Towards a deeper understanding of polymer solar cells

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Outline

- Polymer solar cells
  - Conjugated polymers for Photovoltaics (PV)
  - Basics of polymer solar cells
- Modelling
  - Why model this?
  - How to model this?
- Results
  - Generation of charge carriers
  - Improving the efficiency: influence of band gap

Polymer solar cells

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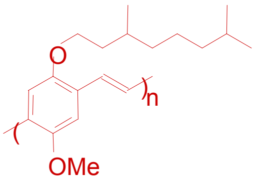
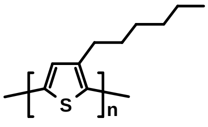
Conjugated Polymers

- Alternating sequences of single/double and/or single/triple bonds result in delocalised π-electron systems.
- MDMO-PPV:
  - Widely characterized and studied (LEDs, mobility known, etc.)
  - Efficiency 2.5% (2001)



- poly(3-hexylthiophene) (P3HT)
  - Efficiency 4-5% (2006)



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Pros and cons of polymer PV

Pros:

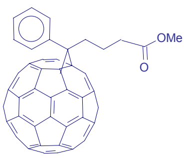
- Mechanically flexible
- Control over band gap, mobility, energy levels, etc. via chemisty
- Cheap and easy to make via spin casting, doctor-blading, etc.

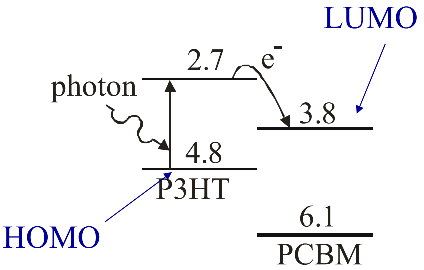
Con(s):

- Upon light absorption an exciton is created, not free charge carriers!

How to break up the excitons

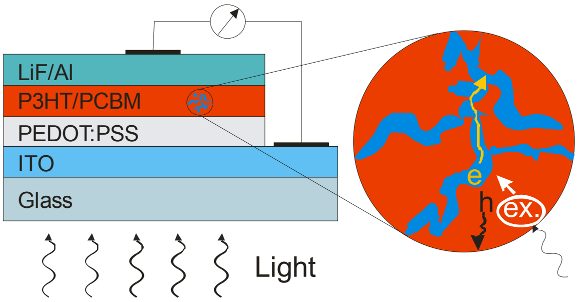
- Binding energy of exciton ~ 0.4 eV!
- Mix polymer with an electron acceptor
- One of the best ones around is a C_{60}-derivative (PCBM)





Bulk heterojunction concept

• Excitons only travel a few nm
• Bulk heterojunction (BHJ): blend of two materials
⇒ large interfacial area for charge separation
⇒ charge separation occurs with unity efficiency!



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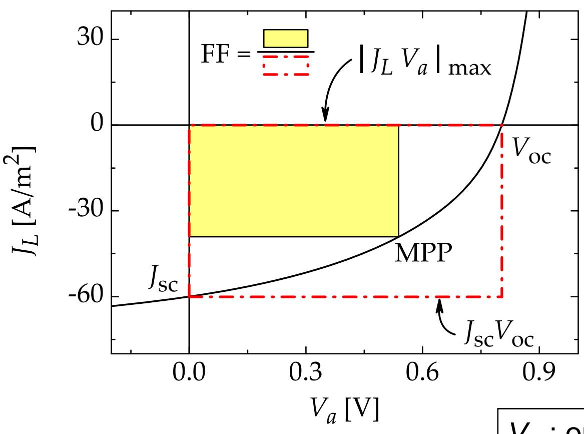
Current-Voltage characteristics



V_{oc}: open-circuit voltage
J_{sc}: short-circuit current dens.
FF: fill factor
MPP: maximum power point

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Modelling

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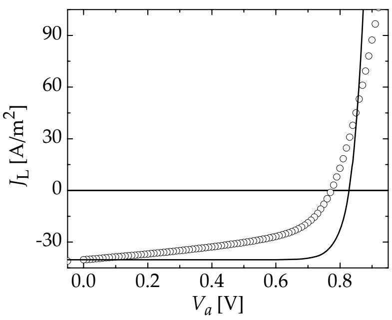
How to start?

