Nanoparticles in Materials and Life Sciences
Hannover, 31. Mai 06

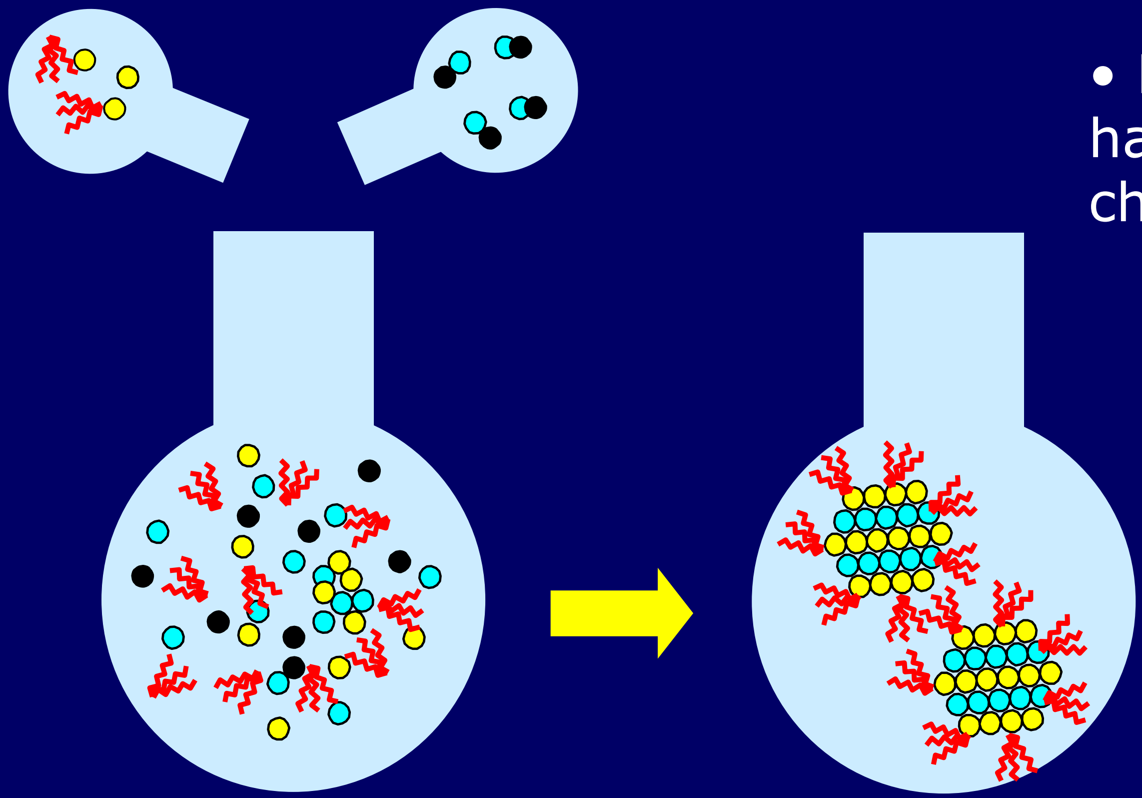
Horst Weller
Institut für Physikalische Chemie und Centrum für Angewandte Nanotechnologie CAN, Hamburg

Synthese and Lumineszenz von Quantum Dots
Magnetische Nanoteilchen
Self Assembly und Drug Delivery

Nanoparticle Synthesis

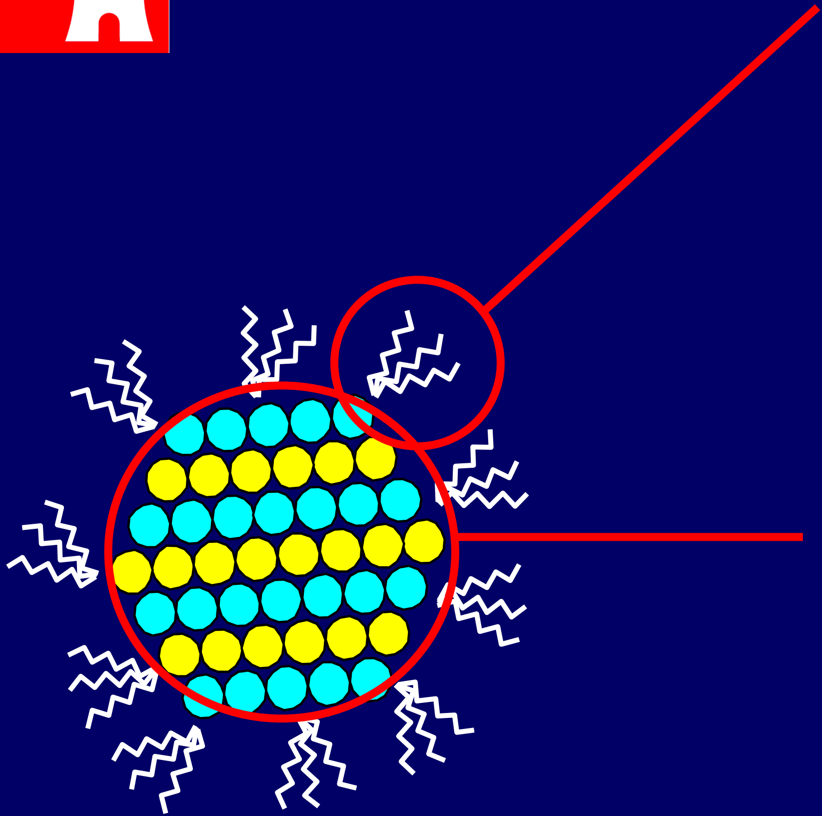
Precursor solutions

- Large variety of materials available
- Nanoparticles can be handled like “normal“ chemicals



Mixing

Arrested precipitation



Ligands keep particles small, determine solubility and allow linking to biological molecules

Chemical and physical properties are determined by the particle size, e.g.

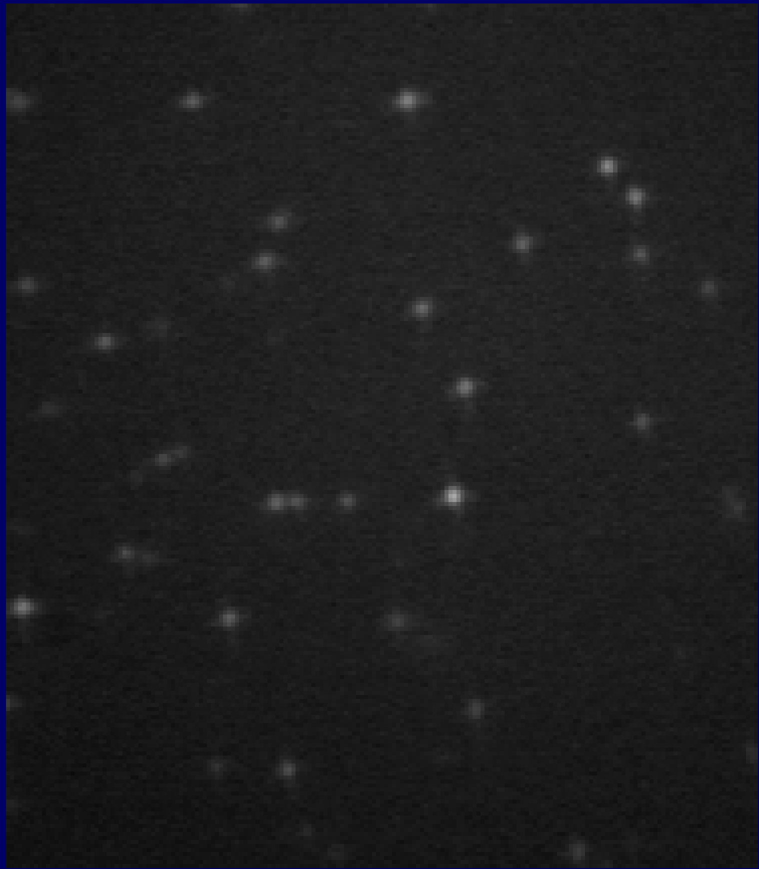
- (fluorescence)-colour
- magnetism
- conductivity
- hardness
- melting point....

Luminescent II-VI nanocrystals (quantum dots)

Room temperature PL quantum efficiencies up to 85%

PL of CdSe/ZnS core-shell nanocrystals in chloroform.

Composites of CdSe/ZnS and CdSe/CdS nanocrystals and polylaurylmethacrylate (PLMA)



Single particle luminescence of CdSe/ZnS nanocrystals (collaboration with Prof. O. Benson, Paul Drude Institut, Berlin)

Monodisperse samples requires separation of nucleation and growth

- Allow spontaneous nucleation
- Reduce temperature or pH after initial nucleation process to avoid further nucleation but allow growth

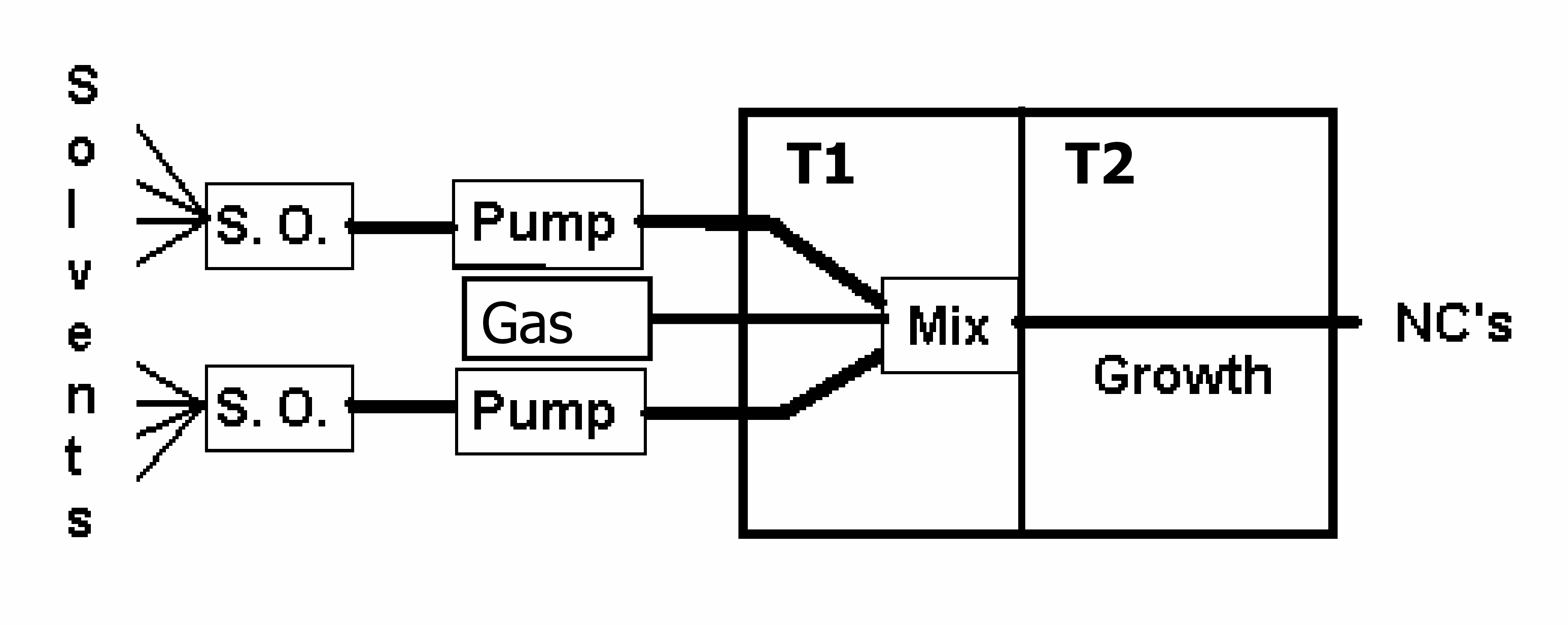
Monodisperse samples requires separation of nucleation and growth

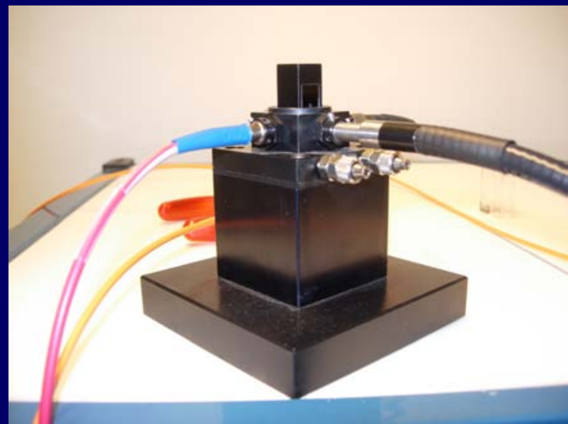
- Allow spontaneous nucleation
- Reduce temperature or pH after initial nucleation process to avoid further nucleation but allow growth

Highly luminescent particles require smooth surfaces

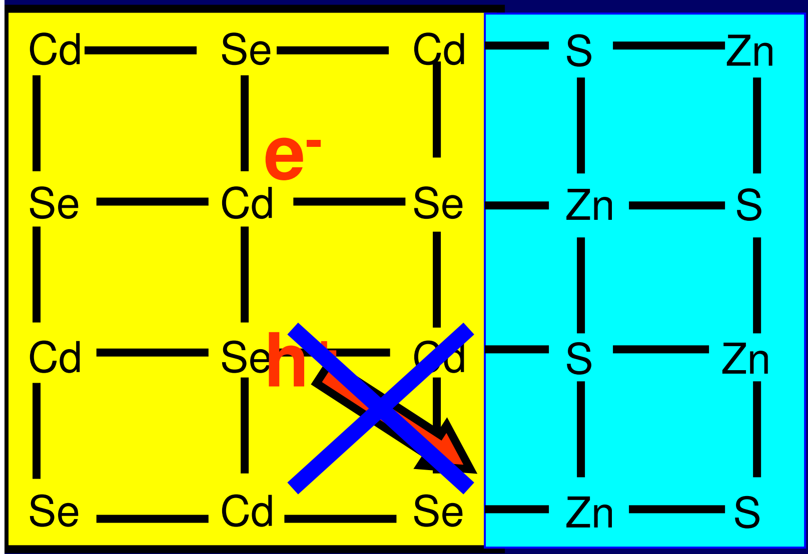
- **Grow under conditions, where monomers undergo rapid surface exchange**
- **Use two types of ligands**

