Exciton Diffusion

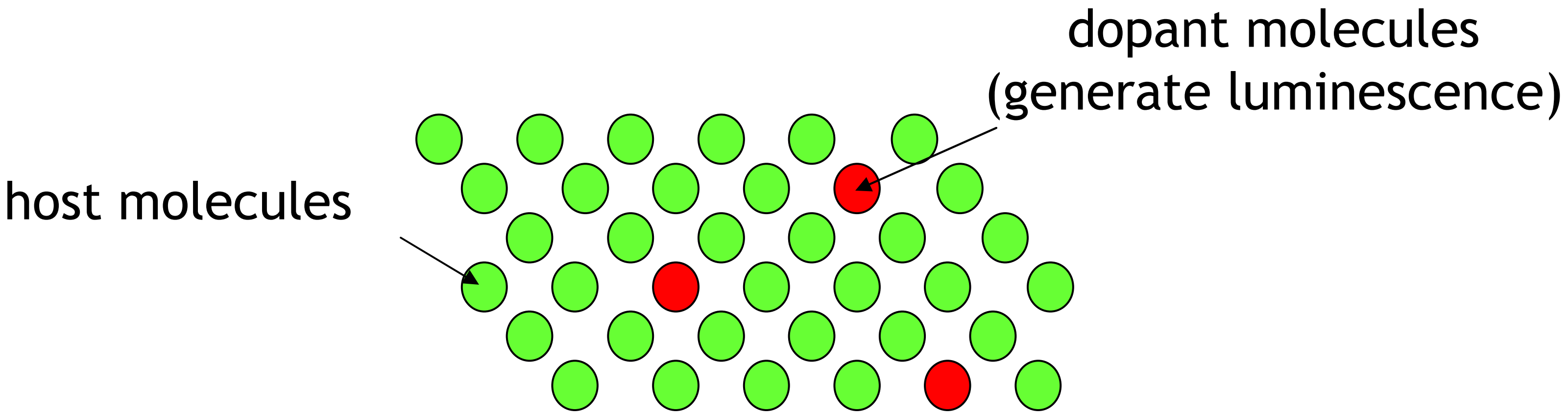
- Exciton Energy transfer
- Exciton Diffusion
  - . Photoluminescence measurement
  - . Photocurrent measurement

Handout on Photocurrent Response:
Bulovic and Forrest., Chemical Physics 210, 13 (1996).

Handout on Solar Cells and Photodetectors:
Peumans, Bulovic, and Forrest., Appl. Phys. Lett. 76, 2650 (2000) & 76, 3855 (2000).

looe
@ MIT

Energy Transfer



How does an exciton in the host transfer to the dopant?

Energy transfer processes:

1. Radiative transfer
2. Förster transfer
3. Dexter transfer

Radiative energy transfer

Transfer of excitation energy by radiative deactivation of a donor molecular entity and reabsorption of the emitted light by an acceptor molecular entity. The probability of transfer is given approximately by:

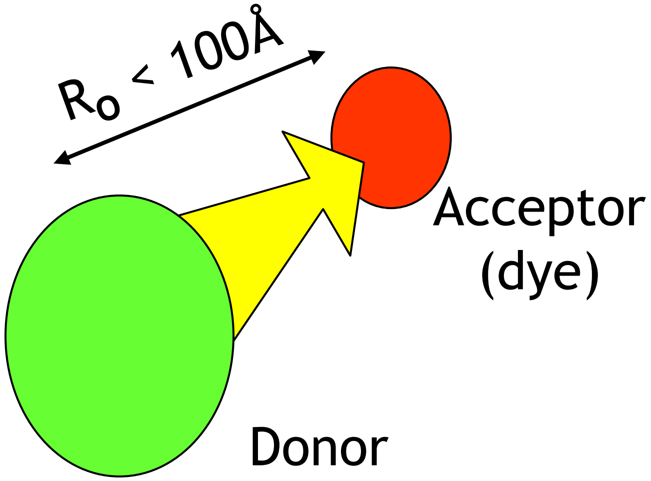
$$\mathrm{P}_{\mathrm{r},\,t} \propto [A]xJ$$

Where J is the spectral overlap integral, $[A]$ is the concentration of the acceptor, and x is the specimen thickness. This type of energy transfer depends on the shape and size of the vessel utilized. Same as trivial energy transfer.

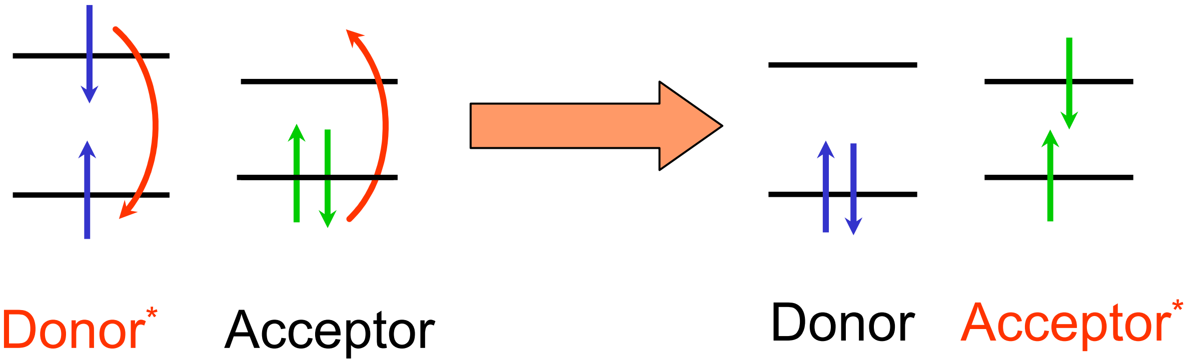
Quoted from IUPAC Compendium of Chemical Terminology compiled by Alan D. McNaught and Andrew Wilkinson (Royal Society of Chemistry, Cambridge, UK).

