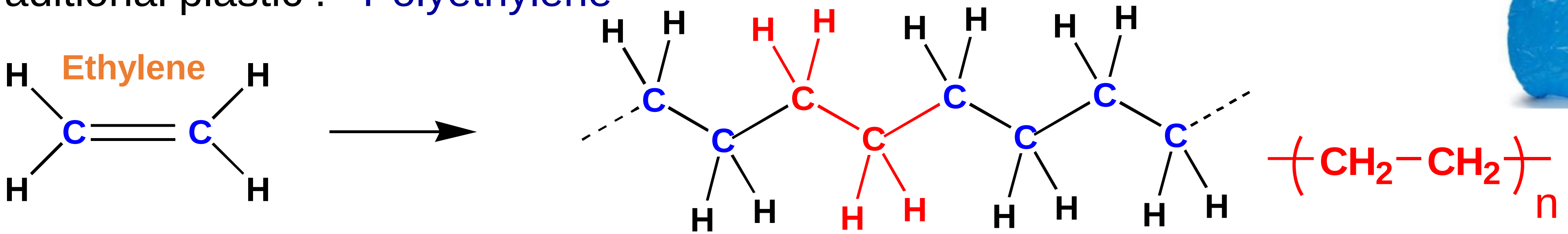
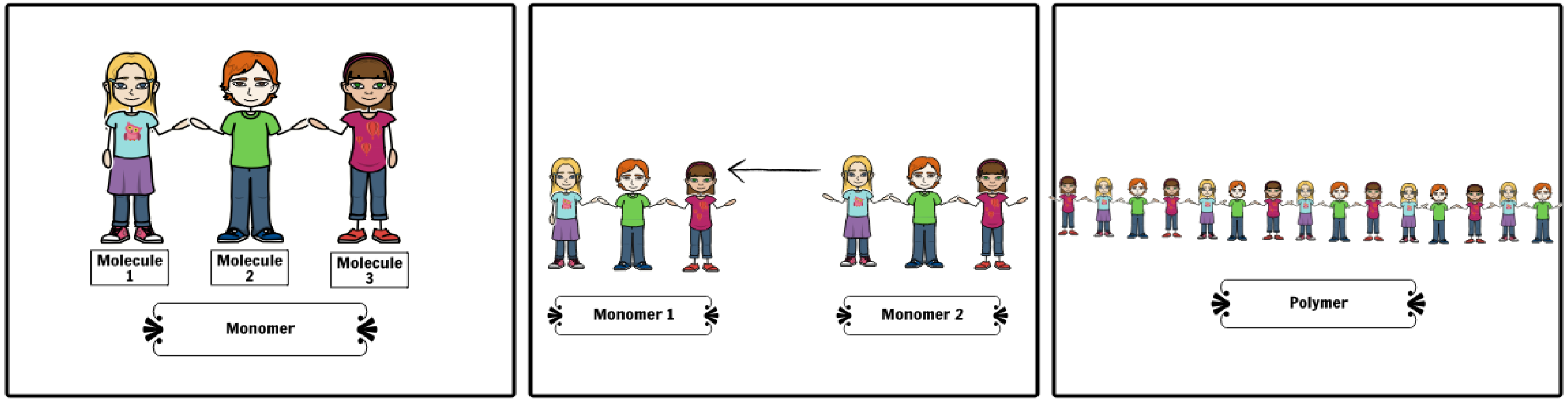
Materials Chemistry III
Day 9

From last class….

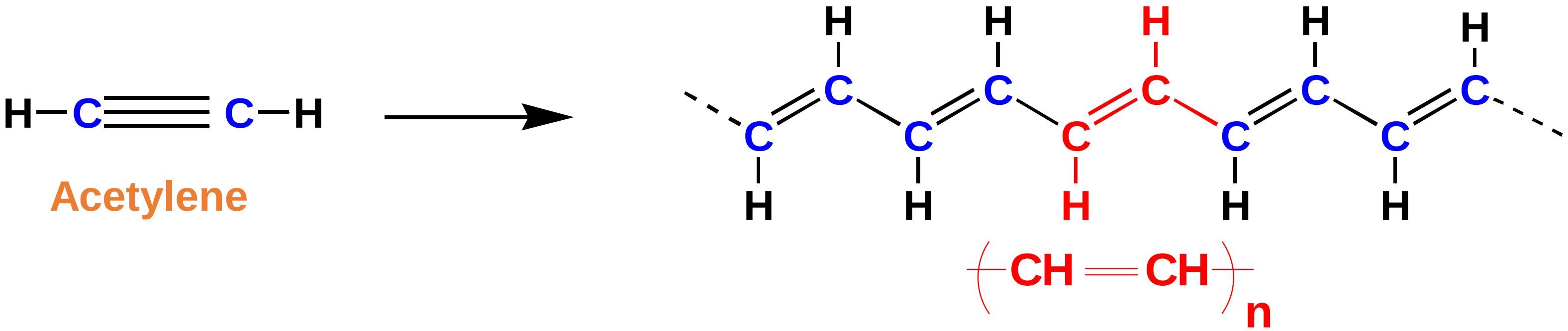
Conjugated Polymers-Plastic solar cells

- Traditional plastic : Polyethylene

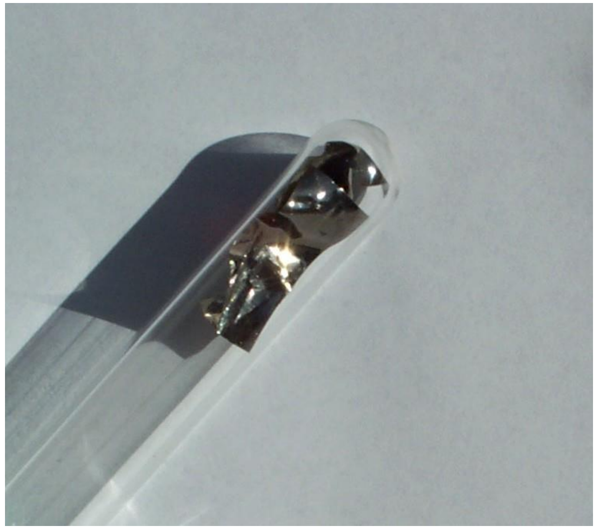


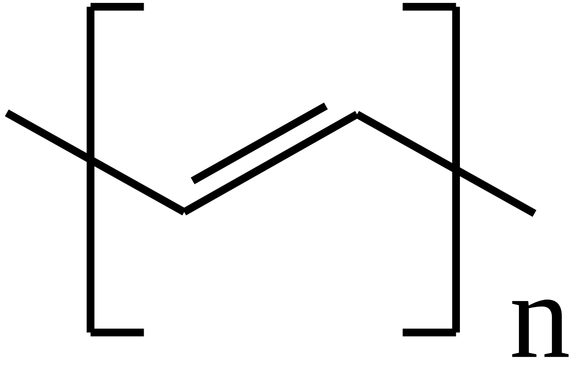


- Conjugated polymer : Trans-polyacetylene



Conjugated Polymers





Trans-polyacetylene (t-PA)

Applications

OLED

OFET

OPV

How do we explain the band properties of large conjugated system?

Nobel Prize in Chemistry 2000

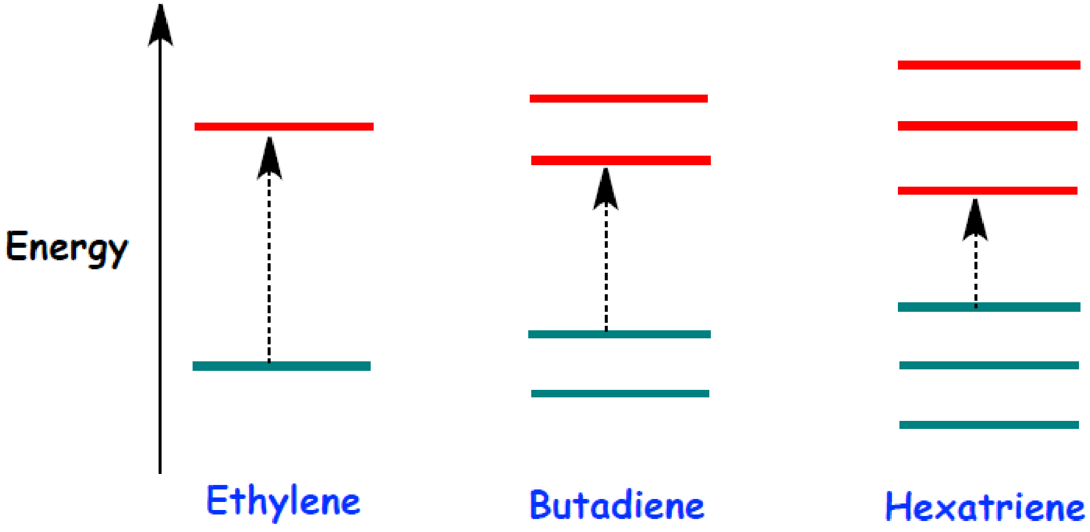
“For the Discovery and Development of Conductive Polymers”