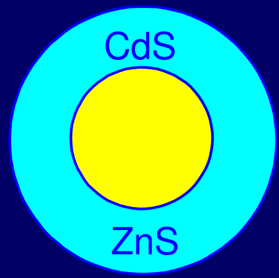
Flow Reactor

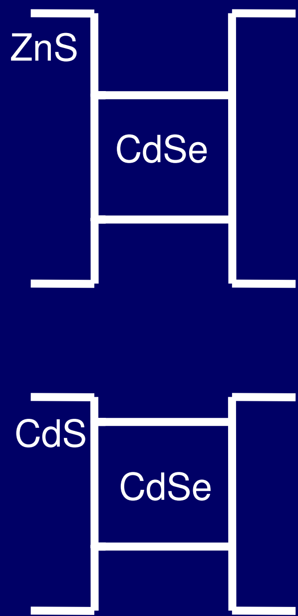


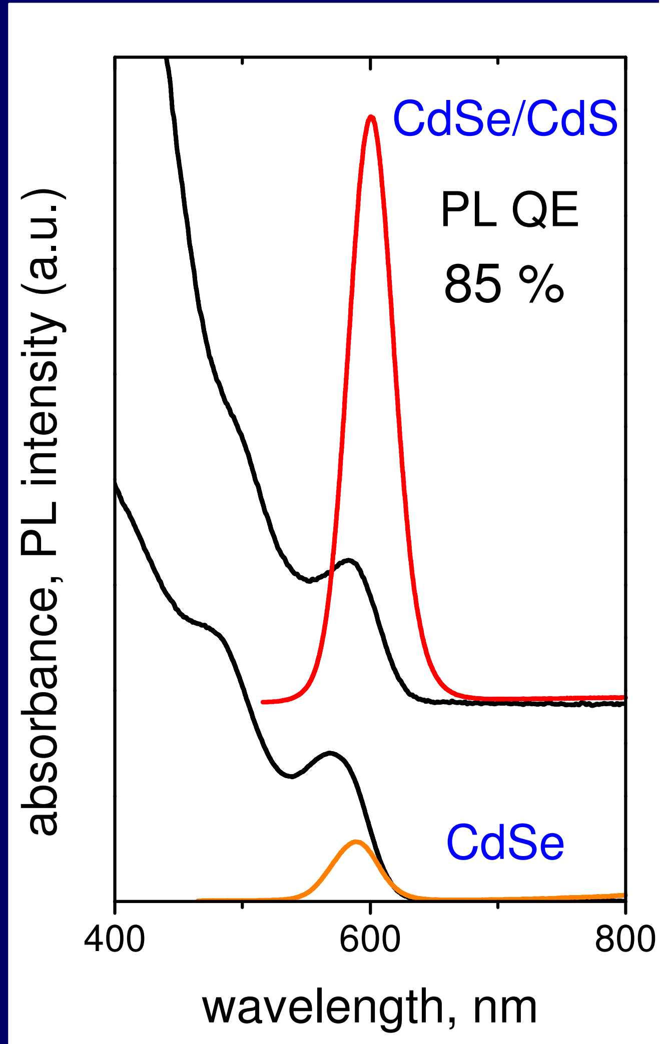


Highly luminescent core-shell nanocrystals



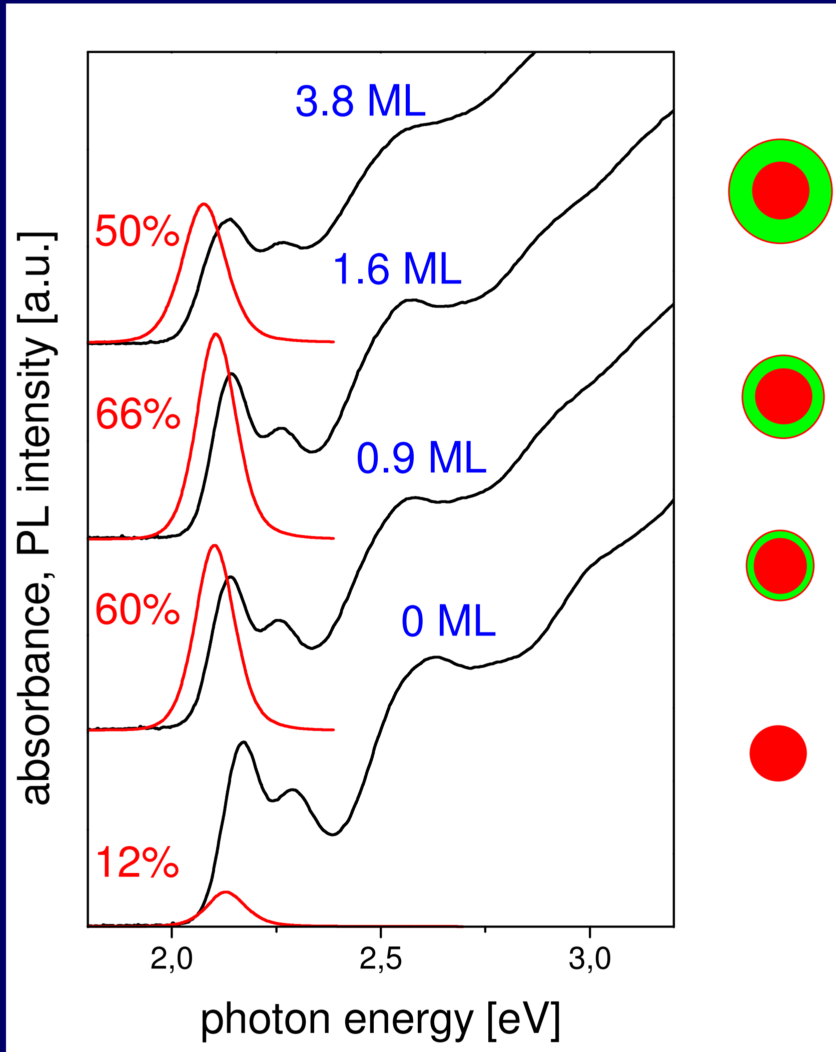




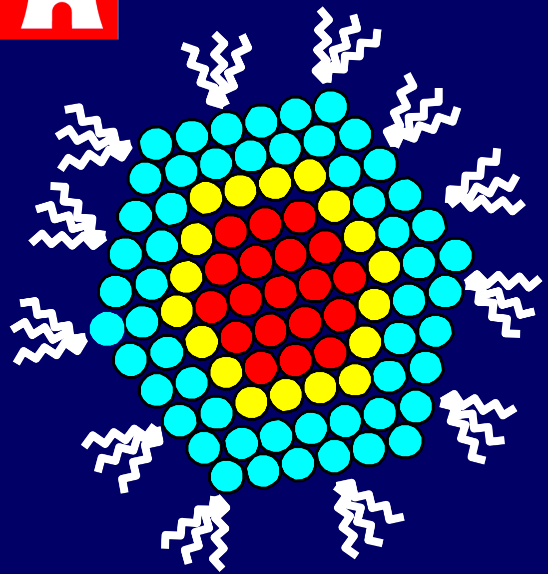


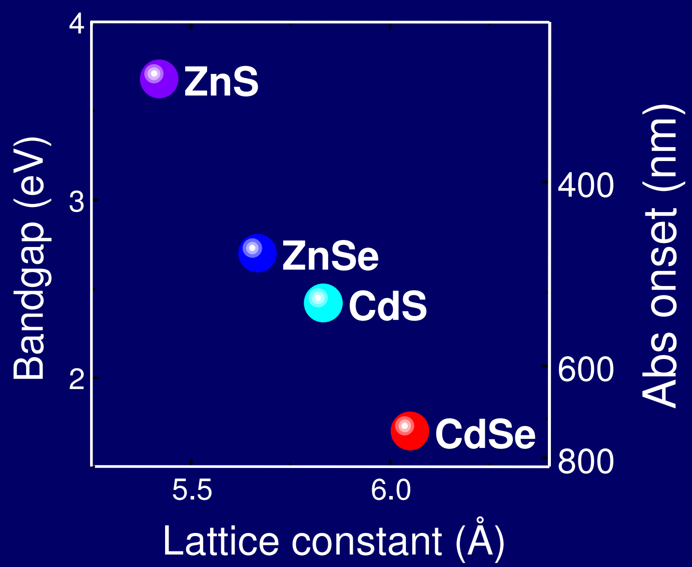
Core-shell CdSe/ZnS nanocrystals

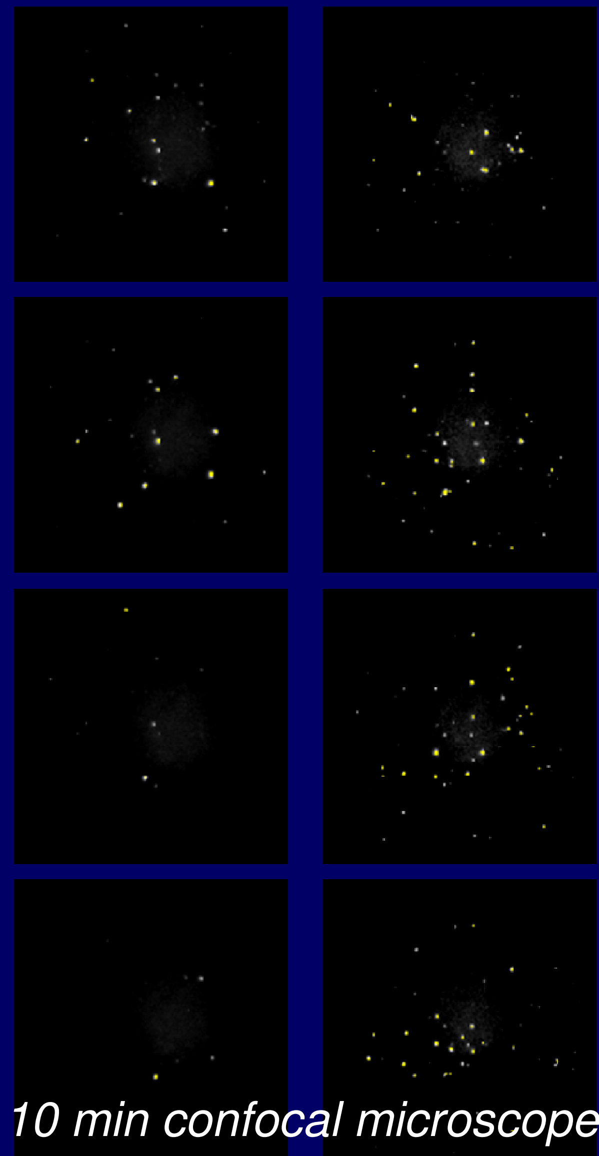
$$\text{nano-CdSe} + Zn(CH_3)_2 + [(CH)_3Si]_2S \xrightarrow{HDA-TOPO-TOP,\ 200°C} CdSe/ZnS$$



CdSe/CdS/ZnS and CdSe/ZnSe/ZnS nanocrystals

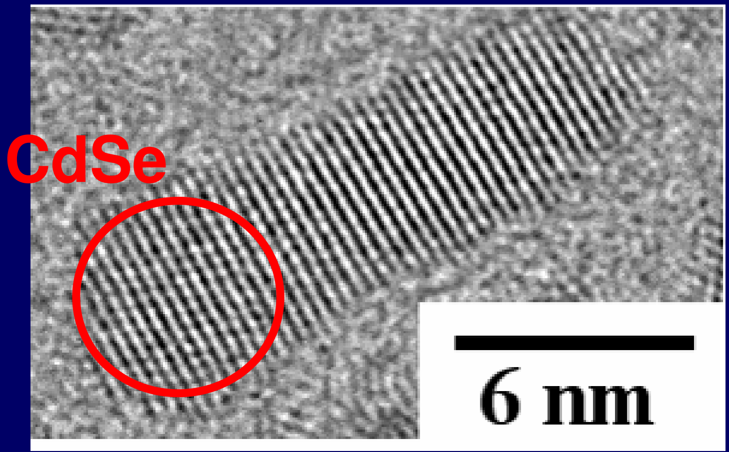


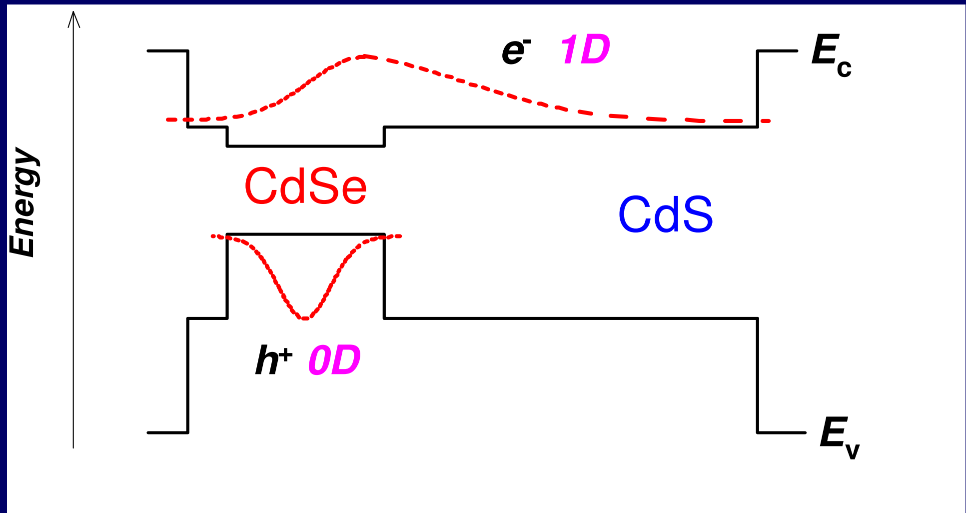




CdSe/ZnS CdSe/ZnSe/ZnS

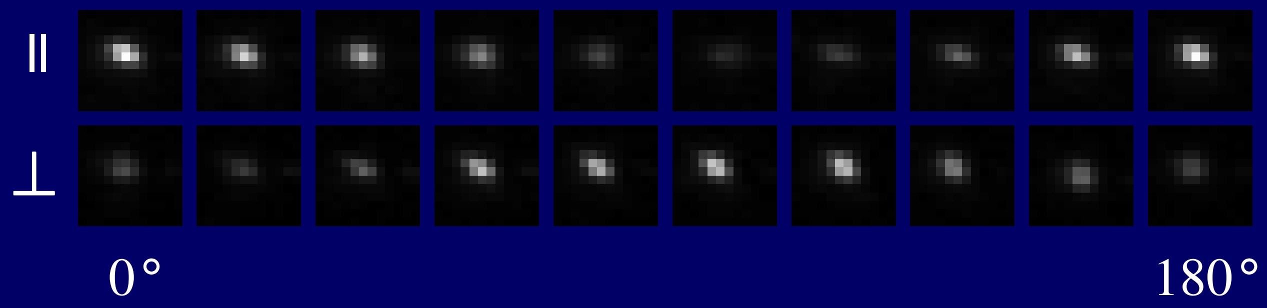
CdSe/CdS quantum dot quantum rods





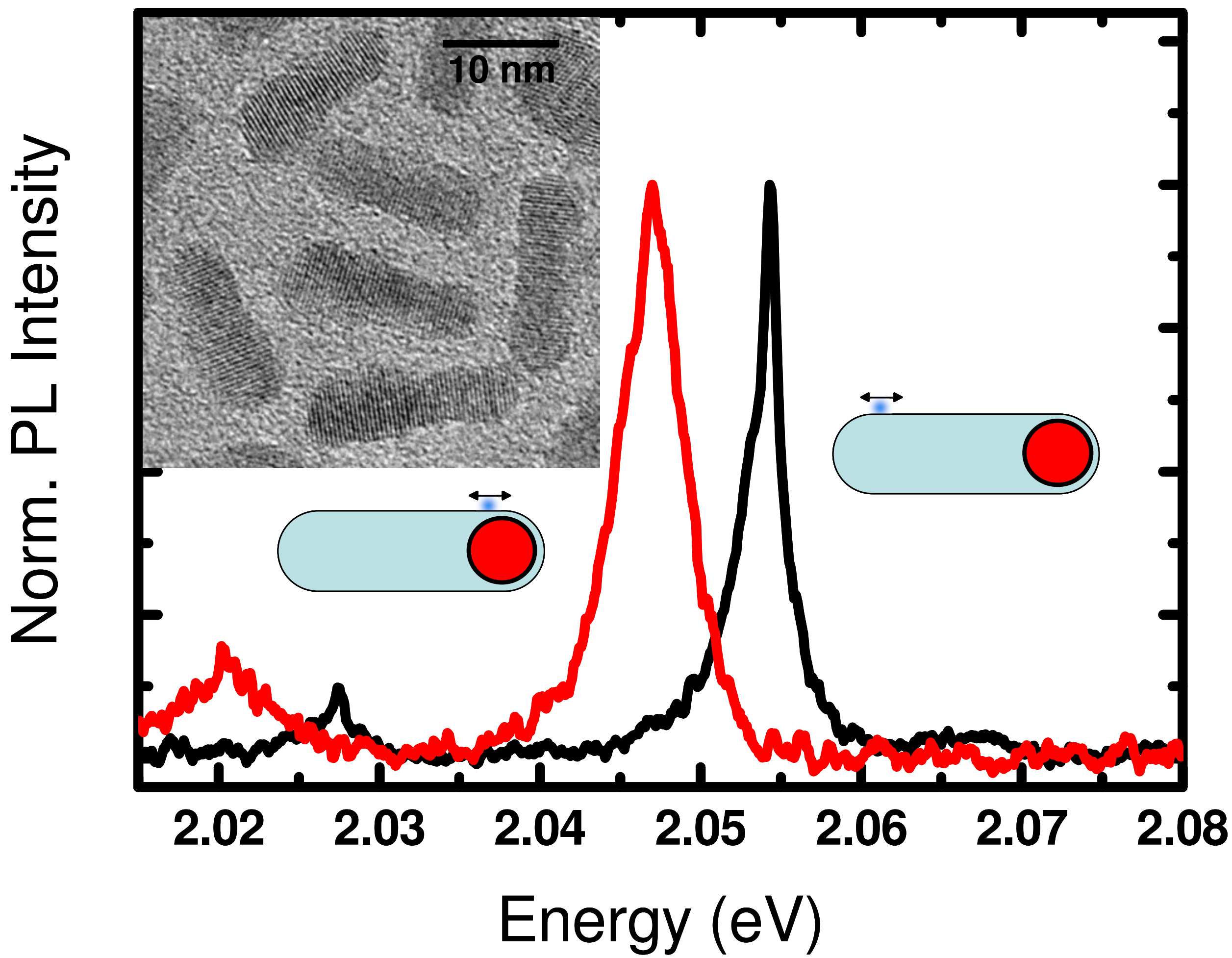
electronic structure of CdSe/CdS QD-QR nanocrystals

Polarized luminescence with quantum efficiency ~60% !



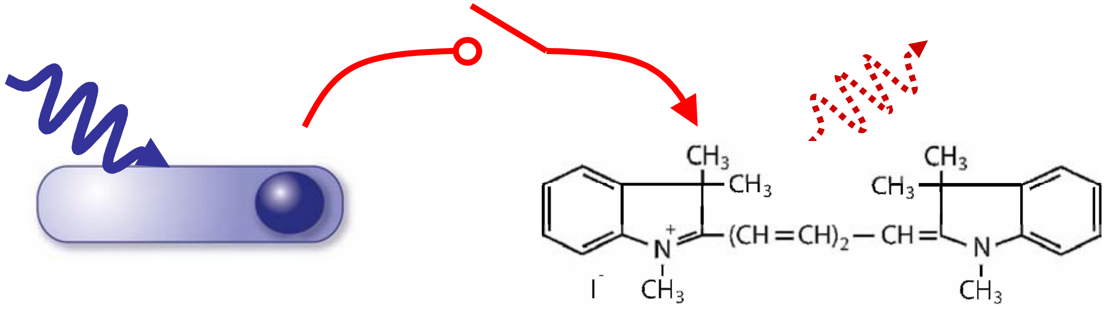
Kooperation mit Oliver Benson (HUB) und Jochen Feldmann (LMU)

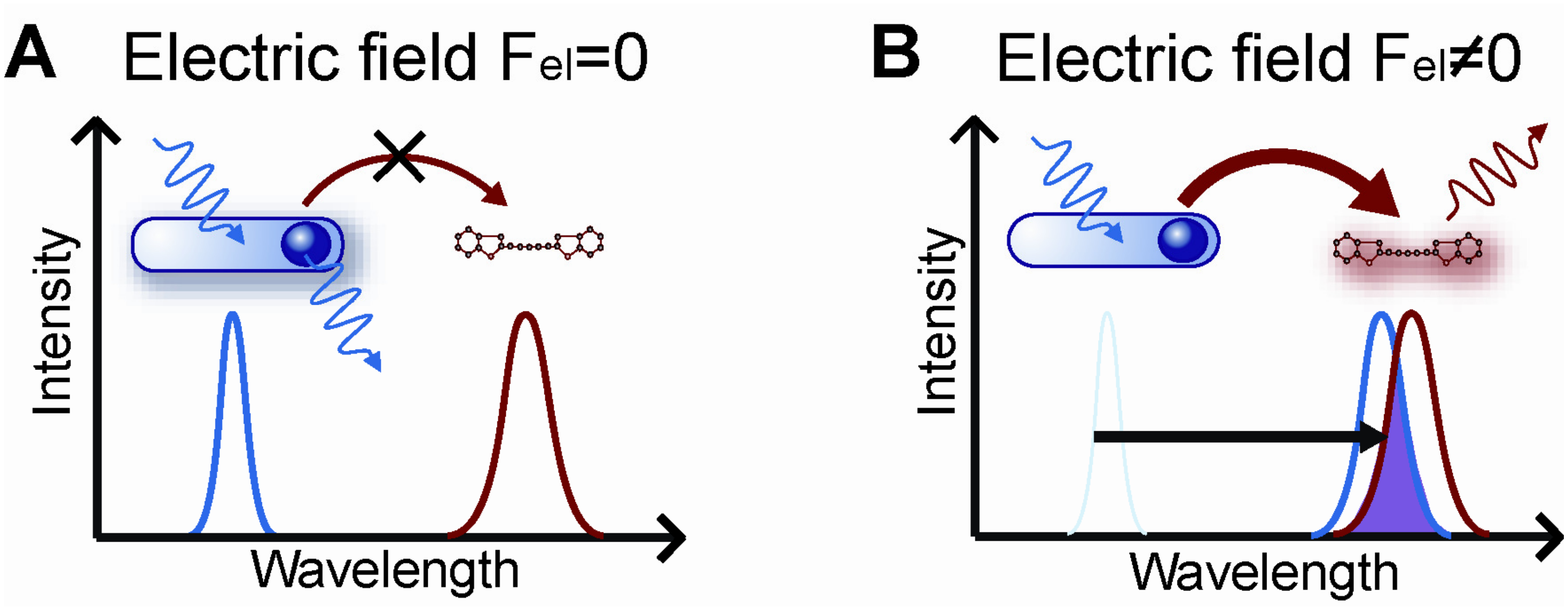
Single quantum dot quantum rod luminescence



Jochen Feldmann, LMU

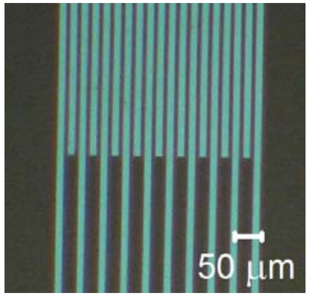
Electrically Switchable Energy Transfer (FRET)

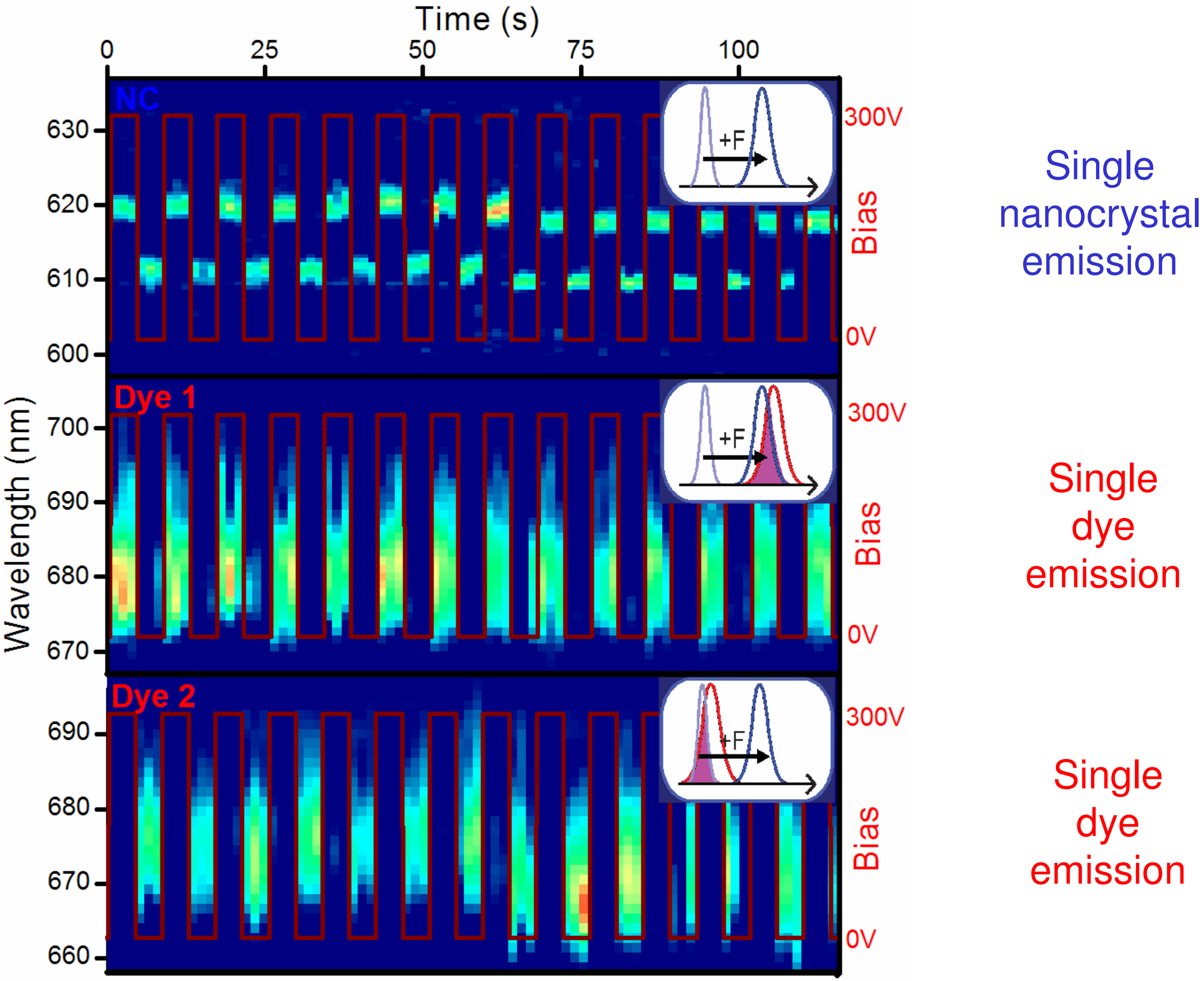




Jochen Feldmann, LMU

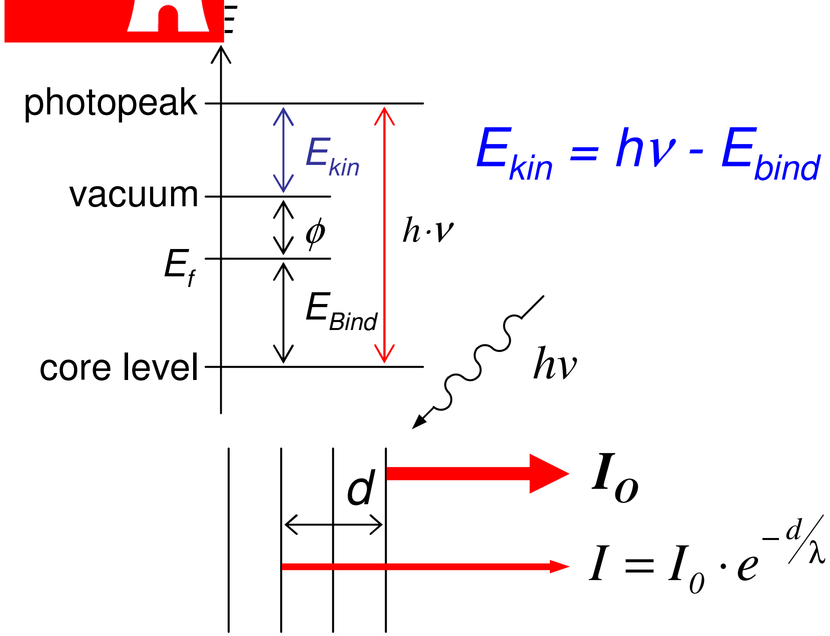
Electrically Switchable Energy Transfer (FRET)

