Introduzione alle nanotecnologie e aspetti applicativi

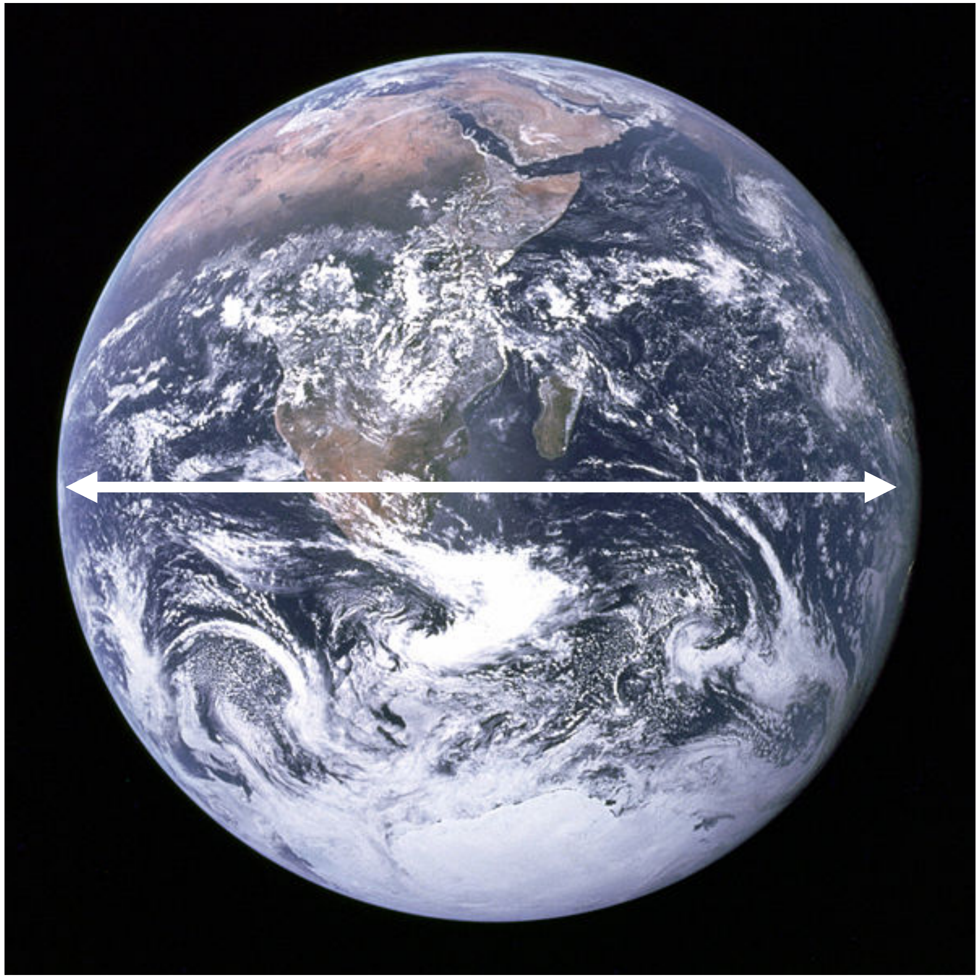
Luca Beverina

Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca
e INSTM
luca.beverina@unimib.it

Scale factors

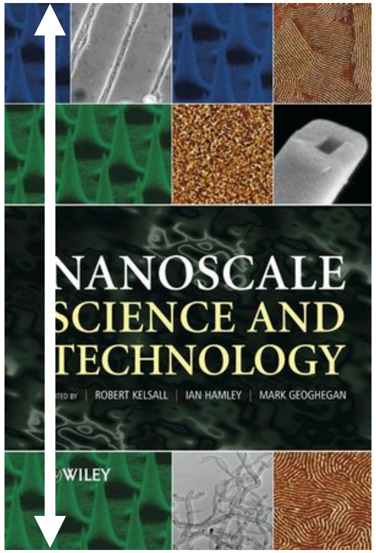
$$1\ \text{nm} = 10^{-9}\ \text{m}$$

Nine orders of magnitude - length



12 745,594 km

10^{-9}



0.13 m

Nine orders of magnitude - Weight

Megaptera novaeangliae

Circa 100 t = 10^8 g

10^{-9}

Ladybug: 0,1 g

Effects of size reduction

- “Physiologic” scaling-laws of classical physics

- Surface to volume ratio

- Just Size Effects

- “Pathologic” quanto-mechanical effects

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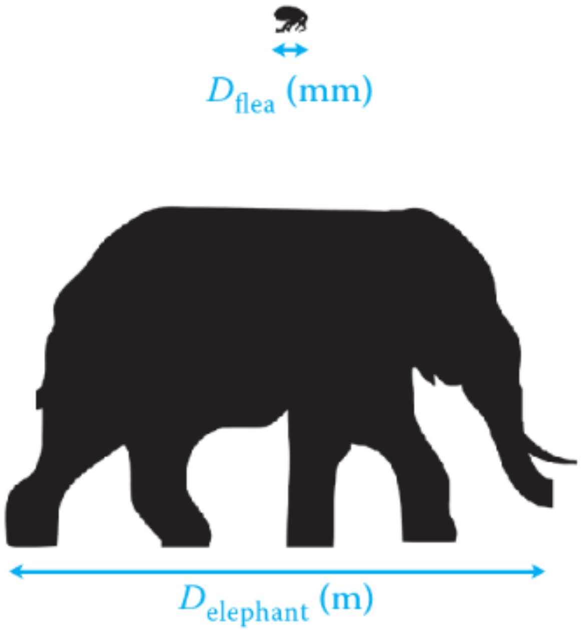
The Elephant and the flea



$$\text{Strength} \propto D^2$$

$$\text{Weight} \propto D^3$$

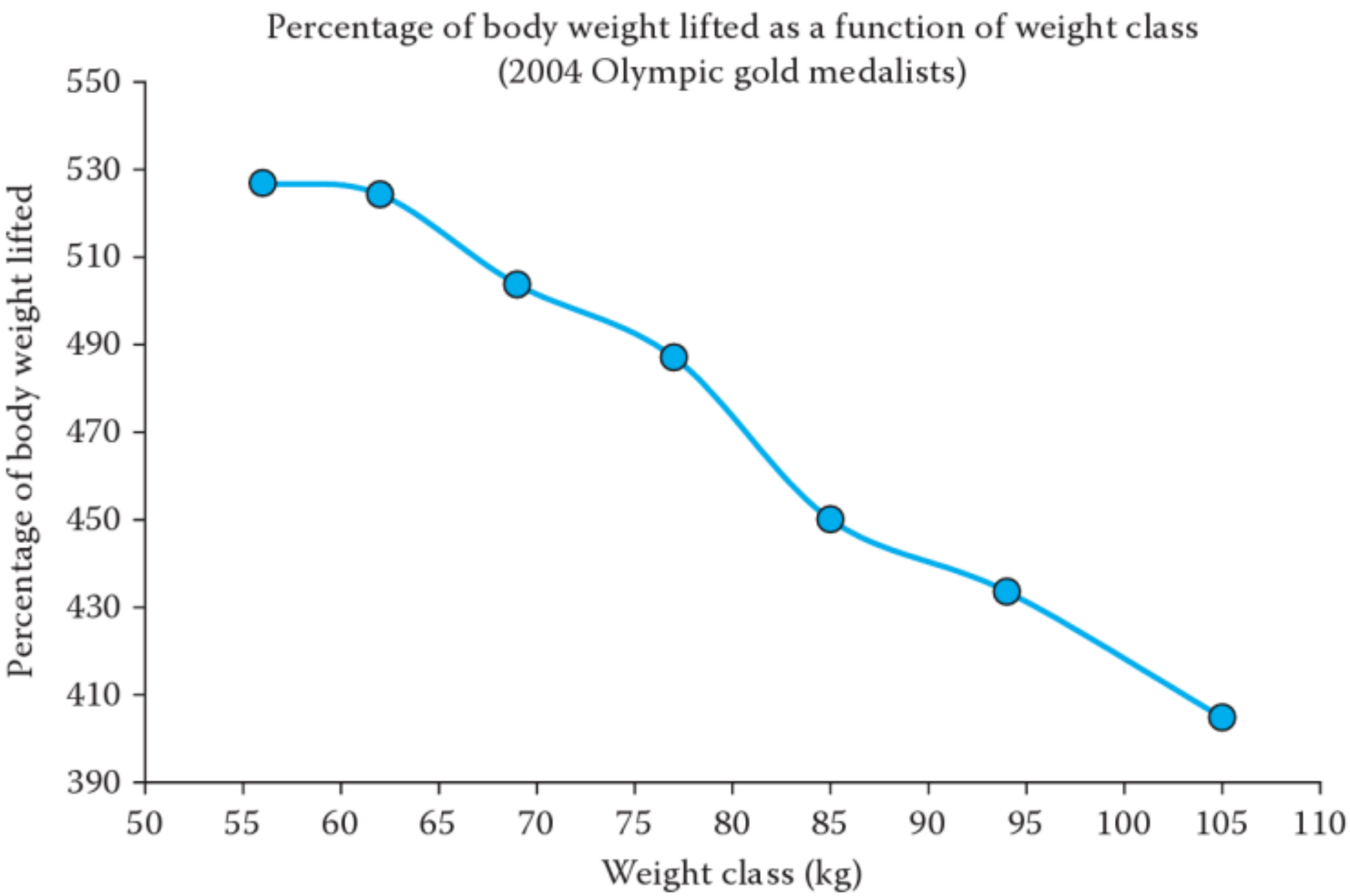
$$\frac{\text{Strength}}{\text{Weight}} \propto \frac{D^2}{D^3} \propto \frac{1}{D}$$

Strength to weight ratio gives an estimate of how far you can jump. An elephant cannot jump, a flea can jump 100 times its body length.

For essentially the same reasons, according to Galileo, mythological giants cannot exist.

Nanotechnology: Understanding Small Systems, Third Edition, Di Ben Rogers,Jesse Adams,Sumita Pennathur

Weightlifting



Nanotechnology: Understanding Small Systems, Third Edition, Di Ben Rogers,Jesse Adams,Sumita Pennathur

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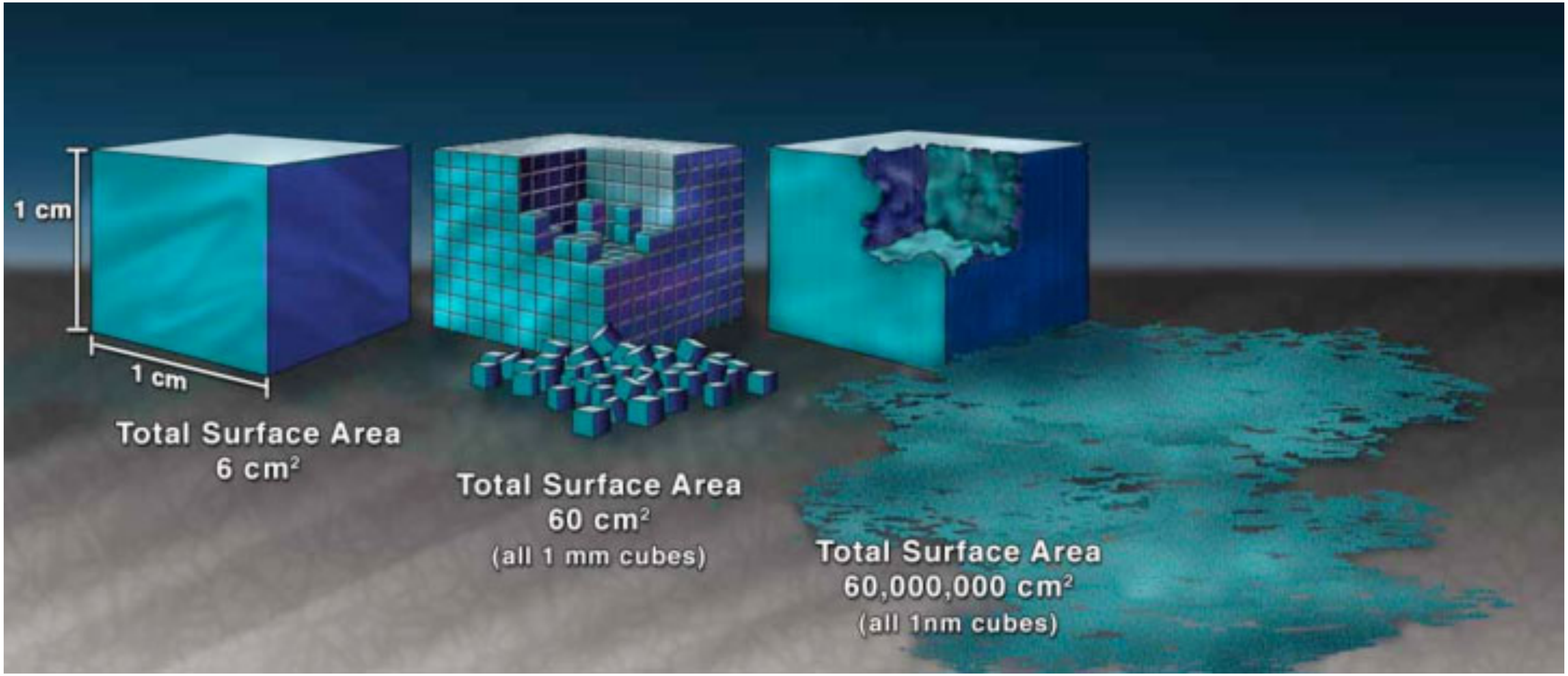
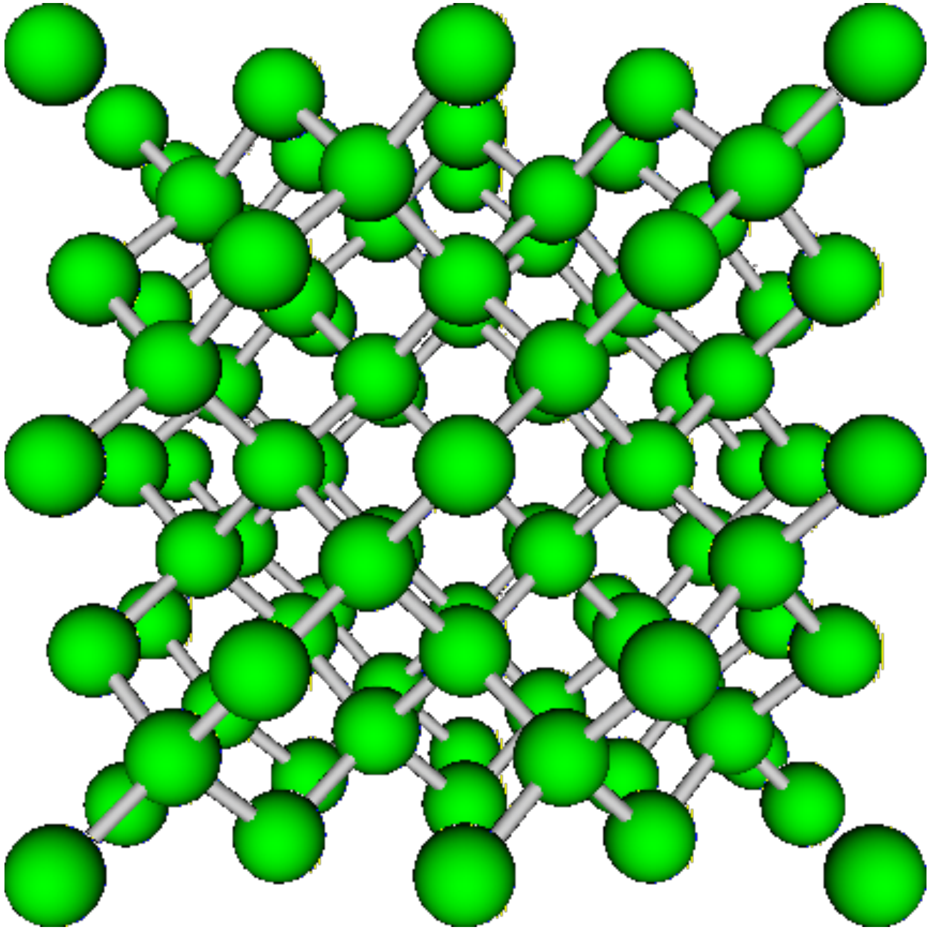
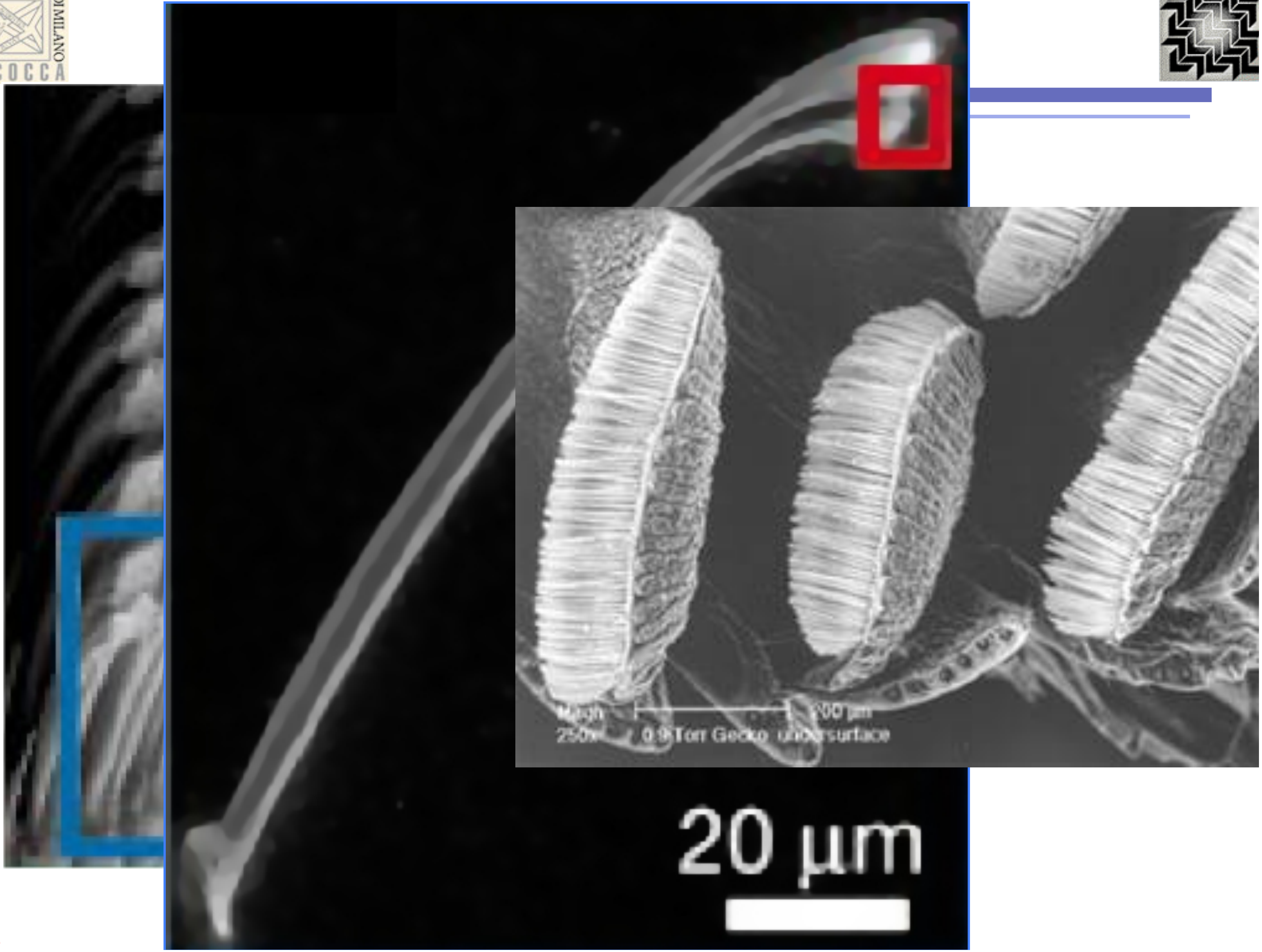
Surface to volume ratio





Si-H, Si-OH, Si-O-Si, ..