- We need: simple model that relates performance to fundamental physics and material properties
- Because: targeted improvement wanted
- Obstacle: complicated morphology
- Literature approach: *pn*-junction model



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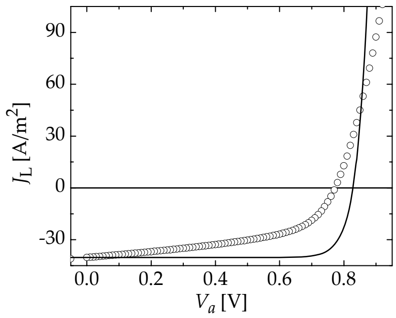

Fails miserably

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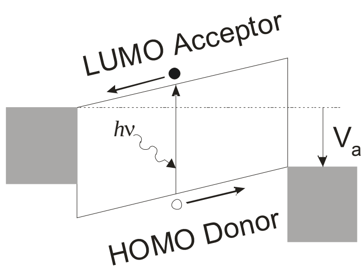
Modelling: MIM model

We developed Metal-Insulator-Metal (MIM) model:

- Effective medium approach
  - Treat blend as one virtual semiconductor
  - Transport occurring in respective bands
- Solve Poisson equation and drift and diffusion equations[1,2]
- Measured mobility electrons and holes as main parameters



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1 Phys. Rev. B. **72**, 085205 (2005)
2 Appl. Phys. Lett. **88**, 052104 (2006)

MIM model clarifies:

- Charge generation and *I-V* characteristics described (incl. temperature dependence)[1]
- How to improve efficiency[2]
- Why so much PCBM is needed (80 wt.%)[3]
- Space-charge effects[4]
- Effect of changing electrodes[5]
- Annealing effects in P3HT:PCBM solar cells[6]
- Intensity dependence of V_{oc}[7] and J_{sc}[8]
- Effect of thickness on efficiency[9]
- Using ZnO nanoparticles as acceptor[10]
- Low fill factor of polymer/polymer solar cells[11]

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2 Appl. Phys. Lett. **88**, 093511 (2006).
3 Adv. Funct. Mater. **15**, 795 (2005)
4 Phys. Rev. Lett. **94**, 126602 (2005)
5 Appl. Phys. Lett. **85**, 970 (2004)
6 Adv. Funct. Mater. **16**, 699 (2006).
7 Appl. Phys. Lett. **86**, 123509 (2005)
8 Appl. Phys. Lett. **87**, 203502 (2005)
9 Appl. Phys. Lett. **88,** 243502 (2006).
10 Adv. Funct. Mater. **17**, 1297 (2007).
11 Adv. Funct. Mater. **17**, 2167 (2007).

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Charge generation and *I-V* curves

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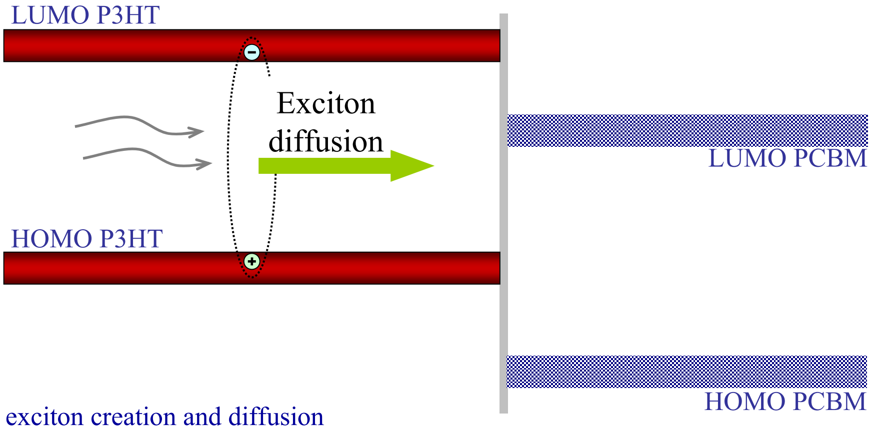
Photovoltaics in a nutshell: *exciton diffusion*



