Charge transport and recombination in bulk-heterojunction solar cells

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FunMat Schematic

Center for Functional Materials

Our vision

We believe that new functional materials will enable the printed intelligence revolution

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To create a strong multidisciplinary research environment for the development of new materials and demonstrating new functionalities by printing

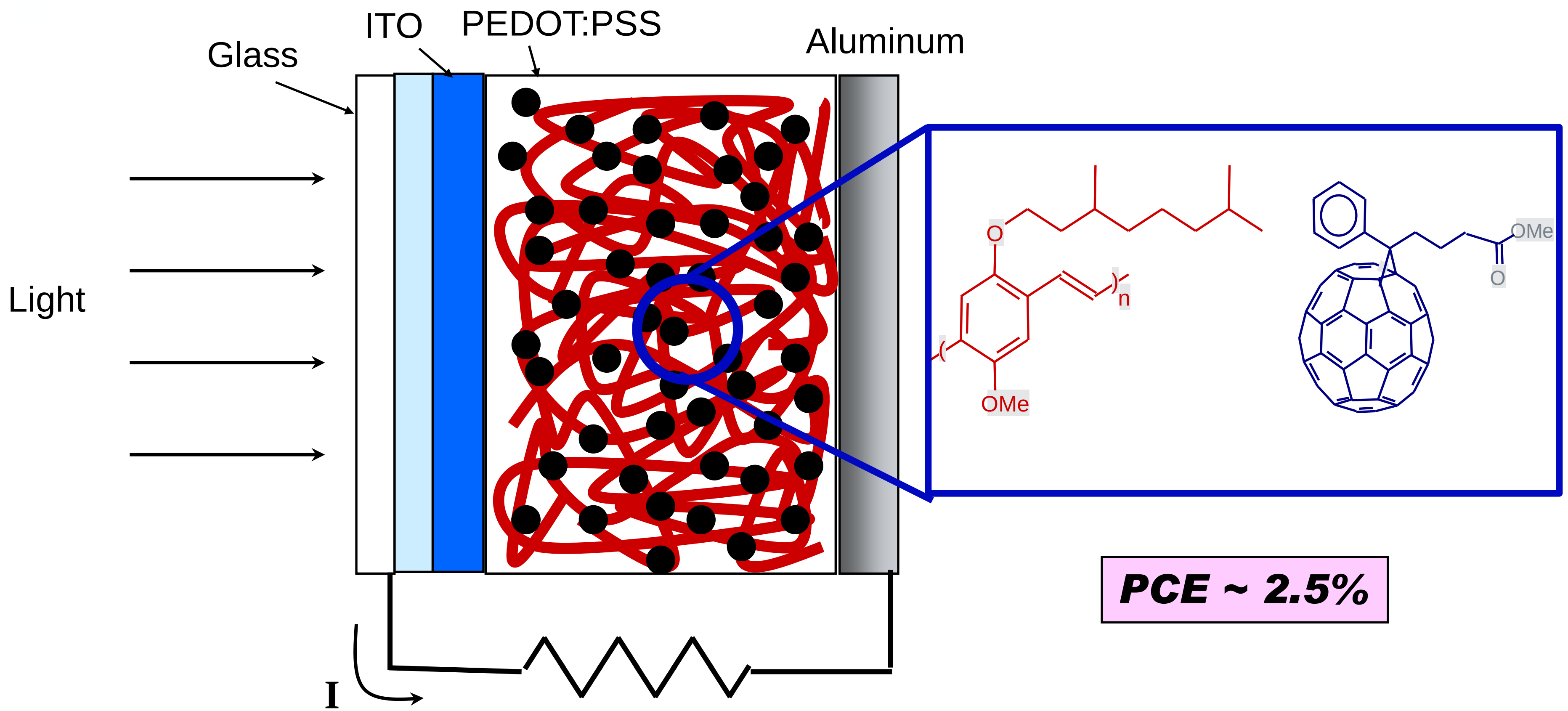
Key objectives

- Excellence and innovativeness in research
- Highly inter- and multidisciplinary approach to research
- Strong national and international networking
- To become the leader in paper based printed intelligence research

Outline

- Introduction to charge transport and recombination
  - Effect of Langevin recombination
- Recombination studies with TOF
  - In pure polymers
  - In annealed bulk-heterojunction solar cells
- Double Injection Transients (DoI)
  - Effect of trapping
- Suggested model
  - Nanomorphology important
  - 2D delocalization of charge carriers
- Effect of reduced recombination on magnetortransport
- Summary

