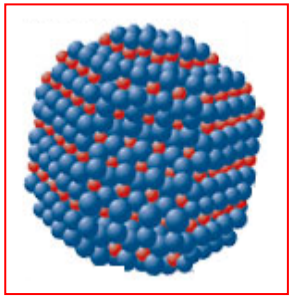
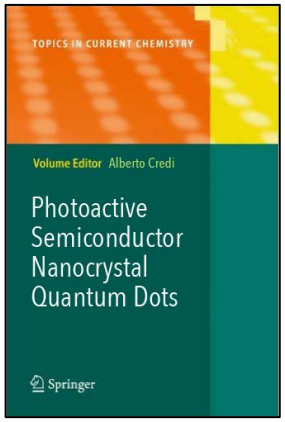
Semiconductor quantum dots

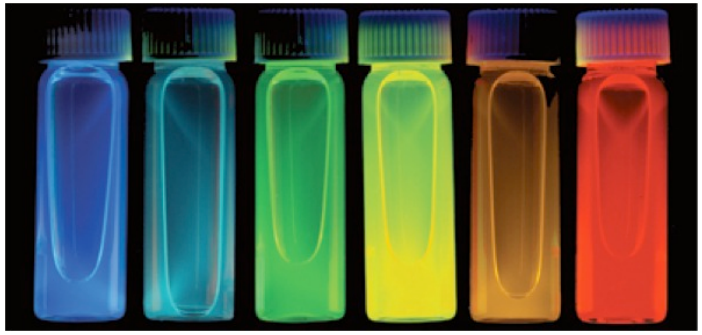


Quantum dots are spherical nanocrystals of semiconducting materials constituted from a few hundreds to a few thousands atoms, characterized by the quantum confinement of the charge carriers.

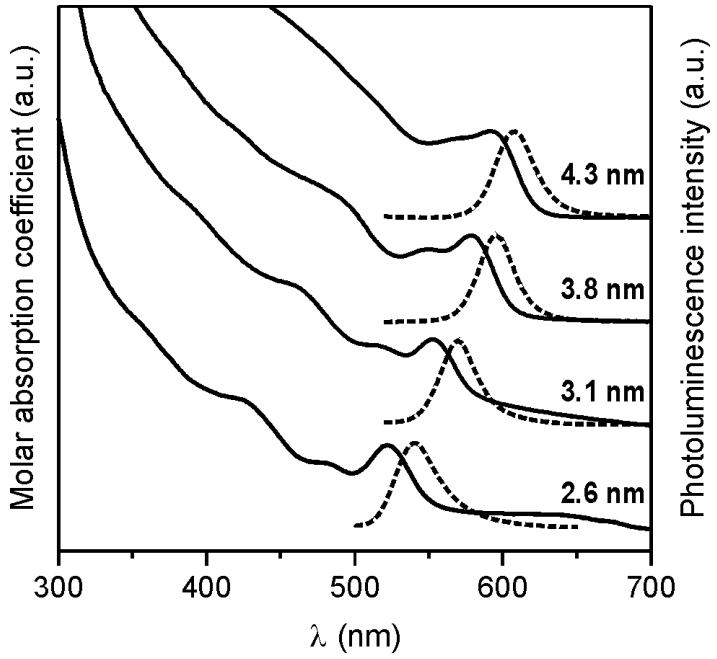
Owing to quantum confinement, their optical and electronic properties are strongly dependent on the particle size



Photoactive semiconductor nanocrystal quantum dots; A. Credi (Ed.), *Top. Curr. Chem.* **2017**



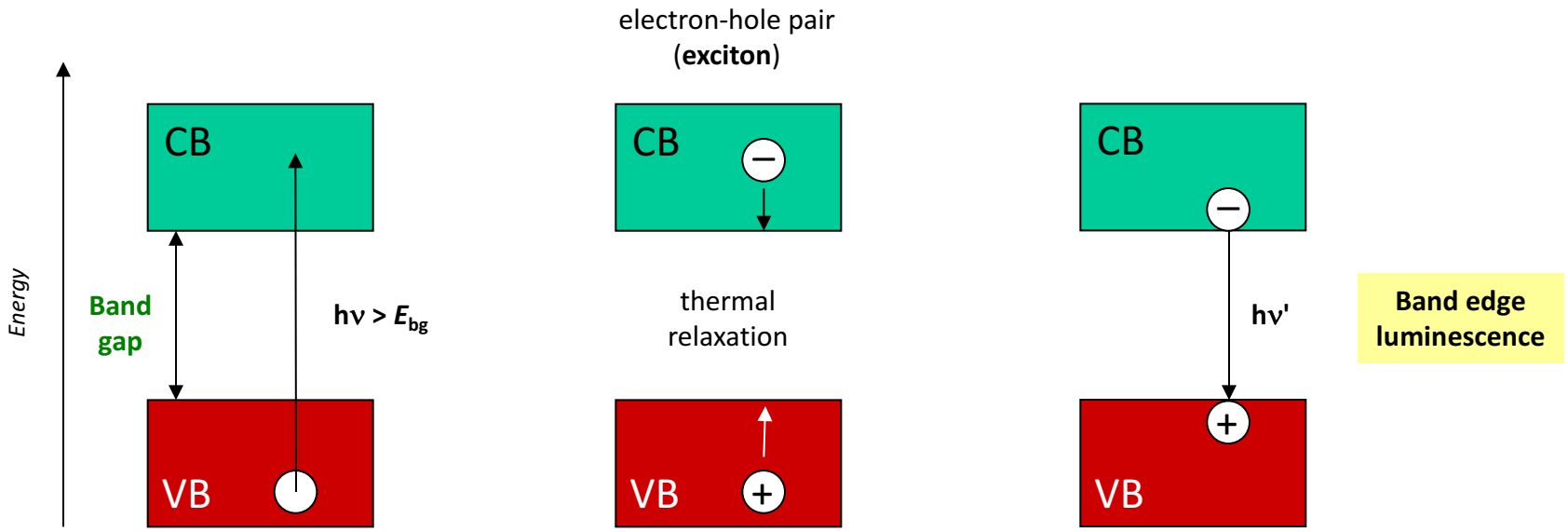
Size tunable fluorescence emission from CdSe/ZnS core shell nanocrystals. The size of the CdSe core dictates the emission wavelength through quantum confinement.