Förster transfer

- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed

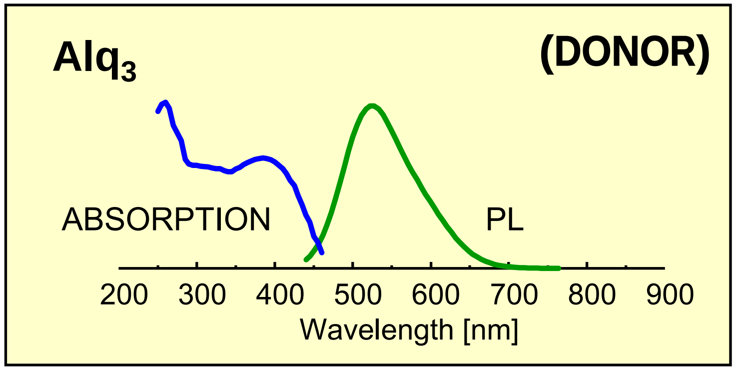


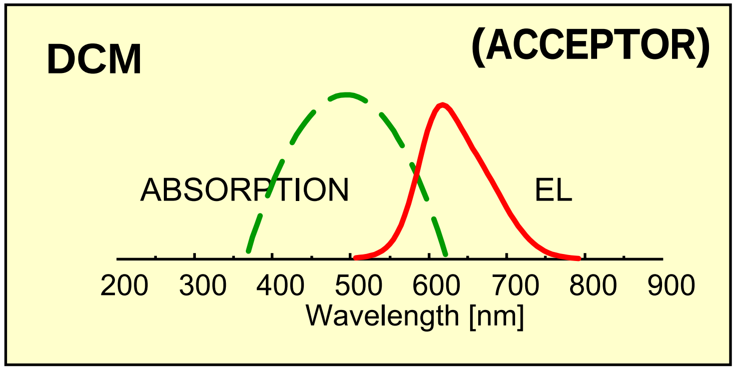
very fast $<10^{-9}$s



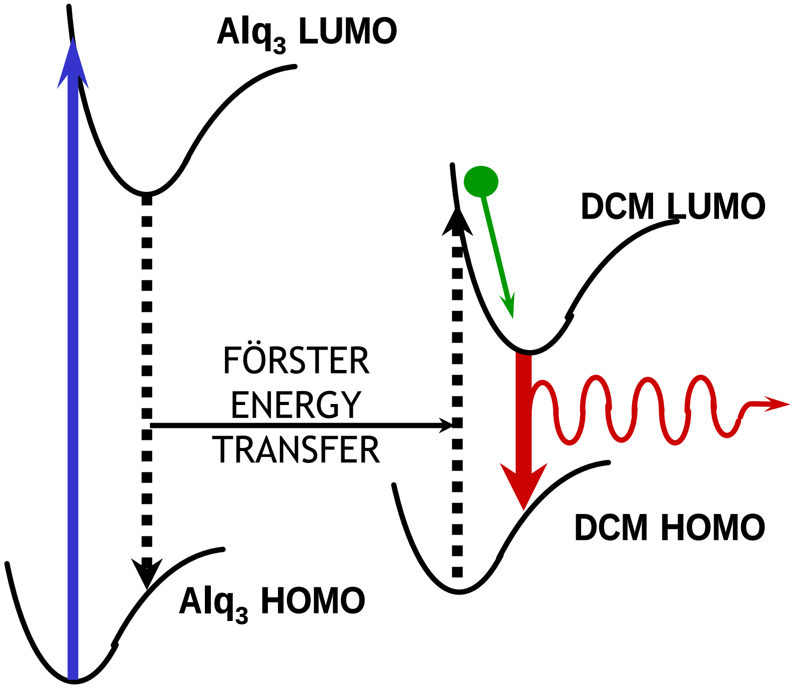
typically singlet- singlet transitions

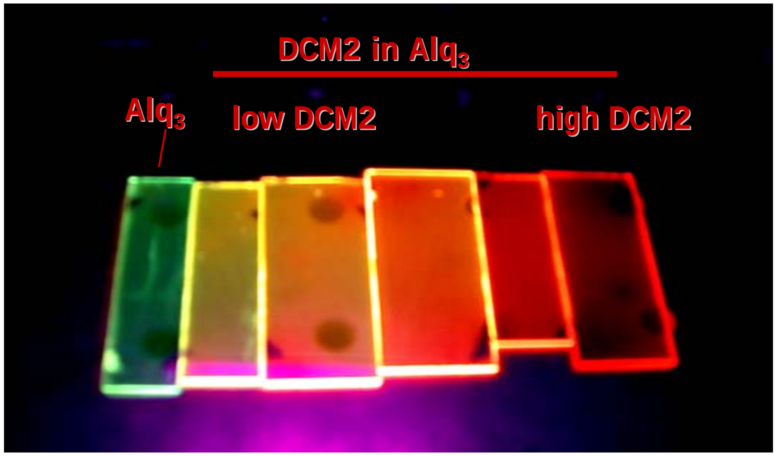
Förster transfer - Example





for efficient transfer donor emission and acceptor absorption must overlap





Förster excitation transfer (dipole-dipole) excitation transfer)

A mechanism of excitation transfer which can occur between molecular entities separated by distances considerably exceeding the sum of their van der Waals radii. It is described in terms of an interaction between the transition dipole moments (a dipolar mechanism). The transfer rate constant $k_D \rightarrow \mathrm{A}$ is given by:

$$k_{\mathrm{D}} \rightarrow \mathrm{A} = \frac{K^2 J 8.8 \times 10^{-28} \mathrm{mol}}{n^4 \varpi r^6}$$

Where *K* is an orientation factor, *n* the refractive index of the medium, ω the radiative lifetime of the donor, *r* the distance (cm) between donor (D) and acceptor (A), and *J* the spectral overlap (in coherent units $\mathrm{cm}^6\ \mathrm{mol}^{-1}$) between the absorption spectrum of the acceptor and the florescence spectrum of the donor. The critical quenching radium r_0, is that distance at which $k_D \rightarrow \mathrm{A}$ is equal to the inverse of the radiative lifetime.

Quoted from IUPAC Compendium of Chemical Terminology compiled by Alan D. McNaught and Andrew Wilkinson (Royal Society of Chemistry, Cambridge, UK).

Förster transfer – Rate Equations

$$K_{ET} = (2\pi/\hbar)\ |\langle D,A^*|H_{DA}|D^*,A\rangle|^2 \boxed{\int g_D(E)\ g_A(E)\ dE}$$

Energy transfer rate (K_{ET}) depends on the overlap integral

FOR DIPOLE-DIPOLE INTERACTION:

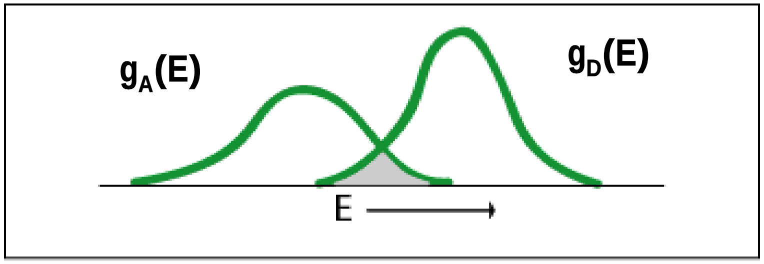
$$K_{ET}(R) = \left(\frac{1}{\tau}\right)\left(\frac{R_0}{R}\right)^6$$

ALLOWED TRANSITIONS:

$$^1D^* + {}^1A \rightarrow {}^1D + {}^1A^*$$

$$^1D^* + {}^3A(T_n) \rightarrow {}^1D + {}^3A^*(T_m)$$

$g_A(E)$



(Adapted from Blasse & Grabmaier)

Dexter transfer

diffusion of excitons from donor to acceptor

'Wigner-Witmer spin conservation rules'

