CHM 696-11: Week 9

Instructor: Alexander Wei

Semiconductor Nanoparticles, Nanorods, and Nanowires:

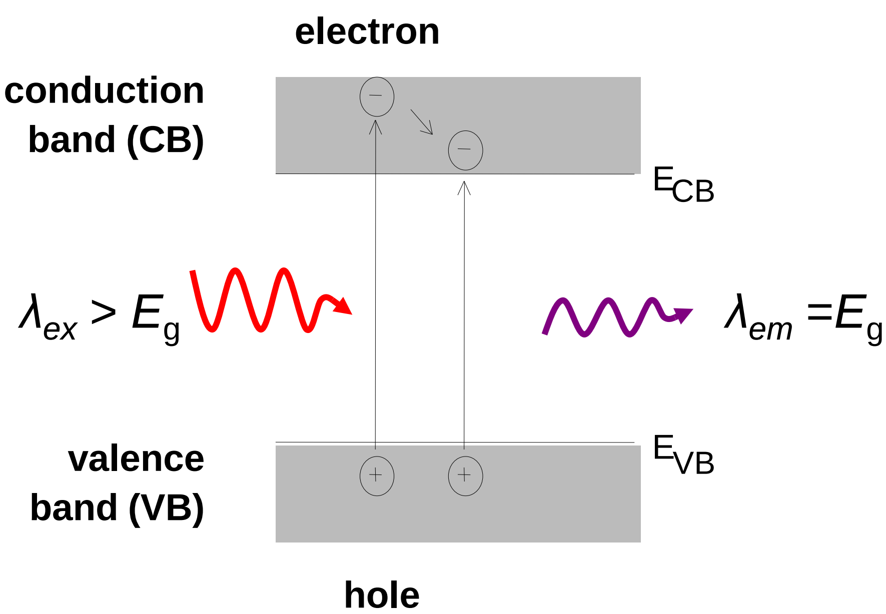
Properties and Applications

Recent review:

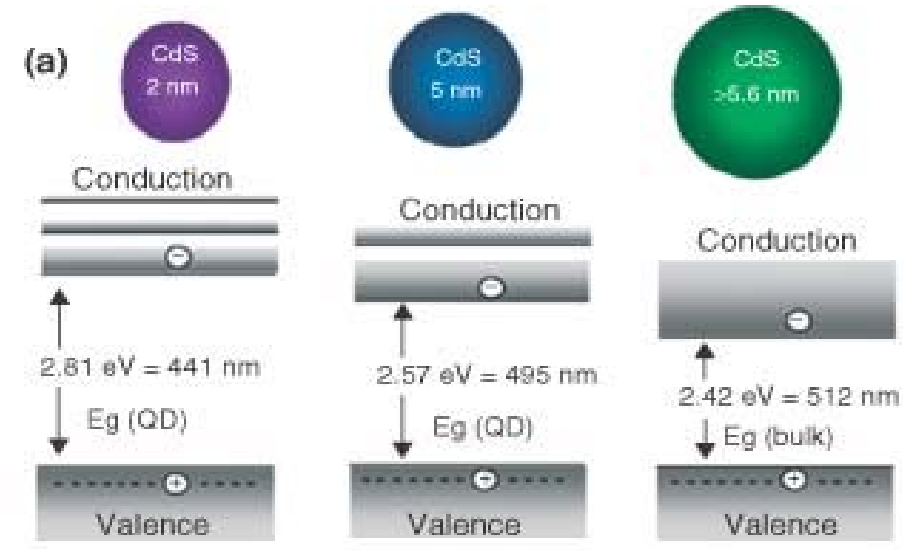
H. M. Mansur, *WIREs: Nanomed. Nanobiotechnol.* **2010**, *2*, 113

Size confinement effects on semiconductor (quantum-dot) nanoparticles

Semiconductor band gap (bulk):



Size-dependent band gap for q-dots (quantum confinement model)