Alan Heeger
University of California
at Santa Barbara

Hideki Shirakawa
University of Tsukuba

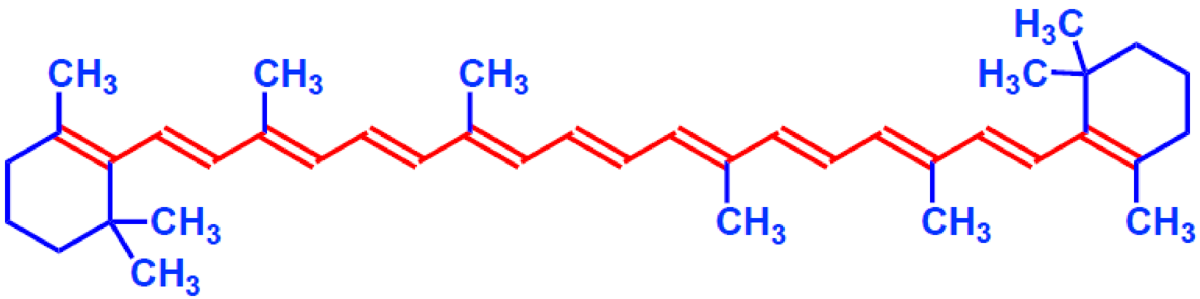
Alan MacDiarmid
University of
Pennsylvania

Effect of Conjugation



Compare 1D box?

Molecule	λ_{max} (nm)
Ethylene	165
1,3-butadiene	217
1,3,5-hexatriene	258
β-Carotene	470

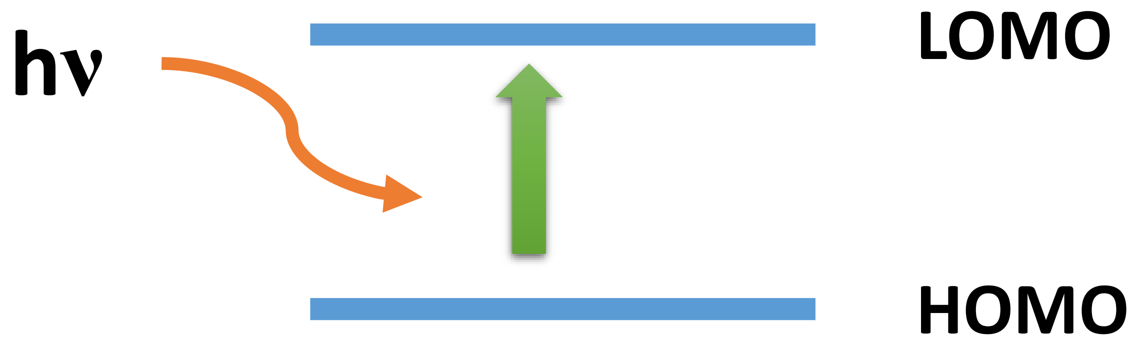


Spectrum?

Why deviation?

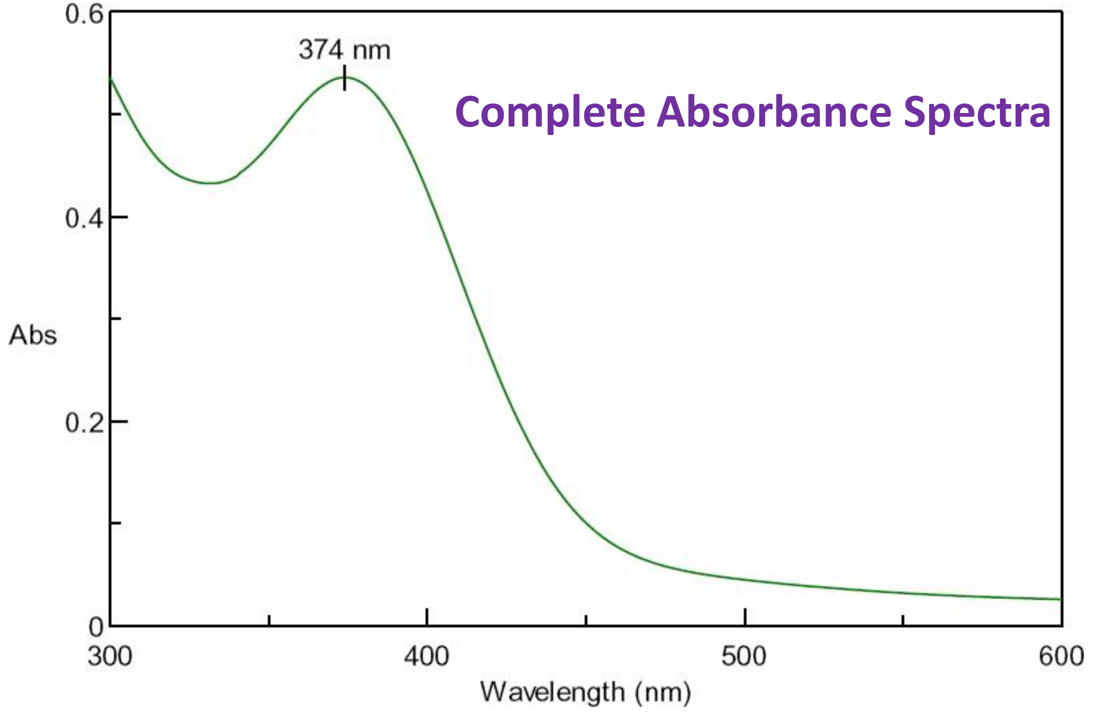
- **Effect of solvent!**
- **Chain rotation!**
- **1D Box model is a crude model, which provides the trend!**

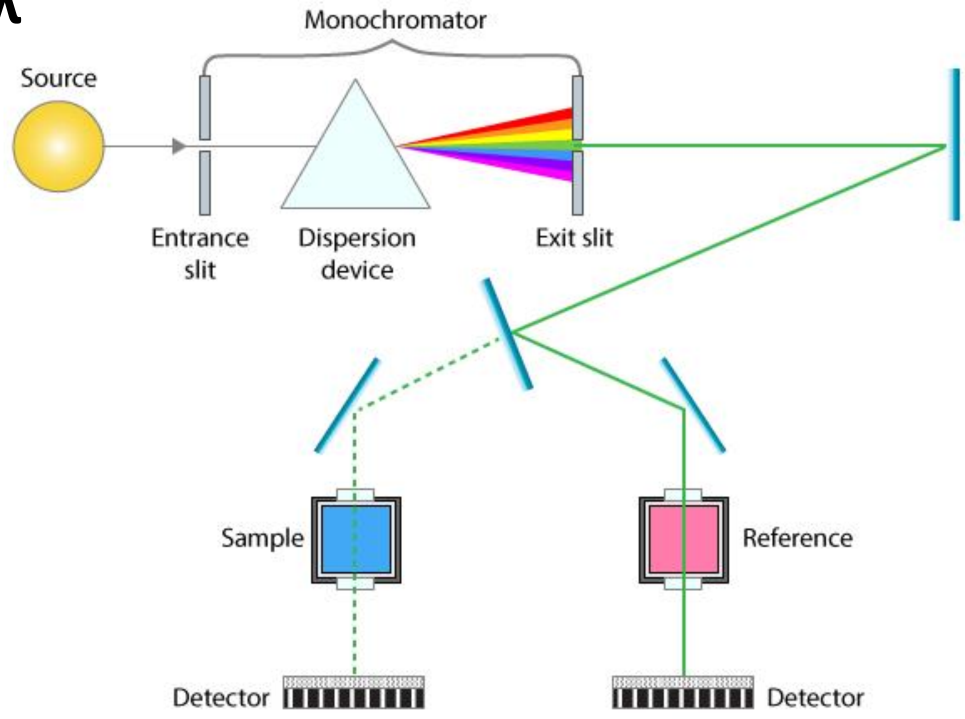
Light Mater Interaction


hν
LOMO
HOMO

Lambert-Beers law: $\log(I_o/I_t)=\varepsilon cL=\text{Absorbance}$

Absorbance at various ‘λ’

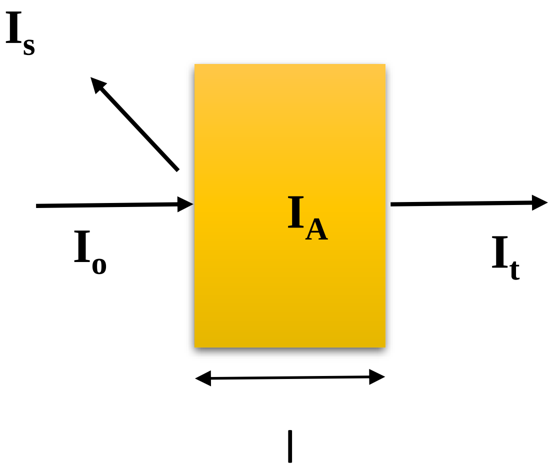


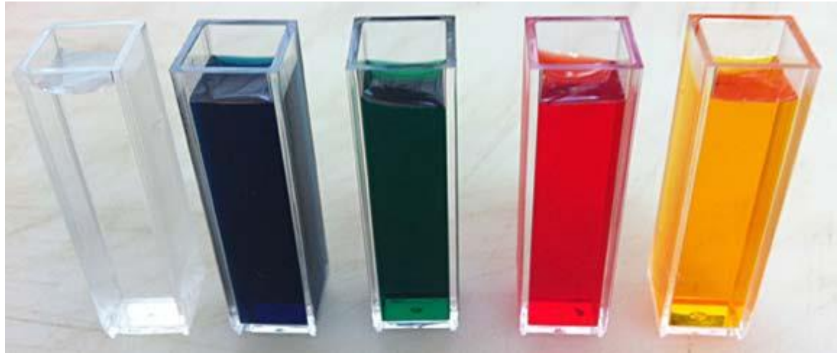


UV-Visible spectroscopy-Measurement of Electronic Transition Electron-Mater Interaction!