20 µm

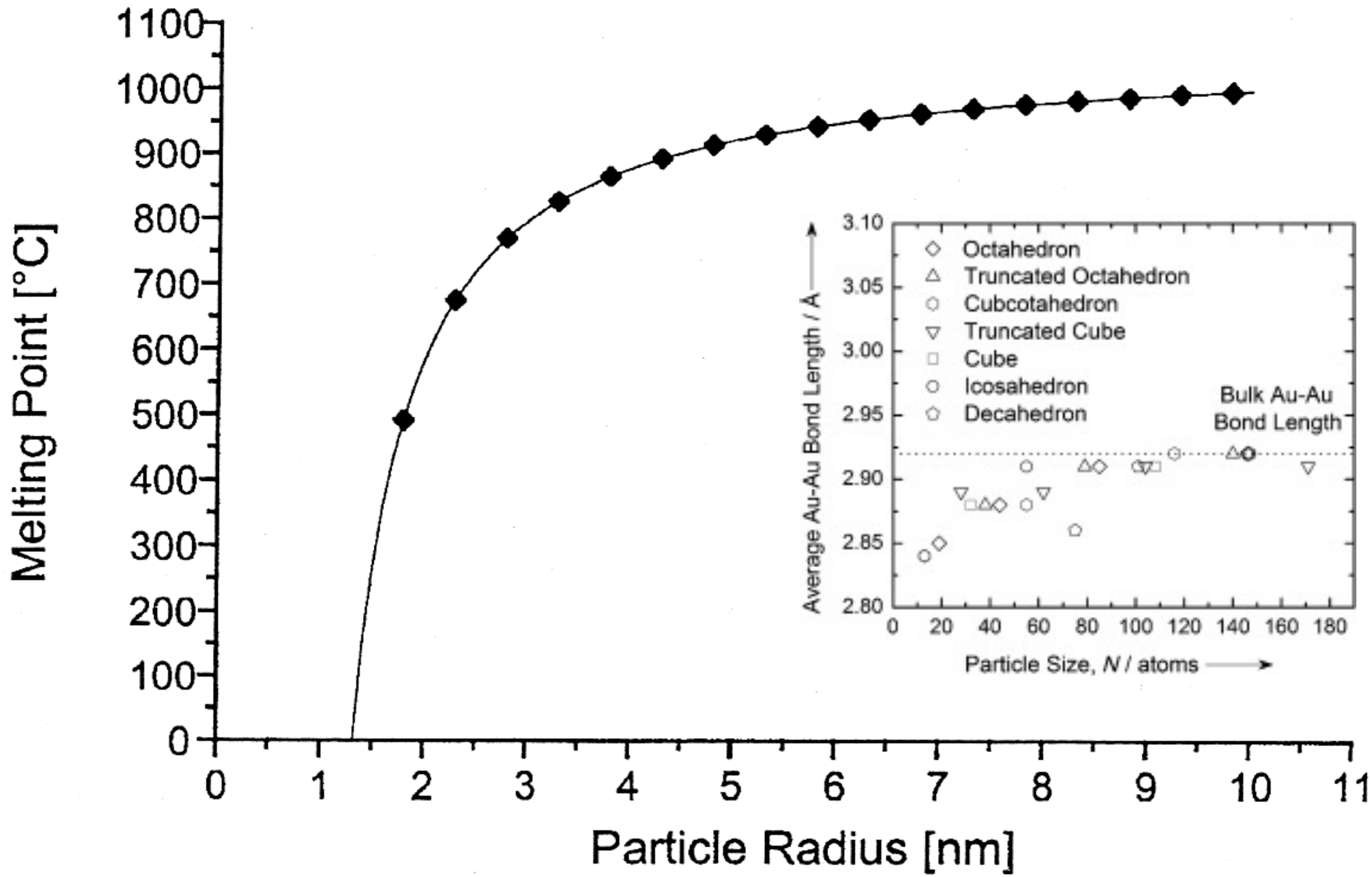
Effects of size reduction

- “Physiologic” scaling-laws of classical physics
- Surface to volume ratio
- Just Size Effects
- “Pathologic” quanto-mechanical effects

Thermodynamics of small systems

- Breakdown of thermodynamic limit $N \to \infty$
- Increase of fluctuations, esp. @ critical points
- Mean values (intensive quantities) are less significant
- Additivity of extensive quantities (S) breaks down

Size dependent melting point



Effects of size reduction

- "Physiologic" scaling-laws of classical physics
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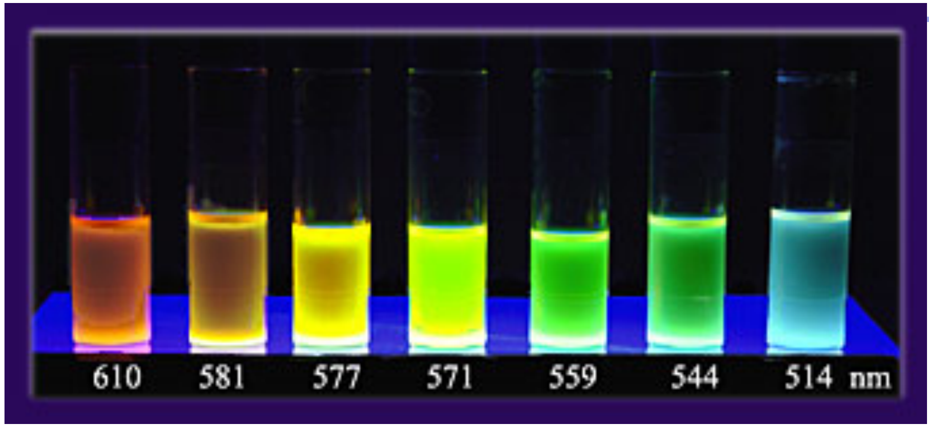
Quanto-mechanical effects

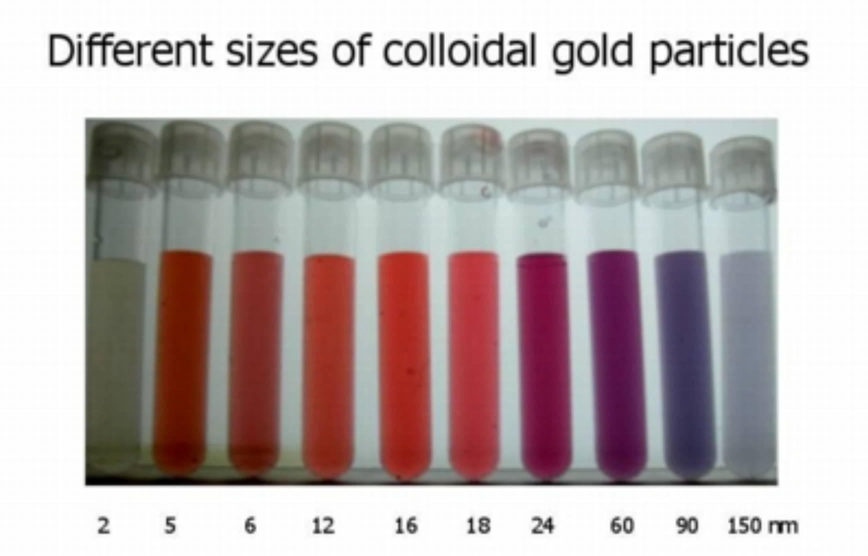
- Quantum confinement: energy levels and their spacings scale as $1/L^2$. Optical shifts with size

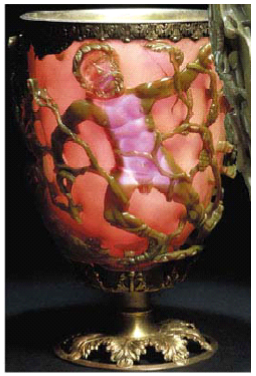
- Tunnelling: current scales as exp $(-2d/\Lambda)$, where d is the thickness of the barrier.

- Scattering: relaxation-time approximation breaks down if $L < \lambda m = v(E_F)\,\Delta t$

Color (optical gap)

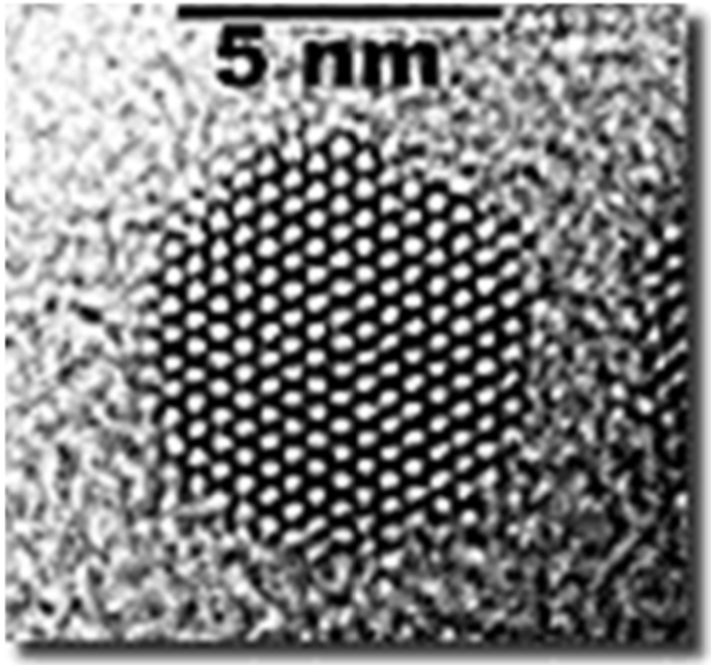






Lycurgus Cup,

nanoparticelle di oro e argento



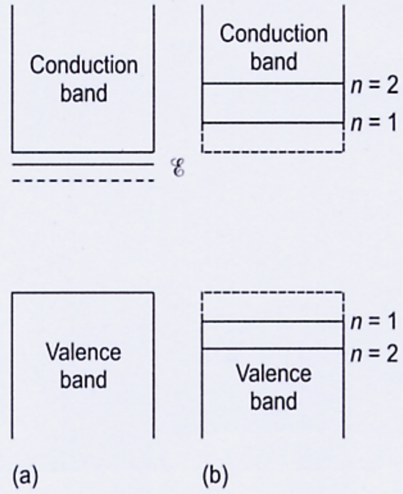


Fig. 8.6 Effects of quantum confinement on the electronic energy levels associated with optical absorption for semiconductor nanocrystals in: (a) the weak-confinement régime. The exciton binding energy ℰ is reduced from the value it has for an infinite crystal (dashed line). (b) the strong-confinement régime. The valence and conduction bands split into a series of sub-bands corresponding to the energy levels of a particle-in-a-box.

uncertainty in momentum

$$\Delta x \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

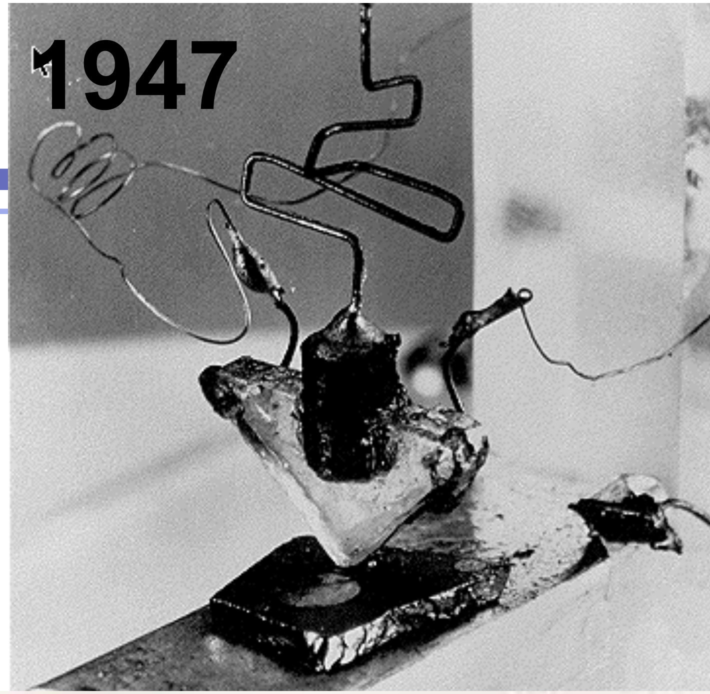
uncertainty in position

$$\Delta E = \frac{n^2 h^2}{8ma^2}$$

1959

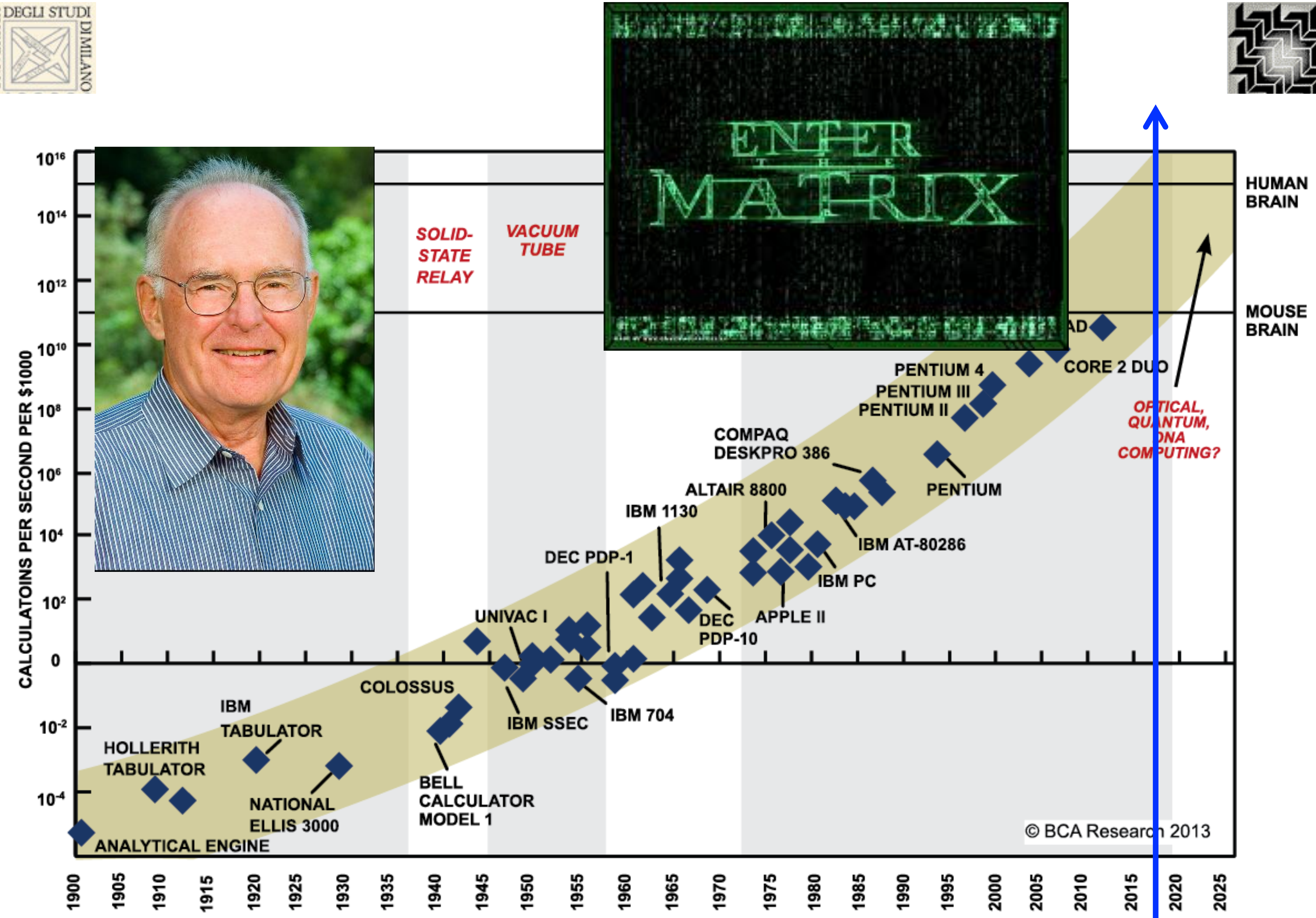
There's Plenty of Room at the Bottom

But I am not afraid to consider the final question as to whether, ultimately, in the great future, we can arrange the atoms the way we want.



John Bardeen (1956)
Nobel 1956 - semiconductors
Nobel 1972 - superconductors

IBM core business 1959

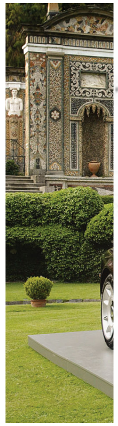


SOURCE: RAY KURZWEIL, "THE SINGULARITY IS NEAR: WHEN HUMANS TRANSCEND BIOLOGY", P.67, *THE VIKING PRESS*, 2006. DATAPOINTS BETWEEN 2000 AND 2012 REPRESENT BCA ESTIMATES.

2017 10^{11} operazioni al secondo

Brains

If the automobile had followed the same development cycle as the computer



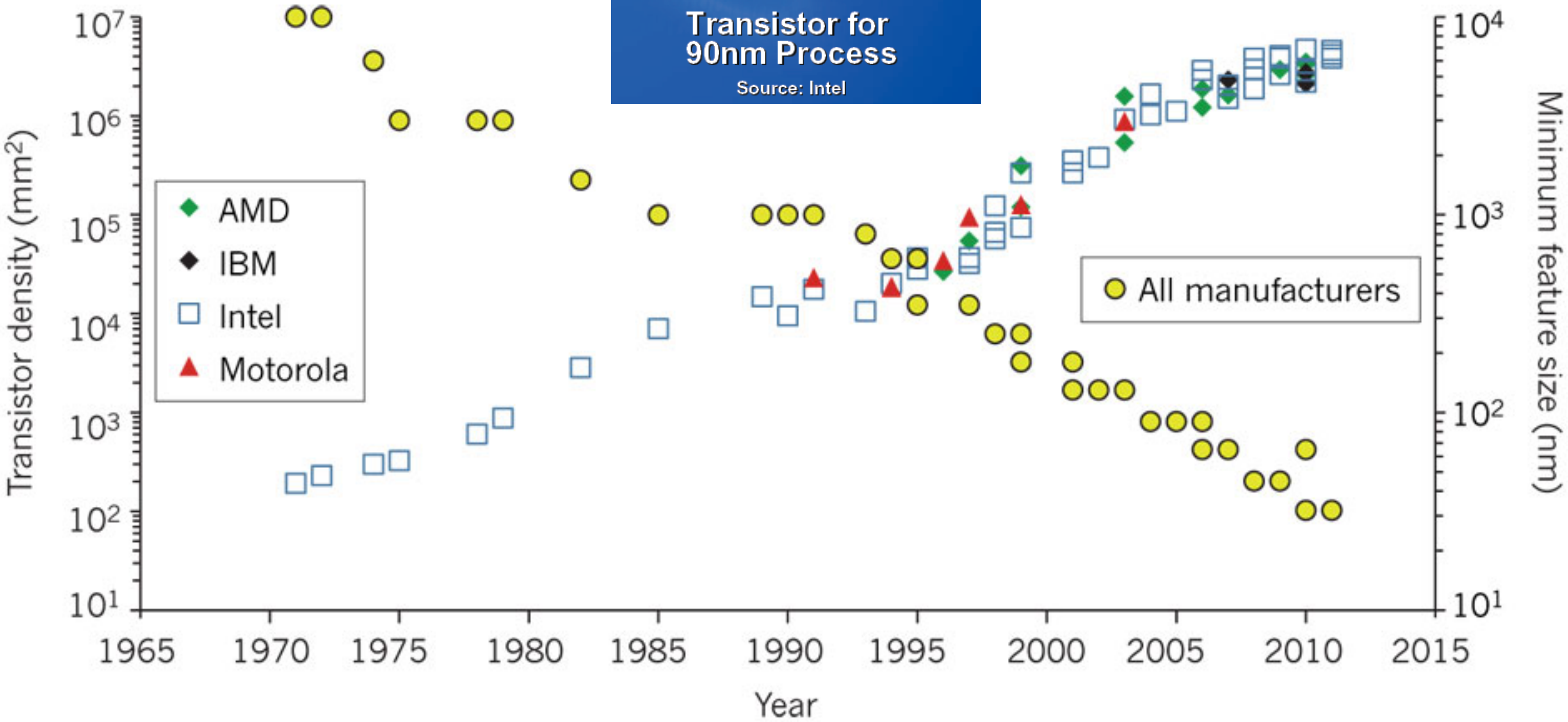
a Rolls-Royce would today cost $100

get a million miles per gallon

and explode once a year, killing everyone inside.

- Robert X. Cringely

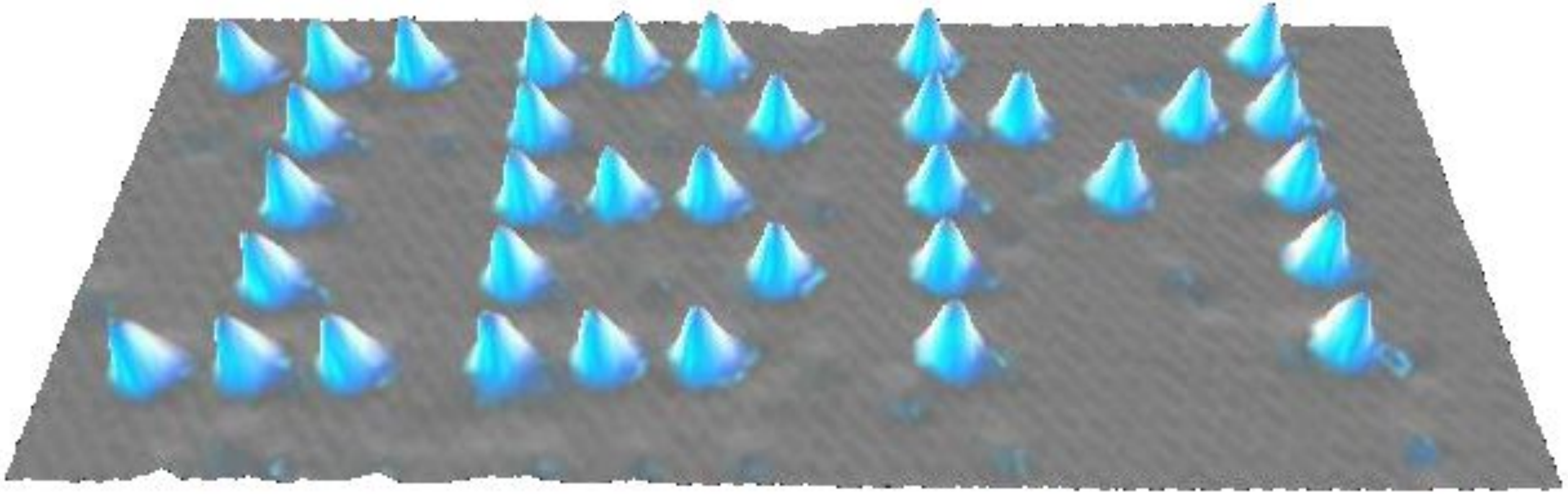
50nm
Transistor for
90nm Process
Source: Intel



Transistor density (mm²)
Minimum feature size (nm)
Year
AMD
IBM
Intel
Motorola
All manufacturers