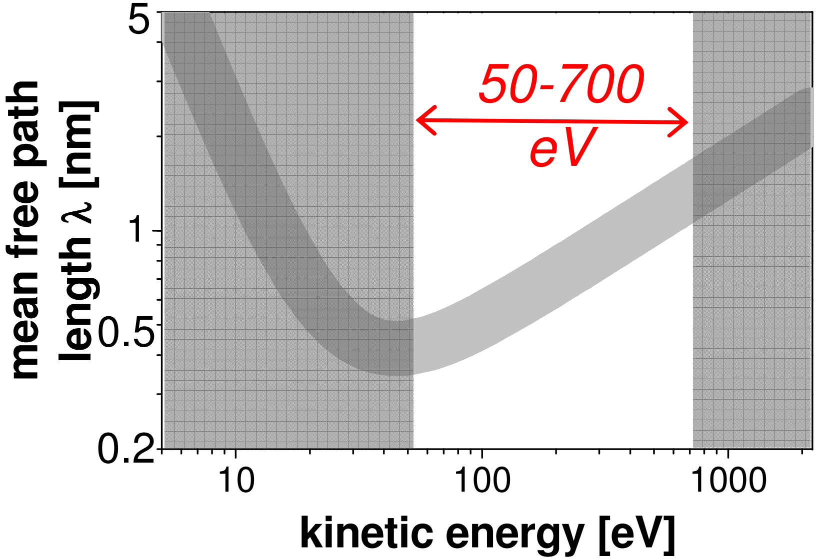




Synchrotron XPS as structural probe for nanoparticles

$$E_{kin} = h\nu - E_{bind} - \phi$$





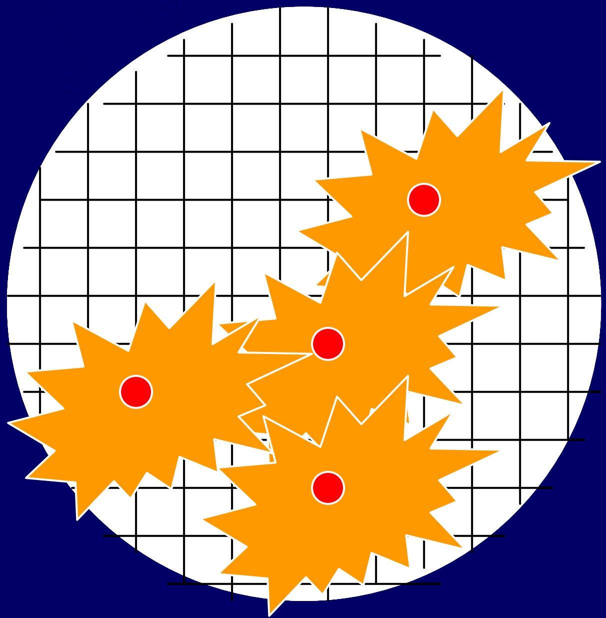
We could identify:

- **core shell growth**
- **surface etching**
- **dopant profiles**

Collaboration with Thomas Möller, HUB

Doped Nanoparticles

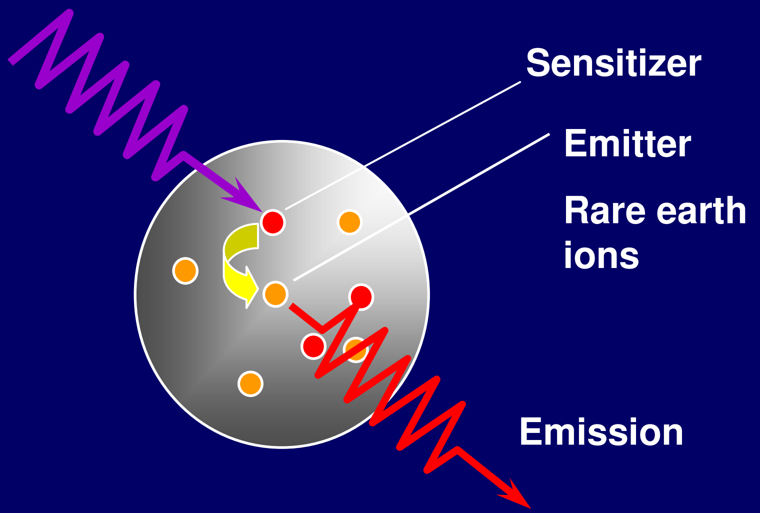
REN-X: Fluorescence of rare earth doped nanoparticles



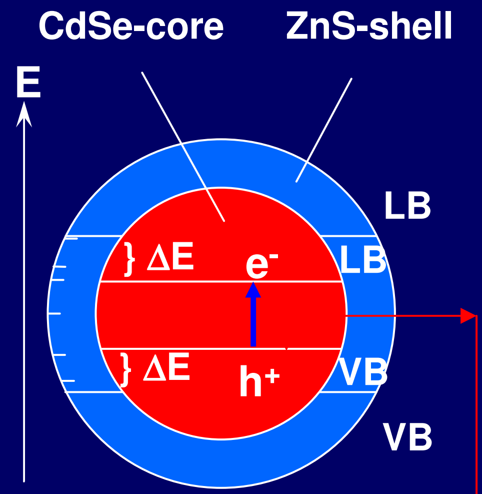
e.g. $LaPO_4$: Ce,Tb

Markus Haase, now University Osnabrück

Semiconductor versus REN-X®



Different colors by different emitters and crystalline hosts

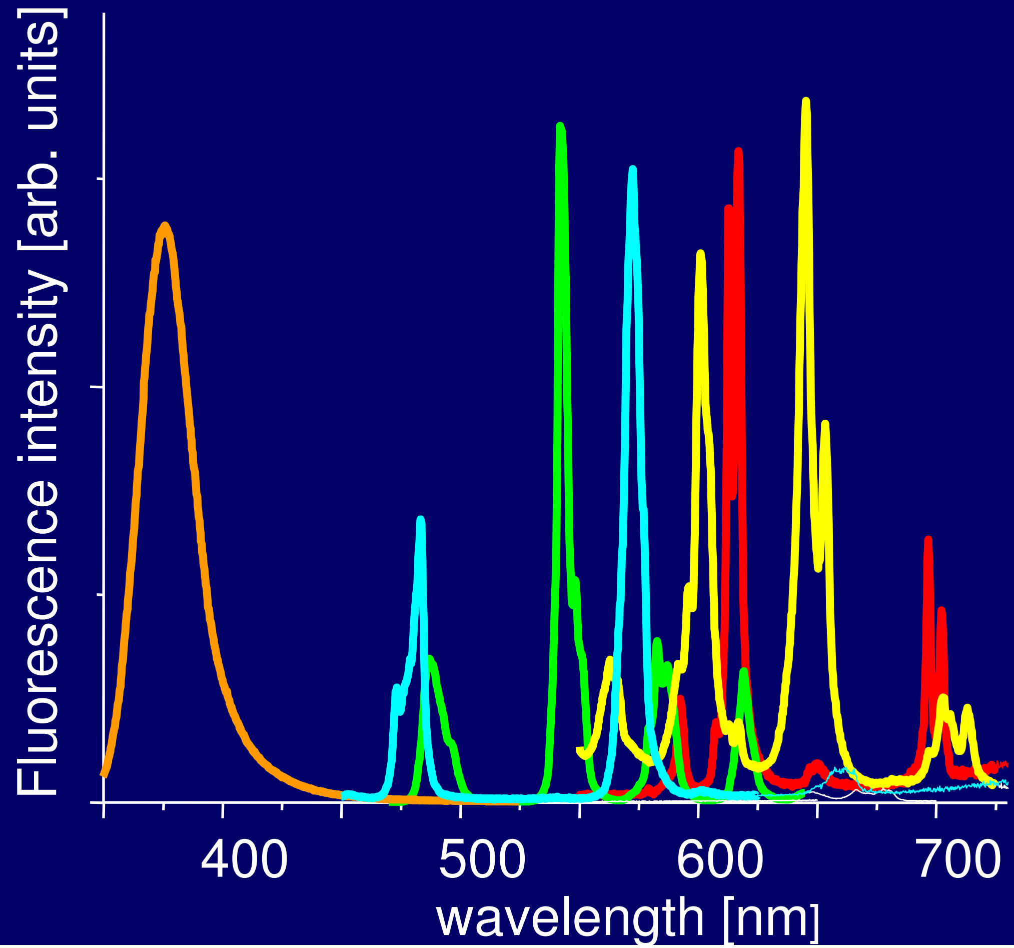


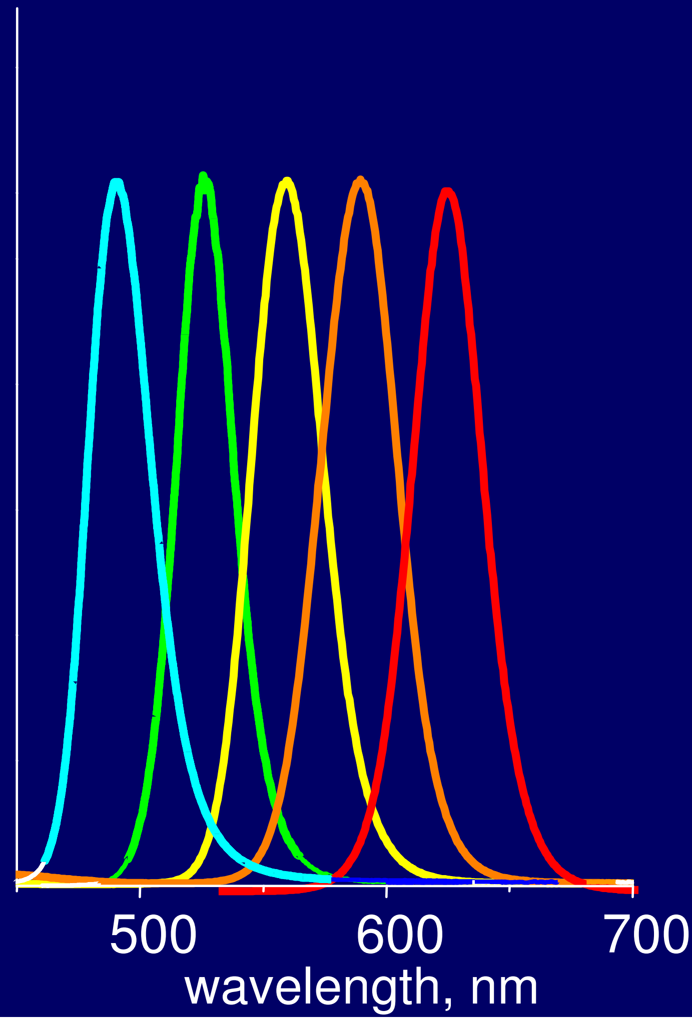
Different colors by size variation

REN-X lables versus quantum dots

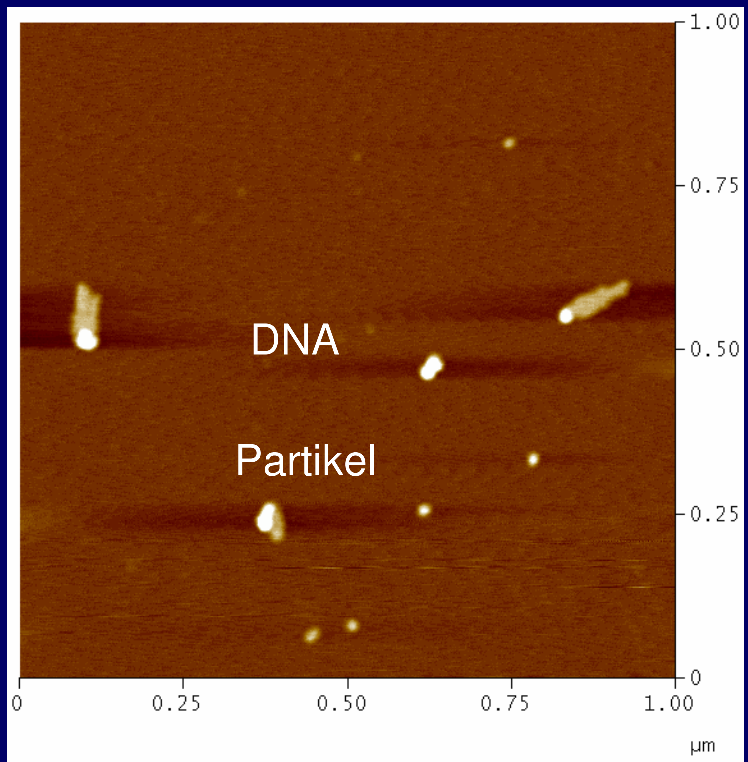
REN-X
- smaller linewidth
- higher stability
- excitation in uv

Q-dots
- shorter lifetime
- excitation in the visible





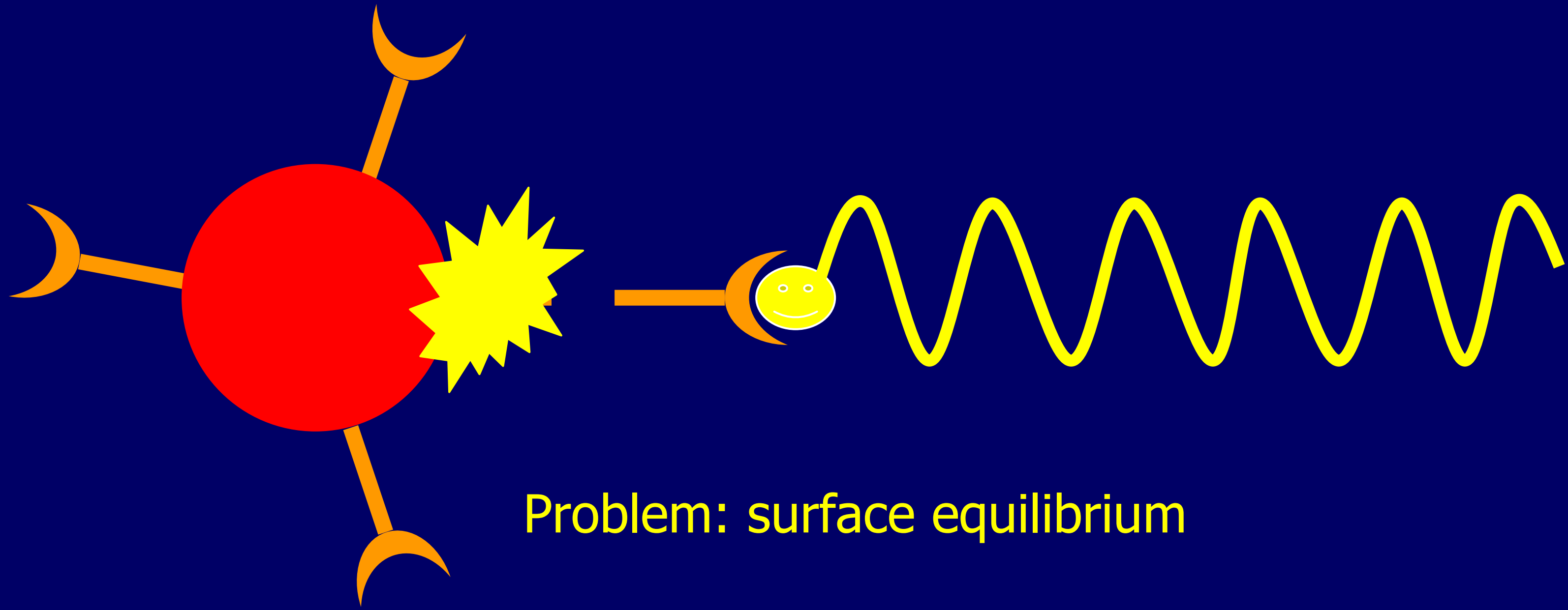
Einsatz von Nanopartikeln in Diagnostik und Therapie



- REN-X, Q-Dots für Lumineszenz
- Magnetische Nanopartikel als Kontrast-mittel für magnetische Resonanz und zur Hyperthermie
- Fast alle Nanopartikel führen zur Erhöhung von Röntgen und Elektronenkontrast
- Einbau von radioaktiven Isotopen
- Multifunktionale Nanopartikel

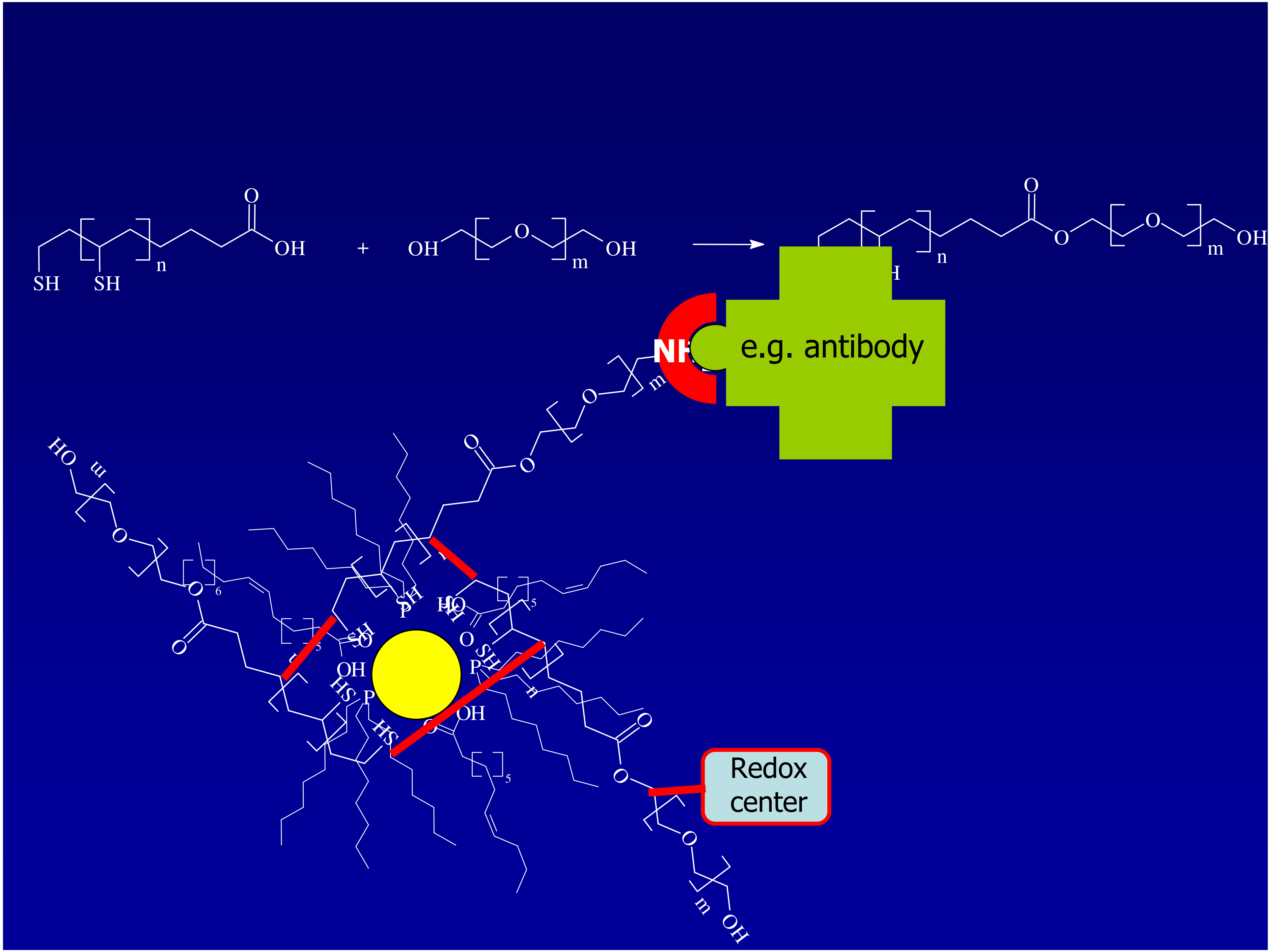
Nanoparticles and biomolecules

Functionality and self-assembly



Problem: surface equilibrium

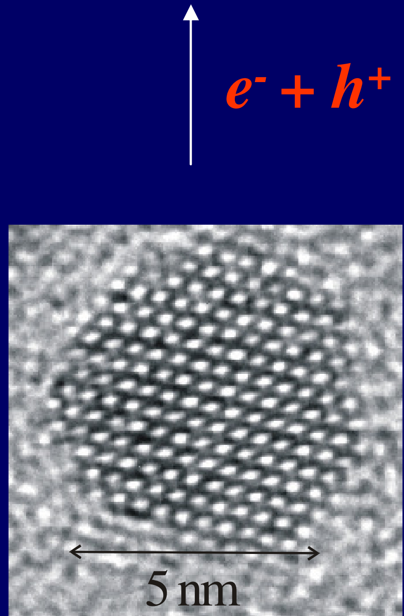
Ligand exchange versus encapsulation


e.g. antibody
Redox
center

How to light up a nanocrystal?

