

PHAS0058

Physics of Advanced Materials

Lecture 3: Organic Photovoltaic (OPV) devices

In this lecture...

- photovoltaic landscape
- OPV devices – basic operation and structures
- fundamental processes
- characterisation of OPVs
- current research topics

Photovoltaic landscape

Motivation for OPVs

Existing PVs:

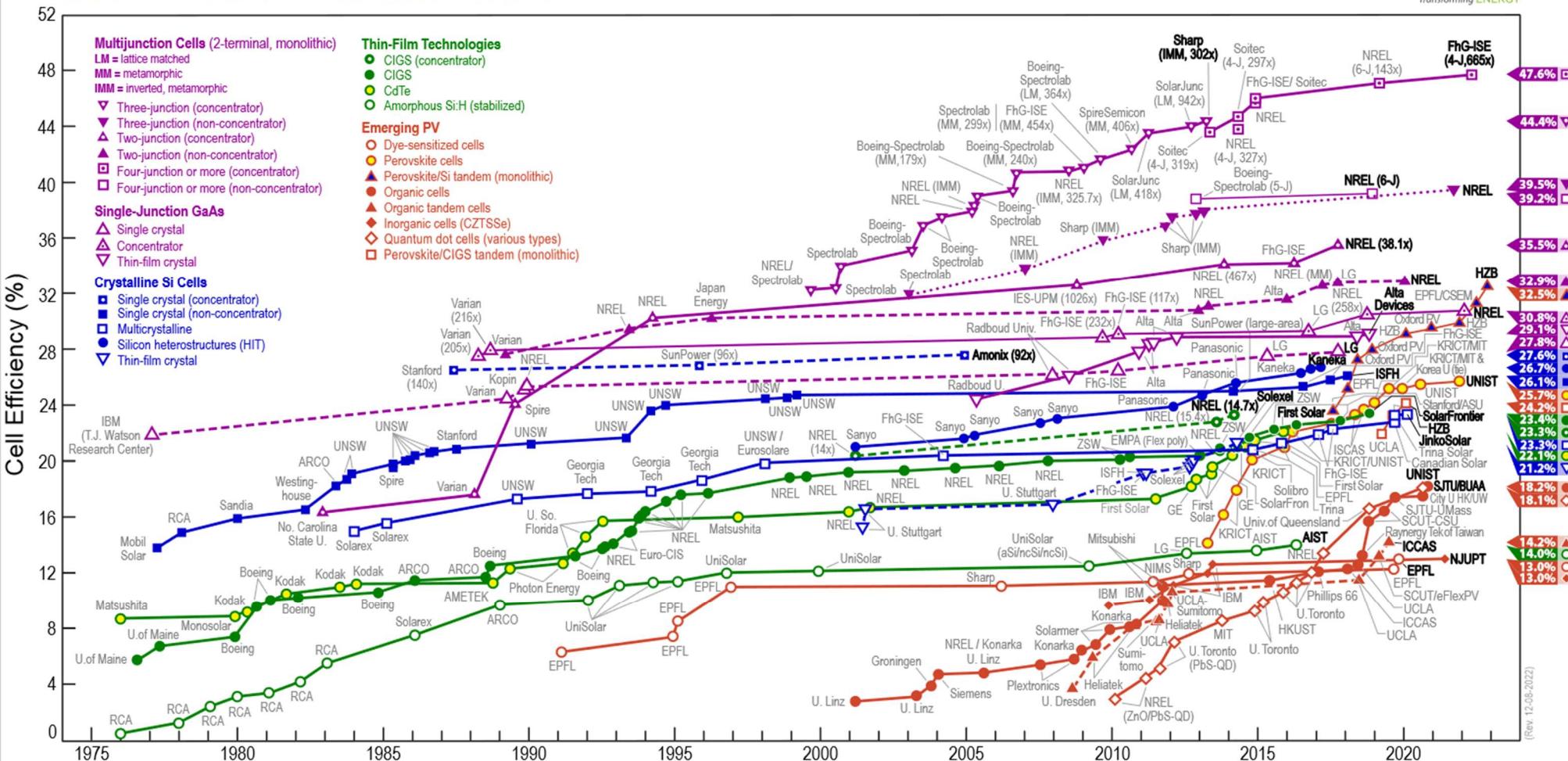
- rigid
- heavy
- low absorption coefficient
- toxic (Cd)
- rare (Te)

Potential for OPVs:

- high absorption coefficient
- cheap large scale fabrication
- low toxicity
- flexible
- lightweight
- possibly biocompatible

