university of groningen / zernike institute for advanced materials

30-fs Hole-Transfer Dynamics in Polymer/PCBM Bulk Heterojunction

Maxim S. Pshenichnikov

Vladivostok, 5 October 2010

Гронинген – Амстердам – Москва - Владивосток

9000 км

Благодарности

Александр Александрович Саранин
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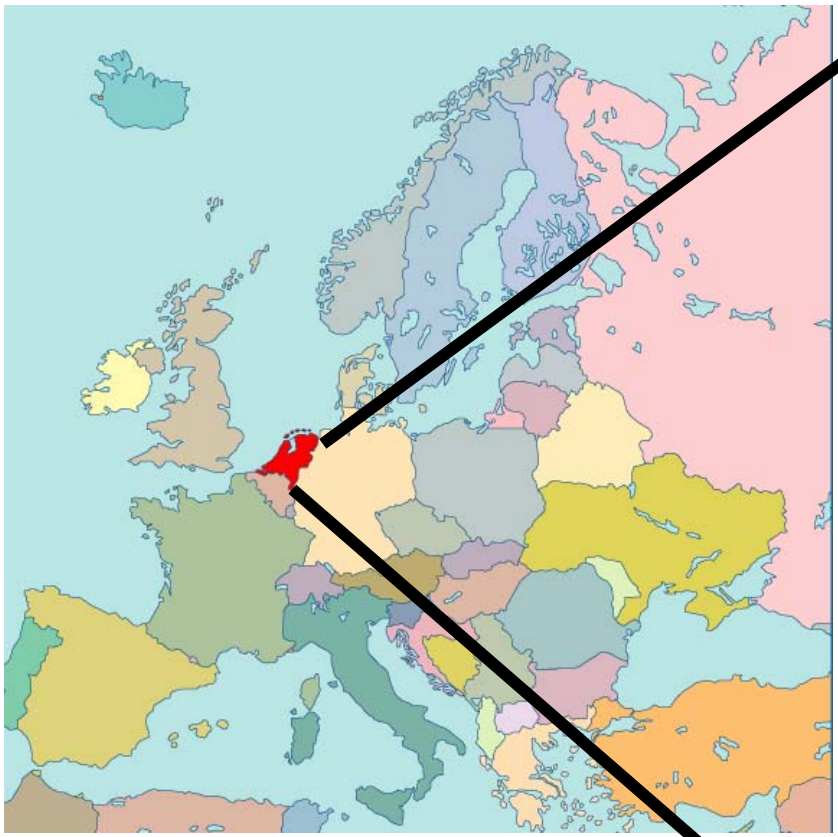
Фонд Дмитрия Зимина
ДИНАСТИЯ

«Нет ничего превыше Гронингена»
“Er gaat niets boven Groningen”



The Netherlands

University of Groningen

Groningen:
170,000 people
Old, youthful, safe, cultural

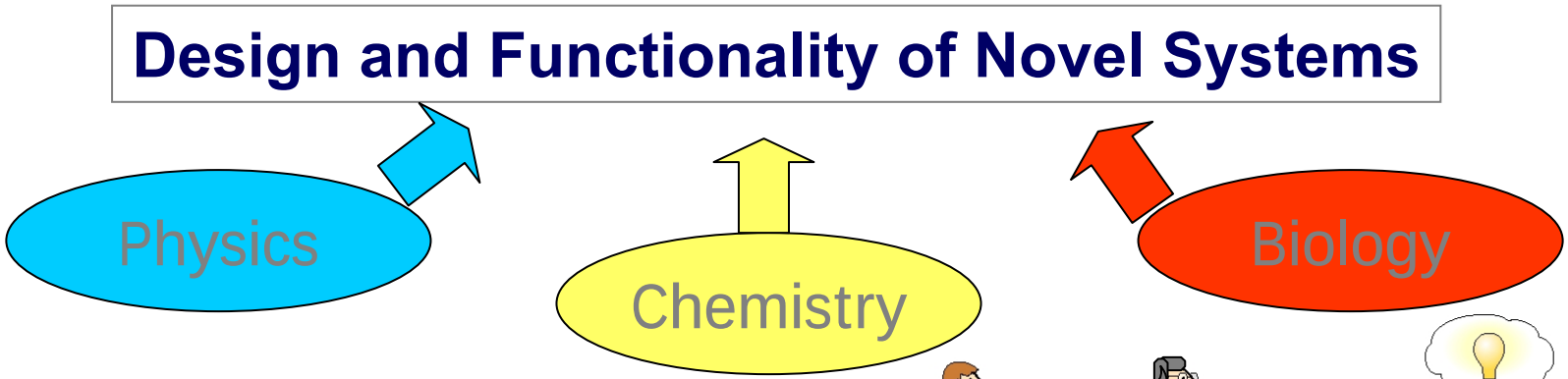
University is founded in 1614
25000 students
6000 staff

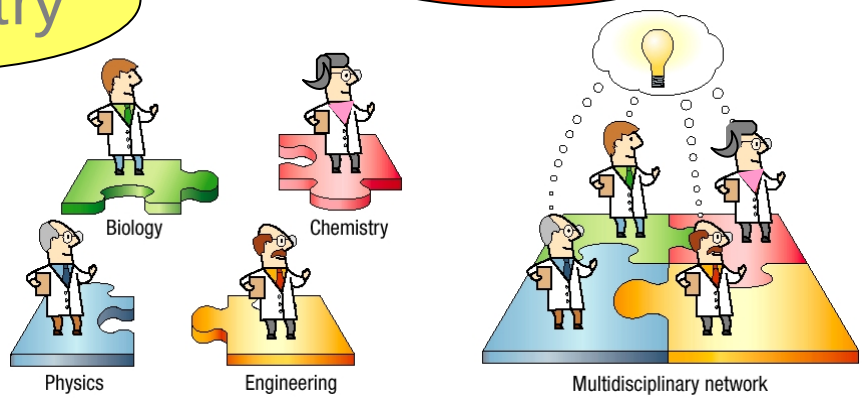
Zernike Institute for Advanced Materials

Frits Zernike (1888-1966)

Professor of Theoretical Physics, University of Groningen
Nobel Prize in Physics in 1953 for
developing phase contrast microscopy

Zernike Institute for Advanced Materials





Facts and Figures
- Founded in 1970
- 20 research groups
- 300 members
- 125 PhD students

- Growing complexity ("smart materials")
- Miniaturisation: nanoscience
- Multidisciplinary approach for breakthroughs
- Focus on curiosity driven research; open eye for technological applications

- *National* Research Center since 1999
- Impact: above twice world average in the field

04 April 2010

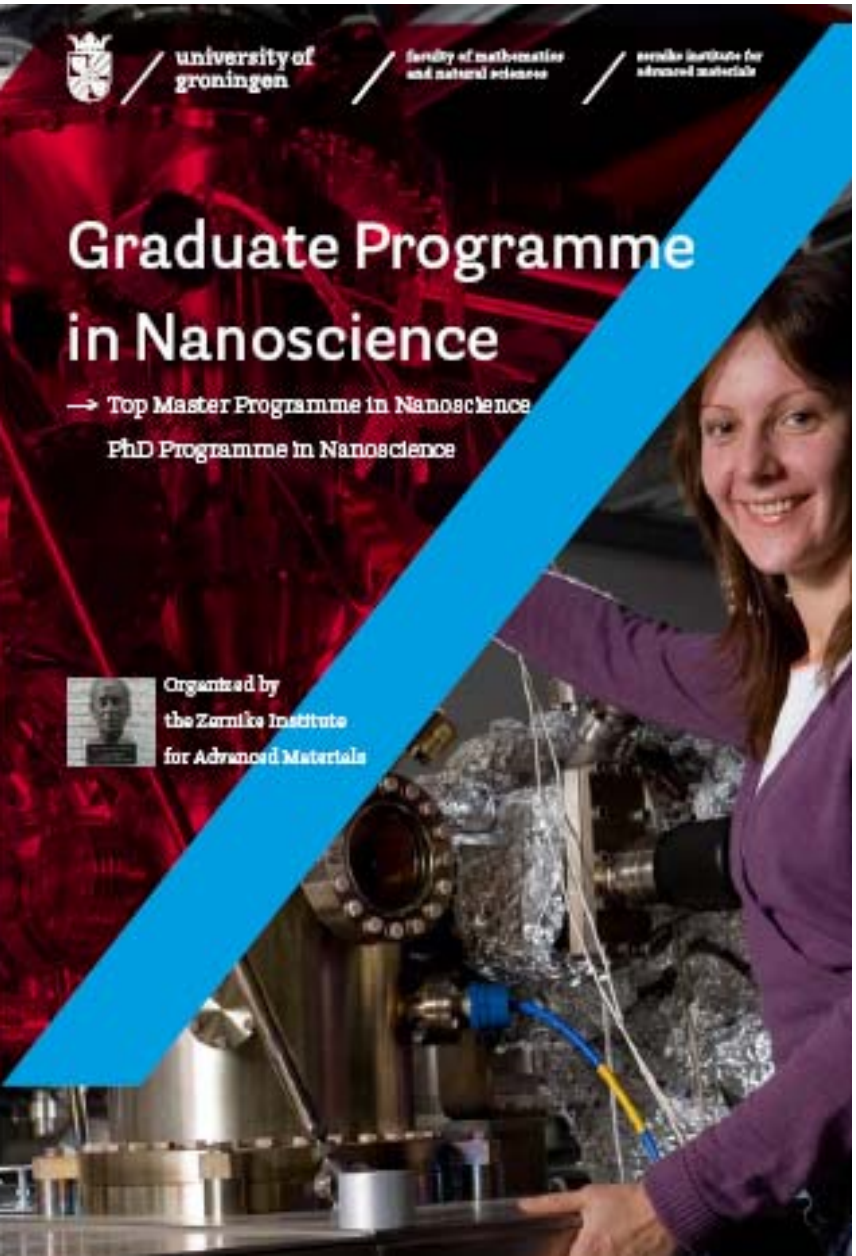
Top institutions in materials science

11 March 2010

Data provided by Thomson Reuters from its Essential Science Indicators database, January 1999-October 2009

	Institution	Papers	Citations	Citations per paper
1	Rice University	381	11,949	31.36
2	Harvard University	596	16,467	27.63
3	University of California, Santa Barbara	964	25,376	26.32
4	University of Washington	822	21,348	25.97
5	IBM Corporation	573	13,822	24.12
6	University of California, Berkeley	1,354	29,963	22.13
7	University of Southern California	552	11,548	20.92
8	Massachusetts Institute of Technology	1,654	34,017	20.57
9	University of Groningen	524	10,547	20.13
10	Princeton University	514	10,085	19.62
11	Stanford University	728	13,853	19.03
12	University of Minnesota	662	11,786	17.80
13	Max Planck Society	3,506	54,175	15.45

Topmaster Program in Nanoscience

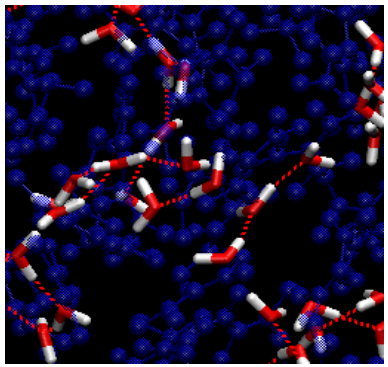


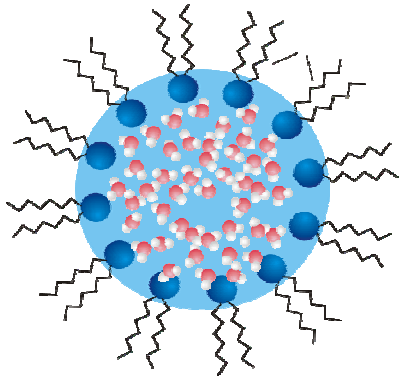
- Two-year MSc study, aims at future PhD's
- Interdisciplinary: physics and chemistry
- International
  - * Courses in English
  - * Selection of top candidates worldwide

- Close contacts with leading experts in the field
- Scholarships !!!
- Graduates pursue scientific career all over the world

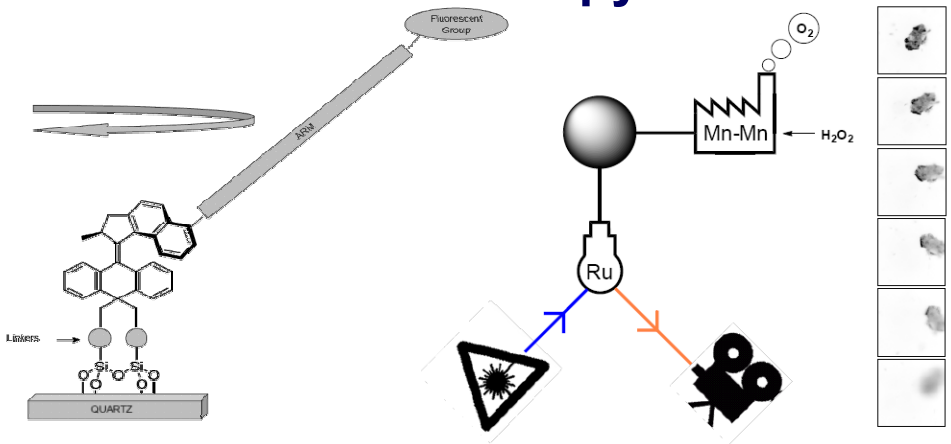
Overview of Current Activities

Water at (bio)interfaces

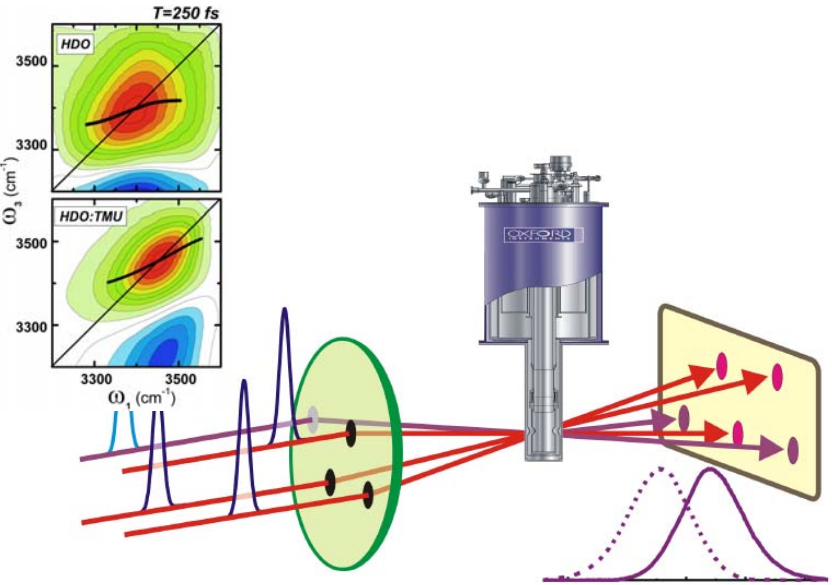




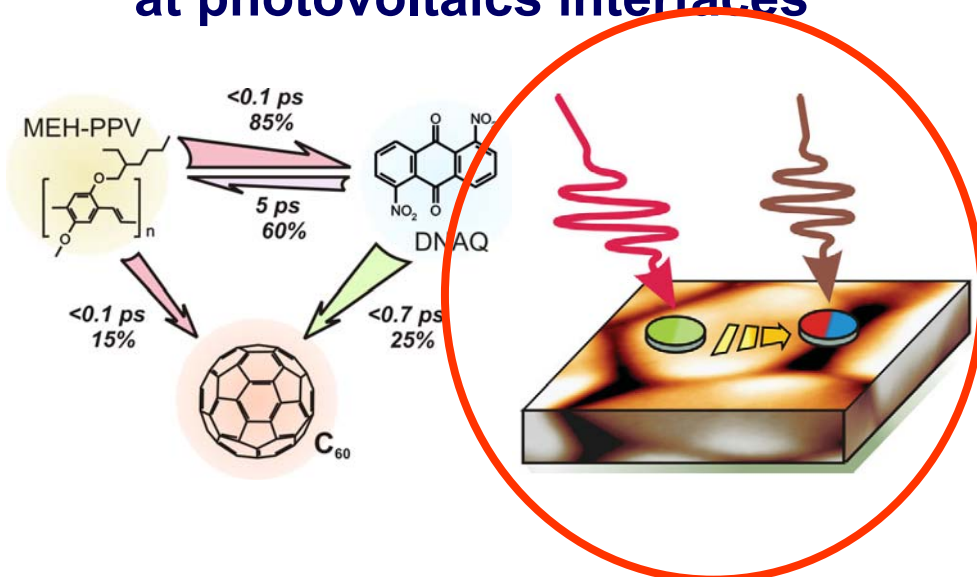
Single-molecule superresolution microscopy



