



Introduzione alle nanotecnologie e aspetti applicativi

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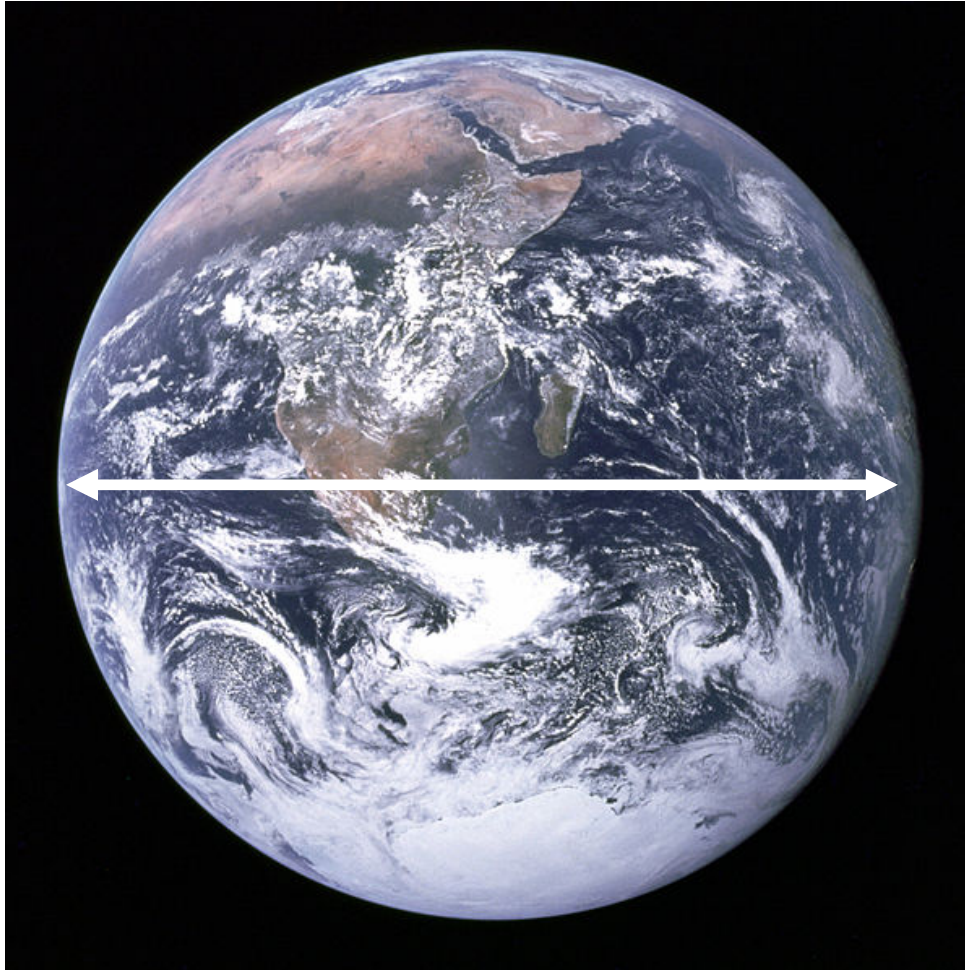
luca.beverina@unimib.it

Scale factors



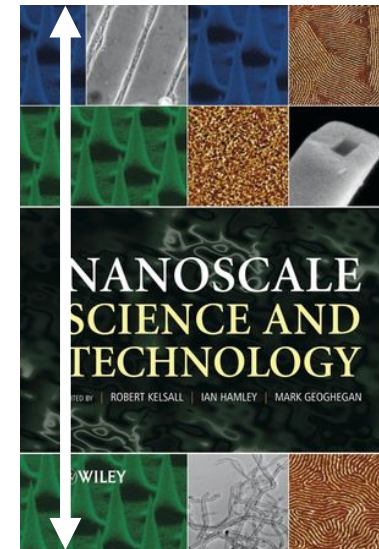
$$1 \text{ nm} = 10^{-9} \text{ m}$$

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



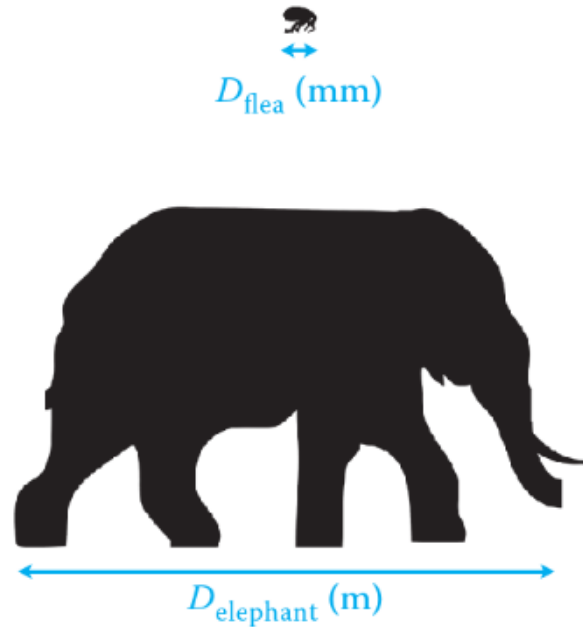
- “Physiologic” scaling-laws of classical physics
- Surface to volume ratio
- Just Size Effects
- “Pathologic” quanta-mechanical effects

Effects of size reduction



- “Physiologic” scaling-laws of classical physics
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The Elephant and the flea



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

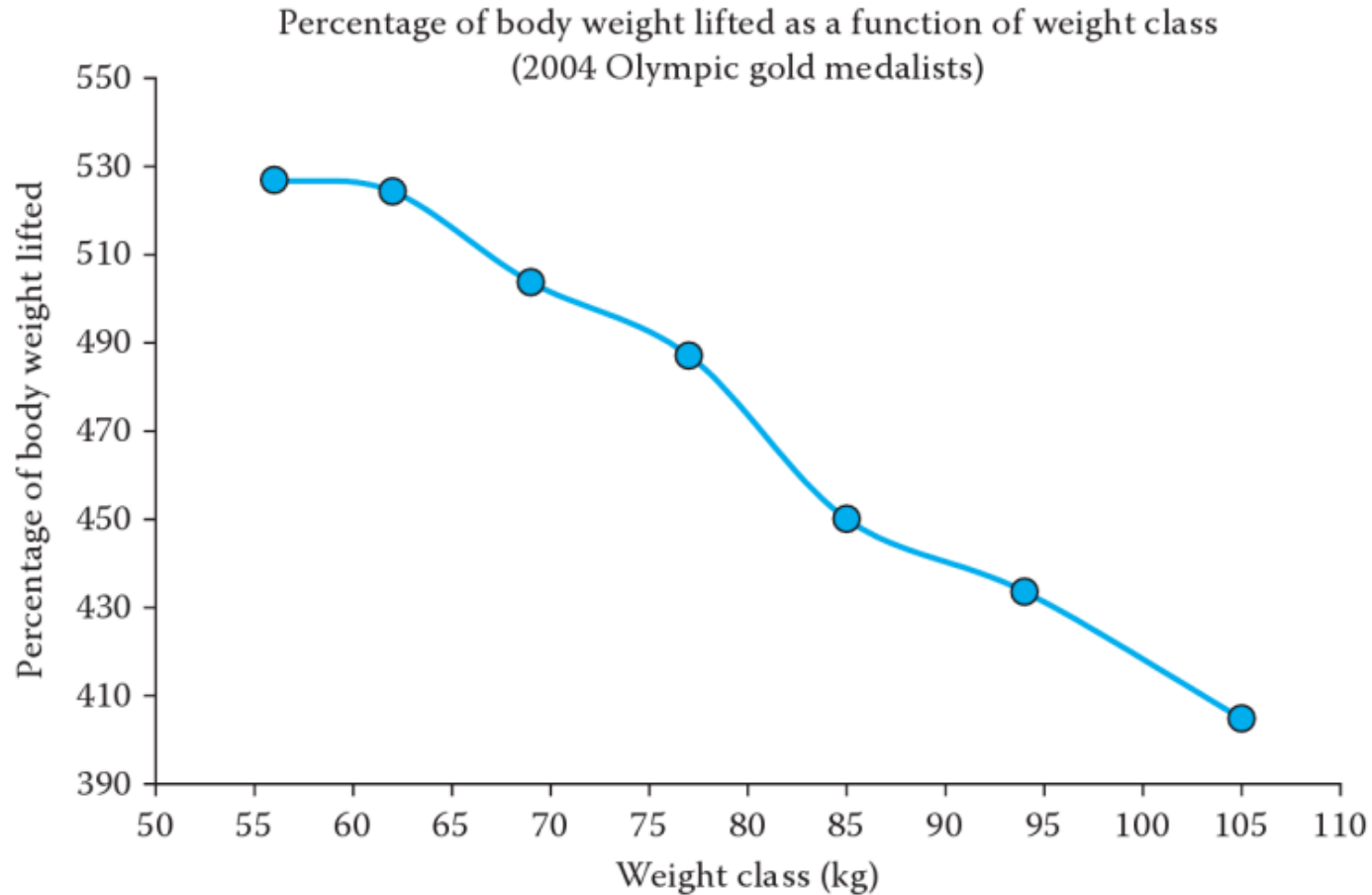
$$\text{Weight} \propto D^3$$

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

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.

Weightlifting

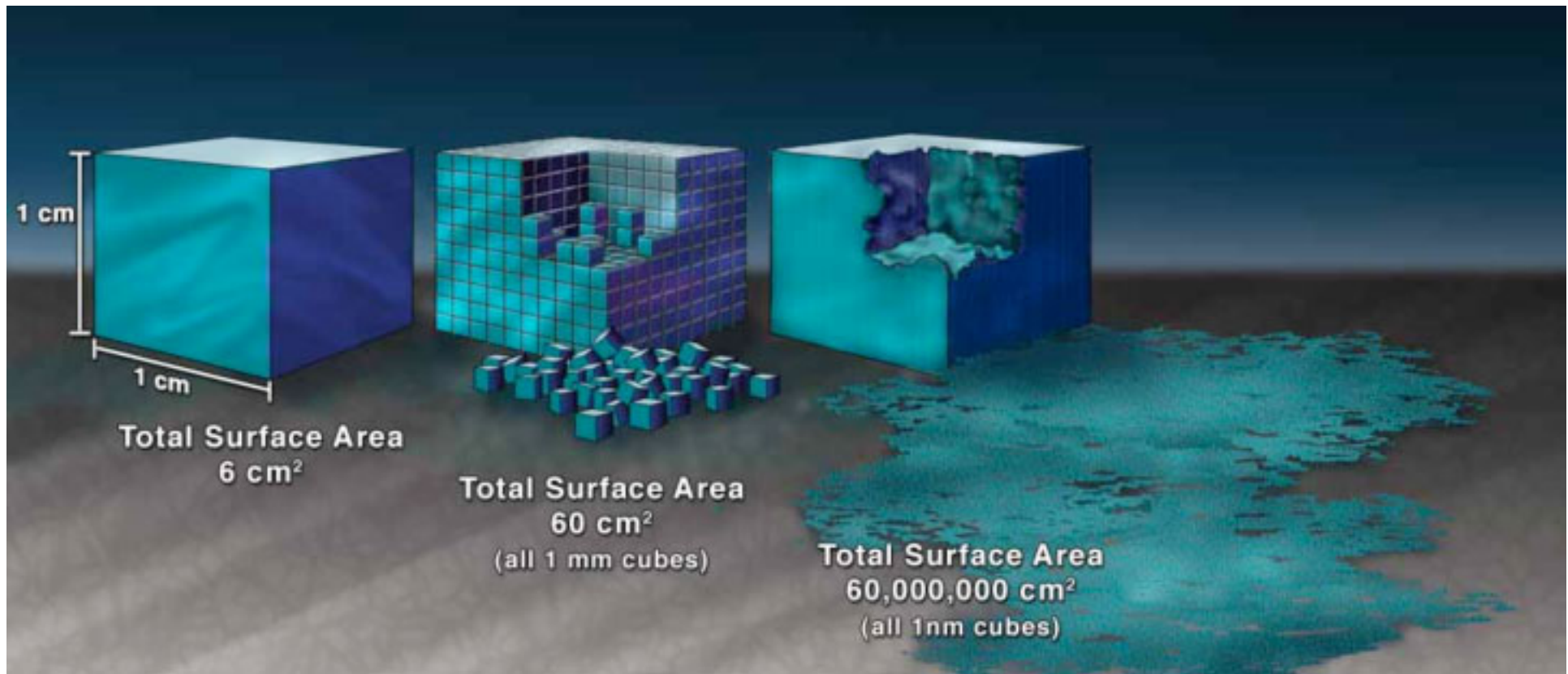


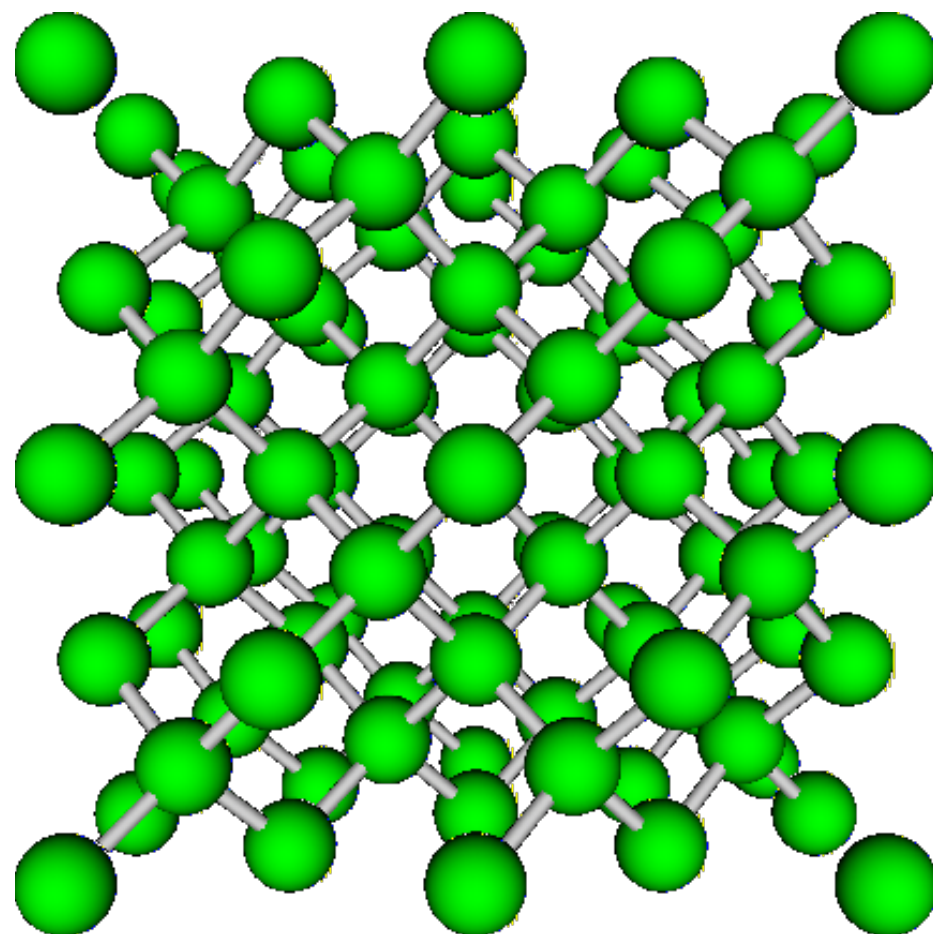
Effects of size reduction



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Surface to volume ratio

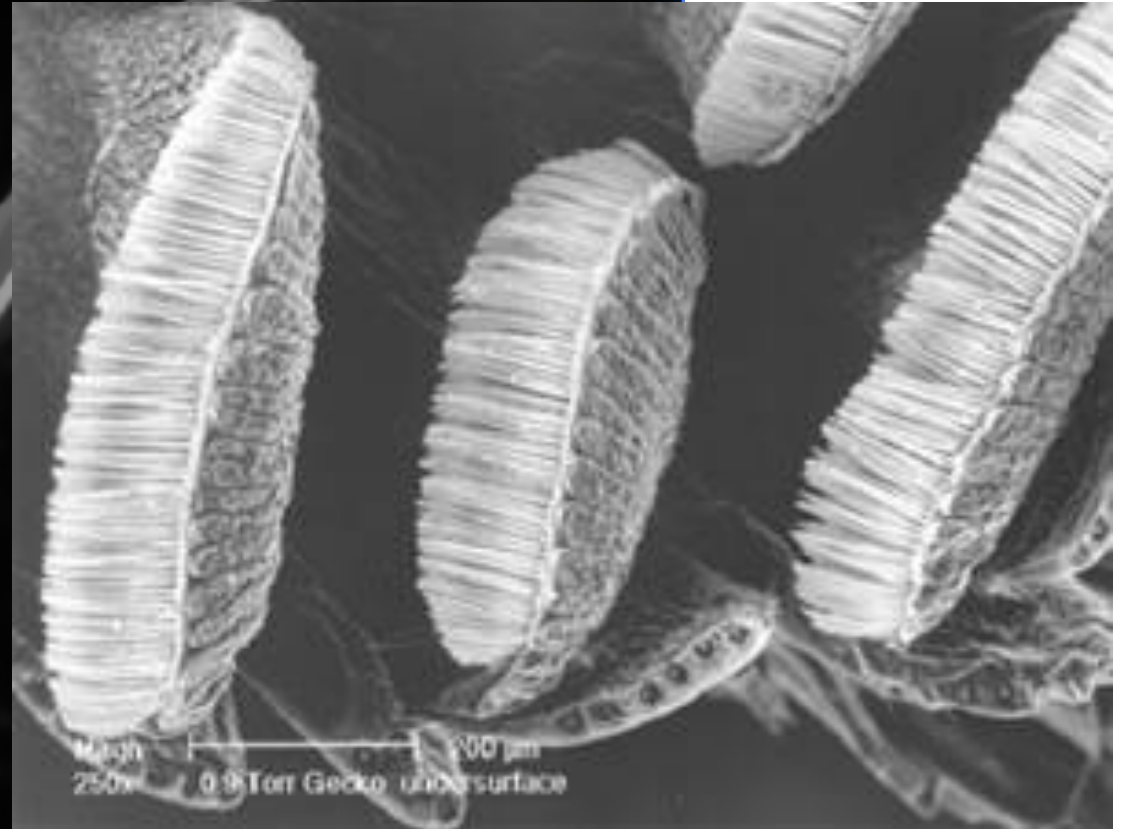
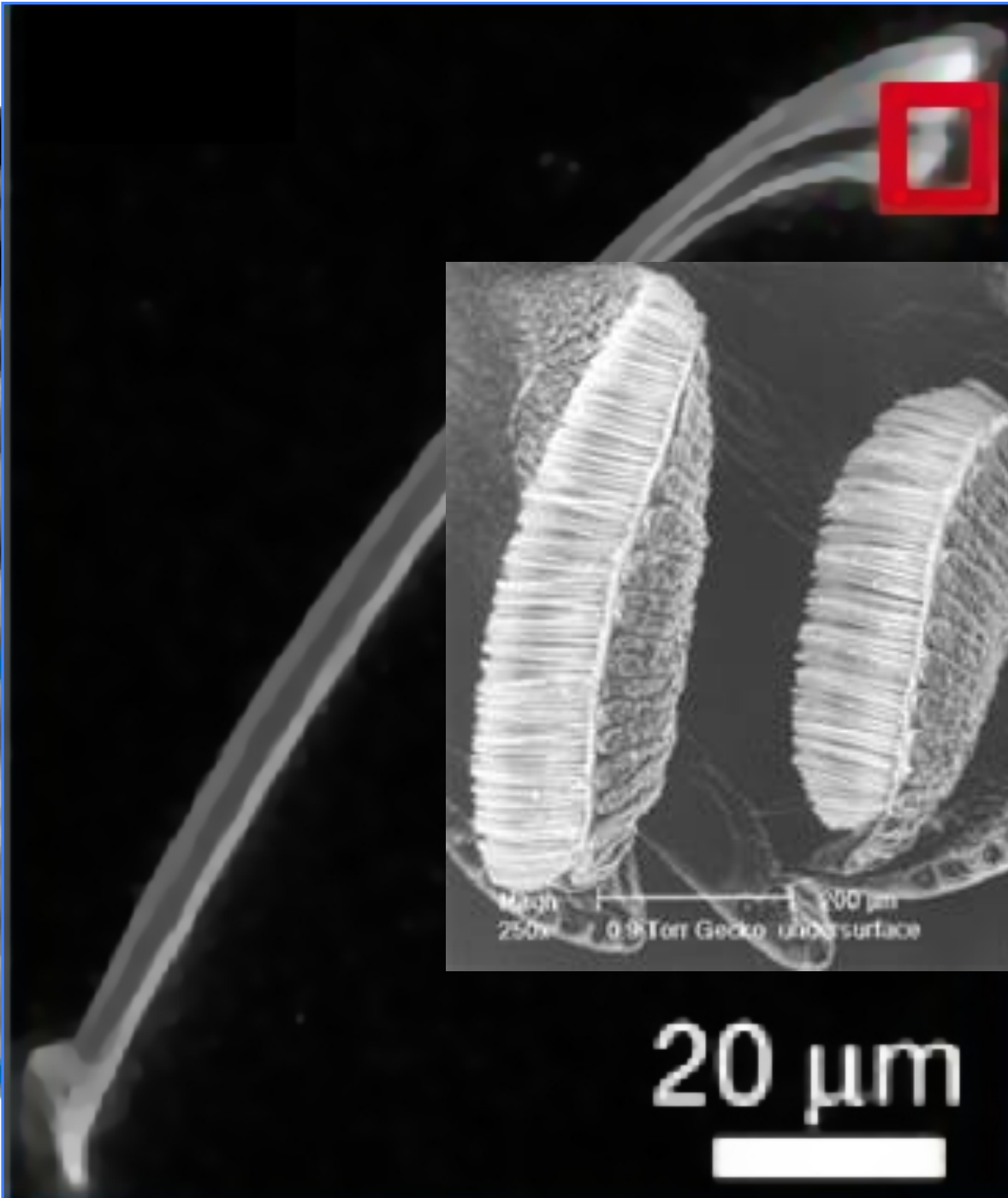




Si-H, Si-OH, Si-O-Si, ..