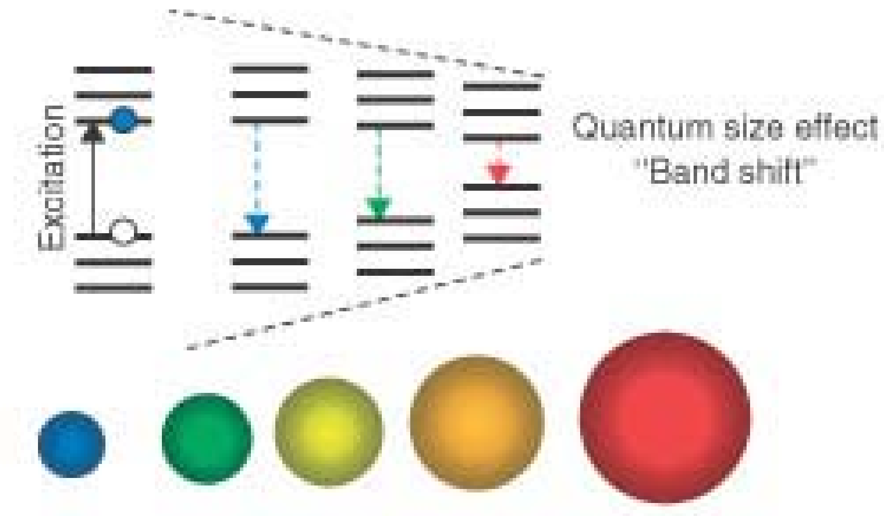


E_g is a material-dependent property

H. M. Mansur, *WIREs: Nanomed. Nanobiotechnol.* **2010**, *2*, 113.

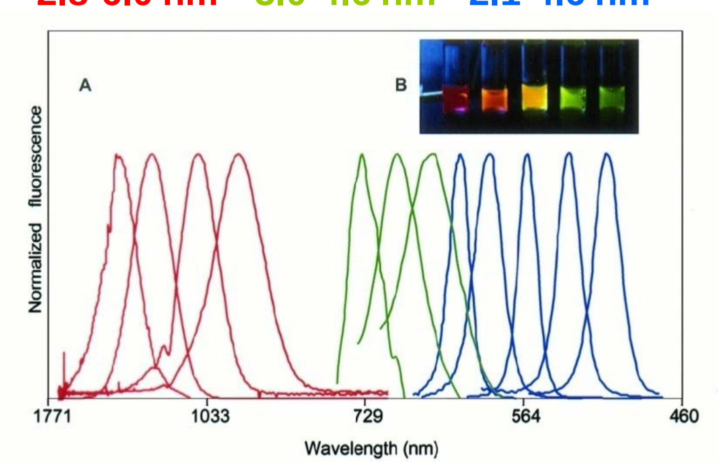
Size-dependent emissions from Q-dot nanocrystals

Typical range of quantum size effect between 2-6 nm



λ_{em} as a function of size and material:

InAs **2.8-6.0 nm** | **InP** **3.0-4.6 nm** | **CdSe** **2.1-4.6 nm**

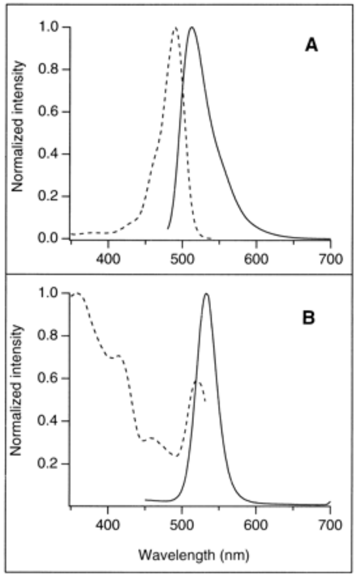


Bruchez et al, *Science* **1998**, *281*, 2013

Organic dyes vs. Q-dots:

Excitation/emission of fluorescent molecule:

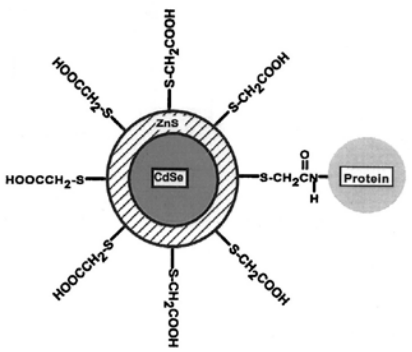
Excitation/emission of CdSe Q-dots:
UV light can be used