Ultrafast spectroscopy



Energy and charge dynamics at photovoltaics interfaces



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30-fs Hole-Transfer Dynamics in Polymer/PCBM Bulk Heterojunction

Maxim S. Pshenichnikov

Artem A. Bakulin (Cambridge U)
Almis Serbenta
Jan C. Hummelen
Paul H.M. van Loosdrecht

Vladivostok, 5 October 2010

Polymer Solar Cells

- **Reason to develop**

  solar cells

  Oil prices, energy consumption, ecology

- **Reason to develop**

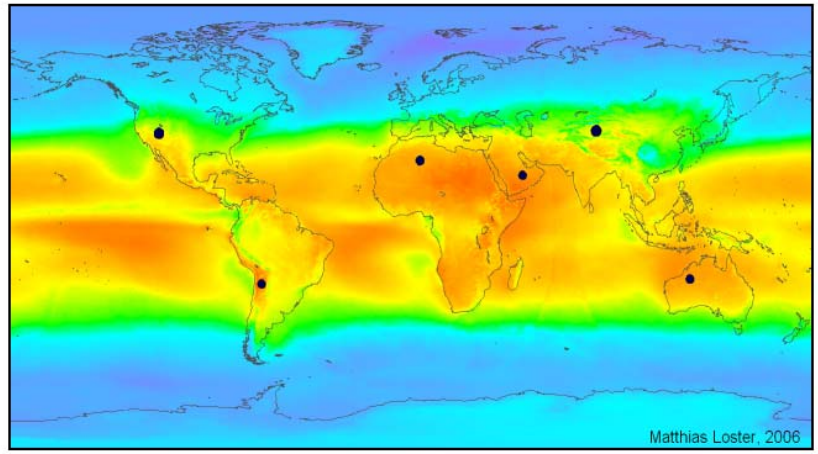
  ***plastic* solar cells**

  They can be cheap: printing technology

- **Reason to *develop***

  plastic solar cells

  Efficiency is the issue



Nature Materials 6, 3 (2007)

Polymer Solar Cells

- Rea

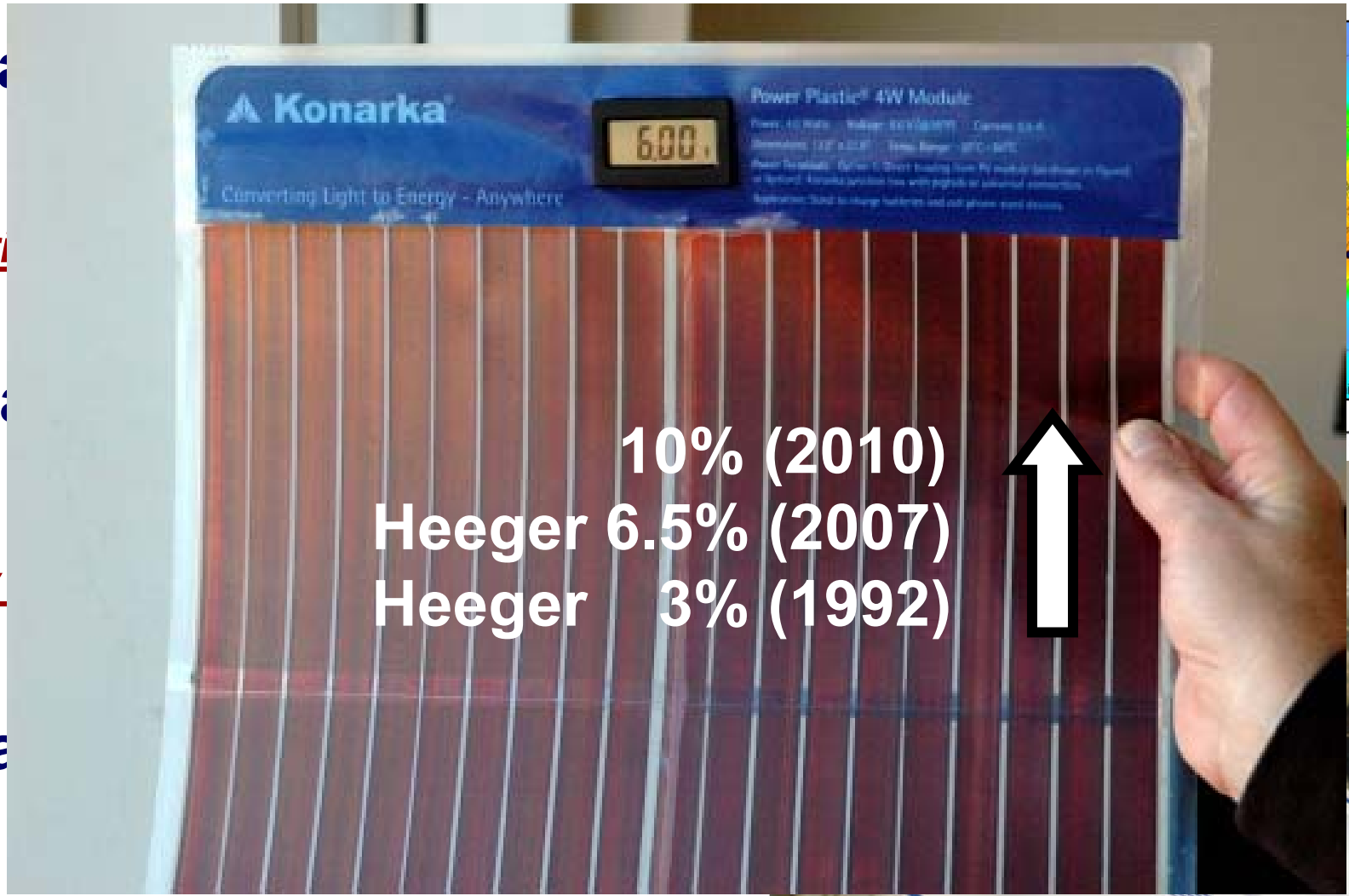
Oil pri

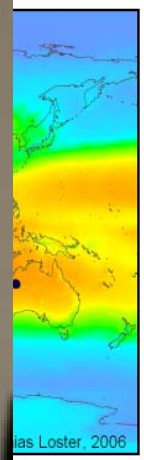
- Rea

They

- Rea

Efficiency is the issue

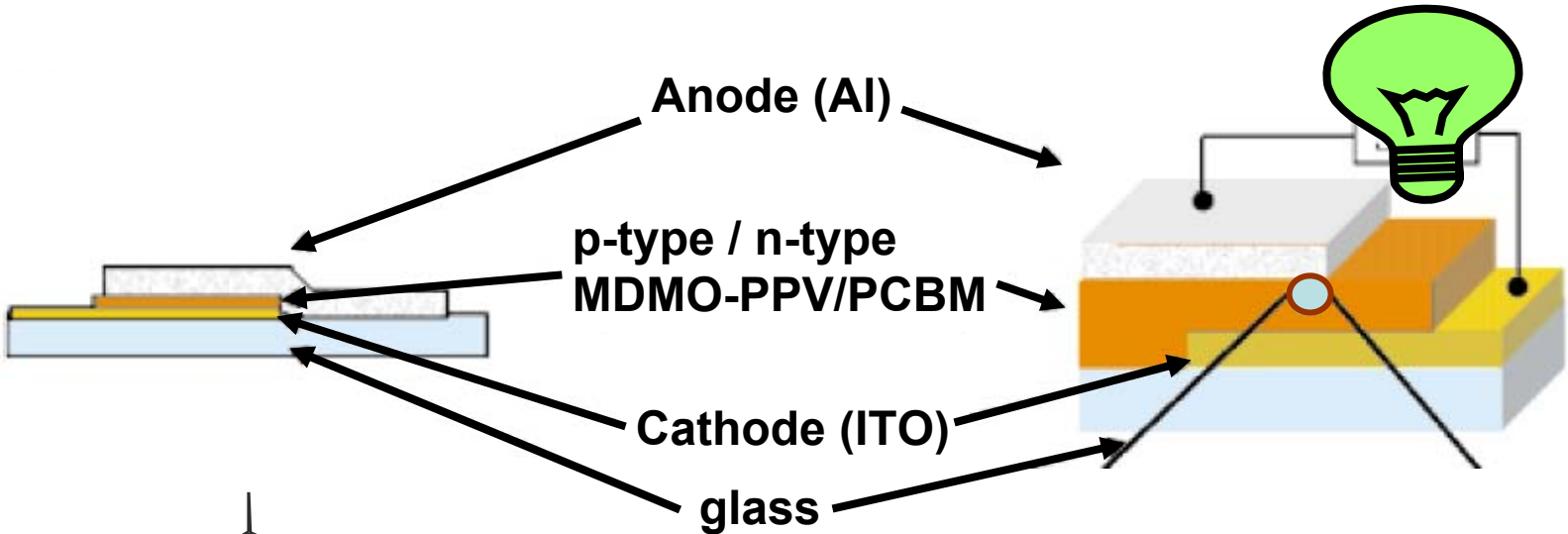




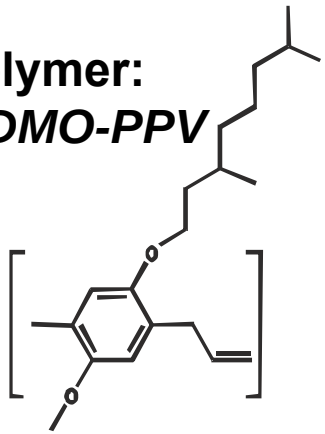
We

Nature Materials 6, 3 (2007)

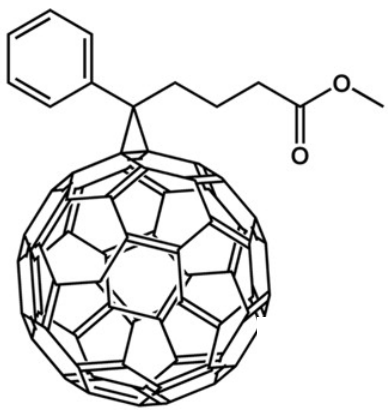
Bulk-Heterojunction Concept



polymer:
MDMO-PPV



Light absorption

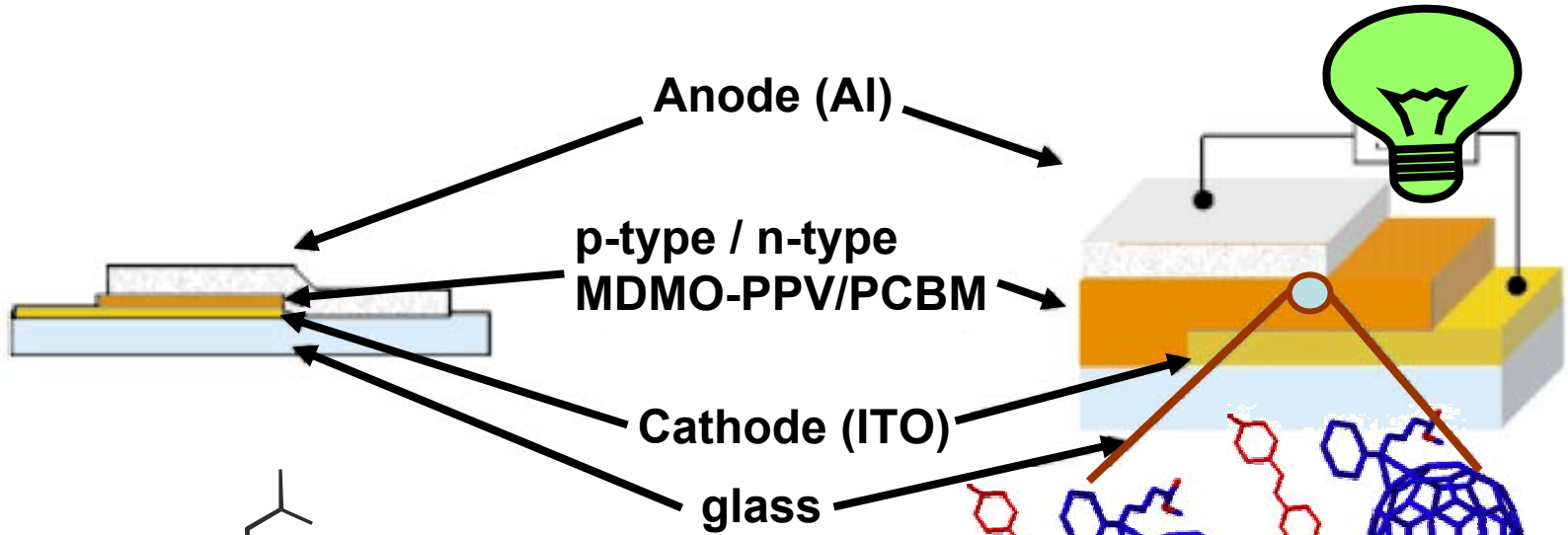


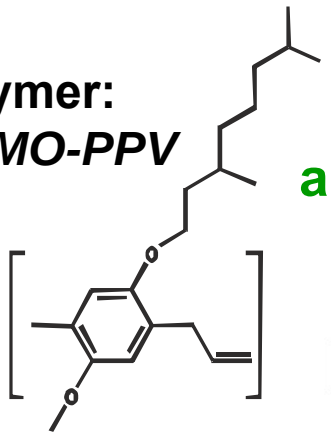
fullerene:
PCBM

Charge separation

Brabec, Sariciftci, Hummelen, AFM 11, 15 (2001)

Bulk-Heterojunction Concept





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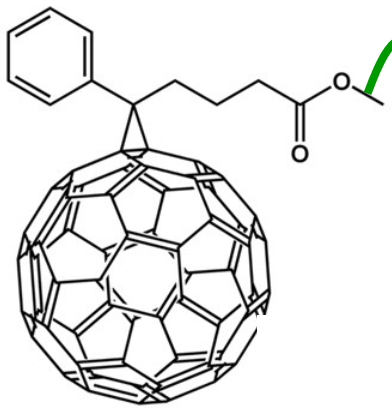

