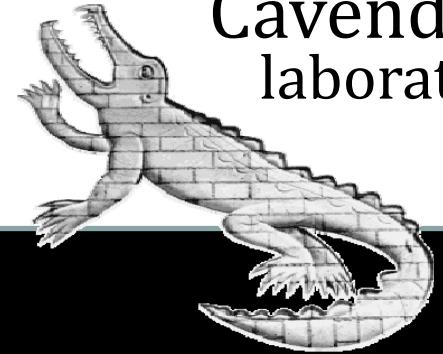




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CAMBRIDGE

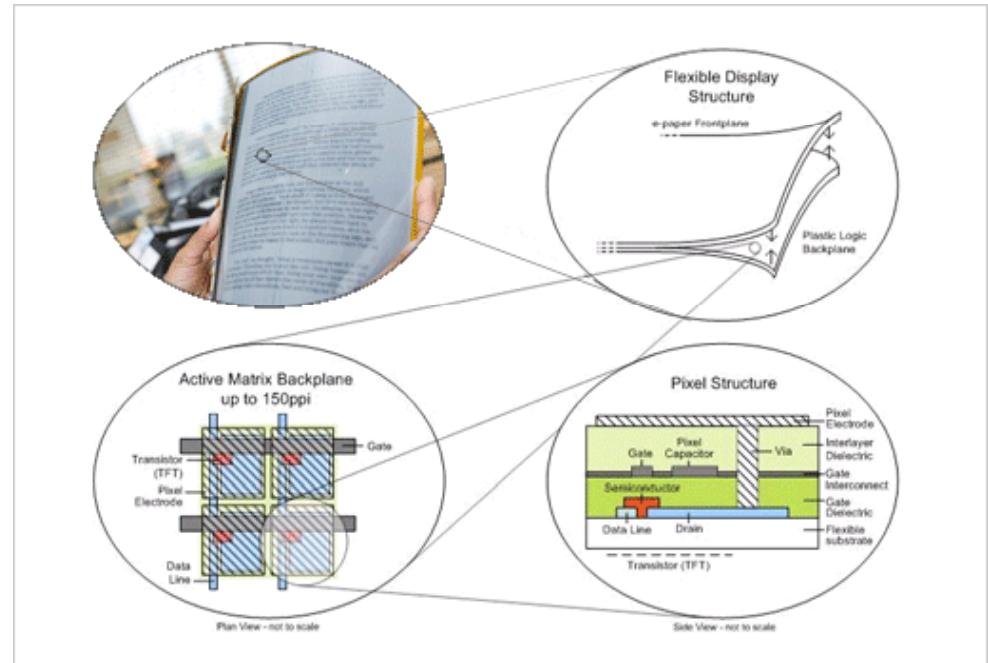


Поляризационная спектроскопия органических полупроводников

Артем Бакулин



Plastic electronics

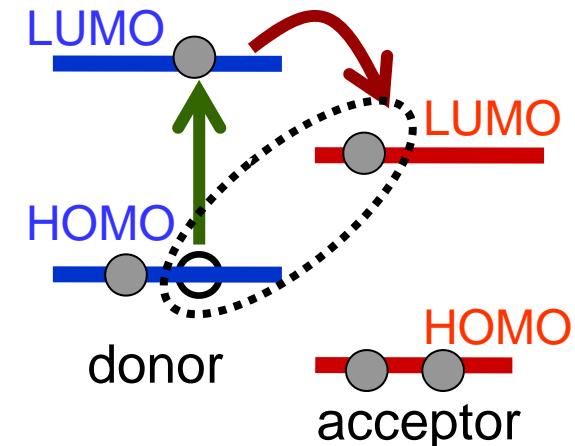
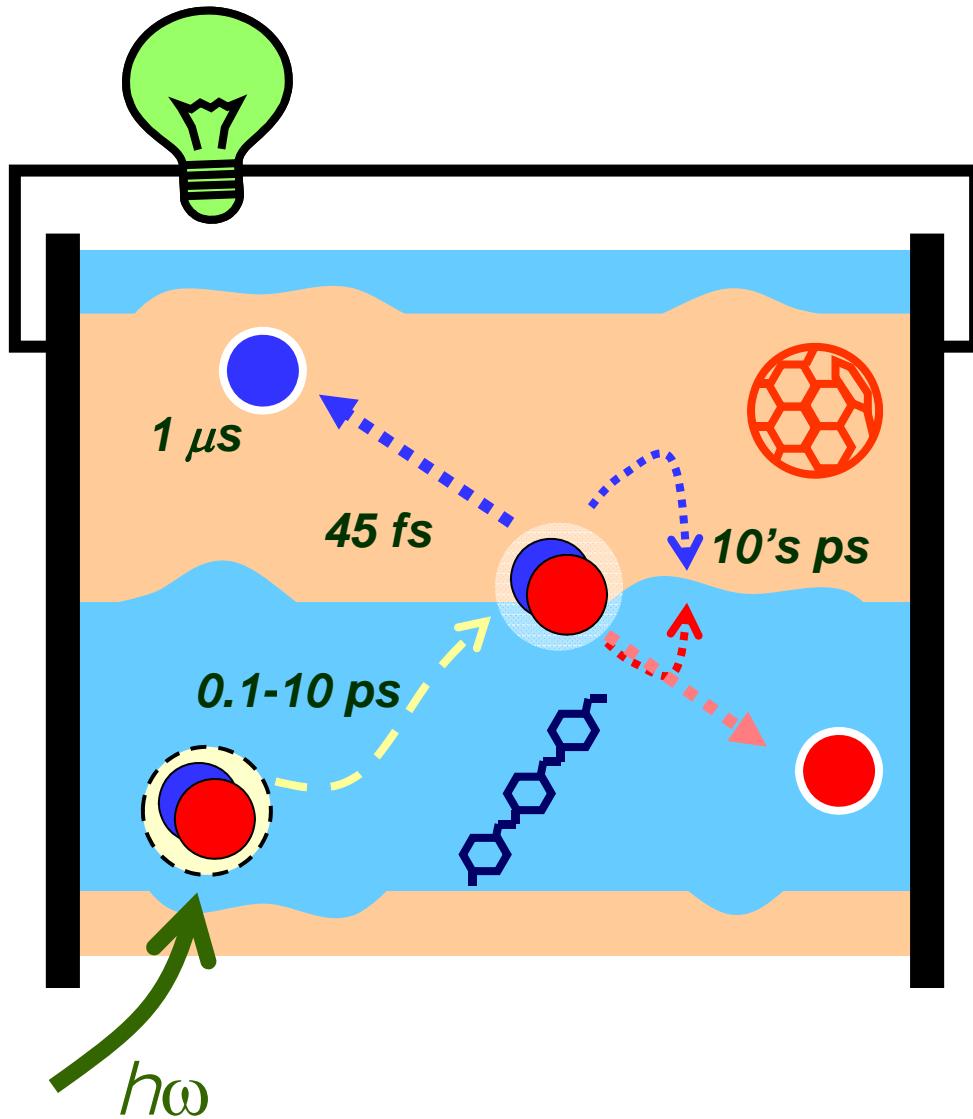


Displays



Solar cells

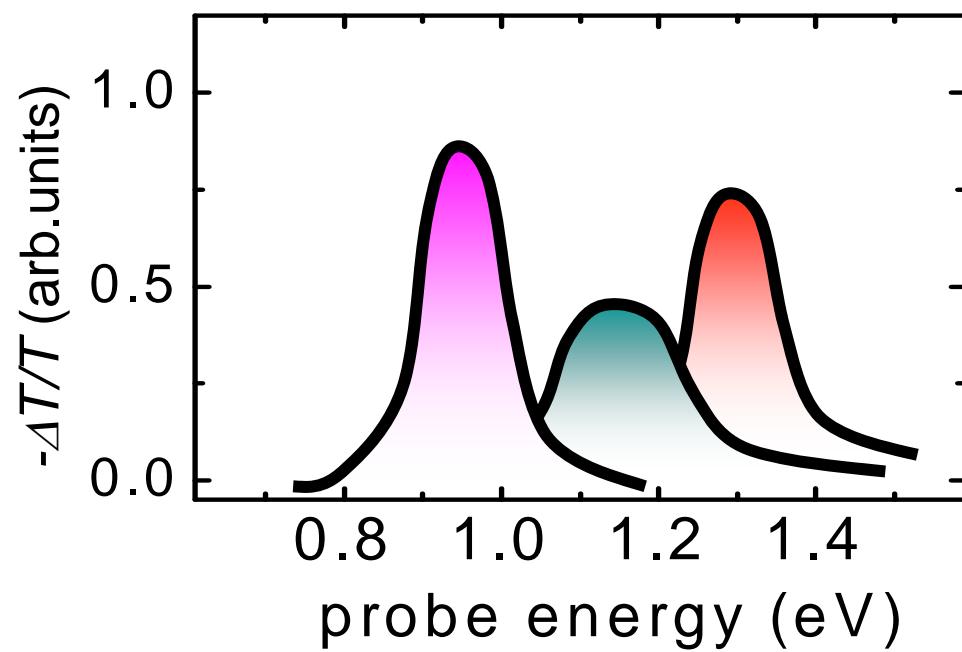
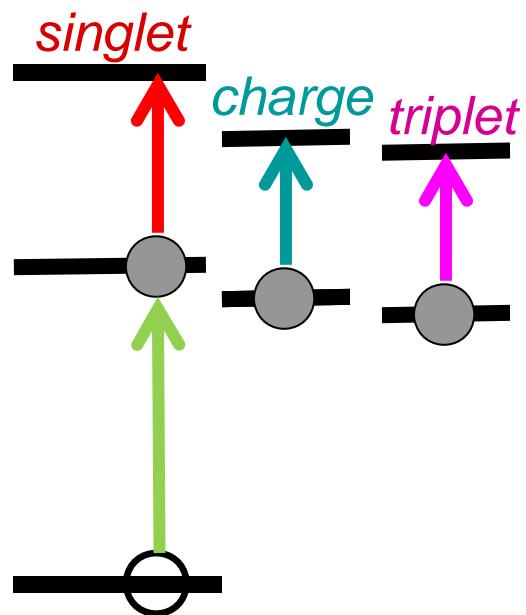
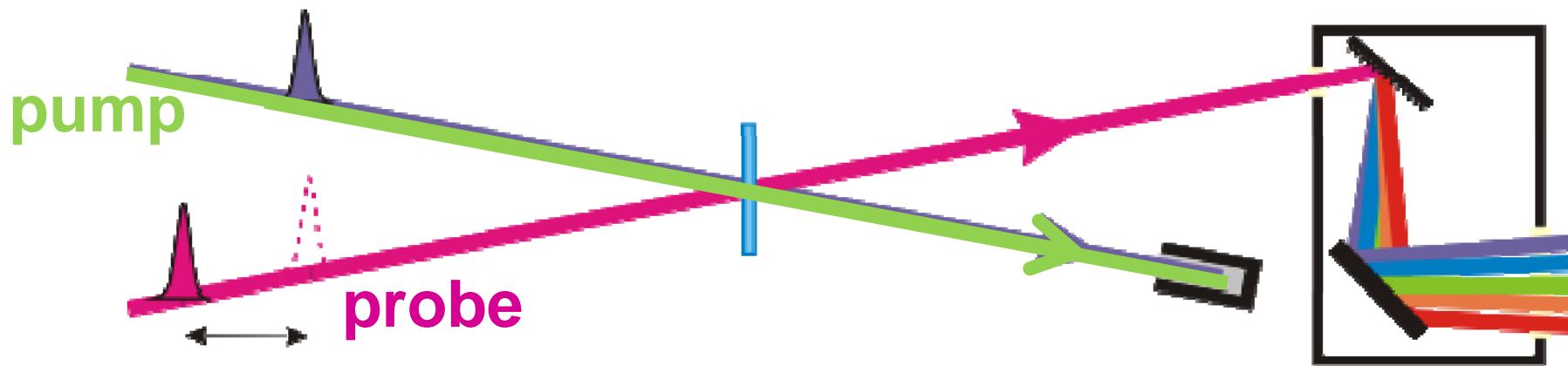
The bulk-heterojunction concept:



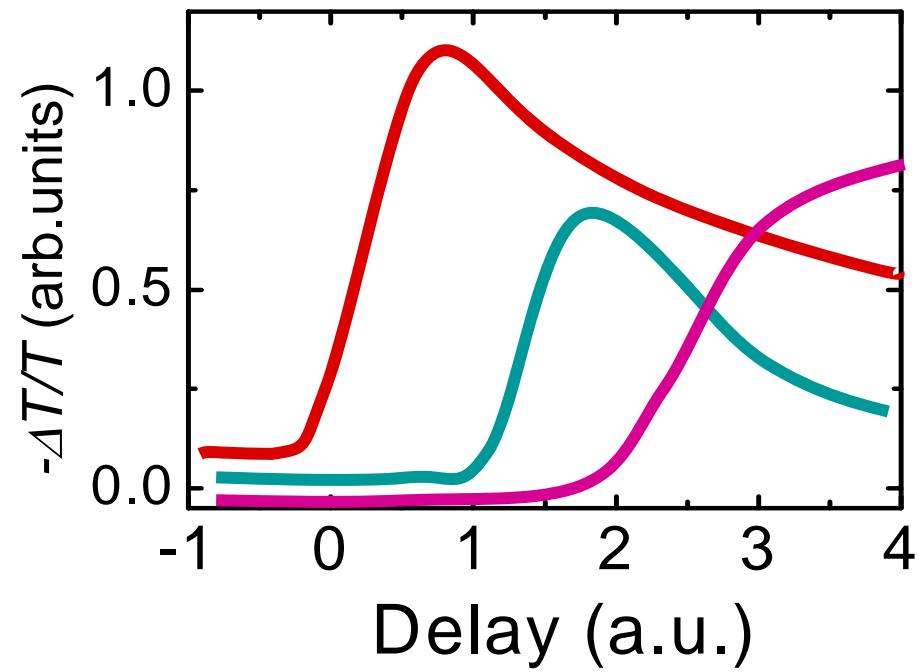
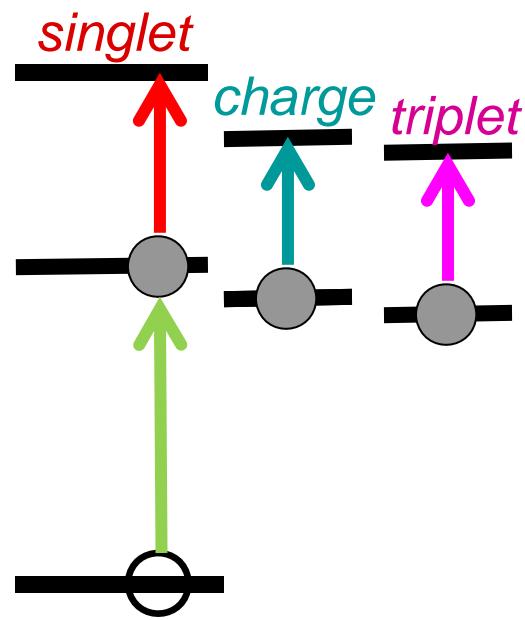
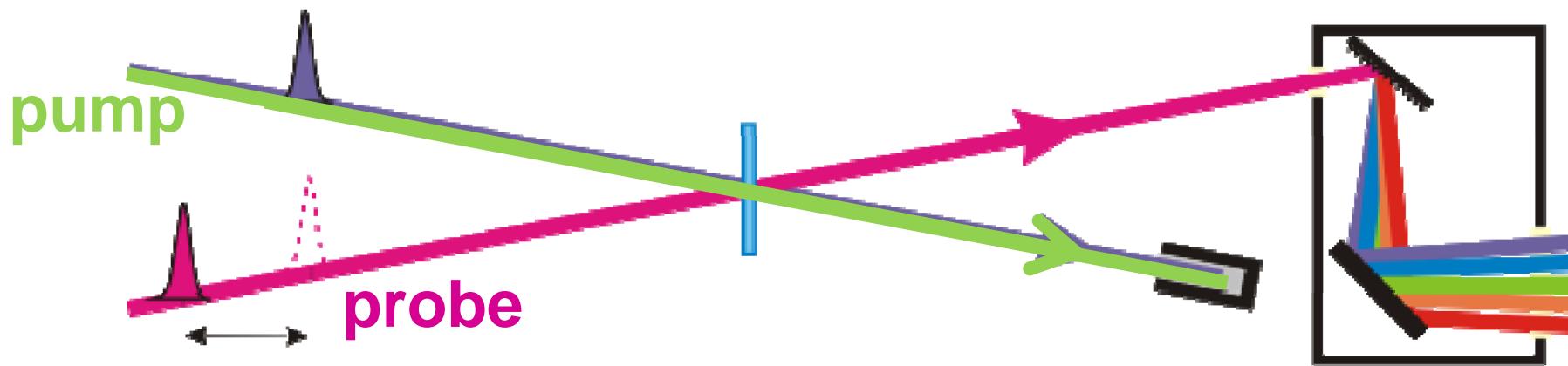
1. Optical excitation
2. Charge separation
3. Charge-transfer state
4. Recombination...
5. ...Or Free charges

What happens in such a PV cell
at the molecular level?

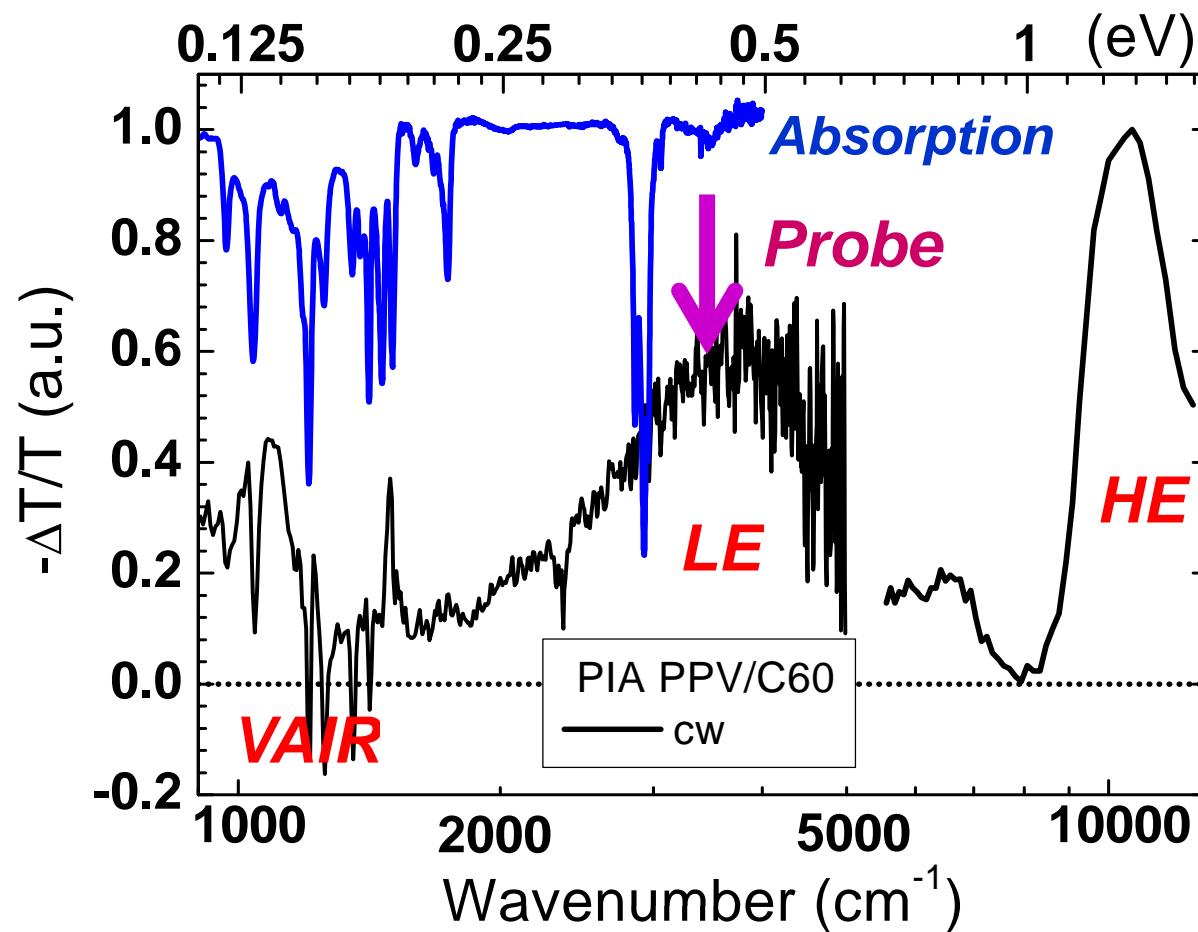
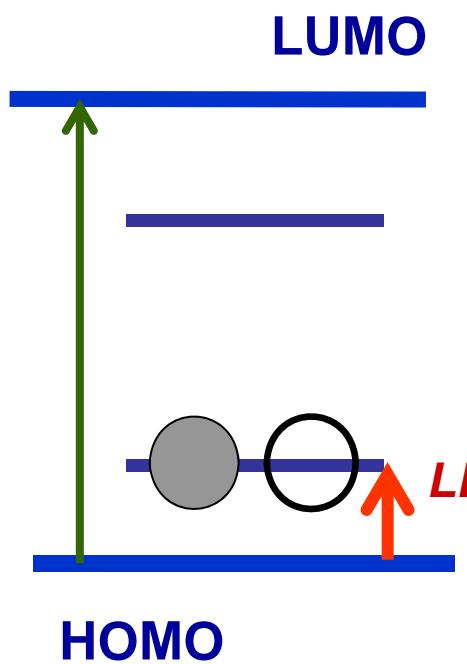
Transient Absorption Spectroscopy



Transient Absorption Spectroscopy

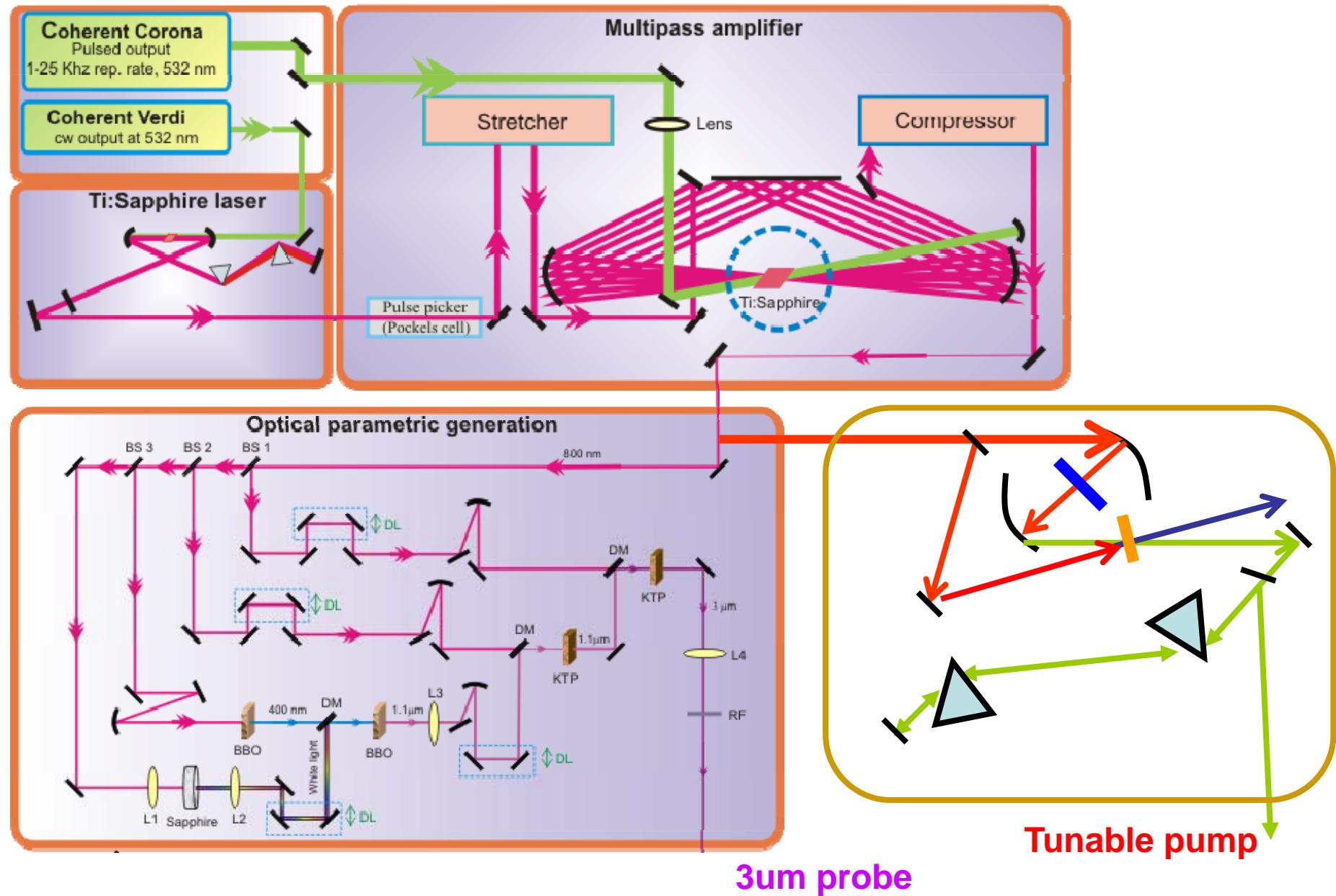


IR Signatures of Charges

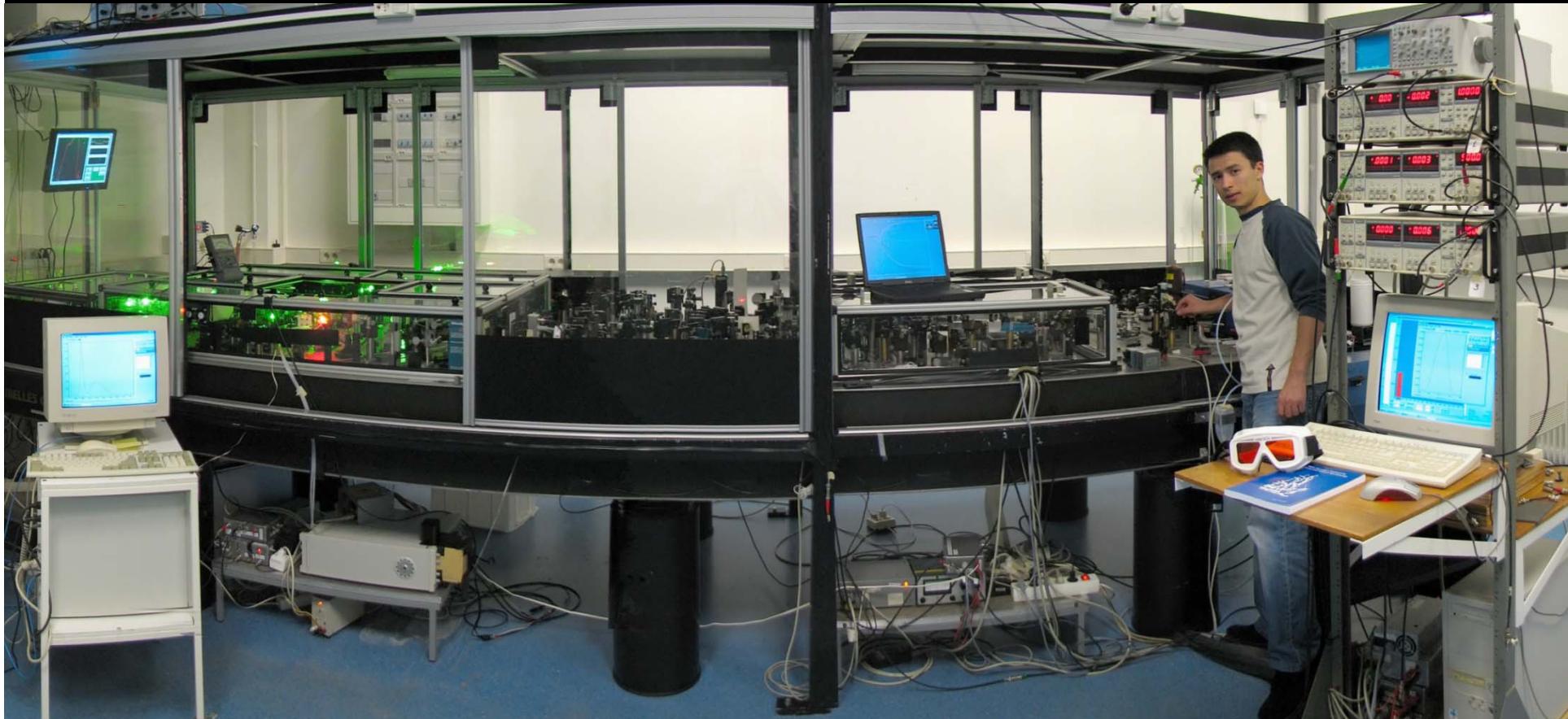


- Photo-Induced Absorption in IR is an excellent probe for the concentration of charges
- Low-energy (LE) peak allows background-free measurements