Electronic transitions in semiconductor materials

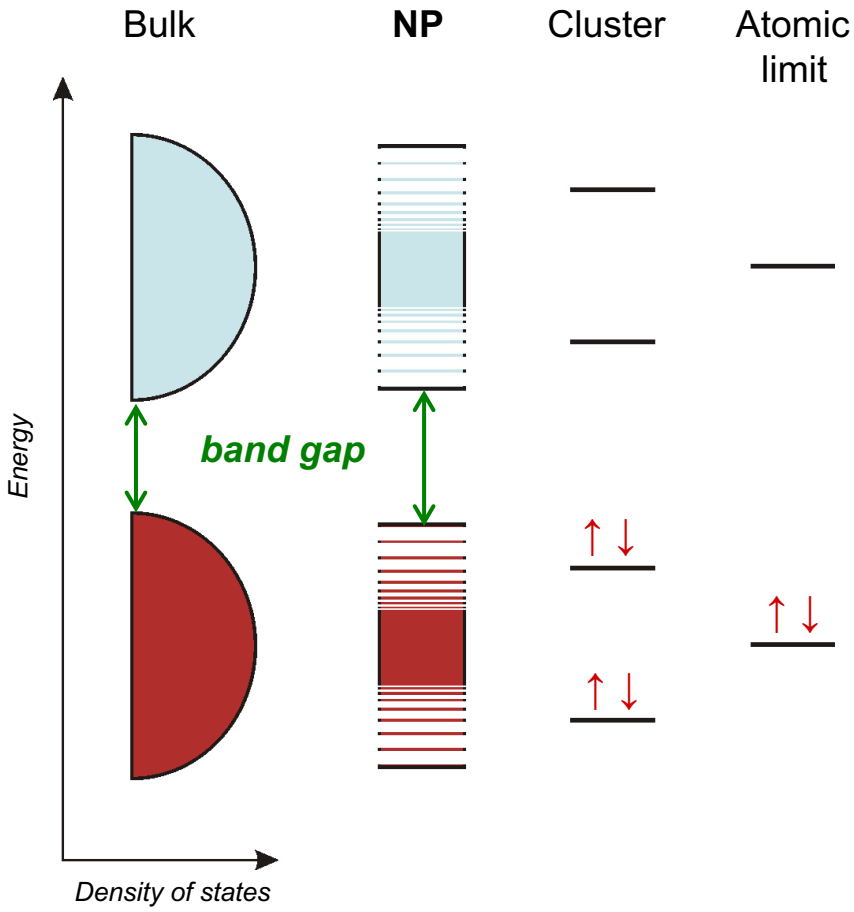
In semiconductors, optical excitation causes the promotion of a valence band electron into the conduction band, leaving behind a valence band hole. Once promotion has occurred, the CB electron quickly relaxes into the lowest energy CB state, while the hole moves to the top of the VB (VB electrons cascade down into lower energy valence states).

The coupled electron-hole pair is electrostatically bound and it is often referred to as a single entity called **exciton**, since one cannot exist without the other.



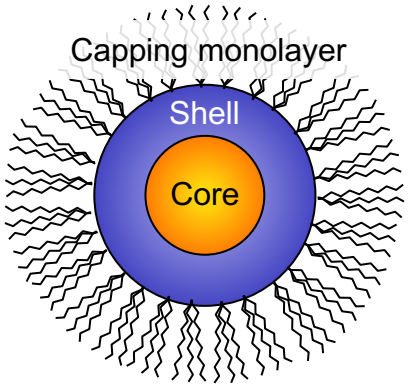
Photoluminescence can arise from radiative recombination of the CB electron with the VB hole. This phenomenon is called *band edge luminescence* and the corresponding emission band is characterized by a very small Stokes shift relative to band edge absorption.

Optical properties of semiconductor quantum dots



Because of quantum confinement, the band gap of semiconductor nanoparticles increases by decreasing the diameter.

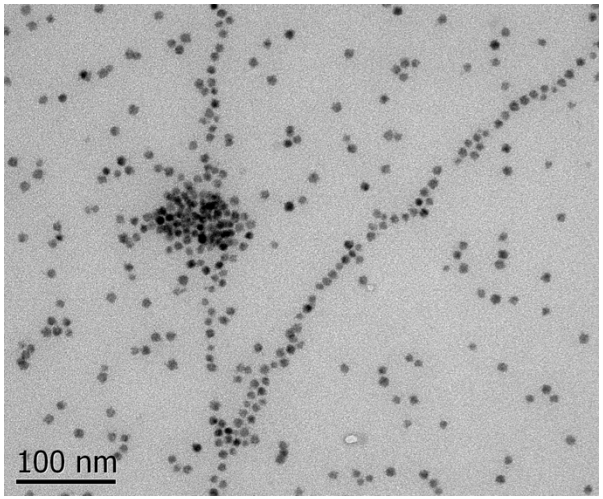
Size-controlled synthesis of monodisperse nanoparticles

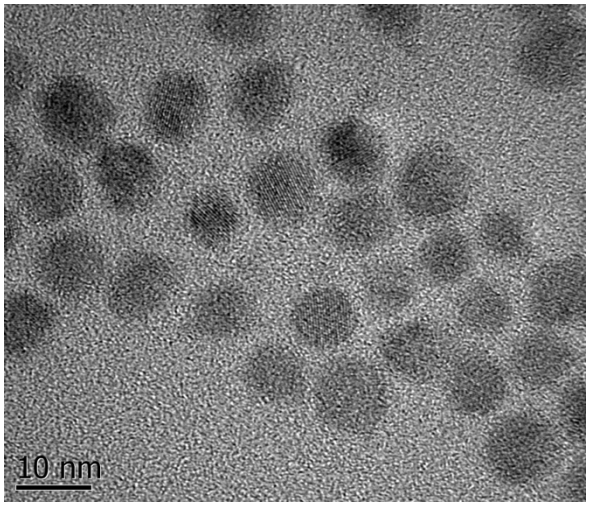


Methods that enable the preparation of NPs of semiconductor materials with a precise control of size and shape are available.