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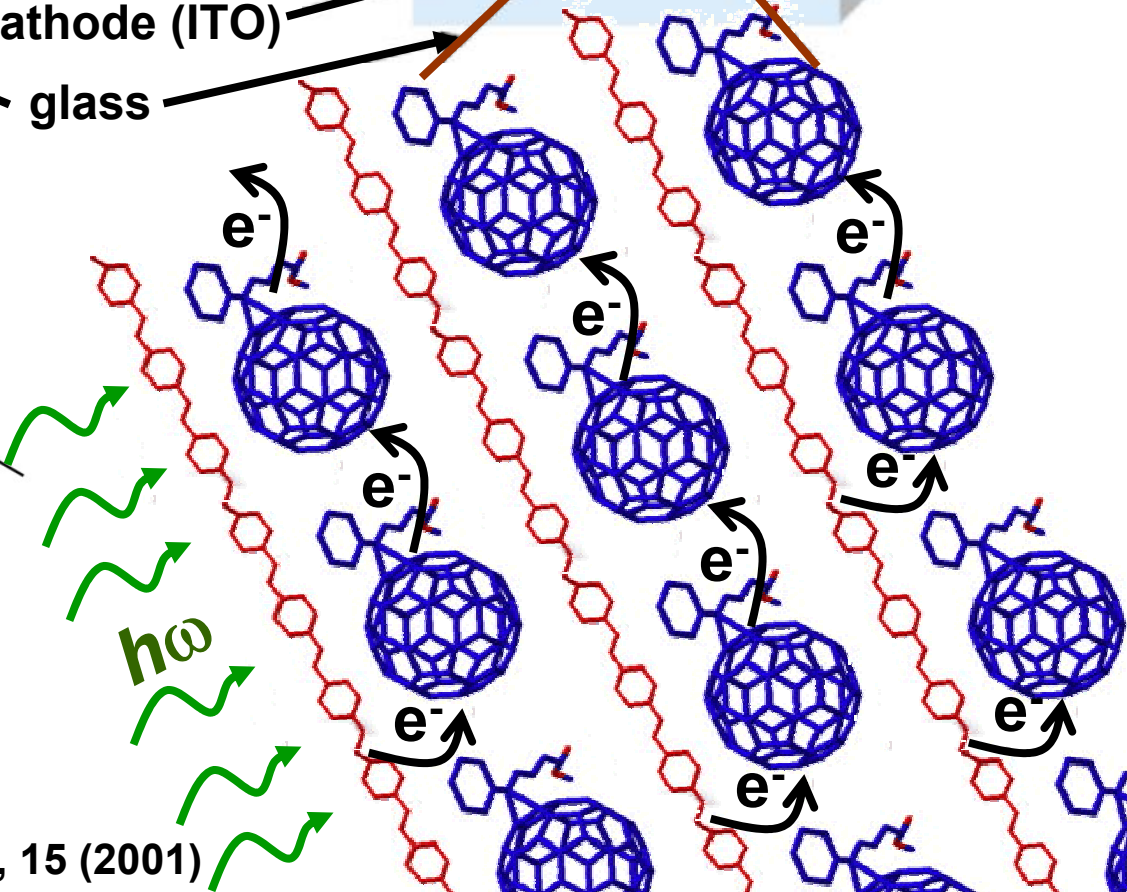
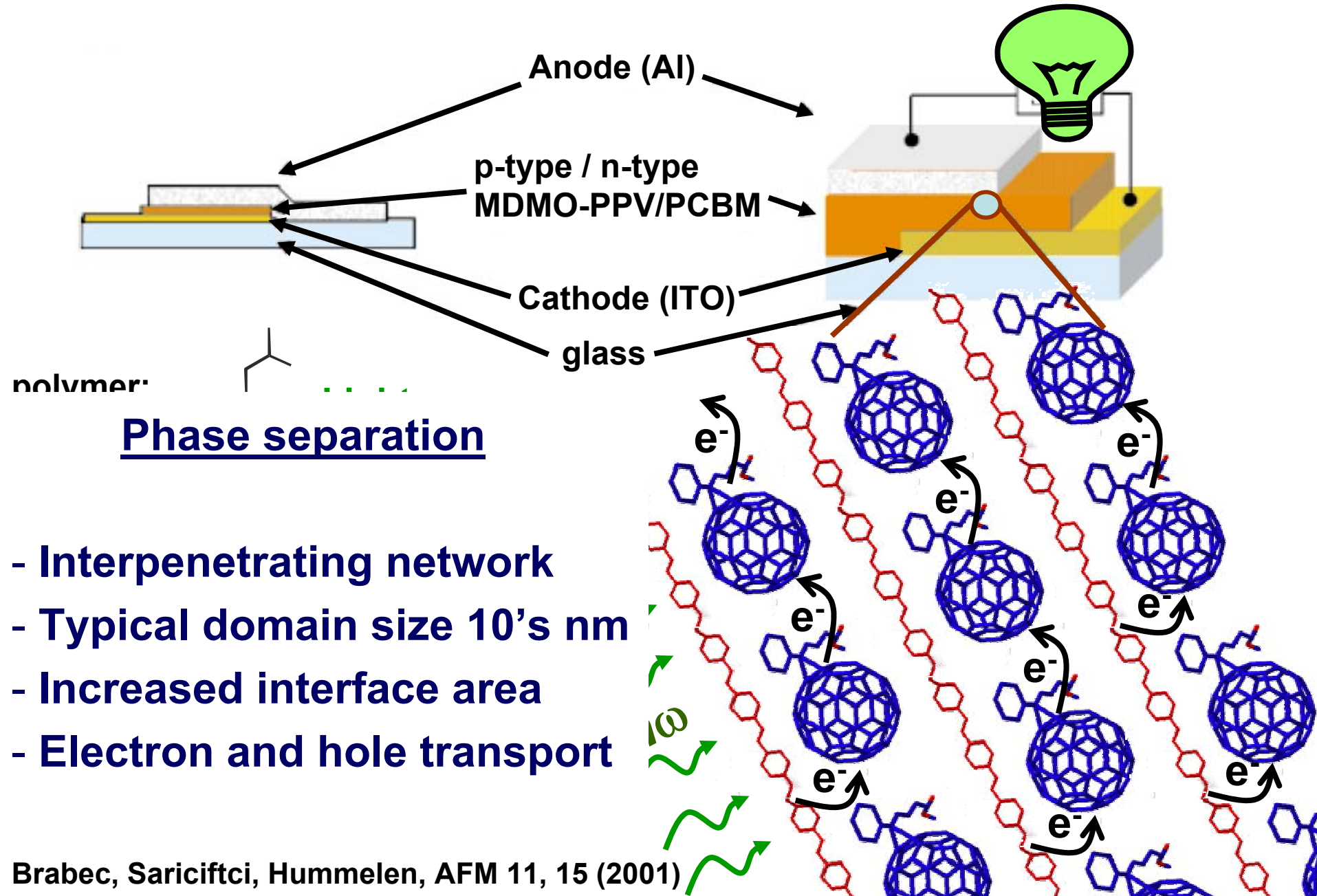


Brabec, Sariciftci, Hummelen, AFM 11, 15 (2001)

Bulk-Heterojunction Concept

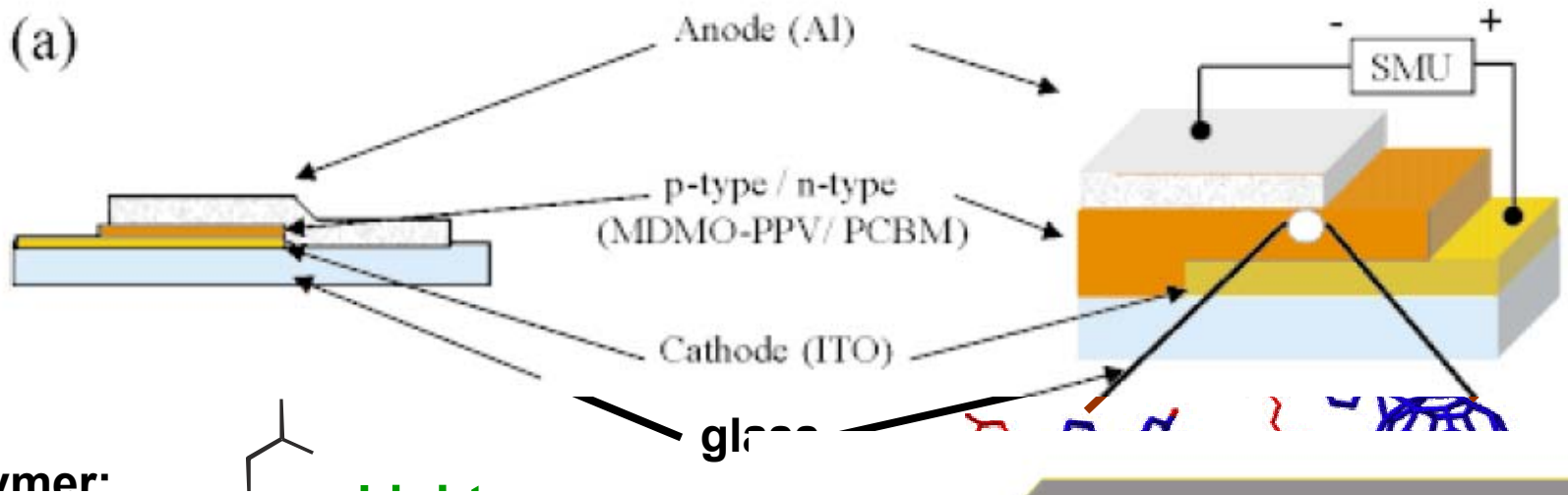


Phase separation

- Interpenetrating network
- Typical domain size 10's nm
- Increased interface area
- Electron and hole transport

Brabec, Sariciftci, Hummelen, AFM 11, 15 (2001)

Bulk-Heterojunction Concept



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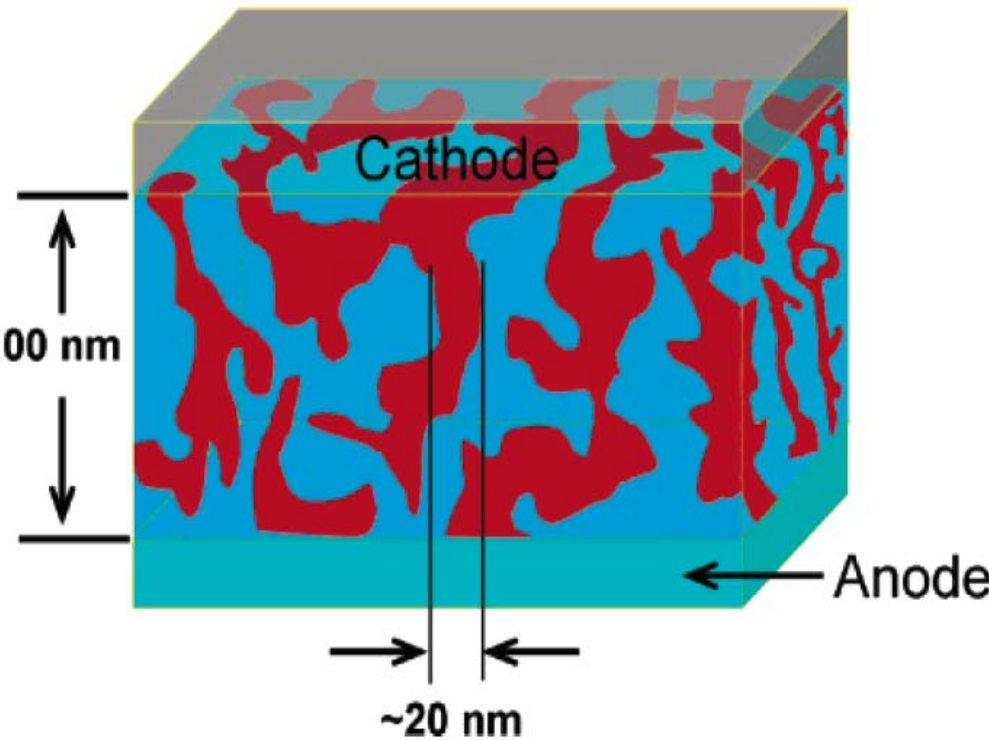
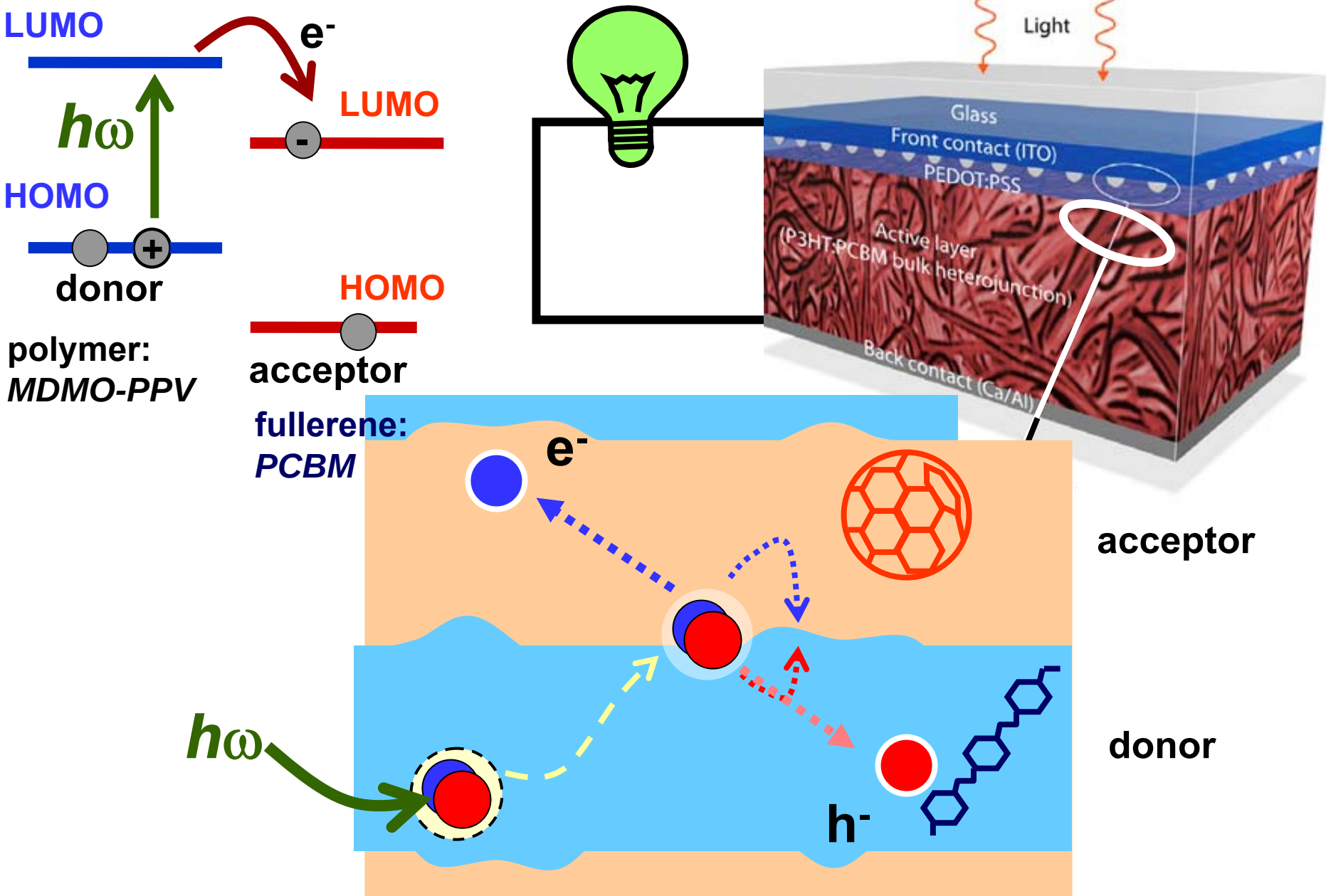
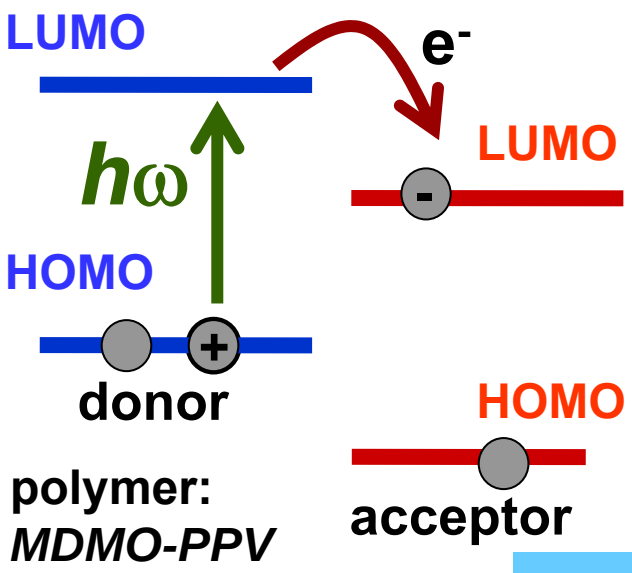


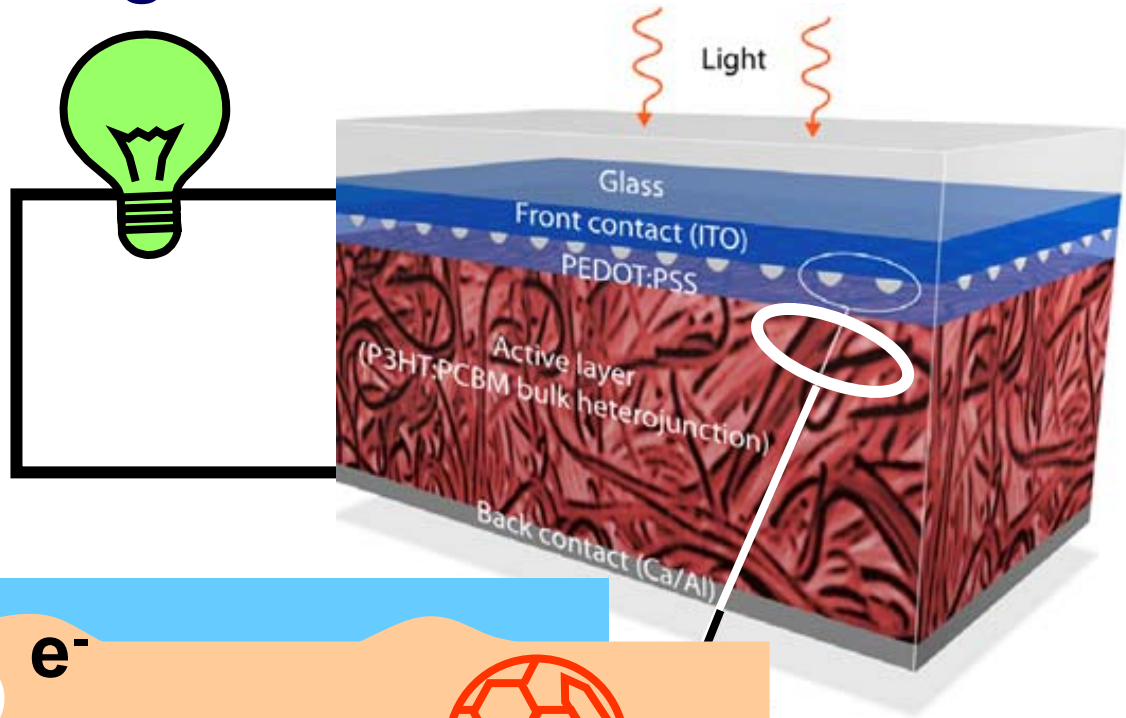
Brabec, Sariciftci, Hummelen, AFM 11, 15