Effects of size reduction



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

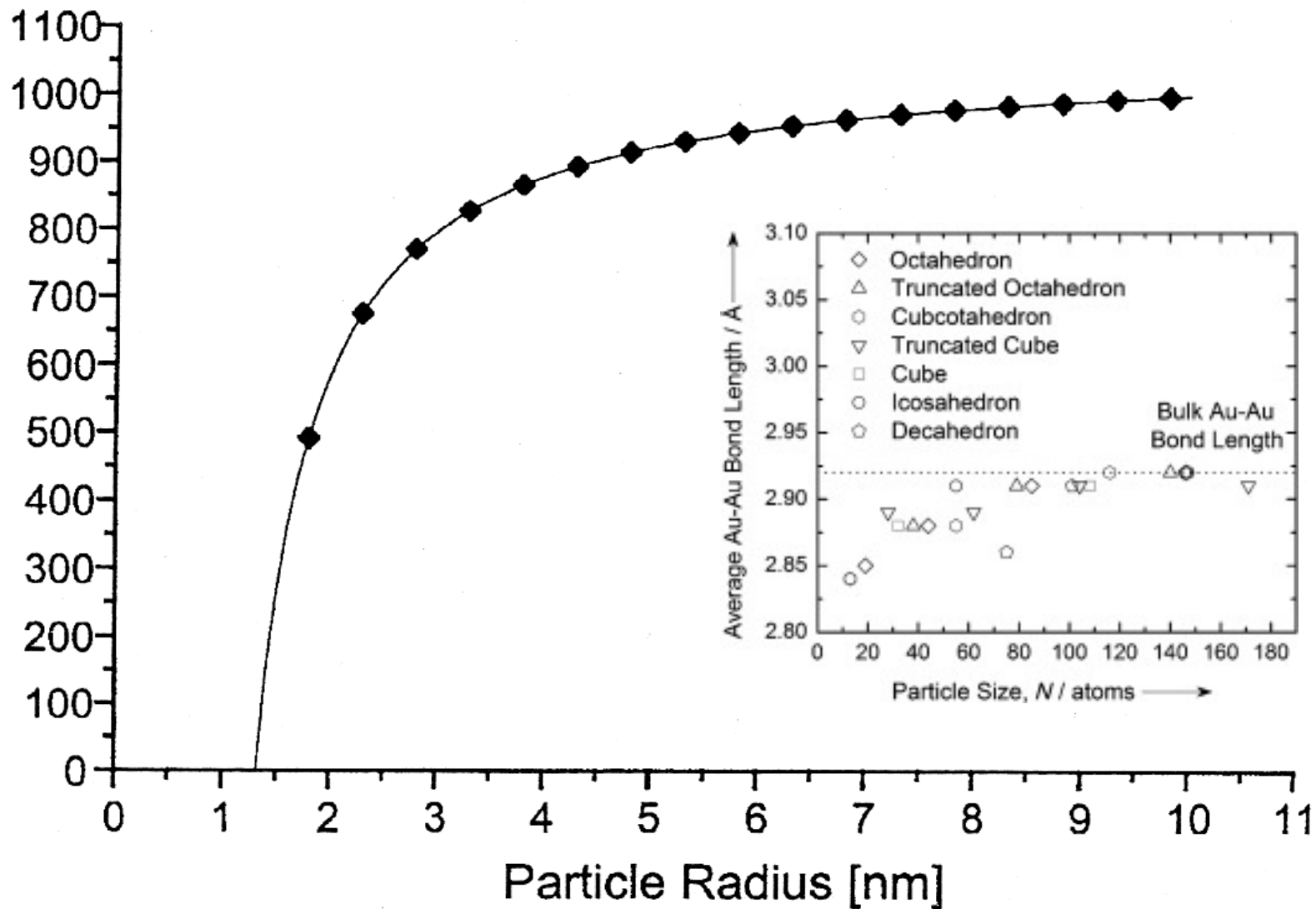


- Breakdown of thermodynamic limit $N \rightarrow \infty$
- Increase of fluctuations, esp. @ critical points
- Mean values (intensive quantities) are less significant
- Additivity of extensive quantities (S) breaks down

Size dependent melting point



Melting Point [°C]



Effects of size reduction

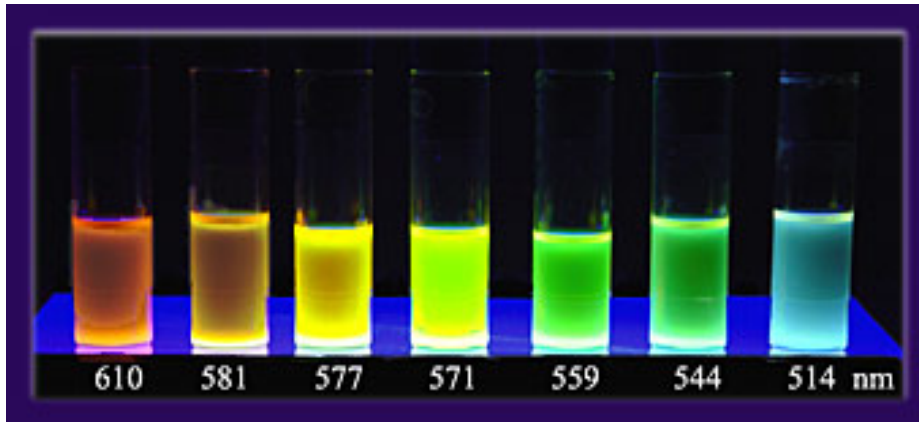


- “Physiologic” scaling-laws of classical physics
- Surface to volume ratio
- Just Size Effects
- “Pathologic” quanta-mechanical effects

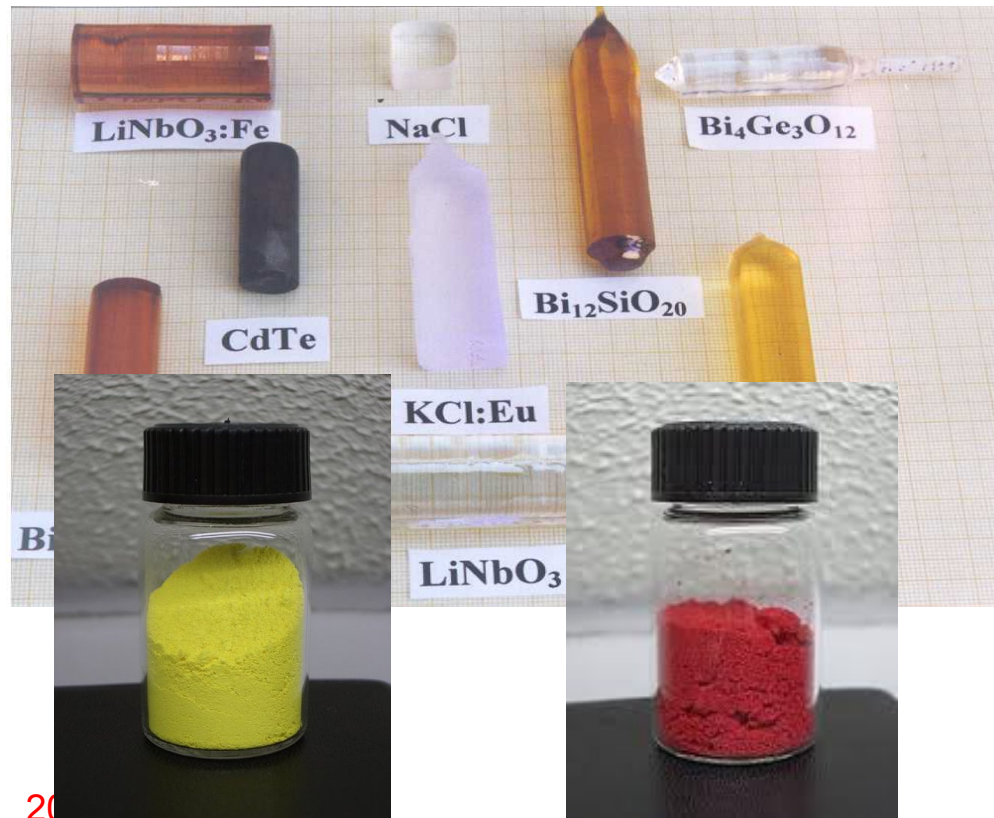
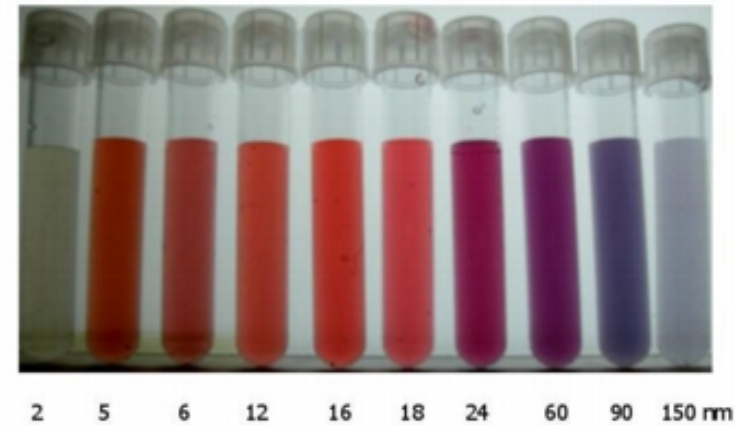


- Quantum confinement: energy levels and their spacings scale as $1/L^2$. Optical shifts with size
- Tunnelling: current scales as $\exp(-2d/\Lambda)$, where d is the thickness of the barrier.
- Scattering: relaxation-time approximation breaks down if $L < \lambda_m = v(E_F) \Delta t$

Color (optical gap)



Different sizes of colloidal gold particles



Lycurgus Cup,

nanoparticelle
di oro e
argento



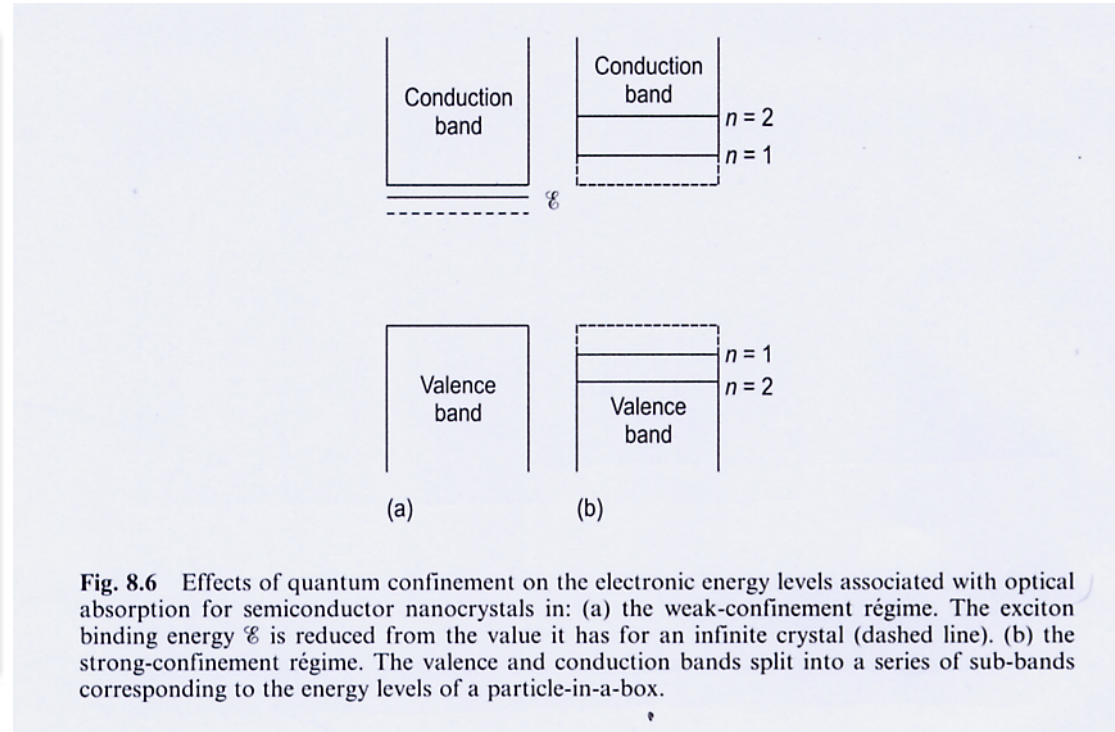
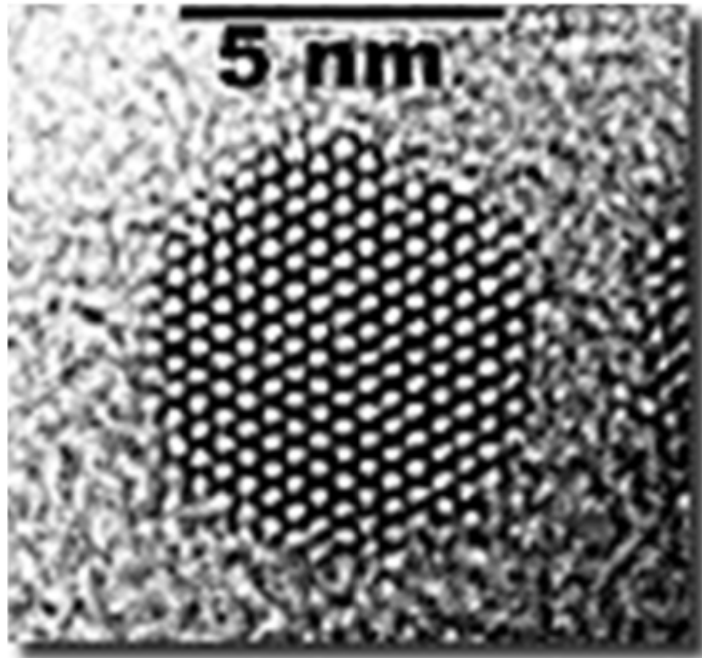


Fig. 8.6 Effects of quantum confinement on the electronic energy levels associated with optical absorption for semiconductor nanocrystals in: (a) the weak-confinement régime. The exciton binding energy \mathcal{E} is reduced from the value it has for an infinite crystal (dashed line). (b) the strong-confinement 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

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



The invention of Nanotechnology



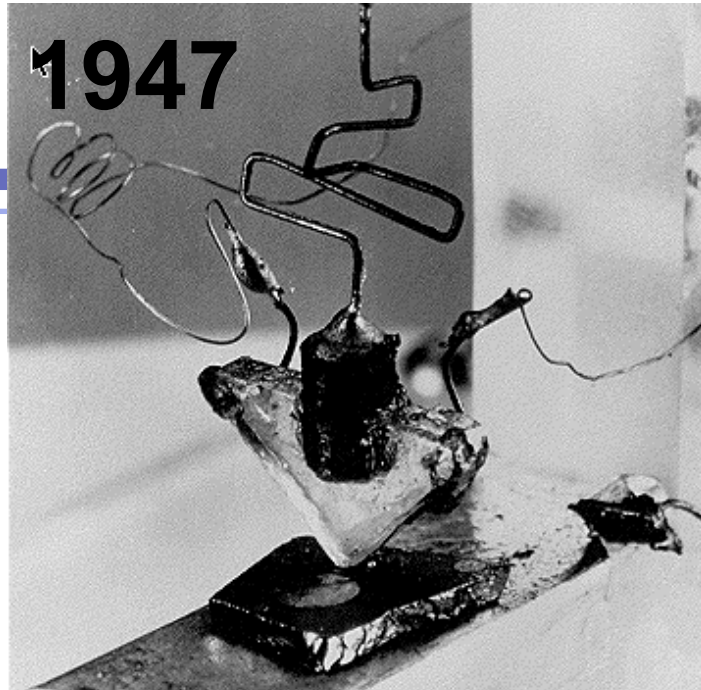
1959

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.



1947

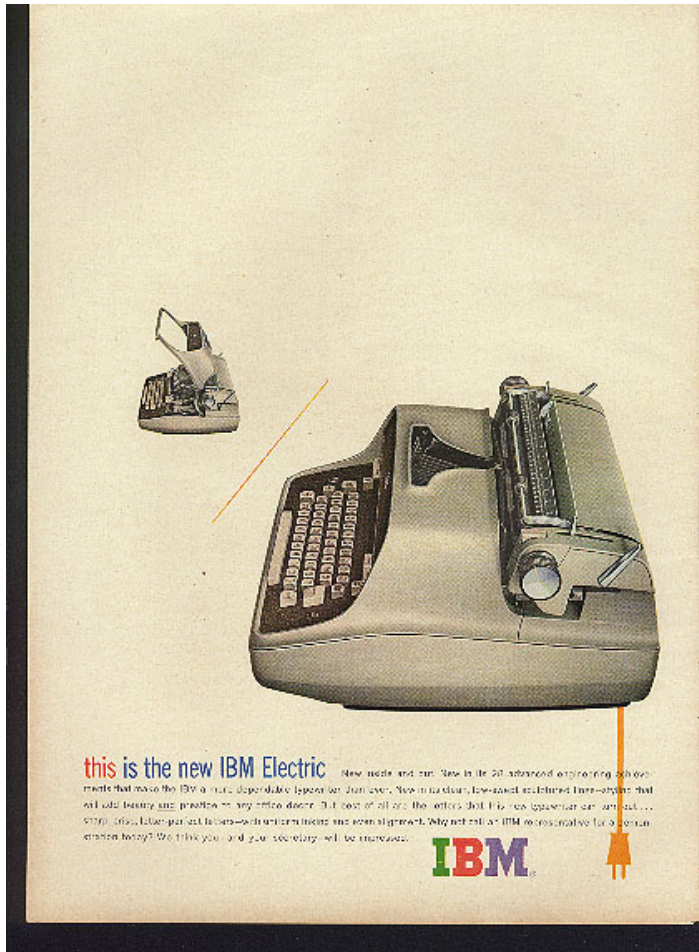


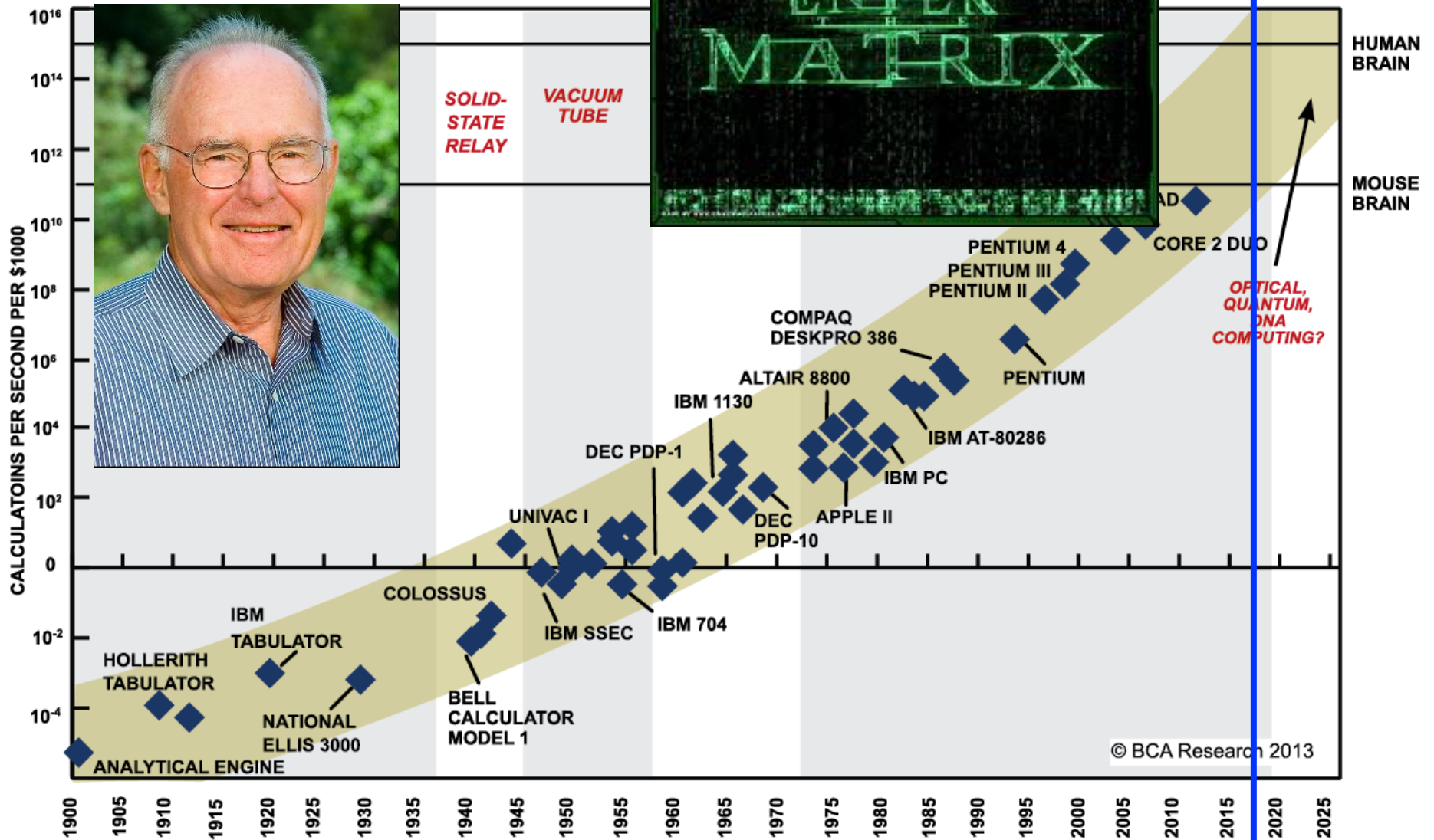
1959



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. DATAPPOINTS BETWEEN 2000 AND 2012 REPRESENT BCA ESTIMATES.

2017 10¹¹ operazioni al secondo

Brains



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

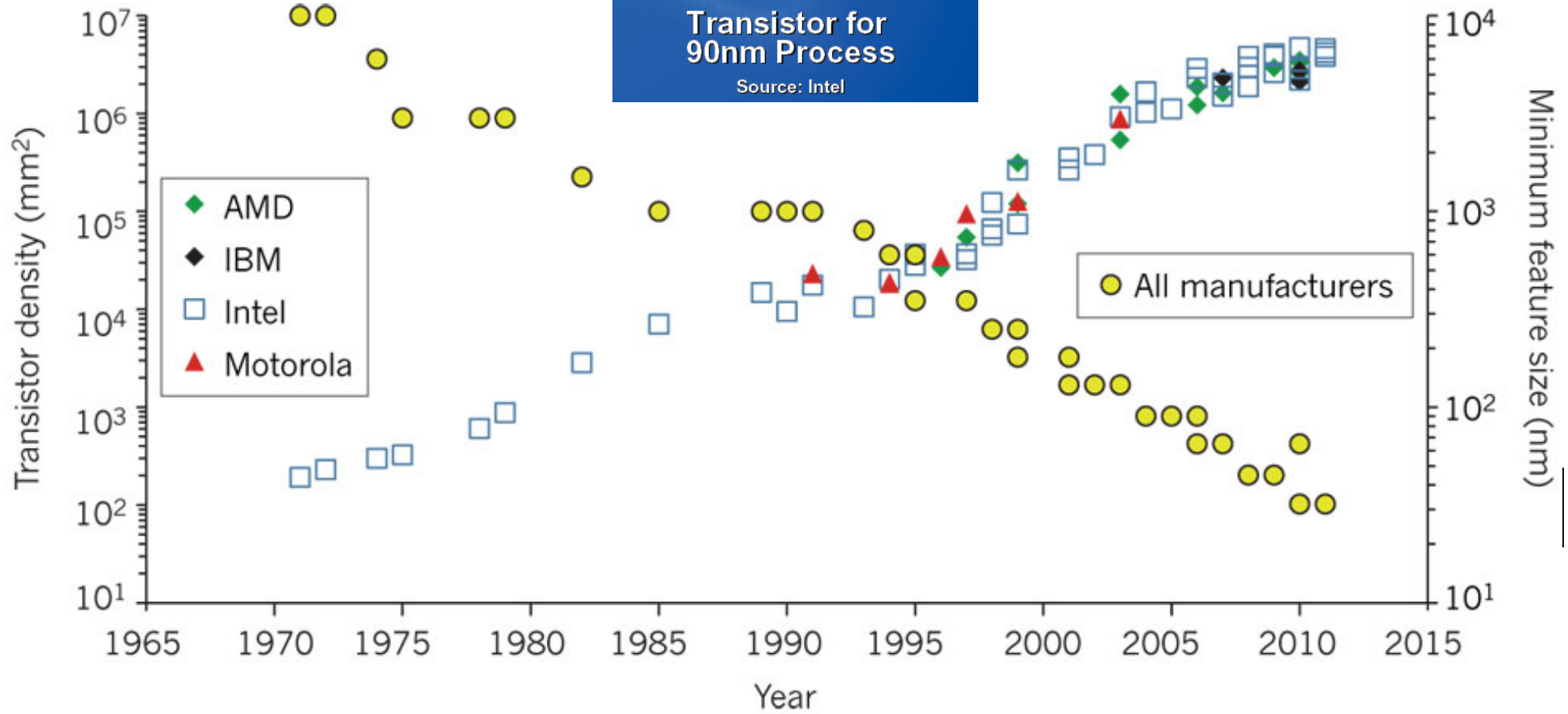
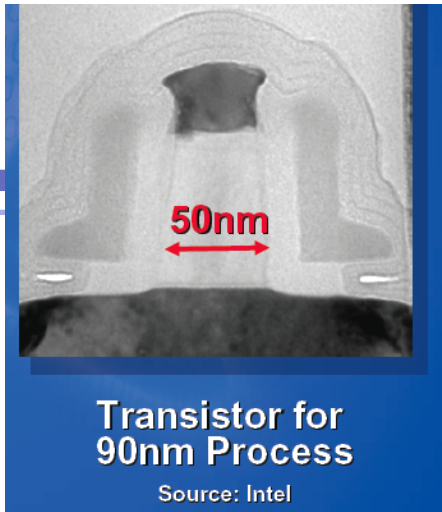
a Rolls-Royce would today cost \$100

get a million miles per gallon

and explode once a year, killing everyone inside.