Best efficiencies

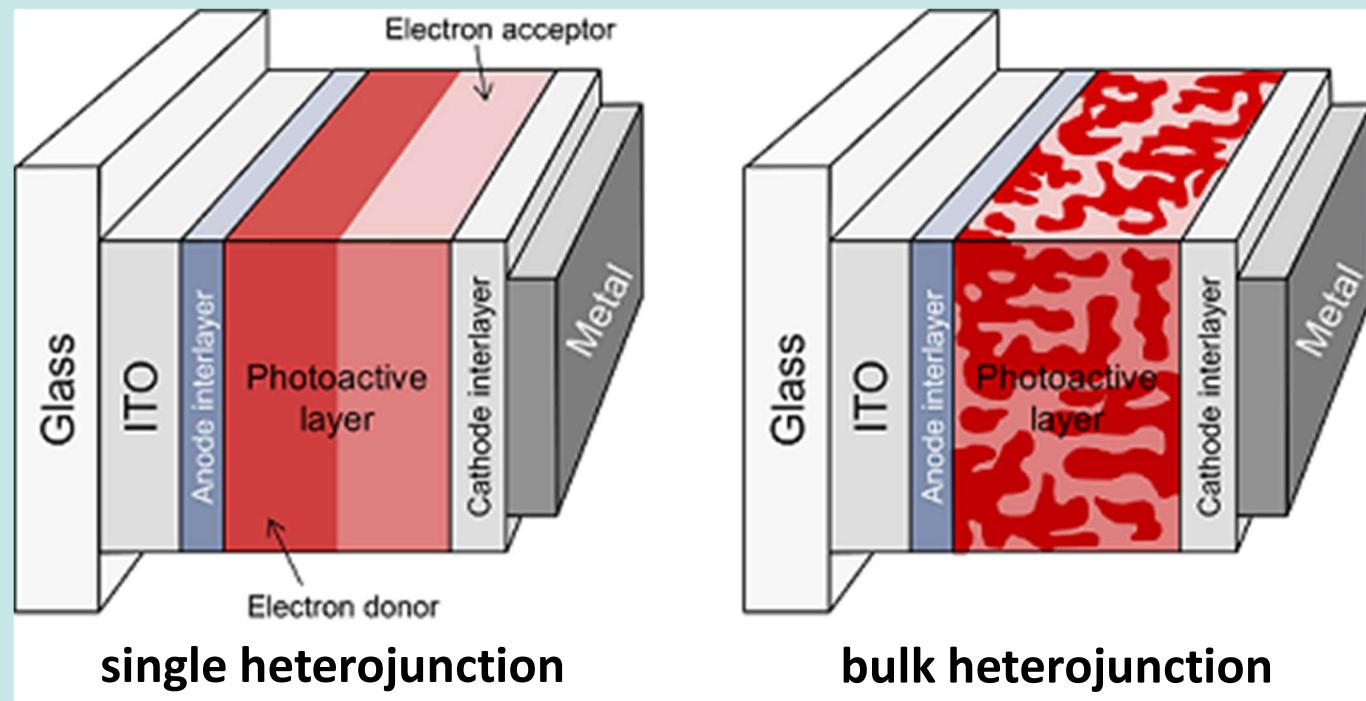
Best Research-Cell Efficiencies



Photovoltaic devices - basics

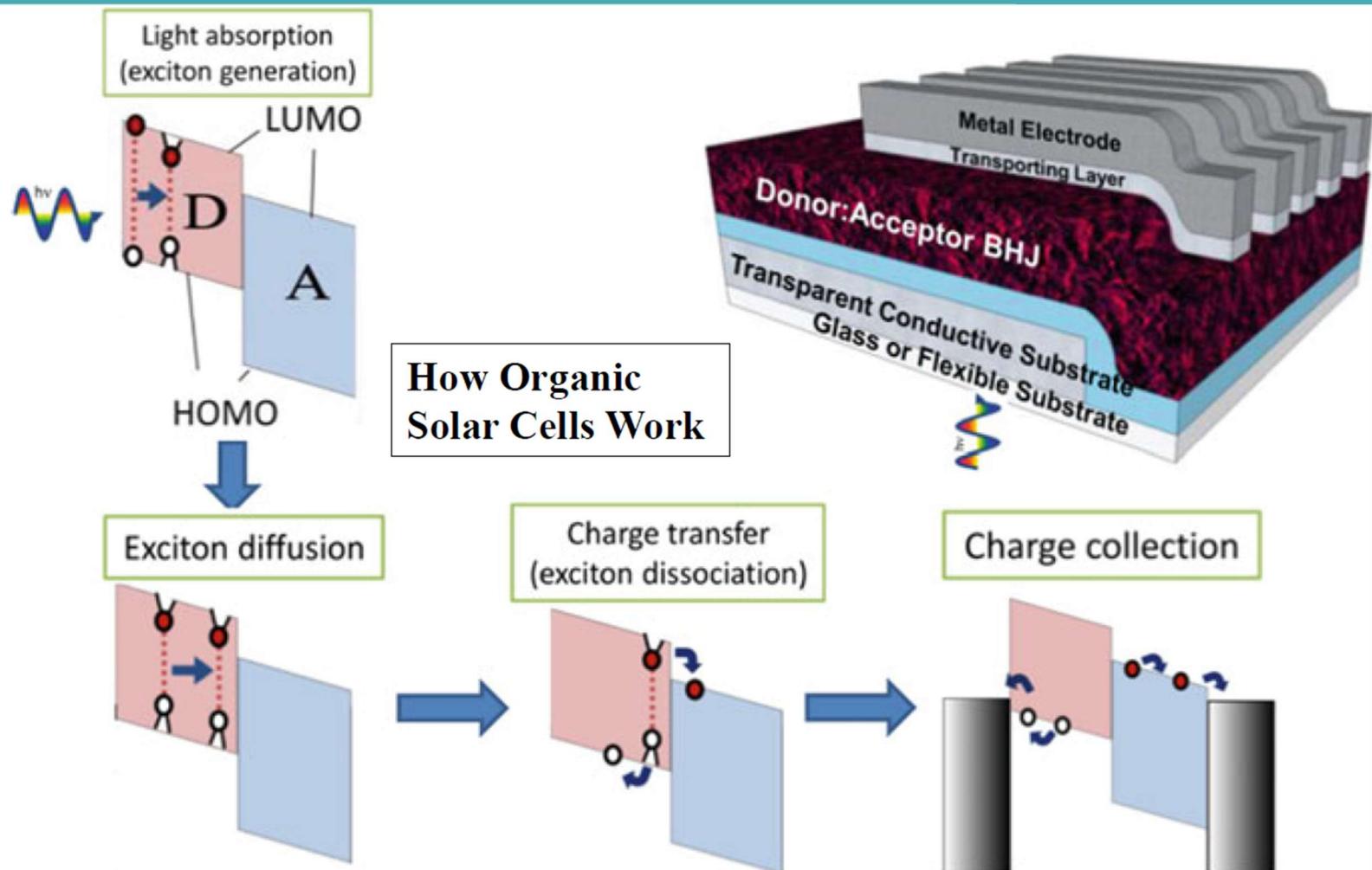
A photovoltaic (PV) cell

- absorption of photons
- creation of excitons
- exciton diffusion
- exciton dissociation
- charge transport
- charge collection

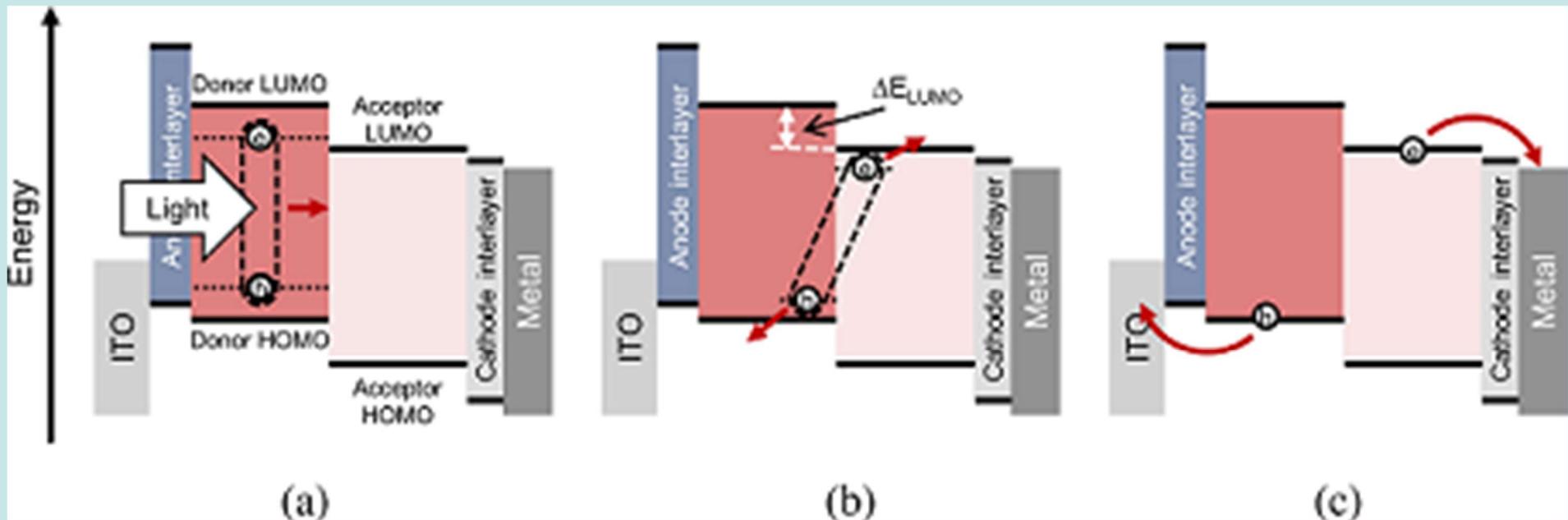


(Image credit: Cavendish OE Group, University of Cambridge)