Donor Excitation and Electron Transfer

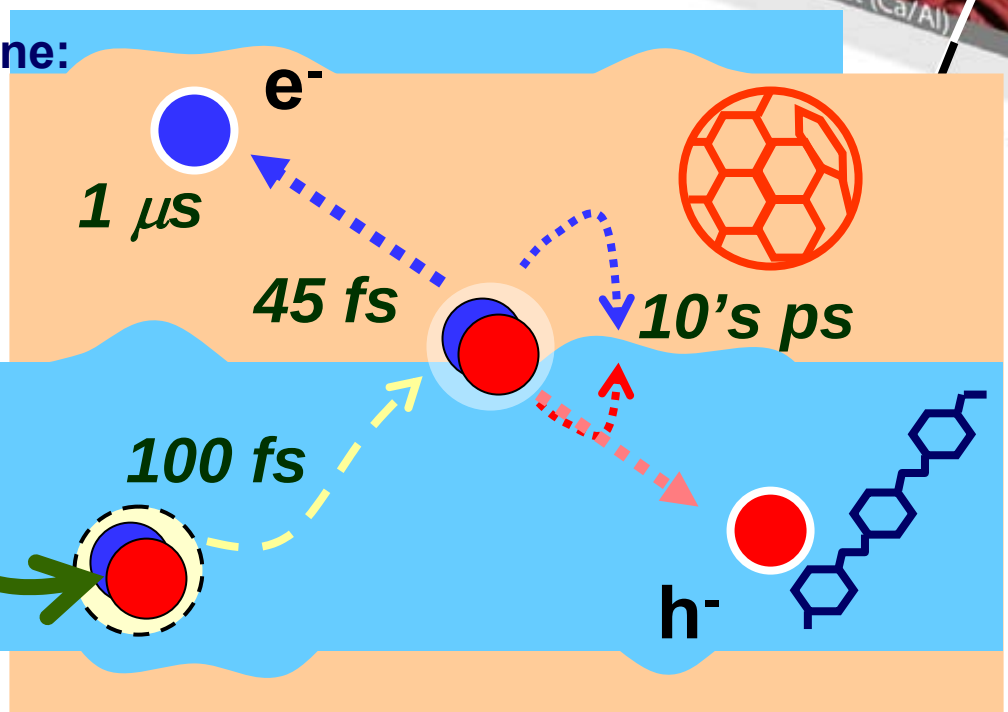


Why Going Nonlinear?





fullerene:
PCBM



1 fs = 10^{-15} s

1 ps = 10^{-12} s

Charge dynamics studies on polymer/fullerene mixtures

Electron transfer

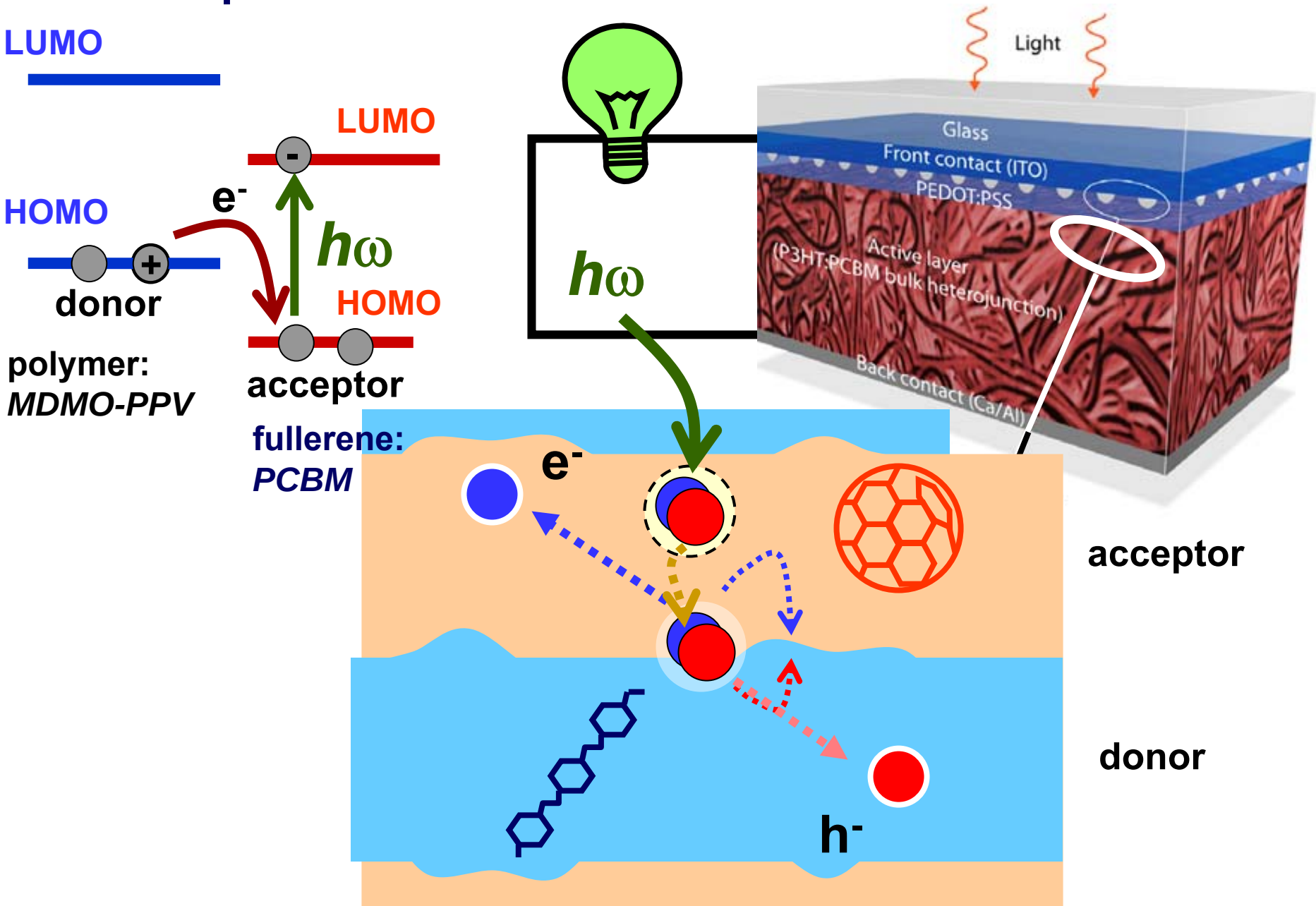
- ***Vardeny (ps-fs broad band probe studies)***
- ***Heeger (100 fs VAIR, sub-ps NIR spectroscopy)***
- ***Saricifici (5 fs resolution ET – 45 fs ET time)***
- ***Friend (100 fs exciton and charge dynamics)***
- ***Sundstrom (low flux spectroscopy)***
- ***Janssen (ET in diads, copolymers &…)***

- **Many, many more …..**

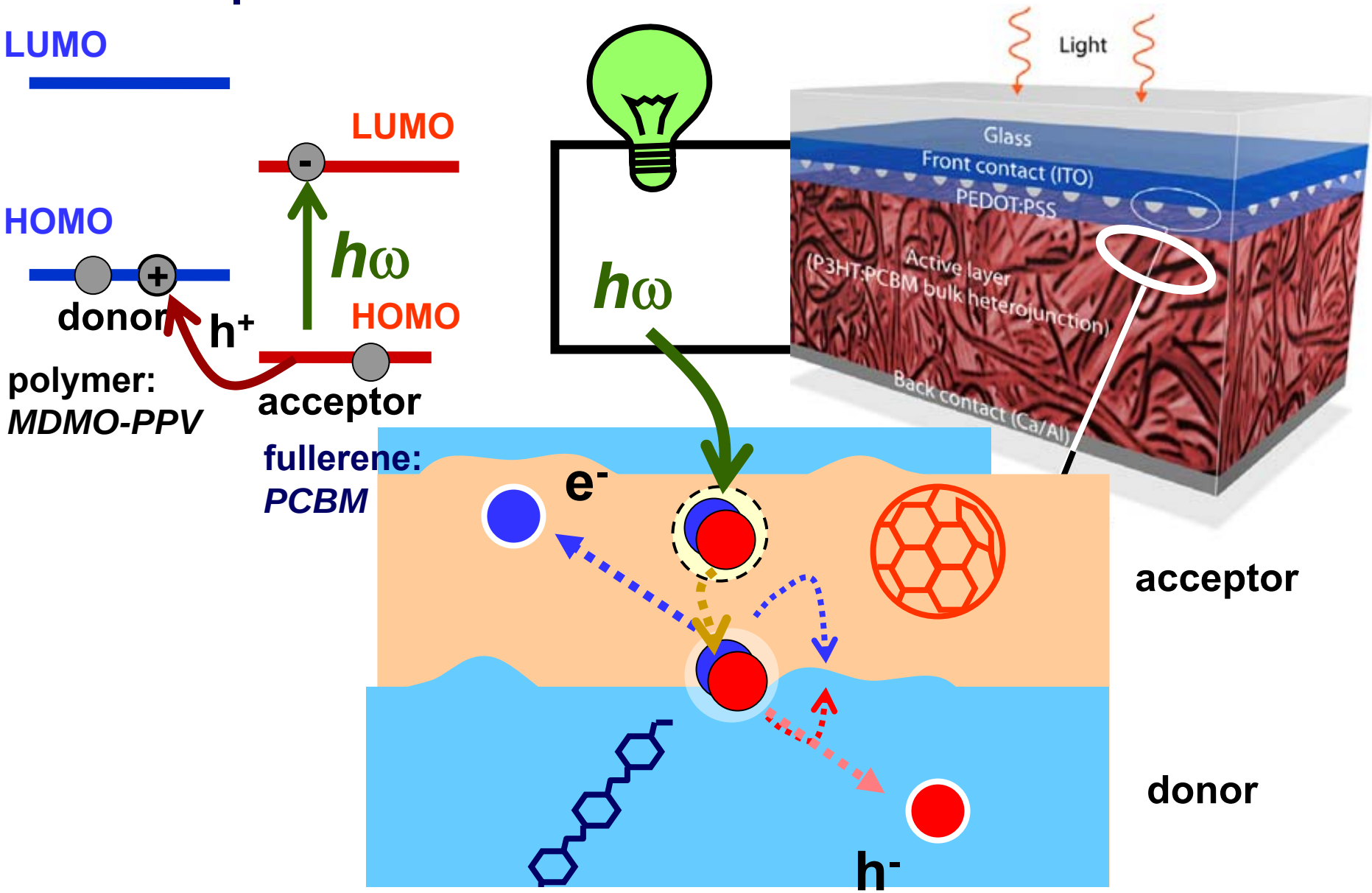
Dynamics of charges after the polymer excitation:

- **Exciton diffusion in polymer (up to 200 ps, ~10 nm)**
- **Photoinduced electron transfer 45 fs**
- **Geminate recombination of charges (10's ps)**

Acceptor Excitation

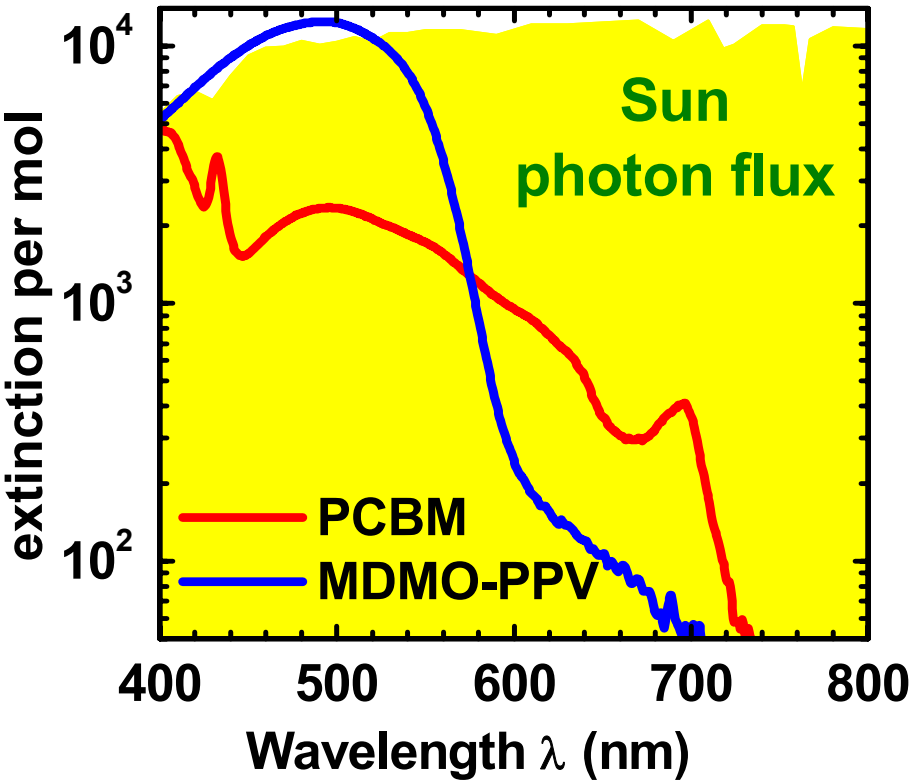


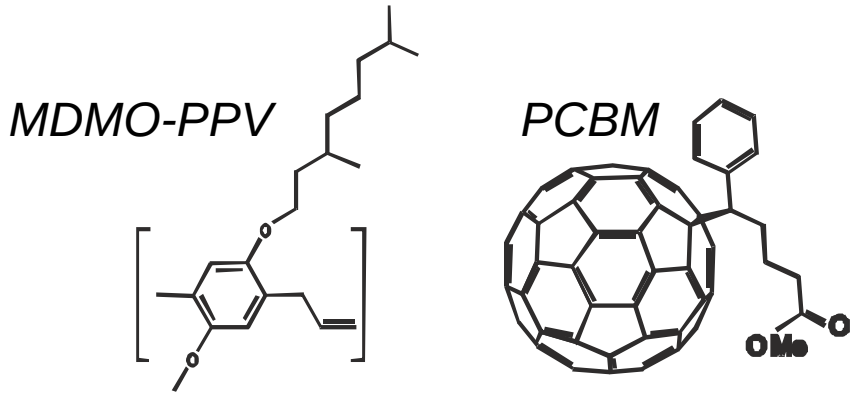
Acceptor Excitation and Hole Transfer



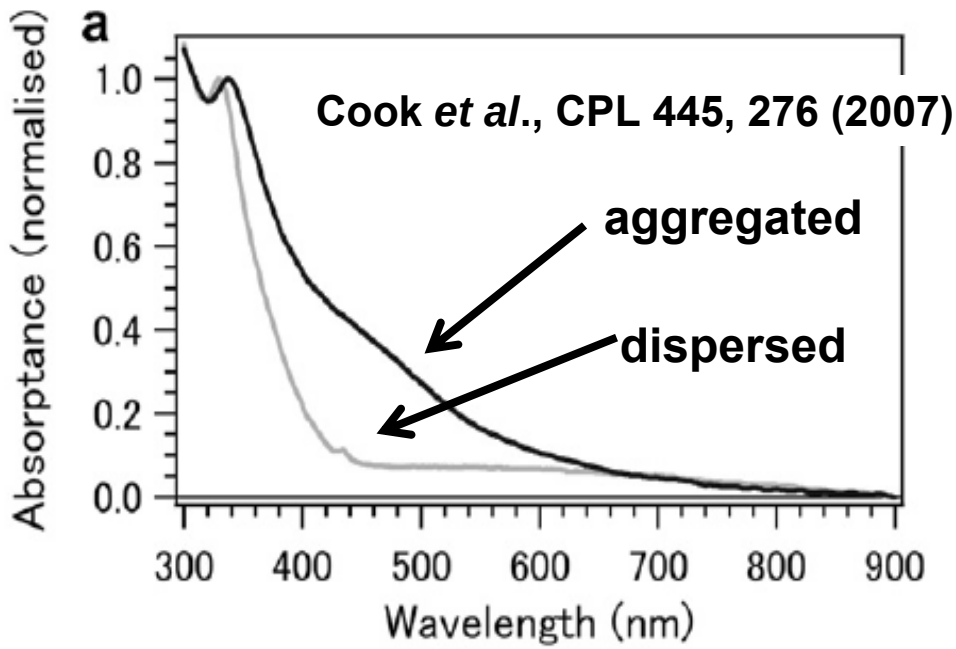
Fullerene accounts for 50-80% of the solar cell active layer

Significance of PCBM Excitation





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



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

For modern materials, fullerene absorption amounts to 30-40%!