Lambert-Beers law

When a monochromatic radiation is passed through an absorbing medium a part of the incident radiation is scattered by the absorbing medium, a part is absorbed and rest of which is transmitted.
Scattering effect may be minimized by using a specific geometry of the sample holder/cuvette.

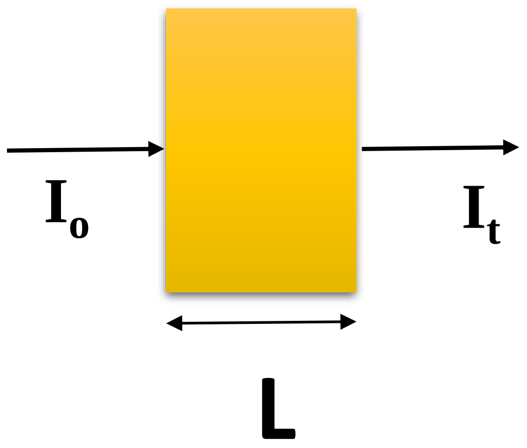




$$I_o=I_t+I_s+I_A$$

Lambert's law

When a monochromatic radiation is passed through a medium, the decrease in intensity of the radiation w.r.t the length of the absorbing medium is proportional to the intensity of the radiation.



$$-[dI/dL] \ \alpha \ I$$

$$\log(I_t/I_o) = -ZL$$

Where Z is the extinction co-efficient.

$$\log(I_o/I_t)=ZL$$

$$\text{If, } \log(I_o/I_t)=1$$

$$\text{Then, } I_0/I_t=10$$

$$Z=1/L$$

Extinction coefficient is defined as the reciprocal of the thickness, expressed in cm at which the intensity of the light falls to 1/10 th of the original value.

Beers law

- Equal fractions of incident light radiation are absorbed by equal changes in concentration of the absorbing substance in a path of constant length.

$$-[dI/l] \; \alpha \; C$$

Lambert-Beers law:

Limitation:
Radiation should be monochromatic

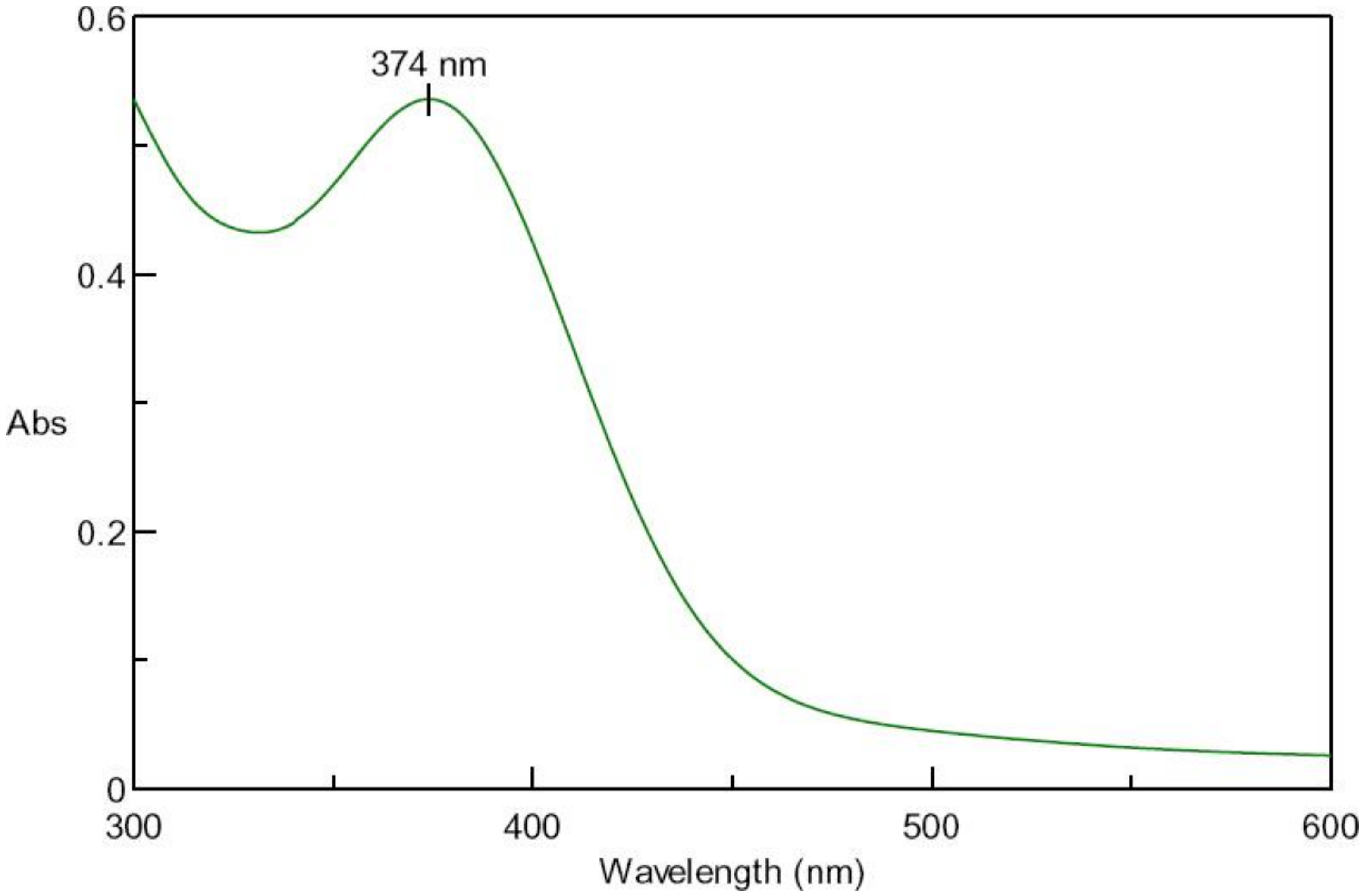
$$-[dI/l] \; \alpha \; C \, dL$$

$$\log(I_o/I_t)=\varepsilon cL=\text{Absorbance}$$

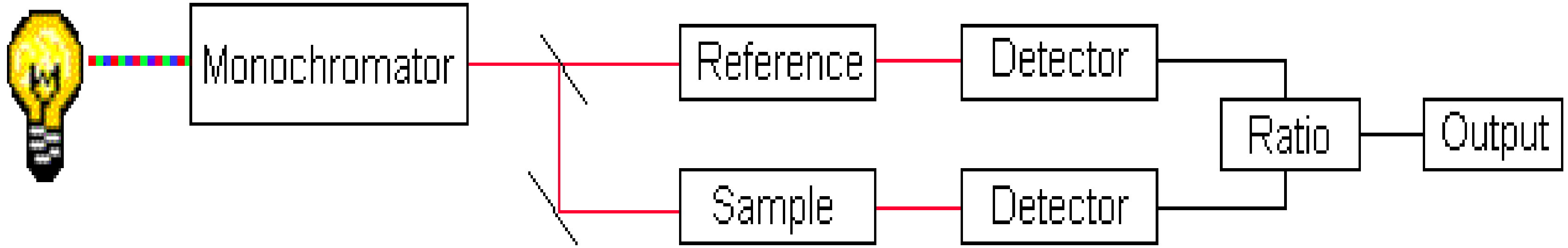
The relationship between transmittance (T) and absorbance (A) can be expressed by the following:

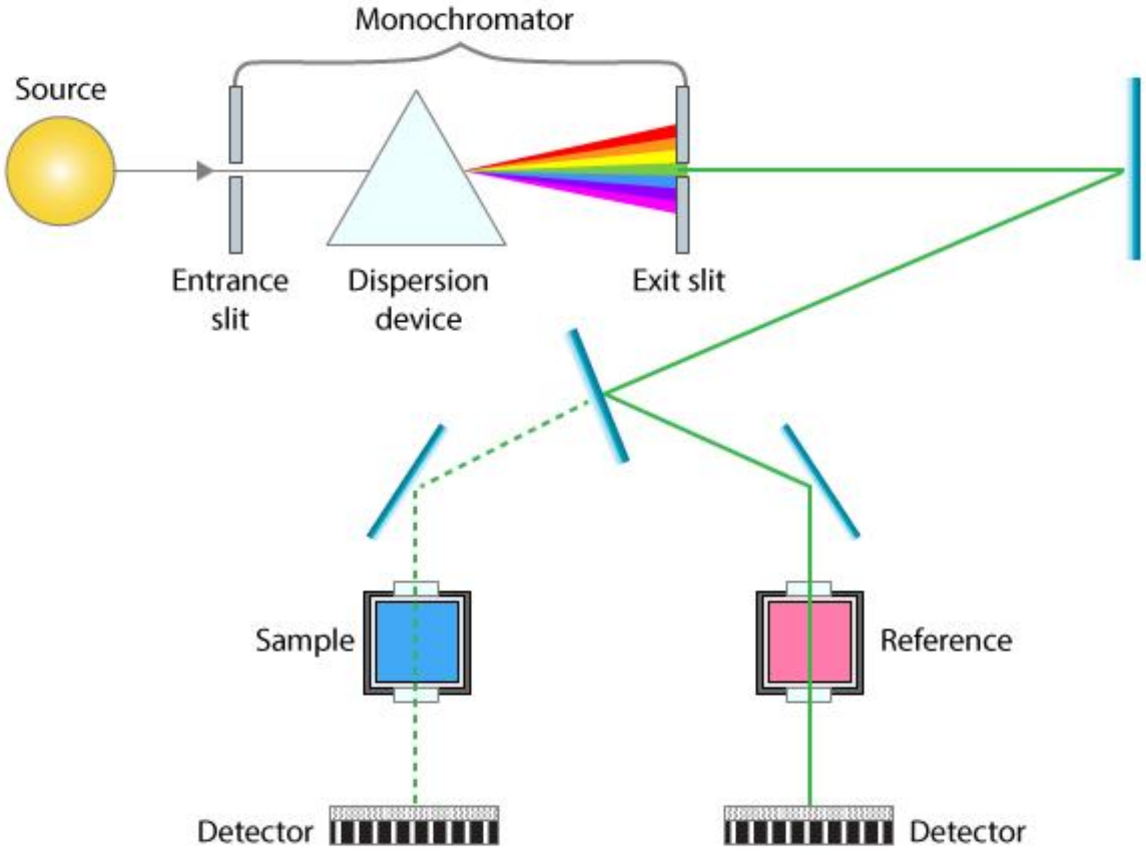
$$\varepsilon cl = A = 2 - \log[I_t]$$

From spectrophotometer

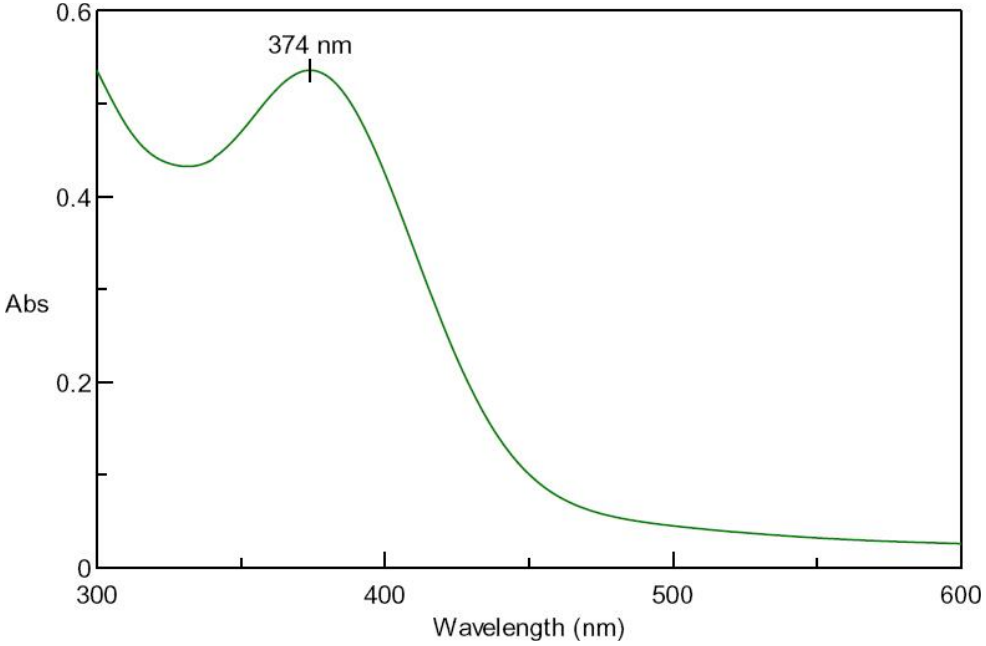


0.6
0.4
0.2
0
Abs
374 nm
300
400
500
600
Wavelength (nm)



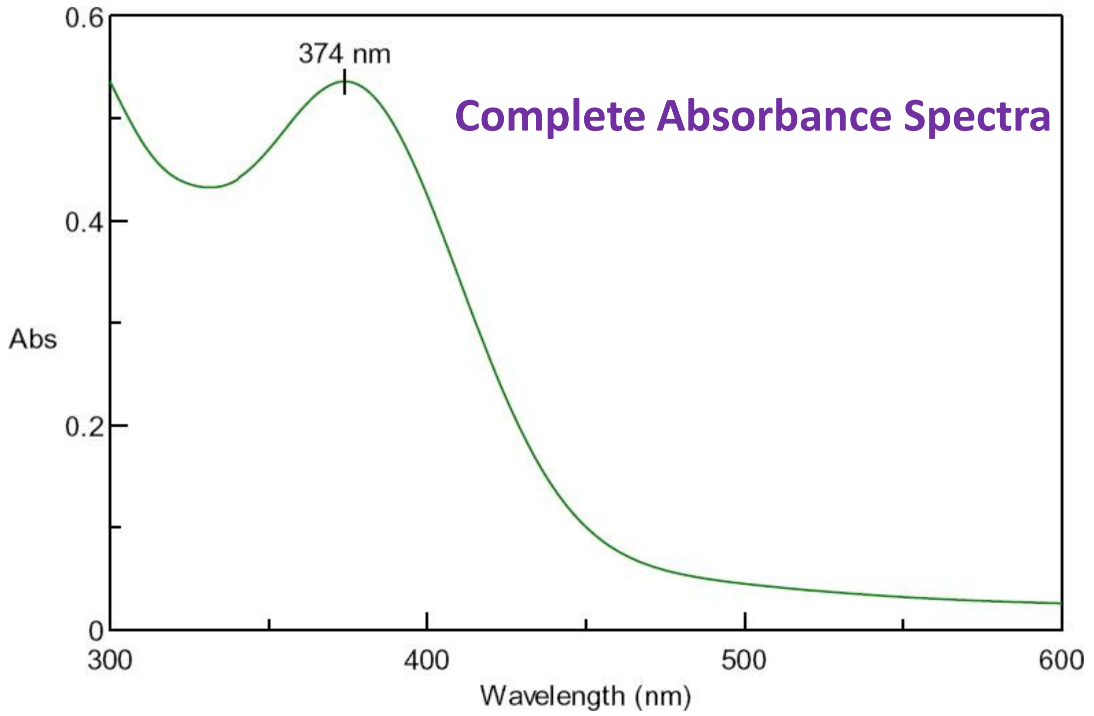


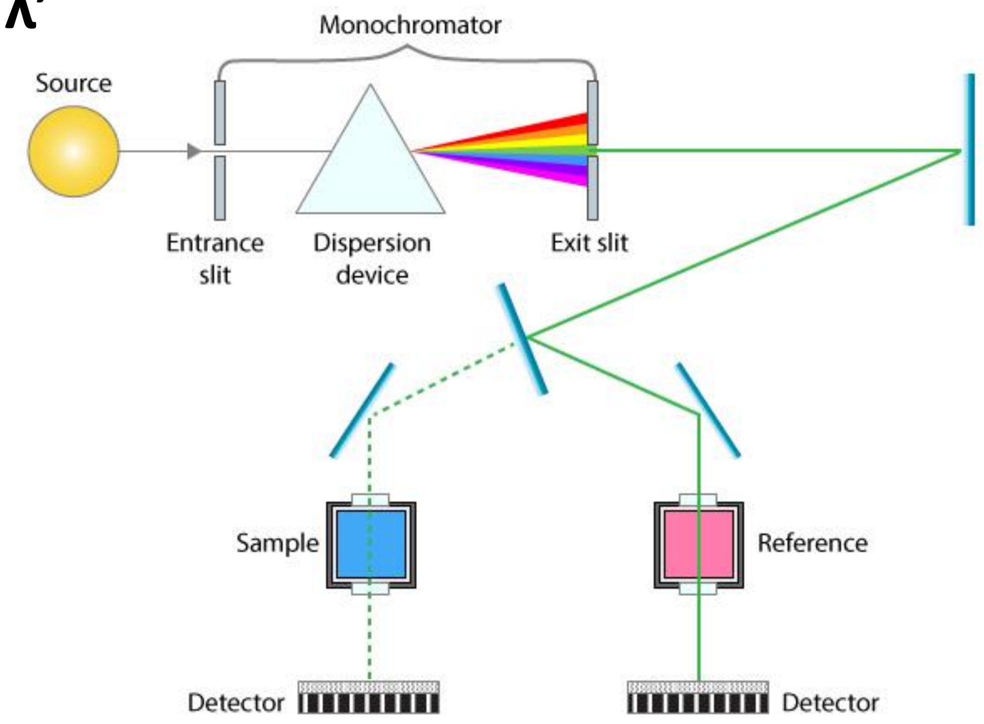
1. Sources (UV and visible)
2. Wavelength selector (monochromator)
3. Sample containers
4. Detector
5. Signal processor and readout