- Robert X. Cringely

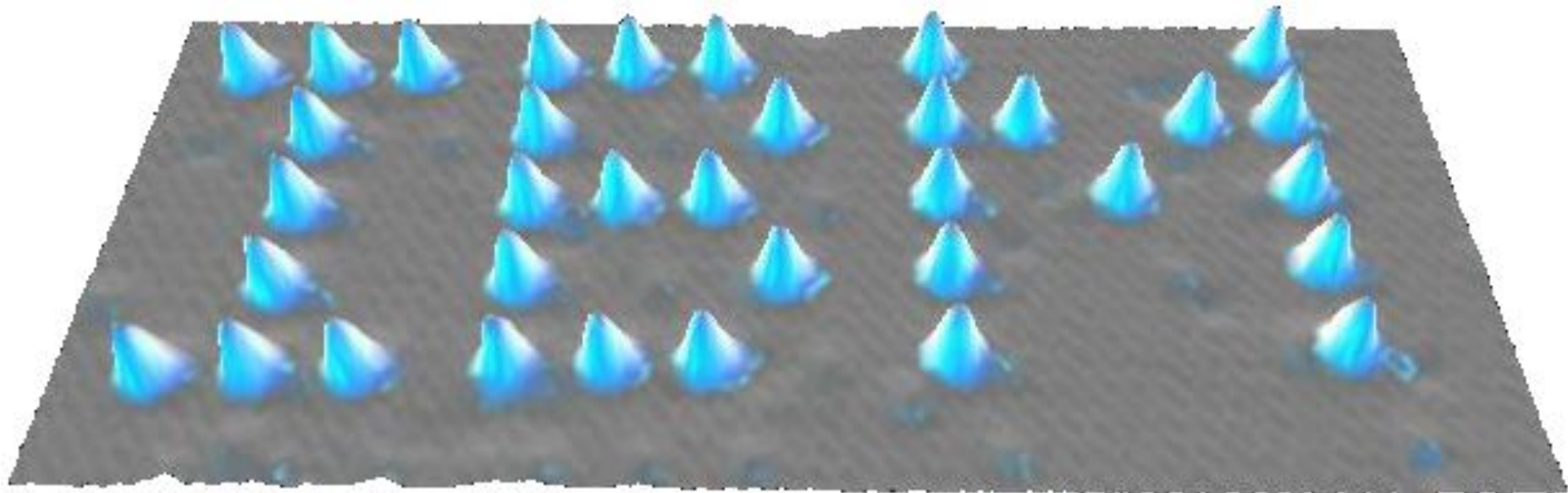






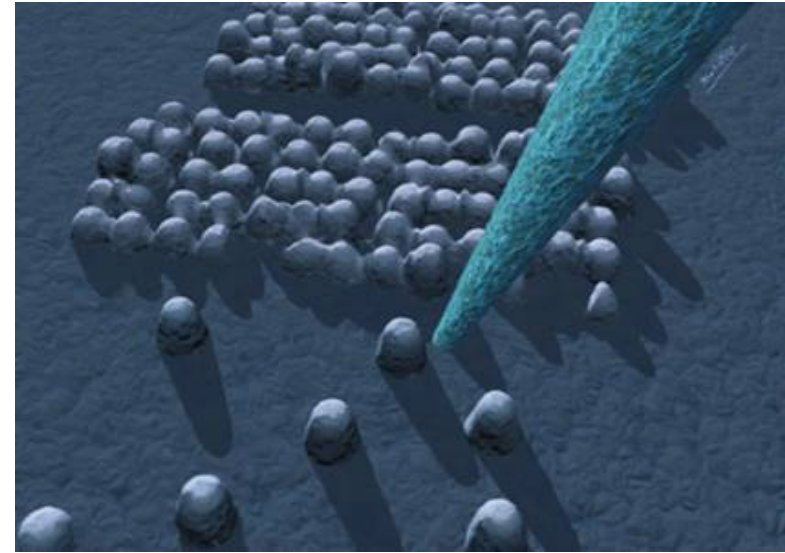
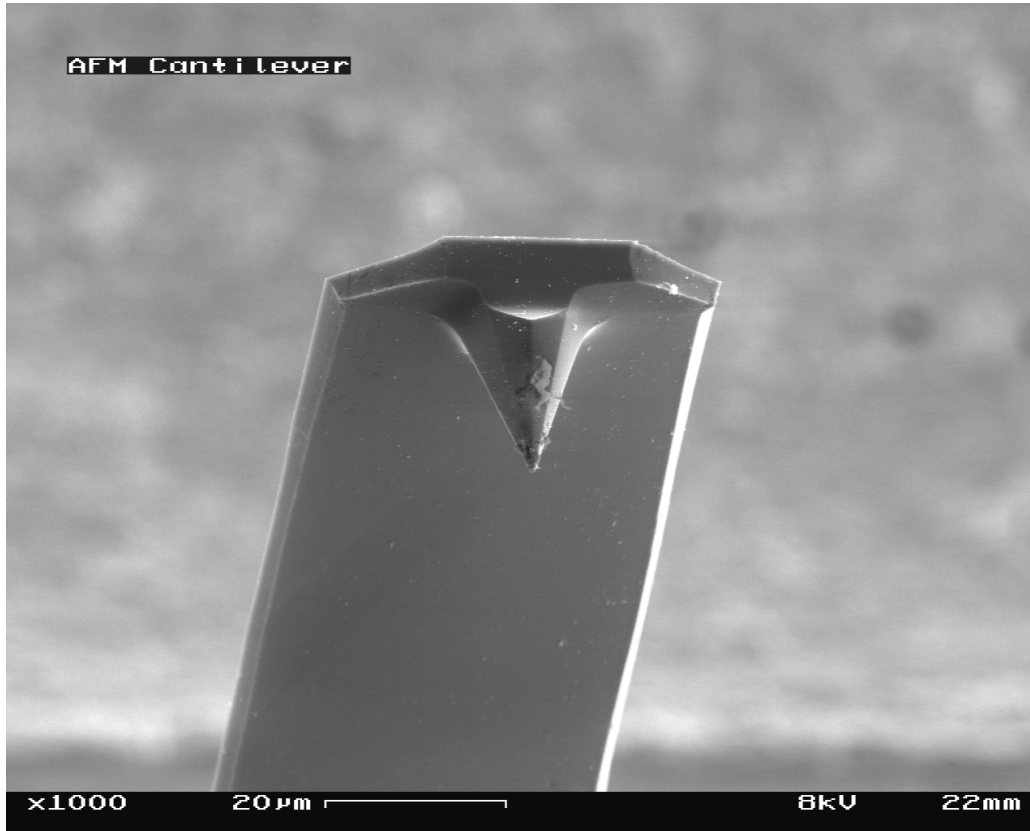
Devices made with single atoms

IBM - 1985

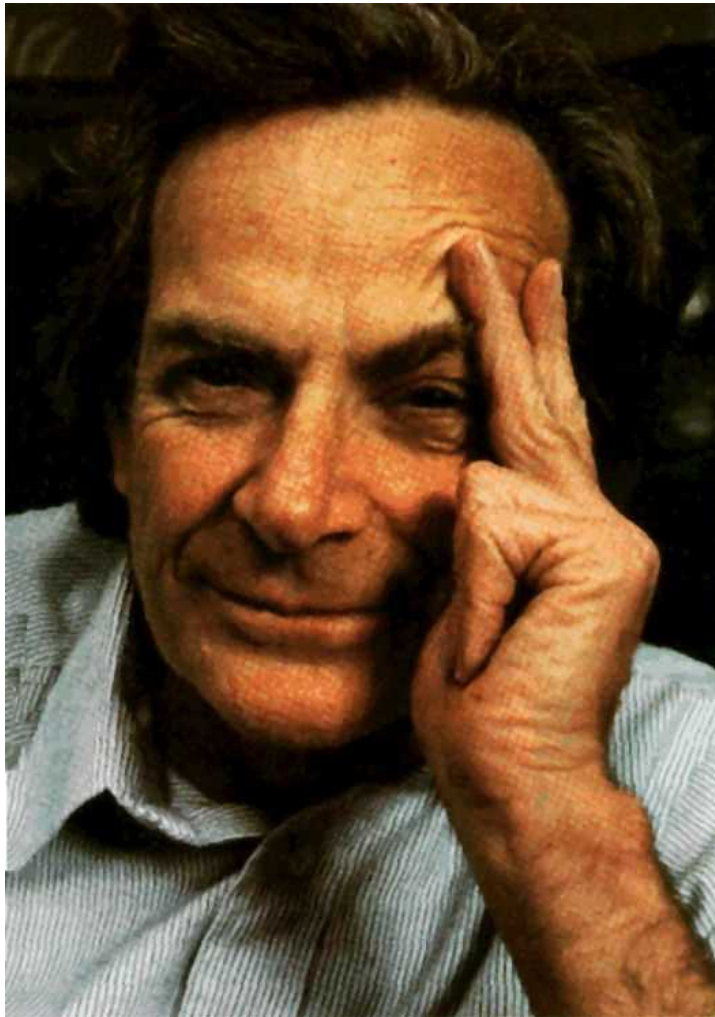


...we can arrange the atoms the way we want...

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

60 nm

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2880, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

400 nm

Richard P. Feynman, 1960

Mole

writing direction

meniscus

Substrate

Plenty of room at the bottom



Dürer, Albrecht

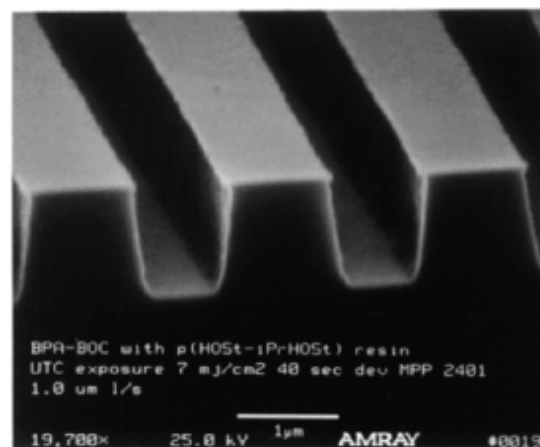
The Knight, Death and The Devil (Le Cheval, la Mort et le Diable)
1514

← **Top**

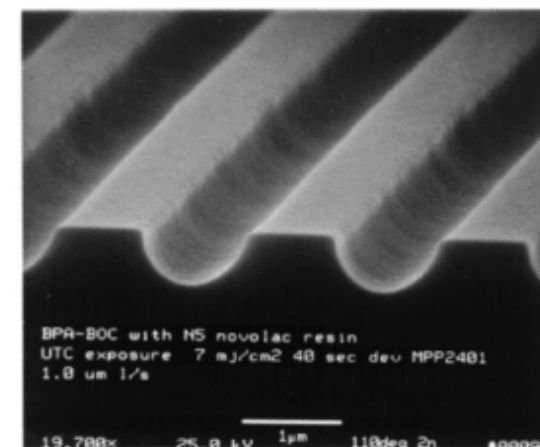
Down



**Design molecules and clusters to self assemble
(Bottom up)**



(a)



(b)

Red pyramid– Dahshur (104 m)



Angle at base = $51^{\circ} 50' 35''$



Giza great pyramid– (147 m)



Angle at base = $52^{\circ} 50' 35''$



Bent pyramid– Dahshur (105 m)



Initial angle at base= 54°





Ge



Si

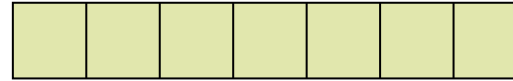


Tavola periodica degli elementi

1/A 18/O

Legend:
 □ solidi □ gas □ liquidi
 □ preparati artificialmente □ delimitazione dei non-metalli * simboli basati sui nomi sistematici IUPAC

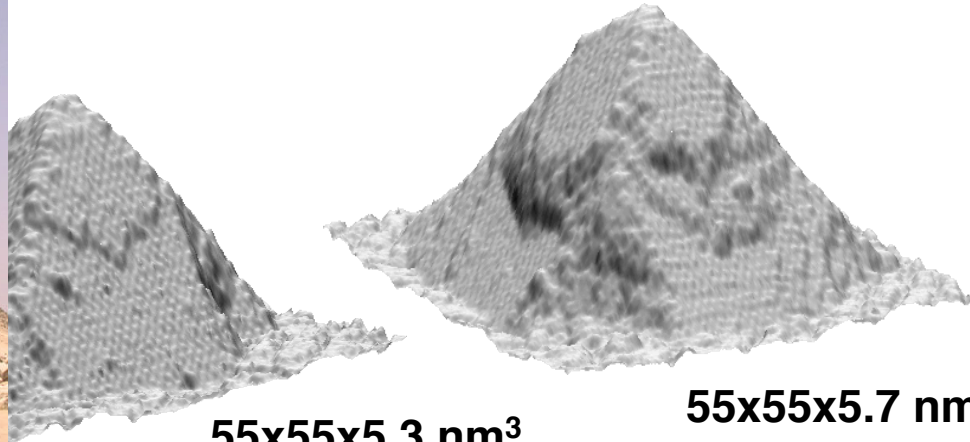
Key for element K:
 - numero atomico: 19
 - simbolo: K
 - nome: potassio
 - peso atomico: 39,0983 (tra parentesi il peso atomico dell'isotopo con vita più lunga)
 - numeri di ossidazione più comuni: +1

1																	2		
H 1,00794 idrogeno																	He 4,002602 elio		
3	4											5	6	7	8	9	10		
Li 6,941 litio	Be 9,012182 berillio											B 10,811 boro	C 12,011 carbonio	N 14,00674 azoto	O 15,9994 ossigeno	F 18,9984032 fluoro	Ne 20,1797 neon		
11	12											13	14	15	16	17	18		
Na 22,989768 sodio	Mg 24,3050 magnesio											Al 26,981539 alluminio	Si 28,0855 silicio	P 30,973762 fosforo	S 32,066 zolfo	Cl 35,4527 cloro	Ar 39,948 argo		
elementi di transizione																			
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
K 39,0983 potassio	Ca 40,078 calcio	Sc 44,955910 scandio	Ti 47,867 titanio	V 50,9415 vanadio	Cr 51,9961 cromo	Mn 54,93805 manganese	Fe 55,845 ferro	Co 58,93320 cobalto	Ni 58,6934 nichel	Cu 63,546 rame	Zn 65,39 zinc	Ga 69,723 gallo	Ge 72,61 germanio	As 74,92159 arsenico	Se 78,96 selenio	Br 79,904 bromo	Kr 83,80 cripto		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
Rb 85,4678 rubidio	Sr 87,62 stronzio	Y 88,90585 ittrio	Zr 91,224 zirconio	Nb 92,90638 niobio	Mo 95,94 molibdeno	Tc (97,9072) tecnecio	Ru 101,07 rutenio	Rh 102,90550 rodio	Pd 106,42 palladio	Ag 107,8682 argento	Cd 112,411 cadmio	In 114,818 indio	Sn 118,710 stagno	Sb 121,760 antimonio	Te 127,60 tellurio	I 126,90447 iodio	Xe 131,29 xeno		
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
Cs 132,90543 cesio	Ba 137,327 bario	vedi lantanidi	Hf 178,49 afnio	Ta 180,9479 tantalio	W 183,84 wolframio (tungsteno)	Re 186,207 renio	Os 190,2 osmio	Ir 192,217 iridio	Pt 195,08 platino	Au 196,96654 oro	Hg 200,59 mercurio	Tl 204,3833 talio	Pb 207,2 piombo	Bi 208,98037 bismuto	Po (208,9824) polonio	At (209,9871) astato	Rn (222,0176) radon		
87	88	89-103	104	105	106	107	108	109										gas nobili	
Fr (223,0197) francio	Ra (226,0254) radio	vedi attinidi	*Unq (261,11)	*Unp (262,114)	*Unh (263,118)	*Uns (262,12)	*Uno	*Une											
lantanidi																			
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71					
La 138,9055 lantano	Ce 140,115 cerio	Pr 140,90765 praseodimio	Nd 144,24 neodimio	Pm (144,9127) promezio	Sm 150,36 samario	Eu 151,965 europio	Gd 157,25 gadolinio	Tb 158,92534 terbio	Dy 162,50 disprozio	Ho 164,93032 olmio	Er 167,26 erbio	Tm 168,93421 tulio	Yb 173,04 itterbio	Lu 174,967 lutecio					
attinidi																			
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103					
Ac (227,0278) attinio	Th 232,0381 torio	Pa (231,0388) protoattinio	U 238,0289 uranio	Np (237,0482) netunio	Pu (244,0642) plutonio	Am (243,0614) americio	Cm (247,0703) curio	Bk (247,0703) berkelio	Cf (251,0796) californio	Es (252,083) einsteinio	Fm (257,0951) fermio	Md (258,10) mendelevio	No (259,1009) nobelio	Lr (262,11) laurenzio					

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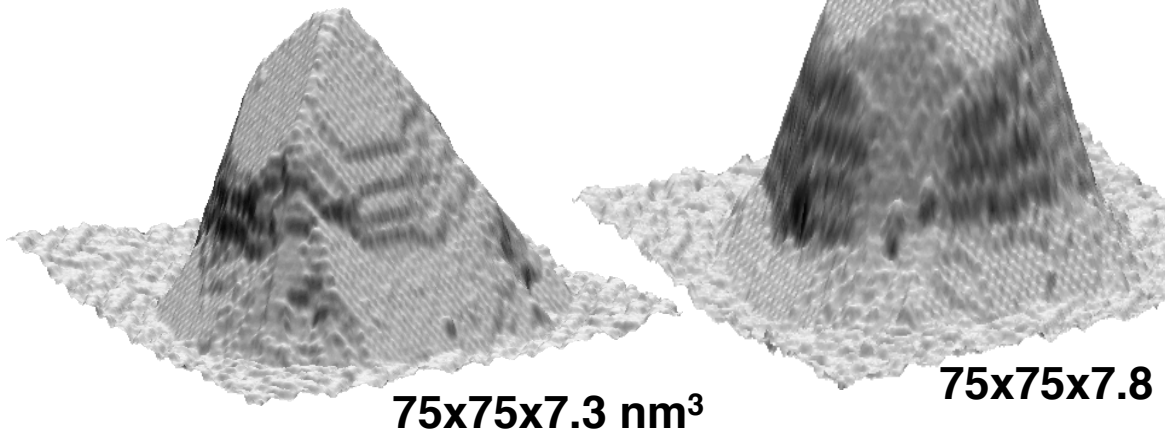
Pyramid-to-dome transition in Ge/Si(001)

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



55x55x5.3 nm³

55x55x5.7 nm³

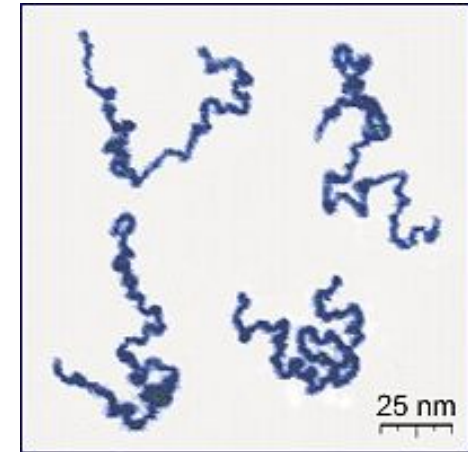
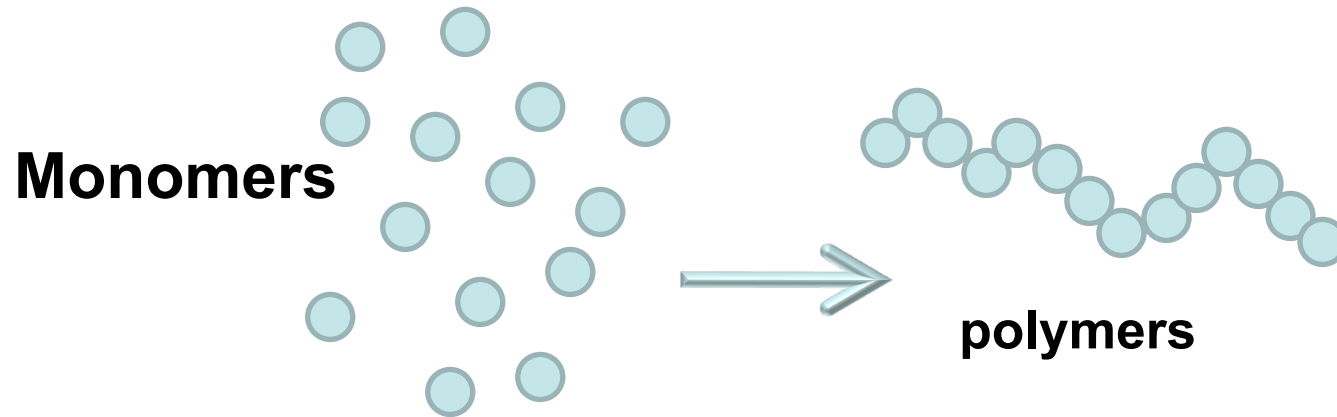