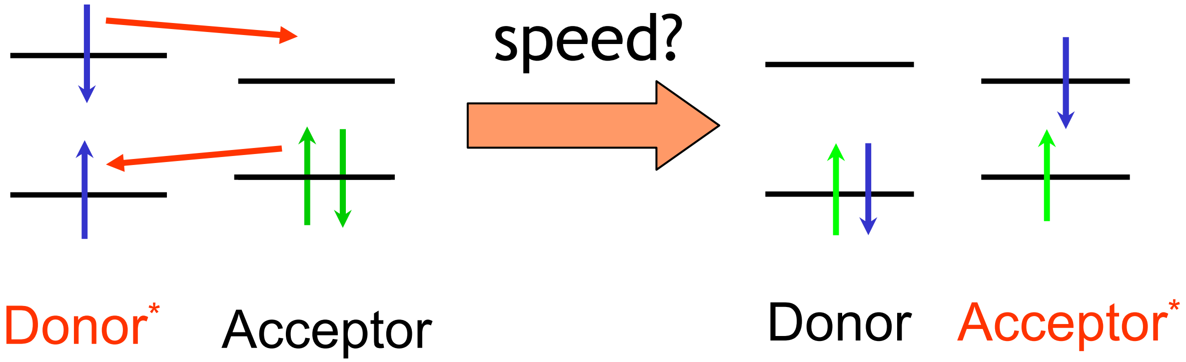
$$A + B \rightarrow C + D$$

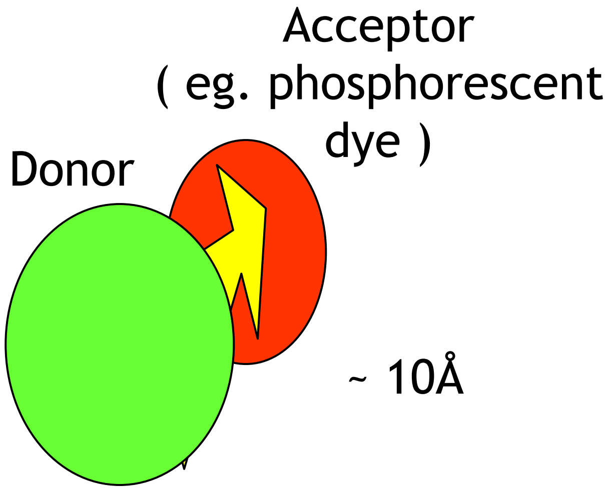
total spin of reactants: $(S_A+S_B),(S_A+S_B-1),\ldots,\left|S_A-S_B\right|$

total spin of products: $(S_C+S_D),(S_C+S_D-1),\ldots,\left|S_C-S_D\right|$

reaction allowed if two sequences have a number in common

only singlet-singlet, triplet-triplet allowed





Dexter excitation transfer (electron exchange excitation transfer)
Excitation transfer occurring as a result of an electron exchange mechanism. It requires an overlap of the wave functions of the energy donor and the energy acceptor. It is the dominant mechanism in triplet-triplet energy transfer. The transfer rate constant, k_{ET}, is given by:

$$k_{\mathrm{ET}} \propto [h/(2\pi)] P^2 J \exp[-2r/L]$$

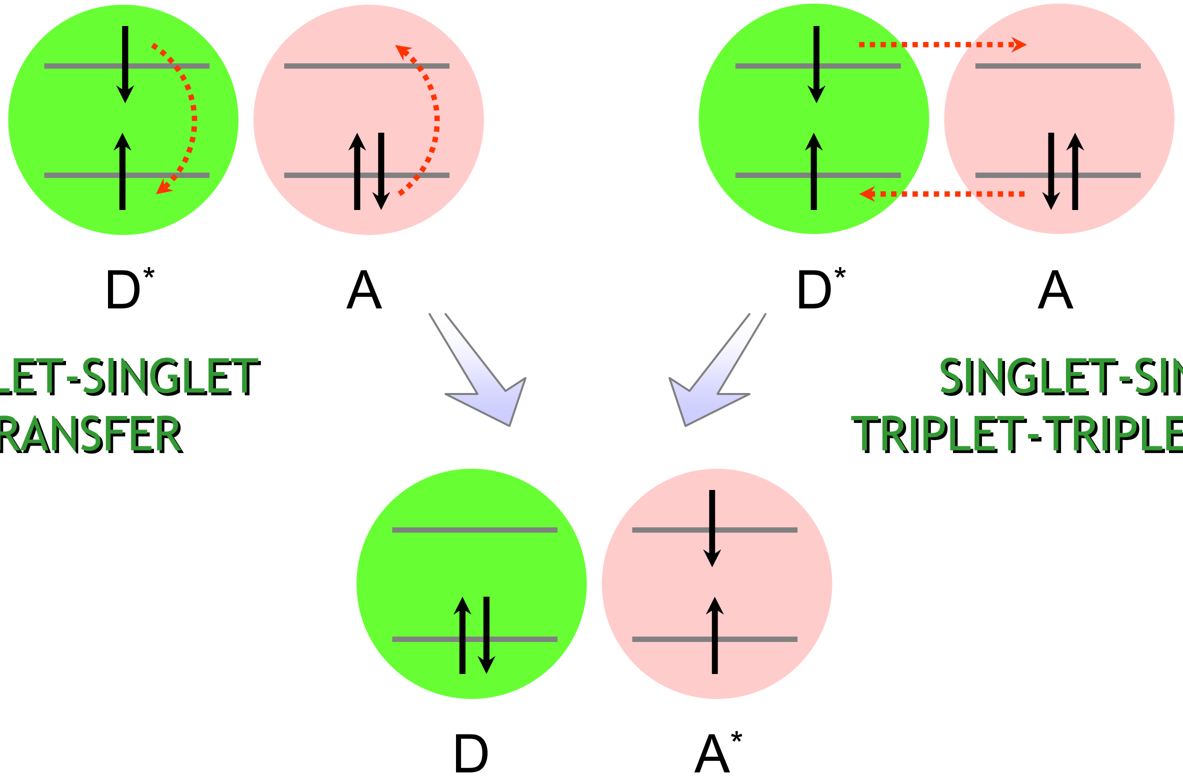
where r is the distance between donor (D) and acceptor (A), L and P are constants not easily related to experimentally determinable quantities, and J is the spectral overlap integral. For this mechanism the spin conservation rules are obeyed.

Quoted from IUPAC Compendium of Chemical Terminology compiled by Alan D. McNaught and Andrew Wilkinson (Royal Society of Chemistry, Cambridge, UK).

Nonradiative Energy Transfer

Förster, Coulombic
(long range ~30-100 Å)

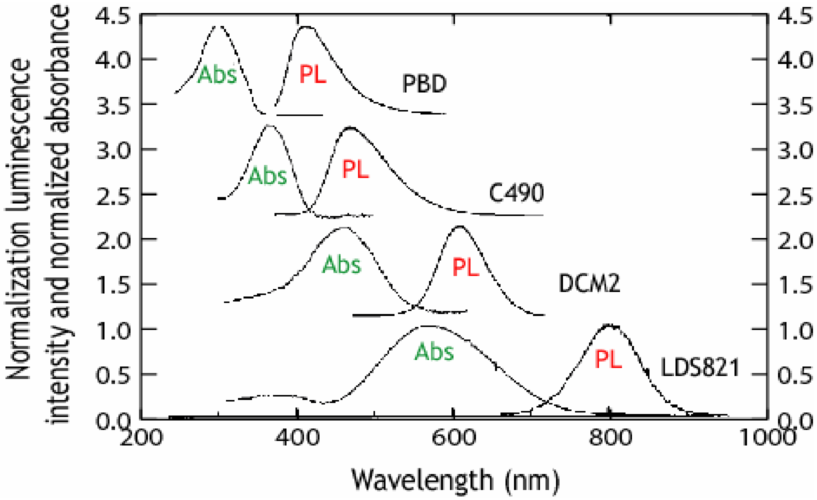
Dexter, e^- exchange
(short range ~6-20 Å)



