ORGANIC-BASED LIGHT HARVESTING ELECTRONIC DEVICES

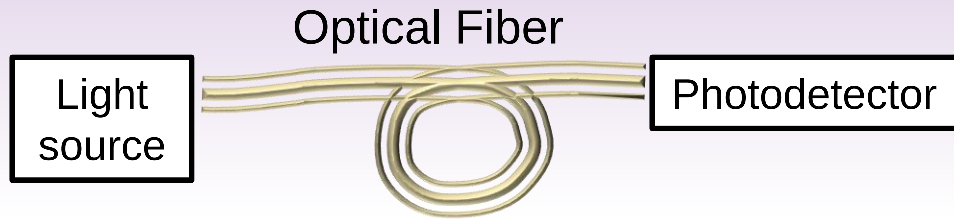
Maddalena Binda

Organic Electronics: principles, devices and applications
Milano, November 23-27th, 2015

Organic-based light harvesting devices

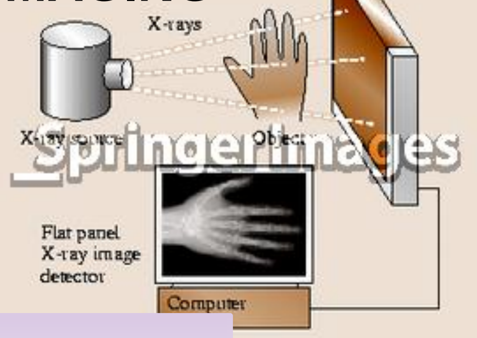
From *power generation* to *signal detection*...

Optical Communications

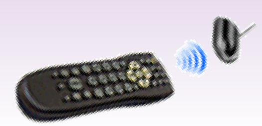


Sensoristics

Imaging

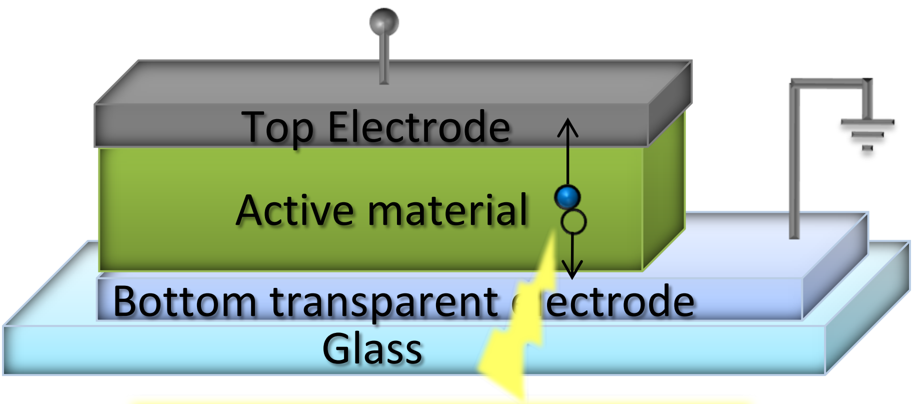


Remote Control



Organic-based light harvesting devices

From *signal detection* to *power generation*...



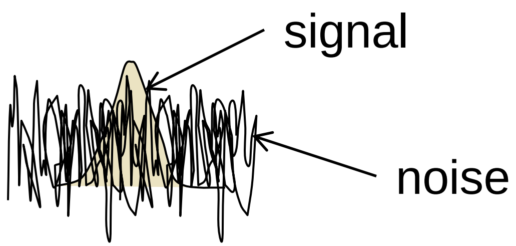
Photogeneration efficiency: EQE

Signal detection	Power generation
High speed	CW operation
Spectral selectivity	Broad responsivity
Bias voltage allowed	Bias voltage not allowed
High signal-to-noise ratio	Power conversion efficiency
Hardiness in critical conditions?	Hardiness in critical conditions

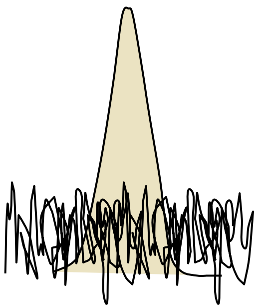
Light sensors:
Organic PhotoDetectors (OPD)

Light sensors: sensitivity

We want to go from this...



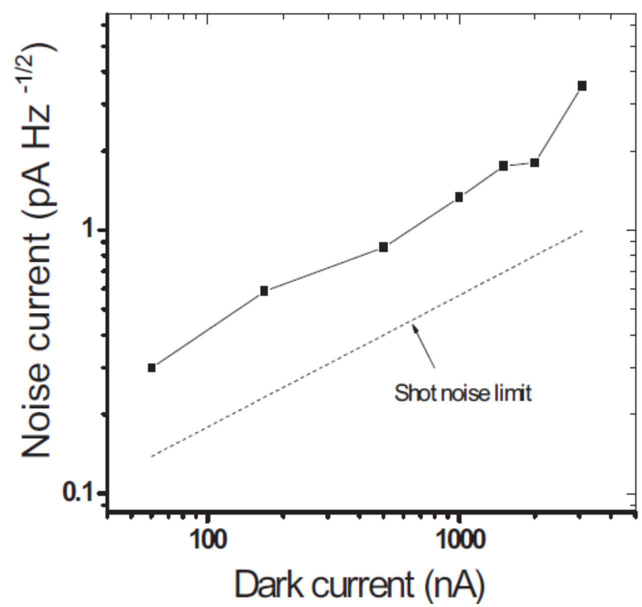
...to this:



High **signal-to-noise ratio (SNR)**

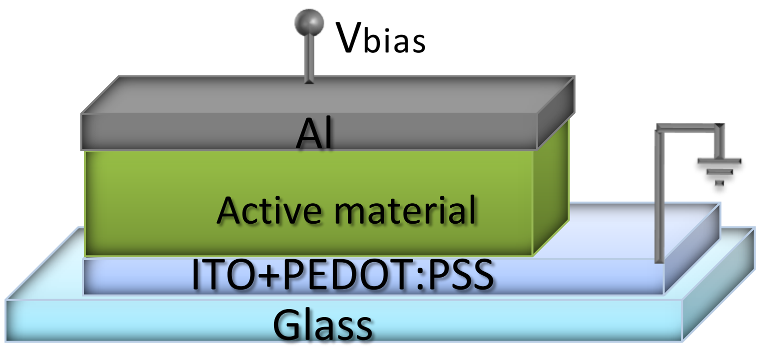
- Increase signal → Increase EQE
- Reduce parasitic effects: leakage current

$$D^* = \frac{R \cdot \sqrt{A}}{\sqrt{2qI_{dark}}} = \frac{R}{\sqrt{2qJ_{dark}}}$$

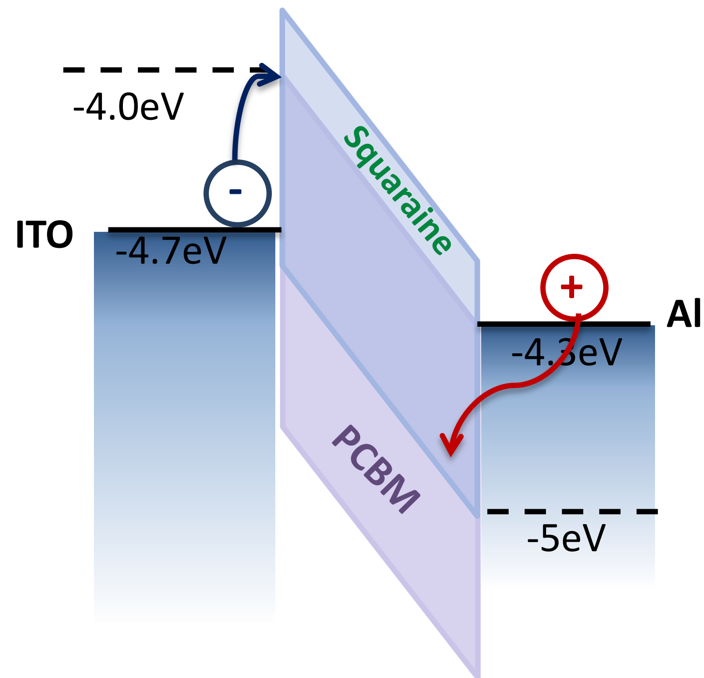


Adv. Mater. **2007**, *19*, 3979–3983

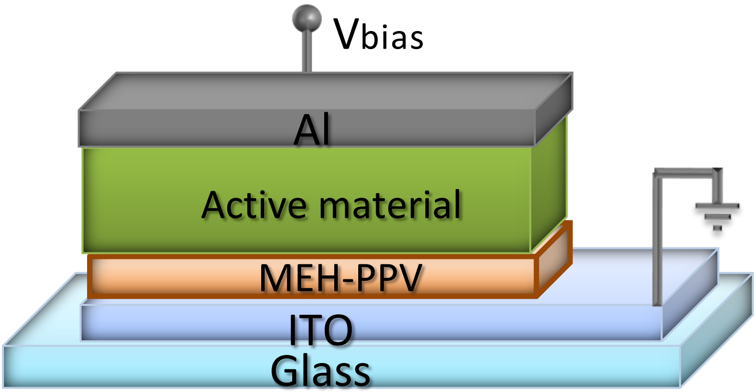
Light sensors: sensitivity



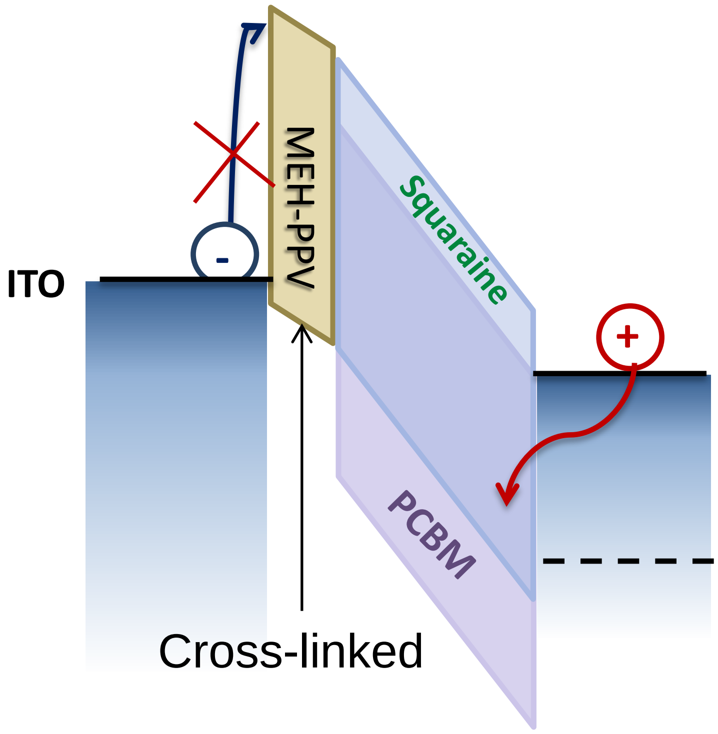
M. Binda et al.
Appl. Phys. Lett. 98 (7), 073303, 2011.