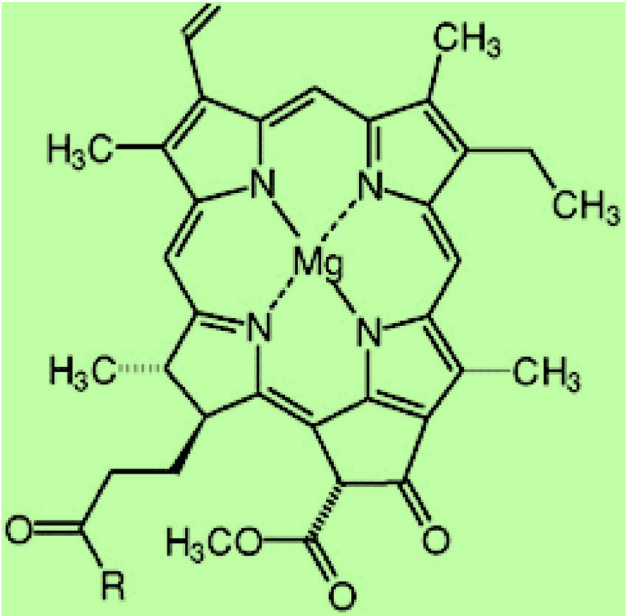
Lambert-Beers law: $\log(I_o/I_t)=\varepsilon cL=\text{Absorbance}$

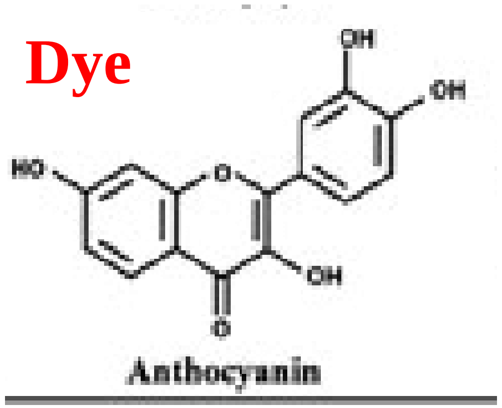
Absorbance at various ‘λ’