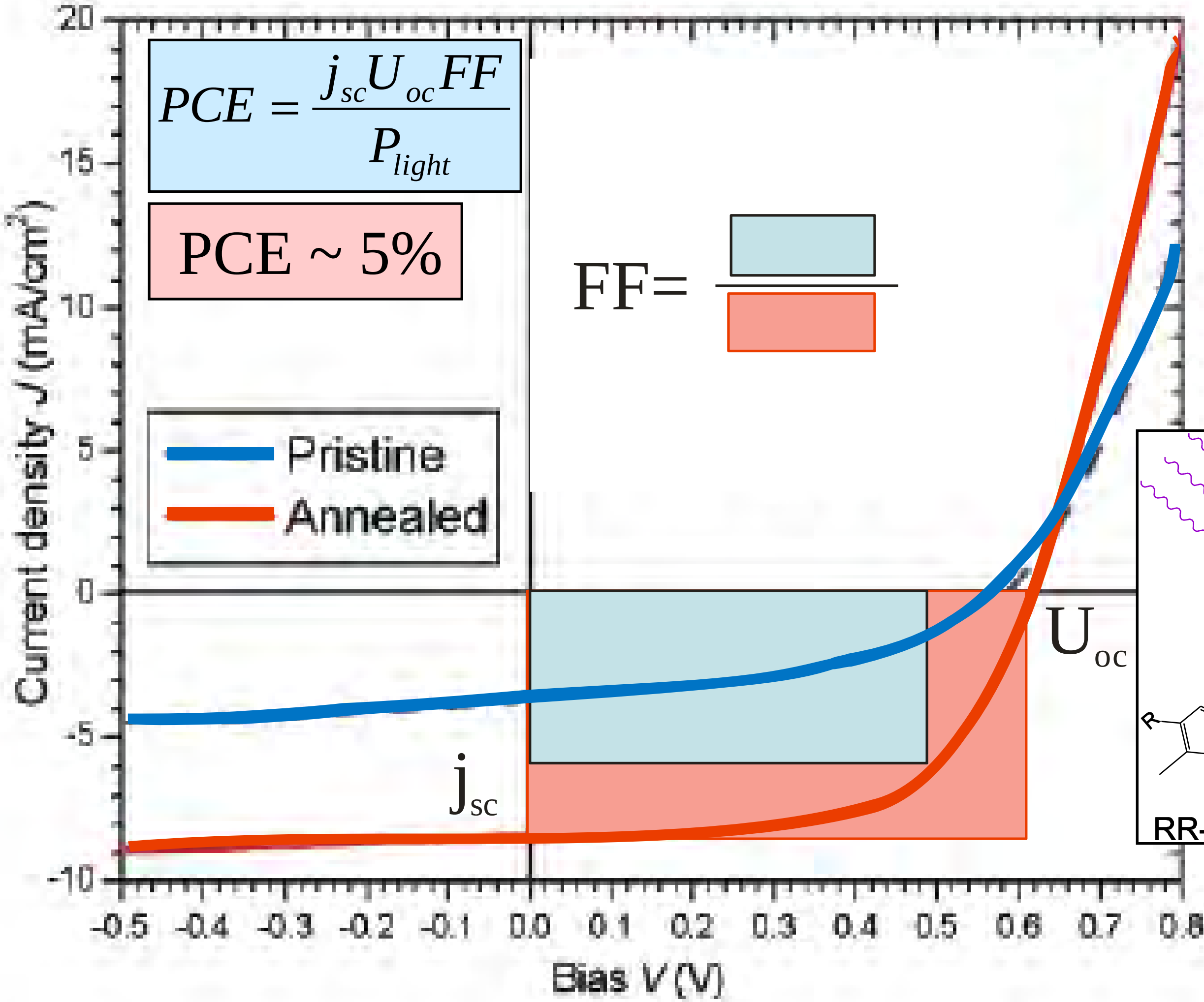
Bulk-Heterojunction Solar Cells

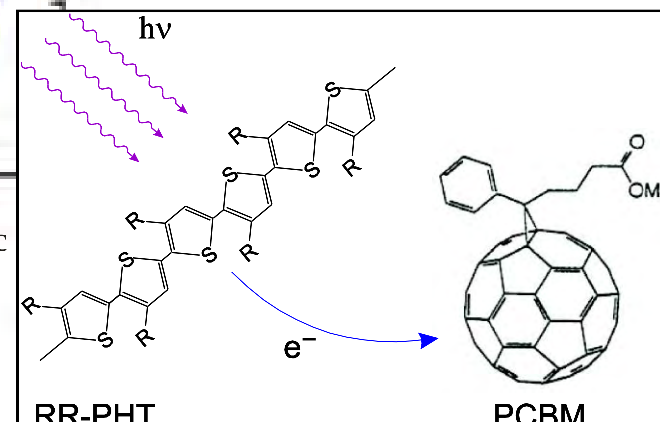


PCE ~ 2.5%

Mixture of electron accepting PCBM and electron donating polymer

Second generation BHSC





Xiaoniu Yang, et al., Nano Letters, **5**, 579-583 (2005)

Why transport and recombination?

Efficiency proportional to the current

$$j = en\mu E$$

n= carrier density

μ= carrier mobility

e= electron charge

E=electric field

- Organic materials have low mobilities
- To have same efficiency we need higher carrier densities
- Higher density leads to lower carrier lifetime -> Lower current!

$$\tau = [n(0)\beta]^{-1}$$

- μ and the second order recombination parameter β are important parameters for testing suitable materials.
- Main goal – to understand transport and recombination in polymeric solar cells.

Langevin Recombination

Expected in low-mobility (μ<1 cm^2/Vs) materials

Langevin recombination is determined by the probability for the charge carriers to meet in space, independent of the subsequent fate of the carriers

$$\frac{dp}{dt} = \frac{dn}{dt} = -\beta_L np = -\beta_L n^2$$

$$\beta_L = \frac{e(\mu_n + \mu_p)}{\varepsilon\varepsilon_0} \propto \mu_f(F,T)$$

Necessary condition: The carrier mean free path is much smaller than the Coulomb capture radius r_c, i.e. $a << r_{C.}$

$$r_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT} \approx 19\text{nm}$$

To reach a photocurrent density of ≥ 15mA/cm^2 for $d=300$ nm and $V_{oc}=0.5$V: **$\mu\beta_L/\beta > 5 \cdot 10^{-3}$ cm^2/Vs**.

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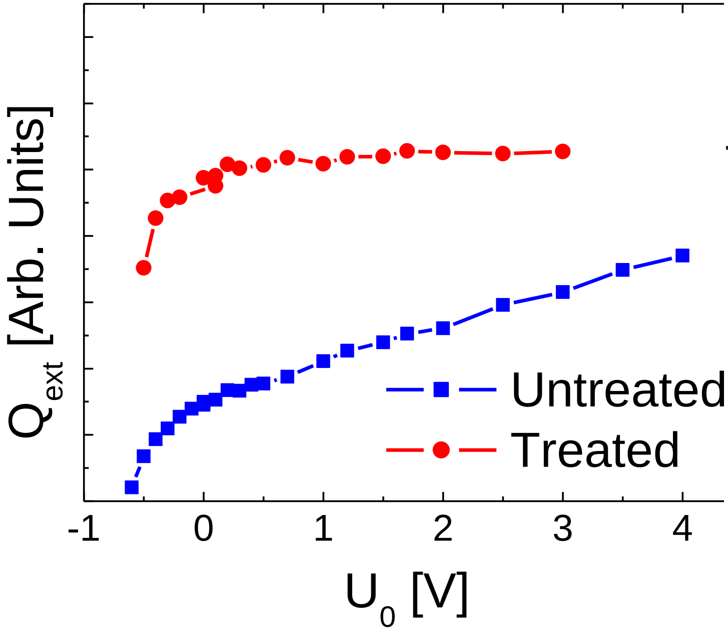
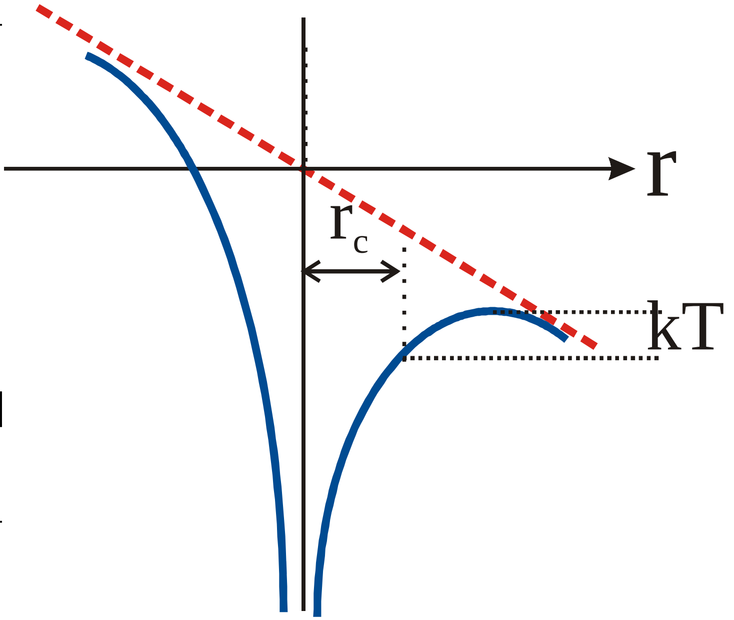
P. Langevin, Ann. Chim. Phys. **28**, 433 (1903).

Consequences of Langevin recombination

- Langevin recombination leads to low photogeneration efficiency of Onsager type
  - –Field-dependent generation!
  - –Lower the Fill-Factor





A. Pivrikas et al, unpublished

Consequences of Langevin recombination

- Langevin recombination leads to low photogeneration efficiency of Onsager type
  - –Field-dependent generation!
  - –Lower the Fill-Factor
- Efficiency will be limited
  - –Only ~CU can be extracted from the device

Photo-SCLC:

$$t_{tr} = t_{\sigma} = \frac{\varepsilon\varepsilon_0}{ne\mu} = \frac{1}{n\beta} = \tau_{\beta}$$

Bimolecular lifetime

Langevin!