Light sensors: sensitivity

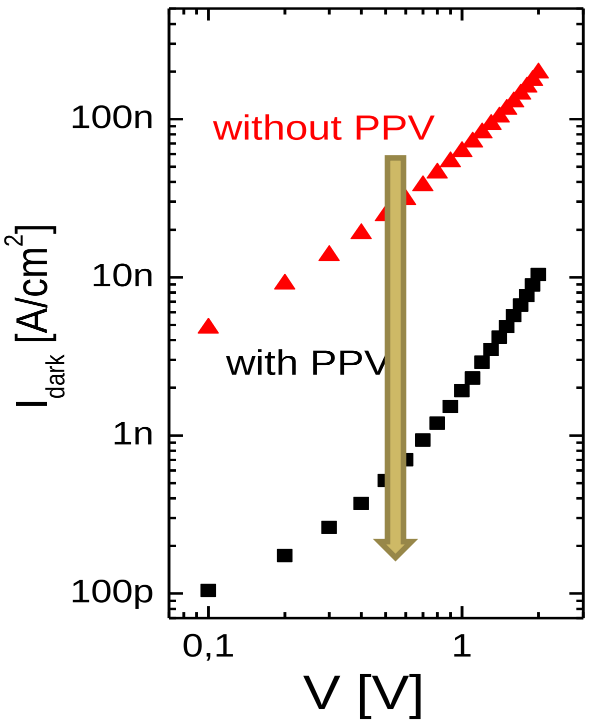


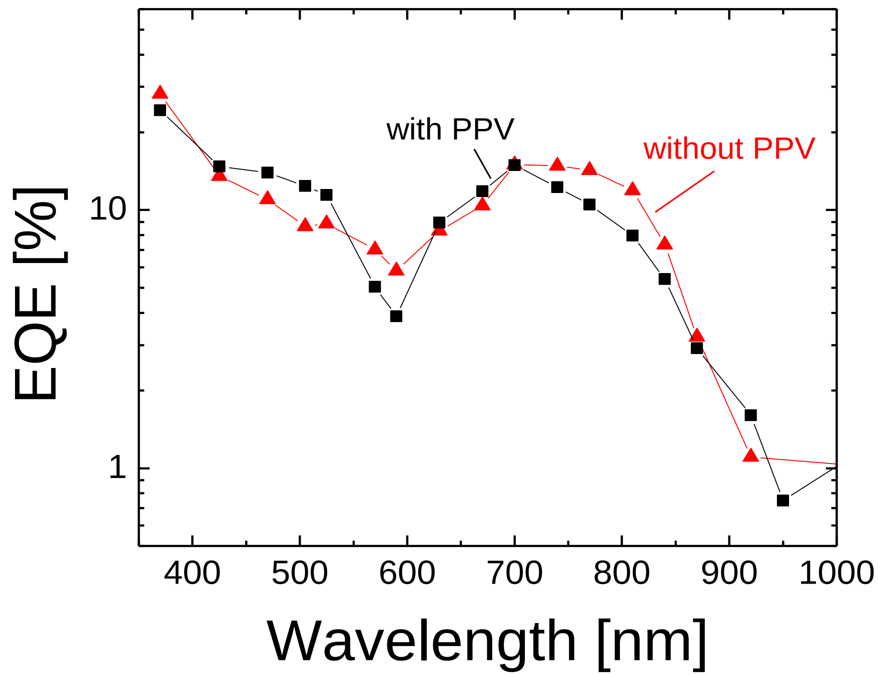
Appl. Phys. Lett. 98 (7), 073303, 2011.



Light sensors: sensitivity

Appl. Phys. Lett. 98 (7), 073303, 2011.





D*: $5.9 \times 10^{11} \rightarrow 3.4 \times 10^{12}$ $Hz^{0.5}cm/W$

SEE ALSO:

Appl. Phys. Lett. 2009, 94, 173303

Science 2009, 325, 1665

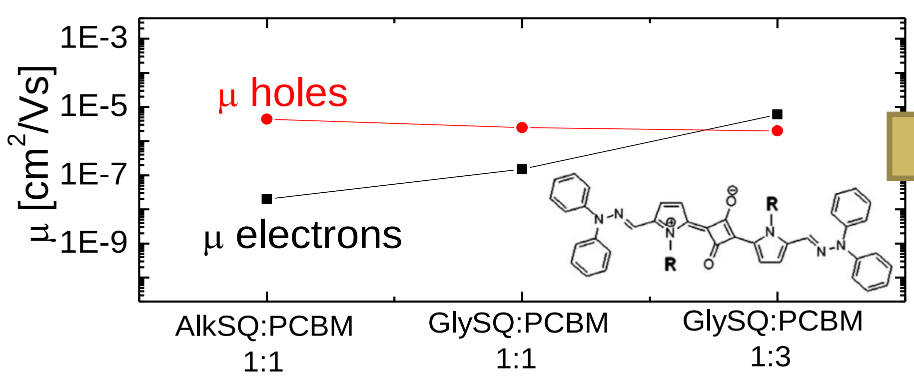
Light sensors: response speed

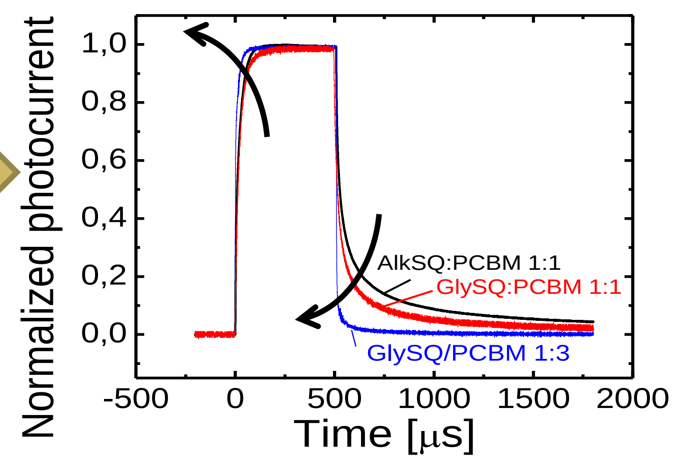
E.g. APPLICATION IN OPTICAL DATA TRANSMISSION

Fast reponse is required!

Play with:

- device geometry –> Reduced interelectrode spacing
- active material composition



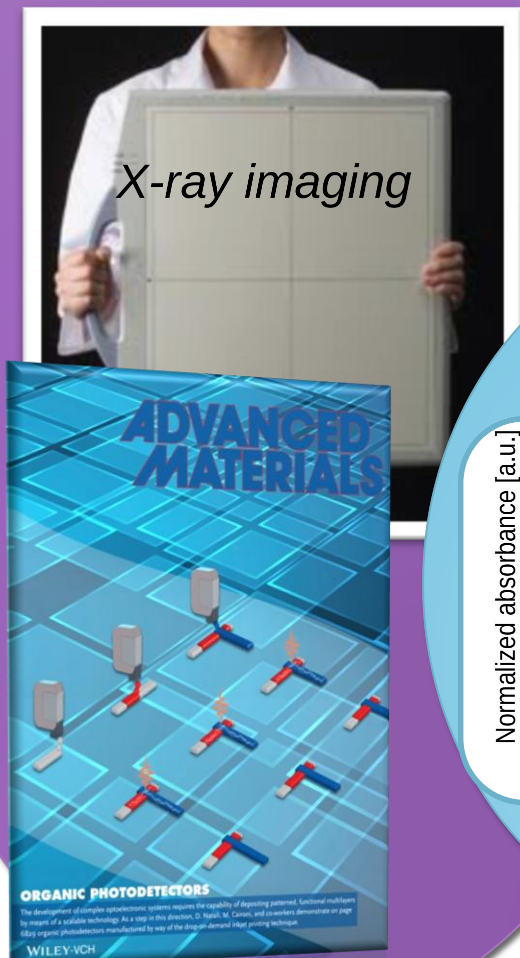


Organic Electronics 10 (2009) 1314–1319

Organic light sensors: applications

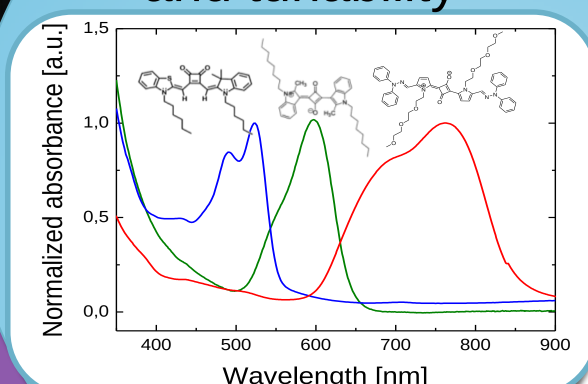
Large area

X-ray imaging



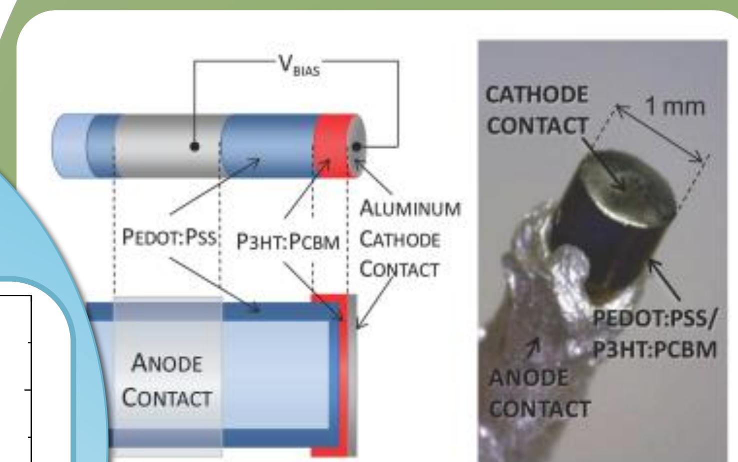
Adv. Mater. 2013, 25, 6829

Spectral selectivity and tunability



Colorimetry, artificial retina, image sensors

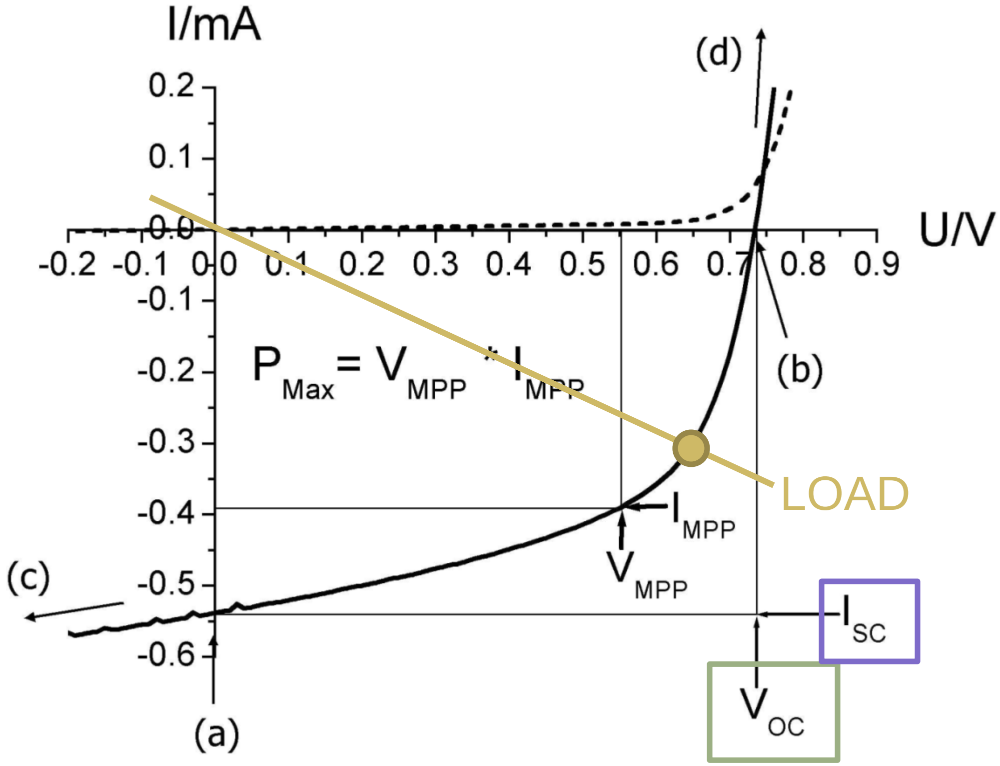
Unconventional shapes

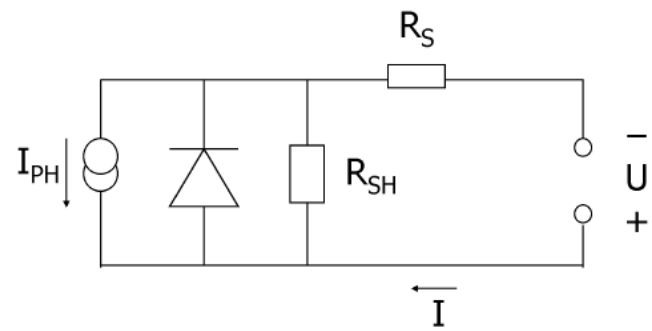


Adv. Mater. 2013, 25, 4335

Organic Solar Cells (OSC)