• exciton creation and diffusion

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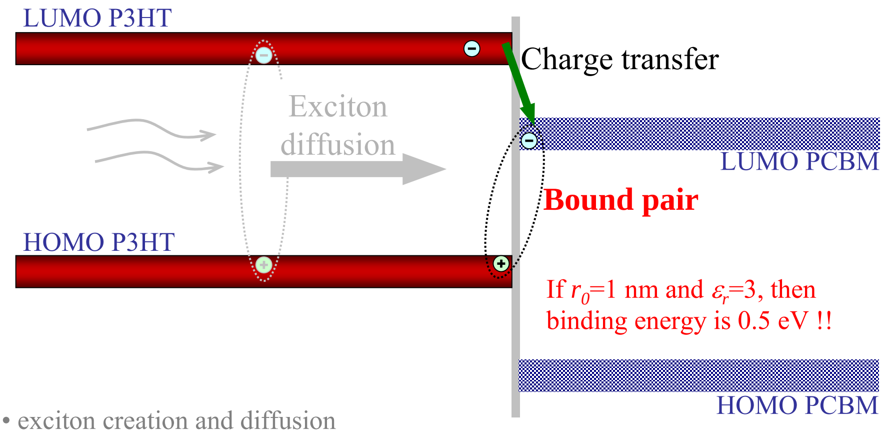
Photovoltaics in a nutshell: *charge transfer*



- exciton creation and diffusion
- charge transfer at D/A interface → metastable bound e-h pairs

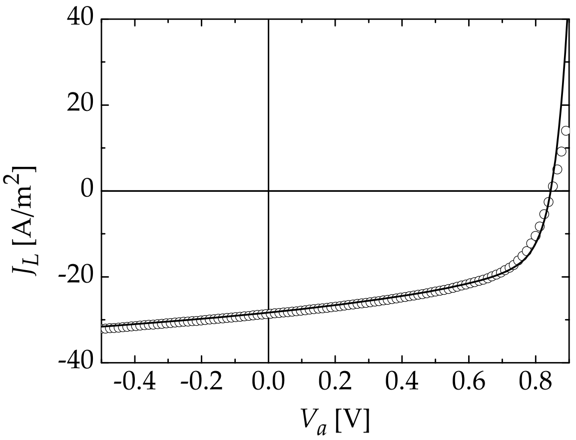
Generation of free carriers: experiments

- Turns out that in MDMO-PPV/PCBM solar cells only ~50% of all electron/hole pairs dissociate![1]
- This process dominates the temperature dependence of current-voltage characteristics.
- Explains low FF in all-polymer devices[2]

[1] Rev. Lett. **93**, 216601 (2004).
[2] Adv. Funct. Mater. **17**, 2167 (2007).

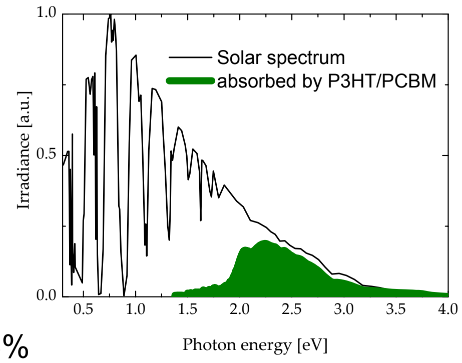
Modelling full *I-V* curve

- Now we can model the full current-voltage curve for MDMO-PPV/PCBM:



Improving the efficiency: influence of band gap

Polymer band gap



•Band gap P3HT 2.1 eV =>16% of incident photons absorbed
•For *pn* junction: optimal band gap is 1.4 eV

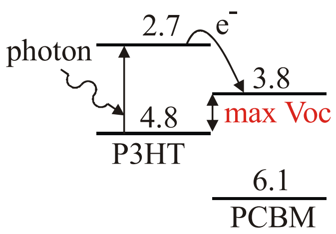
•Several groups* work on low band gap polymers, however...