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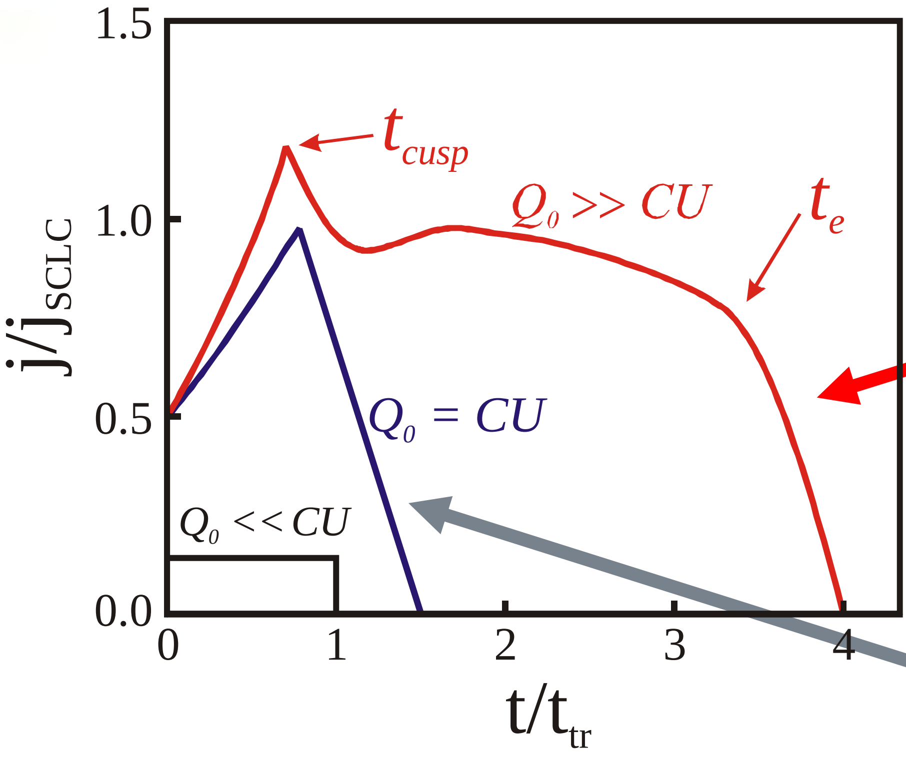
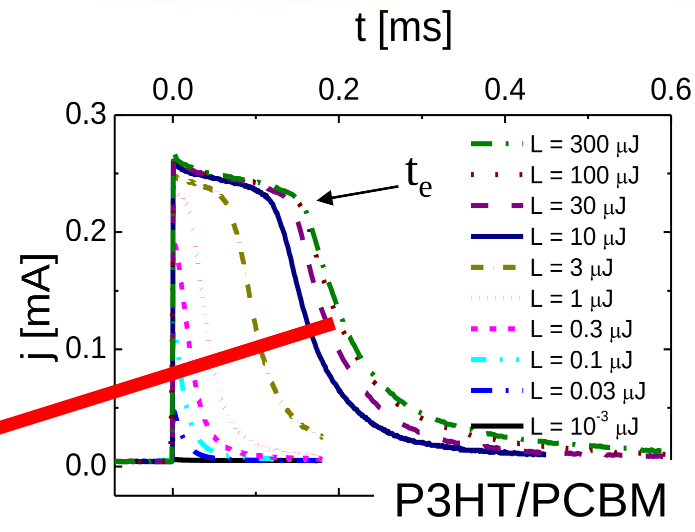
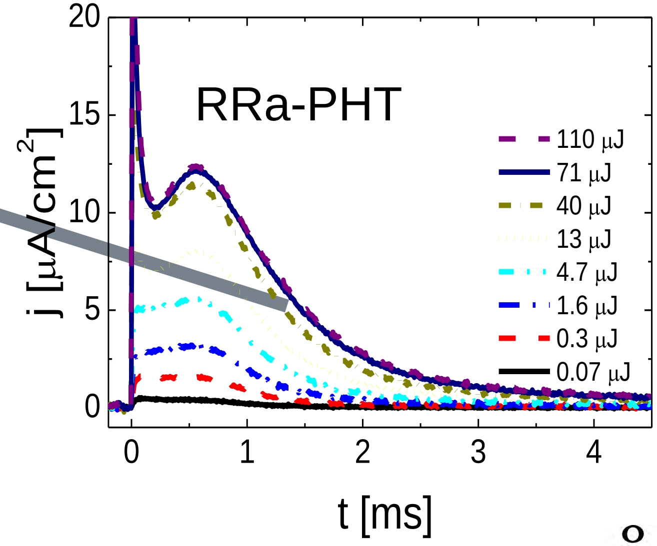
Recombination measured using TOF



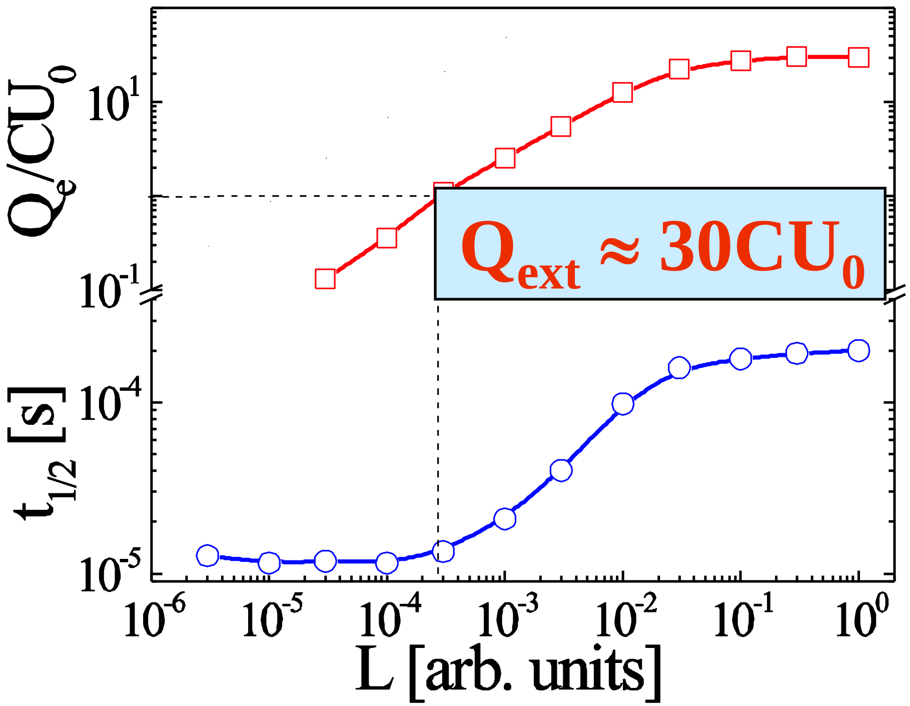




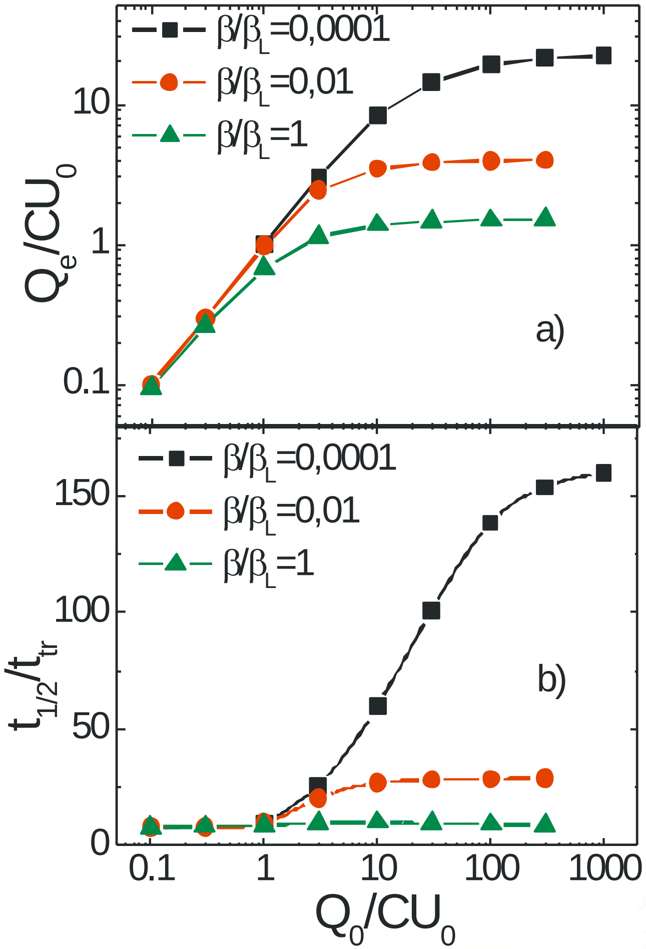
1. Small Charge Current (SCC) mode.
2. Space Charge Perturbed Current (SCPC).
3. Space Charge Limited Current (SCLC).