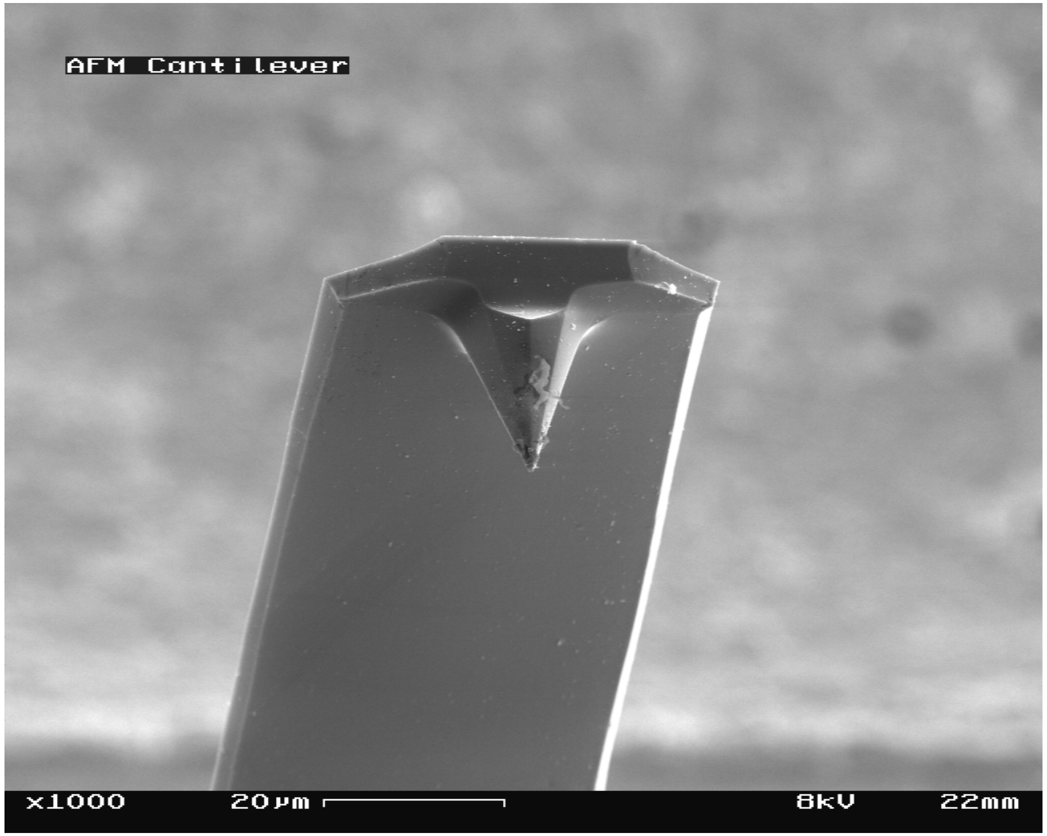
Devices made with single atoms

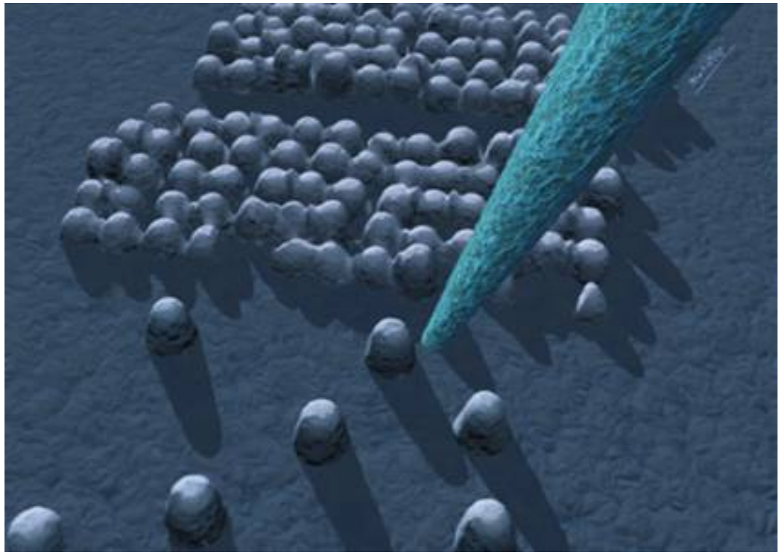
IBM - 1985



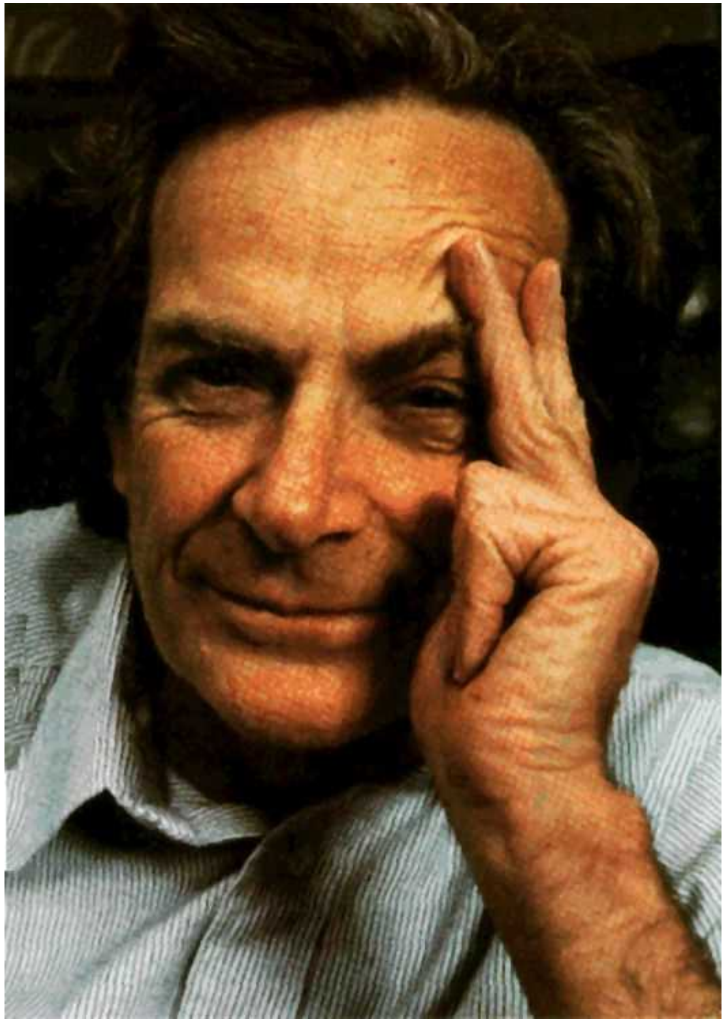
…we can arrange the atoms the way we want…

Scanning Probe devices: STM and AFM.



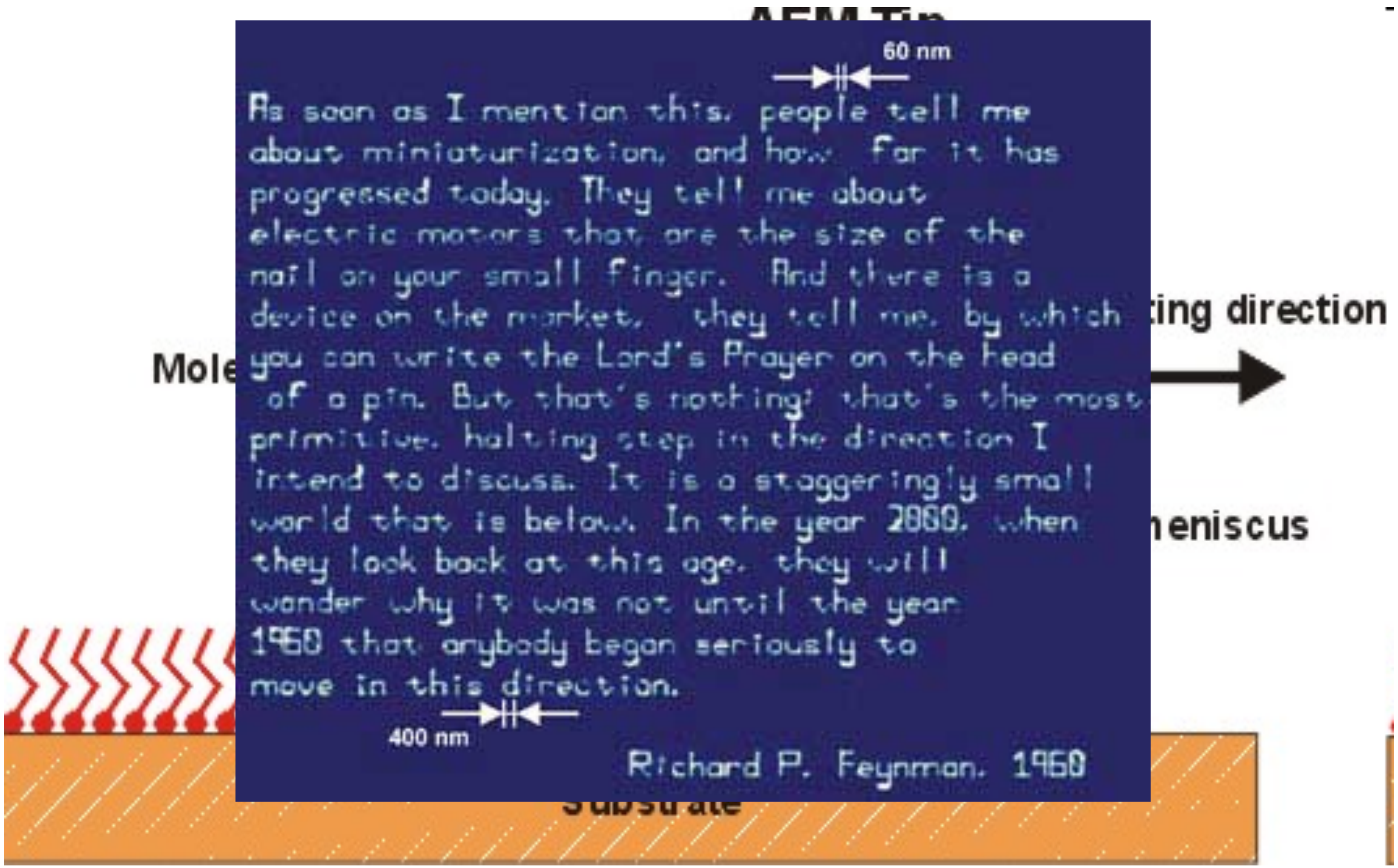


Gerd Binnig and Heinrich Rohrer early 1980s



… write the britannic encyclopedia on the head of a pin…

dip-pen lithography



Plenty of room at the bottom

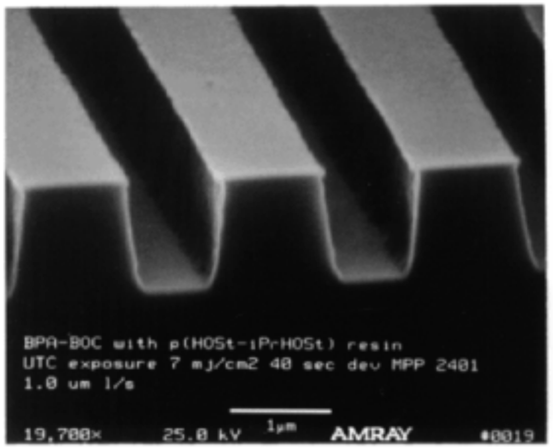
Dürer, Albrecht

The Knight, Death and The Devil (Le Cheval, la Mort et le Diable)
1514

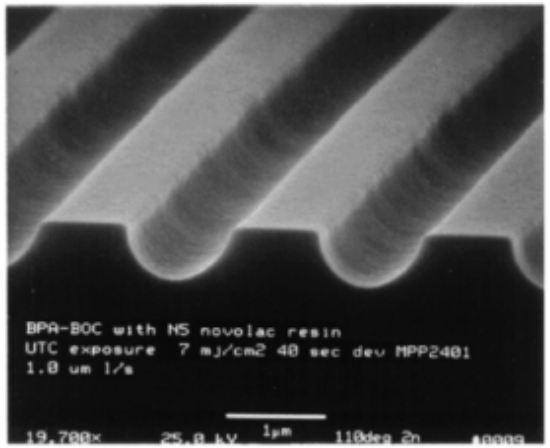
Top

Down

Design molecules and clusters to self assemble (Bottom up)



(a)

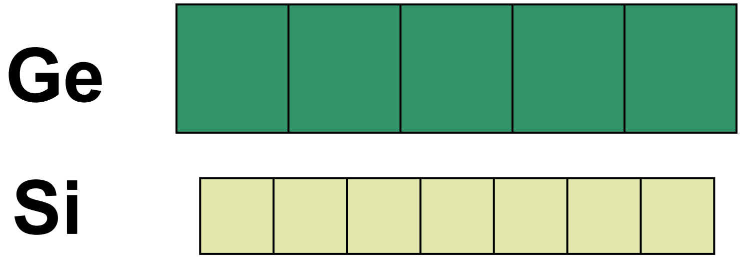


(b)

Red pyramid– Dahshur (104 m)

Giza great pyramid– (147 m)

Bent pyramid– Dahshur (105 m)


Ge
Si

bly

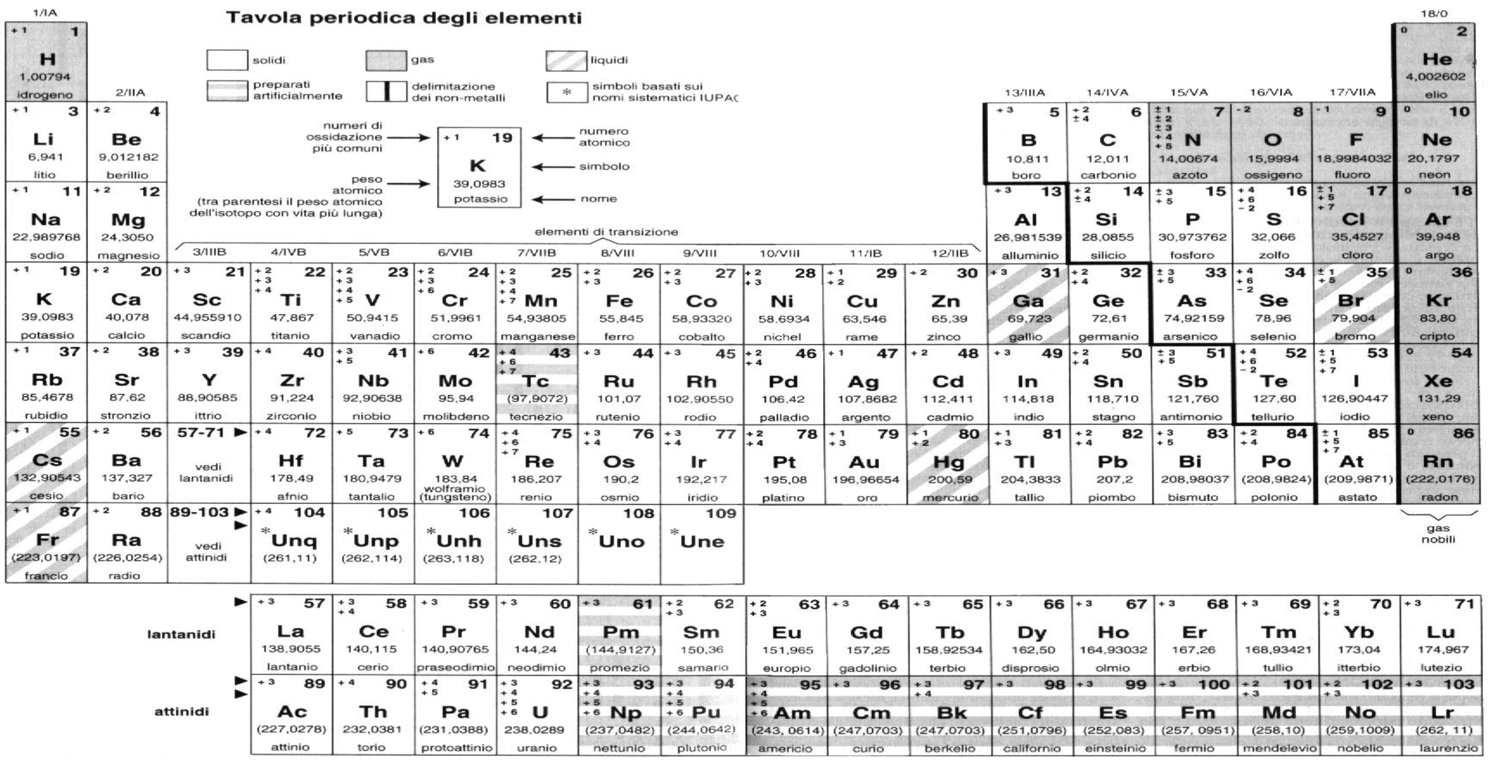
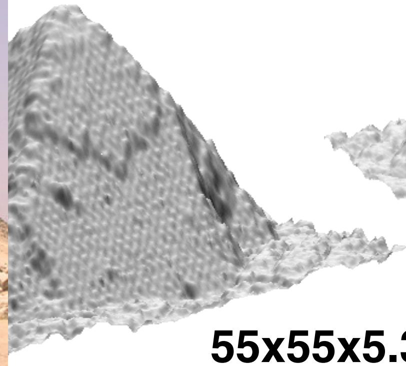


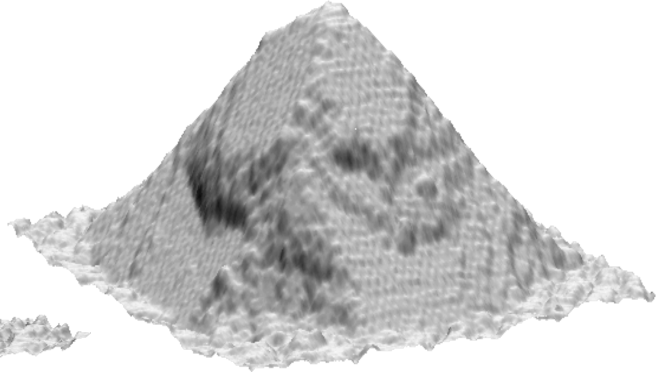
Tavola periodica degli elementi
solidi
gas
liquidi
preparati artificialmente
delimitazione dei non-metalli
simboli basati sui nomi sistematici IUPAC
numeri di ossidazione più comuni
numero atomico
simbolo
peso atomico (tra parentesi il peso atomico dell'isotopo con vita più lunga)
nome
elementi di transizione
gas nobili
lantanidi
attinidi

Pyramid-to-dome transition in Ge/Si(001)

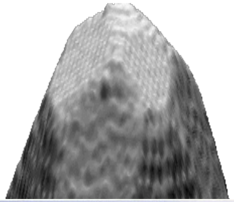
F. Montalenti et al., Phys. Rev. Lett. 93, 216102 (2004)

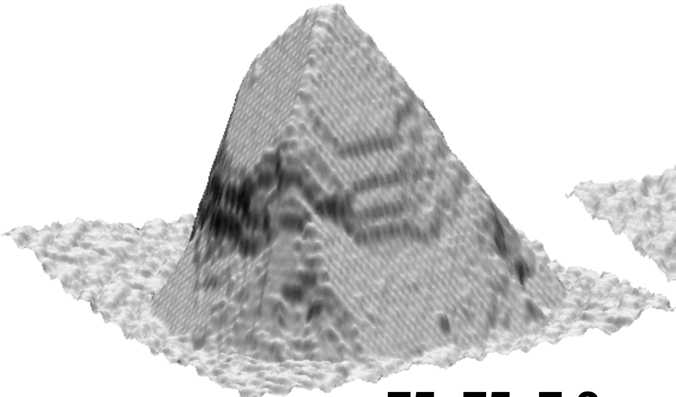


55x55x5.3 nm^3

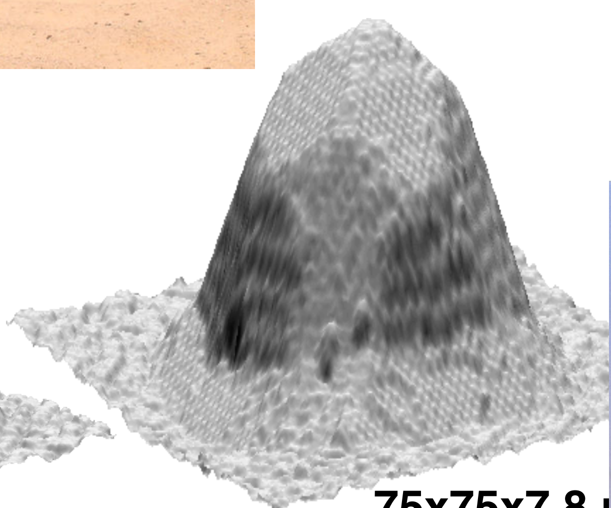


55x55x5.7 nm^3





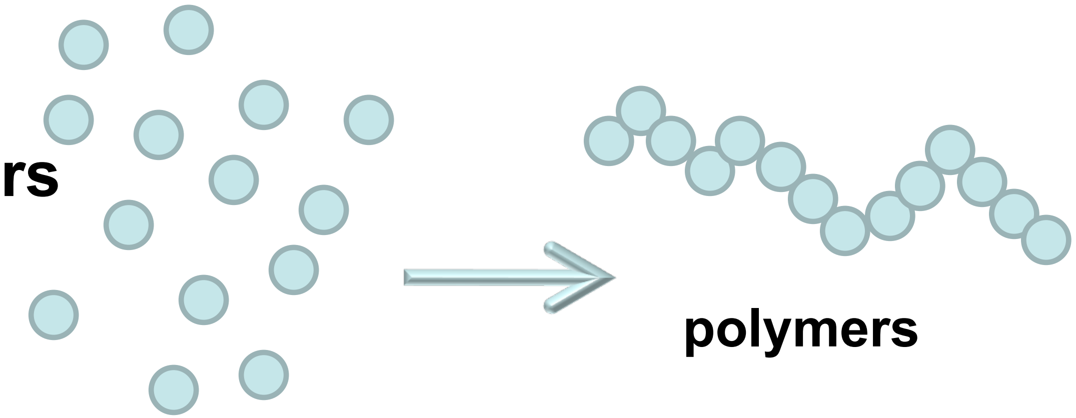
75x75x7.3 nm^3



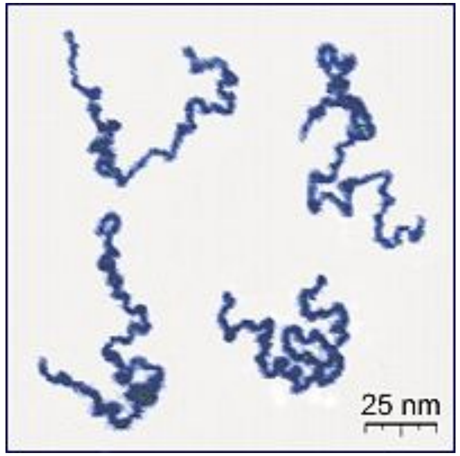
75x75x7.8

Polymers

Monomers



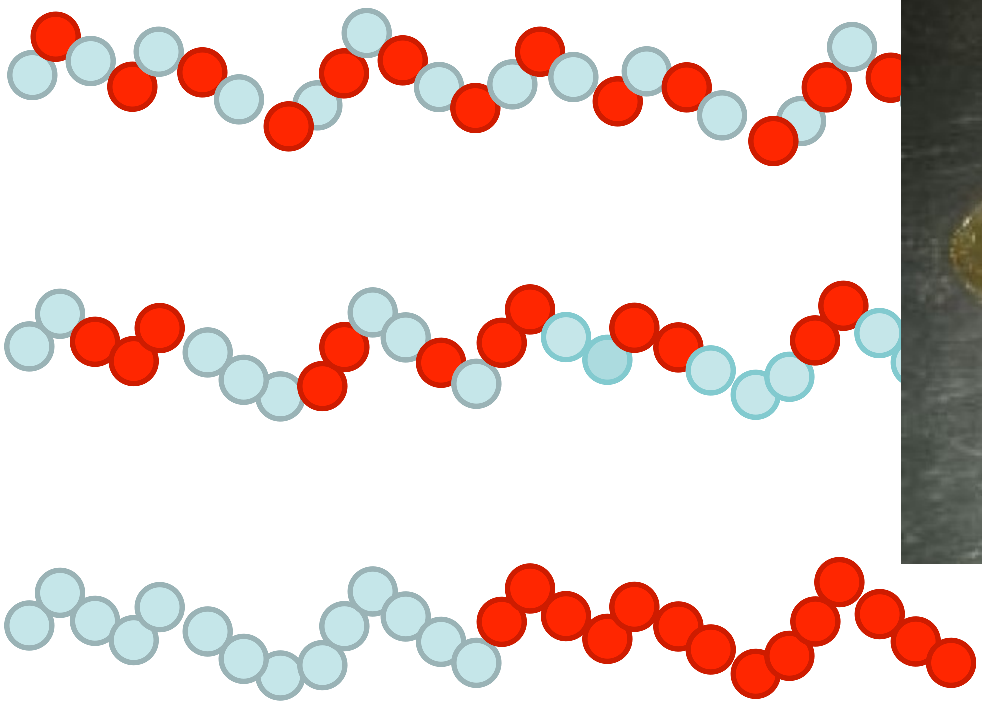
polymers

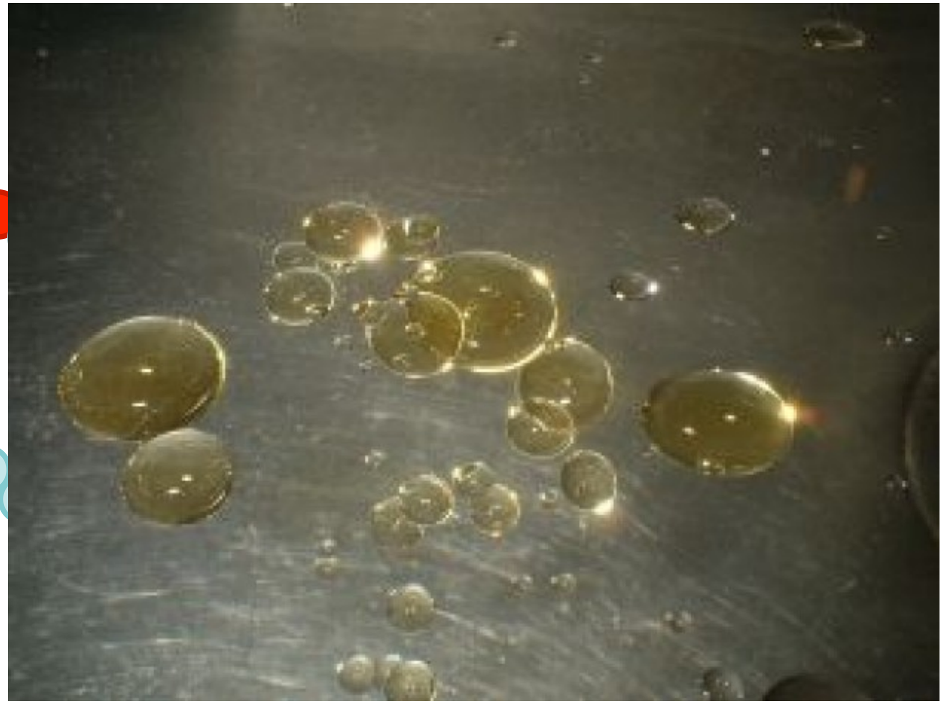


random coil
(spaghetti scotti)