Band diagram of an OPV cell

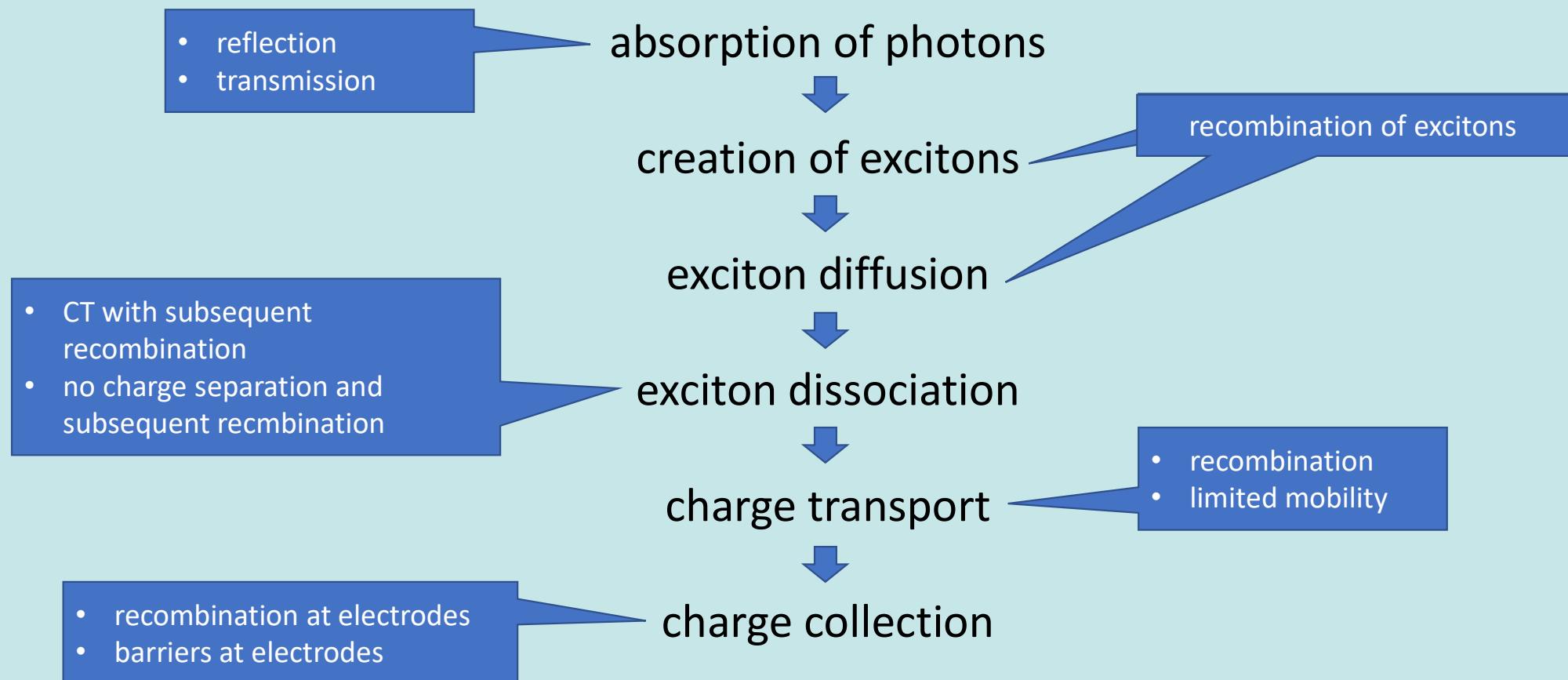


A more detailed view



a) exciton generation; b) charge transfer state dissociation; c) charge transport and extraction
(Image credit: Cavendish OE Group, University of Cambridge)

Losses in PV cells

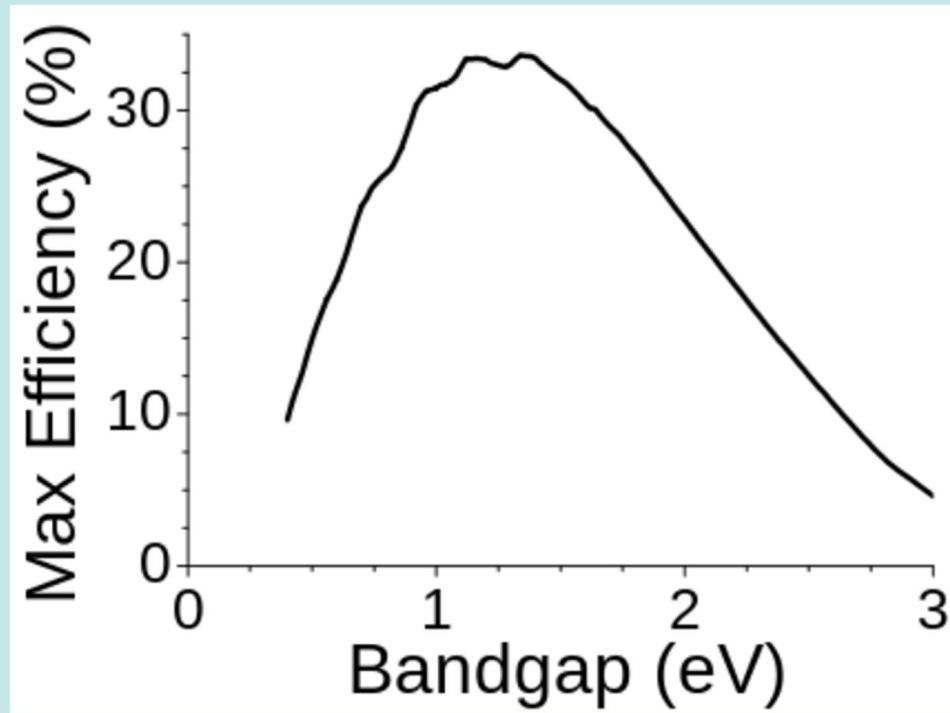


Fundamental processes in an OPV

Charge physics at heterojunctions

Shockley-Queisser limit

What is the maximum theoretical efficiency of a single pn junction solar cell?



33.7% for bandgap 1.34eV

Shockley-Queisser limit - losses

1. black body radiation

- any body at temperature above absolute zero emits radiation
- working PV cell has a higher temperature than surroundings (solar irradiation)

2. recombination

- electrons and holes can recombine
- reason for $V_{OC} < E_G$ in real devices

3. spectral losses

- only photons with energy above bandgap can be used
- any extra energy is lost (spectral losses alone in Si are 52%)

