The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Winter College on Optics and Energy

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Introduction to Polymer Solar Cells (PSCs)

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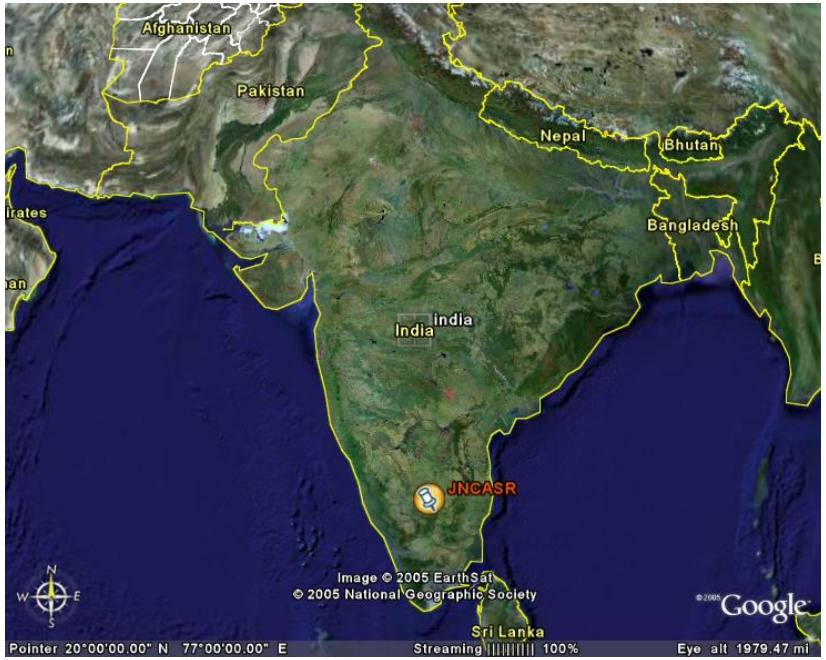
I too have worshipped
at the shrine of science



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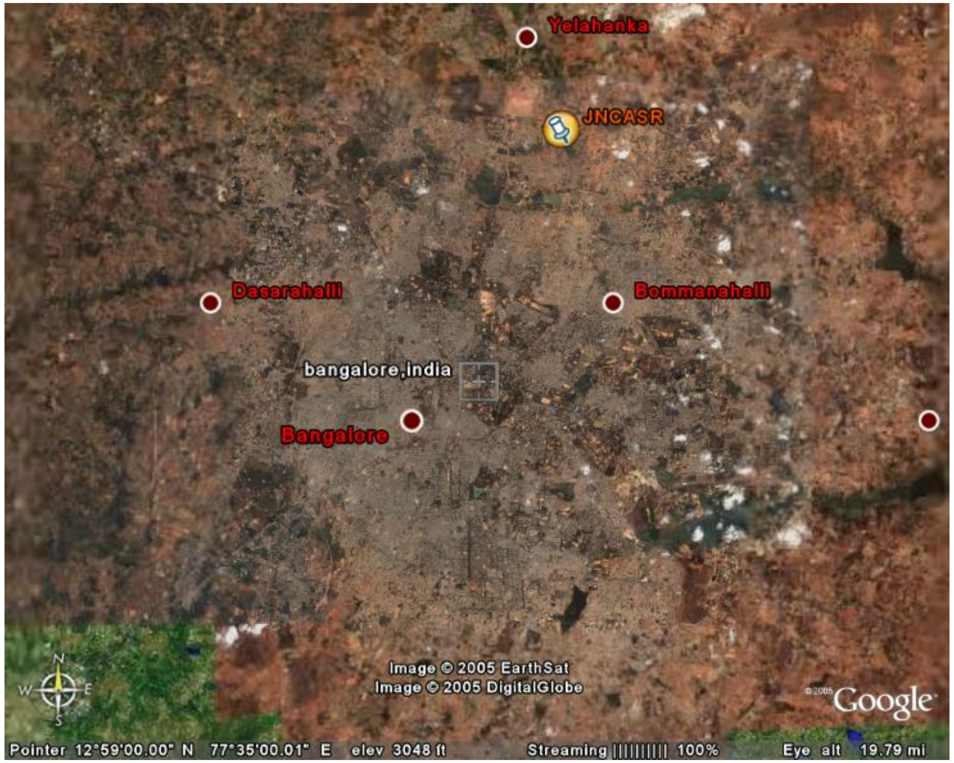

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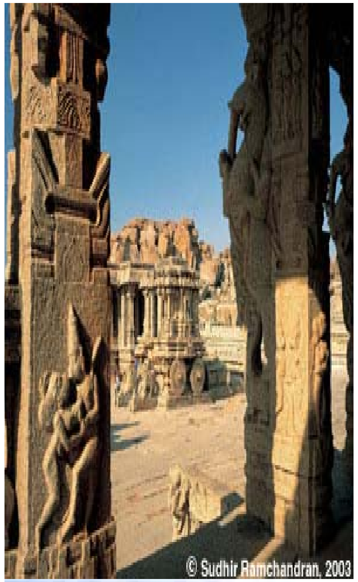
Lalbagh Gardens



- Salubrious Weather < 22 °C >
- Science and Technology Hub (S. Asia's Si-Valley)
- Central Location to Historic and Natural Sites
- Well connected • Culturally Vibrant • Verdant Environment, Academically Stimulating

JAWAHARLAL NEHRU CENTRE FOR ADVANCED SCIENTIFIC RESEARCH

An autonomous institution of Department of Science and Technology, established in 1989

Lecture 1

- Conducting Polymers, Semiconducting Polymers
- Excitons in Semiconducting polymers
- Diodes
- Charge Separation…

Bulk Hetrojunctions

Kinetics-rates-branching factors

Gaussian Model for Transport

Lecture 2

- Jsc- Voc – Fill Factor

Problems and Losses
Bulk limiting factors
Interfaces

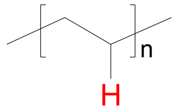
Mobility – Transport Symmetry –

Aging-degradation

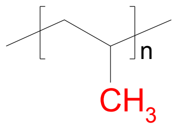
Lecture 3

- General Directions and Present Strategies
- Recent Results from my laboratory

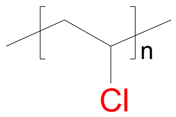
Polymers: Structural variety …



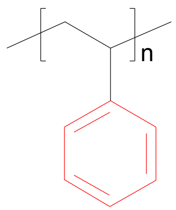
Polyethylene



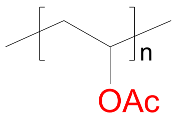
Polypropylene



Polyvinyl chloride PVC



Polystyrene – Styrofoam, thermocole

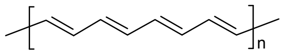


Polyvinyl acetate - Fevicol

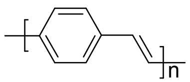
- Insulators
- Semiconductors
- Conductors

Pattern – Colours - ……

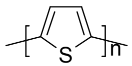
Conjugated Polymers



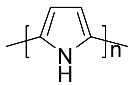
Polyacetylene



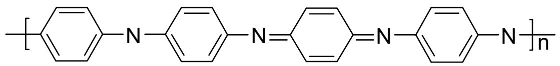
Polyphenylene vinylene



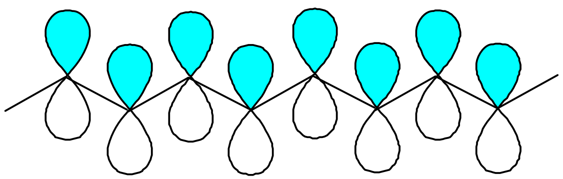
Polythiophene

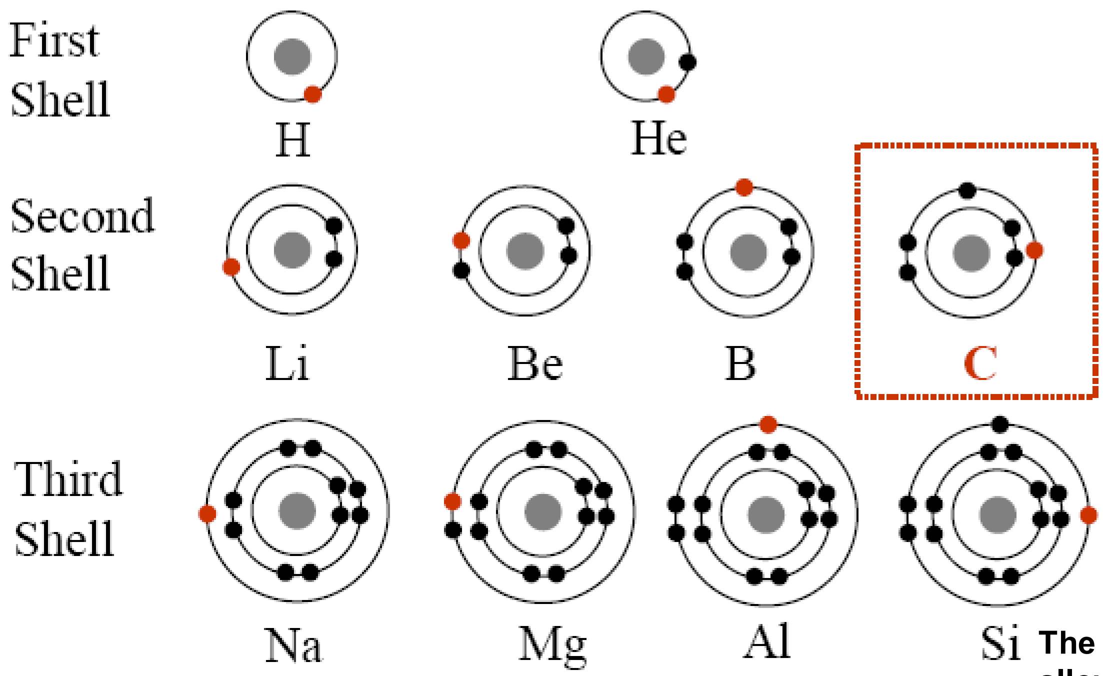


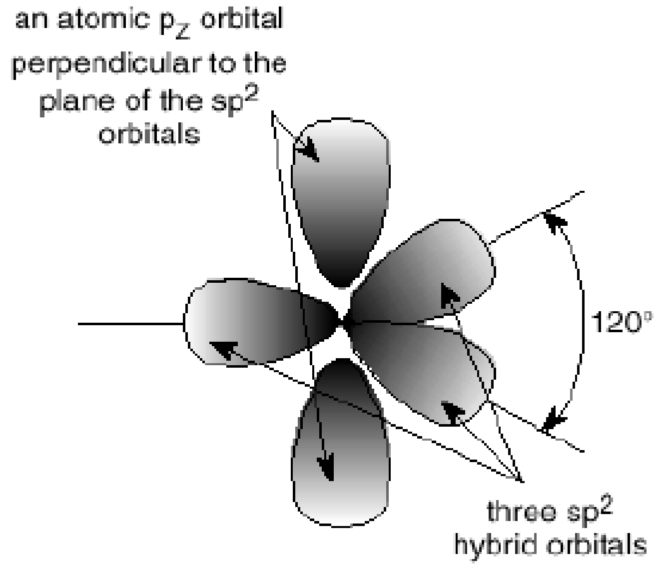
Polypyrrole



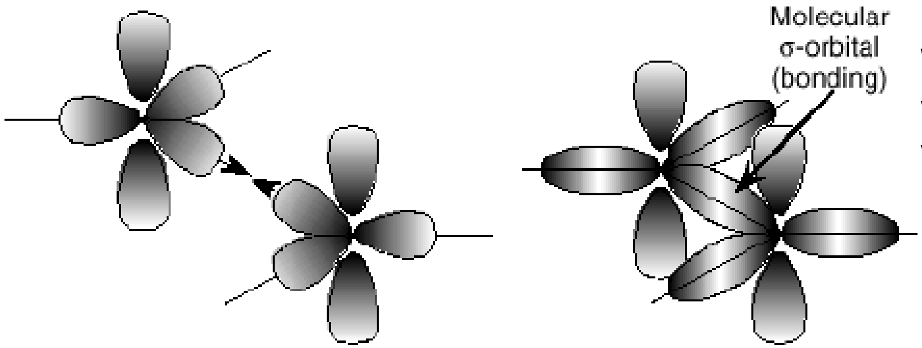
Polyaniline



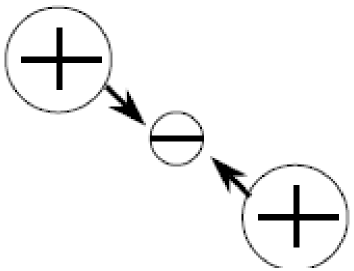




The 4 orbitals of a carbon atom in the form which allows it to couple to other atoms.

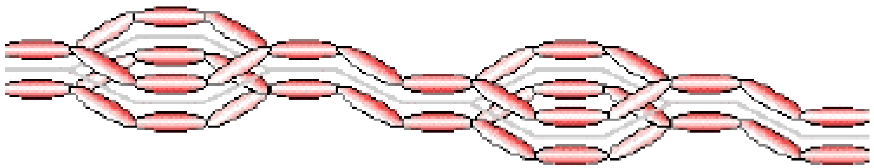


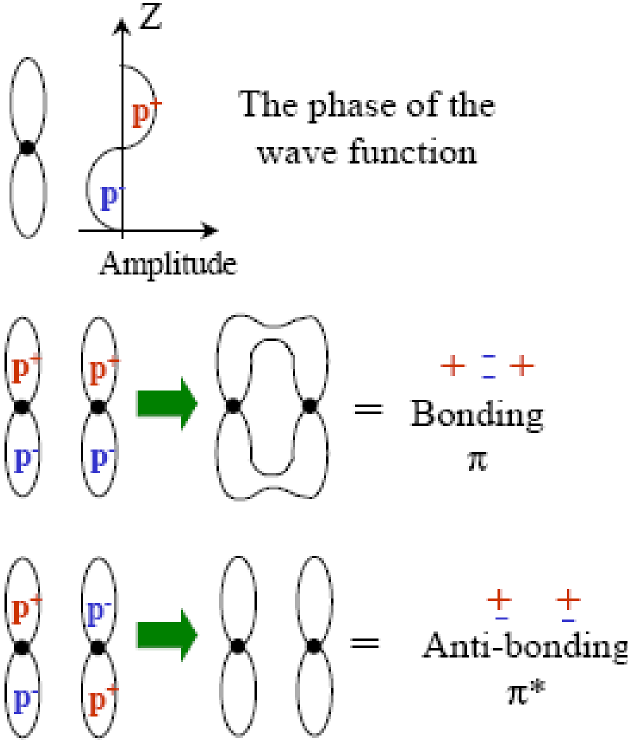
When two atoms are brought together the wavefunctions
which are in the plane overlap and couple.

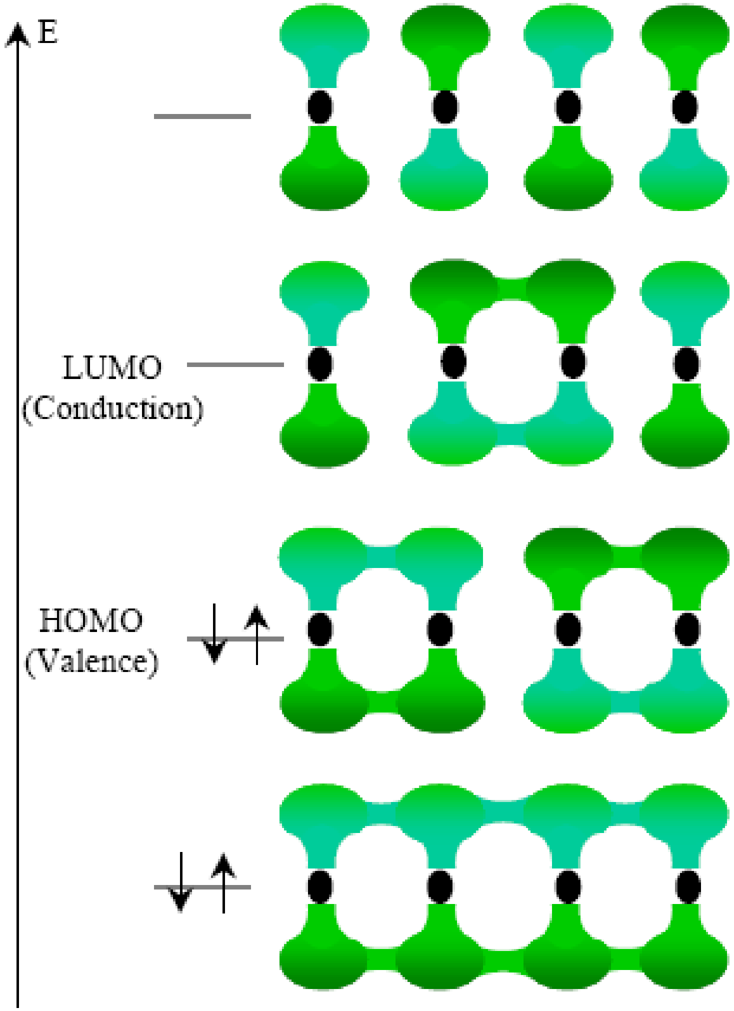


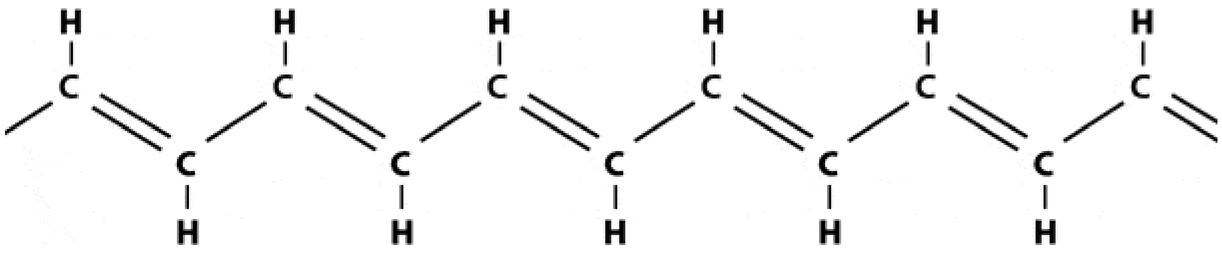
The attraction
(stabilisation) introduced by the overlap.

