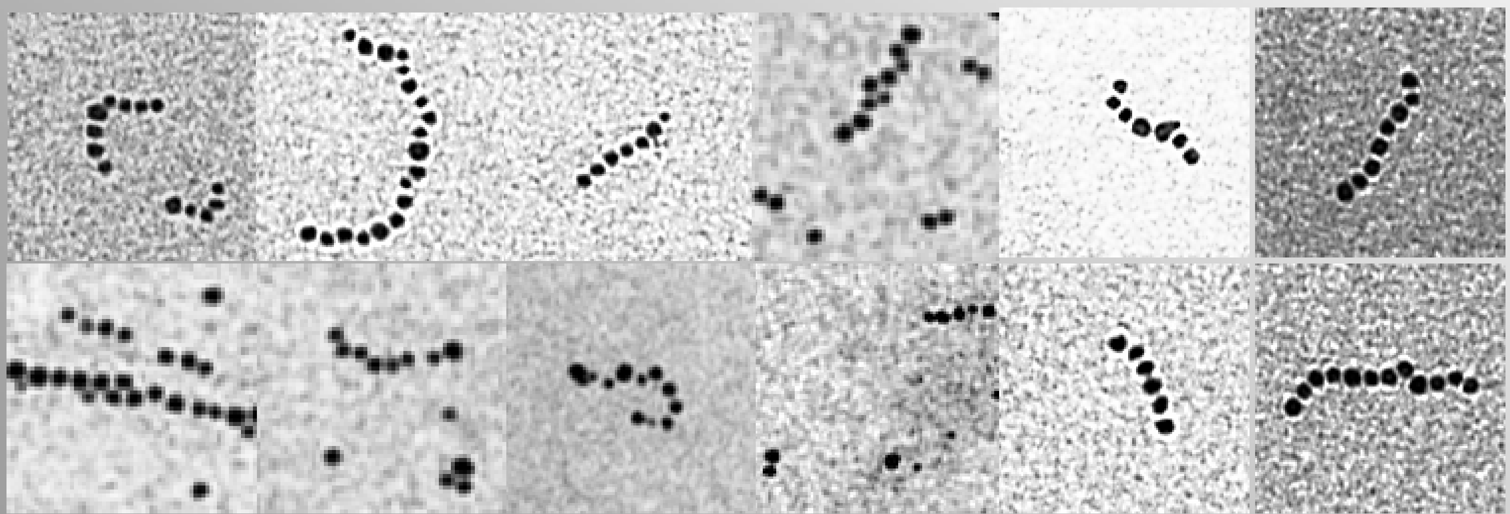
TEM images: All scale bars 20 nm

M. Brunnbauer, F. Stellacci, unpublished

One Phase Chain Formation

S u N M a G



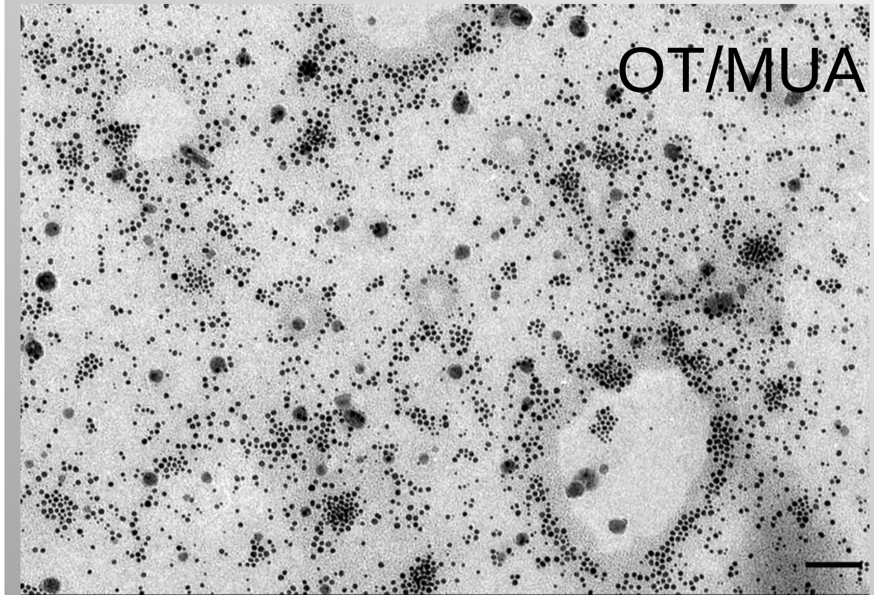


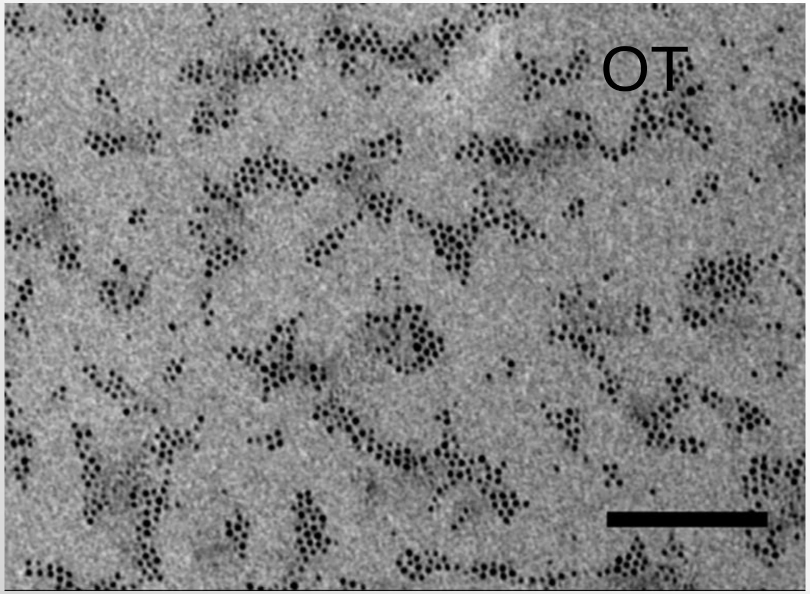
All images are 100 x 100 nm

M. Brunnbauer, F. Stellacci, unpublished

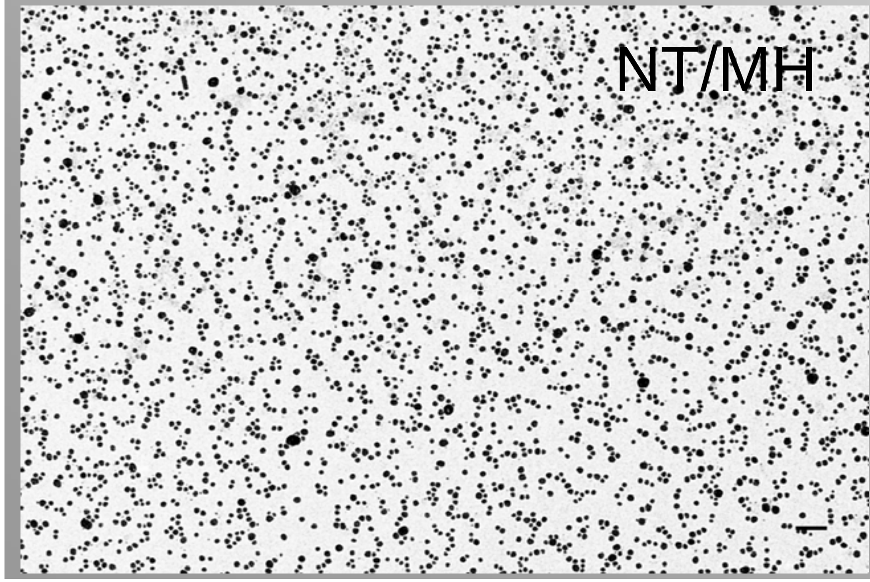
Control Experiments

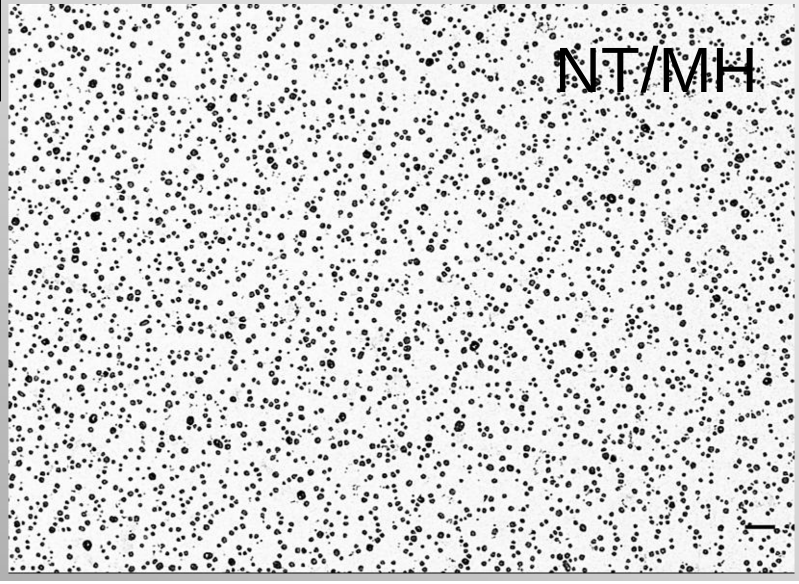
S u N M a G





MUA
@
Poles

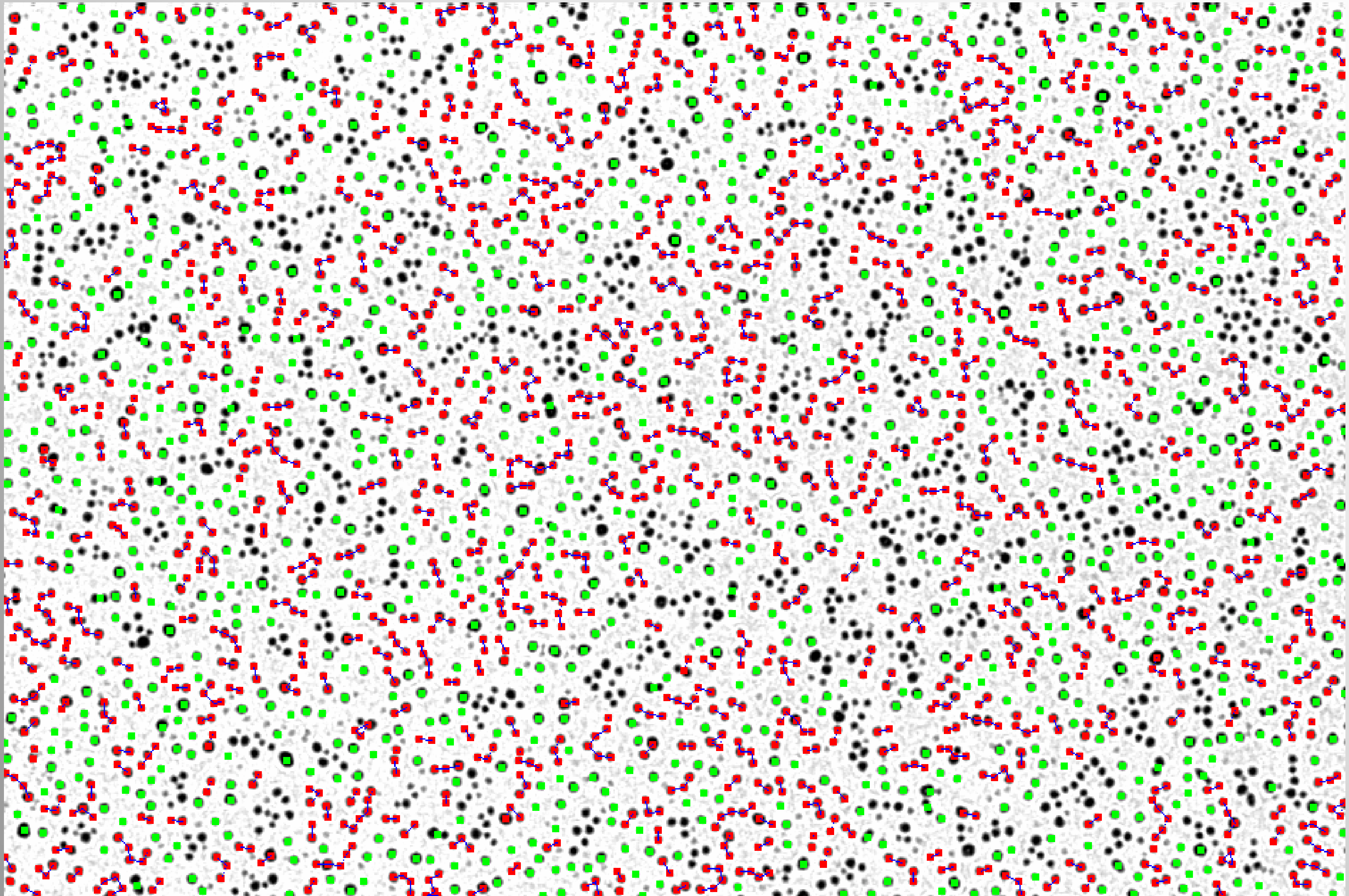




Chain Synthesis Yield

S u N M a G

Scale Bar 50 nm



Nanoparticle Supra-Crystals

S u N M a G

Murray and Kotov

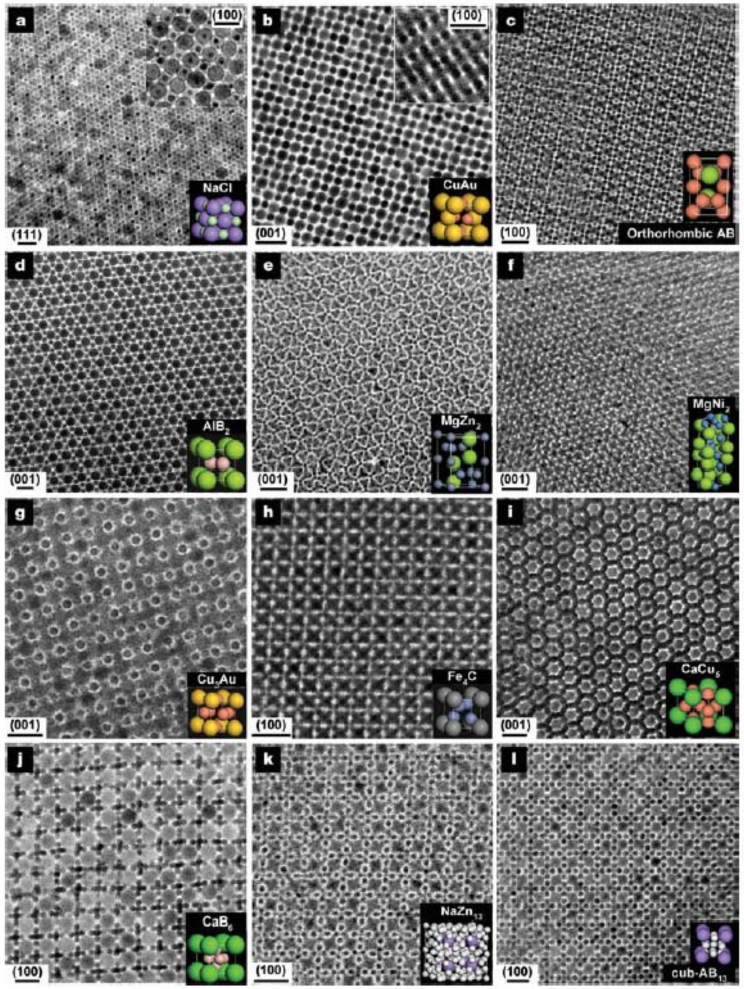


Figure 1 | TEM images of the characteristic projections of the binary superlattices, self-assembled from different nanoparticles, and modelled unit cells of the corresponding