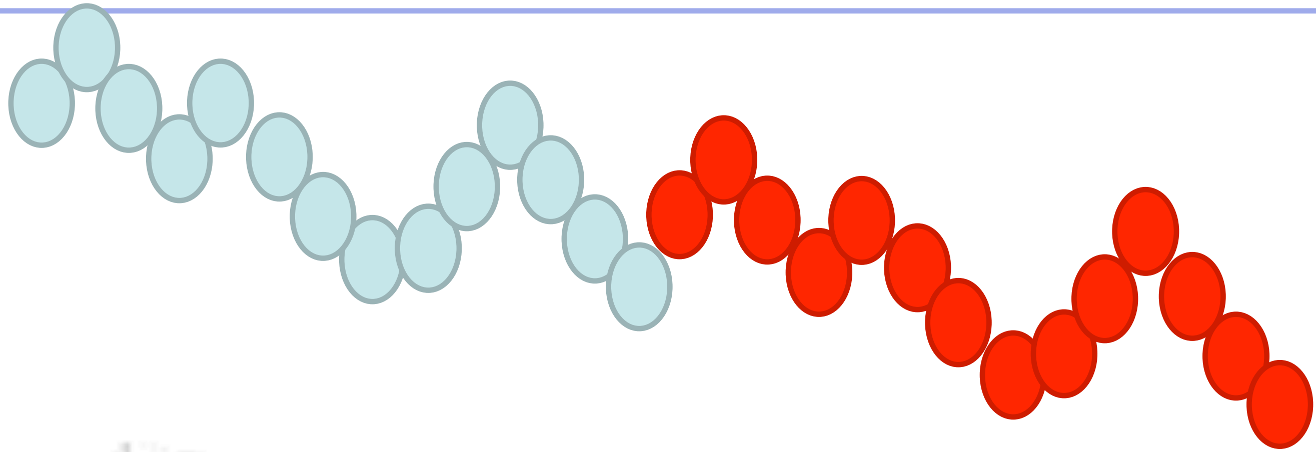
Copolymers

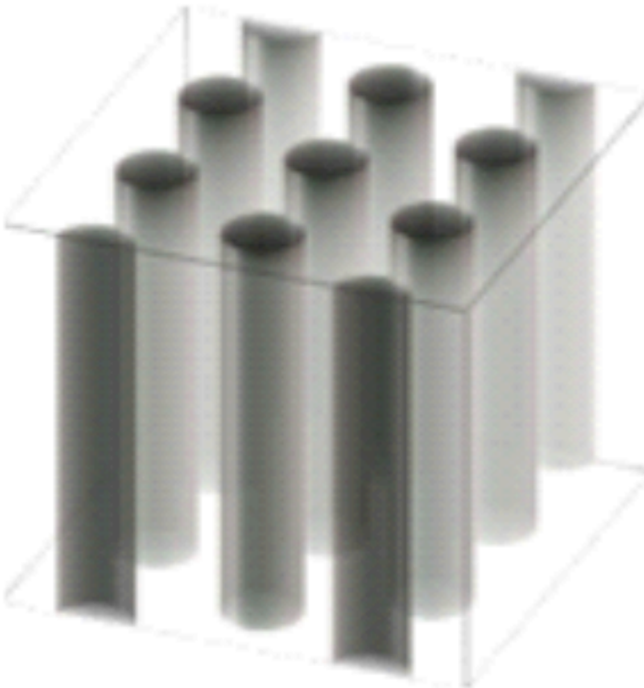
At least two different monomers

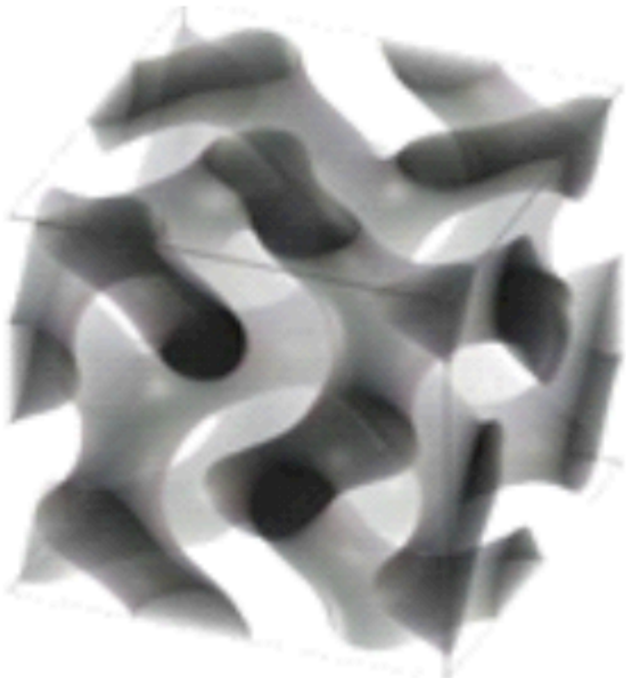




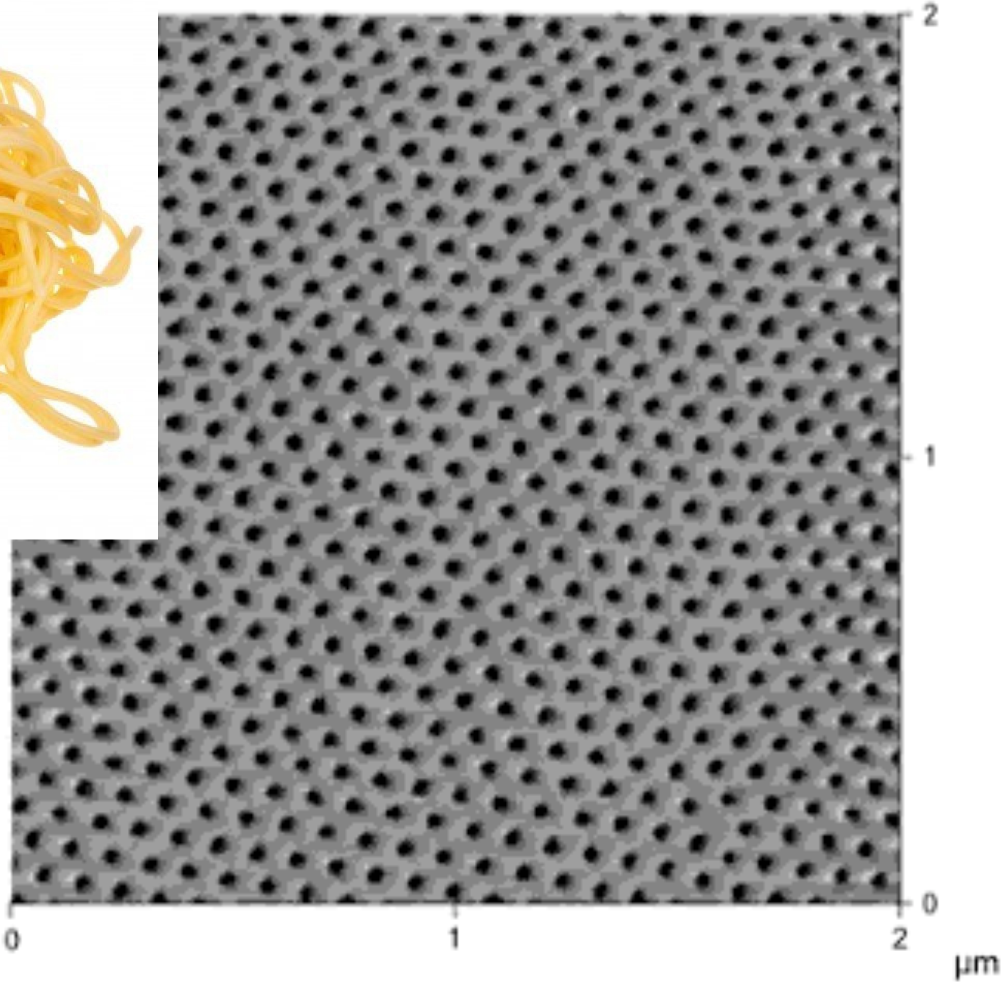
Block







SOLID STATE ORDERING

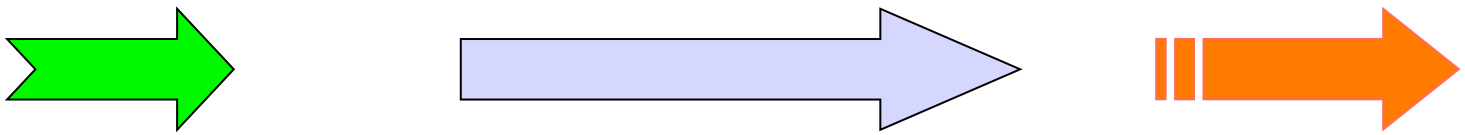


Top view of cylindrical phases packed in an hexagonal lattice

THE BASICS OF INNOVATION

TECHNOLOGY PUSH

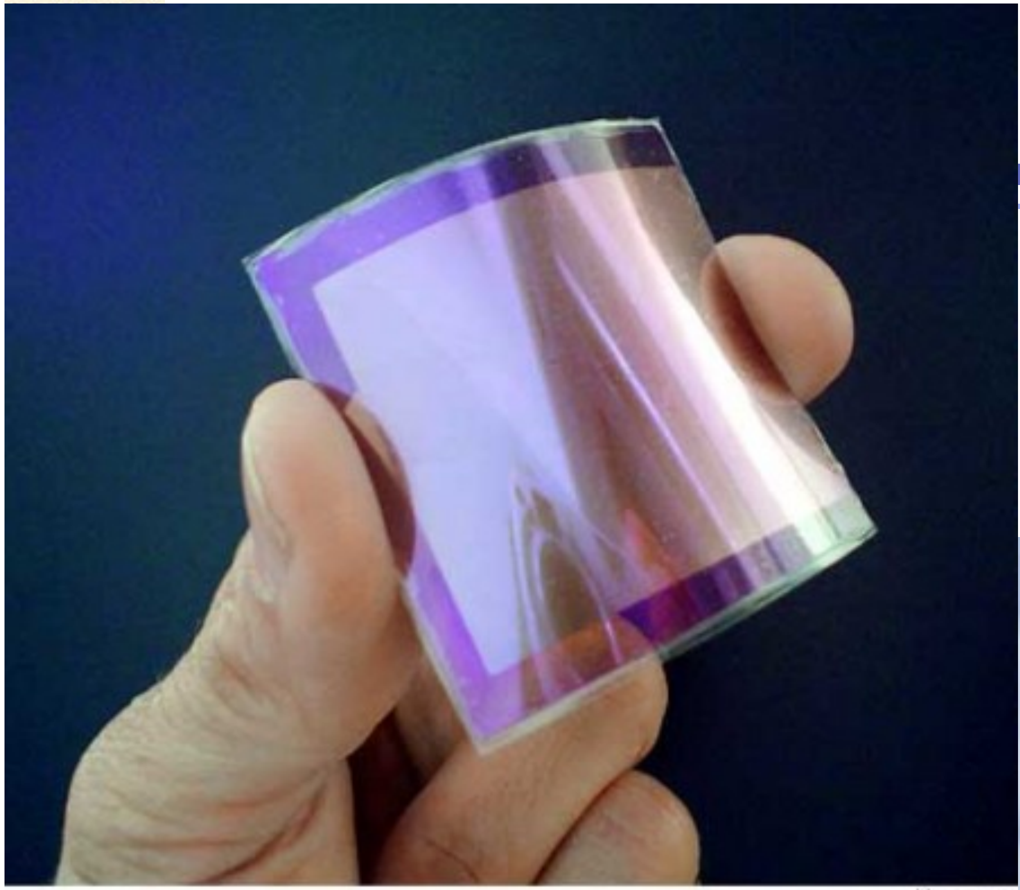
MARKET PULL



INNOVATION

Offer of new materials, processes, devices..

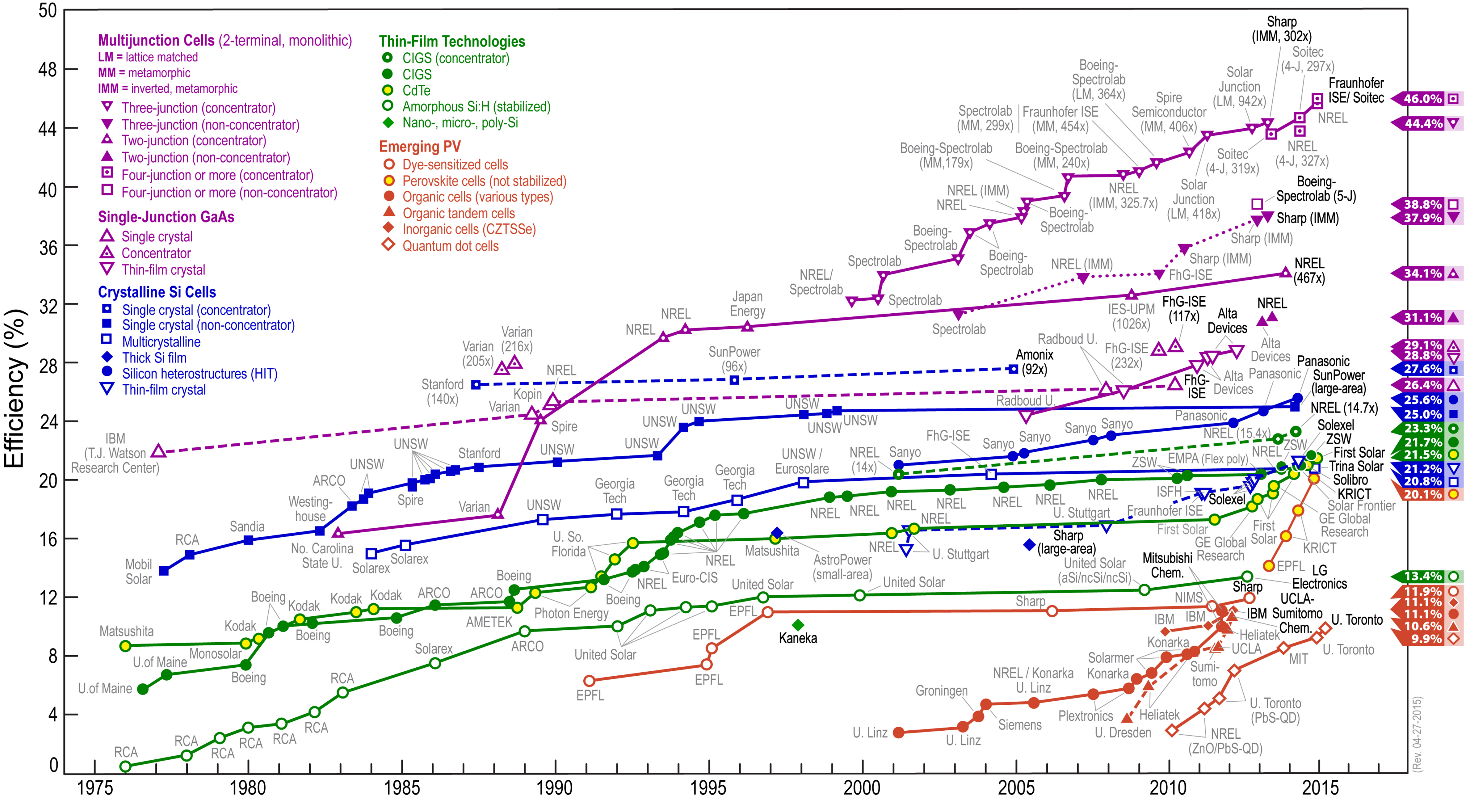
Demand of new products, cheaper/ cleaner processes, new services

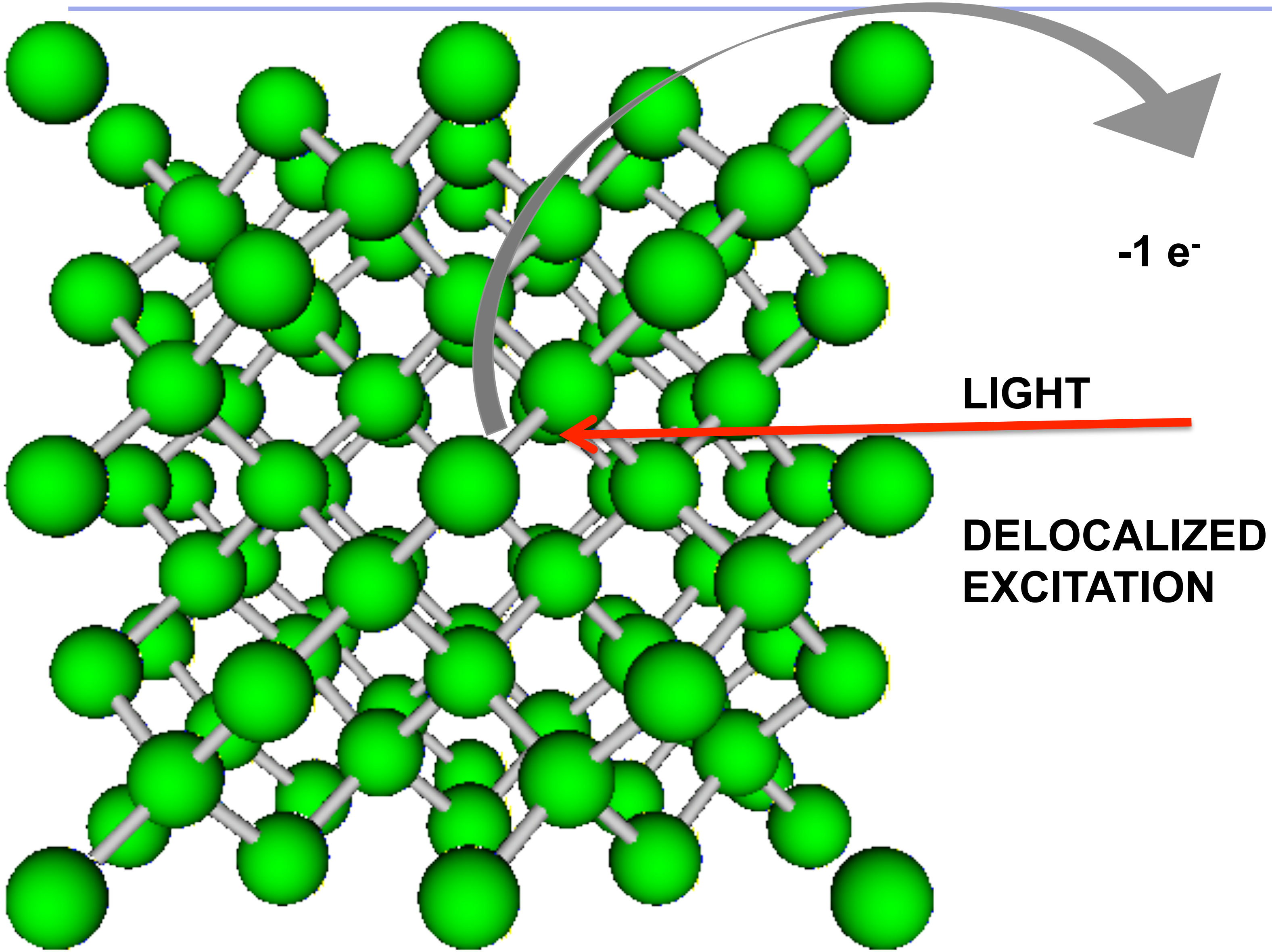


Nanosys

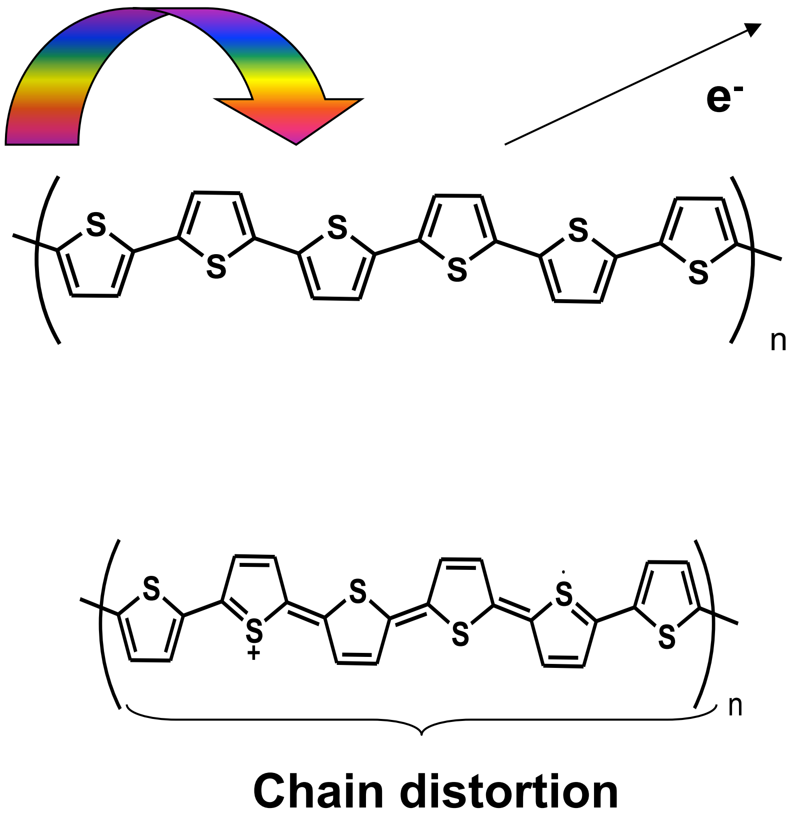
The coming of plastic electronics: flexible devices