*See e.g., Roncali, Chem. Rev. **97**, 173 (1997).

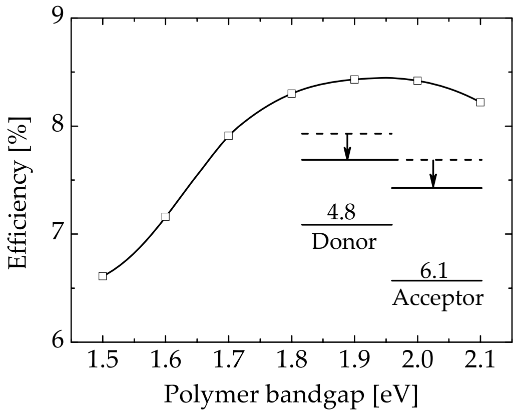
Exciton dissociation

LUMO(D)-LUMO(A) offset drives exciton dissociation
if
LUMO(D)-LUMO(A) offset ≥ exciton binding energy (0.4 eV)

•In P3HT/PCBM: offset = 1.1 eV
•Rest of energy is lost!
•Energy loss is reflected in Voc
•This has implications for band gap



Optimizing band gap



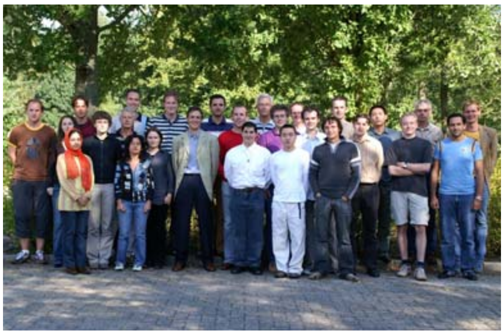
- Optimal band gap 1.9-2.0 eV => not a low band gap!
- Very close to P3HT value (2.1 eV) with broad maximum
- Further optimization can lead to efficiencies >10%

Summary

1. We developed a simple yet accurate model describing the current-voltage characteristics of polymer solar cells.
2. This model relates the current-voltage characteristics to material parameters and basic physics.
3. This model has shed new light on a wide range of issues, including the generation mechanism of free charges and possible strategies for optimising performance.

Acknowlegdements

- Dutch Polymer Institute
- Colaborators in project #323
- Colleagues in the POS group in Groningen



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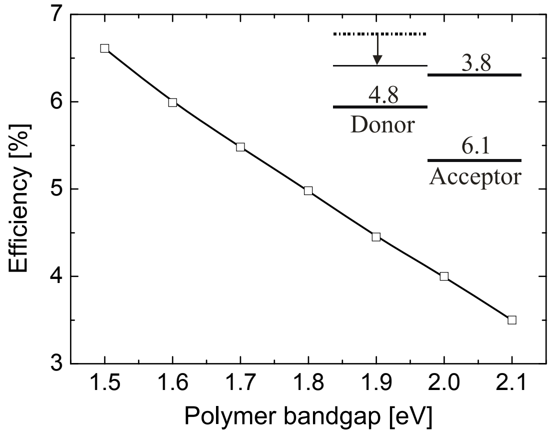
Optimizing band gap