three-dimensional structures. The superlattices are assembled from **a**, 13.4 nm γ-Fe_2O_3 and 5.0 nm Au; **b**, 7.6 nm PbSe and 5.0 nm Au; **c**, 6.2 nm PbSe and 3.0 nm Pd; **d**, 6.7 nm PbS and 3.0 nm Pd; **e**, 6.2 nm PbSe and 3.0 nm Pd; **f**, 5.8 nm PbSe and 3.0 nm Pd; **g**, 7.2 nm PbSe and 4.2 nm Ag; **h**, 6.2 nm PbSe and 3.0 nm Pd; **i**, 7.2 nm PbSe and 5.0 nm Au; **j**, 5.8 nm PbSe and 3.0 nm Pd; **k**, 7.2 nm PbSe and 4.2 nm Ag; and **l**, 6.2 nm PbSe and 3.0 nm Pd nanoparticles. Scale bars: **a–c**, **e**, **f**, **i–l**, 20 nm; **d**, **g**, **h**, 10 nm. The lattice projection is labelled in each panel above the scale bar. The modelled projections of the binary superlattices are shown in Supplementary Fig. 4.

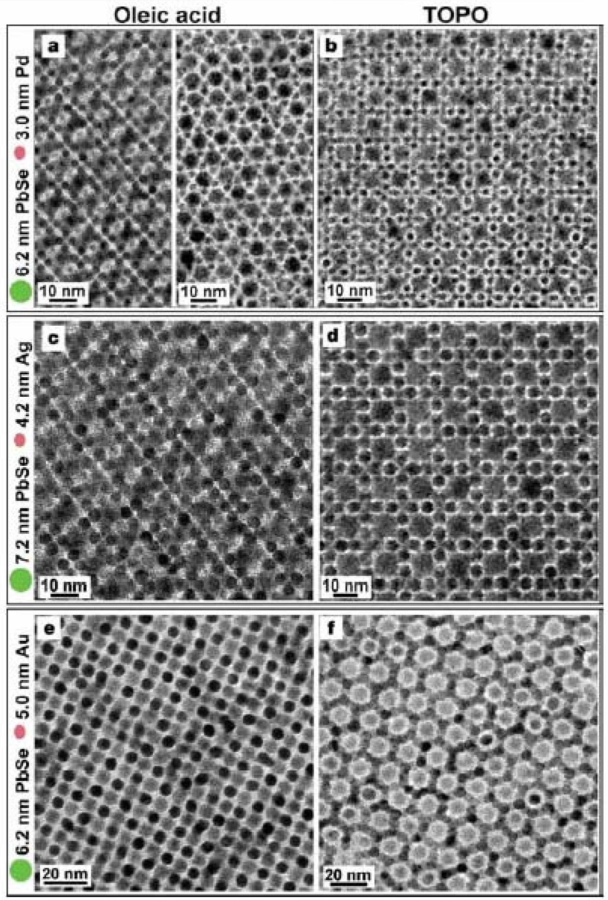