Electroluminescence

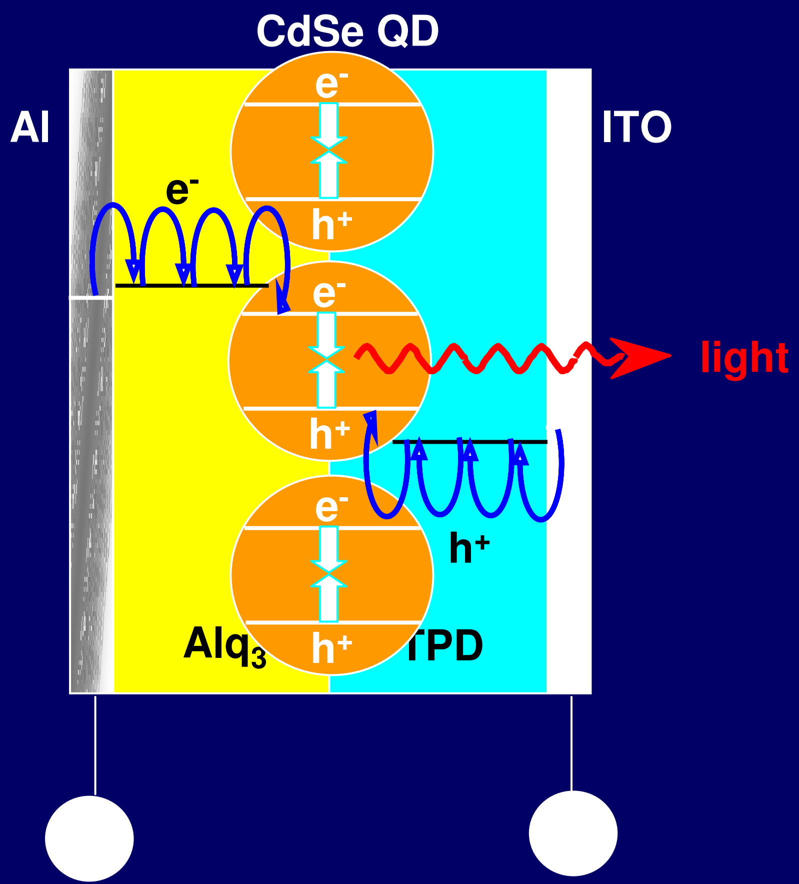
$e^- + h^+$



LED´s with CdSe nanoparticles as emitters

Structure of QD LED

Electron conductor   Hole conductor



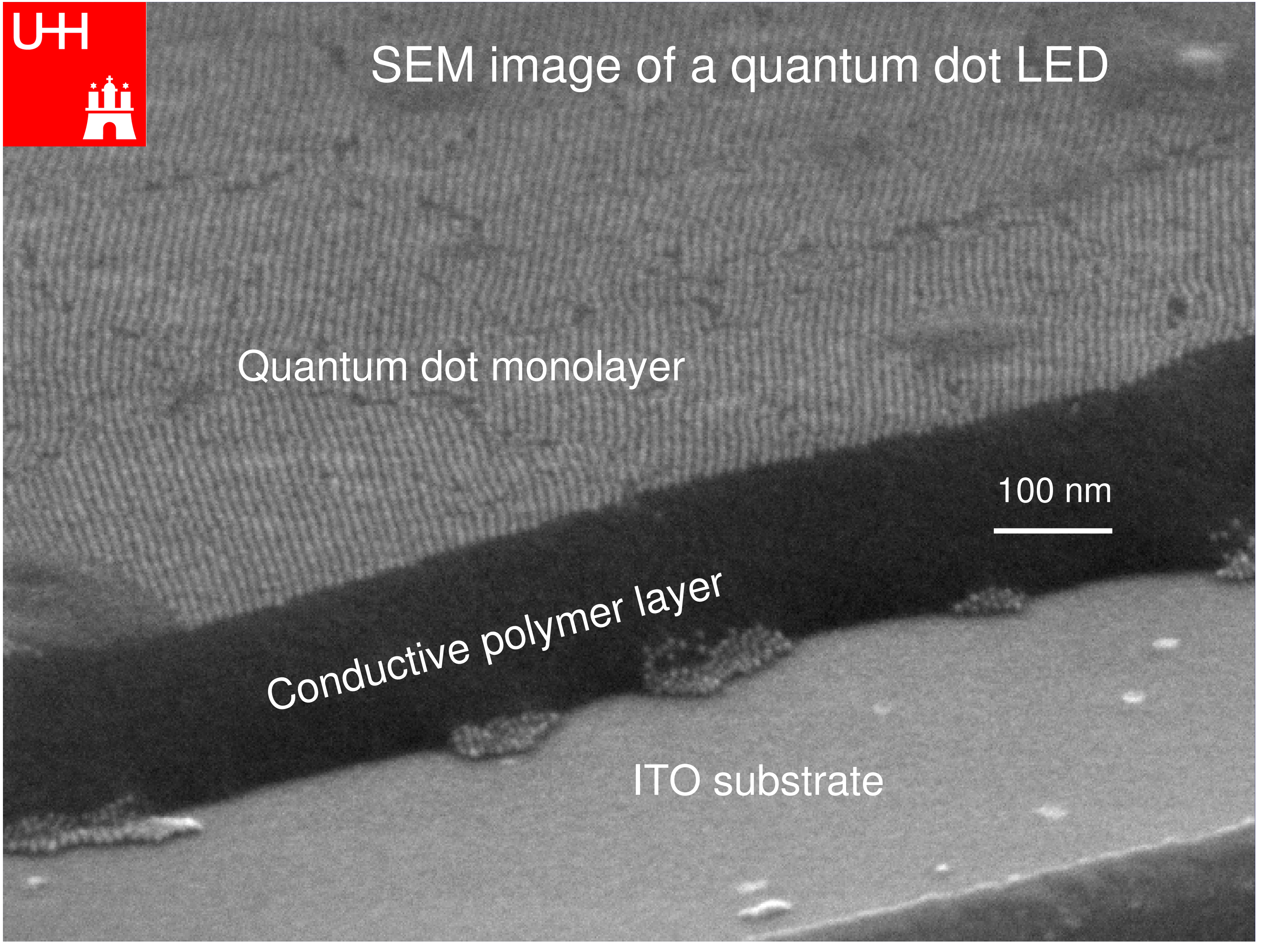
Real device

U = 7 Volt

Philips Aachen (BMBF)

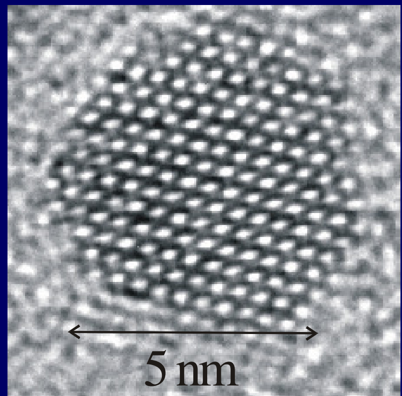
This approach can be applied to IR-emitting quantum dots (IR-emitting QD LED)

InAs, PbSe, PbS


SEM image of a quantum dot LED
Quantum dot monolayer
100 nm
Conductive polymer layer
ITO substrate

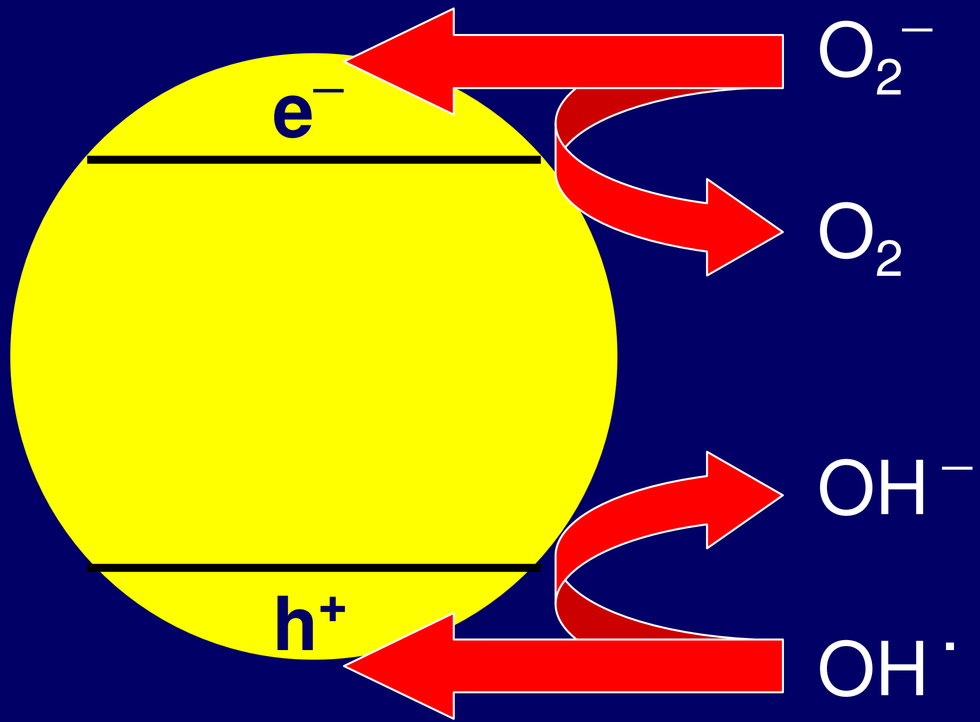
How to light up a nanocrystal?

Chemiluminescence



***Chemiluminescence* is the most sensitive of any non-radioactive method, allowing attomolar amounts of target to be detected.**

Chemiluminescence of quantum dots



$$M + H_2O_2 \rightarrow M^+ + OH^- + OH^\bullet$$

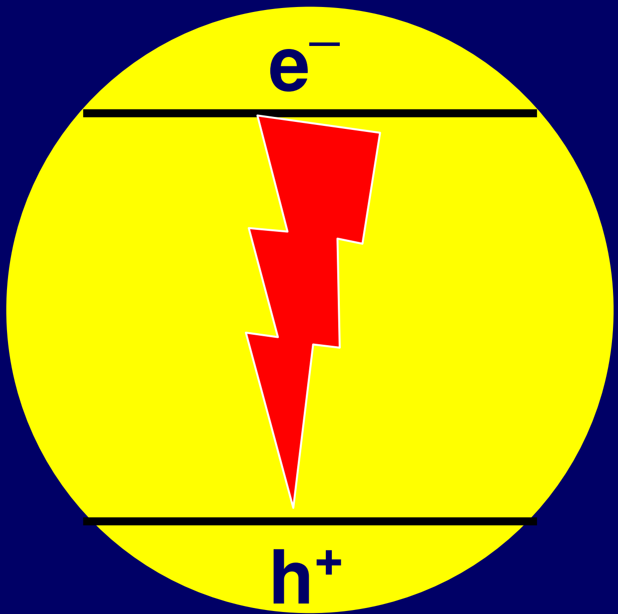
$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$$

$$HO_2^\bullet + OH^- \rightarrow O_2^- + H_2O$$

$$O_2^- + M^+ \rightarrow O_2 + M$$

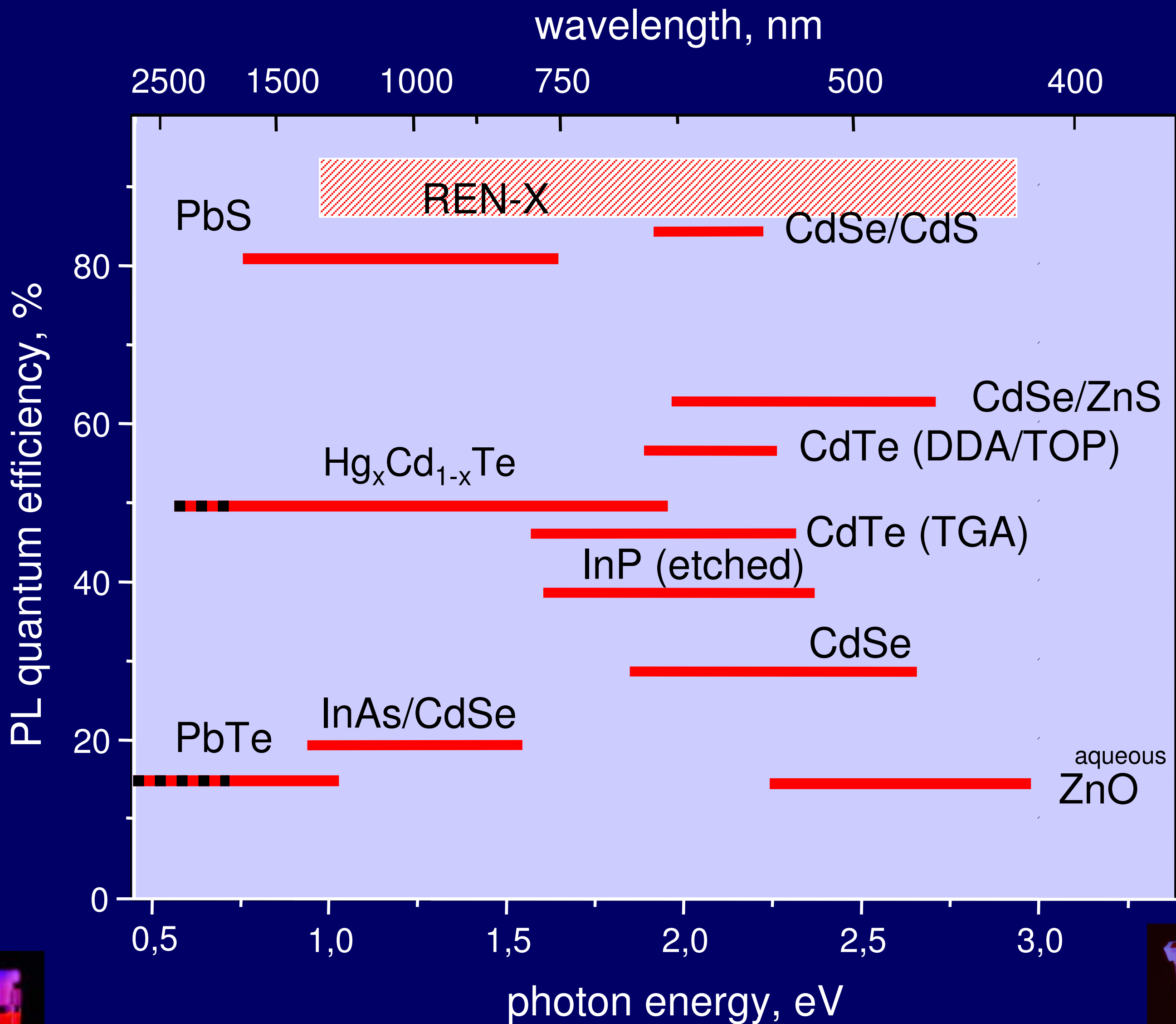
The Haber-Weiss mechanism of H_2O_2 decomposition on metals, etc.

Chemiluminescence of quantum dots

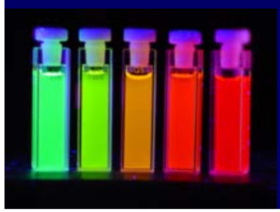


Luminescent nanoparticles

CdTe (aqueous)



InP

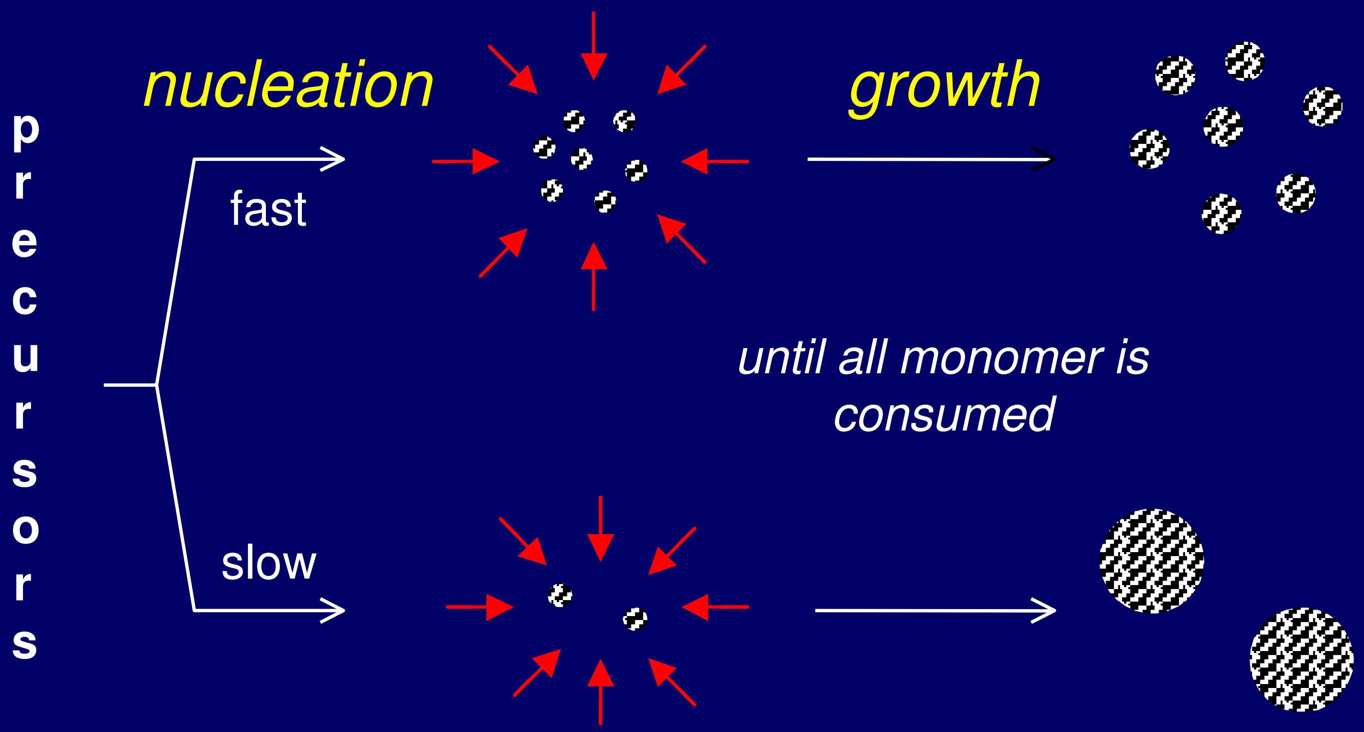


CdSe/ZnS

Magnetic Nanoparticles

Data storage
Magnetic Fluids
Medicine

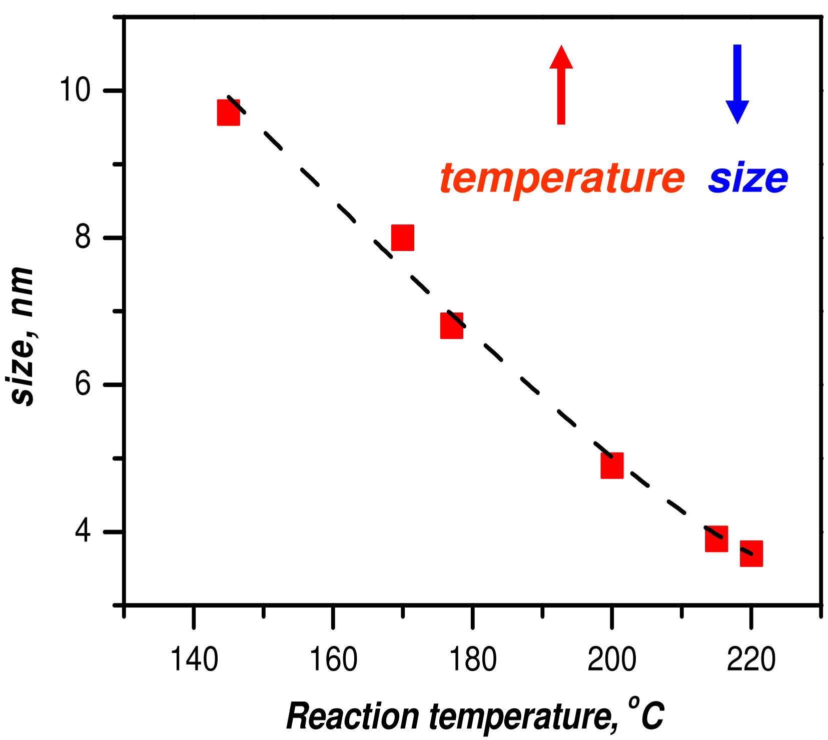
Size control of nanocrystals in the absence of Ostwald ripening, e.g. for $CoPt_x$