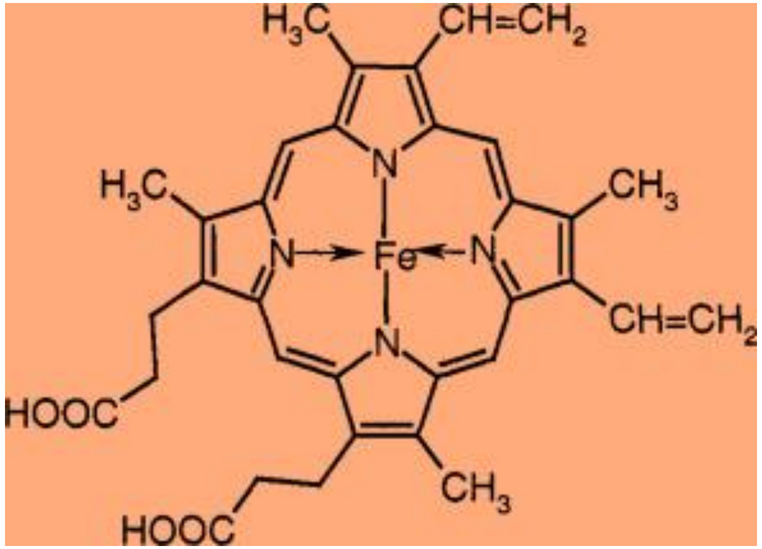




Chlorophyll or Hemoglobin



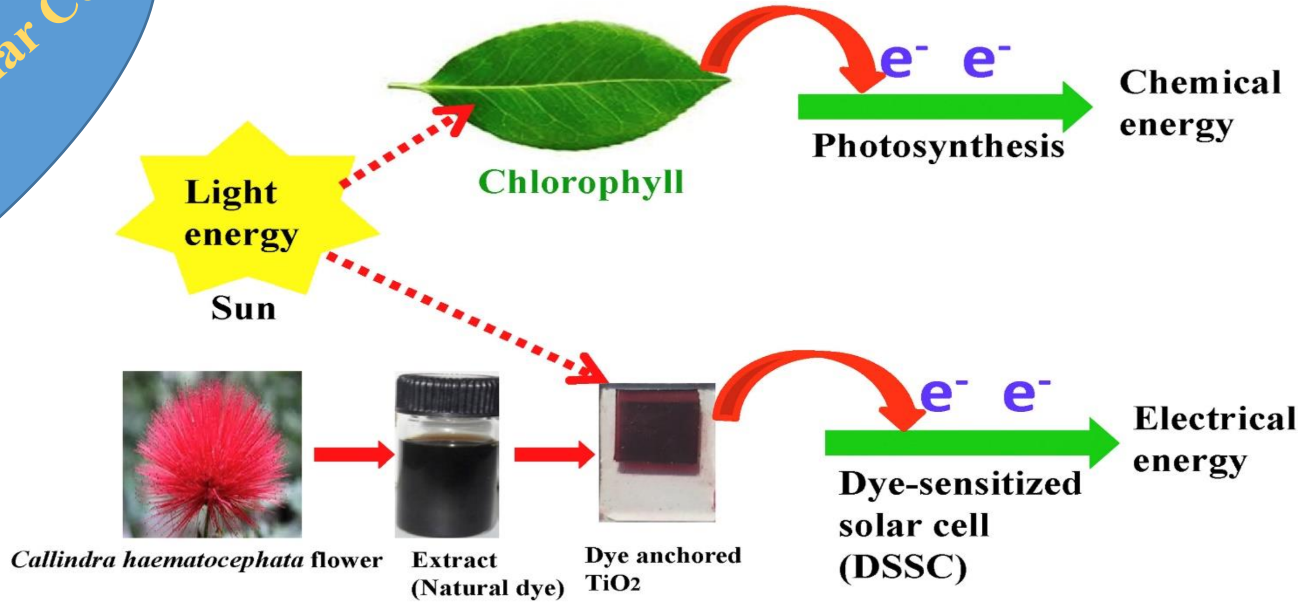


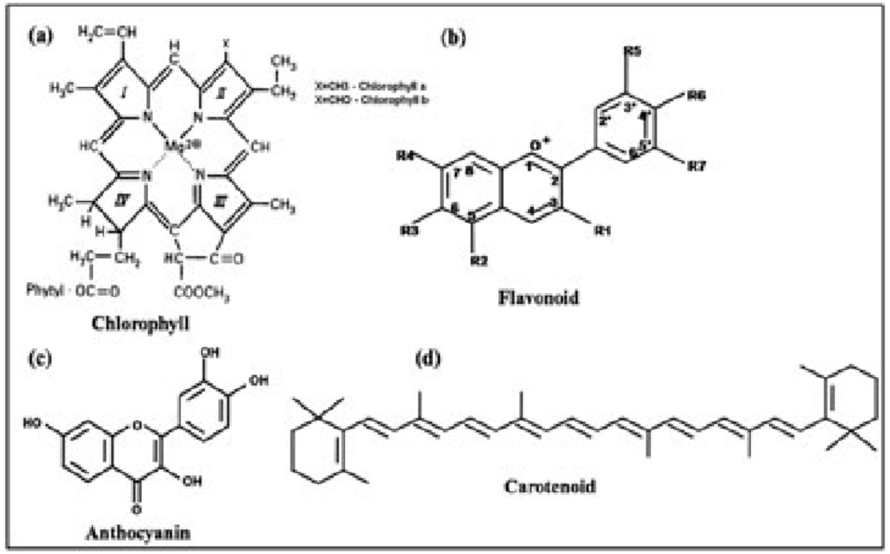


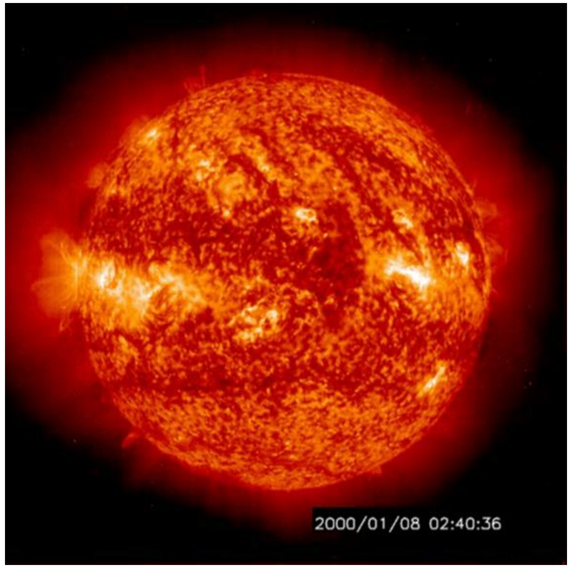
$$2\pi R=n\lambda$$

$$\Delta E=(2n+1)h^2/8\pi^2R^2$$

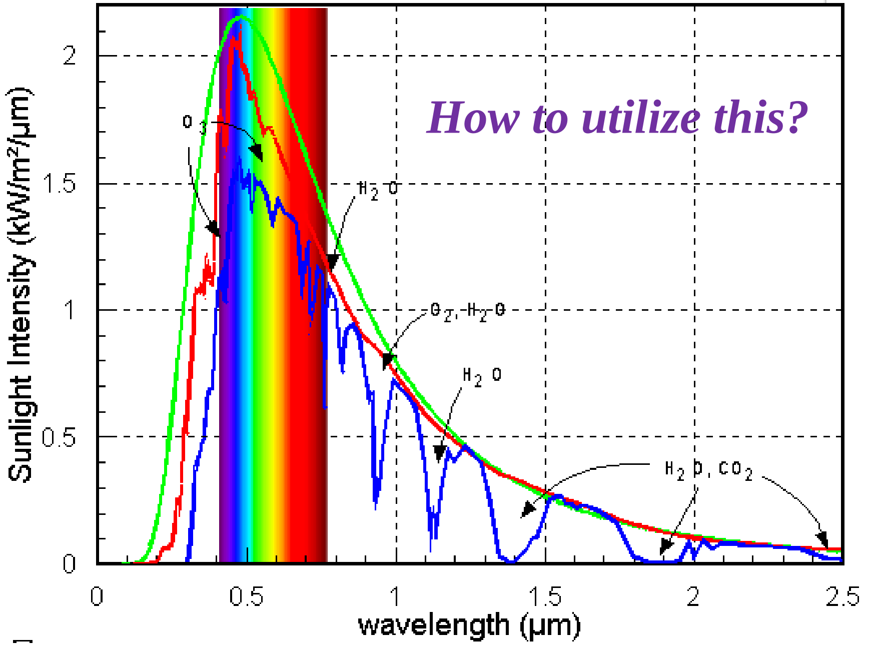
Dye Sensitized Solar Cells







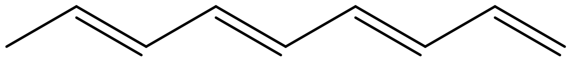
Black-body Radiation



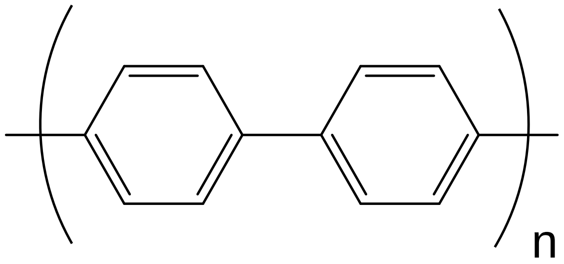
Violet	*~ 3.17 eV*
Blue	*~ 2.73 eV*
Green	*~ 2.52 eV*
Yellow	*~ 2.15 eV*
Orange	*~ 2.08 eV*
Red	*~ 1.62 eV*

If you control chain length, you may control HOMO-LUMO gap and use for flexible solar-cell!

π Conjugated polymers



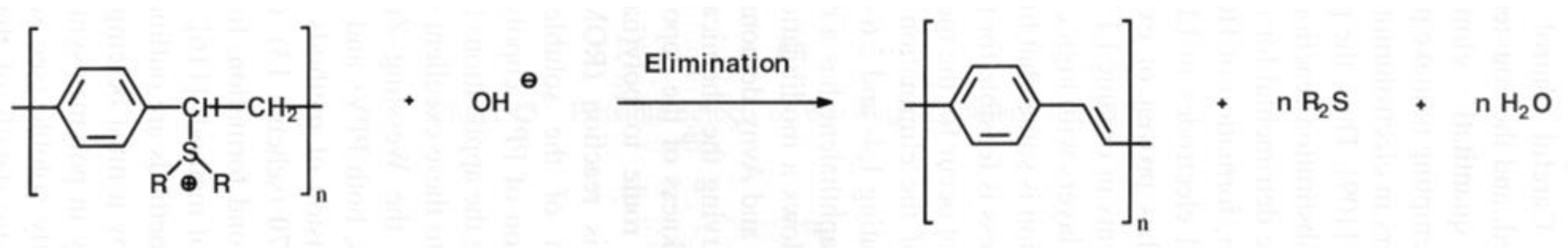
PA: polyacetylene
(1st conducting polymer)



PPP: poly(*para*-phenylene)
(large bandgap)

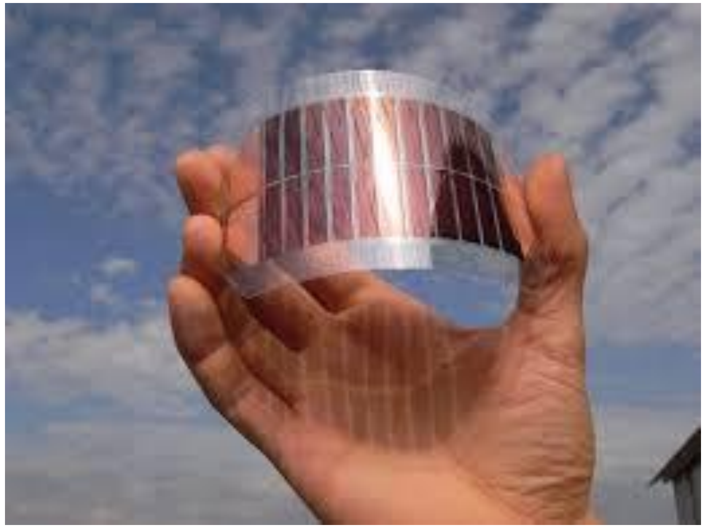
Synthesis by Elimination Route

PVC?