SINGLET-SINGLET
TRANSFER

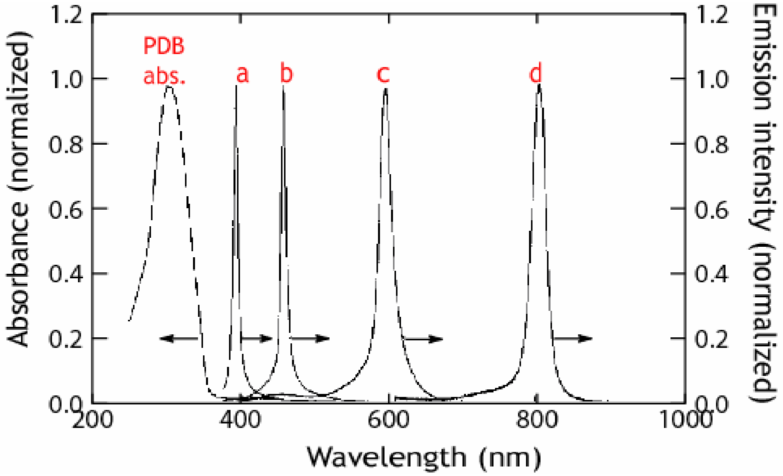
SINGLET-SINGLET &
TRIPLET-TRIPLET TRANSFER

Cascade Energy Transfer Laser



Absorbance and photoluminescence spectra of the host material and fluorescent dyes. The host material is 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole(PBD); the dyes are coumarin 490(C490), DCMII and LDS821. The spectra for PBD are from a pure film whereas the other spectra are from solid solutions of the material in polystyrene.

Threshold Energy ~ 0.1 μJ/cm^2

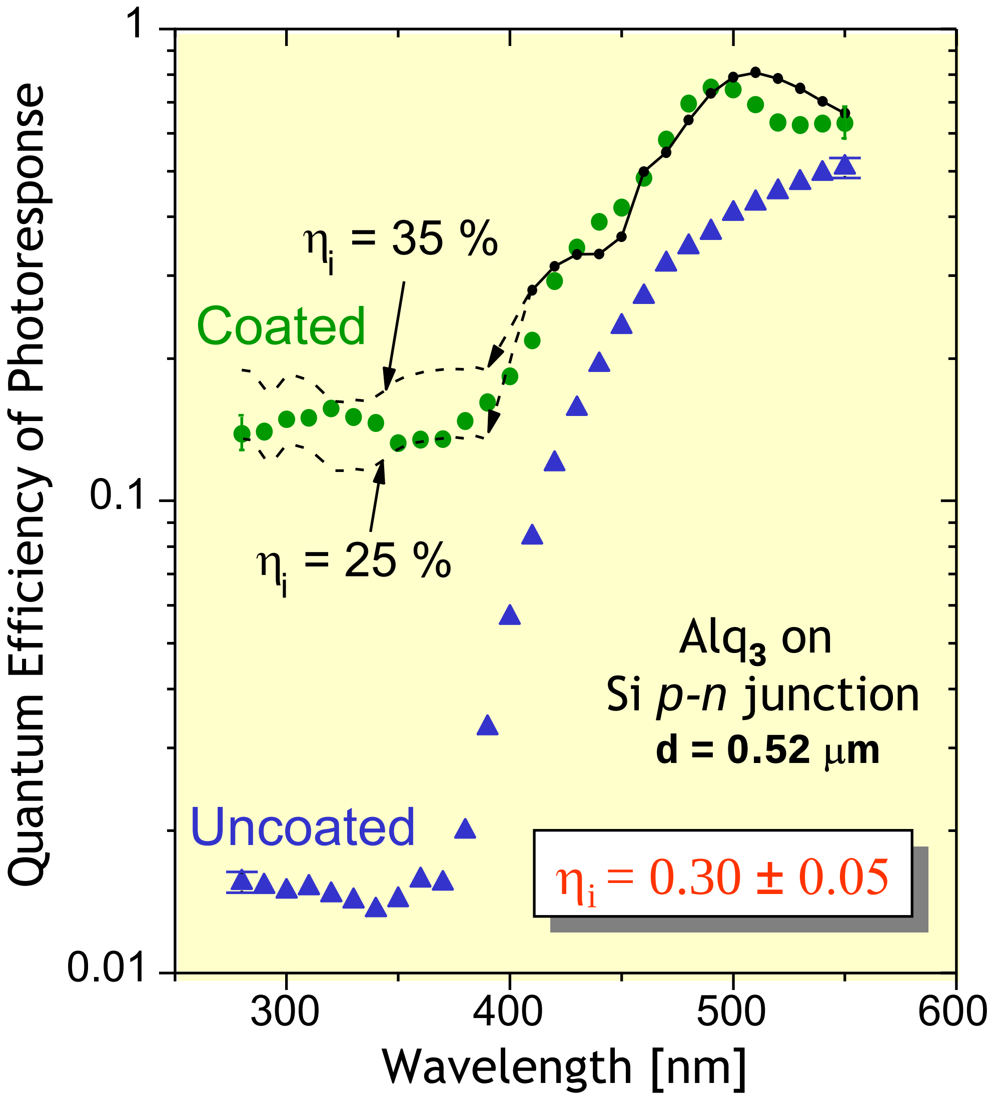


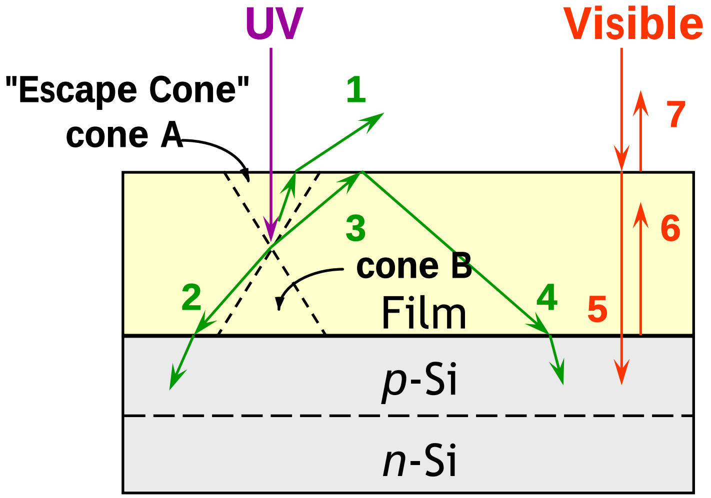
Normalized absorbance of PBD, and stimulated emission spectra from this material alone, and when doped with dyes. Curve:

- (a) PBD only;
- (b) 0.6% C490 in PBD;
- (c) 0.6% C490 + 0.9% DCMII in PBD
- (d) 0.6% C490 + 0.9% DCMII + 0.6% + LDS821 in PBD.