Figure 3 | TEM images of binary superlattices self-assembled in the presence of 4 mM oleic acid (left column) and 6 mM tri-*n*-octylphosphine oxide, TOPO (right column). **a**, 6.2 nm PbSe and 3.0 nm Pd nanoparticles self-assembled into orthorhombic AB- and AlB_2-type BNSLs, and **b**, into $NaZn_{13}$-type BNSL. **c**, **d**, 7.2 nm PbSe and 4.2 nm Ag nanoparticles self-assembled into orthorhombic AB and cuboctahedral AB_{13} BNSLs, respectively. **e**, **f**, 6.2 nm PbSe and 5.0 nm Au nanoparticles self-assembled into CuAu-type and $CaCu_5$-type BNSLs, respectively.

NATURE|Vol 439|5 January 2006

Nanoparticle Liquids

S u N M a G

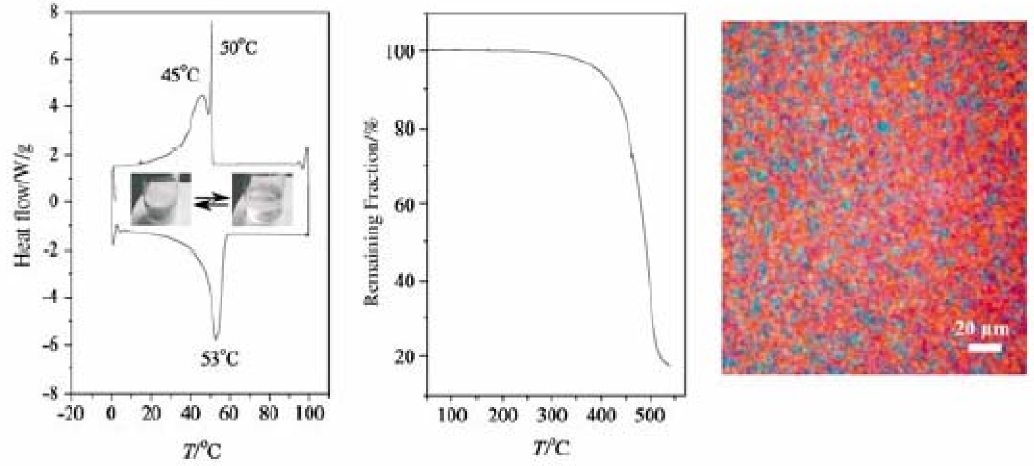
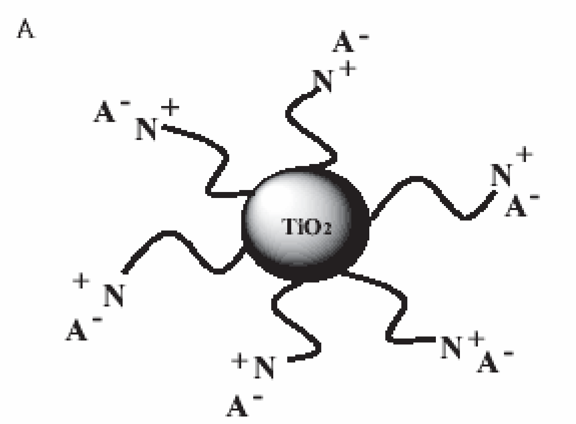


Figure 3. DSC (left) and TGA (middle) traces of the hybrid and the corresponding polarized optical microscopy image after isothermal crystallization (right).