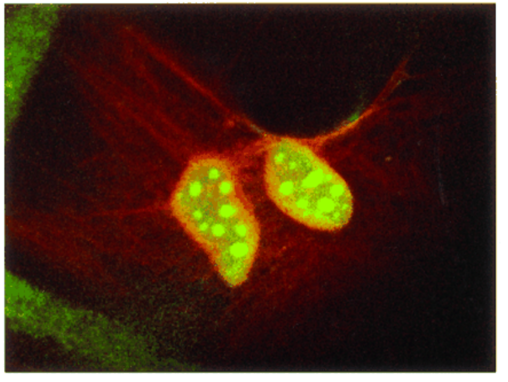


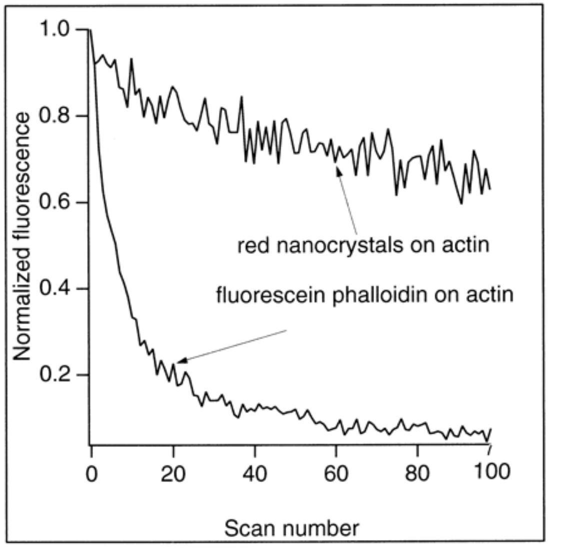
Biological applications of Q-dots

CdSe/ZnS Q-dots as fluorescent biolabels:

Bruchez et al, *Science* **1998**, *281*, 2013;
Chan and Nie, *Science* **1998**, 281, 2016.

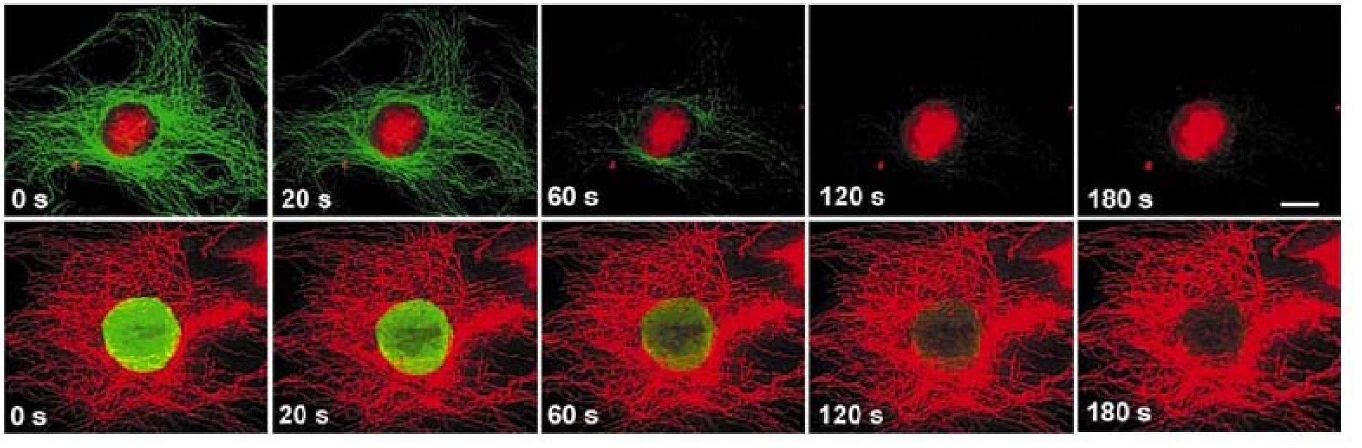






Immunofluorescent labeling: Q-dots vs. dye molecules

Wu et al, *Nature Biotechnol.* **2003**, *21*, 41.



Red: QDs
Green: Alexa Fluor

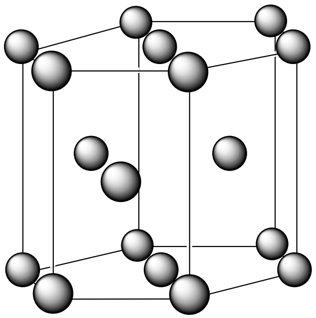
Lattice structures of semiconductor nanocrystals

Zinc blende (diamondoid) structure:

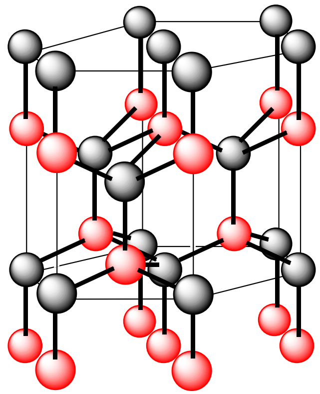
Two interpenetrating fcc lattices (**Cd** & **Se**)