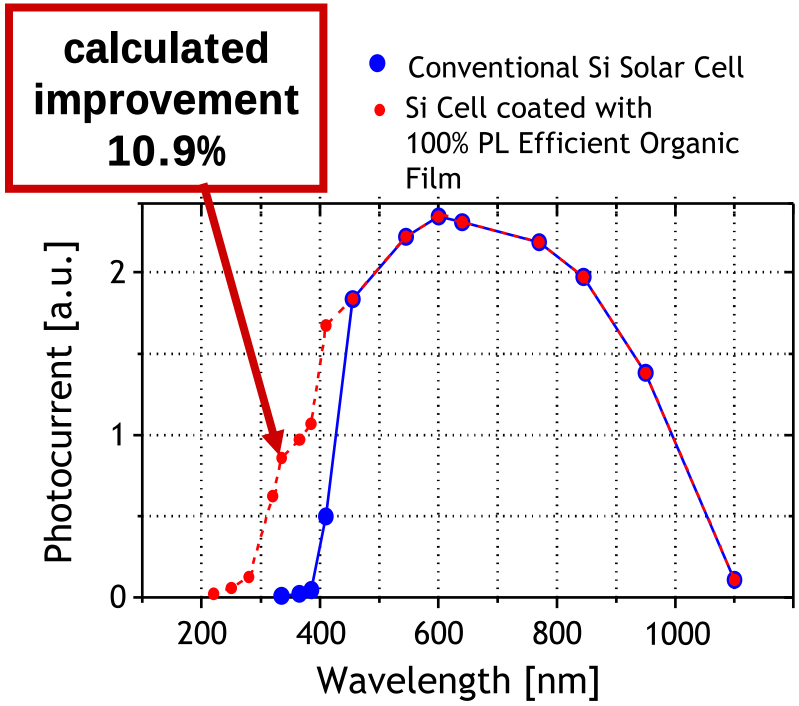
Adapted from Figure 1 and 2 from Berggren, et al., Nature *389*, *466 (1997).*

Luminescent Organic Film on a Si *p-n* Junction



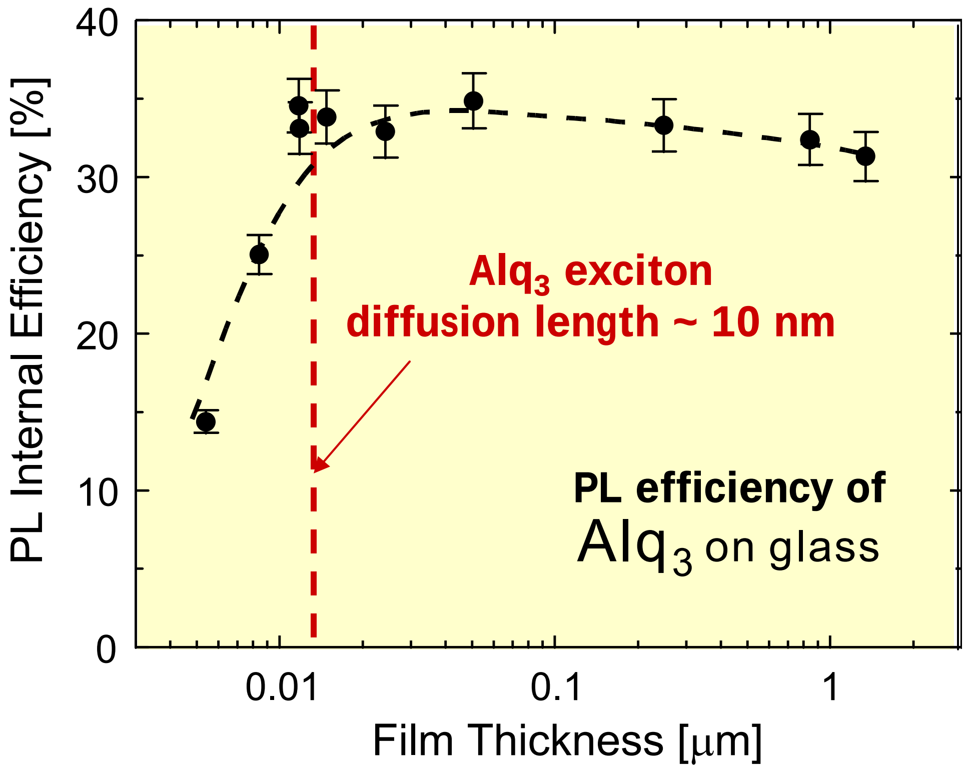


- AR coating in Visible
- Downconverter in UV


calculated improvement 10.9%

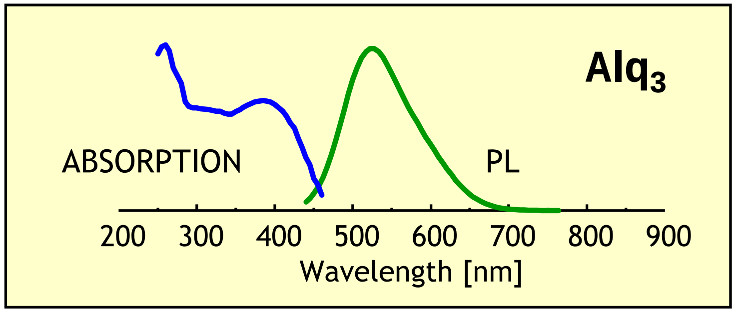
Adapted From: Garboze et al, Journal of Applied Physics, vol 80, pg 4644, 1996

Diffusion of Excitons



If energy transfer occurs between the donor and acceptor molecules of the same species, the term *energy migration* is used.

The four general methods used to measure diffusion of excitons are:
bulk quenching,
surface quenching,
bimolecular recombination,
and photoconduction



Small overlap between Alq_3 absorption and luminescence results in a small Förster radius of ~12 Å

Since the size of Alq_3 molecules is ~10 Å Förster energy transfer can facilitate exciton diffusion

Adapted From: Garboze et al, Journal of Applied Physics, vol 80, pg 4644, 1996

Photosynthetic Machinery

… of Purple Bacteria

exciton transport
followed by
exciton dissociation

(RESULTING IN STABLE
TRANSMEMBRANE
CHARGE SEPARATION)

energy transfer
often occurs in biological
systems

V. Sundström, *et al.*, *J. Phys. Chem. B* 103, 2327 (1999).

Light-induced electron transport
ATP synthesis in a photosynthetic
bacterium

http://www.nobel.se/chemistry/educational/poster/1988/

Schematic picture of a photosynthetic reaction center from the bacterium *Rhodopseudomonas virdis*. The polypeptide chains are drawn as ribbons of different colors for the four different protein subunits.