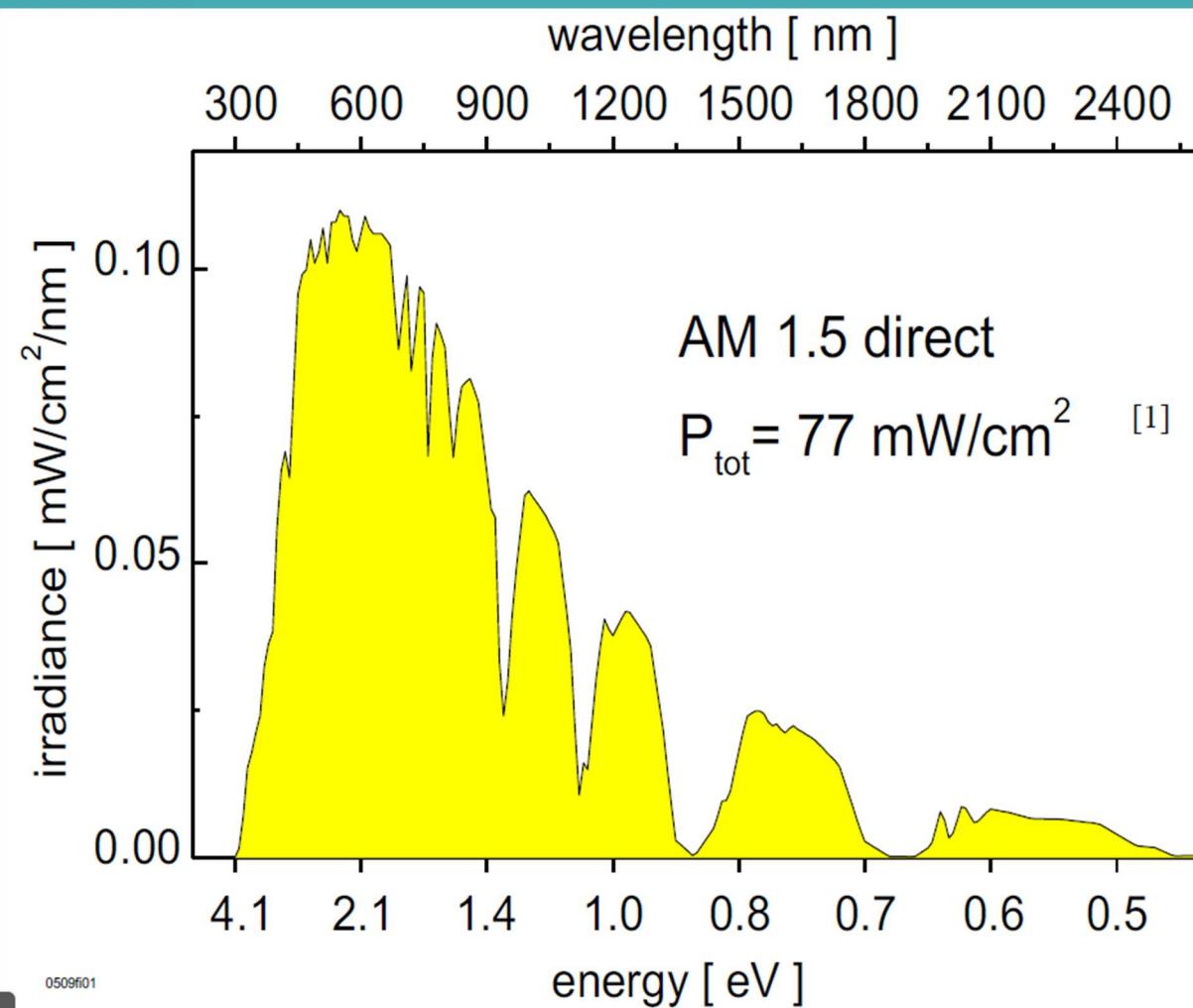
4. impedance matching

- If the resistance of the load is too high, the current will be very low, while if the load resistance is too low, the voltage drop across it will be very low. There is an optimal load resistance that will draw the most power from the solar cell at a given illumination level.

5. other factors

- non-radiative recombination
- limited mobility

Spectral losses



geminate vs. non-geminate recombination

Three possible losses mechanism within recombination:

- 1) **relaxation** of excitons which fail to diffuse to, and separate at, a suitable molecular interface,
- 2) **geminate recombination**: recombination of geminate pairs formed at that interface which fail to fully dissociate
- 3) **non-geminate recombination**: recombination of dissociated carriers generated by different absorption events

Charge transfer: heterojunction

- two materials of different electron affinities create an energetic offset = driving energy for exciton dissociation
- rate of photoinduced e transfer decreases exponentially with separation of D/A -> electrons have to migrate to the interface to dissociate

planar heterojunction

- easy to make
- long distance compared to average exciton diffusion length (5-20nm due to short lifetime)
- thinner layers – worse absorption

bulk heterojunction

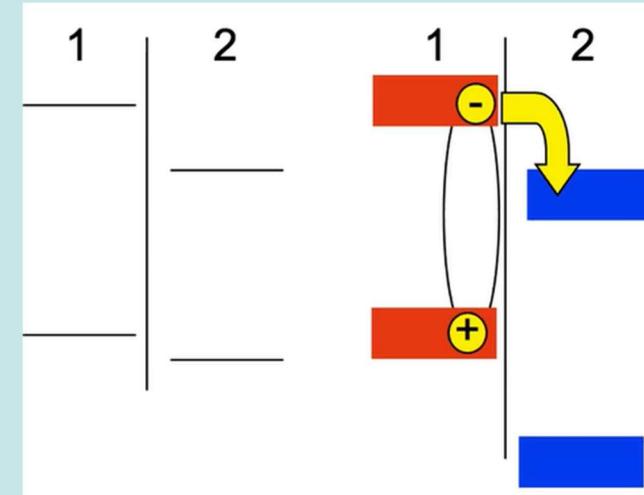
- more common
- shorter distance to interface
- material not always matched with electrode

Charge transfer: heterojunction



type I heterojunction

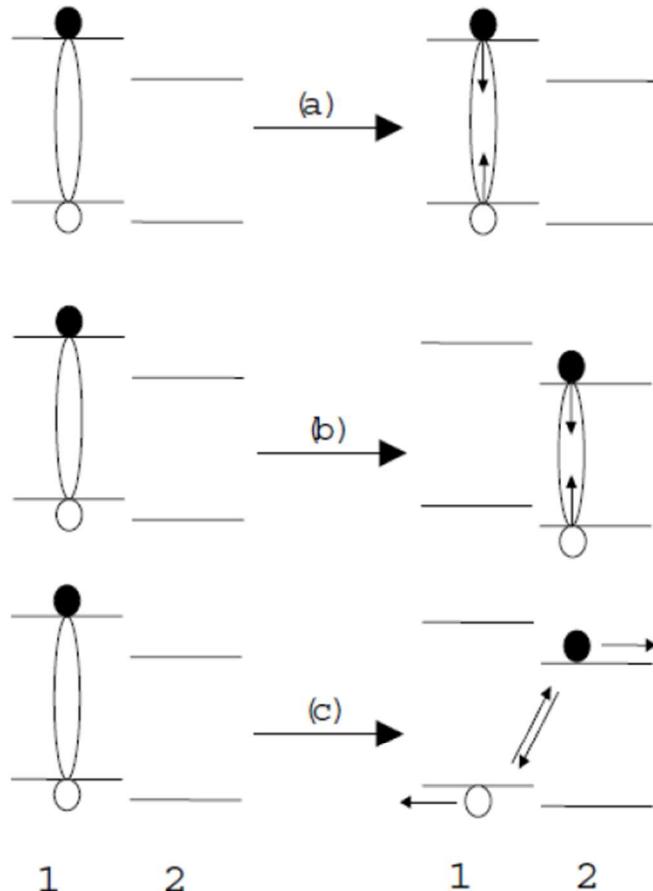
- only energy transfer 1-> 2 possible
- ΔE must be comparable to kT



type II heterojunction

- more complex photophysics
- energy or charge transfer possible
- size of ΔE comparable to binding energy of exciton