π-orbitals




Z
p+
p-
Amplitude
The phase of the wave function
p+ p+
p- p-
+ - +
= Bonding
π
p+ p-
p- p+
+ +
- -
= Anti-bonding
π*


E
LUMO
(Conduction)
HOMO
(Valence)



Polyacetylene

• Despite the expectation of metallic behaviour, pristine polyacetylene was an insulator. Bond alternation due to *Peierls* distortion leads to the formation of a band gap between the valence and conduction band.

• Oxidation of PA (from Shirakawa) using a simple oxidant, like Iodine, (MacDiarmid and Heeger) lead to a 10^7-10^8 fold increase in the conductivity of polyacetylene.

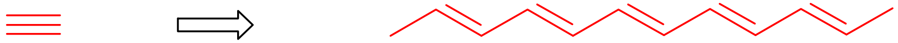
• A similar increase in the conductivity was observed in many of the other conjugated polymers when doped with appropriate oxidants (or reductants).

Doping – oxidation/reduction

Historical evolution

Polyacetylene

Silvery film of *trans*-polyacetylene

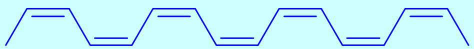


Ziegler-Natta catalyst

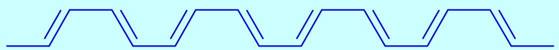
19
po nd
fo

19 ng
sc
th
su
sc !

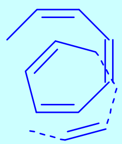
Other isomers of polyacetylene



cis-transoid



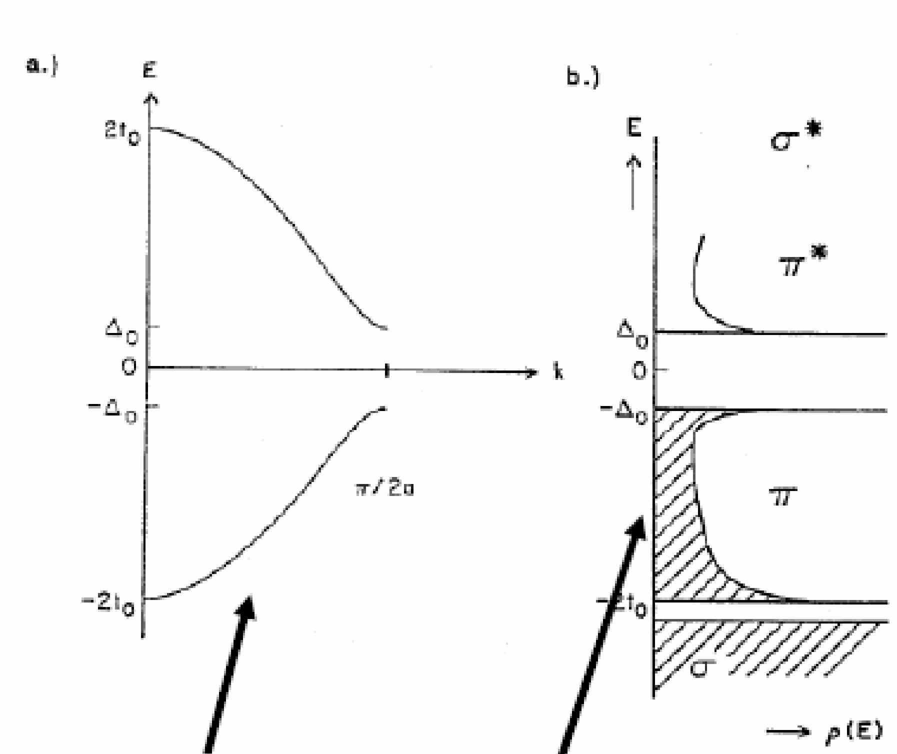
trans-cisoid

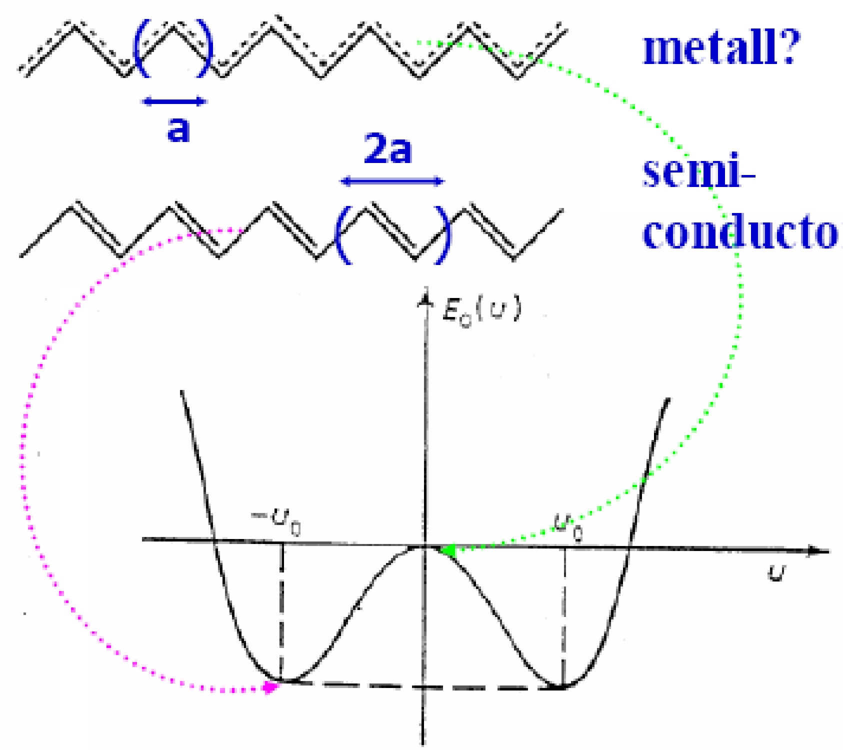


cis-cisoid

Polyacetylene: dimerization

unit cell a and 2a





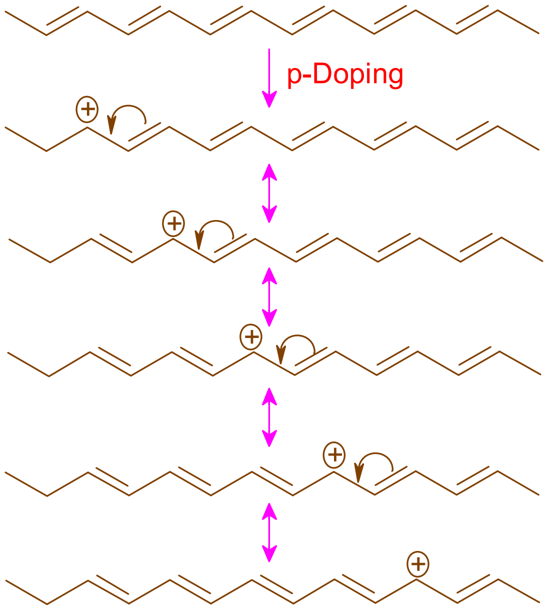
metall?

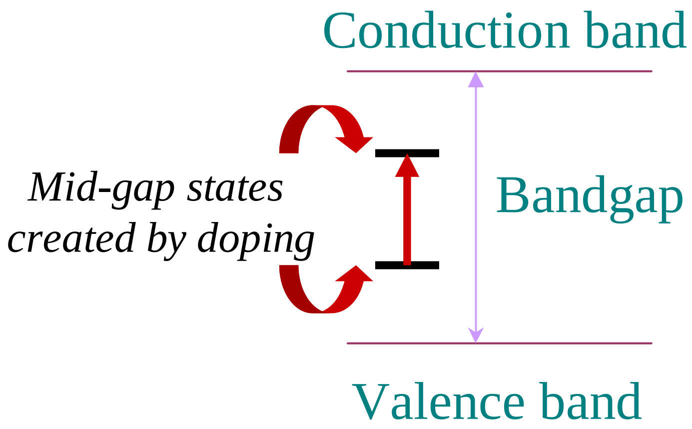
semi-conductor!

Band structure (a) and density of states (b) for trans-(CH)x. The energy gap of $2\Delta_0$ opens up at k=2ð/a due to the Peierls distortion

The total energy (electronic plus lattice distortion) as a function of u. Note the double minimum associated with the spontaneous symmetry breaking and the twofold degenerate ground state.

Electrical conduction





1977 – σ = 38 S/cm

2000 - σ = 30,000 S/cm

Early problems …

Polyacetylene

•Due to the planar structure possessing extended conjugation, all the early conjugated polymers were insoluble and infusible.

•All the virtues of being a polymeric materials, such as ease of processing (solution or melt) were, therefore, lost.

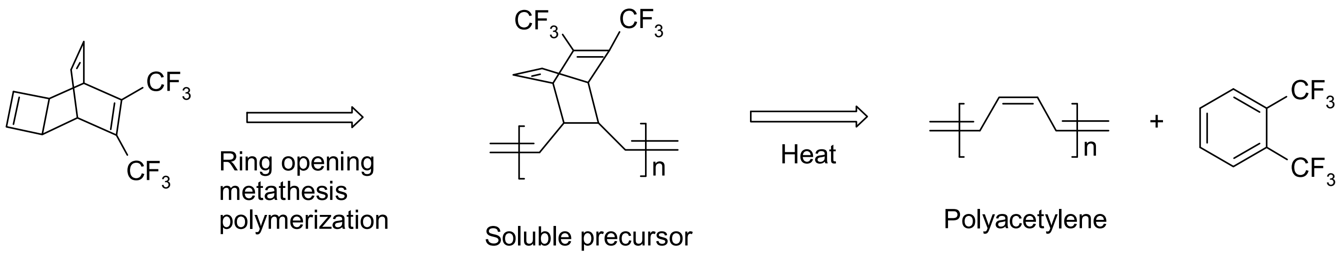
•Films had to be prepared directly or via a *soluble precursor* approach, wherein the precursor was readily and completely transformed to the conjugated polymer at the final stage.

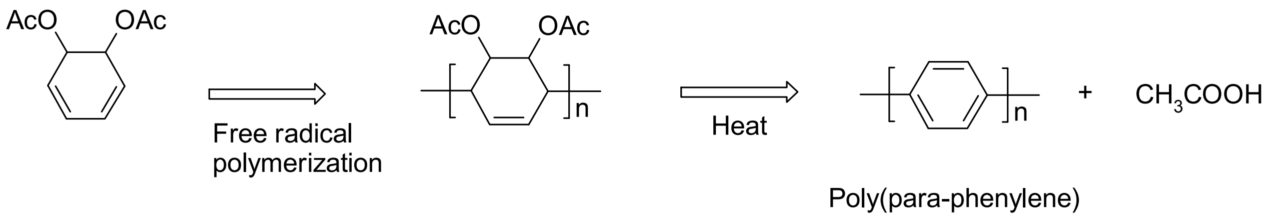
• Alternate approaches involving incorporation of conjugation breakers (*kinks*) *or* introduction of *lateral substitution* needed to be developed.

• Environmental instability.

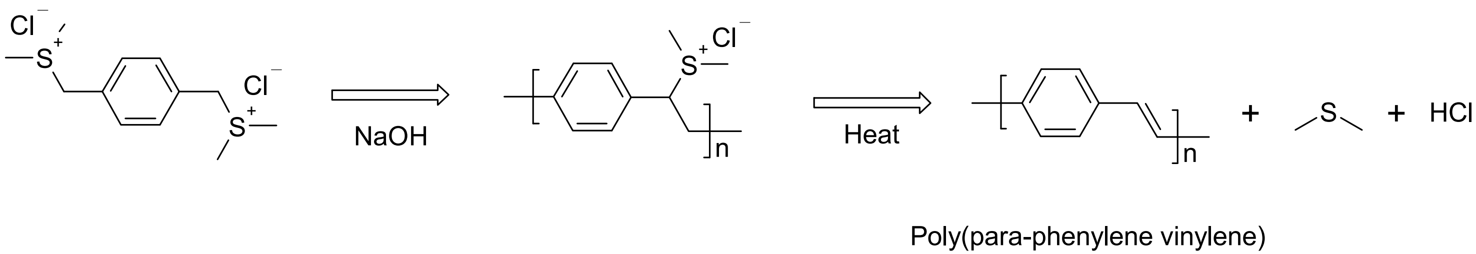
Precursor routes

Feast Approach





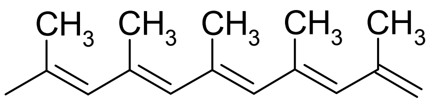
Wessling Route



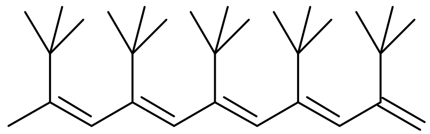
The dilemma of lateral substitution

- Lateral substitution could clearly enhance the solubility but at the same time might be expected to destroy the planarity, and hence the extended conjugation, which is believed to be essential for the electrical properties.

- Early investigators believed this to be an insurmountable problem – *it waseither insoluble good conductor or soluble bad conductor.*

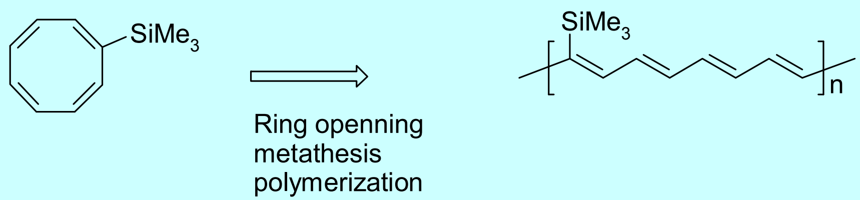


Poor conductor



Pure white colour
Complete absence of conjugation !

Grubb's approach



Conductivity only moderately affected as planarity is retained.

$E_{optical\text{-}gap}$= Electronic transition energy of planar backbone

+

Energy shift introduced by nonplanar subst.

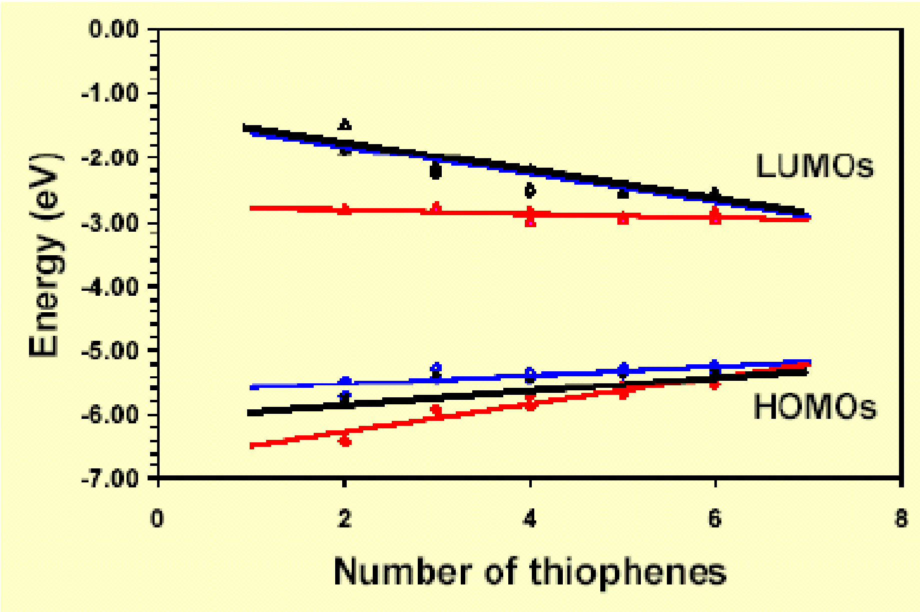
+

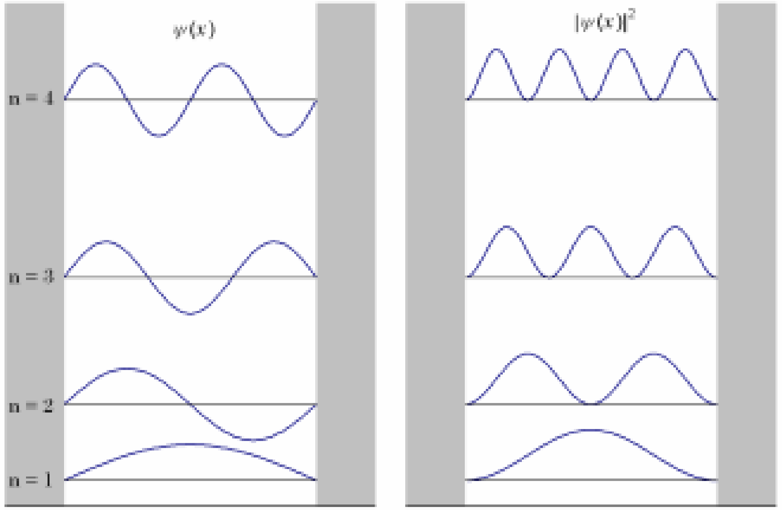
solvent (dielectric effects)

+

Solid state effects (intermolecular)

For oligomers (=„short polymers") a shift of HOMO or LUMO levels towards smaller band-gaps is observed upon increasing the number of repeat units . Compare with quantum-mechanical particle-in-a-box problem.