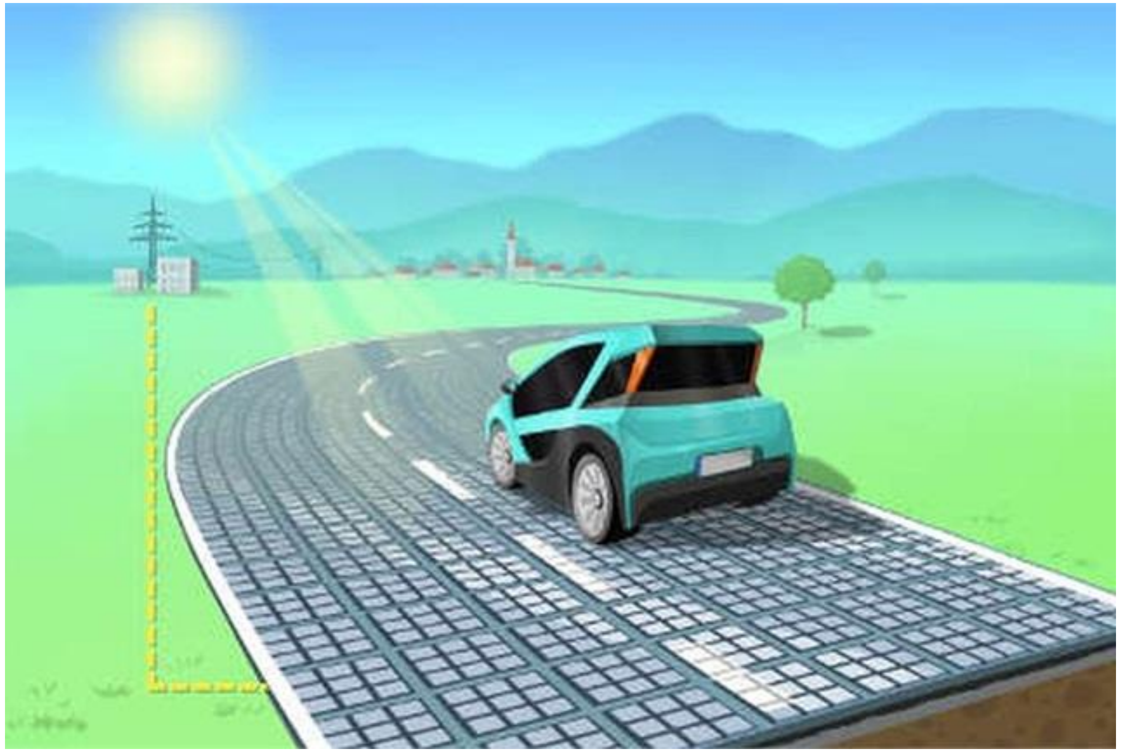






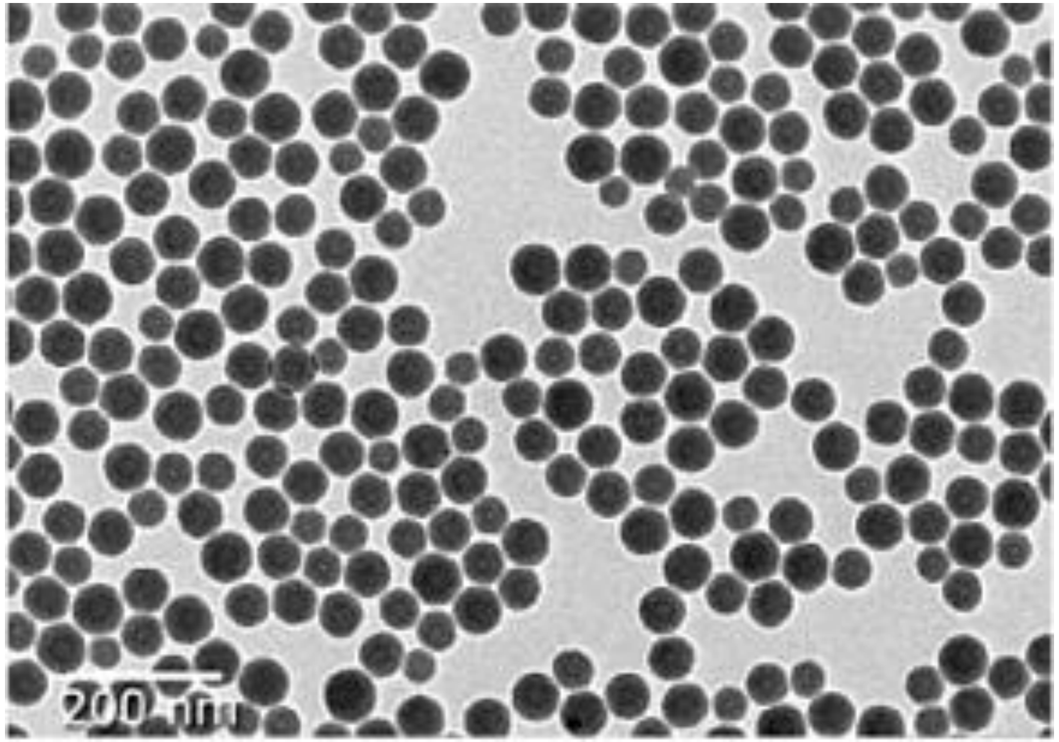
Solar Roadways

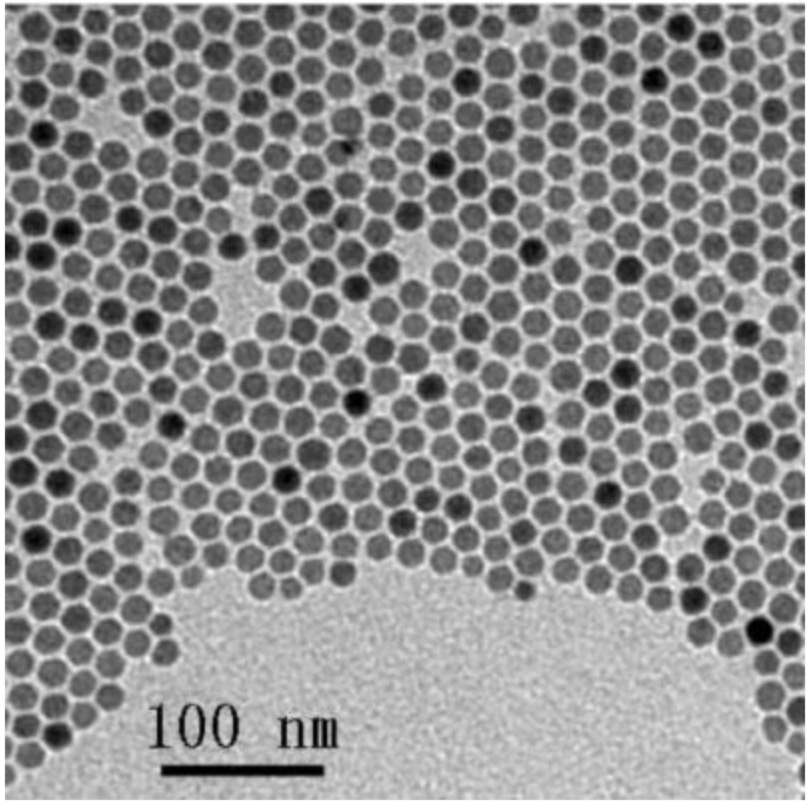


Solar mobile charger

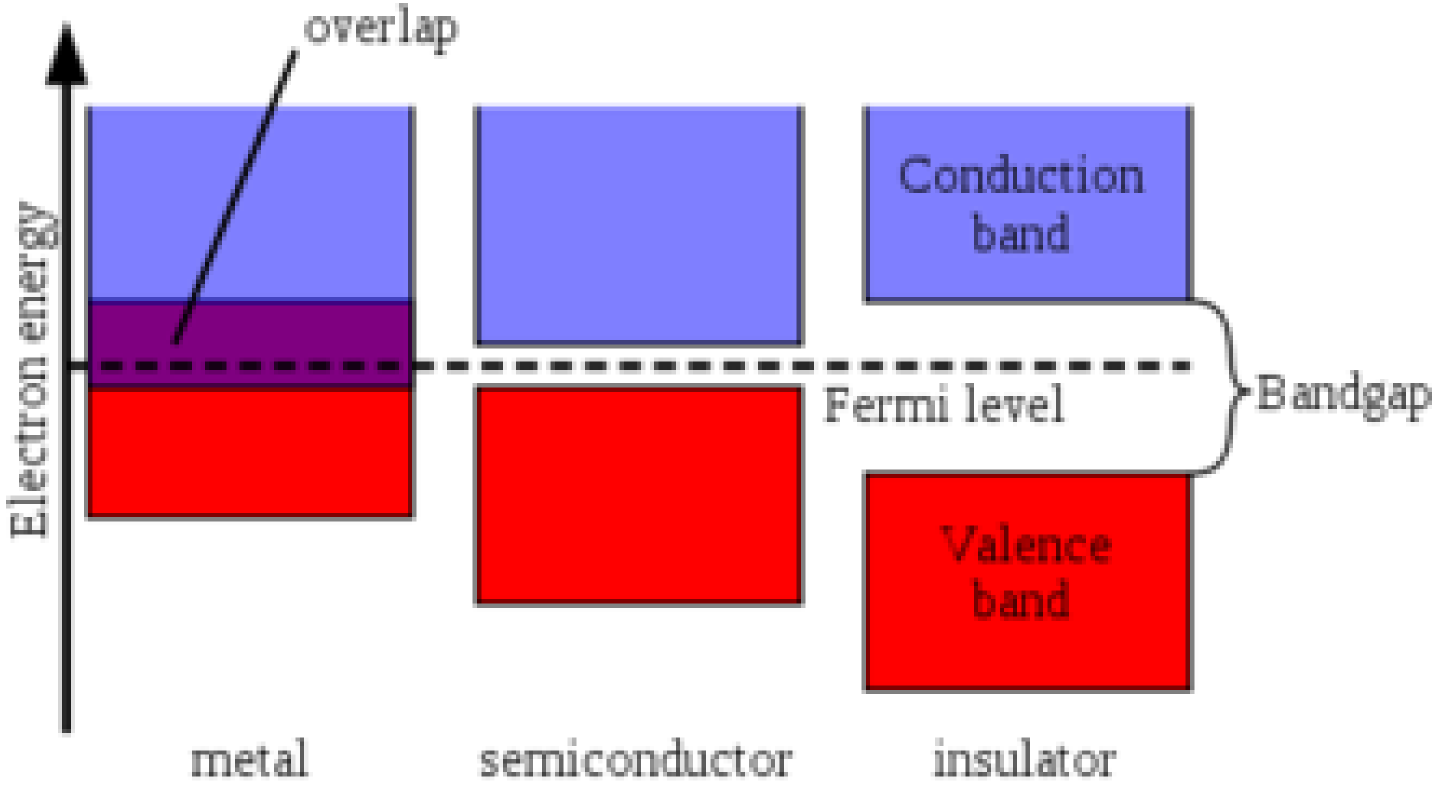
Solar umbrella

Particle in 1D Box
Semiconductor Nanocrystals- Quantum confinement!


