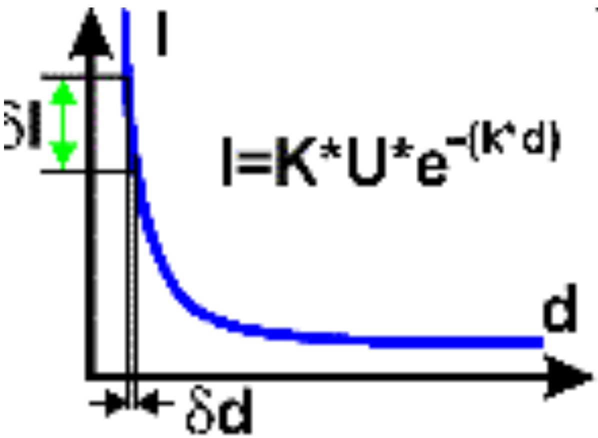
Nanostructure Fabrication

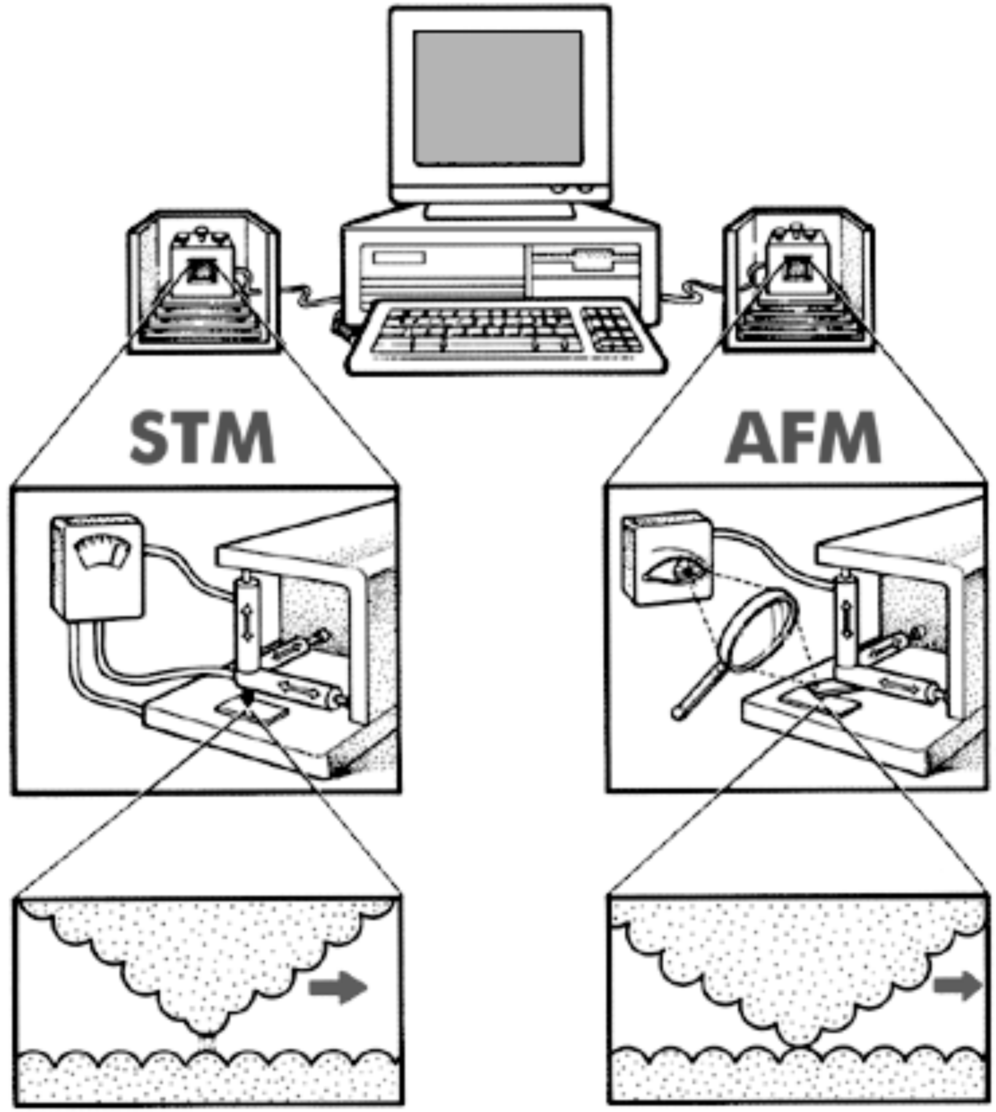
bottom up

- SPM Manipulation
- Molecular Beam Epitaxy
- Self Assembly

General Aspects of SPM Lithography

Instrumentation

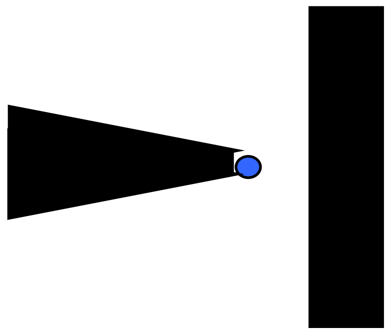




current changes dramatically for a atomic displacement in distance

General Aspects of SPM Lithography

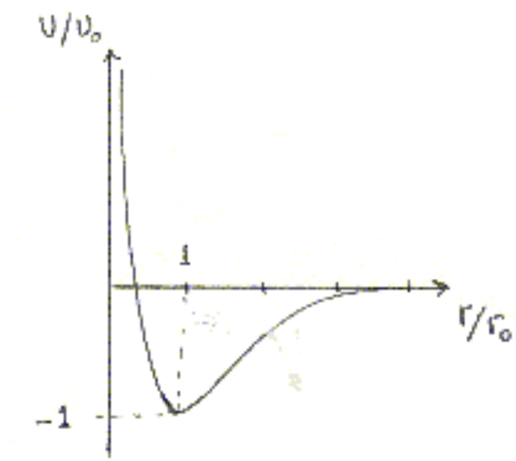
Potentials in the Gap

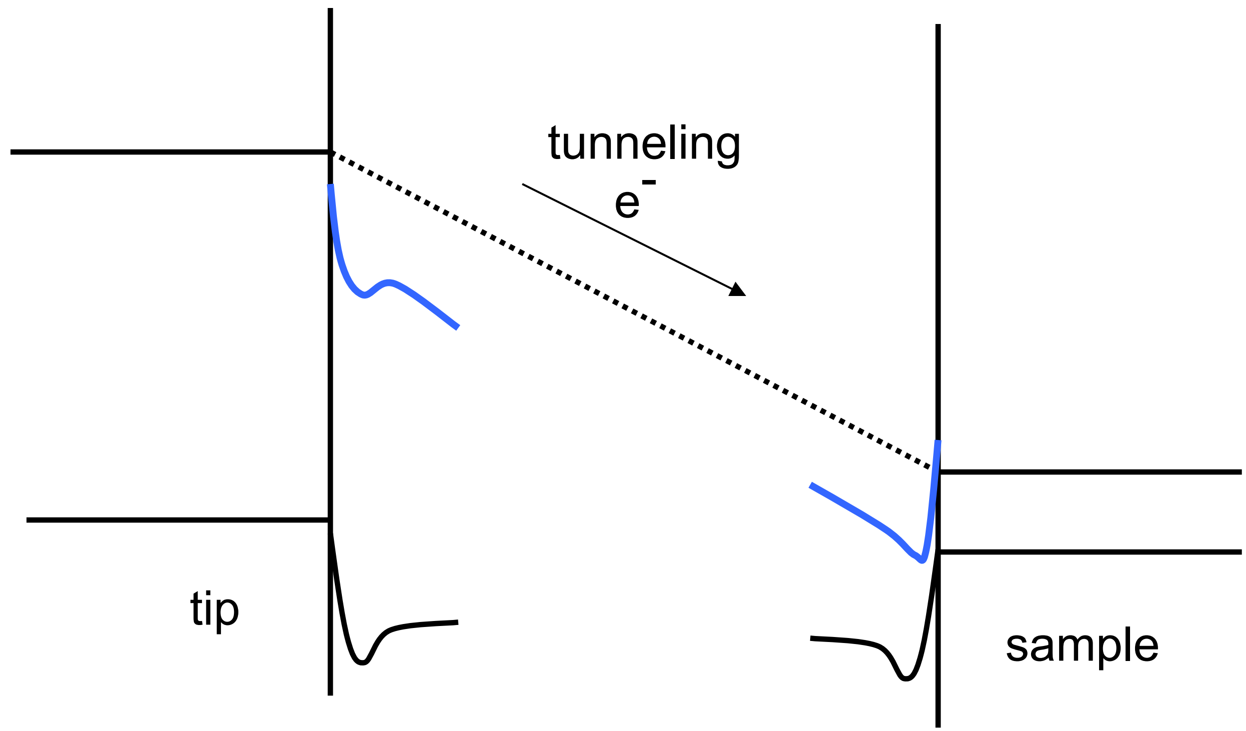


Potential energy diagram net current from occupied states on the tip to unoccupied states on sample

adsorbate potential

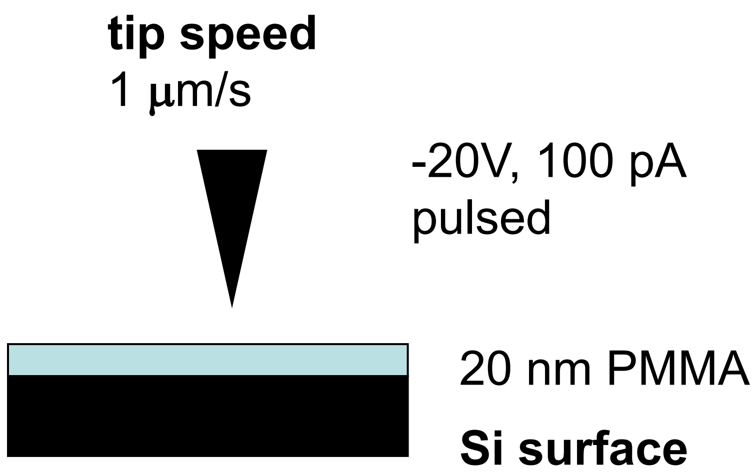
i.e. Lennard-Jones like



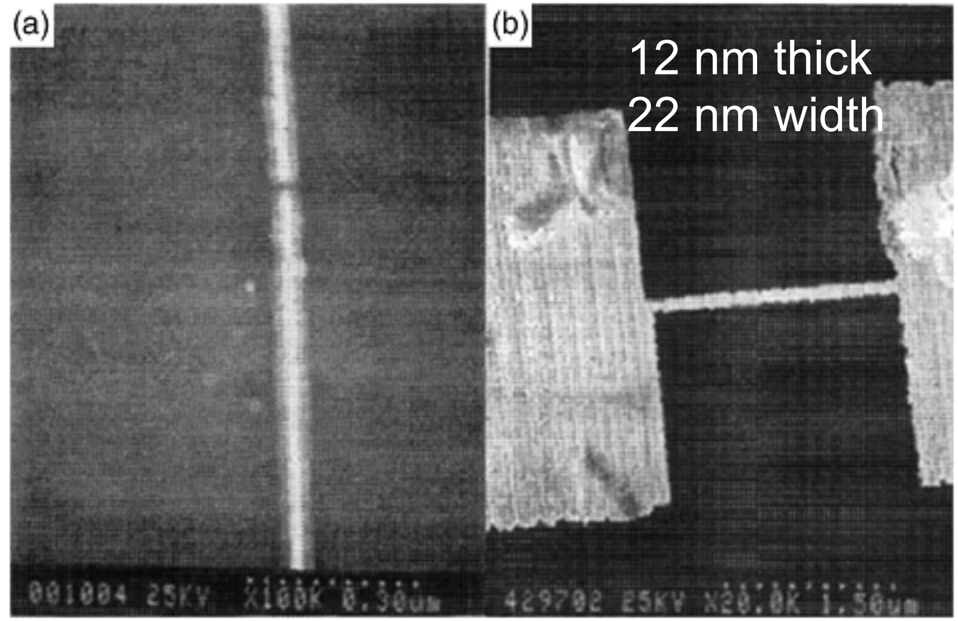


SPM Lithography

DESTRUCTIVE Exposure, Oxidation and Heating

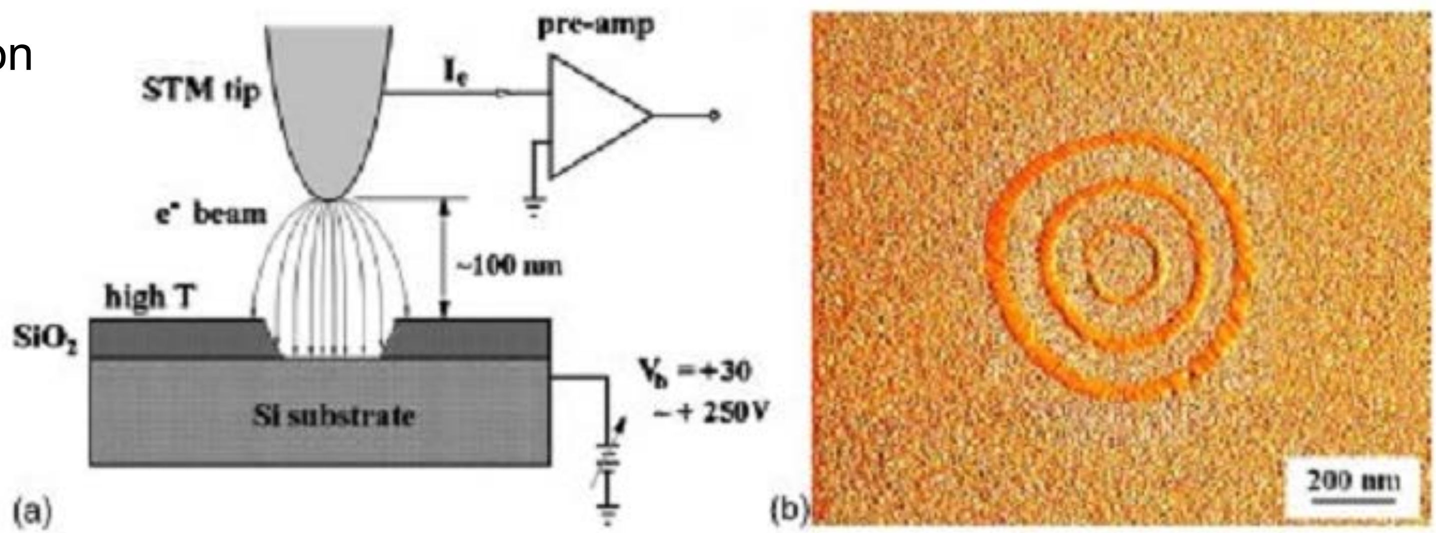


M. A. McCordand, R. F. W. Pease, J. Vac. Sci. Technol. B 6, 293 (1988)



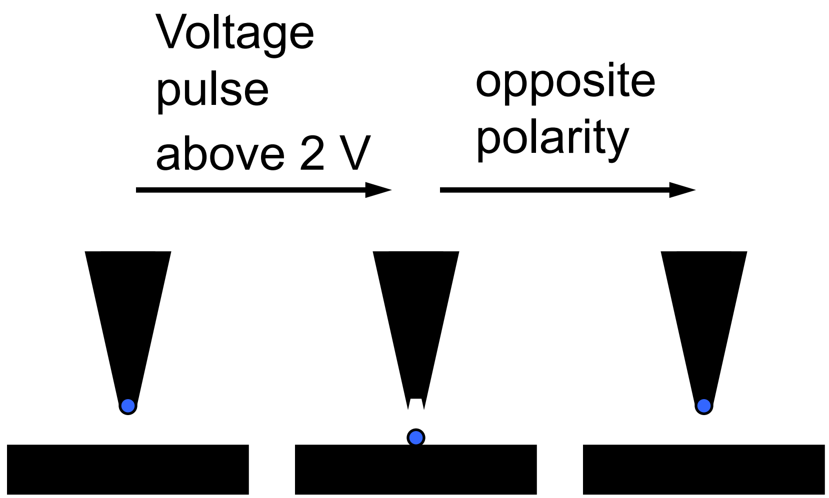
inducing chemical reactions: oxidation

thermal decomposition of a SiO_2 layer

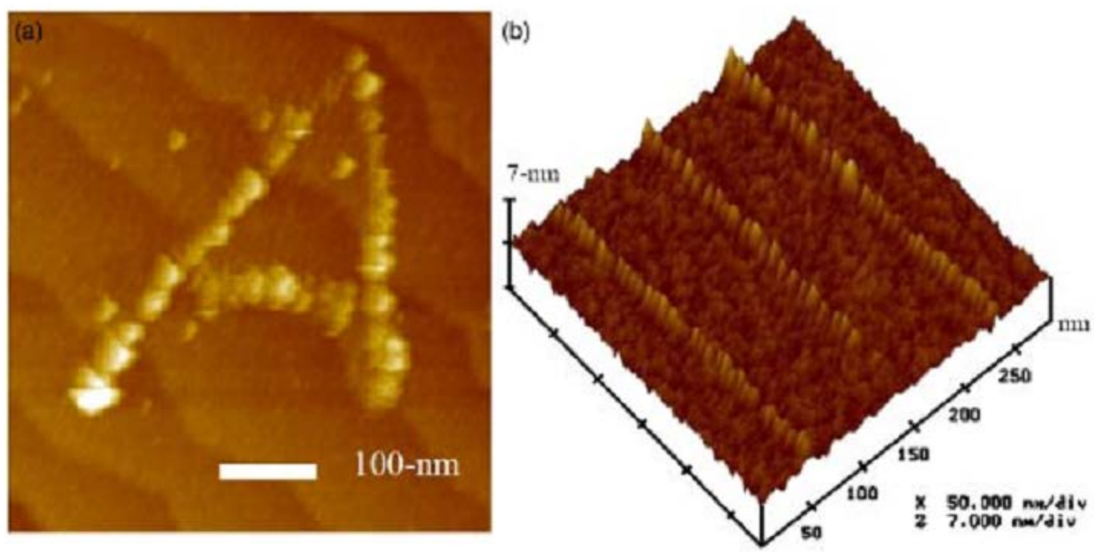


SPM Lithography **Constructive**

Material Deposition

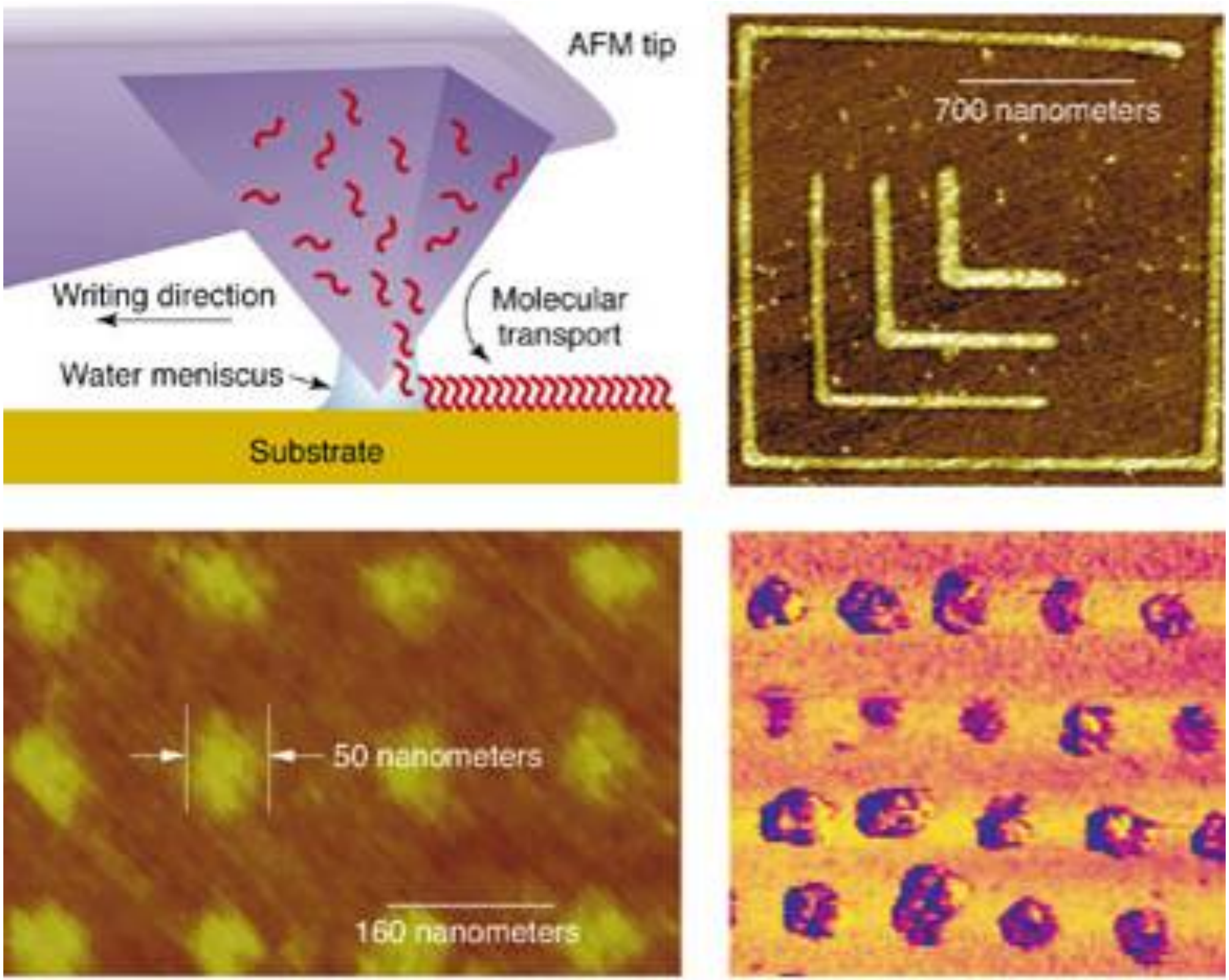


Au on Si-surface



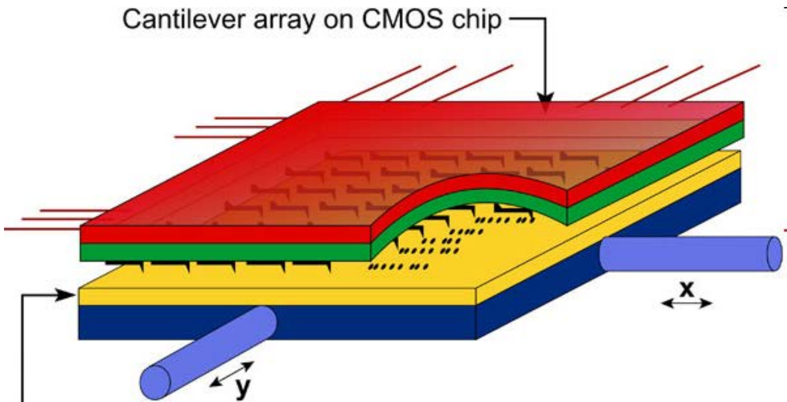
SPM Lithography

Dip Pen Lithography (AFM)

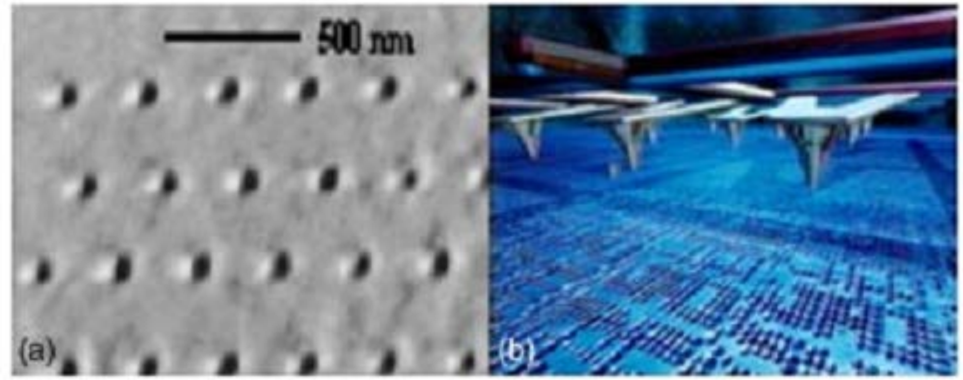


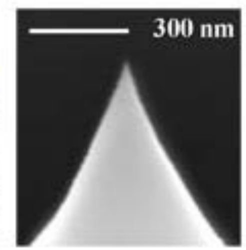
SPM Lithography

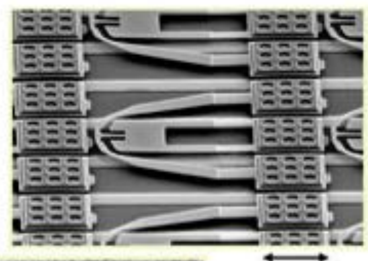
Multiple Cantilever Memory - Millipede



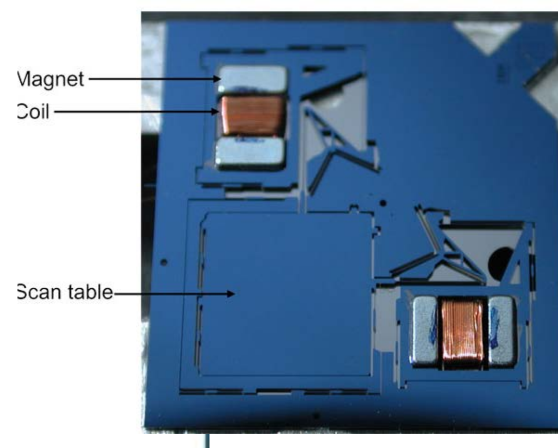
Concept and components.



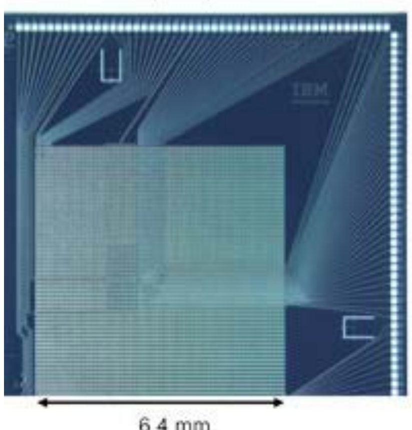


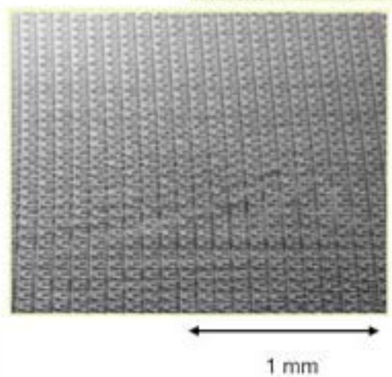


Silicon microscanner.

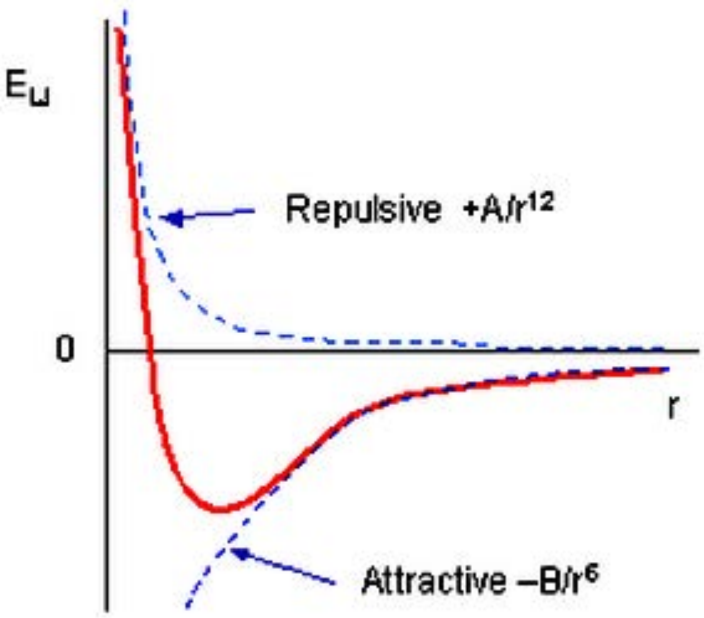


64 x 64 (4096) cantilevers

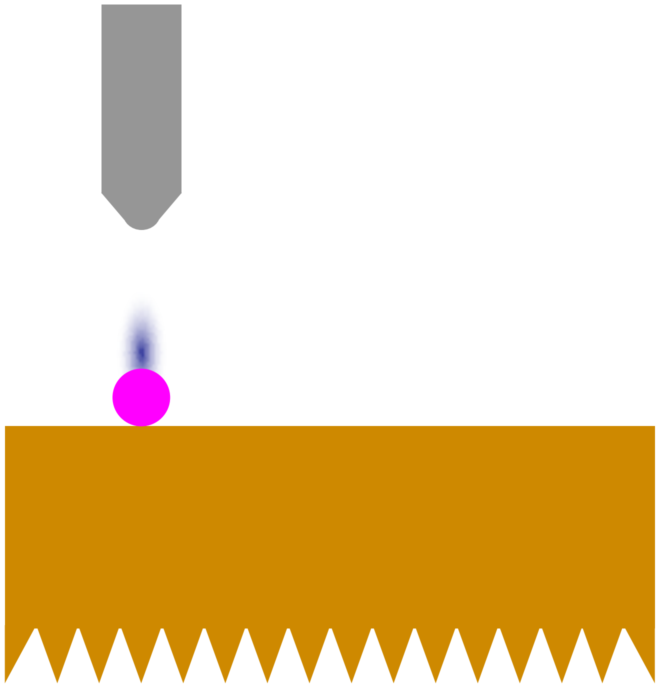




Vertical Manipulation with STM



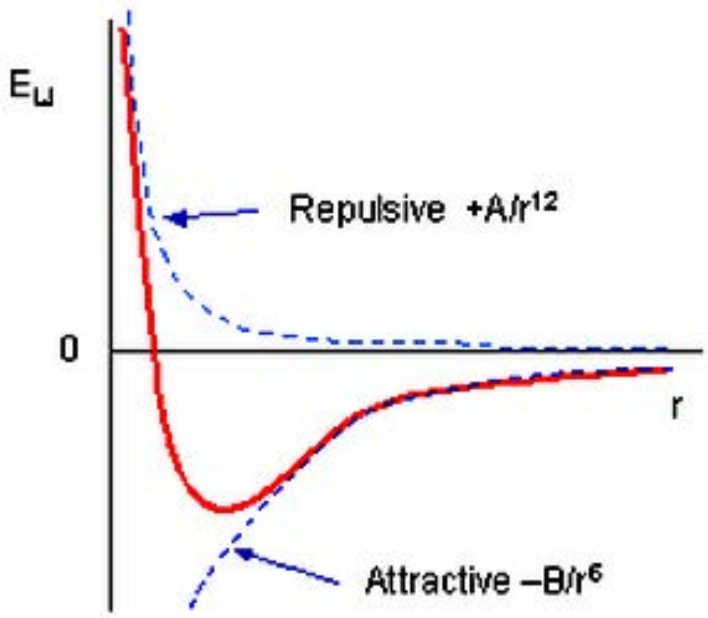
van der Waals interactions



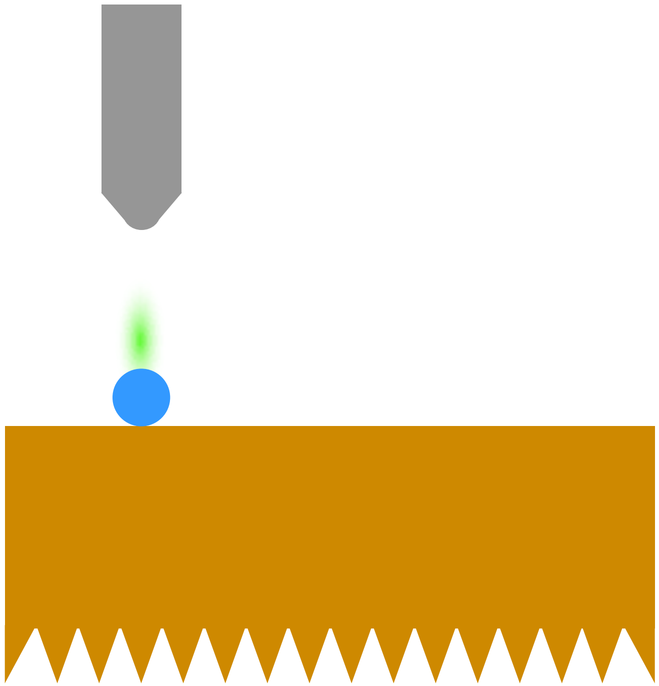
picking-up

Xe atom on tip

Vertical Manipulation with STM



van der Waals interactions



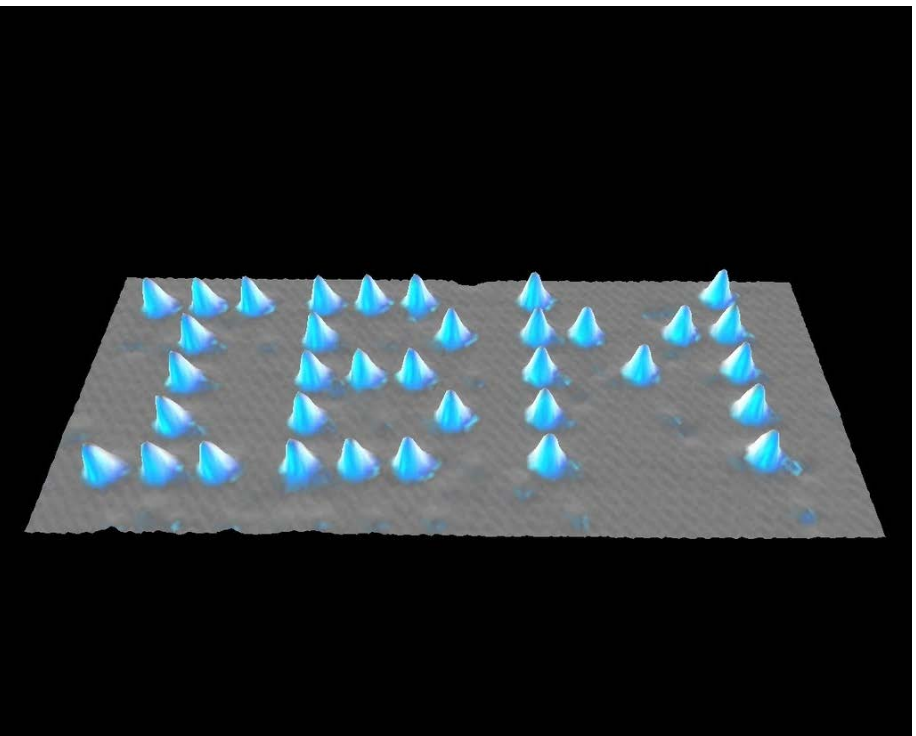
pulling

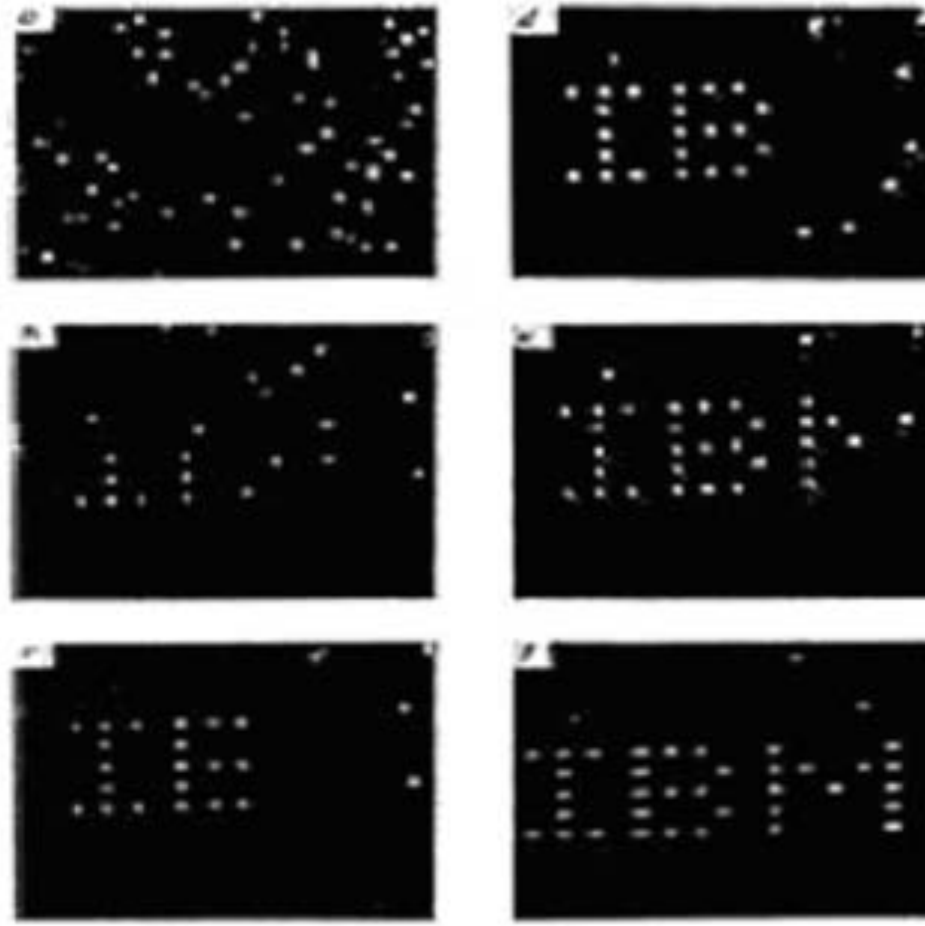
create new material combinations atom-by-atom

SINGLE ATOM MANIPULATION

Xe Atoms on a Nickel Surface

- low temperature STM
- Voltage pulses attach and detach the atom from the tip
- low temperature to induce sticking
- different modes: drag, slide, pick-up





Nature **344**, 534, 1990

Artificial Diffusion of Single Atom Molecule

- Creates an artificial diffusion process along the surface
- Approach the tip toward a target atom/molecule at its initial location to increase the tip-atom/molecule interaction force.
- Scan the tip along a desired path until it reaches a predetermined destination
- Atom/molecule moves along with the tip.
- Tip is retracted back to the normal imaging height.
- Atom/molecule left behind on the surface.