Charge dynamics studies on polymer/fullerene mixtures

Electron transfer

- *Vardeny (ps-fs broad band probe studies)*
- *Heeger (100 fs VAIR, sub-ps NIR spectroscopy)*
- *Saricifici (5 fs resolution ET – 45 fs ET time)*
- *Friend (100 fs exciton and charge dynamics)*
- *Sundstrom (low flux spectroscopy)*
- *Janssen (ET in diads, copolymers &…)*

- **Many, many more …..**

Hole transfer

- *Wienk et al, 2003 (C_{70}PCBM/PPV, 0.5 ps resolution)*
- *Cook et al, 2009 (PCBM/P3HT, 0.2 ps resolution)*

Dynamics of charges after the polymer excitation:

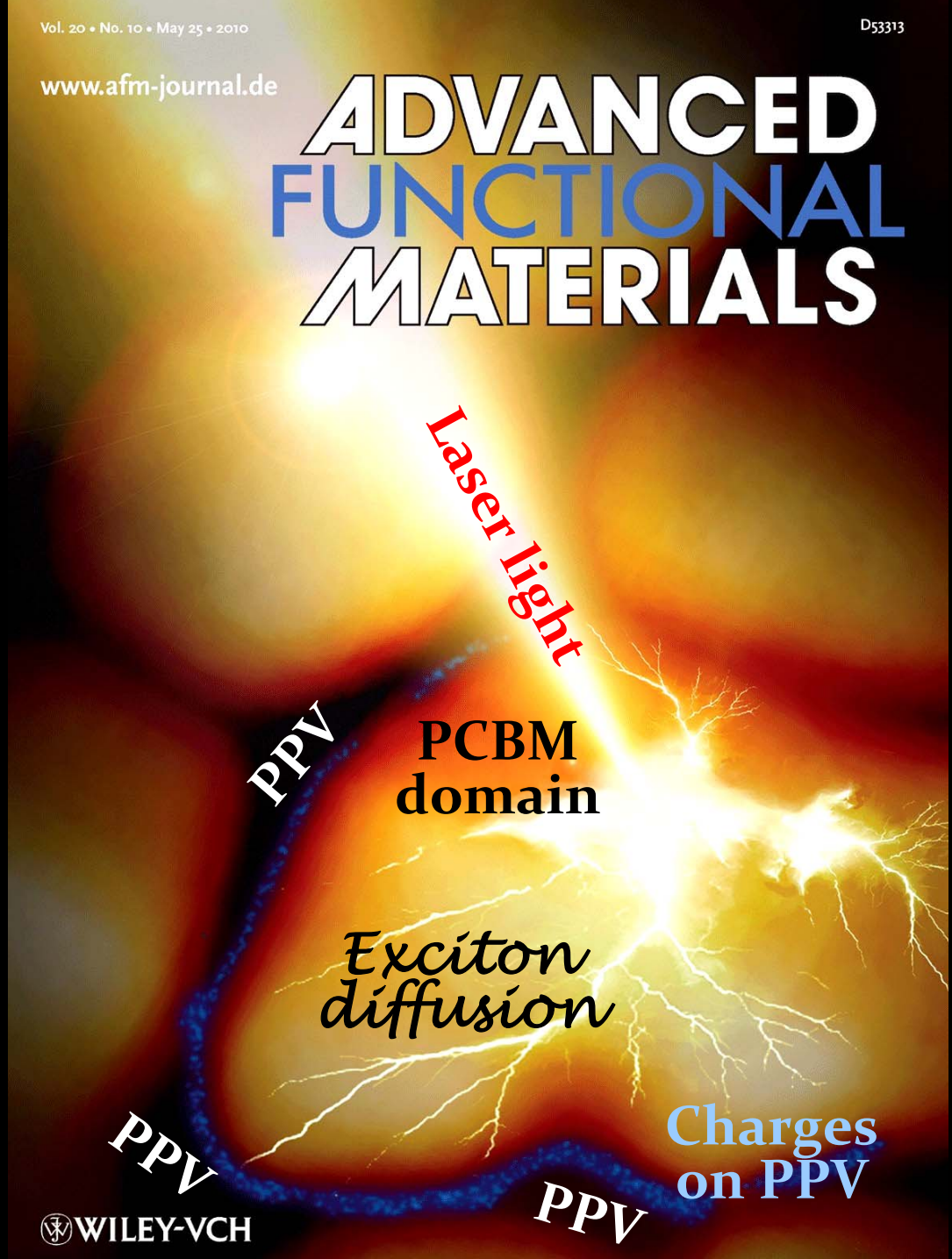
- **Exciton diffusion in polymer (up to 200 ps, ~10 nm)**
- **Photoinduced electron transfer 45 fs**
- **Geminate recombination of charges (10's ps)**

??

The questions to answer

In the blends of polymer (MDMO-PPV) and fullerene (PCBM):

- **What is the Hole-Transfer time?**
- **What are dynamics of PCBM exciton-to-charge conversion?**



The cover story:

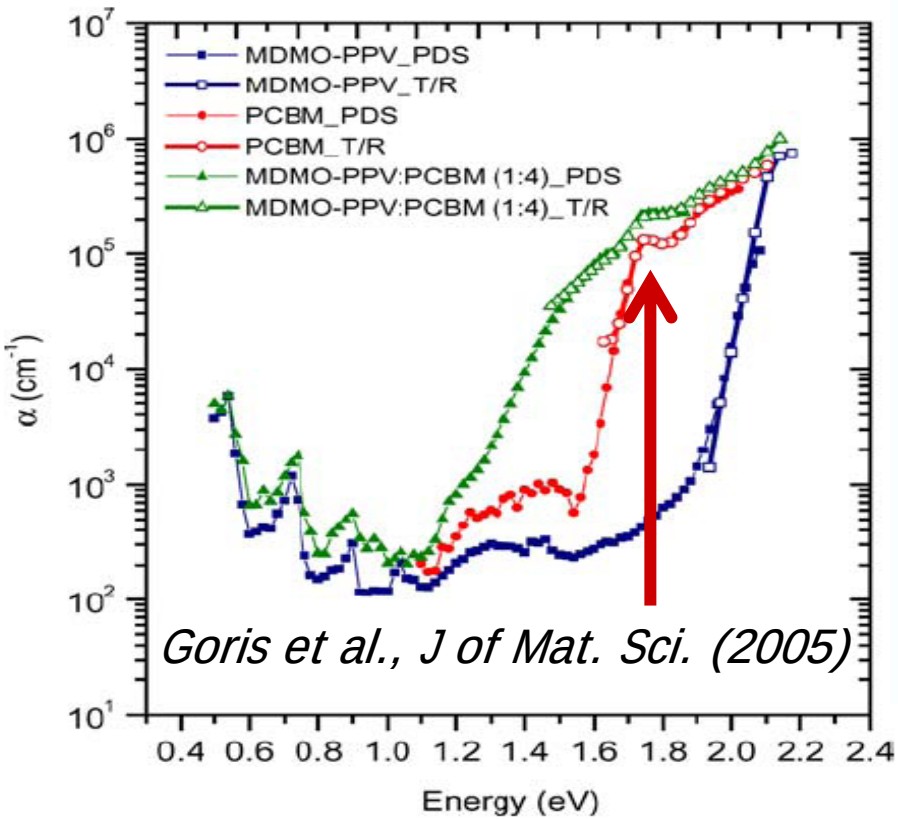
The active layer of the currently most efficient plastic photovoltaic cells is a blend of polymer and methanofullerene molecules. In their article M.S. Pshenichnikov *et al.* show that hole transfer upon methanofullerene excitation operates simultaneously with electron transfer as the charge generation process in plastic photovoltaics, at a staggering timescale of 30 fs.

AFM 20, 1653–1660 (2010)

How to Excite Selectively PCBM?

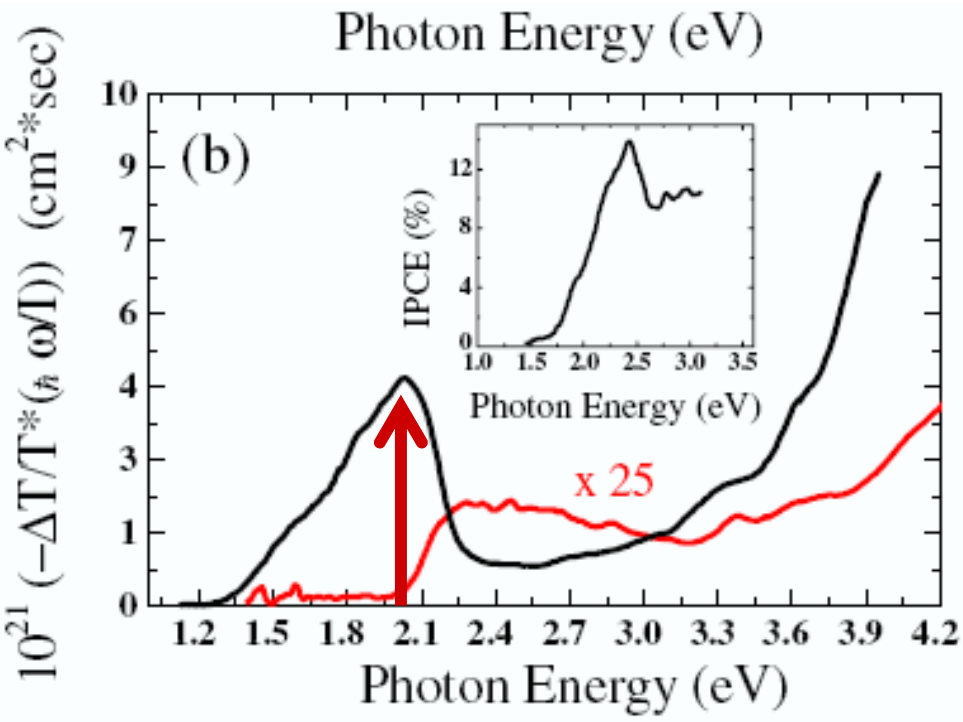
Spectral selectivity!

Linear absorption experiments



Goris et al., J of Mat. Sci. (2005)

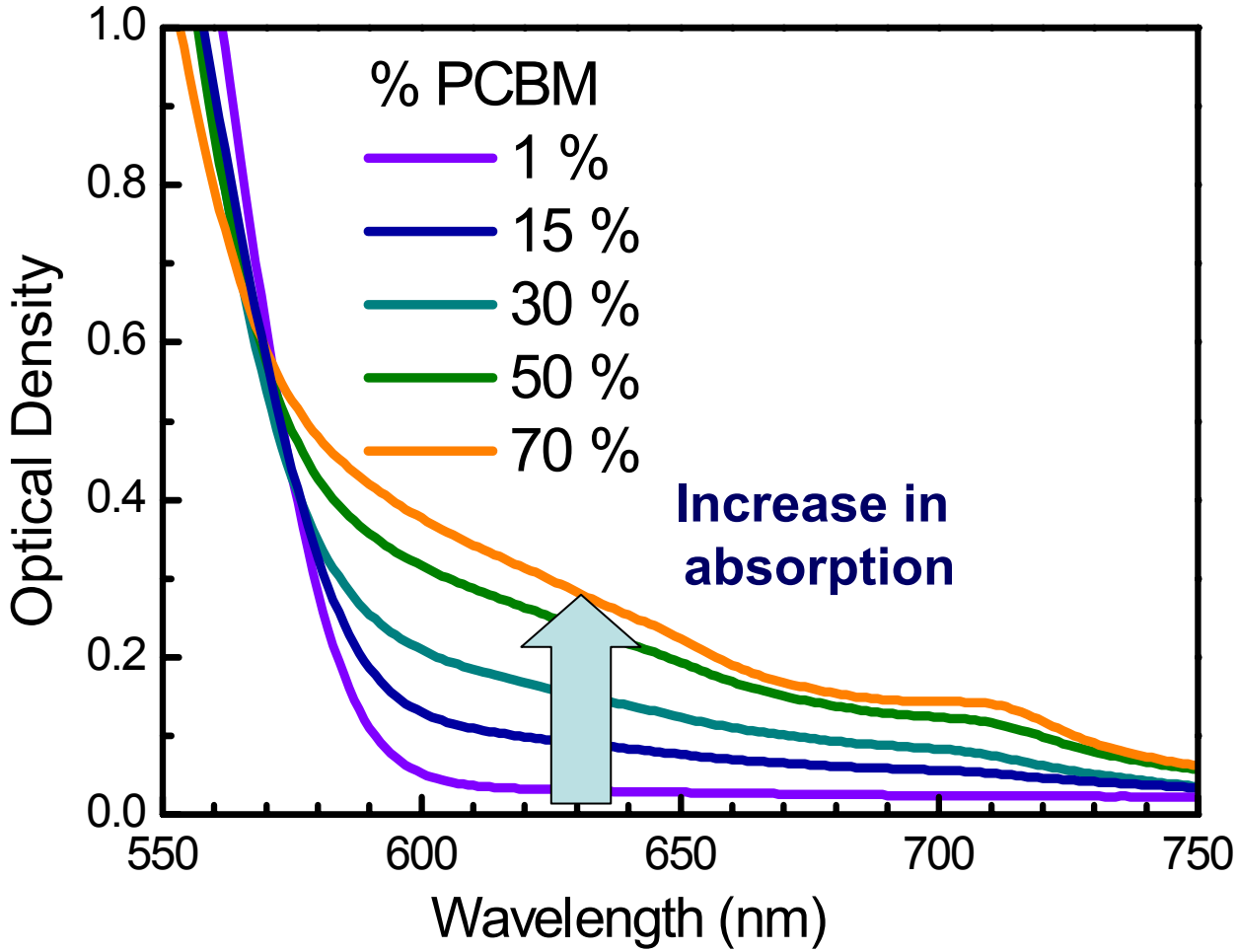
CW PIA photoexcitation



Drori et al, PRL (2008)

Maximum contrast of PCBM excitation is provided by 620-650 nm pump

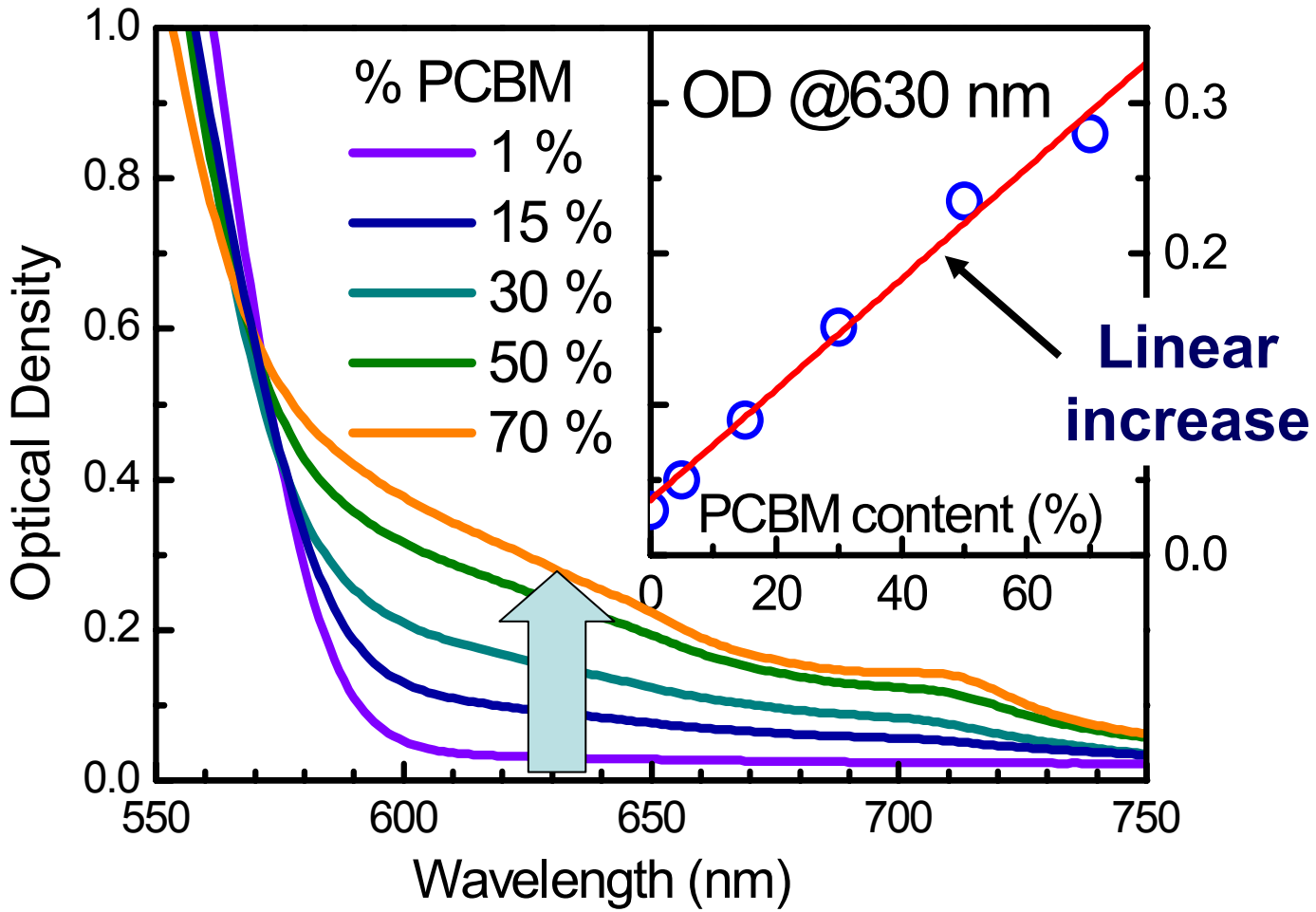
Linear Absorption Spectra



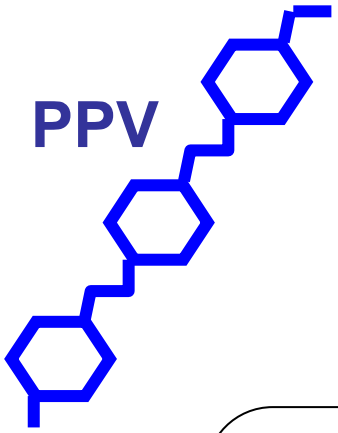
Sample preparation:

Drop-casting from chlorobenzene solution of PCBM and MDMO PPV on 180-μm thick fused silica microscope cover slides sample thickness ~300 nm

Linear Absorption Spectra

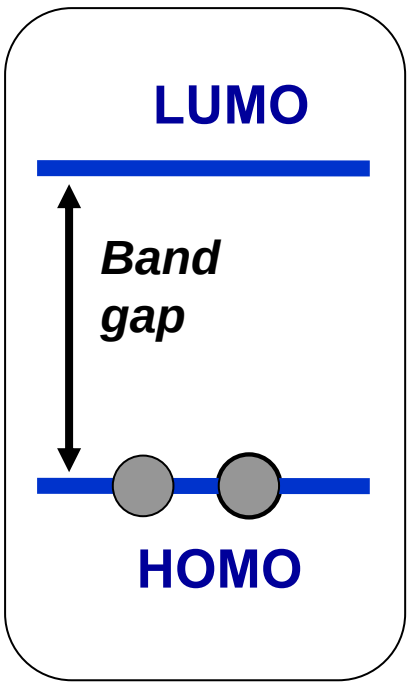


Contrast: $\sigma = \dfrac{\textbf{PCBM extinction}}{\textbf{PPV extinction}} \approx 10$ **(at 630 nm)**

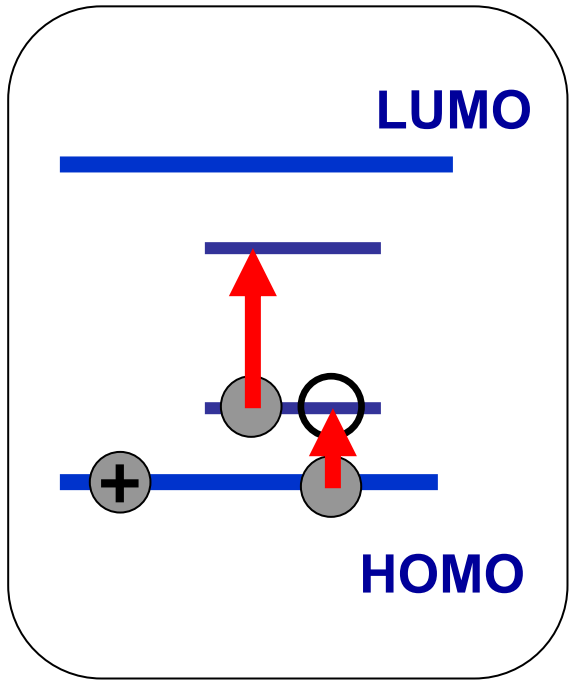


How Can We See Charges on PPV?

Upon *polaron* formation in polymer, new optical transitions are formed



Ground State



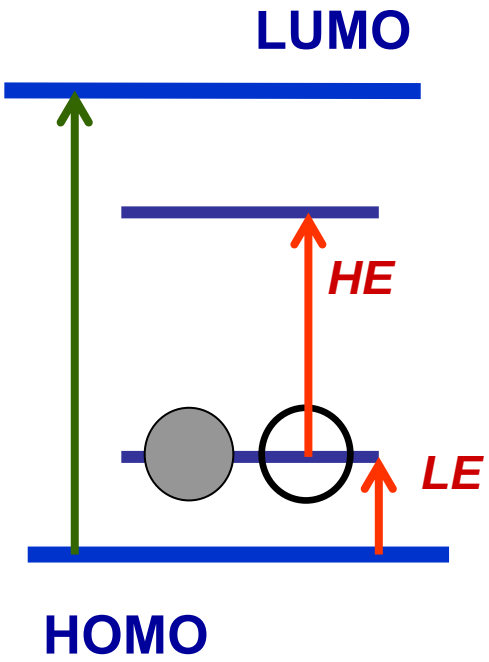
Charged excitations Polarons

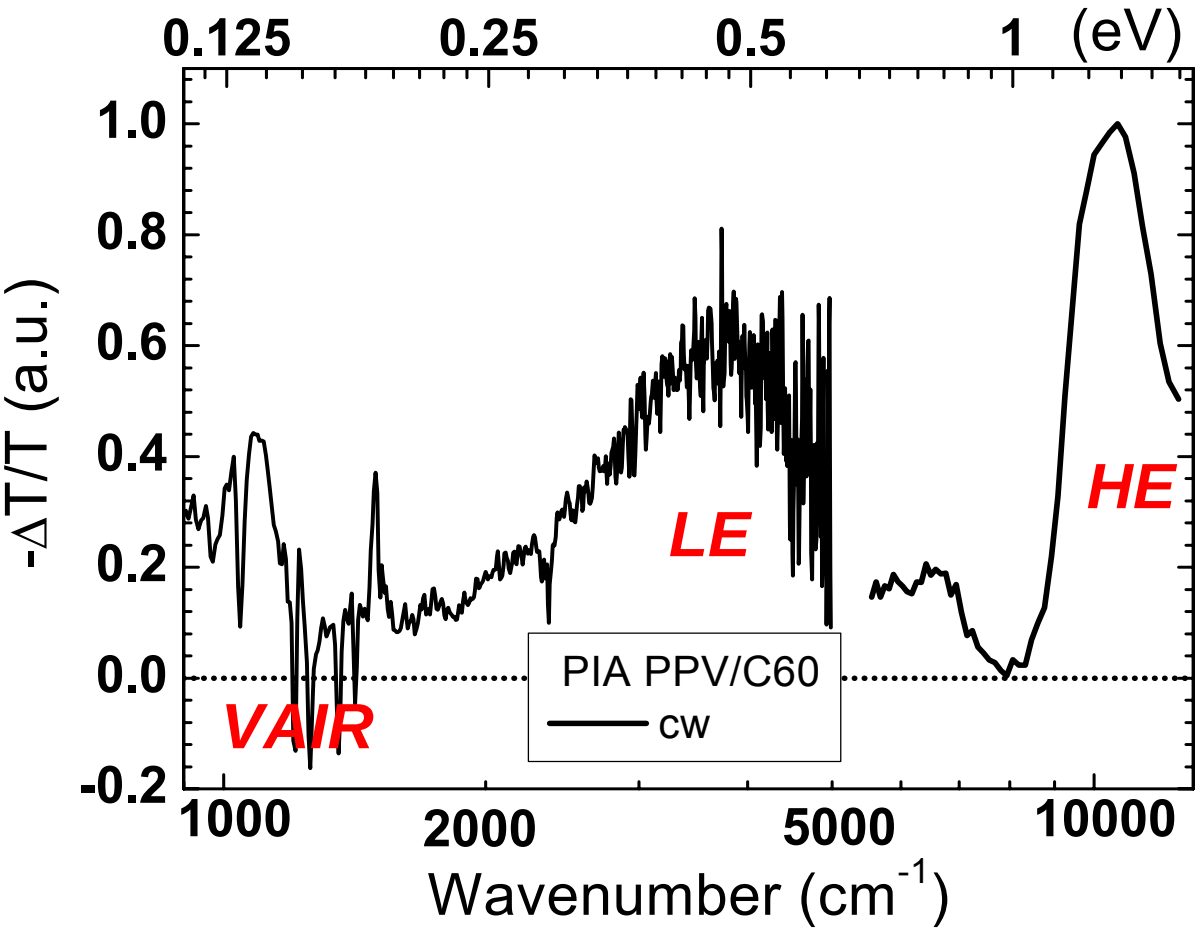
High-energy (HE) polarons

Low-energy (LE) polarons

Heeger 92, 99; Vardeny 96, 03

Optical Signatures of Charges

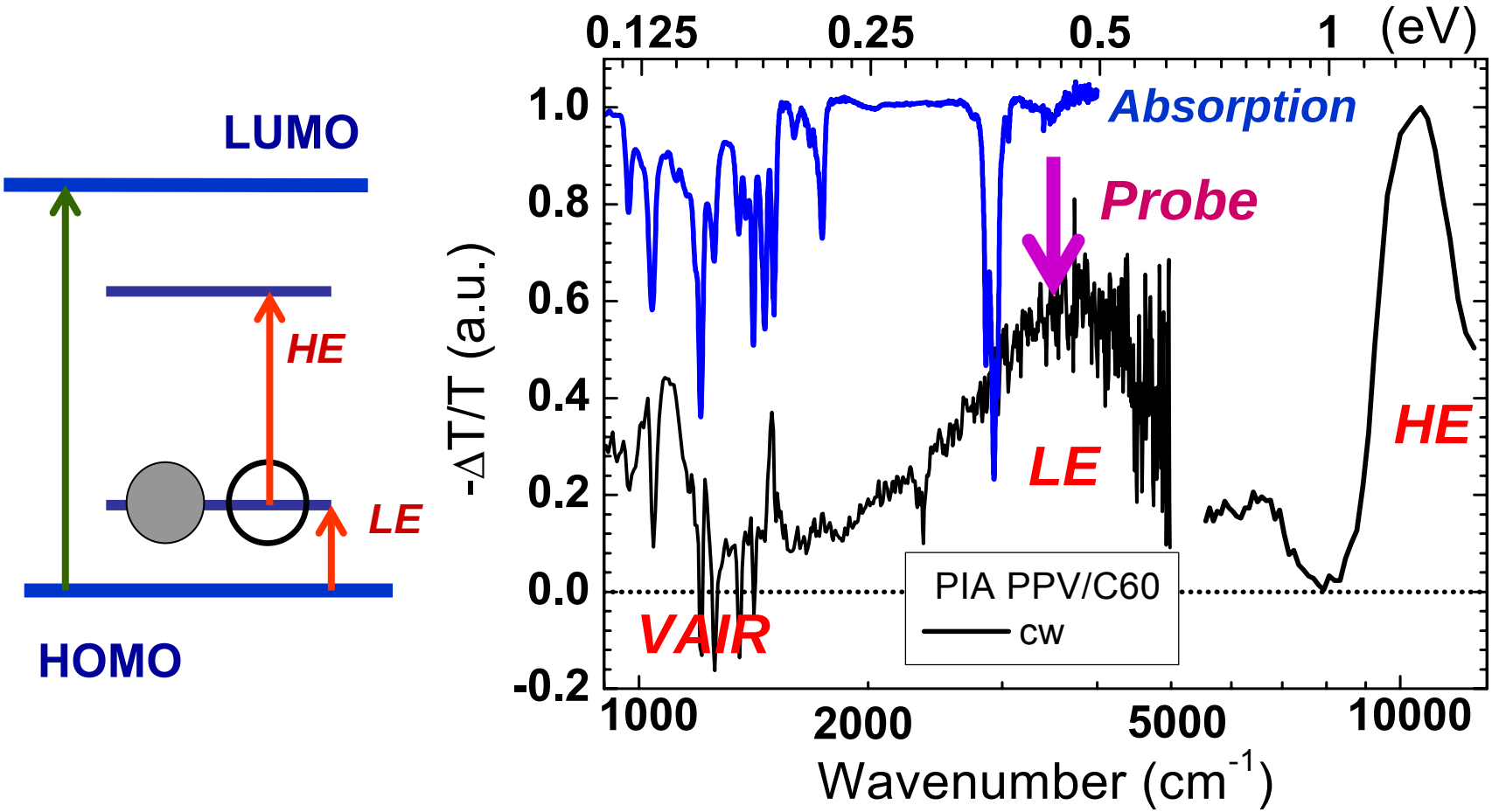




- **Photo-Induced Absorption (PIA) is an excellent probe for concentration of charges**

Bakulin *et al.*, JPC B112, 13730 (2008)

Optical Signatures of Charges

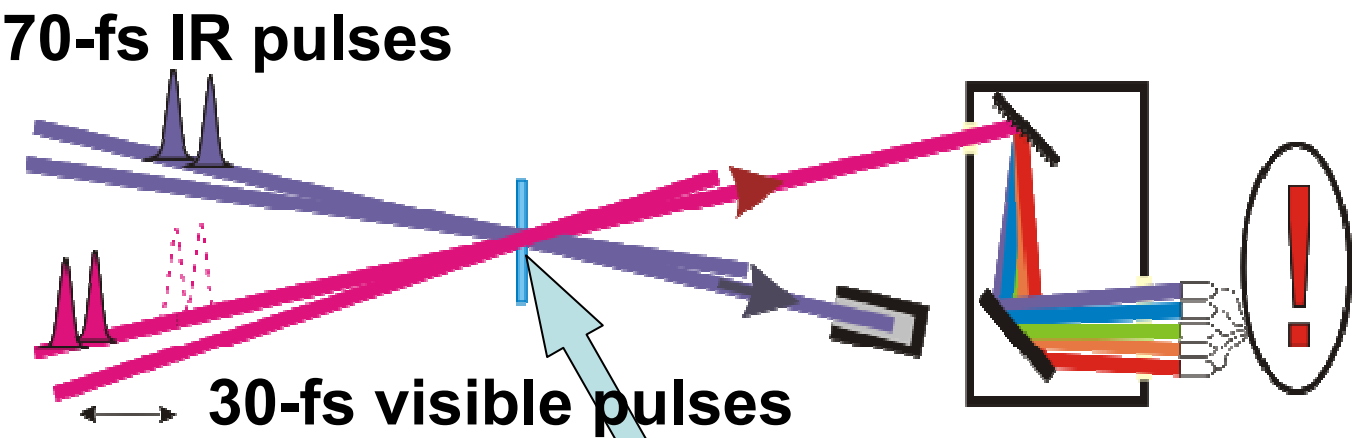


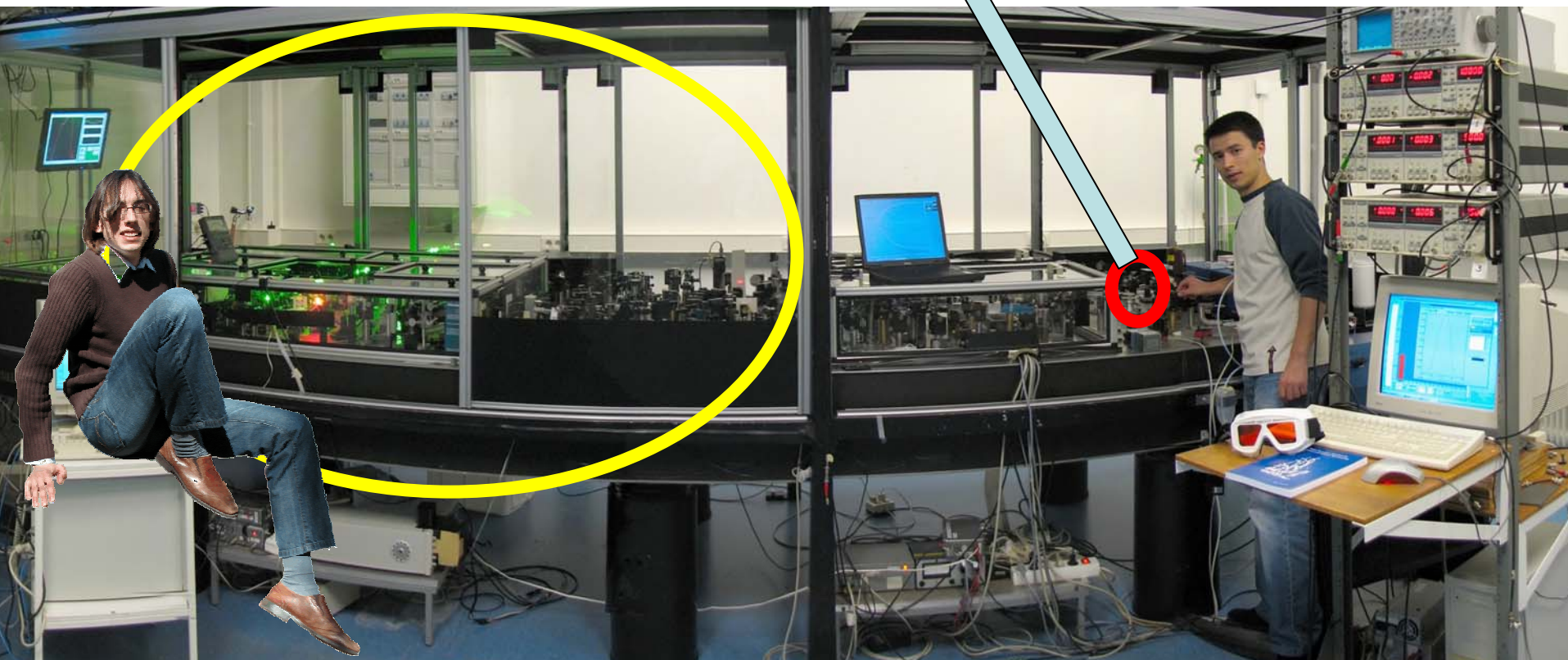
- **Photo-Induced Absorption (PIA) is an excellent probe for concentration of charges**
- **Low-energy (LE) peal allows background-free measurements**

