Hybrid solar energy conversion

Winterschool 2018

theoretical chemistry & spectroscopy

Elizabeth von Hauff

e.l.von.hauff@vu.nl

VU VRIJE UNIVERSITEIT AMSTERDAM

Outline

1) Photovoltaic energy conversion

2) Organic solar cells
   - Charge separation
   - Charge transport
   - State of the art and open questions

3) Perovskite solar cells

Organic semiconductors

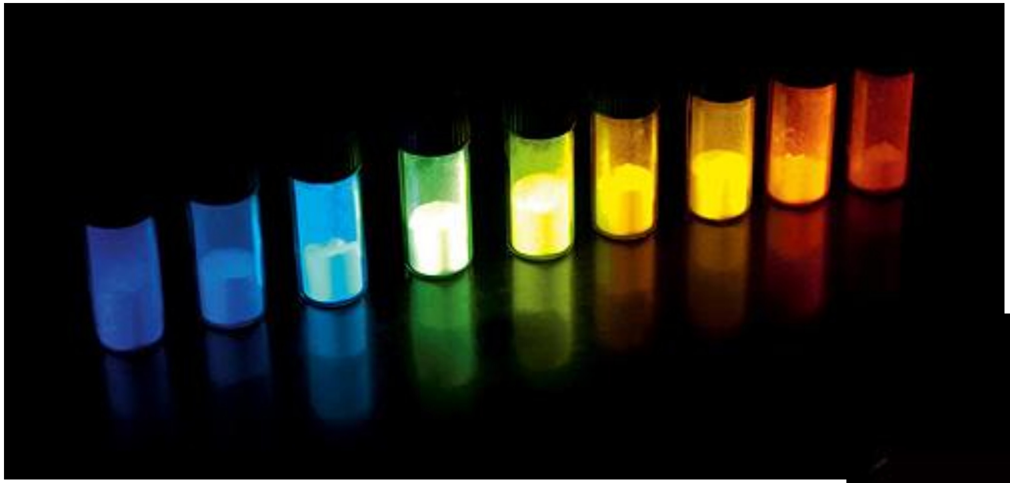
- Molecules as semiconductors
  - Electronic structure
  - Bandgap
  - Optical properties
  - Vibrational properties

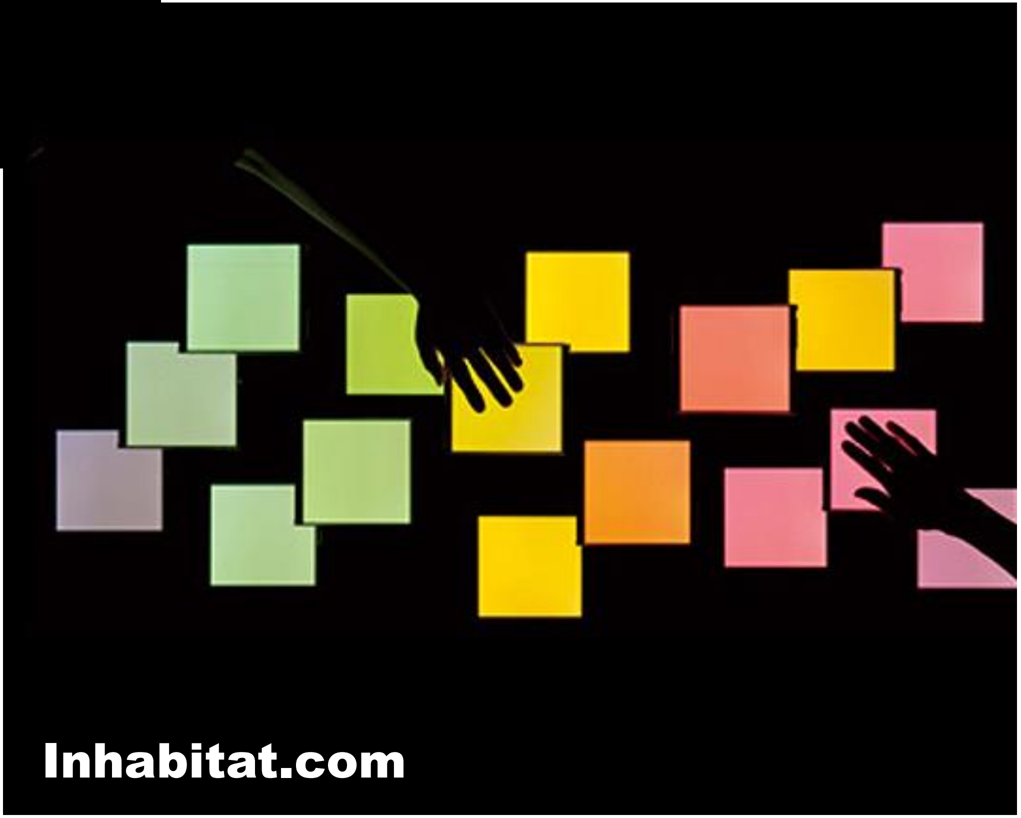
- Donor-acceptor interfaces: charge seperation

- Molecular films and solids

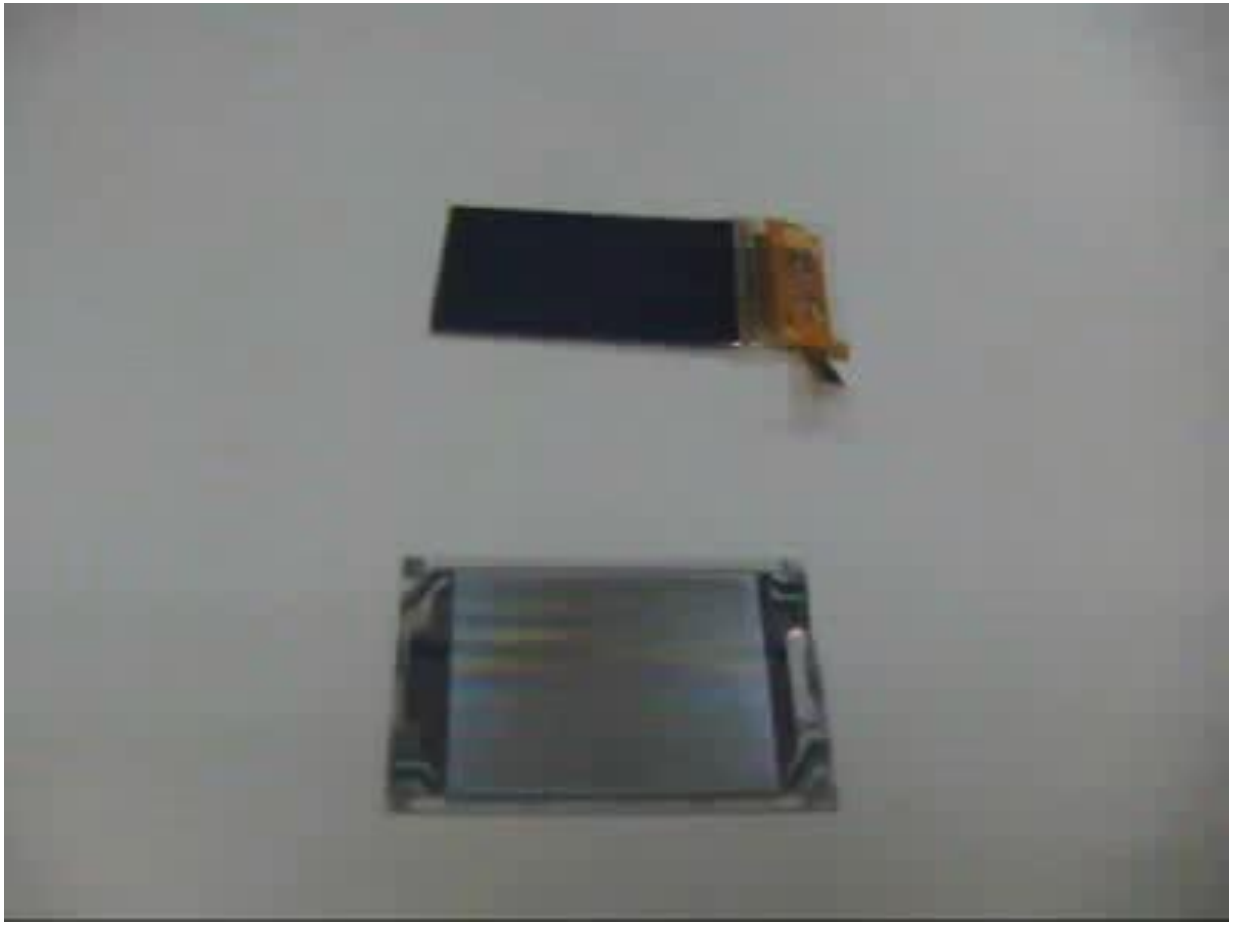
- Device physics of organic solar cells

Advantages – optical properties





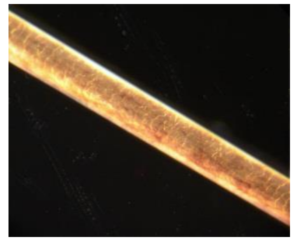
Advantages – mechanical properties



Samsung

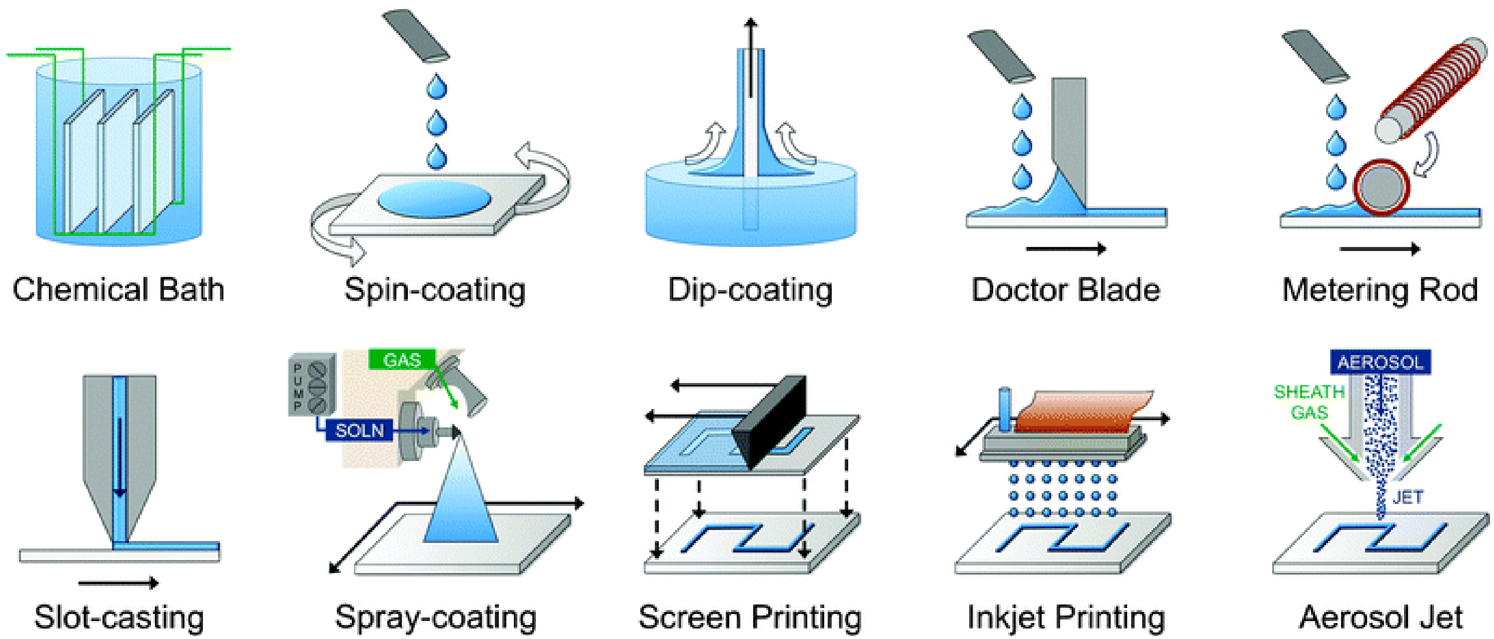
Advantages – Processing

Material reduction



Active layer is 100 nm
(1/100th of a human hair)

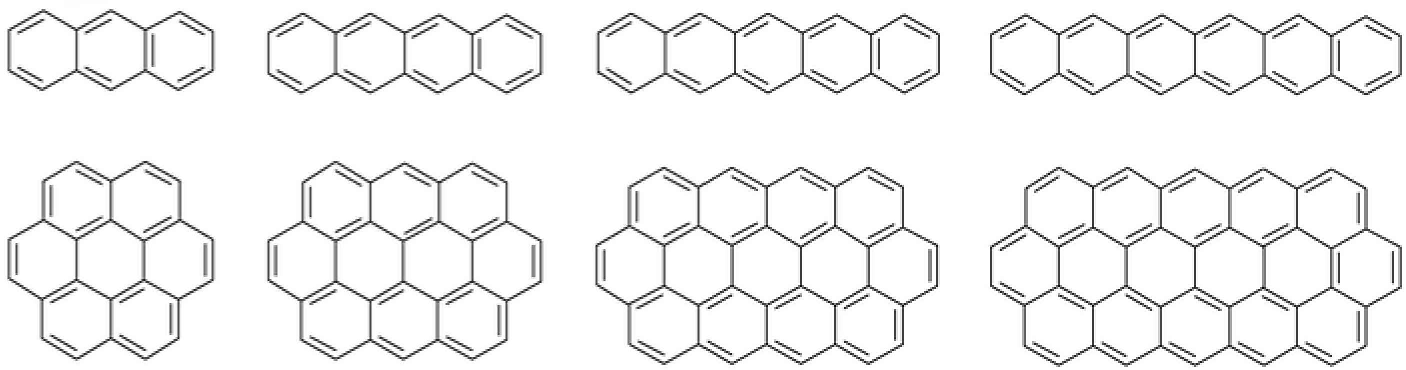
Low cost, large scale processing from solution