The majority of these methodologies exploit precipitation processes resulting from the reaction of appropriate inorganic or organometallic precursors in a solution phase in the presence of organic ligands that eventually form a capping monolayer on the NP surface.

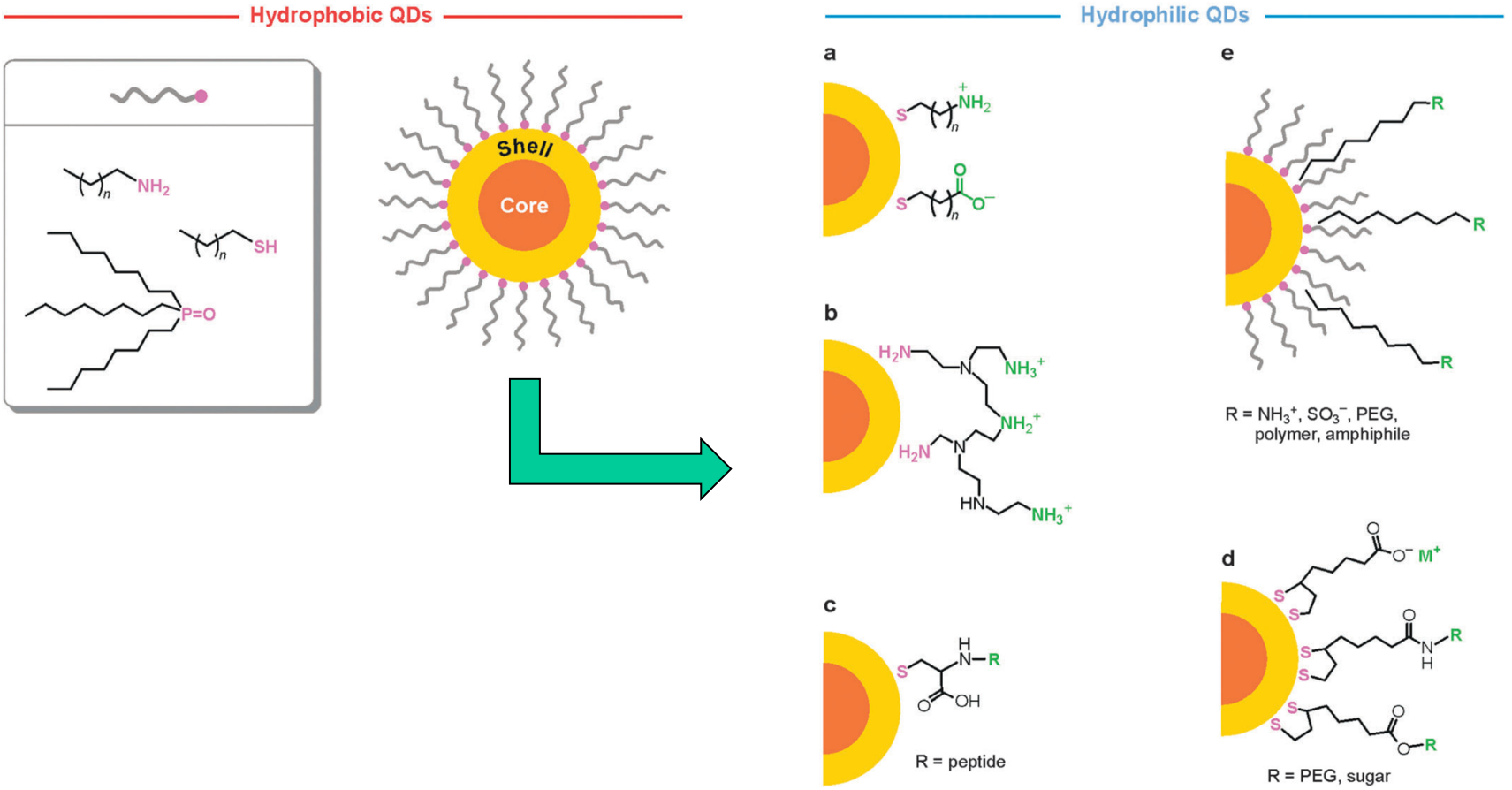
The size and shape accuracy of the product is made possible by a detailed understanding and a precise thermodynamic and kinetic control of the various phases associated with the formation of the nanocrystals, namely *nucleation*, *growth* and *termination*.





TEM images of CdSe-ZnS core-shell NPs

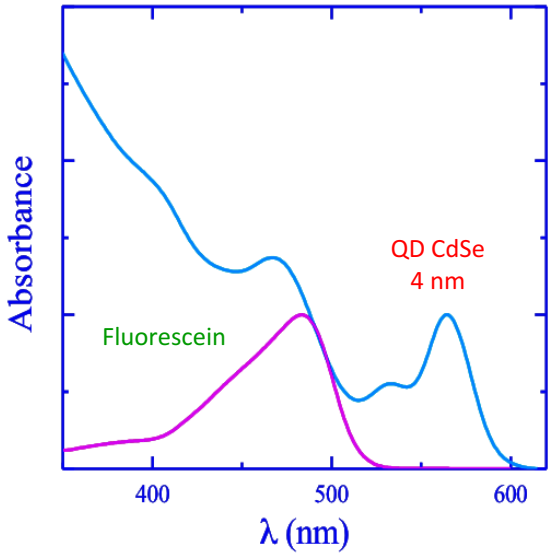
Engineering the surface through ligand exchange

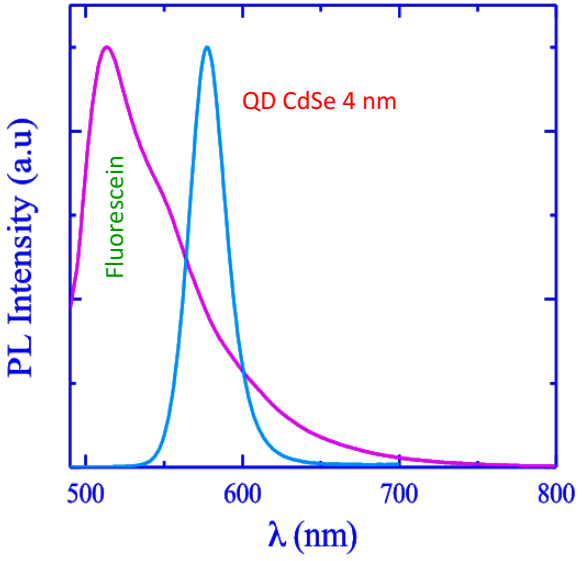


Photophysical properties of semiconductor quantum dots

- Broad absorption spectrum
- Sharp gaussian-shaped emission
- Very small Stokes shift
- Optical properties tunable with size and material type