Wurtzite (hexagonal) structure:

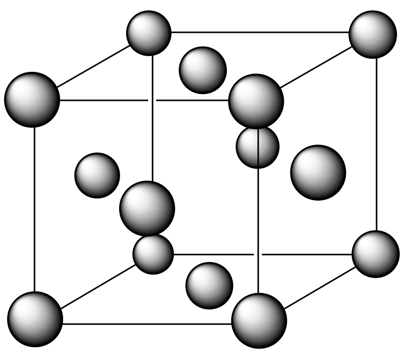
Reduced interatomic **Cd**-**Se** distance

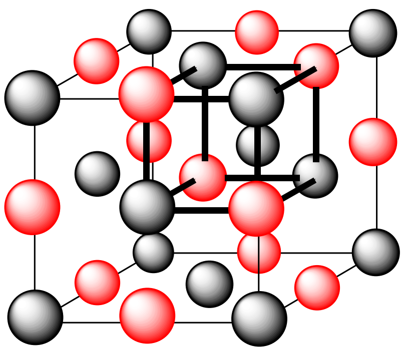


hcp



fcc





Rock salt structure:

Ionic semiconductor lattices;
shortest interatomic distances

CdSe zinc blende and wurtzite nanocrystals have direct band gaps and high quantum yields

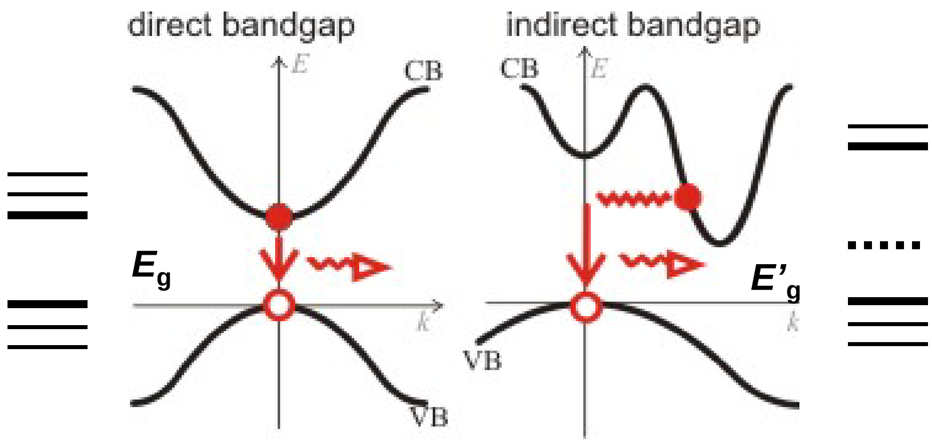
Rock-salt lattice has an indirect band gap

Tolbert et al, *Phys. Rev. Lett*. **1996**, *73*, 3266

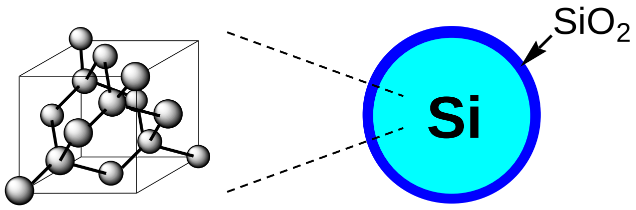
Direct vs. indirect band gaps

Transitions across indirect band gaps are less efficient (lower probability)