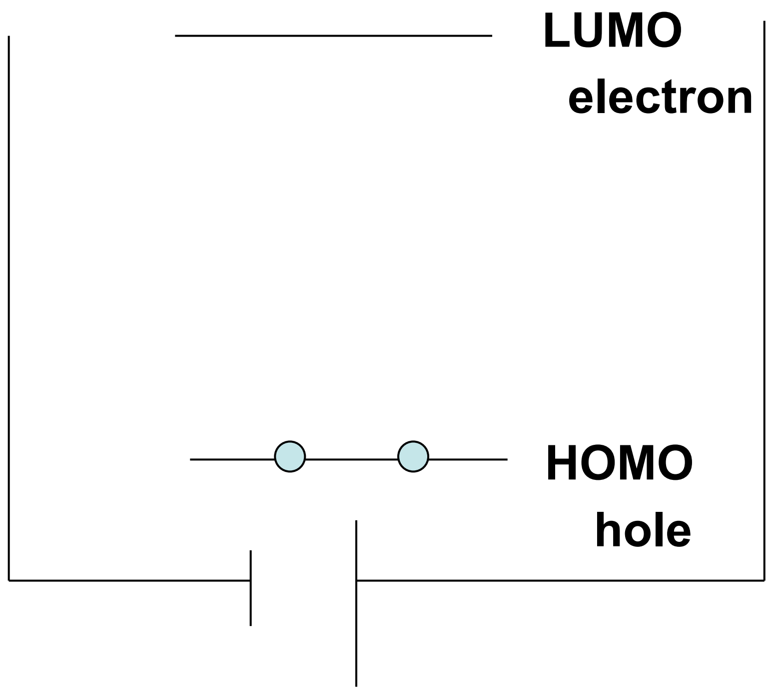
Best Research-Cell Efficiencies



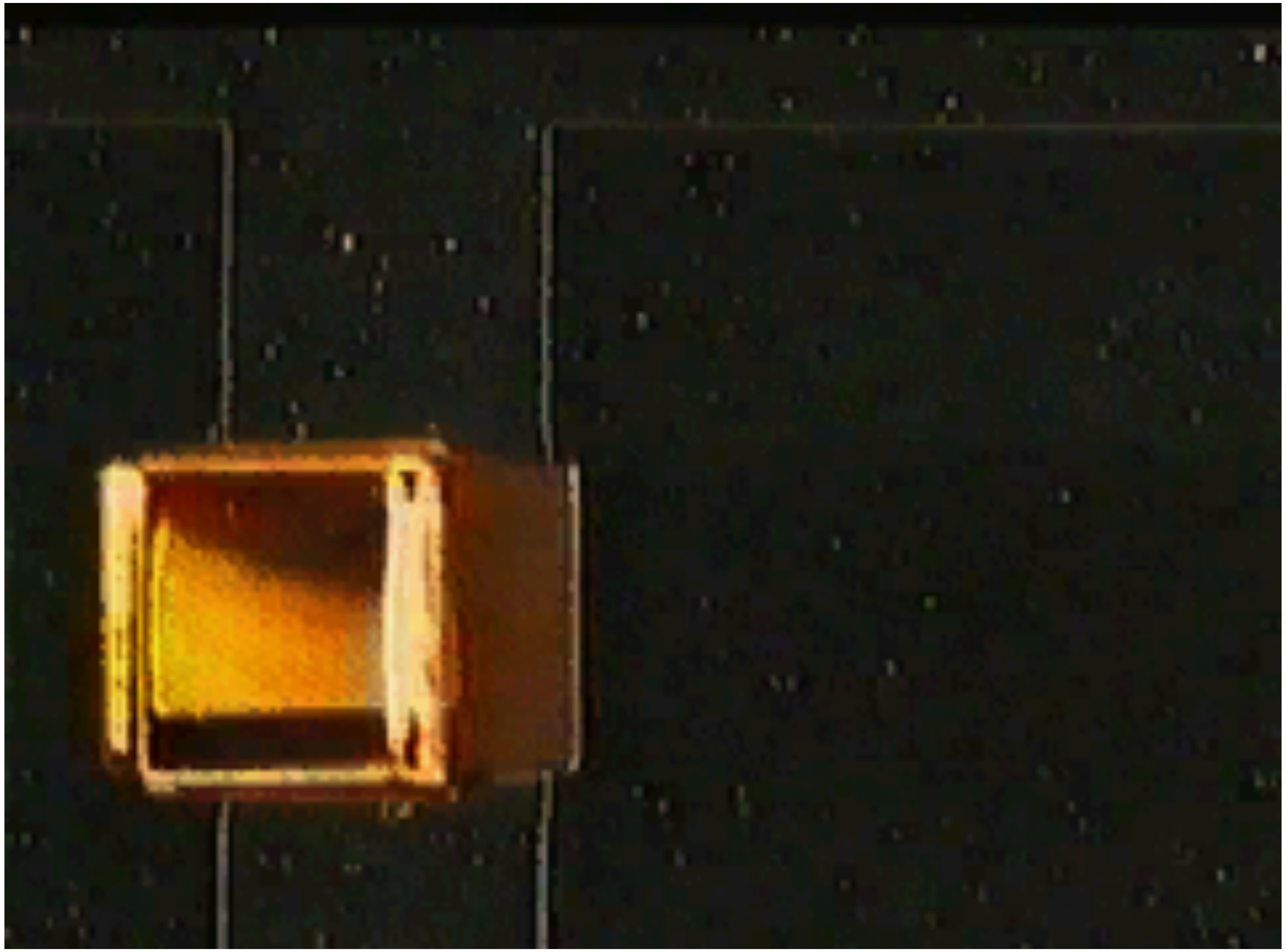

-1 e-
LIGHT
DELOCALIZED
EXCITATION

The exciton concept

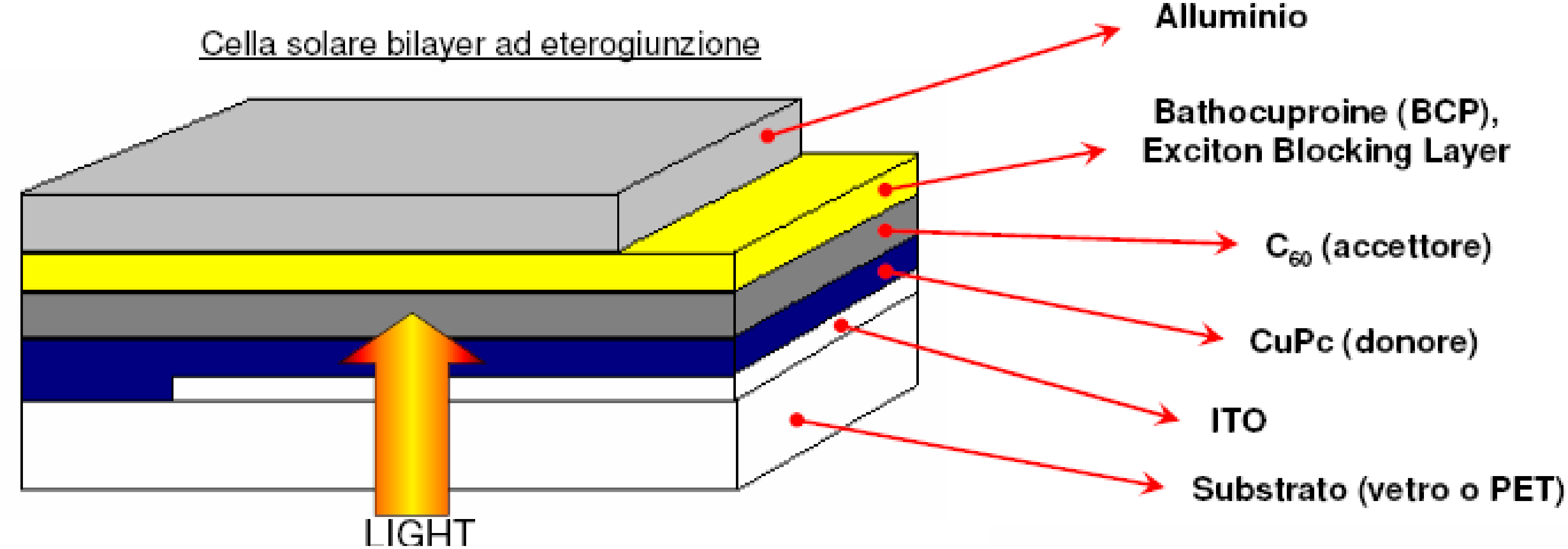




The charge transfer process induces structural distortions, the charges are not free to move



The Heterojunction cell

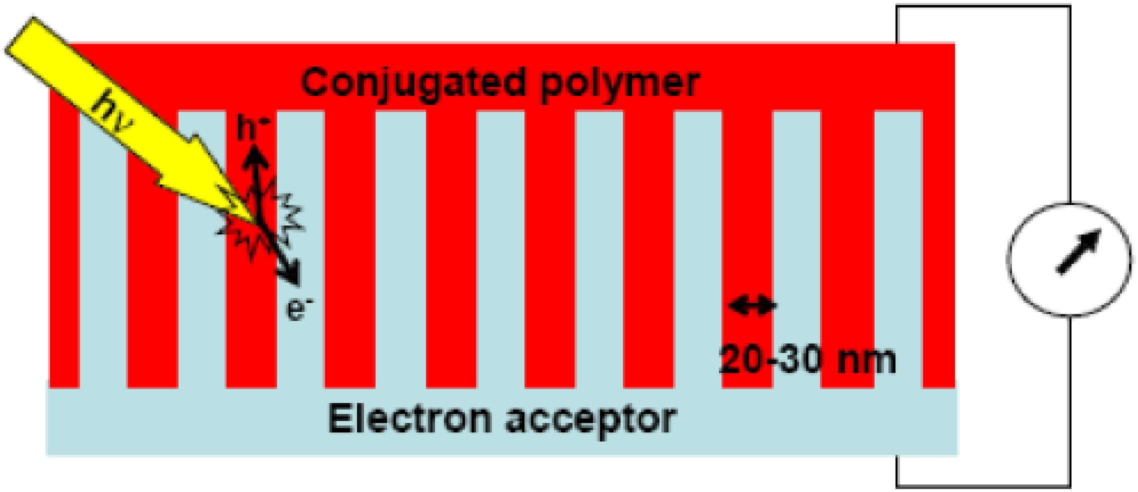


Where is the nano part?

Exctiton diffusion length is in the order of 10 nm, only excitions formed at nanometric distance from the interface can efficiently generate charges

The device active portion is just a very thin (nanoscopic) bilayer. Very low efficiency

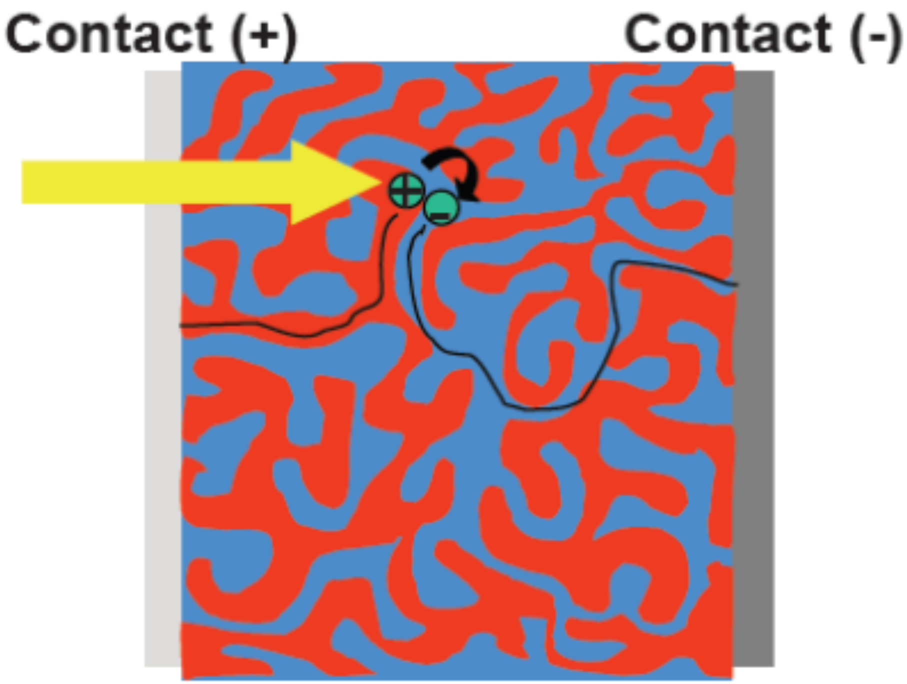
A Desirable Configuration for an Organic Solar Cell



Possible approach: self assembly, use of block-copolymers, learning from nature (use of hydrogen bonded structures)

The Bulk-Heterojunction cell

The idea: to have a distributed surface all over the bulk of the active layer

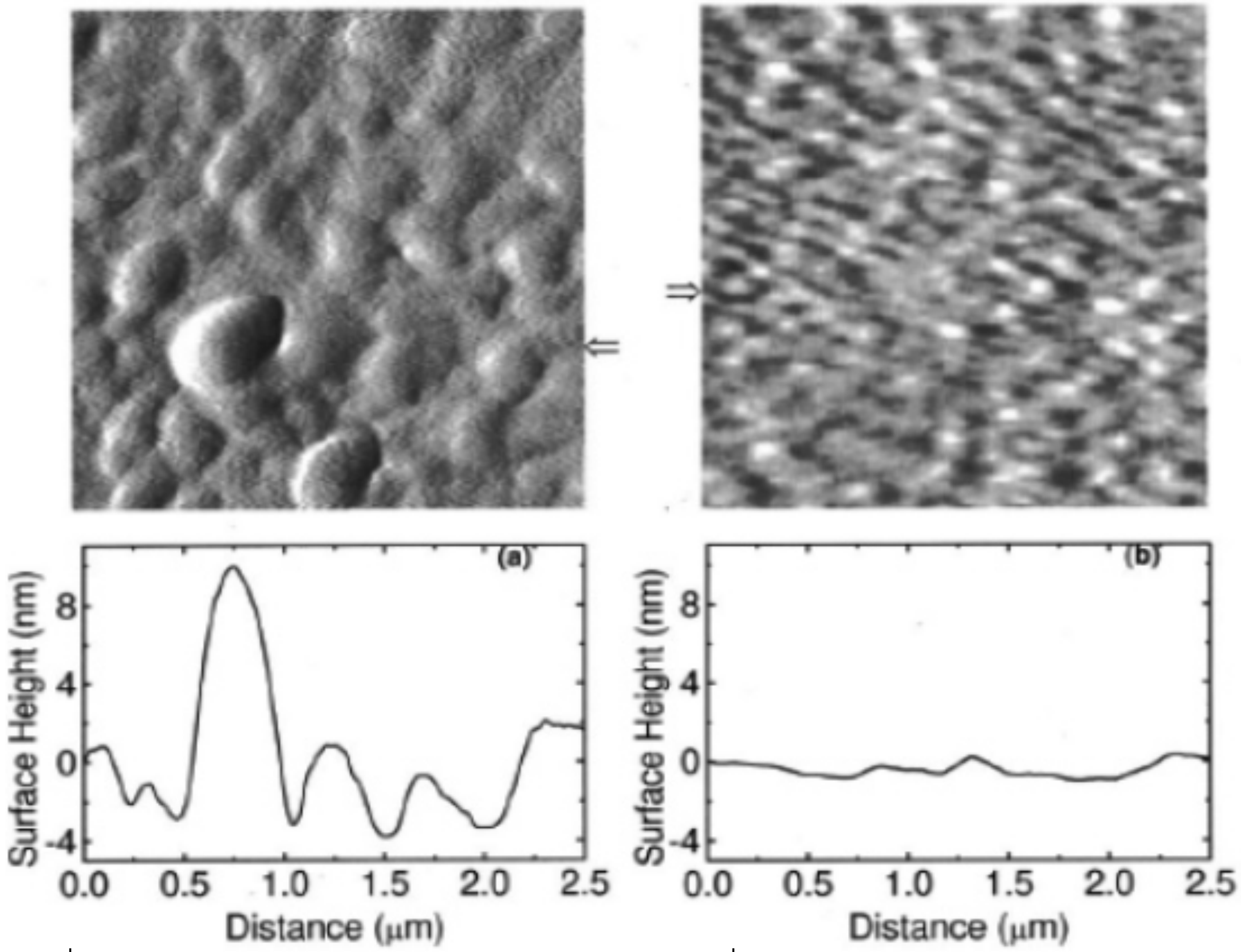


The ideal phase separation should provide 10-20 nm wide channels connecting the two materials to the corresponding electrode

Codeposition of donor and acceptor under controlled conditions

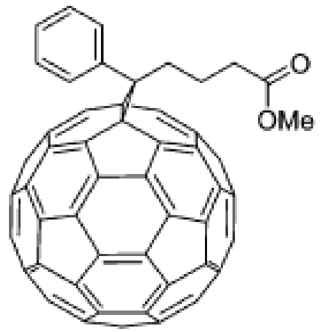
Critical parameters: solvent, deposition conditions (spin coating, doctor blade, casting..), temperature, concentration, nature of the active materials…

Role of the solvent

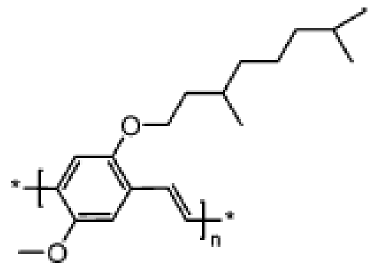


Deposition from toluene

Deposition from chlorobenzene



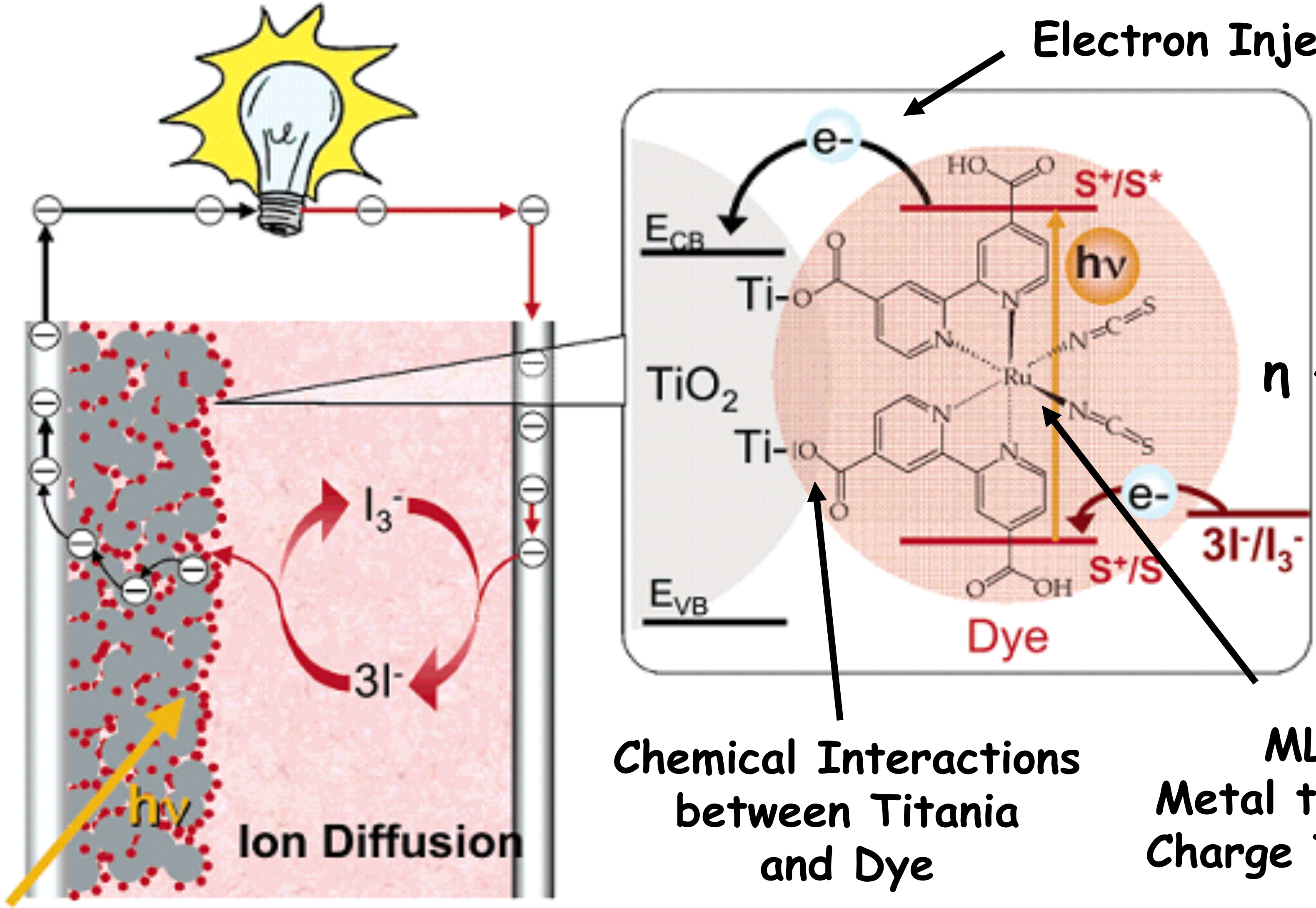
PCBM



MDMO-PPV

Grätzel solar cells

Electron Injection



η ~ 10.4%

Chemical Interactions between Titania and Dye

MLCT
Metal to Ligand Charge Transfer

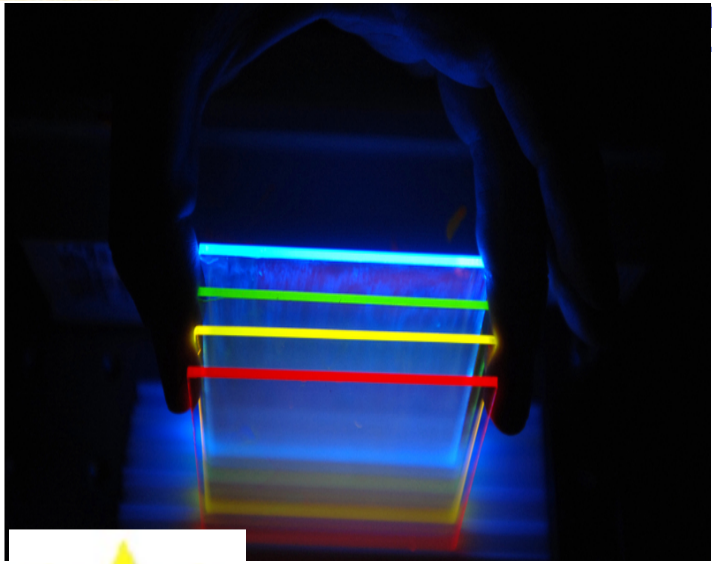
Michael Grätzel, *Chemistry Letters, 34, No.1(2005)*