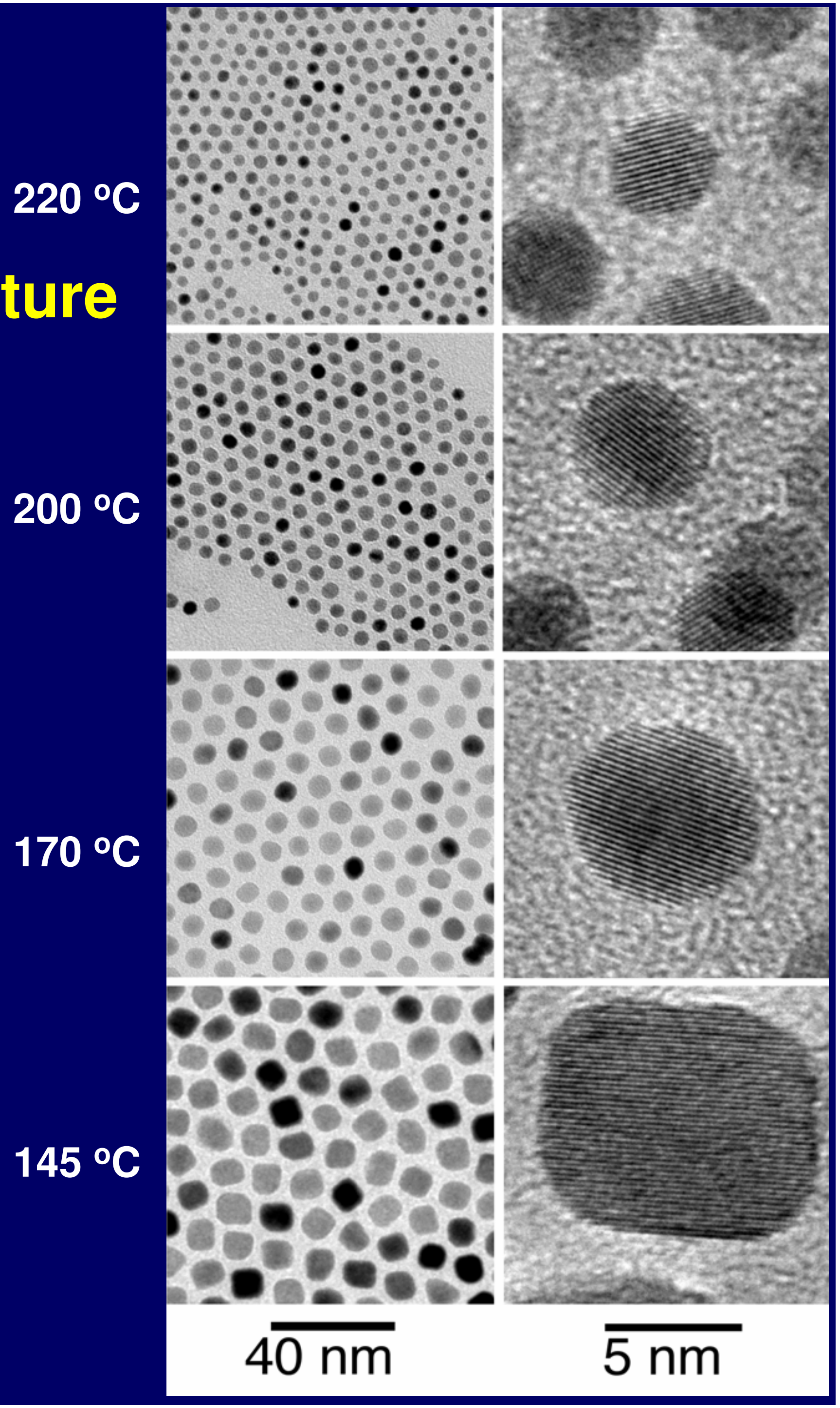


Influence of the reaction temperature

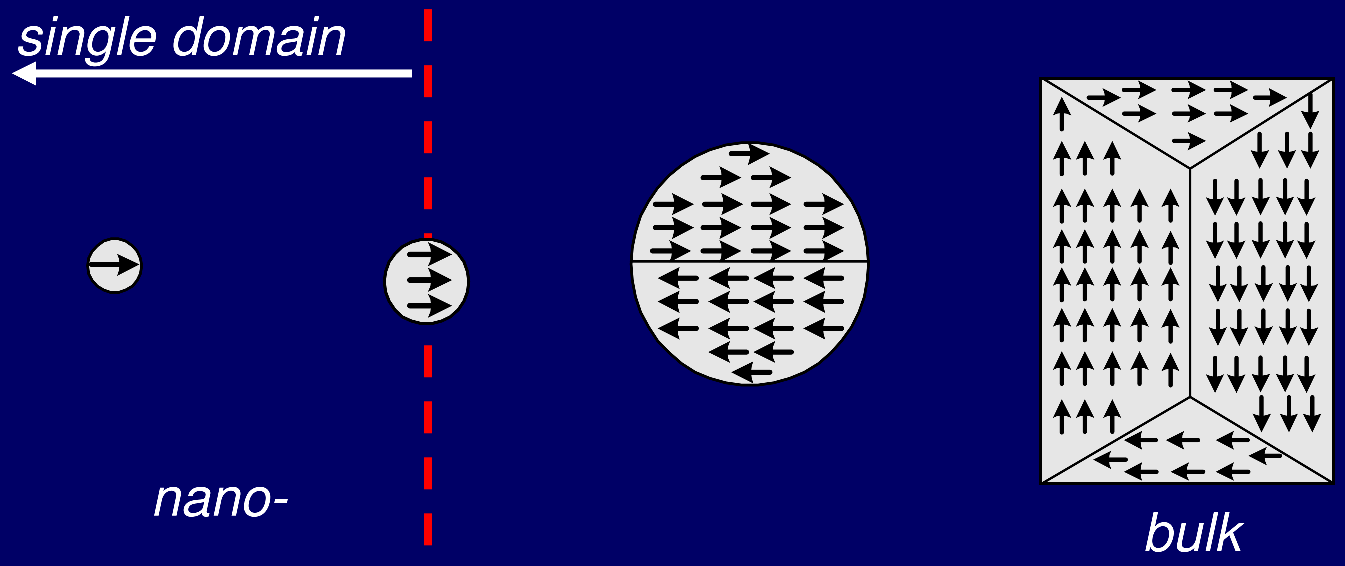
$\Delta G^{Nucleation} >> \Delta G^{Growth}$

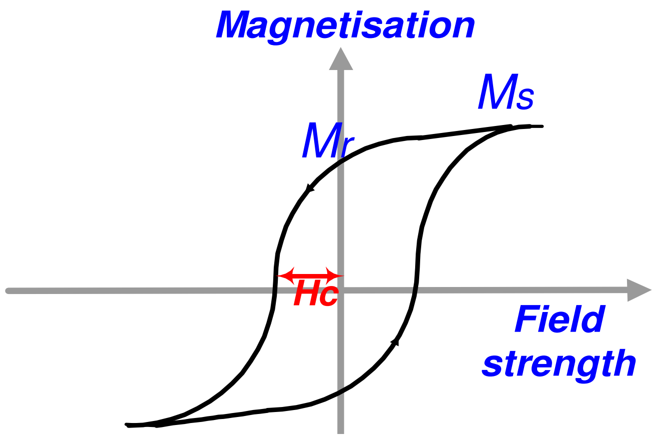
(activation energy for nucleation and growth)



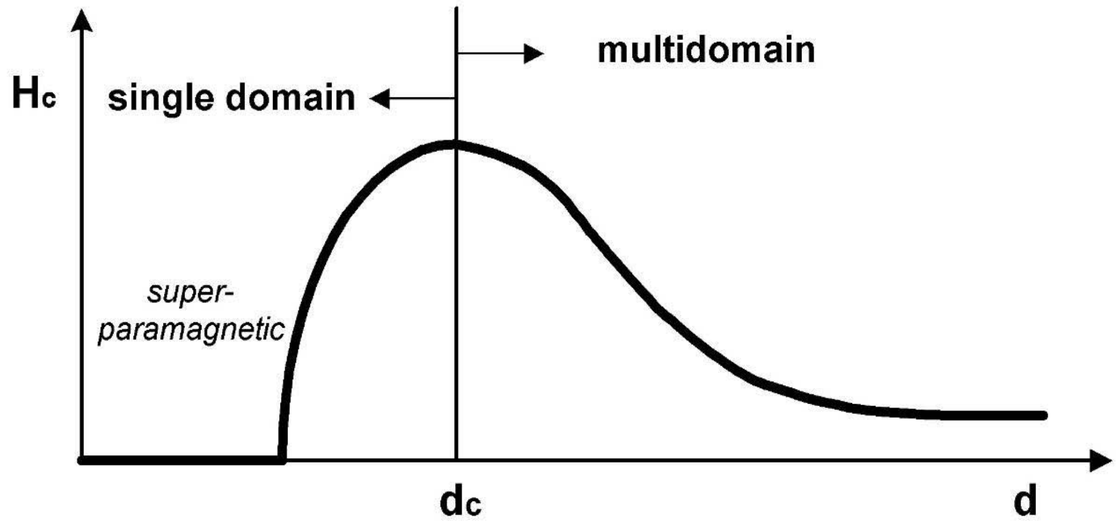


Magnetic behavior of nanoparticles

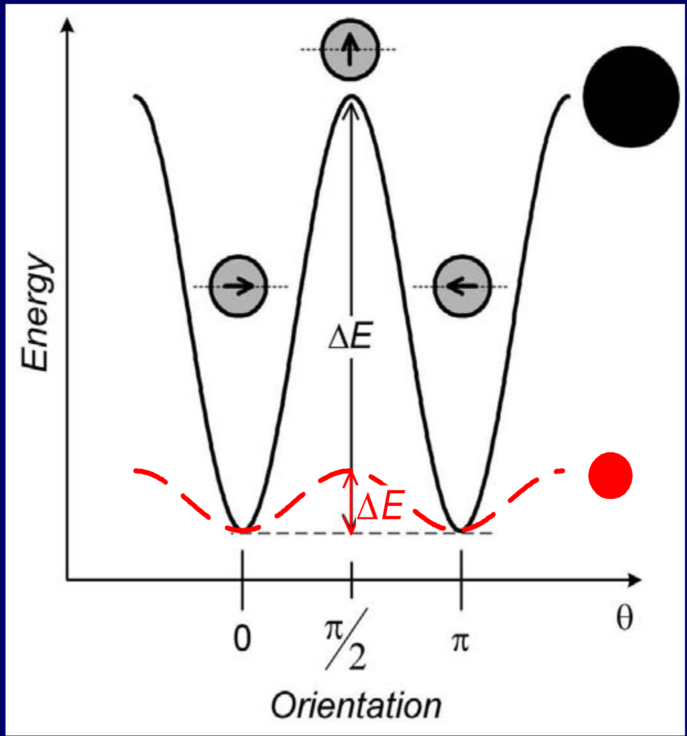


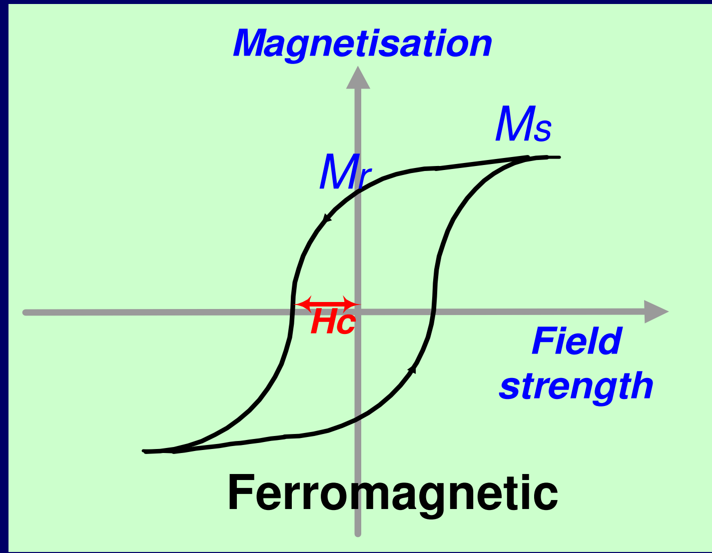


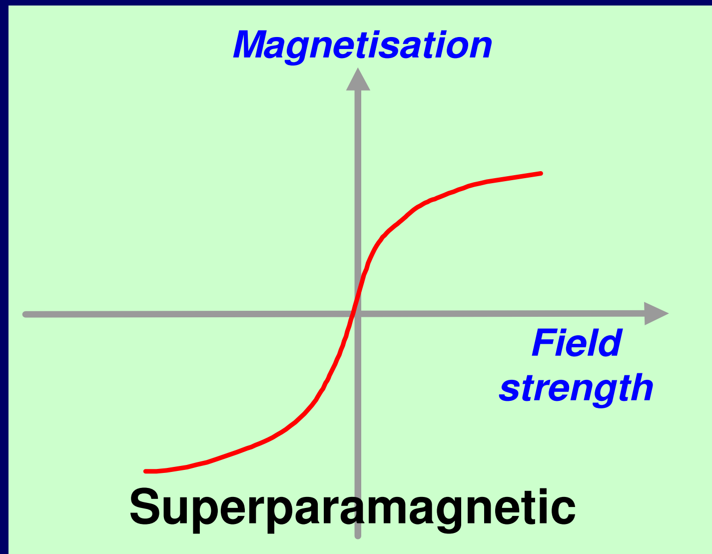
•Coercivity, H_c



Nanomagnetism



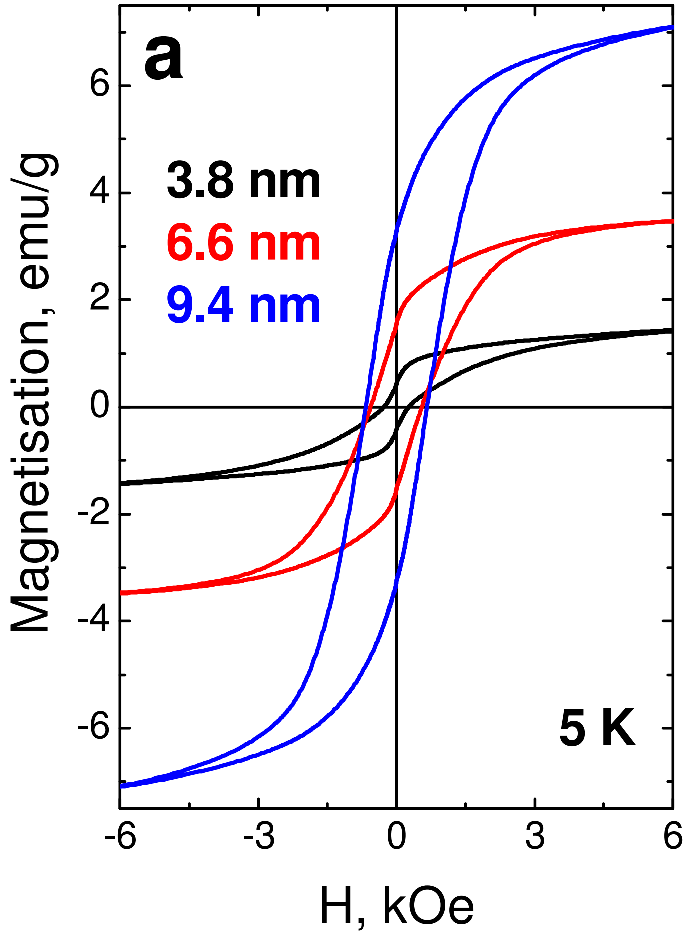




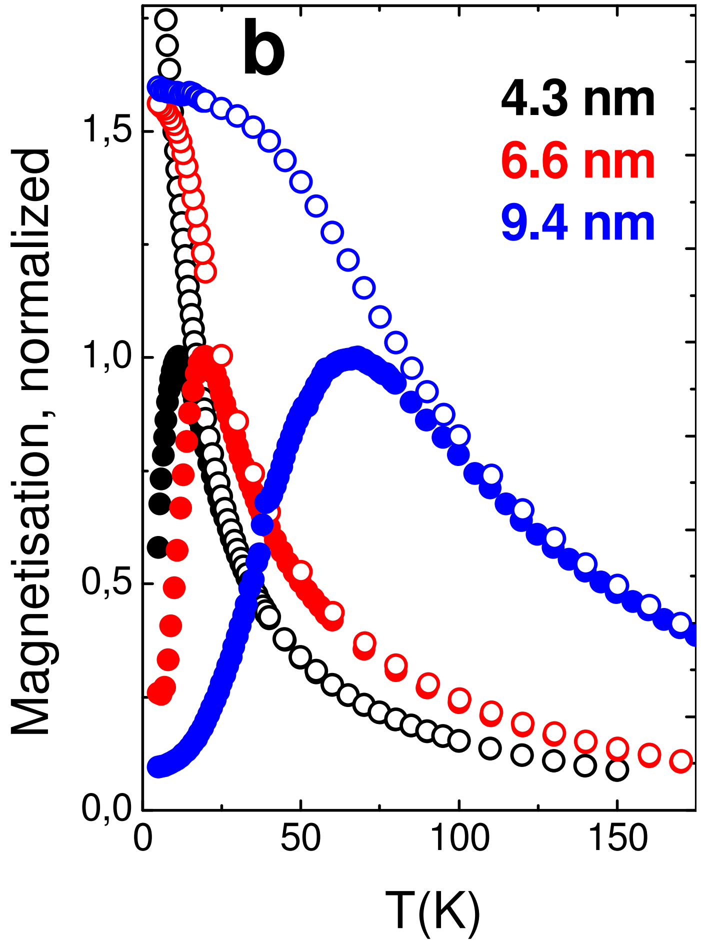
- Orientation determined by anisotropy energy, K.
- Energy barrier, $\Delta E = KV$
- Blocking temperature, $k_B T_B \approx 25\Delta E$

- At $T >> T_B$, particles are superparamagnetic.
- At $T << T_B$, particles are ferromagnetic.