A. Pivrikas et al. PRB **71**, 125205, (2005) A. Pivrikas, et. al., PRL **94**, 176806 (2005).

Reduced Recombination in RRPHT/PCBM Solar cells

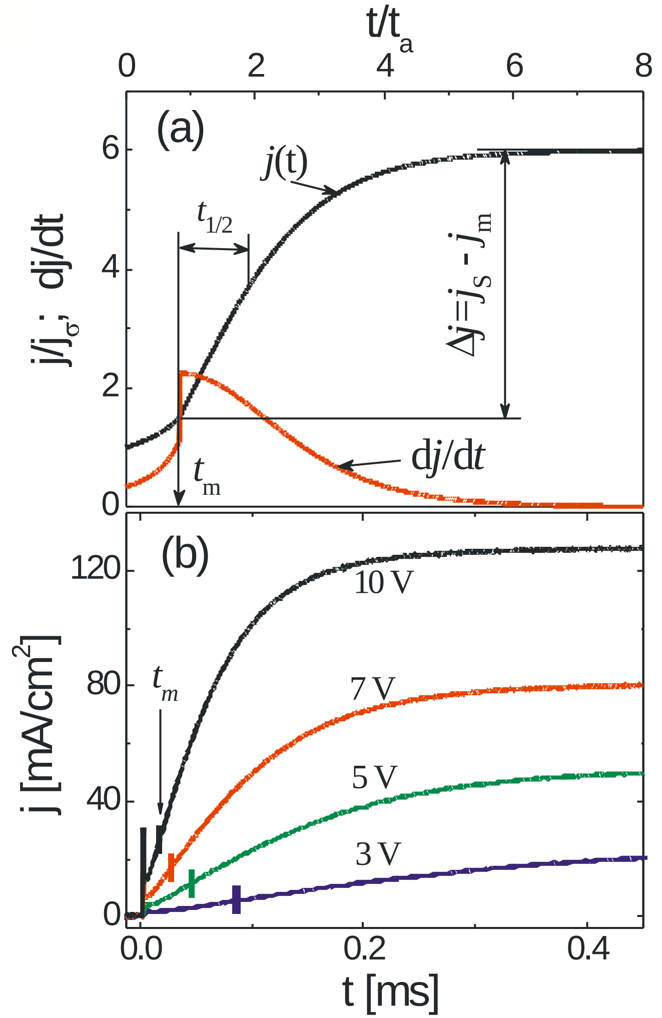


$\beta/\beta_L = 10^{-4}$



A. Pivrikas, et. al., PRL. **94**, 176806 (2005).

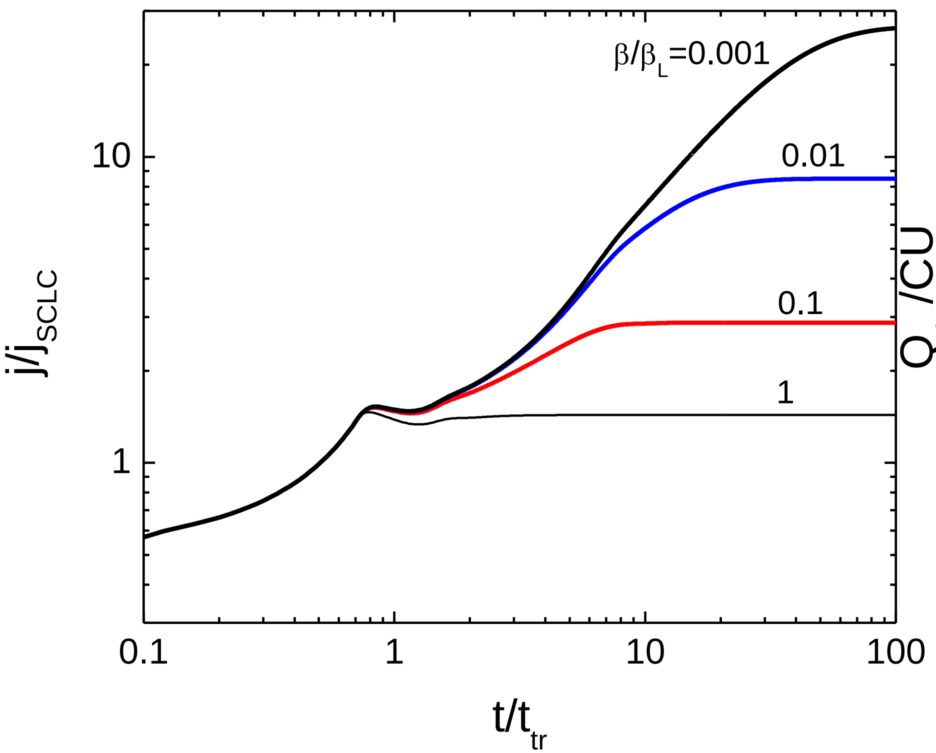
Double Injection (DoI) Currents



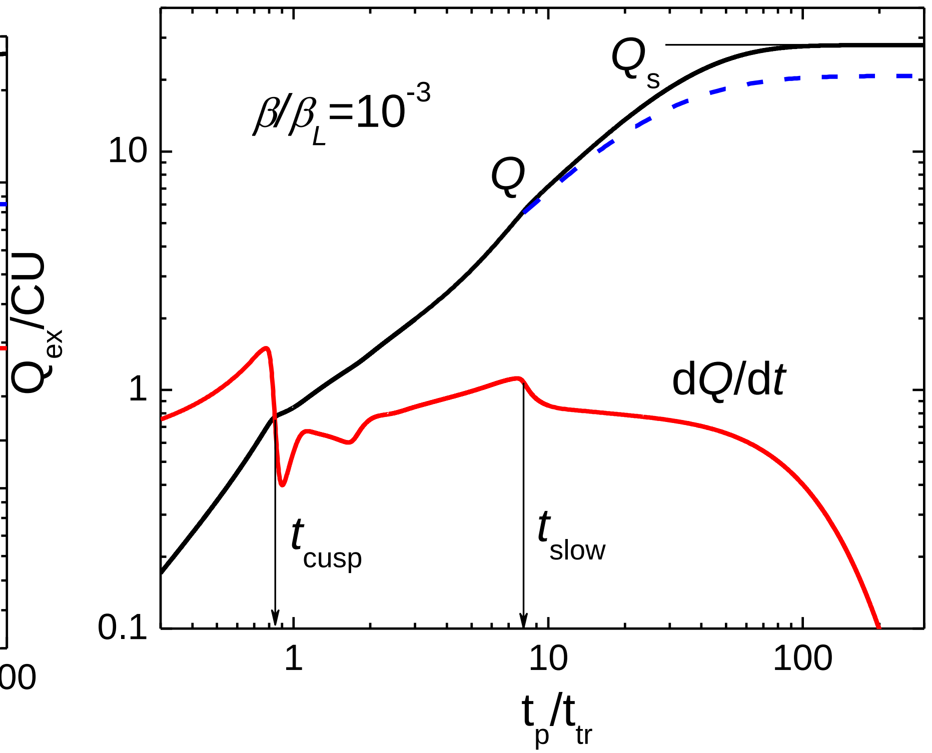
- Apply a voltage pulse
- Record the transient current
- First the RC-current is observed
- Then the build-up of a carrier density is observed
- The saturation curent is limited by recombination
- At switch-off, a reservoir extraction is observed