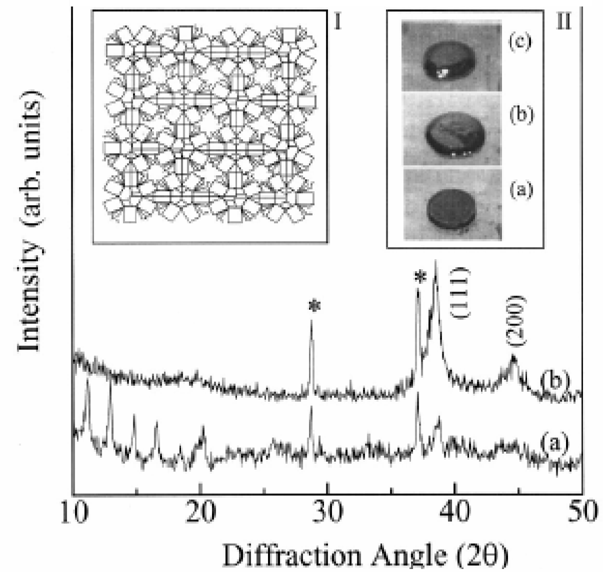
small 2005, 1, No. 1, 80–82

Adv. Funct. Mater. **2005**, 15, 1285–1290

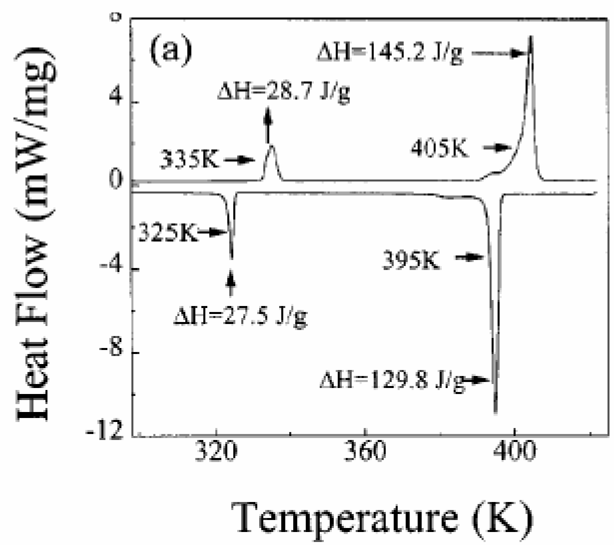
Giannelis' Approach



Pradeep's Approach



PRB 62 R739 ©2000



Free-Standing NanoPolymers

S u N M a G

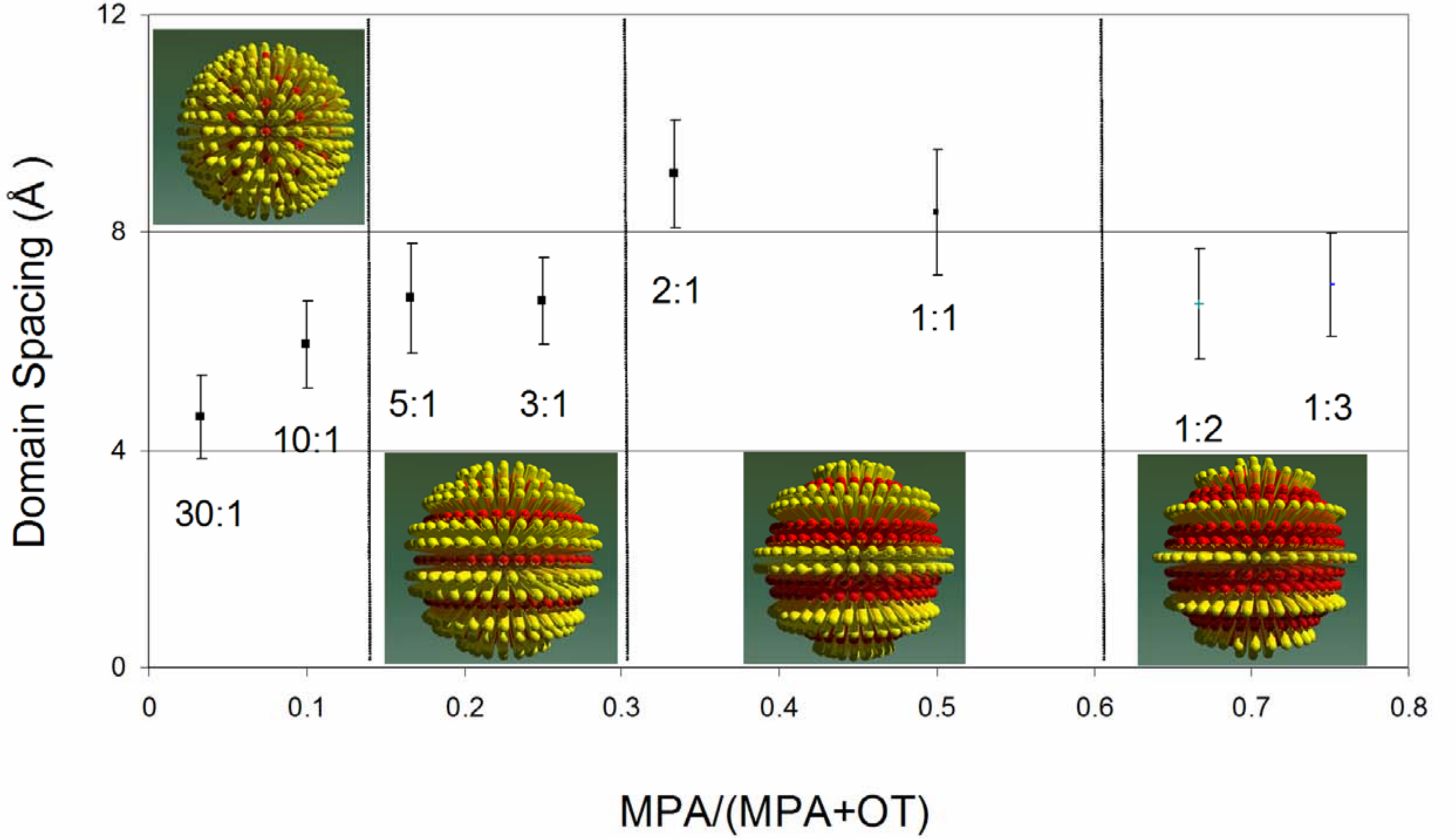
After toluene evaporation

Transferred to ethanol

Ripple Spacing in OT:MPA System

S u N M a G

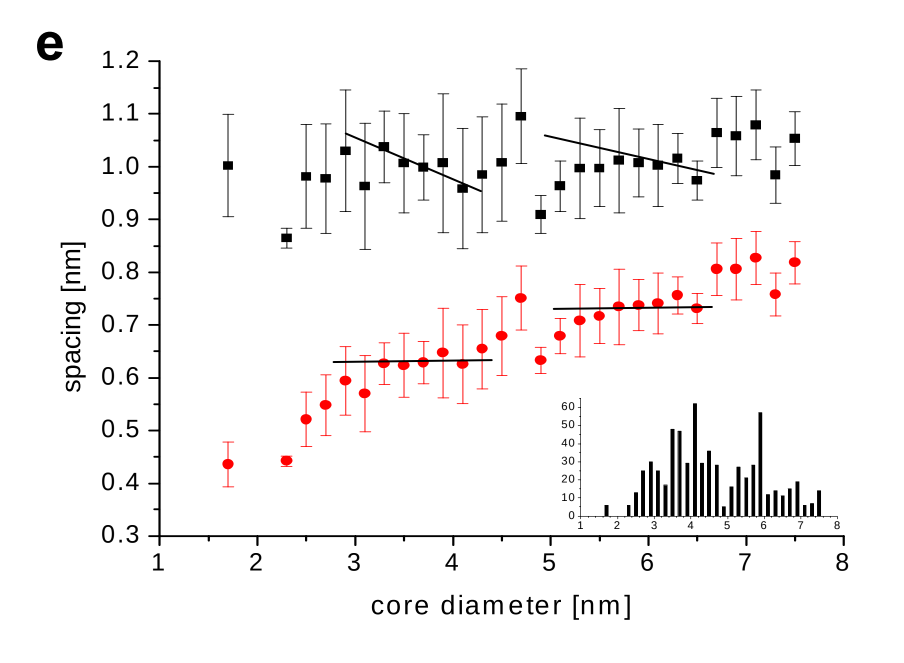
Morphology ranges from discretely packed domains to lamellae-like ripples