Power Conversion Efficiency of a solar cell



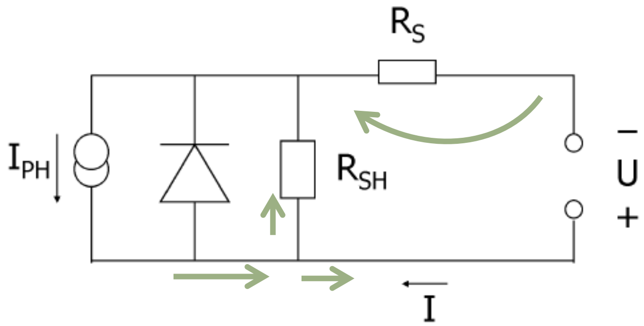


$$FF = \frac{V_{mpp} \cdot I_{mpp}}{V_{oc} \cdot I_{sc}}$$

Power Conversion Efficiency (PCE)

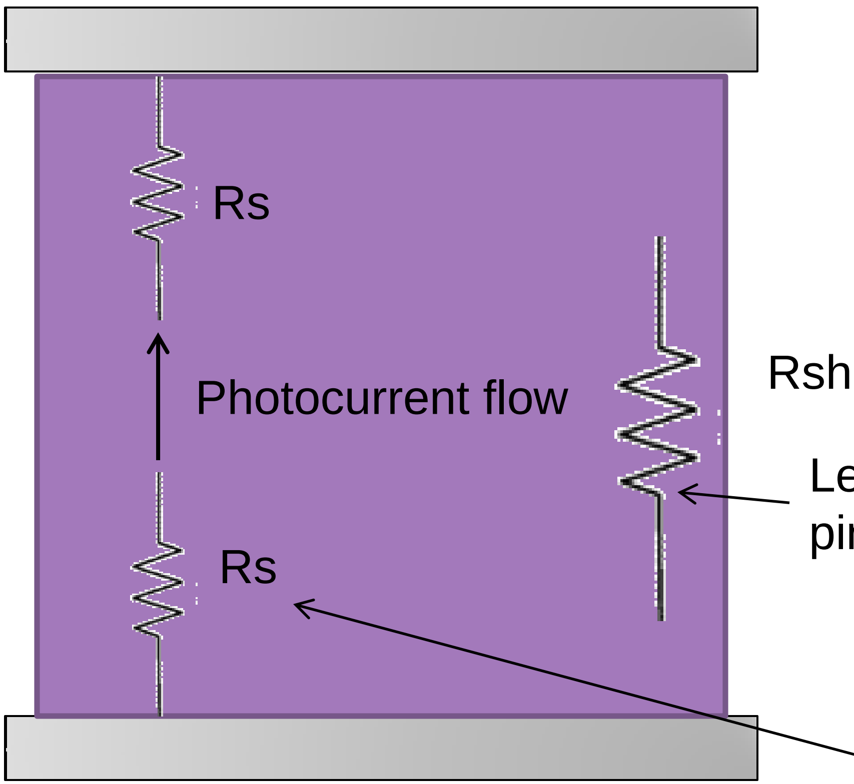
$$\eta_{POWER} = \frac{P_{OUT}}{P_{IN}} = \frac{I_{MPP} \cdot V_{MPP}}{P_{IN}} = \frac{FF \cdot I_{SC} \cdot V_{OC}}{P_{IN}}$$

Series and Shunt resistance of a solar cell



We want:

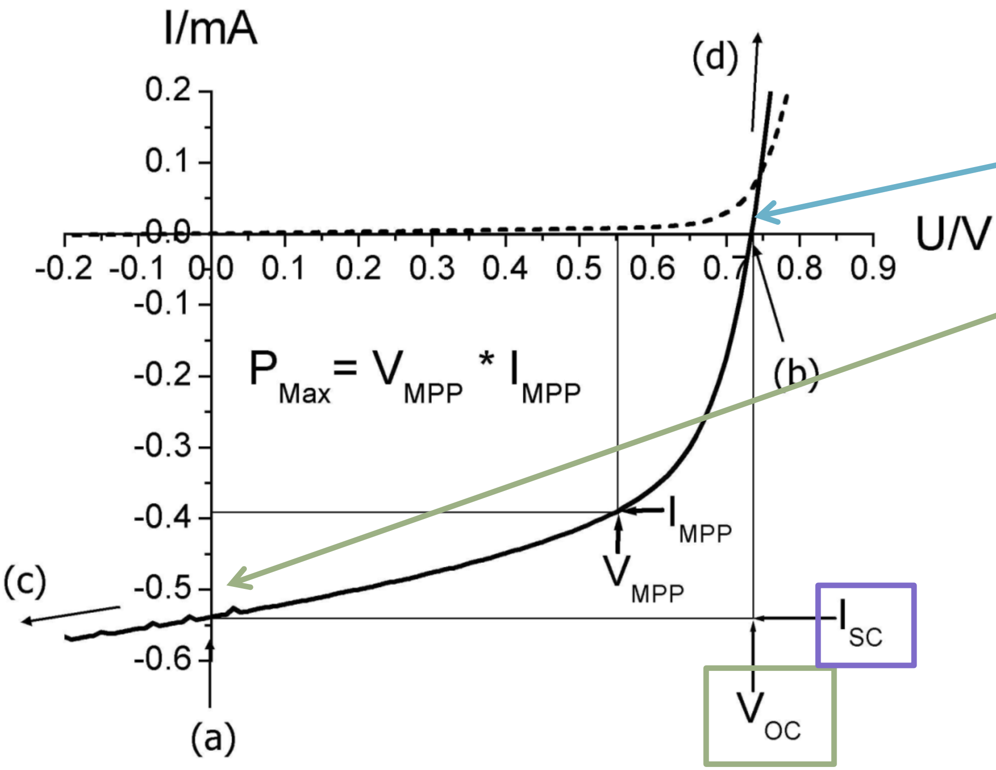
Rs low
Rsh high

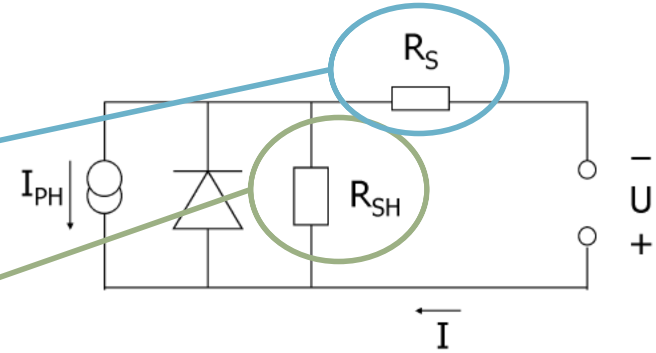


Leakage paths: metal infiltration, pinholes,...

poorly conductive paths in the semiconductor, contact resistance, resistivity of the electrode,...

Power Conversion Efficiency of a solar cell





$$FF = \frac{V_{mpp} \cdot I_{mpp}}{V_{oc} \cdot I_{sc}}$$

Power Conversion Efficiency (PCE)

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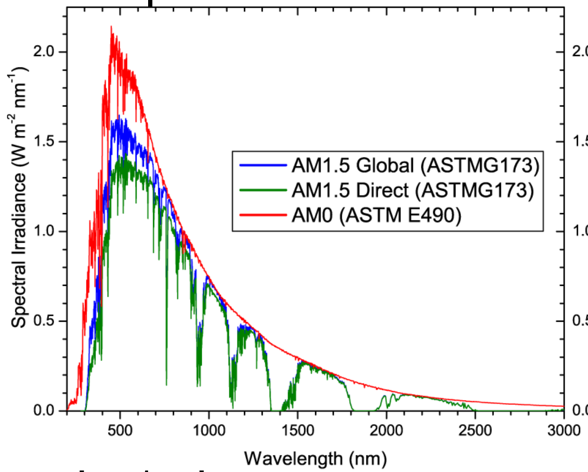
Power Conversion Efficiency of a solar cell

<u>Important notes on cell characterization:</u>

1. The solar emission must be reproduced



Shape & Intensity!