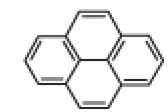


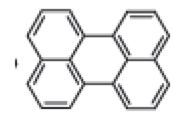
Chem. Soc. Rev., 2011, 40, 5406-5441

Endless possibilities

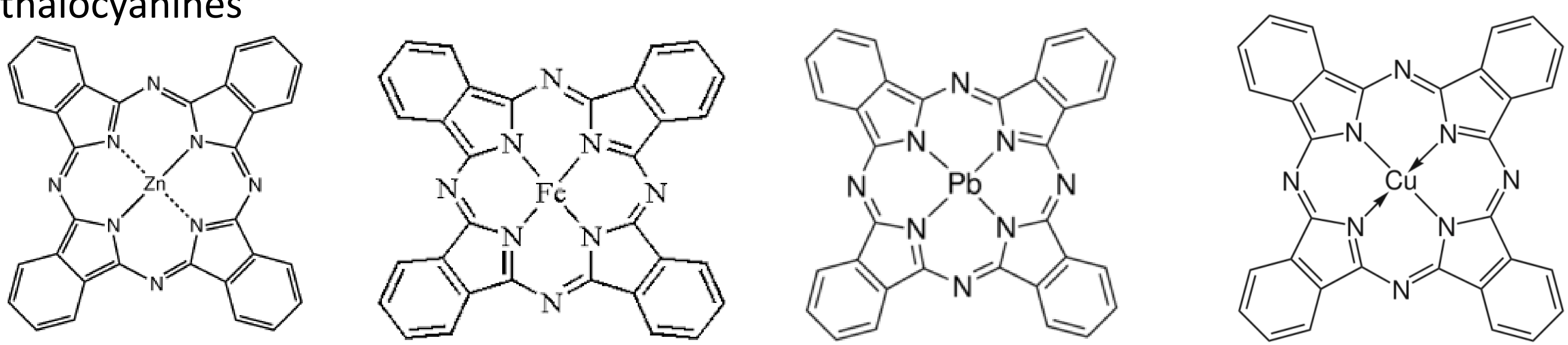
Ancenes



Pyrene 

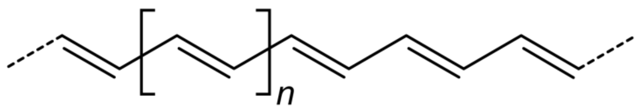
Perylene 

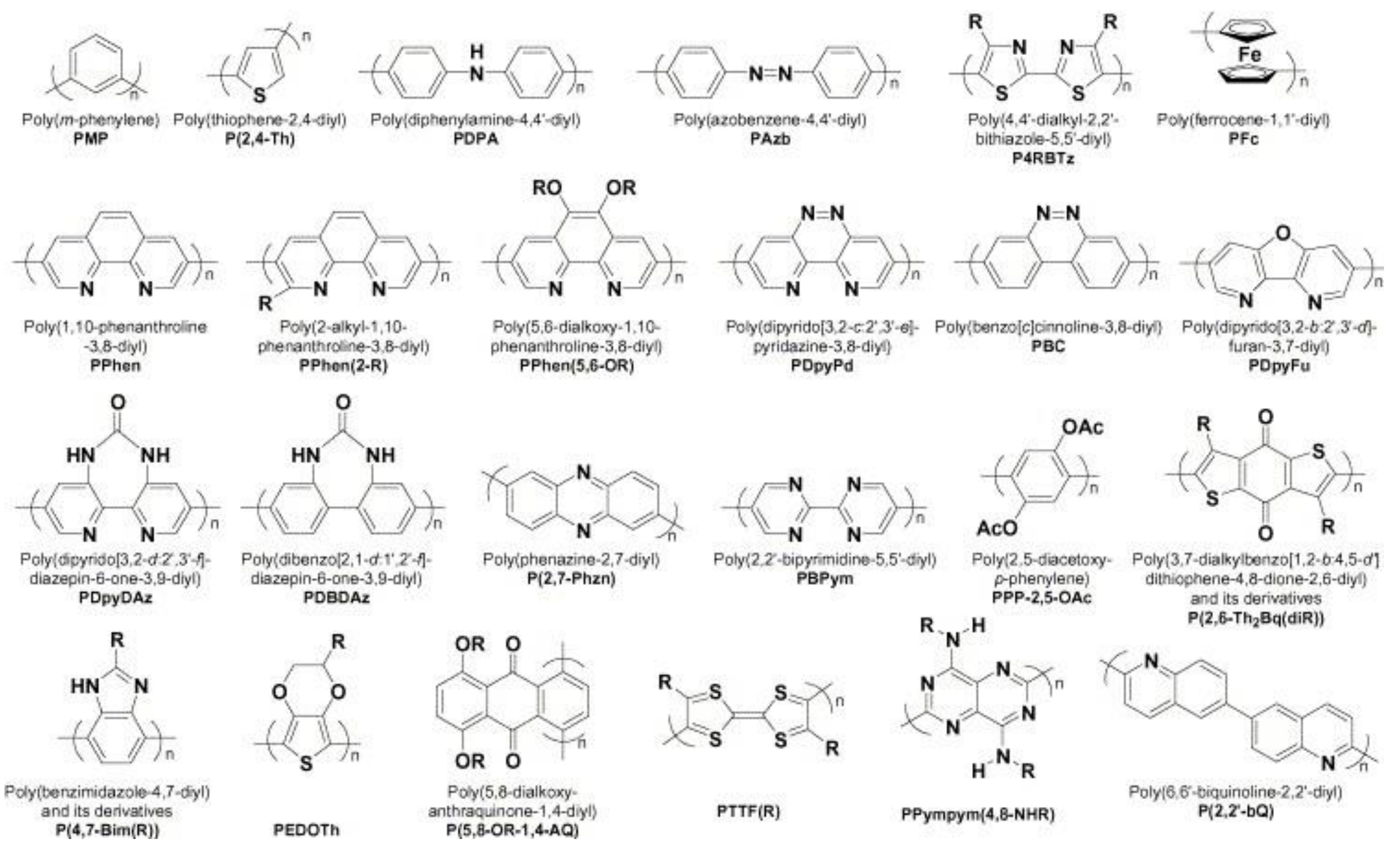
Phthalocyanines



Endless possibilities

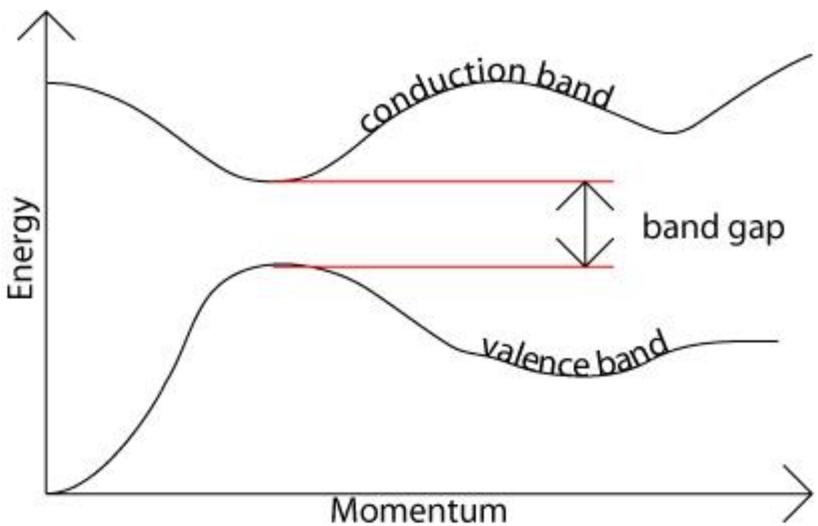
Polymers





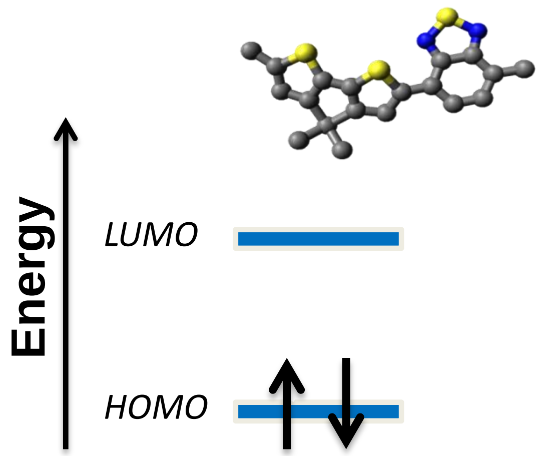
Inorganic vs organic semiconductors

Inorganic semiconductors



- ❑ **photon promotes electron into continuum of states in conduction band**

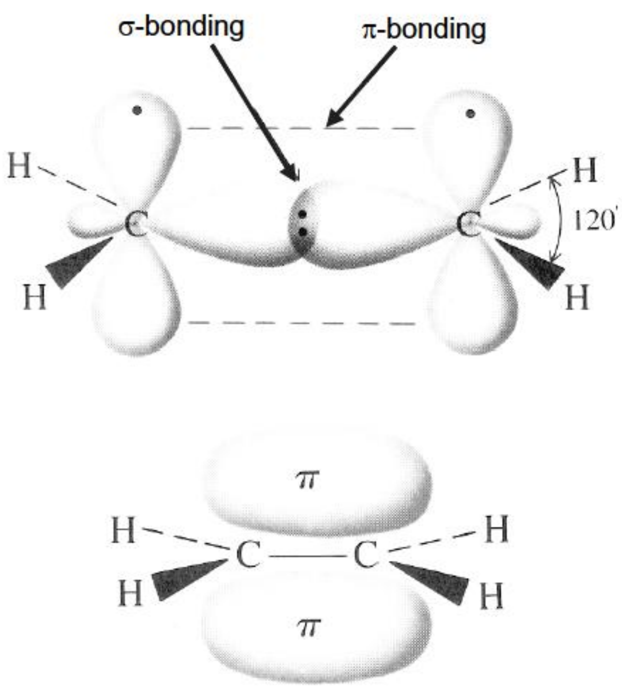
Organic semiconductors

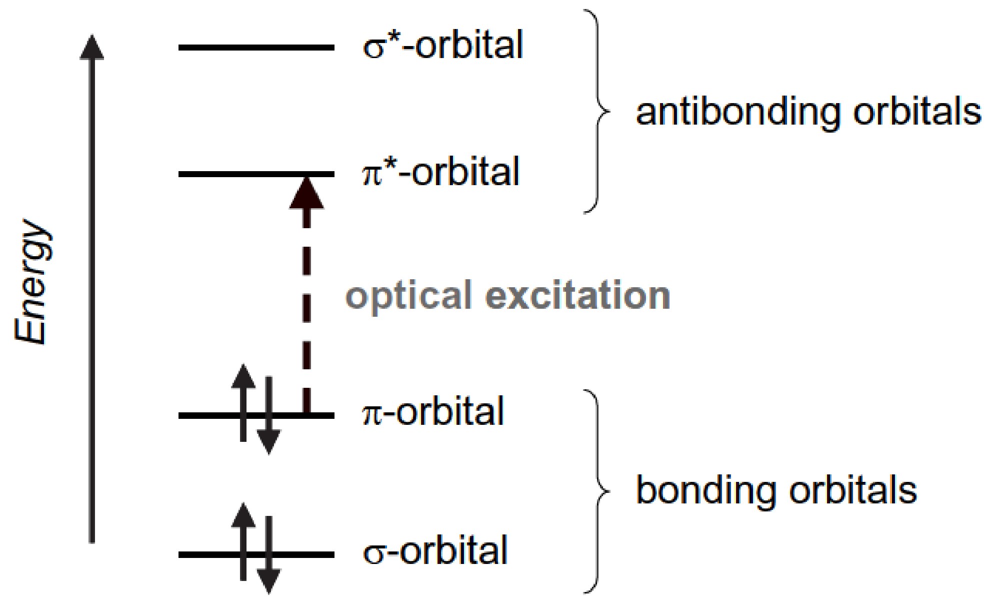


- ❑ **Closed shell molecules**
- ❑ **Photon promotes electron into discrete states**
- ❑ **Electrical transport complex**

Optical bandgap

- Single bonds = σ bond (covalent, in molecular plane)
- Double bonds = π bond (delocalised, perpendicular to σ bonds)
- Optical excitation of π bonds in the visible regime

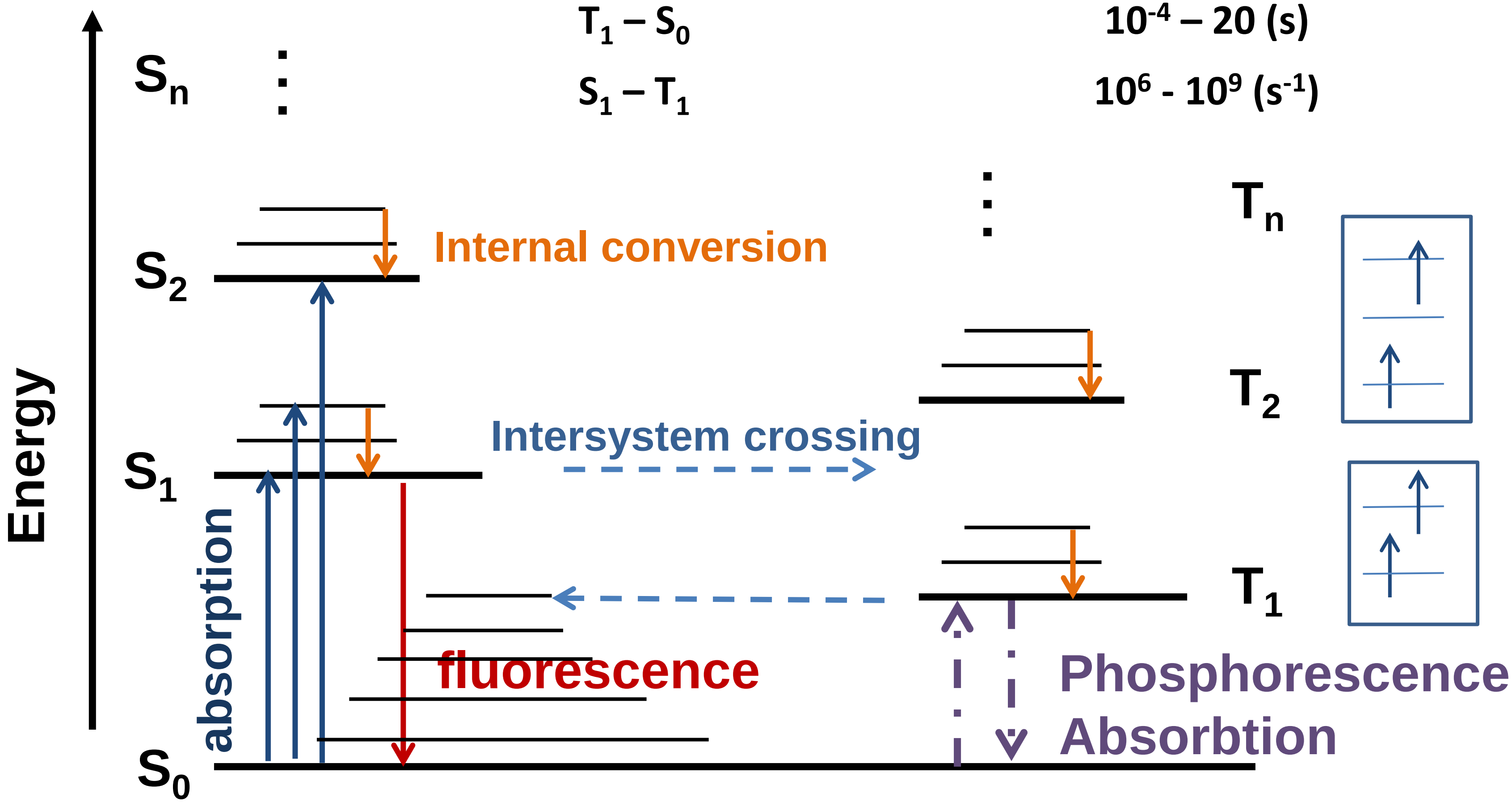




W. Bruetting, Uni Augsburg

Excited states in organic semiconductors

Transition	Lifetime (s)/Rate (s^{-1})
$S_1 - S_0$	$10^{-9} - 10^{-6}$ (s)
$T_1 - S_0$	$10^{-4} - 20$ (s)
$S_1 - T_1$	10^{6} - 10^{9} (s^{-1})



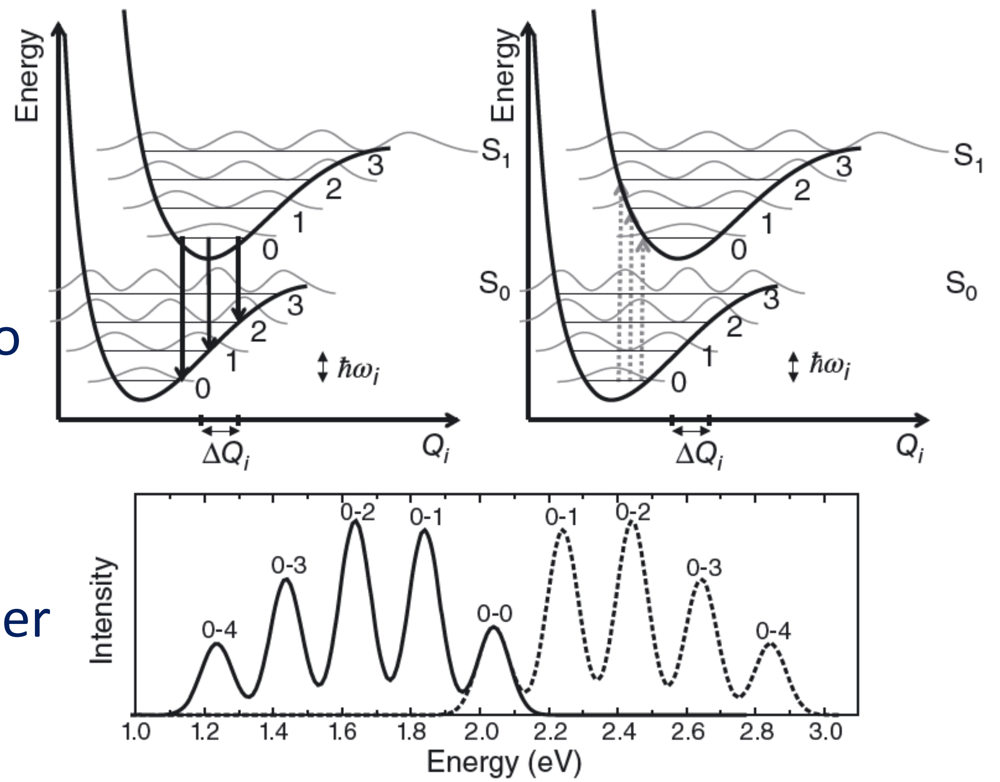
Absorption/emission

<u>Electronic transitions</u>

- Emission is characteristically red shifted when compared to absorption (Stokes shift)

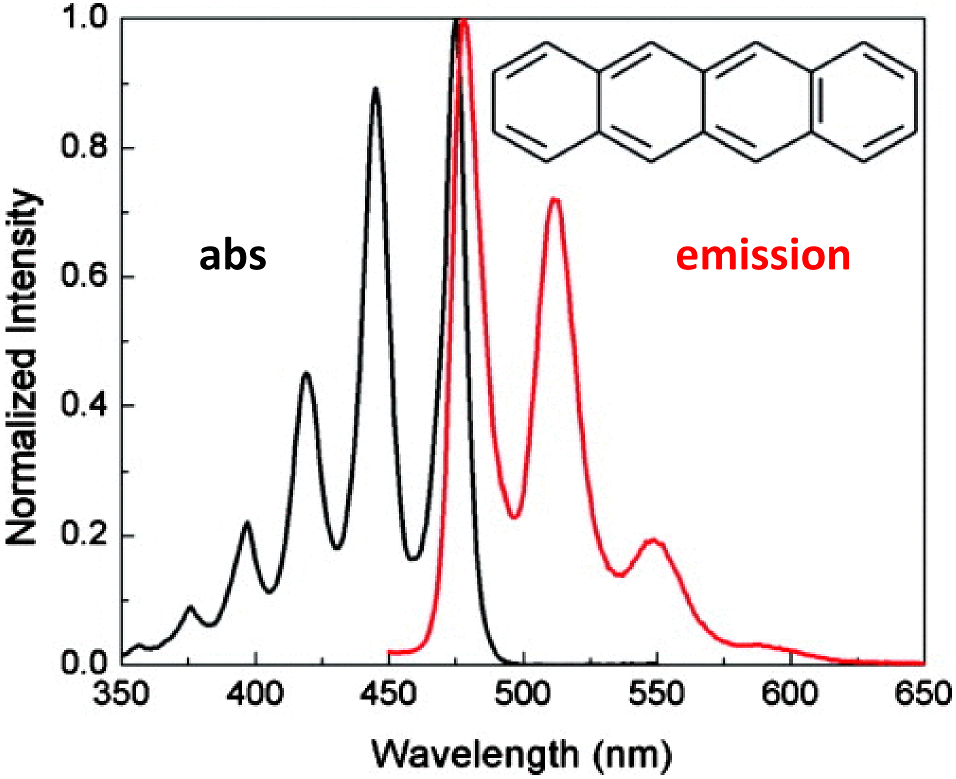
- Absorption – from ground state to a higher vibrational state (e.g. $S_{0\text{-}2} \rightarrow S_{1\text{-}3}$)