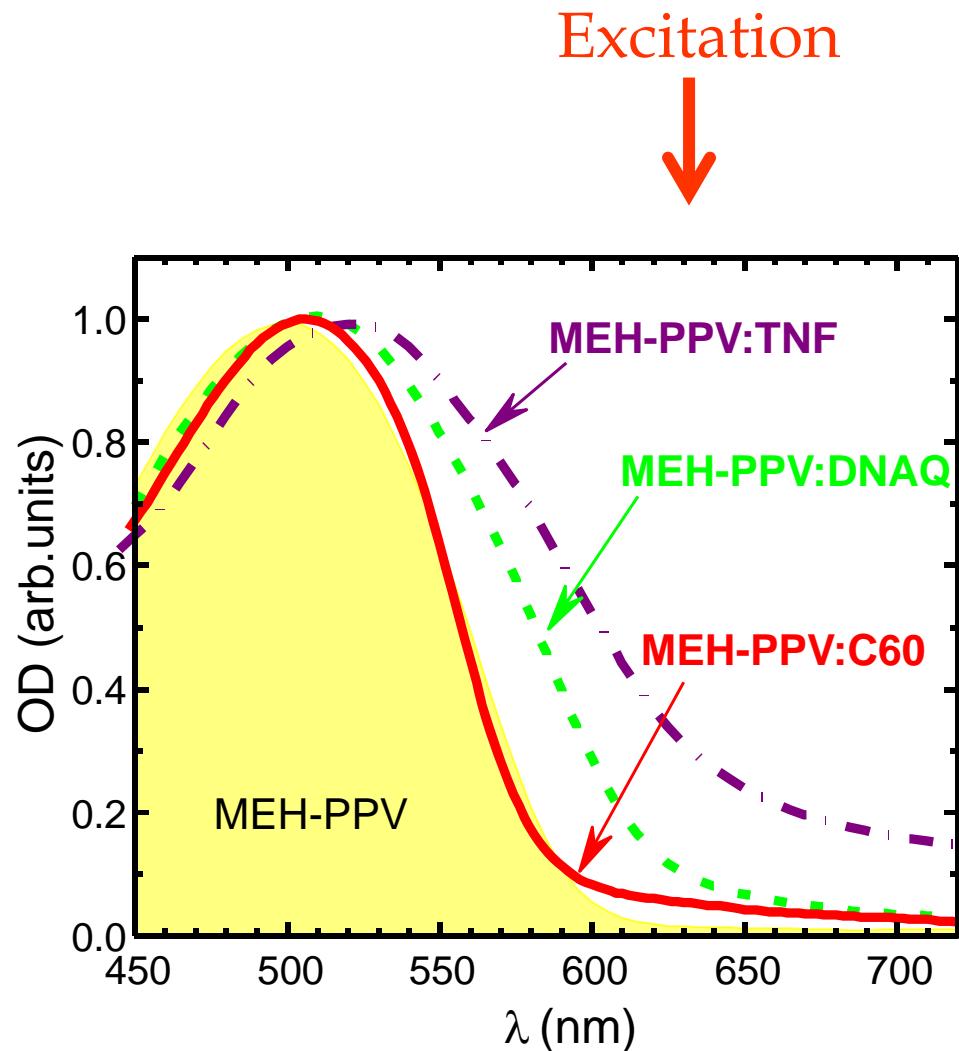
Vis (35 fs) – IR (70 fs) spectroscopy set-up



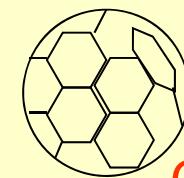
Vis (35 fs) – IR (70 fs) spectroscopy set-up



Samples: donor- acceptor blends



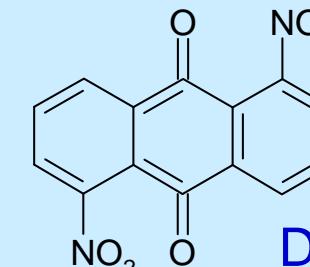
Acceptors:



C₆₀

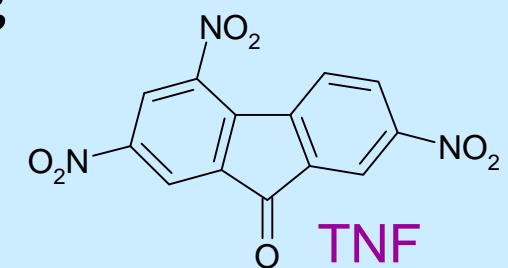
Weak
CTC

Goris *et al*, J of Mat. Sci. (2005)
Drori *et al*, PRL (2008)



DNAQ

Strong
CTCs

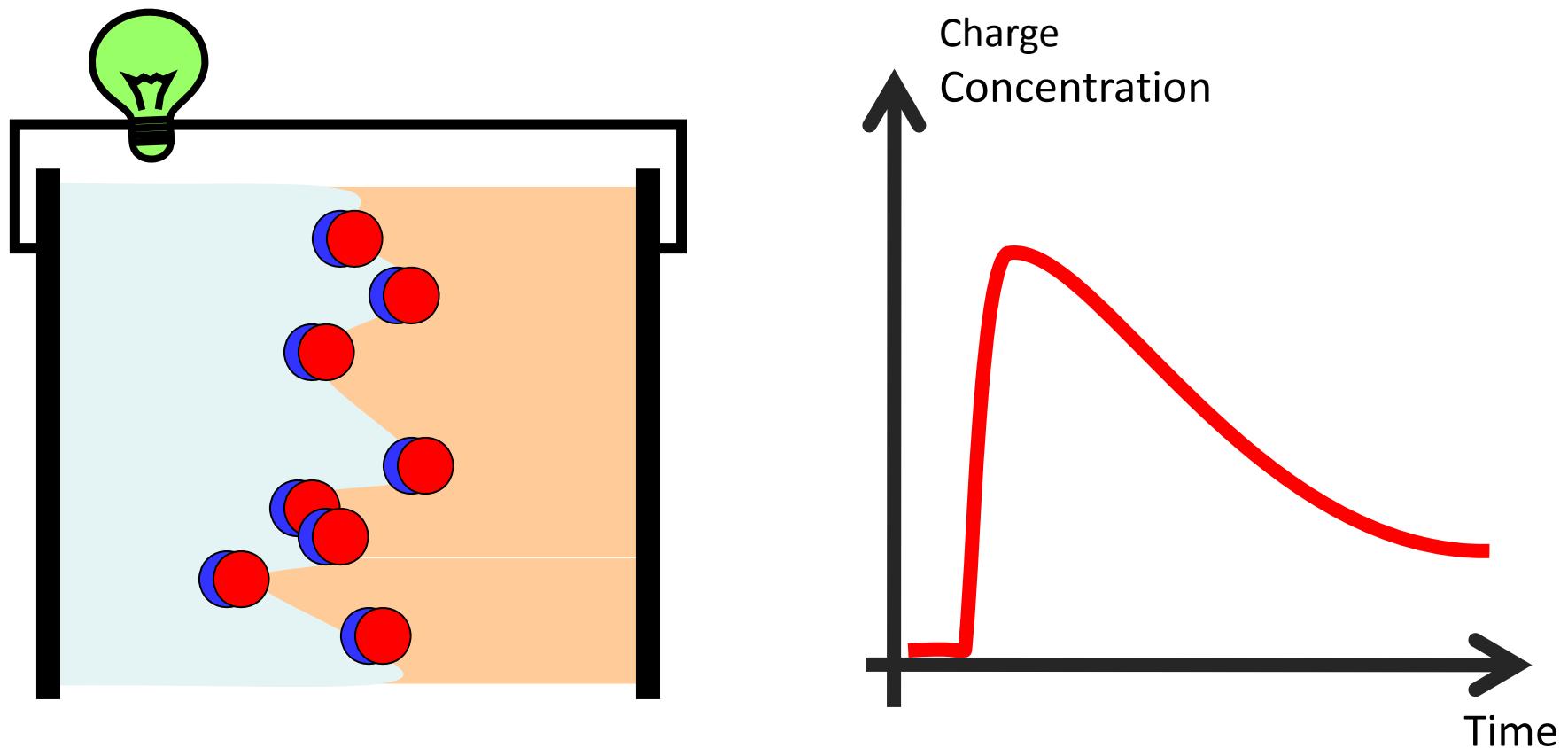


TNF

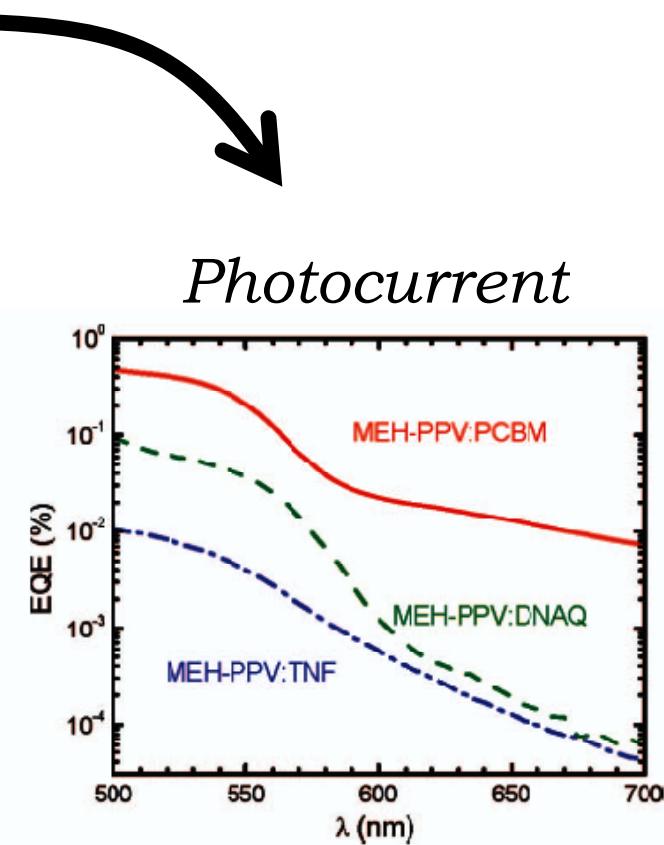
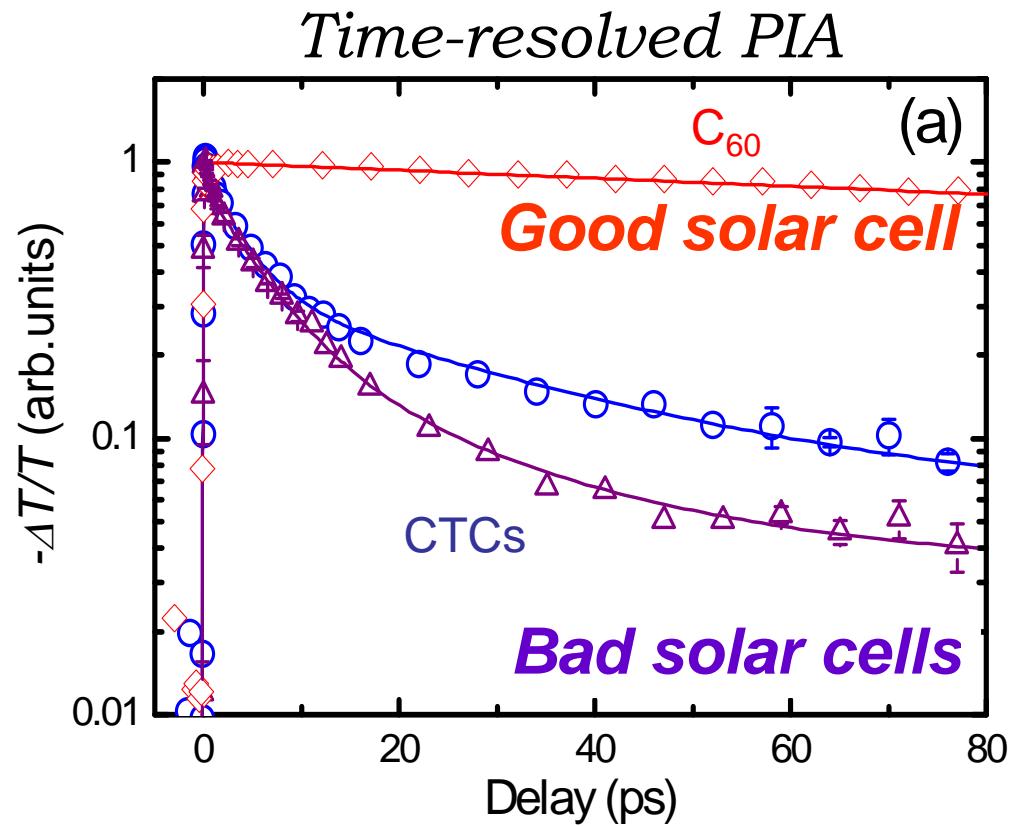
Bakulin *et al*, Synth. Met. (2004)