TDK
STAF

Total reflection

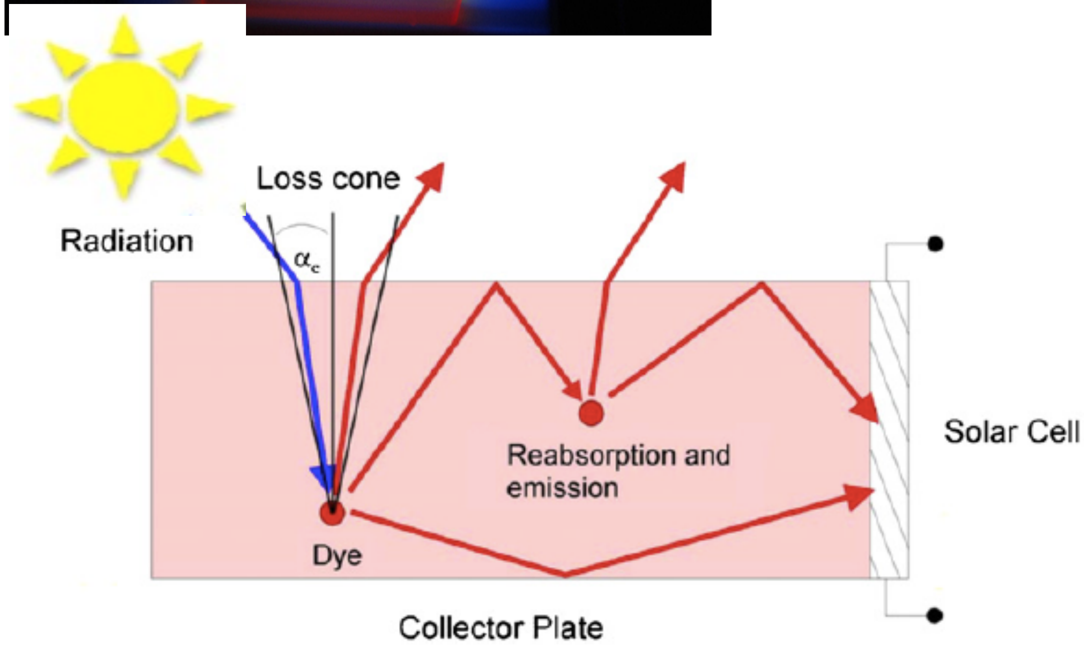
$$\theta_{\text{crit}} = \arcsin\left(\frac{n_2}{n_1}\right)$$

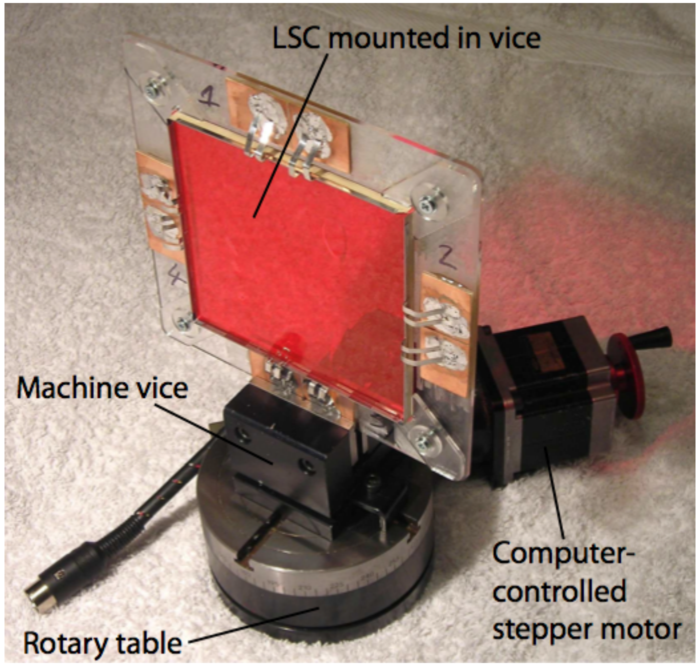
LUMINESCENT SOLAR CONCENTRATORS



Slabs of transparent materials doped with luminescent molecules/nanoparticles

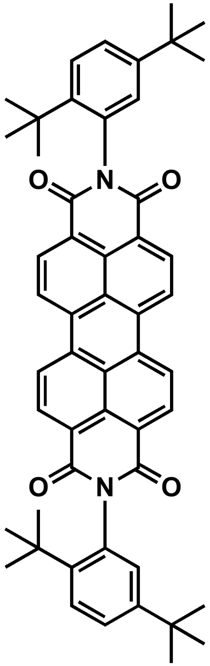
- Inexpensive materials (Polymers, glass)
- Reduced amount of expensive PV cells
- Large scale and building integration (Building integrated photovoltaics)
- Compatibility with diffuse illumination conditions

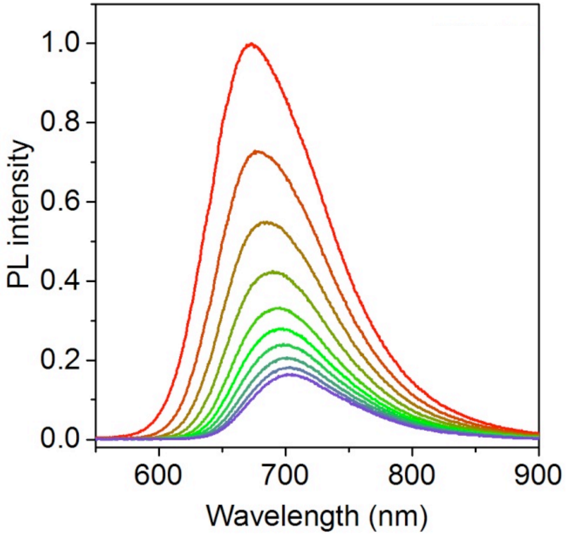


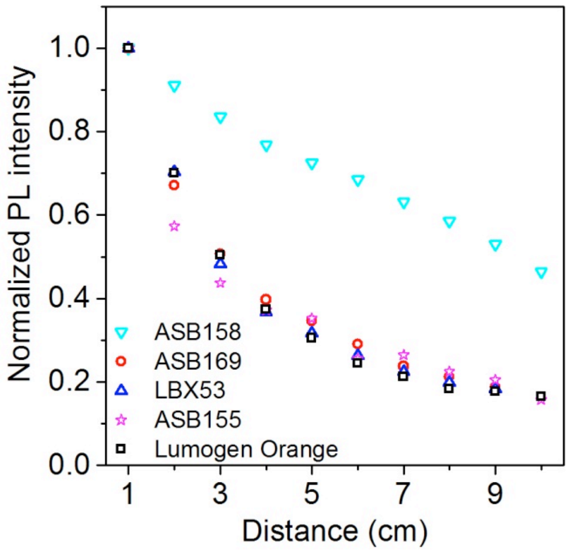


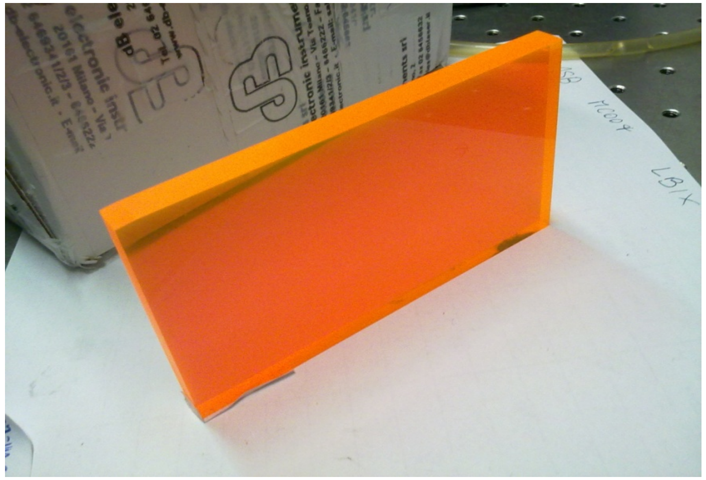
Goldschmidt, J. C. *et al.*, *Solar Energy Materials & Solar Cells*, 2009, *93*, 176