- Emission – from a lower to a higher vibrational state (e.g. $S_{1\text{-}0} \rightarrow S_{0\text{-}3}$)



Electronic processes in organic semiconductors, Kohler, Baessler

Example: tetracene



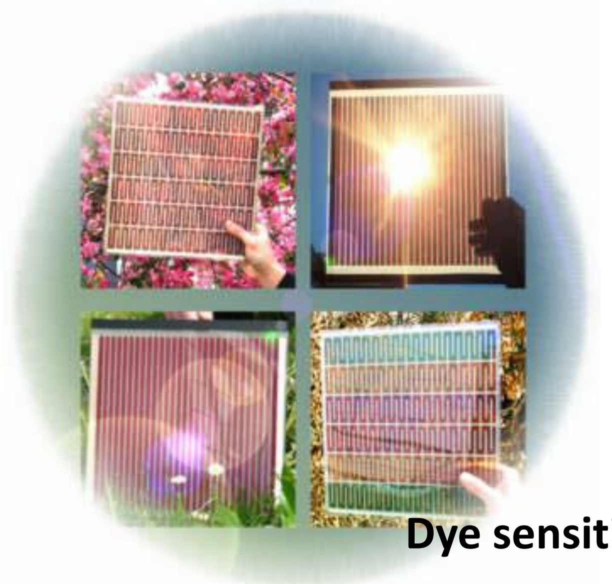
Burdett, J Chem Phys, 2011

Organic molecules in photovoltaics

Organic solar cells are sometimes compared to dye sensitised or Grätzel solar cells

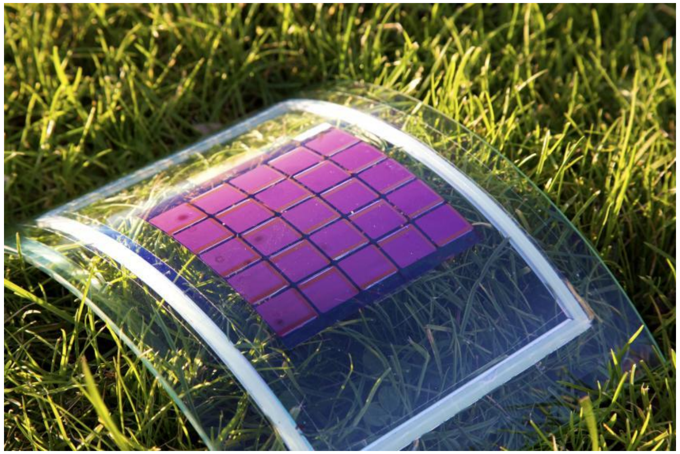
Similarity use of organic molecules for light absorption

Difference electrochemical vs solid state device



Dye sensitised

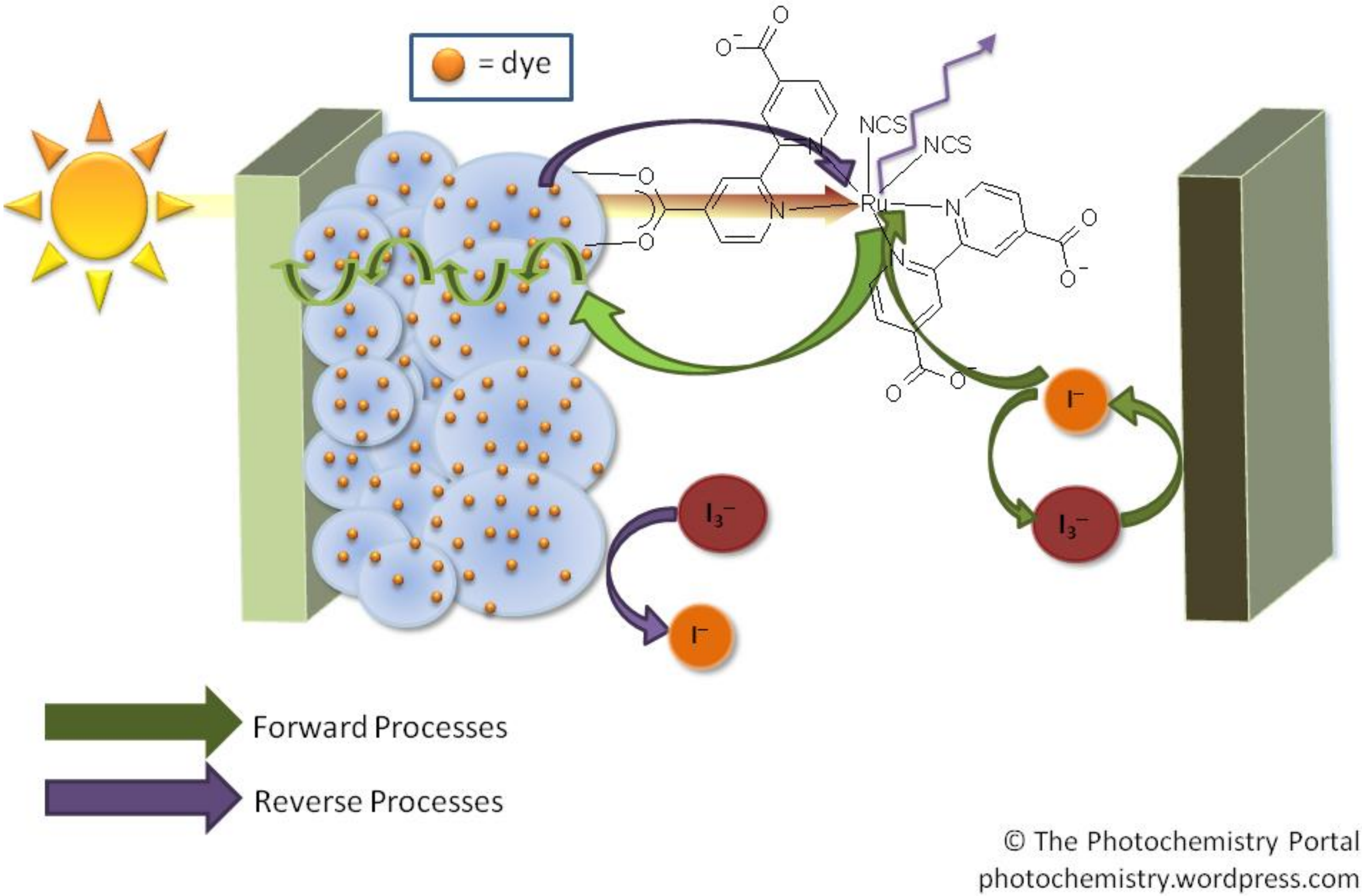
Wiki



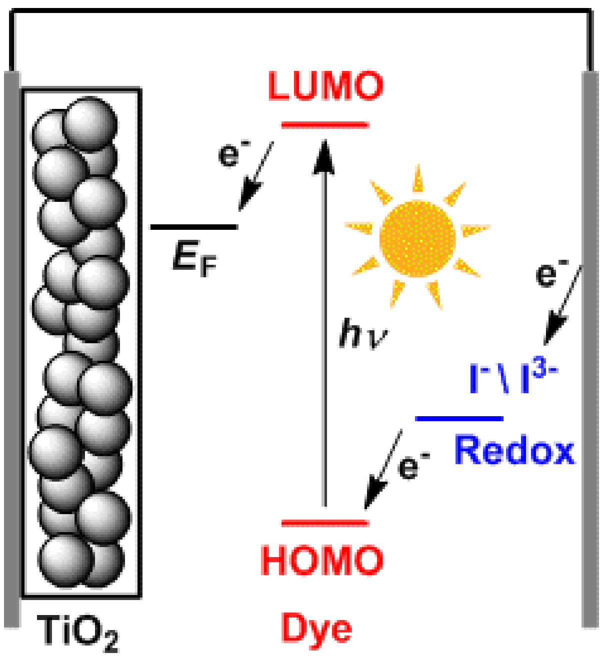
Organic

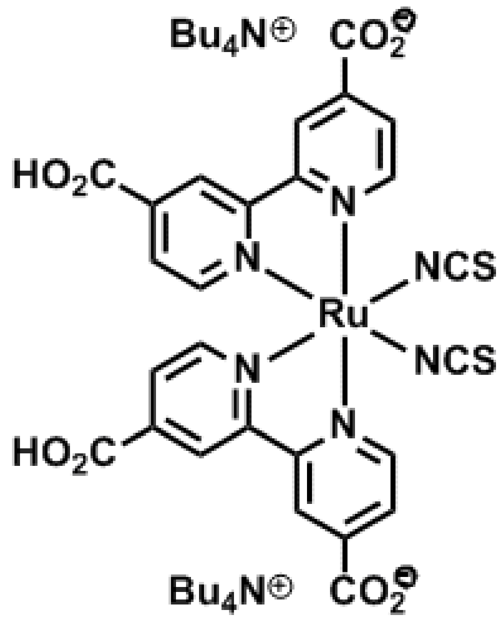
Phys.org

Dye sensitised solar cell



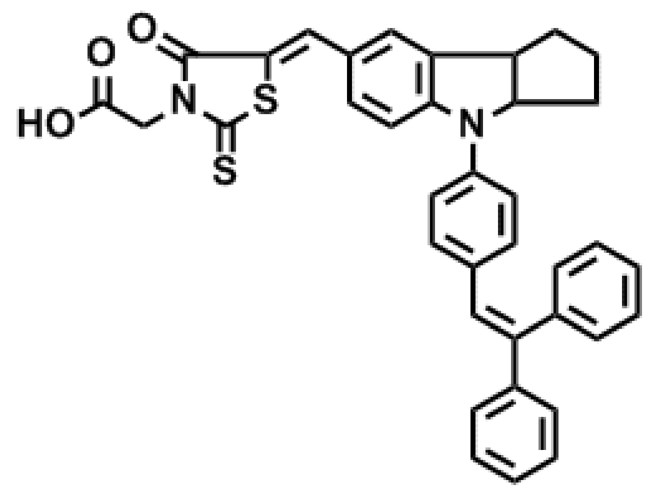
Dye sensitised solar cell





N719 dye

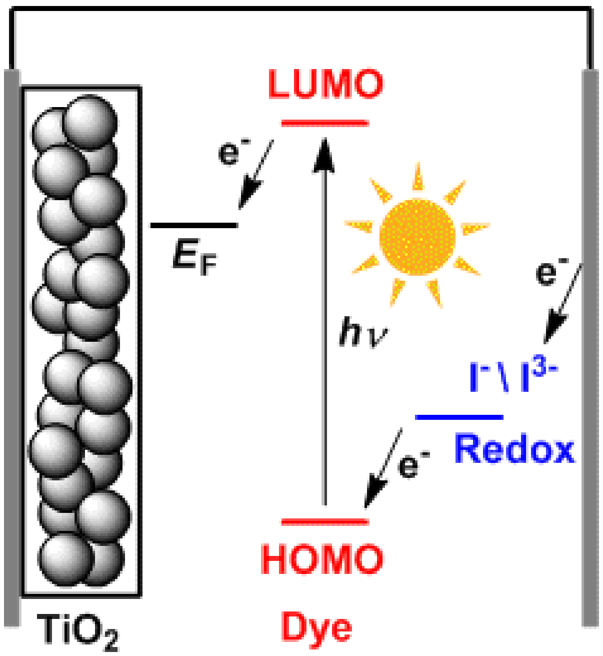
[B3514]



D102 dye

[D4430]

Dye sensitised solar cell



Components

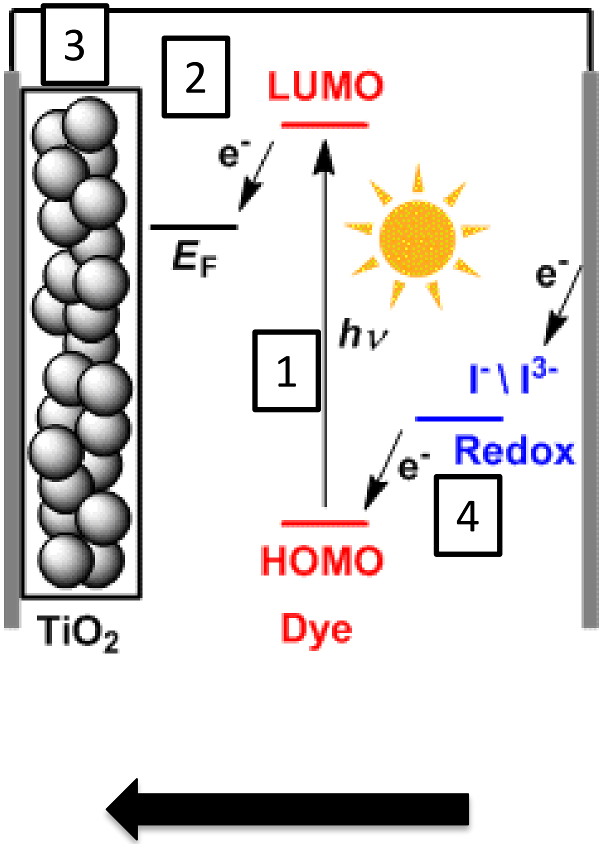
1) Dye (high absorption coefficient)

2) Wide band gap semiconductor
   TiO2 - mesoporous

3) Electrolyte with different redox states

4) Electrodes with suitable energetics

Dye sensitised solar cell



Processes

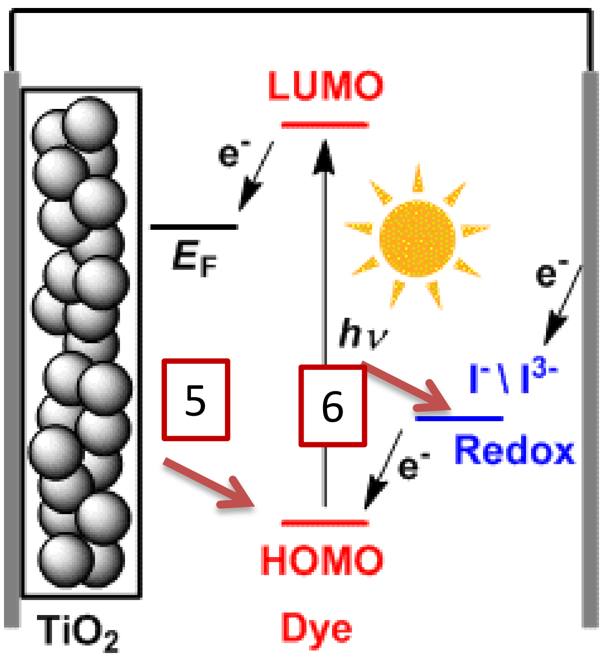
1) Light absorption (dye)

2) Electron transfer from LUMO of dye to conduction band of TiO_2

3) Electron transport to electrode

4) Electron transfer from electrolyte to HOMO of dye (S1 -> S0)