R.H. Dean. J. Appl. Phys. **40**, 585 (1969)
Mark & Lampert, *Current Injection in Solids*, Academic Press NY (1970)

Simulated current transients



As a function of β



As a function of pulse width

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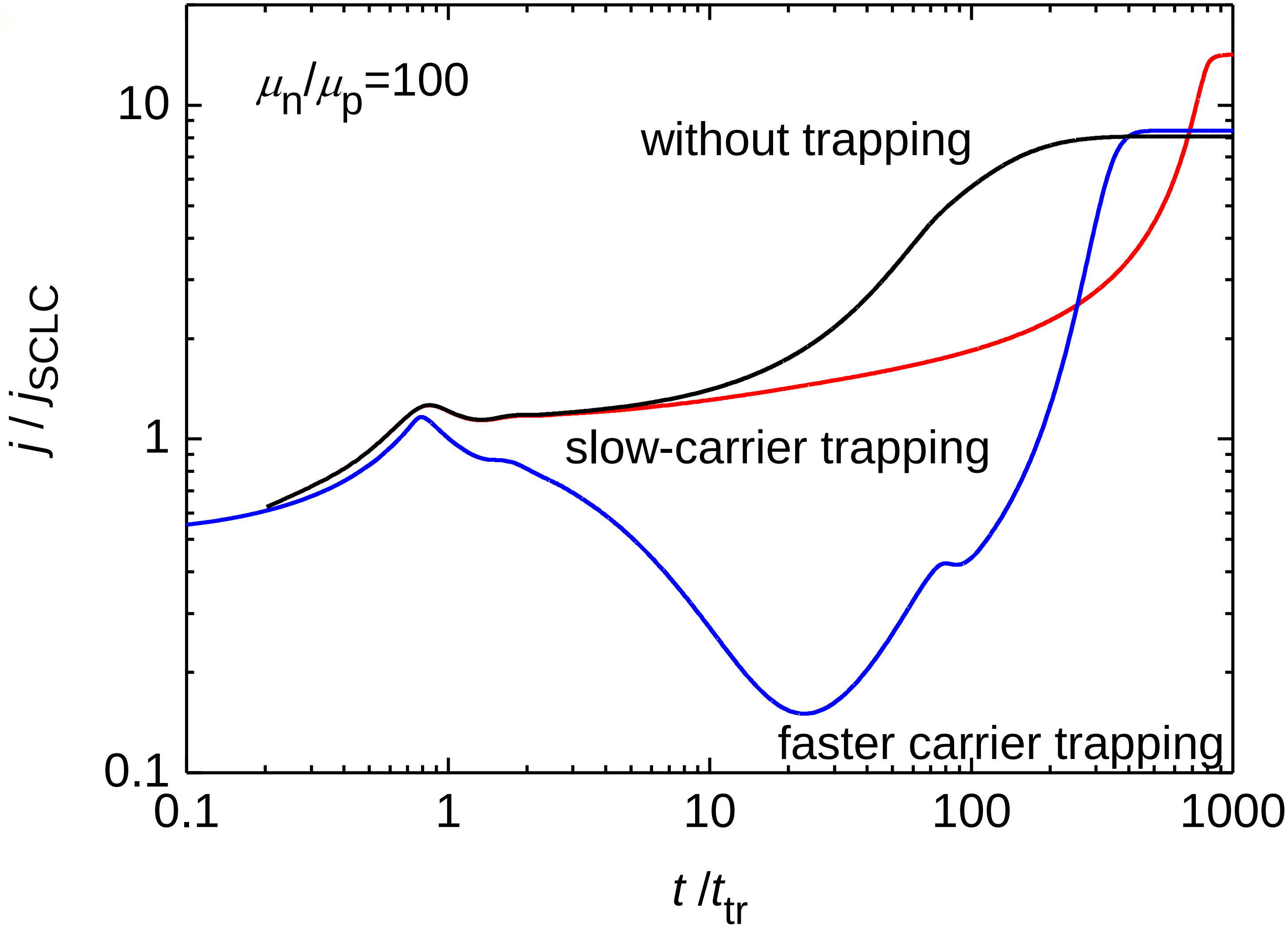
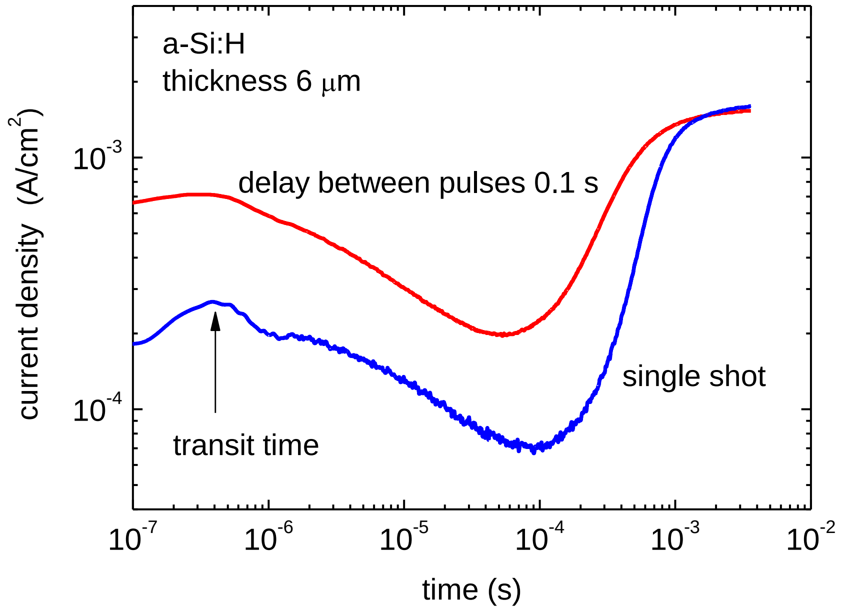
G. Juska et al., JAP 101, 114305 (2007)