75x75x7.3 nm³

75x75x7.8 nm³



Polymers



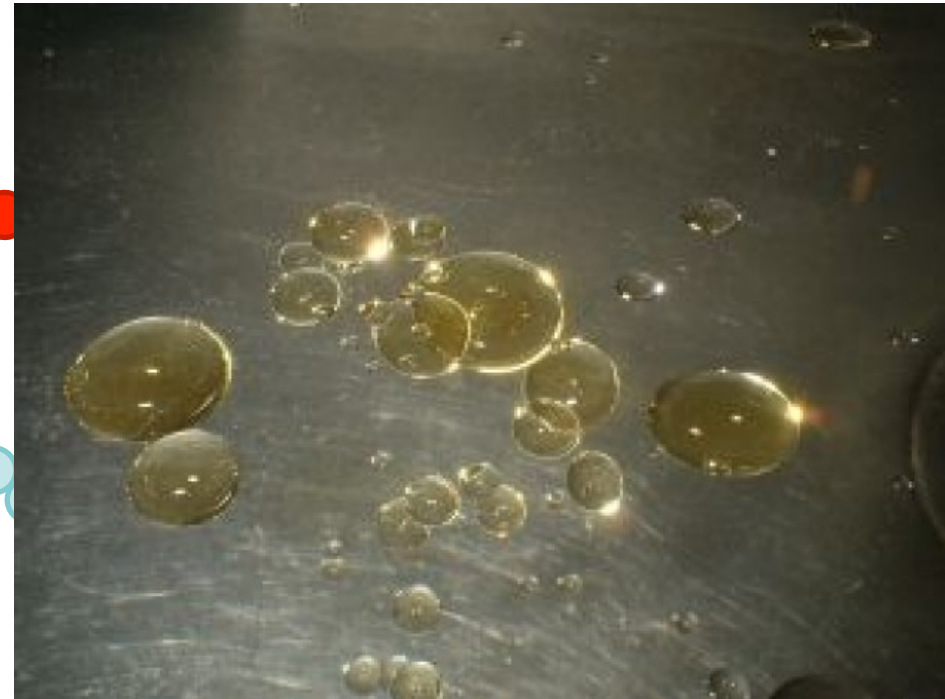
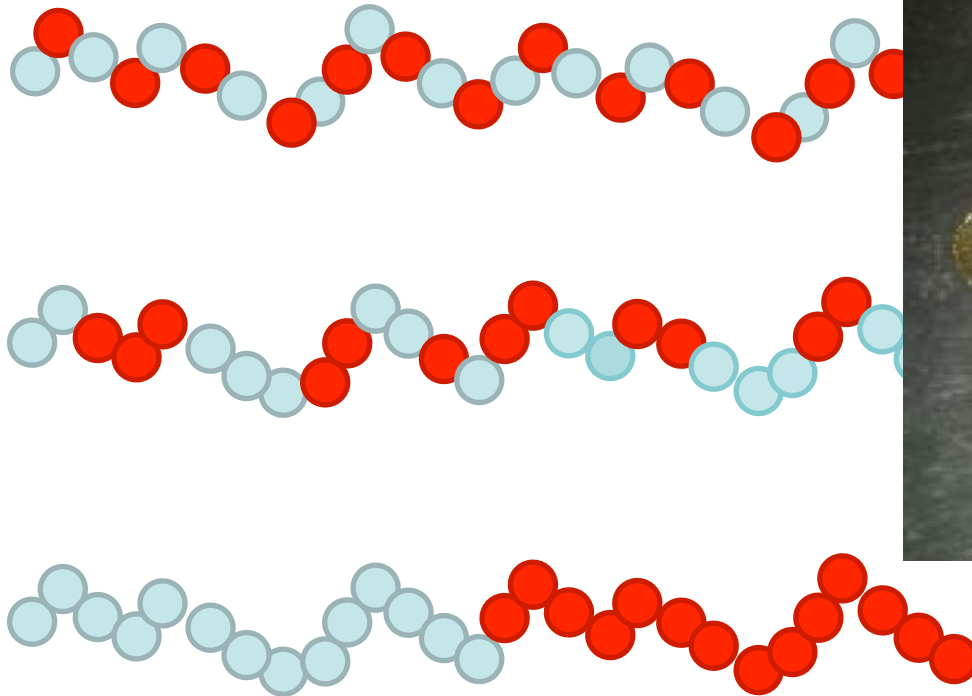
**random coil
(spaghetti scotti)**



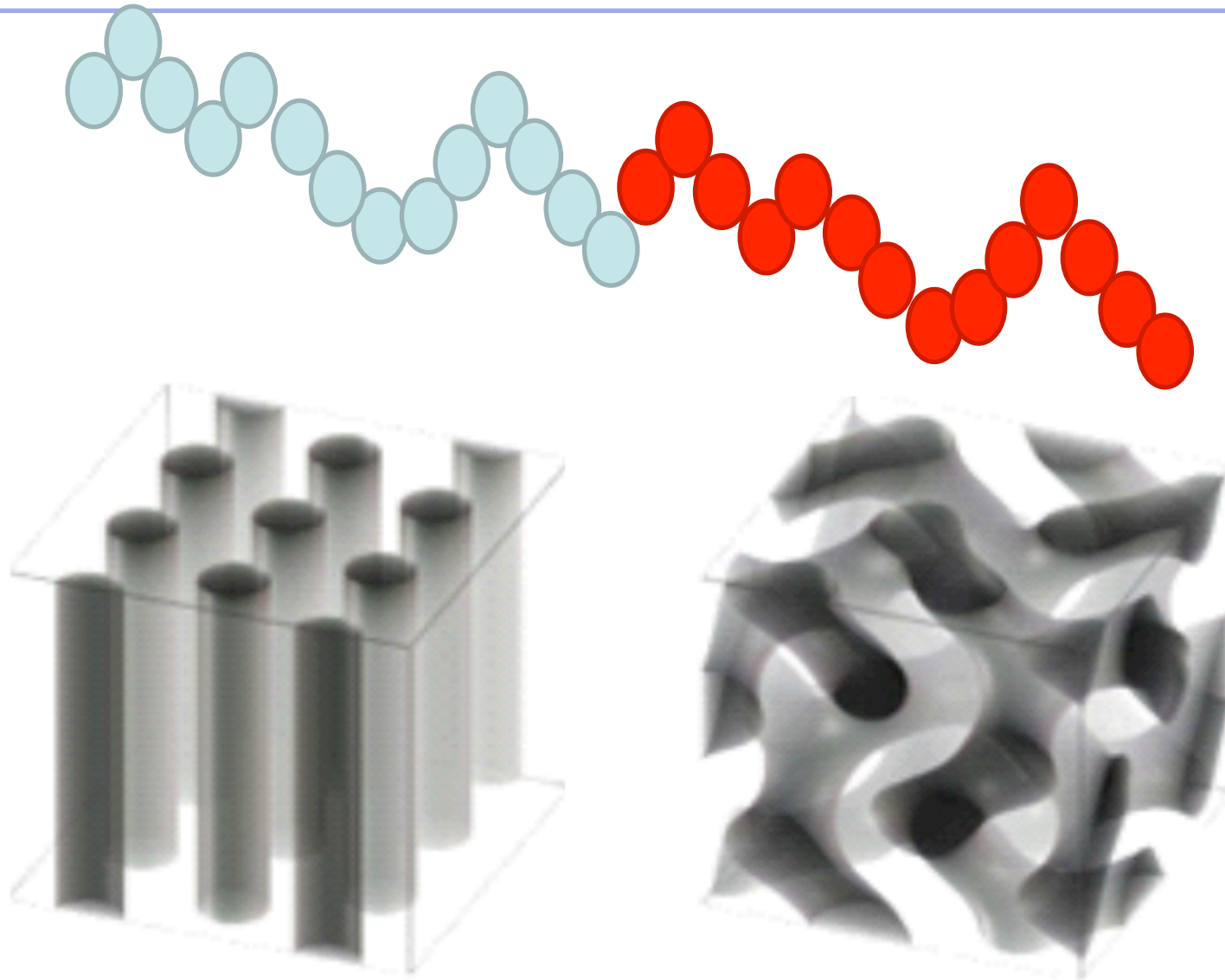
Copolymers



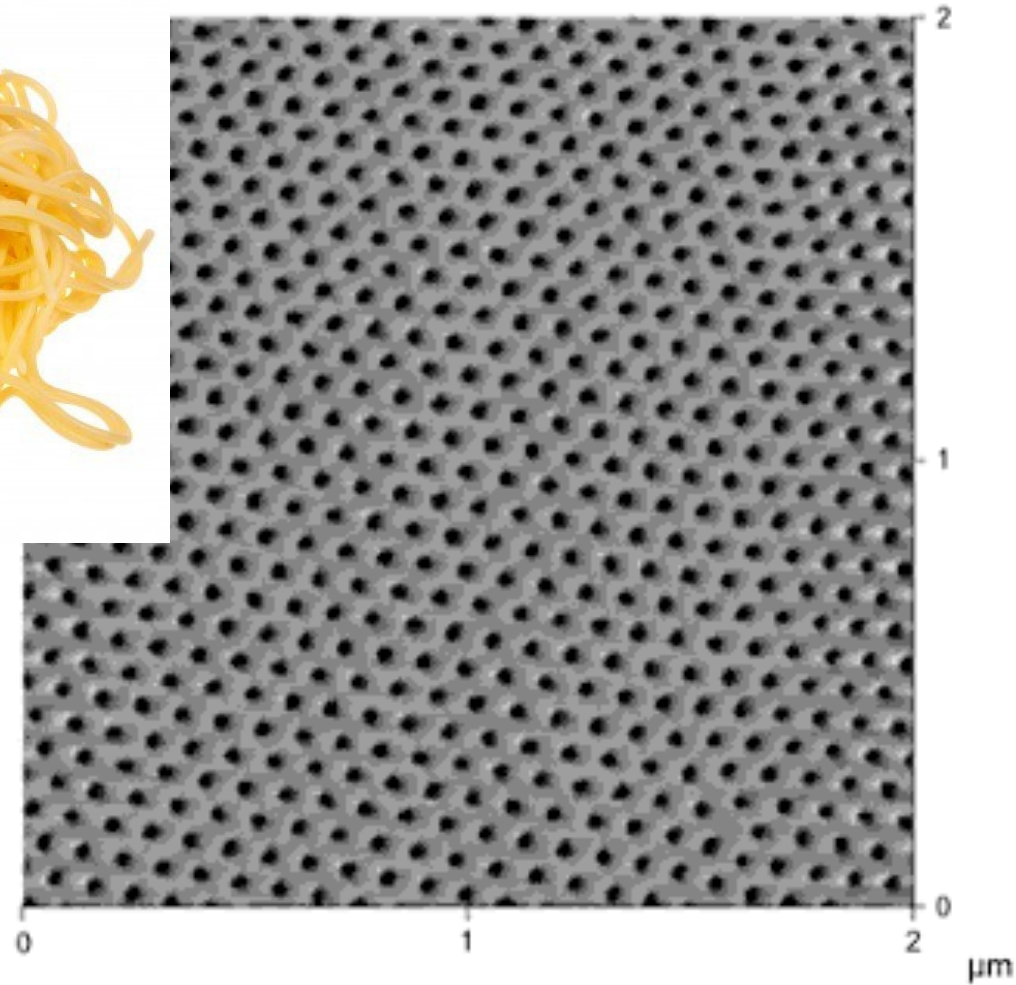
At least two different monomers



Block



SOLID STATE ORDERING

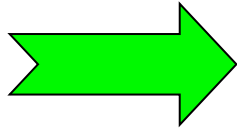


Top view of cylindrical phases packed in an hexagonal lattice



TECHNOLOGY

PUSH



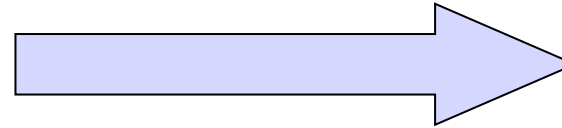
Offer of new materials, processes, devices..

MARKET

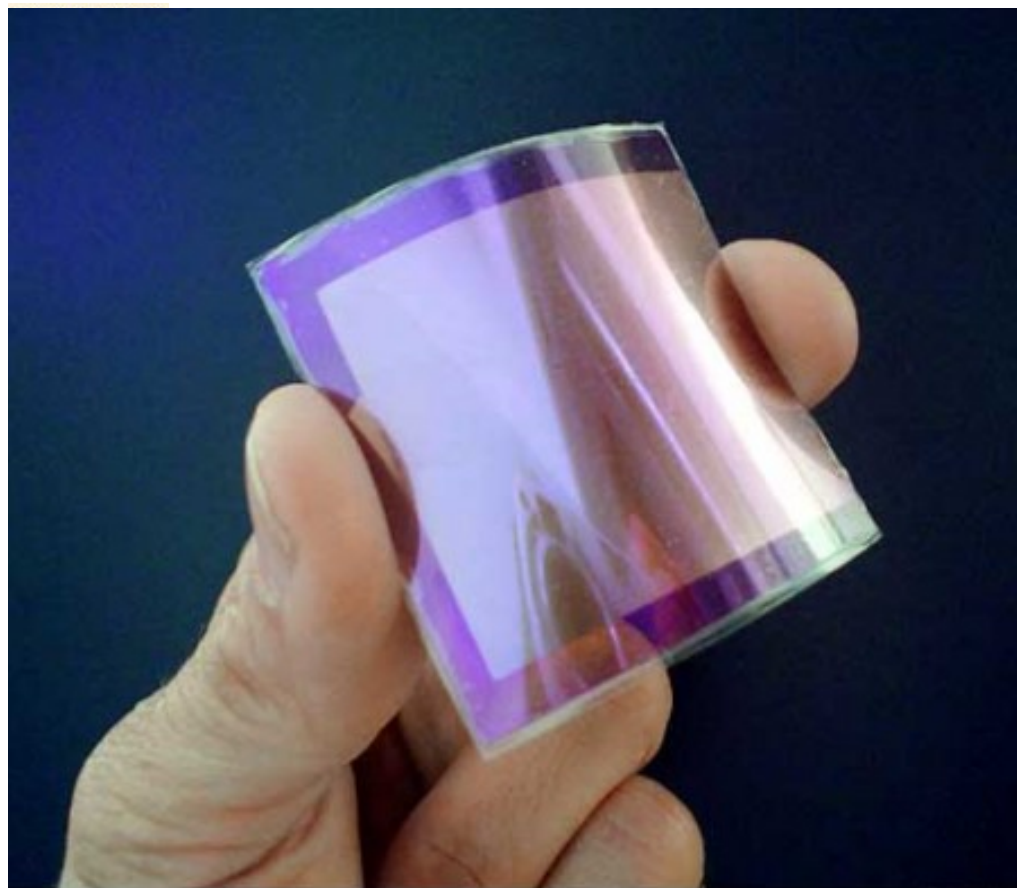
PULL



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



INNOVATION



Nanosys

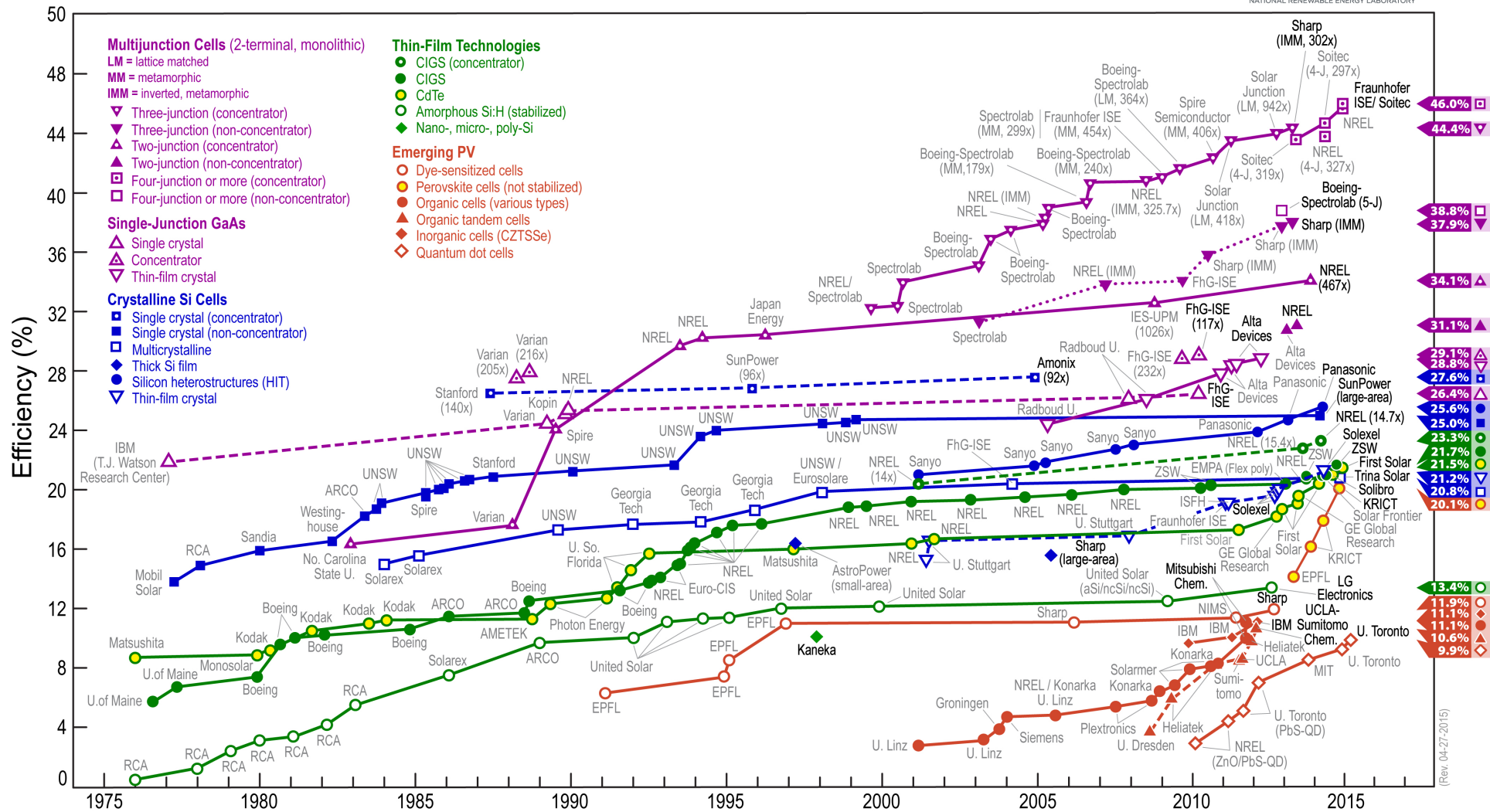


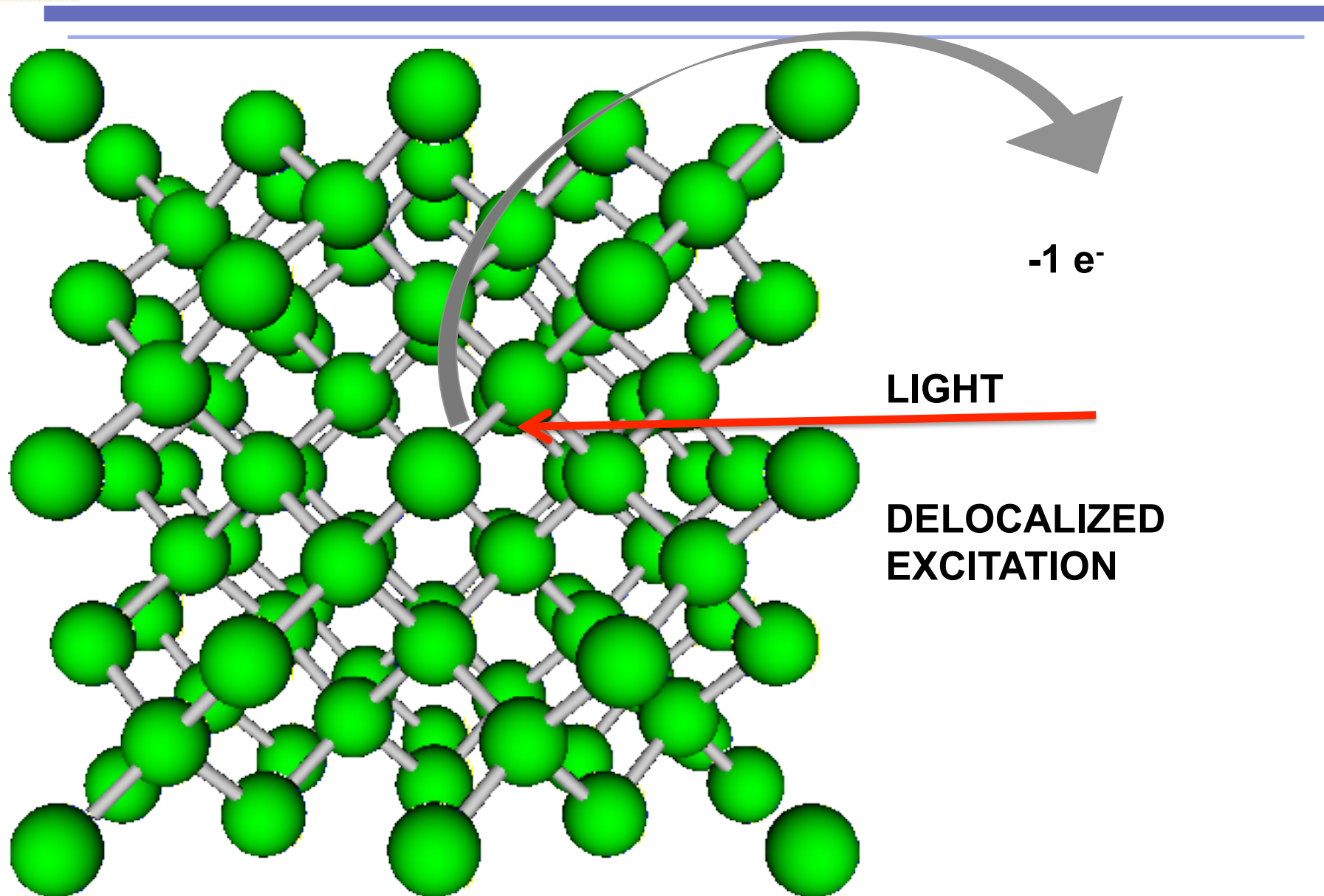
The coming of plastic electronics: flexible devices





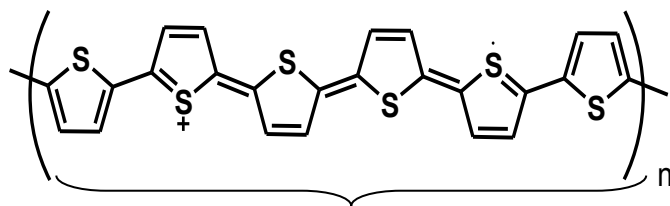
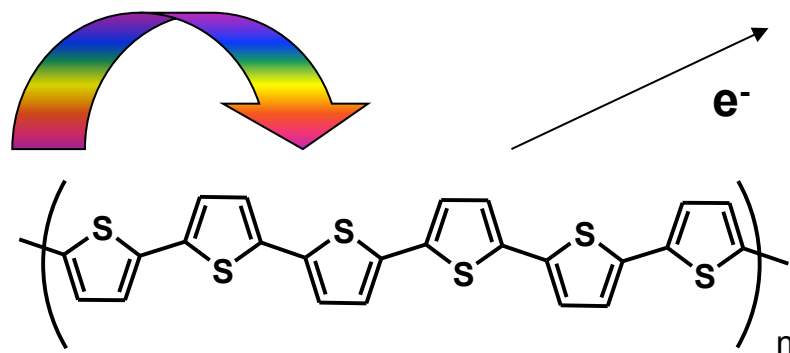
Best Research-Cell Efficiencies