2. A standard path must be adopted

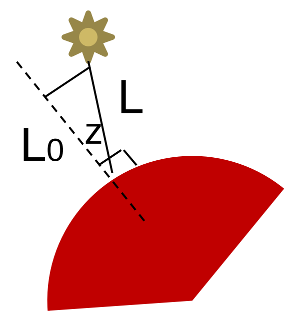
<u>air-mass:</u>
optical path through the Earth athmosphere

scattering ← → absorption

Standard AM1.5 - 1 sun

AM1.5 ⇔ ~1000W/m^2

<u>AM *X*</u>

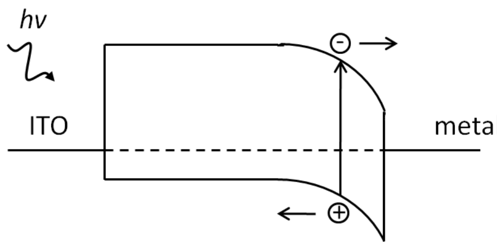


$$X = \frac{L}{L_0} \approx \frac{1}{\cos z}$$

L_0=zenit path length at see level
L=effective path length

Es. z=0 → AM1

Organic solar cell: a brief history



1950's: first studies on photovoltaic effect in organic solids
(single semiconductor material and Schottky effect)
PCE<0.1%

1986: first demonstration of donor/acceptor OPV
(small molecule bilayer p-type /n-type CuPc/PTCBI)
PCE=1%

1990: ultrafast charge transfer phenomenon demonstrated between polymer and fullerene

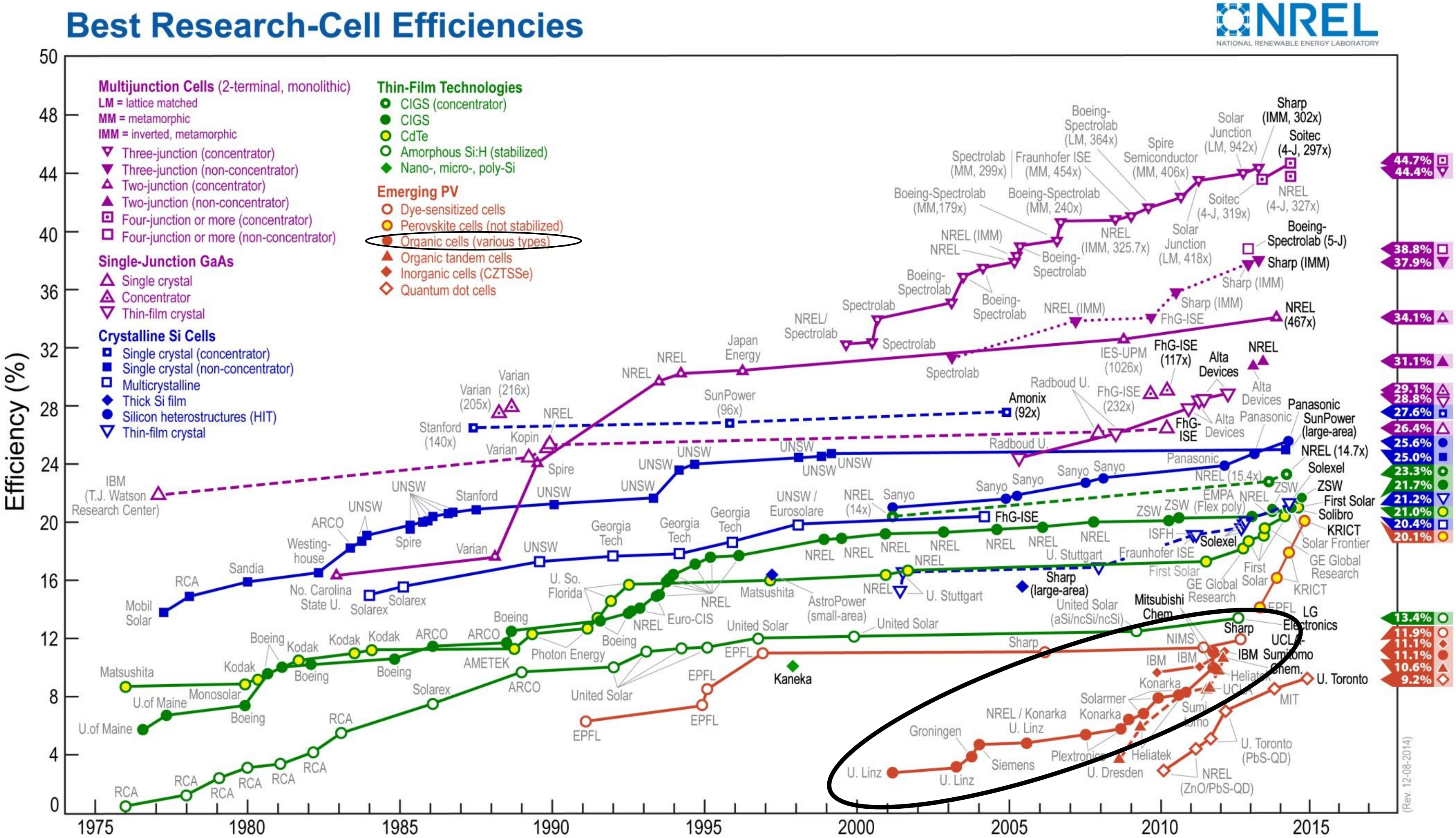
1992: first demonstration of BHJ

Appl. Phys. Lett., 1986, 48, 183
Science, 1992, 258, 1474
Solid State Commun. 1992, 82, 249
Synth. Met., 1993, 59, 333

A.J. Heeger, N.S. Sariciftci, Patent US 1992/5331183
Science, 1995, 270, 1789
Nature, 1995, 376, 498

Energy Environ. Sci., 2014, 7, 2123

Power Conversion Efficiency of a solar cell



Power Conversion Efficiency of a solar cell

Different parameters must be simoultaneously optimized:

$$PCE = \frac{FF \cdot V_{OC} \cdot I_{SC}}{P_{IN}}$$

But they are indeed strongly correlated!!!

Open Circuit Voltage (V_{OC})

empirical

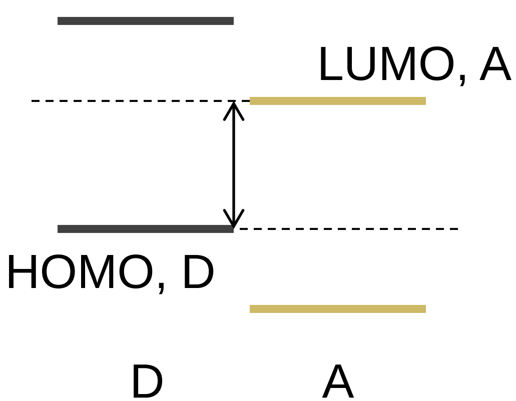
$$qVoc = \underbrace{HOMO_D - LUMO_A}_{E_{g,tr}} - 0.3$$

at solar intensity

$$qVoc = E_{g,tr} + mk_B T \ln\left(\frac{\ldots G}{\ldots}\right)$$

G=photogeneration rate

$m > 1$



See: Adv. Funct. Mater. 11, 5, 2001.
Adv. Funct. Mater. 2011, 21, 2744–2753
Adv. Mater. 2010, 22, 4987–4992
Nat. Materials, 8, 904-909, 2009
Adv. Mater. 18, 789 (2006)

Open Circuit Voltage (V_{OC})

empirical

$$qVoc = \underbrace{HOMO_D - LUMO_A}_{E_{g,tr}} - 0.3$$

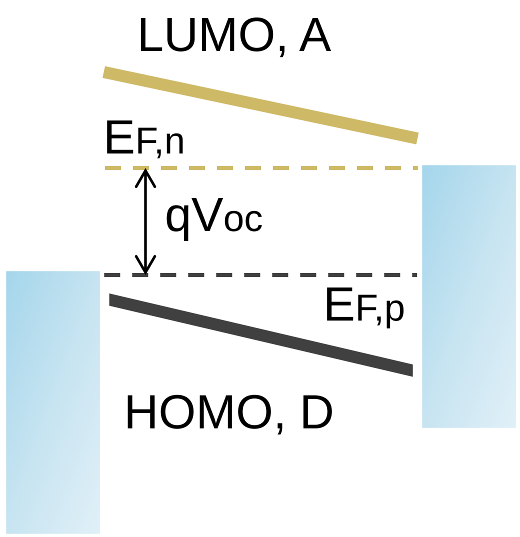
at solar intensity

$$qVoc = E_{g,tr} + mk_BT\ln\left(\frac{\dots G}{\dots}\right)$$

G=photogeneration rate

$m > 1$

$J_{net}(x)=0$



$qVoc = E_{Fh} - E_{Fe}$

$G = R(x)$

?

$G=R_{geminate}$

$G=R_{langevin}$

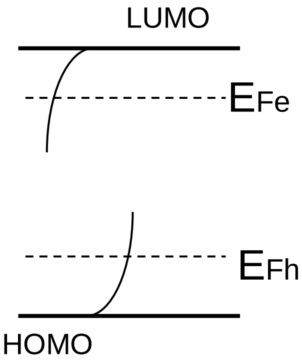
$G=R_{SRH}$

....

Open Circuit Voltage (V_{OC}): example

R=Rlangevin=$\gamma n_h(x) n_e(x)$
Energetic disorder with exponential tail distribution

$$\begin{cases} qVoc = E_{g,tr} + mk_B T \ln\left(\dfrac{G}{\gamma N_{t,h} N_{t,e}}\right) \\ m = E_t / k_B T > 1 \end{cases}$$



Physical Review B 2011, 84, 075210

$N_{t,h}$, $N_{t,e}$ density of states in the tail
Et = tail slope

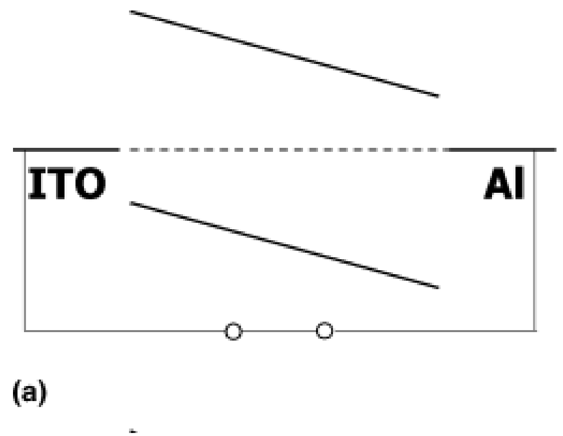
Voc depends on:

1. Eg
2. Recombination
3. Energetic disorder
4. Light intensity
5. Electrodes

Origin of the V_{OC}: role of the electrodes

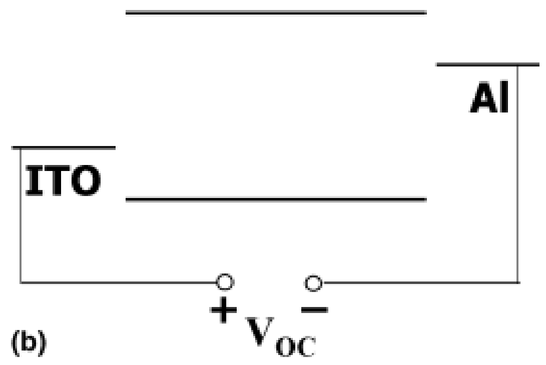
MIM: Metal Insulator Metal model

Short-circuit condition



Open-circuit condition

or "flat band" condition



Built-in field due to metals workfunction mismatch

No net current flow. Voc given by the difference between the metal workfunctions

J_{PHOTO}: photogenerated carriers need a driving force

- Internal Electric Field→Drift current
- Charge concentration gradient→Diffusion current