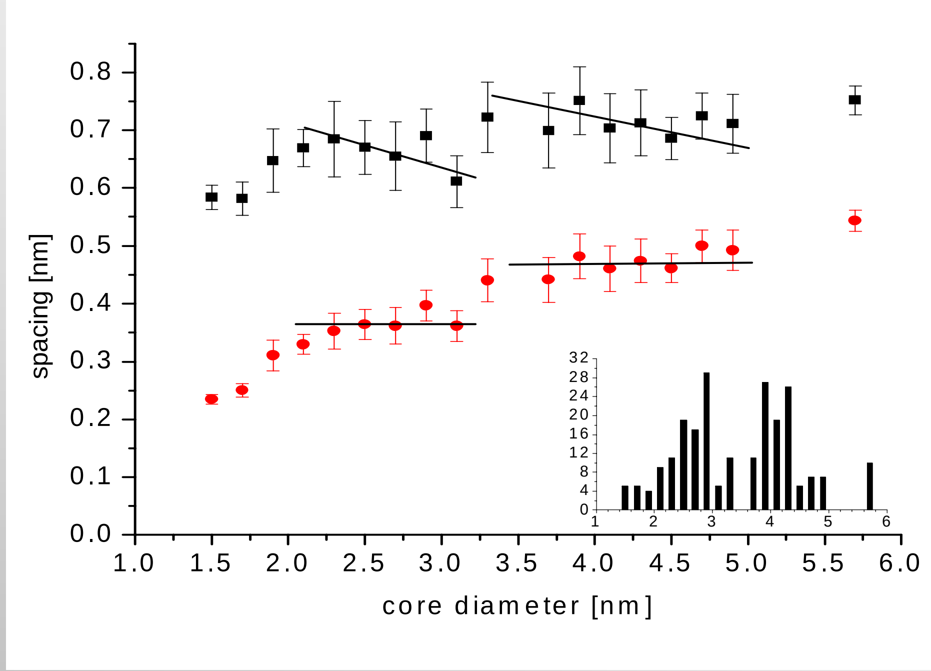


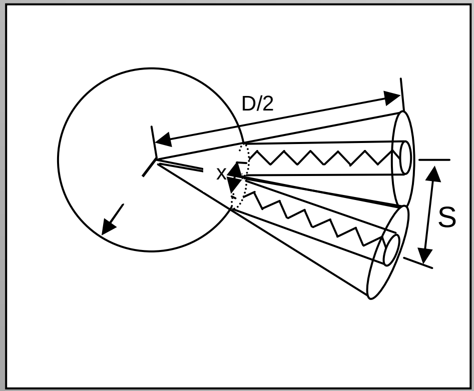
For OT and MPA the starting reaction stoichiometry ratio (r_r) corresponds to the final ratio found in the nanoparticles' ligand shell (r_n). Typically r_r / r_n=const.

Ripple Spacing vs. Particle Diameter

S u N M a G







Ripple Spacing and Core Structure

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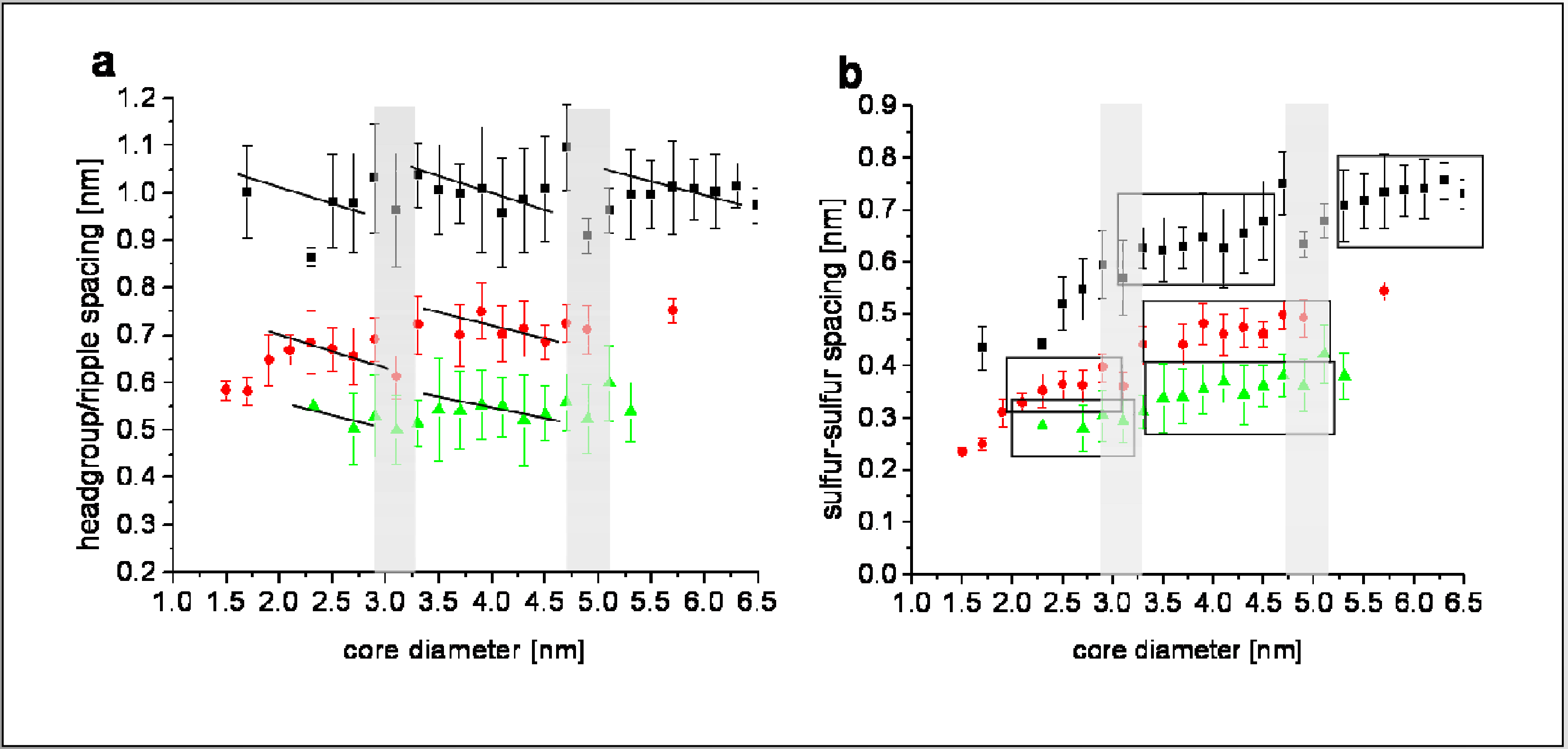

Zanchet, D.; Hall, B. D.; Ugarte, D. *J Phys Chem B* **2000**, *104*, 11013-11018.

Cleveland, C. L.; Landman, U.; Shafigullin, M. N.; Stephens, P. W.; Whetten, R. L. *Z Phys D Atom Mol Cl* **1997**, *40*, 503-508.