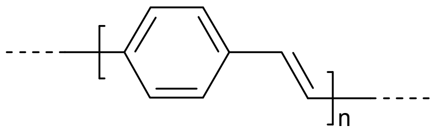
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad (1)$$

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \quad (9)$$

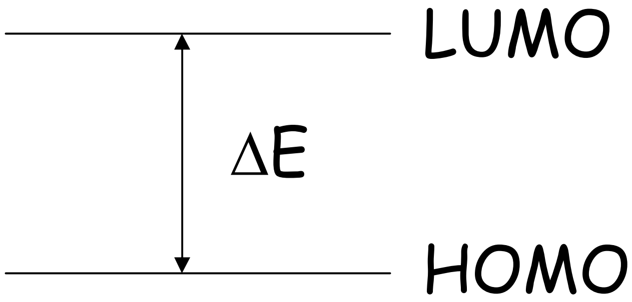
$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

longer chain/wider box
→ decrease in „band-gap"

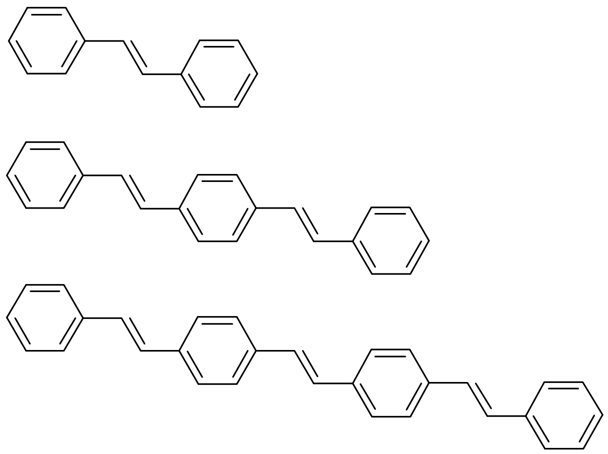
What is the chromophore in a CP?



Polymer chains are very long – 1000's of repeat units!



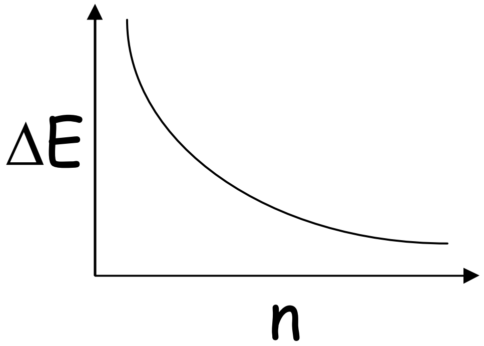
Molecular conjugation Length "n"



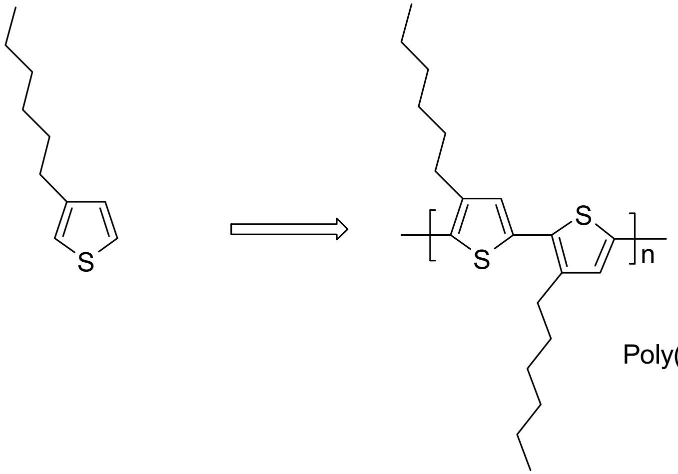
n = 1

n = 2

n = 3



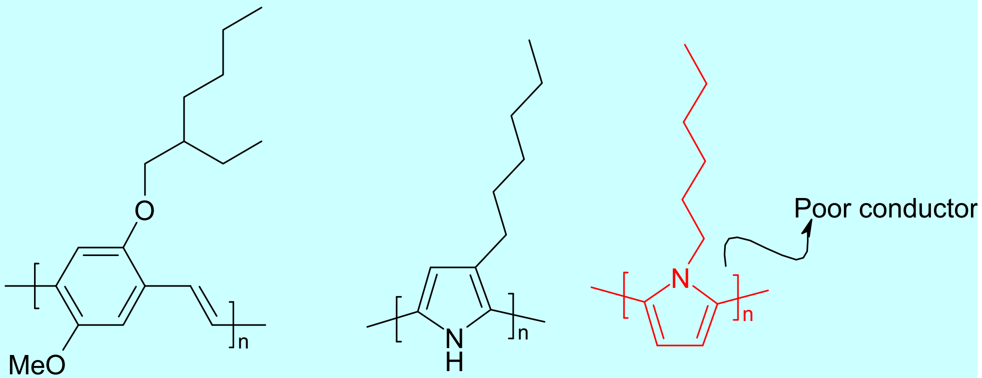
Lateral substitution – the solution



Poly(3-hexyl-thiophene) P3HT

- In polyarylenes and polyarylenevinylenes, lateral substitution became the method of choice for attaining processability while at the same time retaining reasonably good transport properties.

Other examples of soluble conjugated polymers

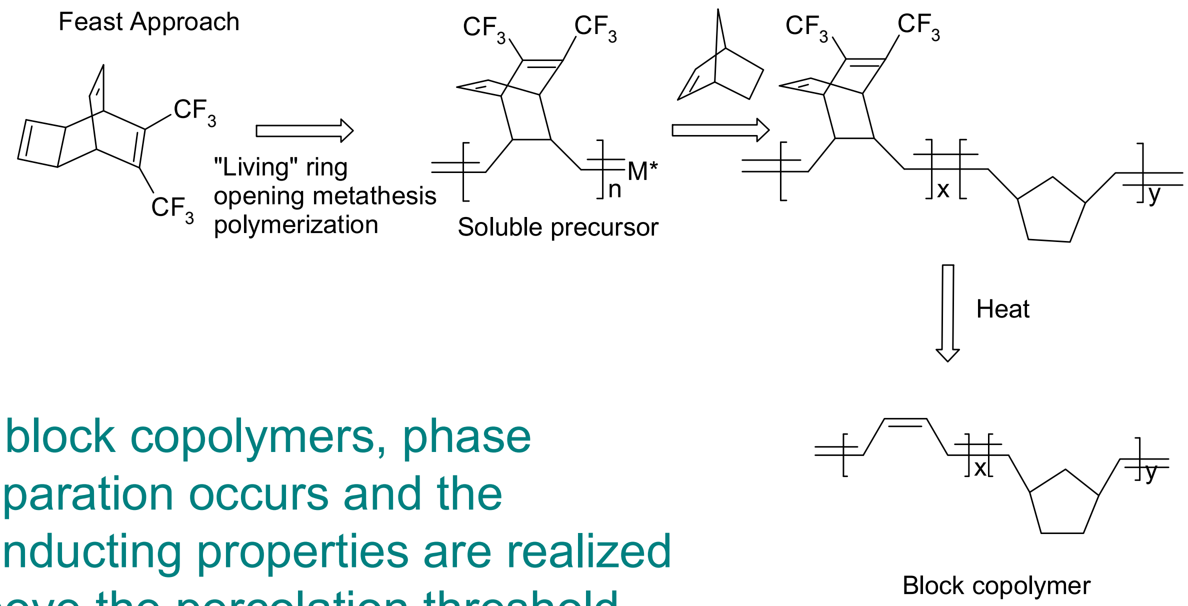


MEHPPV

Substituted polypyrole's

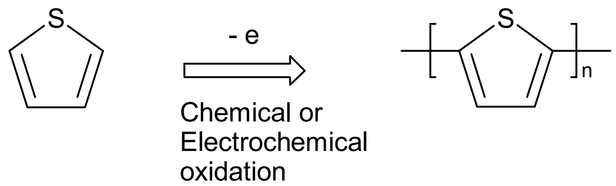
Copolymerization routes

• Inclusion of solubilizing comonomer – one segment that improves solubility and the other that imparts transport behaviour.



In block copolymers, phase separation occurs and the conducting properties are realized above the percolation threshold.

Common preparative routes



- Oxidative coupling approach works very well for the preparation of a variety of poly(aromatic)s, such as polythiophene, polypryrrole, polyphenylene (electron-rich variety), polyaniline, etc.

- Most preparations can be done in aqueous medium and therefore is amenable to direct preparation of emulsions under suitable conditions.

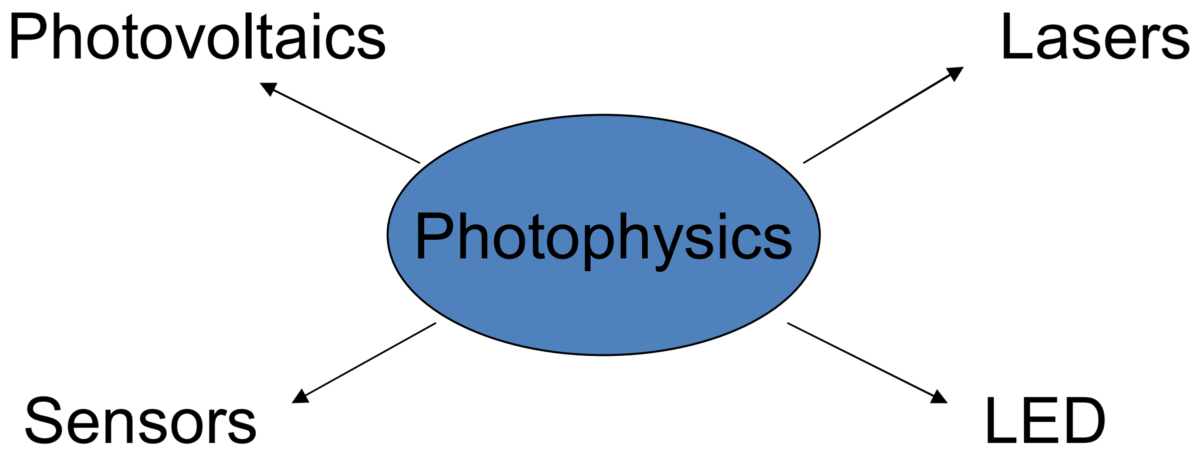
- Preparation of conducting polymer composites, such as on paper, cloth, membranes etc. are also readily achieved. This is especially suitable in the case of pyrrole and aniline.

Sustained Interest in CPs

- Discovery of of photoluminescence and electroluminescence (1990)
- Potential for flexible all-plastic LEDs
- Potential for all-plastic photovoltaics
- Luminescence-based sensors
- Feasibility nano-patterning and nanostructuring

Most of these applications rely on the photophysical properties of conjugated polymers

Photophysics of conjugated polymers



nature of the excited state

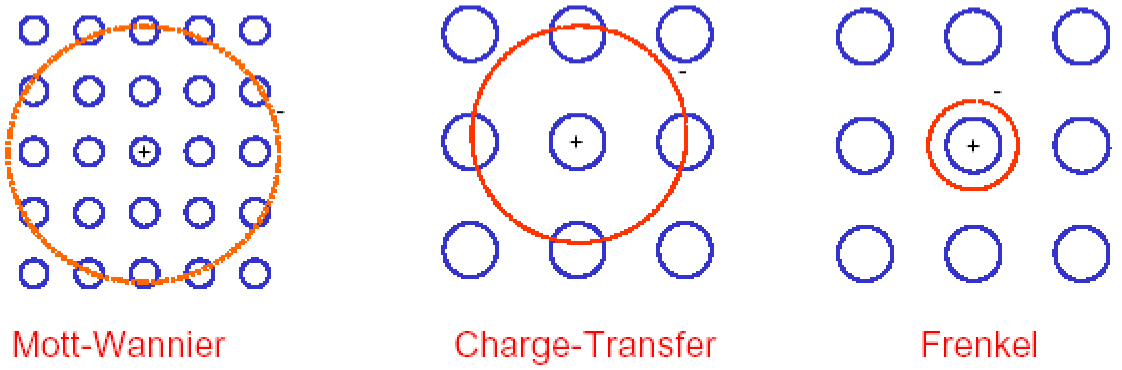
- when we promote e^- from HOMO to LUMO
- we change the distribution of electrons
- "exciting the molecule means moving the electrons"

- this creates large variations in local charge
- in other words we create
  - a local pocket of positive charge (hole); and
  - a local pocket of negative charge

- the positive & negative regions attract each other
  - "restoring force" encourages return to ground state
  - excess energy is often shed as a photon

different types of exciton

excitons are highly localised in molecular materials



	found in	properties
Mott-Wannier	inorganics, - Si, GaAs higher exc. states in mol. crystals	hydrogen-like, radius 40 – 100 Å $E = E_G - G/n^2 , n = 1,2\ldots$ binding energy ~ meV
Frenkel	low density mol. crystals semiconducting polymers	correlated e^-/h^+ pair on same molecule radius < 5 Å binding energy ~ 500 meV
Charge-Transfer	dense mol. crystals	radius 1 – 2 times nearest neighbour separation, e^- on neighbouring mol.

Wannier-Mott Excitons

Columbic interaction between
the hole and the electron is given by
$E_{EX} = -e^2/\in r$

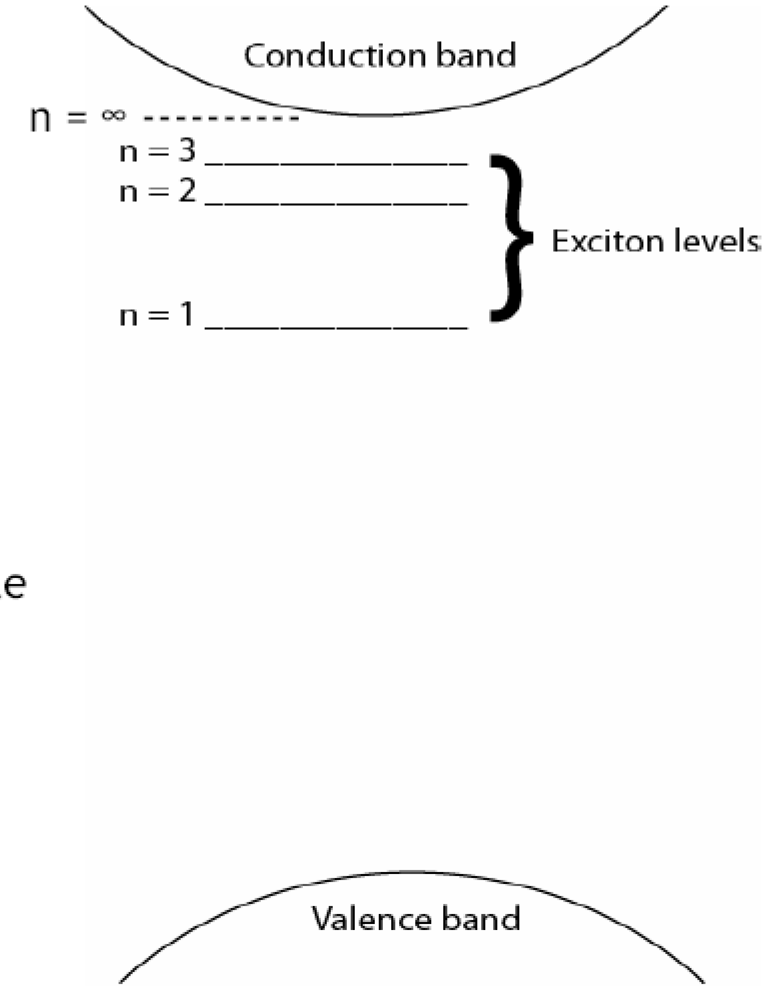
The exciton energy is then

$$E = E_{ION} - E_{EX}/n^2 \text{ , } n = 1,2, \ldots$$

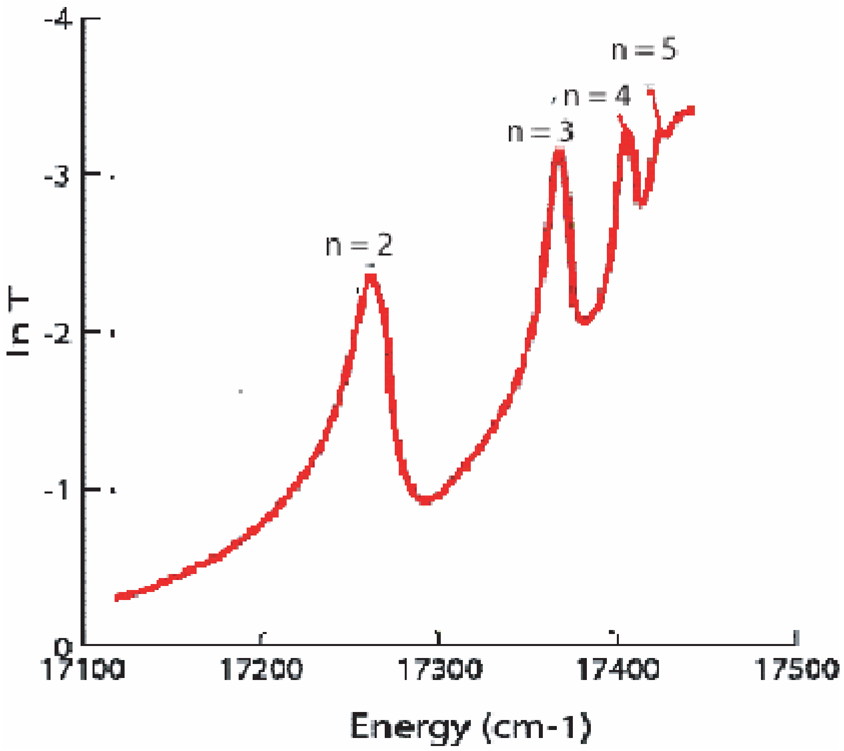
E_{ION} – energy required to ionize the molecule
n – exciton energy level

$$E_{EX} = 13.6 \text{ eV } \mu/m\in$$

μ- reduced mass = $m_e m_h$ / (m_e+m_h)



An Example of Wannier-Mott Excitons



exciton progression
fits the expression

$$\nu[\text{cm-1}] = 17{,}508 - 800/n^2$$

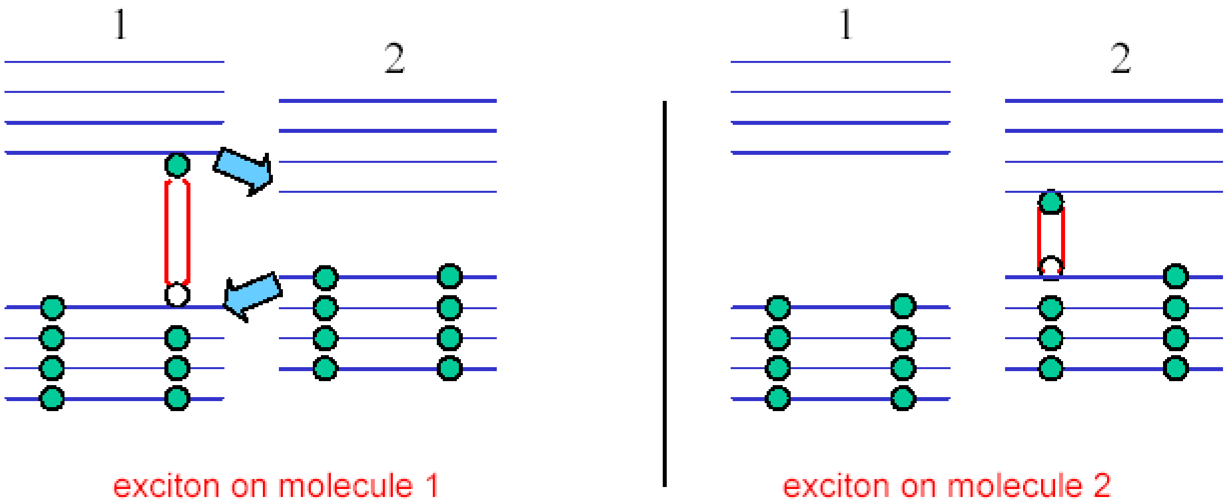
corresponding to
$\mu = 0.7$ and $\in = 10$

The absorption spectrum of Cu_2O at 77 K, showing the exciton lines corresponding to several values of the quantum number *n*. (From Baumeister 1961).