Magnetic properties of non-interacting $CoPt_3$ nanocrystals



Hysteresis loops



ZFC/FC dependence of magnetisation

Örjan Festin, Peter Svedlindh (Sweden)

Iron oxide as contrast agent in MRI

Detection of Water

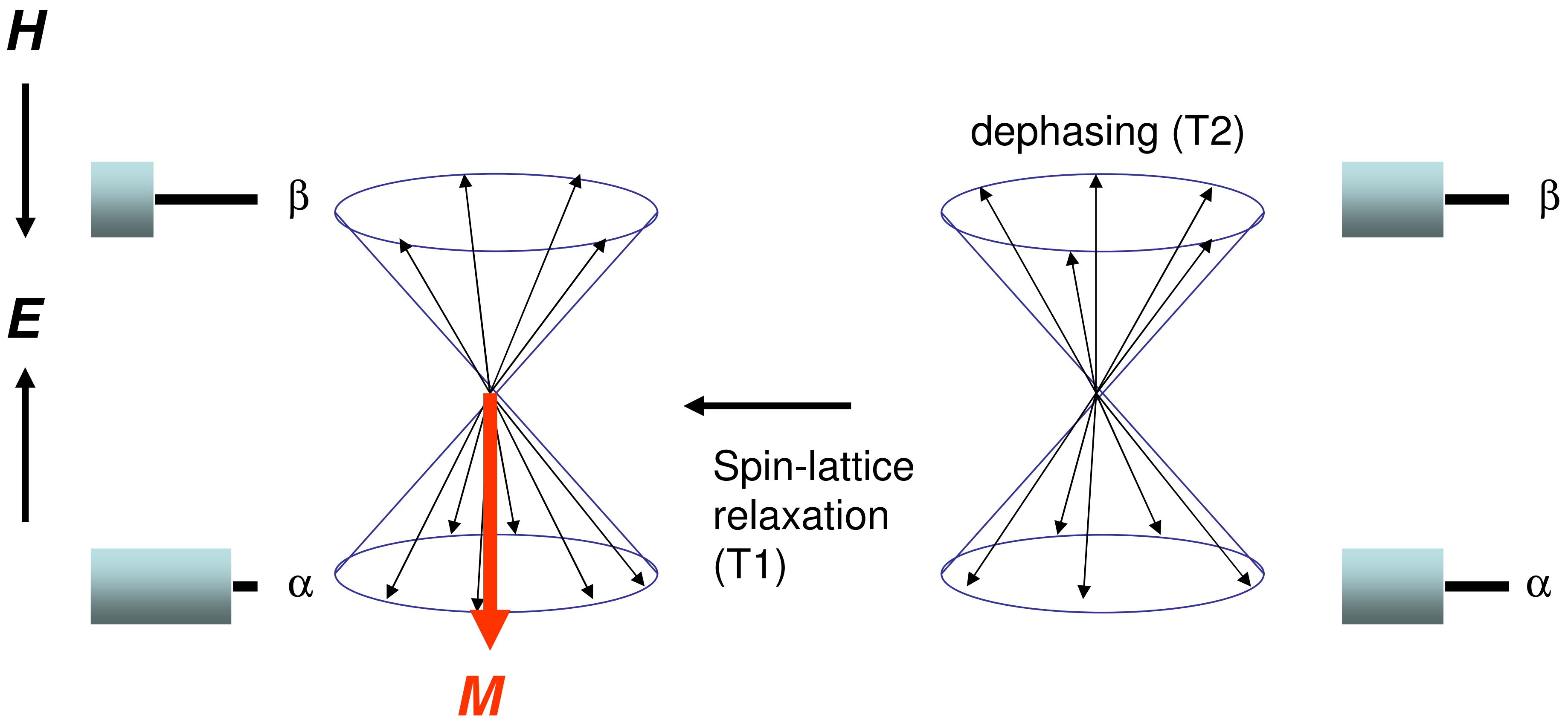
Saturation of Nuclear Spins

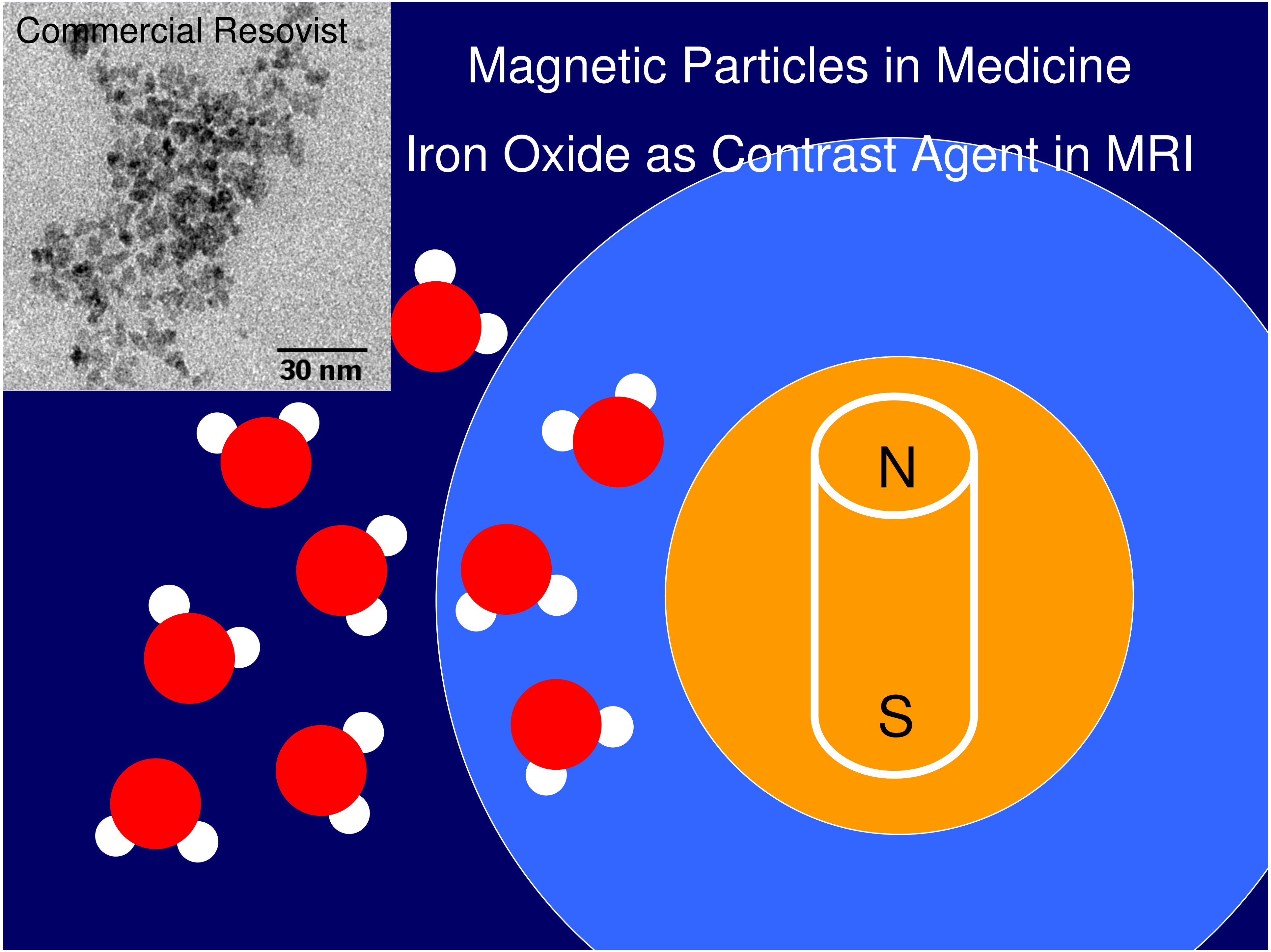
Differences in Relaxation Times

(T1 or T2)

→ Contrast

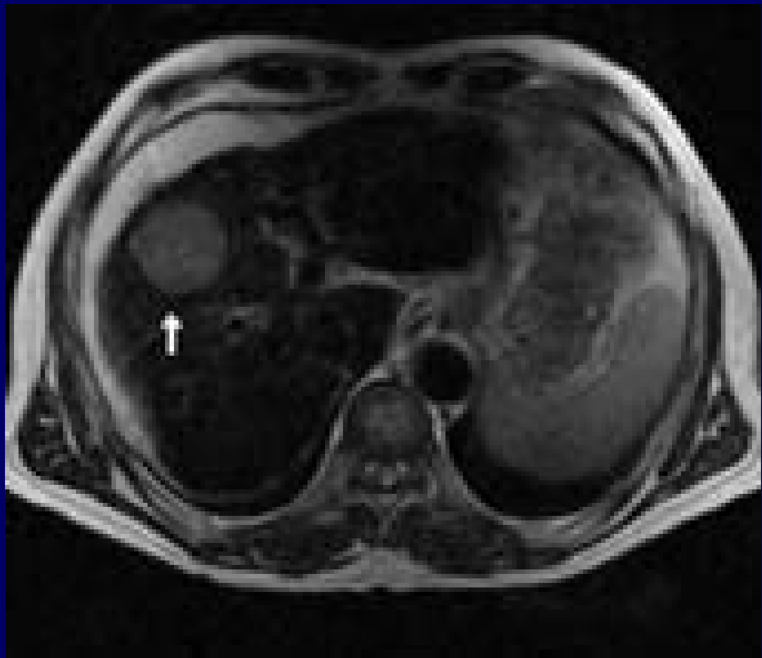
Saturation and Relaxation of Magnitisation




Commercial Resovist
30 nm
Magnetic Particles in Medicine
Iron Oxide as Contrast Agent in MRI
N
S

Magnetic Particles in Medicine

Iron Oxide as Contrast Agent for MRI



Detection of Water

Saturation of Nuclear Spins

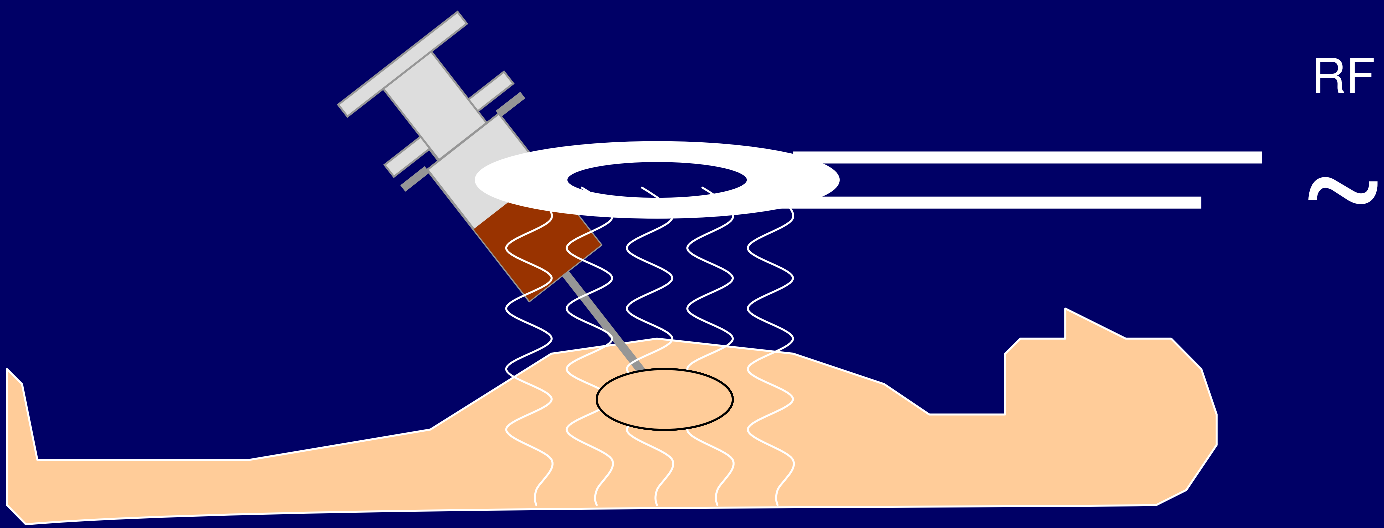
Differences in Relaxation Times

(T1 or T2)

→ Contrast

The Classical Approach

The Nanoparticle Approach

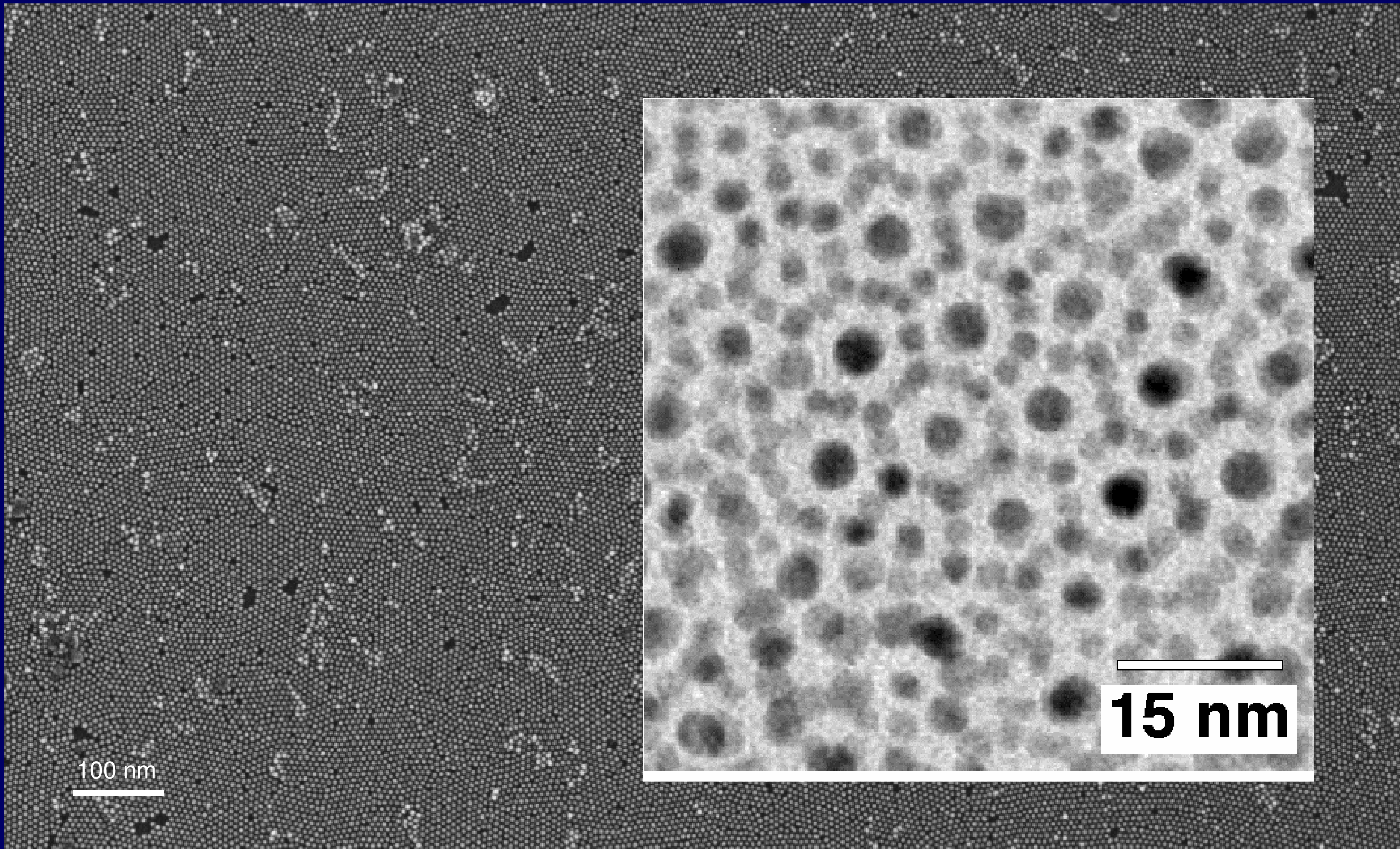


Hyperthermal therapy with magnetic iron oxide particles

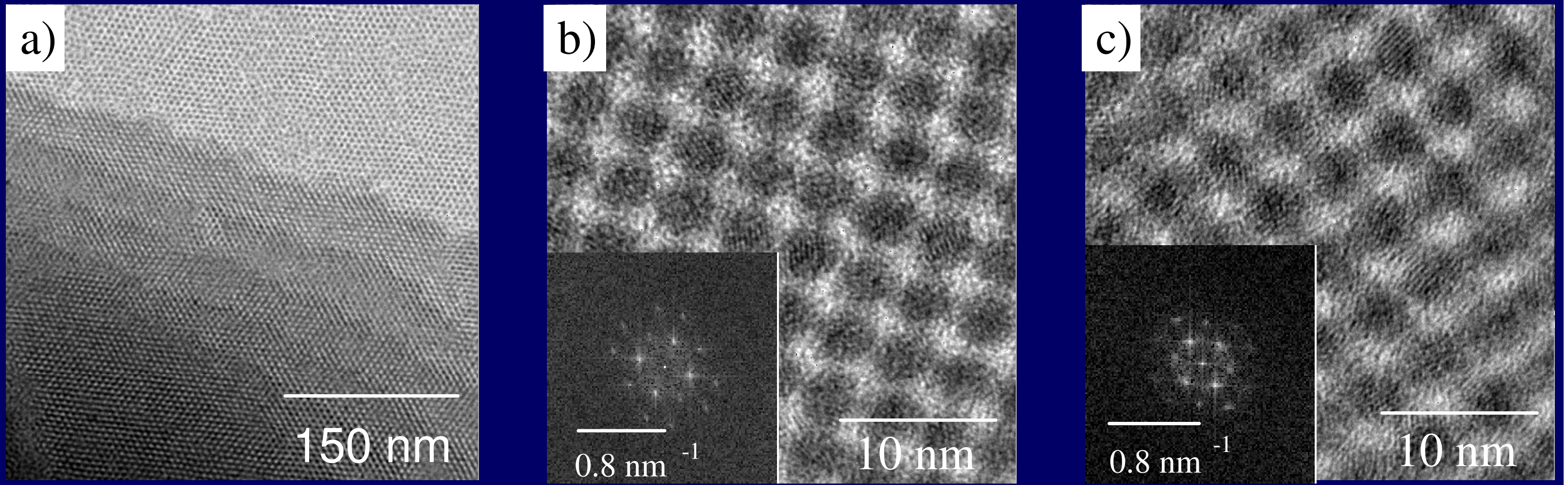
(Jordan, Berlin)

Self assembly

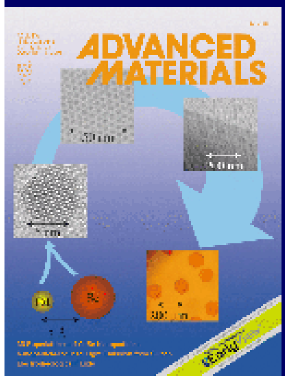
2D Self Assembly

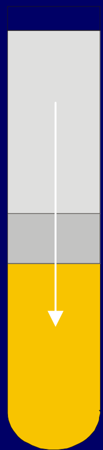


3D Self-Assembly of CdSe Nanocrystals



(111) *(100)* *(110)*



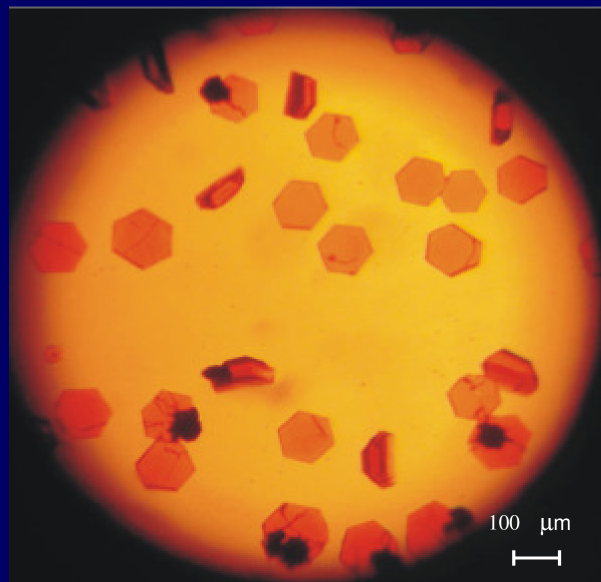


Non-solvent: (methanol)

Buffer layer („semi-solvent"): (propan-1-ol)