Solubility in different solvents

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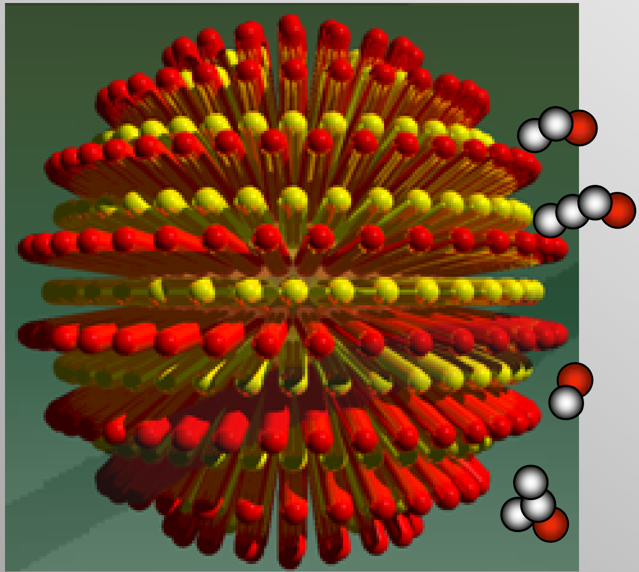
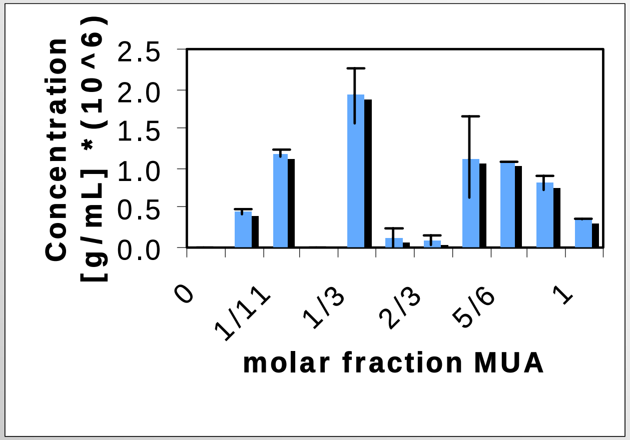
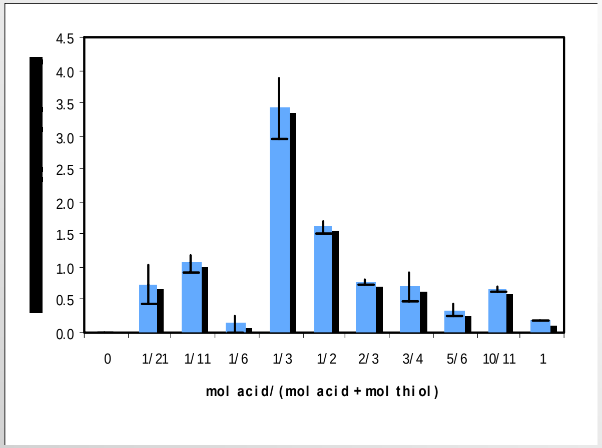
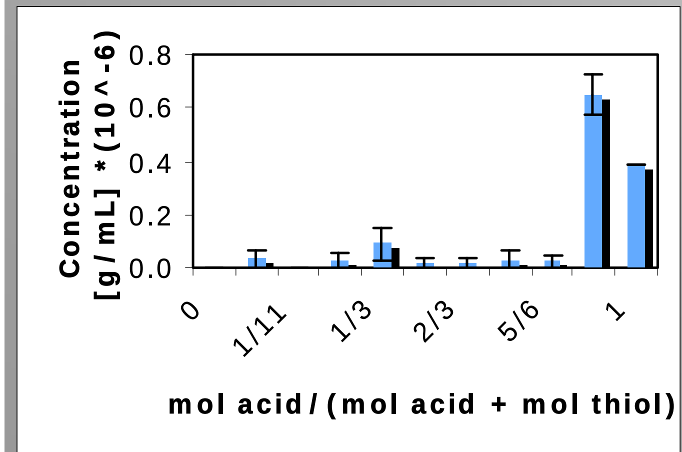
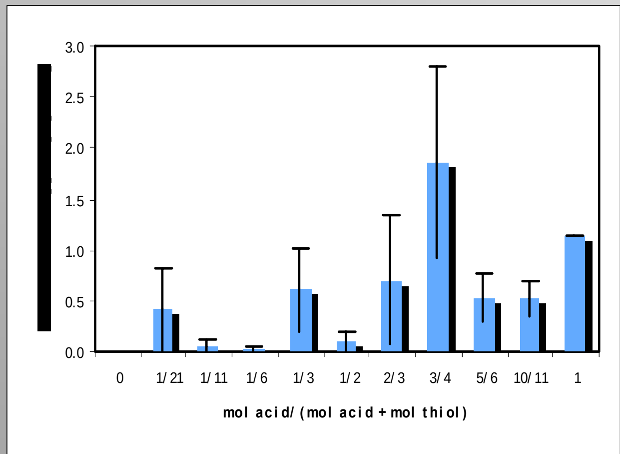


Morphology partially determines solubility









Surface Energy and Morphology

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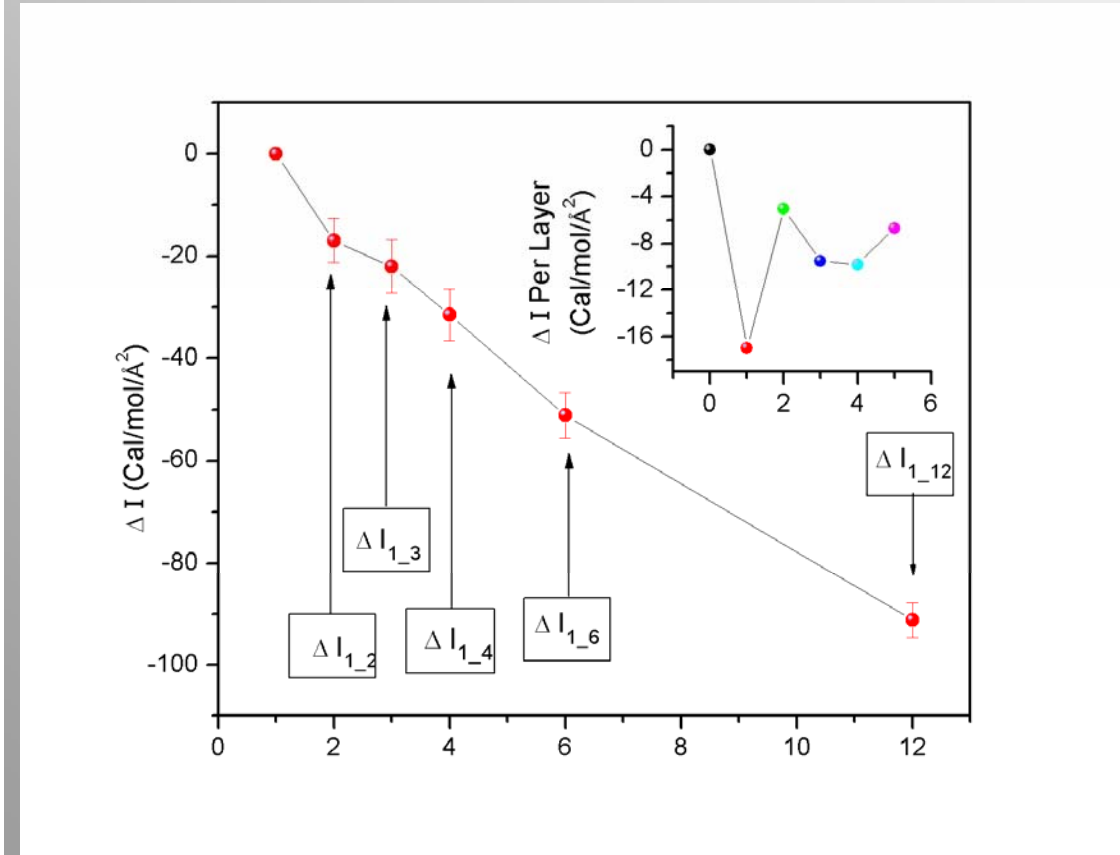