Quoted from Figure I.D.28. <u>Electronic Processes in Organic Crystals and Polymers</u> by M. Pope and C.E. Swenberg

excitons behave like single particles

- they "hop" from one molecule to the next
- excitons "sniff out" longest chains (lowest energy)



exciton on molecule 1
molecule 2 in ground-state

exciton on molecule 2
molecule 1 in ground-state

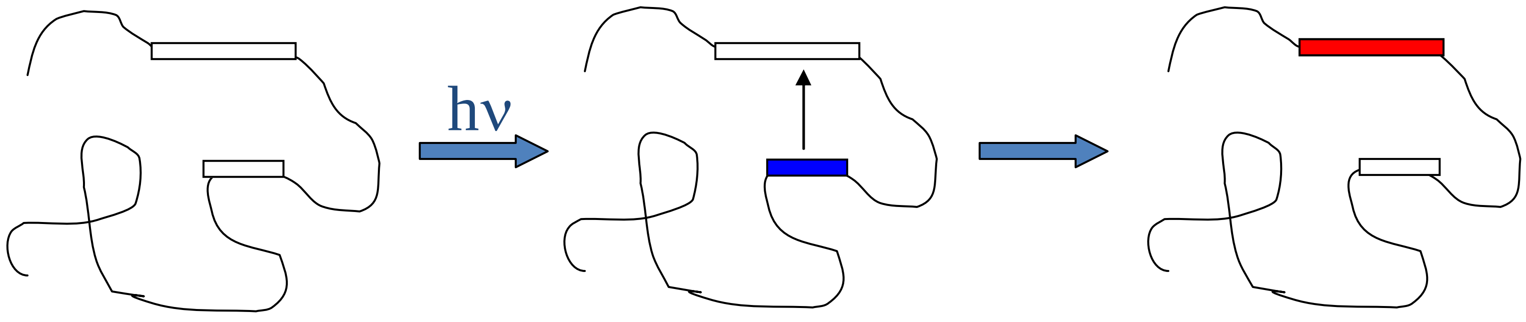
detailed transfer mechanism depends on type of exciton

- singlet: Dexter or Forster
- triplet: Dexter only

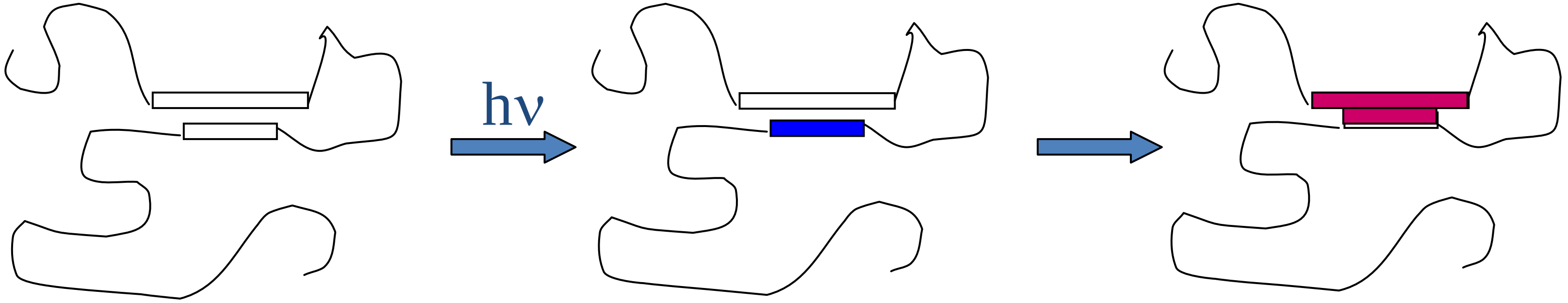
} see http://tiger.technion.ac.il/~nir/excitons.pdf for discussion

Aftermath of photoexcitation

Energy Migration



Intra-chain exciton formation



J. C. deMello 2004

the spin of the exciton?

KSN

there are four possible states for the two spins

- -both spins "up": 1(↑)2(↑)
- -both spins "down": 1(↓)2(↓)
- -one spin "up" and one spin down: 1(↑)2(↓) or 1(↓)2(↑)

but this last form suggests we can distinguish between the spin "up" electron and the spin "down" electron, which is **never** true (Pauli principle). we must therefore rewrite the spin-states as the following linear combinations:

1(↑)2(↓) + 1(↓)2(↑)
1(↑)2(↓) - 1(↓)2(↑)

Three of these states have S = 1: 1(↑)2(↑), 1(↓)2(↓), 1(↑)2(↓) + 1(↓)2(↑)
(triplet)

One of these states has S = 0: 1(↑)2(↓) - 1(↓)2(↑)
(singlet)

optical transitions

- optical transitions are governed by the following selection rule

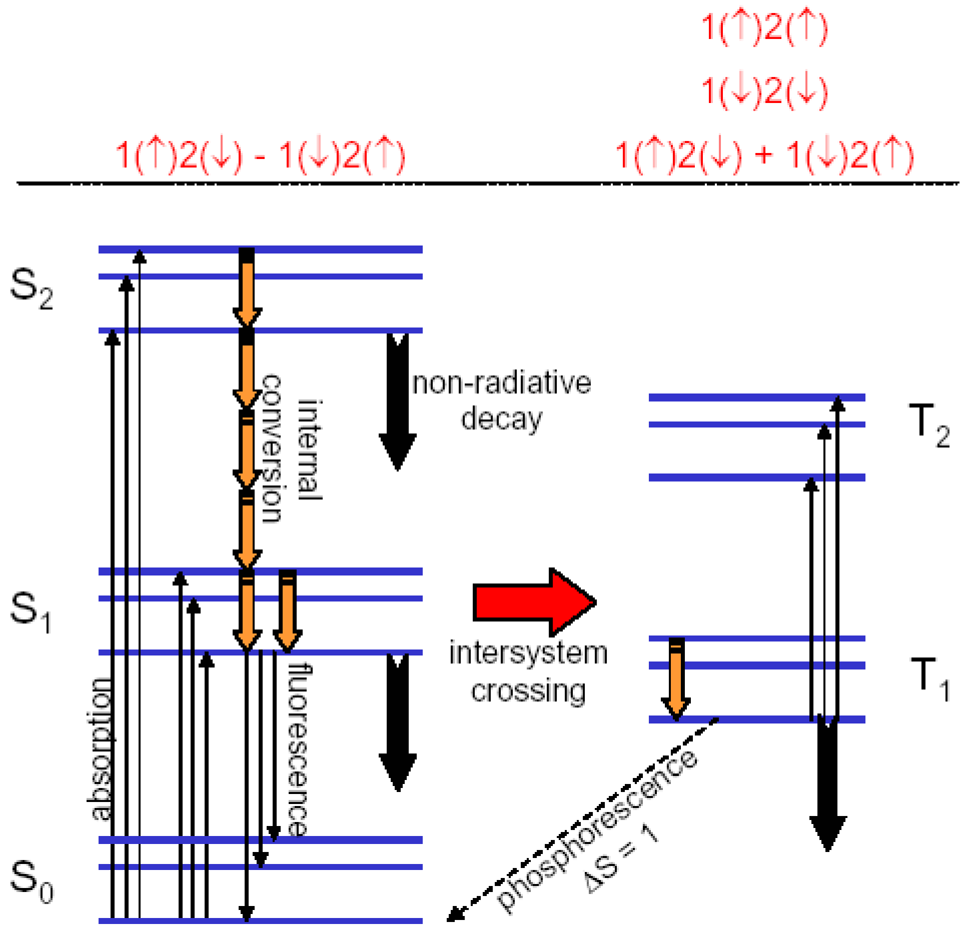
$$\Delta S = 0$$

hence, since the spin of the ground-state is zero (all bonding orbitals being fully occupied), we can only generate singlet excitons by absorbing light and, *importantly, only singlet excitons can decay radiatively to the groundstate!*

BUT

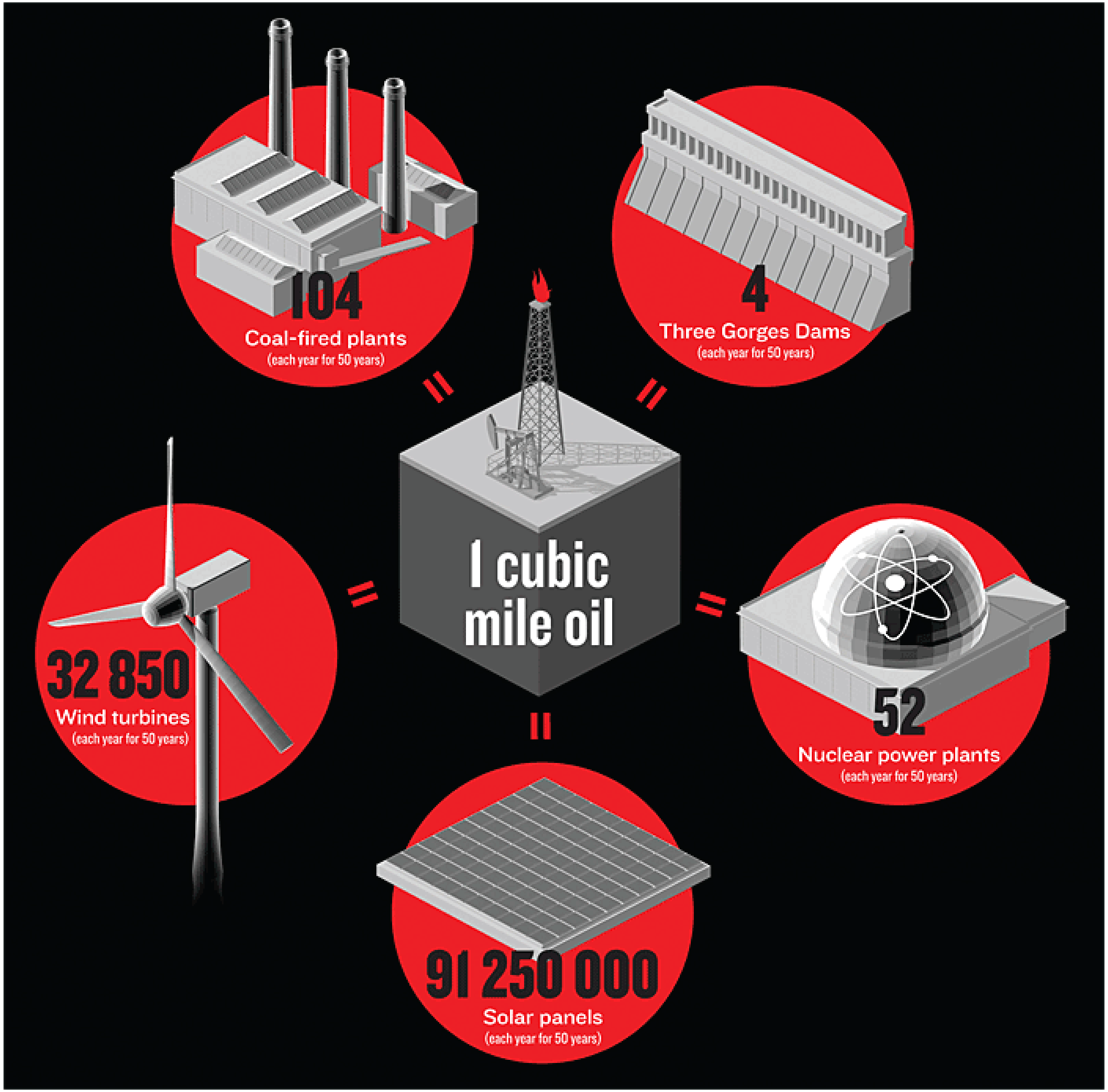
- we can create both singlets and triplets electrically
- so in an LED all triplets will be wasted
- if singlets and triplets created with equal probability, max EL efficiency may be 25 %.

exciton transition processes



$T_1 \rightarrow S_0$ spin forbidden
hence $\tau_{triplet} >> \tau_{singlet}$

$\tau_{singlet}$ ~ 1 – 100 ns
$\tau_{triplet}$ ~ μs - ms



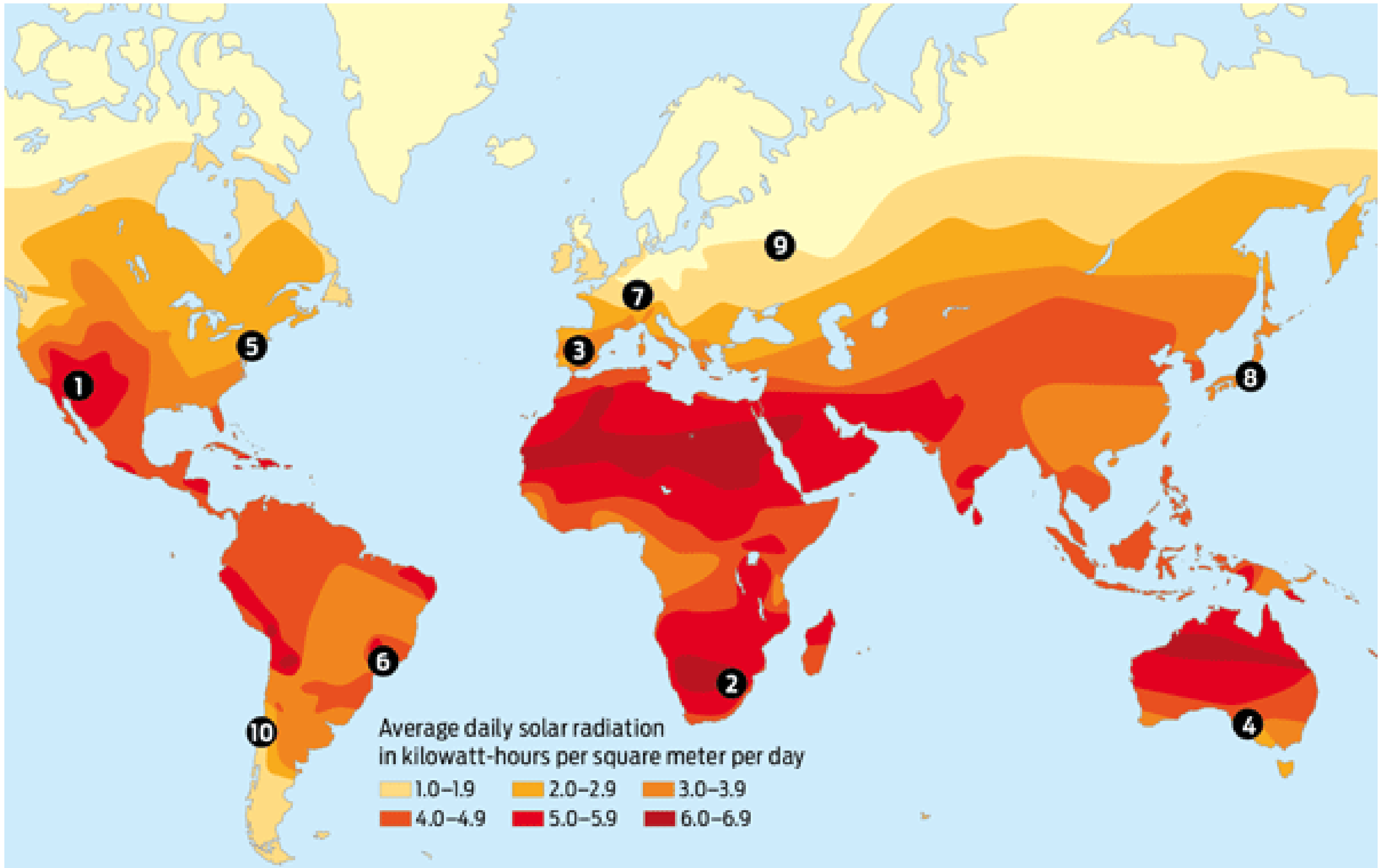
IEEE spectrum 2007

Fact files

- The sun provides us with 10,000 times as much energy as we need
- Solar power contributes 0.039 percent of the world's electricity needs
- PV installations in 4 percent of the deserts would meet global energy needs

the energy we get from all of the world's reserves of coal, oil and natural gas can be matched by ~ 20 days' supply of sunshine.