Watching charge dynamics in solar cell

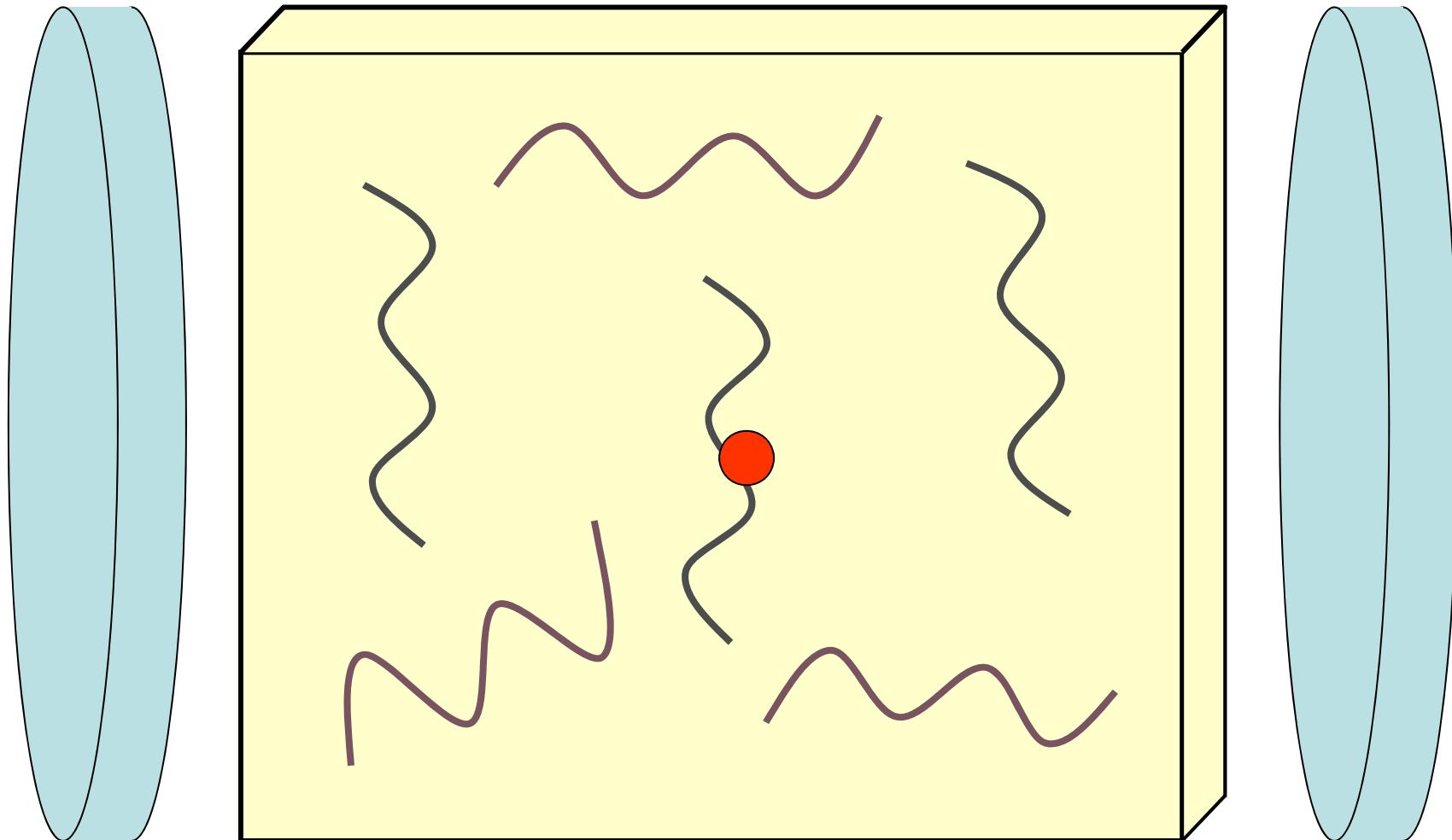
Excitation by the Ultrafast Laser



Spectroscopy vs. cell performance

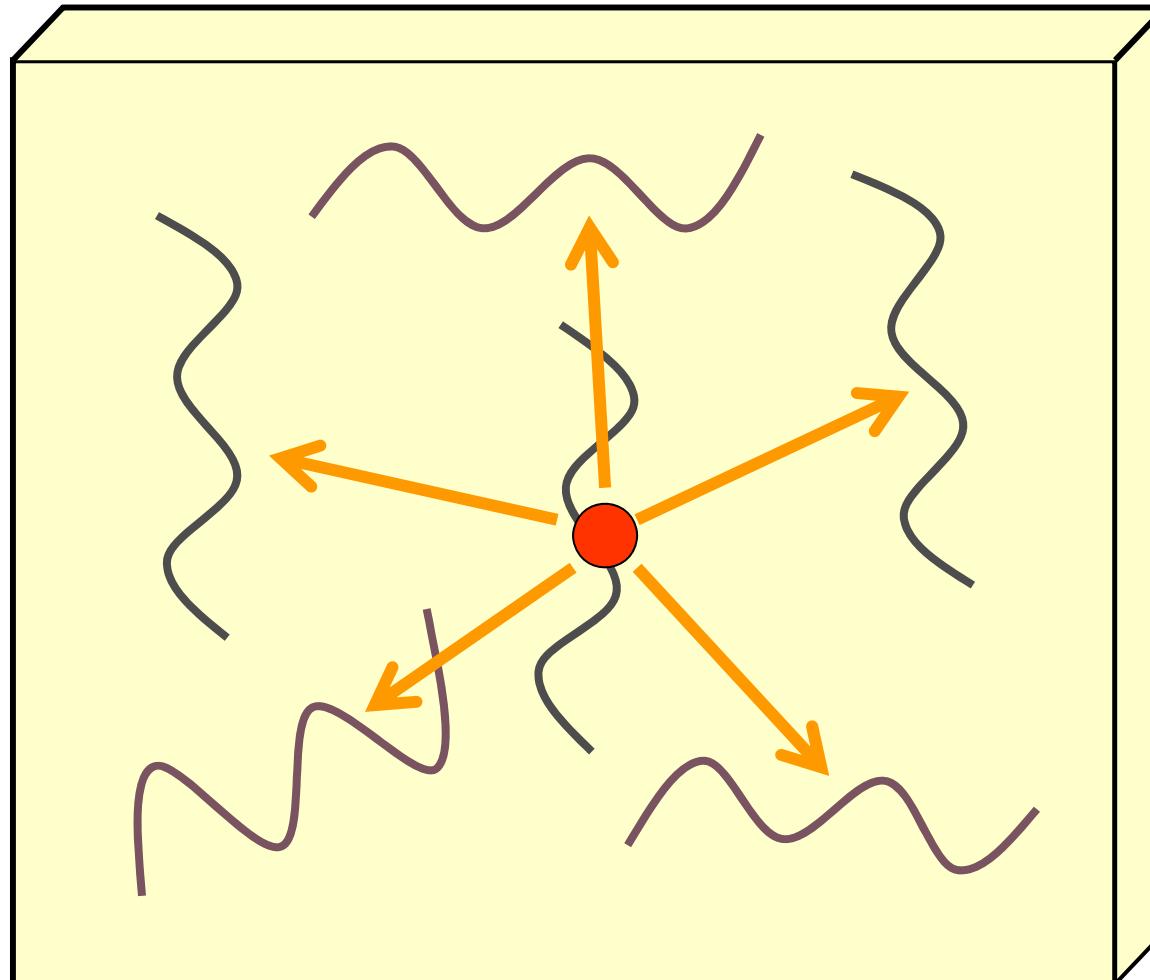


What do we know about charge transport?



Conductivity **within chain** and through the **complete device**.

One can build a microscopic model



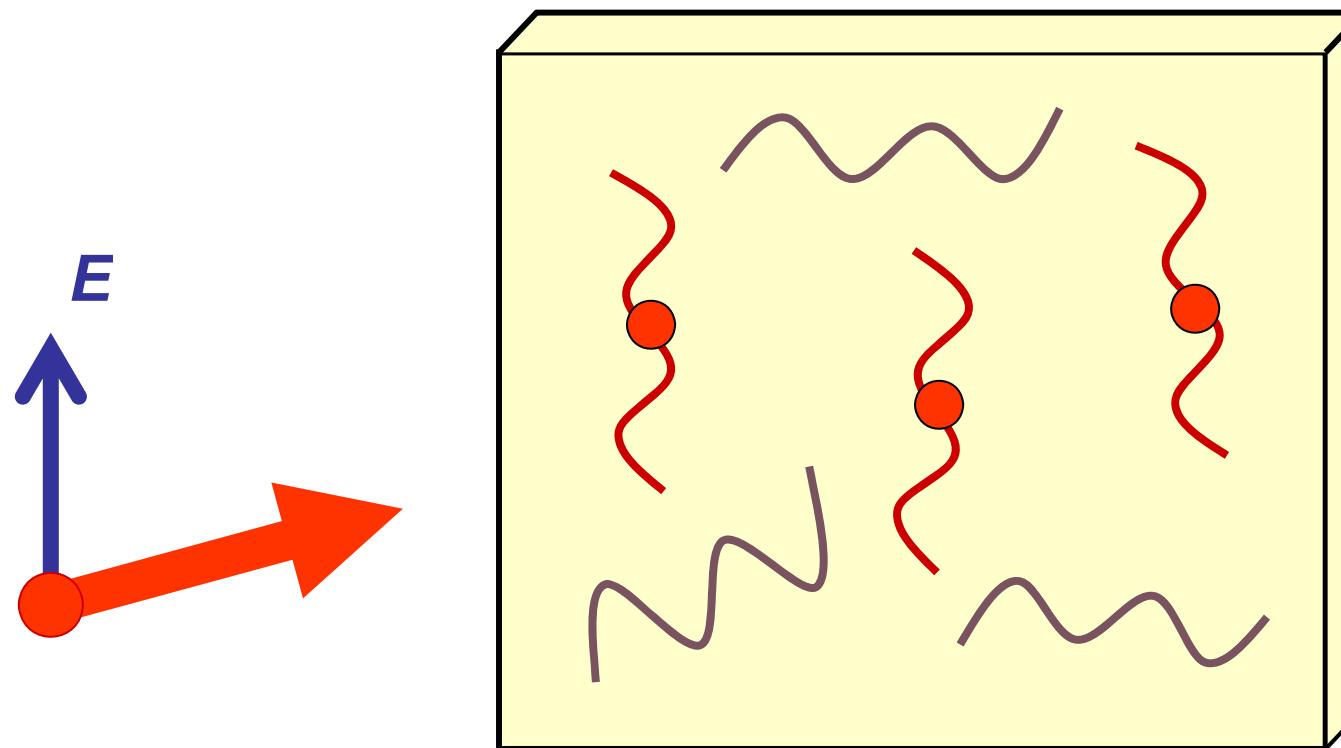
Distribution of states + hopping rates $V_{ij} (E, T, \dots)$

Remember Nir's talk

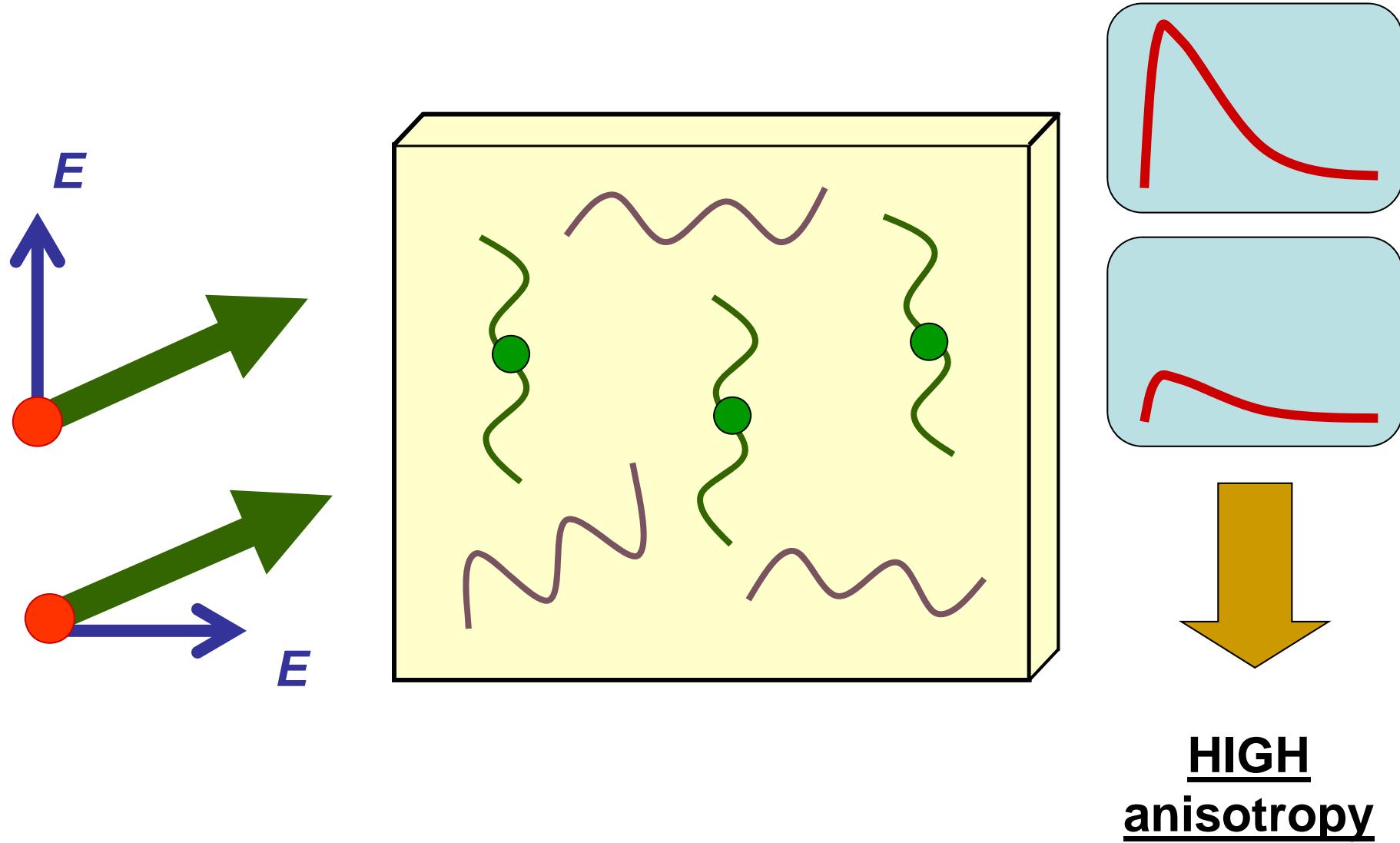
Can we **measure** the distribution of hopping rates?