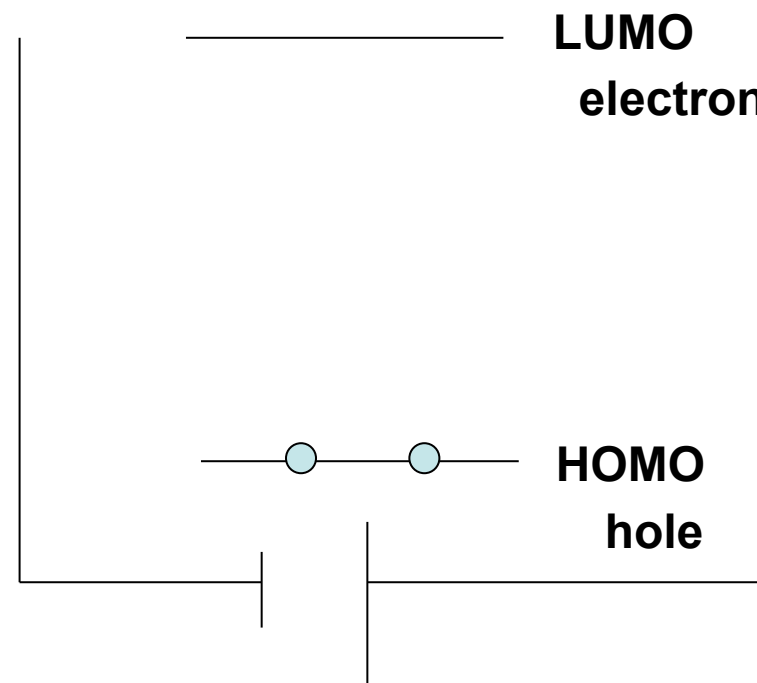




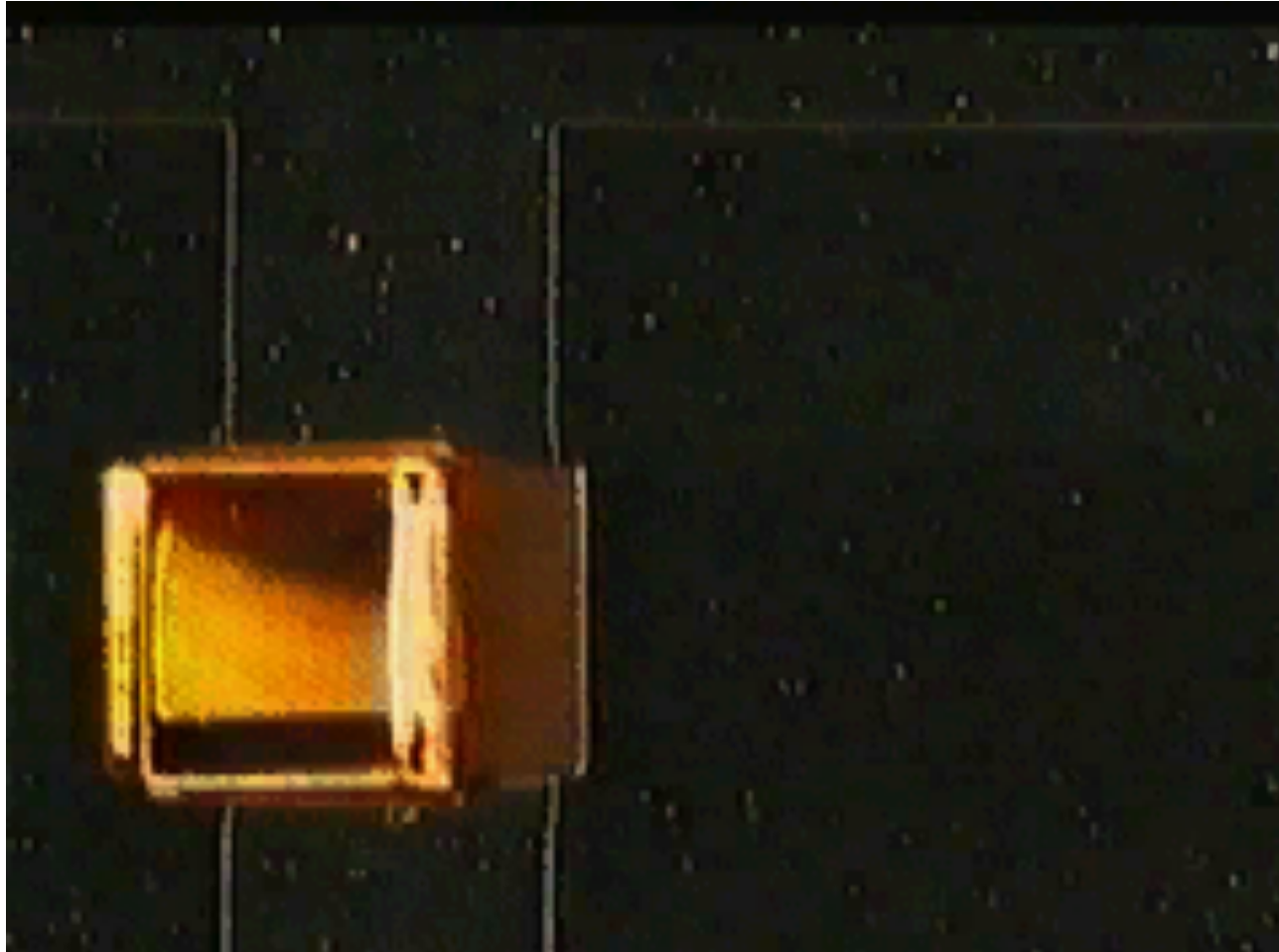
The exciton concept



Chain distortion

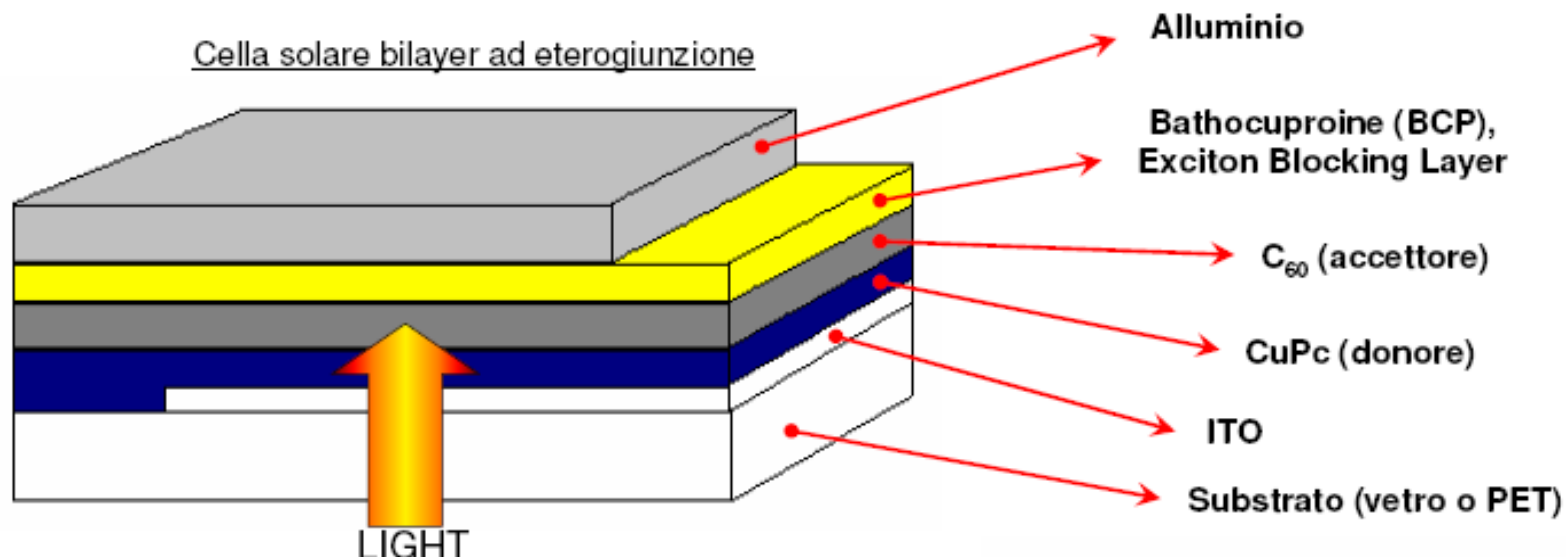


The charge transfer process induces structural distortions, the charges are not free to move





The Heterojunction cell



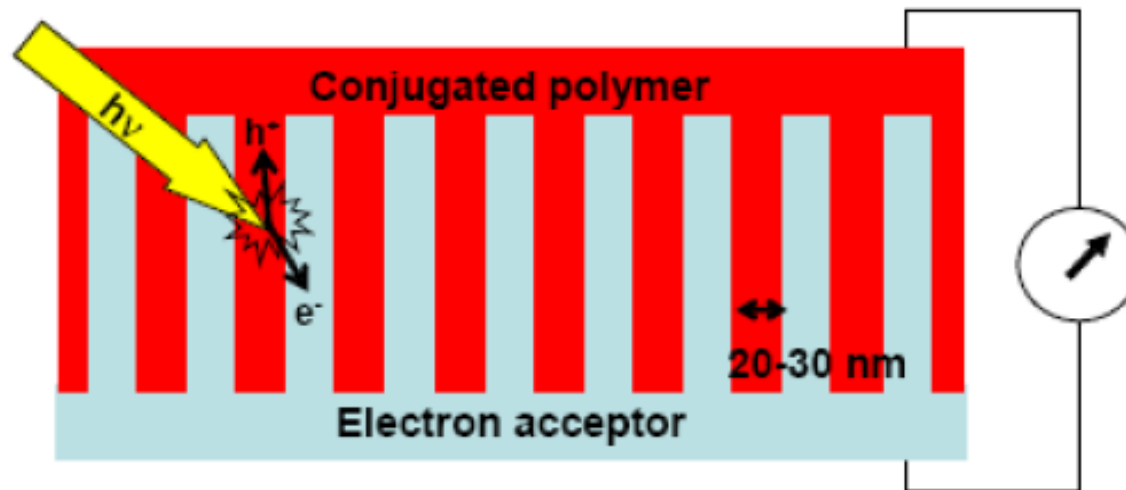
Where is the nano part?

Exciton diffusion length is in the order of 10 nm, only excitations 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

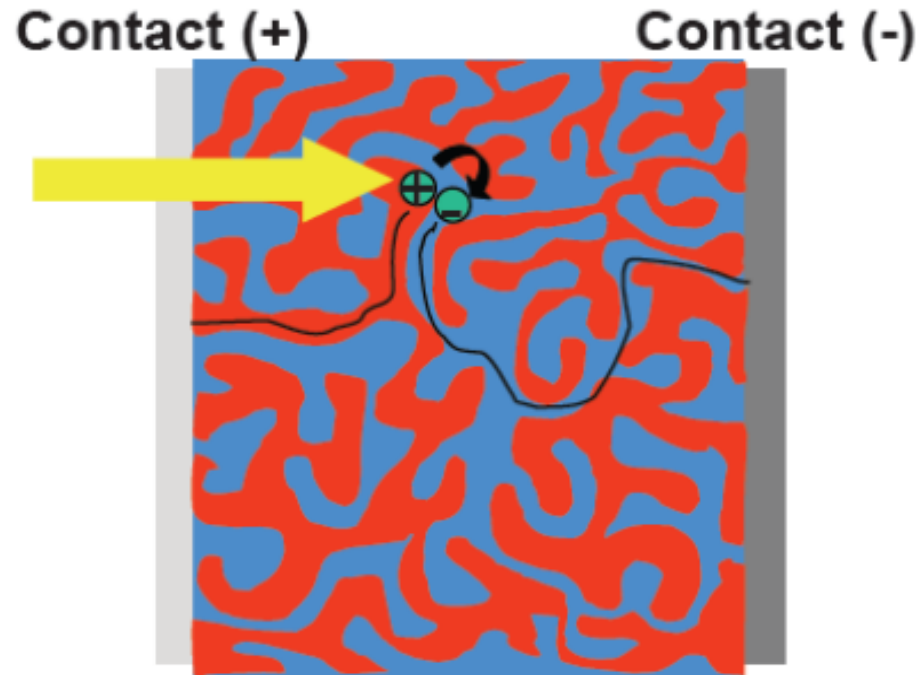


Possible approach: self assembly, use of block-copolymers, learning from nature (use of hydrogen bonded structures)

The Bulk-Heterojunction cell



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

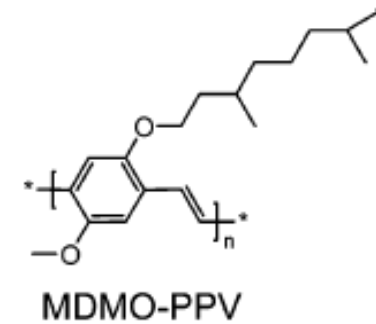
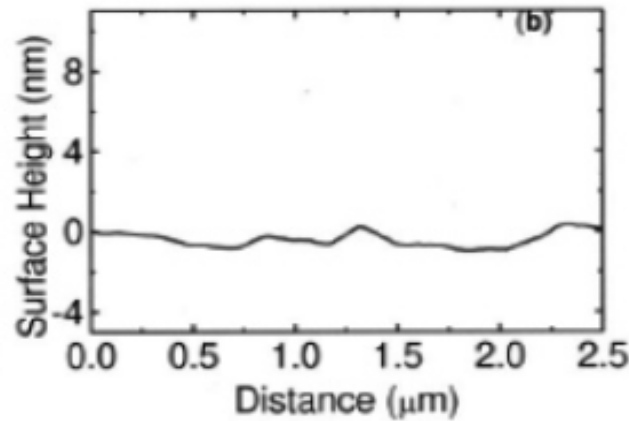
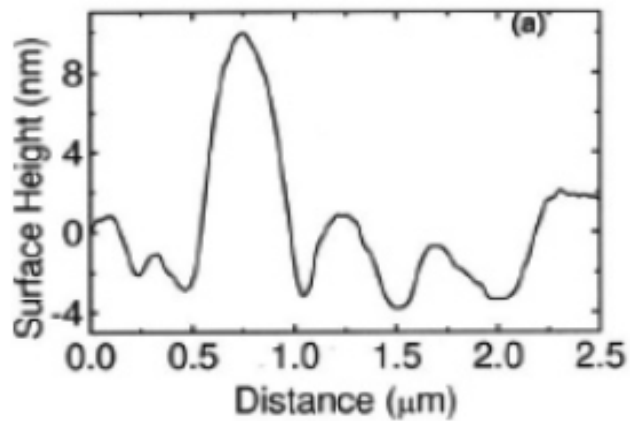
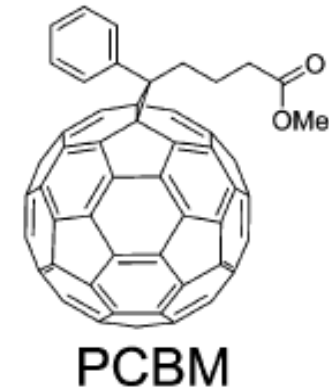
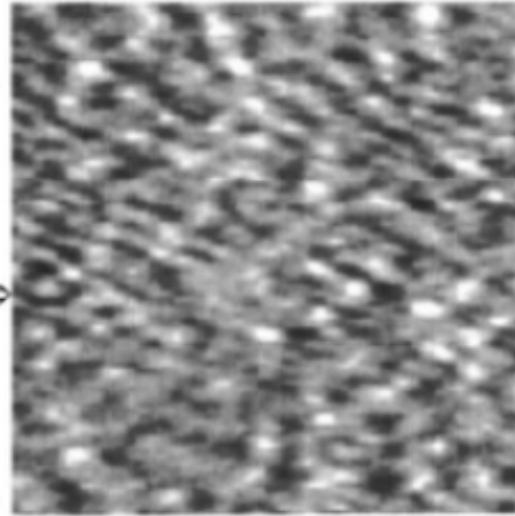
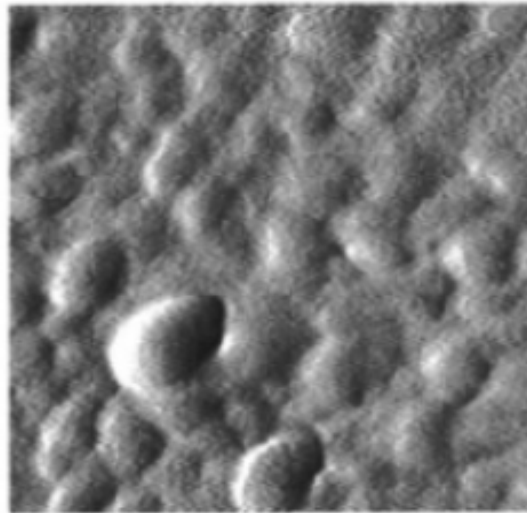


The ideal phase separation should provide 10-20 nm wide channels connecting the two materials to the corresponding electrode

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

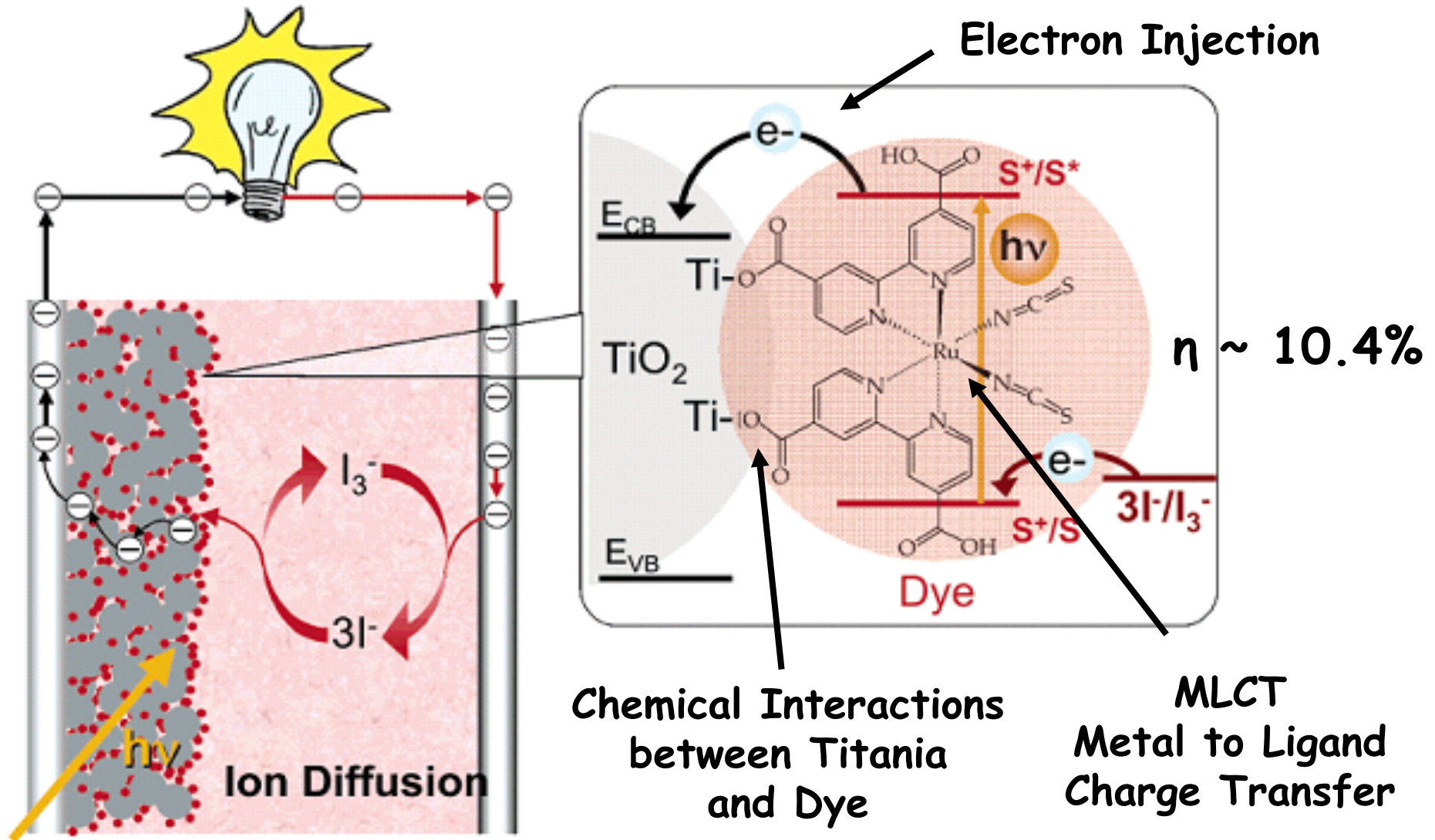


↓
Deposition from toluene

↓
Deposition from chlorobenzene



Grätzel solar cells

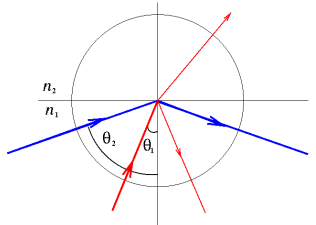
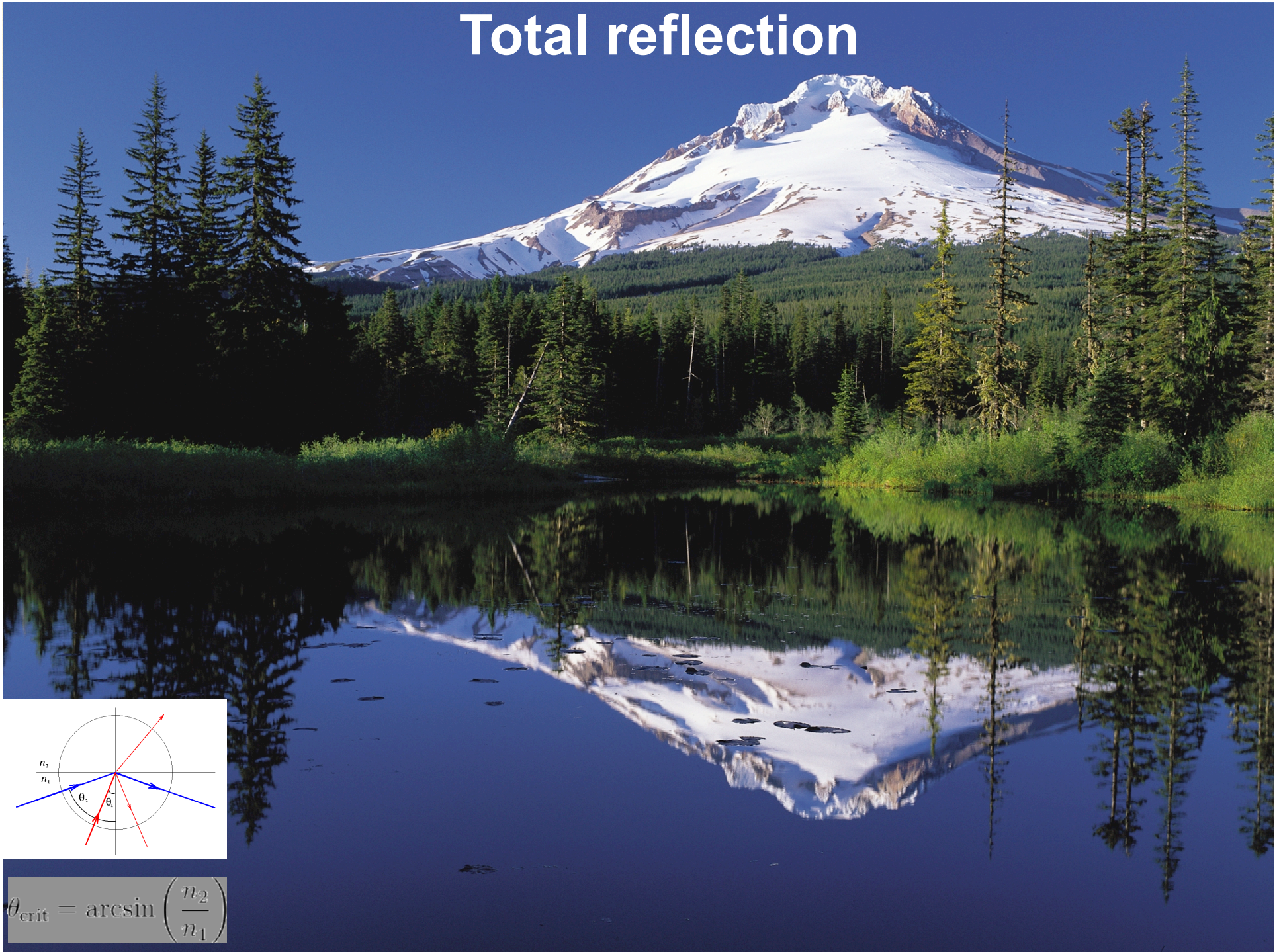