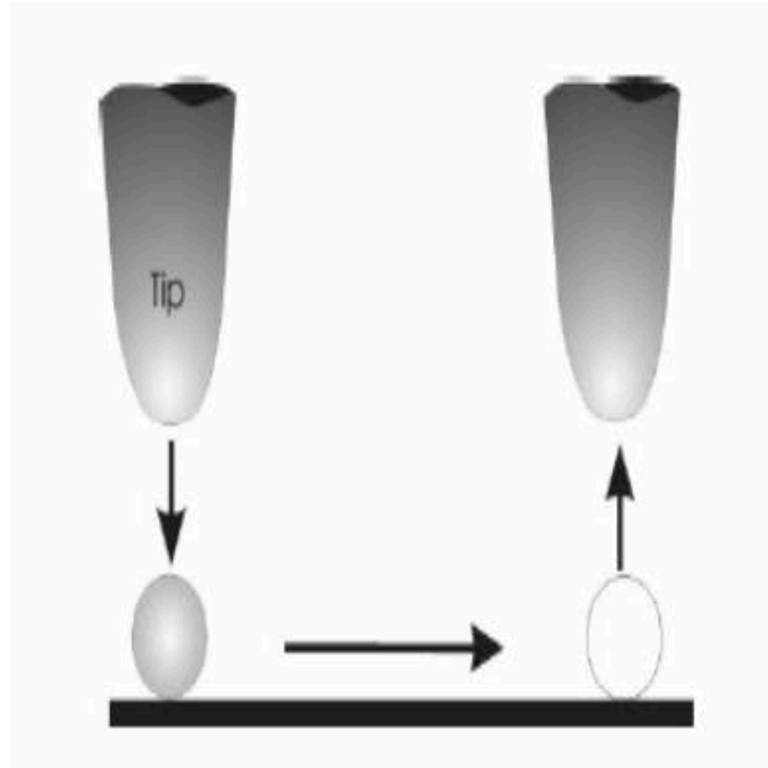
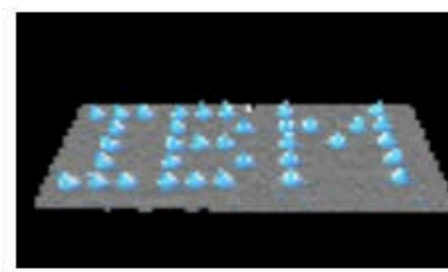
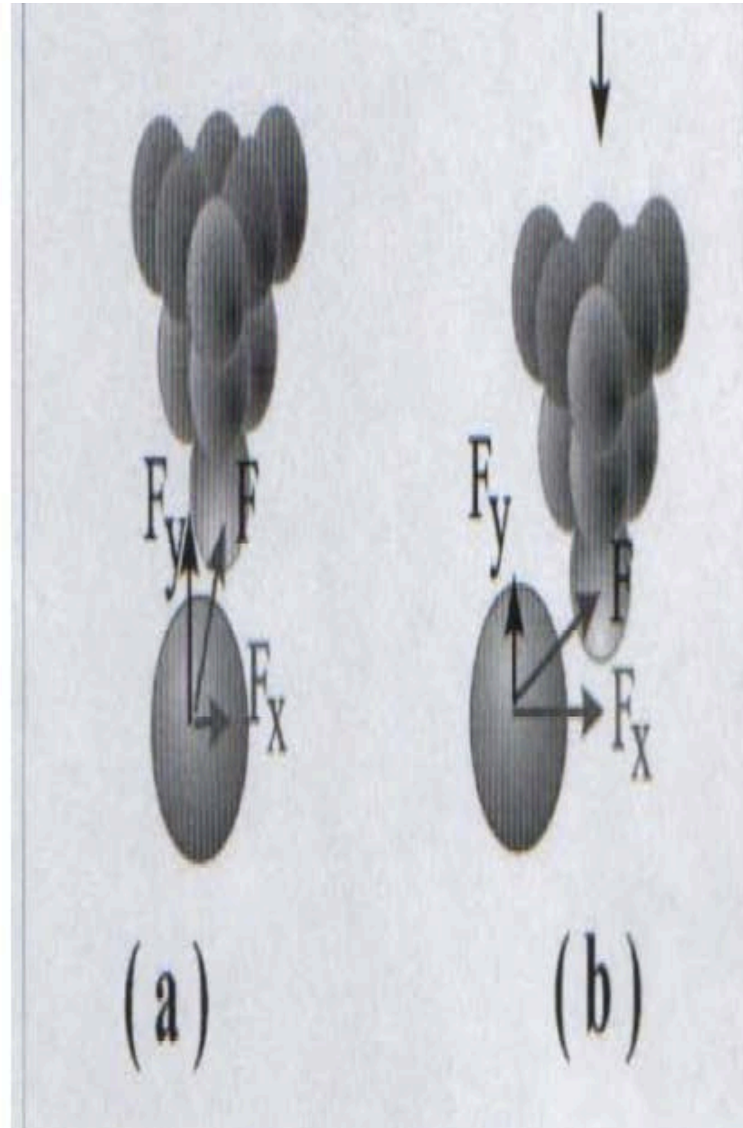


Figure 2 STM lateral manipulation procedure.



- As tip moves down slope of the contour the lateral component F_x increases.
- Increase in F_x causes the molecule to overcome the surface potential barrier and hop into the next absorption site.
- This hopping causes the tip to retract abruptly producing the tip height to increase.
- This is known as "stick-slip" movement regime.

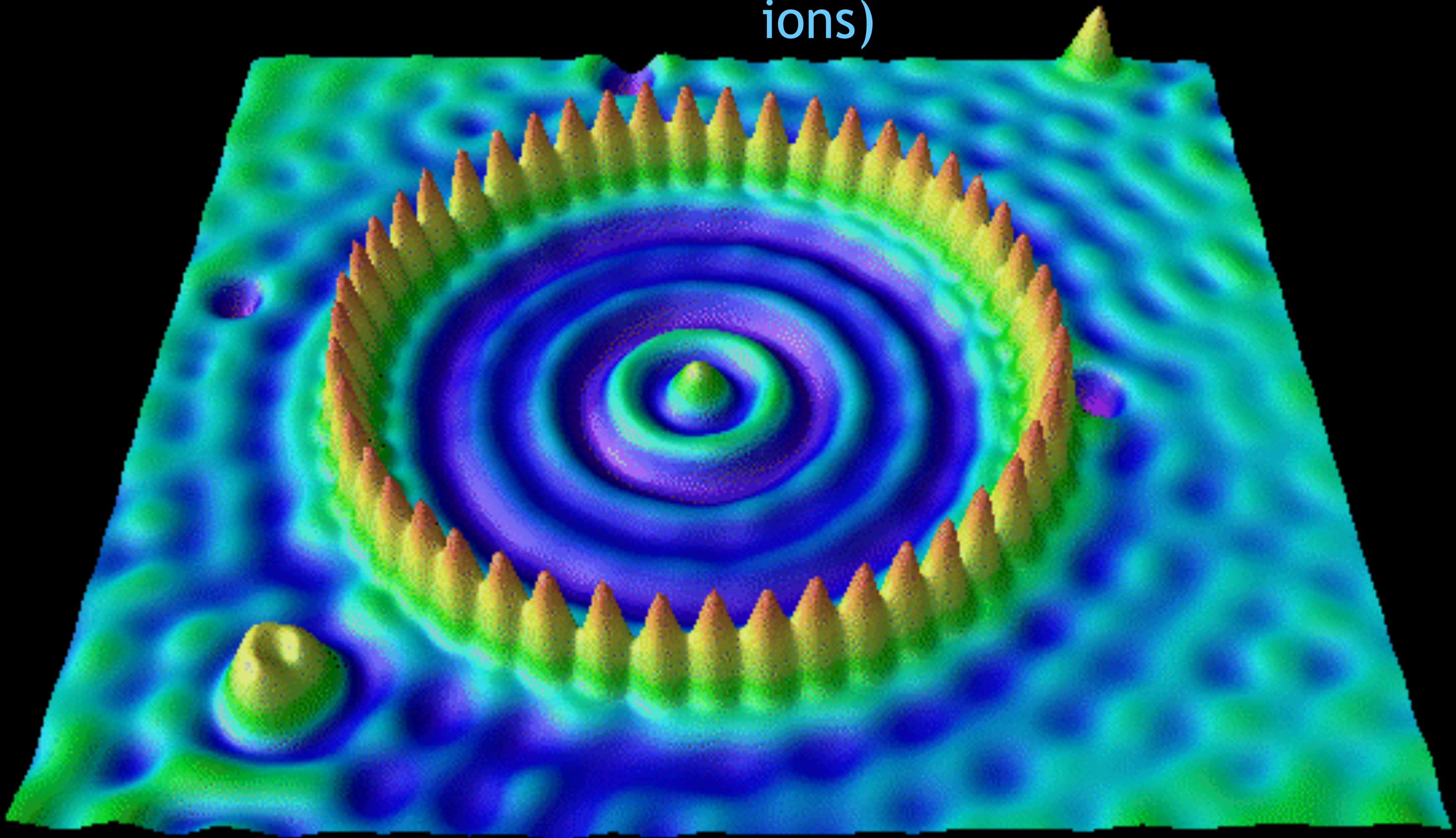


SINGLE ATOM MANIPULATION

Nanostructures

Quantum Coral: Adatoms scatter the surface state

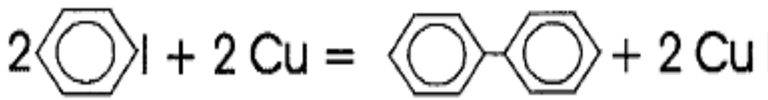
Quantum mechanical analog of electric charge screening (charge species in a pool of ions)

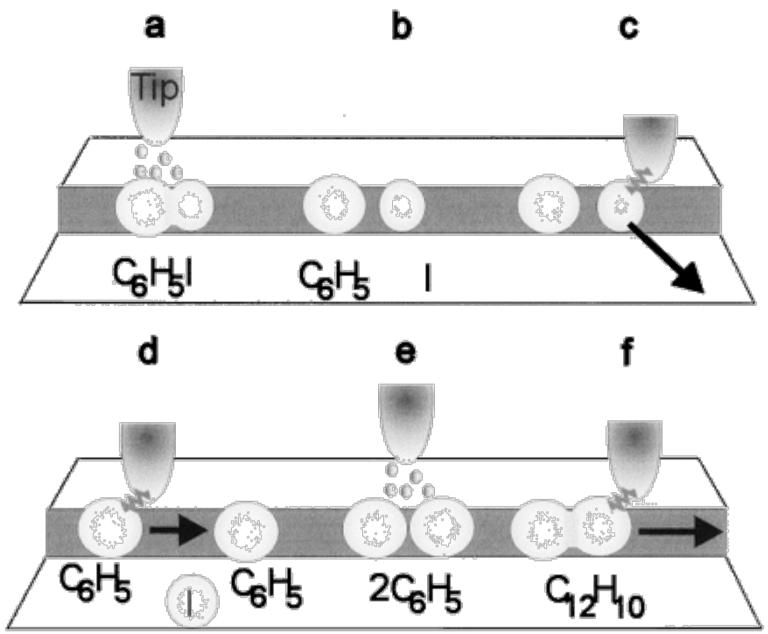


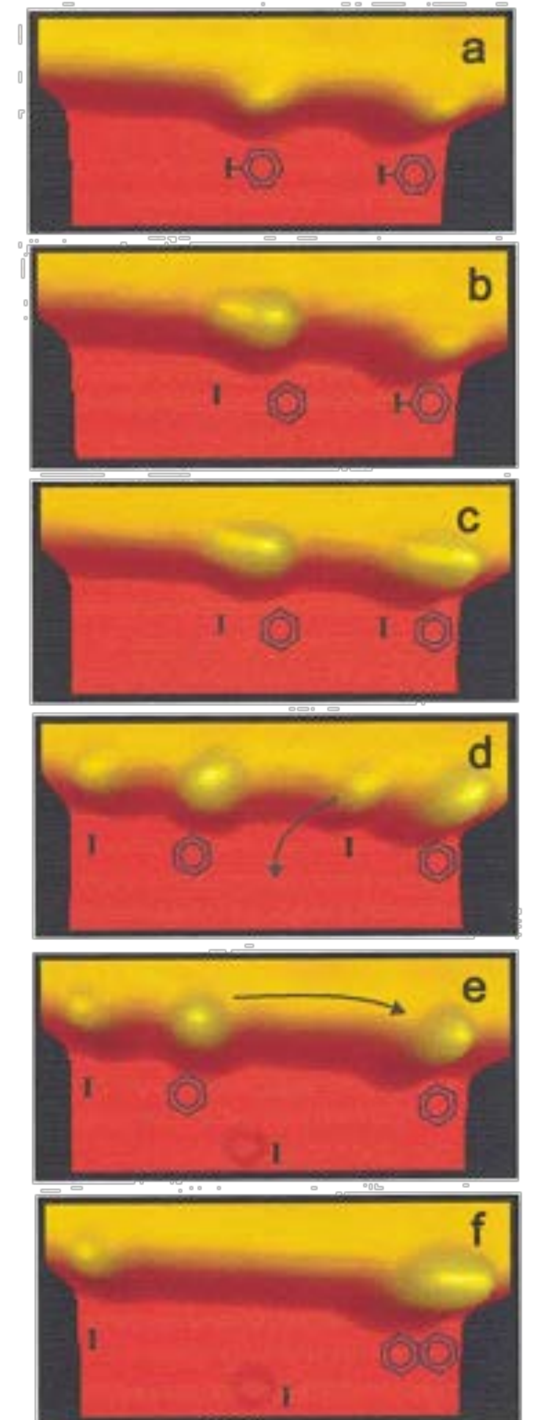
D.M. Eigler, E.K. Schweizer, Nature **344**, 524 (1990)

SINGLE ATOM MANIPULATION
STM induced Chemical Reaction

Cu 111
20 K



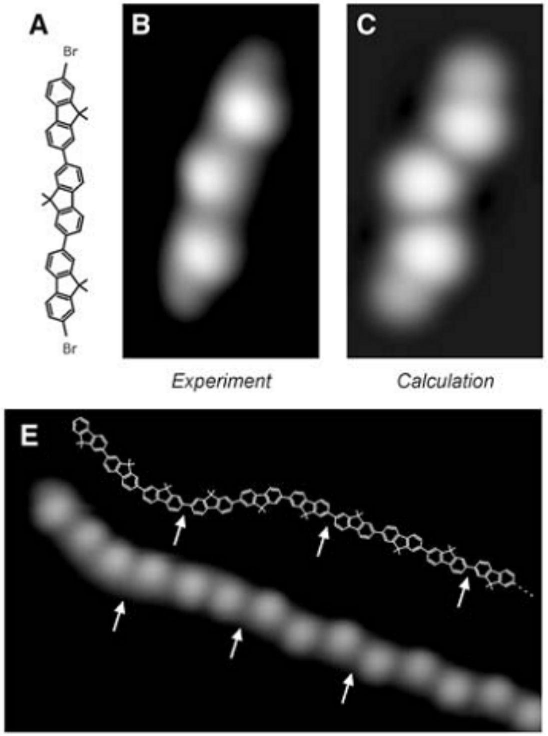


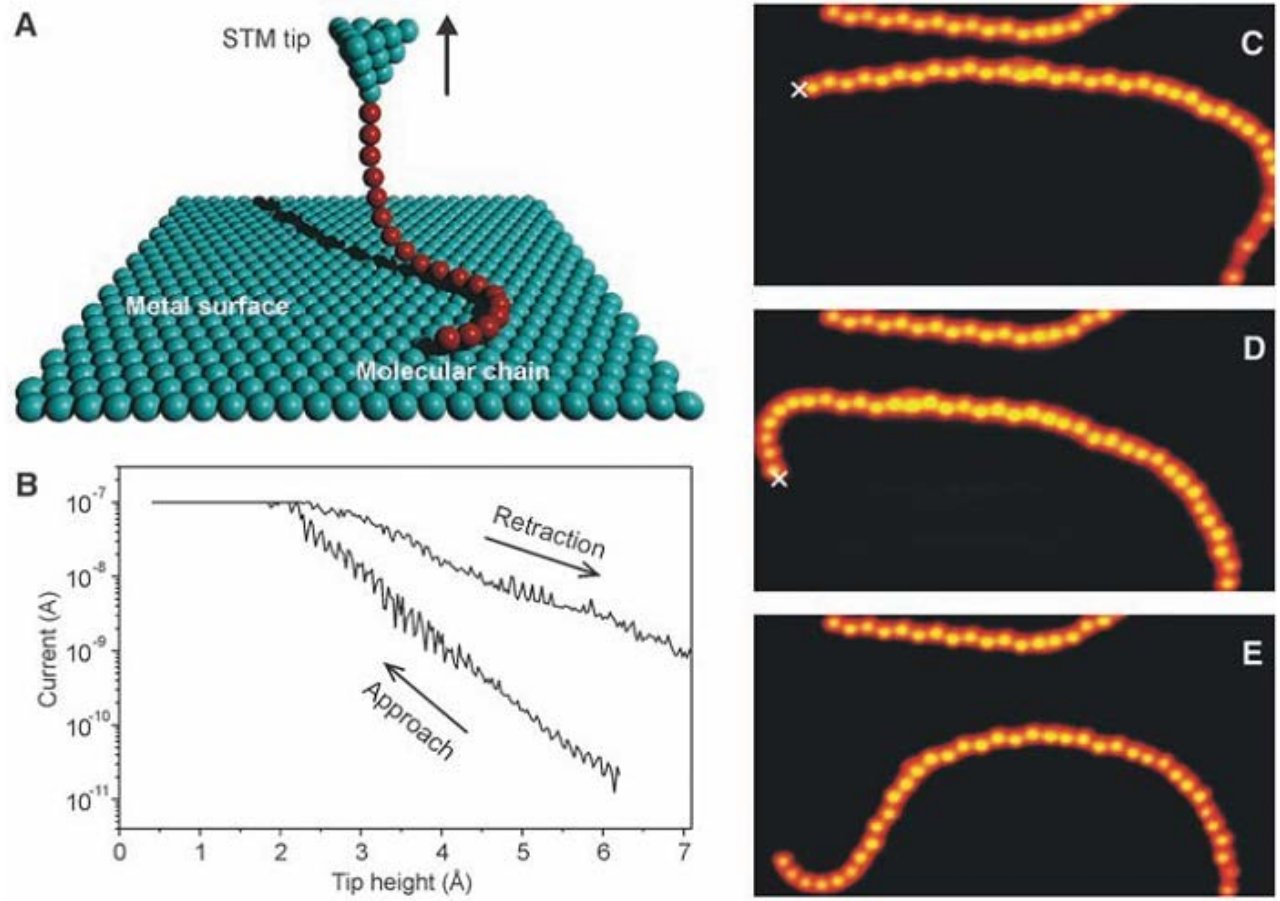


Hla et al., Phys Rev Lett **85** (2000)

SINGLE ATOM/MOLECULE MANIPULATION

Conductivity of a Molecular Wire





Lafferentz et al., Science **323** (2009)

Nanostructure Fabrication

bottom up

- SPM Manipulation
- Molecular Beam Epitaxy
- Self Assembly

SELF-ASSEMBLY and SELF ORGANIZED GROWTH

Definitions

Self Organized Growth

ordering during growth process

determined by mesoscopic forces and kinetics- a priori not identical

Examples:

semiconductor quantum dots

Self Assembly

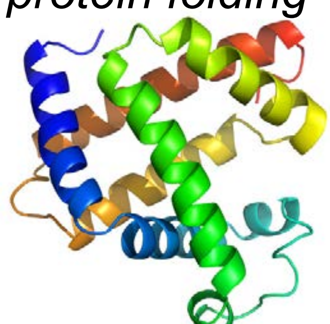
spontaneous association of molecular components into a <u>supramolecular</u> architecture

Free energy minimization, can proceed in closed systems, stable under equilibrium

Examples:

supramolecular networks

protein folding



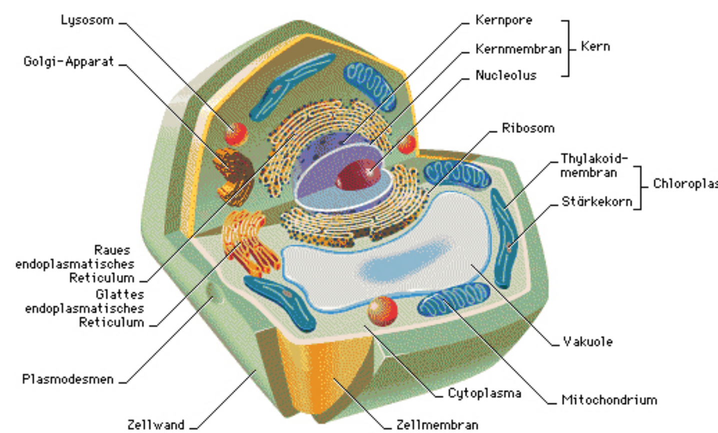
Self Organization

(i) Open systems dissipative structure formation far from equilibrium

(ii) initial emergence of biological macromolecules

Examples:

Cells



SELF-ASSEMBLY and SELF ORGANIZED GROWTH

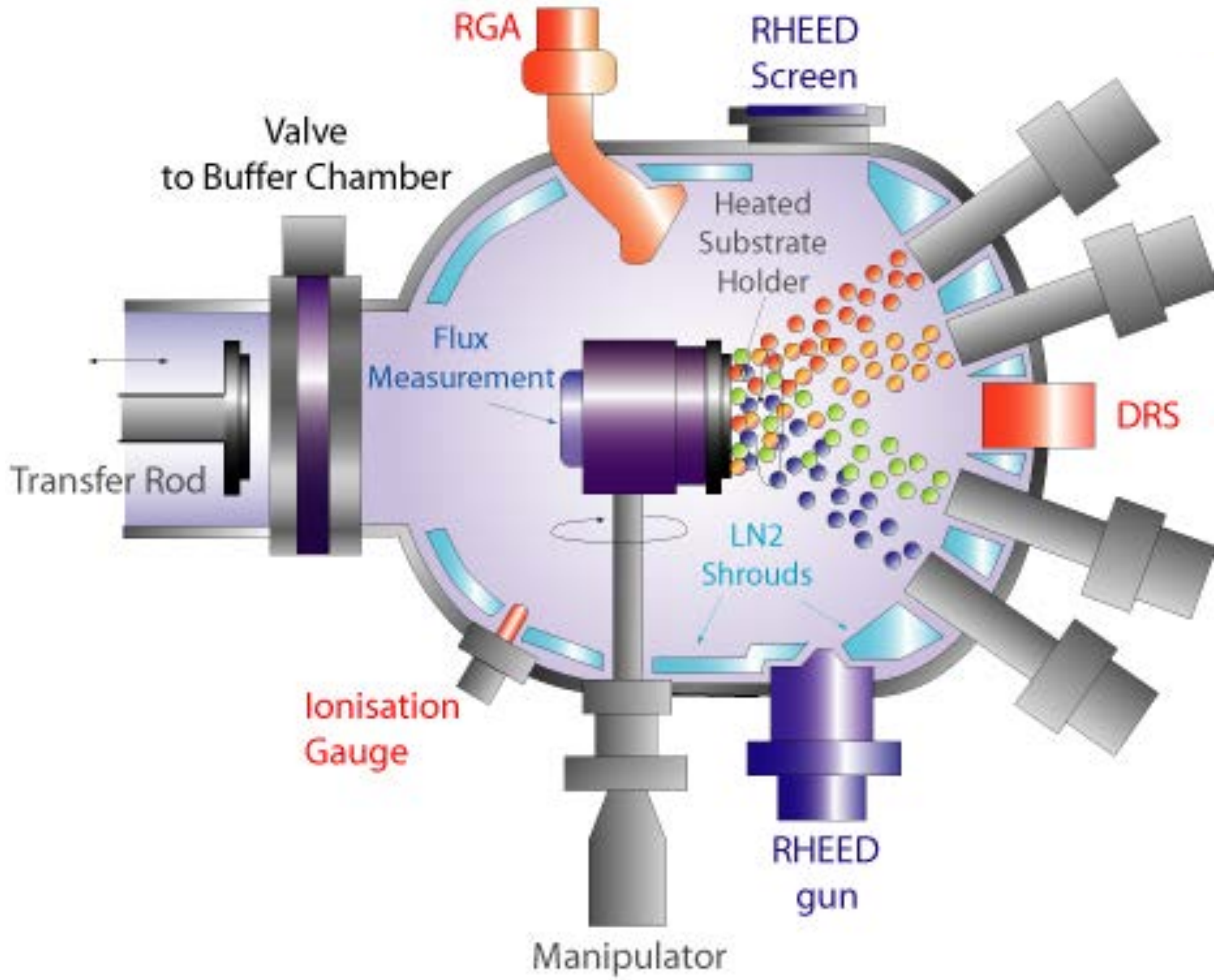
Molecular Beam Epitaxy

Ultrahigh Vacuum (UHV)
$<10^{-10}$ mbar
cryo shrouds to reduce wall desorption

Effusion Cell
Knudsen Cell
for organic and inorganic materials

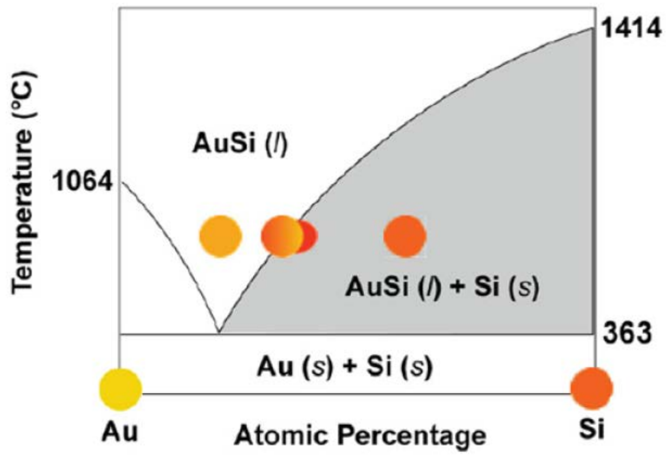
Substrate Heating

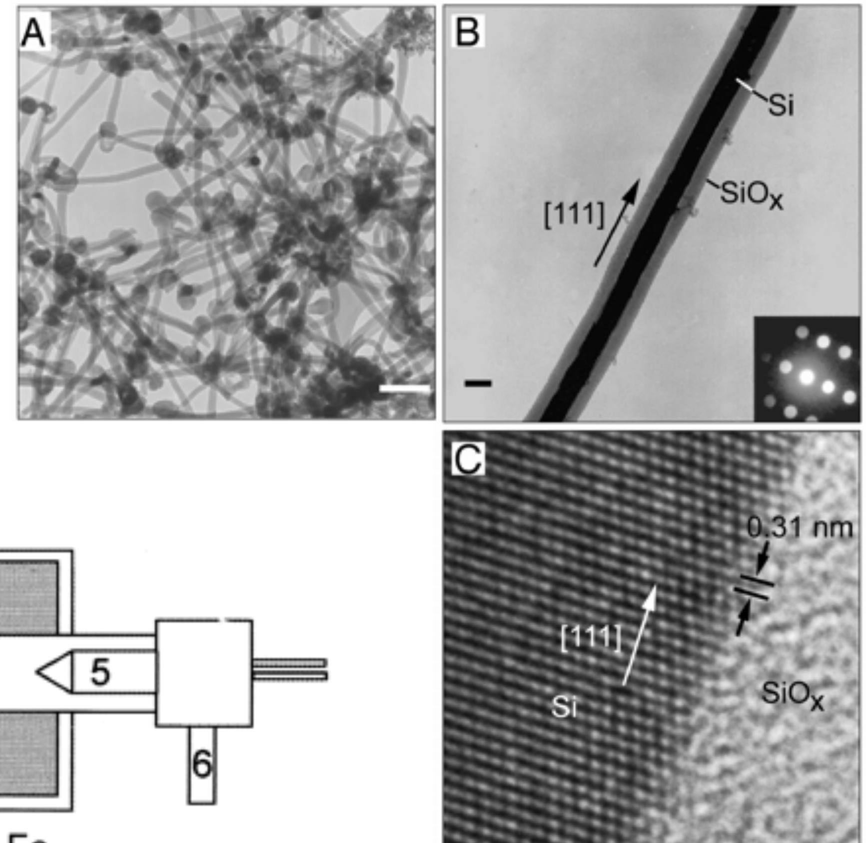
Reflection High Energy Electron Diffraction
(RHEED) for in-situ monitoring