Dye sensitised solar cell

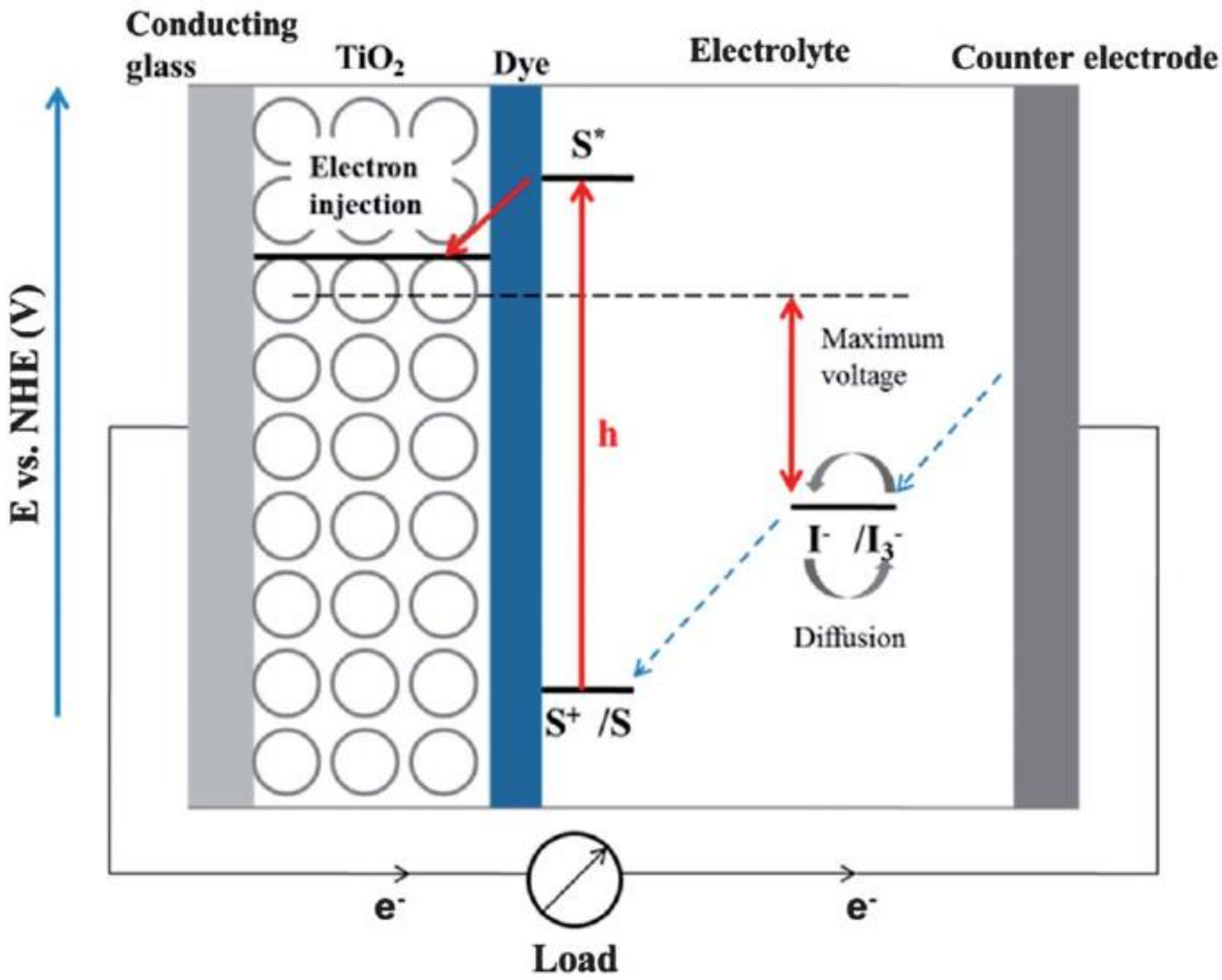


Loss mechanisms

5) Electron back transfer from TiO_2 to dye

6) Electron back transfer to electrolyte

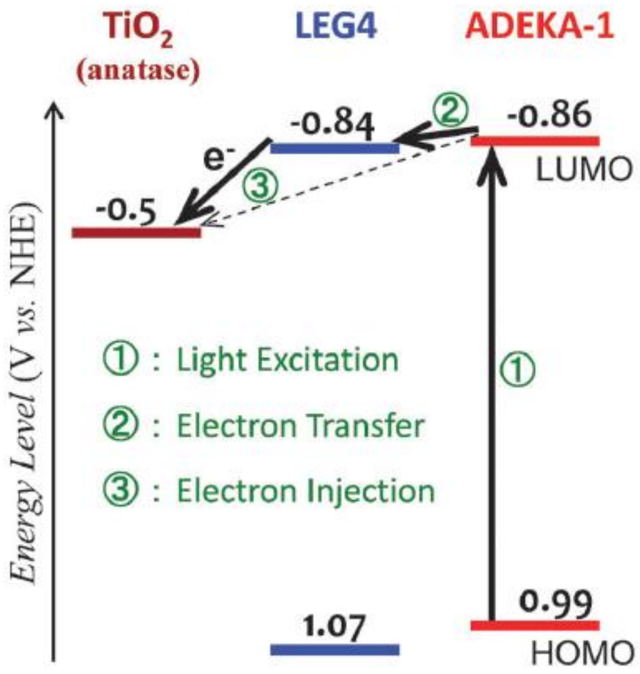
Dye sensitised solar cell



Singh, RCS Adv. 2014

Dye sensitised solar cell

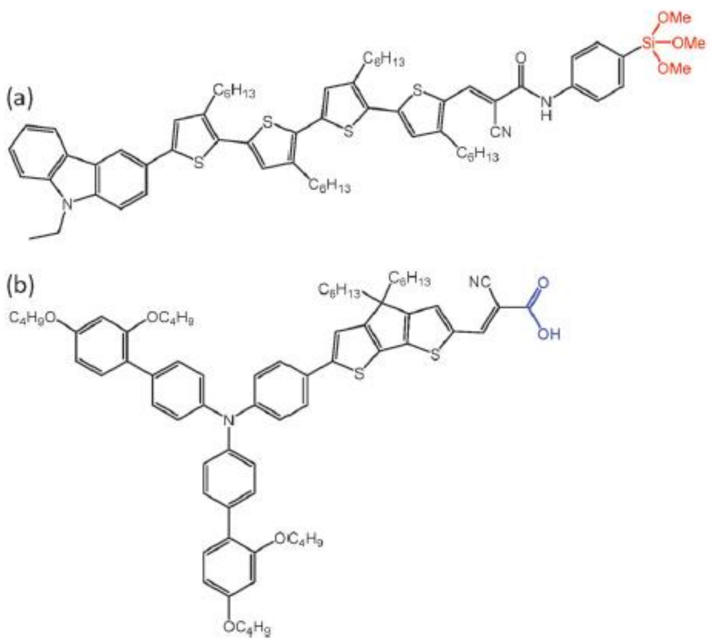
2015 – new record of > 14 %



Combination of dyes

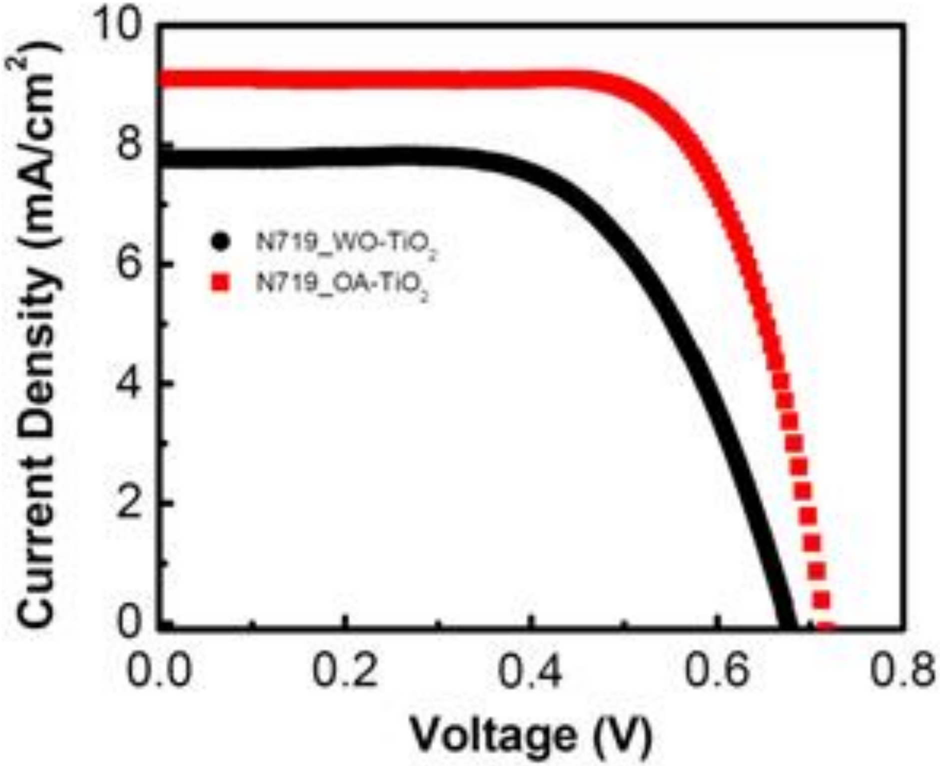
1) Absorber

2) Dye with anchoring group to attach to TiO_2 for enhanced carrier extraction (FF)



Kakiage et al Chem. Commun., 2015, 51, 15894

Dye sensitised solar cell



(a)

(b)

Saxena, Semiconductor Science and Technology 2015

Dye sensitised solar cell

1) Stability – electrolyte! corrosive

2) Absorption of dye (thickness)

3) Photovoltage of cell – limited by redox potential of electrolyte

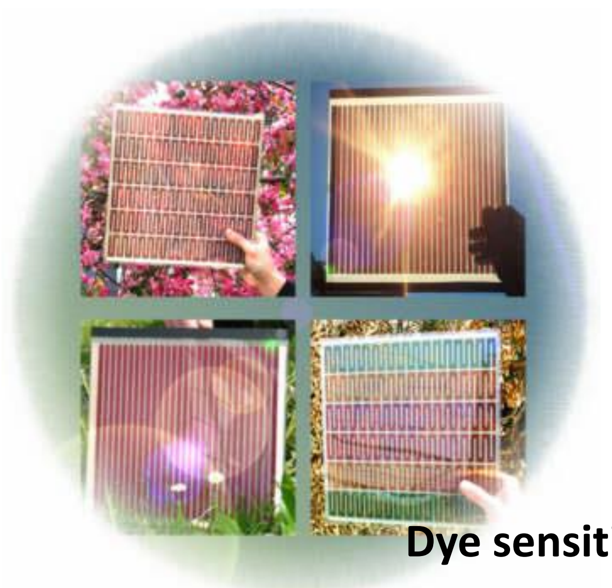
4) Loss processes at solid/liquid interface

Organic solar cells

Organic solar cells are sometimes compared to dye sensitised or Grätzel solar cells

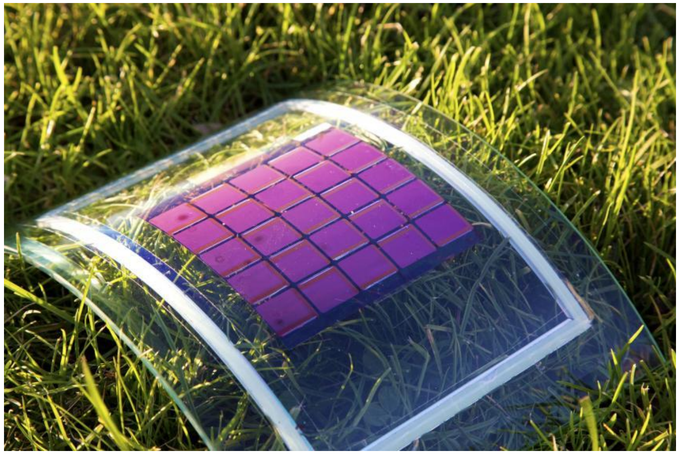
Similarity use of organic molecules for light absorption

Difference electrochemical vs solid state device



Dye sensitised

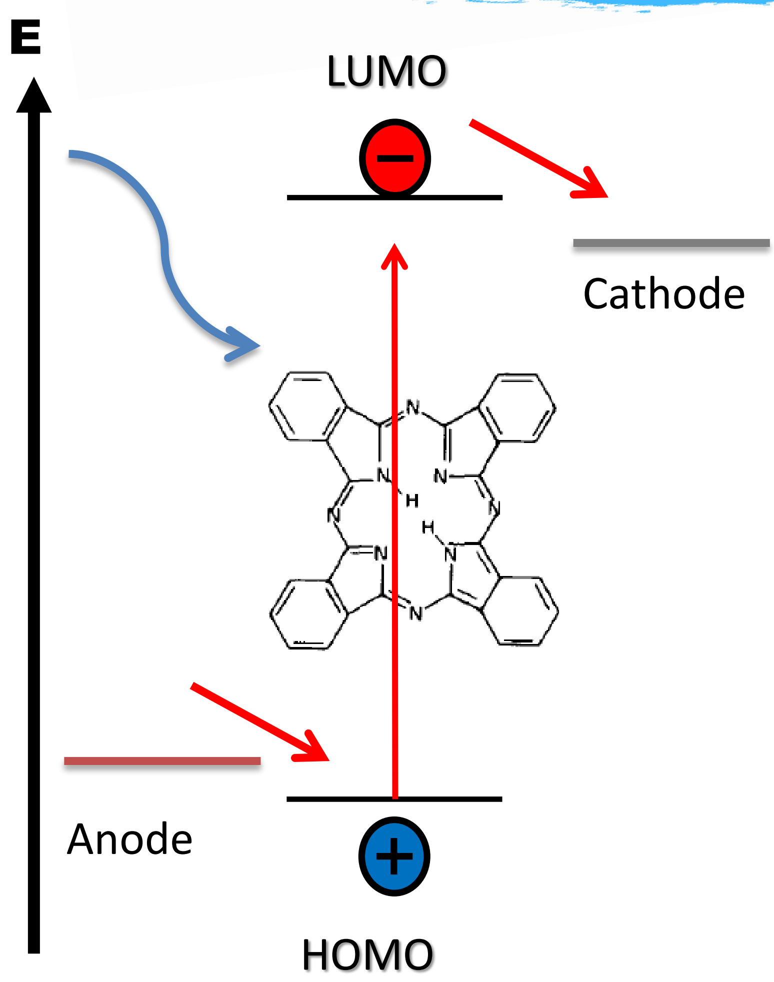
Wiki



Organic

Phys.org

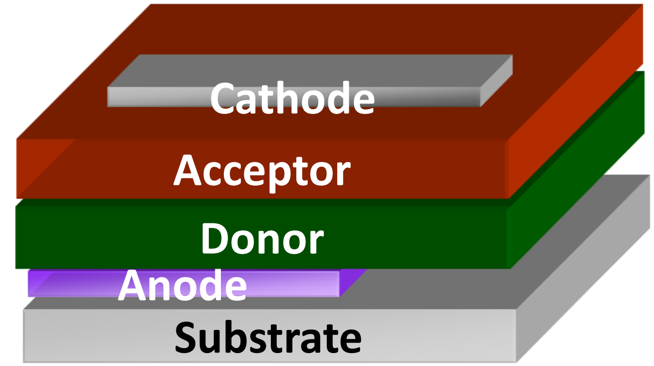
Organic solar cells - beginnings



Functional principles

- Organic absorber (~100 nm)
- Electron transfer from organic to Cathode (photoinduced carriers)
- Electron transfer from Anode to organic (regeneration)
- But in thin organic layers, many excitons recombine before or at the contacts)
- Inefficient charge separation!

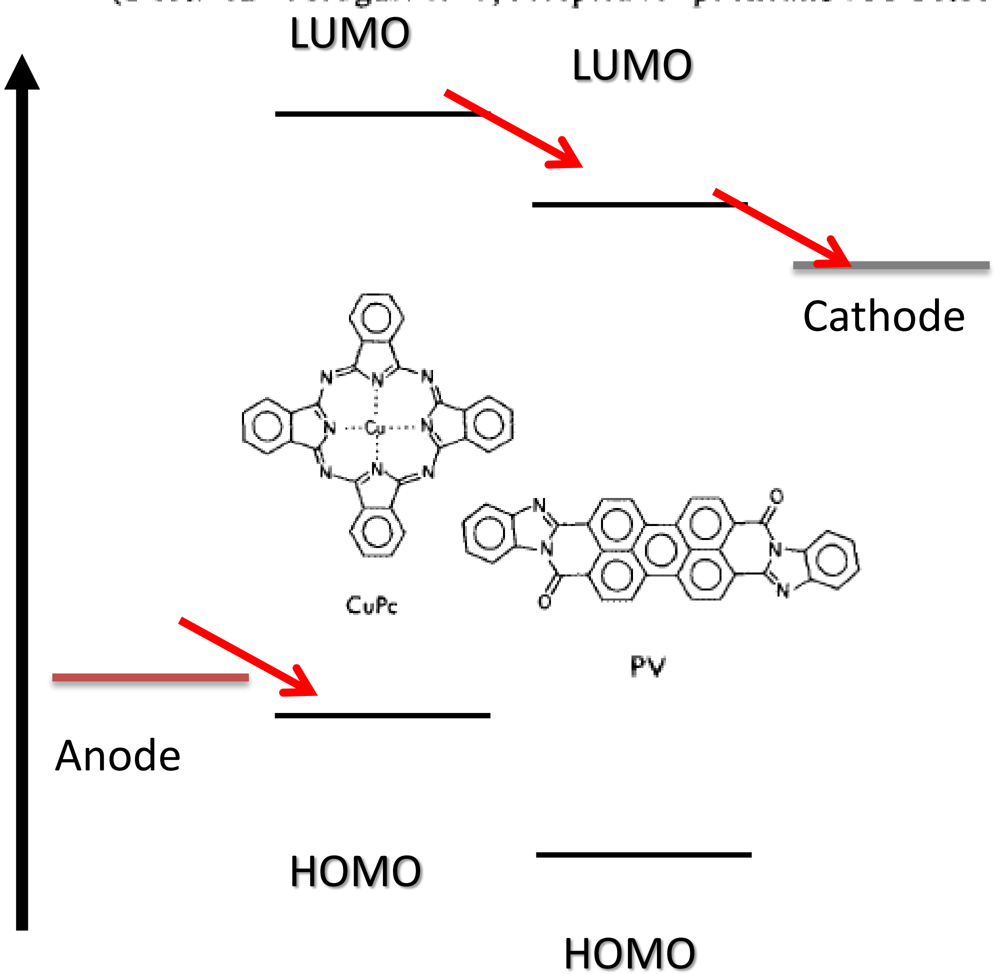
The Tang solar cell



Two-layer organic photovoltaic cell

C. W. Tang
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

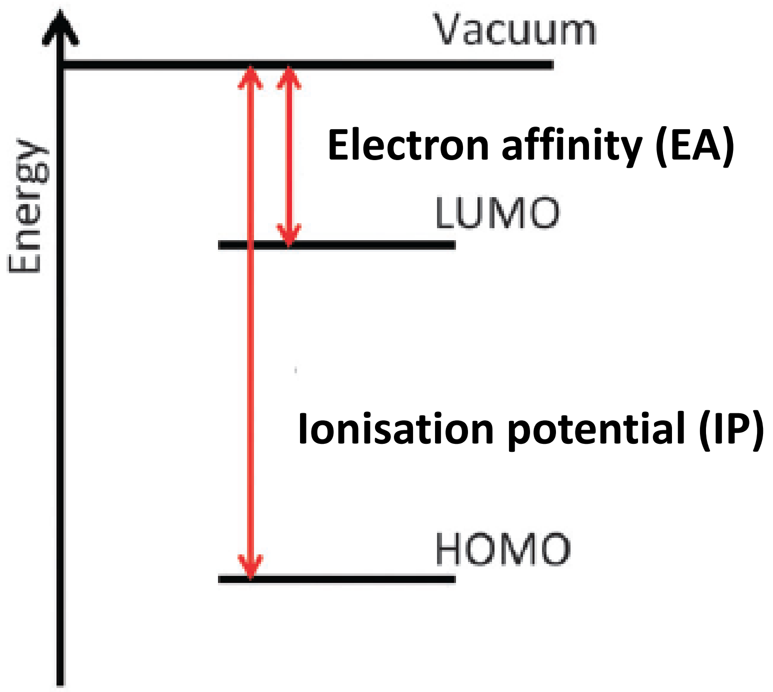
(Received 28 August 1985; accepted for publication 31 October 1985)