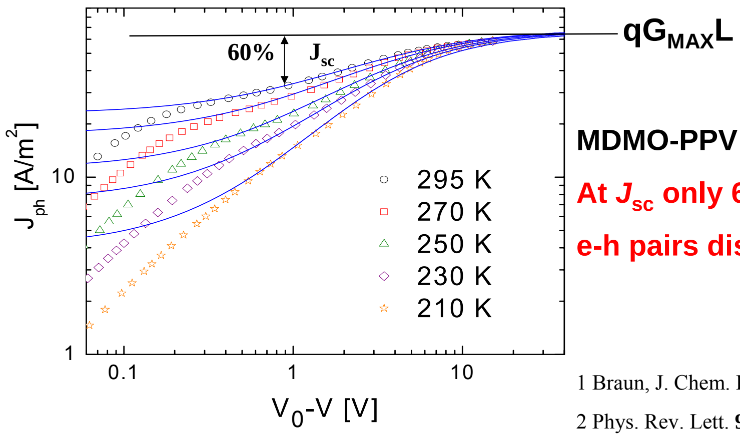


- Keep HOMO of P3HT as is => Voc same
- Max. efficiency 6.6%
- Improvement all due to larger Jsc

Generation of free carriers: experiments

MDMO-PPV:PCBM

Saturated regime: photocurrent J=q G(V,T) L due to dissociation of bound electron-hole pairs[1,2]



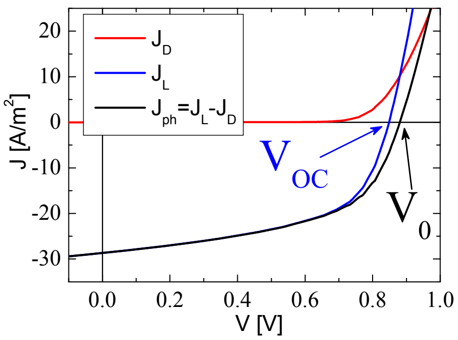
MDMO-PPV:PCBM:

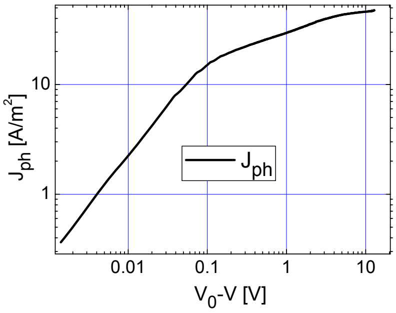
At J_{sc} only 60% of bound e-h pairs dissociated!

1 Braun, J. Chem. Phys. **80**, 4157 (1984).

2 Phys. Rev. Lett. **93**, 216601 (2004).

Photocurrent: J_{ph}





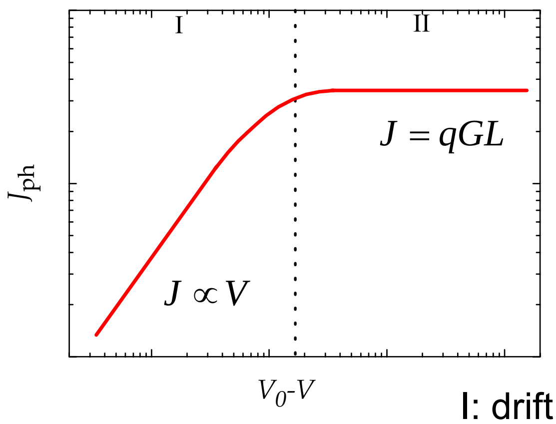
$J_{ph}=J_L-J_D$: photocurrent

$J_{ph}(V_0)=0$: definition of compensation voltage

V_0-V : represents the effective applied voltage

Log(J_{ph}) vs. Log(V_0-V) very useful: easy to relate to analytical models!