Direct gap; vertical transition but higher energy
Indirect gap; lower energy

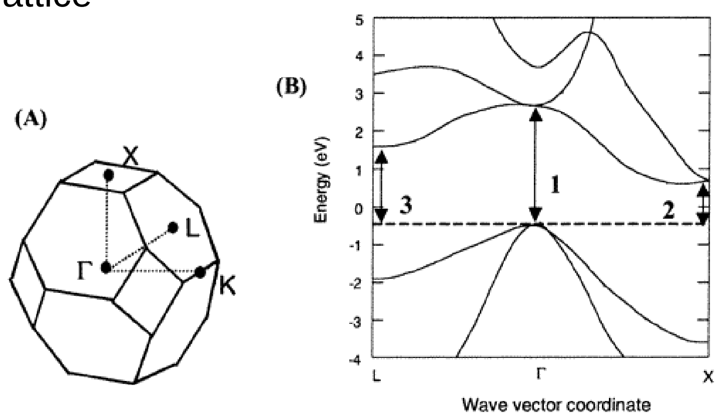


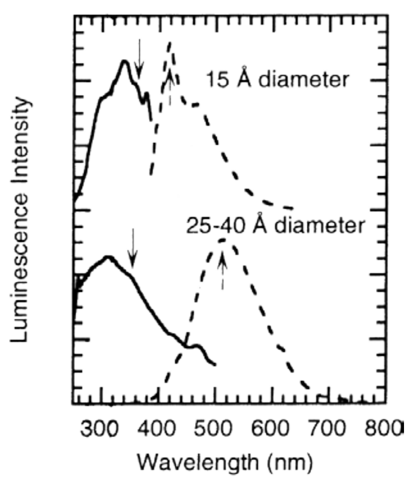
<u>Ex</u>. Silicon has an indirect band gap;
Passivated Si-NPs have low quantum yields

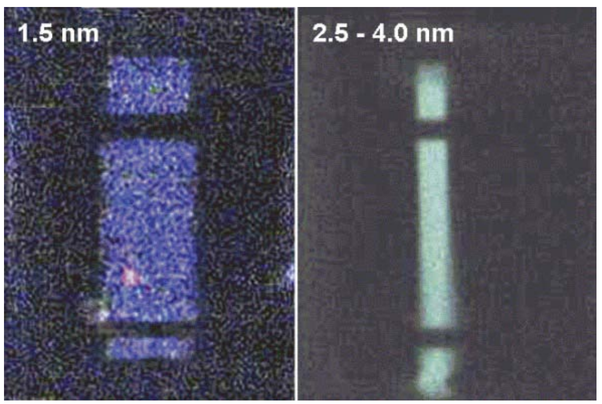


diamondoid lattice

2-6 nm







Holmes et al, *J. Am. Chem. Soc.* **2001**, *123*, 3743.

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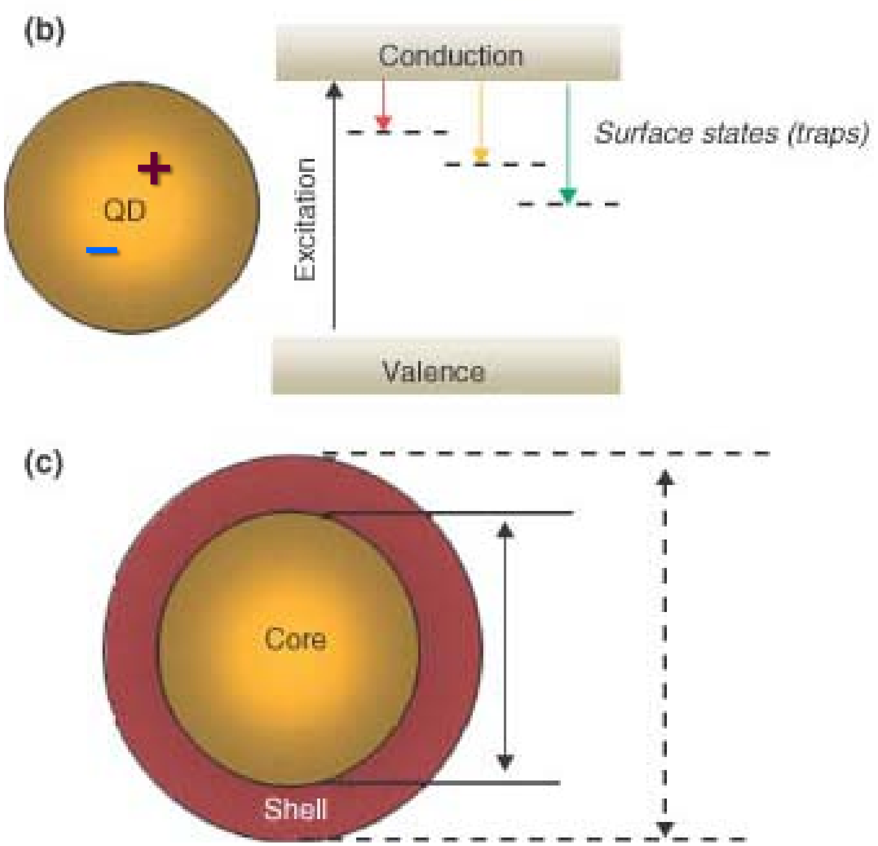
Excitons in quantum-dot nanoparticles

<u>excitons</u>: localized electron–hole pair

Electrons can be trapped in lower-energy surface states, lowering quantum yield (radiationless decay);
also creates "dark" states