- High luminescence quantum yield and relatively long lifetime
- High photostability
- Large two-photon absorption cross section
- Possibility of surface passivation by inorganic and organic layers



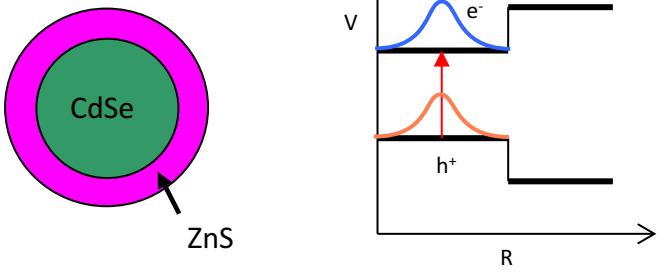


J. Phys. Chem. C **2010**, *114*, 7007; *Pure Appl. Chem.* **2011**, *83*, 1; *ChemPhysChem*, **2011**, *12*, 2280; *Chem. Soc. Rev.* **2012**, *41*, 5728

Core-shell quantum dots

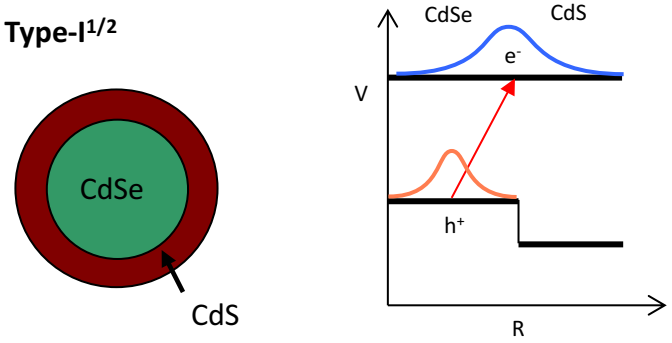
Core-shell QD: a nanocrystal of a given semiconductor coated with a thin layer of another semiconductor.

Type-I



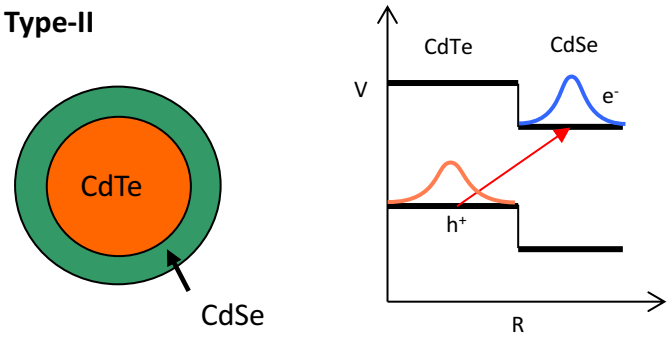
Both electron and hole are confined in the core

Type-I$^{1/2}$



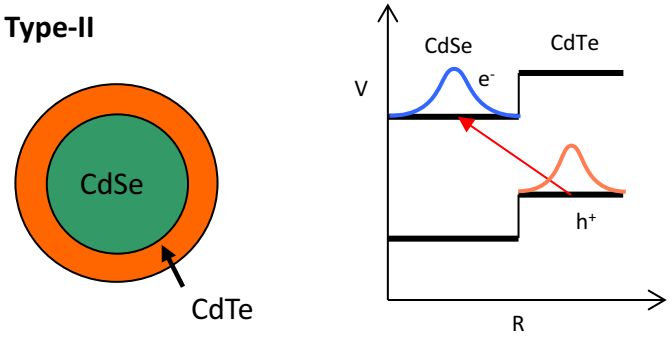
Electron is delocalized over the entire QD
Hole is confined in the core

Type-II



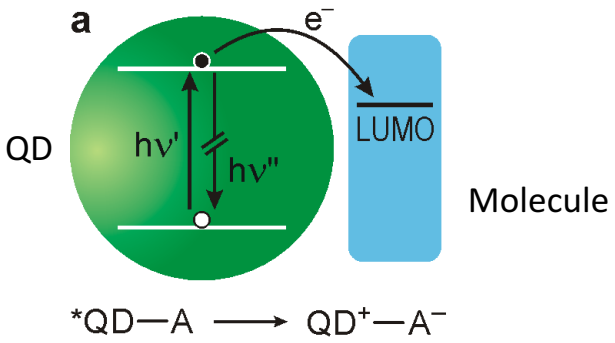
Electron is confined in the shell
Hole is confined in the core

Type-II

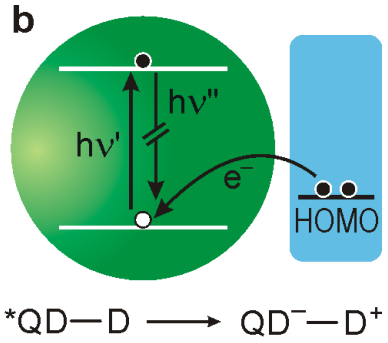


Electron is confined in the core
Hole is confined in the shell

Luminescence modulation mechanisms in QD-molecule conjugates

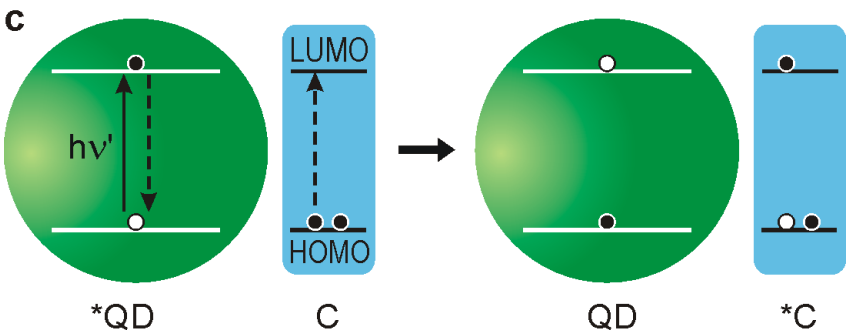


Photoinduced electron transfer from the conduction band of the quantum dot to the LUMO of a bound molecular electron acceptor (A)