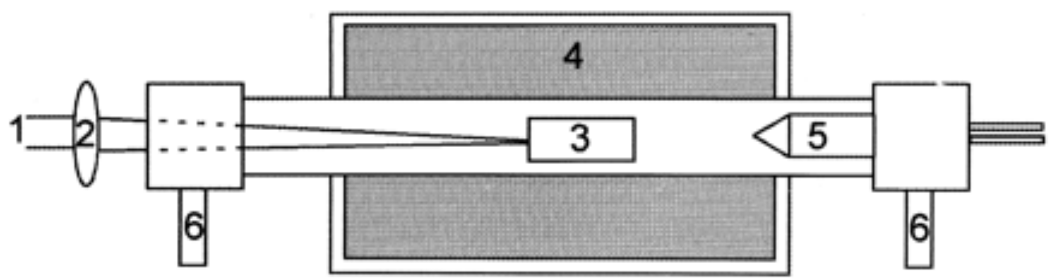


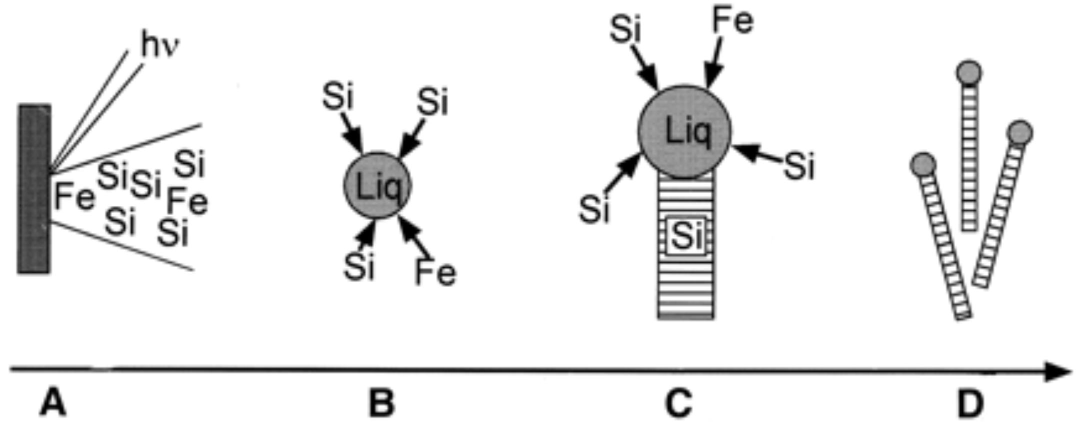
Vapor-liquid-solid growth mechanism

Si nanowire synthesis:

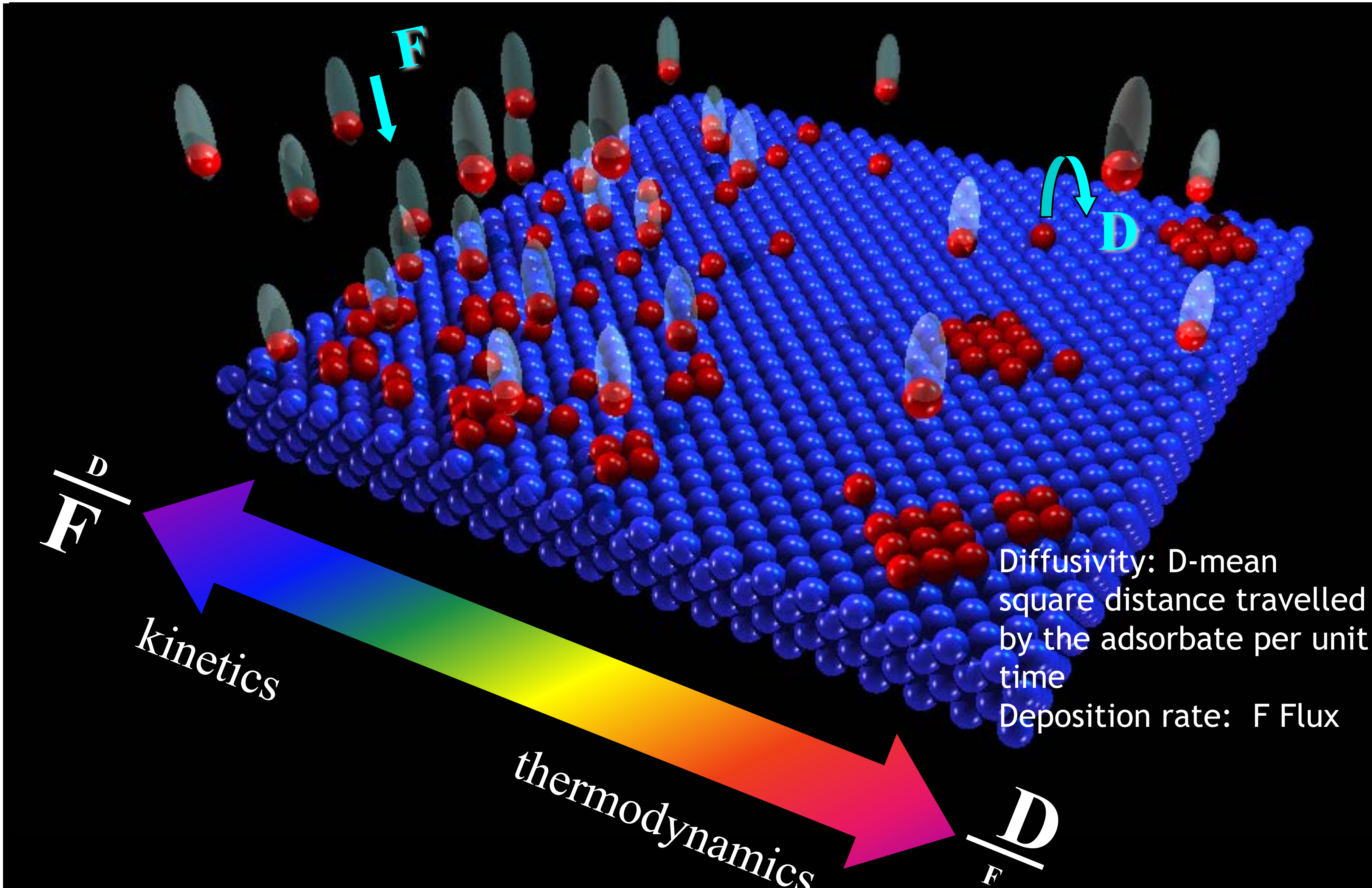








Thin Film Growth



The ratio determines outcome (average distance that the molecule needs to travel to meat another, nucleation or aggregation).

Self-Organized Growth at Surfaces

$\frac{D}{\mathbf{F}}$

$\frac{\mathbf{D}}{F}$

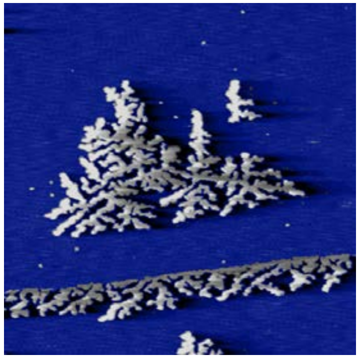
kinetics

thermodynamics

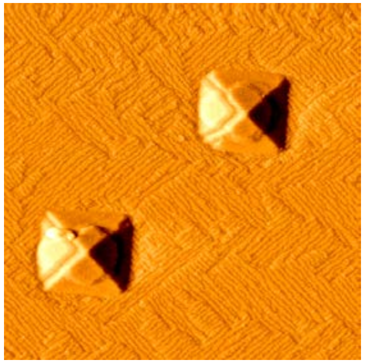
Deposition Rate F ⟷ **Diffusion D**

Arrhenius Law (Temp. T)

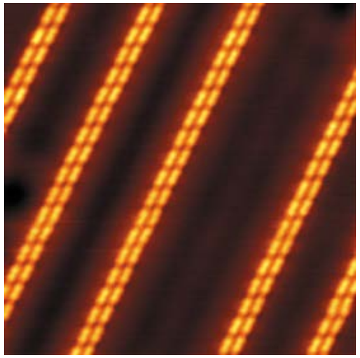
$D \sim n_0 \exp(E_{barr}/k_B T)$



metal epitaxy



semiconductor MBE



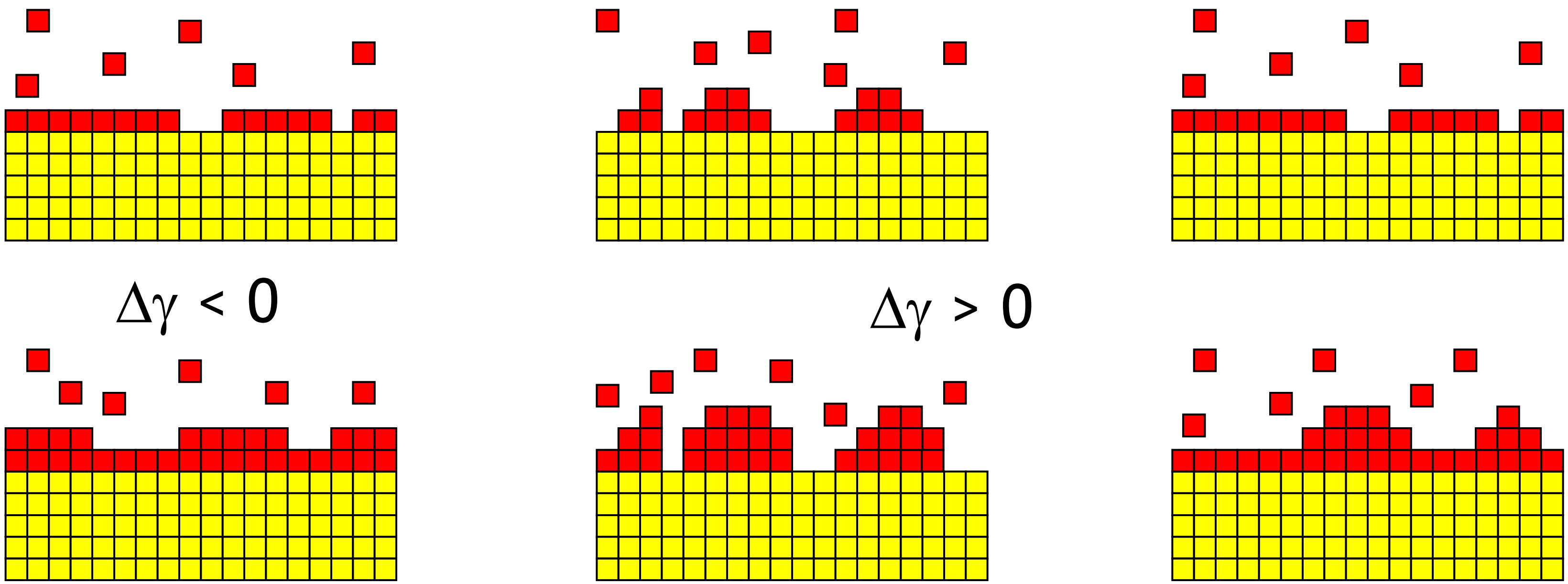
molecular self-assembly

https://www.nature.com/articles/nature04166

Growth modes

Surface tensions (free energy/unit area) of overlayer-vacuum: overlayer-substrate, substrate-vacuum

$$\Delta\gamma = \gamma_F + \gamma_{S/F} - \gamma_S$$



layer - by - layer growth
(Frank - van der Merve)
a-s stronger than a-a

island growth
(Volmer - Weber)
a-a stronger than a-s

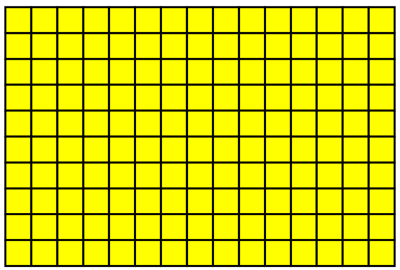
layer - by - layer
+ island growth
(Stranski - Krastanov)

quantum dots

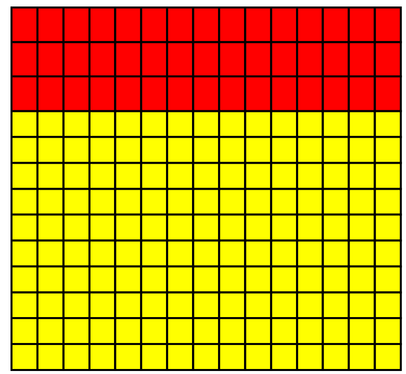
a: adsorbate
s: surface

Stranski-Krastanov Growth of Semiconductor QDs

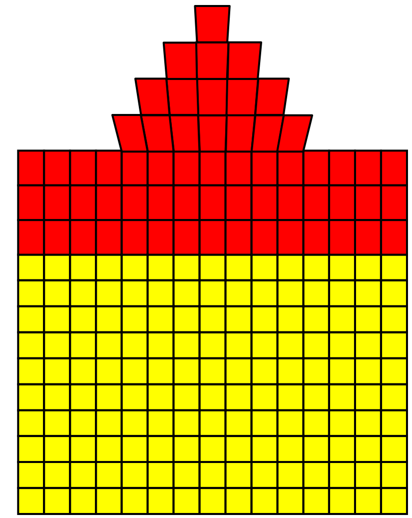
lattice constants: $a_A > a_B$



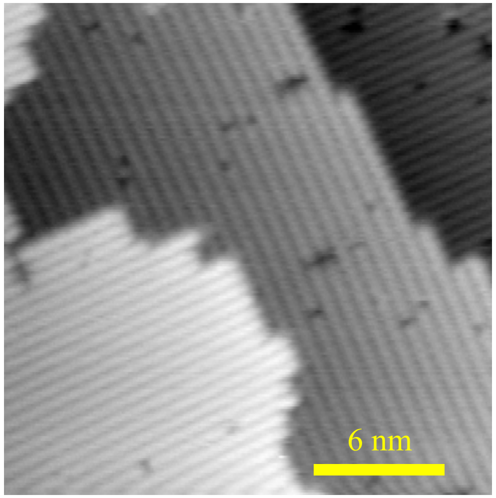
substrate



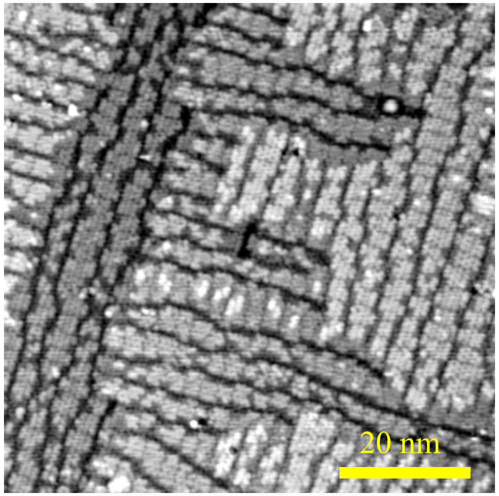
wetting layer



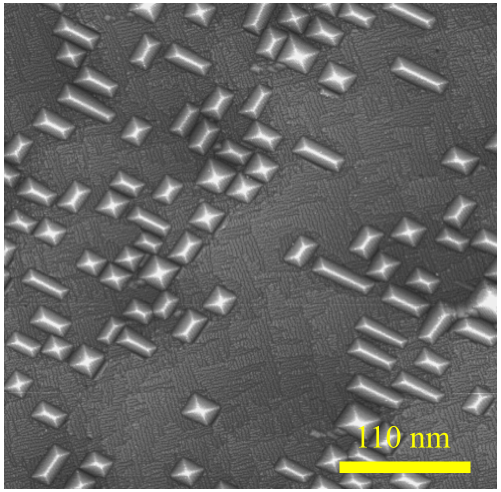
islands



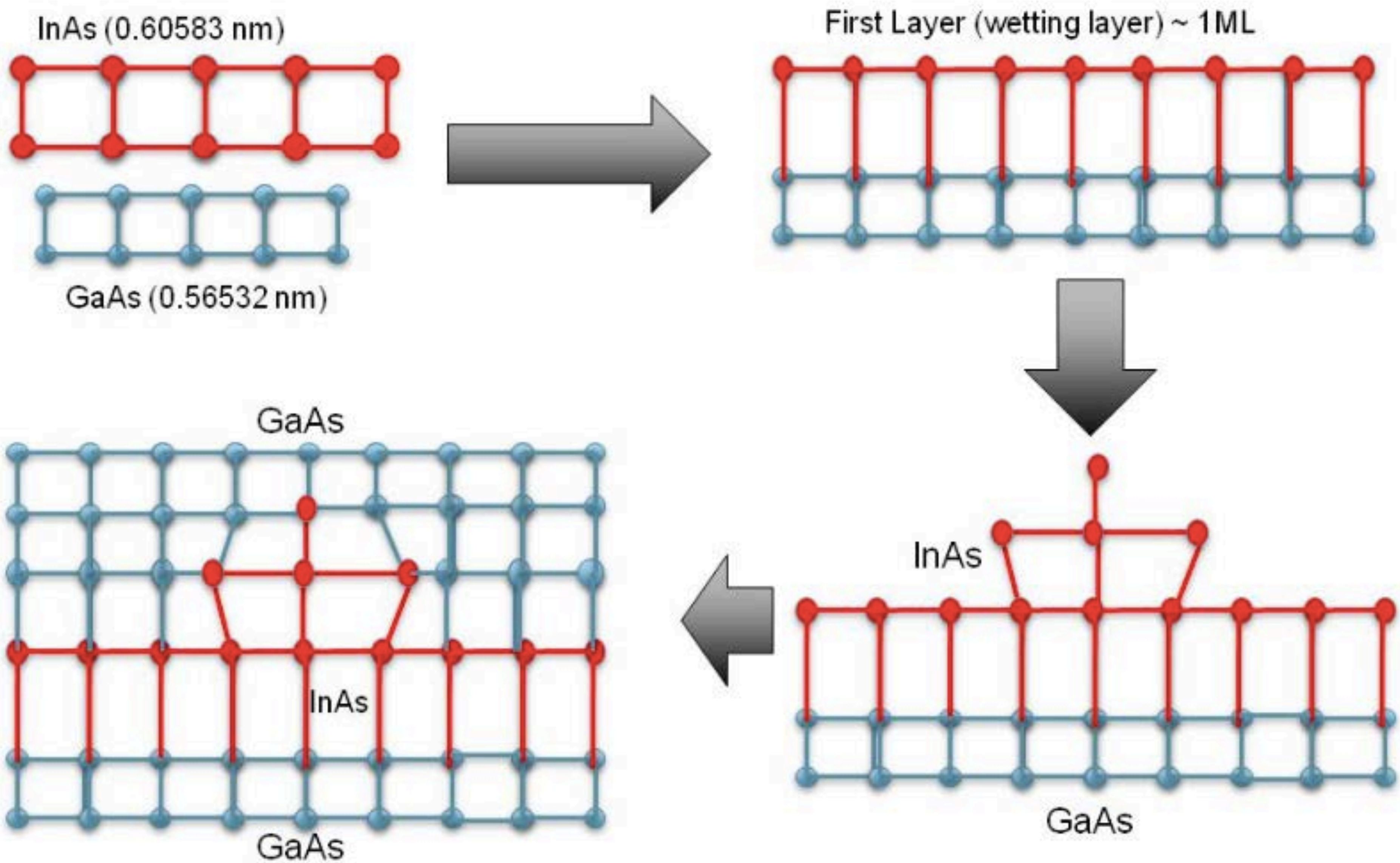
Si(001)



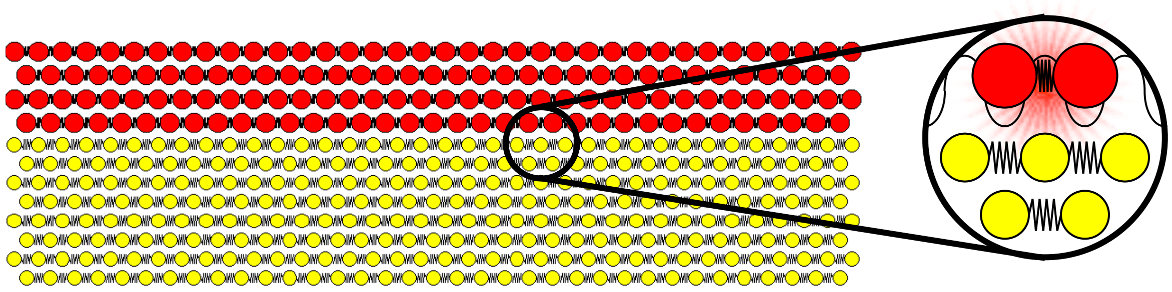
3ML Ge on Si(001)



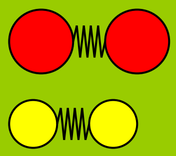
6ML Ge on Si(001)


InAs (0.60583 nm)
GaAs (0.56532 nm)
First Layer (wetting layer) ~ 1ML
InAs
GaAs
GaAs
InAs
GaAs

Stranski-Krastanov Growth



Equilibrium lattice parameter:



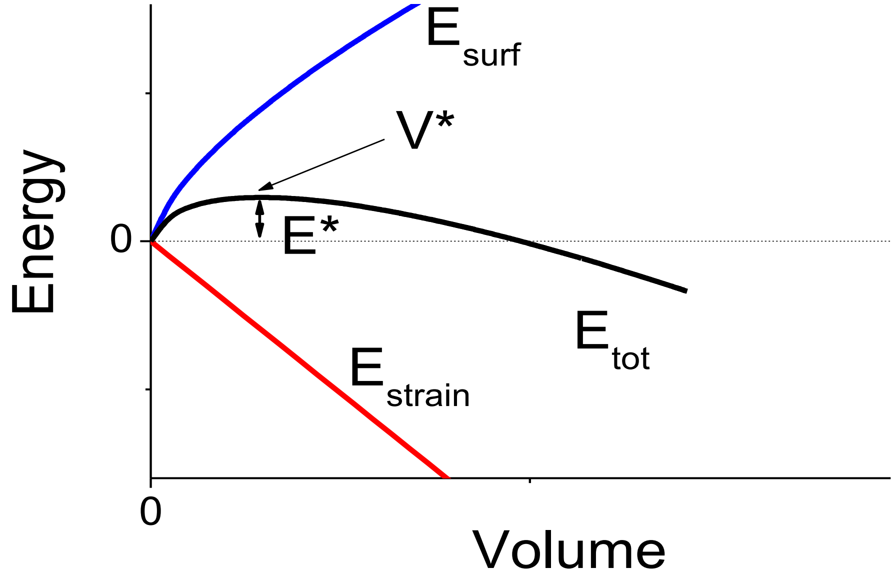
Material A

Material B

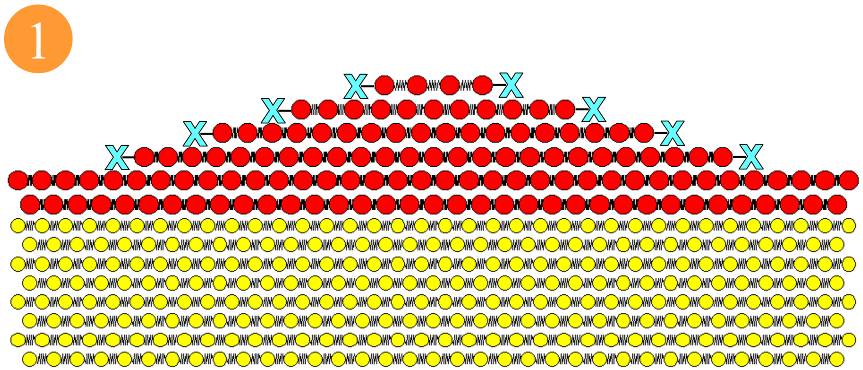
$$E_{tot} = E_{strain} + E_{surf}$$

$$E_{strain} = -\alpha V$$

$$E_{surf} = +\beta V^{2/3}$$

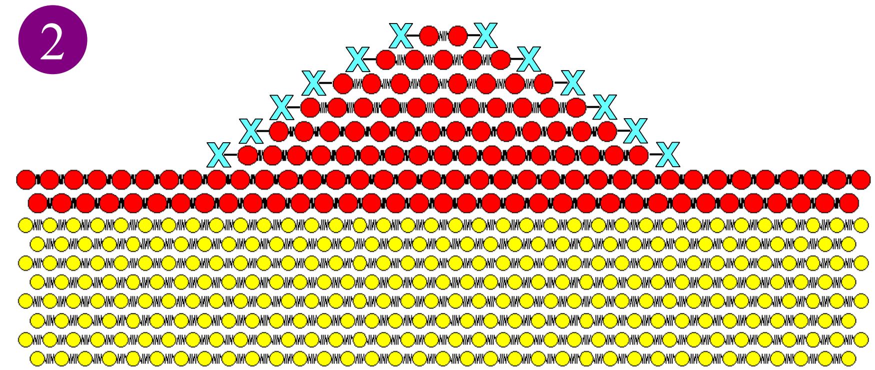


Stranski-Krastanov Growth



more strain energy

less surface energy



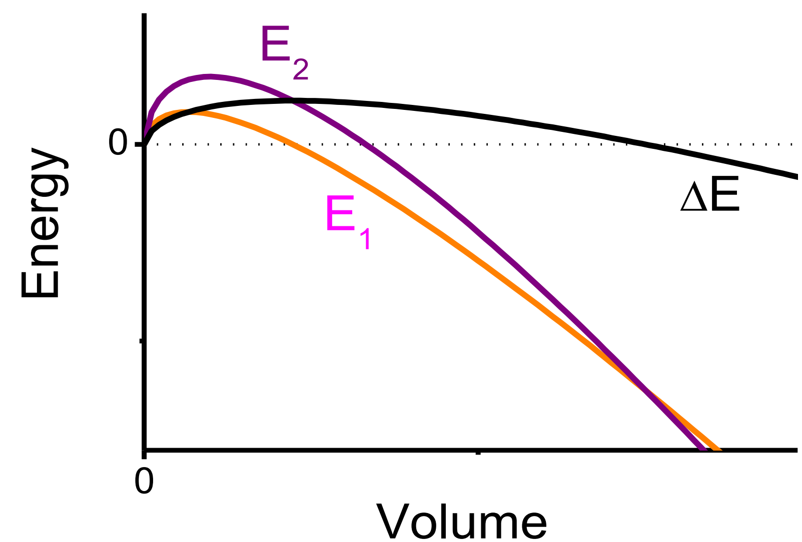
less strain energy

more surface energy

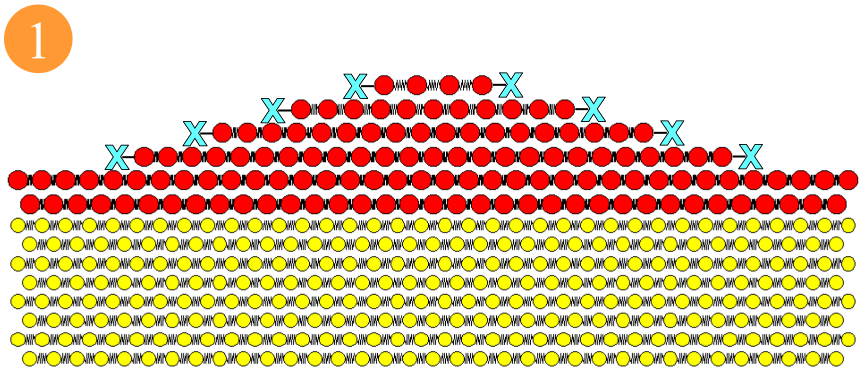
$E_1 = -\alpha_1 V + \beta_1 V^{2/3}$; $E_2 = -\alpha_2 V + \beta_2 V^{2/3}$

$\alpha_2 > \alpha_1$ $\beta_2 > \beta_1$

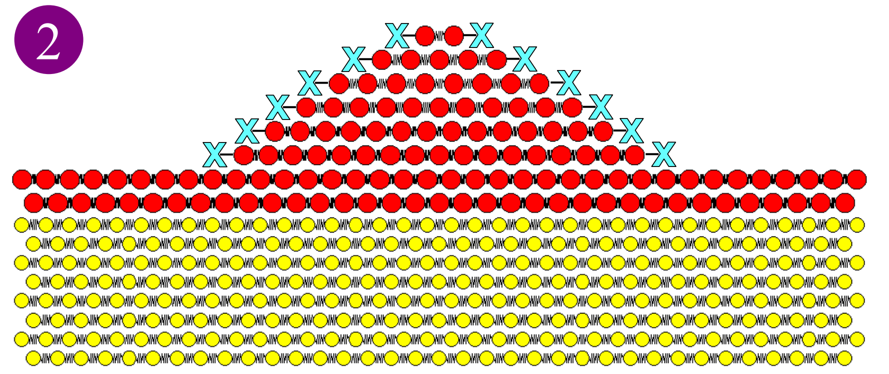
$$E_2 - E_1 = -(\alpha_2 - \alpha_1)V + (\beta_2 - \beta_1)V^{2/3}$$