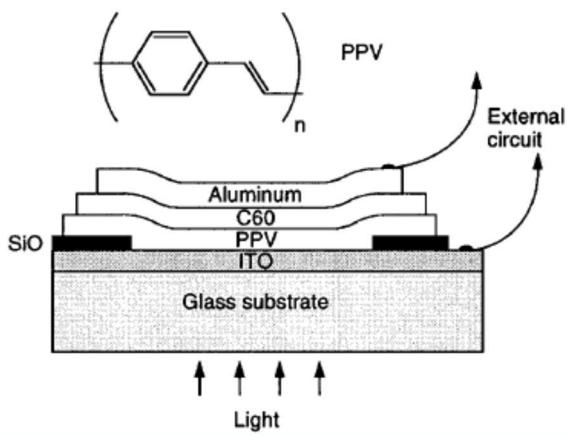
Type II heterojunction



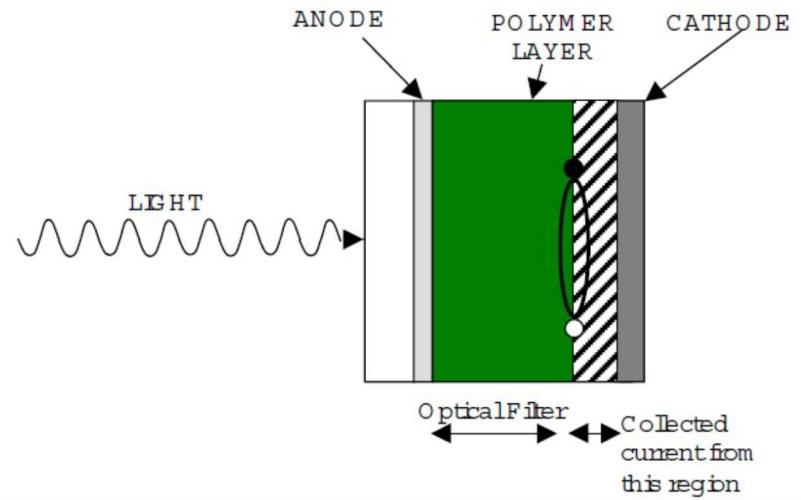
- a) No transfer:** exciton decays radiatively or non-radiatively in Polymer 1 with energy = E_G of polymer 1 (minus relaxation energy)
- b) Energy transfer:** exciton transfers to Polymer 2 and then decays radiatively or non-radiatively. Radiative recombination will result in emission of a photon with an energy characteristic of Polymer 2. This can only happen if the distance of the exciton from interface is comparable with Förster transfer radius.
- c) Charge transfer:** One of the charges transfers to Polymer 2 leaving the opposite charge on Polymer 1. They could then become trapped, recombine with a free opposite charge, recombine geminately across the interface or move as free charges through the system. This is what is particularly interesting for PVDs. Only possible within a Förster radius or so from interface and if LUMO or HOMO mismatch > exciton binding energy.

Double layer structure

- most of implementations use good electron acceptor + polymer
- electron acceptor traditionally C₆₀
- example below: 1% efficiency (FF=0.48)



Sariciftci et al APL (1993), Halls et al (1996)

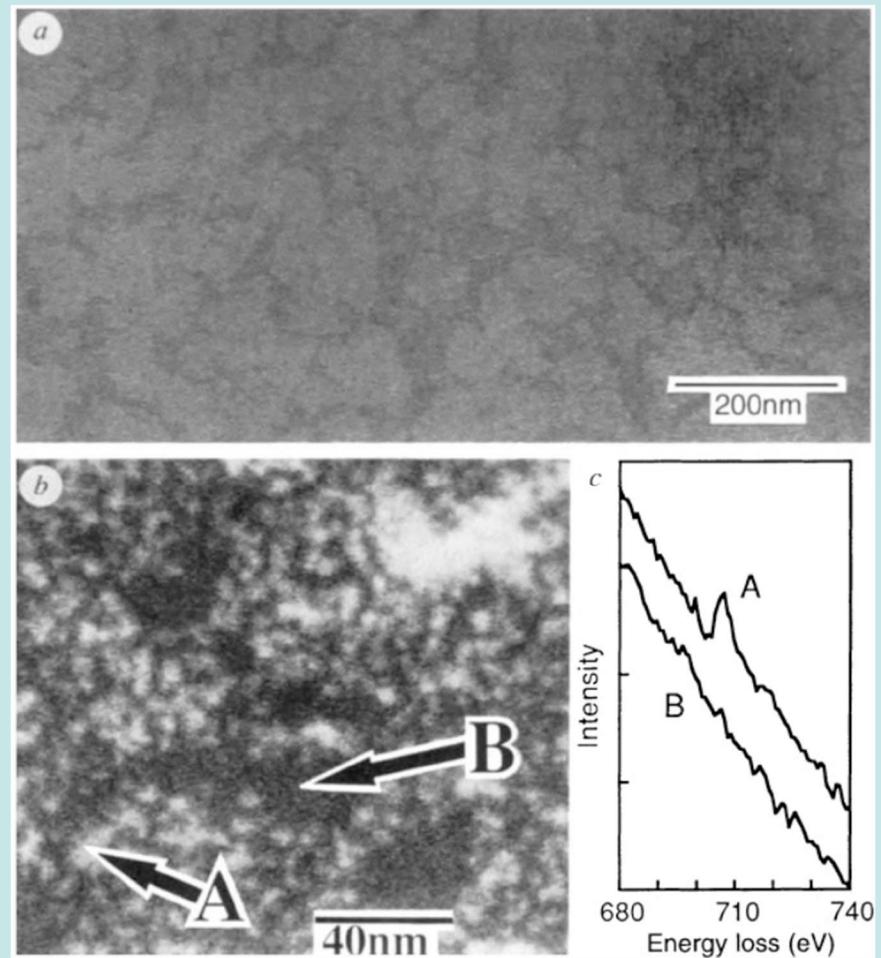


issues:

- filter effect
- only 1 interface
- large distance for charge transport (favours recombination)

Interpenetrating polymer networks

- aka bulk heterojunction
- mix donor and acceptor in the same solvent
- exploit phase separation tendency of polymers (small entropy of mixing)
- good PL quenching
- MEH-PPV/CN-PPV : 6% efficiency



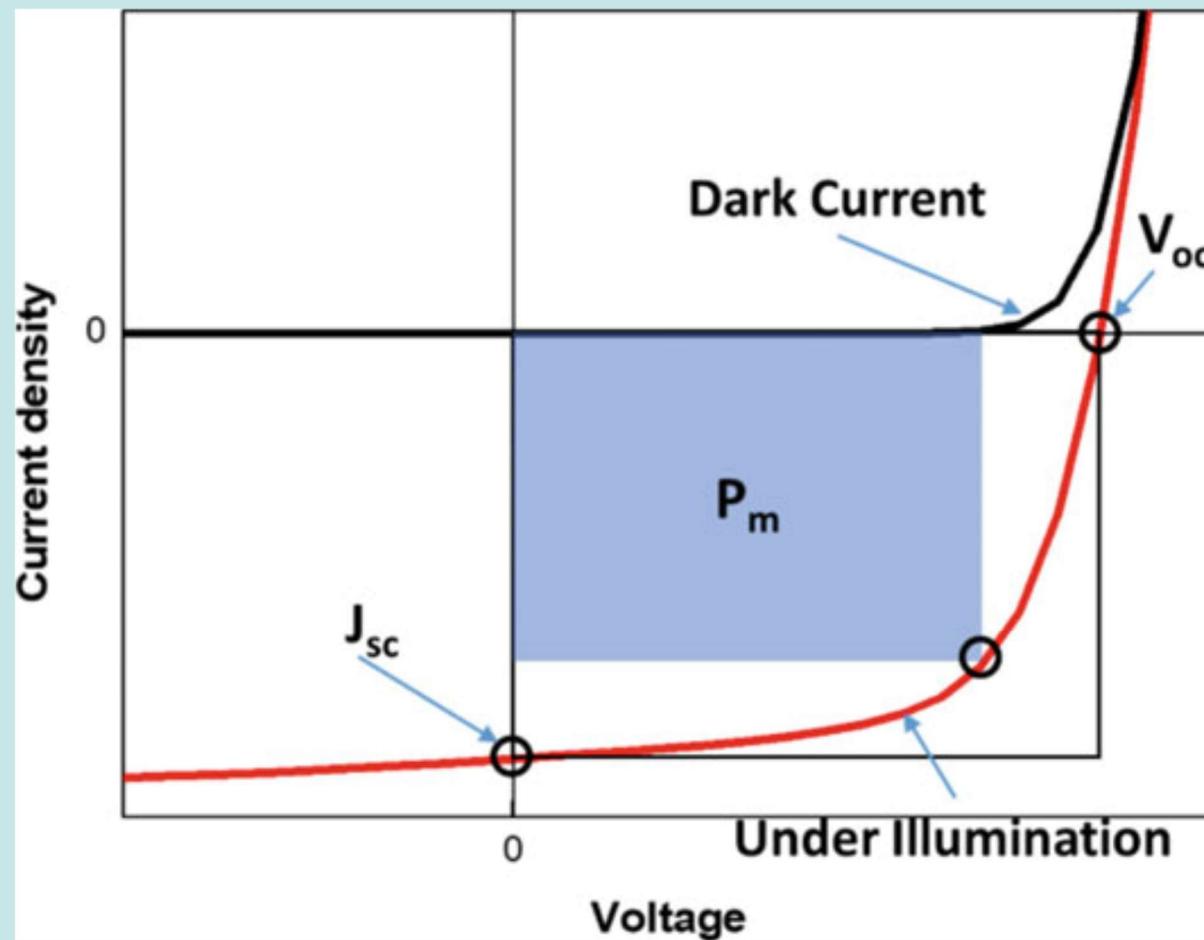
JJ Halls et al. Nature , 376, 498 (1995)