Effect of trapping

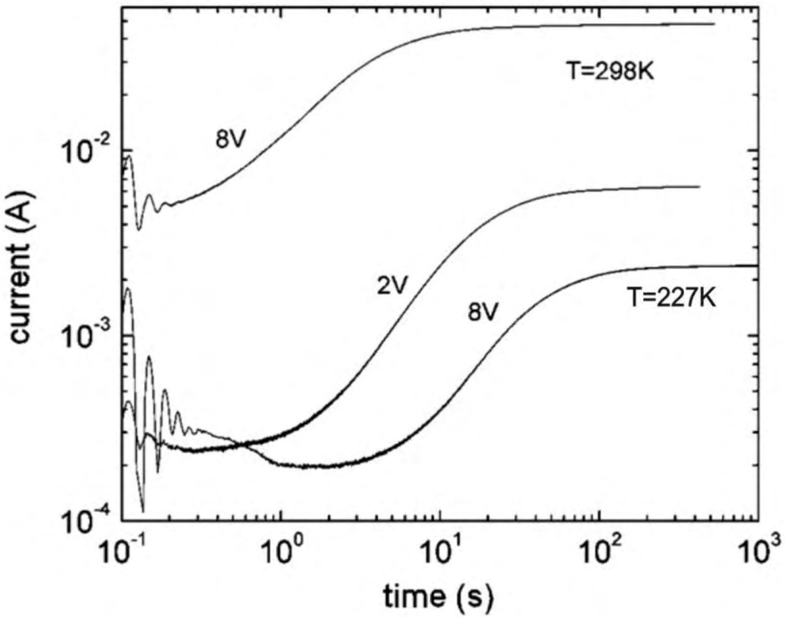


Trapping in real solar cells

a-Si:H



RR-P3HT/PCBM

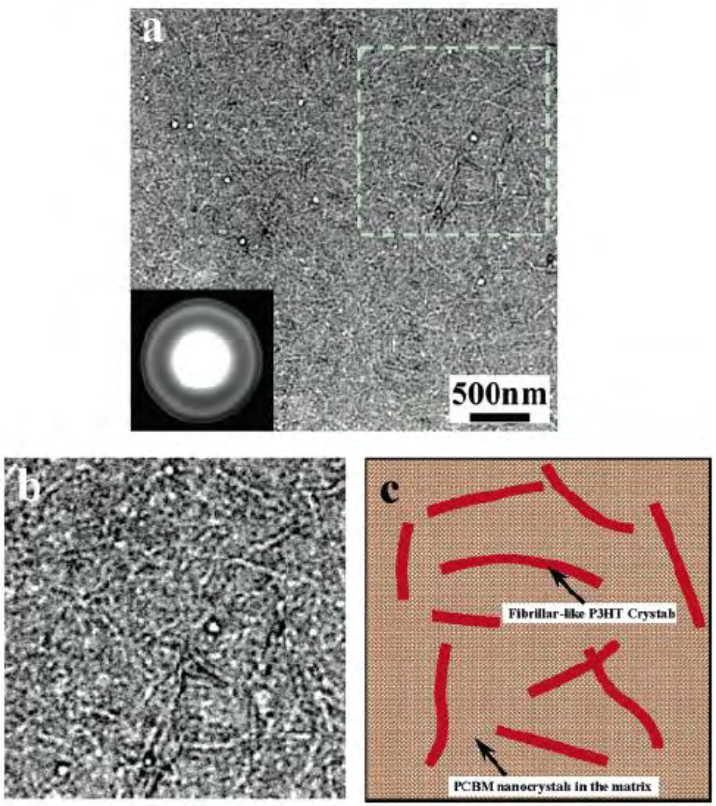


Note the absence of trapping in annealed RRPHT/PCBM BHSC!

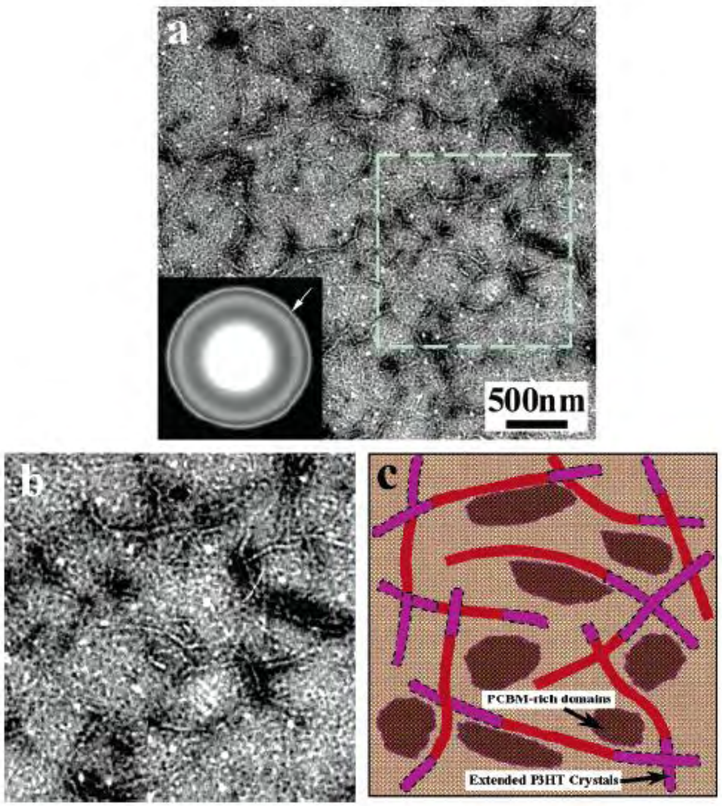
Juska et al., in press

Why is there reduced recombination?

Before annealing

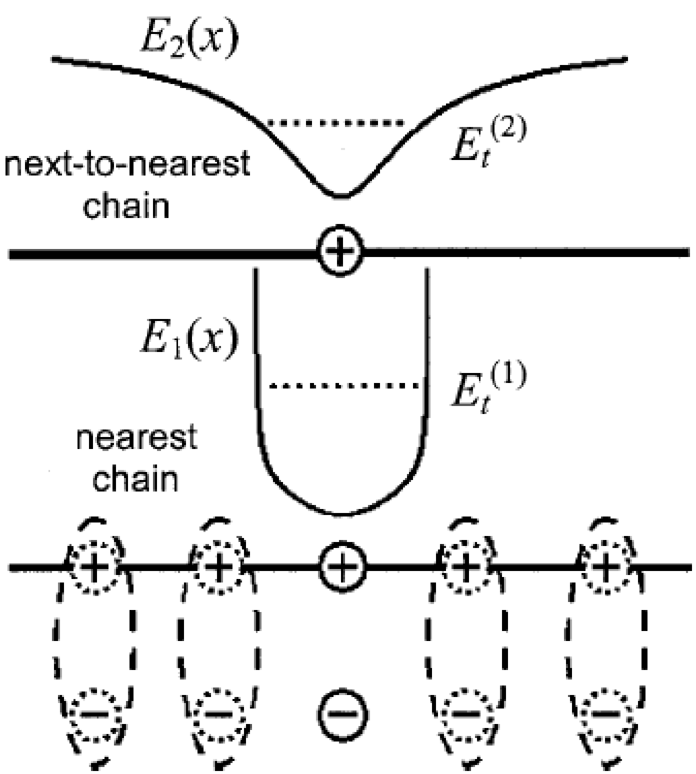


After annealing



Xiaoniu Yang, et al., Nano Letters, **5**, 579-583 (2005)

A possible model for reduced recombination in RR-PHT/PCBM

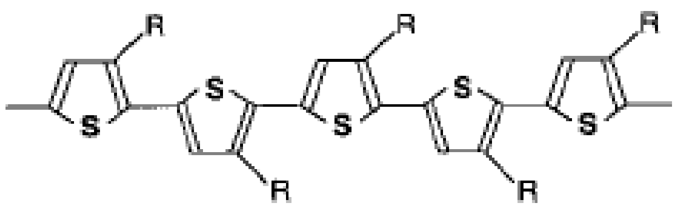


- Increased carrier generation / reduced recombination due to an effective energy barrier for geminate pair recombination at the interface (Δ~0.5 eV Osikowicz et al.)
- To reach the chain nearest the interface the hole on the polymer has to overcome the same barrier
- Probability for carriers to meet in space is reduced!
- Requires lamellar structures at the interface

V. Arkhipov et al., APL **82**, 4605 (2003); Osikowicz et al., Advanced Materials **19**, 4213 (2007)

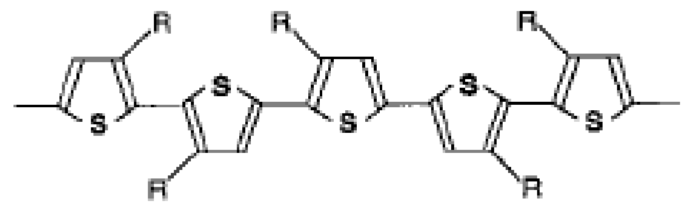
Lamellar structures important

A Regioregular (RR)