ideal BHJ

Origin of the V_{OC}: role of the electrodes

MIM: Metal Intrinsic Metal model

Short-circuit condition

Open-circuit condition

or "flat band" condition

built-in voltage

$$V_{oc,max}=(1/q)(\Phi_{M1}-\Phi_{M2})$$

Vs

$$V_{oc,max}=(1/q)(HOMO_D-LUMO_A-\Delta E)$$

tions

J_P

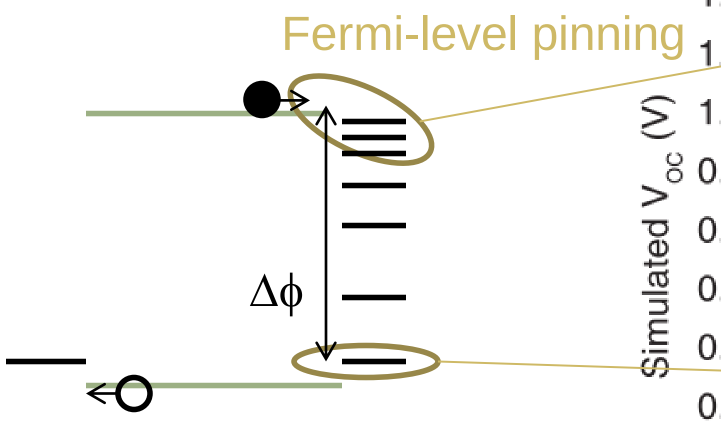
•Internal Electric Field→Drift current

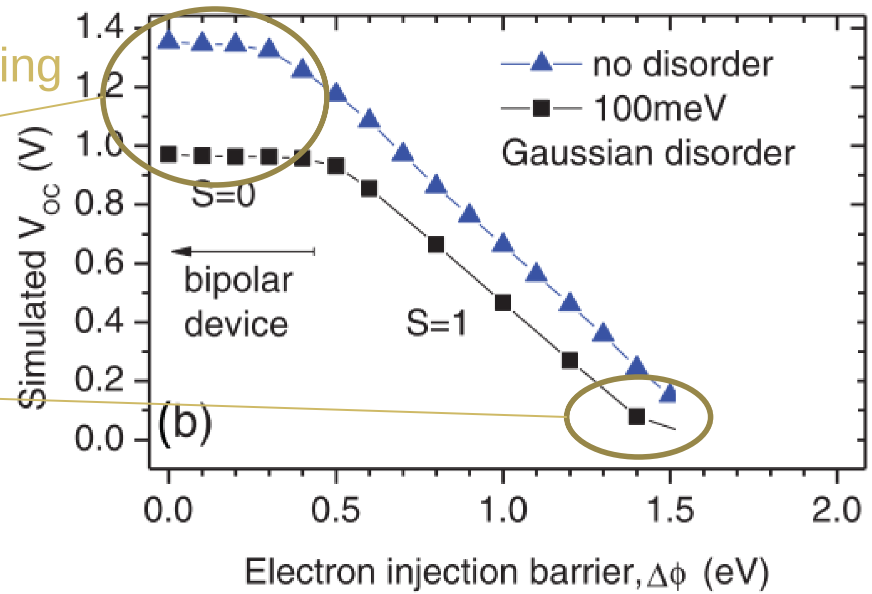
•Charge concentration gradient→Diffusion current

ideal BHJ

Origin of the V_{OC}: role of the electrodes

Contacts have little effect… if I choose them right!

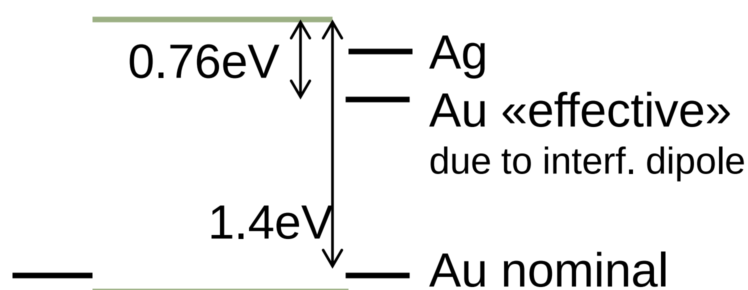




Physical Review B 2011, 84, 075210

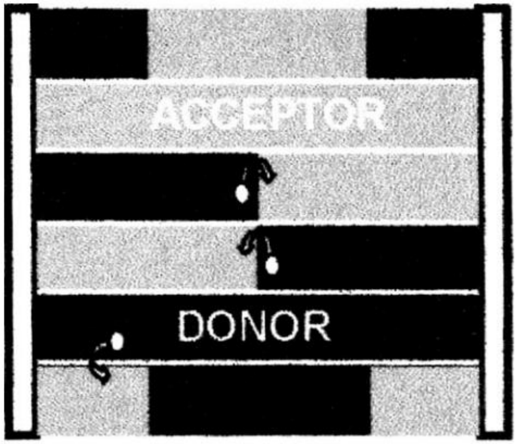
Cathode	φ_b (eV)	V_{OC} (V)	ΔV_b (V)	$\varphi_b+V_{OC}+\Delta V_b$ (eV)
LiF/Al	0	1.28[a]		
Ag	0.65	0.84	0	1.49
Au	0.76	0.74	0	1.5

J. Appl. Phys., Vol. 94, No. 10, 15 November 2003



Origin of the V_{OC}: role of the electrodes

- V_{oc} can exceed the built-in of the contacts if the bulk-heterojunction is not so “ideal”



J. Appl. Phys. 2006, 99, 104503

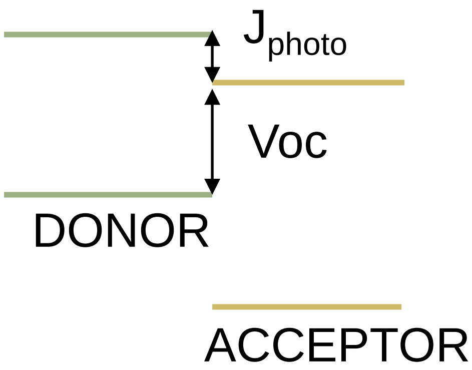
- Complex, more realistic device architectures provide asymmetry to the system (i.e. blocking layers)

Current flow can be driven by diffusion!

Phys. Rev. B 2008, 77, 165332

Improving the V_{OC}: active material

1. D/A energy level alignment



TRADE OFF with charge dissociation!!!

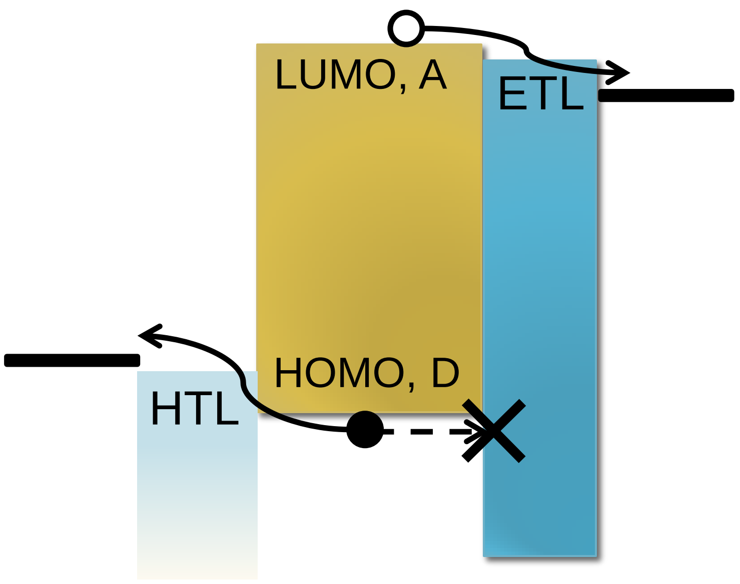
2. Reducing recombinations

? material level ?

Increase phase separation: slow down the rate at which charges meet each other... But TRADE OFF with charge generation (reduced D/A interface)!!!

Improving the V_{OC}: device

INTERLAYERS FOR SELECTIVE COLLECTION AT THE ELECTRODES



1. Block excitons
2. Block misdirected carriers
3. Improve collection efficiency

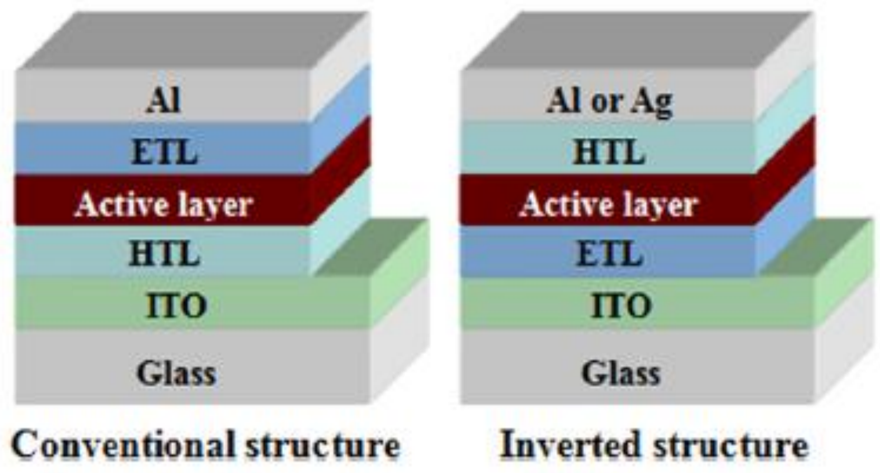
Reduced recombination

4. Optimize light absorption (*optical spacer: coming soon…*)

… Active material protection
Influence active material growth

Improving the V_{OC}: device

INTERLAYERS FOR SELECTIVE COLLECTION AT THE ELECTRODES



Main specs

Suitable energy levels
Transparency
Processability

Typical interlayers

HTL

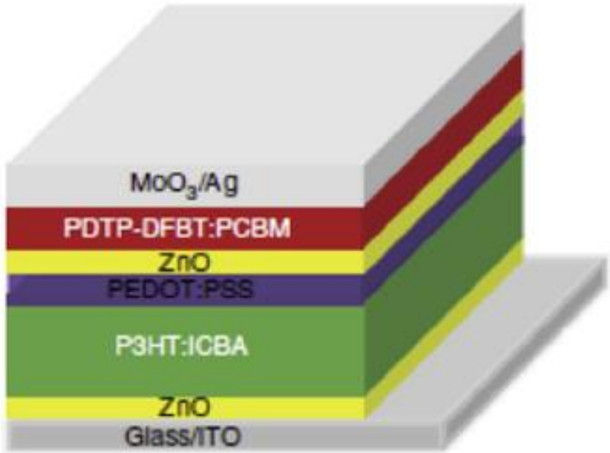
Polymer (PEDOT:PSS)
Transition metal oxides (MoO_3, V_2O_5, WO_3)

ETL

Inorganic salts (LiF, CsF, MgF)
Polymers (PFN,PEIE)
Metal oxides (TiO_x, ZnO)

SOLUBLE!