Charge transport: polarons

- in OPVs charge transport takes place by polarons hopping
- mobilities strongly affected by morphology of the film
- typical mobilities in bulk heterojunction: 10^{-4} - $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
- trap sites reduce mobility

Characterisation of OPVs

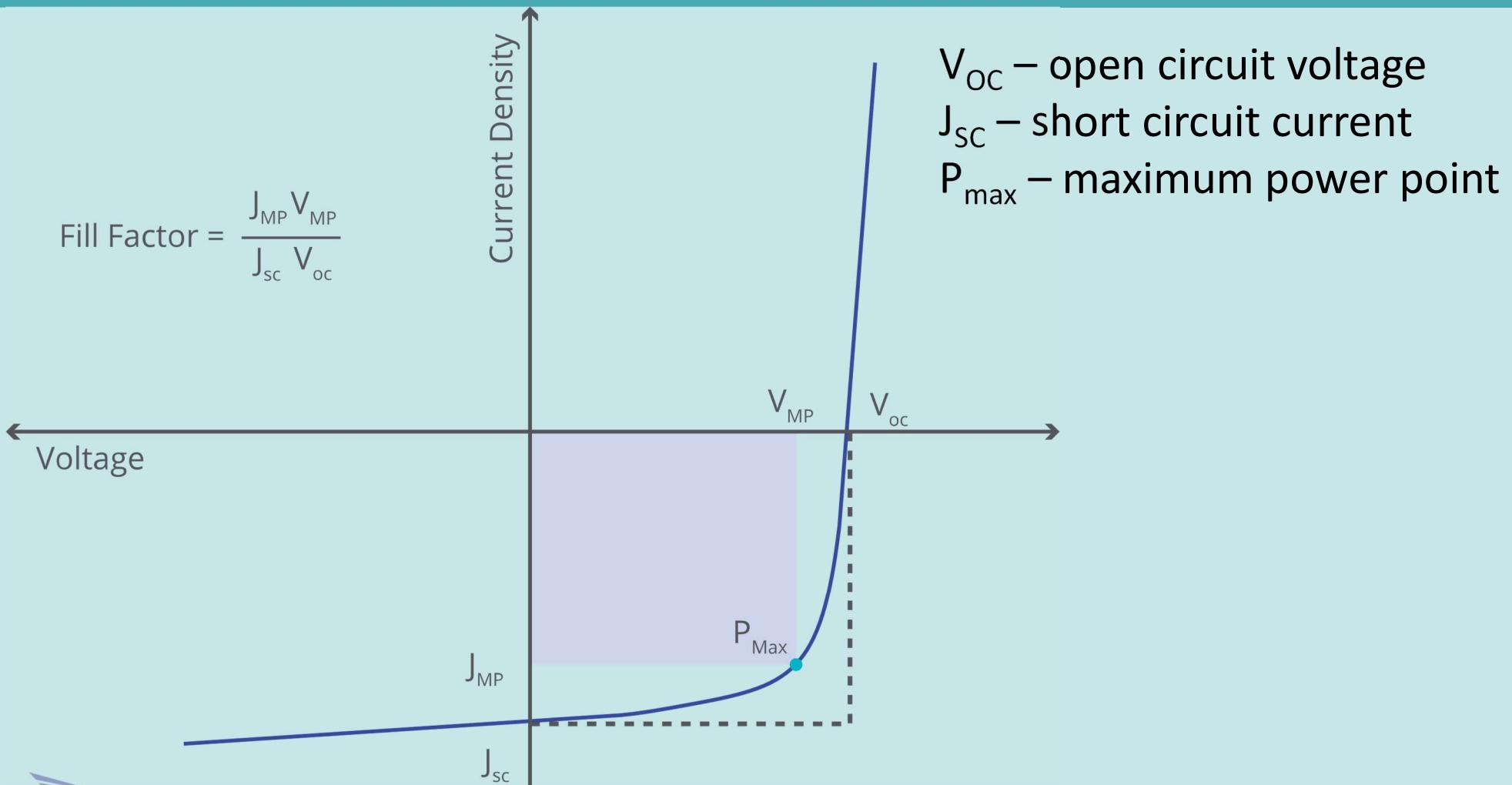
JV curve



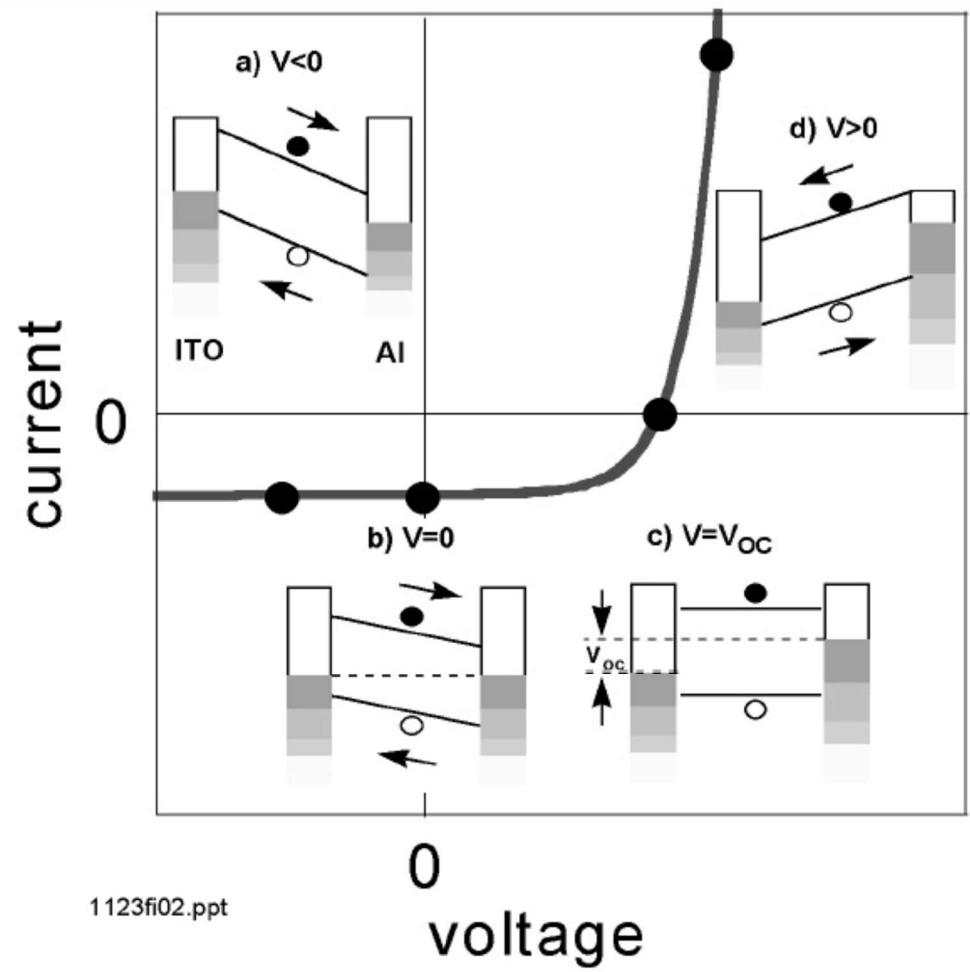
V_{oc} – open circuit voltage
 J_{sc} – short circuit current
 P_m – maximum power point