Photoinduced electron transfer from the HOMO of a bound molecular electron donor (D) to the valence band of the quantum dot

The rate of these processes depends on the electronic coupling between the QD and the molecule, and on their distance



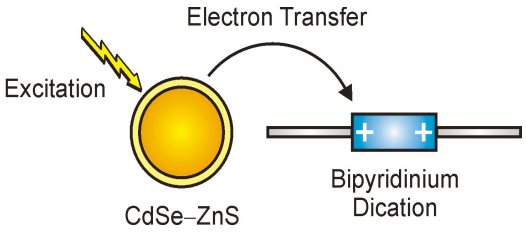
Photoinduced energy transfer by dipole-dipole (FRET) mechanism: the energy of the QD exciton level is transferred to the electronic levels of the bound molecule

The efficiency of this process depends on the spectral overlap between the QD emission and the molecule absorption, and on the QD-molecule distance.

Curr. Phys. Chem. **2011**, *1*, 181; *Chem. Soc. Rev.* **2015**, *44*, 4275

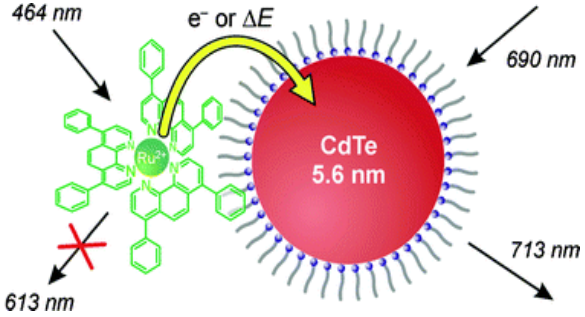
Luminescence quenching in self-assembled QD-molecule conjugates

CdSe-ZnS / 4,4'-bipyridinium derivatives



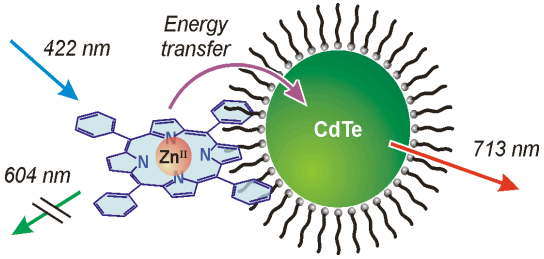
J. Mater. Chem. **2008**, *18*, 2022

CdTe / $[Ru(dpp)_3]^{2+}$



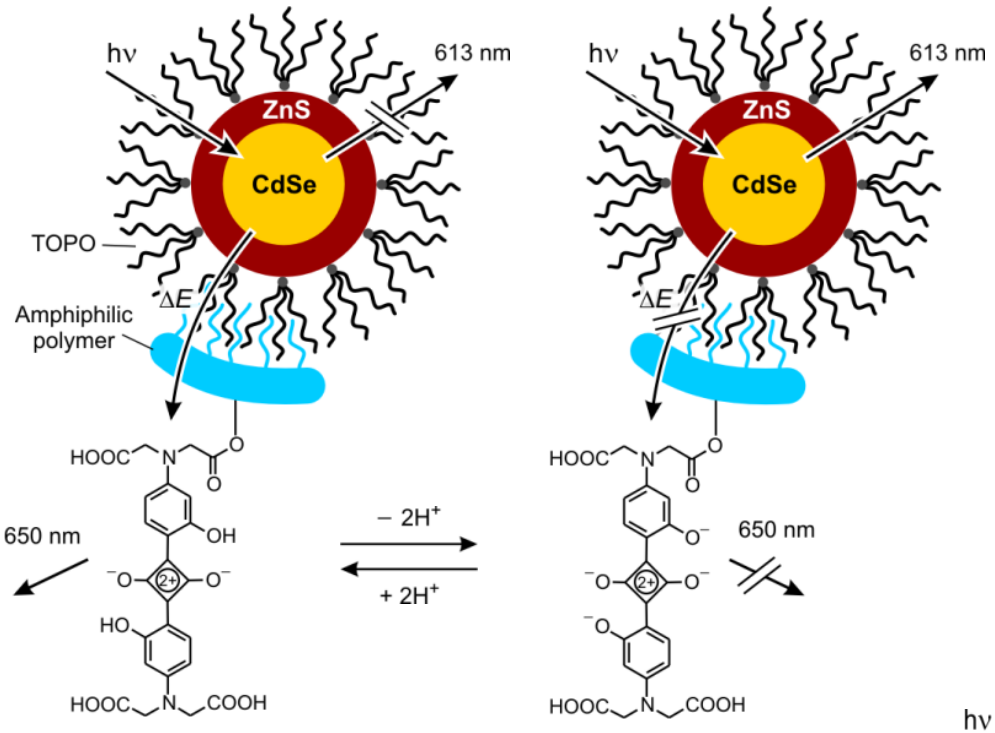
Dalton Trans. **2011**, *40*, 12083

CdTe / Zn(TPP)