Michael Grätzel, *Chemistry Letters*, 34, No.1(2005)



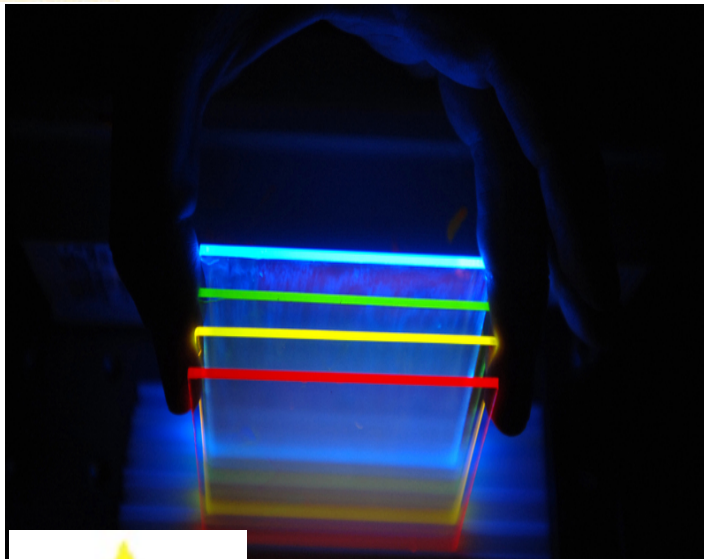


Total reflection



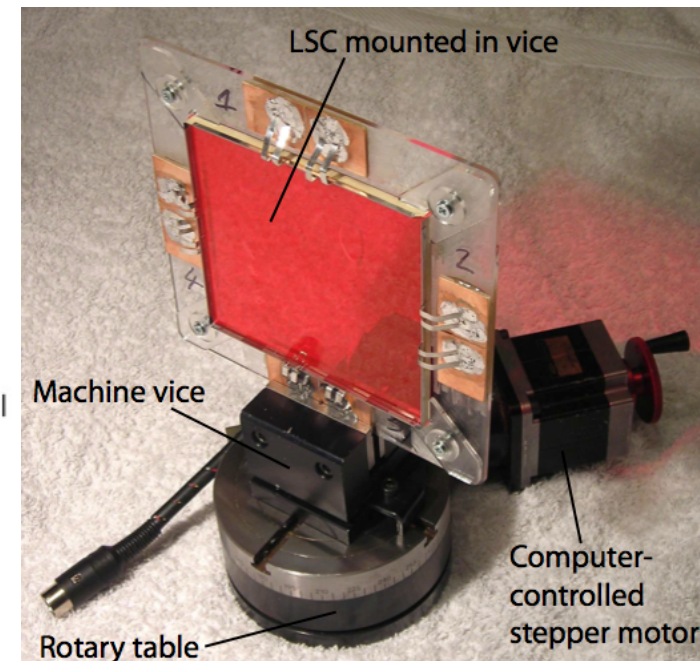
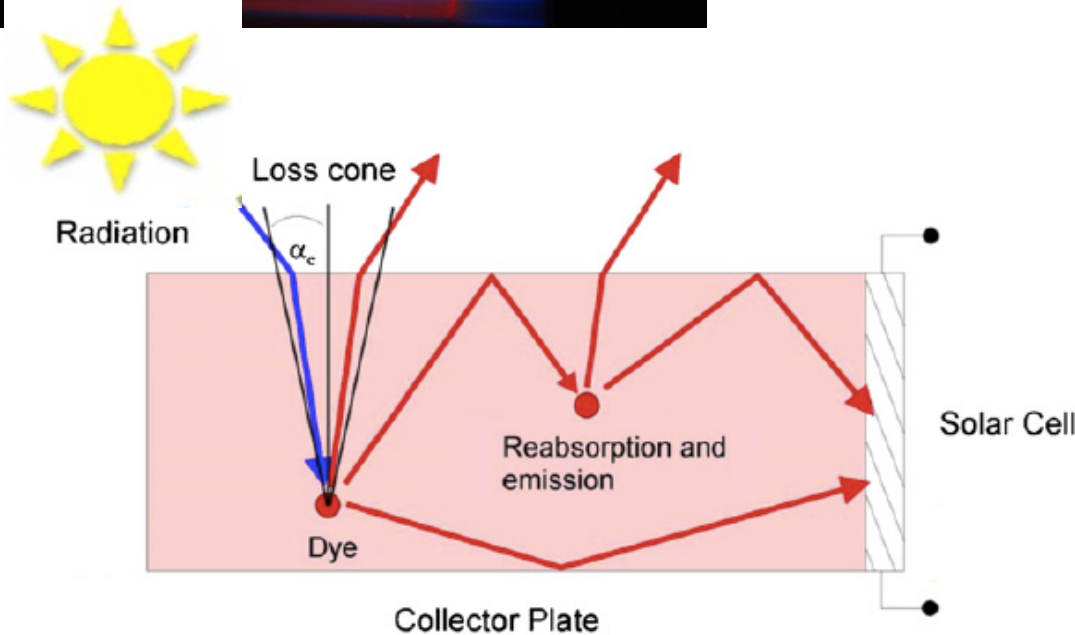
$$\theta_{\text{crit}} = \arcsin\left(\frac{n_2}{n_1}\right)$$

LUMINESCENT SOLAR CONCENTRATORS



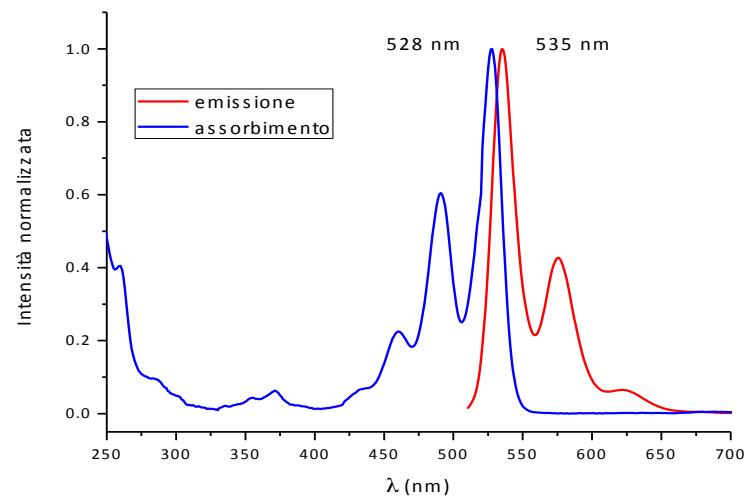
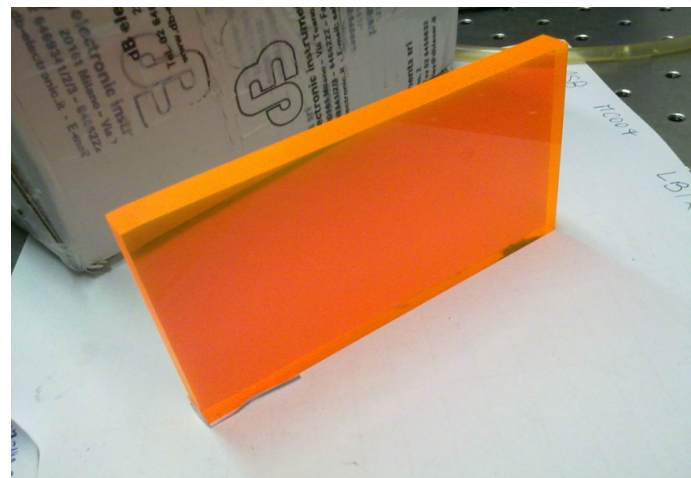
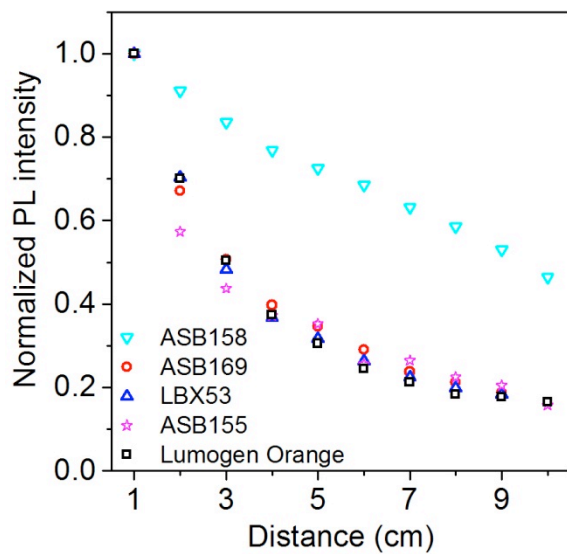
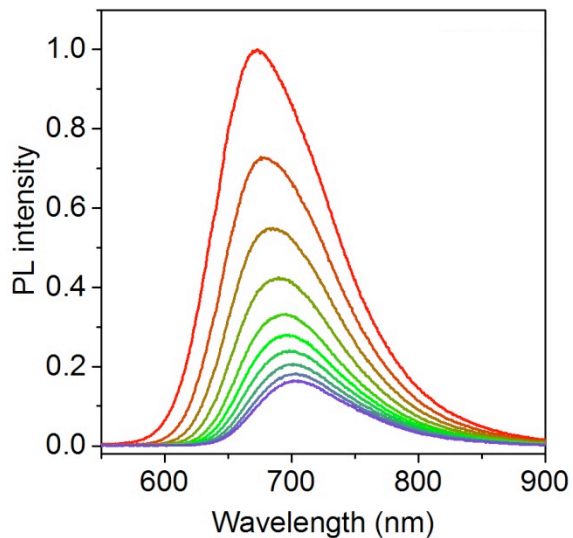
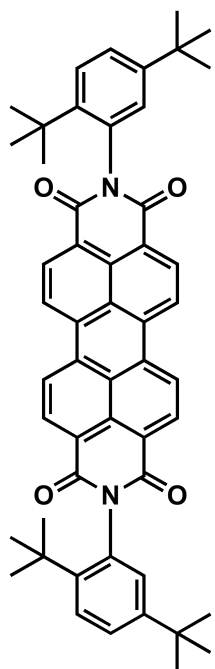
Slabs of transparent materials doped with luminescent molecules/nanoparticles

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



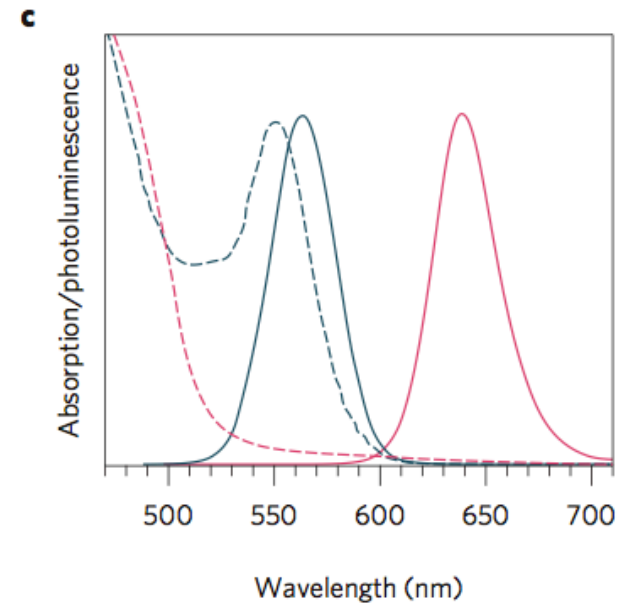
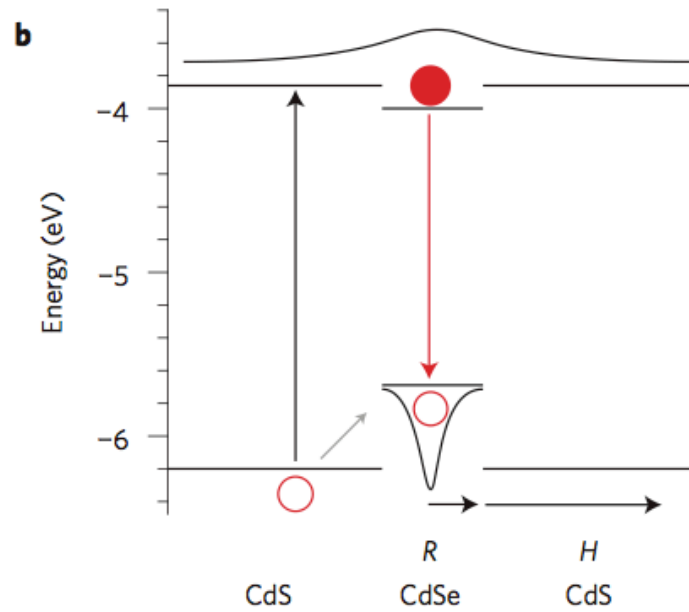
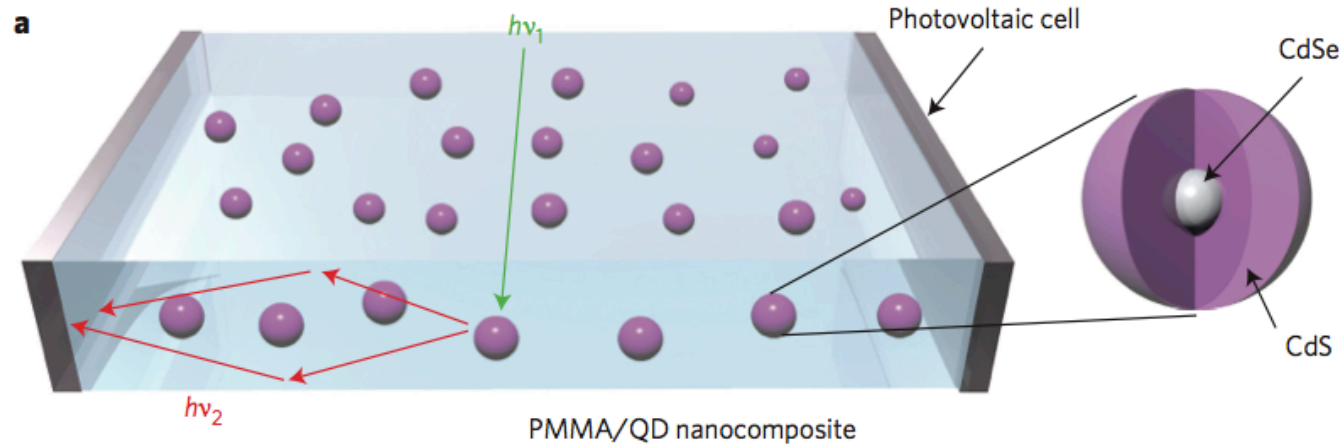
Goldschmidt, J. C. et al., *Solar Energy Materials & Solar Cells*, 2009, 93, 176

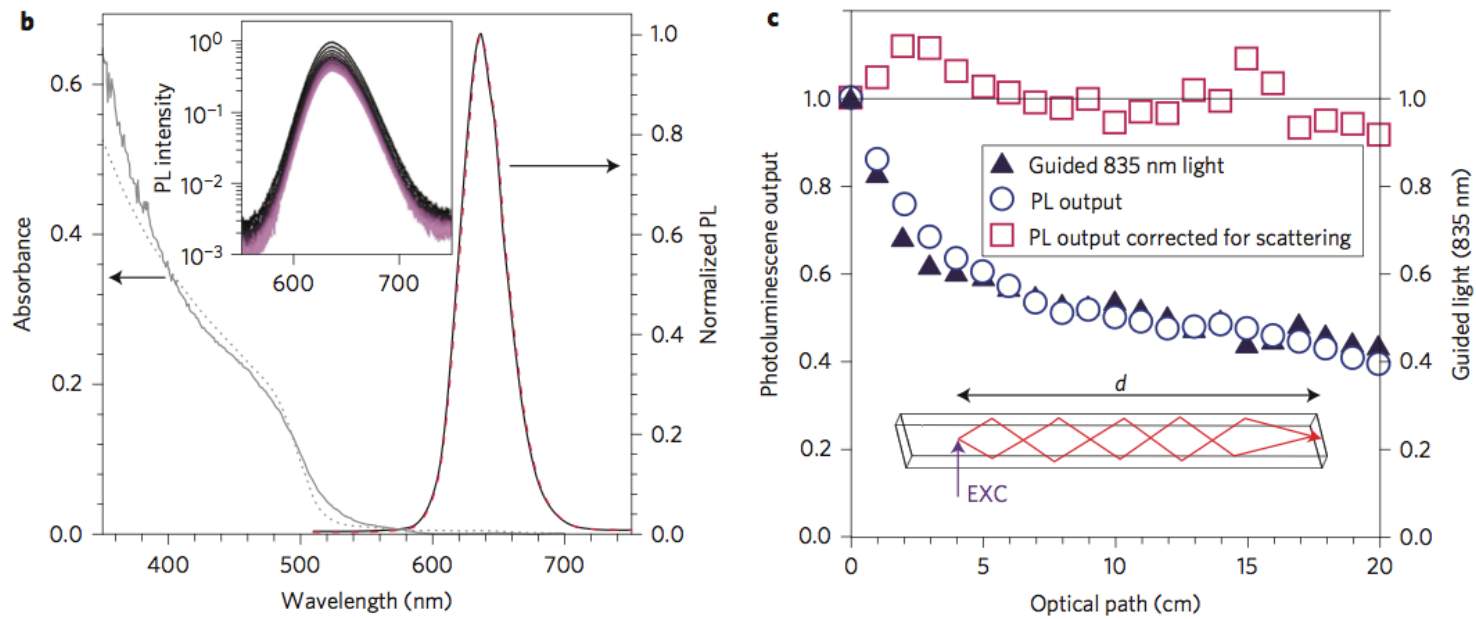
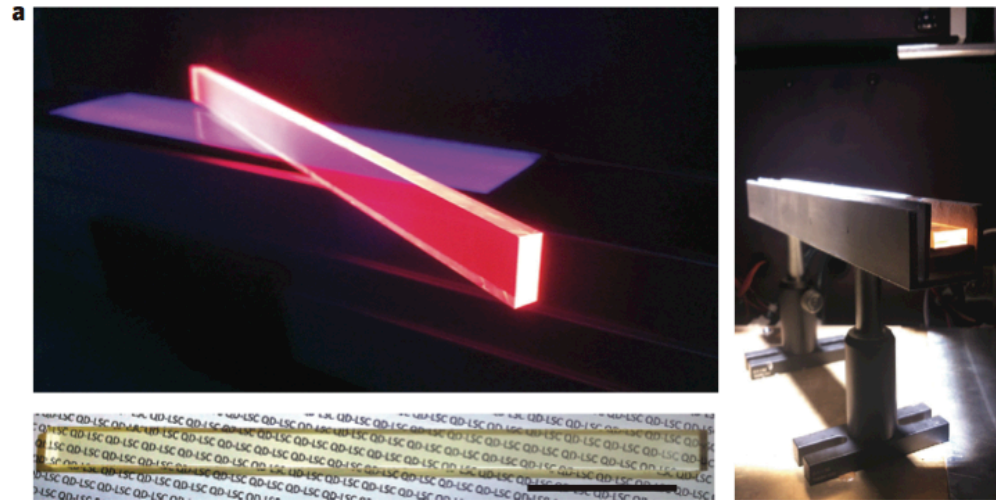
Re-absorption and emission efficiency