Extracting Fill Factor

$$\text{Fill Factor} = \frac{J_{MP} V_{MP}}{J_{SC} V_{oc}}$$



Band regimes



Relevant parameters

PCE – Power Conversion Efficiency

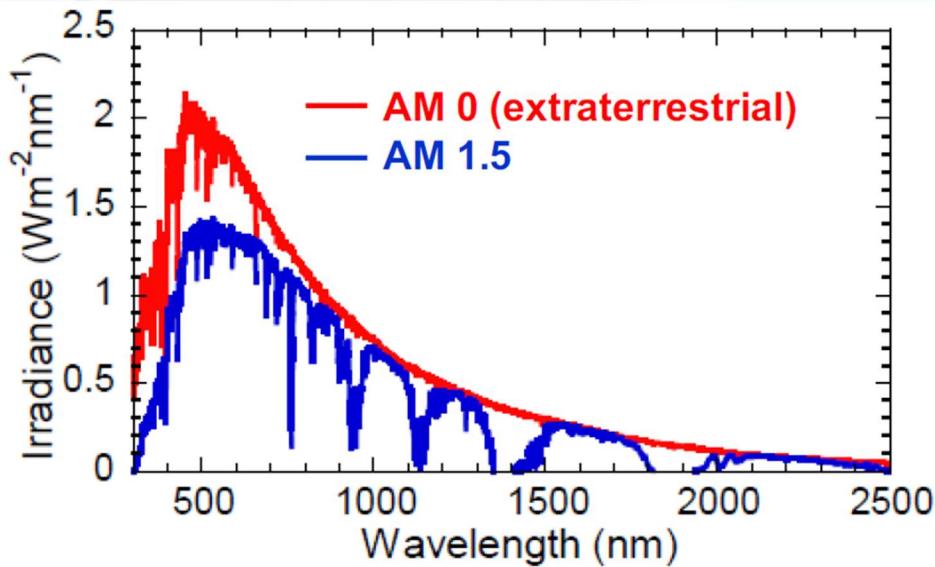
$$PCE = \frac{P_m}{P_{in}} = \frac{I_{SC} \times V_{OC} \times FF}{P_{in}}$$

V_{OC} – open circuit voltage
 I_{SC} – short circuit current
 P_m – maximum power point
 P_{in} – incident light power
FF – fill factor $FF = \frac{P_m}{V_{OC}I_{SC}}$

EQE – external quantum efficiency

$$EQE = \frac{I_{SC}(\lambda)hc}{P_{in}(\lambda)e\lambda}$$

Solar simulator

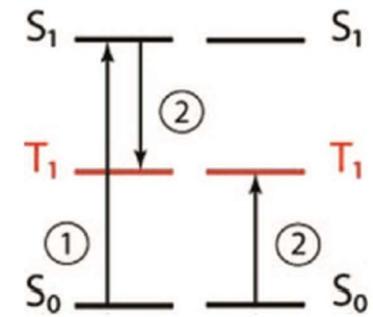
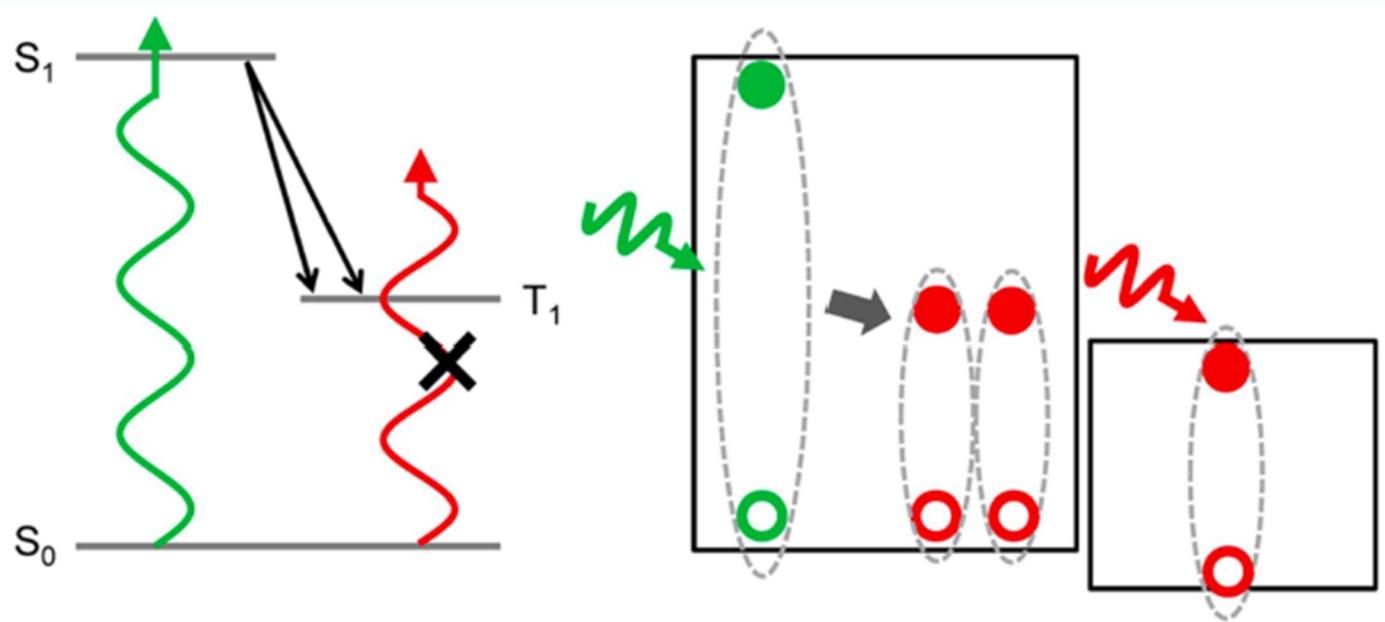


- broadband lamp with filters
- simulates intensity and spectral composition of sunlight
- usually set to AM1.5:
 - radiation that crossed 1.5 x mass of air compared to irradiation along the normal
 - corresponds to a solar angle of 48°

Research directions in OPVs

Singlet fission

S-Q limit raised: max theoretical efficiency
now above 40%



(1) Initial excitation of left chromophore to S_1 . (2) excited chromophore shares its energy with chromophore on the right, creating a T_1 state on each