$$V_{ij}(E, T, \dots)$$

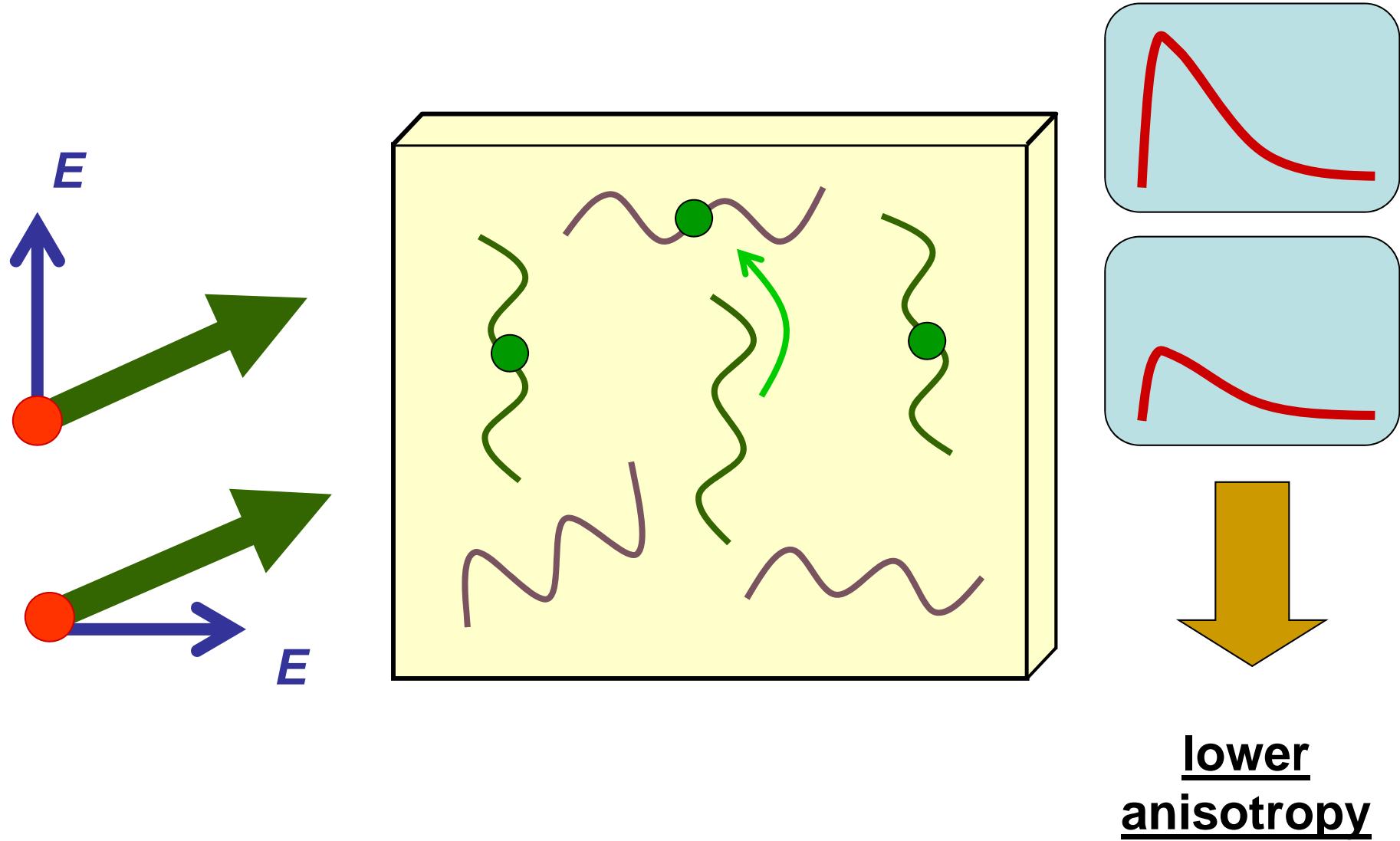
Polarization sensitive technique



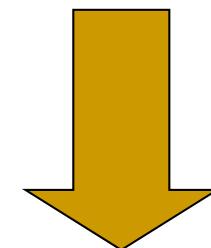
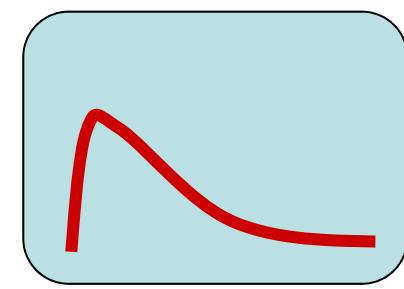
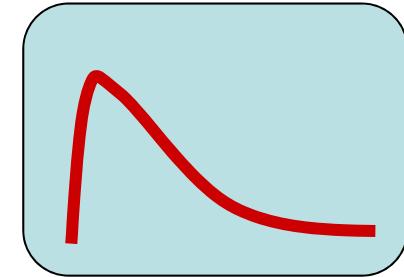
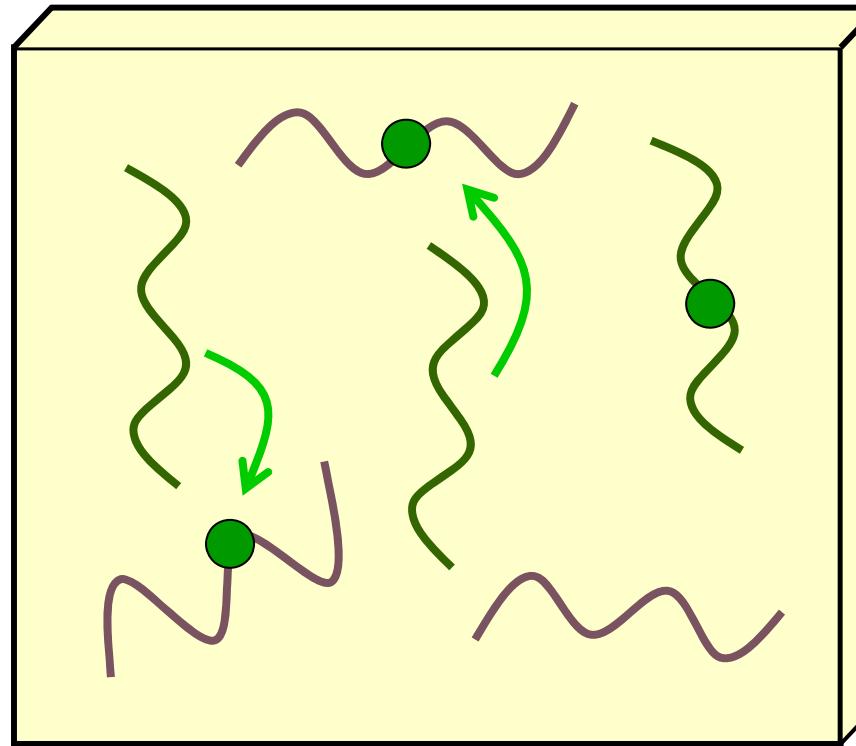
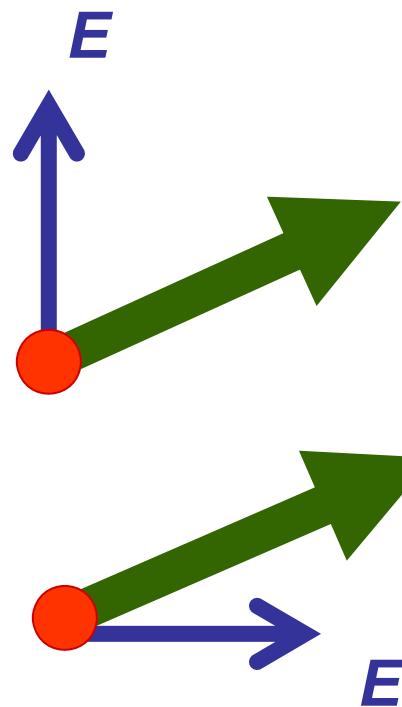
Polarization TA in CTCs



Polarization TA in CTCs

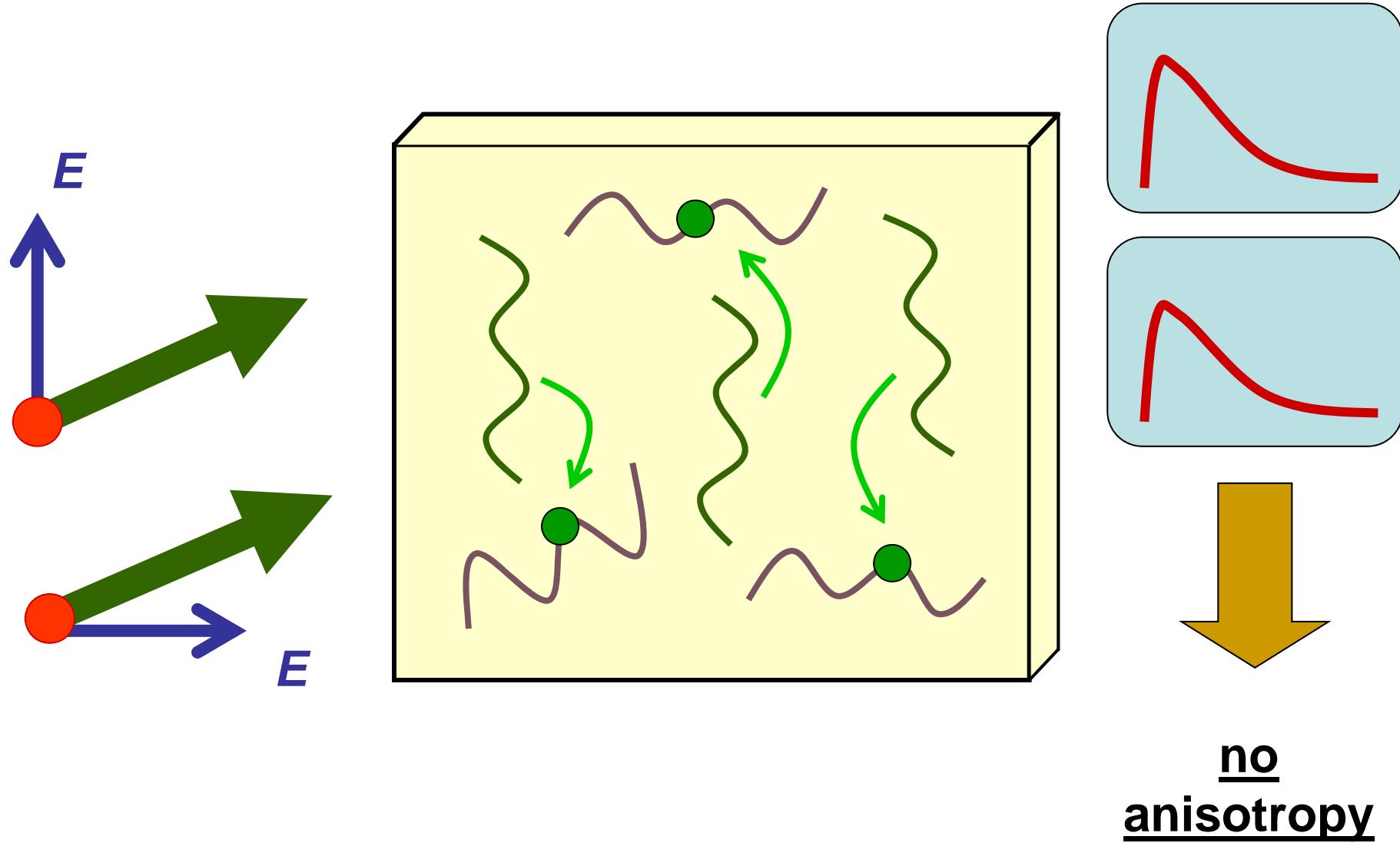


Polarization TA in CTCs

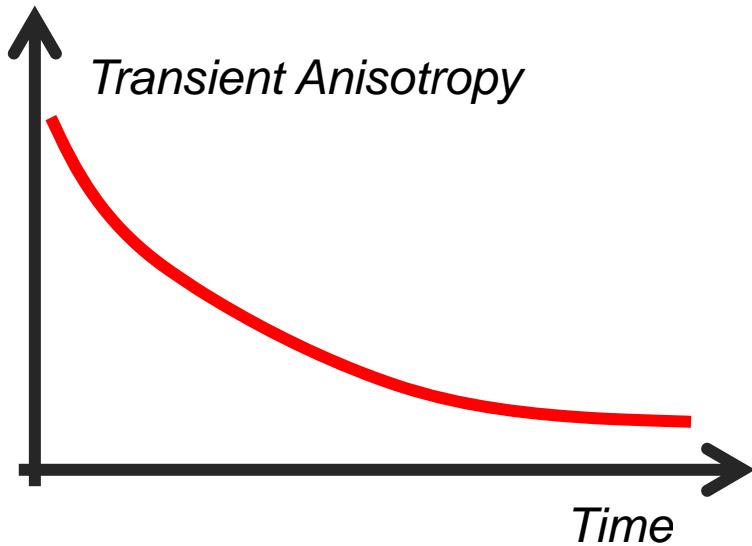


lower
anisotropy

Polarization TA in CTCs



Measuring transient anisotropy – information about hopping (V_{ij})

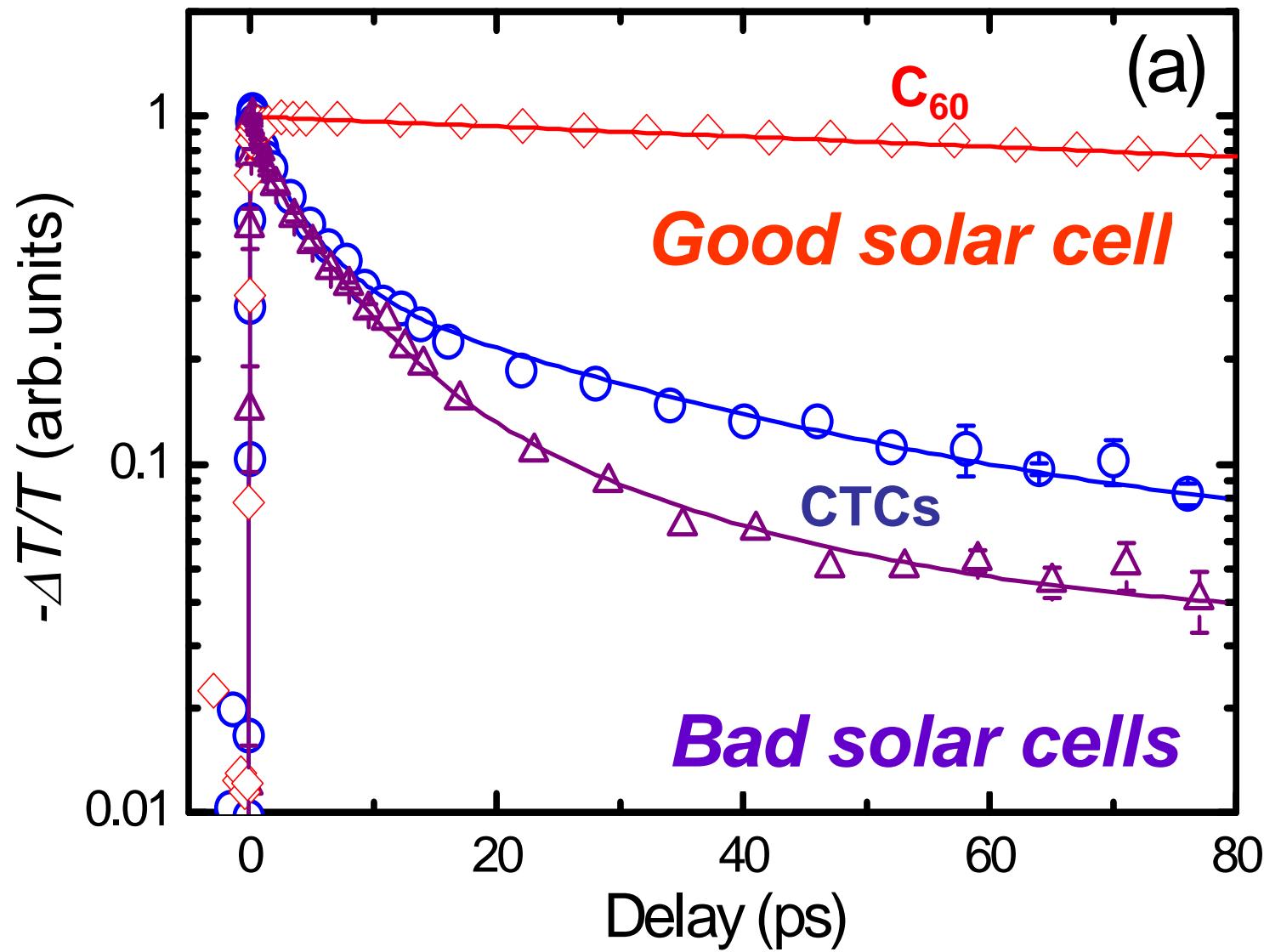


The distribution of hopping probabilities (V_{ij}) will depend on:

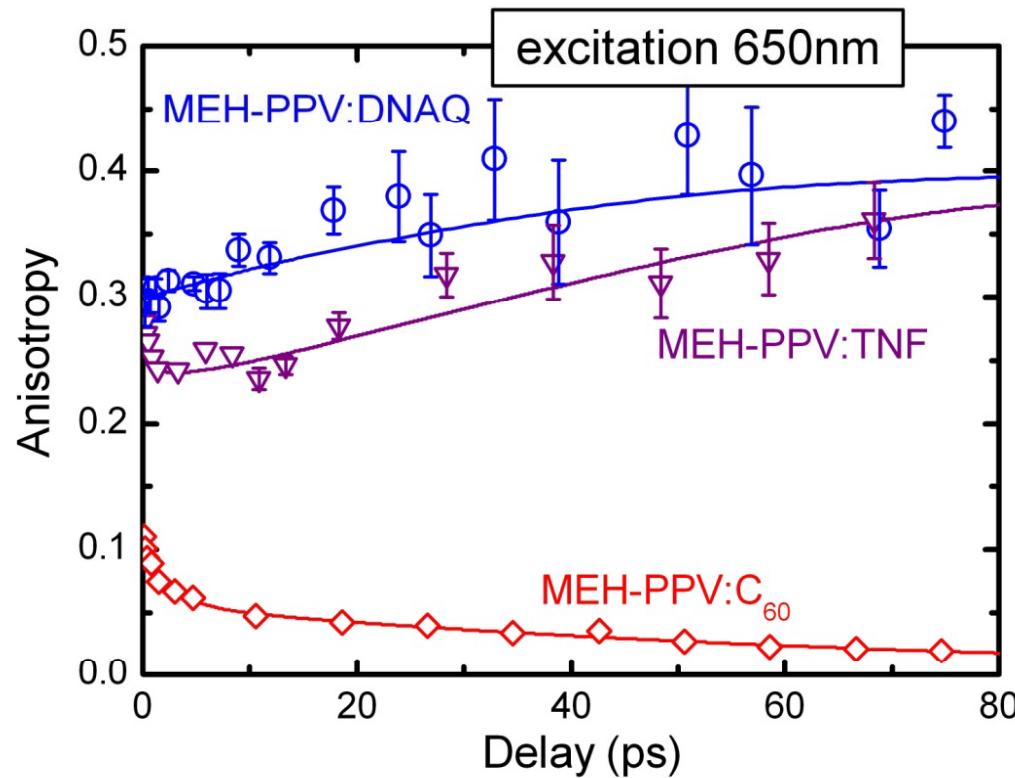
- polymer
 - doping
 - external field
 - temperature
 - morphology
-
- ... and modeling is essential

Example I. Localization of charges

Photophysics in CTCs



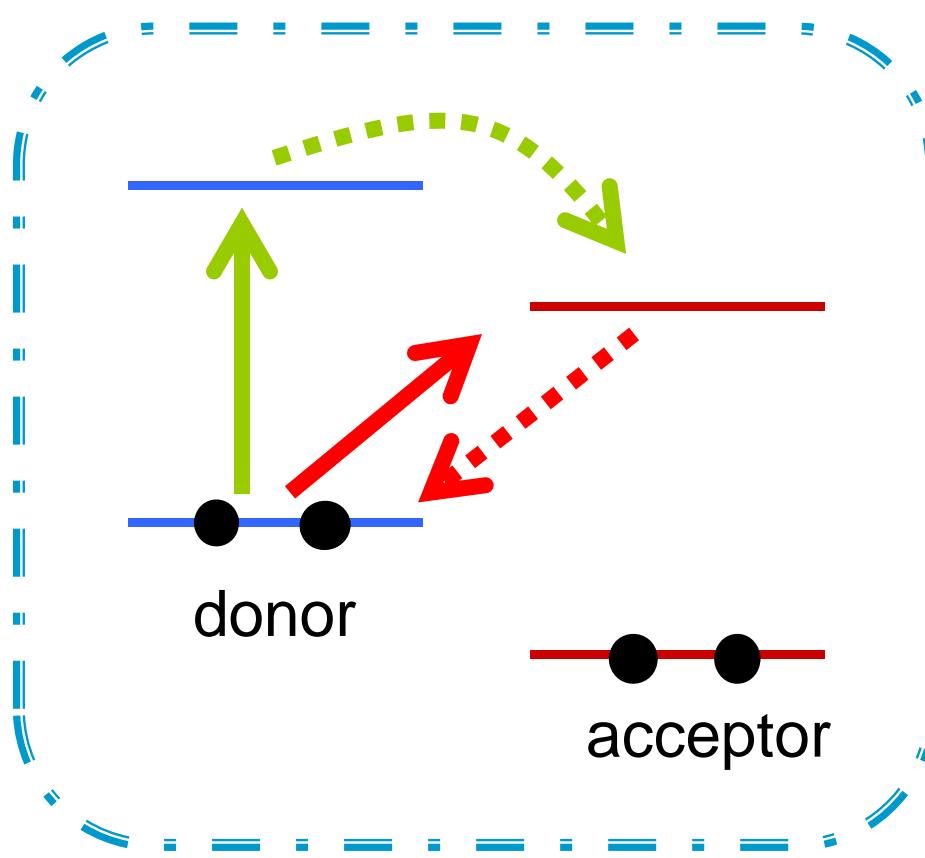
Transient Anisotropy in CTCs



- Localization of charges in pronounced CTCs
- Dynamics do not depend on wavelength -
same pathway of charge generation

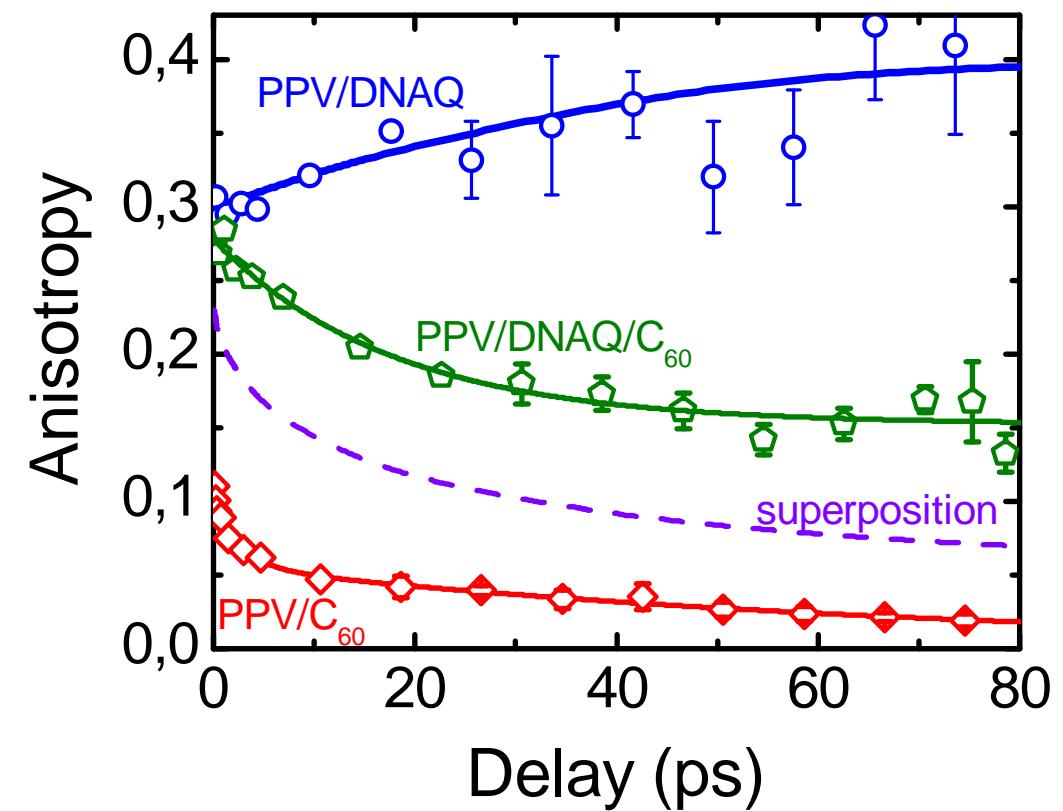
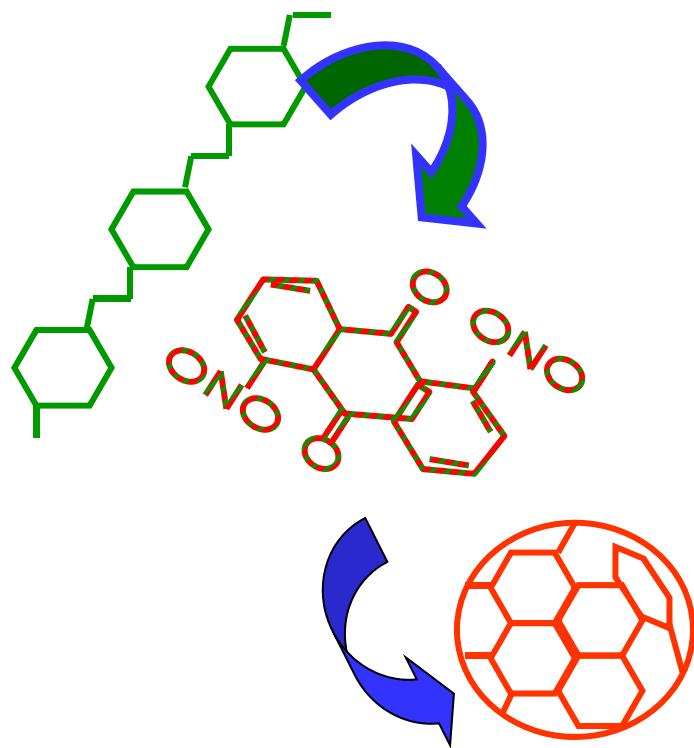
Chem. Phys. Lett. 482, 99 (2009)