Quantum yield up to 99 %

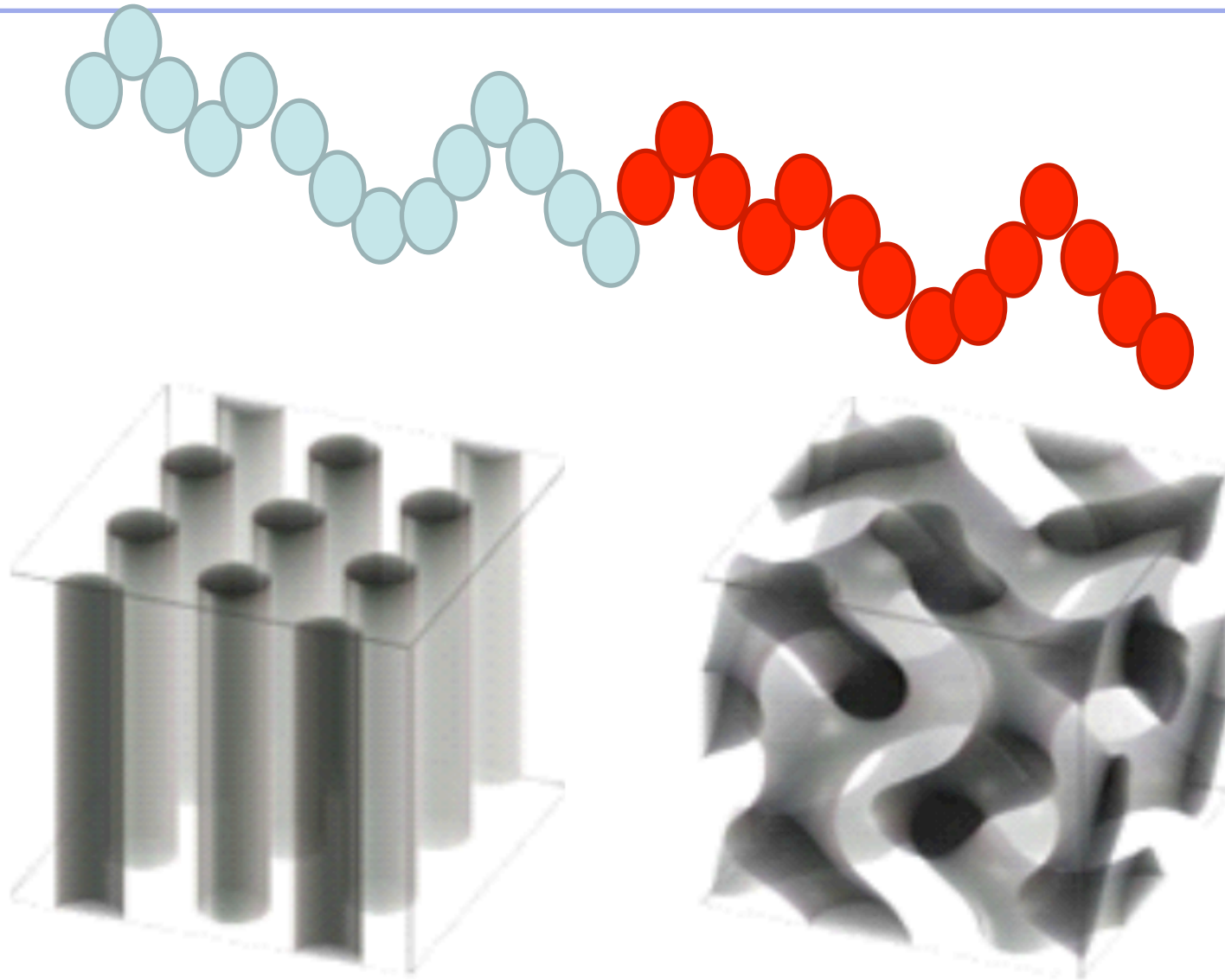
LSC and Quantum Dots





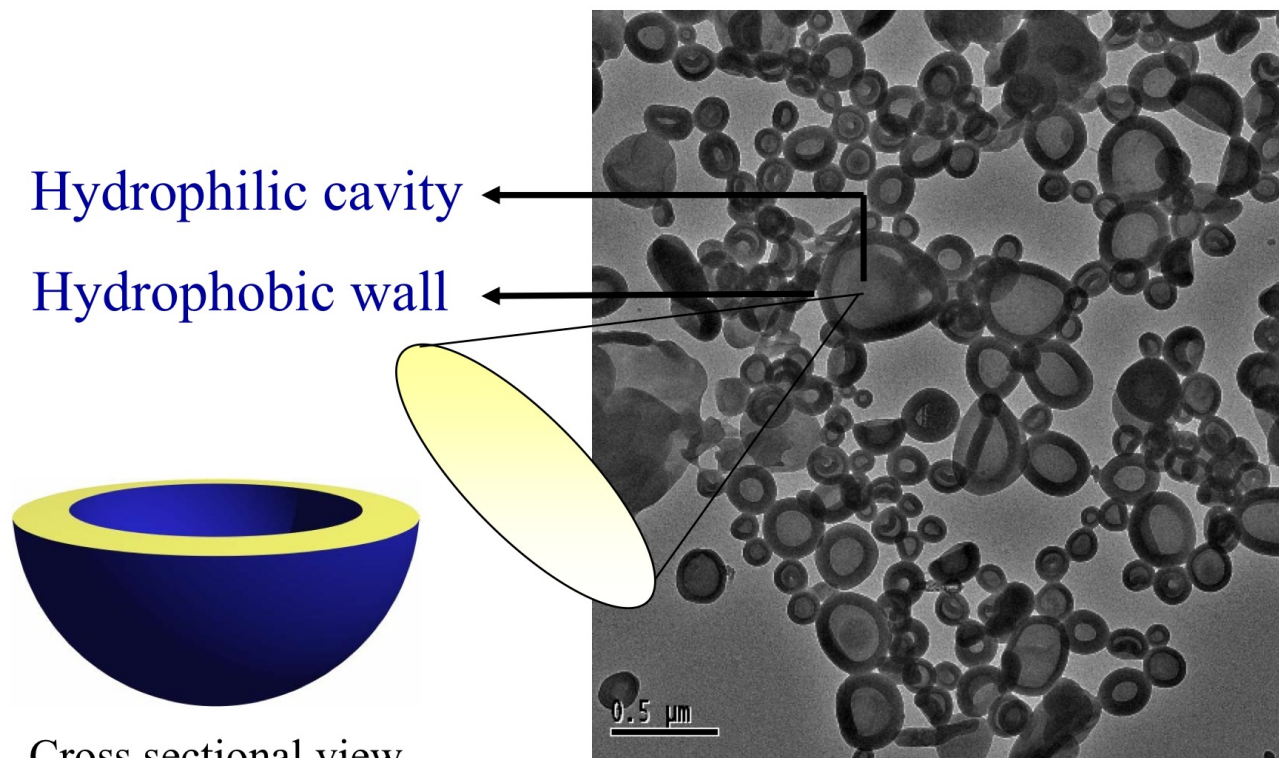
Meinardi, F. et al., 2014. Large-area luminescent solar concentrators based on “Stokes-shift-engineered” nanocrystals in a mass-polymerized PMMA matrix. *Nature Photonics*, pp.1–8.





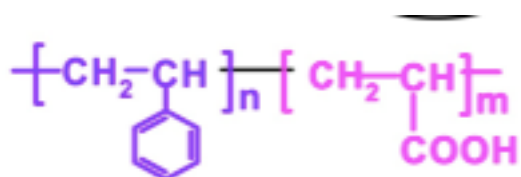


Active Loading into Vesicles



Cross sectional view

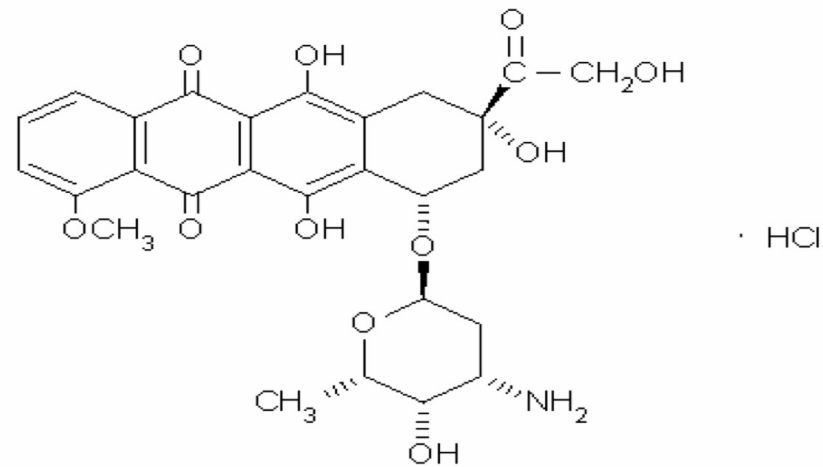
Vesicles prepared from 0.5 % (w/w)
Polystyrene₃₁₀-*b*-poly(acrylic acid)₃₆ in dioxane





What's DXR

- DXR.HCl: doxorubicin hydrochloride

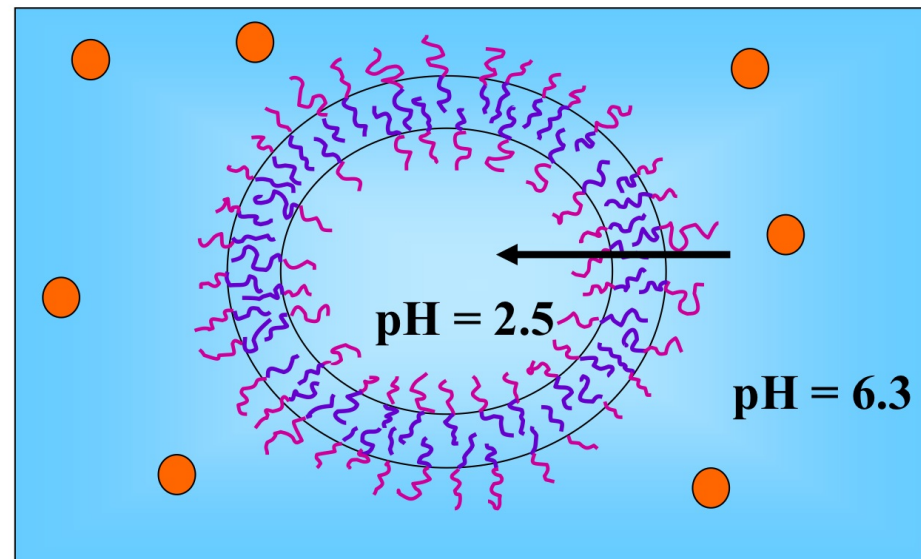


- Anti-cancer drug
- Molecular weight = 580 (g/mol)
- Water soluble (50 mg/ml)



Loading Mechanism

- = XNH_2 : neutral form can diffuse
- ⁺ = XNH_3^+ : protonated form can NOT diffuse

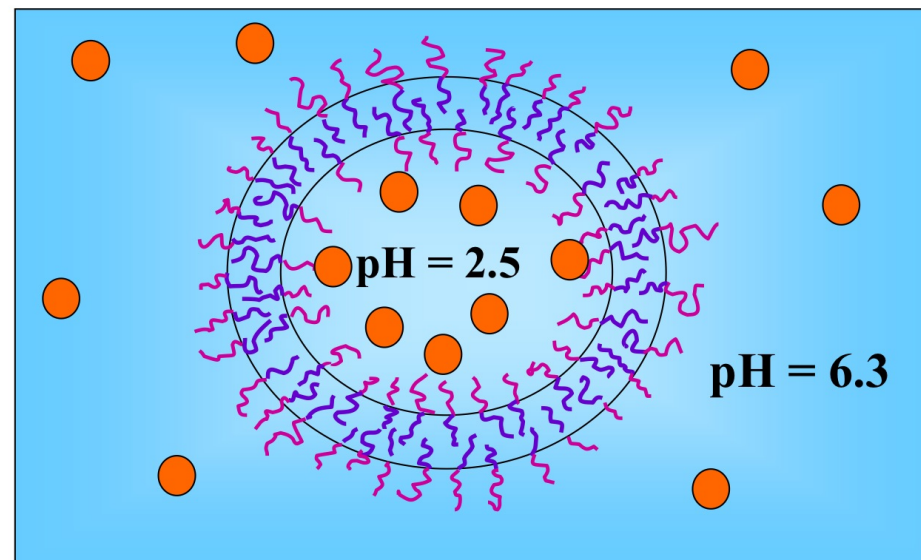




Active Loading into Vesicles

Use vesicles as model carriers for Doxorubicin

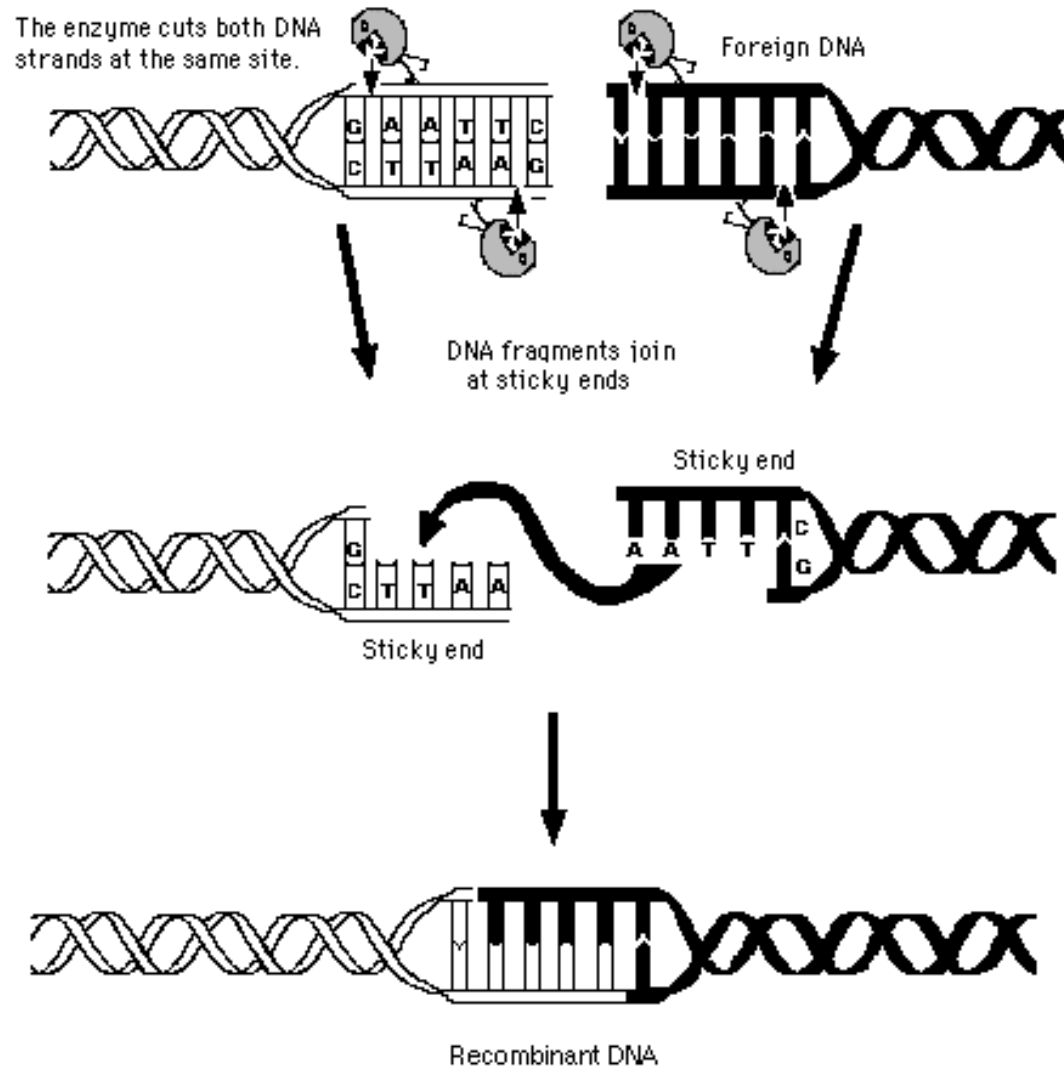
Induce loading by creating a transmembrane pH gradient



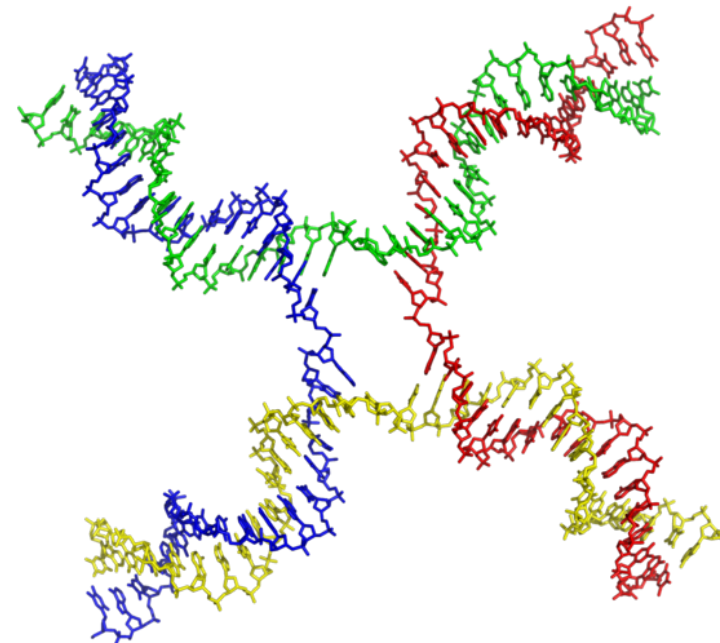
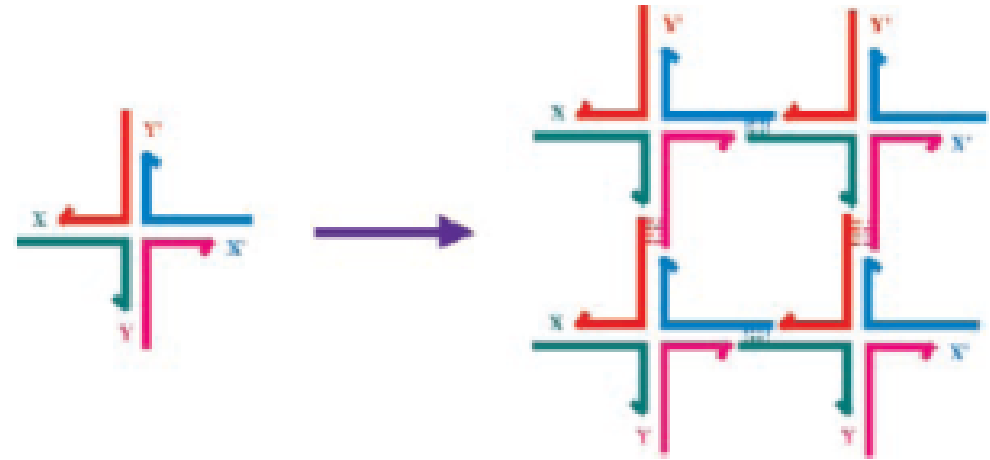
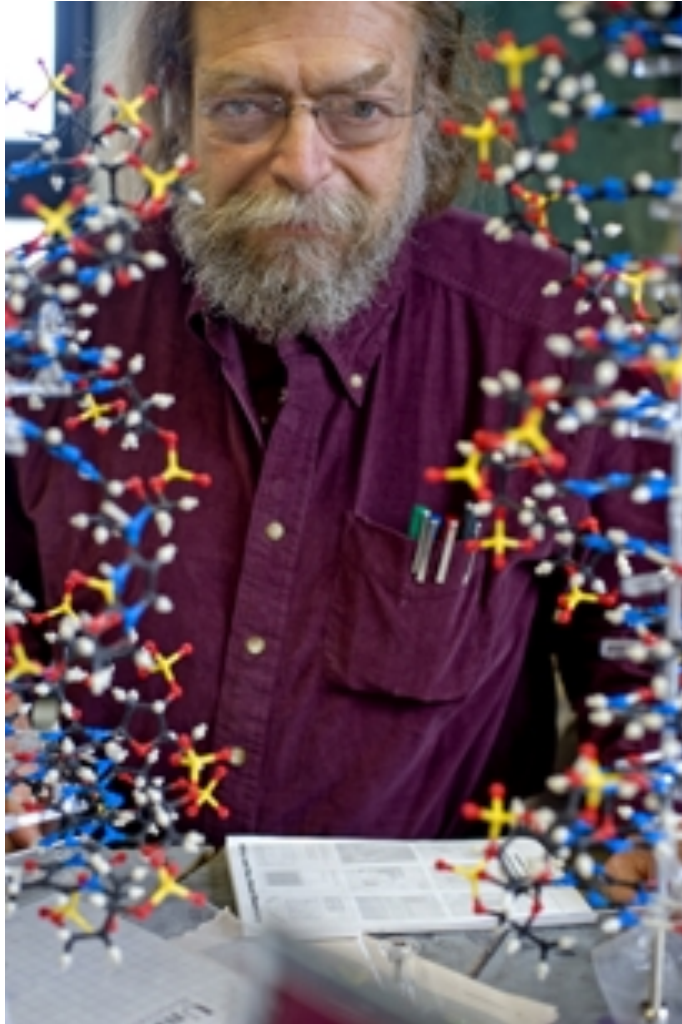