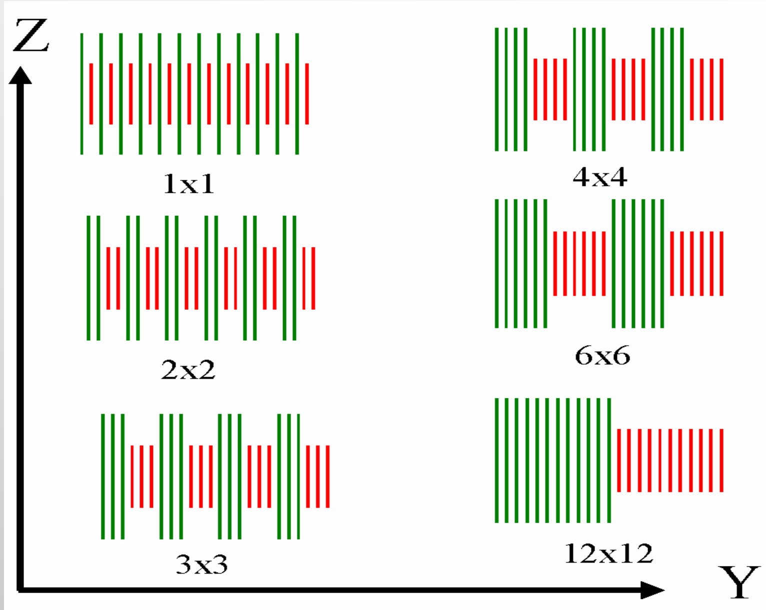

From Manu Sharma and Nicola Marzari

Protein Nonspecific Absorption

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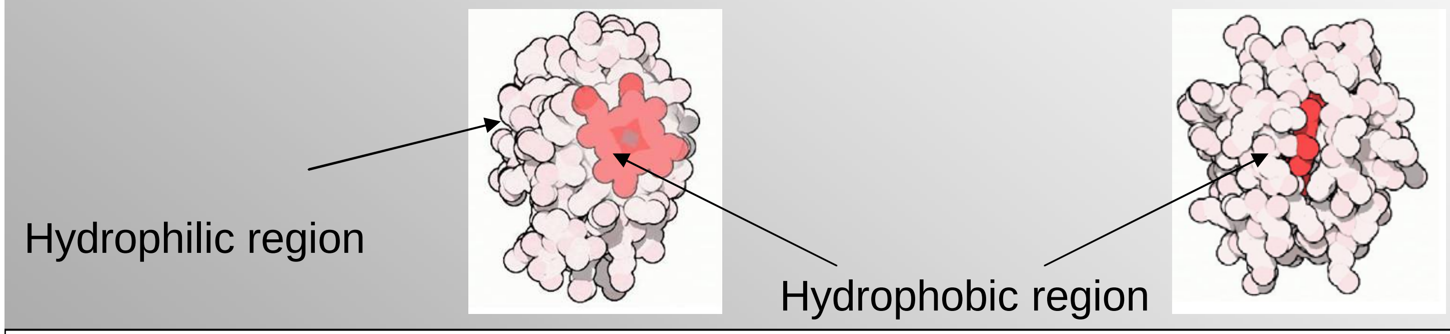
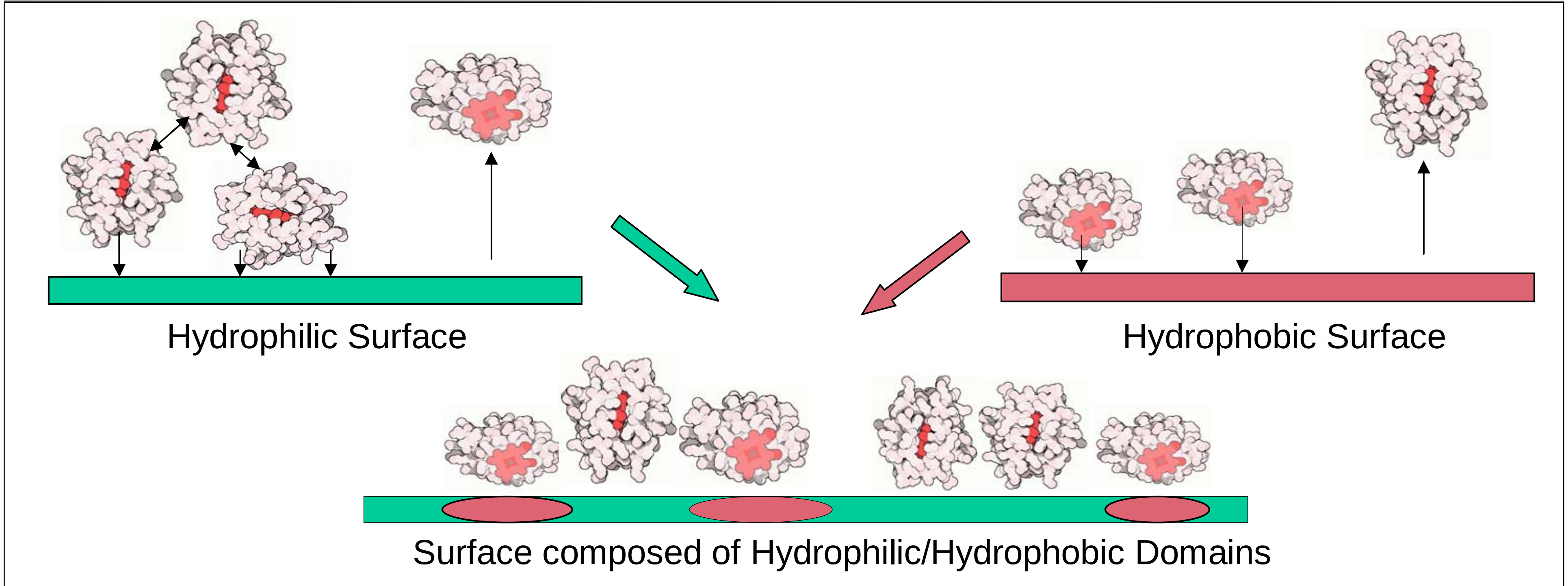
Proteins can assume a few possible conformations as determined by molecular structure

1) Maximizes exposure of hydrophobic region

2) Minimizes exposure of hydrophobic region





The Nano Lotus Leaf Effect

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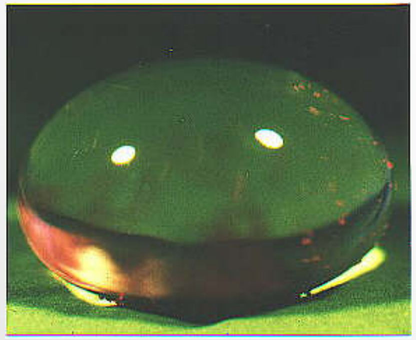