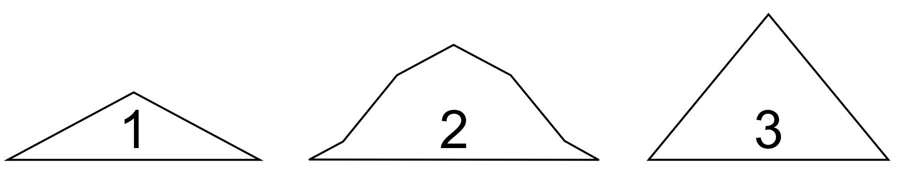
Stranski-Krastanov Growth

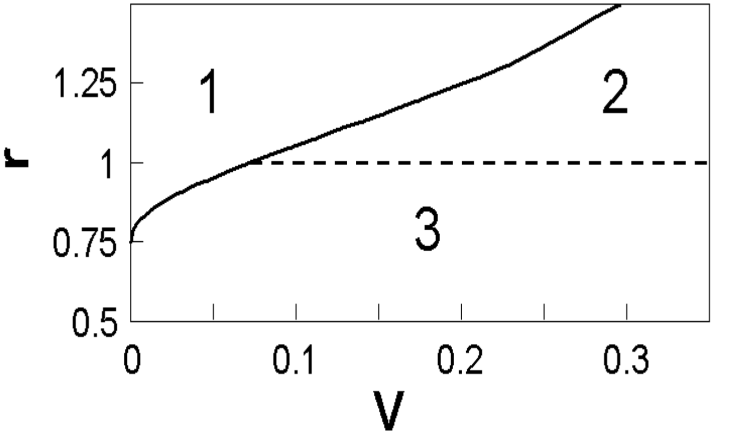


more strain energy
less surface energy



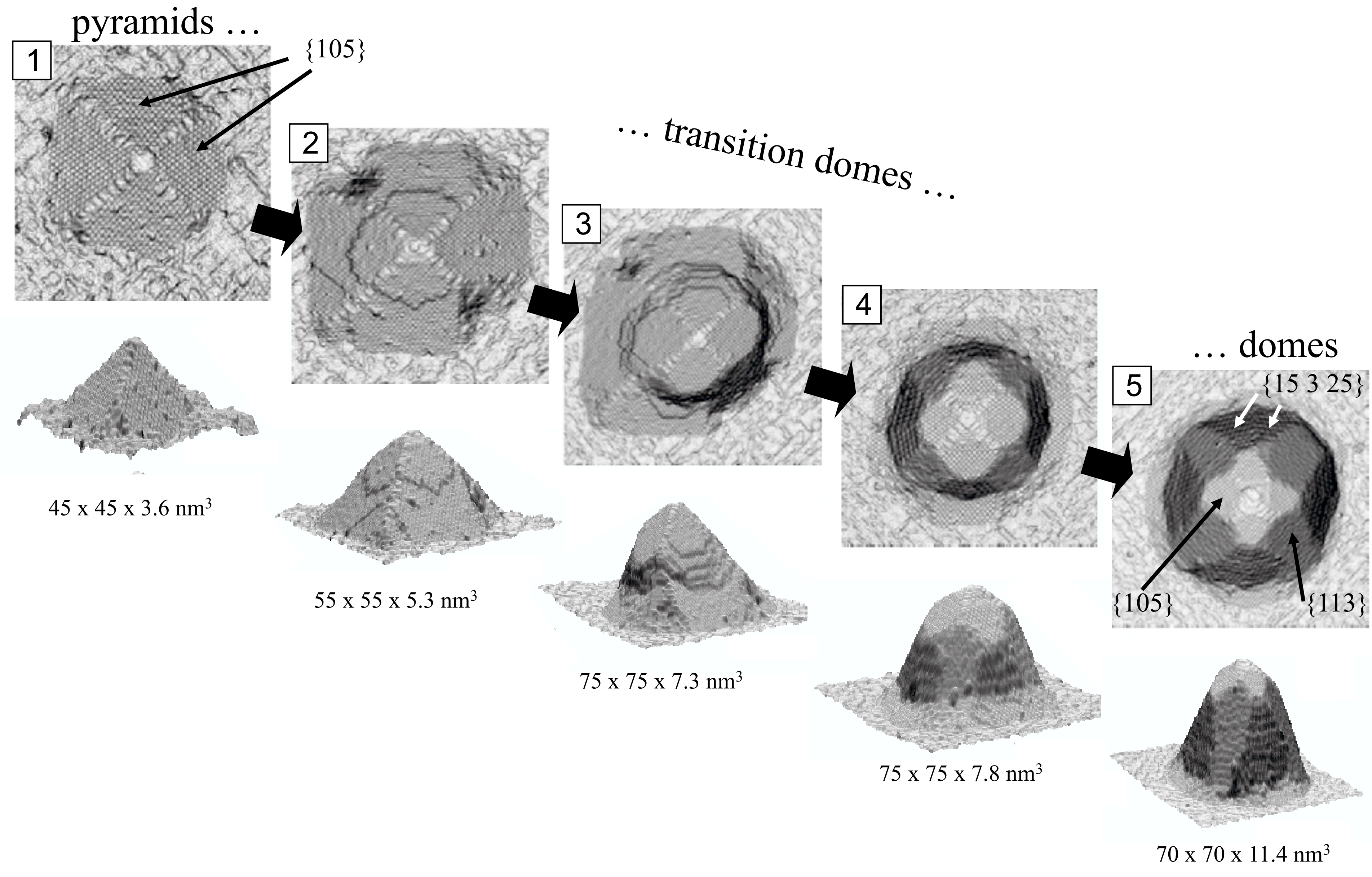
less strain energy
more surface energy



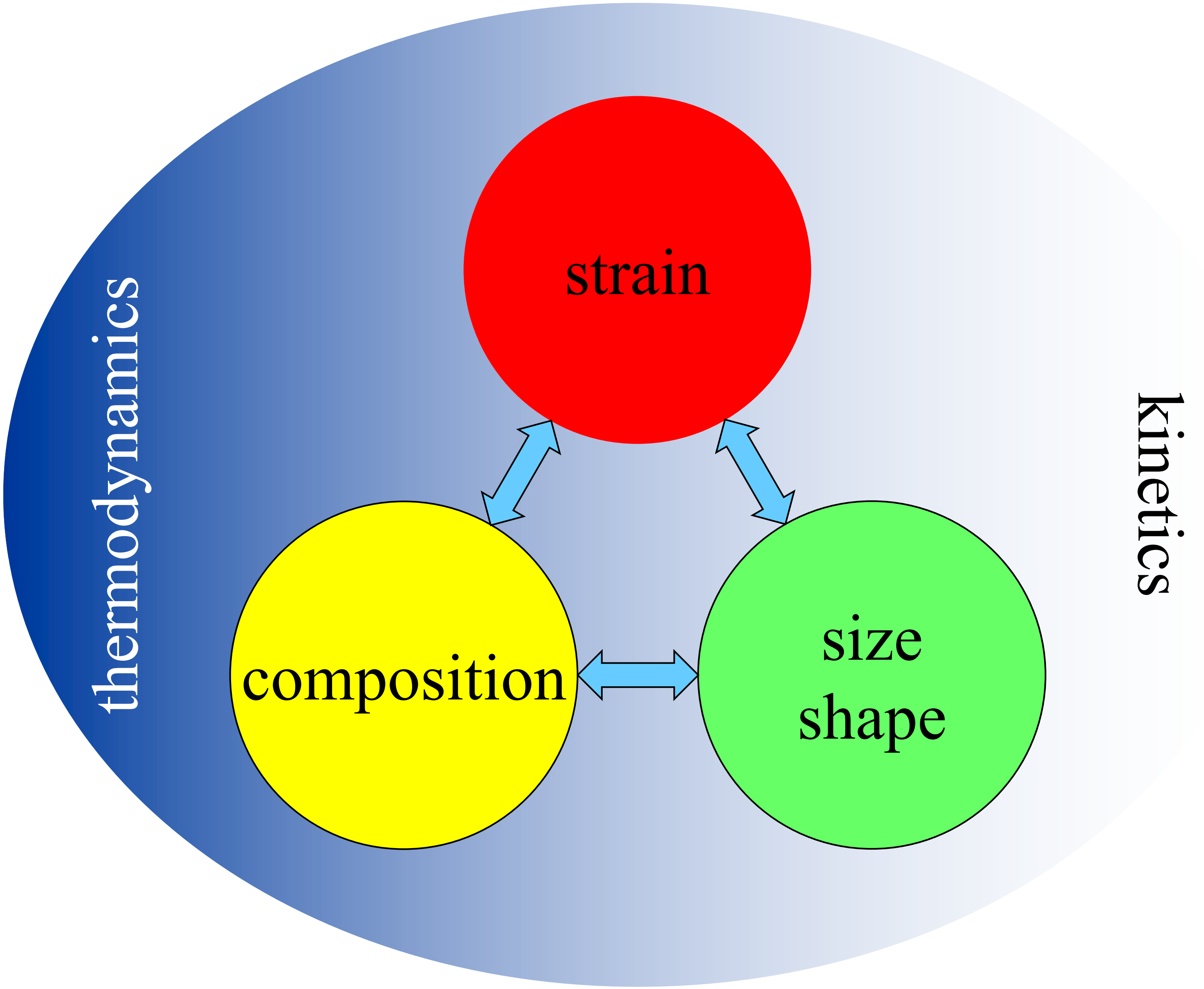


I. Daruka et al., PRL**87**, 2753 (1999); PRB**66**, 132104 (2002)

Pyramid-to-Dome transformation : Ge/Si(001)

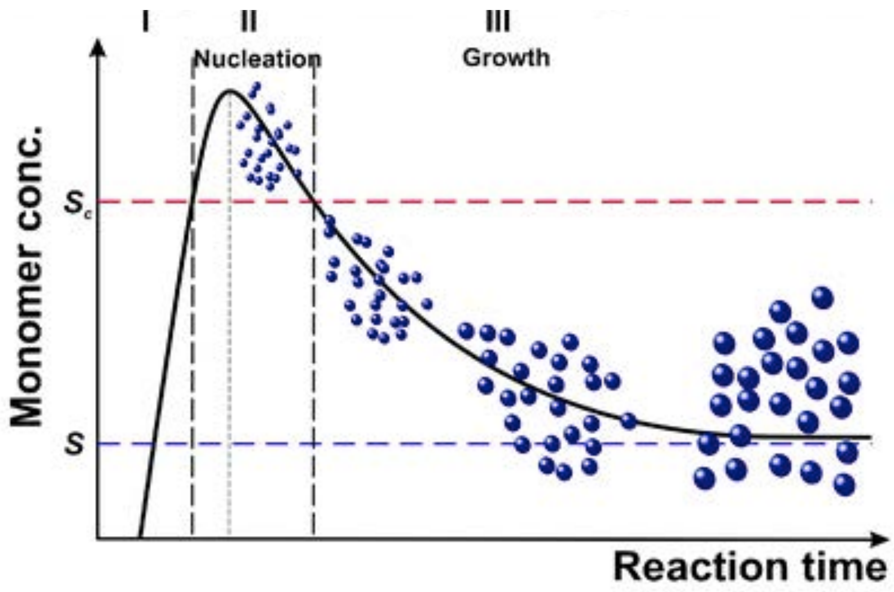


Self – organized semiconductor quantum dots



Solution-based nanocrystal synthesis

Degree of supersaturation vs. reaction time (LaMer plot):



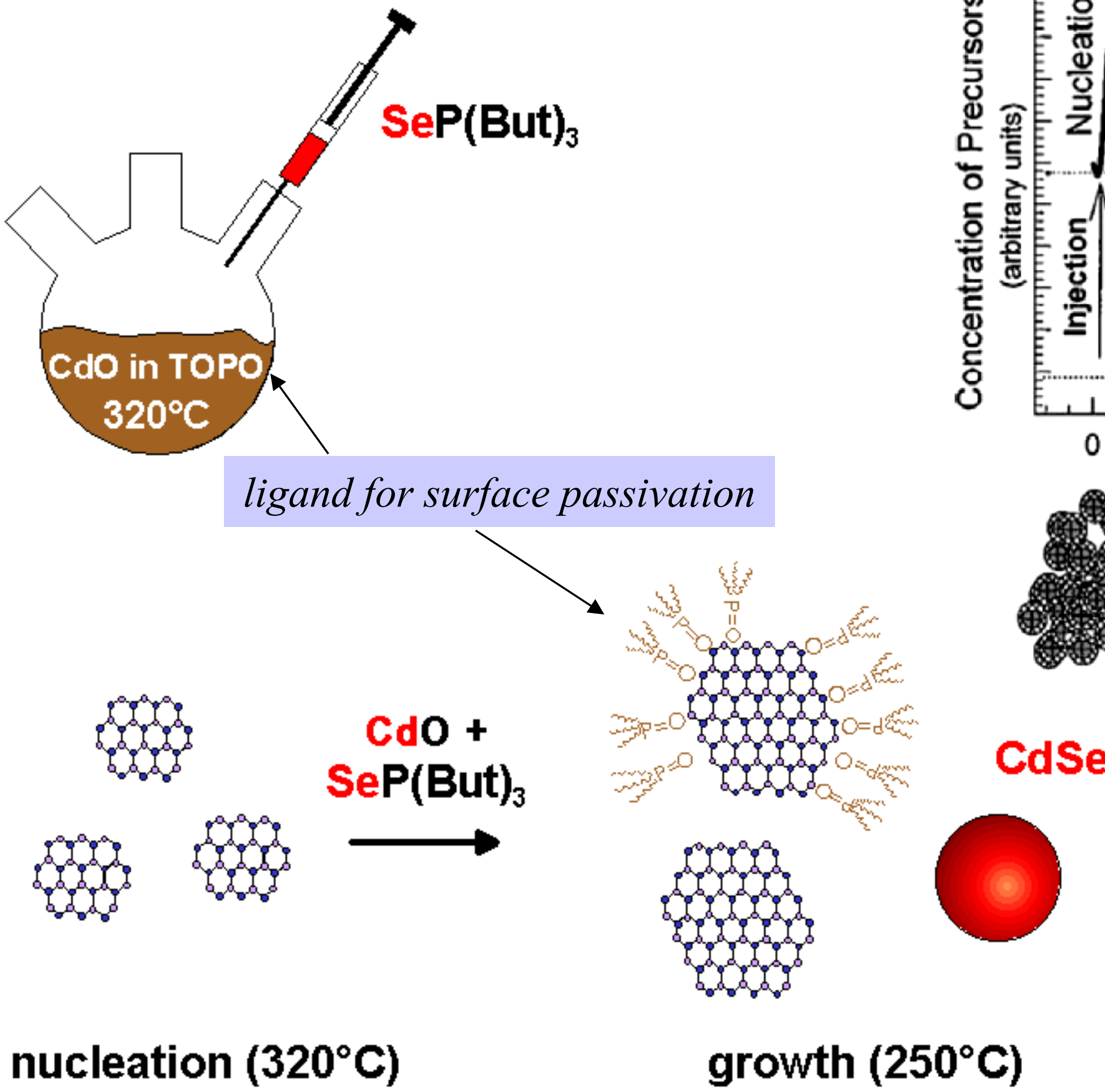
nucleation threshold

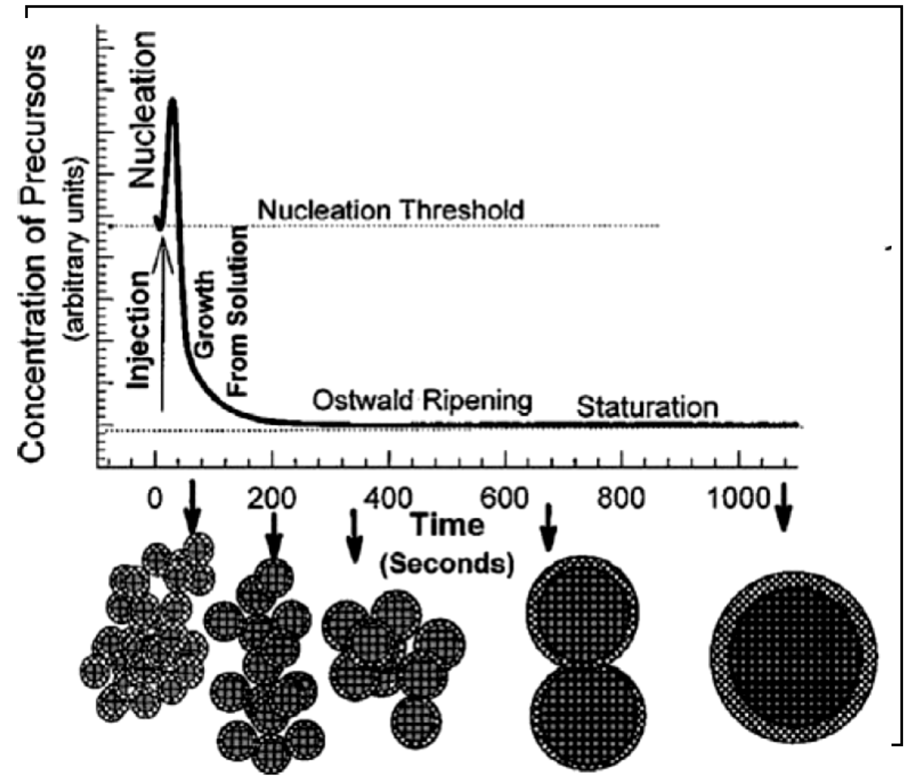
→ homogeneous nucleation requires temporal separation of nucleation and growth of the seeds.

hot injection method (instantaneous nucleation)

heating-up method (in situ formation of reactive species)

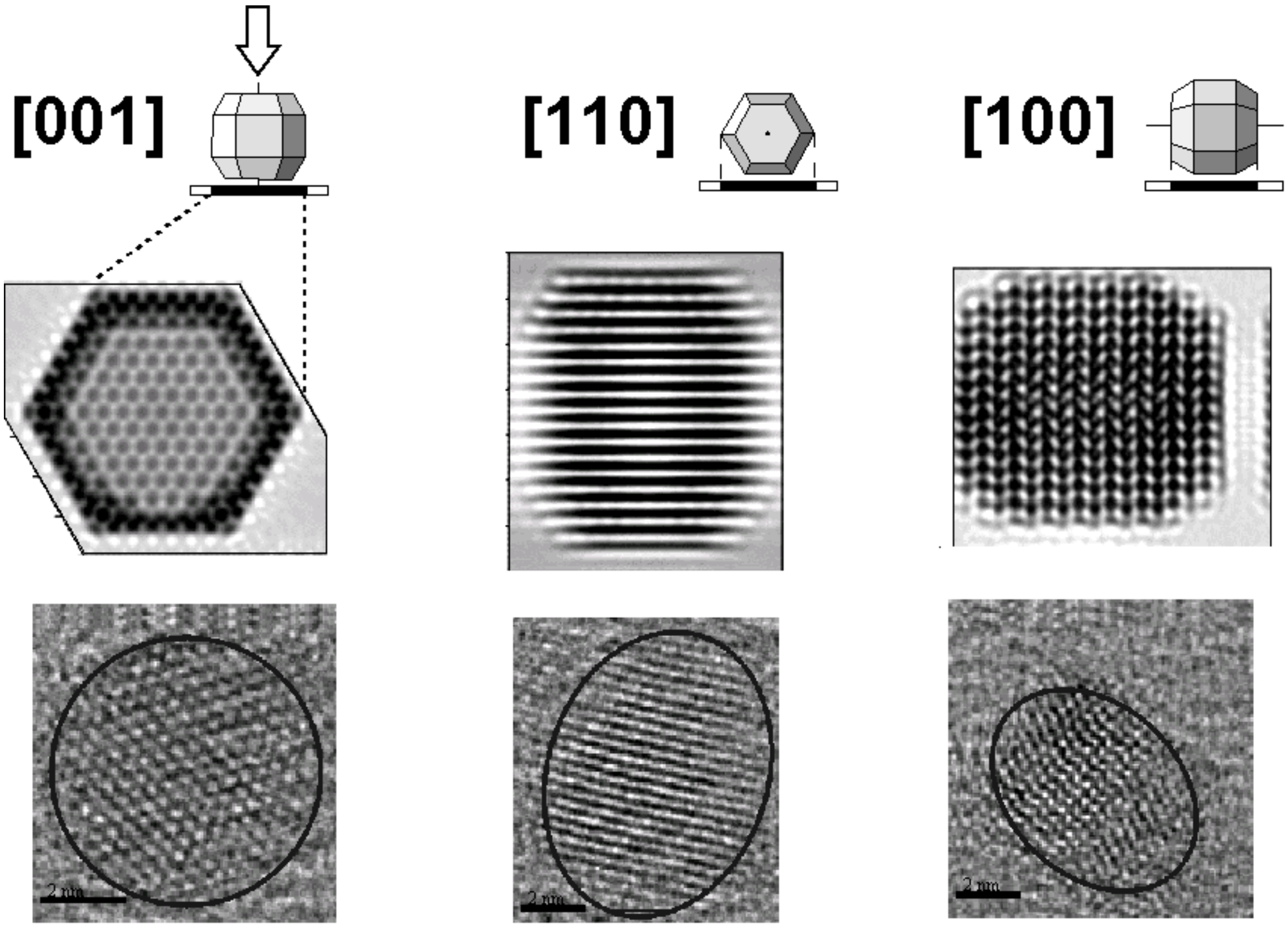
CdSe nanocrystal synthesis



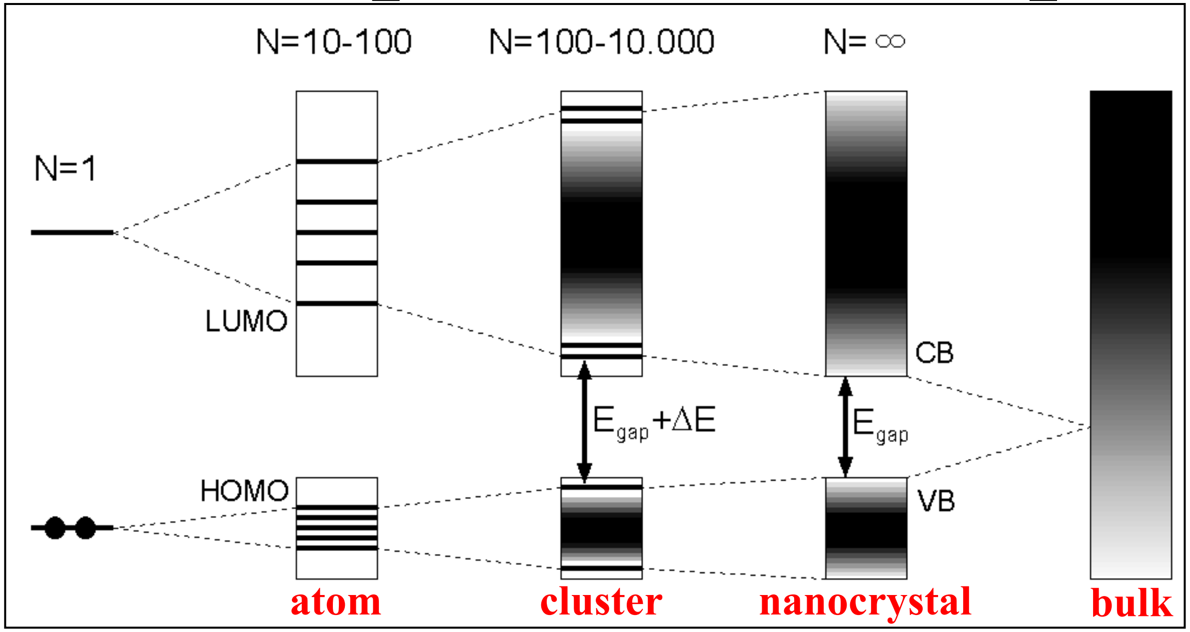


Microscopic structure

HRTEM images of hexagonal CdSe nanocrystals:



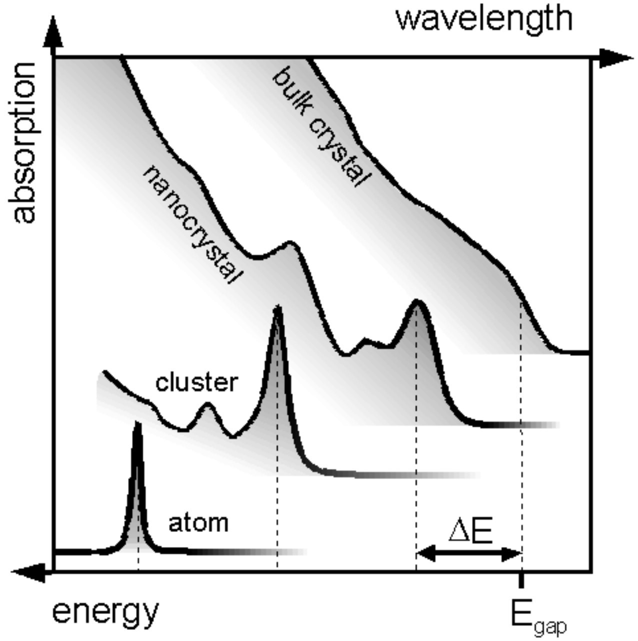
Size-dependence of optical absorption



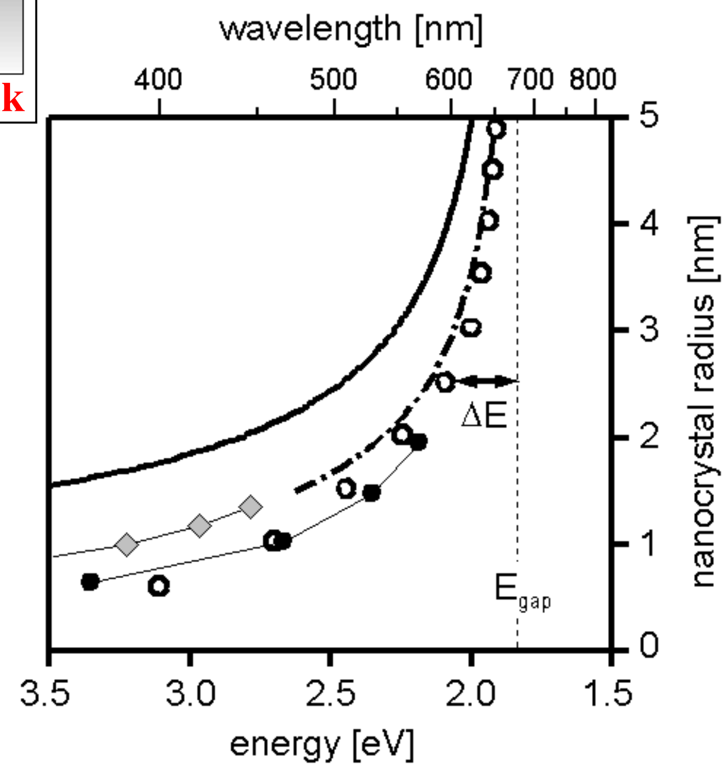
Inorganic:

CB min

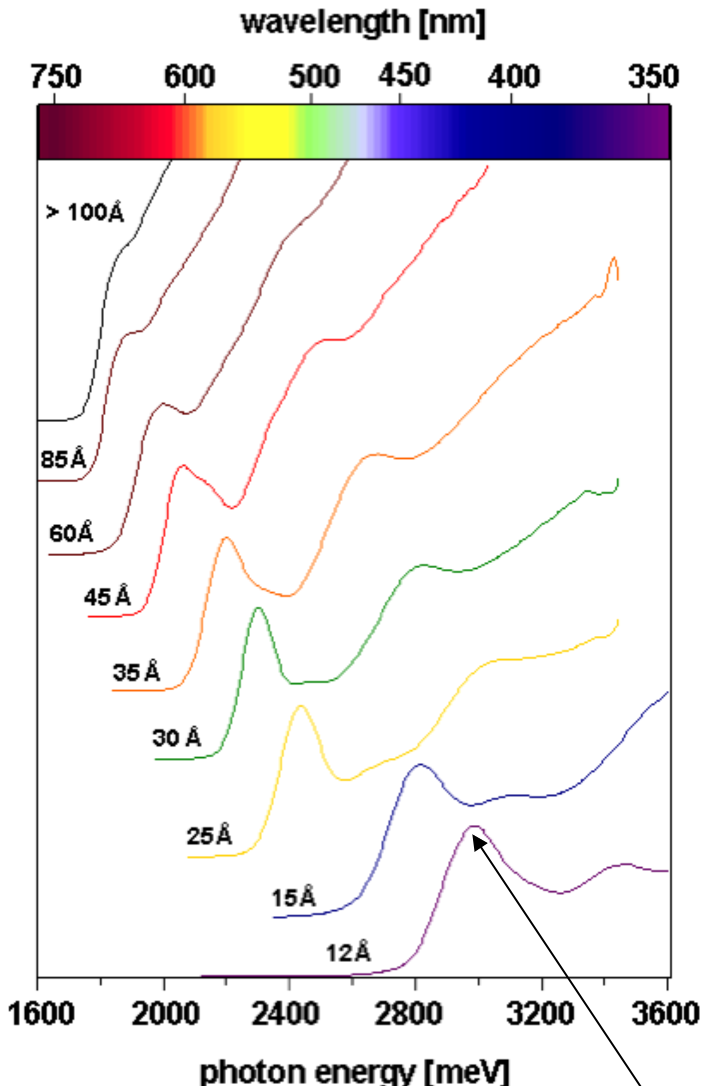
VB max



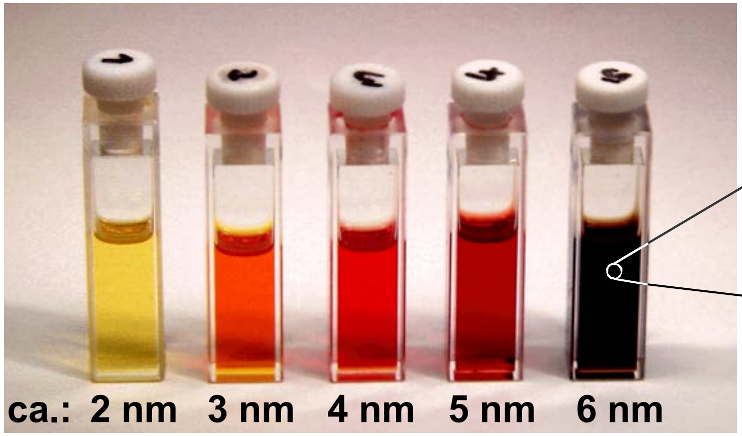
band gap as a function of nanocrystal size:

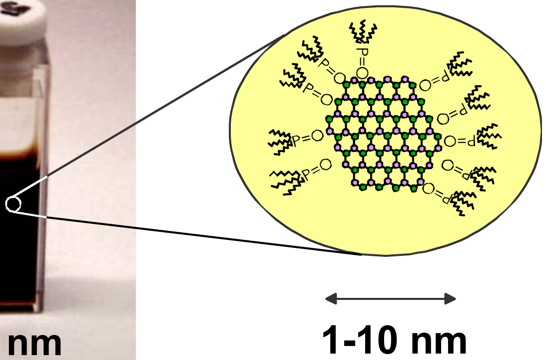


Size-dependence of optical absorption



CdSe nanocrystals





- very large molar extinction coefficients (how strongly a substance absorbs light at a given wavelength) (1-5 x 10^6 M^{-1} cm^{-1}), ~ 10-50 times larger than that of organic dyes

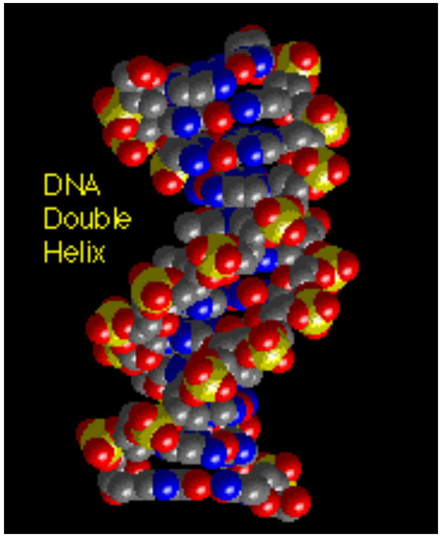
excitonic peak (e-hole pair)

Nanostructure Fabrication

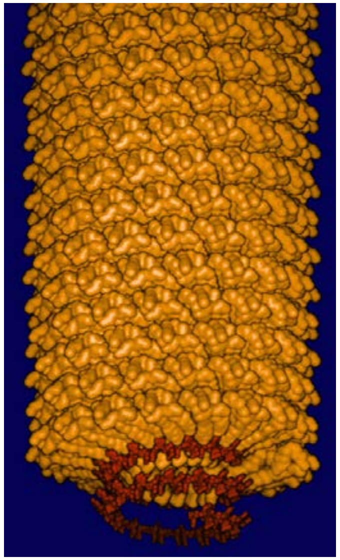
bottom up

- SPM Manipulation
- Molecular Beam Epitaxy
- Self Assembly

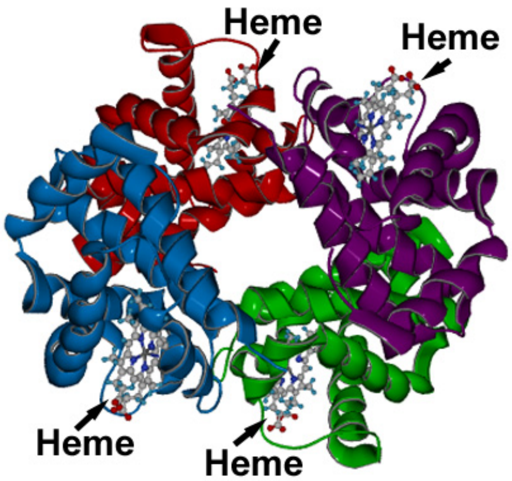
Self-Assembly: Nature's Choice



DNA



virus



Protein

(Folding)

- Noncovalent interactions :
  reversible, selective and directional bonding
- Assembly:
  self-recognition and error correction

Did you know..?

- person of 60Kg (~70% water) ~ 1,4 x 10(27) molecules
- the human body has 6x10(13) cells and that each human cell has on average ~ 1x10(14) molecules :~6x10(27) molecules (total=water+proteins, sugars, etc)

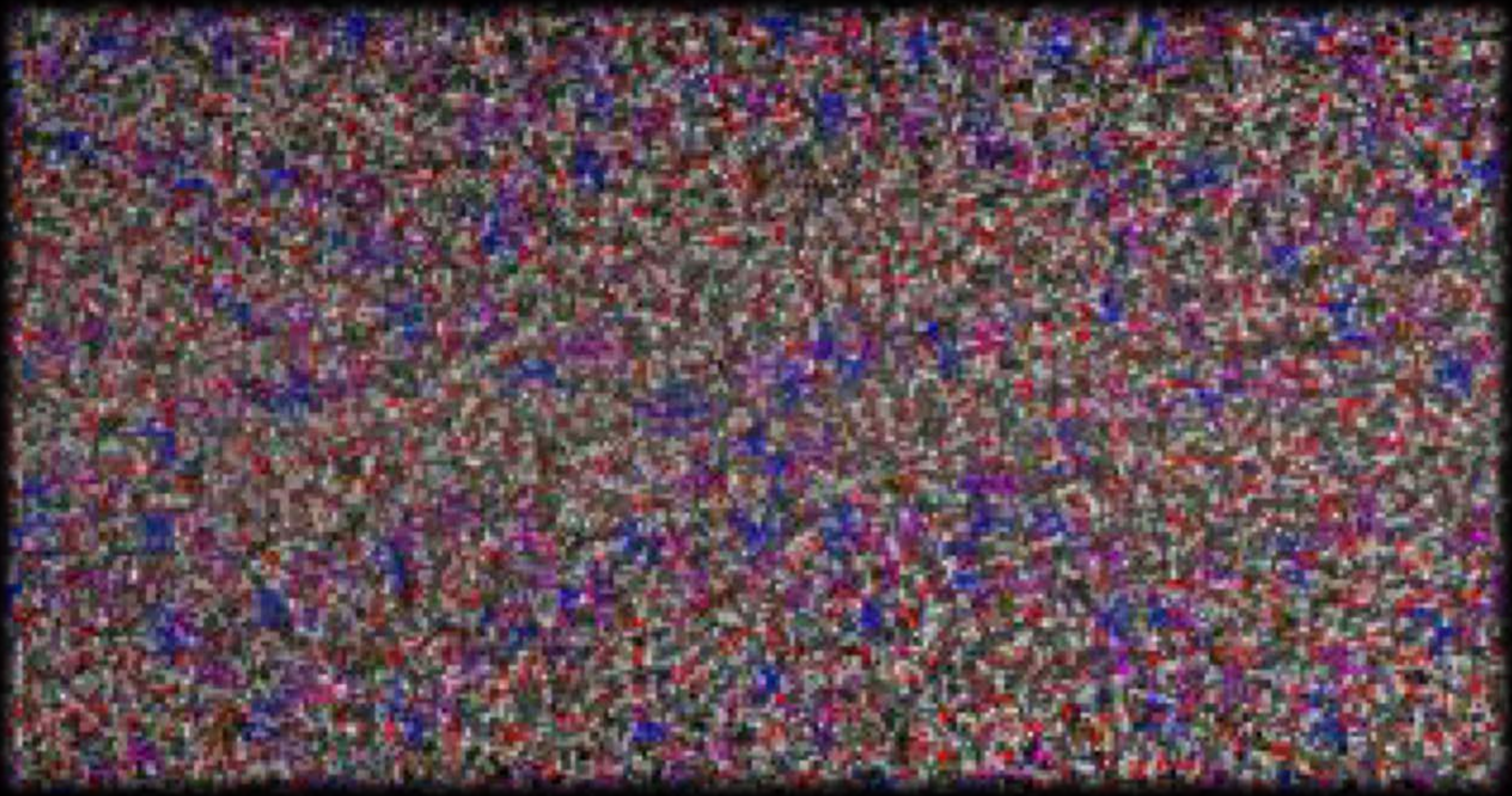
- ~ 10(21)-10(24) stars in the universe

1000 times more molecules forming our body than stars are in the universe….