Restriction Enzyme

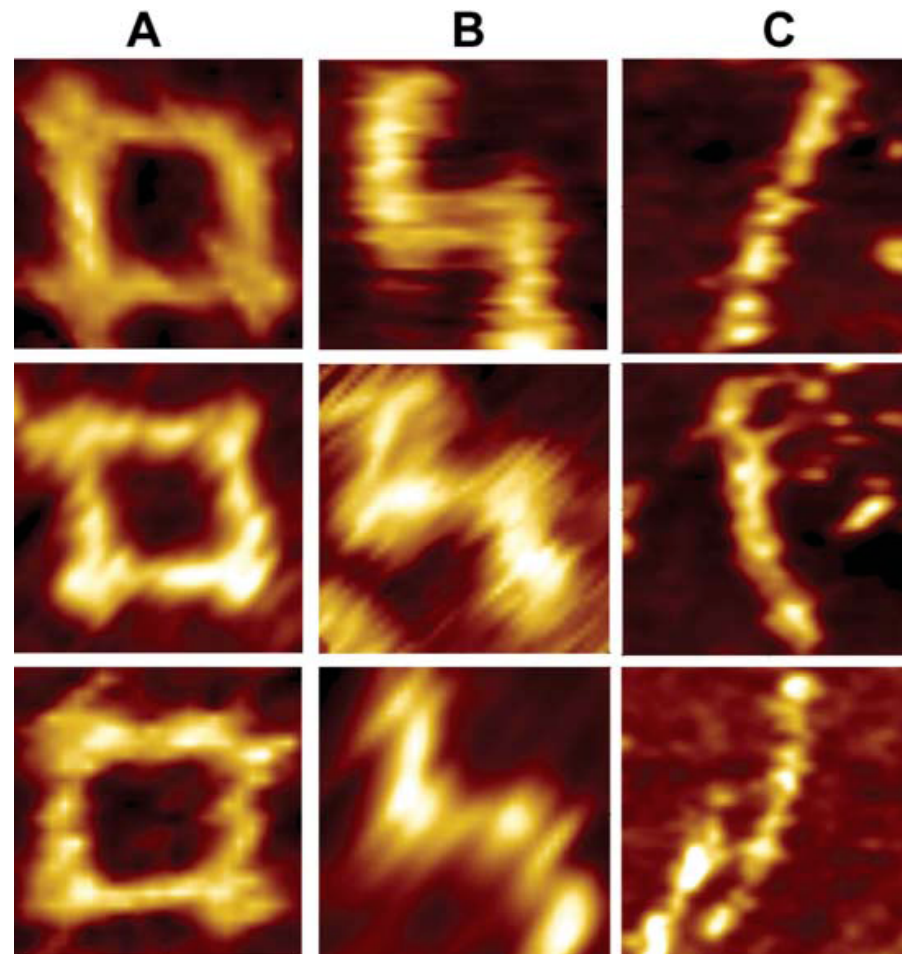
Action of EcoRI



self-assembly of DNA nanostructures

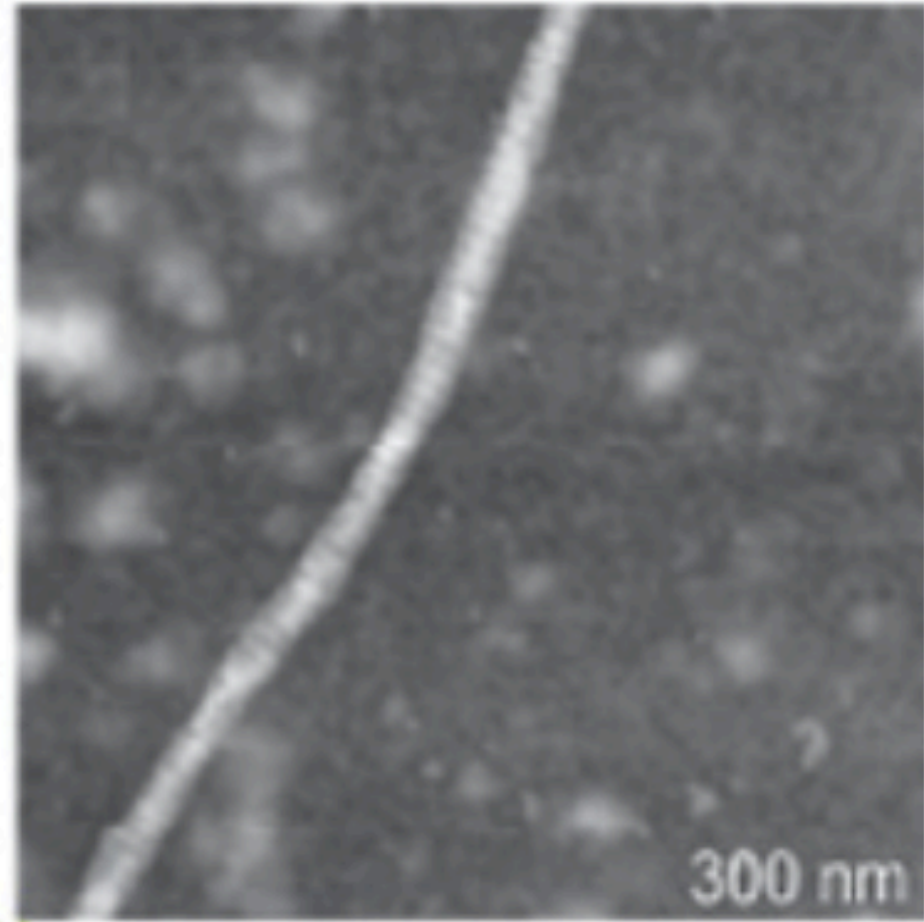
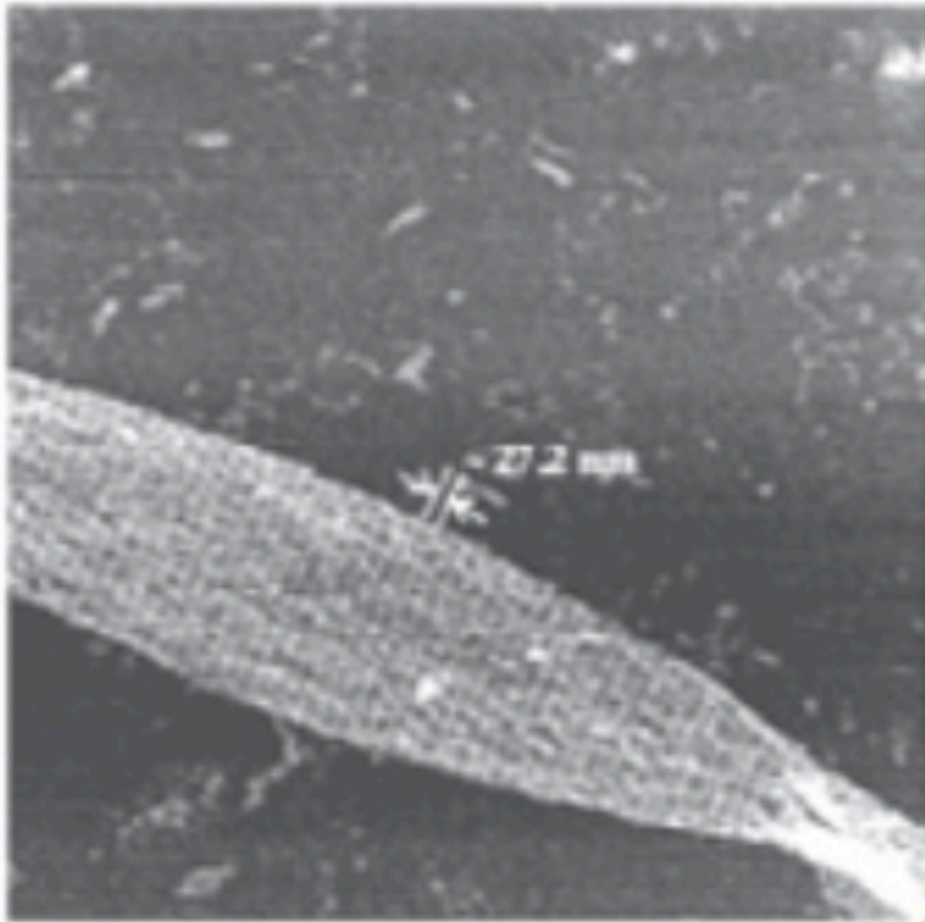
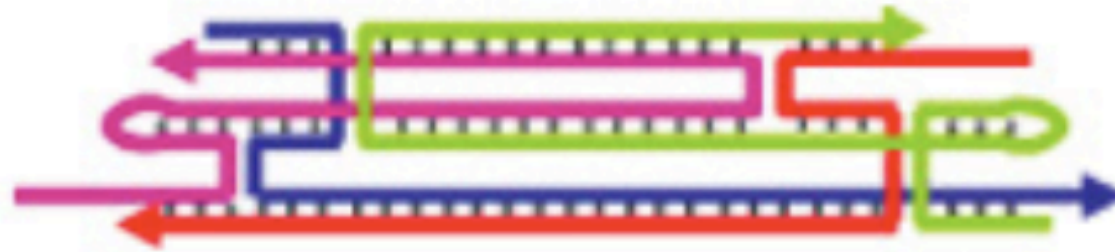


AFM pictures of DNA tiles combinations





(b)

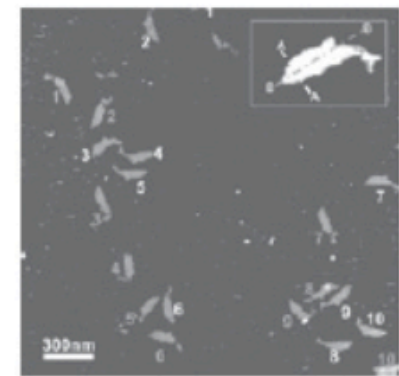
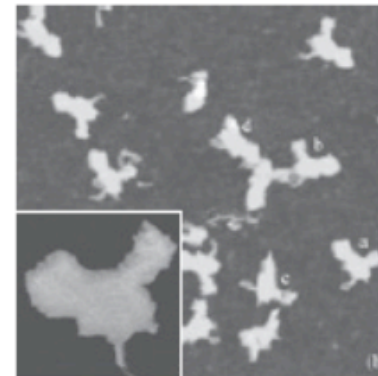
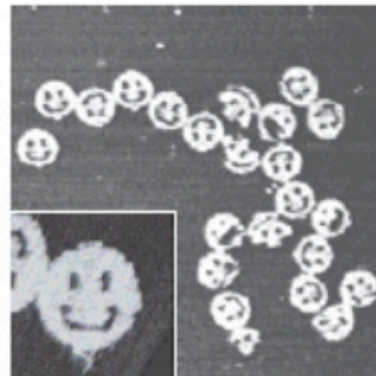
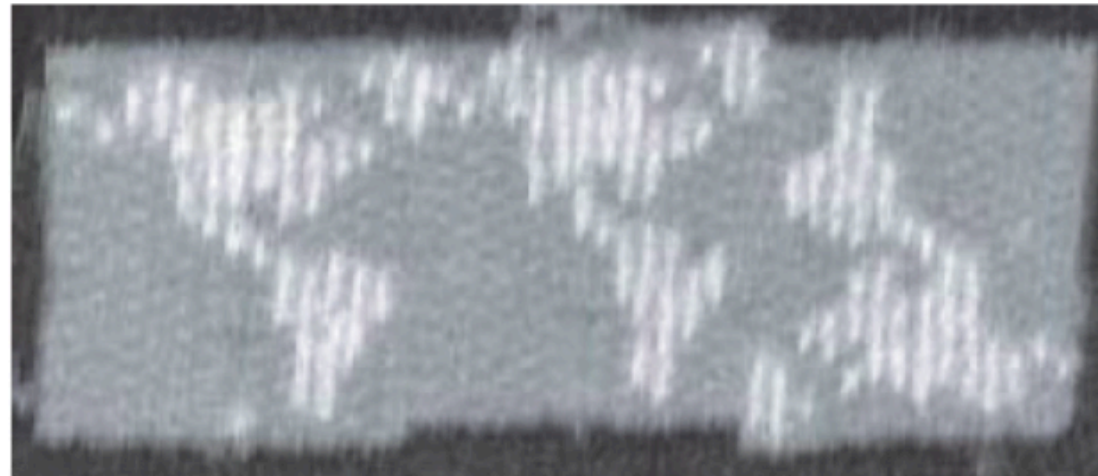
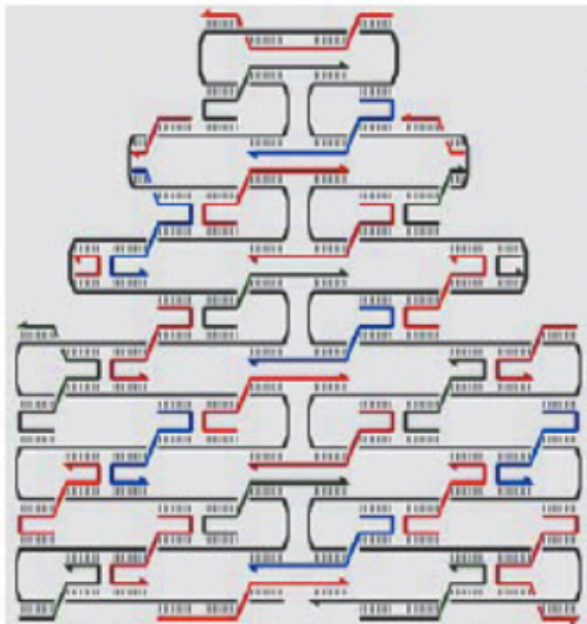


DNA triple crossover complex and resulting 2D arrays and tubes

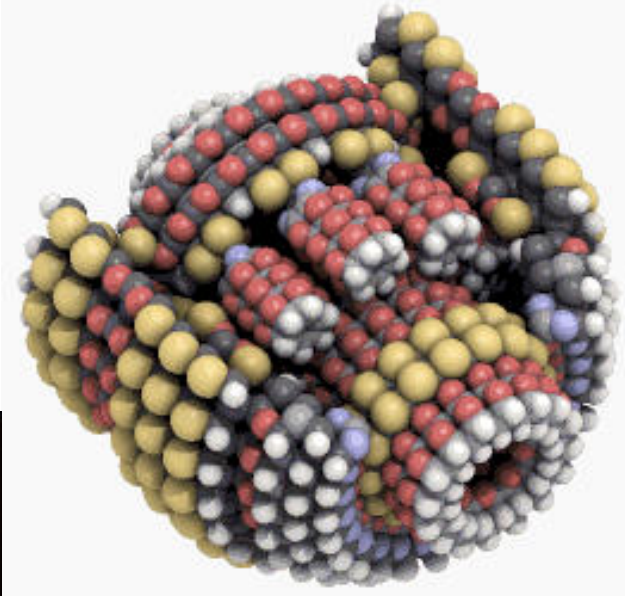
Extreme self assembly



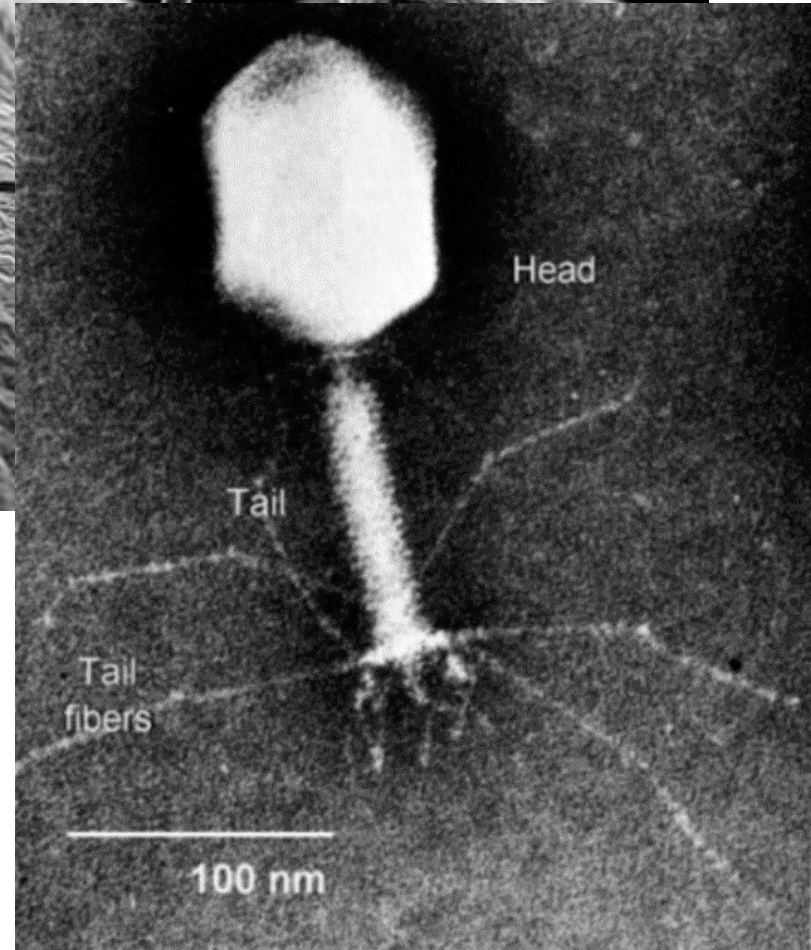
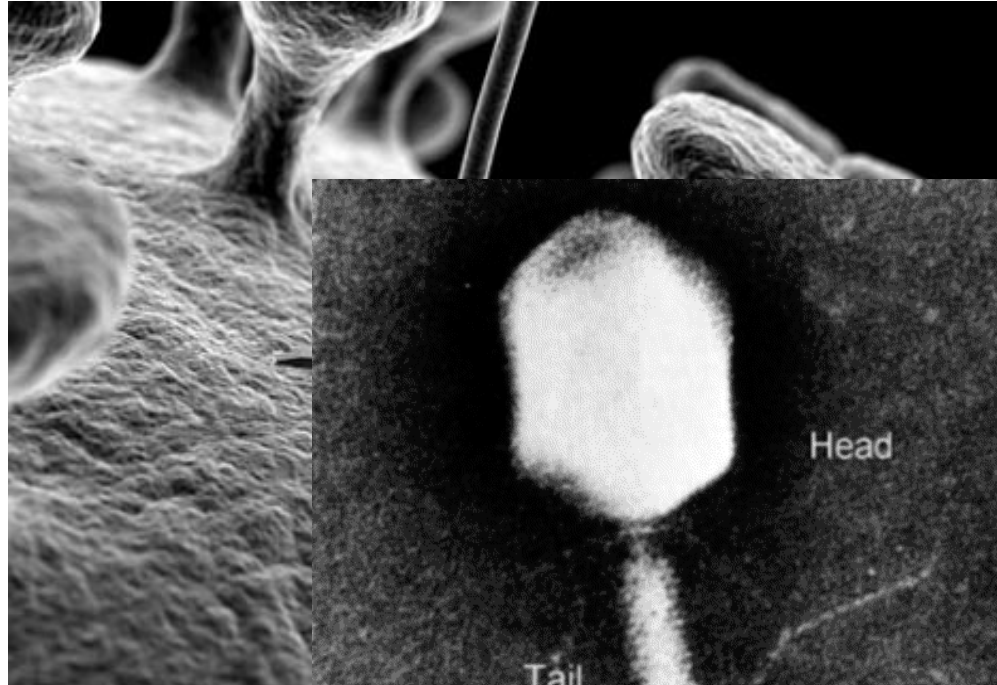
(b)



Eric Drexler and self replicating nanomachines



versatile
independent
deterministic
Self replicating



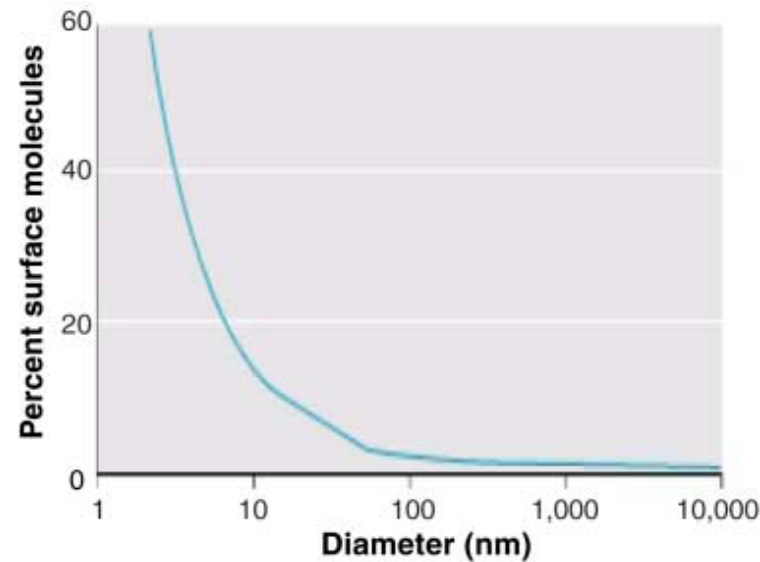


Risks

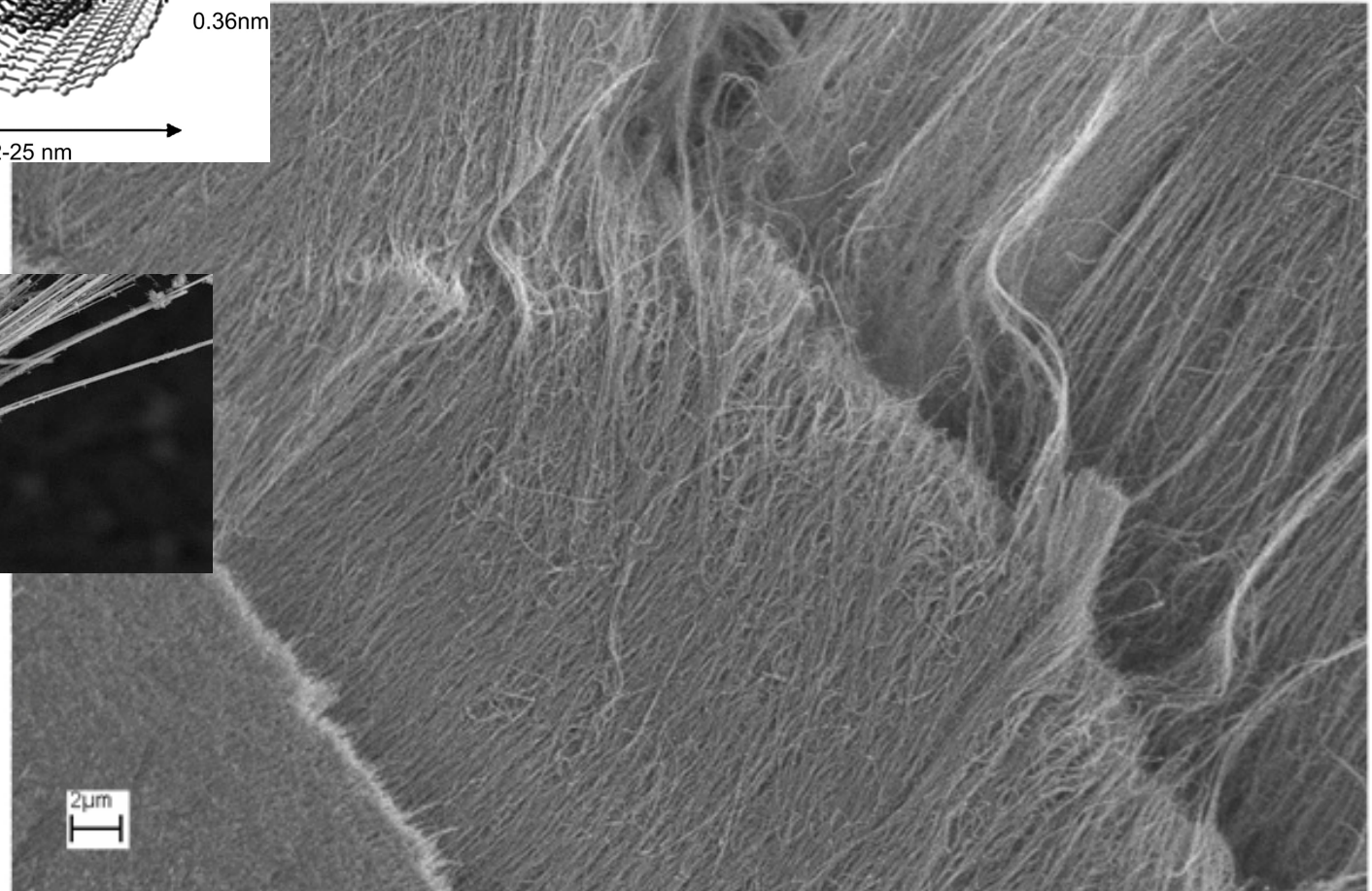
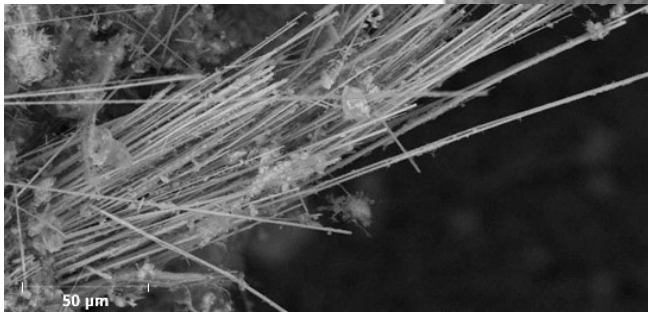
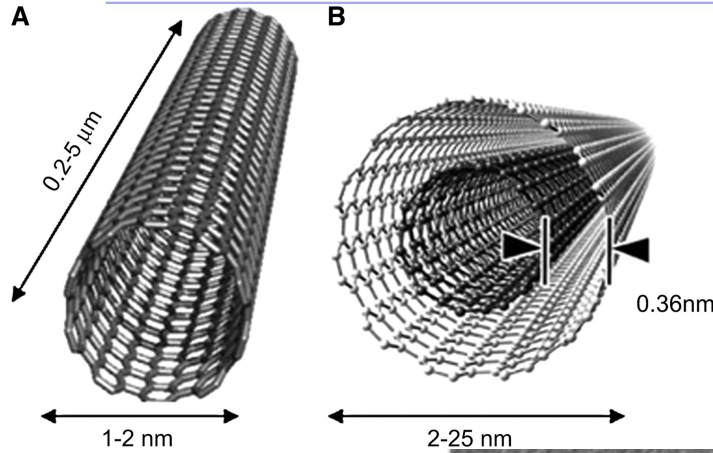


Benefits

Exposed surface = chemical reactivity



Morphology and toxicity



Thanks!



image courtesy of The Boeing Company