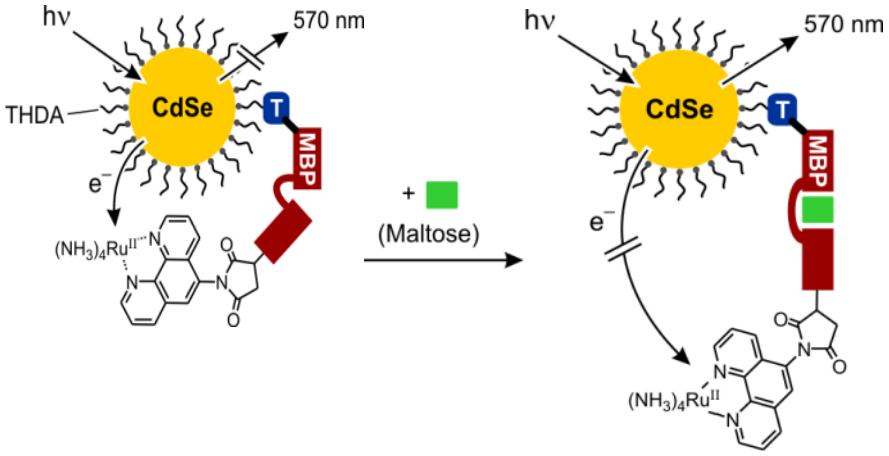
Inorg. Chim. Acta **2012**, *381*, 247

QD-molecule conjugates as luminescent sensors



Ratiometric pH sensor

Bawendi, Nocera et al., *J. Am. Chem. Soc.* **2006**, *128*, 13320



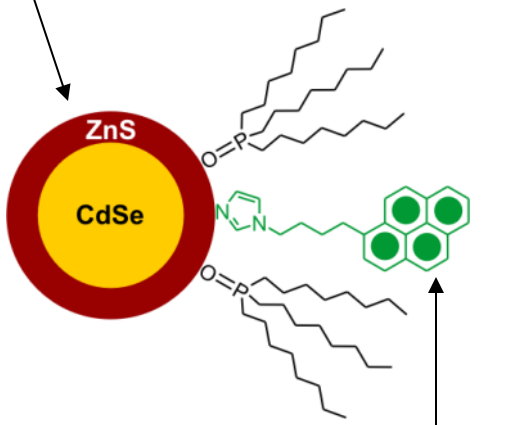
Maltose sensor in water

Benson et al., *J. Am. Chem. Soc.* **2005**, *127*, 12198

QD-molecule conjugates as luminescent sensors

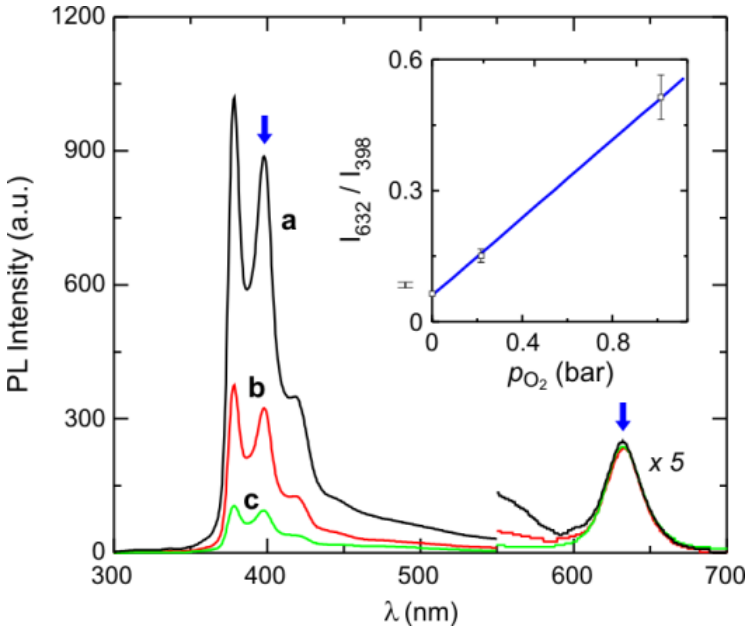
Ratiometric O_2 sensor for organic solvents

Band edge emission
λ_{max} = 632 nm
Insensitive to oxygen



Fluorescence
λ_{max} = 375 nm
Strongly quenched
by oxygen

Chem. Commun. **2011**, *47*, 325

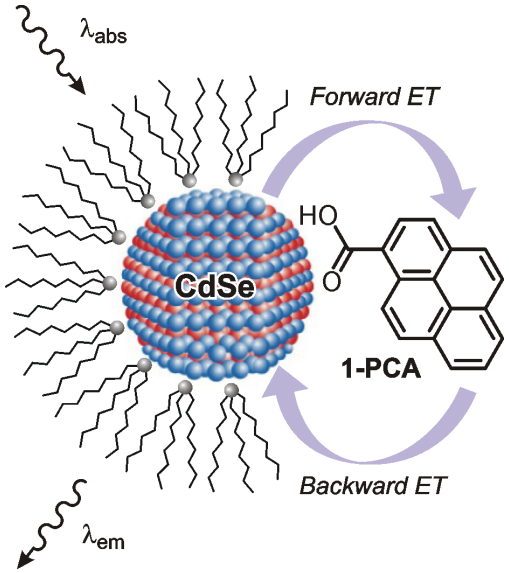


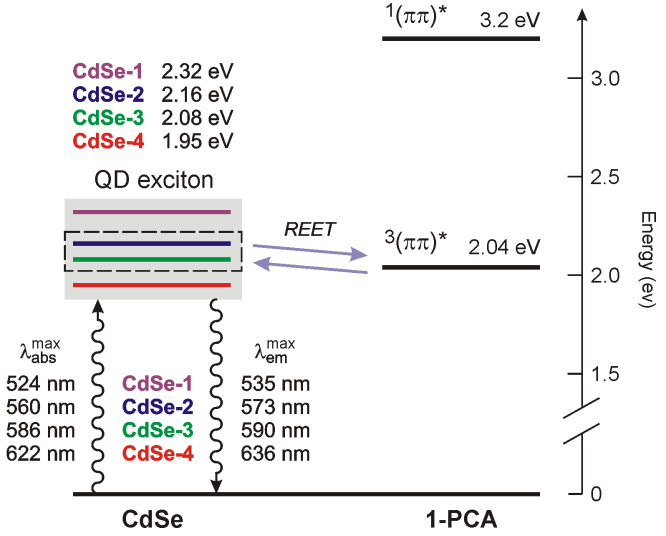
$$I_{632}/I_{398} = (0.061 \pm 0.004) + (0.445 \pm 0.007) \times p_{O_2}$$

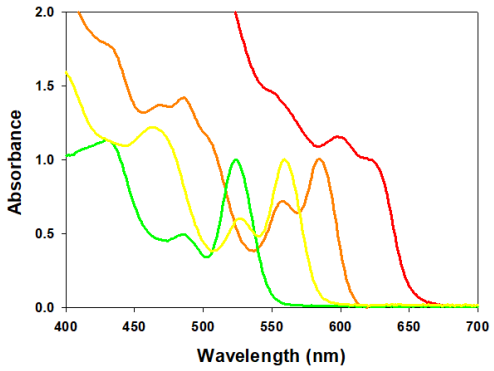
With Nathan McClenaghan, Université de Bordeaux