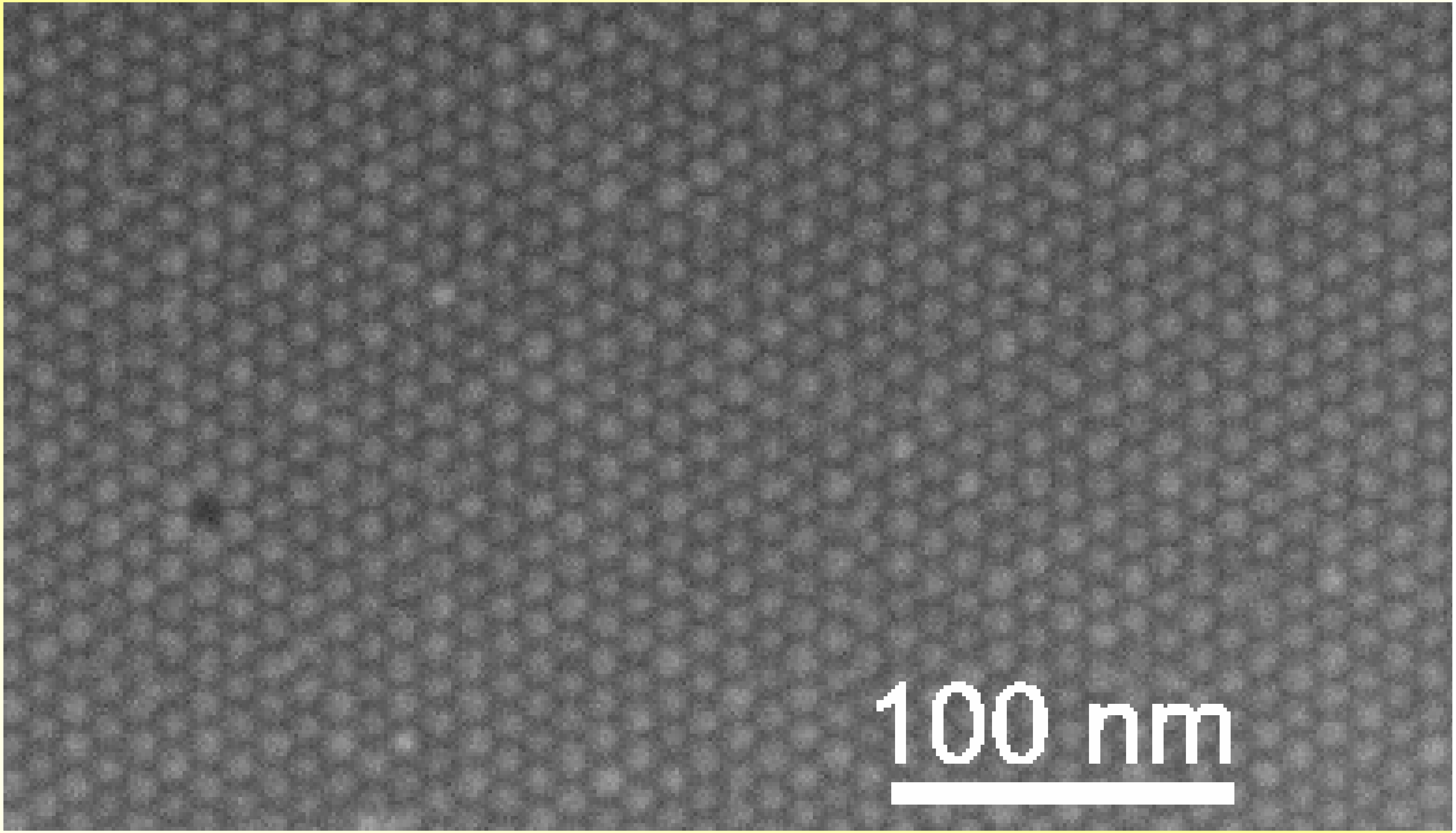
CdSe nanocrystals in a solvent (toluene)

b



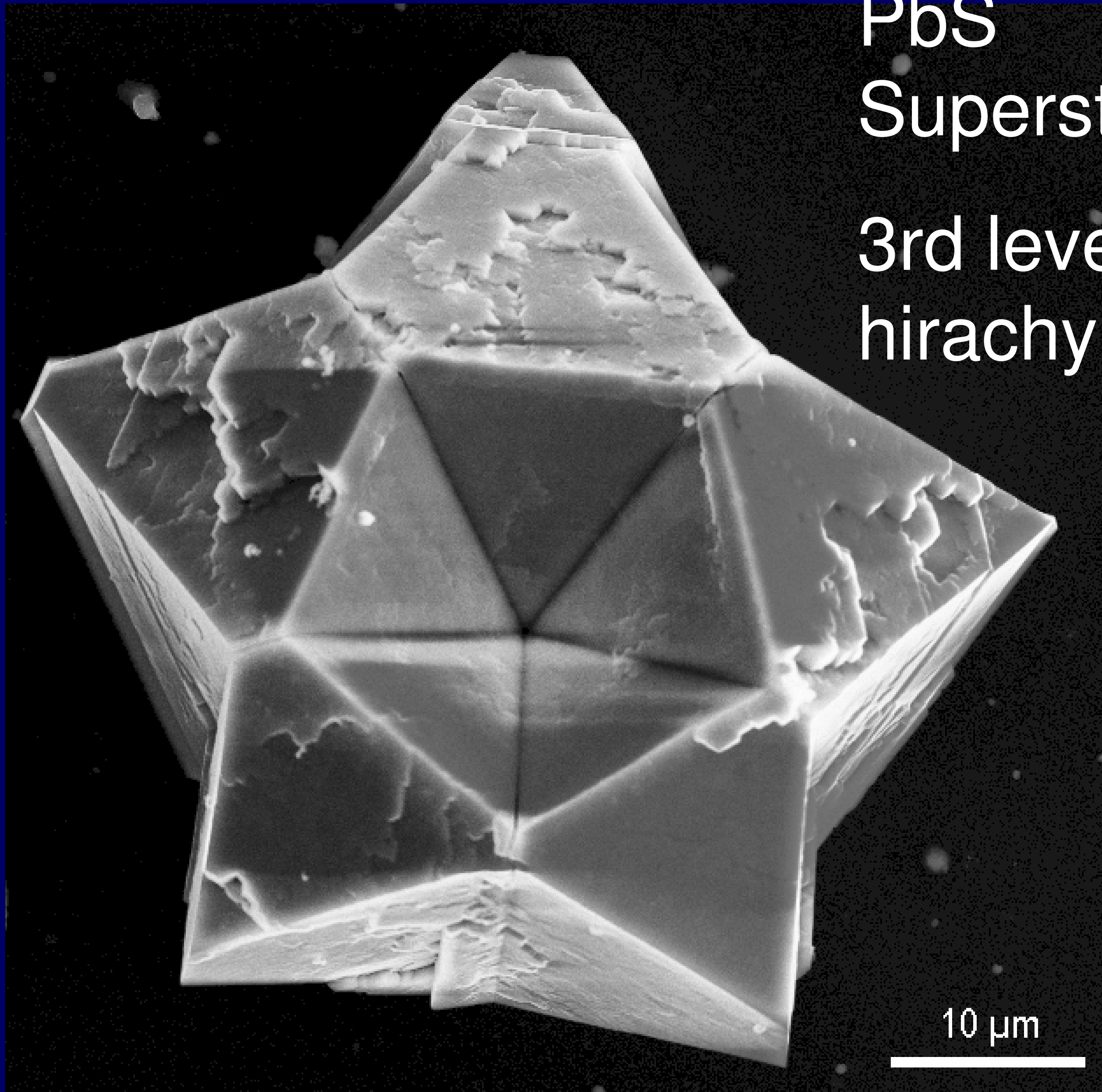
Adv. Mater. **2001**, 13, 1868.

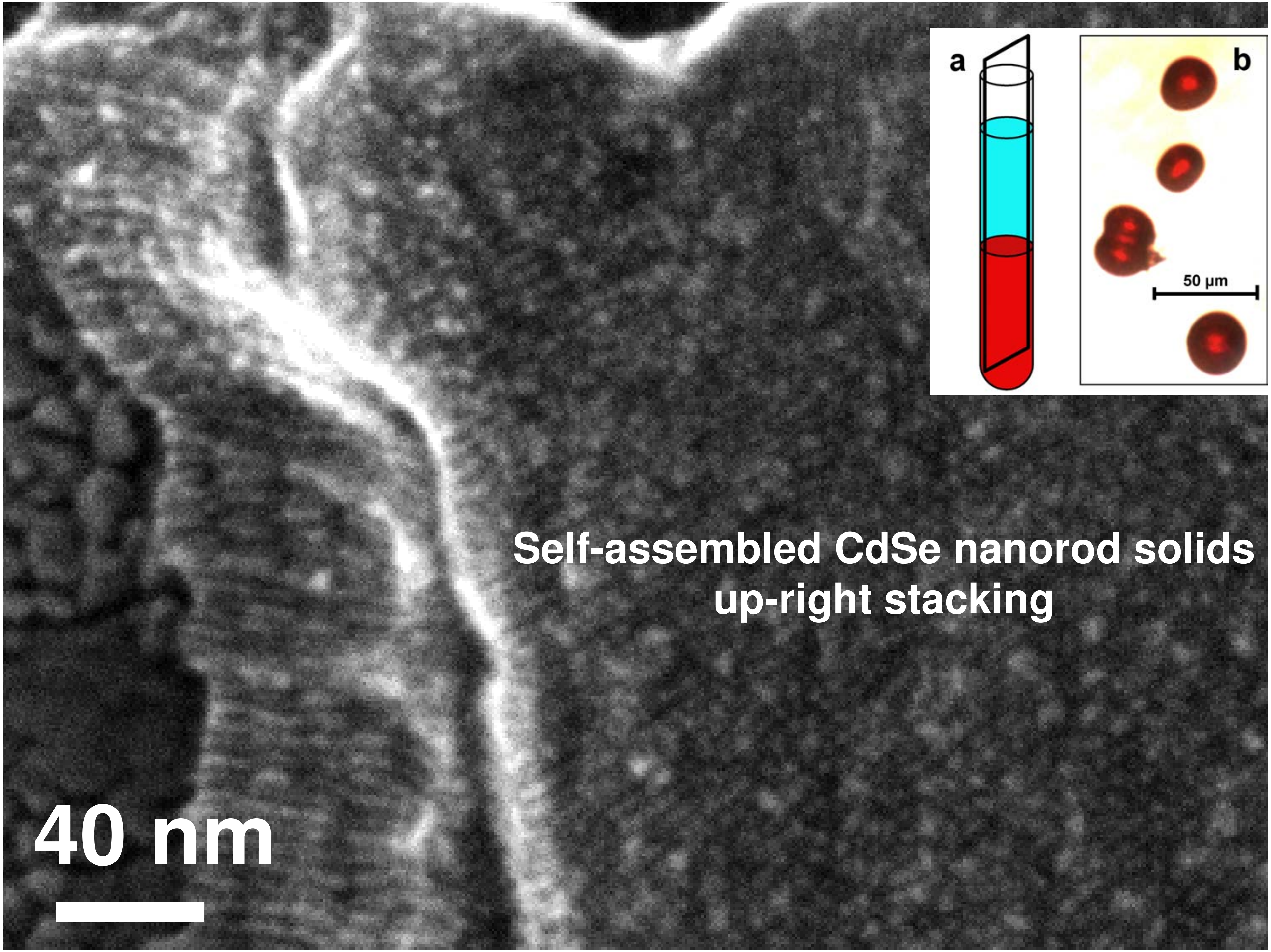
Colloidal crystals from PbS



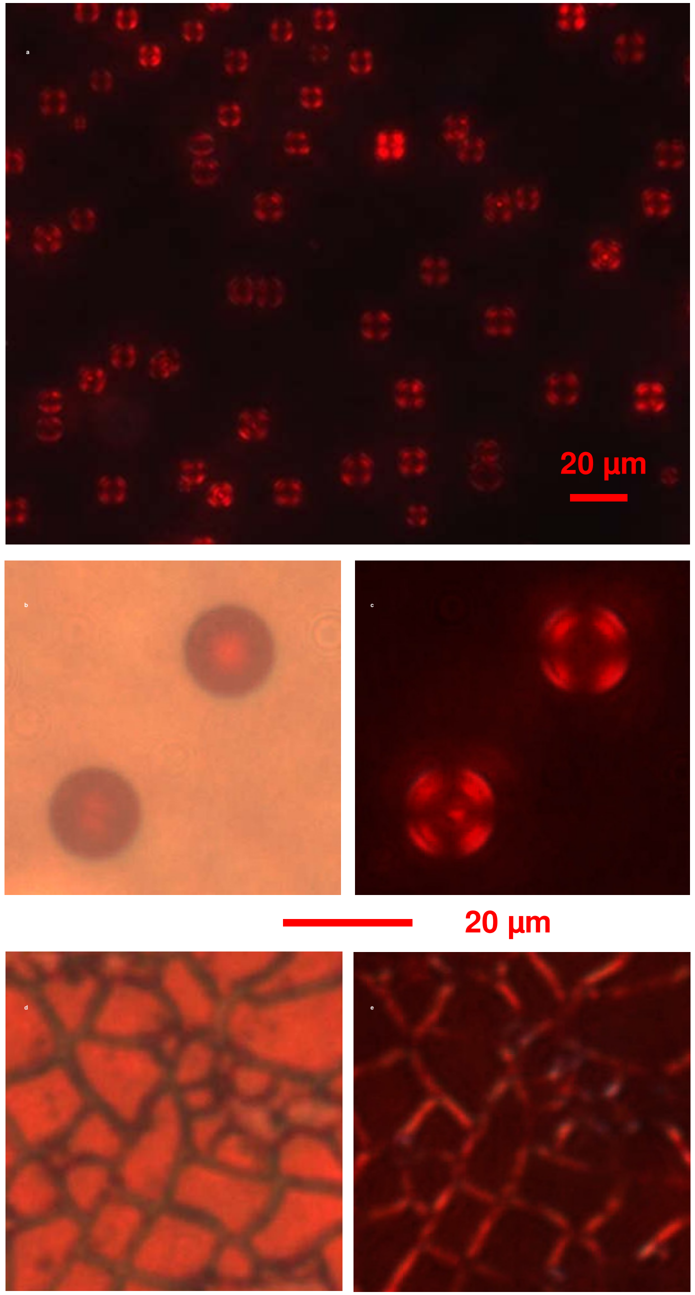
PbS Superstars

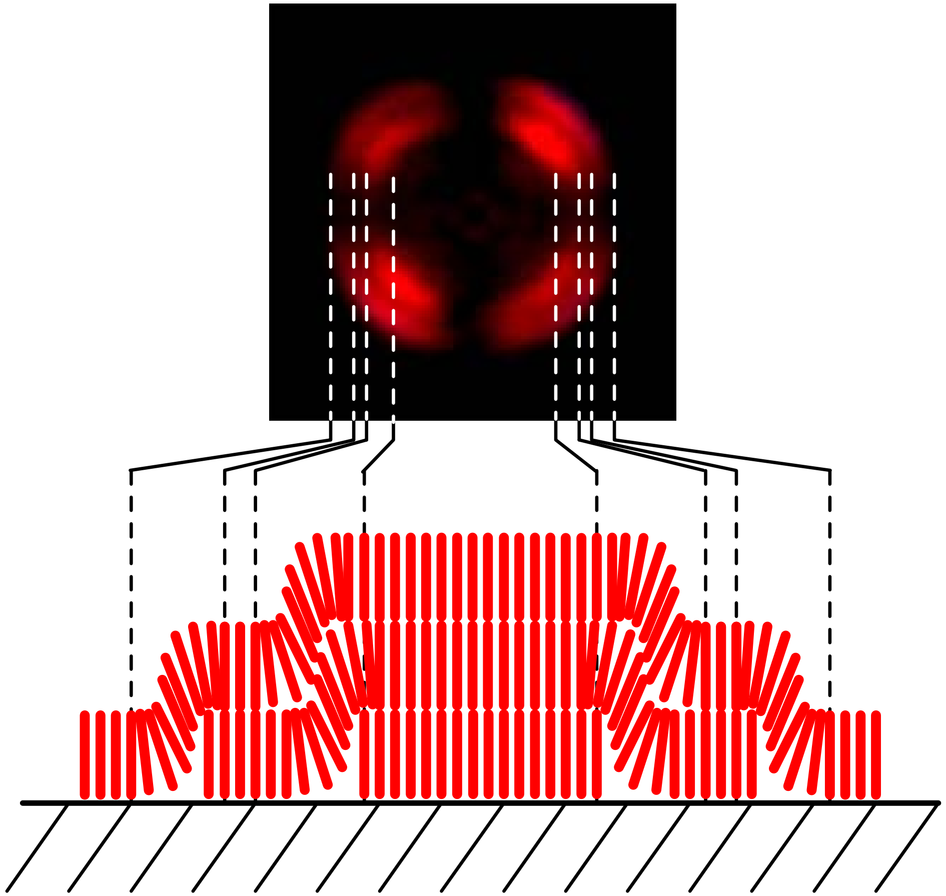
3rd level of hirachy



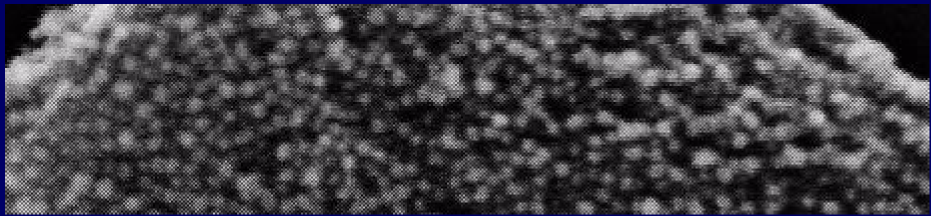

a
b
50 µm
Self-assembled CdSe nanorod solids
up-right stacking
40 nm

Characteristic birefringence of CdSe nanorod solids

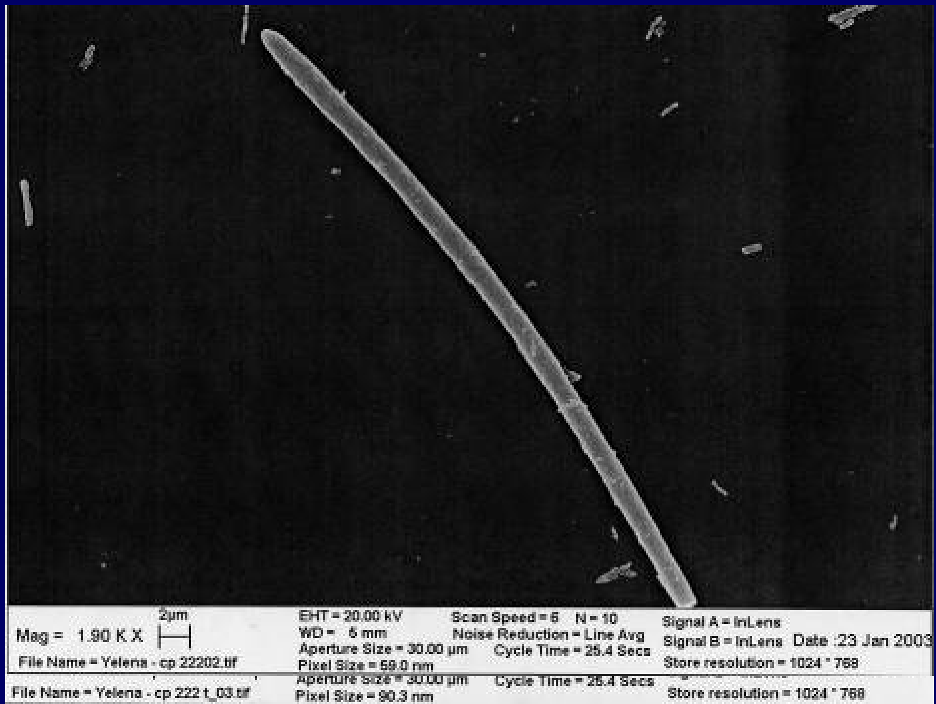




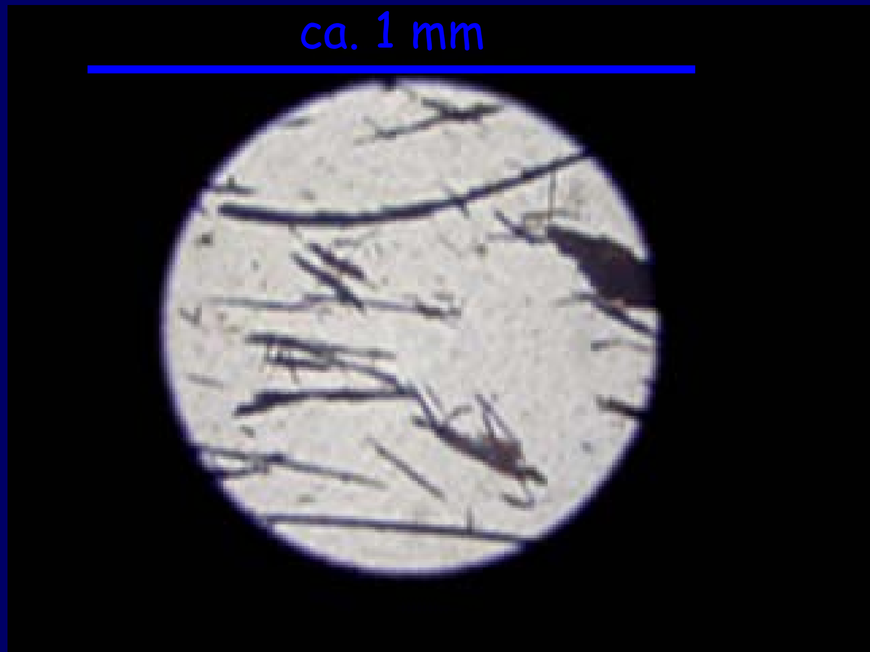
Magnetic alignment of $CoPt_3$ particles