Core-shell semiconductor NPs

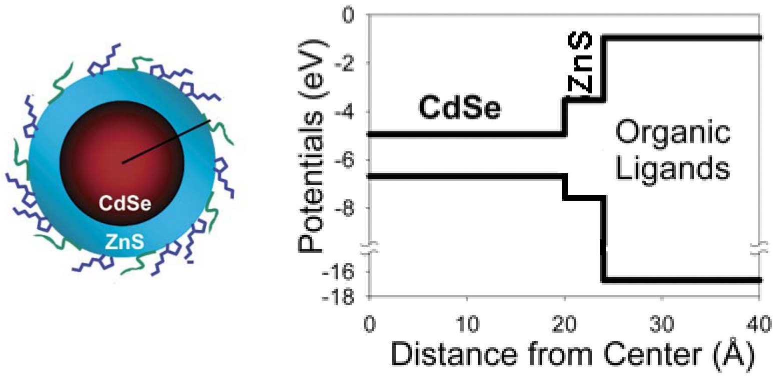
Surface passivation greatly reduces the probability of exciton trapping

H. M. Mansur, *WIREs: Nanomed. Nanobiotechnol.* **2010**, *2*, 113.

Photoexcited states of Core-Shell Q-dots

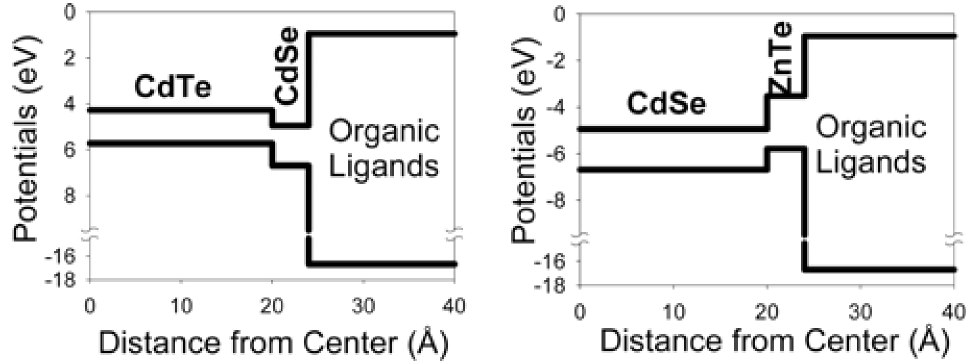
"Band-gap engineering"

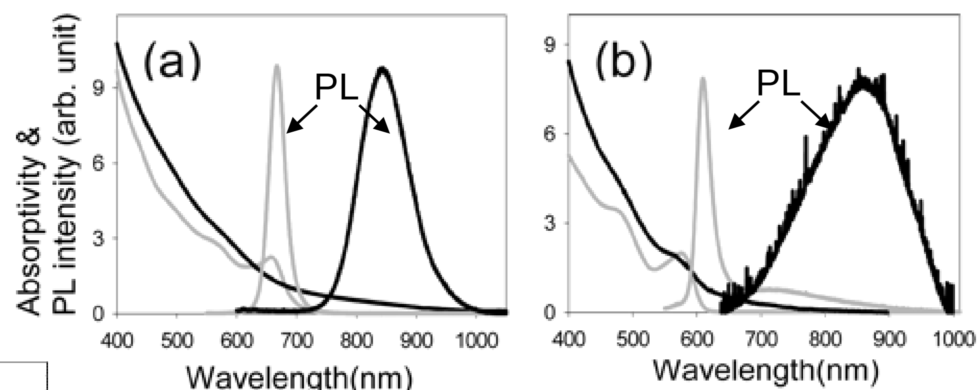
Type I: Shell has larger band gap than core



CdSe/ZnS core-shell QD + organic ligands; shell material has minimal effect on band gap