According to the BP Statistical Review of World Energy 2007, solar, wind and geothermal combined only account for around 1 percent of the world's electricity generation, (IEA) putting solar power's contribution to global energy supply at ~ 0.039 %

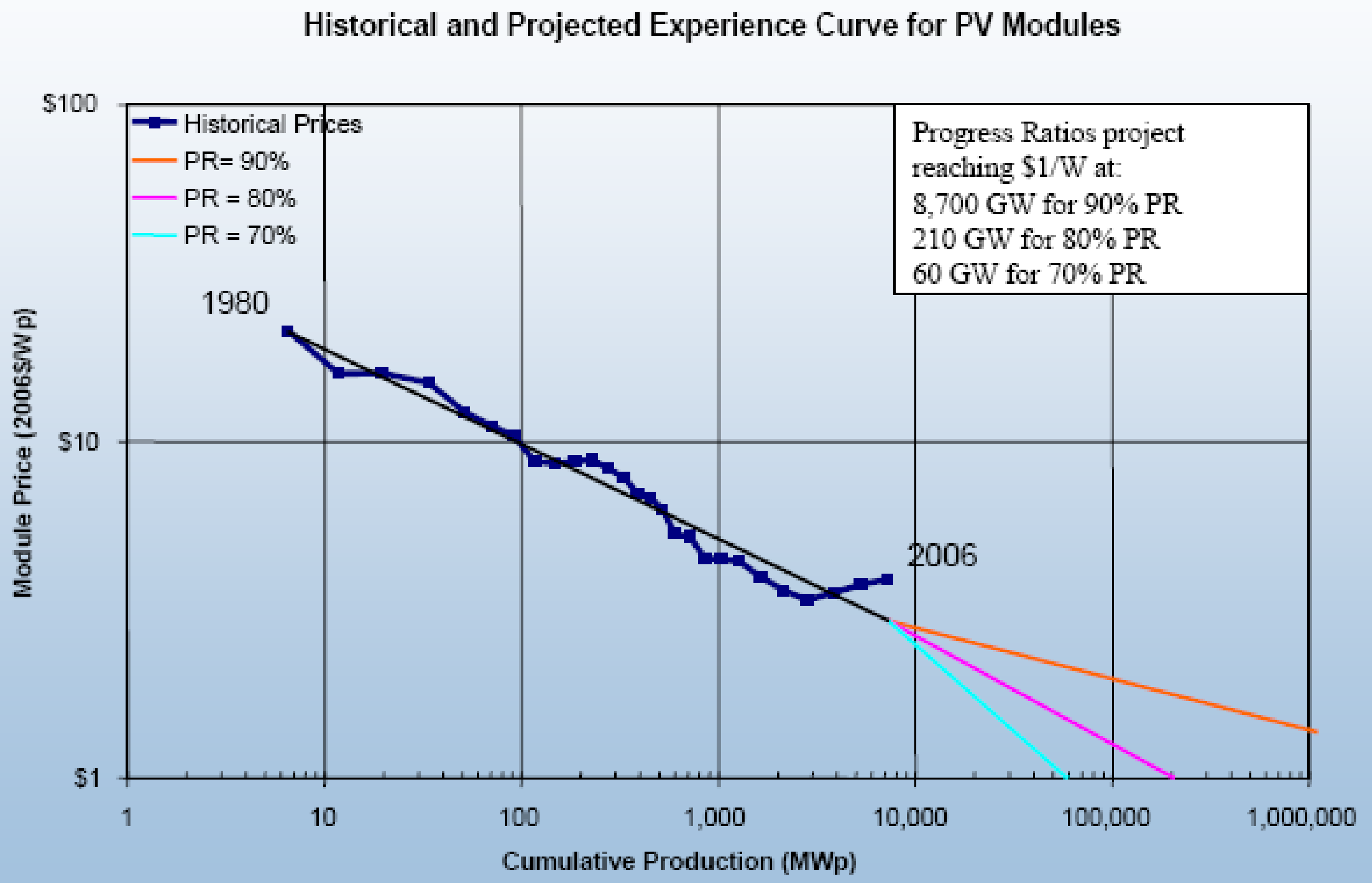


energy input from the sun in a single day could supply the needs for all of the Earth's inhabitants for a period of about 3 decades.

- **India is endowed with rich solar energy resource.**

"The average intensity of solar radiation received on India is 200 MW/km square (megawatt per kilometre square). With a geographical area of 3.29 million km square, this amounts to 657.4 million MW. However, 87.5% of the land is used for agriculture, forests, fallow lands, etc., 6.7% for housing, industry, etc., and 5.8% is either barren, snow bound, or generally inhabitable. Thus, only 12.5% of the land area amounting to 0.413 million km square can, in theory, be used for solar energy installations. Even if 10% of this area can be used, the available solar energy would be 8 million MW, which is equivalent to 5 909 mtoe (million tons of oil equivalent) per year."

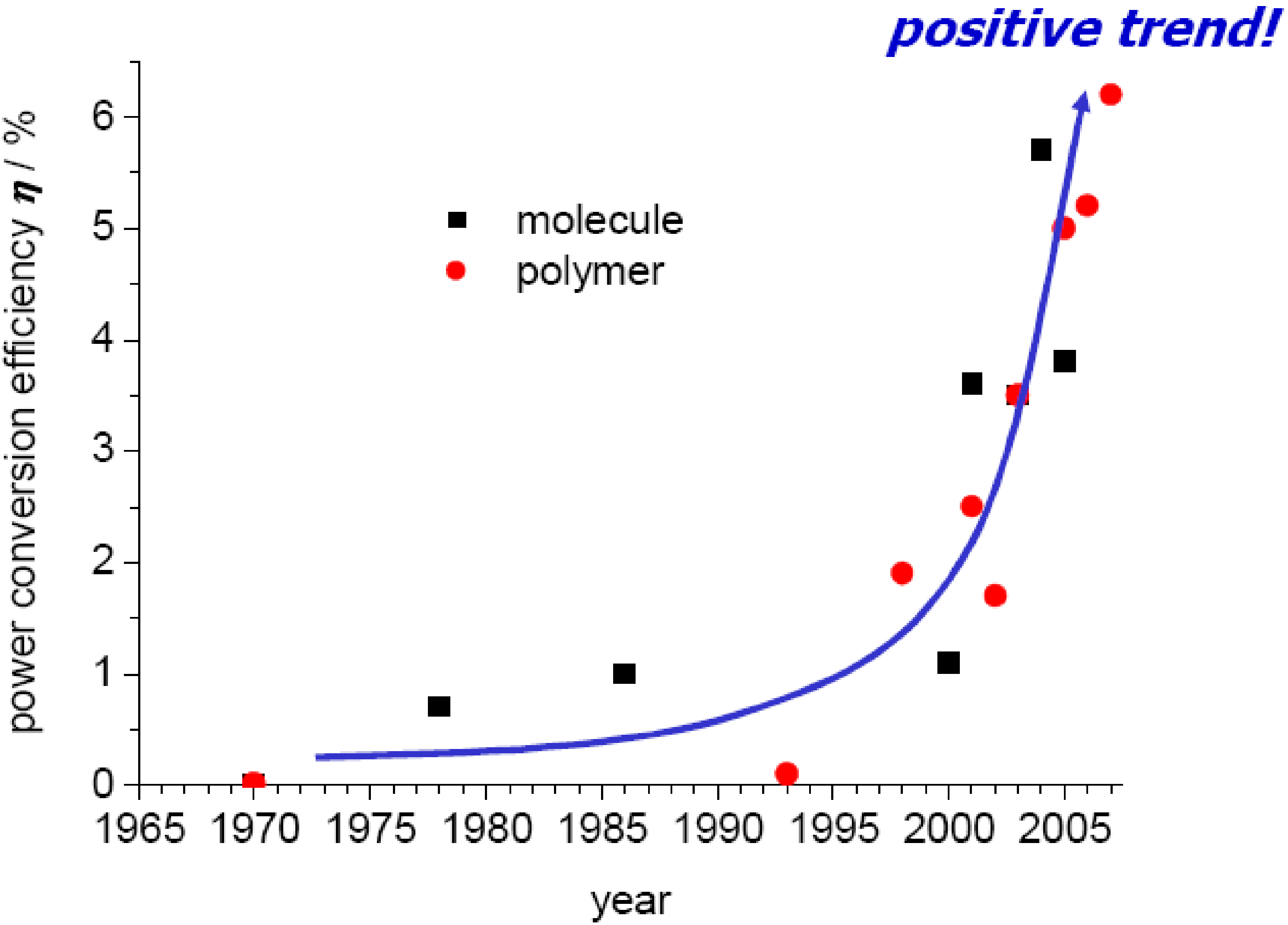
Projection at different PRs



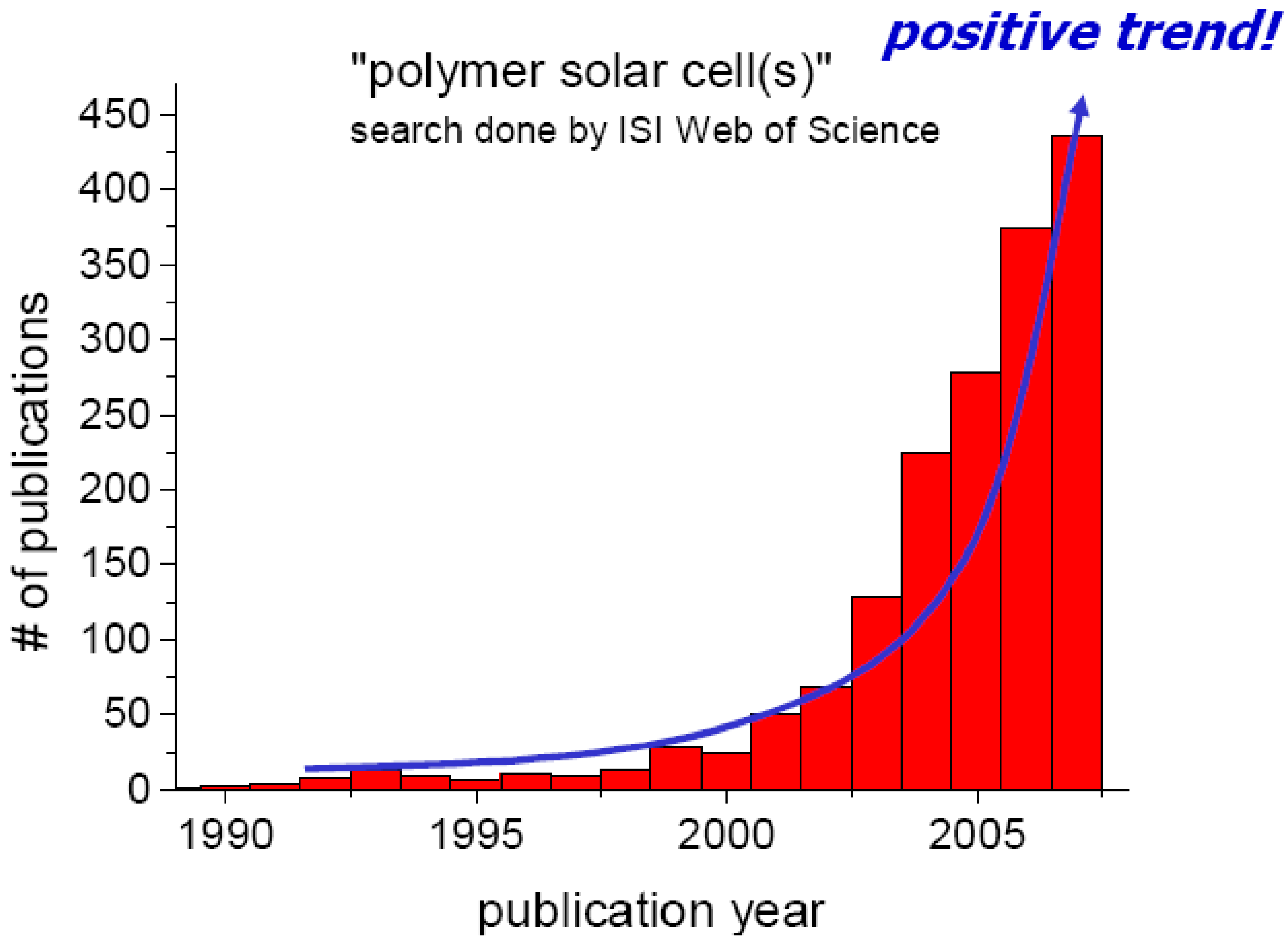
Source: NREL 2007

Energy Payback Time

Renewable-energy technologies promise to liberate us from fossil fuels. But this implies that their energy payback periods—the time it takes for a system to recover the energy used to produce it—is just as important as financial payback



H. Hoppe and N. S. Sariciftci, *Organic solar cells: an overview,* **J. Mater. Res. 19, p. 1924 (2004)**



positive trend!
"polymer solar cell(s)"
search done by ISI Web of Science
# of publications
450
400
350
300
250
200
150
100
50
0
1990
1995
2000
2005
publication year

www.solarmer.com

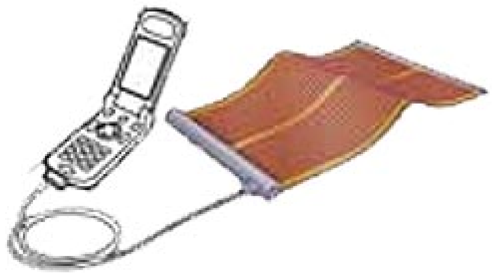
For the Bright Future - Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4% (p NA)

Yongye Liang, ZhengXu, Jiangbin Xia, Szu-Ting Tsai, Yue Wu, Gang Li, Claire Ray, Luping Yu

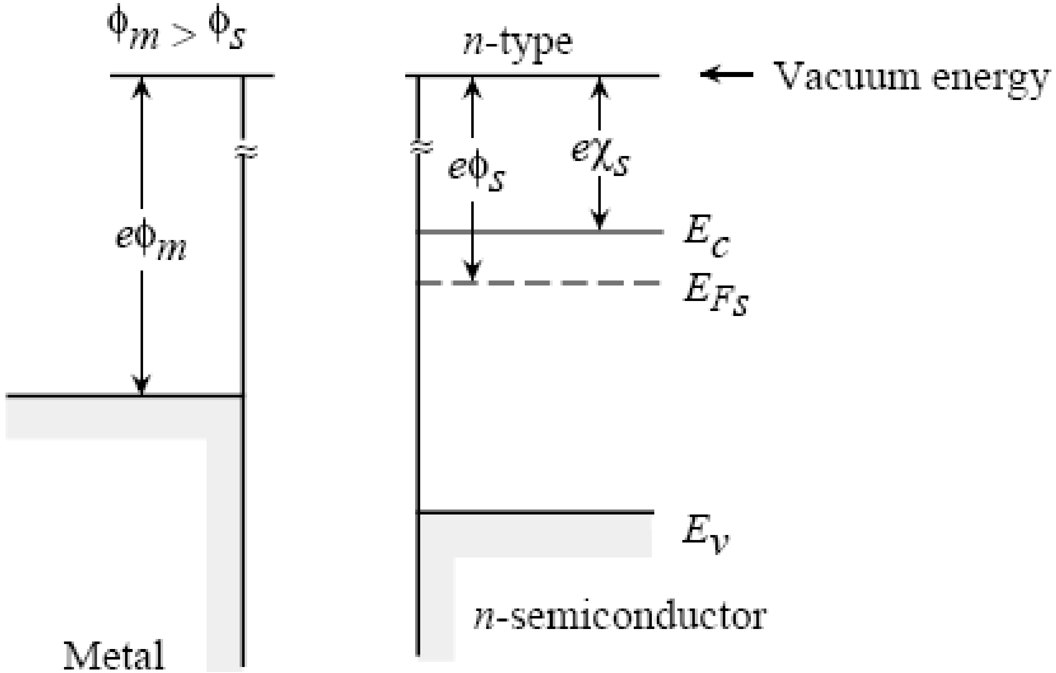
Published Online: Jan 4 2010 8:30AM

DOI: 10.1002/adma.200903528 **Advanced Materials**

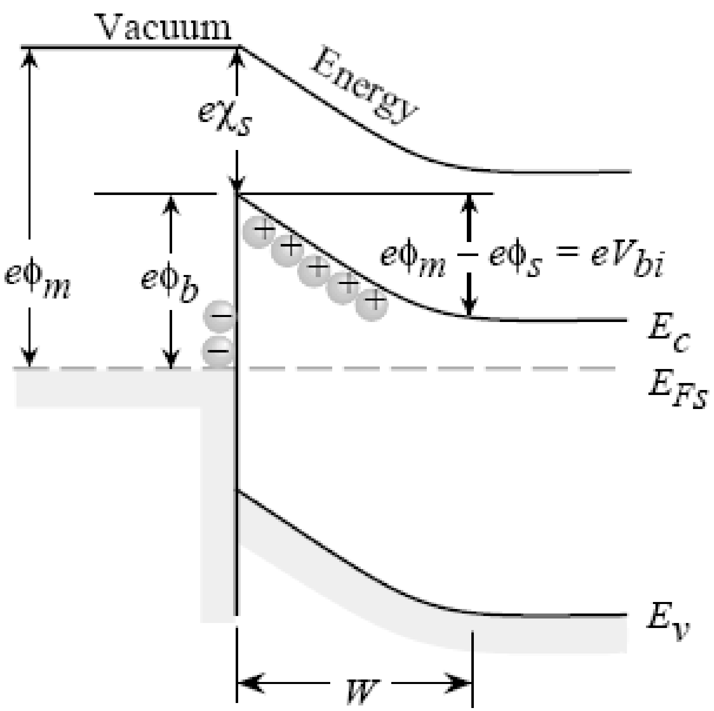
portable, electric-generating buildings for the military.