Tandem solar cells for increased V_{oc}



(a)

Equivalent Voc= sum of single cells Voc

Equivalent Jsc= Jsc of the worst cell in the stack

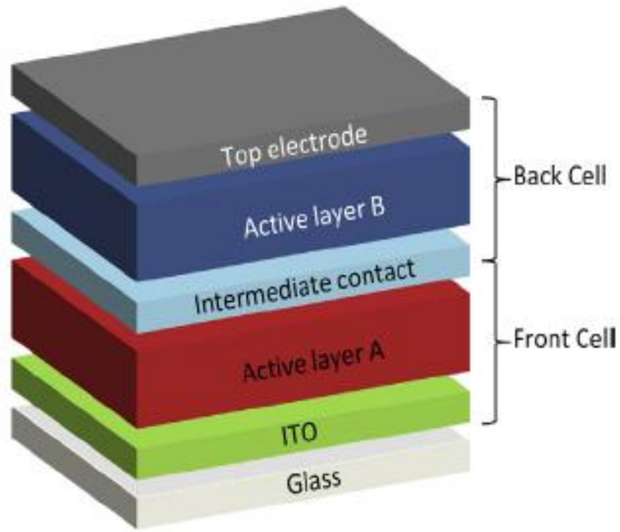
Devices		V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
P3HT:ICBA	single cells	0.84	10.3	71.1	6.1
PDTP-DFBT:$PC_{61}BM$	single cells	0.70	15.4	66.2	7.1
PDTP-DFBT:$PC_{71}BM$	single cells	0.68	17.8	65.0	7.9
P3HT:ICBA/PDTP-DFBT:$PC_{61}BM$ (Tandem 1)	stack	1.53	10.1	68.5	10.6
P3HT:ICBA/PDTP-DFBT:$PC_{71}BM$ (Tandem 2)	stack	1.51	9.8	69.2	10.2

Nat. Commun. 2013, 4, 1446

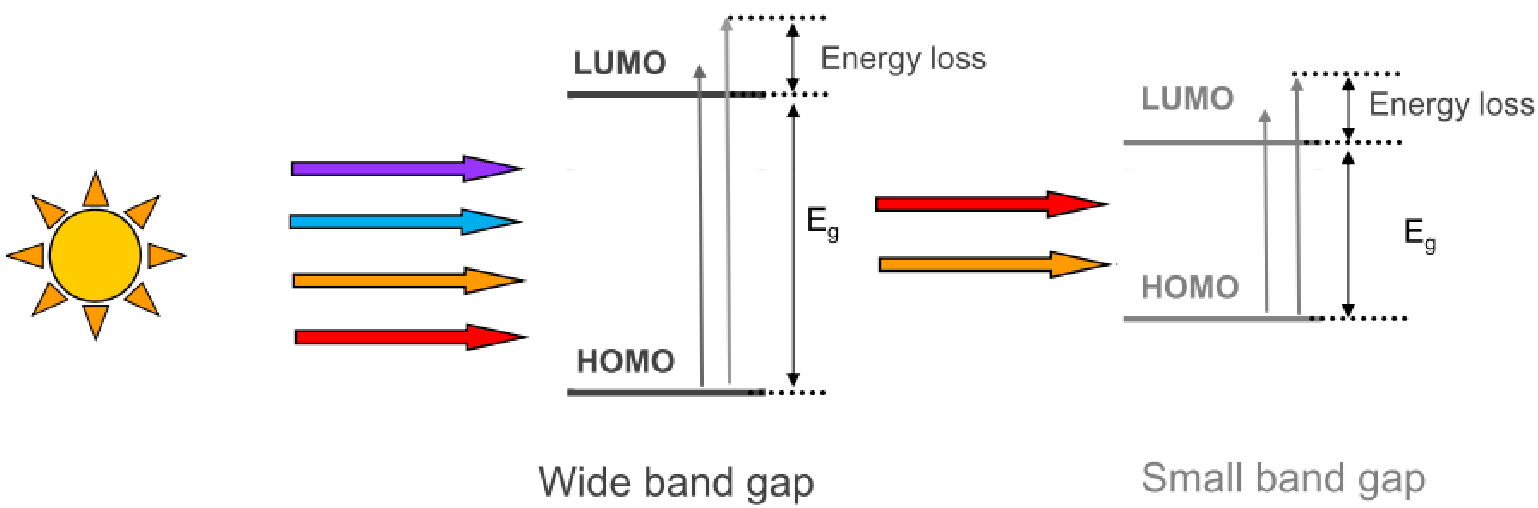
REVIEW ART.: *Energy Environ. Sci.*, 2013,6, 2390-2413
Org. Electron. 2015, 19, 34

$PCE \propto V_{oc} \cdot J_{sc} \cdot FF$

Tandem solar cells for increased V_{oc}



(b)



Short-circuit current (J_{sc})

EQE →
- Light absorption
- Charge photogeneration efficiency
- Charge transport and collection

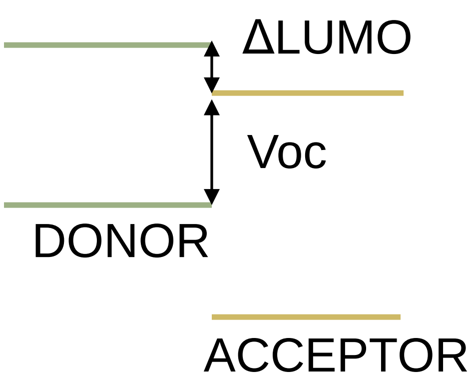
$$EQE = \frac{\text{Number of collected charges/s}}{\text{Number of incoming photons/s}} = \frac{n_c/s}{n_v/s} = \eta_{abs} \cdot \eta_{ed} \cdot \eta_{cc}$$

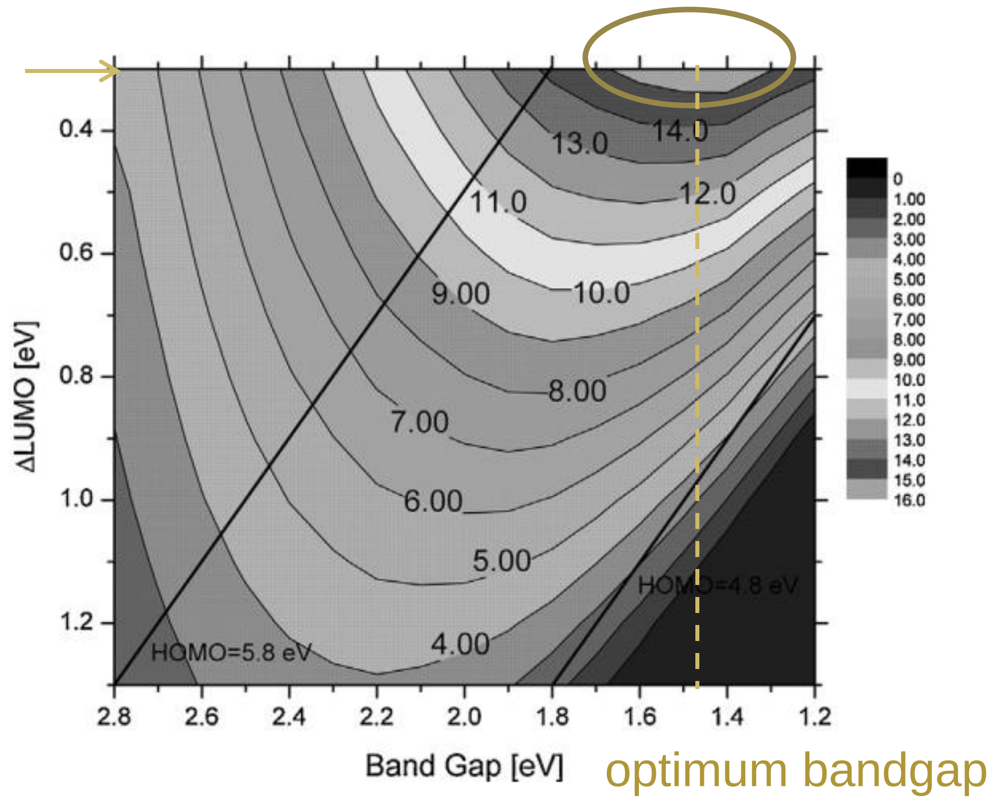
$PCE \propto V_{oc} \cdot J_{sc} \cdot FF$

Short-circuit current (J_{sc}): light absorption – active material

Extending the responsivity to low energy photons

As much as half of the energy of the solar spectrum is carried by long wavelengths photons!

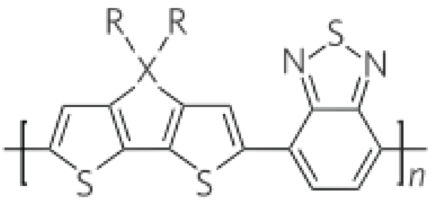




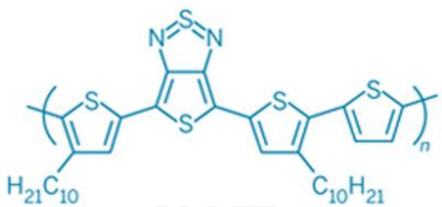
Progress in Polymer Science 38 (2013) 1929–1940

Red-light responsivity

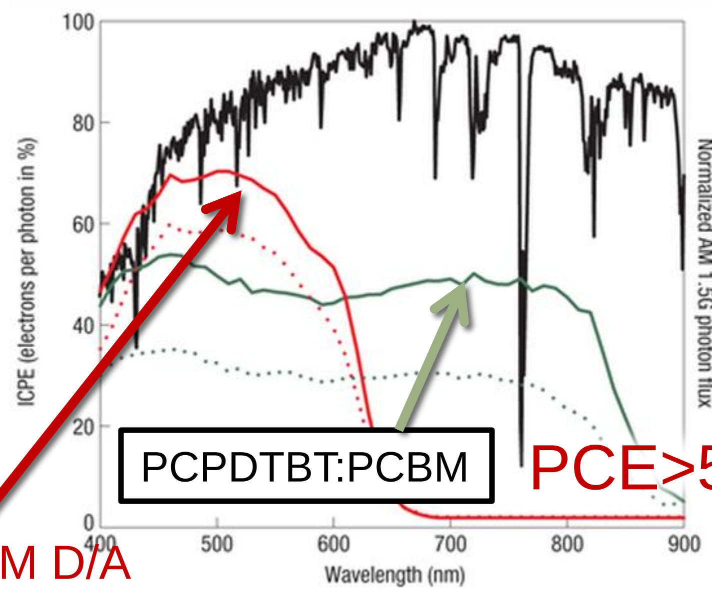
EXAMPLE 1: POLYMERS



X = C, PCPDTBT
X = Si, PSBTBT



PDDTT



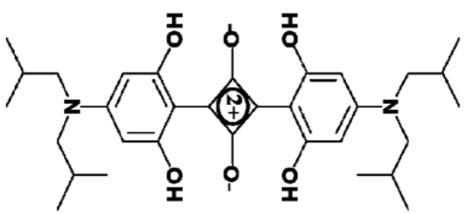
PCE>5%

Nature Materials 2007, 6, 497

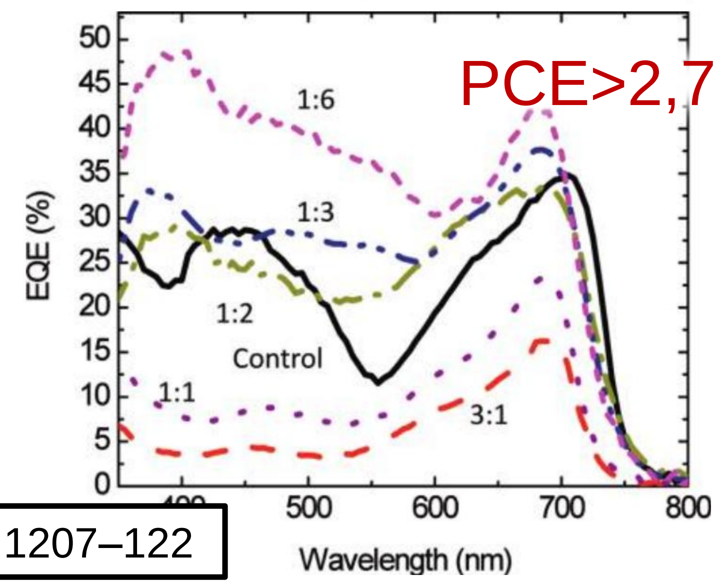
Science 2009, 325, 25

Standard P3HT:PCBM D/A

EXAMPLE 2: SMALL MOLECULES



SQUARAINES



PCE>2,7%

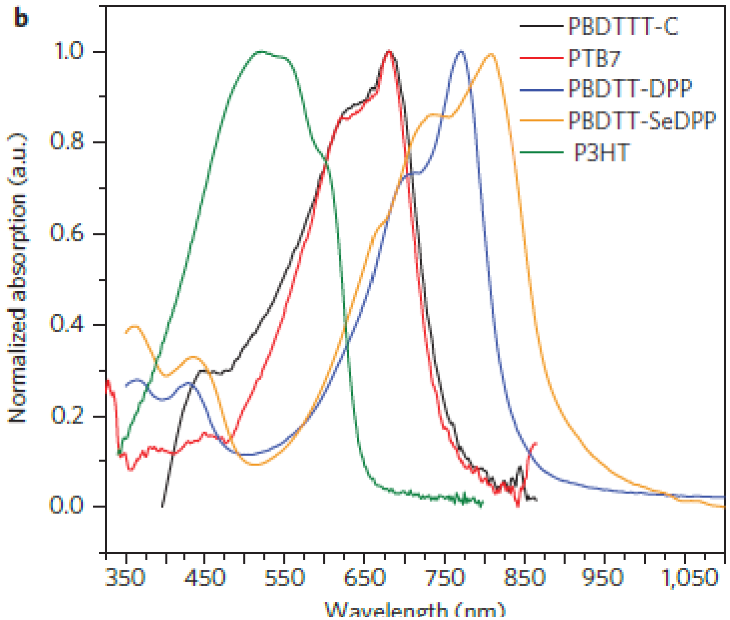
G. Wei et al., ACSNano 4, 4, 2010.
Other works: Muhlbacher et al., 2006; Kooistra et al., 2006; Yao et al., 2006; Soci et al., 2007; Wang et al., 2008; Hou et al., 2008)