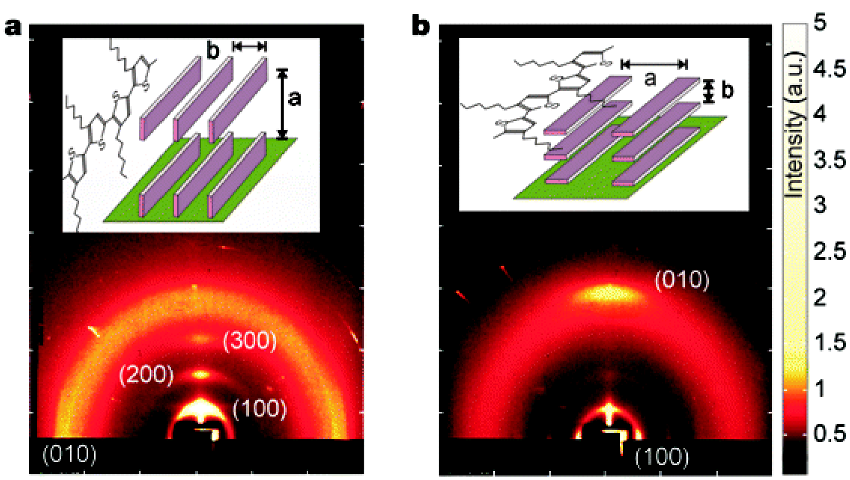


Head-to-tail = 100%

B Regiorandom (RRa)

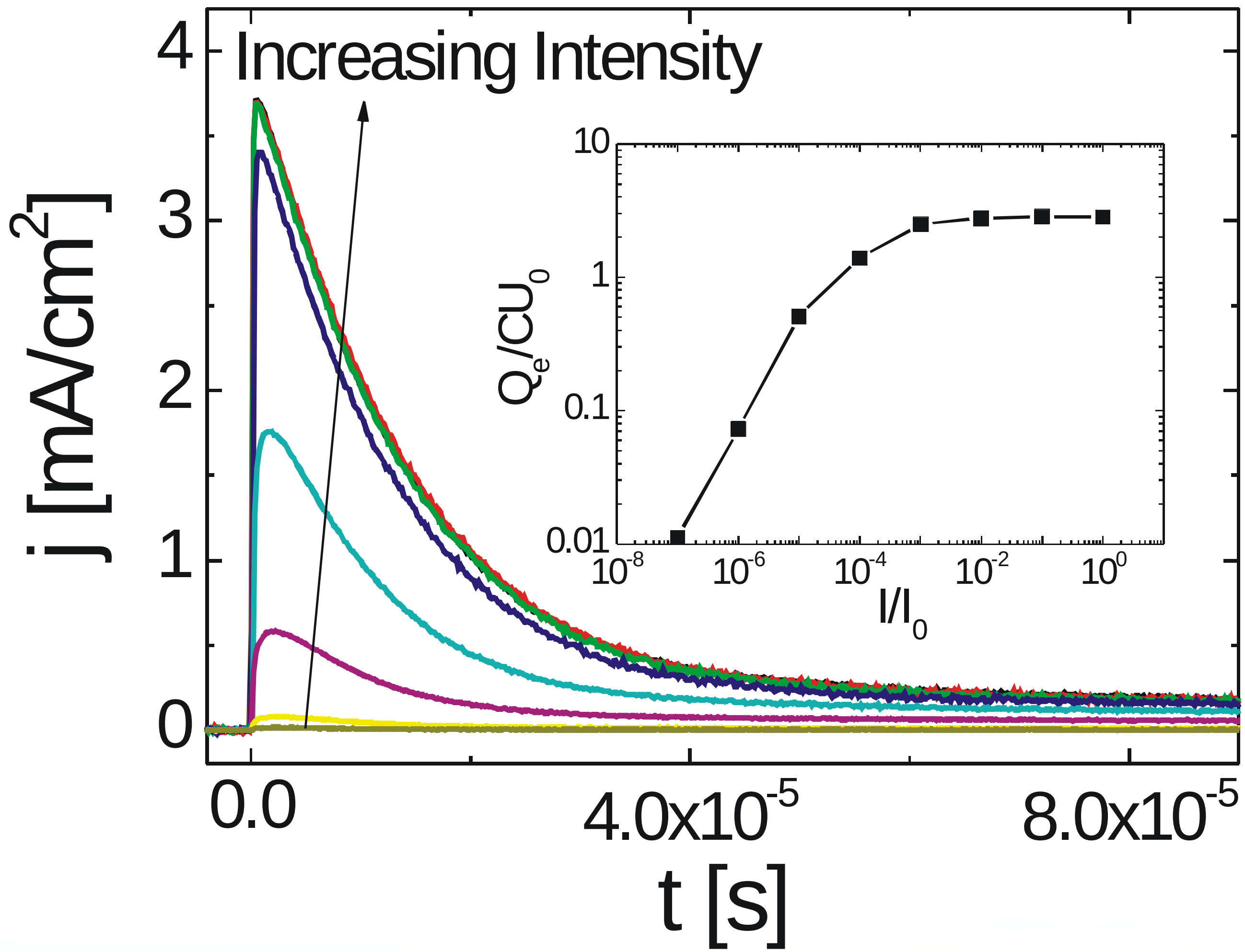


Head-to-tail ~ 80%



Sirringhaus et al., Nature **401**, 685 (1999); Österbacka et al., Science **287**, 839 (2000)

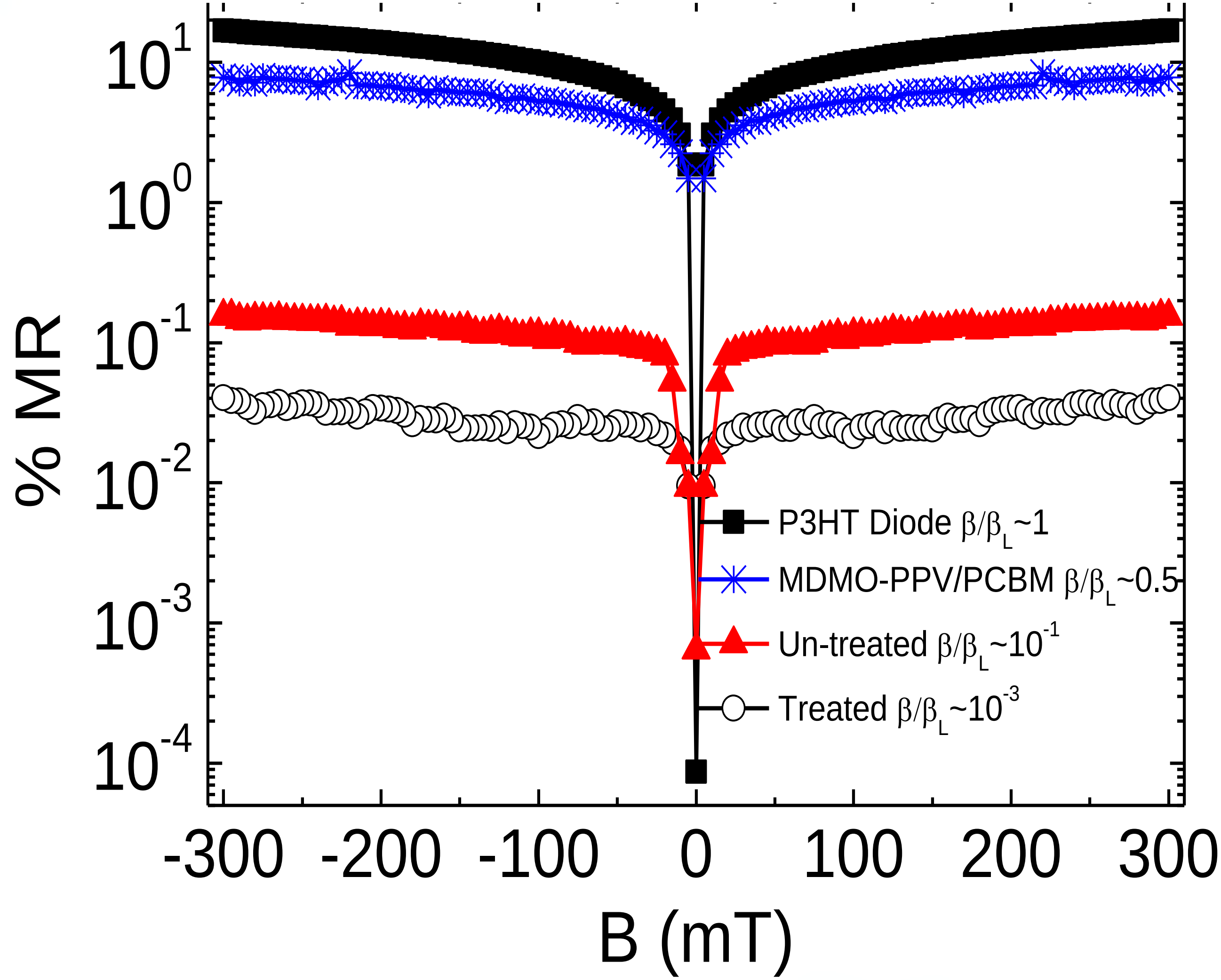
Langevin recombination in MDMO-PPV/PCBM systems