Metal/semiconductor junction for n-type semiconductor

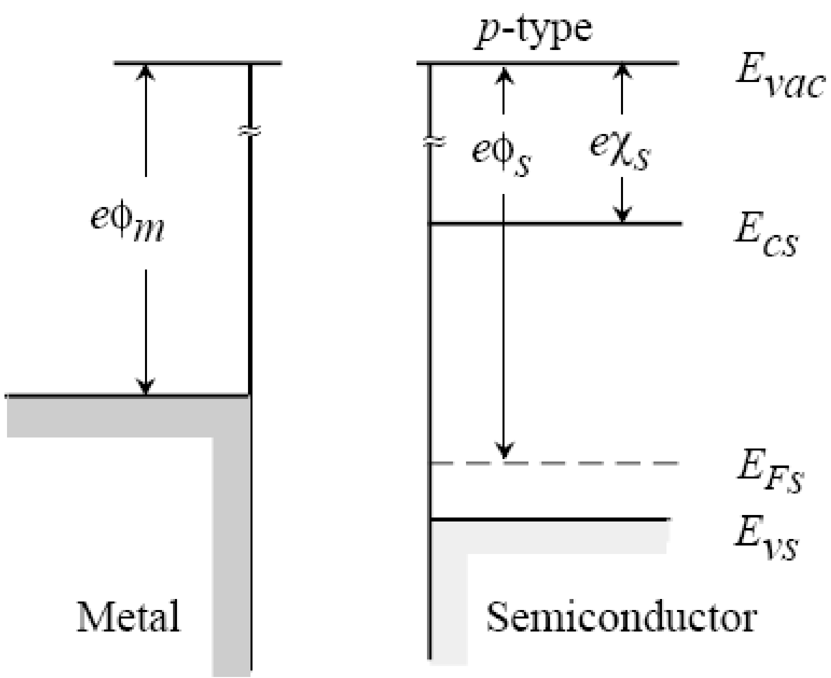


Before junction formation

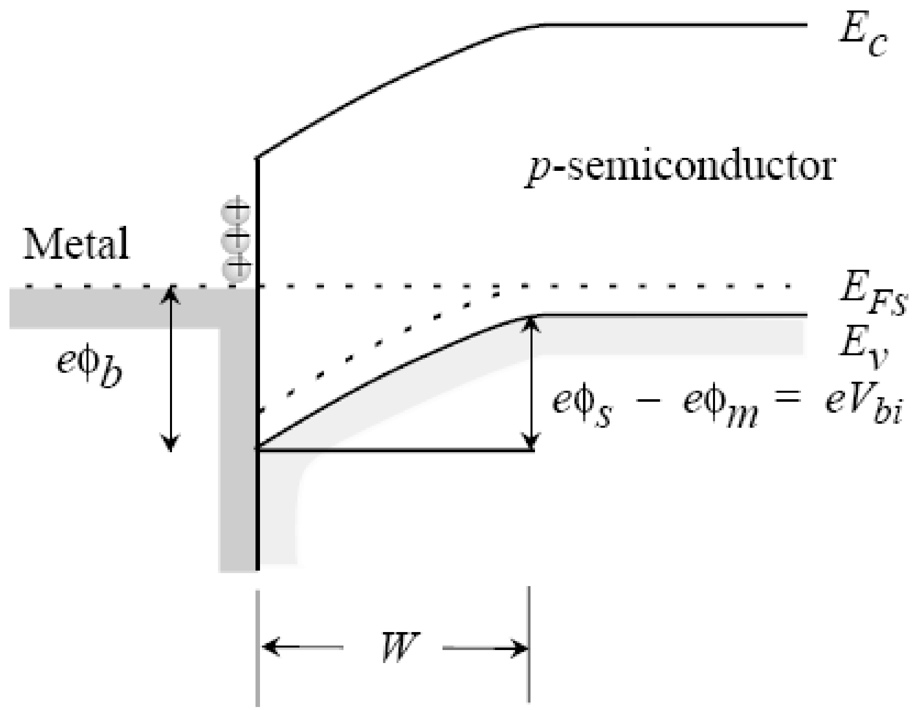


After junction formation

Metal/semiconductor junction for p-type semiconductor

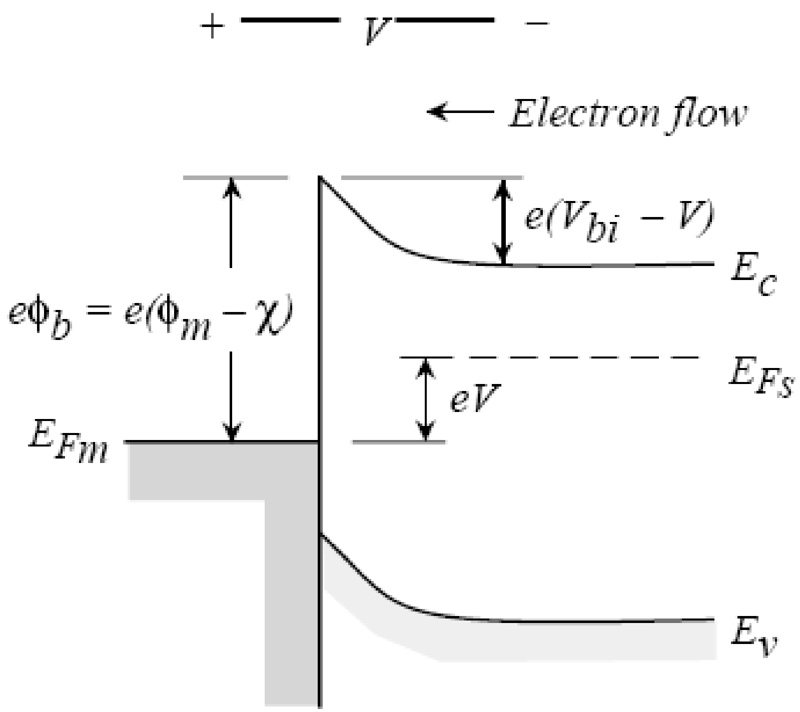


Before junction formation

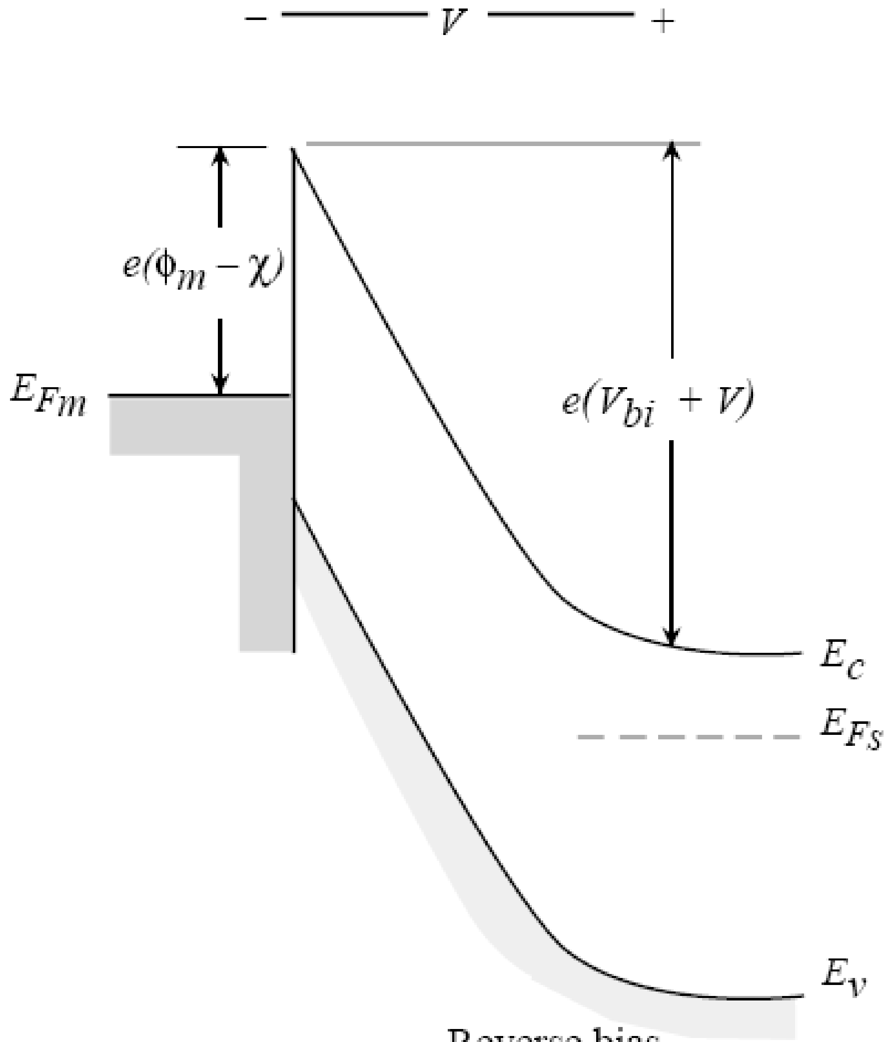


After junction formation

Metal/semiconductor junction: forward and reverse bias

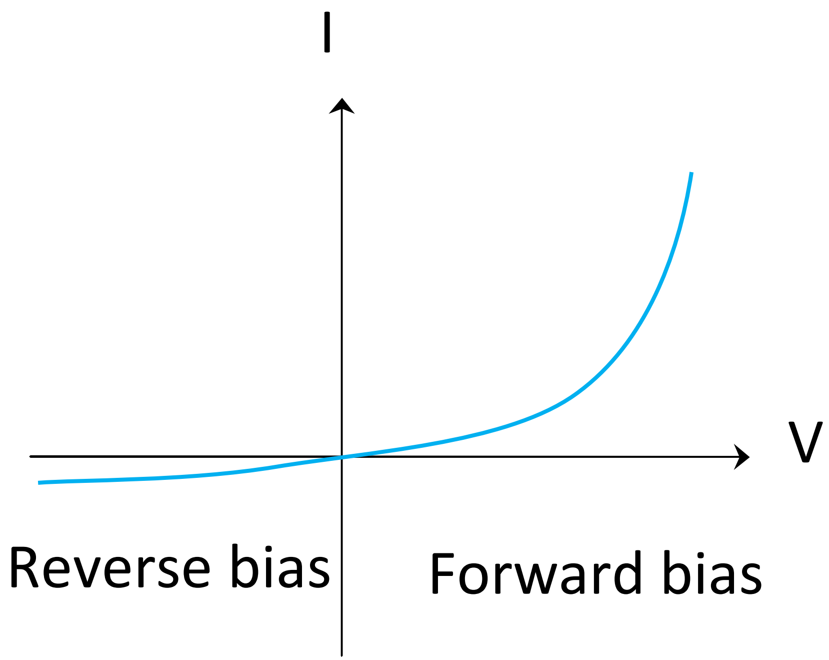


Forward bias



Reverse bias

Current flowing through metal/semiconductor Schottky diode

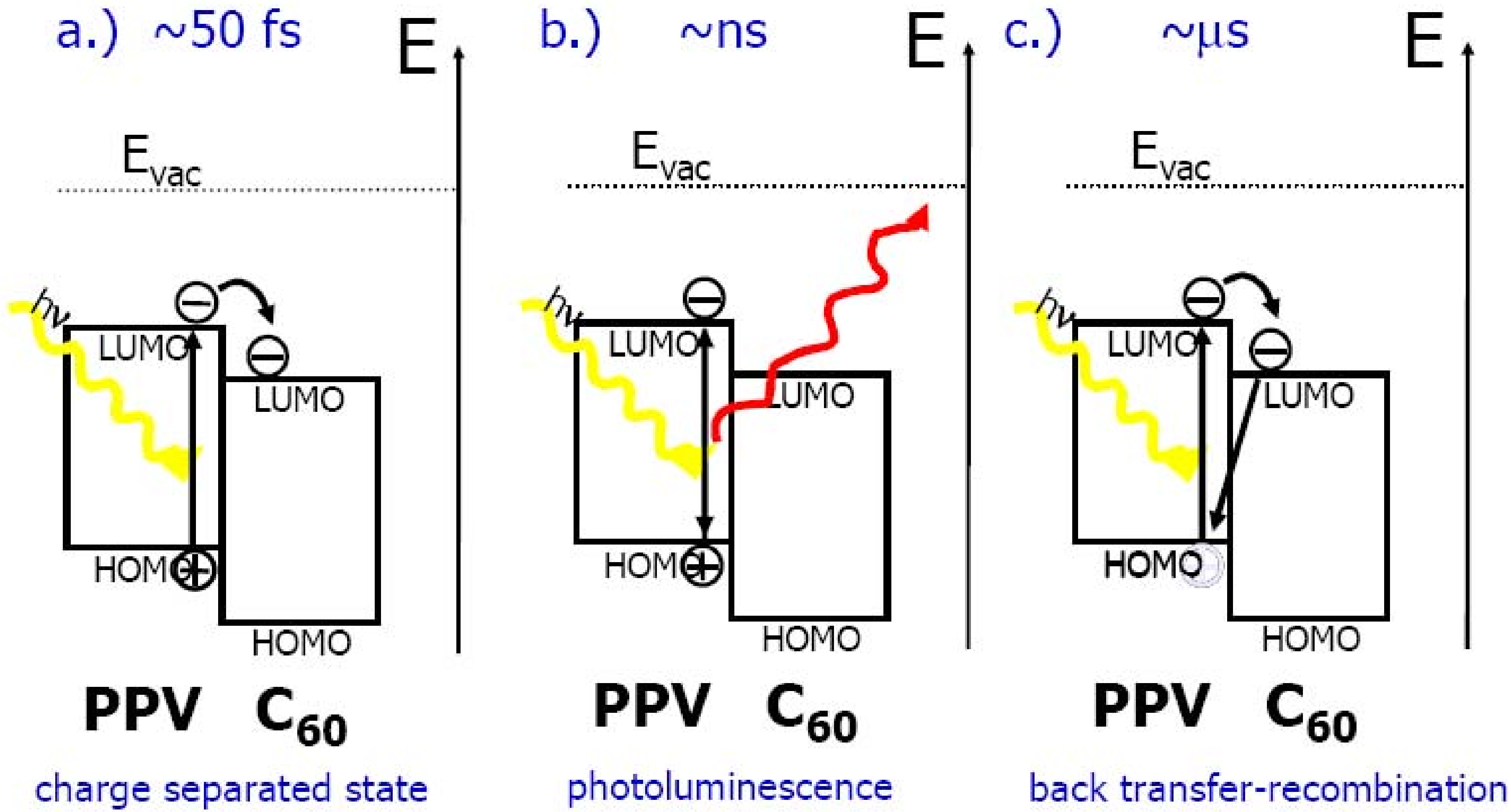


$$I = I_s \left[\exp\left(\frac{eV}{k_B T} \right) - 1 \right]$$

$$I_s = A \left(\frac{m^* e k_B^2}{2\pi^2 h^3} \right) T^2 \exp\left(\frac{-e\phi_b}{k_B T} \right)$$

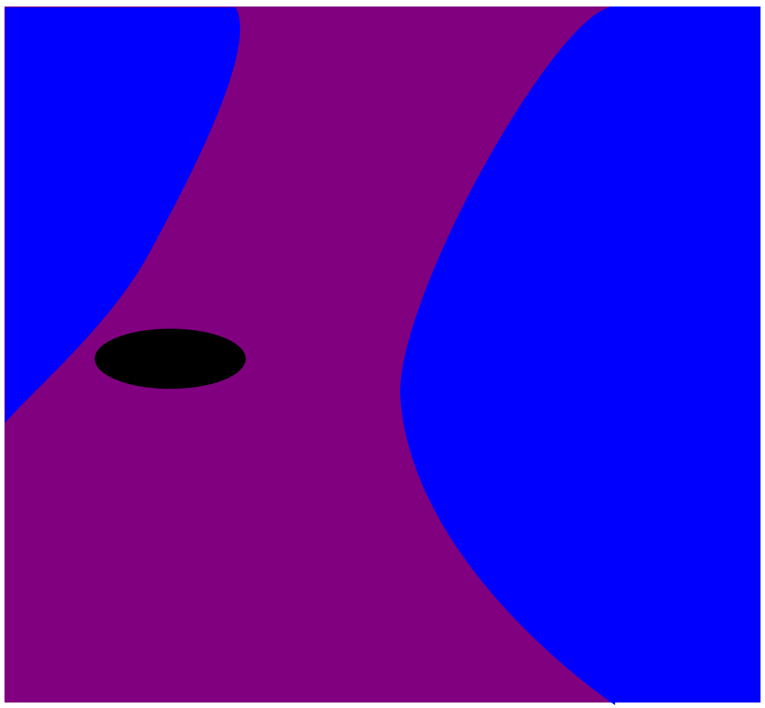
$$= AR^* T^2 \exp\left(\frac{-e\phi_b}{k_B T} \right)$$