Type II: induces hole-electron separation



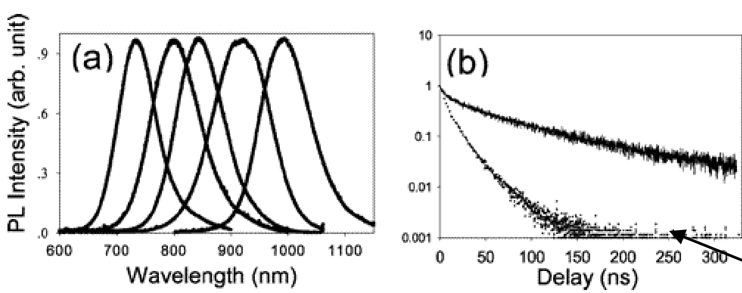


CdTe **CdTe/CdSe**

CdSe **CdSe/ZnTe**

CdTe/CdSe NPs:
emission range and PL decay

1.6/1.9
1.6/3.2
3.2/1.1
3.2/2.4
5.6/1.9 nm

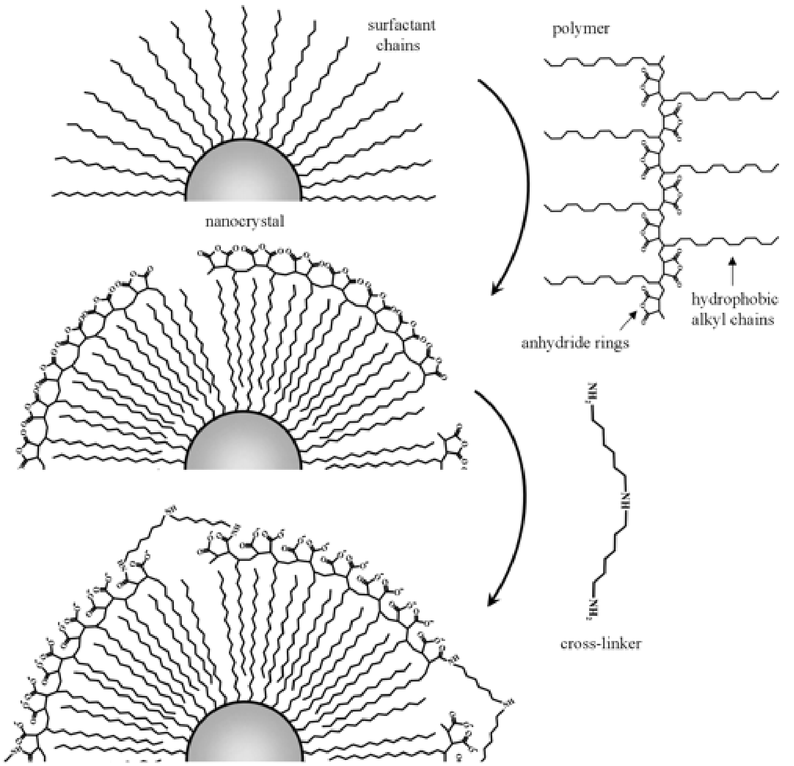


CdTe/CdSe
CdTe only

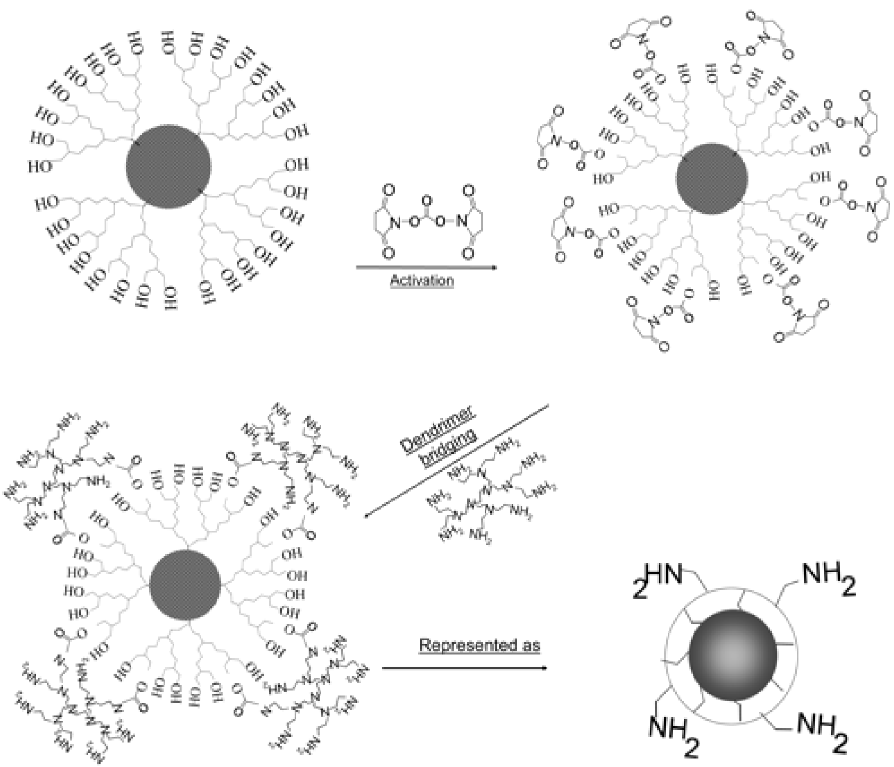
Kim et al, *J. Am. Chem. Soc.* **2003**, *125*, 11466

Surface functionalization of Q-dots: crosslinked surfactant layers

Polymer interdigitation and crosslinking:
Pellegrino et al, *Nano Lett.* **2004**, *4*, 703.