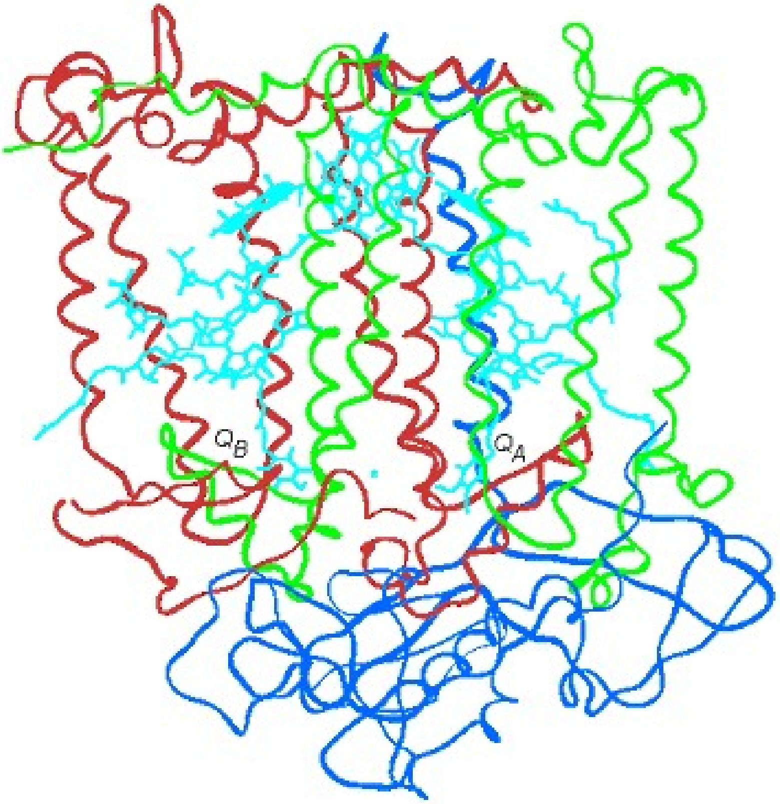


Image from http://www.bio.anl.gov/

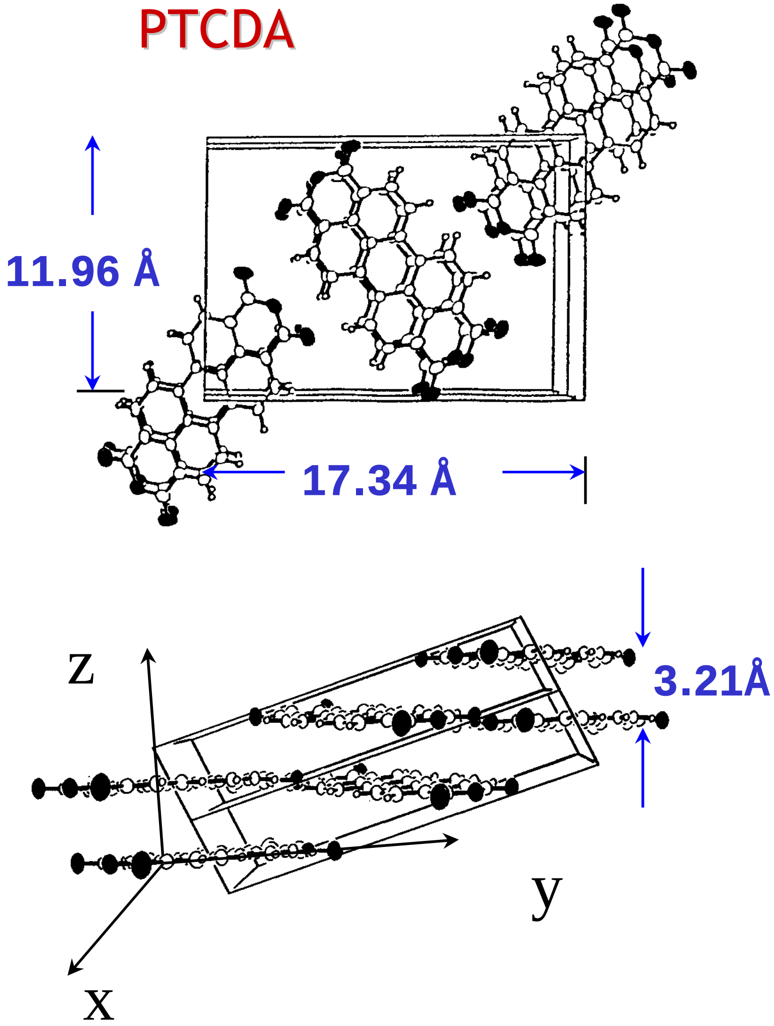
The reaction center is composed of four protein subunits. Two of these, the L and M subunits, each form five membrane-spanninghelices. The structure shows the precise arrangement in the L and M subunits of the photochemically active groups – two chlorophyll molecules forming a dimer, two monomeric chlorophylls, two pheophytin molecules (these lack the central magnesium ion of chlorophyll), one quinone molecule, called QA (a second quinone molecule, QB, is lost during the preparation of the reaction center) and one iron ion (Fe). The L and M subunits and their chromophores are related by a twofold symmetry axis that passes through the chlorophyll dimer and the iron. A third subunit, H, without active groups and located on the membrane inner surface, is anchored to the membrane by a protein helix. The remaining subunit, a cytochrome with four heme groups (related to the blood pigment hemoglobin), binds at the outer surface of the membrane.

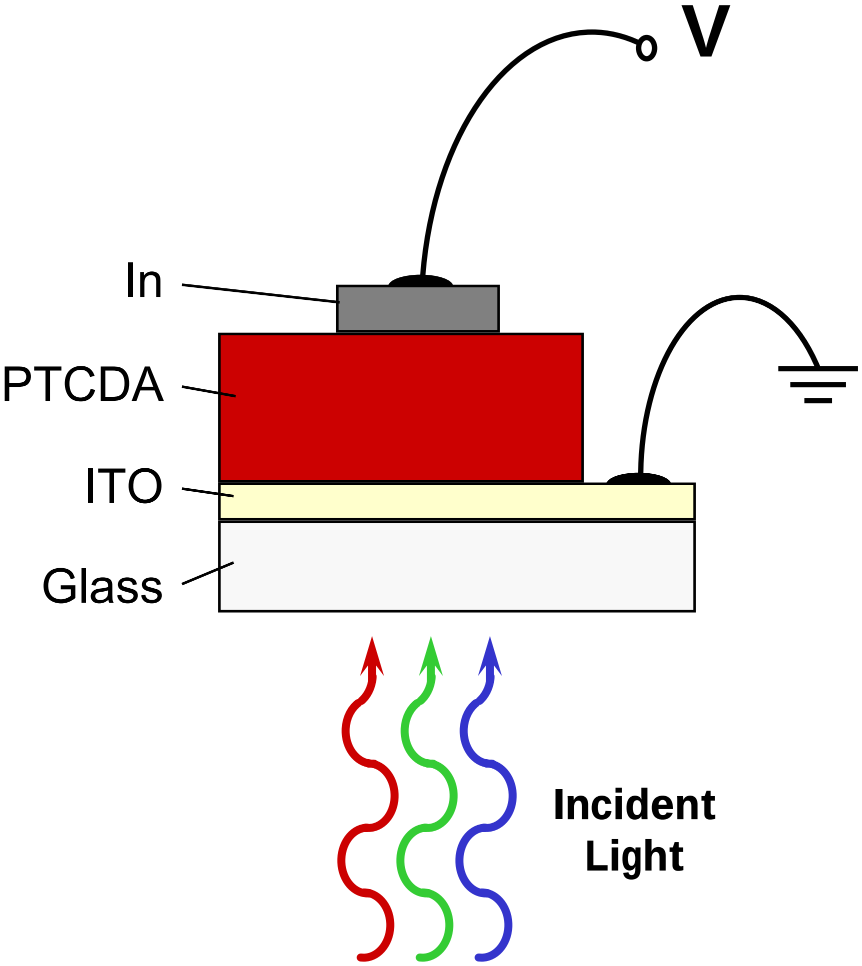
Photosynthesis and respiration are based on the transfer of electrons between donor and acceptor molecules bound to biological membranes – sheet-like structures composed of lipids and proteins which surround the cells and their inner compartments. The photosynthetic reactions in plants take place in the inner membranes of the chloroplasts, the organelles which contain the chlorophyll. Some bacteria have a simpler form of photosynthesis, to some extent similar to that in plants but without the ability to form oxygen.