Photophysics of CTC

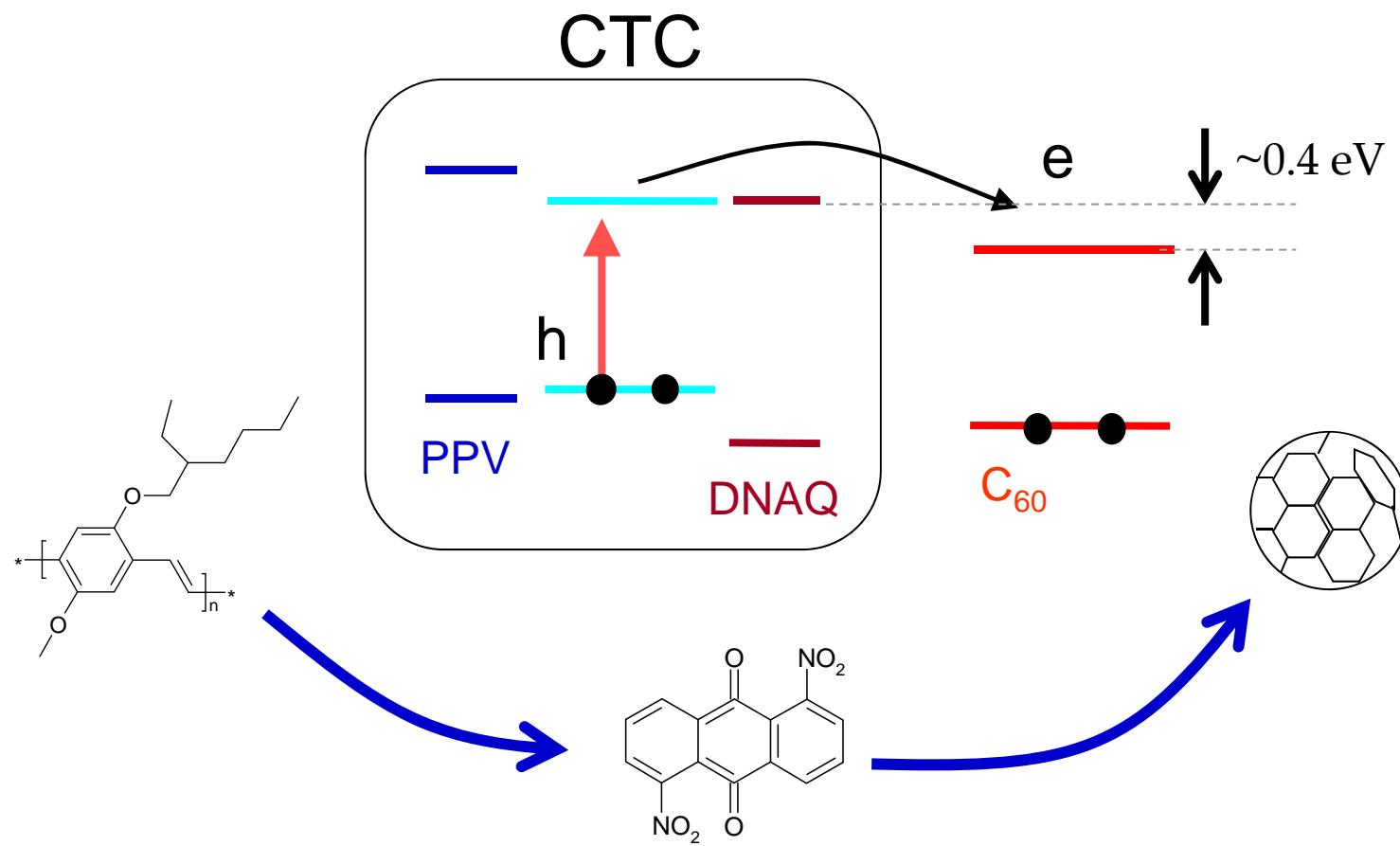


- Efficient pathway of geminate recombination
- Charges are localized

Photophysics in ternary PPV/DNAQ/C₆₀ blend



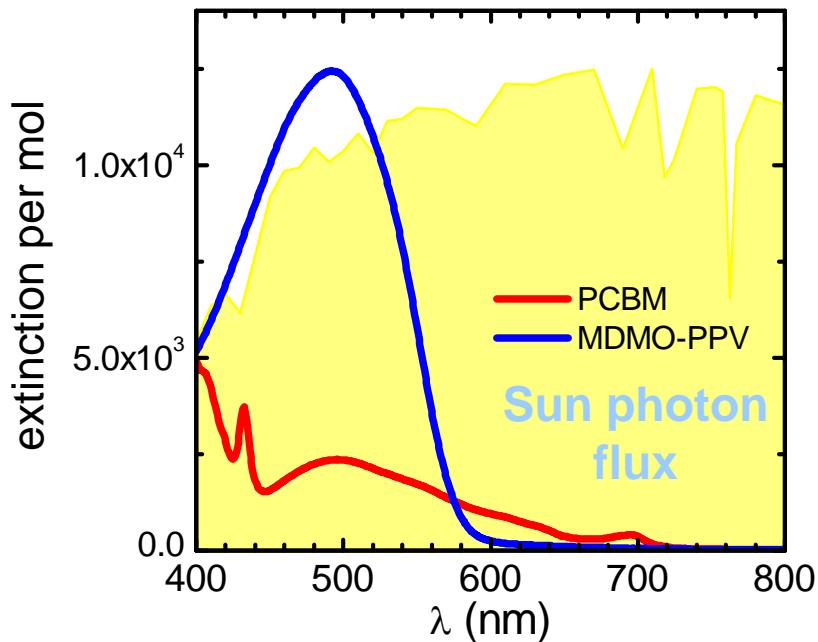
Charge dynamics in ternary blend



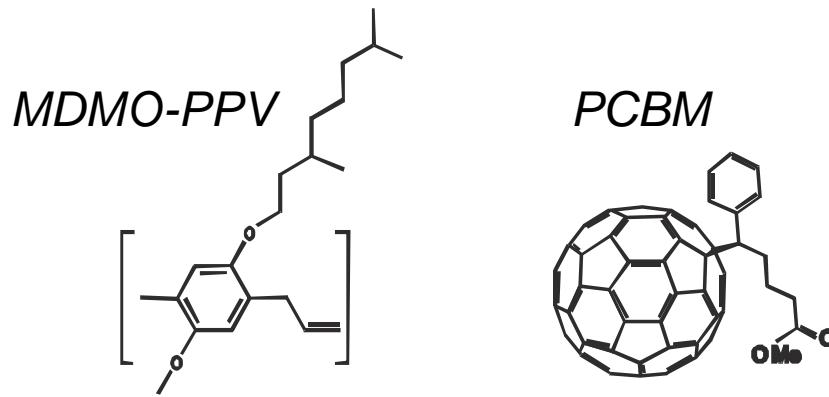
$$1 + 1 + 1 = 2$$

Example II. Charge photogeneration pathway.

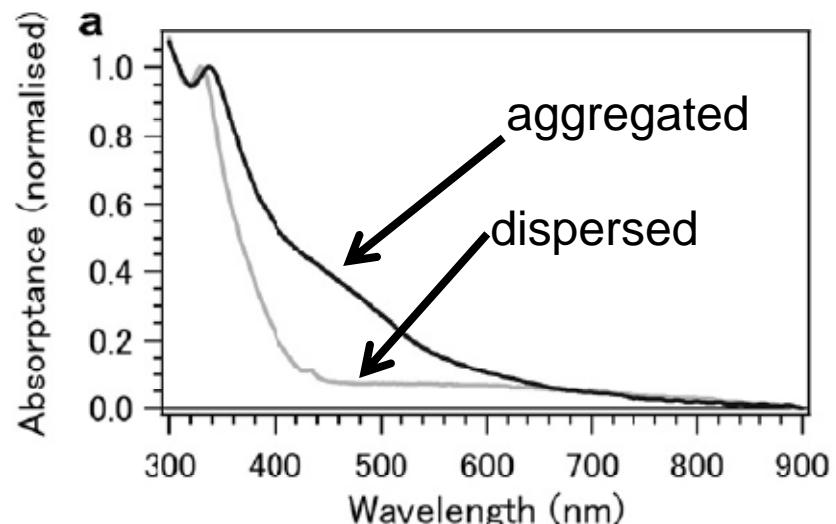
Significance of PCBM excitation



- **Fullerene absorption in Visible is probably underestimated**

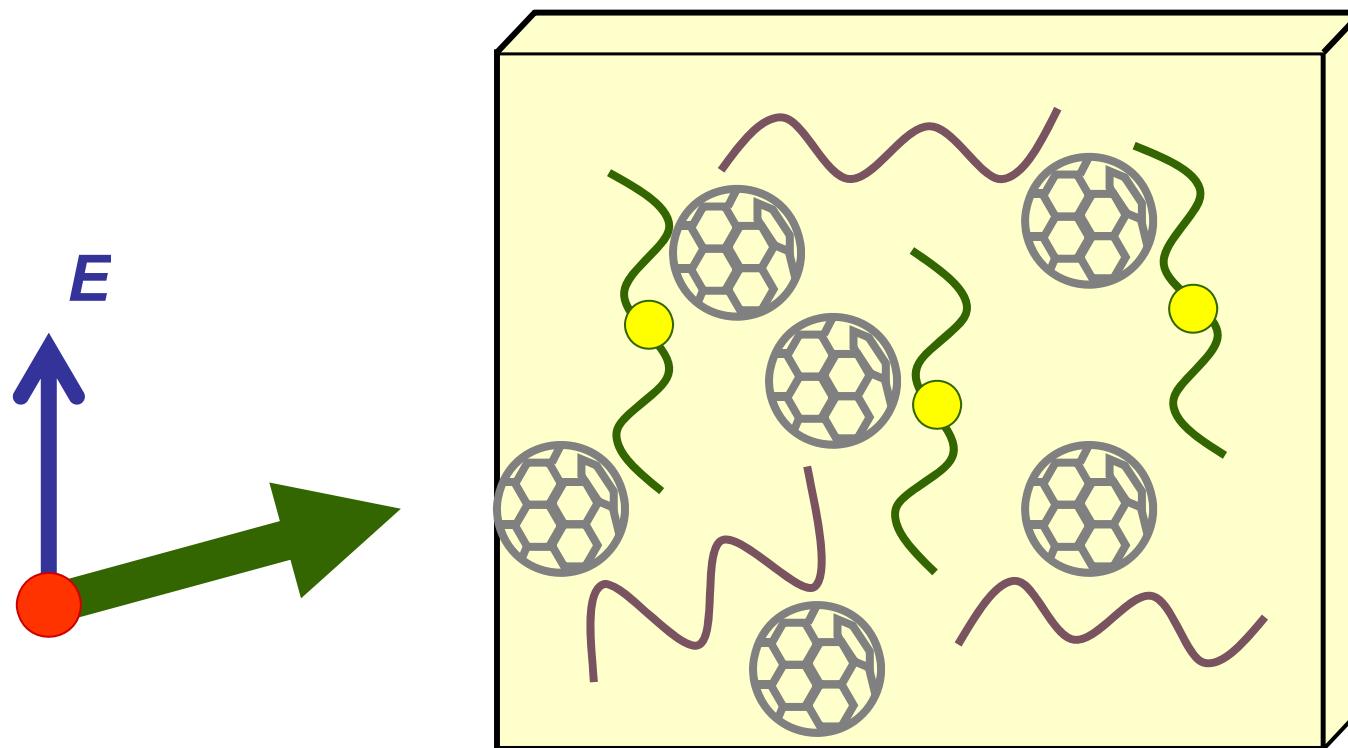


- **Fullerene provides absorption in the IR region**



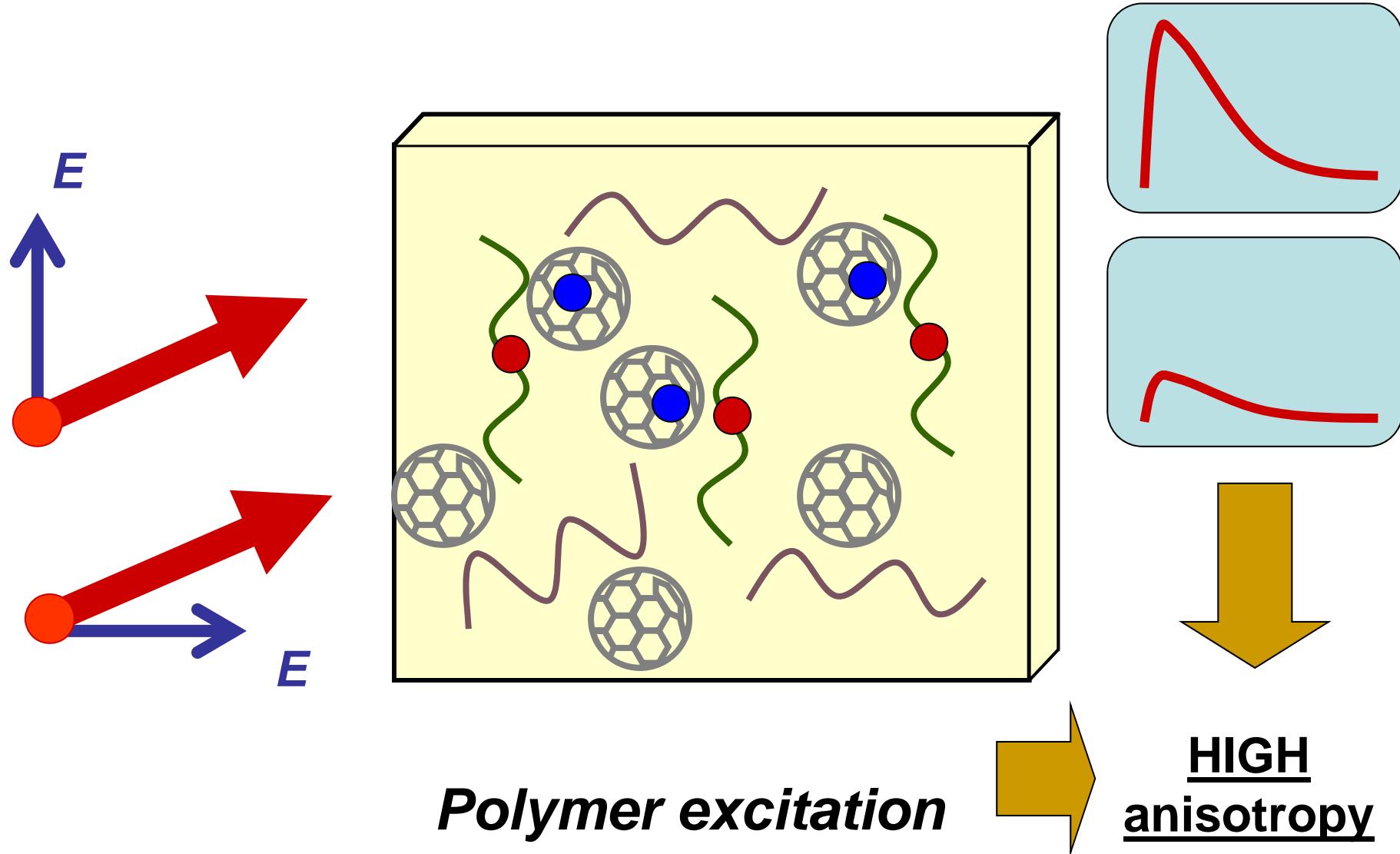
Polarization sensitive technique

Muller et al, PRB (2005)
Westenhoff et al, JACS (2008)
Bakulin et al, JPC B (2008)