Chem. Rev. 2010, 110, 6891

ACCOUNTS OF CHEMICAL RESEARCH 2013, 46, 1300

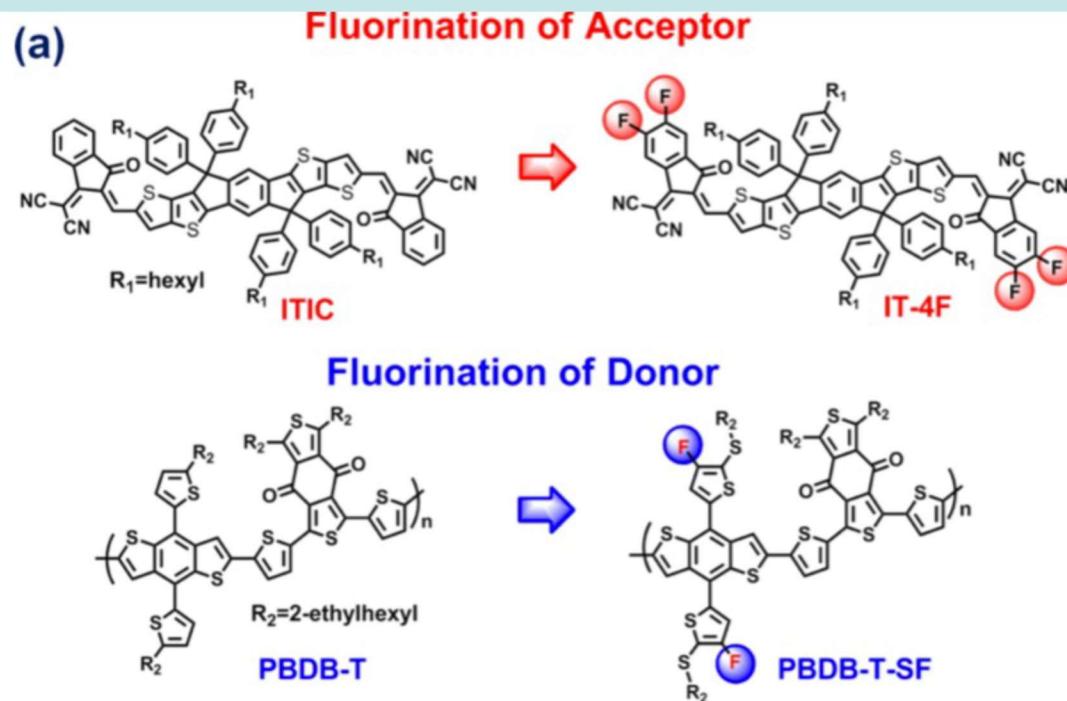
Choice of acceptor

- fullerenes:
 - very low LUMO (fast energy transfer) but large energy losses
 - electron transfer to C₆₀ facilitates exciton dissociation
 - toxic
- non-fullerene:
 - low toxicity
 - currently the most promising (>18% efficiency)
 - fluorination of non-fullerenes
 - shifts HOMO and LUMO down without strong steric hindrance
 - increases crystallinity and charge transport
 - higher polarisation (screening of Coulombic interactions of e-h)
 - often increased absorption

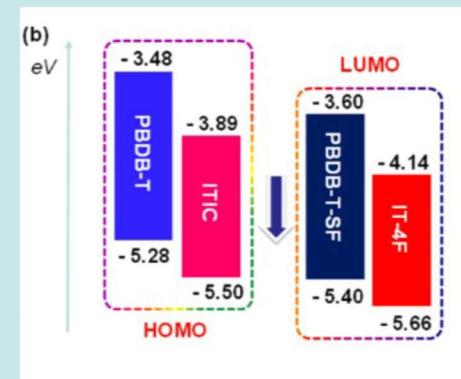
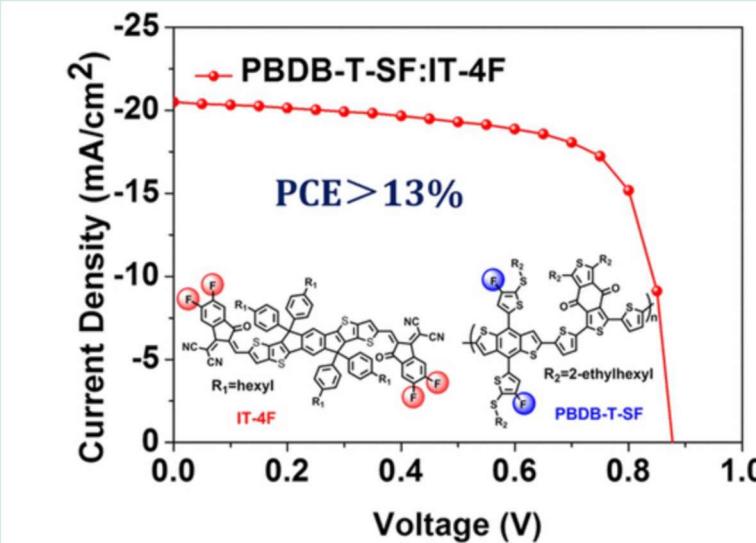
Zhao W. et al JACS 139, 7148 (2017)

Fluorination

(a)

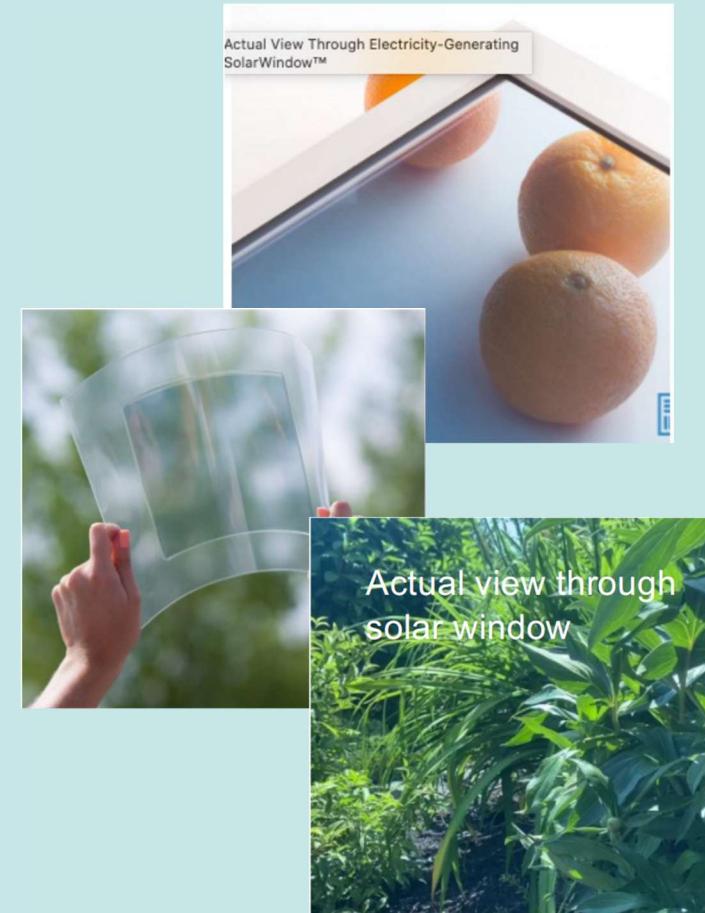


Zhao W. et al JACS 139, 7148 (2017)



(Semi)transparent OPVs

- absorb invisible part of spectrum
- March 2021: SolarWindow Technologies reported a record 14.72% (+/- 0.29%) PCE using industry-standard single-cell patterning for performance testing (though transparency not stated for this particular cell – possibly fully absorbing).
- Technology: organic semiconductors (OS) coating (that they term "LiquidElectricity™ coatings")



www.solarwindow.com/2021/03/solarwindow_sets_new_record_doubling_its_power_conversion_efficiency/

Summary

- Challenges:
 - stability of devices
 - active layer films with uniform morphology
 - fabrication methods suitable for large scale applications

Next week:

Organic Field Effect Transistors (OFETs)

Consider 2 organic PVDs for which the following parameters are known:

Diode A: $I_{sc} = 1$ mA, $V_{oc} = 1.2$ V, $FF = 0.75$

Diode B: $I_{sc} = 2$ mA, $V_{oc} = 1.2$ V, $FF = 0.35$

Say which of the two diodes is more efficient under an illumination of 10 W/m²