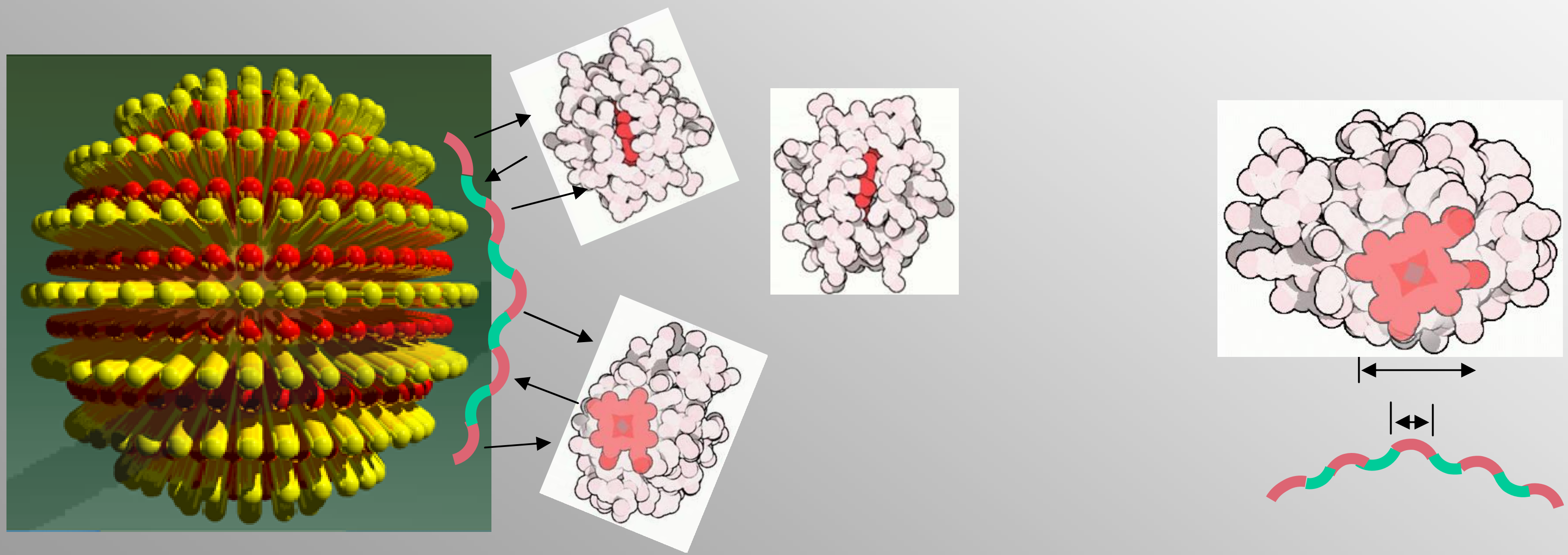

Size of hydrophobic/hydrophilic regions of protein are greater than size scale of ligand domains on the nanoparticles.

Proteins are conformationally frustrated and cannot adsorb to nanoparticle surface.

Cytochrome C: a large Protein

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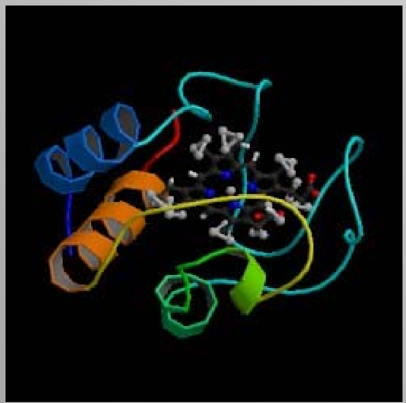
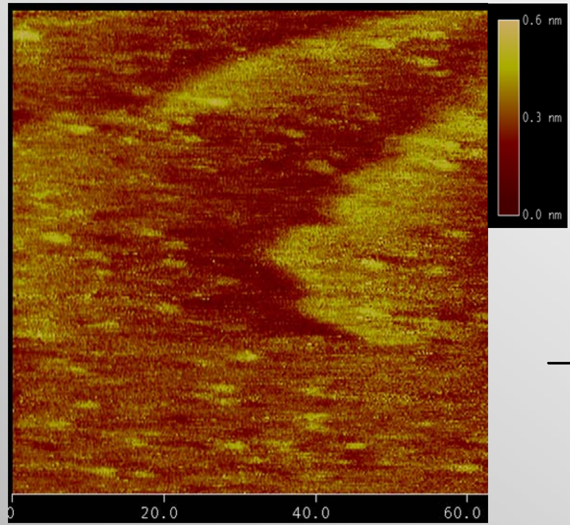
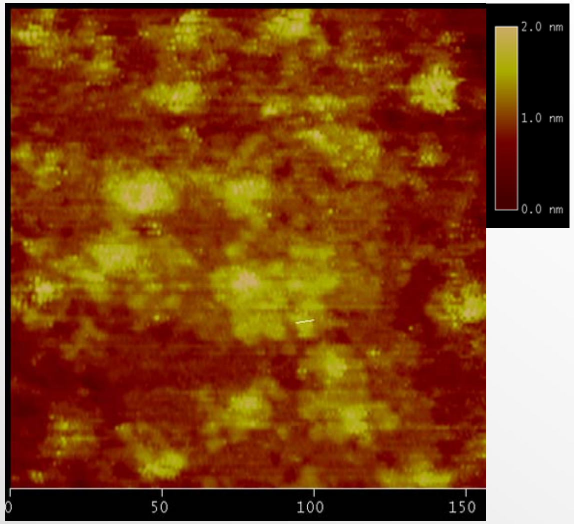


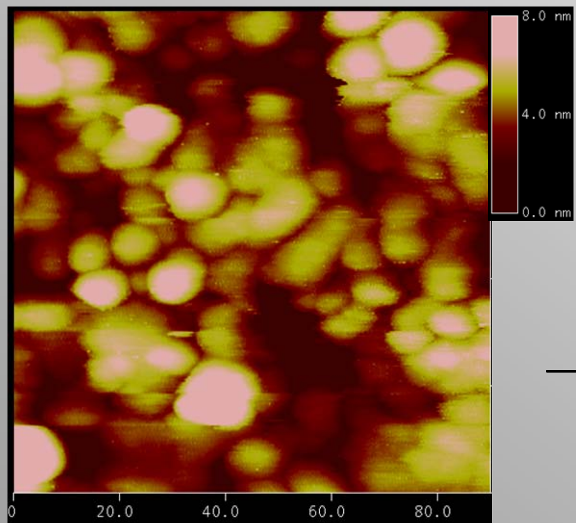
3.6 x 3.6 x
13.7 nm



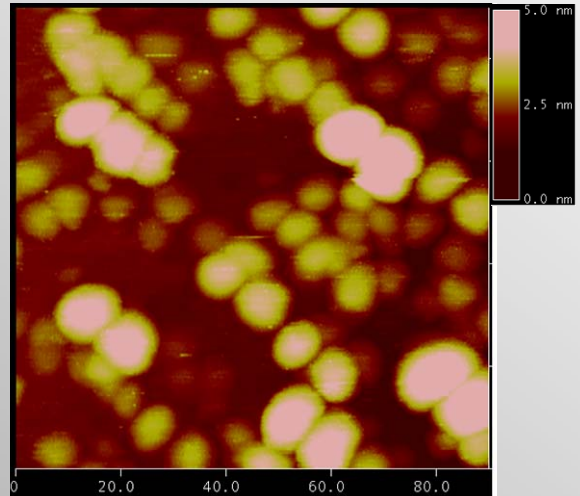
Protein
24 h



Extensive Adsorption of Protein onto Monolayer



Protein
24 h



No Adsorption of Protein

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MARCO
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DuPont Young Professor Award
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