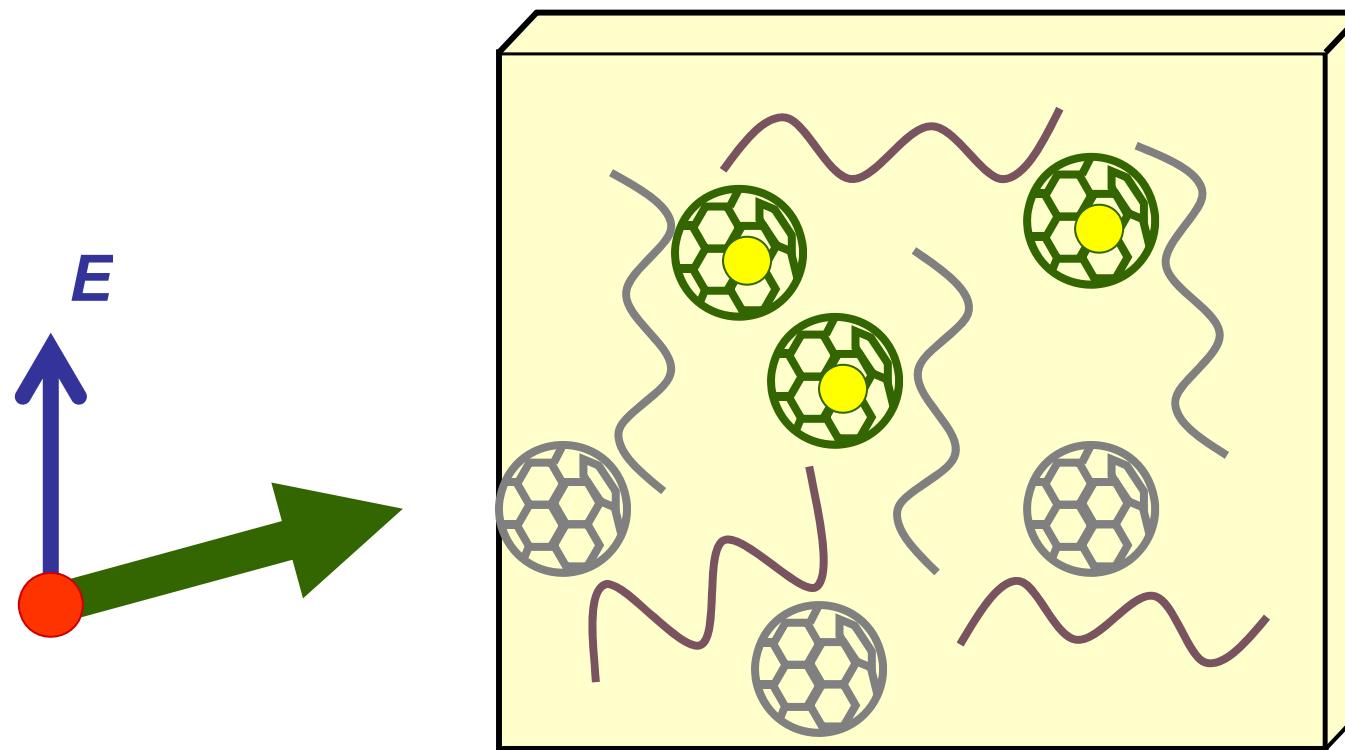


Polymer excitation

Polarization sensitive technique

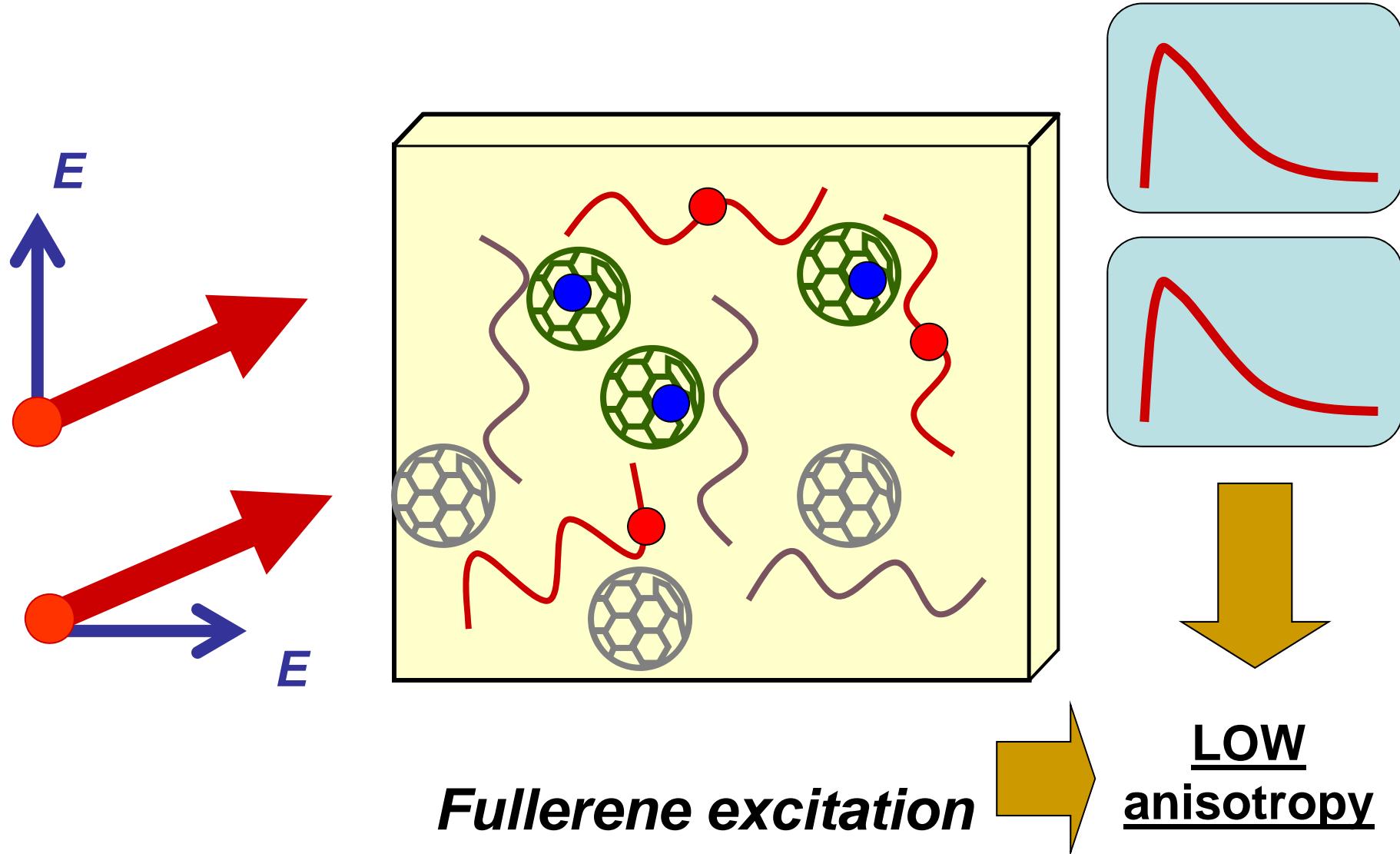


Polarization sensitive technique



Fullerene excitation

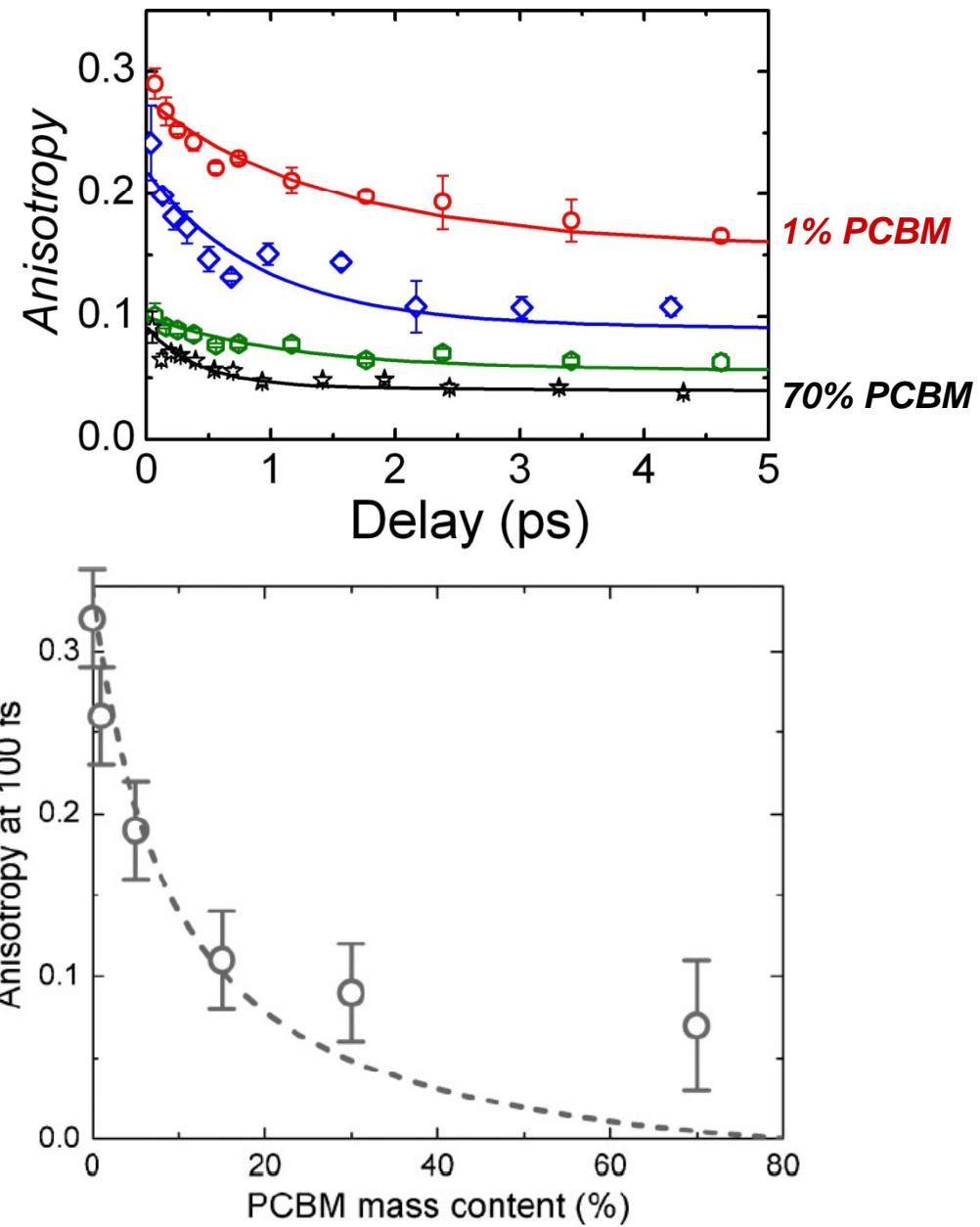
Polarization sensitive technique



PCBM excitation contrast

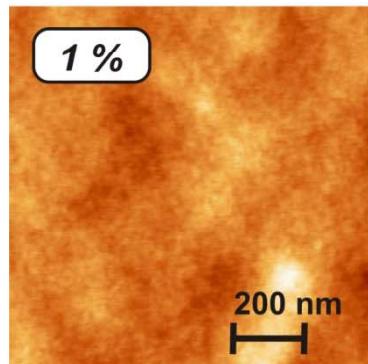
The contrast of
PCBM excitation
vs.
excitation of
polymer/CTC

$$\sigma \sim 10$$

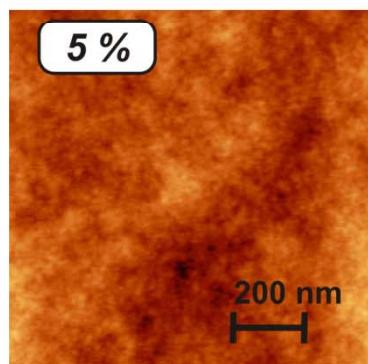


AFM Images

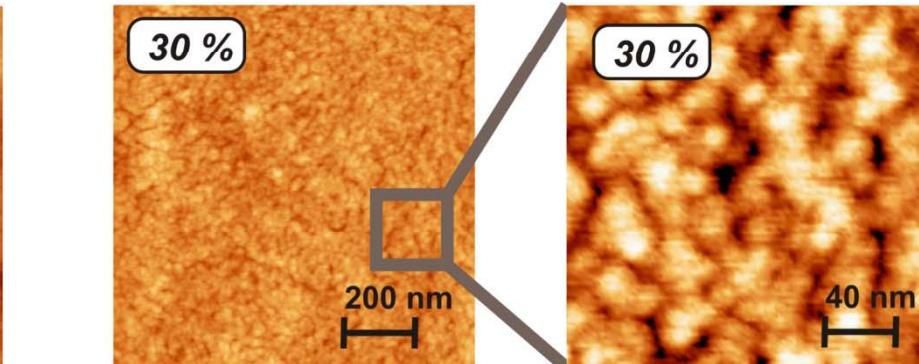
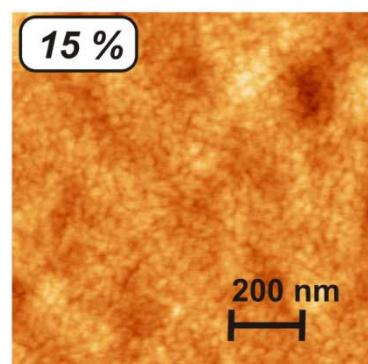
1x1 μm



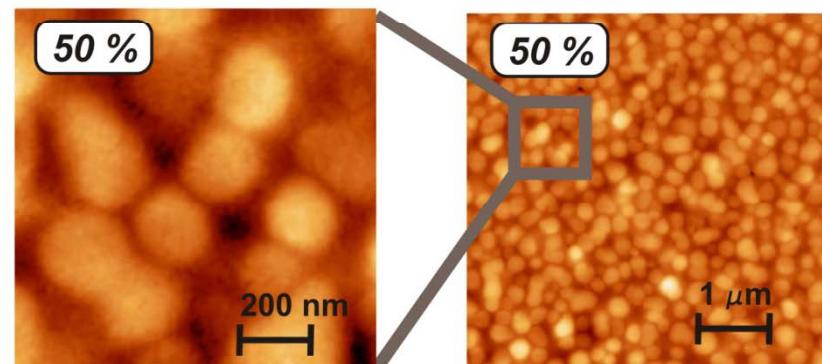
1x1 μm



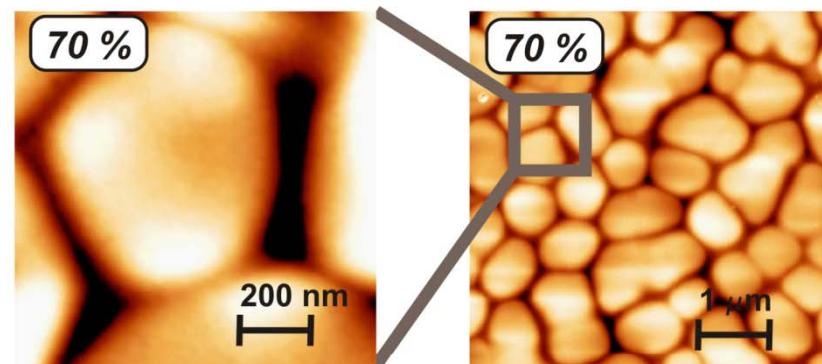
1x1 μm



0.2x0.2
 μm



5x5 μm



5x5 μm

- Charge generation pathways
- Evidence of the morphology change

Conclusions

- Ultrafast spectroscopy is a powerful tool for studying charge dynamics
- Anisotropy of nonlinear response provides information about delocalization of charges and charge generation pathway
- Potential for development of charge-transport models

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Sergey Zapunidy (Moscow State University)

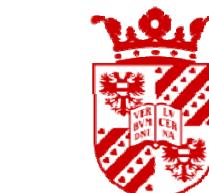
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University of Groningen & Zernike Institute for Advanced Materials,
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University of Groningen
Zernike Institute
for Advanced Materials



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