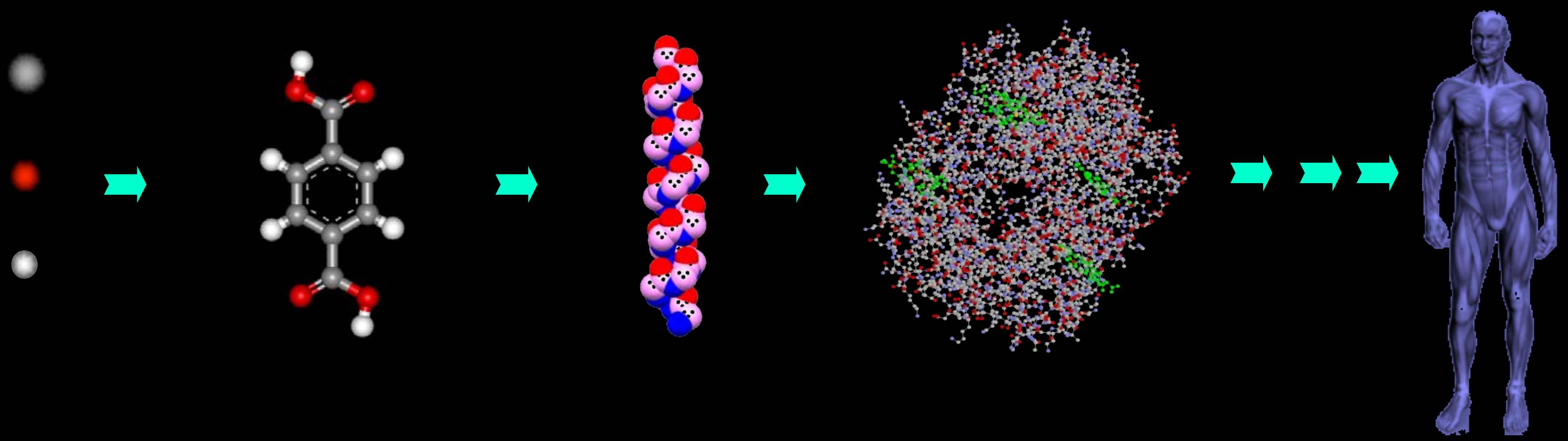
about one hundred thousand molecules with different shapes and functions found specific function and location out of countless possibilities... interactions between molecules are responsible for structure and function!

RECOGNITION (and Folding)!!!

Lipid Bilayer formation



Interactions determine order, increasing complexity

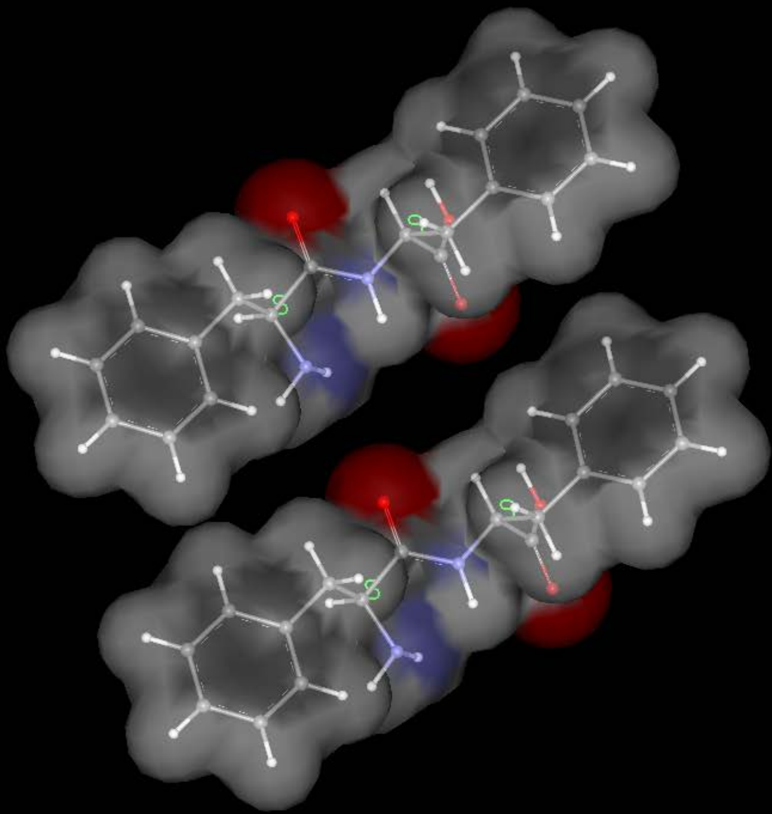


Self-assembly

Molecular Recognition

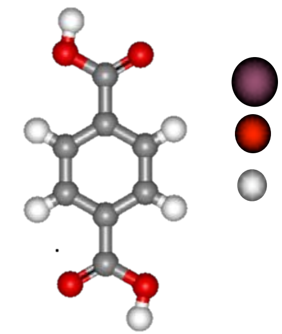
Function

How is the transfer of molecular information?



Supramolecular Chemistry

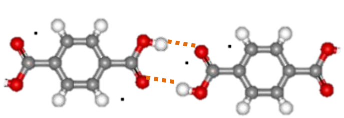
„The chemistry beyond the molecule"   J.M. Lehn



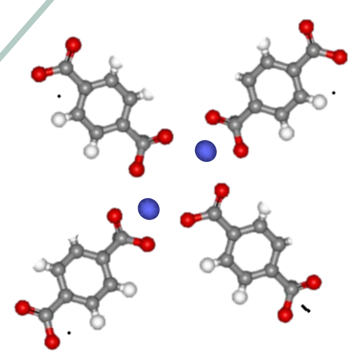
Molecular Chemistry → Covalent Bonds

Supramolecular Chemistry → Noncovalent Bonds

- π–π stacking
- Hydrogen bonding



- Coordination complexation

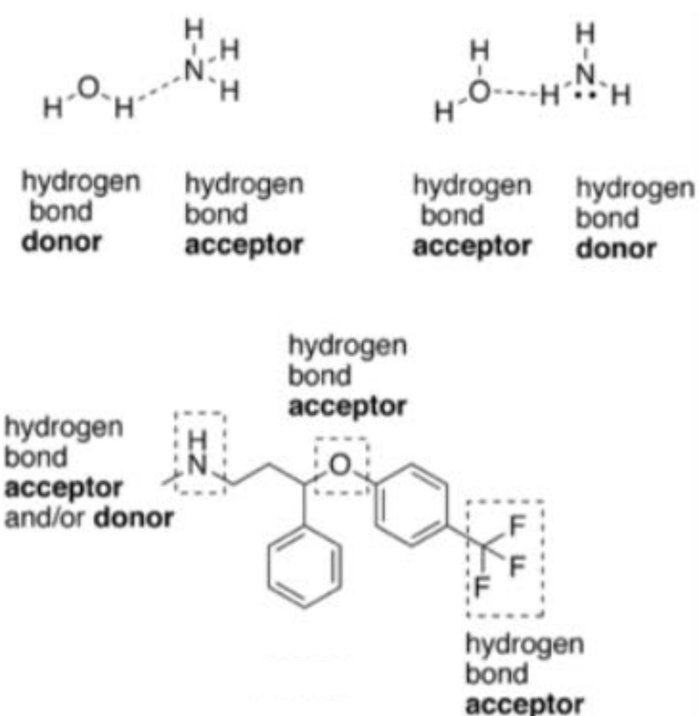


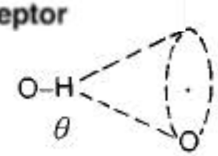
- Van der Waals
- Ionic interactions

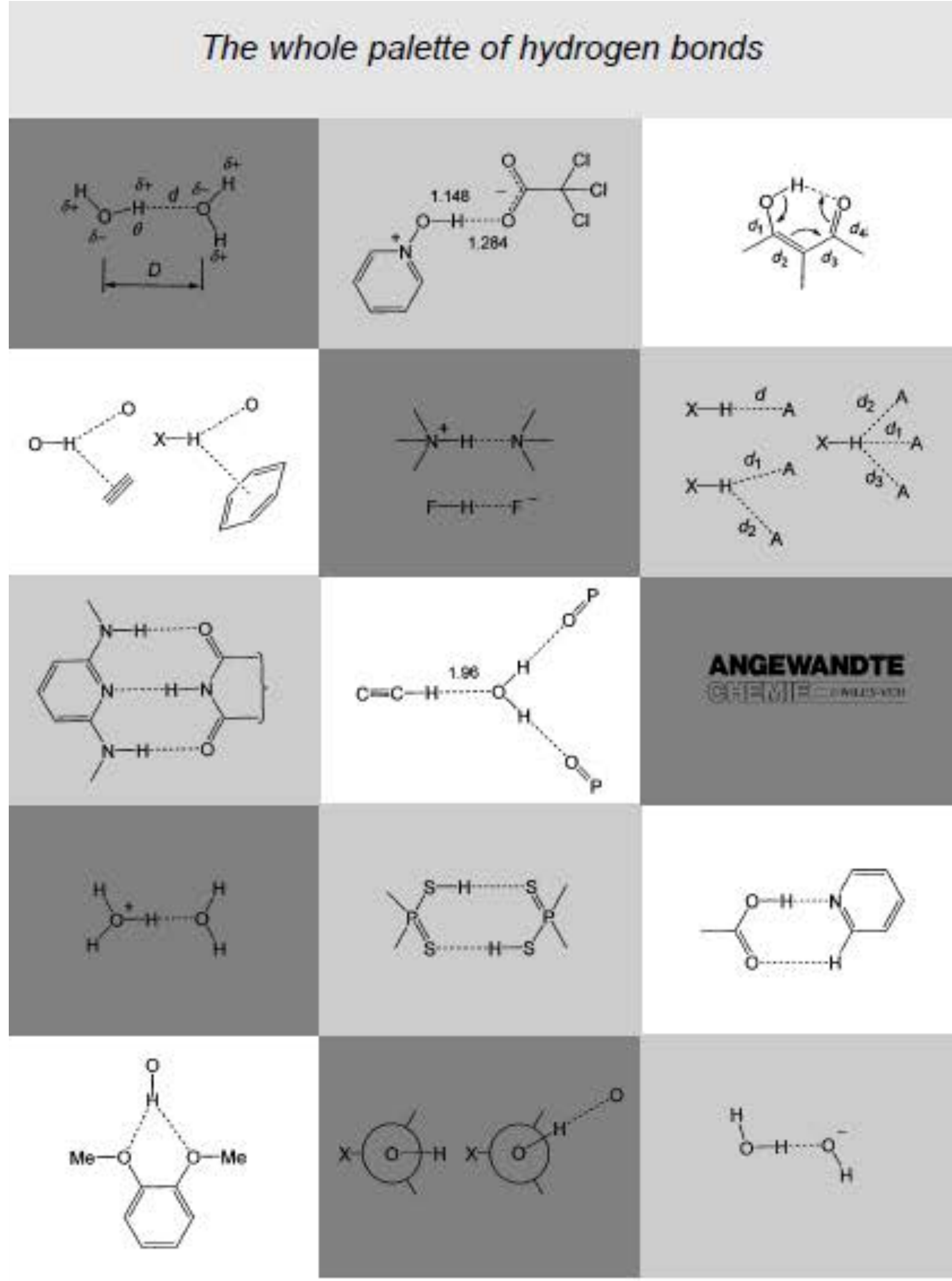
Hydrogen bond

Acceptor atoms have to have a lone-pair electron.

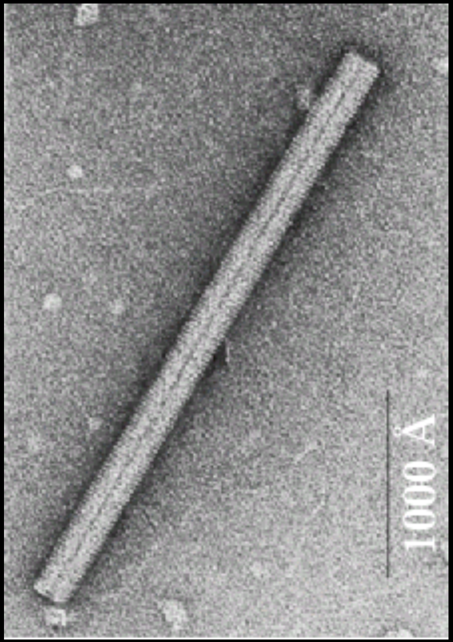
A **donor** atom is connected with at least one H atom.

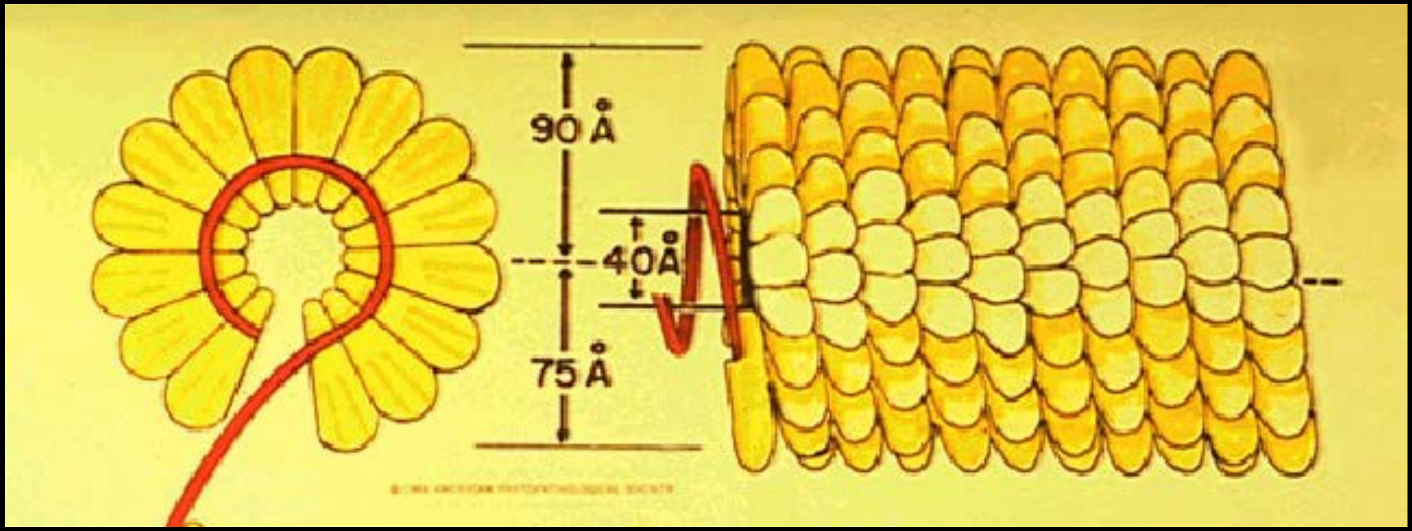






Self-Assembly in Biological Systems





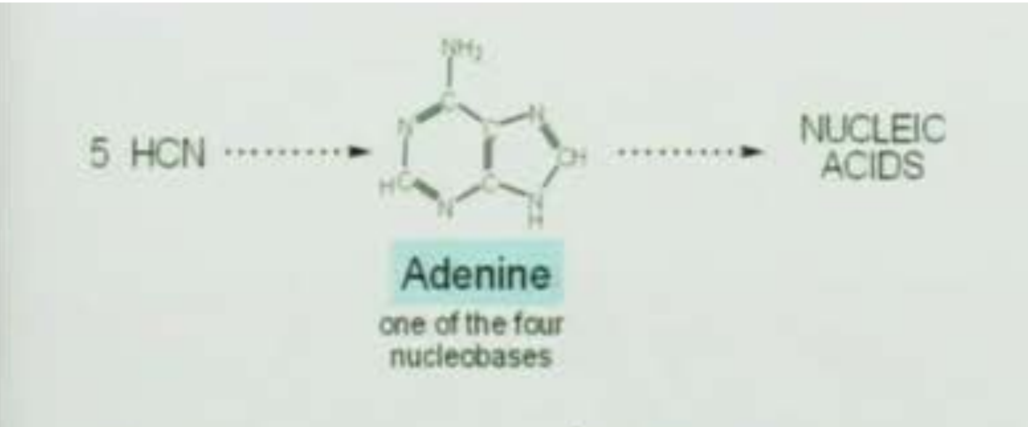
Tobacco Mosaic Virus

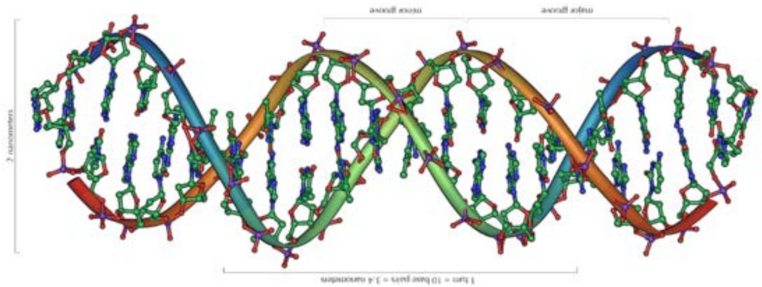
(Length : 300 nm, Diameter : 18 nm)

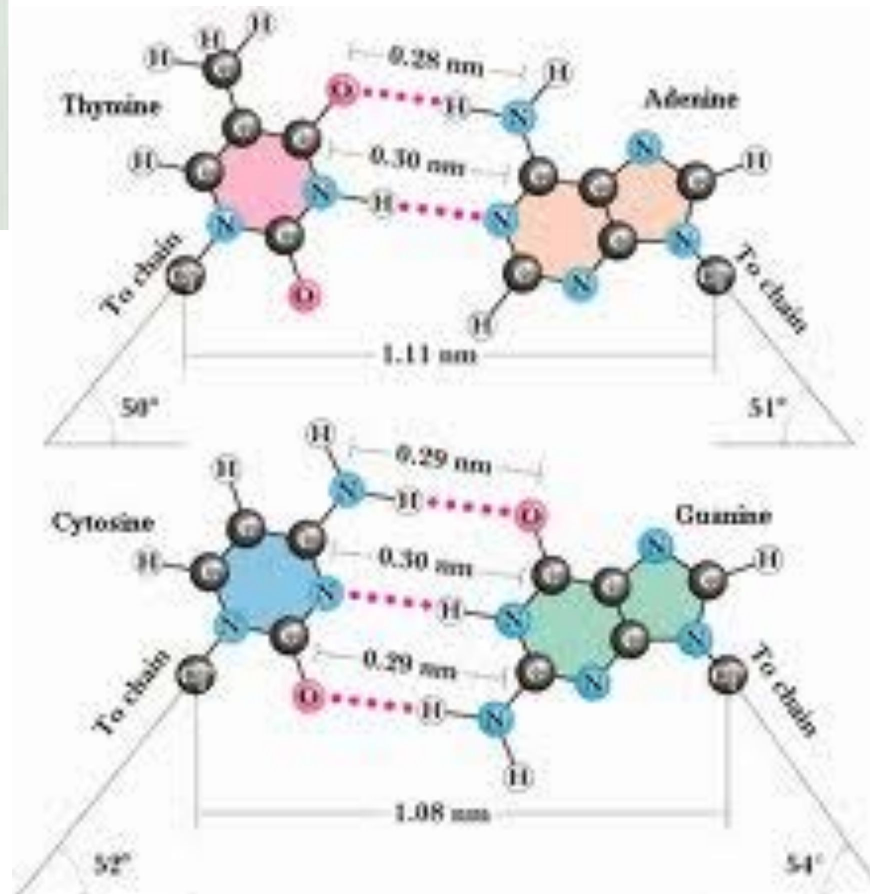
- helix stabilized by hydrogen bonds
  - ca. 2130 identical protein units (à 158 amino acids)
  - central RNA strand (6390 base pairs)

⇒ self-assembly of entire virus under equilibrium conditions

Towards Complexity



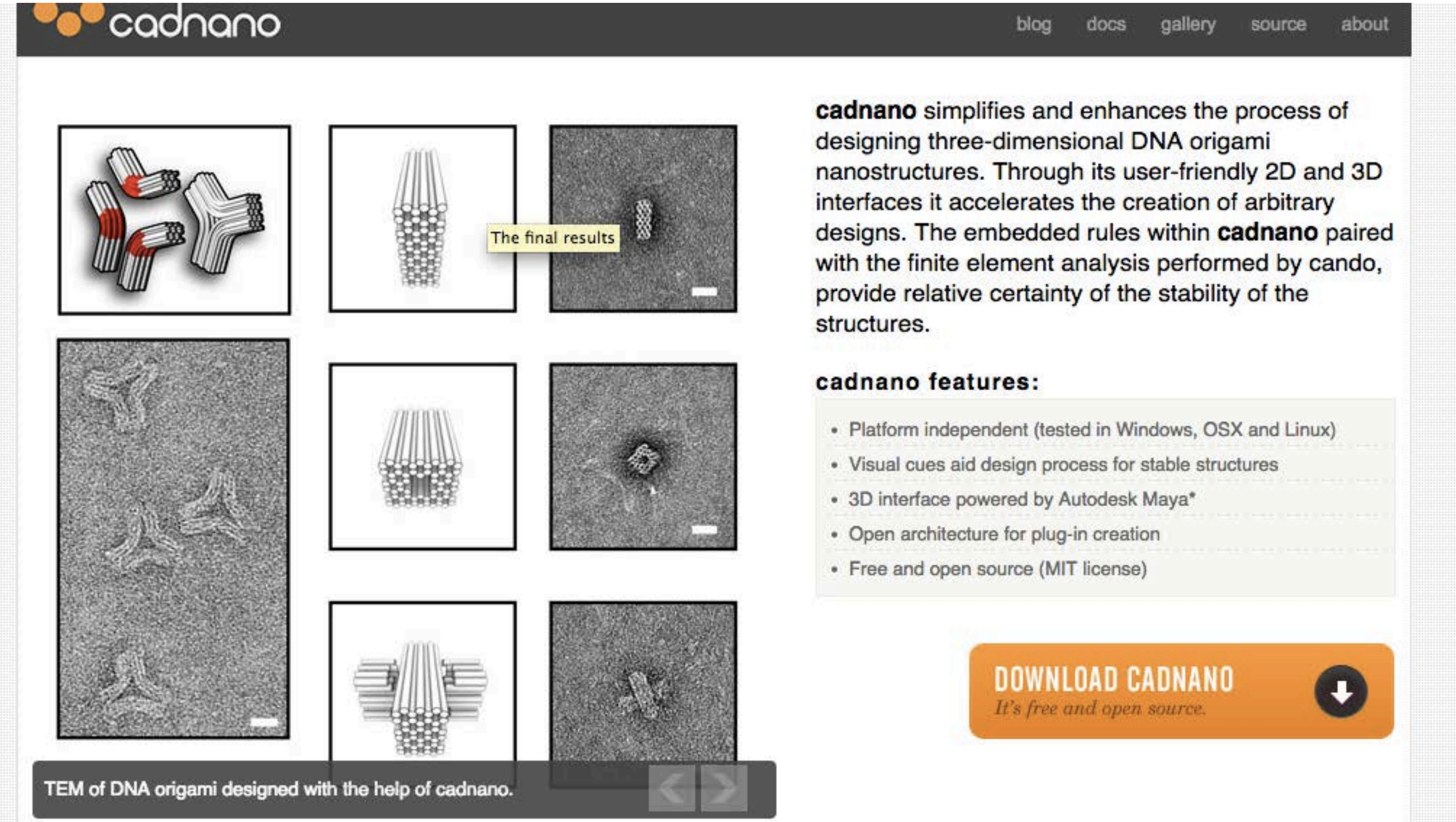




Chemical information coded
Read by intermolecular interactions

Using the predictability of DNA interactions

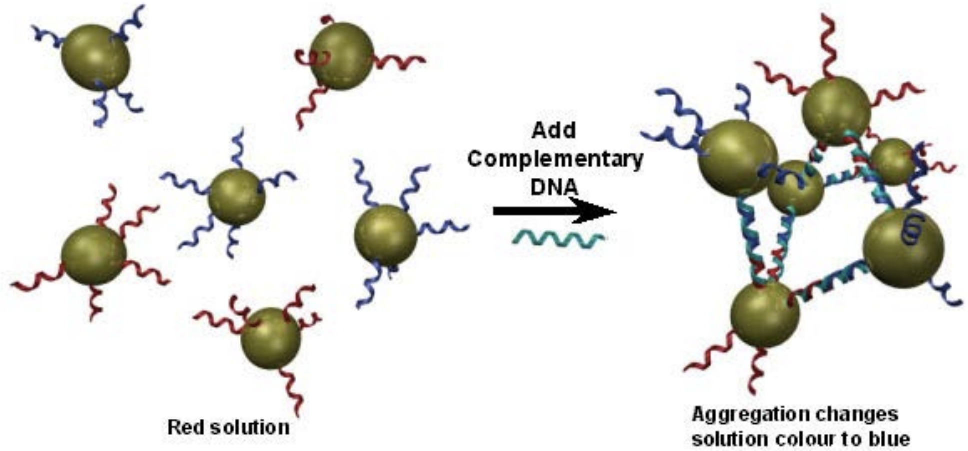
A software to synthesize DNA structures

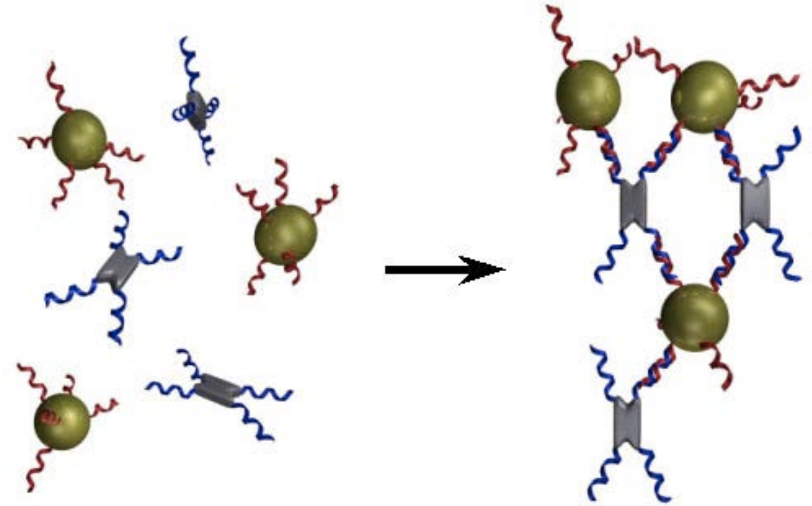


Cadnano.org

Nature. 459:414–8. 21 May 2009.
Science, 325:725–730, 7 August 2009.

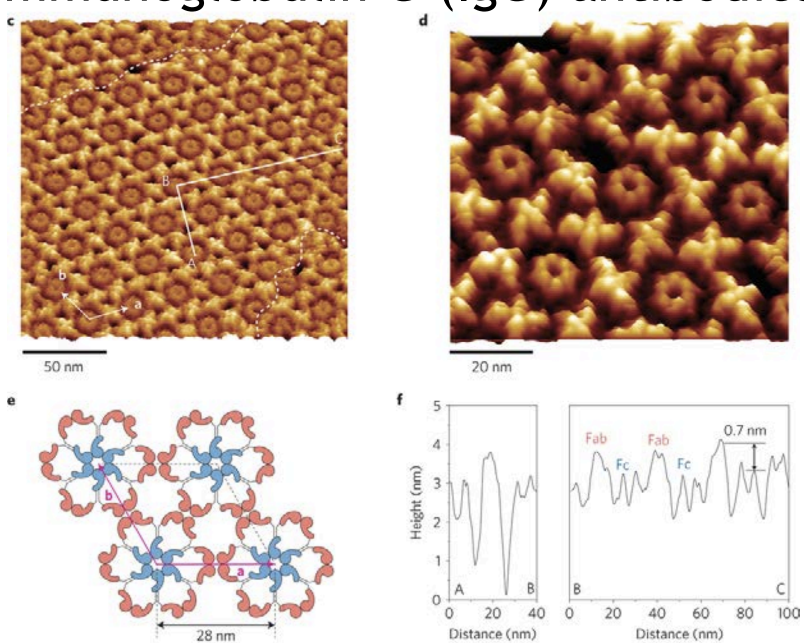
SELF-ASSEMBLED Systems Nanoscience



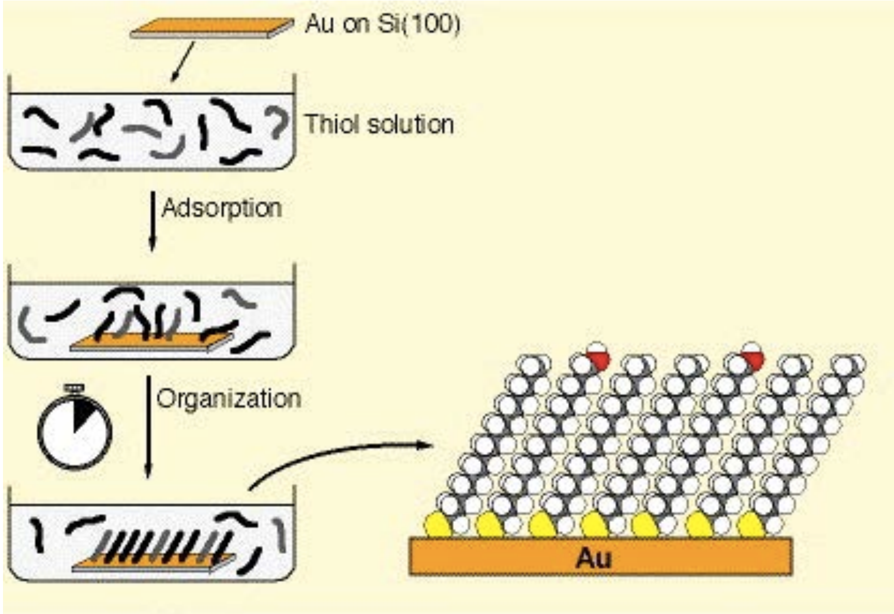


http://barrett-group.mcgill.ca/tutorials/nanotechnology/nano07.htm

immunoglobulin G (IgG) antibodies



Nature Materials 13, 264–270 (2014)



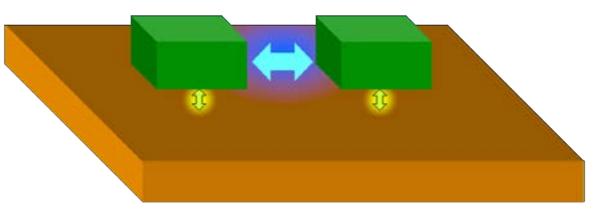
https://www.ifm.liu.se/applphys/molphys/research/self/

Supramolecular chemistry on surfaces?