MIM-model: photocurrent

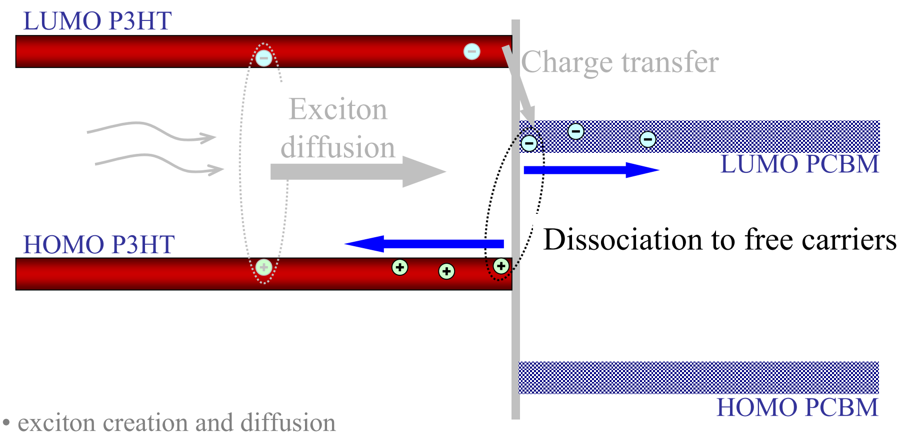


I: drift vs. diffusion, [1] $J \sim V$

II: saturated[1,2] $J=qGL$

[1] R. Sokel & R.C. Hughes, J. Appl. Phys. **53**, 7414 (1982).
[2] Goodman & Rose, Appl Phys **42,** 2823 (1971).

Photovoltaics in a nutshell: *bound e/h pairs*



- exciton creation and diffusion
- charge transfer at D/A interface
- dissociation of e-h pairs at D/A interface → field- and temperature dependent process

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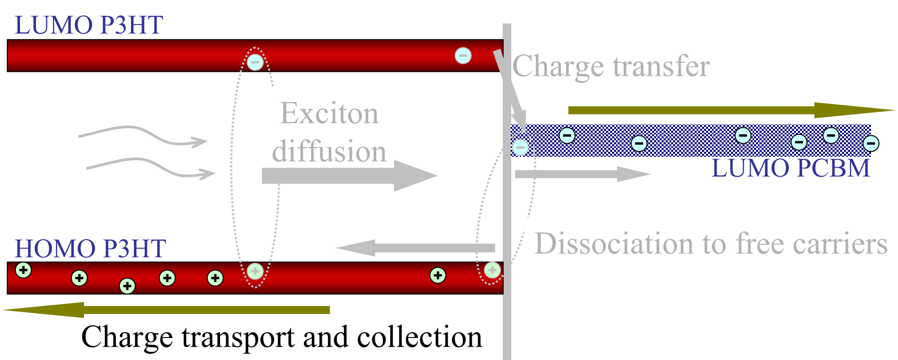
Photovoltaics in a nutshell: *charge transport*



HOMO PCBM

- exciton creation and diffusion
- charge transfer at D/A interface
- dissociation of e-h pairs at D/A interface
- transport of free charge carriers to the electrodes

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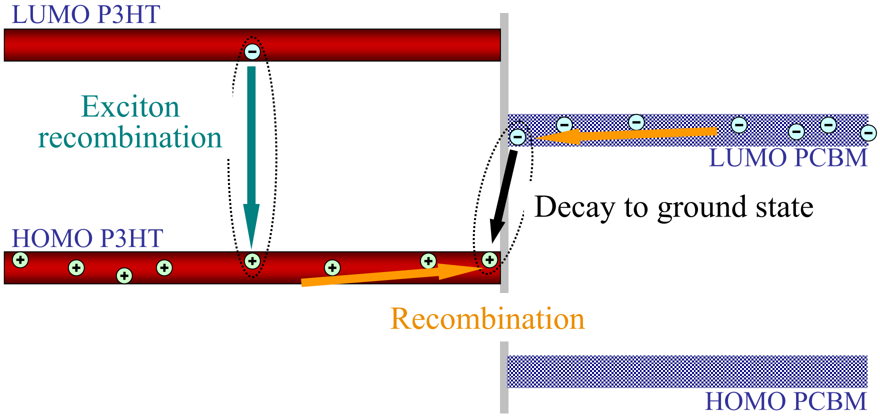
Photovoltaics in a nutshell: *recombination*



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Open-circuit voltage

- Ohmic contacts
  =>Voc determined by HOMO(D)-LUMO(A)[1]
- More specific:[2]

$$V_{oc} = \text{HOMO(D)} - \text{LUMO(A)} - \frac{kT}{q}\ln\left[\frac{(1-P)\gamma N_c^2}{PG_M}\right]$$

0.3-0.4 V

- Efficiency superlinear in Voc

[1] Brabec *et al.*, Adv. Funct. Mater. **11**, 374 (2001).
[2] Koster *et al.*, Appl. Phys. Lett. **86**, 123509 (2005).