Bakulin *et al.*, JPC B112, 13730 (2008)

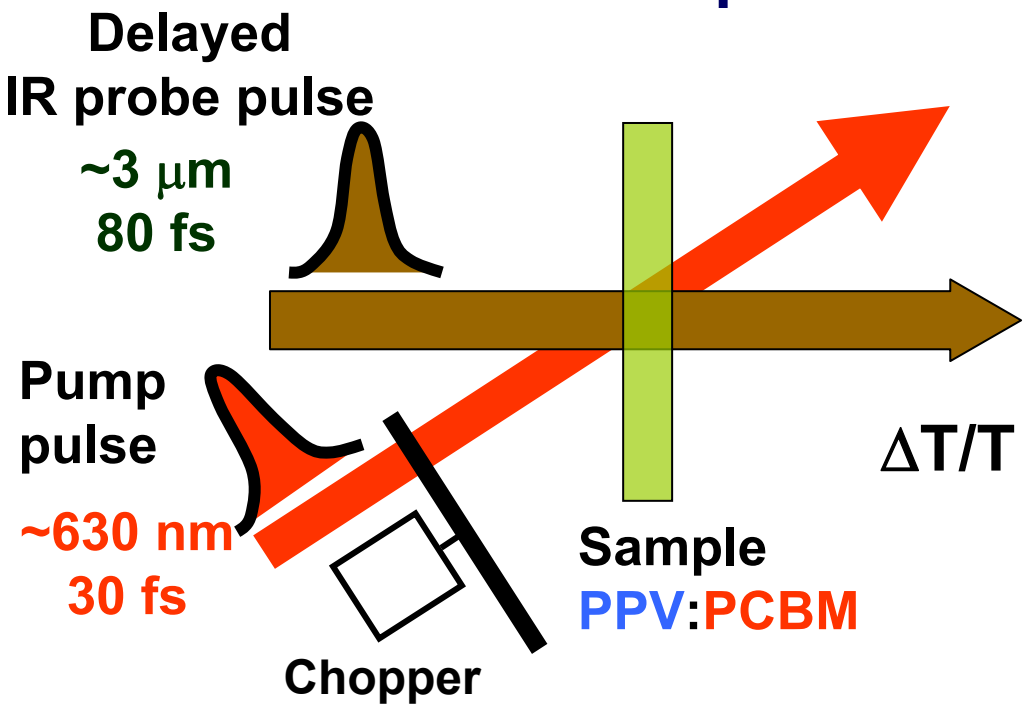
The Instrument – Photocamera

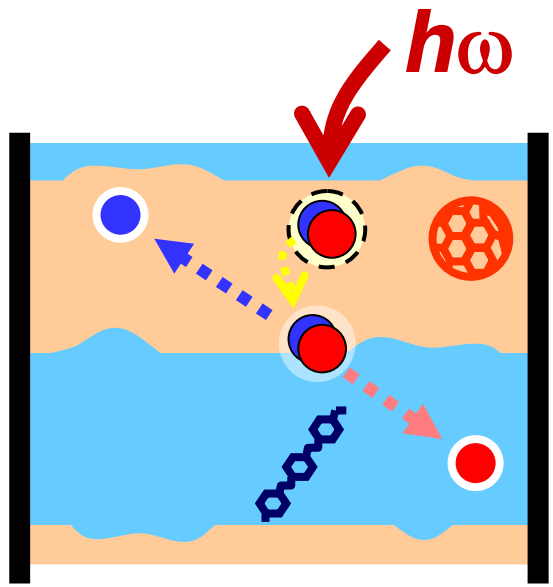
The Instrument – Ultrafast Photocamera



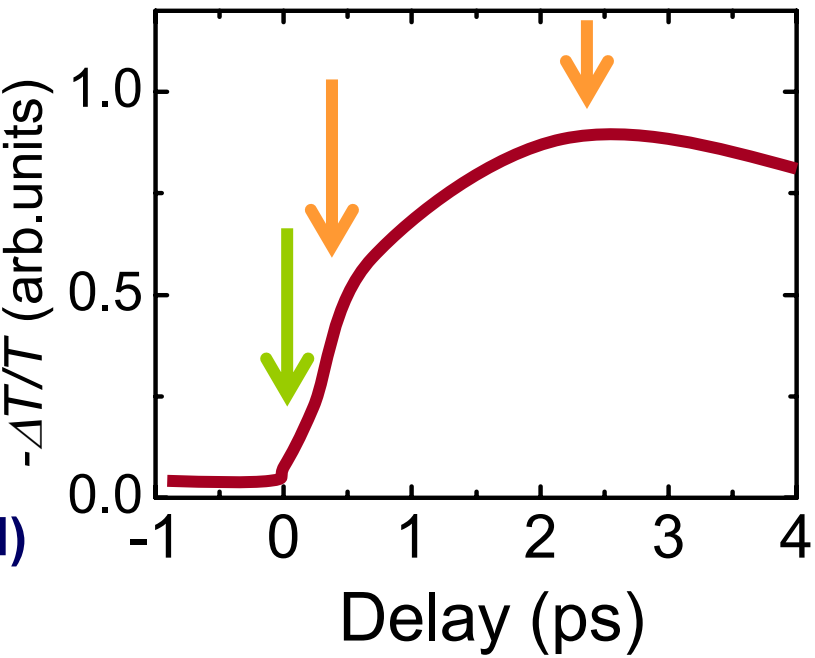


Concept of Experiment

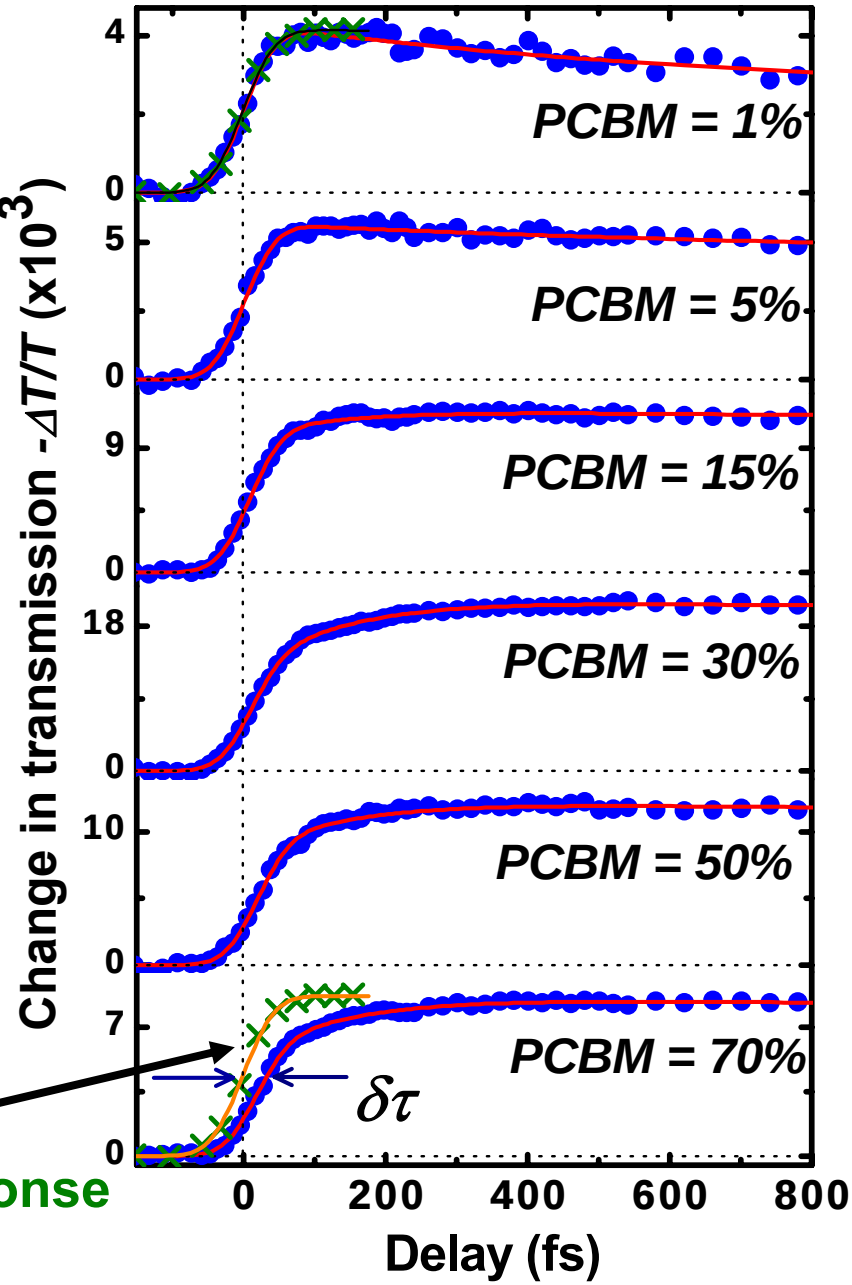




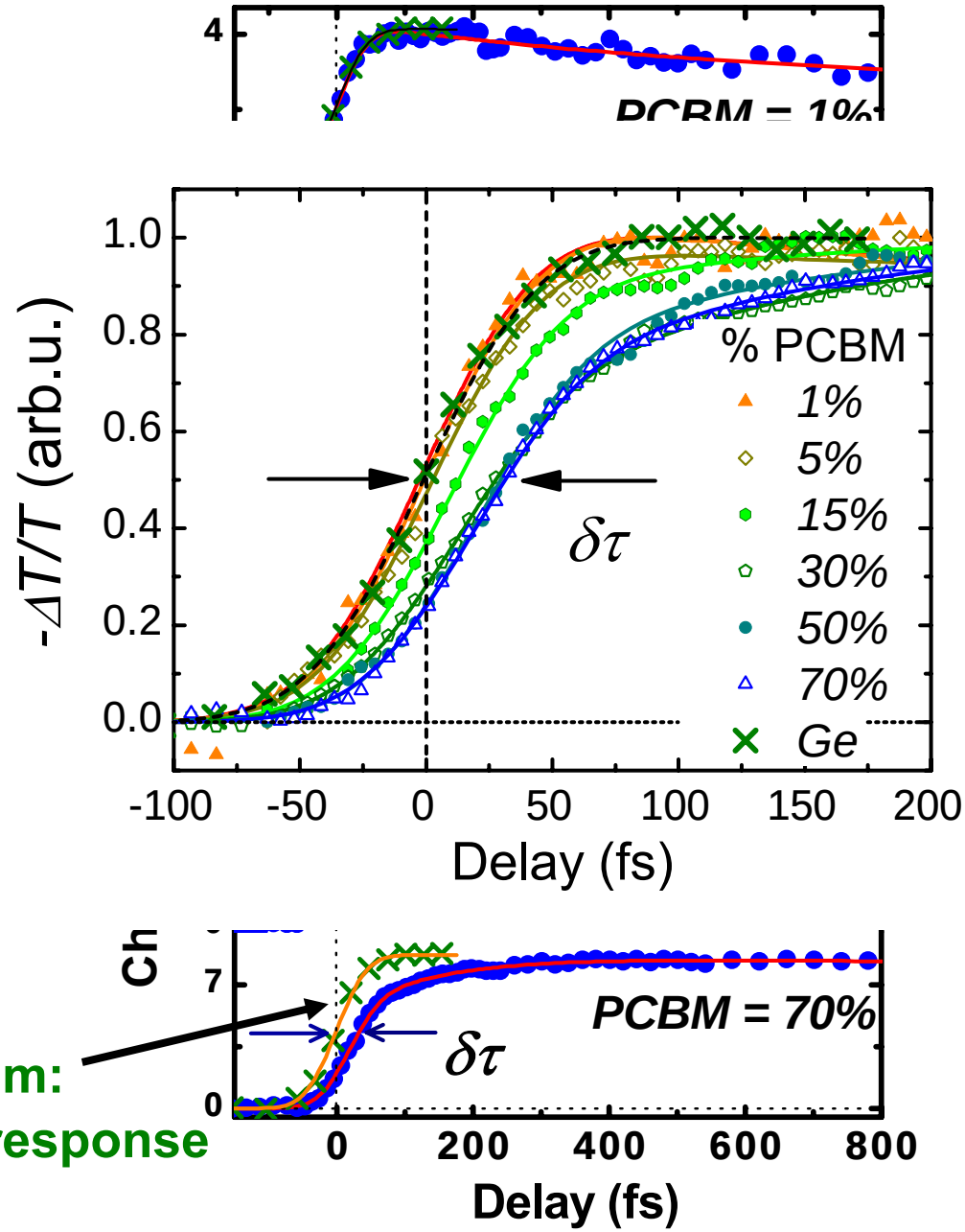
- Excite spectral-selectively PCBM
- Watch for arrival of the hole to PPV
- Hole arrival should be delayed by:
  - hole-transfer time (low % PCBM)
  - exciton diffusion time (high % PCBM)