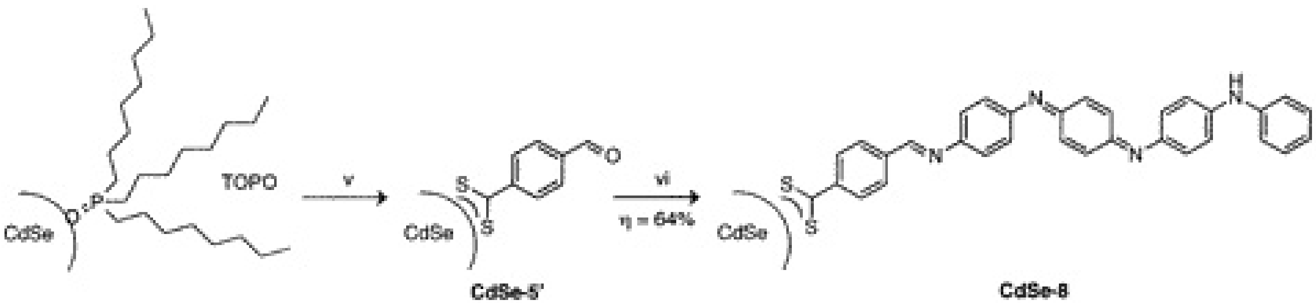
Dendrimer crosslinking:
Guo et al, *Chem. Mater.* **2003**, *15*, 3125.

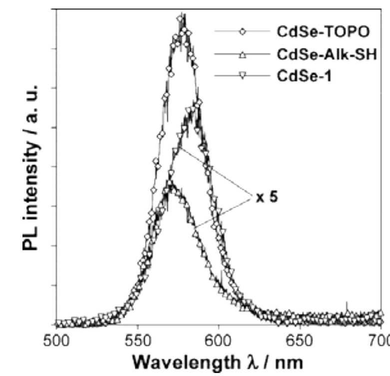


Direct chemisorption onto Q-dots can often reduce quantum yield

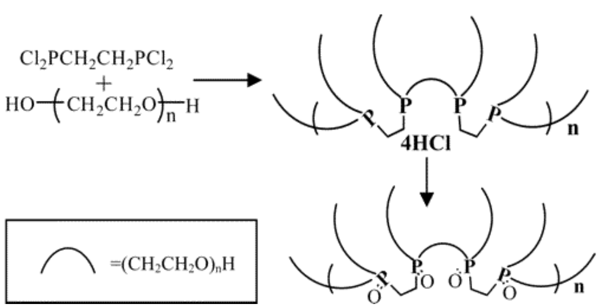
Surface functionalization of Q-dots: more recent approaches

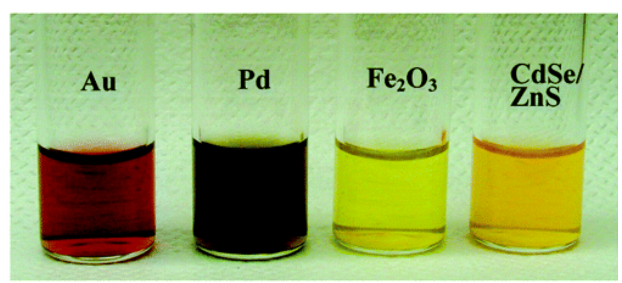
Chelating carbodithioates: Querner et al, *J. Am. Chem. Soc.* **2004**, *126*, 11574.

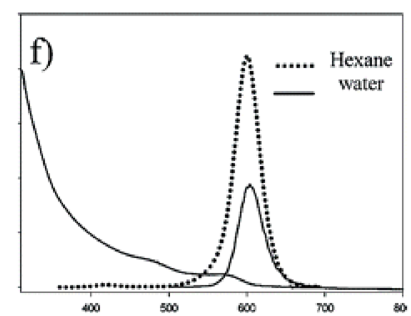




Poly(dioxyethylenephosphonates): Kim et al, *J. Am. Chem. Soc.* **2005**, 127, 4556







CdSe/ZnS photoluminescence spectra:
50% retention of PL in water