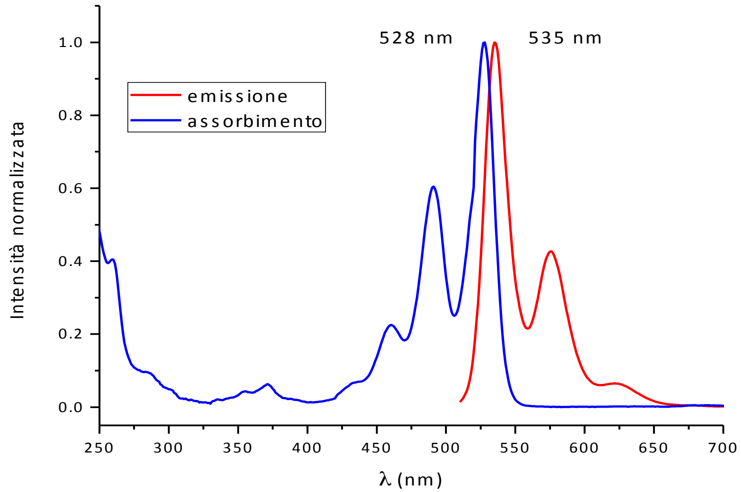
Re-absorption and emission efficiency





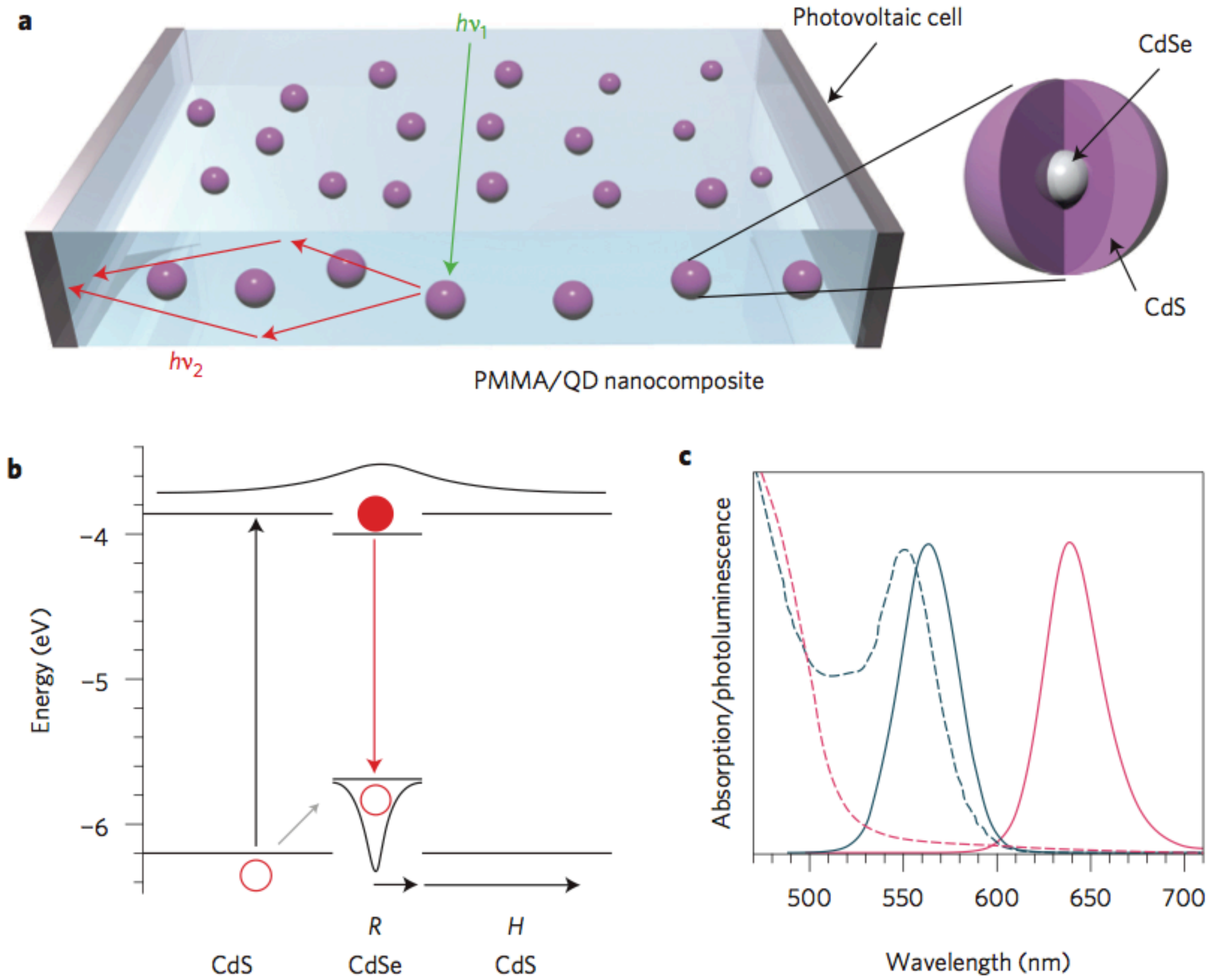


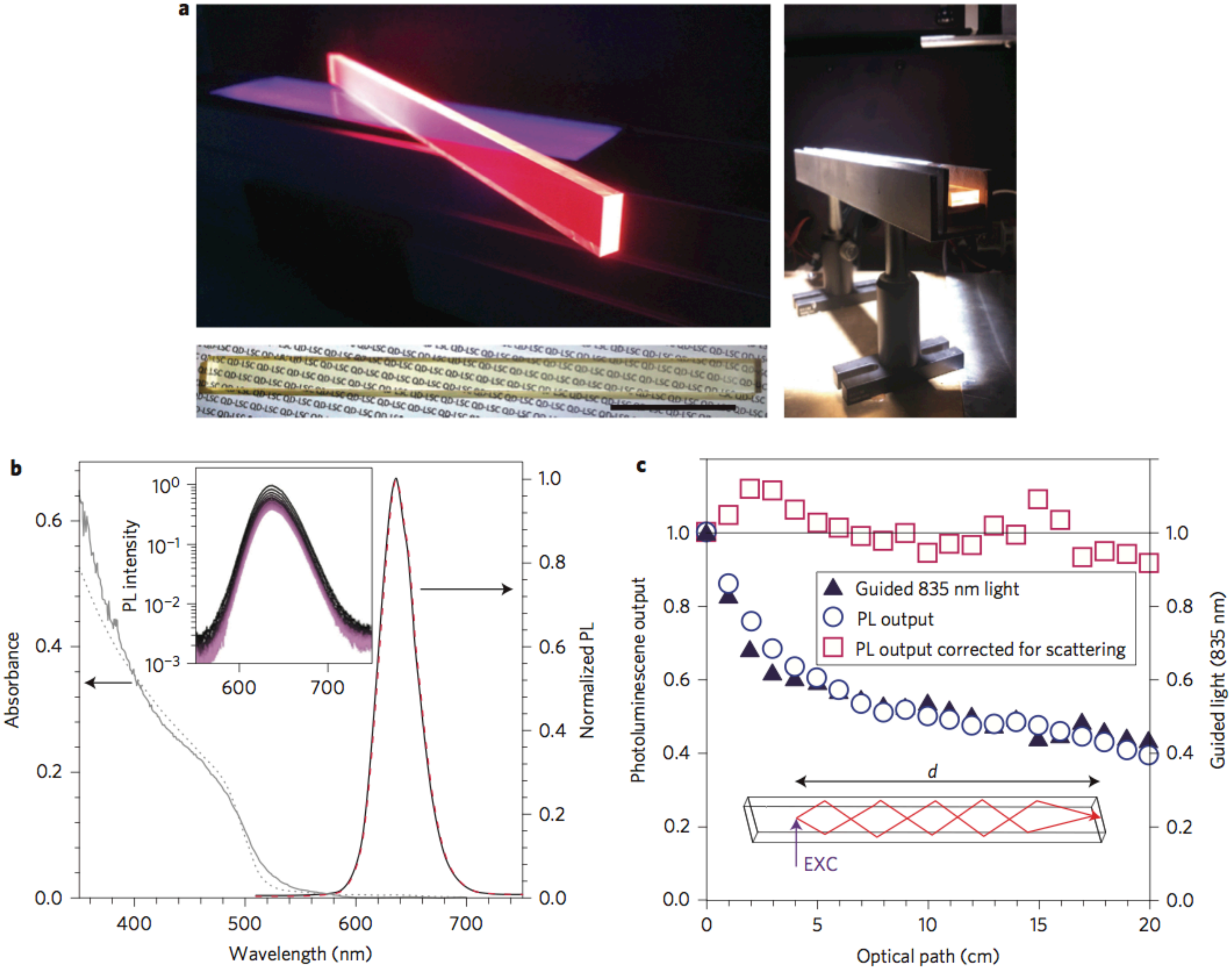




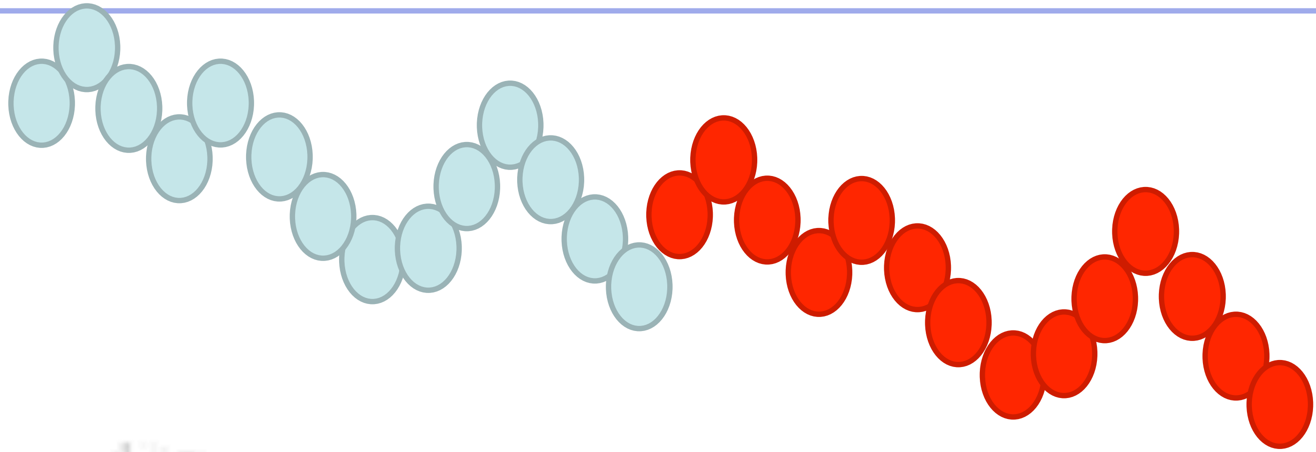
Quantum yield up to 99 %

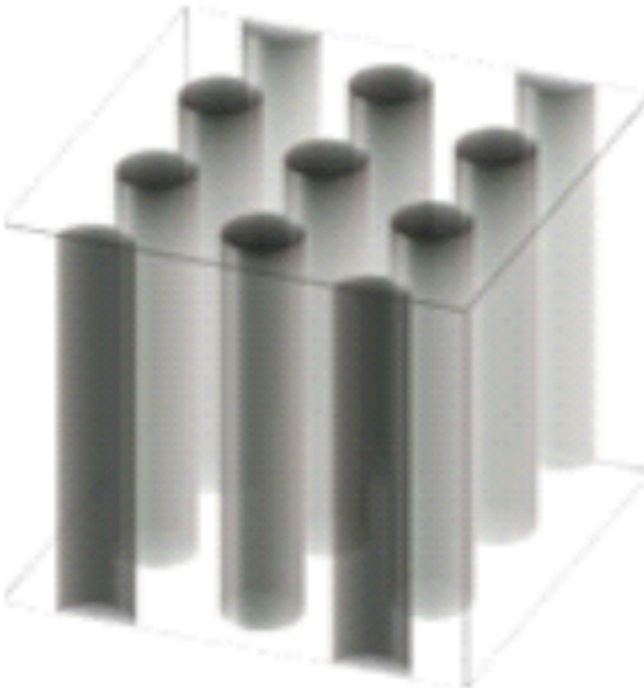
LSC and Quantum Dots

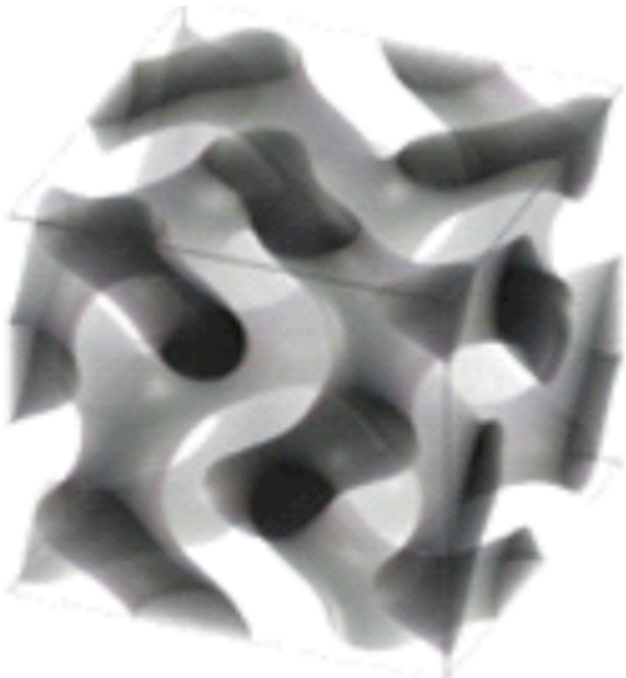




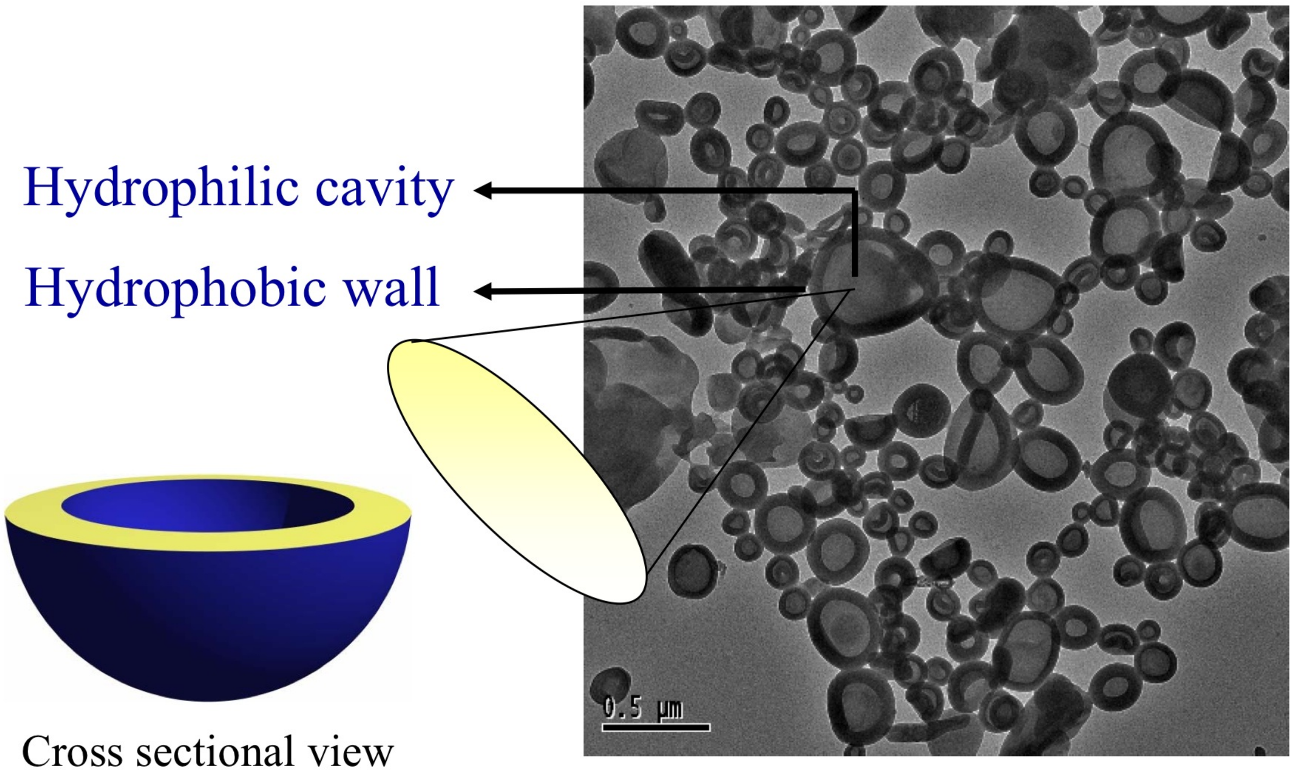
Meinardi, F. et al., 2014. Large-area luminescent solar concentrators basedon "Stokes-shift-engineered" nanocrystals in amass-polymerized PMMA matrix. Nature Photonics, pp.1–8.





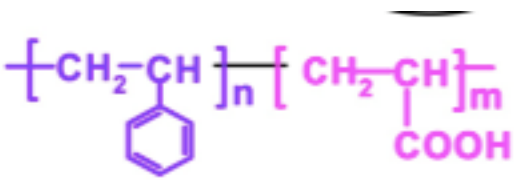


Active Loading into Vesicles



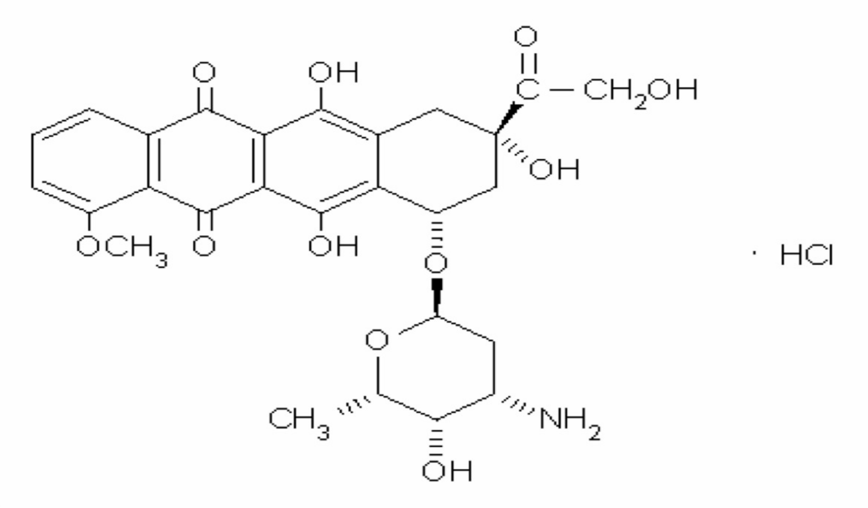
Cross sectional view

Vesicles prepared from 0.5 % (w/w) Polystyrene$_{310}$-*b*-poly(acrylic acid)$_{36}$ in dioxane



What's DXR

- DXR.HCl: doxorubicin hydrochloride

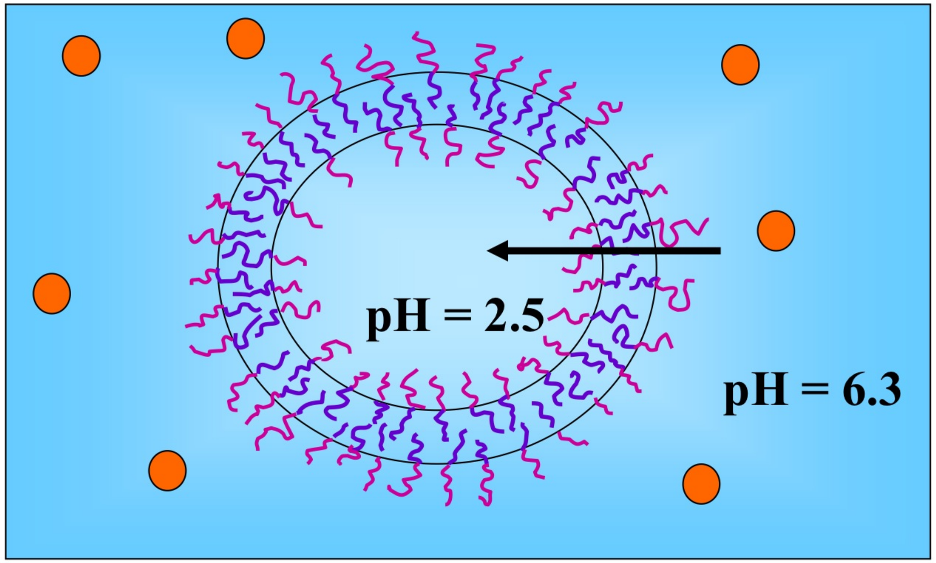


- Anti-cancer drug
- Molecular weight = 580 (g/mol)
- Water soluble (50 mg/ml)

Loading Mechanism

● = XNH_2 : neutral form can diffuse

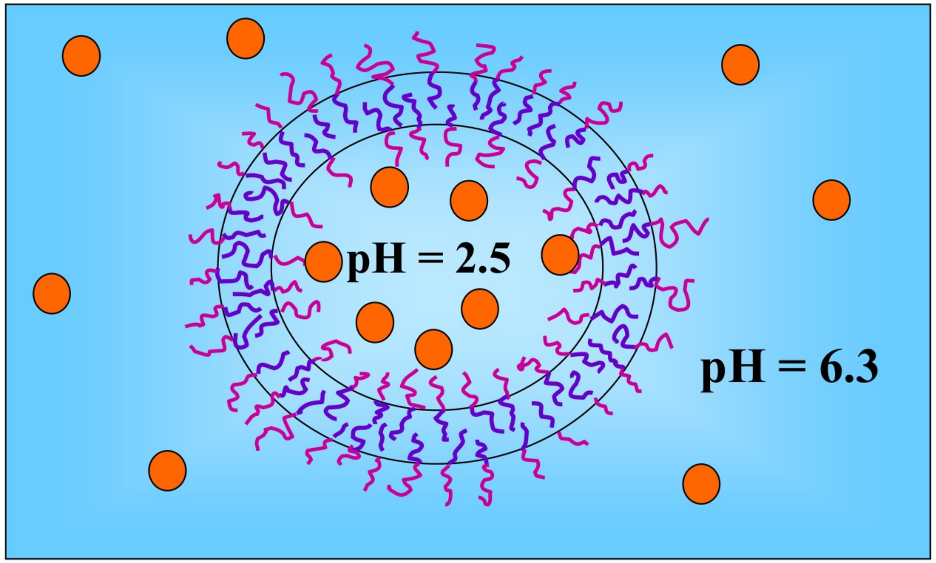
●+ = XNH^{+}_{3} : protonated form can NOT diffuse



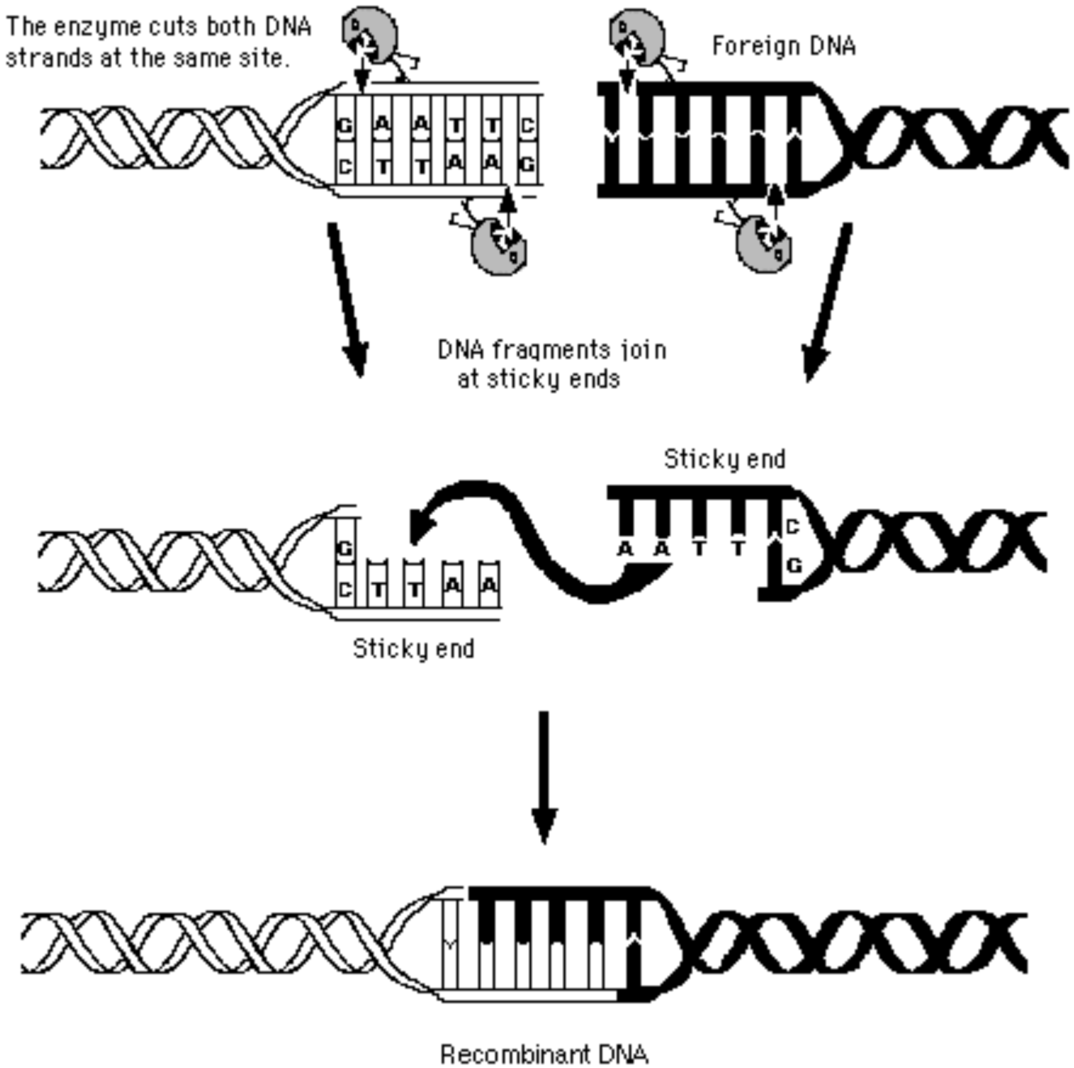
Active Loading into Vesicles

Use vesicles as model carriers for Doxorubicin

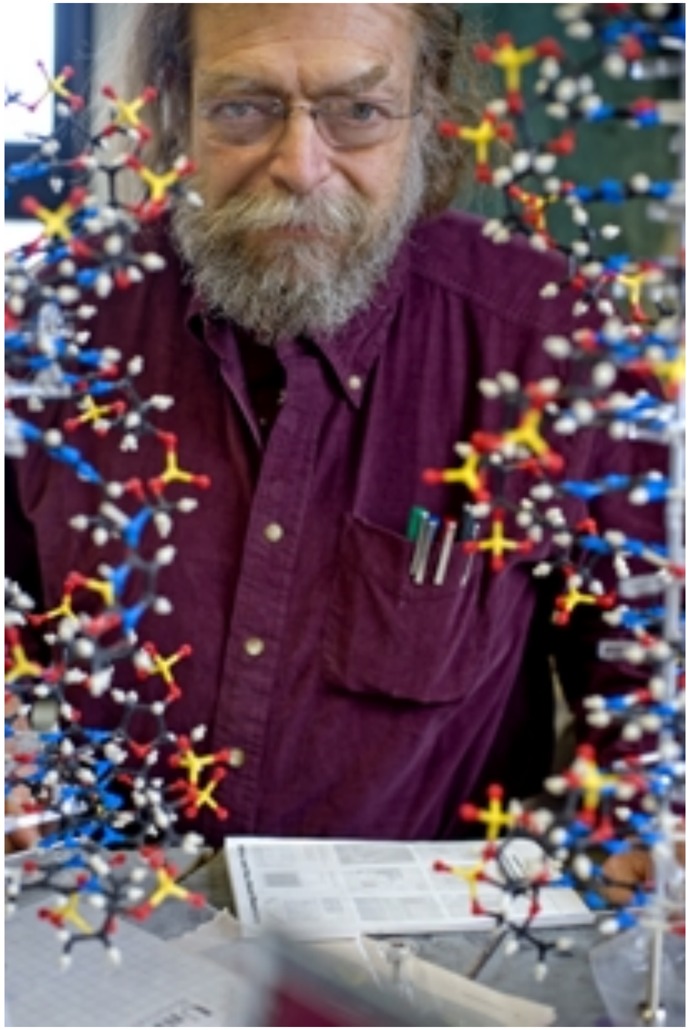
Induce loading by creating a transmembrane pH gradient