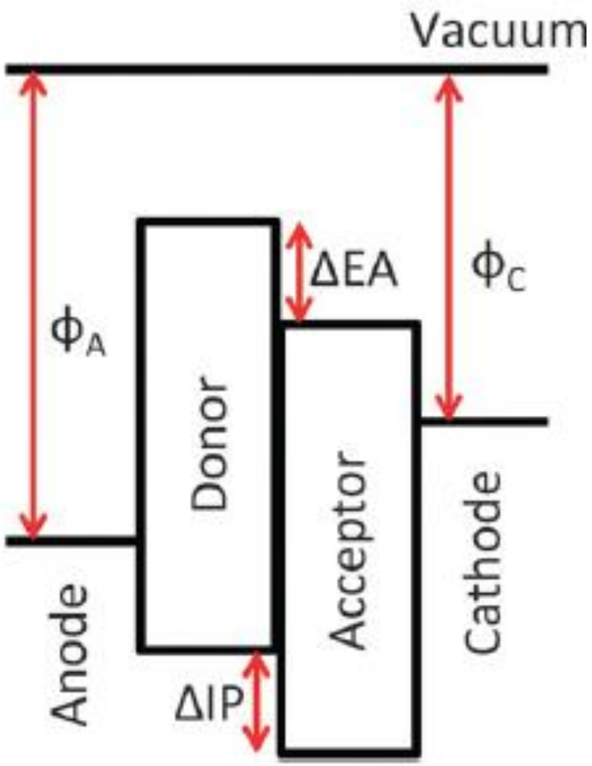


<u>Donor-acceptor system</u>

- Exciton dissociation at the interface between a donor and acceptor
- Transport of electrons and holes in separate organic phases
- Charge collection at the contacts
- 1% barrier was broken!

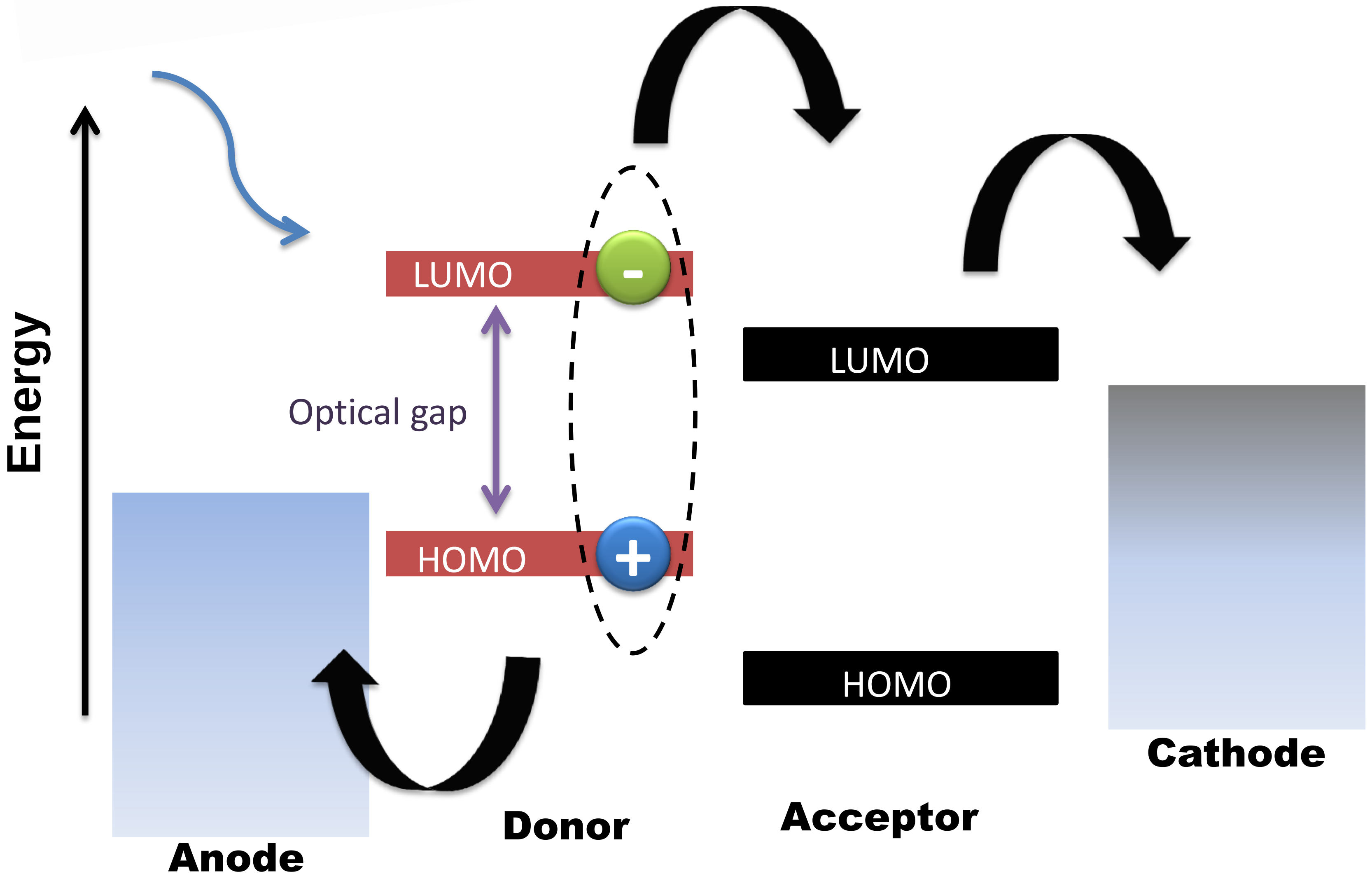
Organic solar cells





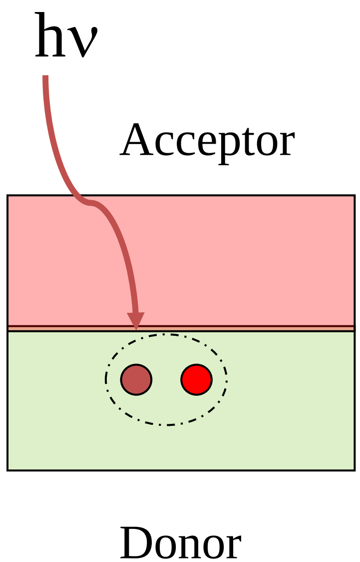
Excitation of donor
Electron transfer to acceptor
What is the optimal ΔEA? Loss in energy vs back transfer?

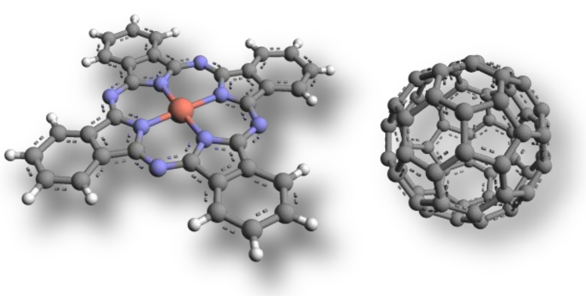
Organic solar cells – band diagram



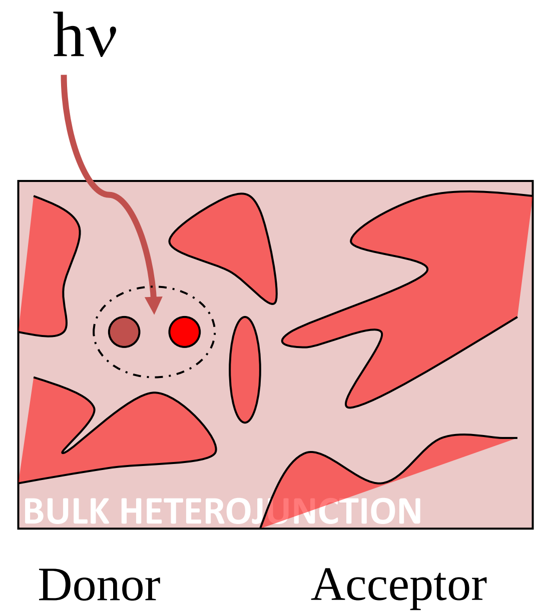
Organic solar cells – active layer structure

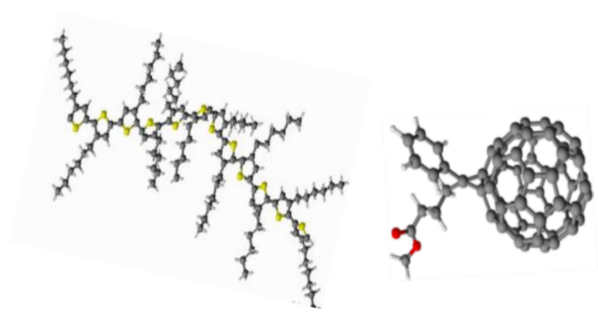
Well ordered organic films
Vacuum processed



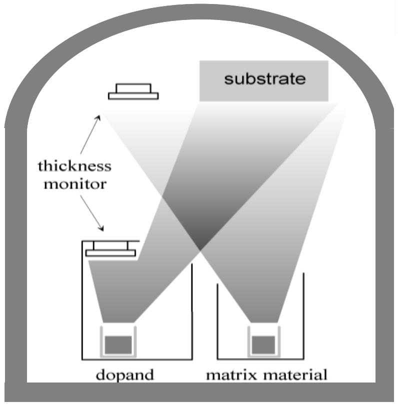


Disordered
Solution processed





Thermal deposition of organic films



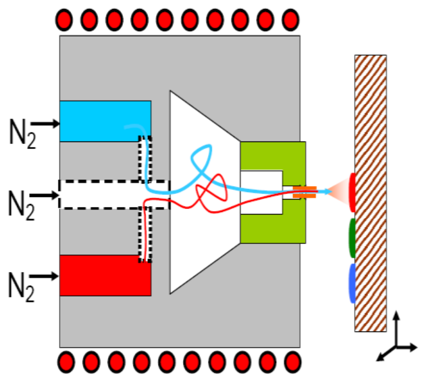
Small molecules sublimate around 200 C

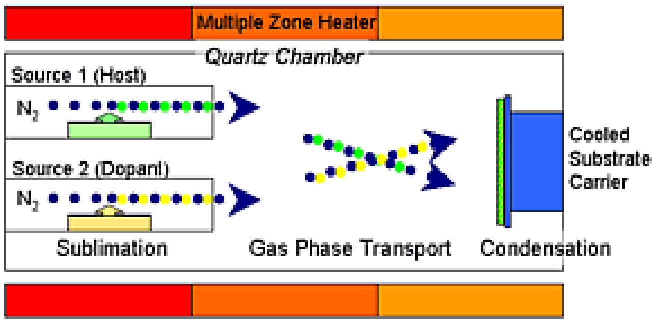
Heat a source, collect molecules on substrate

Ultra thin (100 nm) ordered molecular films

Crucible with organic material heated
Low temperature sublimation

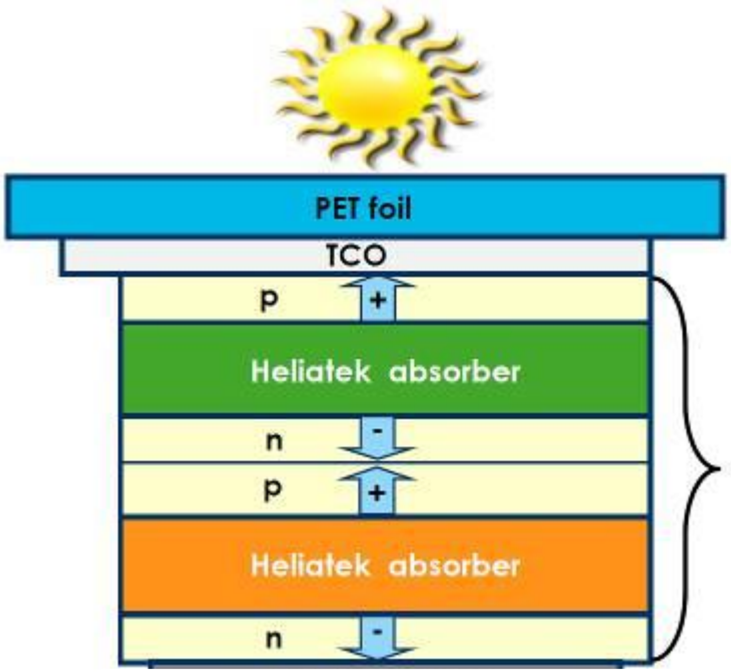
Carrier gas used to structure the organic film

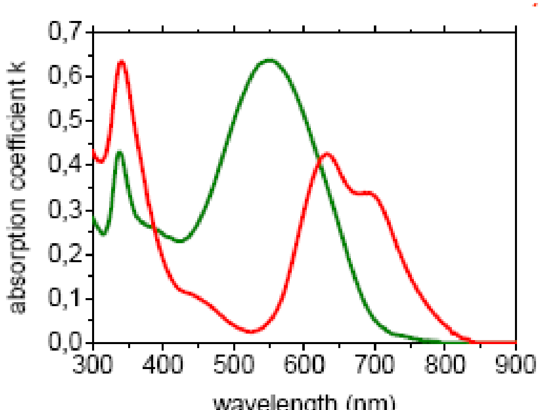




Universial Display

Organic tandem solar cells





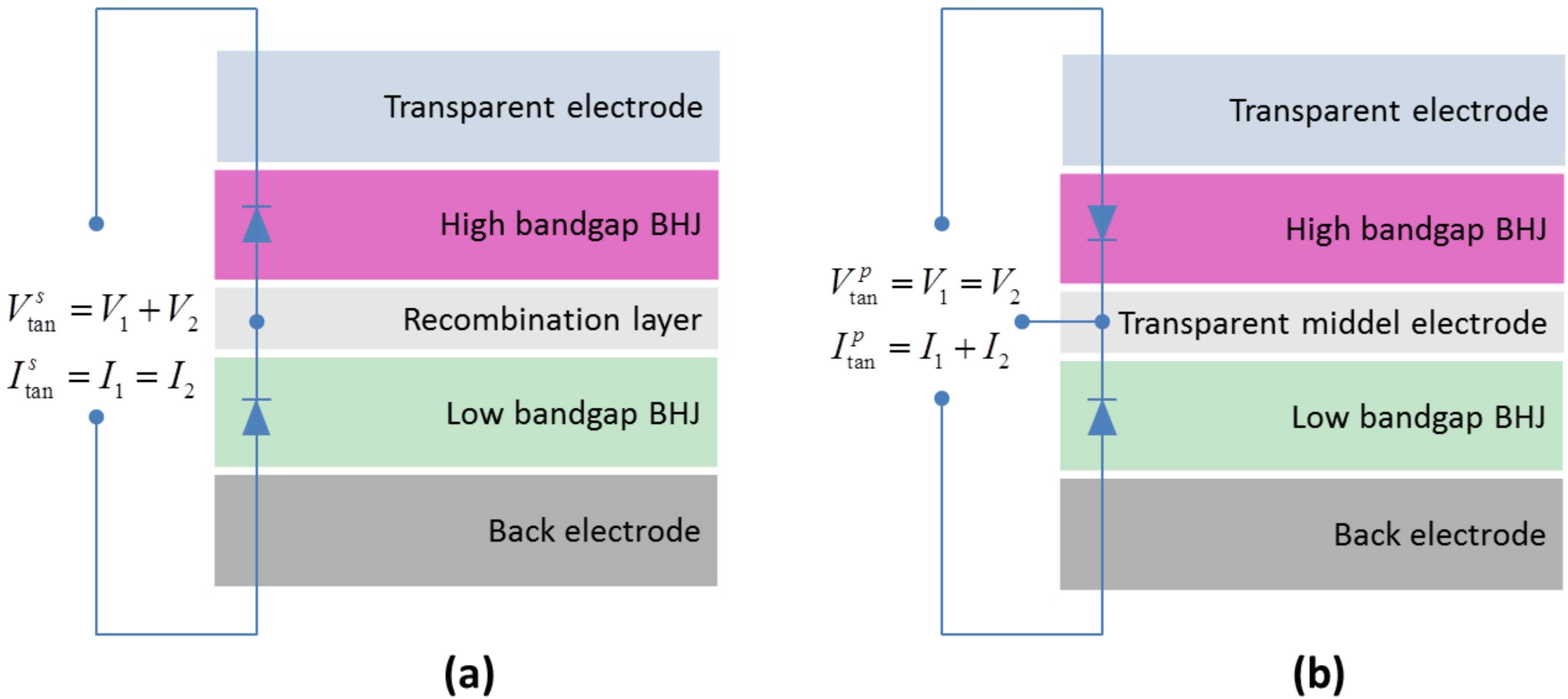
<u>Vacuum processed layers</u>

- Vacuum processed semiconductors can easily be used to form tandem structures
- Slight increase in price is balanced by increase in efficiency
- Tandems harvest more solar spectrum
- Top efficiencies (>12%)