200 nm


100 nm

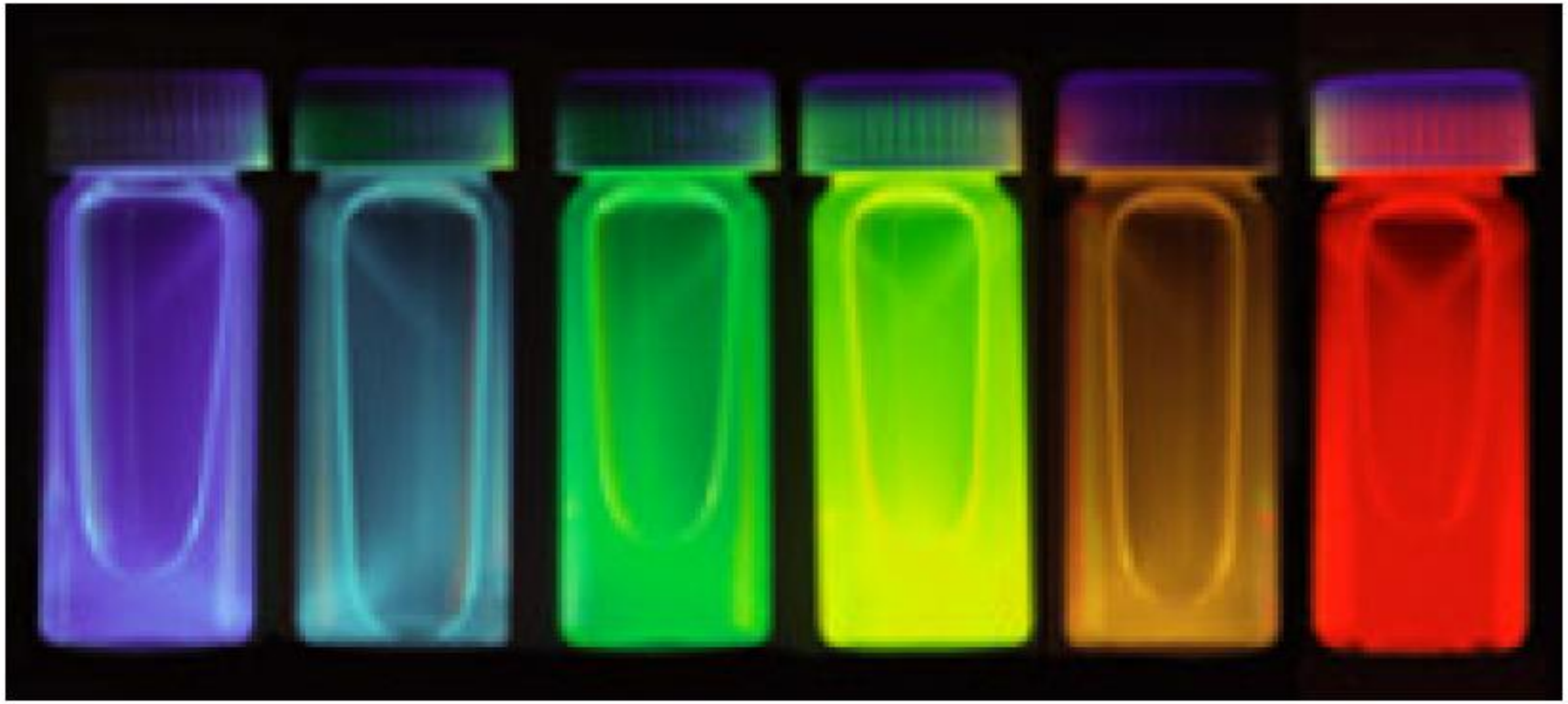
What are semiconductors?



Particle in 1D Box-allows us to understand the trend in bandgap in nanoparticles

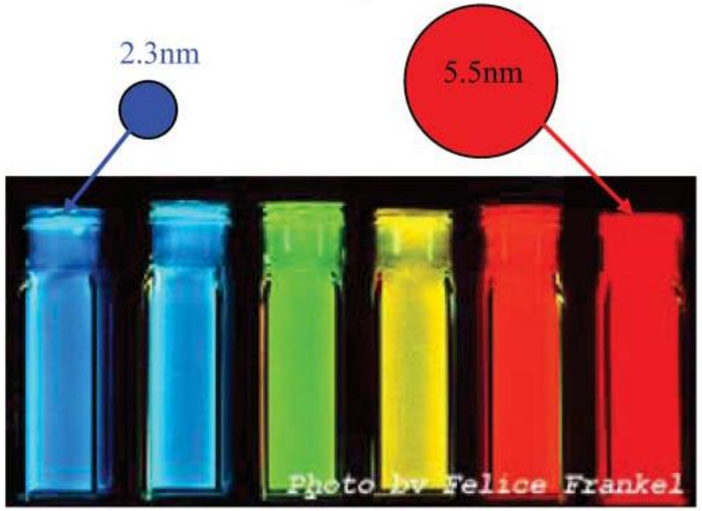
$$\Delta E \propto \frac{1}{L^2}$$

Quantum confinement



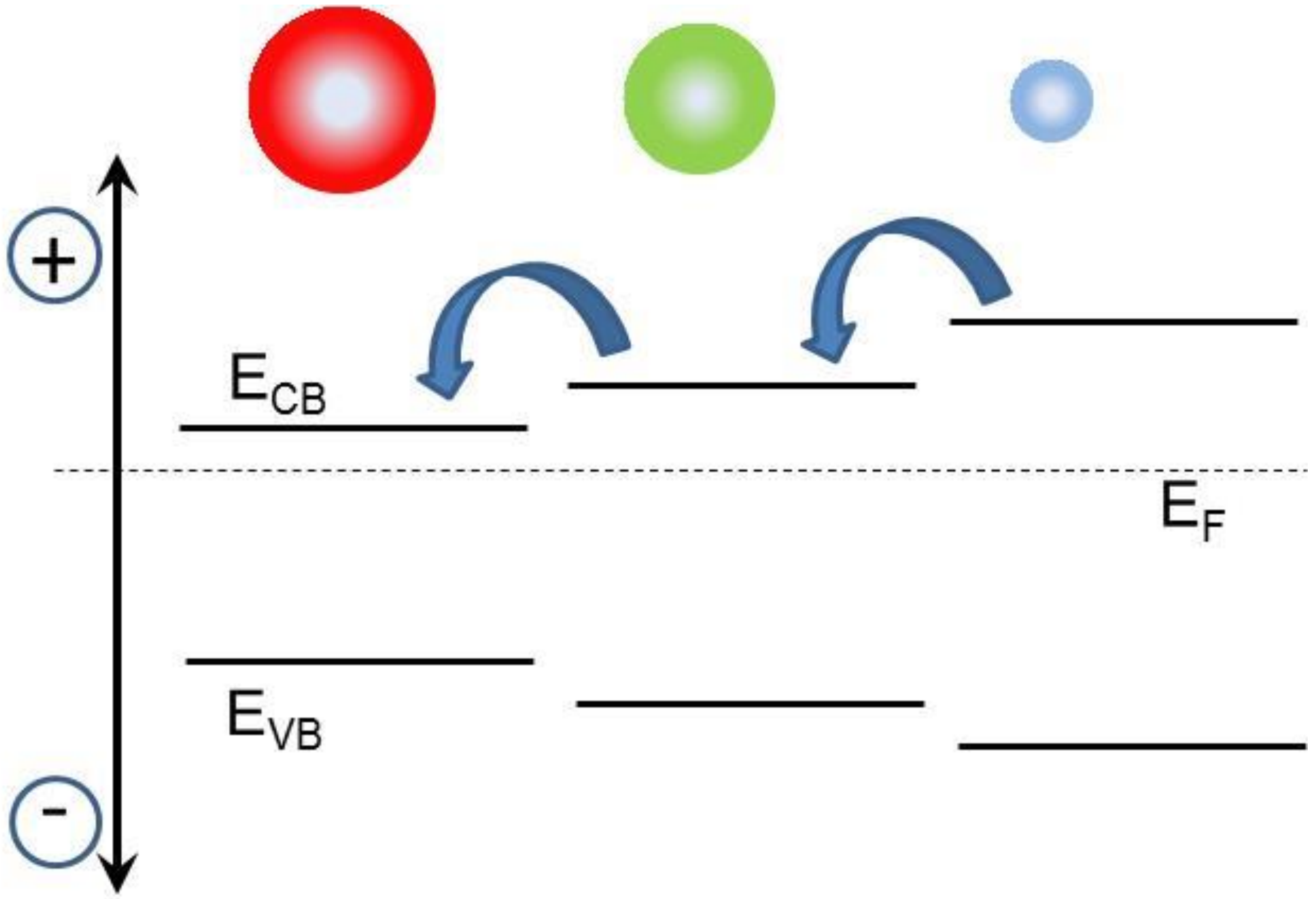
Colloidal CdSe quantum dots dispersed in hexane

CdSe Nanoparticles



Particle in 1D Box?

Size effect in semiconductors



$E=h^2/8ml^2$ **For one electron system**

$E_A=h^2/8l^2[1/m_e+1/m_h]$ **For electron and hole**

Quantum confinement is a result of size of nanocrystals (NCs), smaller than that of Bohr's exciton radius of the bulk semiconductor.

$$E_{dot}=E_{bulk} + E_{ex}$$

$E_{ex}=E_A+E_{Coul}$ $E_{coul}= -1.8e^2/4\pi\epsilon_0 R$ **(small quantity)**

$$E_{dot}=E_{bulk} + h^2/8l^2[1/m_e+1/m_h]+E_{coul}$$

Brus Equation

$$E_{QD} = E_{bulk} + h^2/8\mu R^2 - 1.8e^2/(\epsilon R)$$

Quantum confinement

Coulombic attraction- Screening of charges-can be neglected as inorganics have high ‘Є’

R= Bohrs Radius