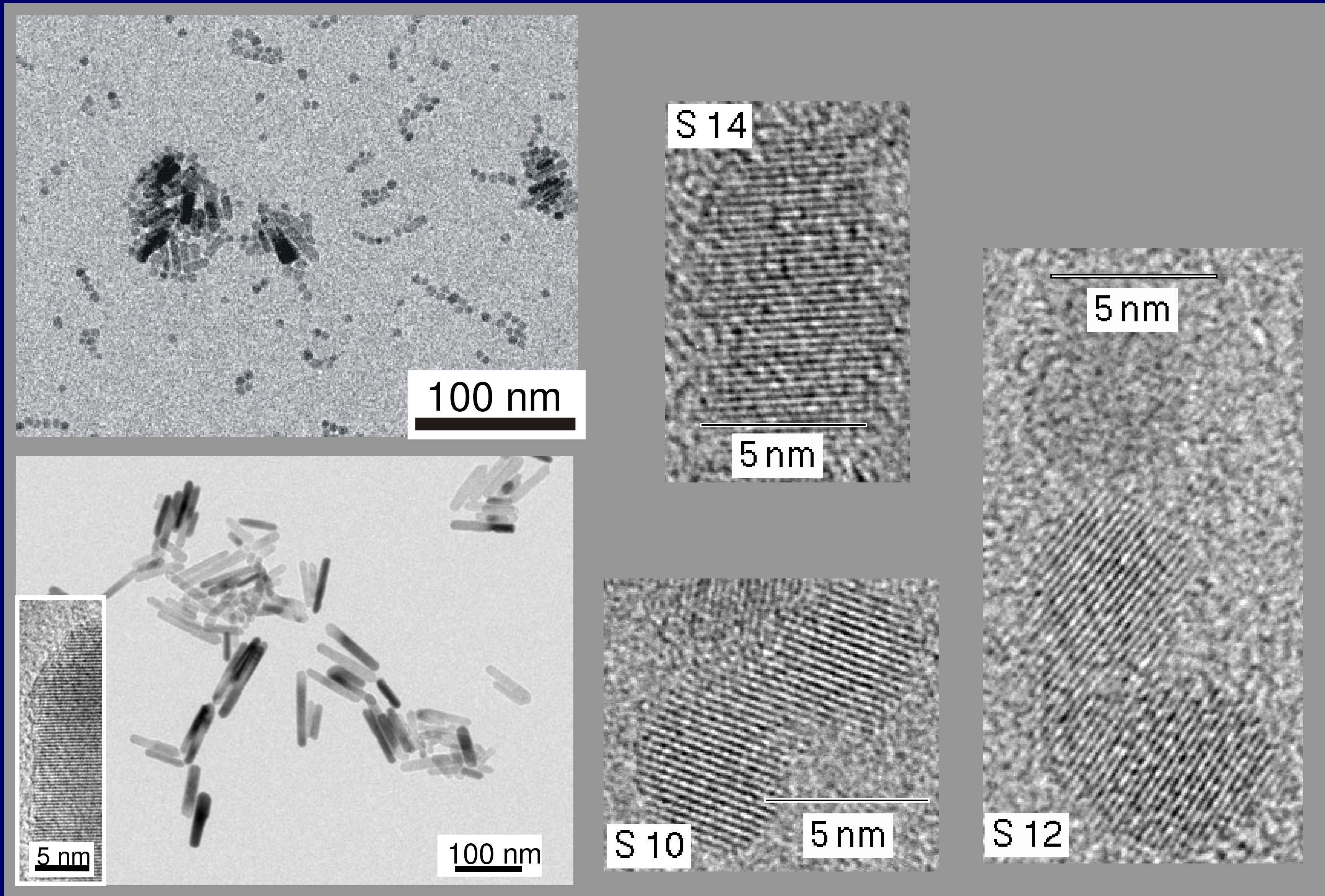
SEM



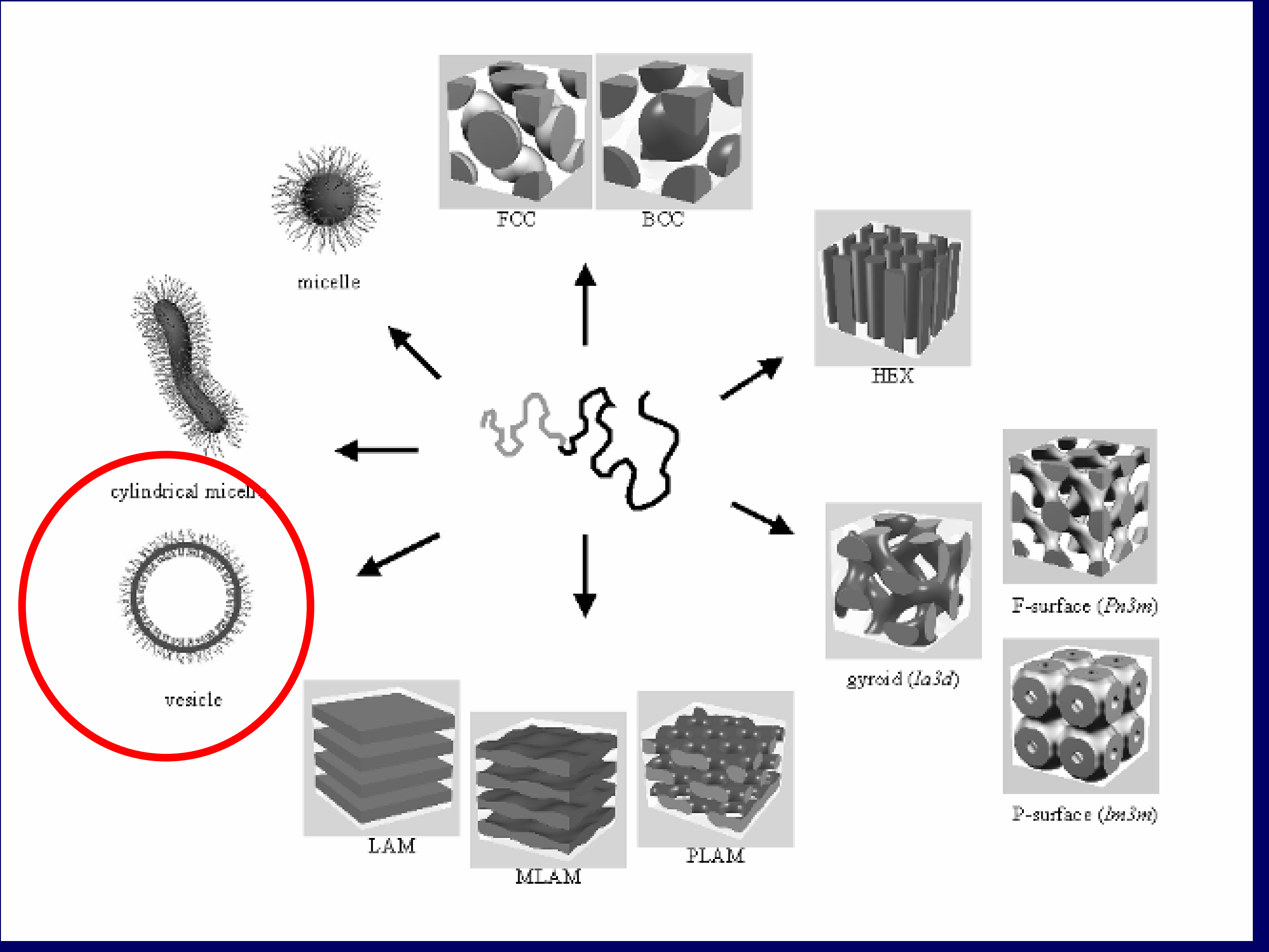
optical microscope



Self assembled oriented attachment
From nanodots to nanorods



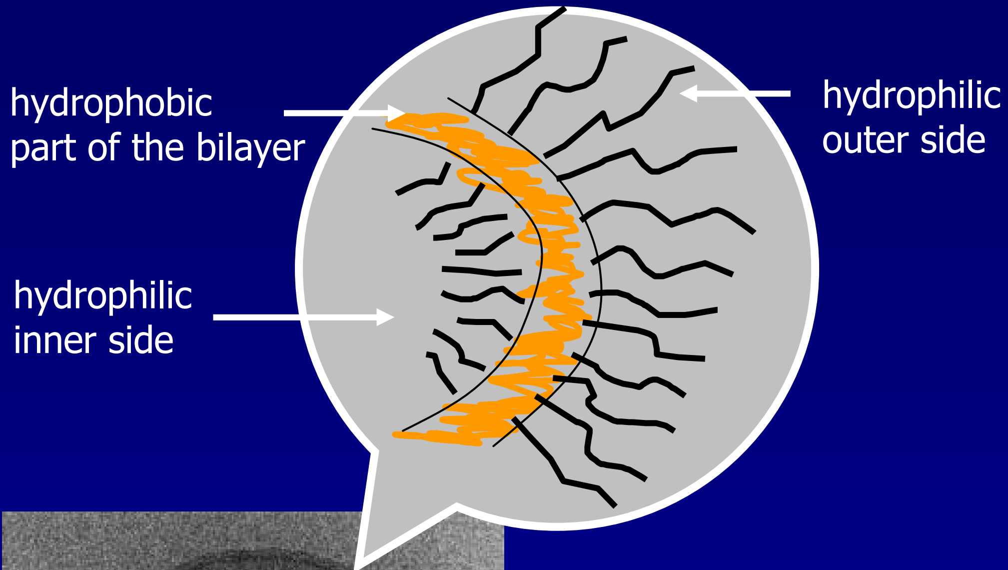
Self-organisation of block copolymers

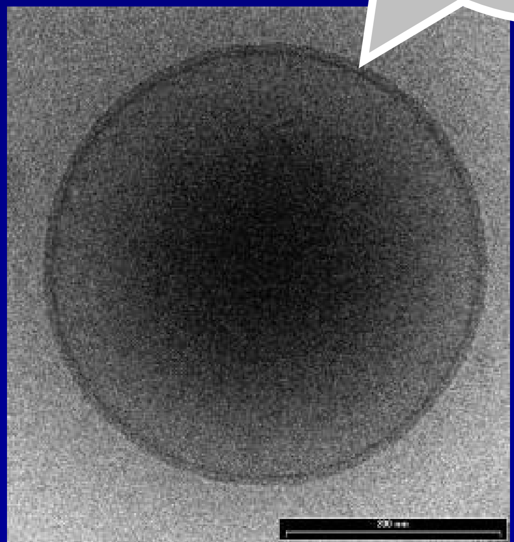


Angew. Chem. Int. Ed. 41, 688 (2002)

S. Förster

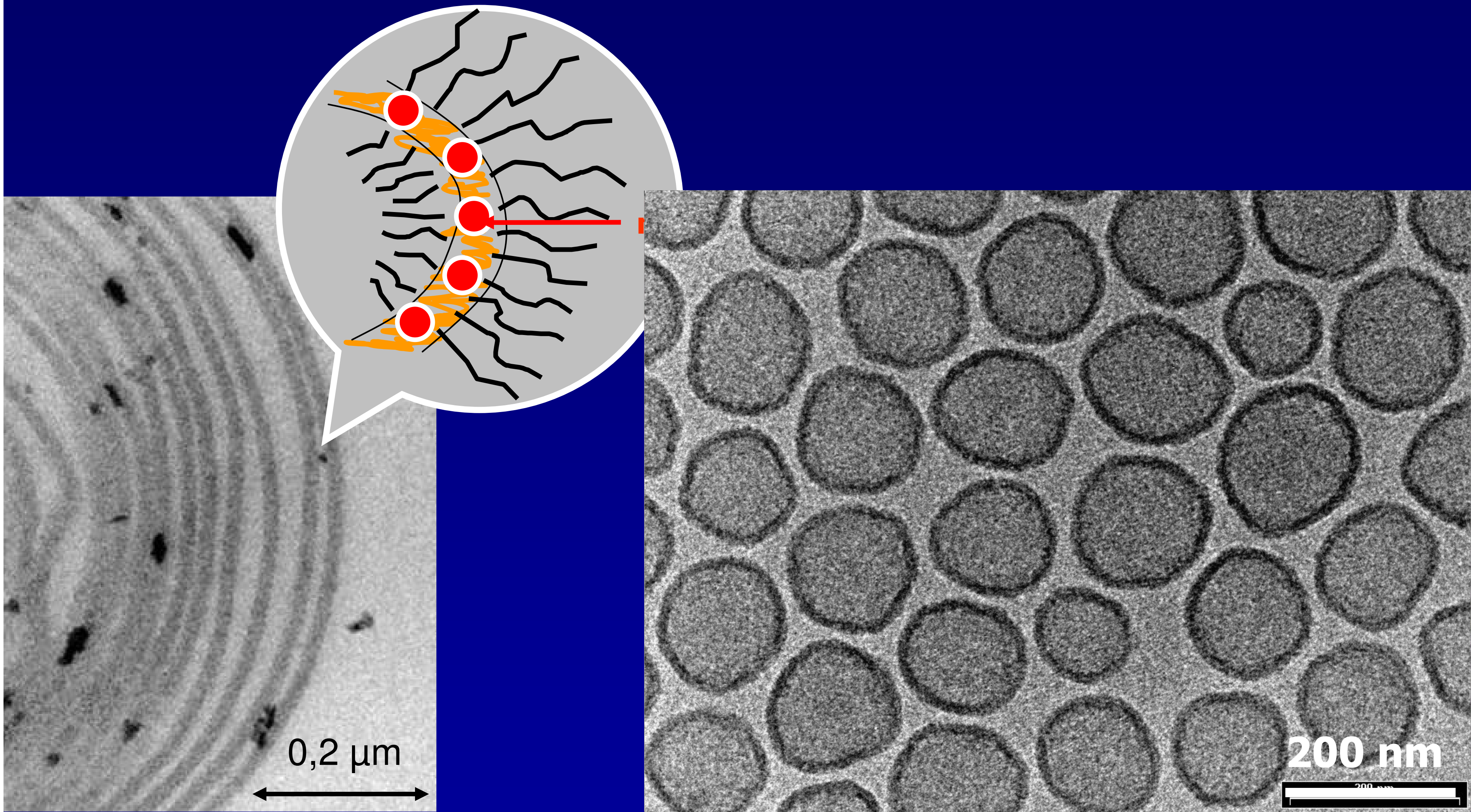
Artificial Vesicles from Polymers: Drug Delivery



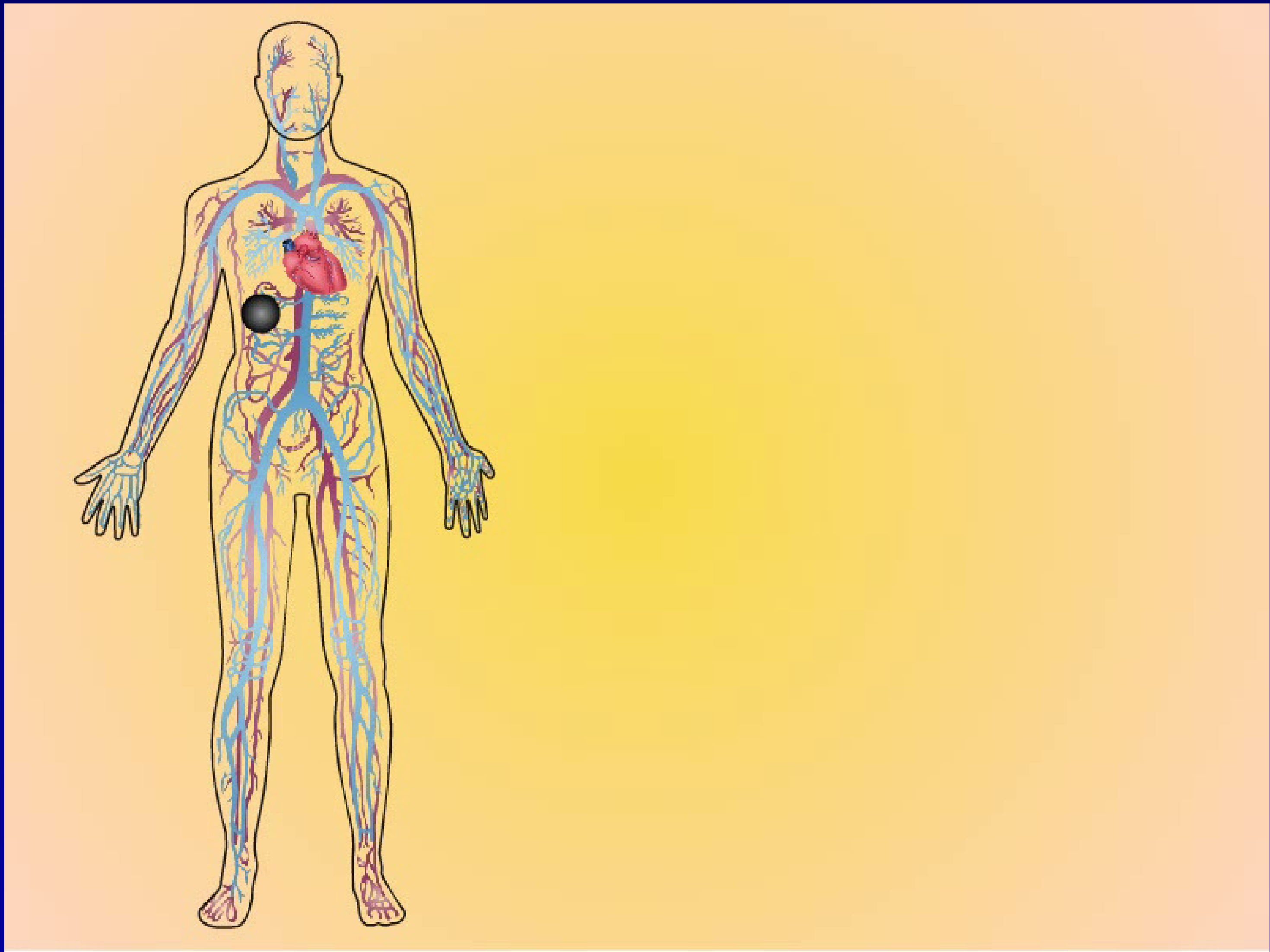


Stefan Förster

Artificial Vesicles from Polymers: Drug Delivery



The future



Animation by H. Fuchs, HanseNanoTec

Thanks to

- Andreas Kornowski
- Maren Krack
- Ivo Mekis
- Jan Niehaus
- Kirsten Ahrenstorf
- Mona Nagel
- Nadja Biegal
- Marija Nicolic
- Hauke Heller
- Vesna Alexandrovic
- Steven Hickey
- Elena Shevchenko, now Berkeley
- Dima Talapin, now Berkeley

Collaboration: Jochen Feldmann (LMU), Thomas Möller (HUB), Gerhard Adam (UKE), Stefan Förster (UHH)

€ from: SFB 508, BMBF, EU, FCI, GIF

Nano-Activities at Hamburg

UH

INCH

interdisciplinary nanoscience center
hamburg

can

Historie CAN

Sommer 2004	Nanotechnologie Studie von HH und SH empfiehlt Gründung eines Centrums für Angewandte Nanotechnologie
November 2004	„Go“ zur Erstellung eines Business Plans für CAN in PPP
April 2005	Business Plan liegt vor
M[illegible]	[illegible]ördeninte[illegible]ung, Se[illegible]he
Juli 2005	[illegible]at beschl[illegible]g von C[illegible]en des SIP
September 2005	Bürgerschaft stimmt Gründung zu, Mittelfreigabe
[illegible]e 2005	[illegible]er[illegible]nd[illegible]
November 2005	Gründung der CAN-Hamburg GmbH
	Unterzeichnung der ersten Forschungsaufträgen
Dezember 2005	Einstellung der ersten Mitarbeiter
	Einrichtung der Labore im Inst. Phys. Chem.
Januar 2006	Beginn der Forschungsprojekte
15. Februar 2006	Offizielle Einweihung von CAN, Hamburger Nanotech Tage
1. März 2006	Operativer Geschäftsführer Dr. Schroeder Oeynhausen