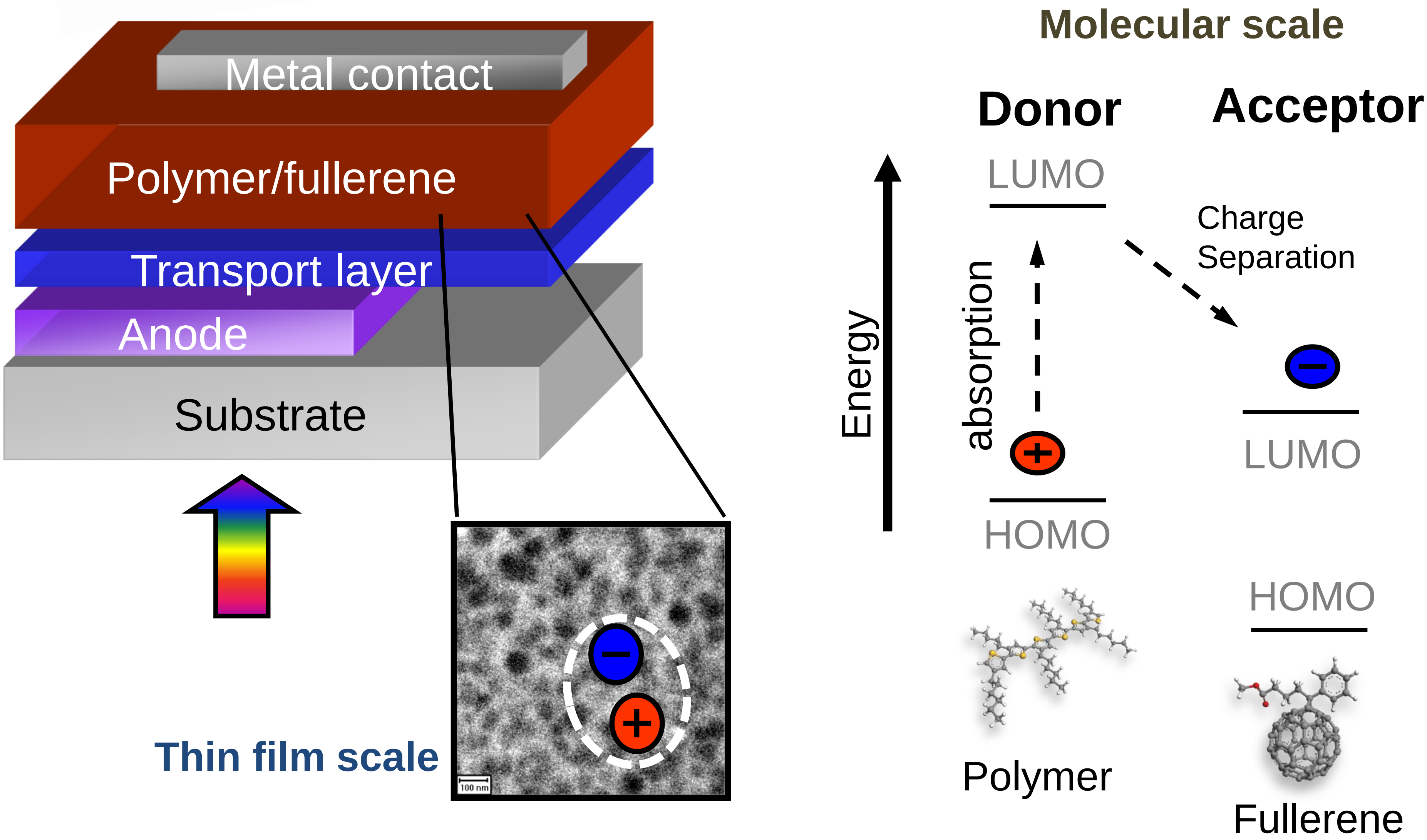
Organic tandem solar cells

Two alternatives for contacting a tandem structure
Remember: the solar cells are in series.

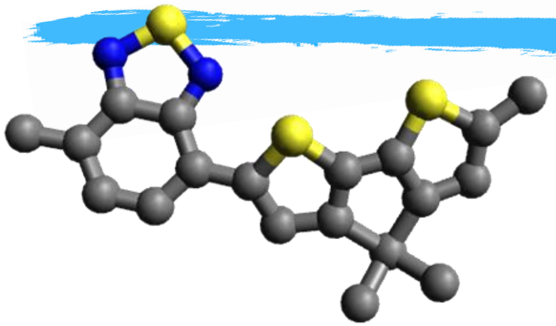
- *The current is the same through the cell*
- *The voltage is additive*

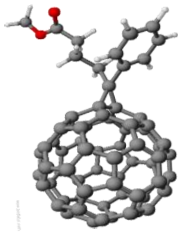


Organic bulk heterojunction solar cells



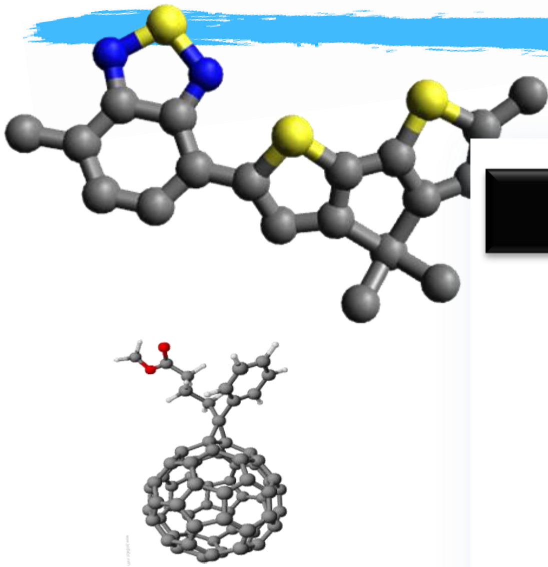
Organic bulk heterojunction solar cells



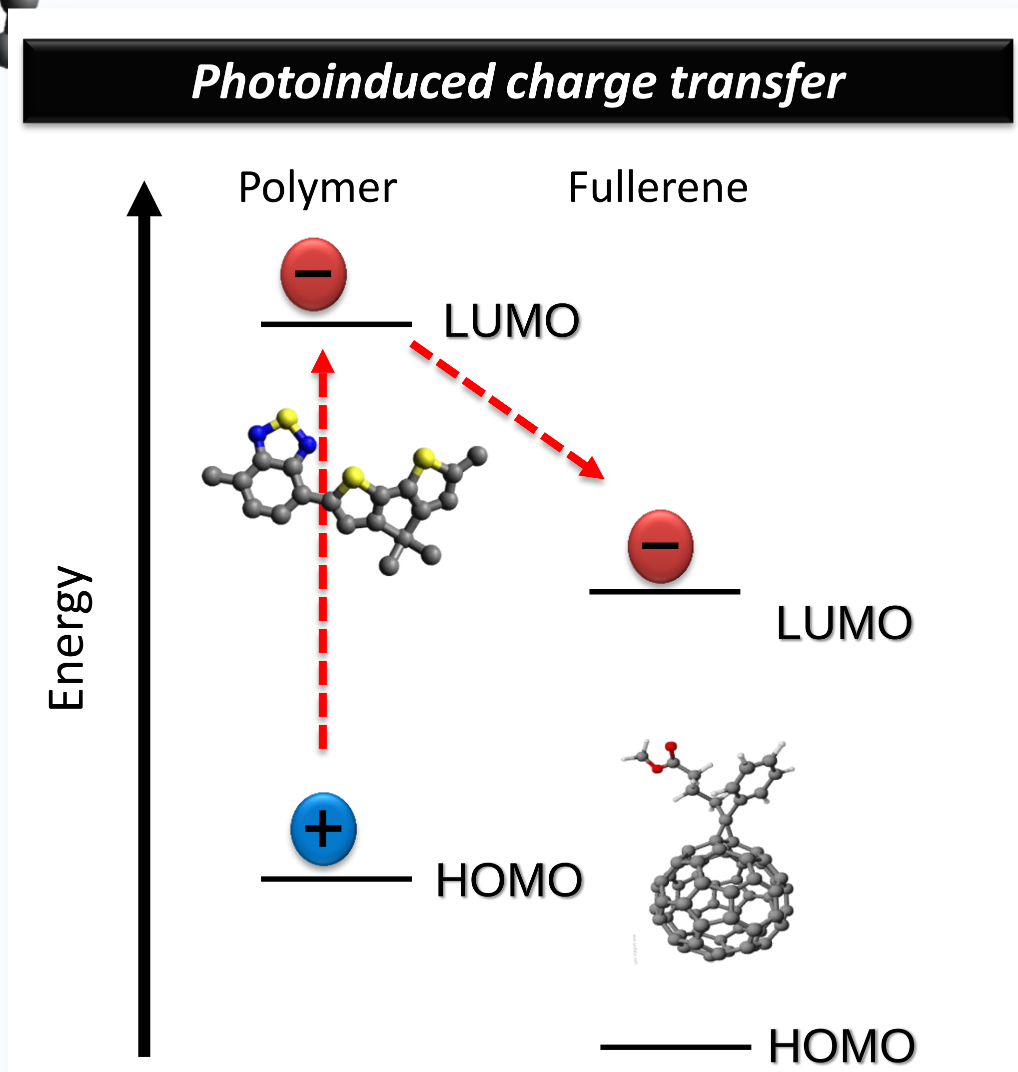


Donor-Acceptor

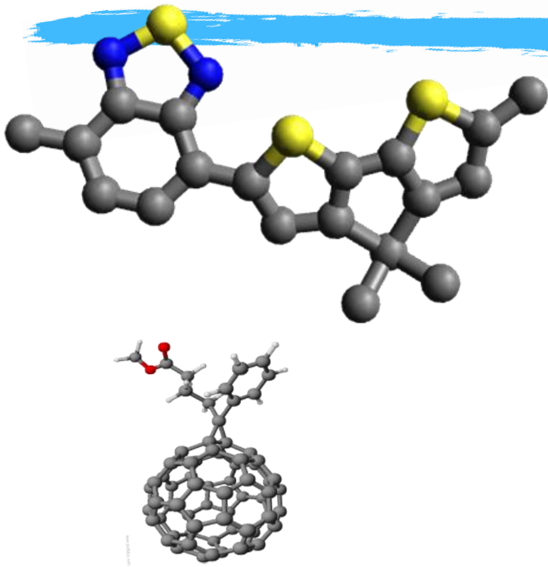
Organic bulk heterojunction solar cells

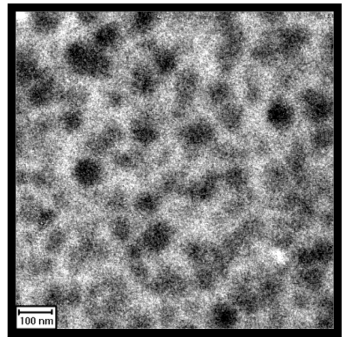


Donor-Acceptor



Organic bulk heterojunction solar cells

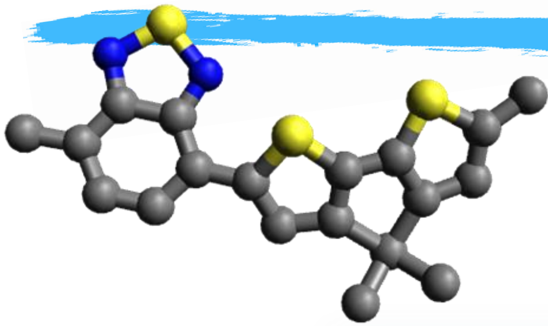


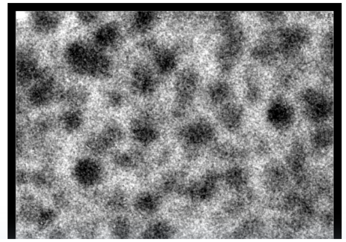


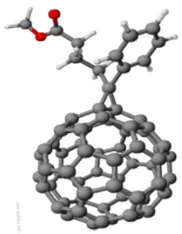
Donor-Acceptor

Bulk heterojunction

Organic bulk heterojunction solar cells

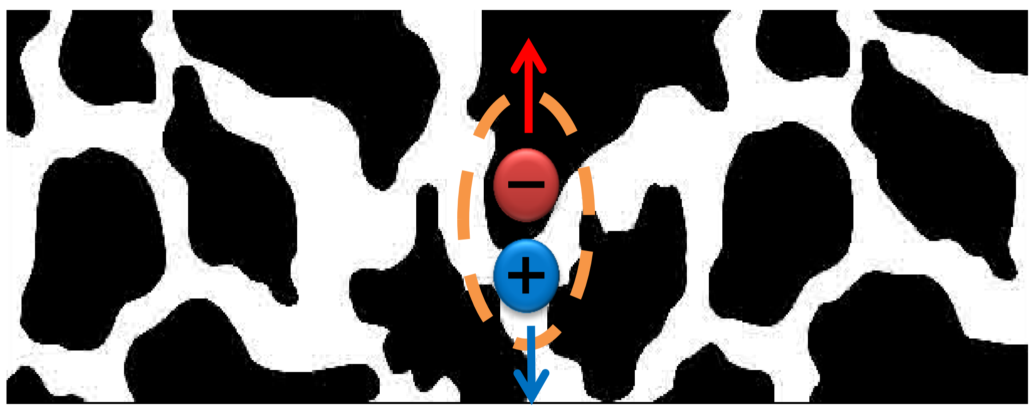




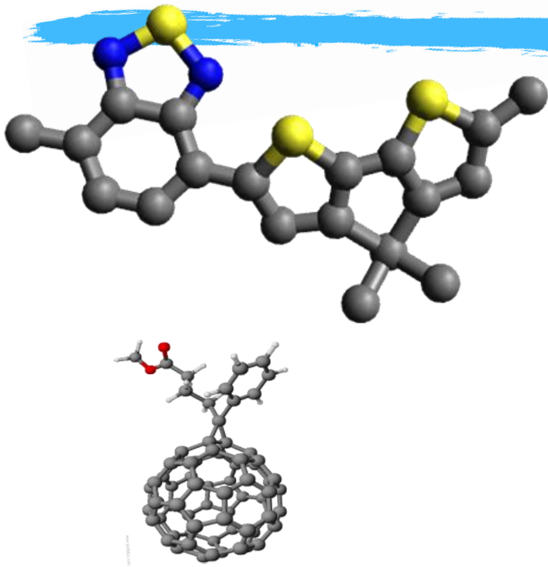


Donor-Accept

Charge separation & transport

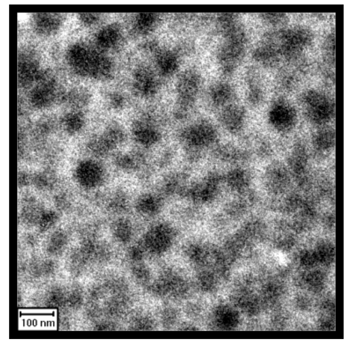


Organic bulk heterojunction solar cells



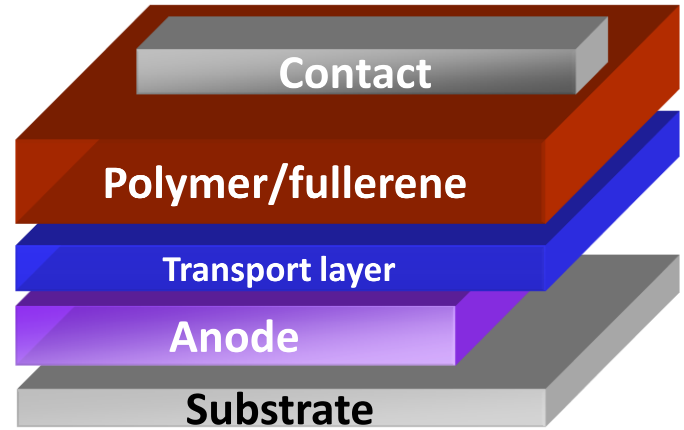
Donor-Acceptor

10^{-9} m



Bulk heterojunction

10^{-7} m



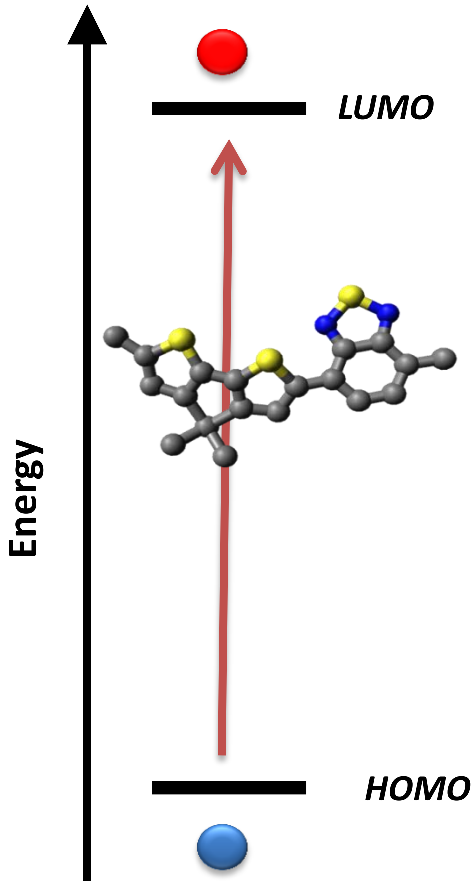
Solar cell

10^{-2} m

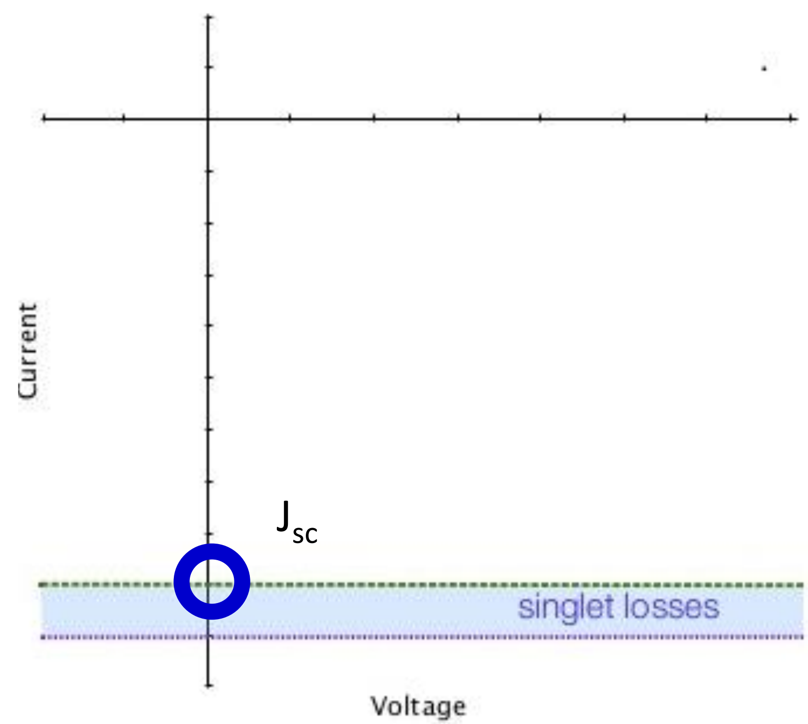
Material interfaces @ different length scales