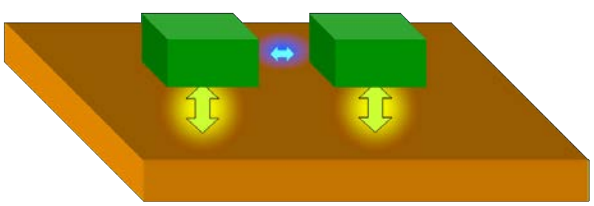
Molecule-molecule

Molecule-surface

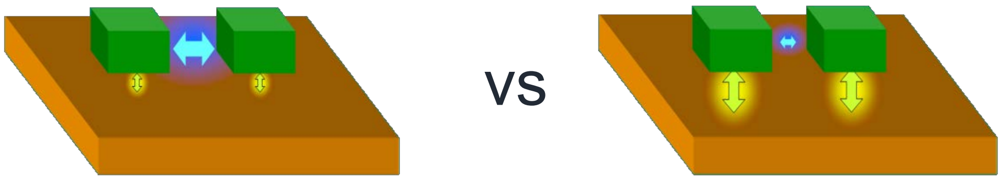
Symmetry and chemistry of the surface



vs

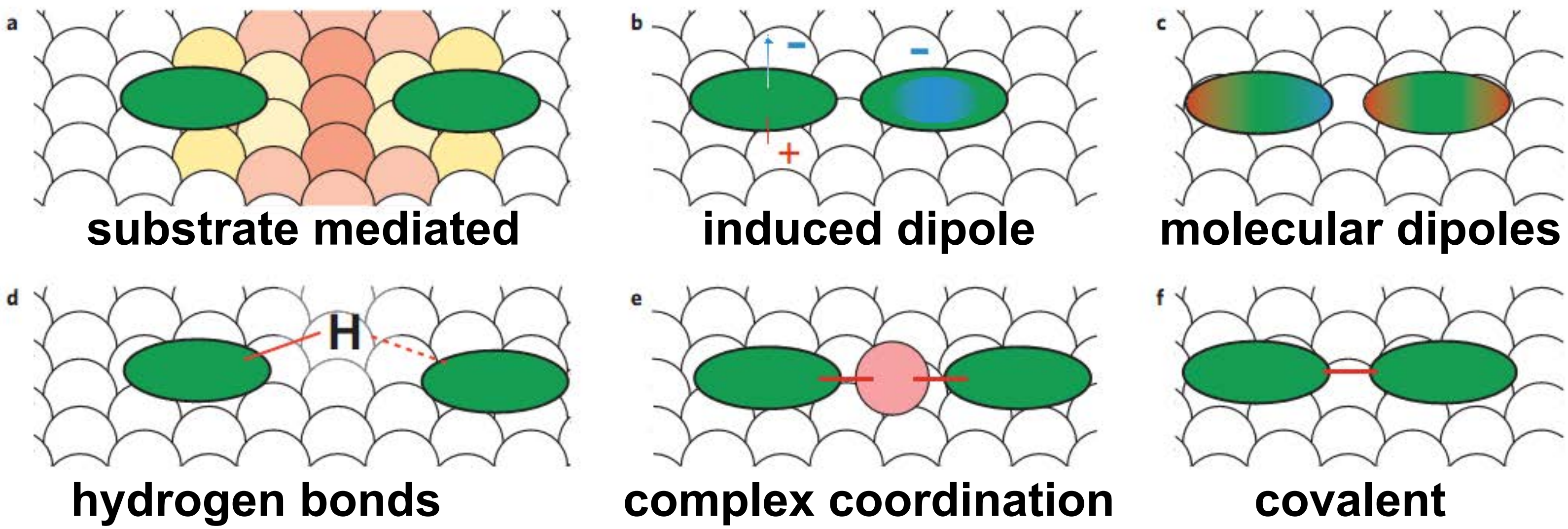


Molecules that can participate in weak and directional non-covalent bonds may be programmed to form desired supramolecular structures



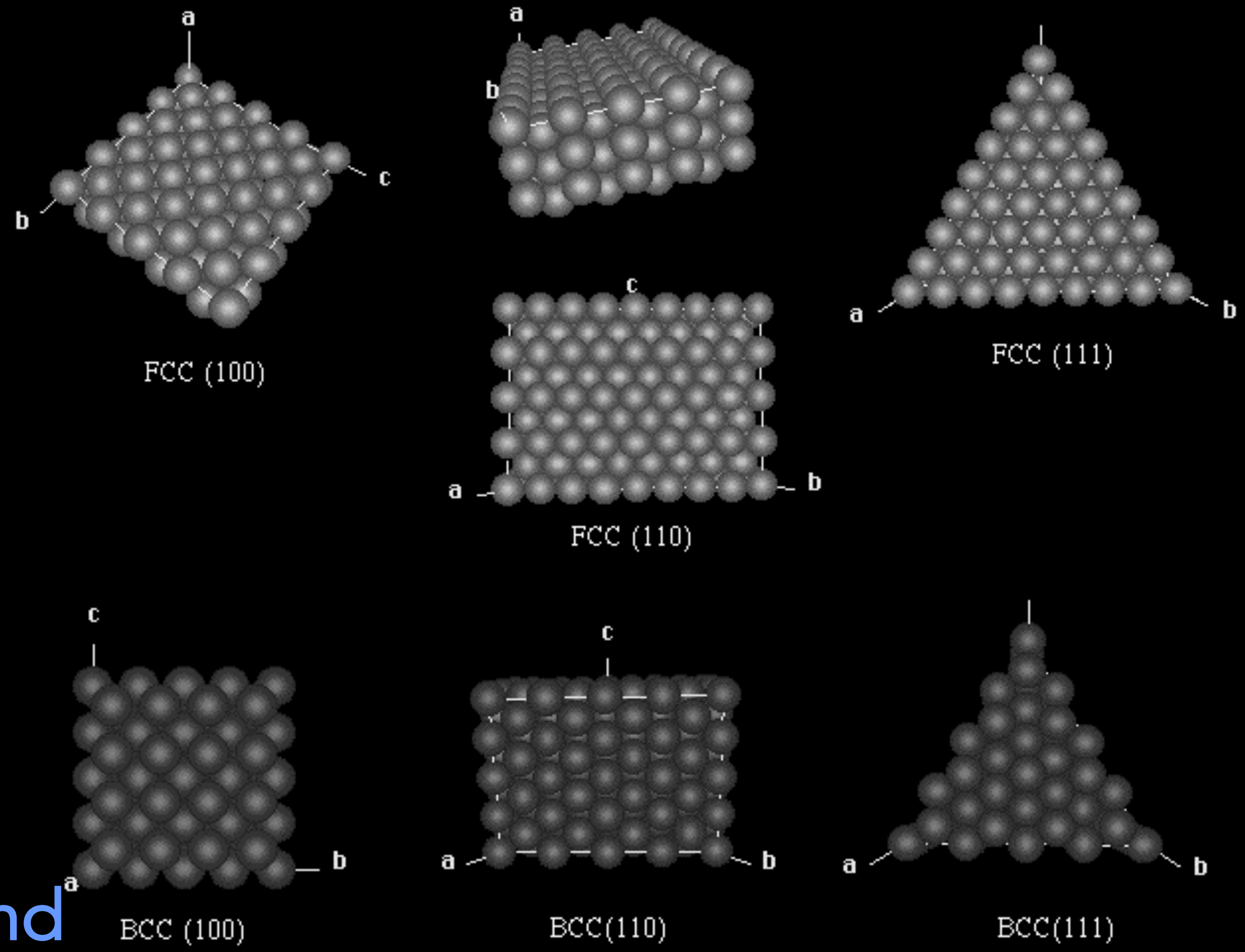
To allow for supramolecular self-assembly based on molecular recognition, conditions close to equilibrium are required (large *D/F values*, *or post-deposition* equilibration)

SELF-ASSEMBLED MOLECULAR NETWORS
Binding forces



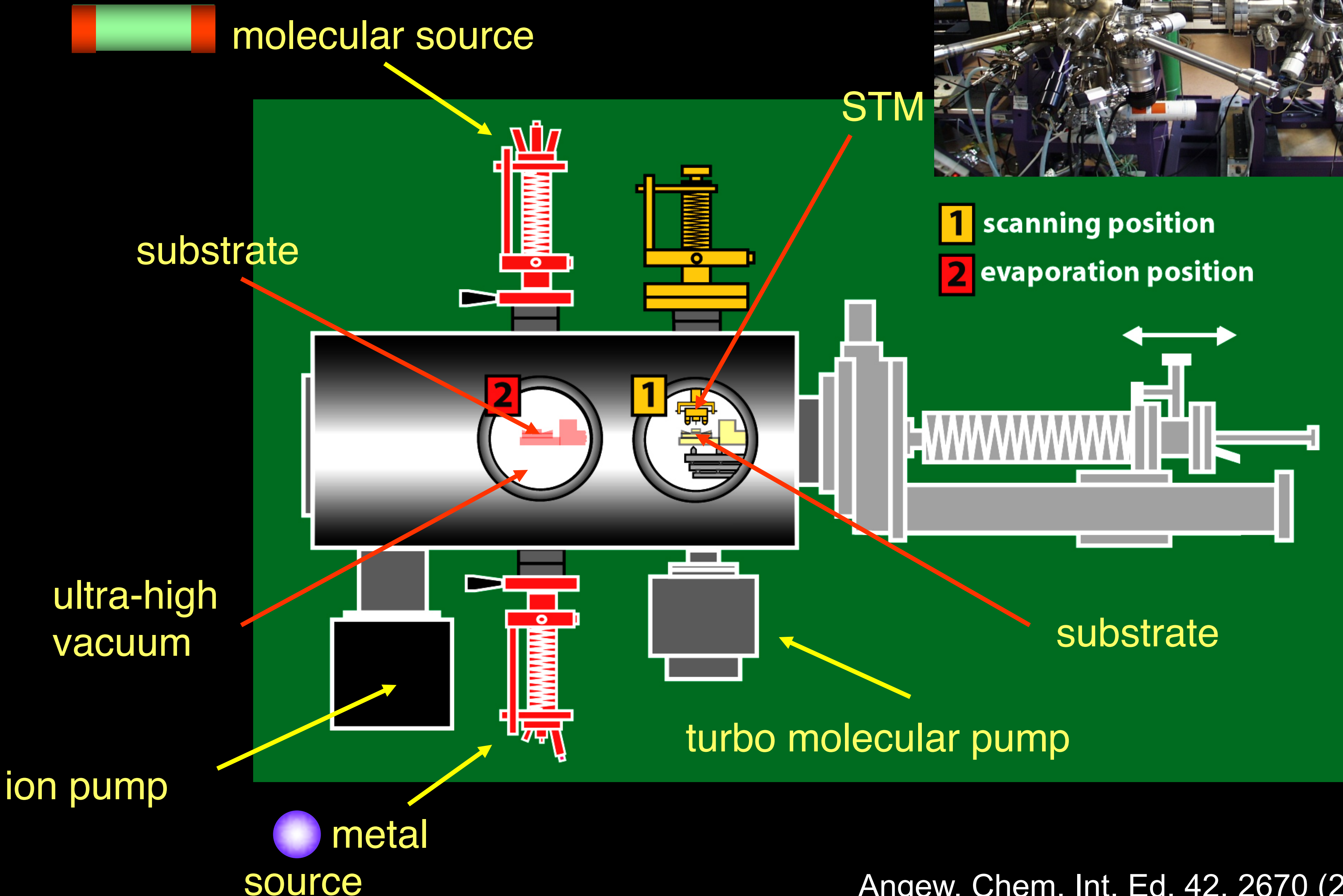
	Energy range	Distance	Character
Adsorption	$E_{ad} \approx 0.5–10$ eV	≈1.5–3 Å	Directional, site selective
Surface migration	$E_m \approx 0.05–3$ eV	≈2.5–4 Å	1D / 2D
Rotational motion	$E_{rot} \sim dim\,(E_m)$	s	2D
Indirect substrate mediated	$E_s \approx 0.001–0.1$ eV	a to nanometerrange	Oscillatory
Reconstruction mediated	$E_s \sim 1$ eV	short	Covalent
van der Waals	$E_{as} \approx 0.02–0.1$ eV	< 1 nm	Nonselective
Hydrogen bonding	$E_{as} \approx 0.05–0.7$ eV	≈1.5–3.5 Å	Selective, directional
Electrostatic ionic	$E_{as} \approx 0.05–2.5$ eV	Long range	Nonselective
Metal-ligand interactions	$E_{as} \approx 0.5–2$ eV	≈1.5–2.5 Å	Selective, directional

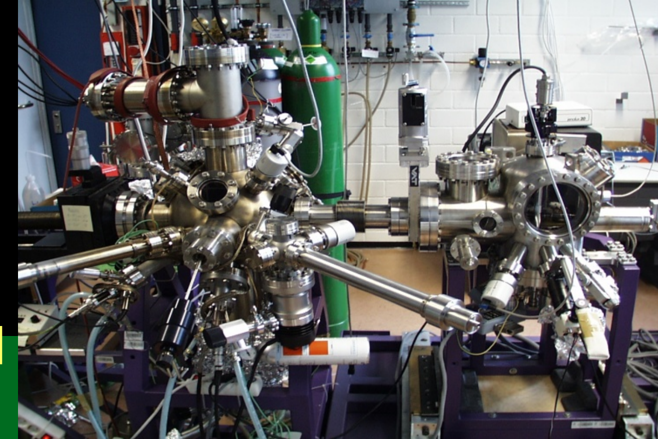
Metal Surface



- Predictability and control over the formation of low dimensional arrangements

Preparation and Characterization





Angew. Chem. Int. Ed. 42, 2670 (2003)

SELF-ASSEMBLY MOLECULAR NETWORS

Hydrogen Bonded Networks

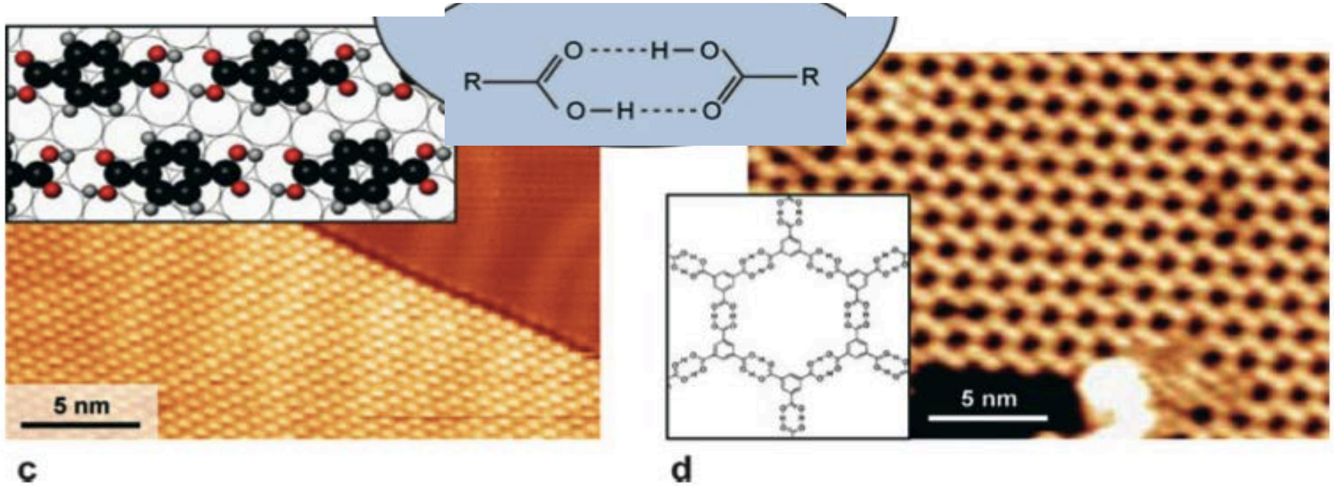
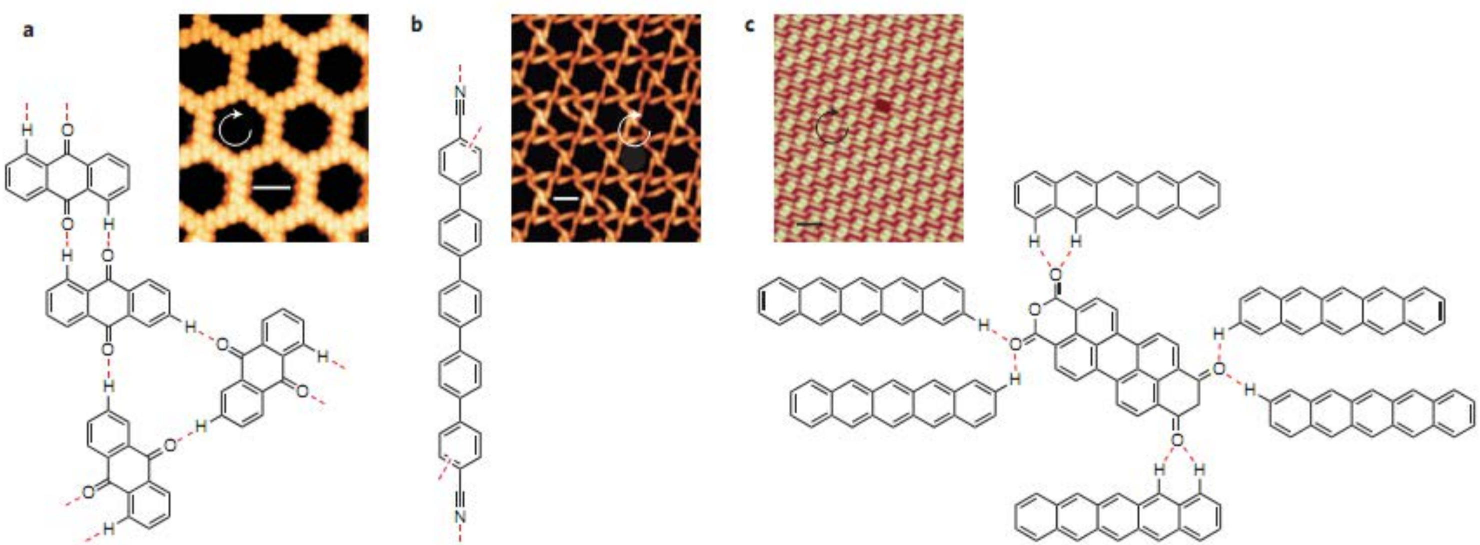
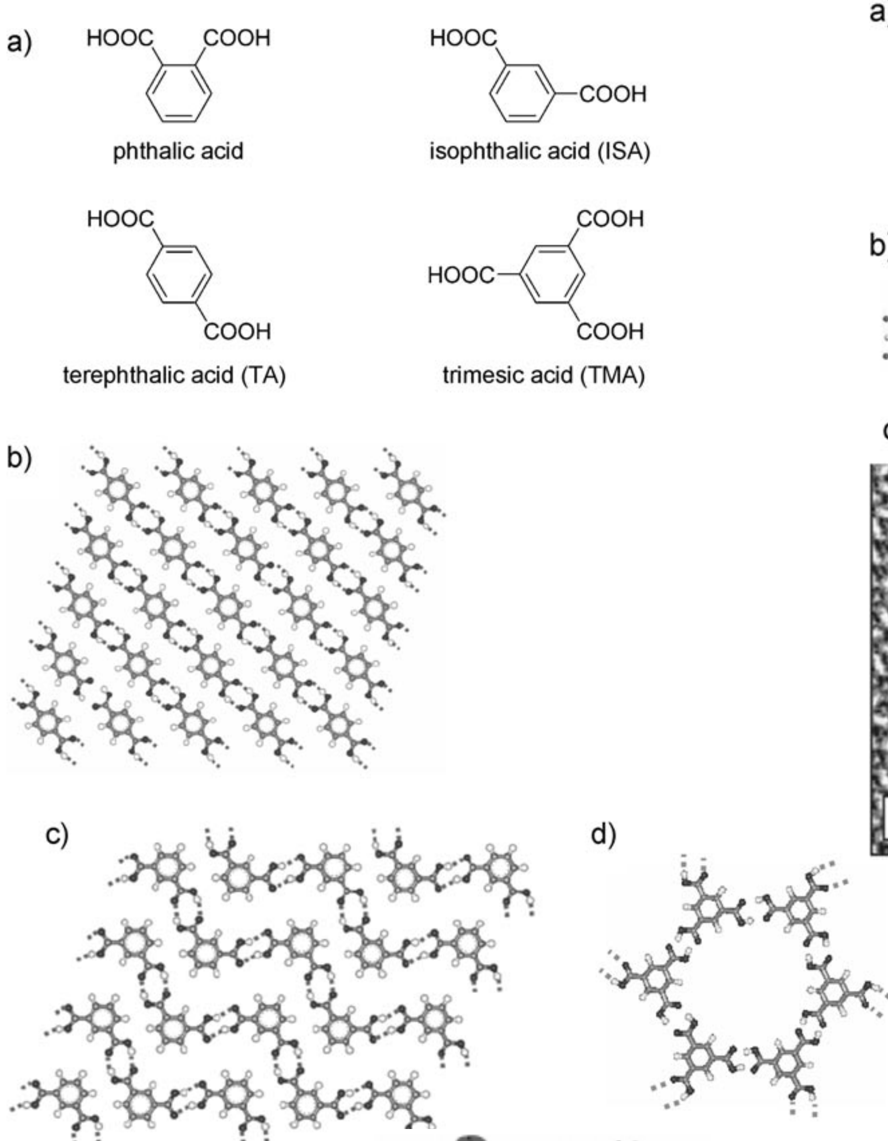
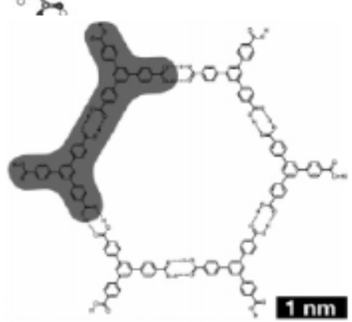


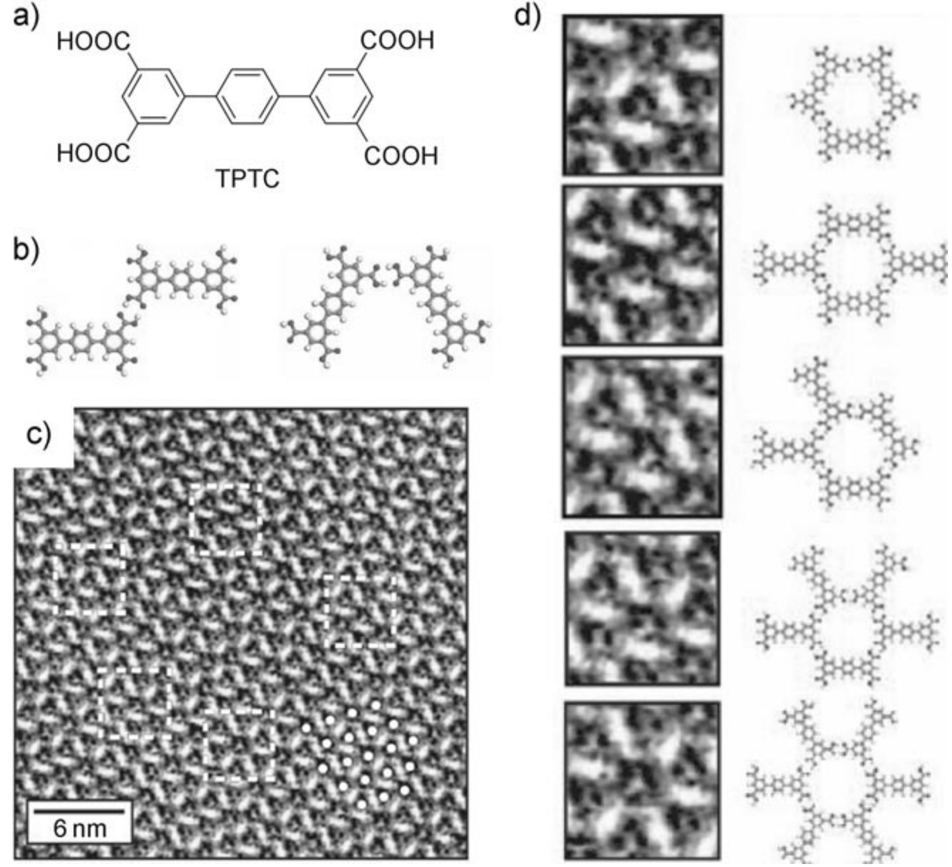
Figure 2

Self-complementary dimerization of carboxylic acid groups as a supramolecular synthon to engineer supramolecular assemblies on surfaces. (*a*) Two- and (*b*) four-membered clusters of carboxyphenyl-substituted porphyrins (65) on Au(111). (*c*) A molecular sheet from terephthalic acid on Au(111) comprising a linear-chain motif (104). (*d*) The open-honeycomb network structure of a trimesic-acid layer on Ag(111) (106).

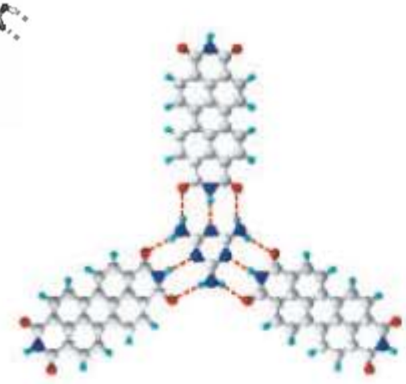


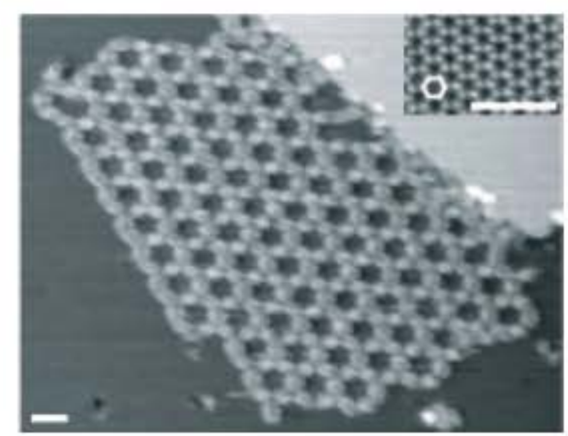




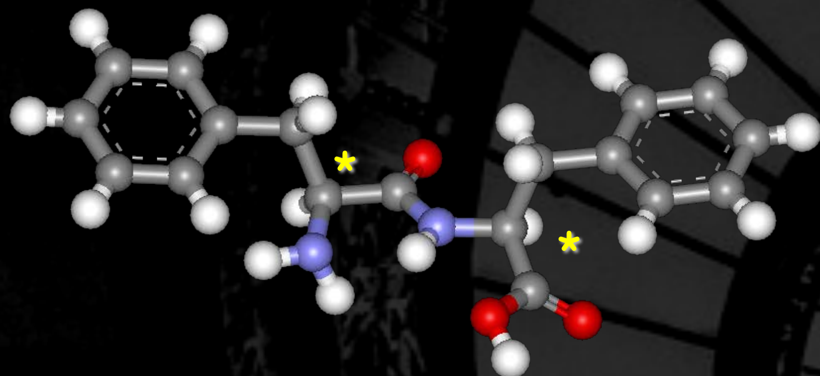


Solid/liquid

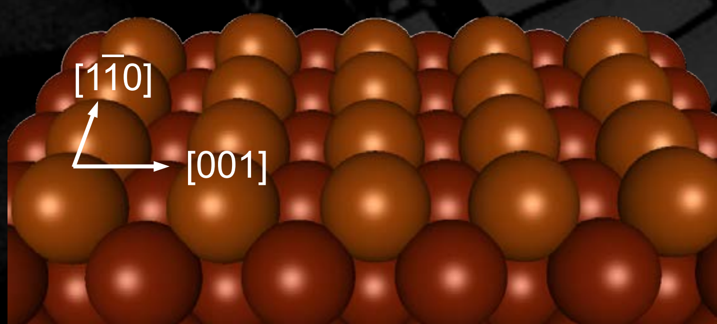




Diphenylalanine: A key Recognition motif



Diphenylalanine

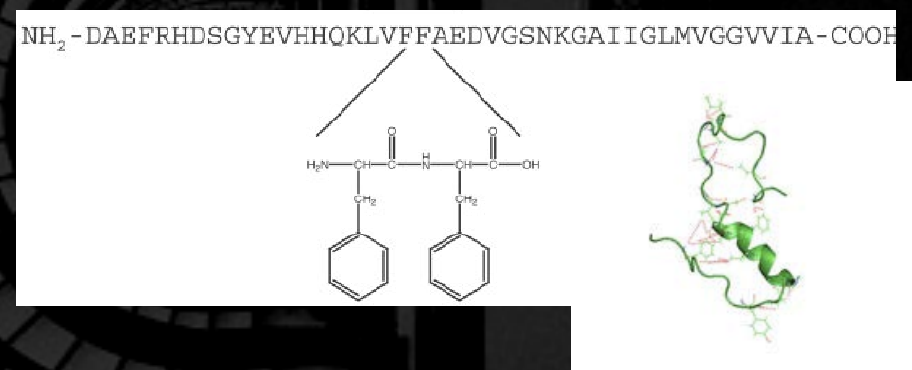


Cu(110)

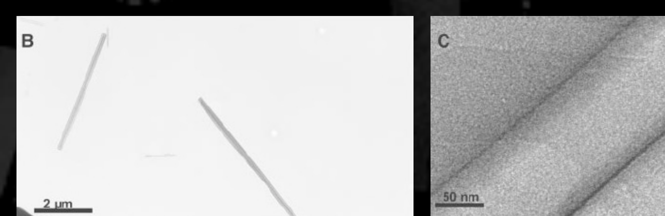
-involved in the recognition of cargo proteins for transport between cellular organelles

Kirchhausen, Nature reviews, Nature, 2000.
D. C. Pimenta, J. Chao, L. Chao, M. A. Juliano, L. Juliano, Biochem. J. 339, 473, 1999.

-core recognition motif of Aβ peptide (Alzheimer's disease)

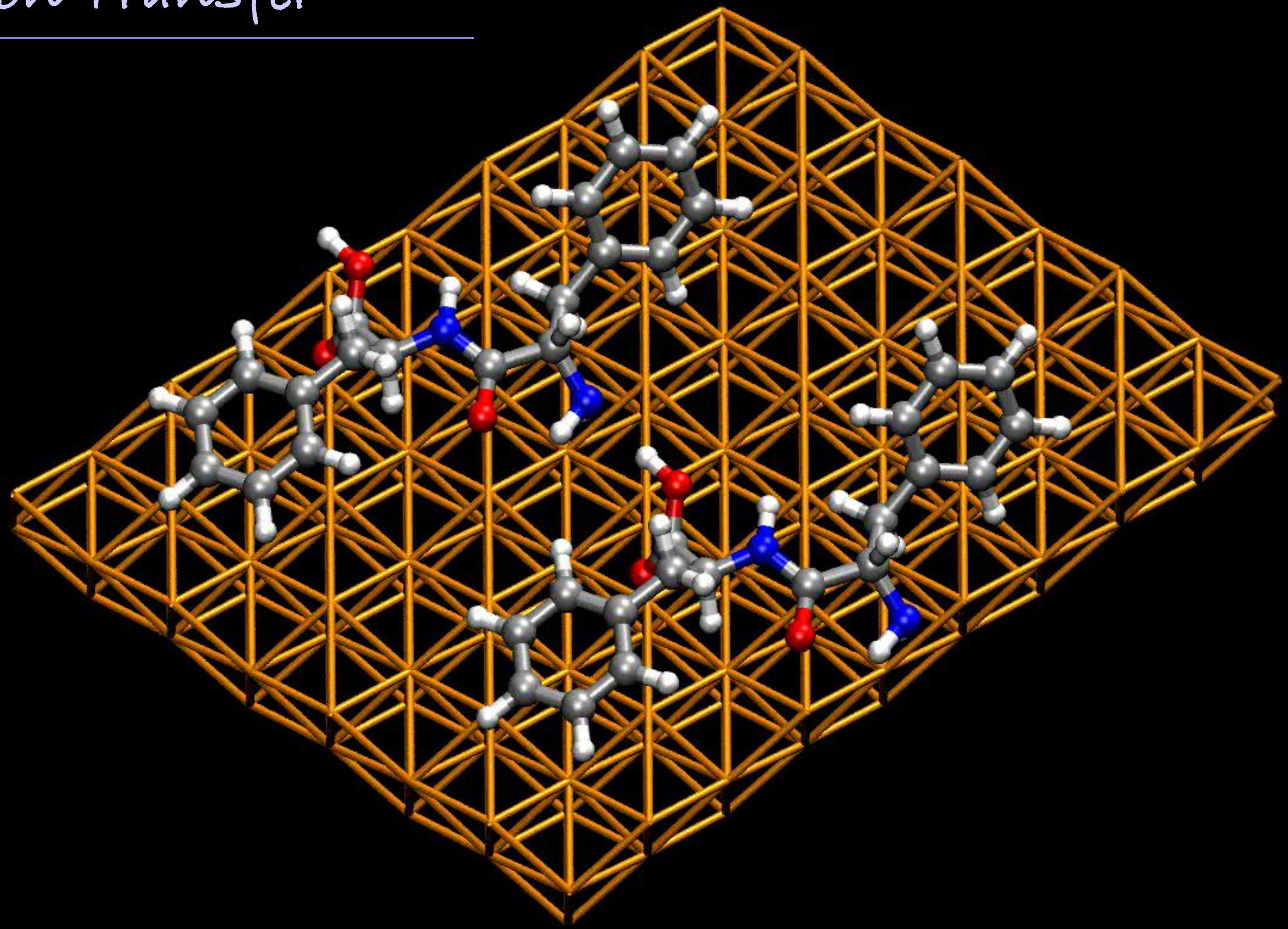


-forms self-assembled nanotubes



M. Reches and E. Gazit, Science **300**, 625 (2003)
M. Reches and E. Gazit, Nature Nanotech **1**, 195 (2006)

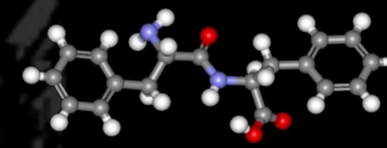
Proton Transfer

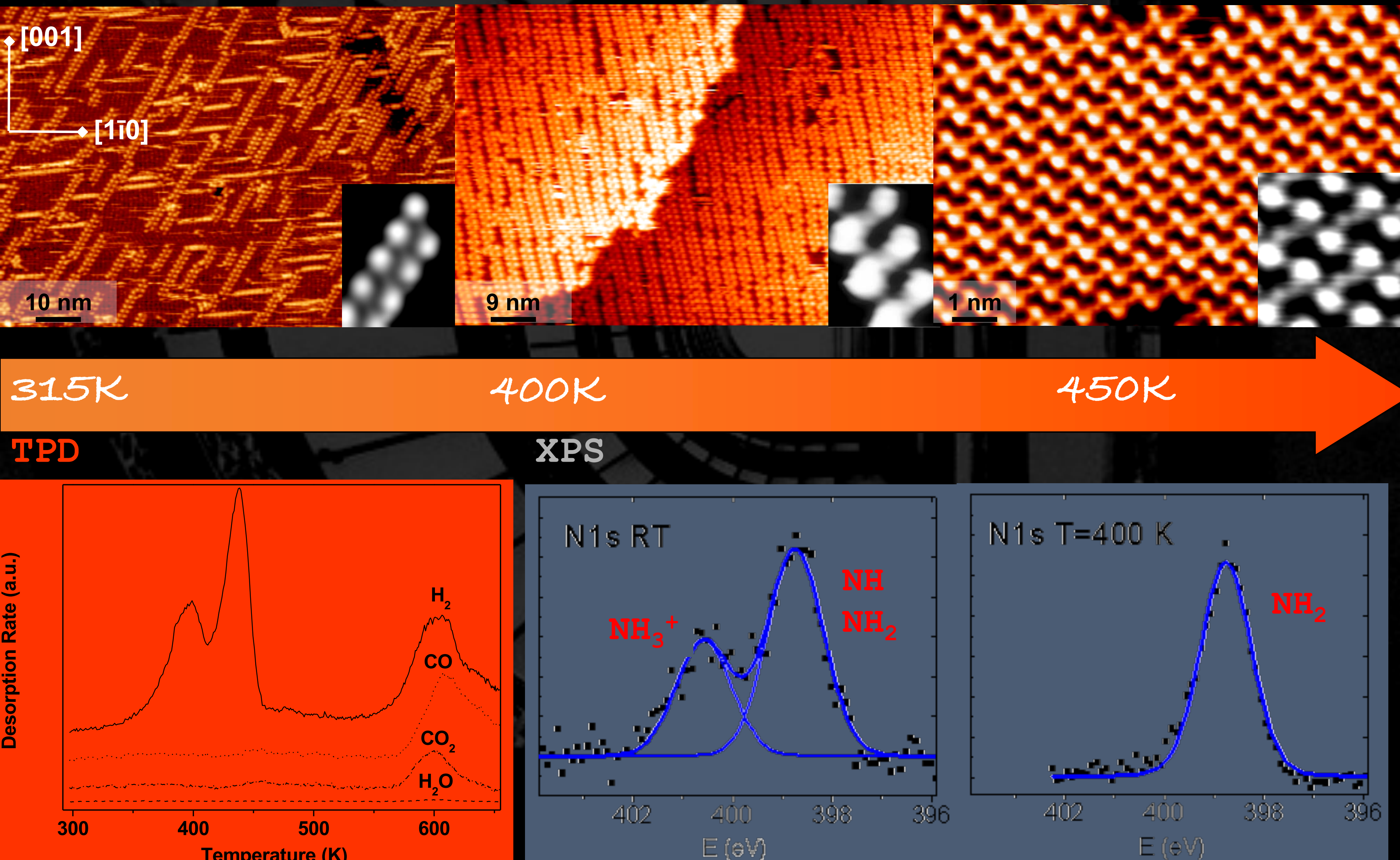


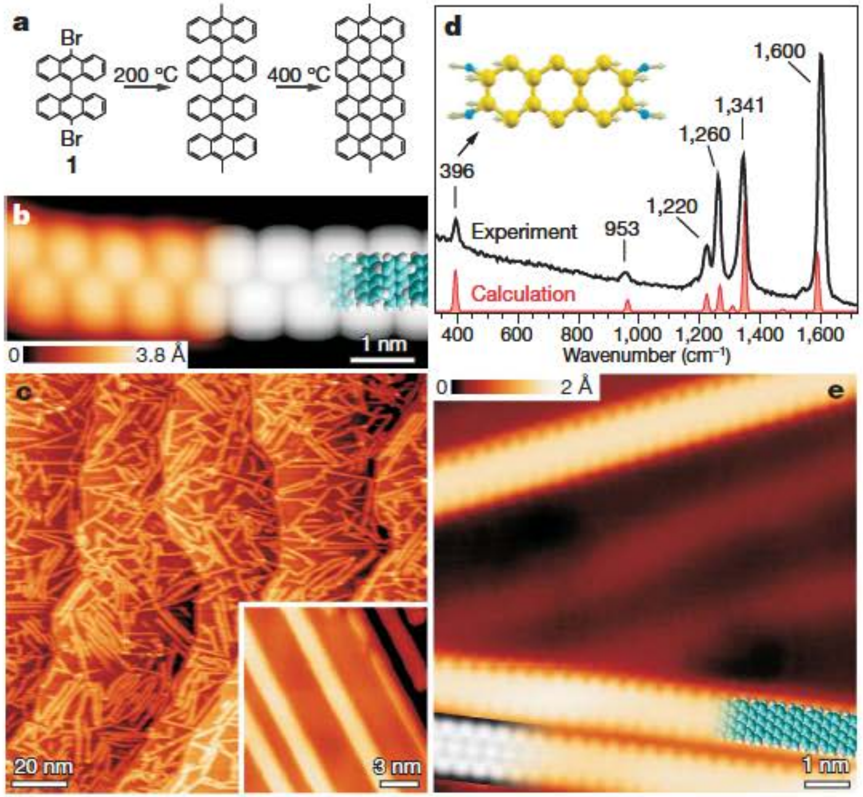
Angew. Chem. Intl. Ed. 46, 4492 (2007)