In all types of photosynthesis, the light energy absorbed by chlorophyll is transferred to membrane-bound protein-pigment complexes, known as reaction centers. In these complexes the light energy initiates electron-transfer reactions which are coupled to the translocation of hydrogen ions across the membrane. The resulting pH gradient is utilized by another membrane-bound protein, ATPase, to synthesize ATP, a compound used as a fuel in energy-demanding biological processes. In cell respiration, too, electron transport is coupled to proton translocation and ATP synthesis.

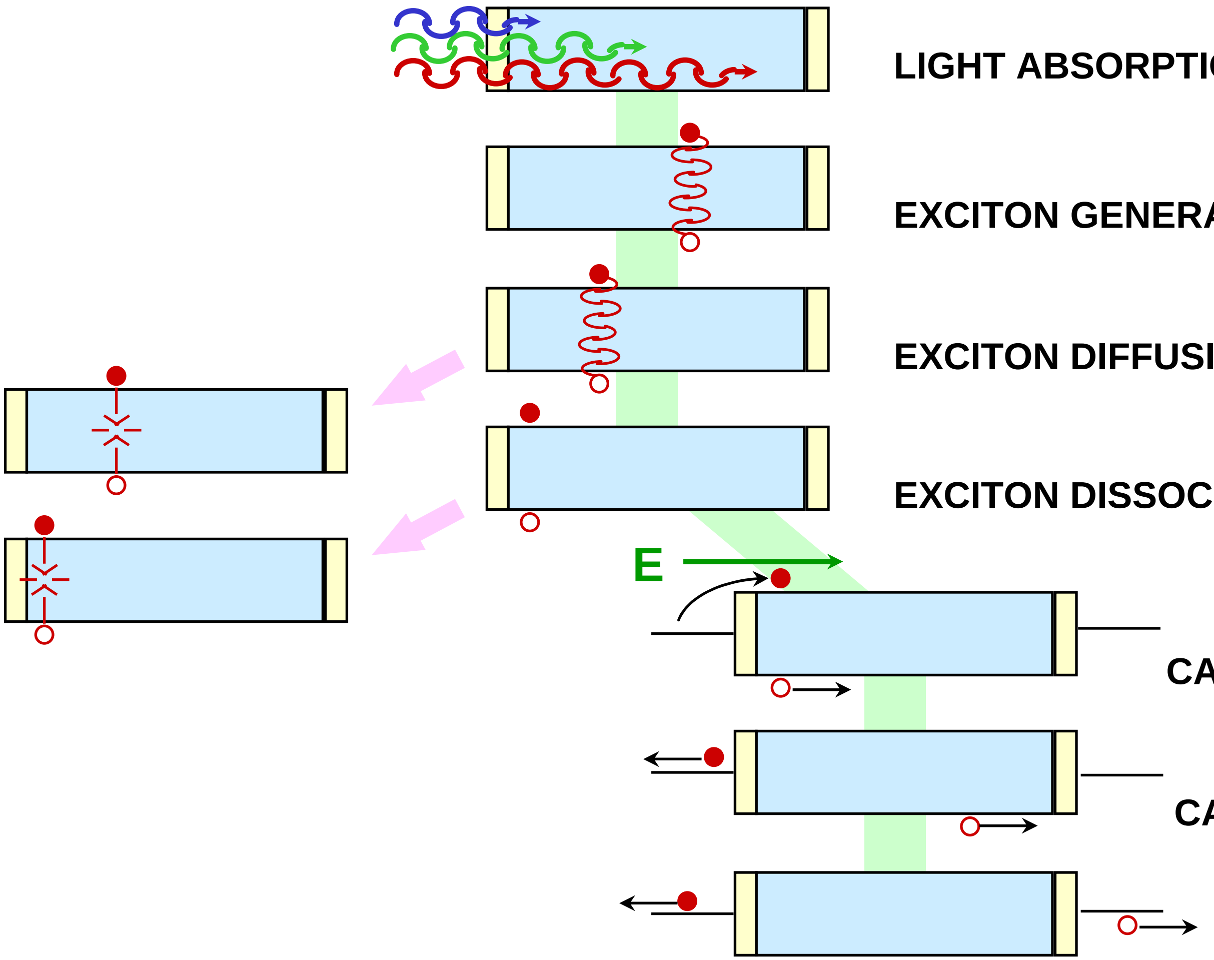
From
http://www.nobel.se/chemistry/educational/poster/1988/