- ❑ Molecular scale: donor-acceptor
- ❑ Thin film: electrical transport pathways
- ❑ Device: transport layers and contacts

Organic solar cells – the current-voltage curve

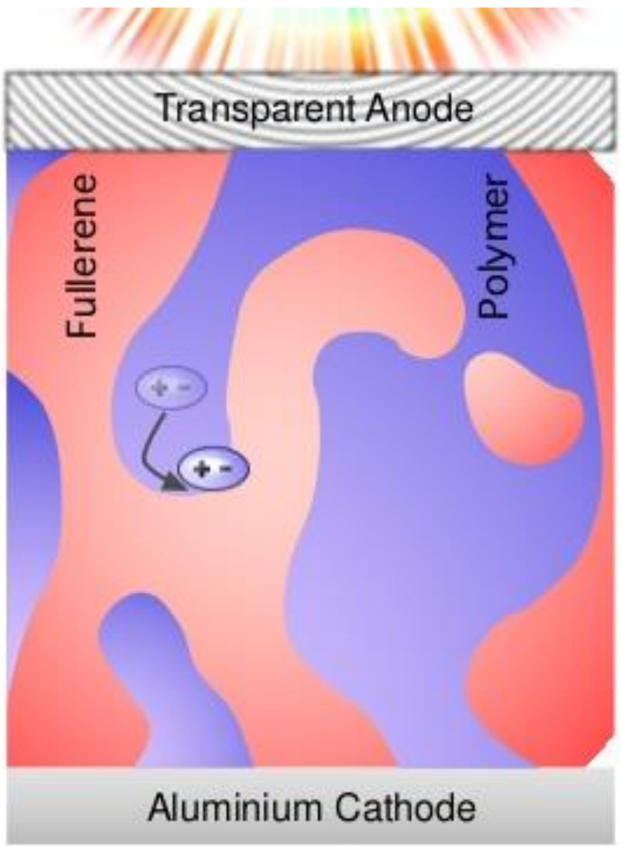


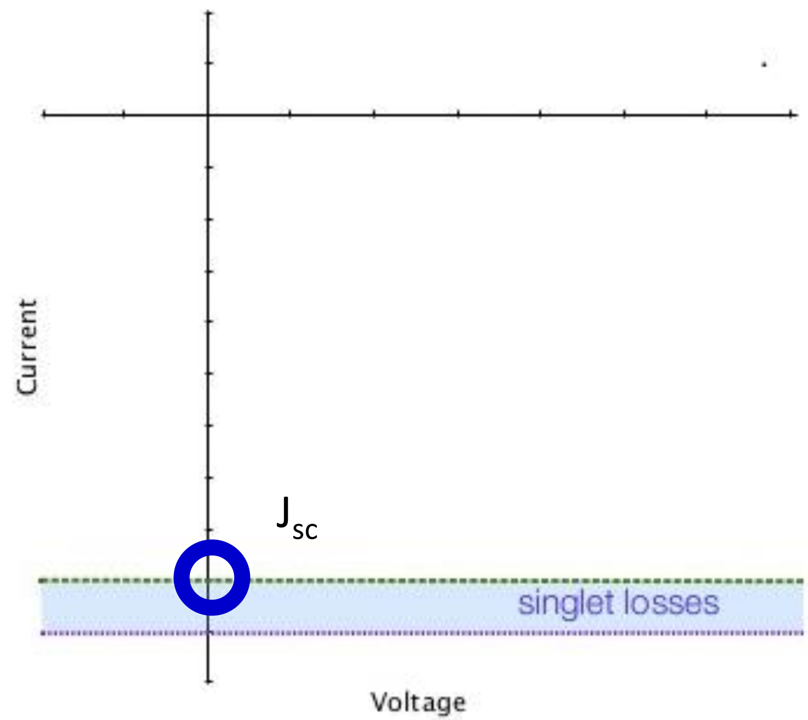
Geminate recombination reduces photocurrent



Singlet excitons – dont reach the donor-acceptor interface

Organic solar cells – short circuit current

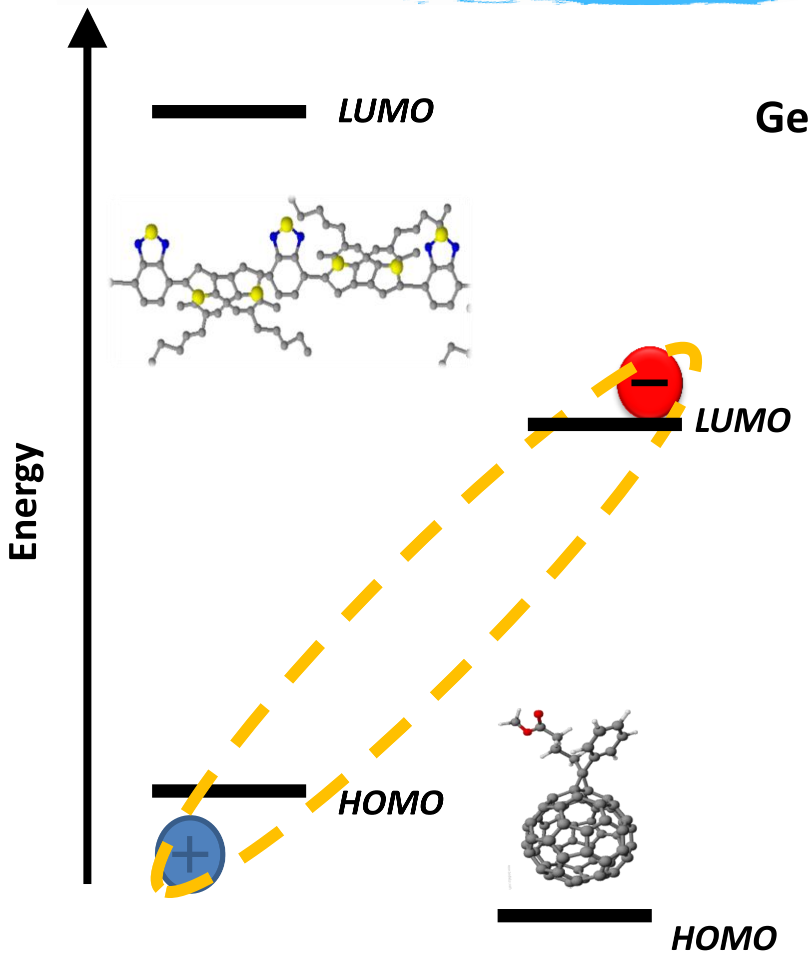




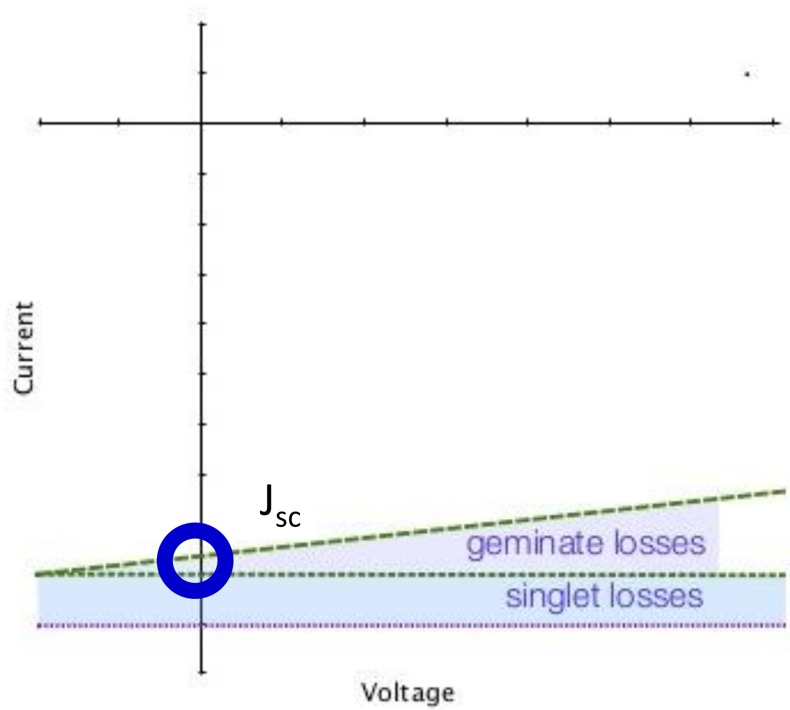
Singlet excitons – dont reach the donor-acceptor interface

C. Deibel, Uni Würzburg

Organic solar cells – fill factor



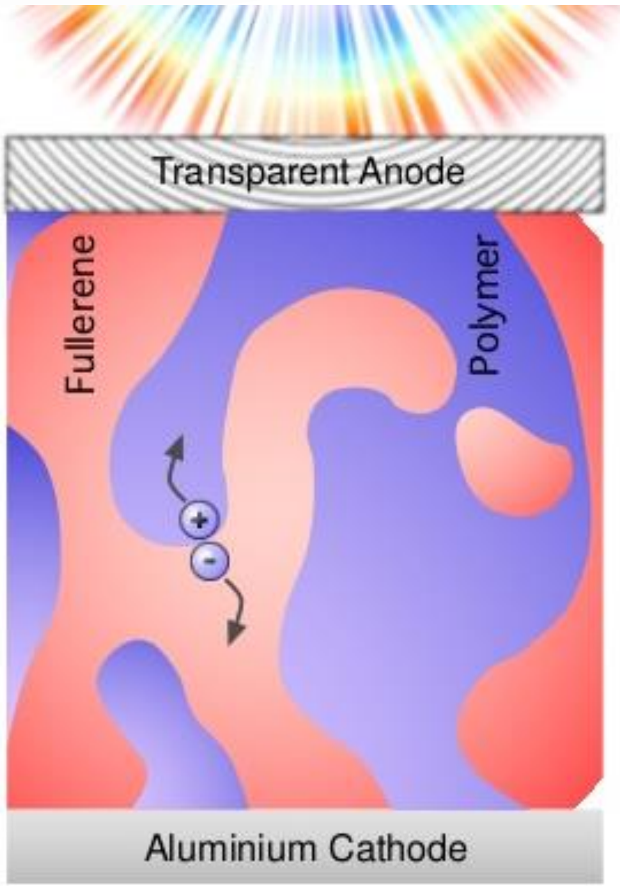
Geminate recombination reduces photocurrent

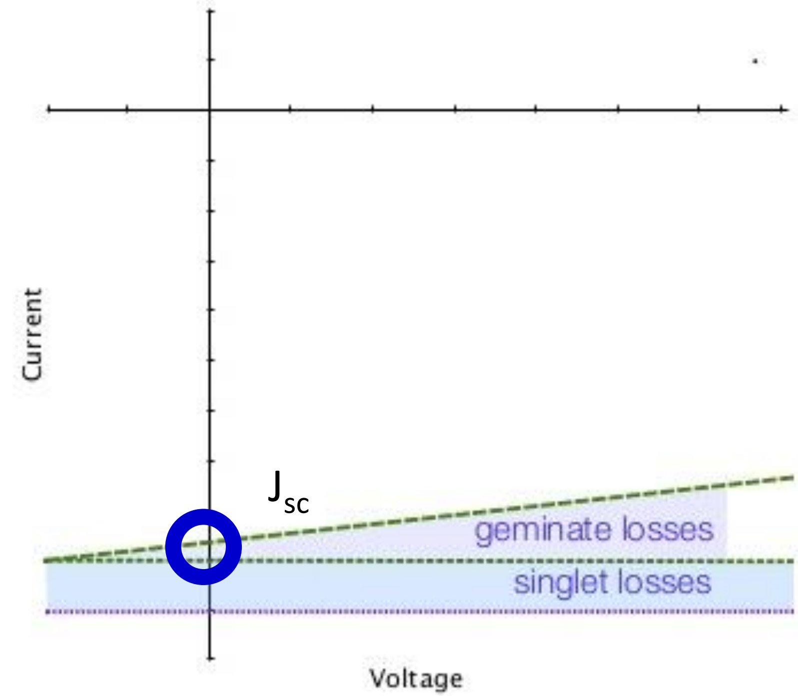


Charge transfer excitons – losses at the donor-acceptor interface

C. Deibel, Uni Würzburg

Organic solar cells – fill factor

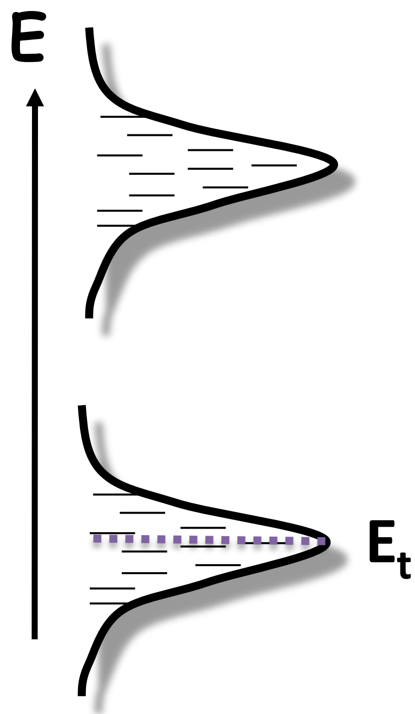


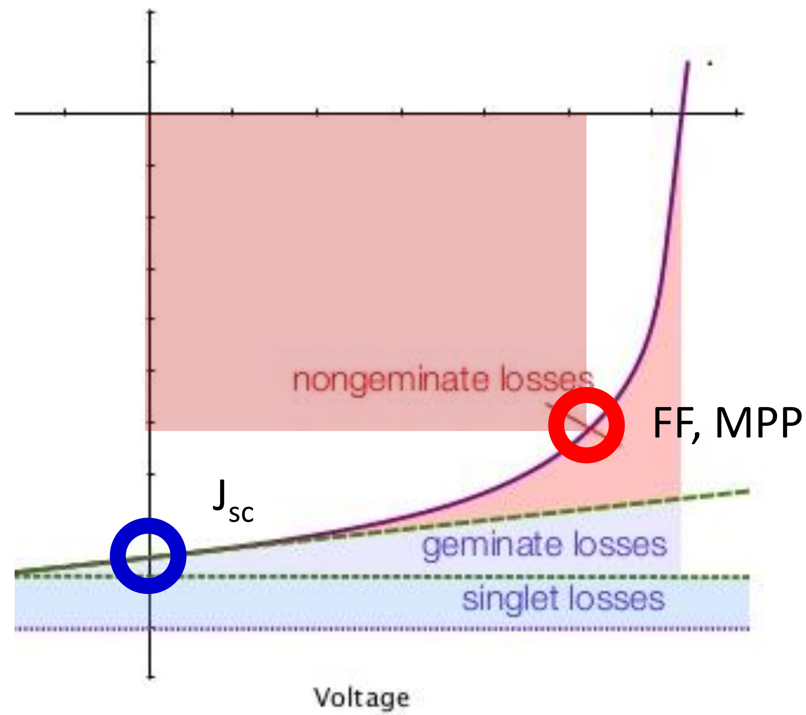


Charge transfer excitons – losses at the donor-acceptor interface
Inefficient charge separation