Adsorption phase diagram L-Phe-L-Phe on Cu (110)

Angew. Chem. Intl. Ed. 46, 4492 (2007)







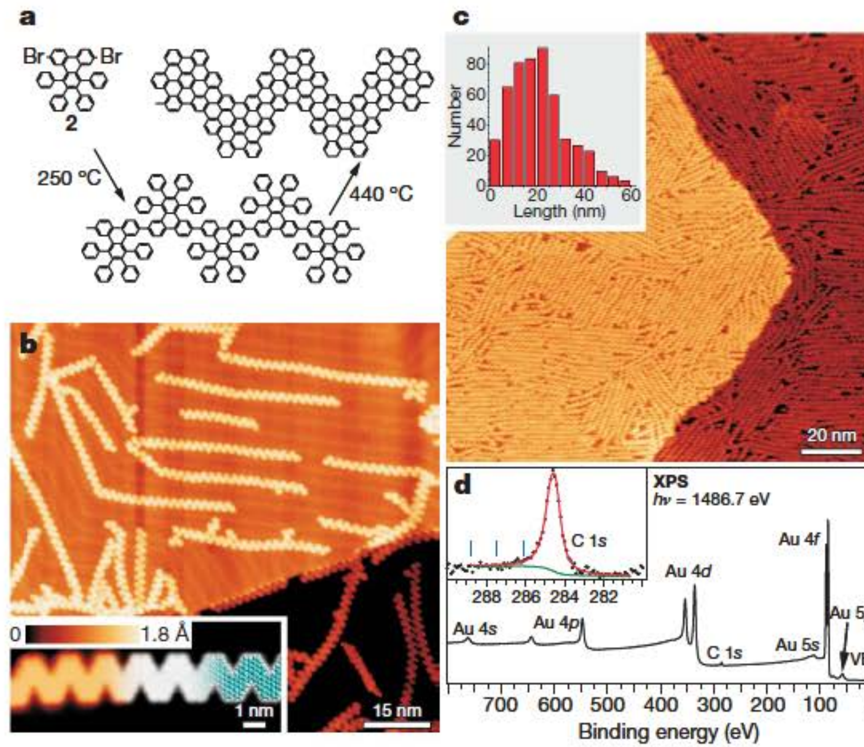


Figure 3 | Chevron-type GNRs from tetraphenyl-triphenylene monomers.
a, Reaction scheme from 6,11-dibromo-1,2,3,4-tetraphenyltriphenylene

T controlled

nature Vol 466|22 July 2010|doi:10.1038/nature09211

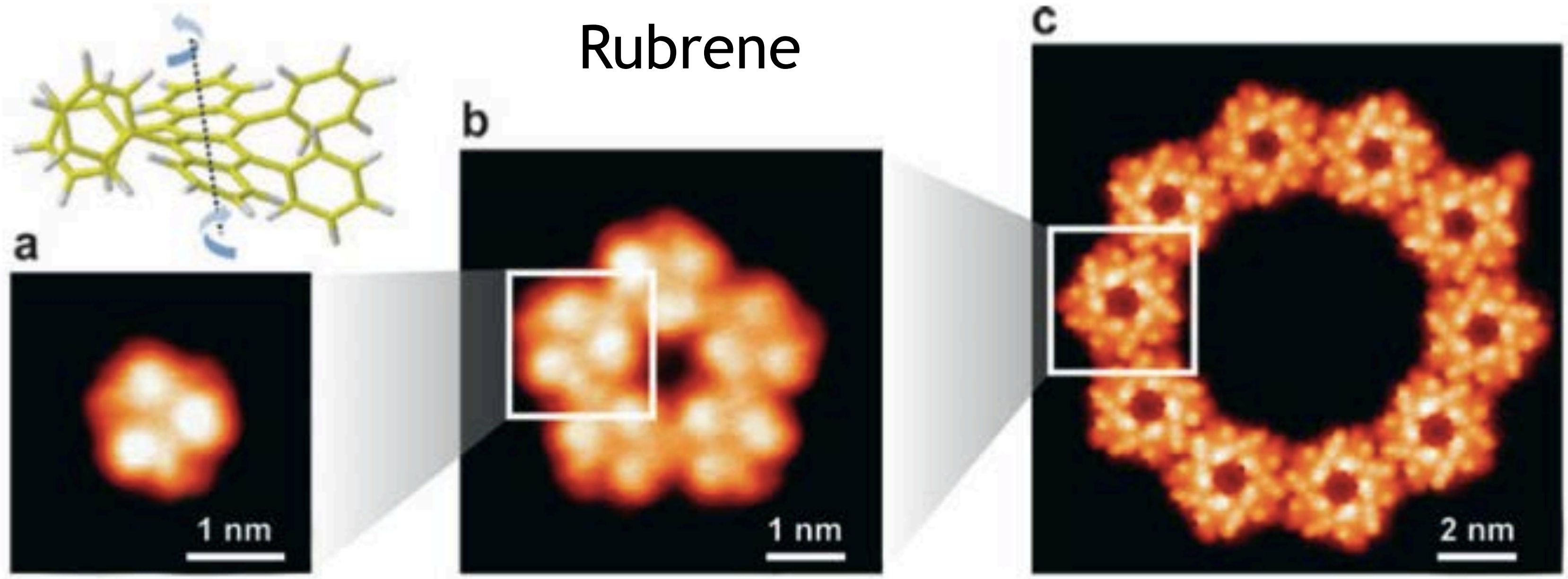
LETTERS

Atomically precise bottom-up fabrication of graphene nanoribbons

Jinming Cai[1]*, Pascal Ruffieux[1]*, Rached Jaafar[1], Marco Bieri[1], Thomas Braun[1], Stephan Blankenburg[1], Matthias Muoth[2], Ari P. Seitsonen[3,4], Moussa Saleh[5], Xinliang Feng[5], Klaus Müllen[5] & Roman Fasel[1,6]

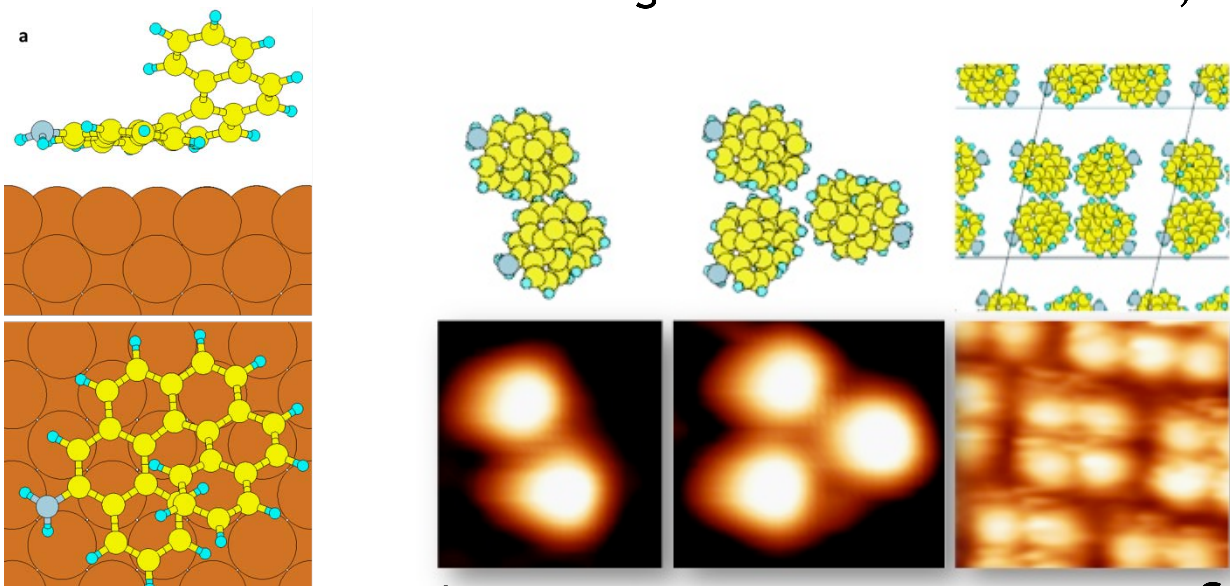
Van der Waals

Rubrene



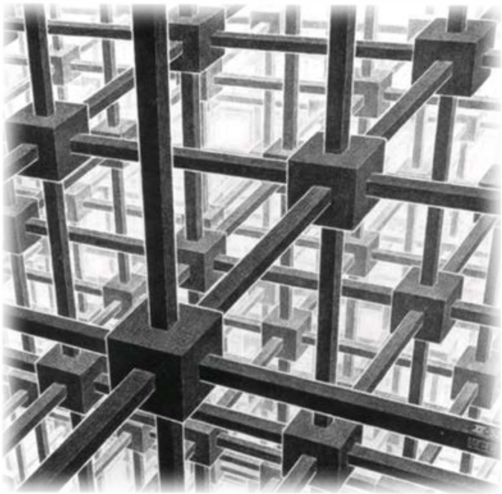
Angew. Chem. Int. Ed. 2005, 44, 5334

Helicenes

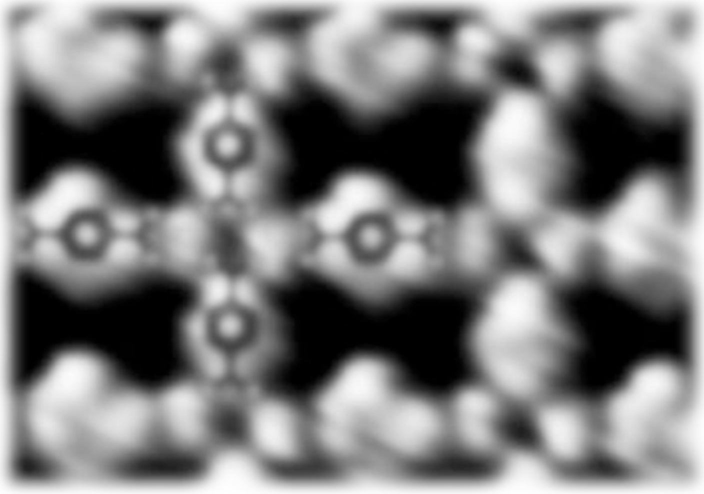


Chem. Commun., 2014, DOI: 10.1039/C4CC04338C

Arquitectonics



Escher
architectonics



Molecular
architectonics

Self-assembly

Molecular
Recognition

Function

Goals

1.The Synthesis:
Rational design of functional architectures by self-assembly

2.The path:
How is the transfer of molecular information at the single molecule level?

Nanometer cavity

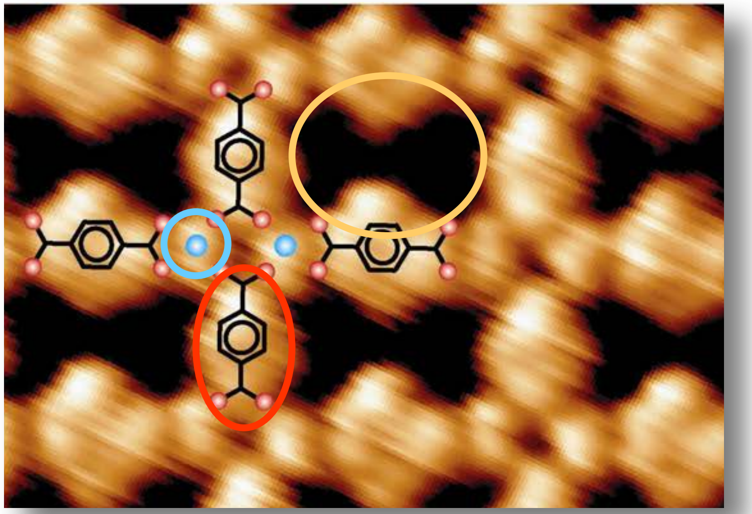
- Host-guest chemistry
- Gas storage, etc

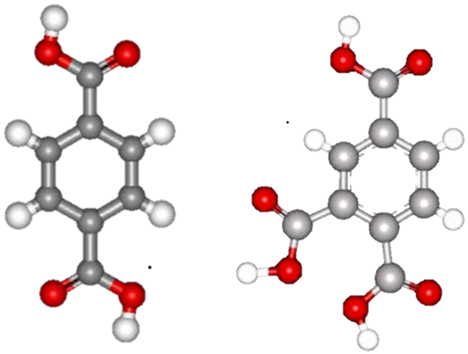
Organic linker

- Recognition unit
- Functionalization by side groups

Metal center

- catalytic center
- Magnetic, photochemical, properties



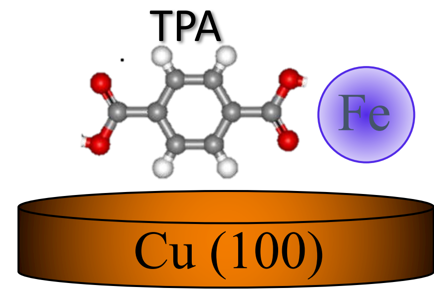


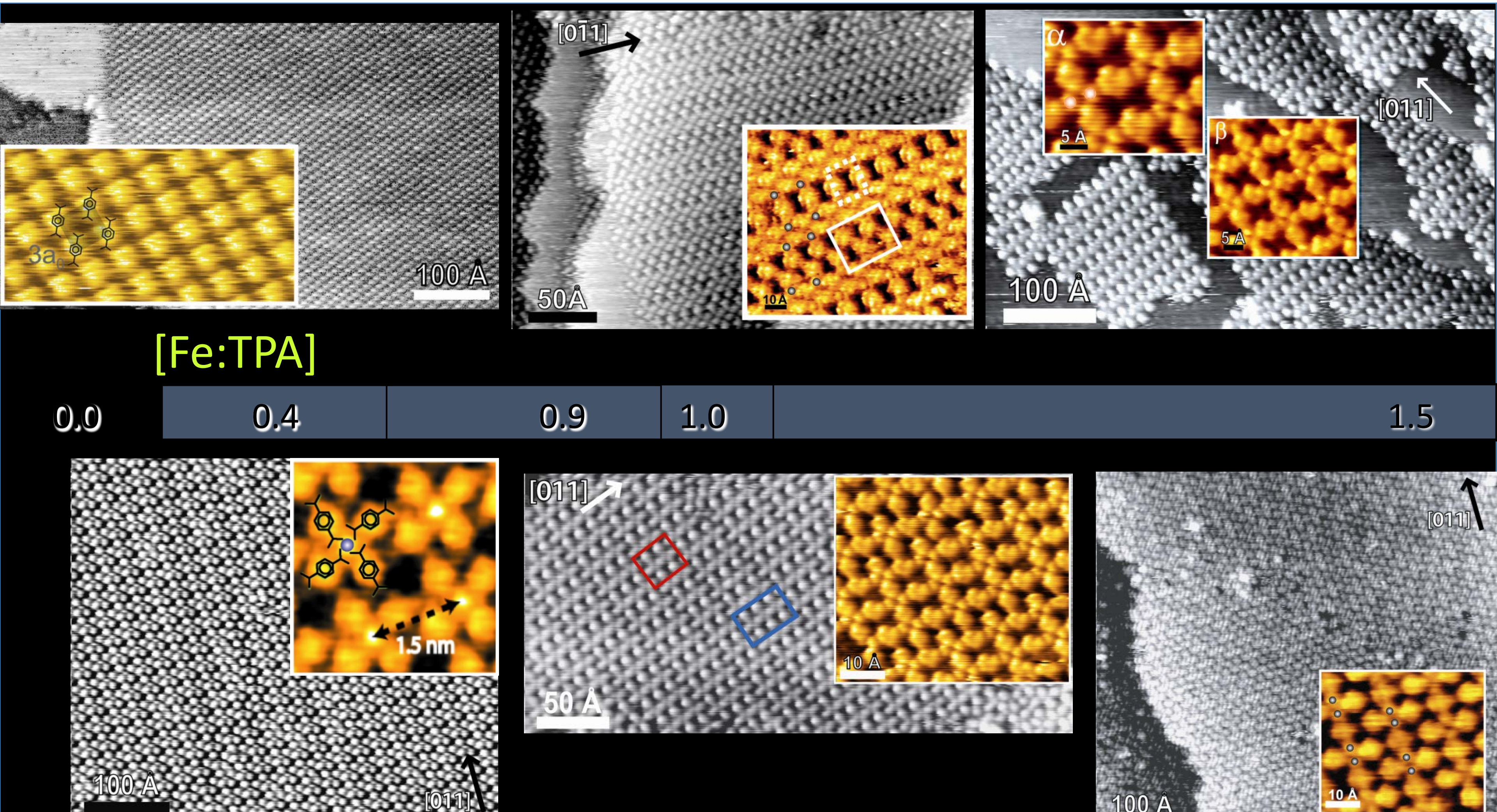
- ✓ The relative concentration of constituents.
- ✓ The selection of substrate (reactivity and single crystal symmetry).

Chem. Eur. J. 10, 1913 (2004)

Rational design: Tailored coordination assembly

Metal:Molecule



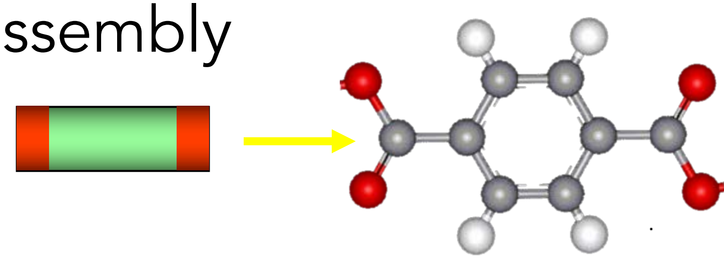


J. Phys. Chem B 108, 19392 (2004),

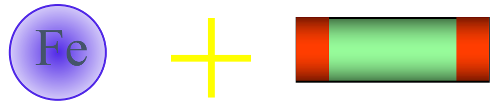
Chem. Eur. J. 10, 1913 (2004)

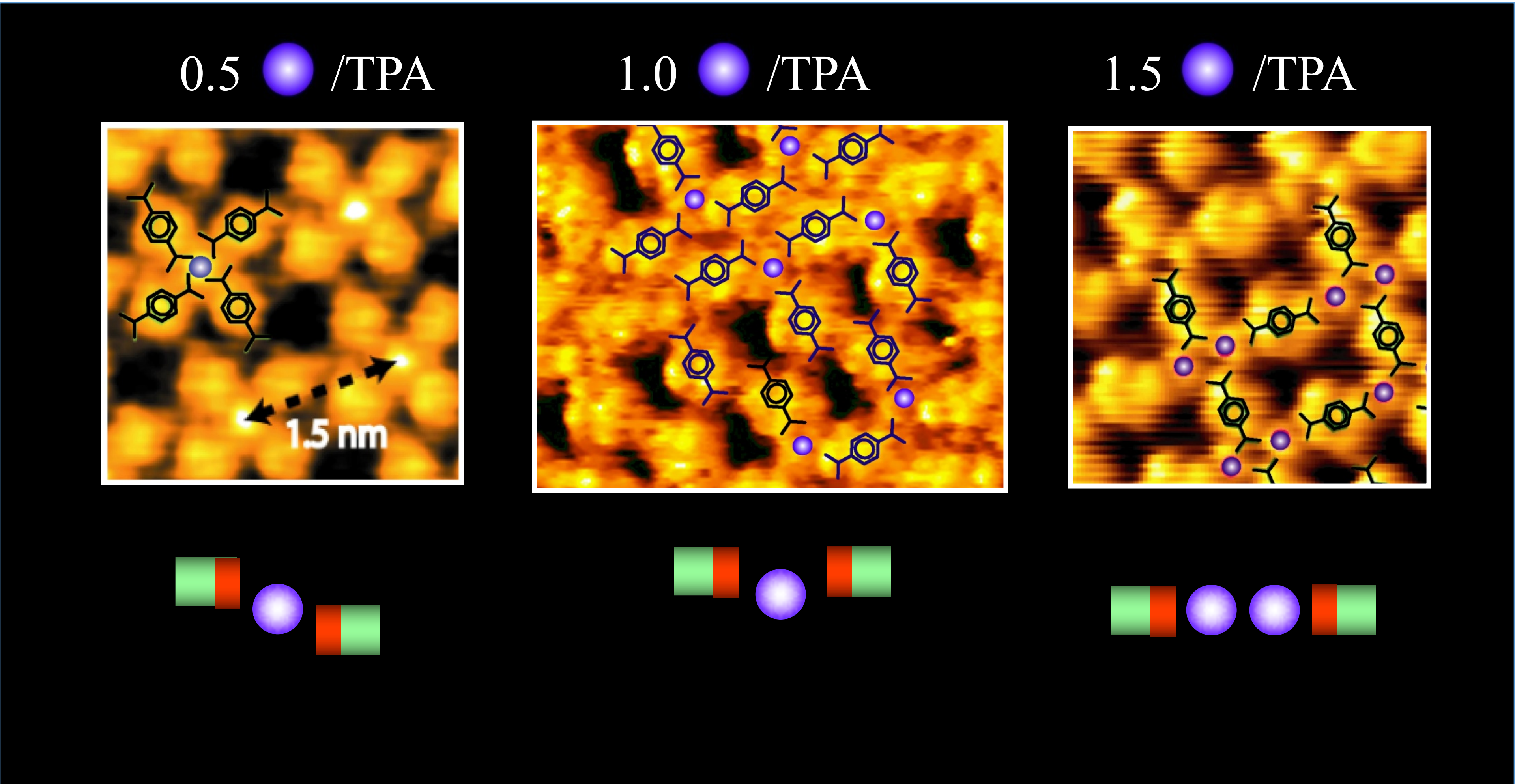
Rational design: Tailored coordination assembly

Metal:Molecule



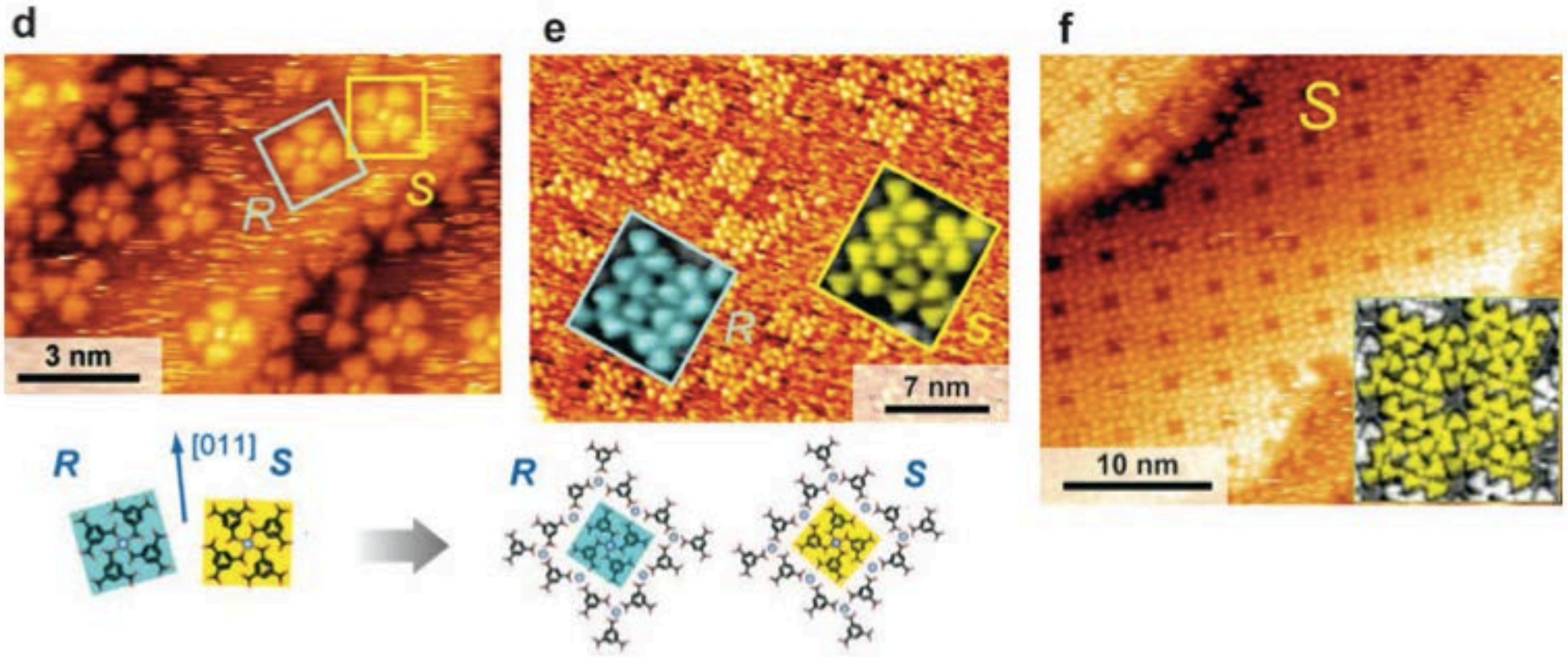
TPA





J. Phys. Chem B 108, 19392 (2004), Chem. Eur. J. 10, 1913 (2004)

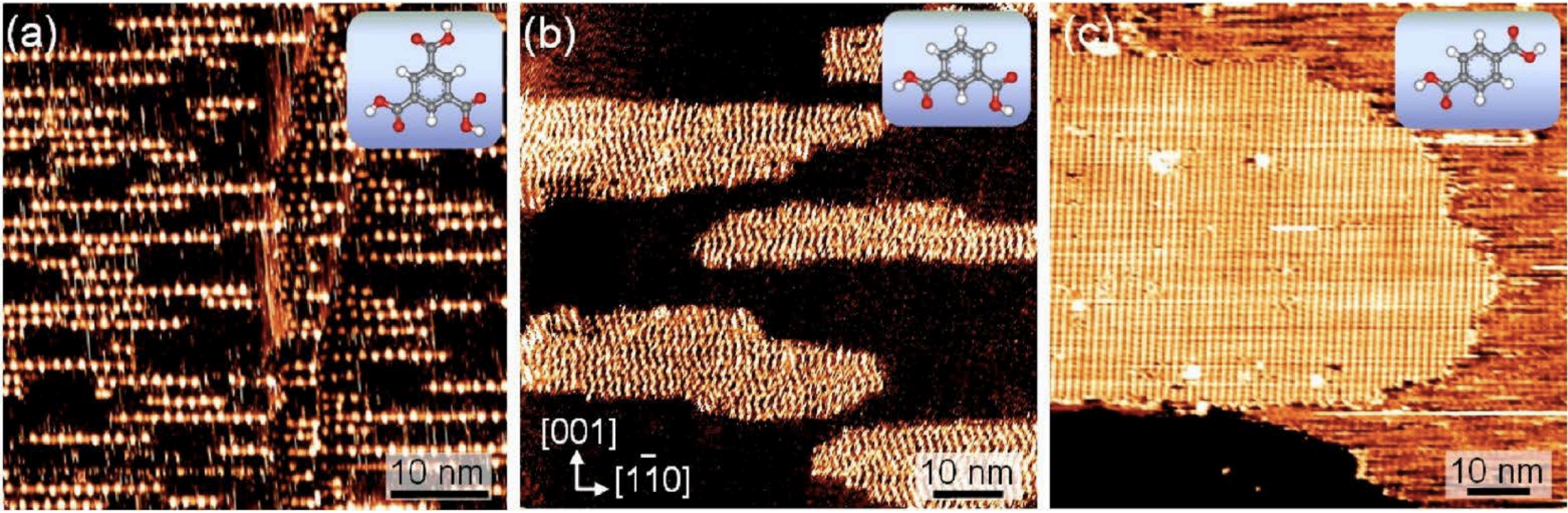
Metal Organic plus H bonding Hierarchical order

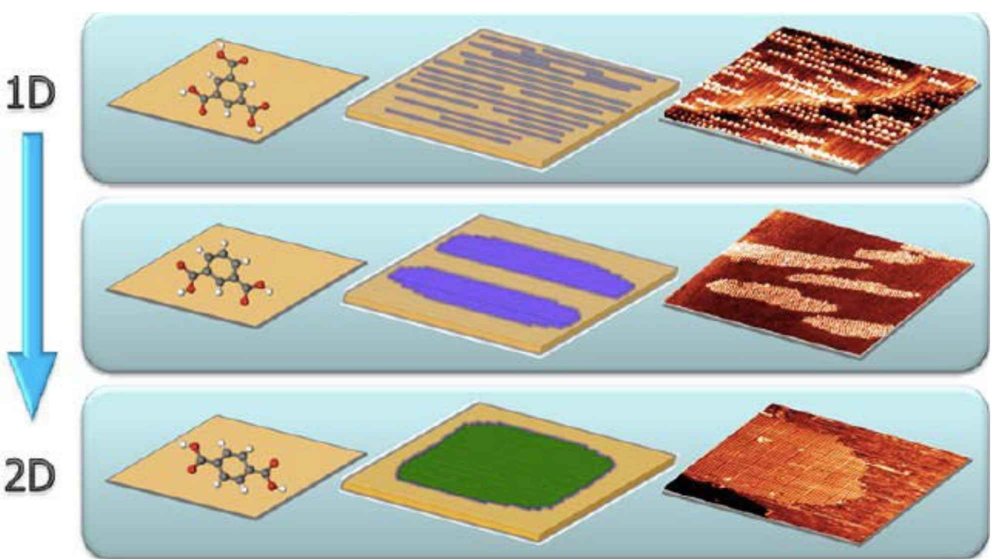


Rational design: Tailored coordination assembly

Cu (110)