REVIEW: L. Beverina et al., Eur. J. Org. Chem. 2010, 1207–122

$PCE \propto V_{oc} \cdot J_{sc} \cdot FF$

Ternary blends

Nature Photonics, 2015, 9, 190



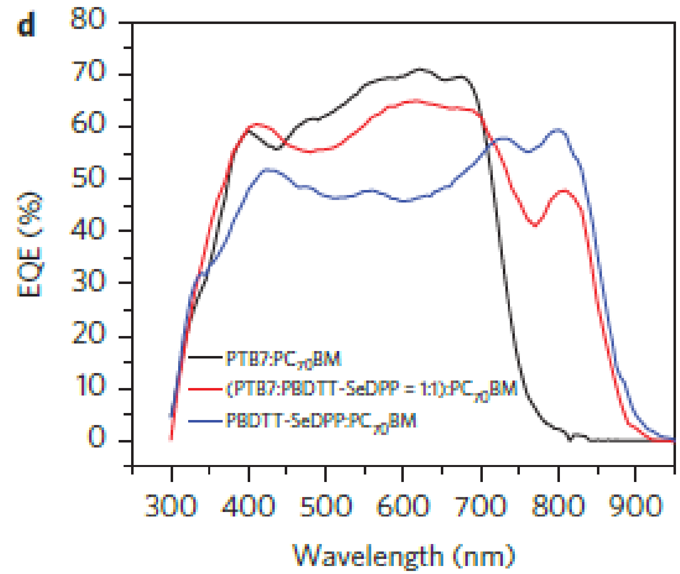
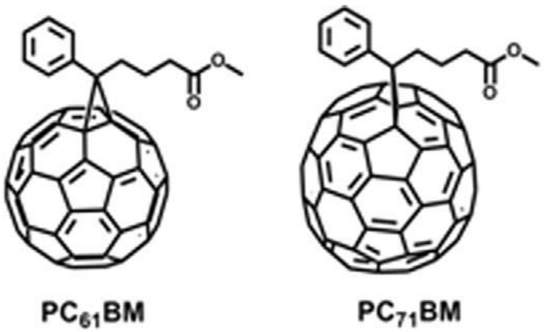


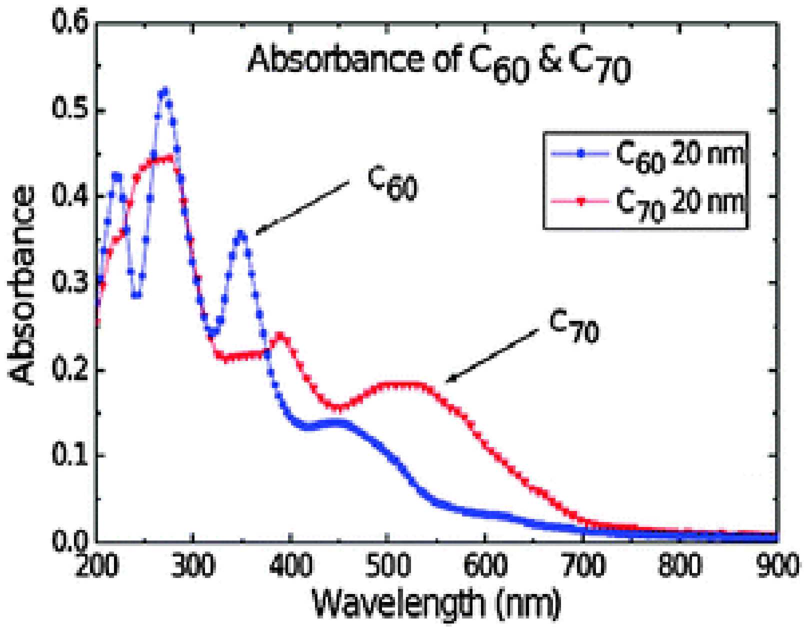
Table 1 | Device performance of the (PDBTTT-C:PBDTT-DPP):$PC_{70}BM$ ternary BHJ solar cell system and the (PTB7:PBDTT-SeDPP):$PC_{70}BM$ ternary BHJ solar cell system.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%) max./avg.
PBDTTT-C:$PC_{70}BM$	0.70	14.1	64.0	6.4/6.3
(PBDTTT-C:PBDTT-DPP = 3:1):$PC_{70}BM$	0.70	15.7	65.6	7.2/7.2
(PBDTTT-C:PBDTT-DPP = 1:1):$PC_{70}BM$	0.70	15.6	64.9	7.1/7.0
(PBDTTT-C:PBDTT-DPP = 1:3):$PC_{70}BM$	0.72	13.1	65.0	6.2/6.1
PBDTT-DPP:$PC_{70}BM$	0.74	13.0	64.2	6.2/6.0
PTB7:$PC_{70}BM$	0.72	15.1	66.3	7.2/7.0
(PTB7:PBDTT-SeDPP = 3:1):$PC_{70}BM$	0.69	16.2	70.0	7.8/7.7
(PTB7:PBDTT-SeDPP = 1:1):$PC_{70}BM$	0.69	18.7	67.4	8.7/8.5
(PTB7:PBDTT-SeDPP = 1:3):$PC_{70}BM$	0.69	17.9	62.4	7.7/7.7
PBDTT-SeDPP:$PC_{70}BM$	0.68	16.9	62.9	7.2/7.1
(PBDTTT-C:PBDTT-DPP:PTB7:PBDTT-SeDPP = 1:1:1:1):$PC_{70}BM$	0.70	17.3	64.6	7.8/7.6

PCE∝ Voc · J_{sc} · FF

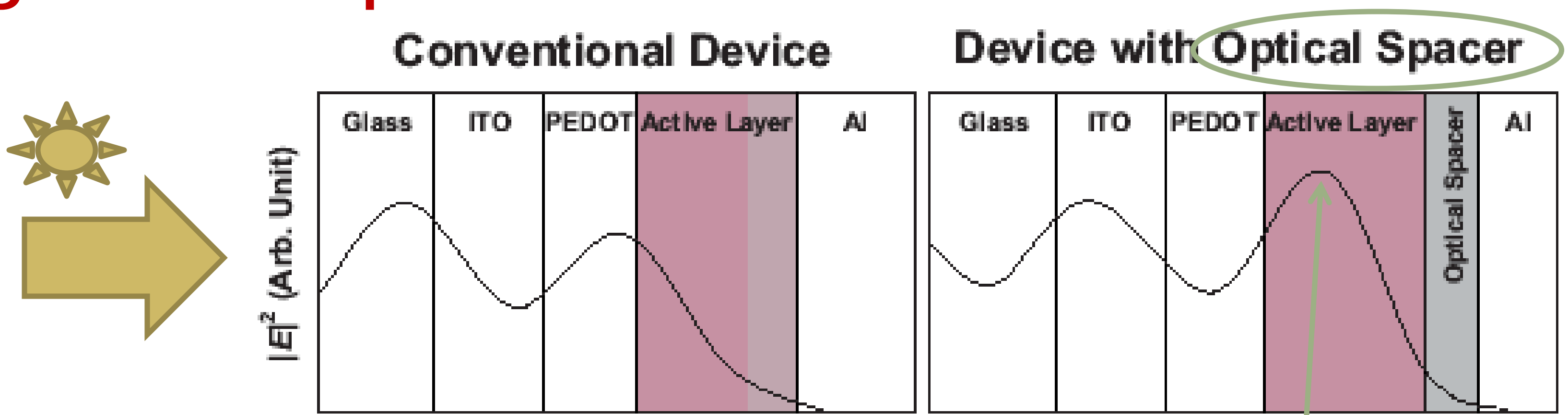
Fullerene-based acceptors





$PCE \propto V_{oc} \cdot J_{sc} \cdot FF$

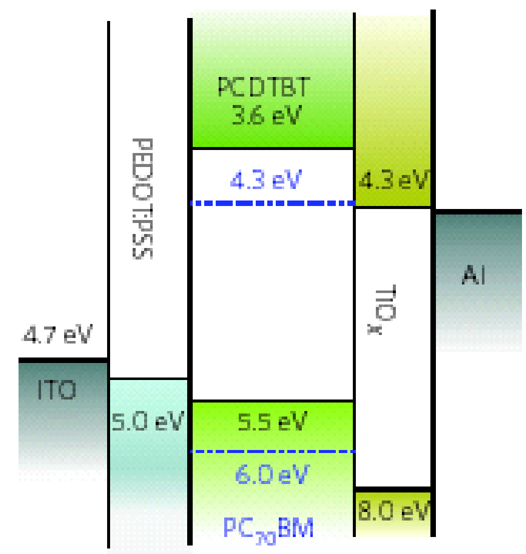
Short-circuit current (J_{sc}): light absorption - device



Maximum of the stationary optical field inside the active region

Requirements:

- Transparent
- Electron transporter
- Energy level alignment



Nature Photonics 2009, 3, 297

Short-circuit current (J_{sc})

EQE
- Light absorption
- Charge photogeneration efficiency
- Charge transport and collection

$$EQE = \frac{\text{Number of collected charges/s}}{\text{Number of incoming photons/s}} = \frac{n_c/s}{n_v/s} = \eta_{abs} \cdot \eta_{ed} \cdot \eta_{cc}$$

Short-circuit current (J_{sc}): photogeneration and charge transport

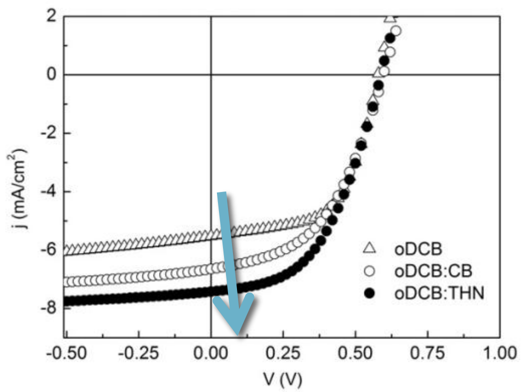
BULK-HETEROJUNCTION OPTIMAL FOR EXCITON DISSOCIATION...
...BUT REQUIRES CAREFUL CONTROL OF MORPHOLOGY!