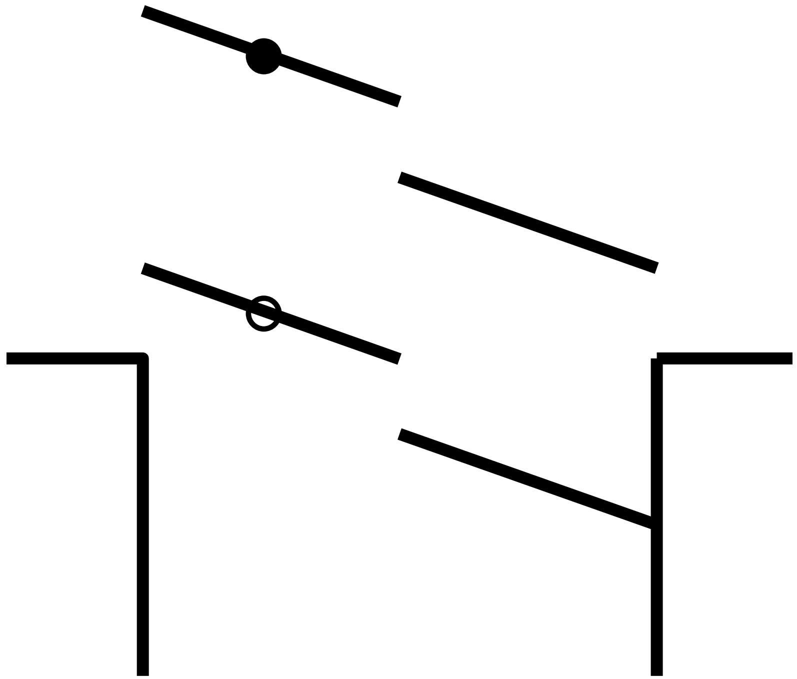
Richardson constant R^*


a.) ~50 fs
E
E
vac
hv
LUMO
LUMO
HOMO
HOMO
PPV
C
60
charge separated state
b.) ~ns
E
E
vac
hv
LUMO
LUMO
HOMO
HOMO
PPV
C
60
photoluminescence
c.) ~μs
E
E
vac
hv
LUMO
LUMO
HOMO
HOMO
PPV
C
60
back transfer-recombination

heterojunctions

- Exciton is generated and diffuses to interface

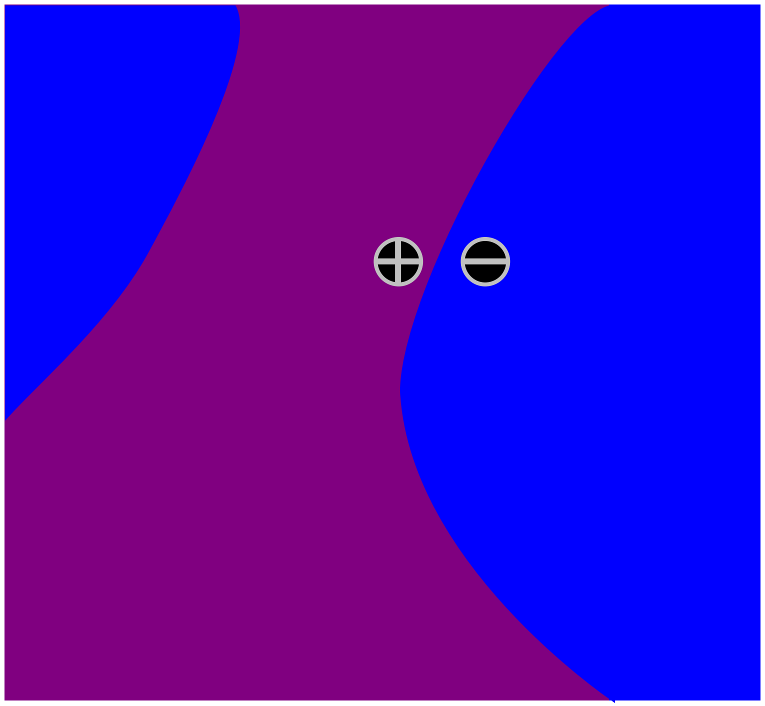


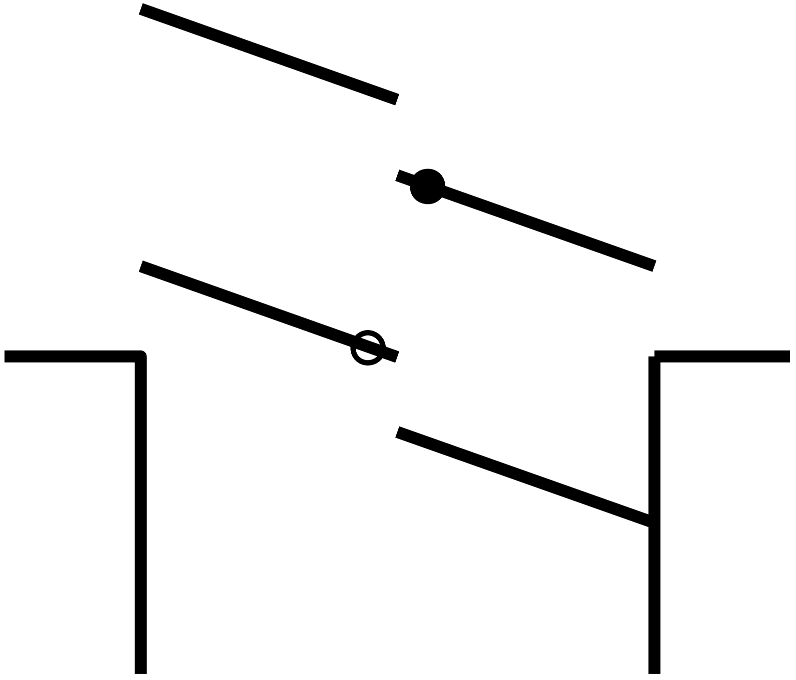


Hole transporter / Electron transporter

heterojunctions

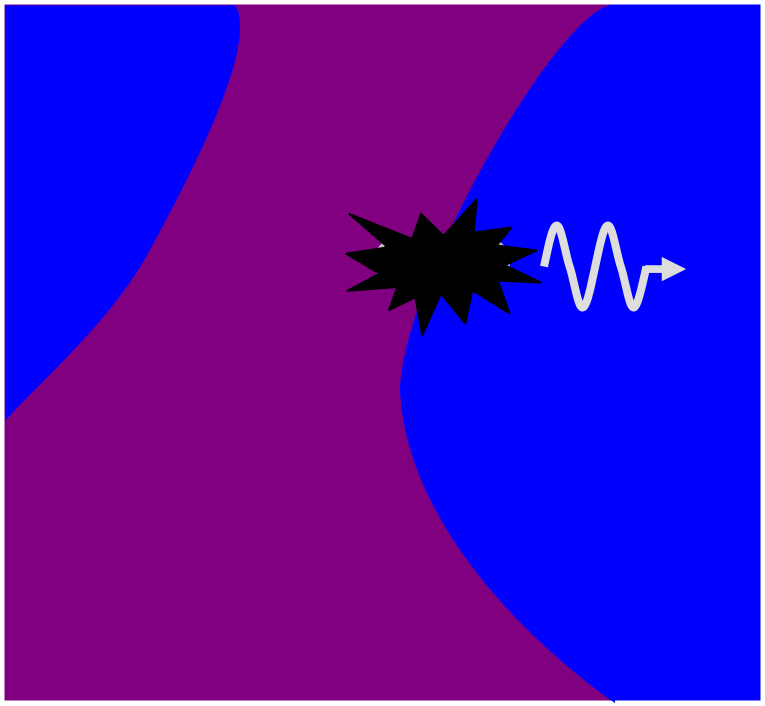
- Charge is transferred across the junction



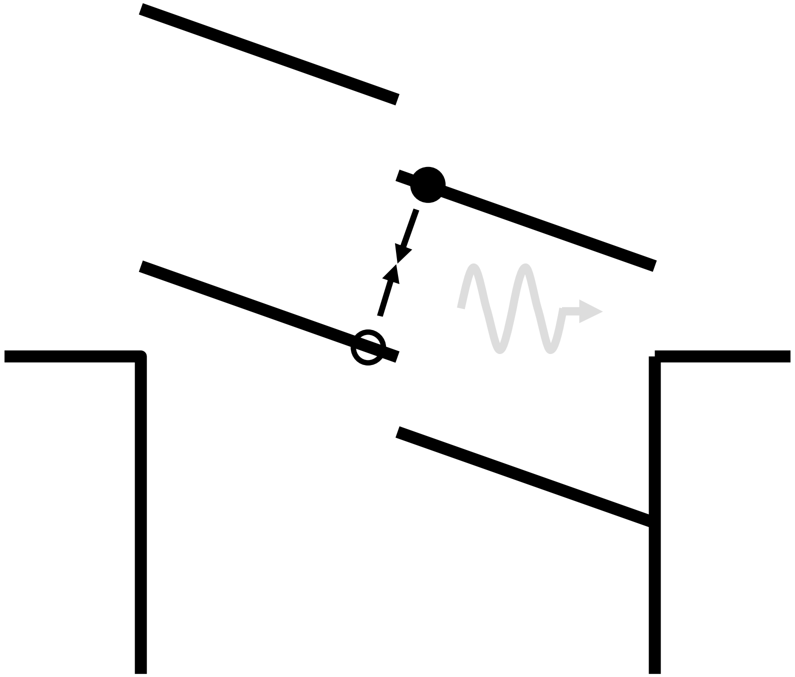


heterojunctions

- Charges either recombine or escape



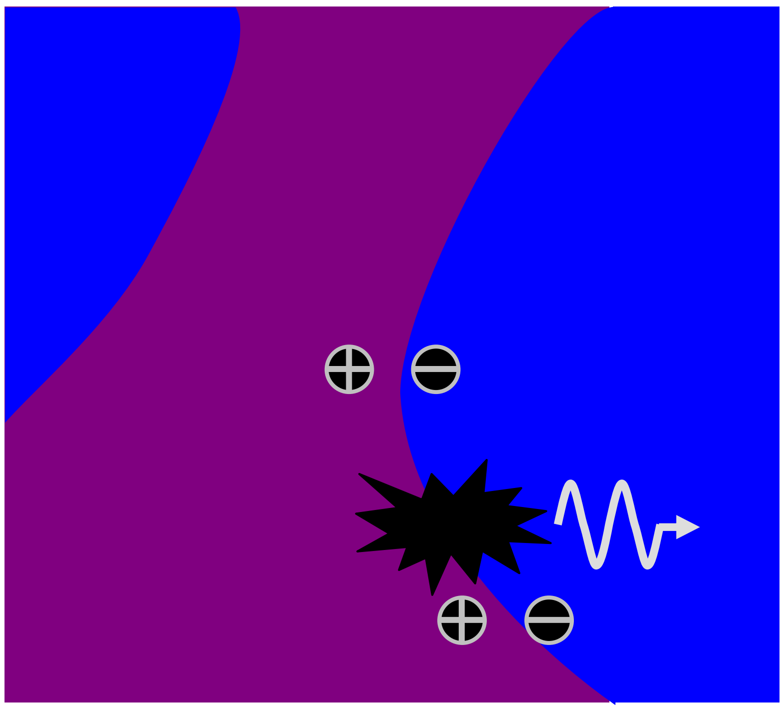
Geminate recombination



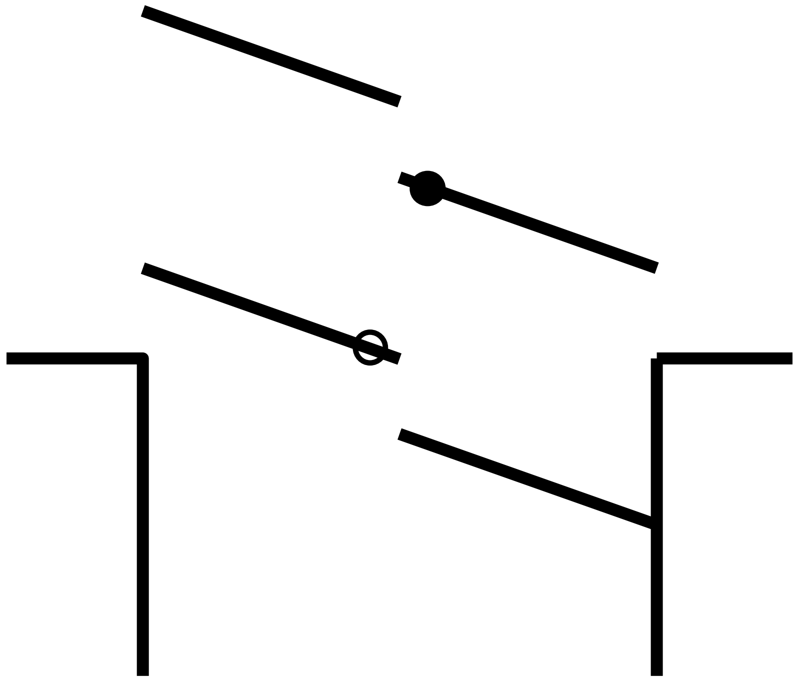
Hole transporter / Electron transporter

Bulk heterojunctions

- Charges either recombine or escape



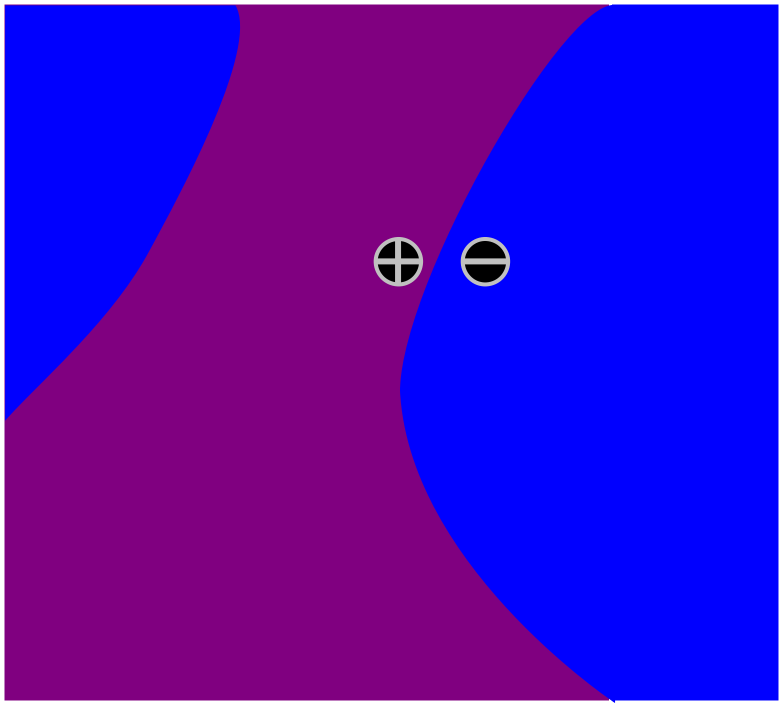
Bimolecular recombination



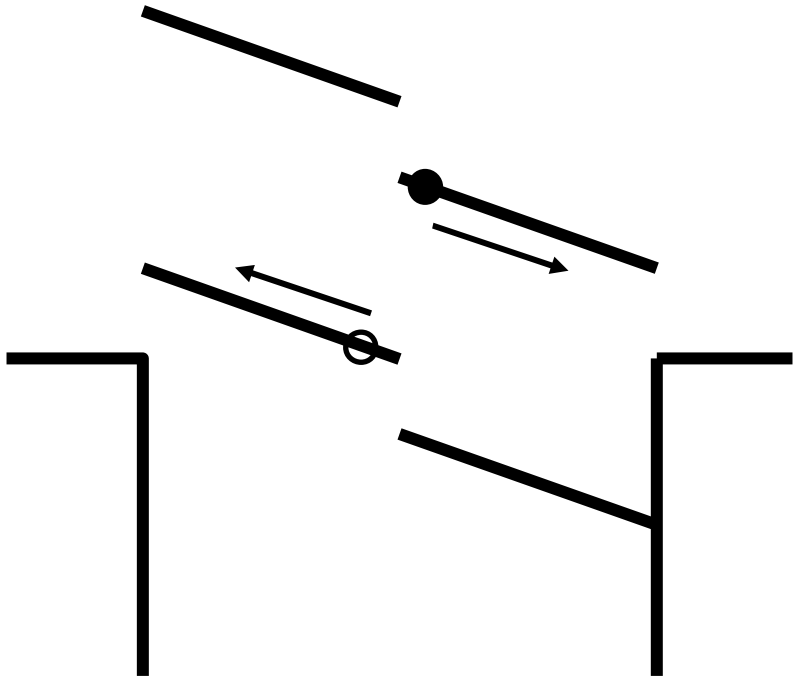
Hole transporter / Electron transporter

Bulk heterojunctions

- Charges either recombine or escape



Charges drift to electrodes



Hole transporter / Electron transporter

Efficiency

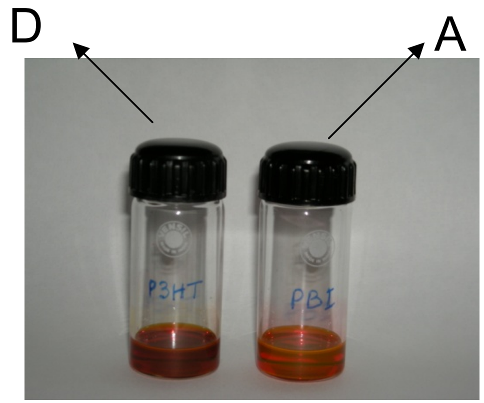
- Total efficiency is found by multiplying the efficiency of all the steps described above