Single Layer Organic PV Cells





Photocurrent Generation



LIGHT ABSORPTION

EXCITON GENERATION

EXCITON DIFFUSION

EXCITON DISSOCIATION

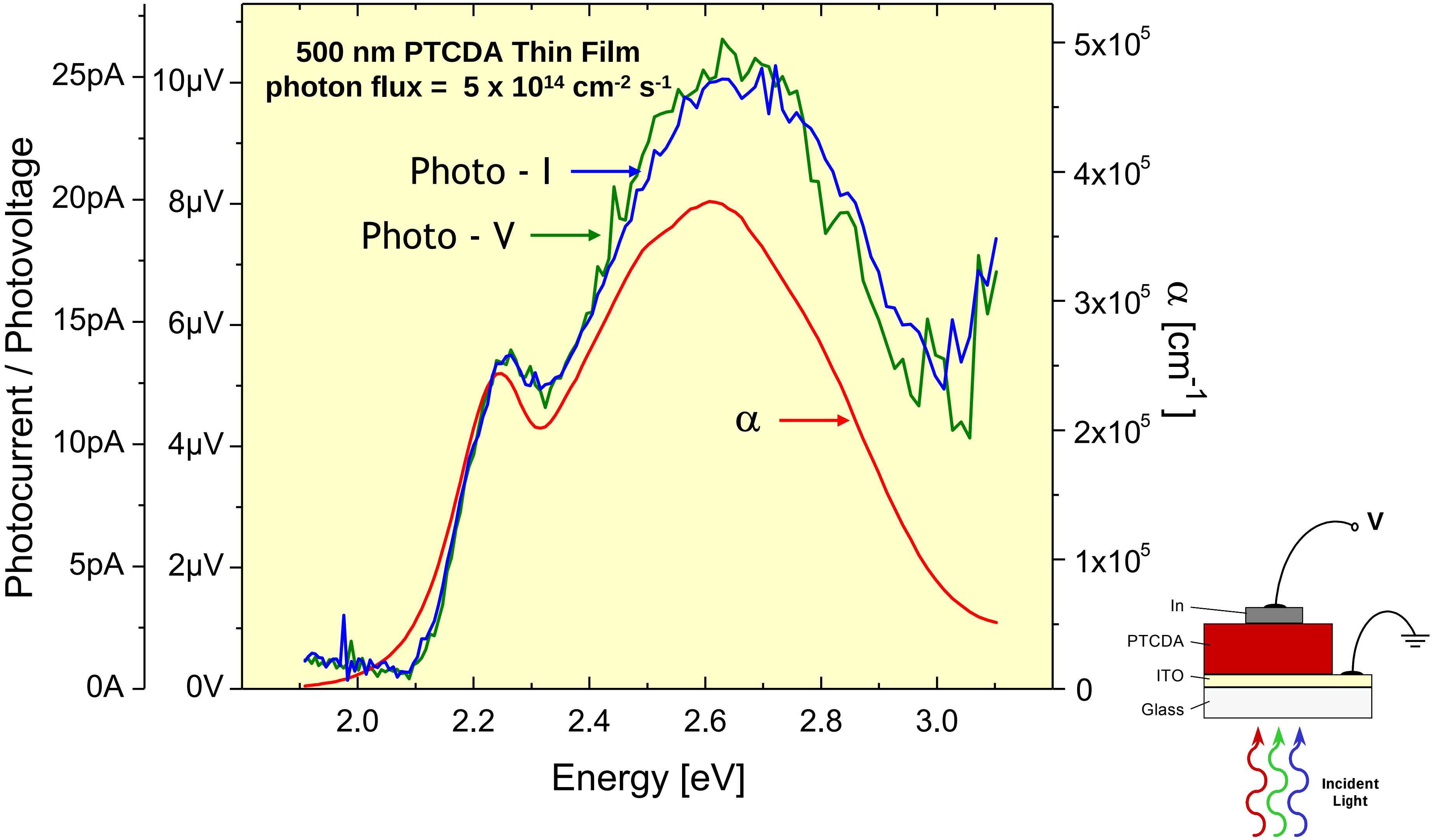
CARRIER SEPARATION

CARRIER TRANSPORT

DELIVERY TO
EXTERNAL CIRCUIT

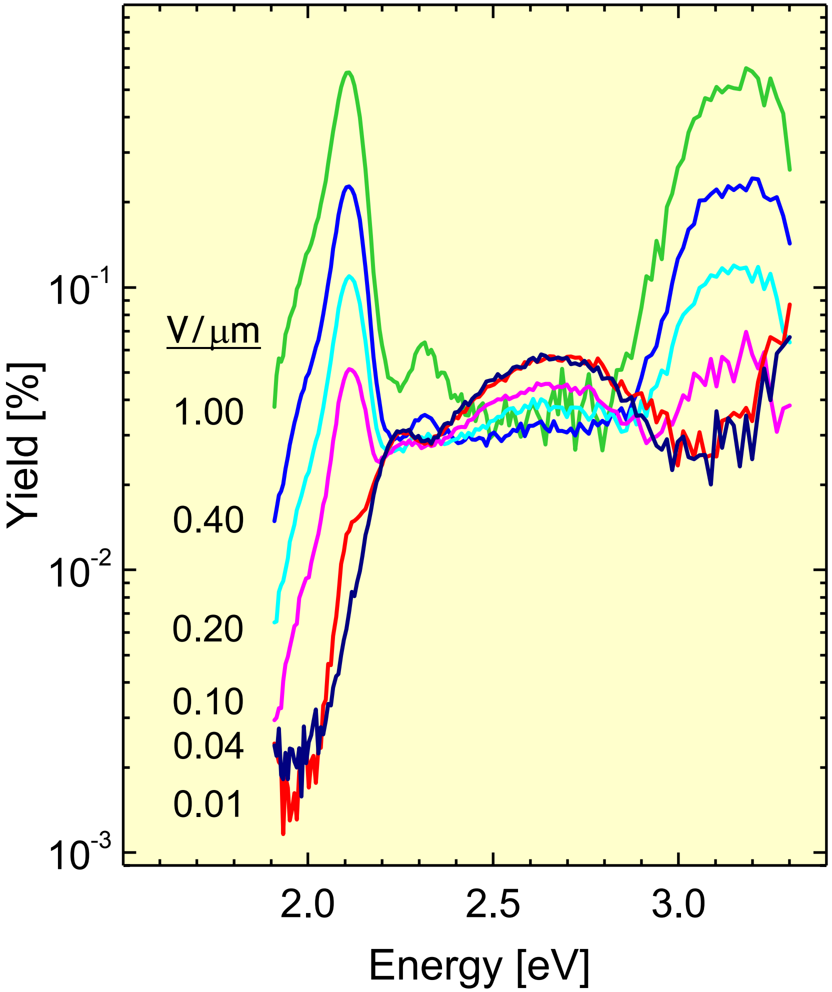
Photocurrent, Photovoltage, Absorption

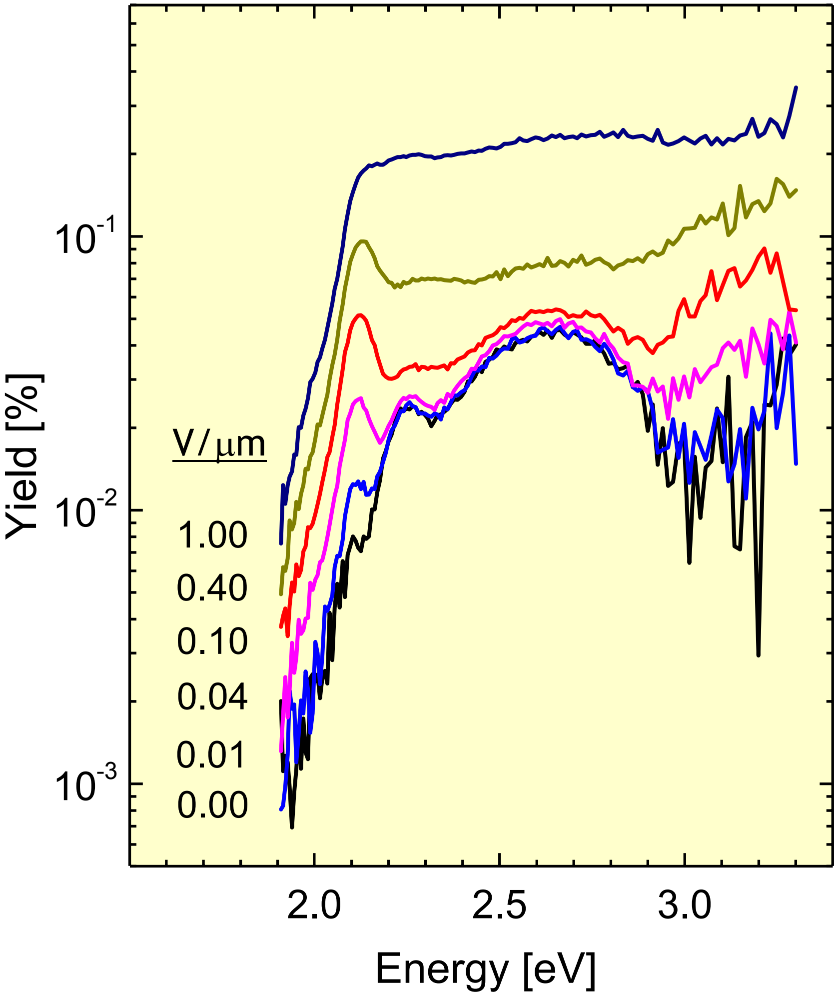
Photocurrent measured at 0V external bias



Photocurrent Dependence on Electric Field

Different photocurrent response for positive and negative applied bias


positive field (In +, ITO -)


negative field (In -, ITO +)