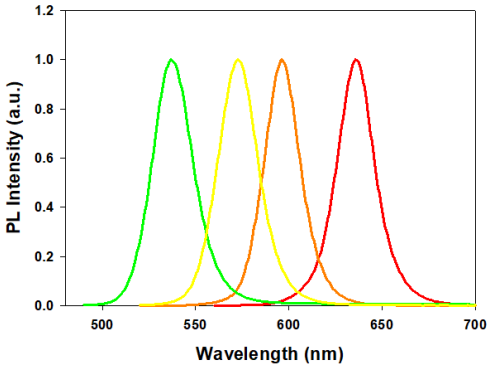
Matteo Amelia

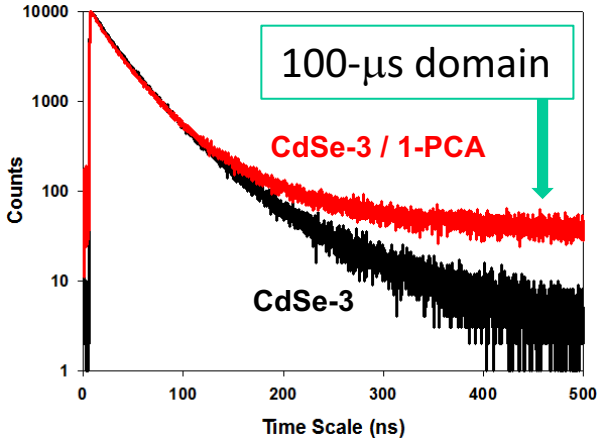
Engineering the luminescence lifetime of semiconductor quantum dots







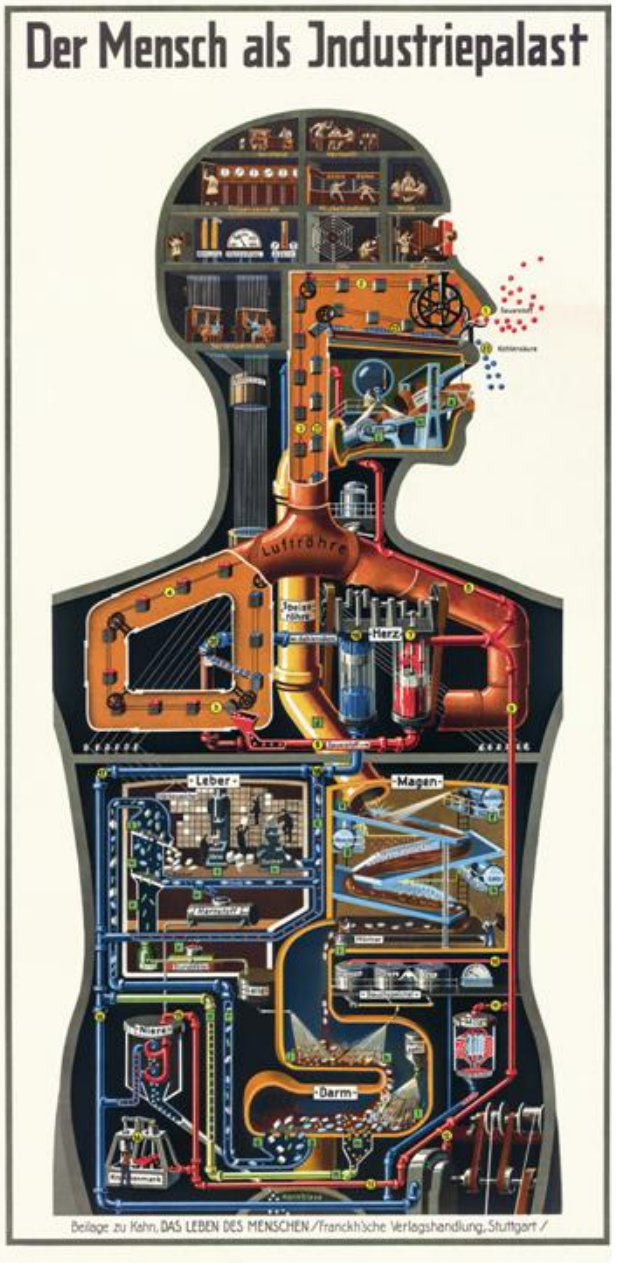




With Nathan McClenaghan, Université de Bordeaux

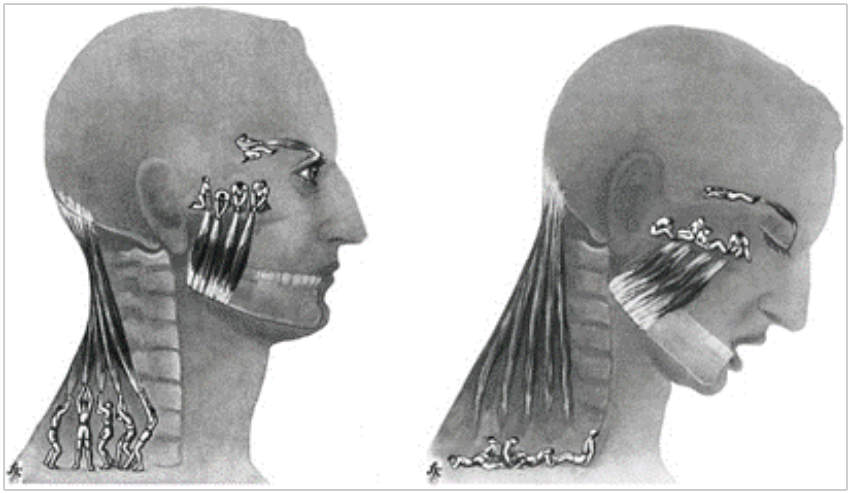
Marcello La Rosa

Molecular machines and motors



'Man as Industrial Palace'
Fritz Kahn, 1926

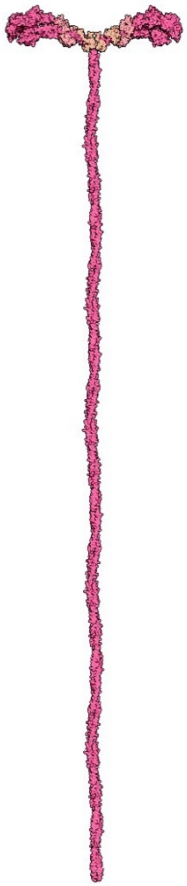
Natural molecular motors in skeletal muscles