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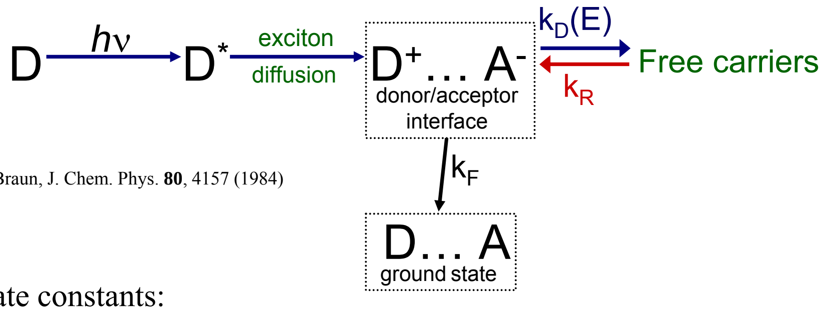
Generation of free carriers

Schematic diagram for charge-carrier formation in polymer(donor)/fullerene(acceptor) films



Braun, J. Chem. Phys. **80**, 4157 (1984)

Rate constants:

k_D - production free carriers, field dependent

k_F - decay to ground state

k_R - recombination of free carriers back to D/A interface

Why is the efficiency not 30%?

pn-junction:
Detailed balance limit by Shockley and Queisser*

- Absolute limit!
- Sun and solar cell as two black bodies (6000 K and 300 K resp)
- 30% efficiency (AM1.5) at E_{gap} = 1.4 eV => V_{oc} = 1.06 V

BHJ:

- Suppose LUMO-LUMO offset = 0.5 eV
- E_{gap}=1.4 eV => V_{oc} < 0.9 V
- Therefore, gain in J_{sc} counteracted by loss in V_{oc}

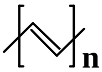
⇒ max. efficiency < 30%
optimal band gap > 1.4 eV

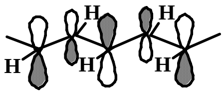
- JV characteristics will be different!

* J. Appl. Phys. **32**, 510 (1961).

Conjugated polymers

- Simplest conjugated polymer is *trans*-polyacetylene:





- Alternating sequences of single/double and/or single/triple bonds give delocalised π-electron systems.
- Polyacetylene important historically but not of current practical interest.
- Chemistry Nobel Prize (2000) awarded to Heeger, MacDiarmid and Shirakawa for development of conducting polymers.

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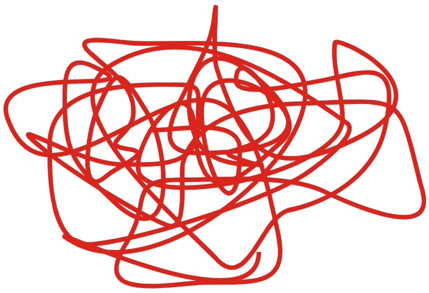
Conjugated polymers

A physicist's view:



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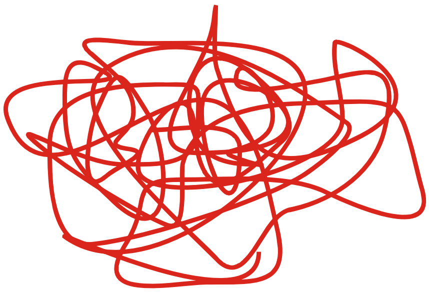

After being around chemists:

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