$$\frac{\beta}{\beta_L} \approx \frac{1}{2}$$

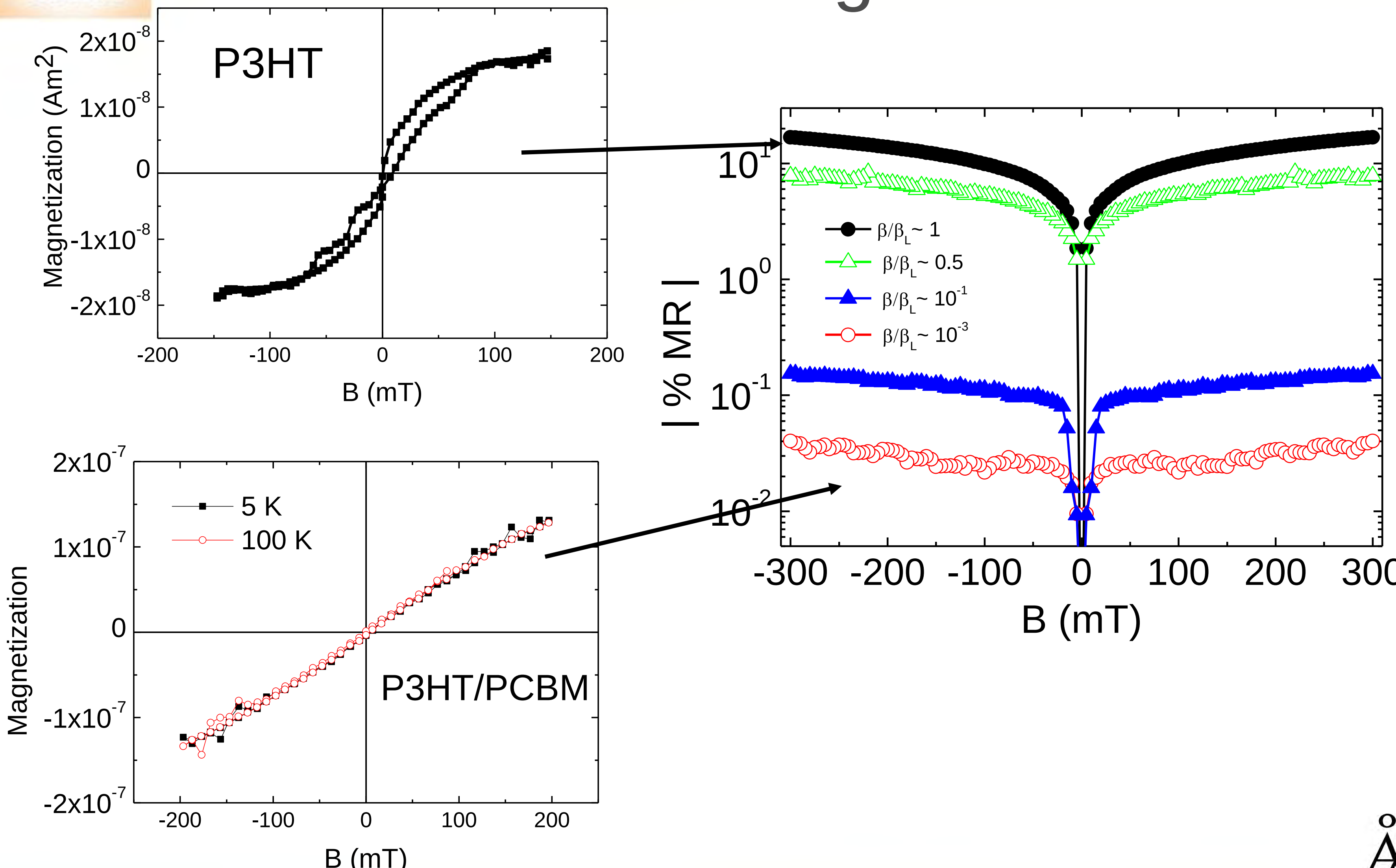
Pivrikas et al., Nonlinear Optics, Quantum Optics: Concepts in Modern Optics, **37**, 169-177 (2007)

Role of e-h recombination on OMAR



S. Majumdar et al., Physical Review B **79**, 201202R (2009).

Correlation with magnetic behavior

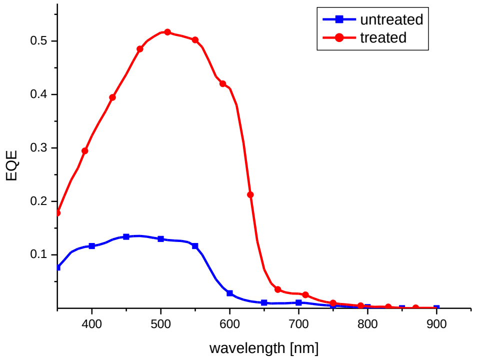


S. Majumdar et al., submitted.

V.I. Krinichnyi, Solar cells and Solar energy Materials **92**, 942 (2008).

Summary

- Bimolecular recombination is important for characterization of solar cell materials
- Langevin recombination:
  - Probability for charge carriers to meet in space
  - Field dependent generation of Onsager type
  - Lower extraction efficiency



- Treated RR-PHT/PCBM blends shows greatly reduced recombination compared to Langevin **$\sim\beta/\beta_L \sim 10^{-3}$**
- Untreated RR-PHT/PCBM blends show **$\sim\beta/\beta_L \sim 0.1$**
- MDMO-PPV/PCBM blends show **$\sim\beta/\beta_L \sim 0.5$**
- Nanomorphology important ->delocalization in lamellas important!
- DoI is an extremely useful measurement technique for materials with reduced recombination
- Take-home message: The probability to form electron – hole pairs is crucial for the magnetotransport response.

The people!

- S. Majumdar, H. Majumdar, T. Mäkelä, L. Jian, R. Mohan, ÅA
- H. Aarnio, G. Sliauzys, J.K. Baral, N. Kaihovirta, D. Tobjörk, F. Jansson, N. Björklund, M. Nyman, S. Sanden, F. Petterson, ÅA
- H. Stubb (emeritus), K.-M. Källman (lab engineer), ÅA

- Left the group: A. Pivrikas (Linz), T. Bäcklund (UPM), H. Sandberg (VTT), M. Westerling (Perkin-Elmer)

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Organic Electronics group 2008

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