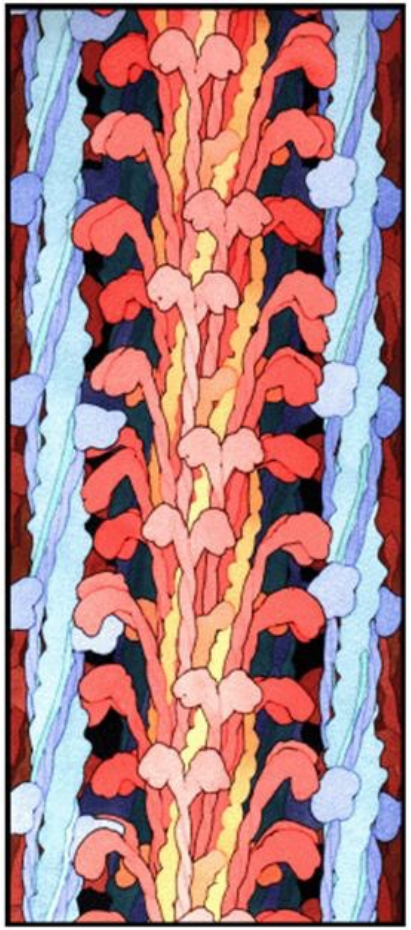


'Wenn wir wachen' *'Wenn wir schlafen'*

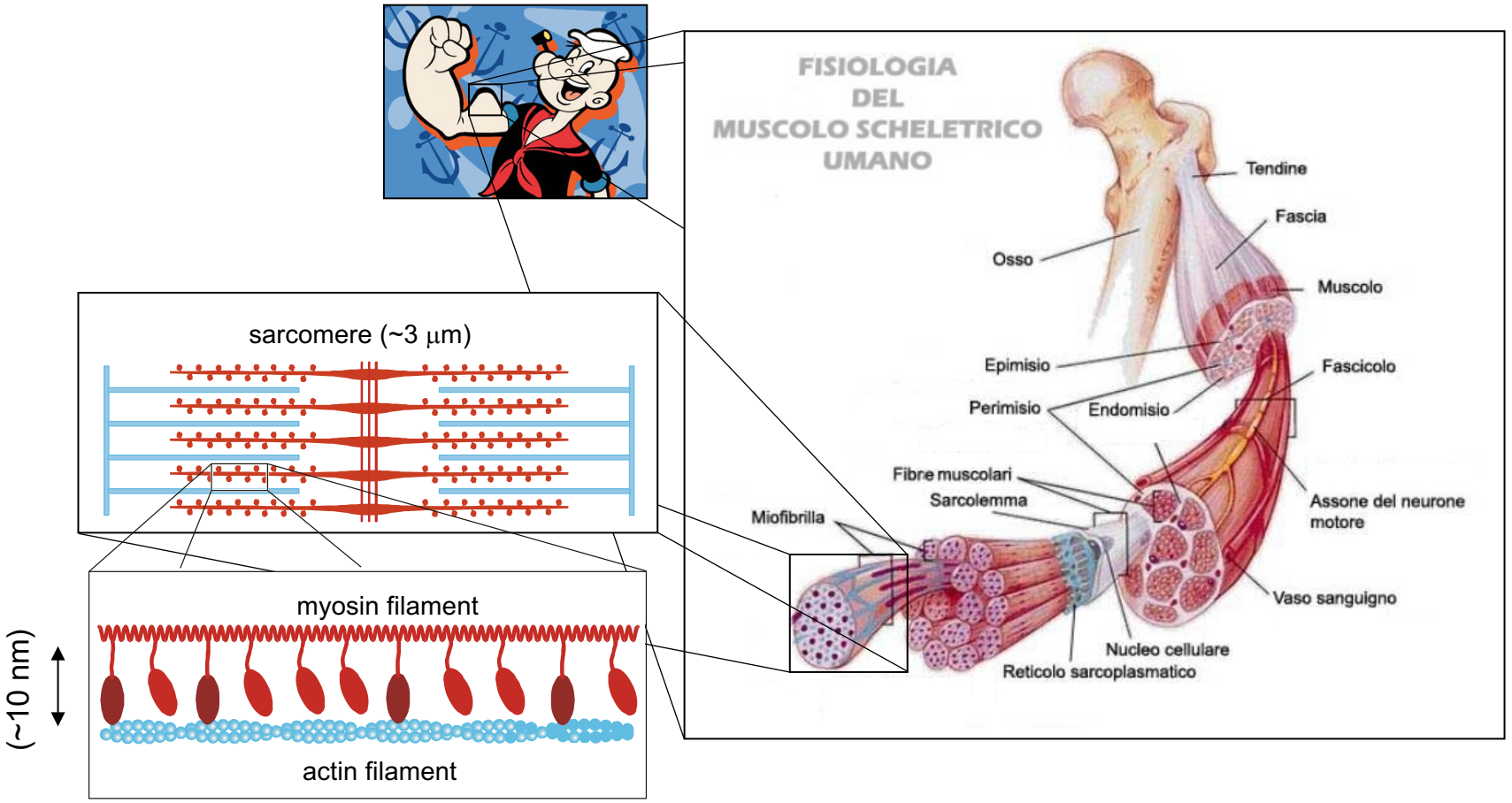
Fritz Kahn, 1939

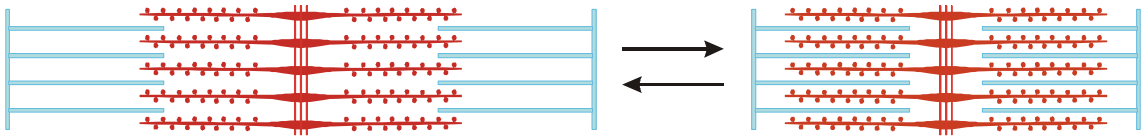
Myosin





Actin





expanded form

contracted form