1. Additives (solvents mixtures):

selective solubility

One phase still in solution while the other is already in solid state

Higher degree of phase separation, higher cristallinity

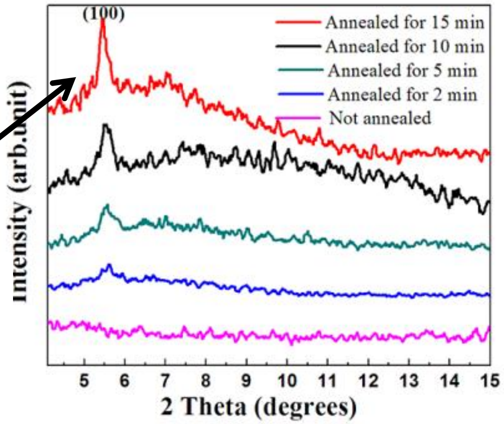


Solar Energy Materials & Solar Cells 2011, 95, 3536

2. Post deposition treatments: thermal annealing, vapor annealing

Energy/motion capability for the molecules to rearrange

XRD, increased P3HT crystallinity



Appl. Phys. A 2011, 105, 1003

Fill Factor (FF)

Prone to practical/technological accidents…

Pinholes in the active film
Metal diffusion from the electrodes
…

High R_{shunt}

Low R_s

- ❑ High mobility materials (↓Rs)
- ❑ Highly conductive electrodes (↓Rs)
- ❑ Low recombination (↑Rsh)
- ❑ Transporting/blocking layers
  - effectively collect photo-charges (↓Rs)
  - block undesired charge paths between the electrodes (misdirected carriers, pin-holes, metal diffusion…) (↑Rsh)

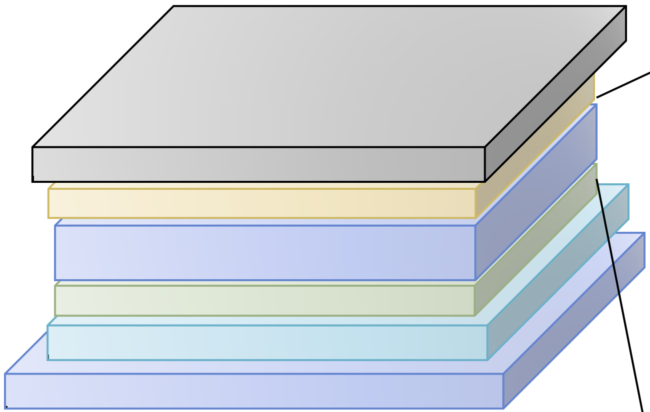
Stability of organic solar cells

* on rigid substrates

* *projected* lifetimes > 7 years ⟺ *projected* energy payback time ~ days

Energy Environ. Sci., 2015, 8, 55–80
Adv. Mater. 2012, 24, 580

Stability of organic solar cells



ACTIVE MATERIAL

Chemical instability

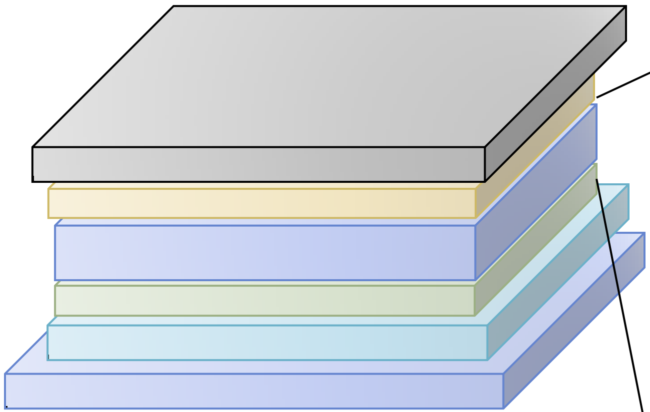
Photo-degradation (photo-oxidation)

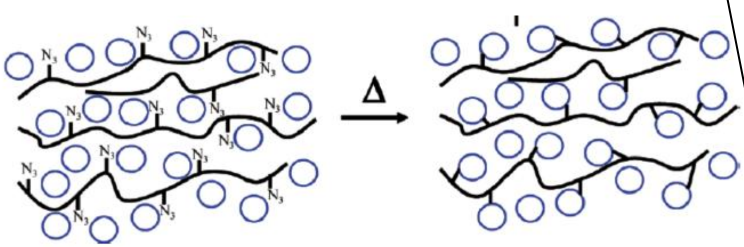
1. Oxygen/moisture induced
   UV light induced
2. Side chains have negative effects

Possible solutions

a. Encapsulation
b. Remove chains after deposition
   heat labile groups

Stability of organic solar cells





D-to-A linking after deposition

Active material

Morphological instability

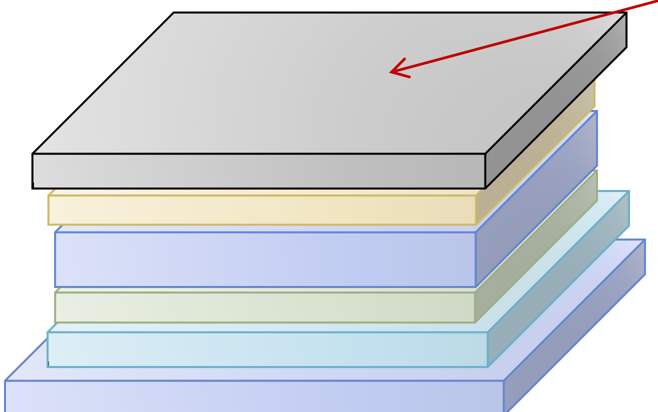
BHJ morphology evolves over time at room T

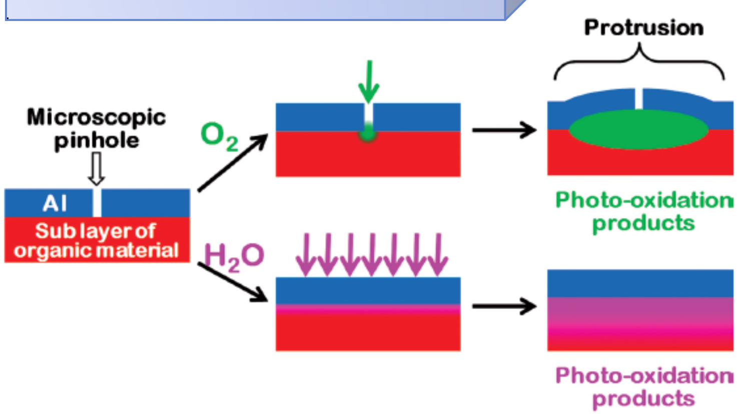
1. Speeden up by operating T (~80°C)
2. Depends strongly on BHJ processing conditions

Possible solutions

a. Chemically link D and A: block copolymers, cross-linking
b. Remove side chains post deposition

Stability of organic solar cells





O2/H2O infiltration through the metal electrode

ELECTRODES

METAL

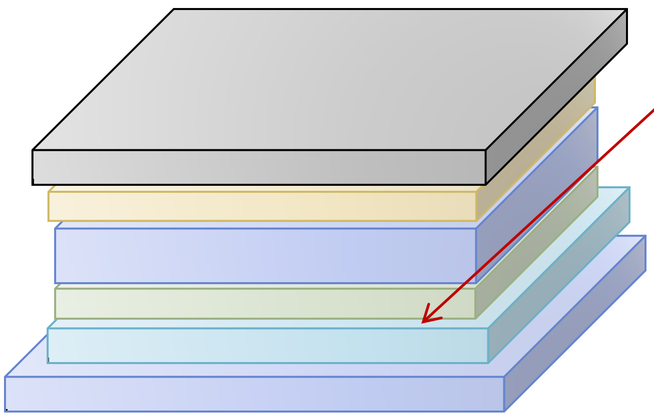
Oxygen/moisture diffusion through the electrode

Oxide formation at the interface with active material (especially with low work function electrodes)

__Possible solutions__

- a Thicker electrodes
- c Inverted structure
- b Encapsulation

Stability of organic solar cells



ELECTRODES

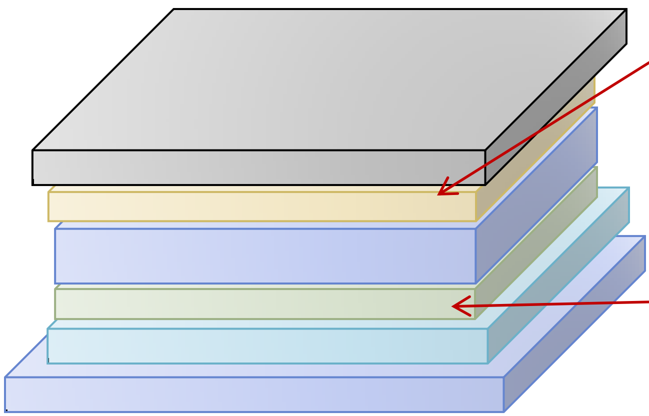
TRANSPARENT

ITO work function change upon UV irradiation

Possible solutions

Interlayers for stabilizing the electrode work function

Stability of organic solar cells



INTERLAYERS

N-TYPE

Protection of the layer towards:
- oxygen/moisture penetration
- electrodes related damages (deposition, chemical reactions,…)

P-TYPE

PEDOT:PSS:
- phase segregation over time
- highly acidic
- deposited from water

- corrosion of metal contacts (ITO)
- …even in dry/enacpsulated athmosphere (residual water)

__Possible solutions__

a Non-acidic formulations of PEDOT:PSS

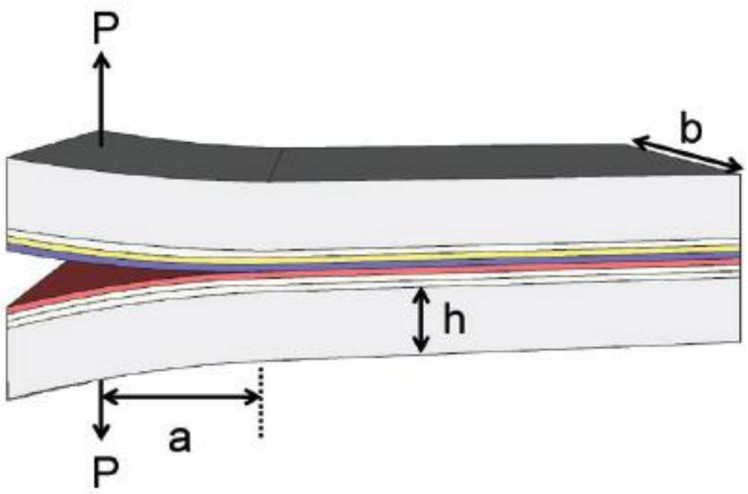
b replacement with other interlayers (MoO_3, WO_3)

Stability of organic solar cells

mechanical degradation

Stresses:
- Pressure of wind, weight of rain and snow,…
- Daily thermal expansion/contraction cycles

Cracking, delamination



1. thin films are good
2. polymeric materials (e.g. electrodes, interlayers) better than metals or inorganic oxides
3. control over intermolecular and surface forces that control:
   i) active material brittleness and stiffness
   ii) adhesion