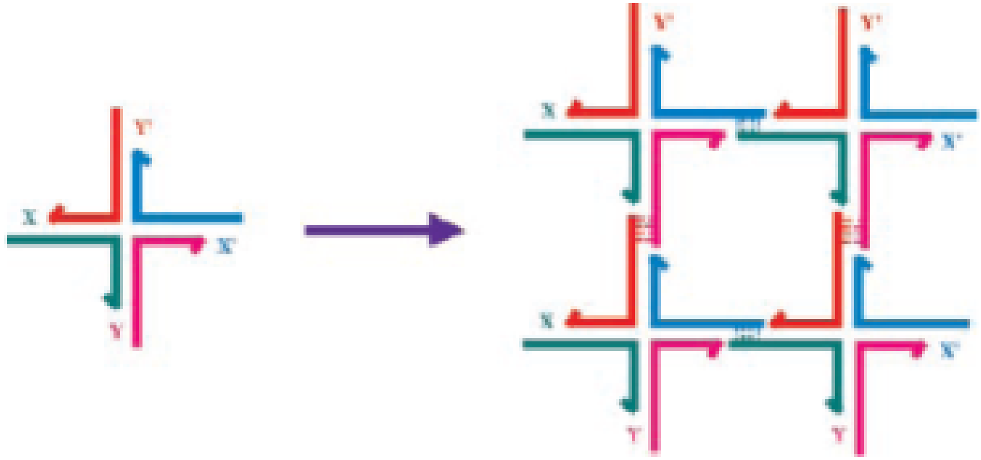


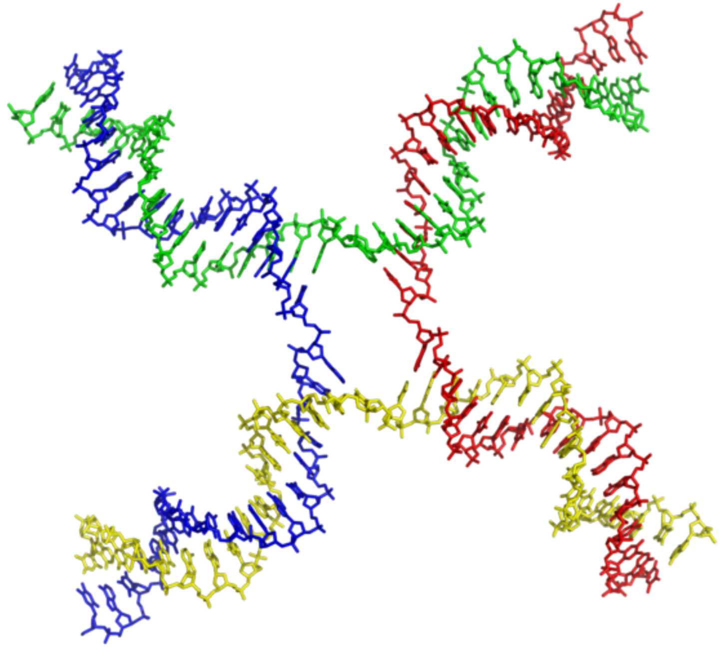
Restriction Enzyme
Action of EcoRI



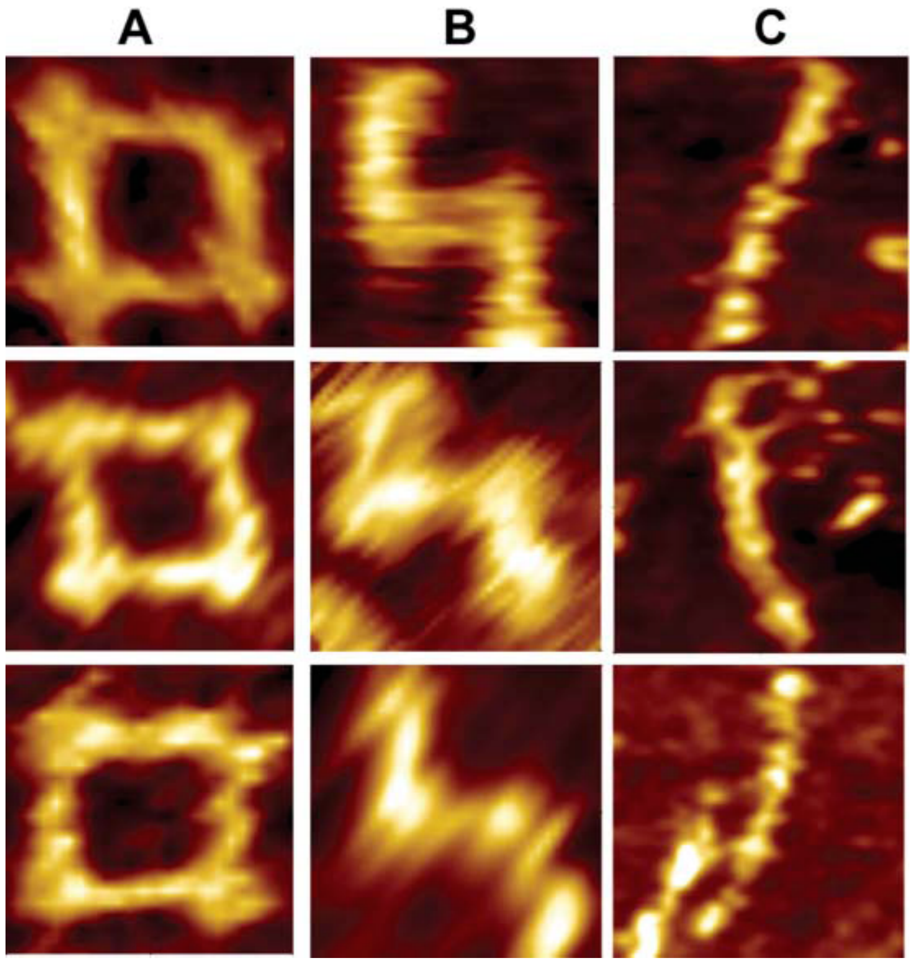
self-assembly of DNA nanostructures



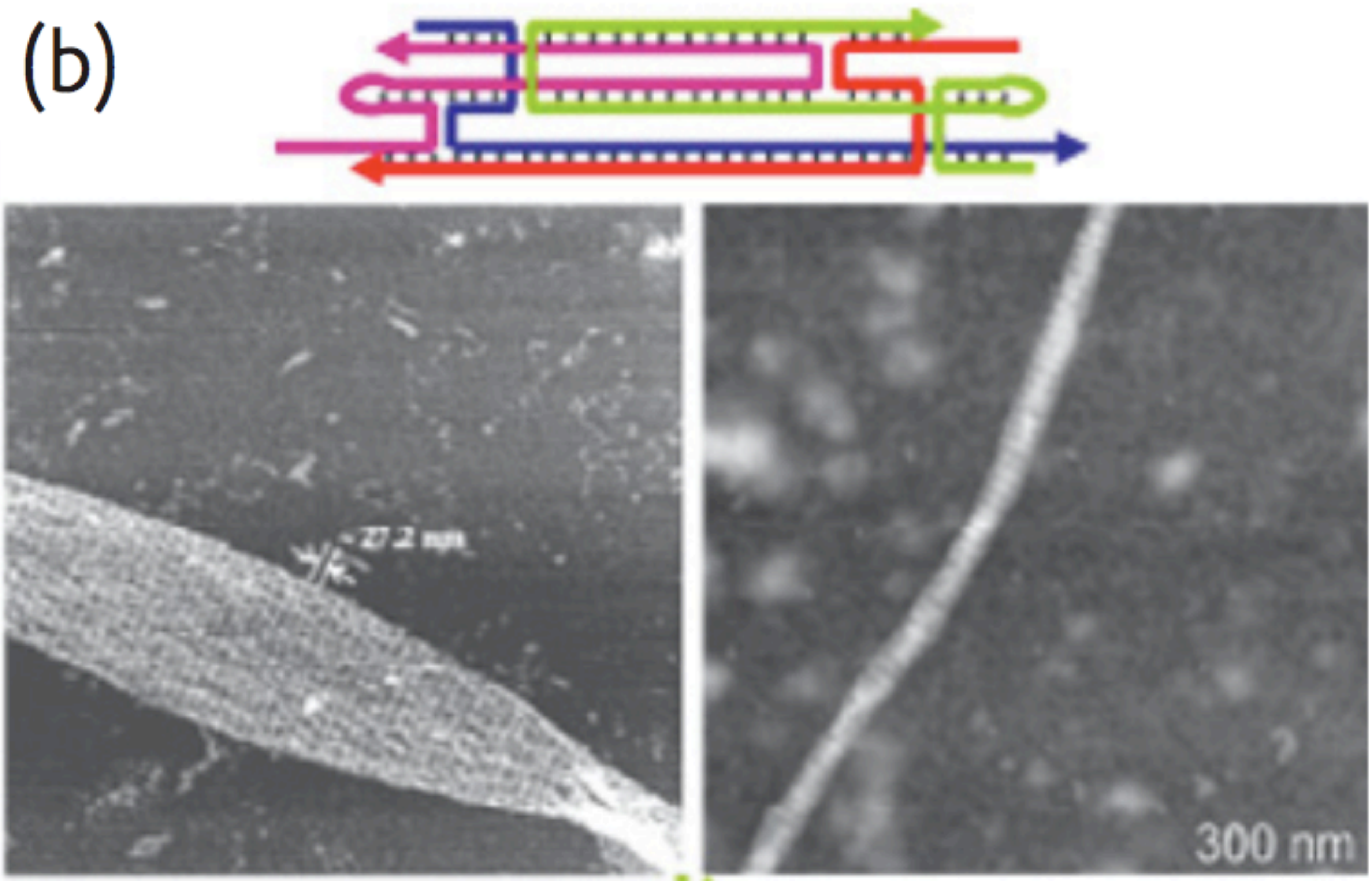




AFM pictures of DNA tiles combinations



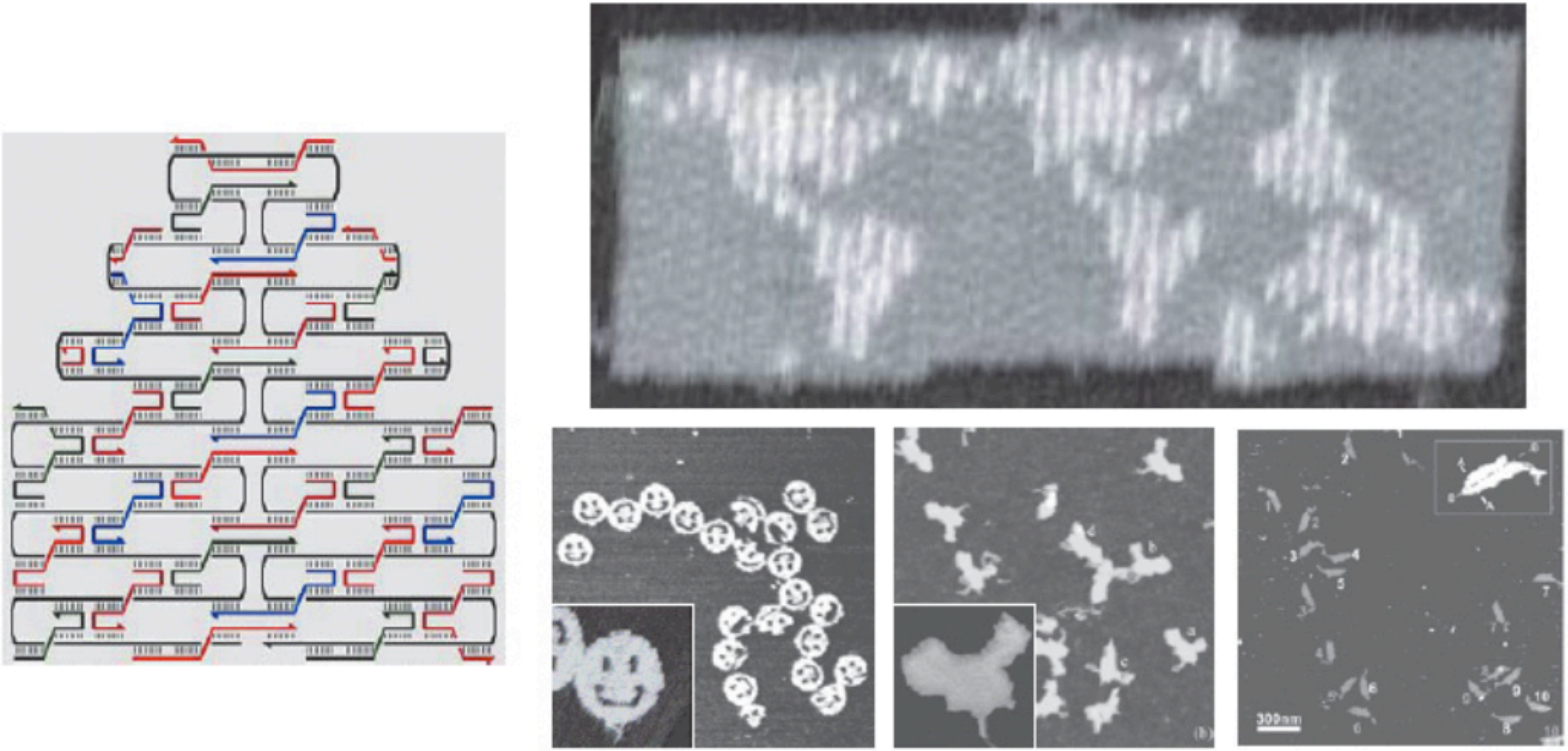
(b)



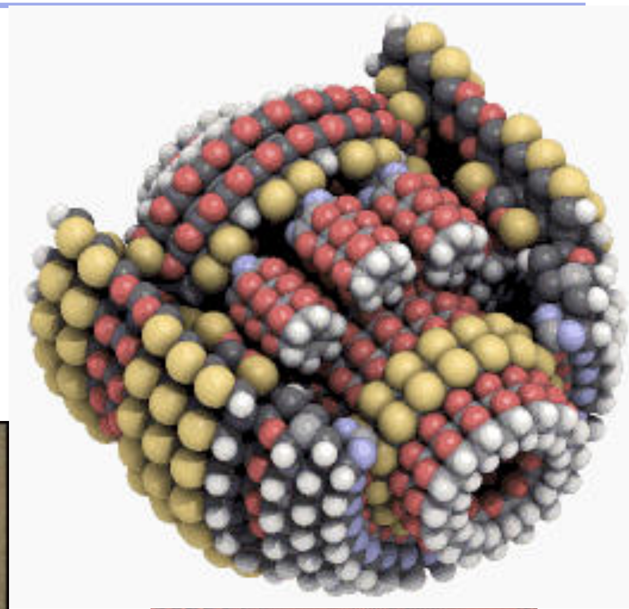
DNA triple crossover complex and resulting 2D arrays and tubes

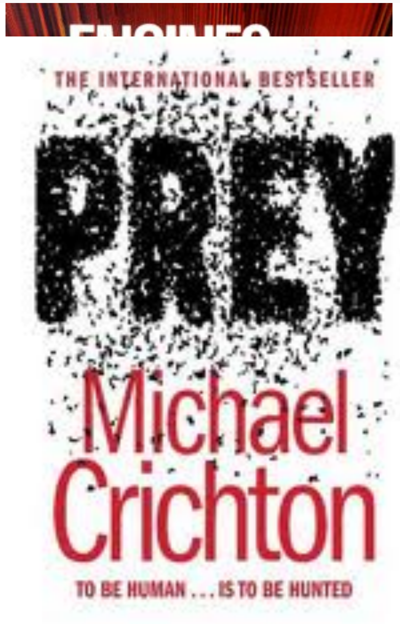
Extreme self assembly

(b)

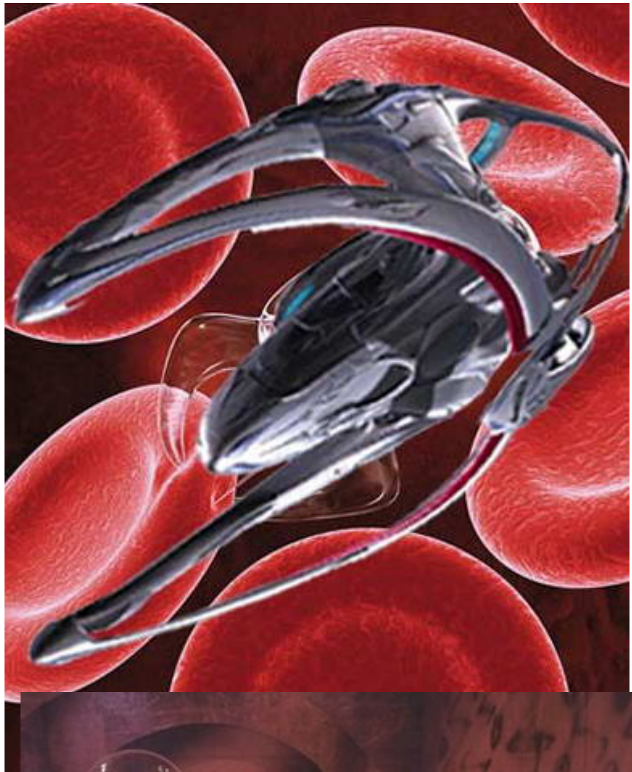


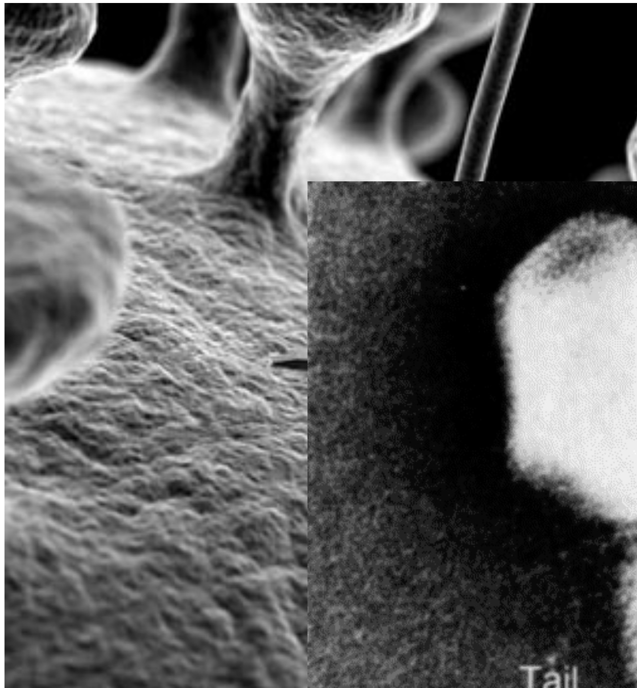
Eric Drexler and self replicating nanomachines

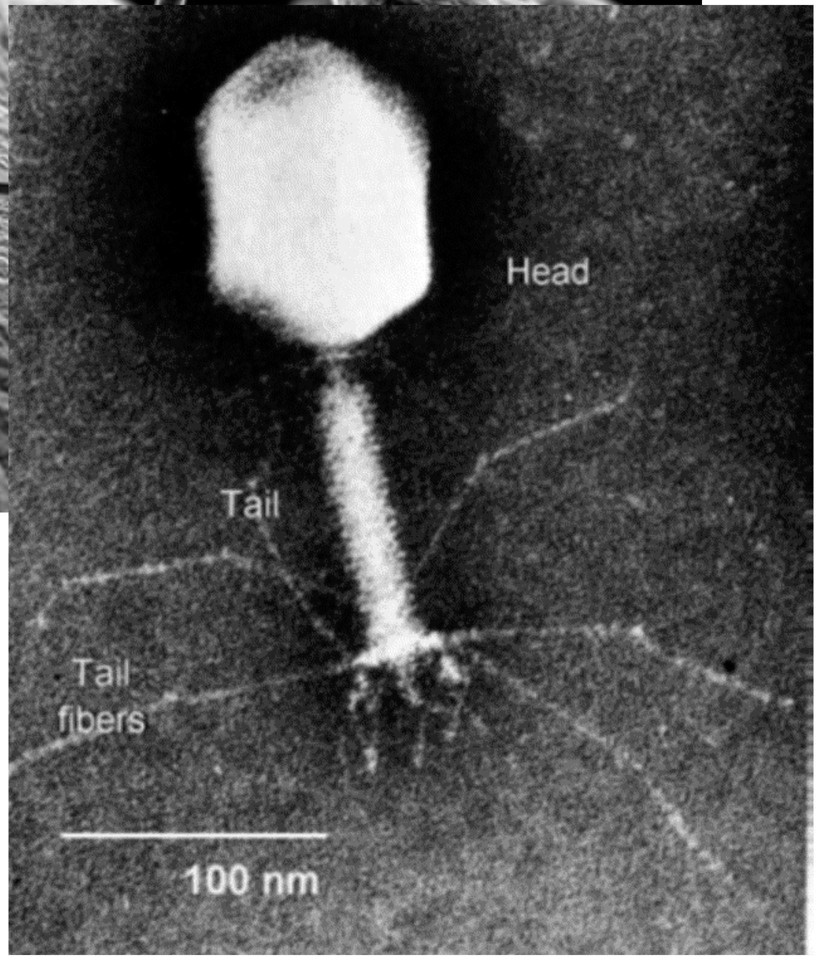




versatile
independent
deterministic
Self replicating

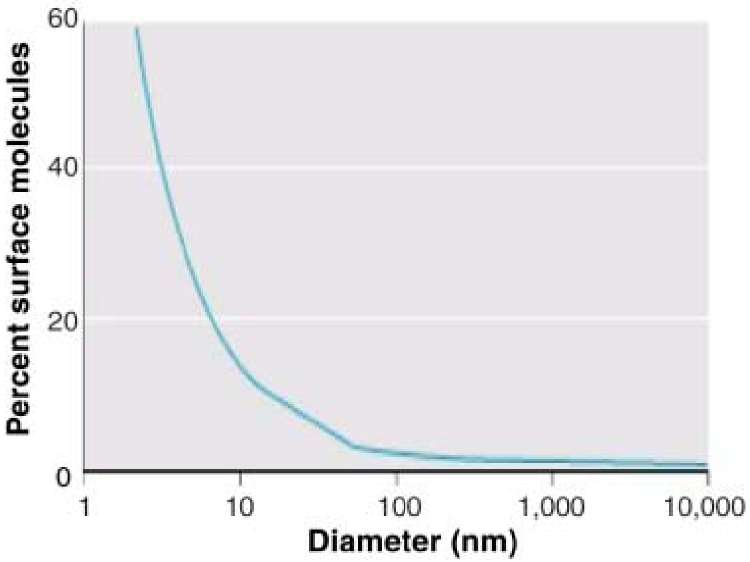




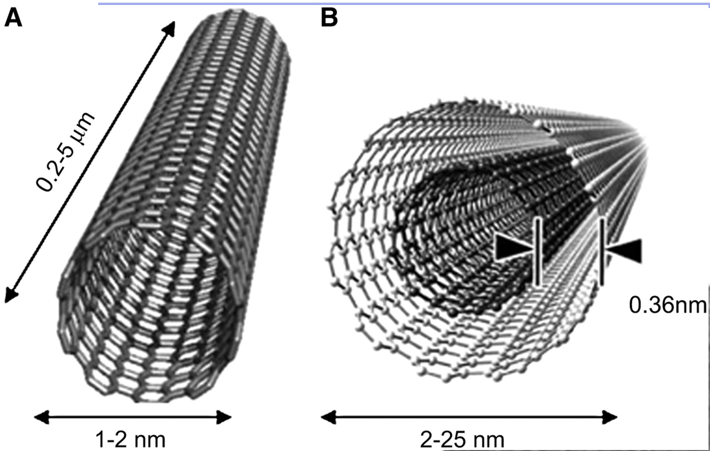

Head
Tail
Tail
fibers
100 nm

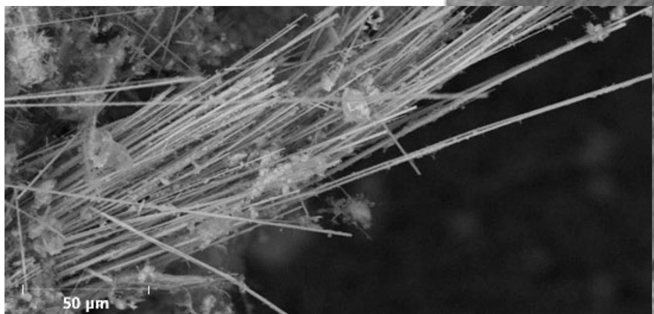
Risks ⟷ **Benefits**

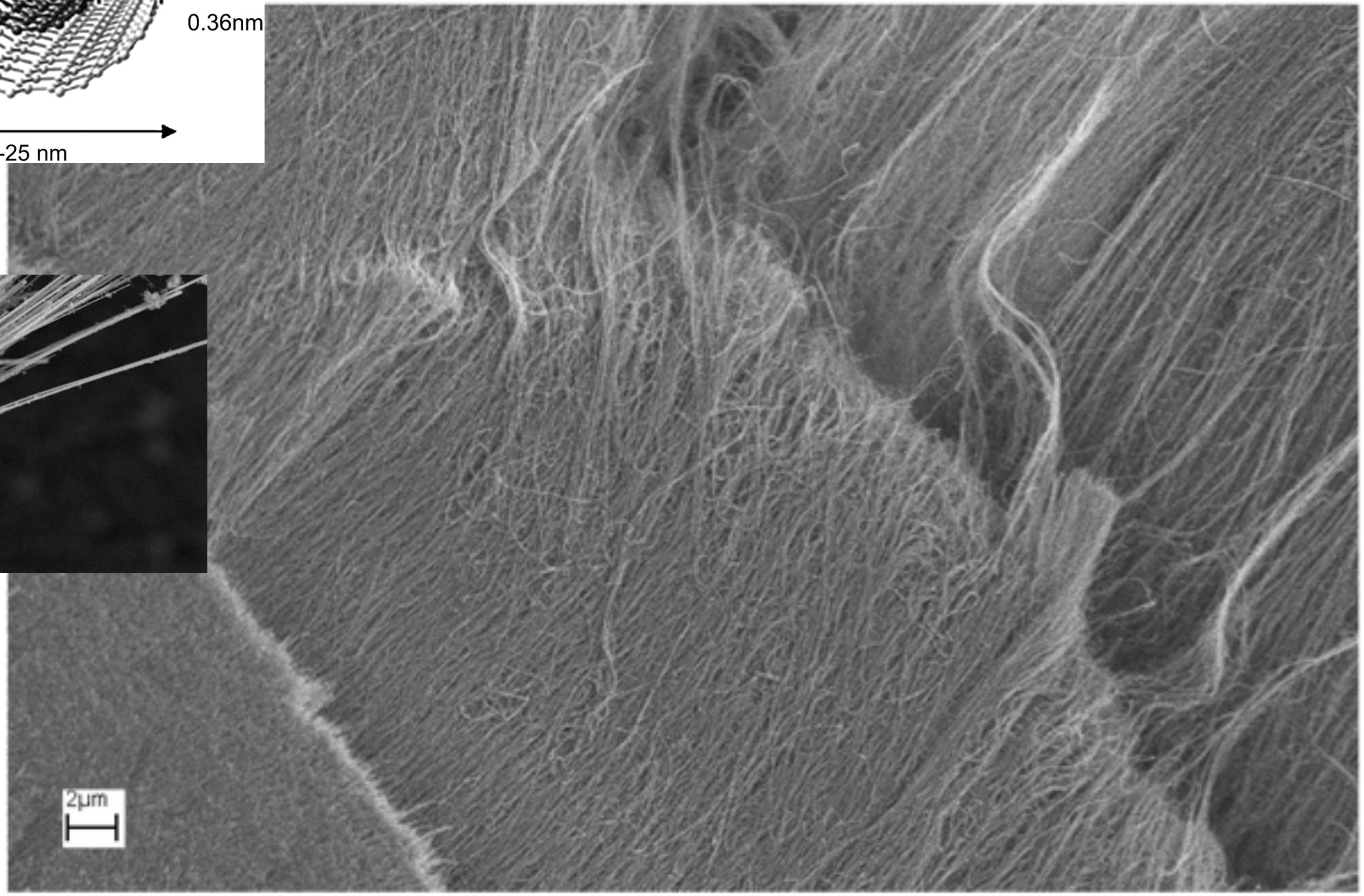
Exposed surface = chemical reactivity



Morphology and toxicity







Thanks!