C. Deibel, Uni Würzburg

Organic solar cells – fill factor

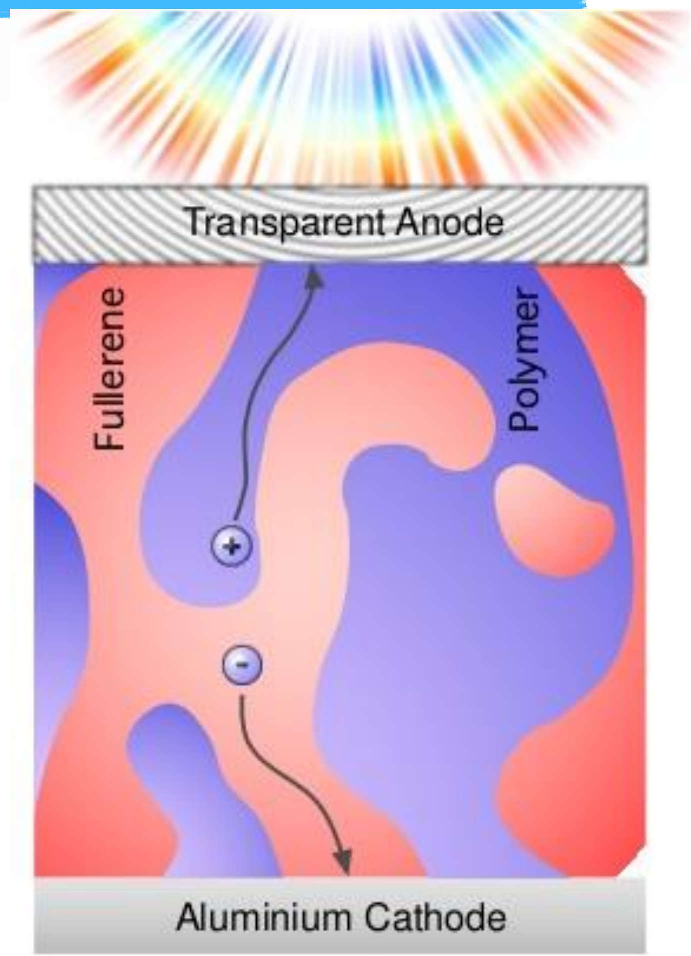


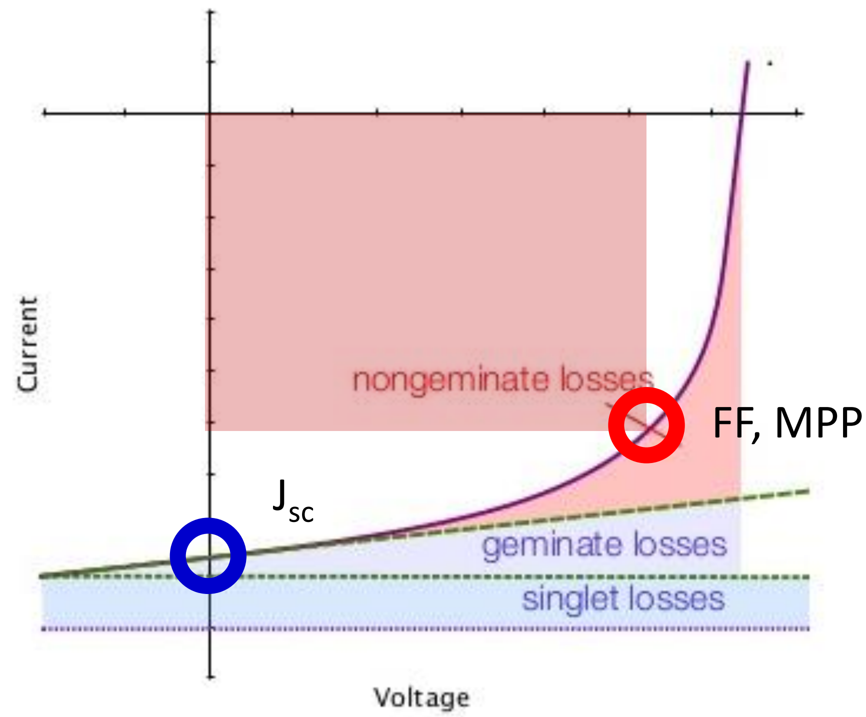


Carrier trapping, low mobility
Trap-assisted Recombination

C. Deibel, Uni Würzburg

Organic solar cells – fill factor

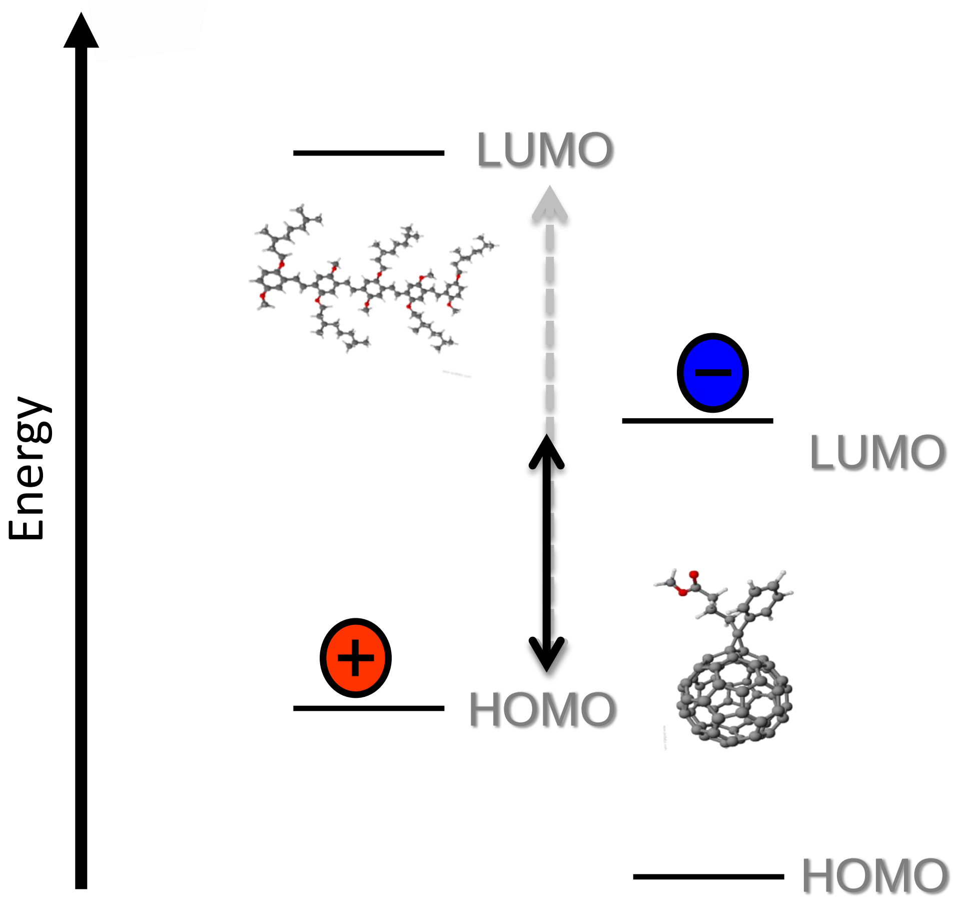


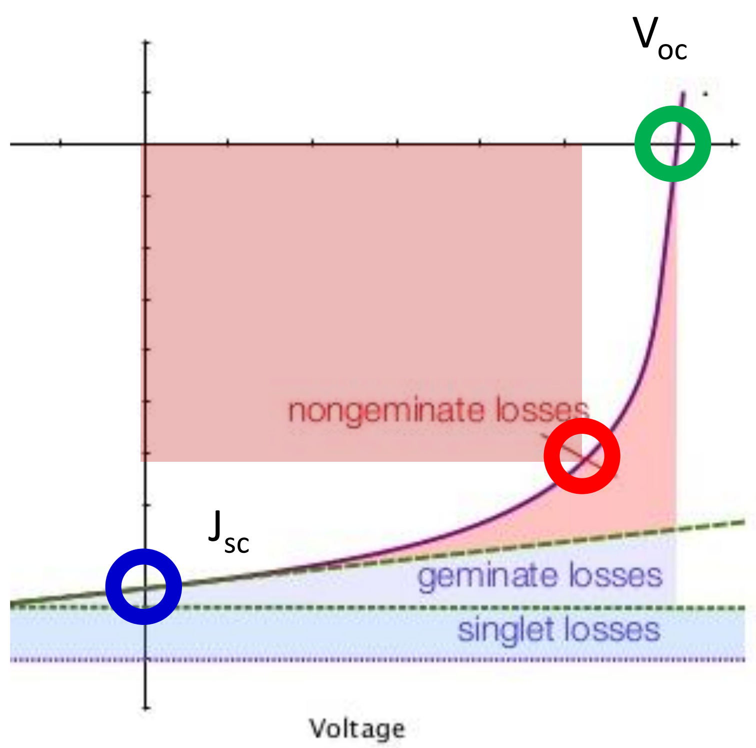


Carrier trapping, low mobility
Trap-assisted Recombination

C. Deibel, Uni Würzburg

Organic solar cells – open circuit voltage

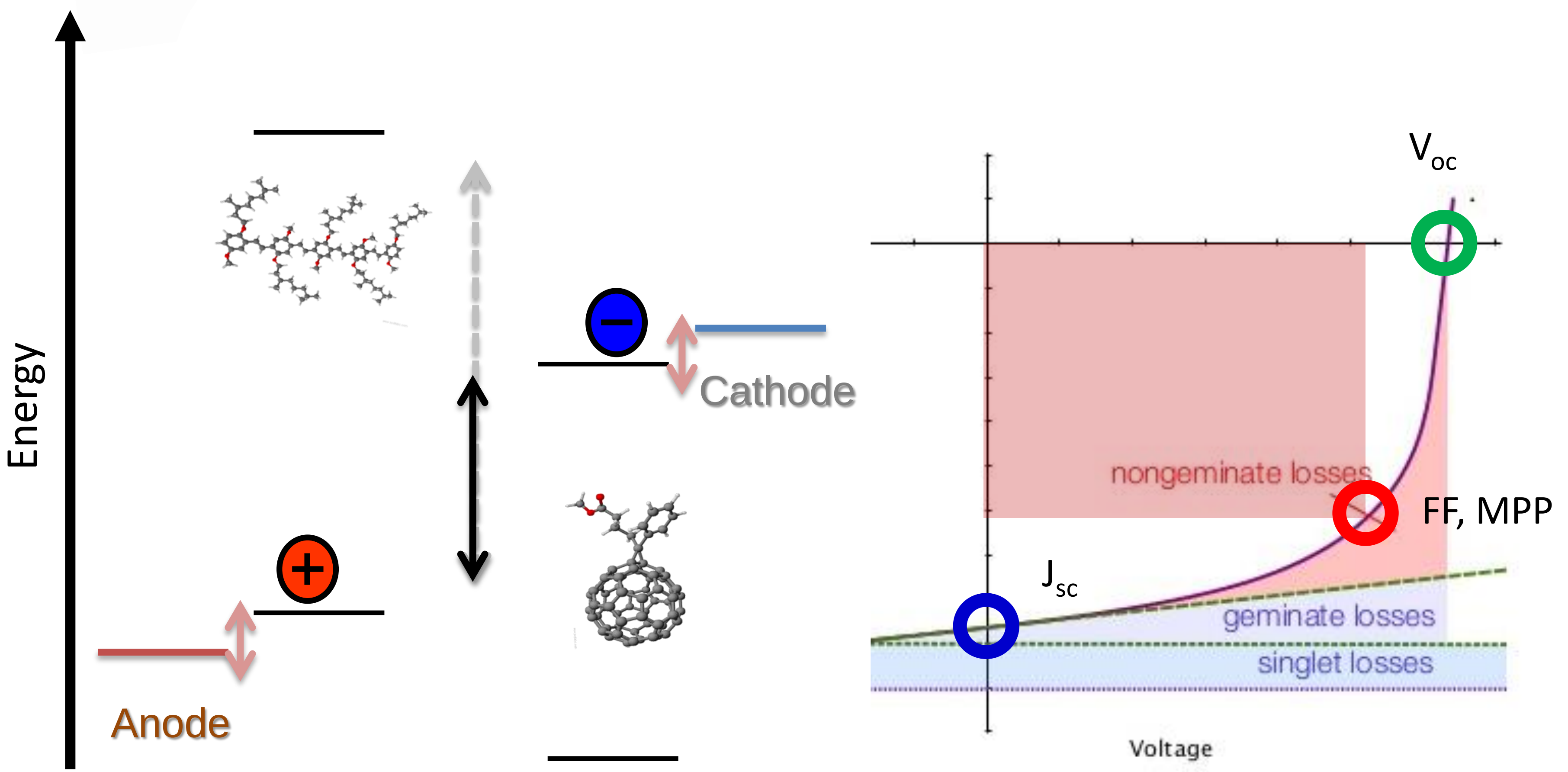




Energy loss between LUMOs of donor and acceptor

C. Deibel, Uni Würzburg

Organic solar cells – open circuit voltage

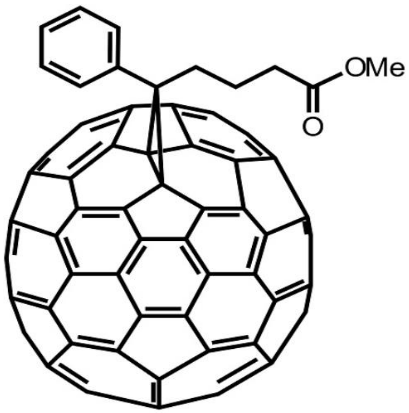


Energy loss between semiconductor and contacts

C. Deibel, Uni Würzburg

Organic solar cells – nonfullerene acceptors

Fullerenes



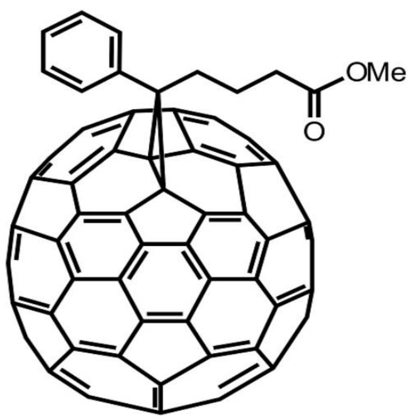
Certified PCE of 11.5% with high performance donor materials

<u>Advantages</u>

- High electron affinitys
- High electron mobility (μ_e)
- Ability to form favorable morphologies with donor
- Isotropy of charge transport
- Reversible electrochemical reduction

Organic solar cells – nonfullerene acceptors

Fullerenes



Certified PCE of 11.5% with high performance donor materials

Advantages

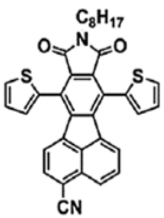
- High electron affinitys
- High electron mobility (μ_e)
- Ability to form favorable morphologies with donor
- Isotropy of charge transport
- Reversible electrochemical reduction

Disadvantages

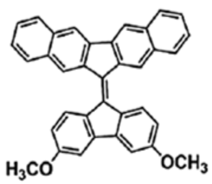
- Weak absorption in the visible and near-infrared
- Fullerene derivatives bandgap can also not be easily tuned
- Fullerene derivatives crystallize and aggregates leading to long term stability issues.
- PCBM solar cells suffer from large open circuit voltage losses (V_{OC})

Organic solar cells – nonfullerene acceptors

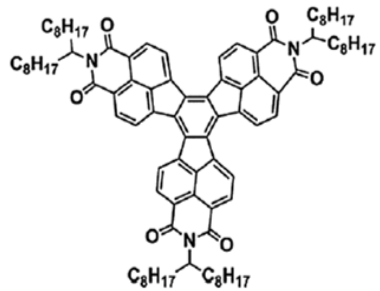
Small molecule acceptors



FFI-1

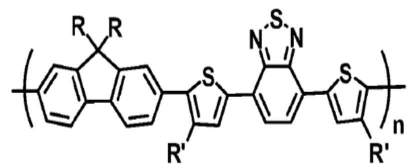


D99'BF

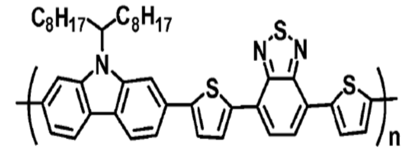


DTI

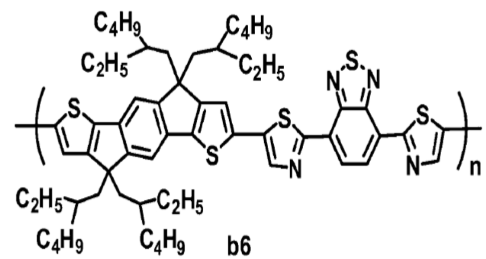
Polymer acceptors



b3 R = n-octyl R' =n-hexyl
b4 R = n-dodecyl R' =H



b5



b6

- Certified PCEs > 13%
- Tunable bandgap, broad absorption
- High oscillator strength
- Tunable energy levels to suitable energy offsets and high V_{OC}
- Tunable planarity and crystallinity
- Tunable morphology behaviour

State of the art

Science

REPORTS

Cite as: L. Meng *et al.*, *Science*
10.1126/science.aat2612 (2018).

Organic and solution-processed tandem solar cells with 17.3% efficiency

Lingxian Meng[1], Yamin Zhang[1], Xiangjian Wan[1*], Chenxi Li[1], Xin Zhang[1], Yanbo Wang[1], Xin Ke[1], Zuo Xiao[2], Liming Ding[2*], Ruoxi Xia[3], Hin-Lap Yip[3], Yong Cao[3], Yongsheng Chen[1*]