Molecular Design



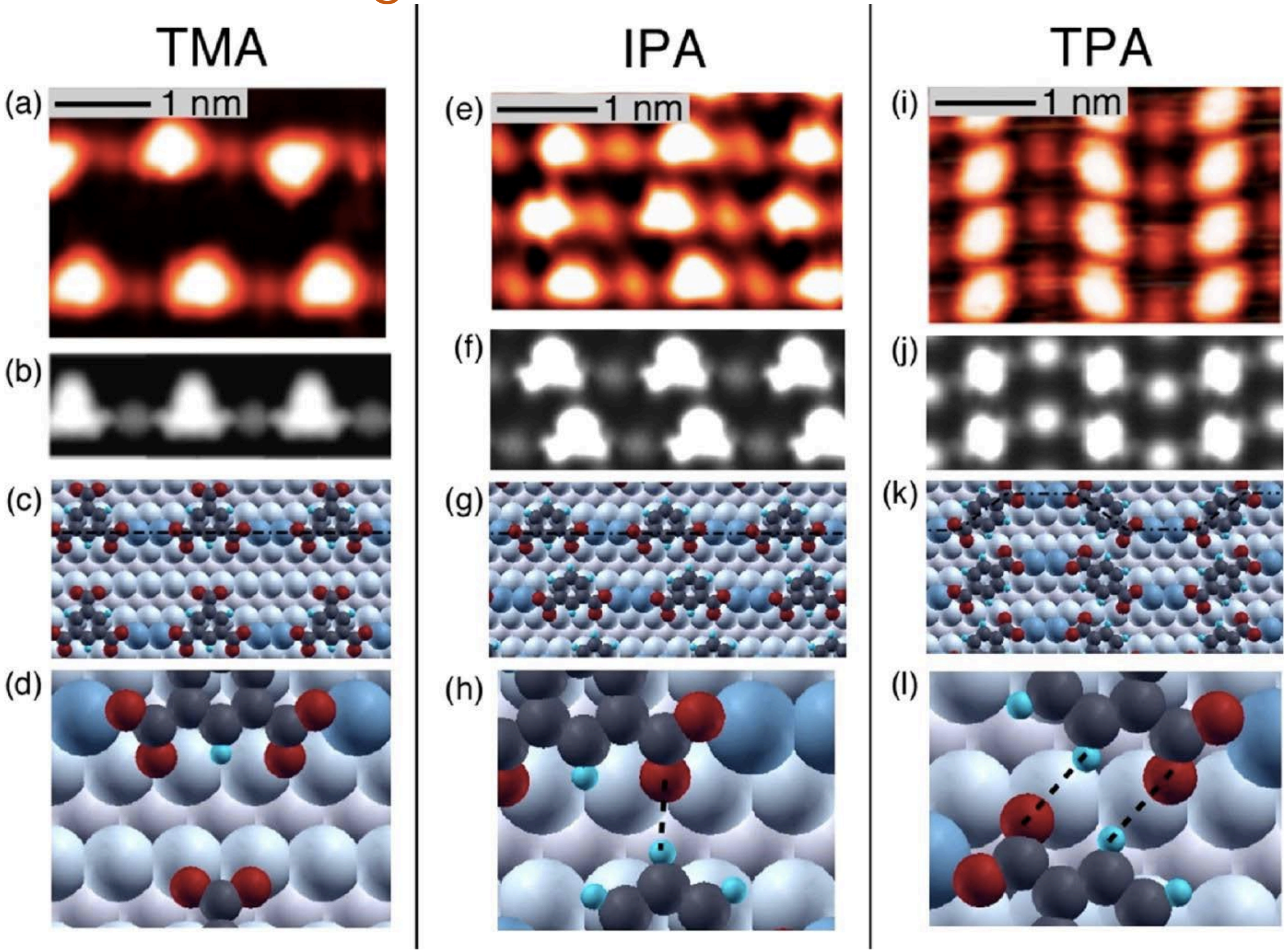


Dimensionality tuned by molecular design

J. Phys. Chem B 108, 19392 (2013)

Rational design: Tailored coordination assembly

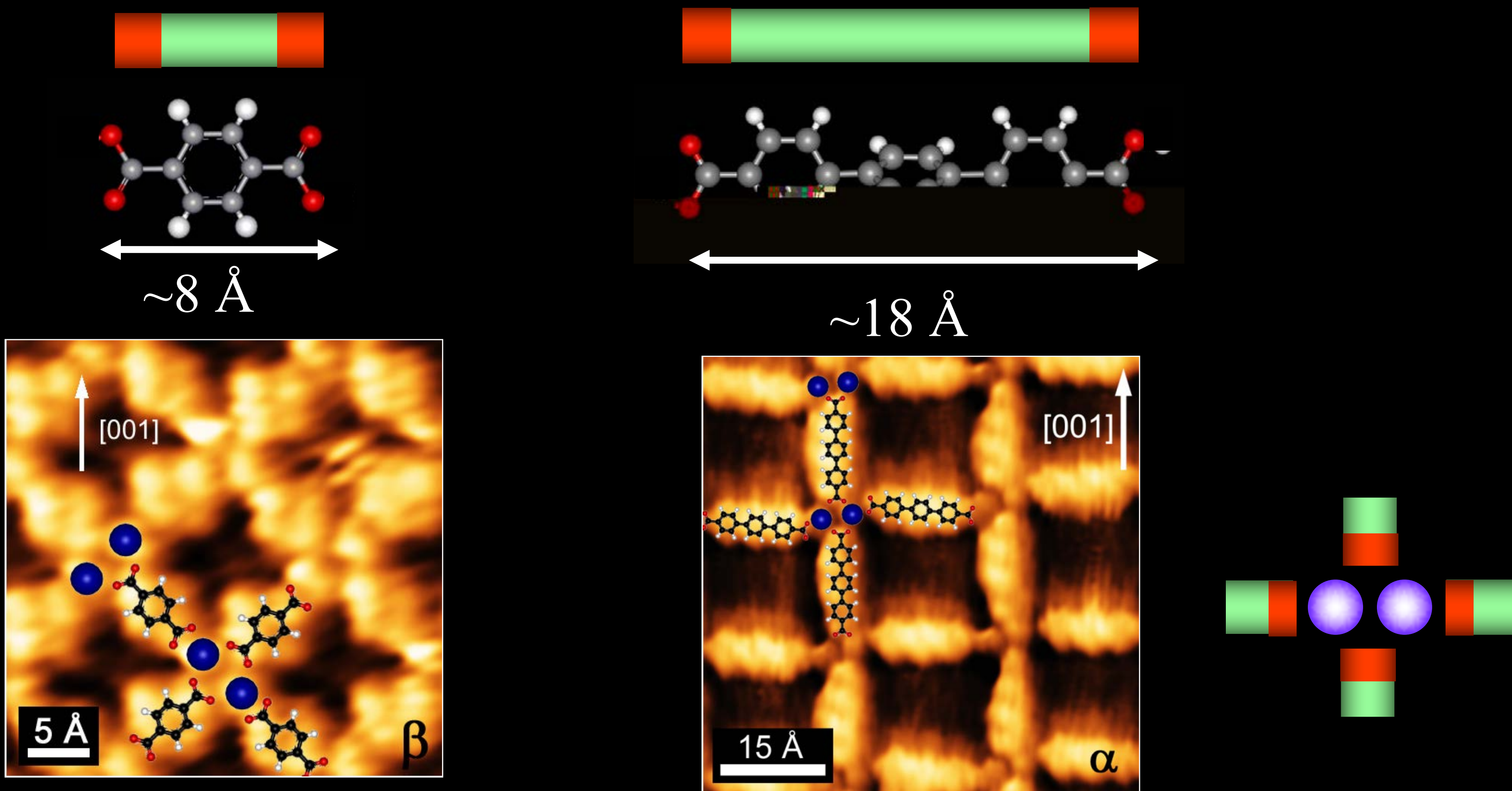
Molecular Design



Metal organic coordination plus week C−H···O hydrogen bonding

J. Phys. Chem B 108, 19392 (2013)

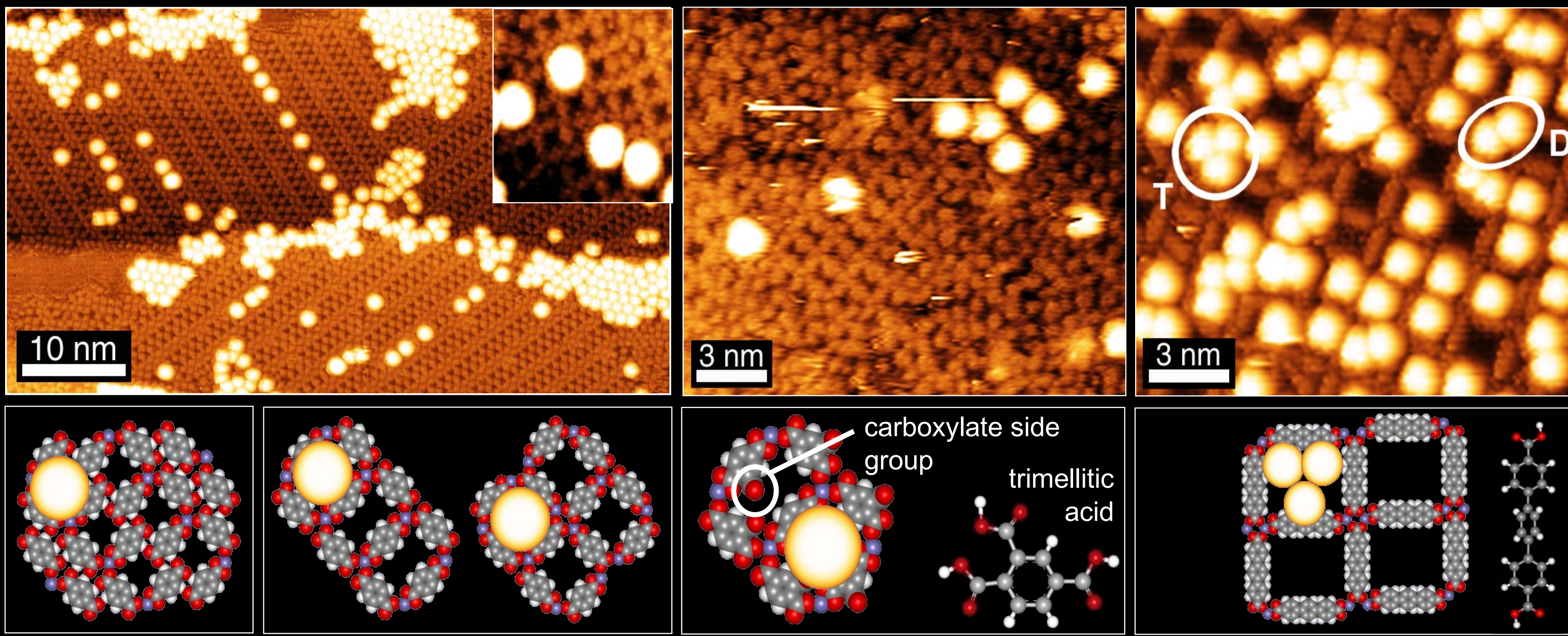
Rational design: Steering the cavity size



coordination	square planar	coordination	threefold
Fe-Fe spacing	4.7 Å	Fe-Fe spacing	4.3 Å
cavity size	25-35 $Å^2$	cavity size	220-290 $Å^2$

Function : Host-Guest chemistry

steering
host-guest chemistry → adsorption of C_{60} guest molecules

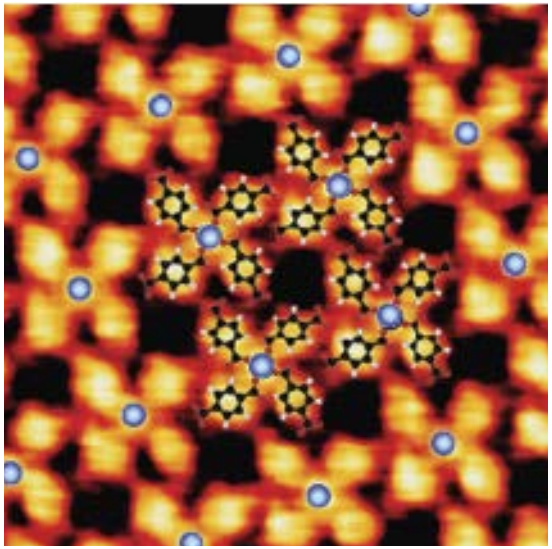


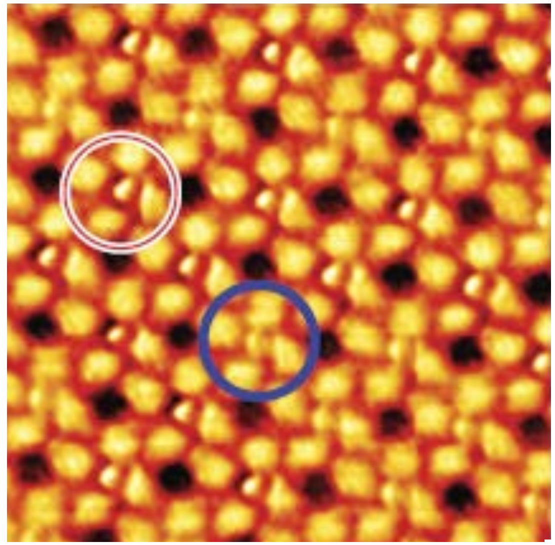
thermal desorption

< 300 K	~370 K	destructive	> 500 K
C_{60} to phenyl	C_{60} to Cu (loose contact)	C_{60} to carboxylate	C_{60} to Cu (close contact)

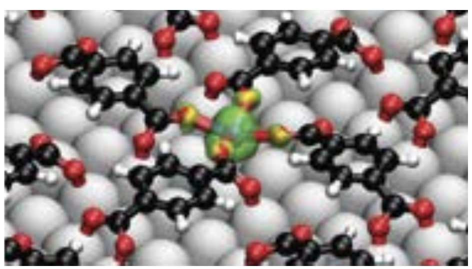
Nature Materials, 3, 229 (2004)

Function : Tunable magnetic properties

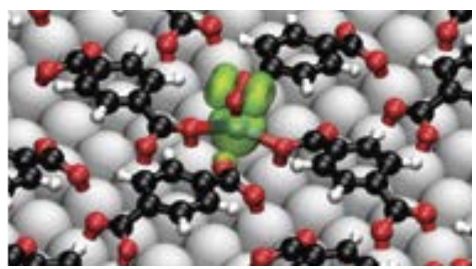




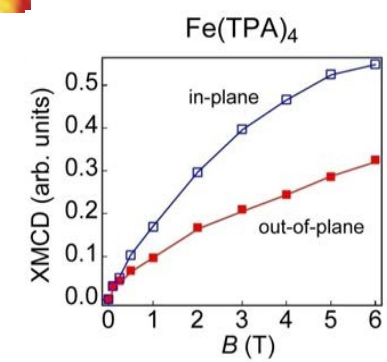
Control of magnetic anisotropy:
O_2 adsorption turns the easy direction of magnetization out of plane!

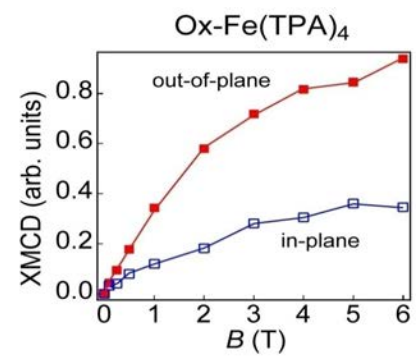


Fe(TPA)$_4$



O$_2$- Fe(TPA)$_4$

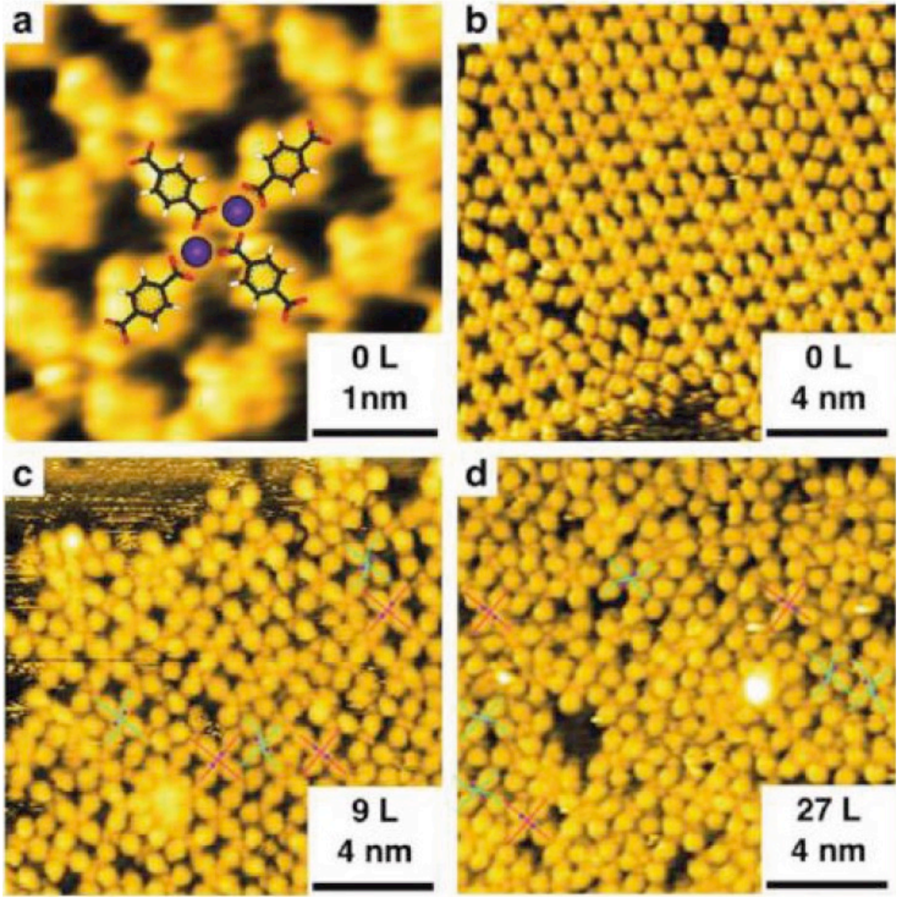


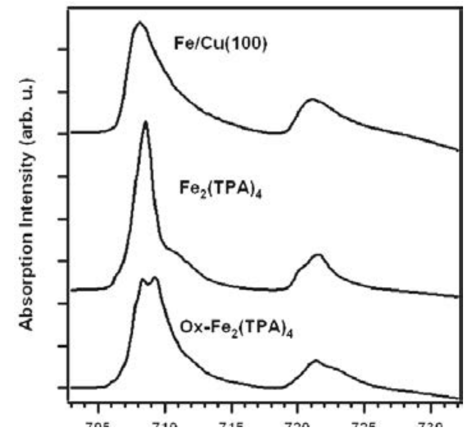


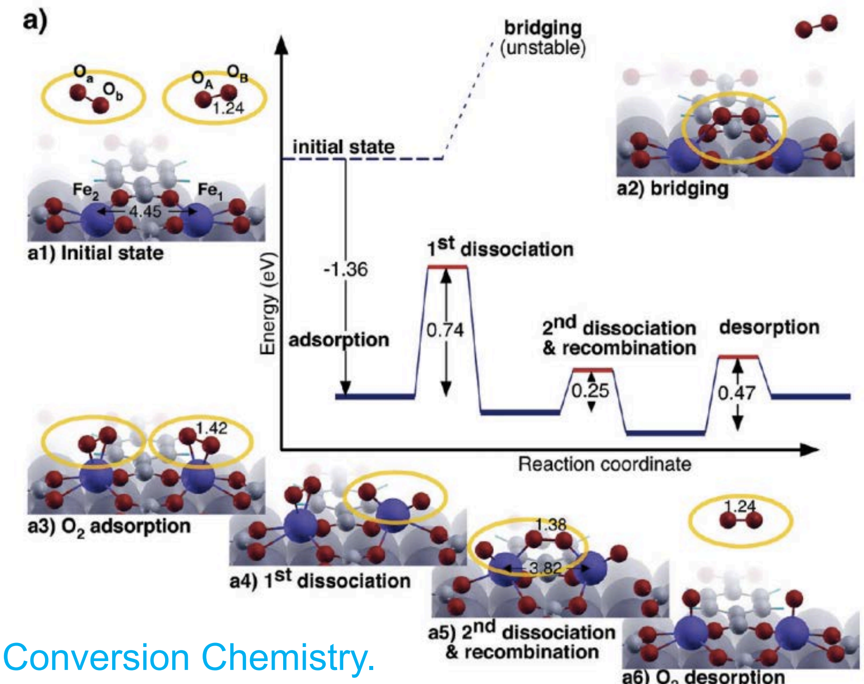
Nature Materials, 8, 189 (2009)

Function : Catalytic properties

O_2 dissociation on self-assembled molecular networks (TPA-Fe)



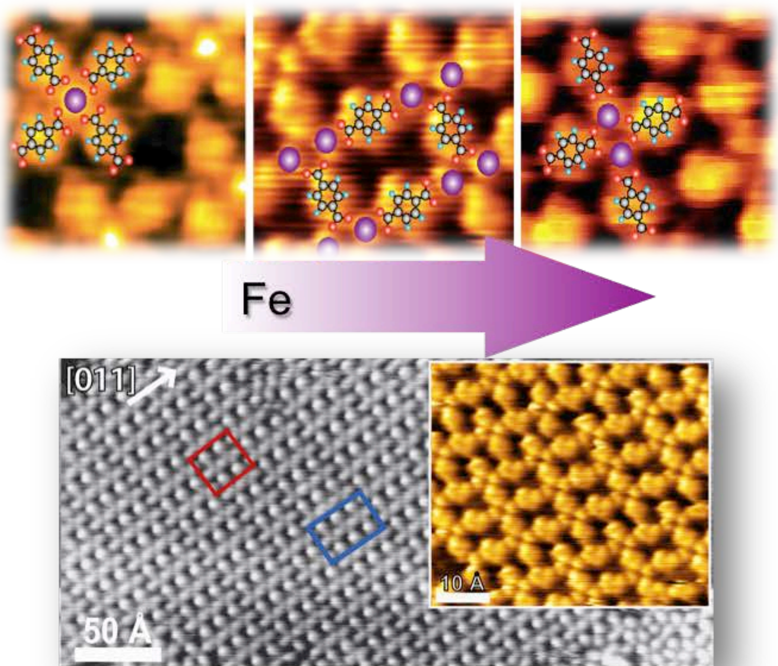


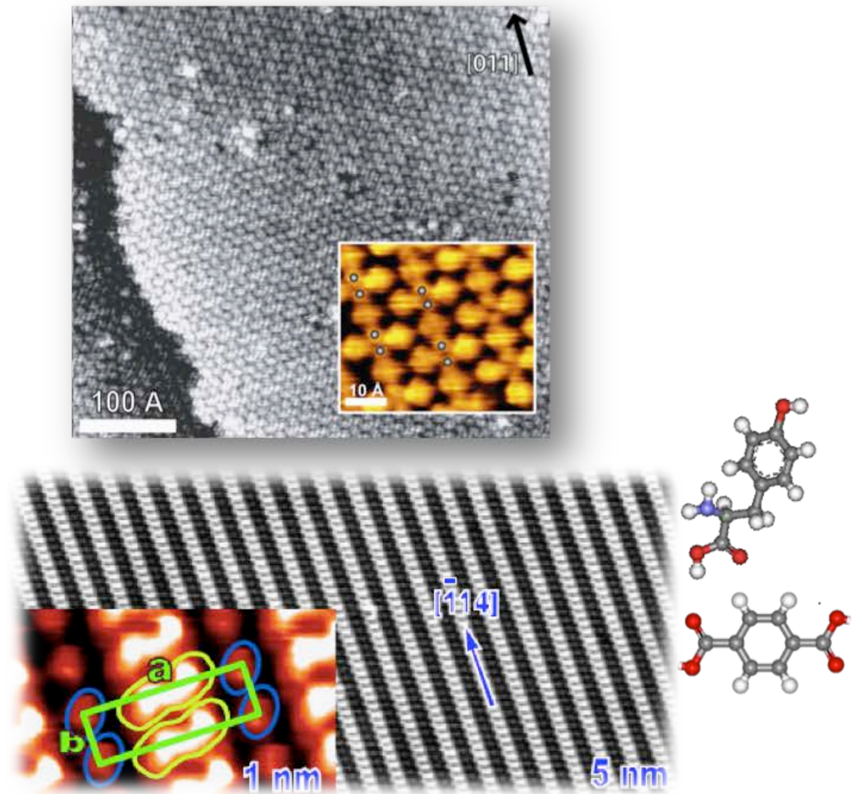


Mimicking Enzymatic Active Sites on Surfaces for Energy Conversion Chemistry. Accounts of Chemical Research 2015; 48(7). DOI:10.1021/acs.accounts.5b00172

Structure-Function

Control: Structure is tuned by T, symmetry and chemistry of the surface,metal/molecule ratio, Co-deposition of different molecules, chirality, etc





Using self assembly, tuning intermolecular forces…

J. Phys. Chem B 108, 19392 (2004), Chem. Eur. J. 10, 1913 (2004), Nature Materials, 3, 229 (2004)

Nature Materials, 8, 189 (2009), Angewantde Chemie International Ed. (2007) Nature 437, 671 (2005)

J. Phys. Chem. A 111, 12589 (2007), Nano Letters 11,5414 (2011), Chem. Commun. 48, 534 (2012),

Nat. Commun. 3, 940 (2012), etc

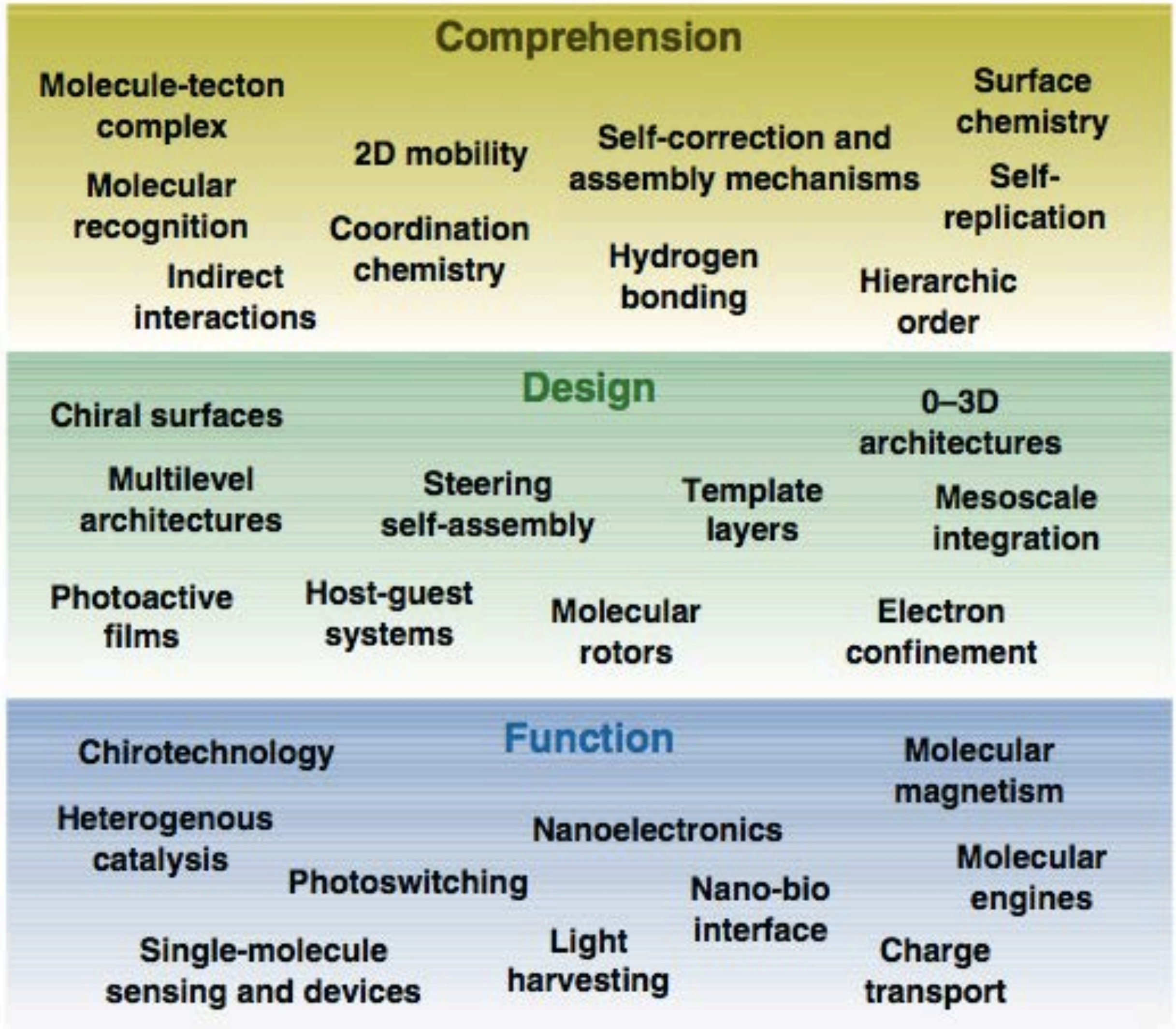


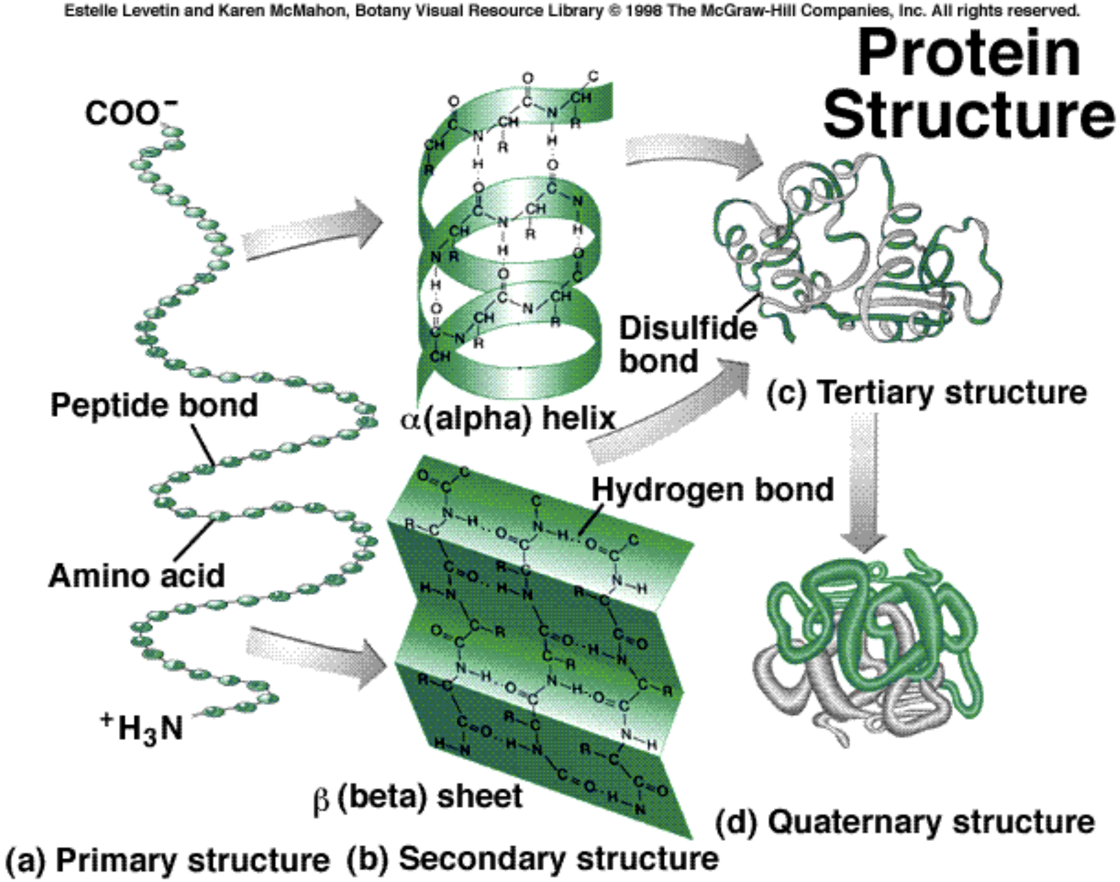
Figure 10

Molecular architectonic on surfaces is bound to advance at three levels: the fundamental understanding of basic interactions and processes, the conceiving and engineering of low-dimensional nanosystems, and the development of nanomaterials and devices performing specific tasks.

Botton up and top down

3D-4D printing combining smart materials

Self folding-self assembled-functional



http://www.youtube.com/watch?v=GIEhi_sAkU8

Quiz

Building blocks in Nanoscience?
Factors determining self-assembly?