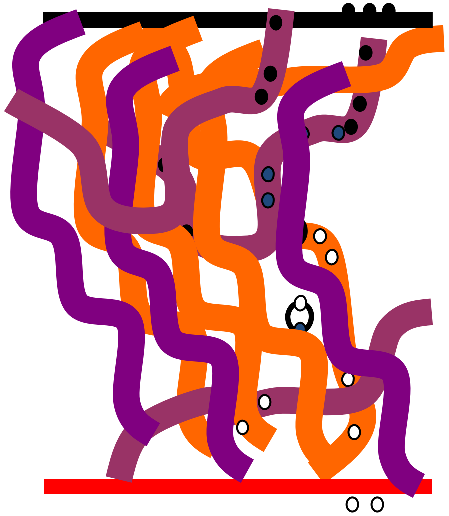
- $\eta = \eta_{abs} \cdot \eta_{exdiff} \cdot \eta_{sep} \cdot \eta_{coll}$

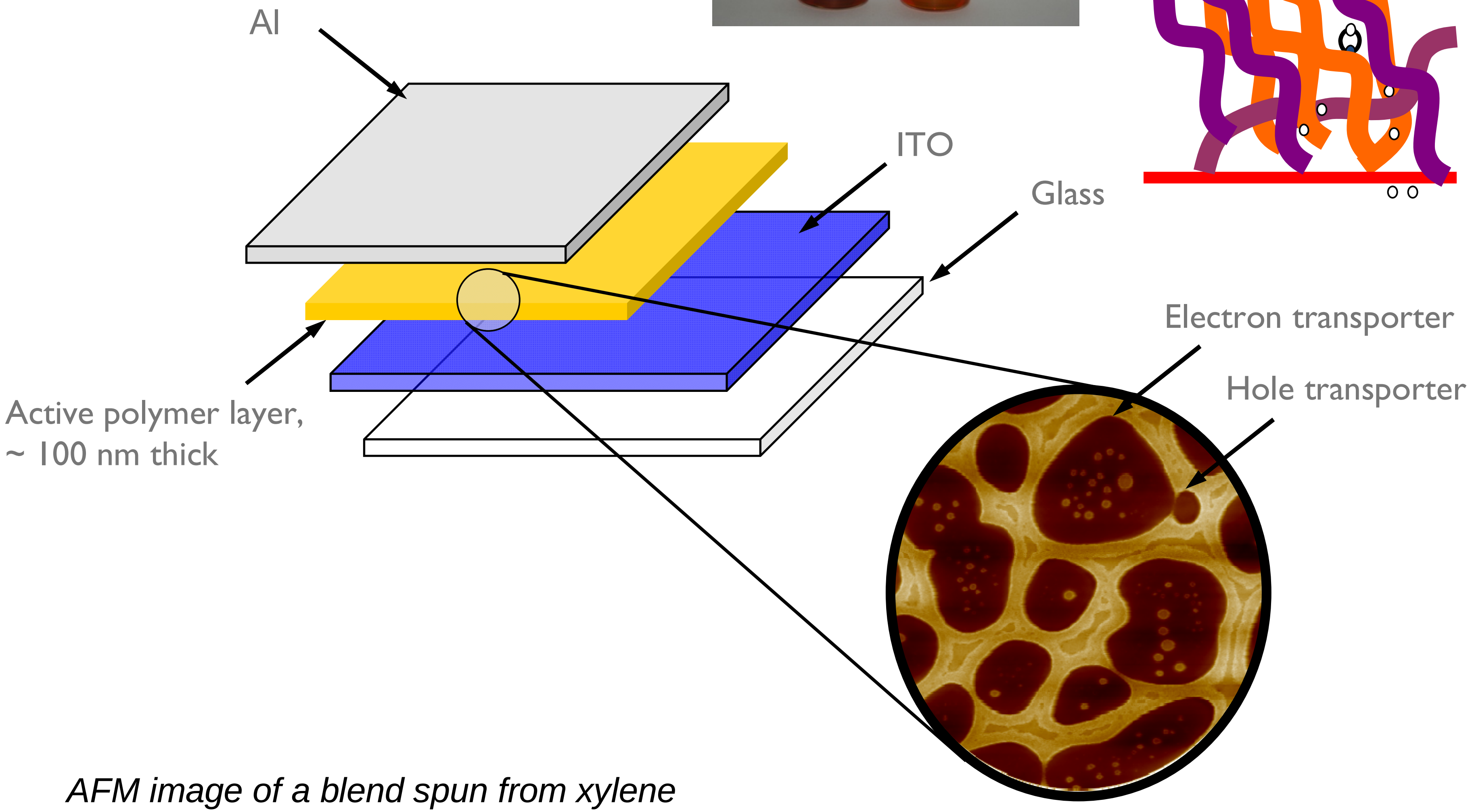
- Trade-offs between step-efficiencies are often necessary.

E.g. A thicker device would increase η_{abs} but (by lowering the external field) reduce η_{sep}

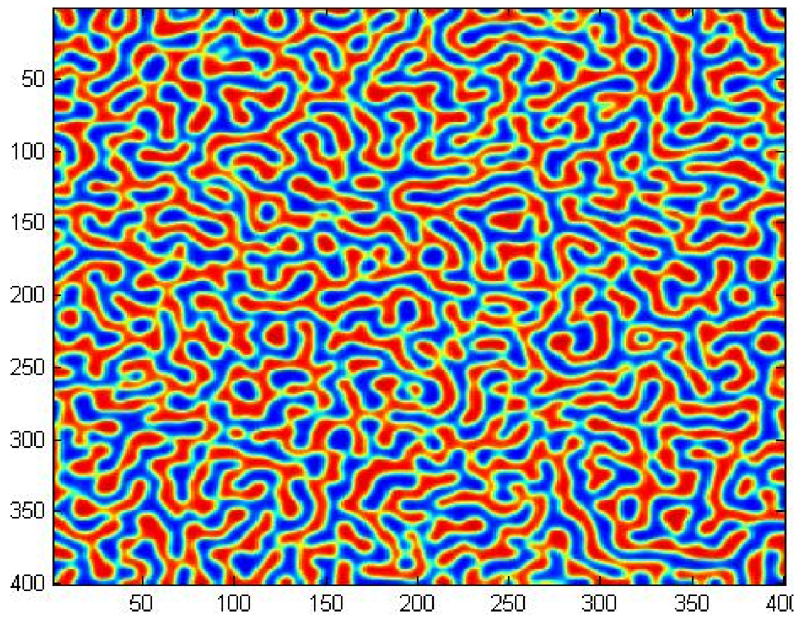
Bulk heterojunctions (BHJ)

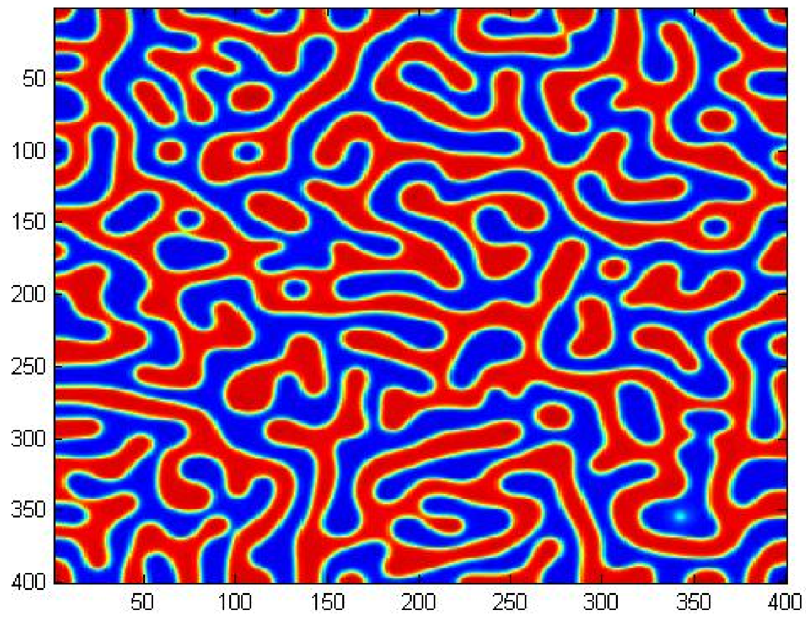






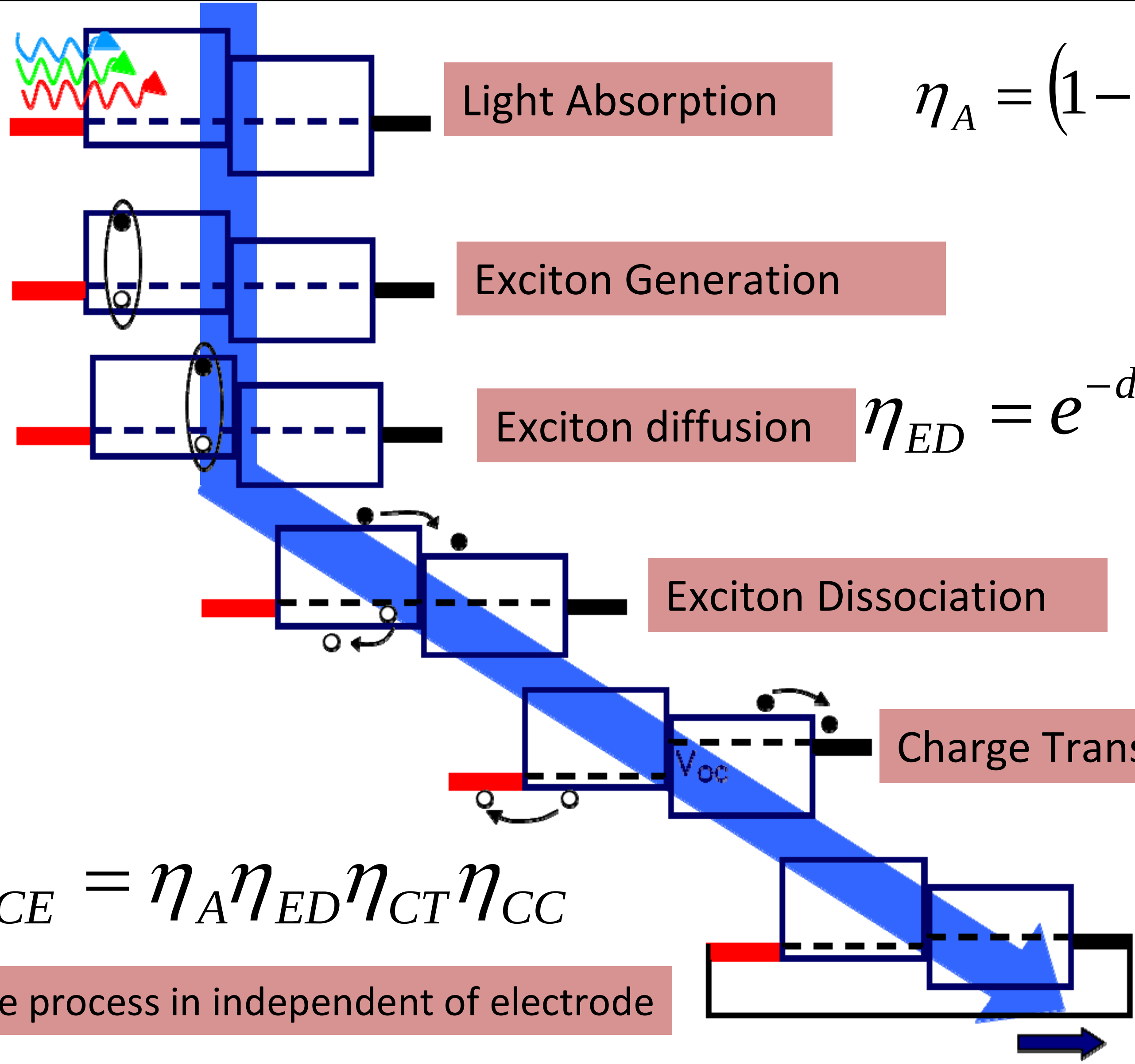
AFM image of a blend spun from xylene





BLEND Bulk Heterostructure Solar Cells

Incident Photon to Current Conversion in BHJ



$$\eta_A = \left(1 - e^{-\alpha(\lambda)d}\right)$$

$$\eta_{ED} = e^{-d/L_d}$$

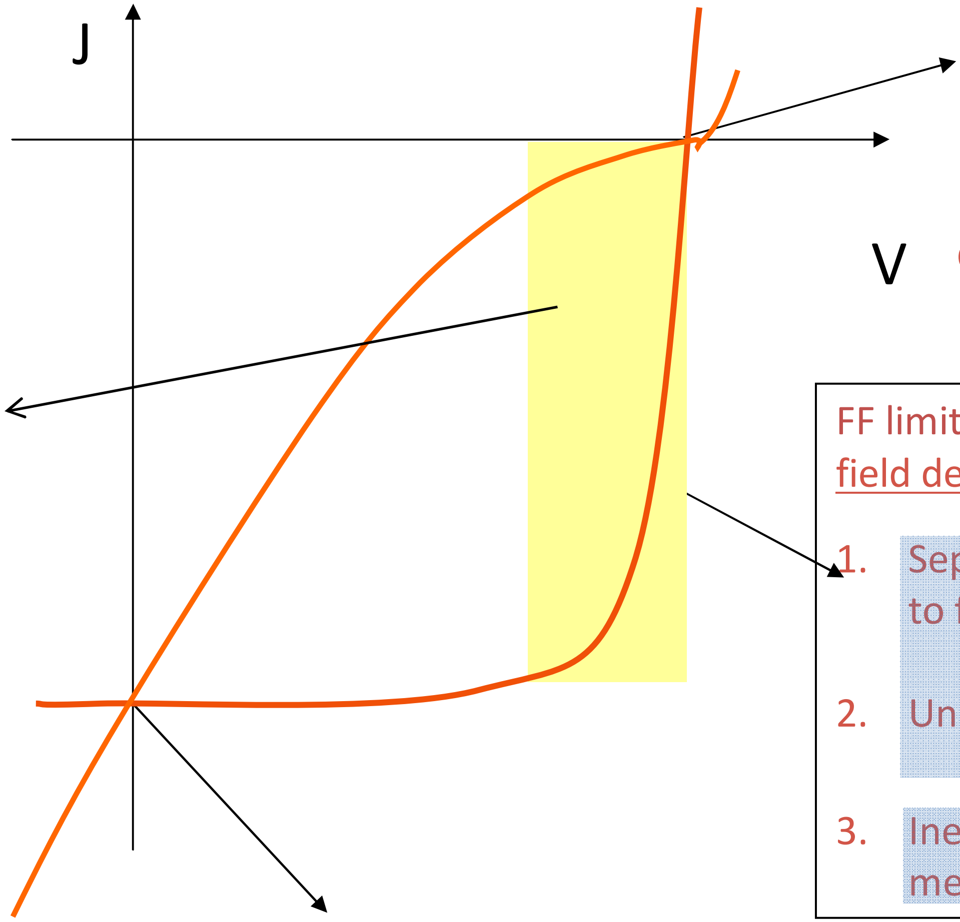
$$\eta_{CT}$$

$$\eta_{CC}$$

$$\eta_{IPCE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

Whole process in independent of electrode

η_{CC} and FF



V_{oc} limited by:
Donor-acceptor energy levels

$V_{sat} < V < V_{OC}$
Low effective field region, strong field dependence of exciton dissociation rate changes the curvature

FF limited by:
field dependence of η_{CC}

1. Separation of geminate e-h pair to form free carriers.

Transport (Bulk)

2. Unbalanced 'e' and 'h' transport.

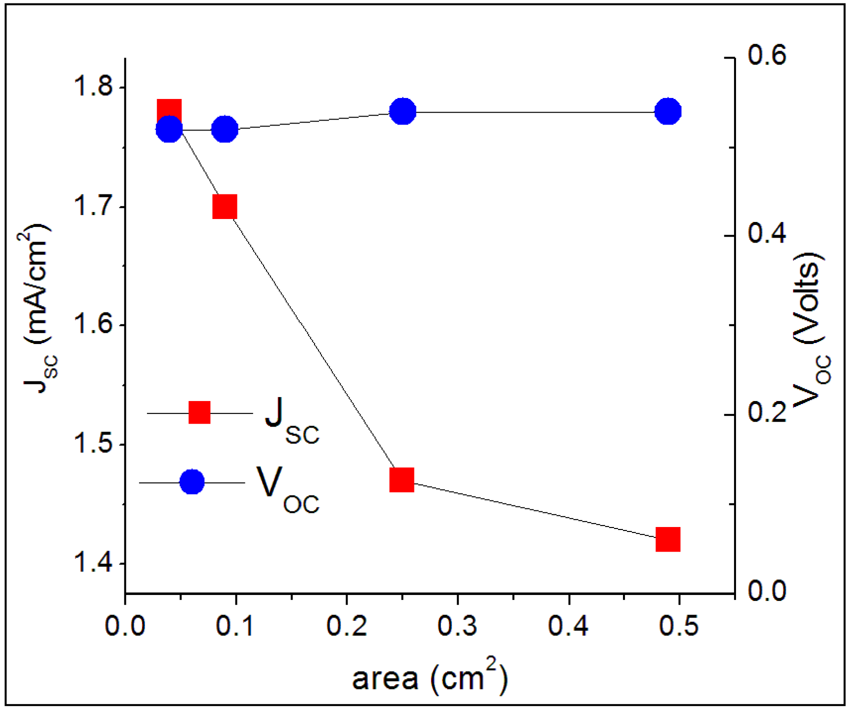
3. Inefficient collection at the metal-polymer interface.

Collection (Interface)

J_{sc} limited by: η_{IPCE}

$$J_{sc} = q\int \text{photon flux density}(\lambda) \times \eta_{\text{IPCE}}(\lambda)\, d\lambda$$

- Power conversion efficiency for a BHJ-PSC not a universal constant.
- Device dimensions extremely critical.



Narayan et. al.
Appl. Phys. Lett. 2008
SPIE News 2009