Experimental Transients

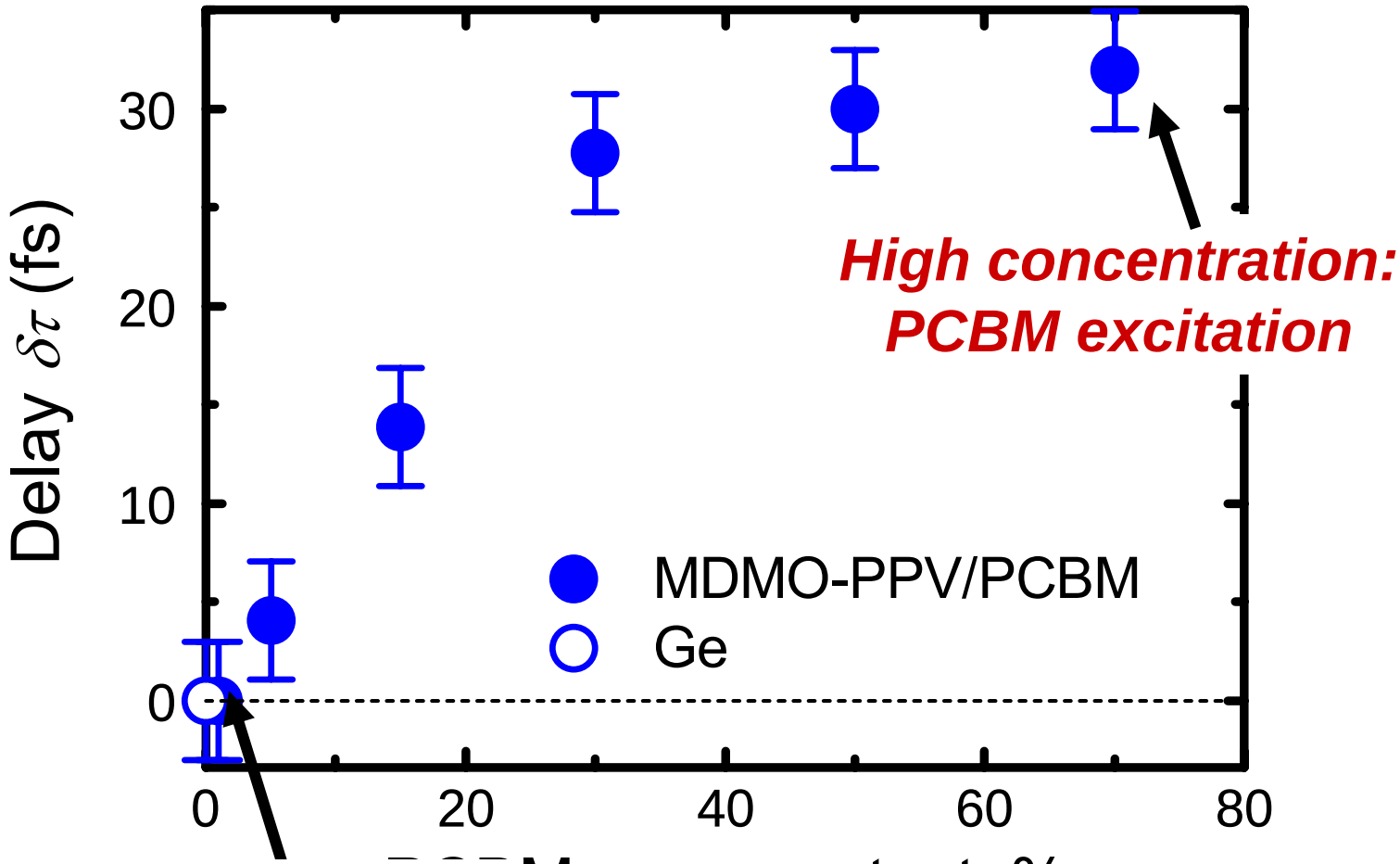


Results I. Hole-Transfer Time

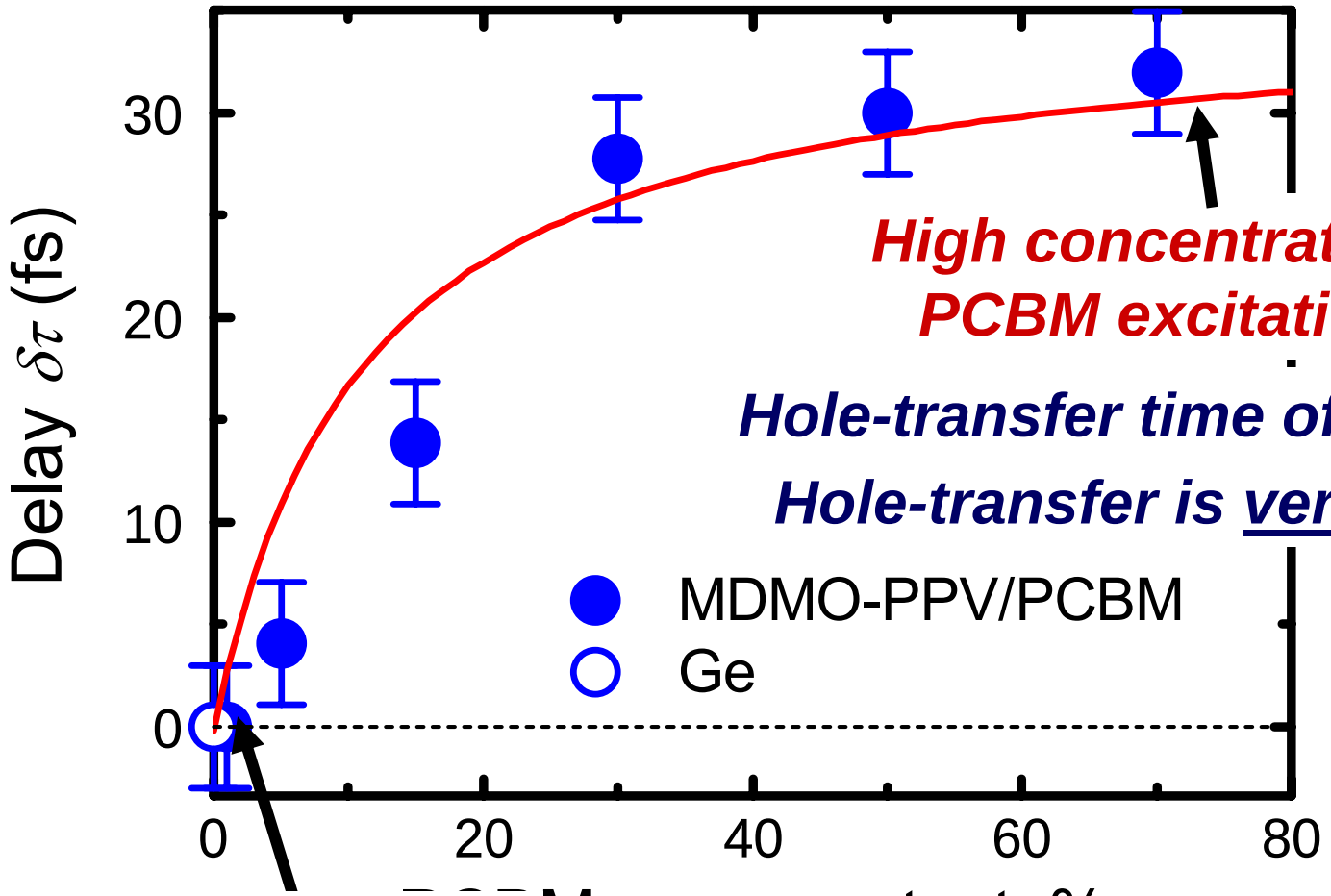


Ge thin film:
Instantaneous response

Results I. Hole-Transfer Time



Results I. Hole-Transfer Time



High concentration: PCBM excitation

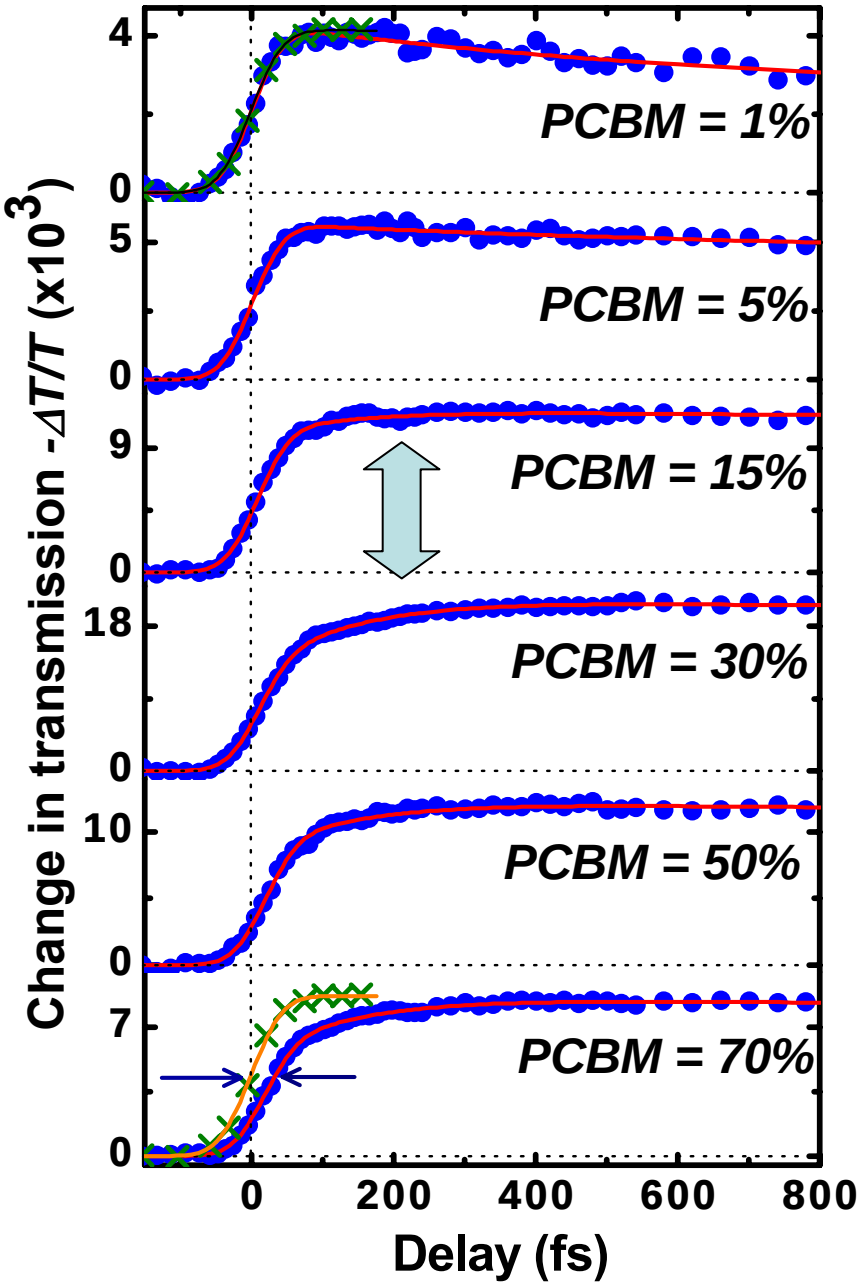
Hole-transfer time of 30 fs

Hole-transfer is very efficient!

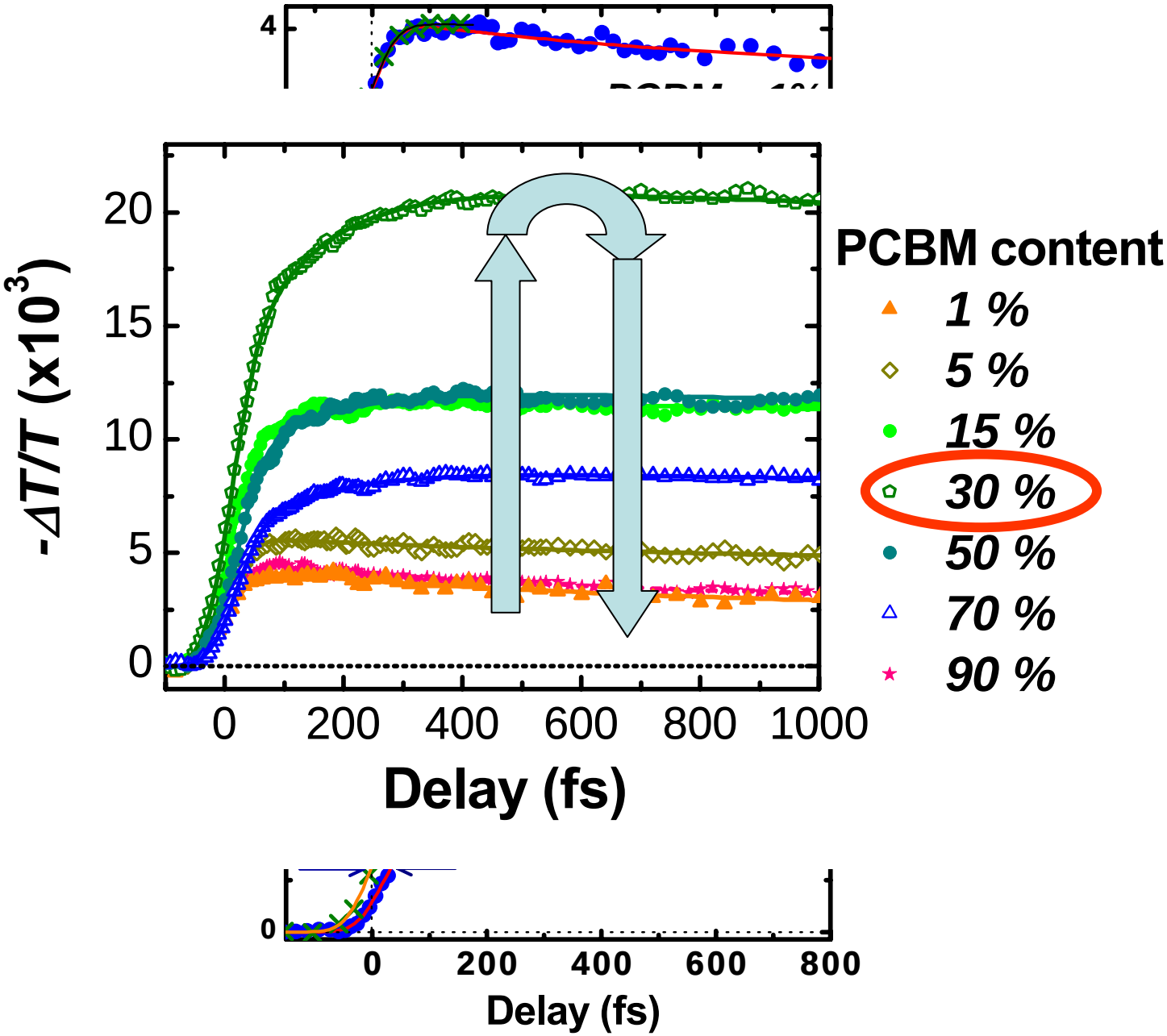
Low concentration: Polymer excitation

Two-component model: $$\delta\tau = \frac{\sigma N}{\sigma N + (1 - N)} \cdot \delta\tau_{MAX}$$

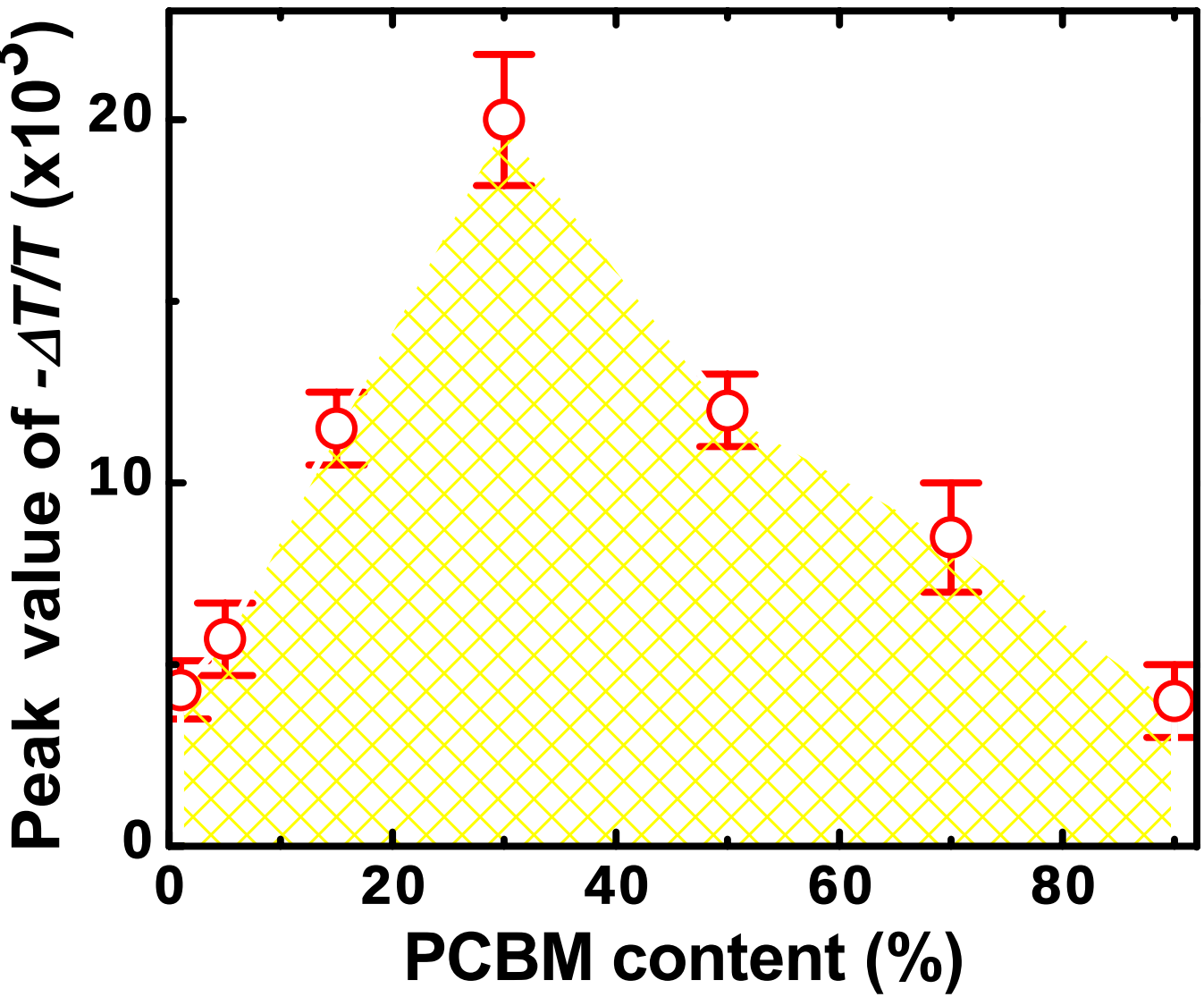
Results II. PIA Amplitudes



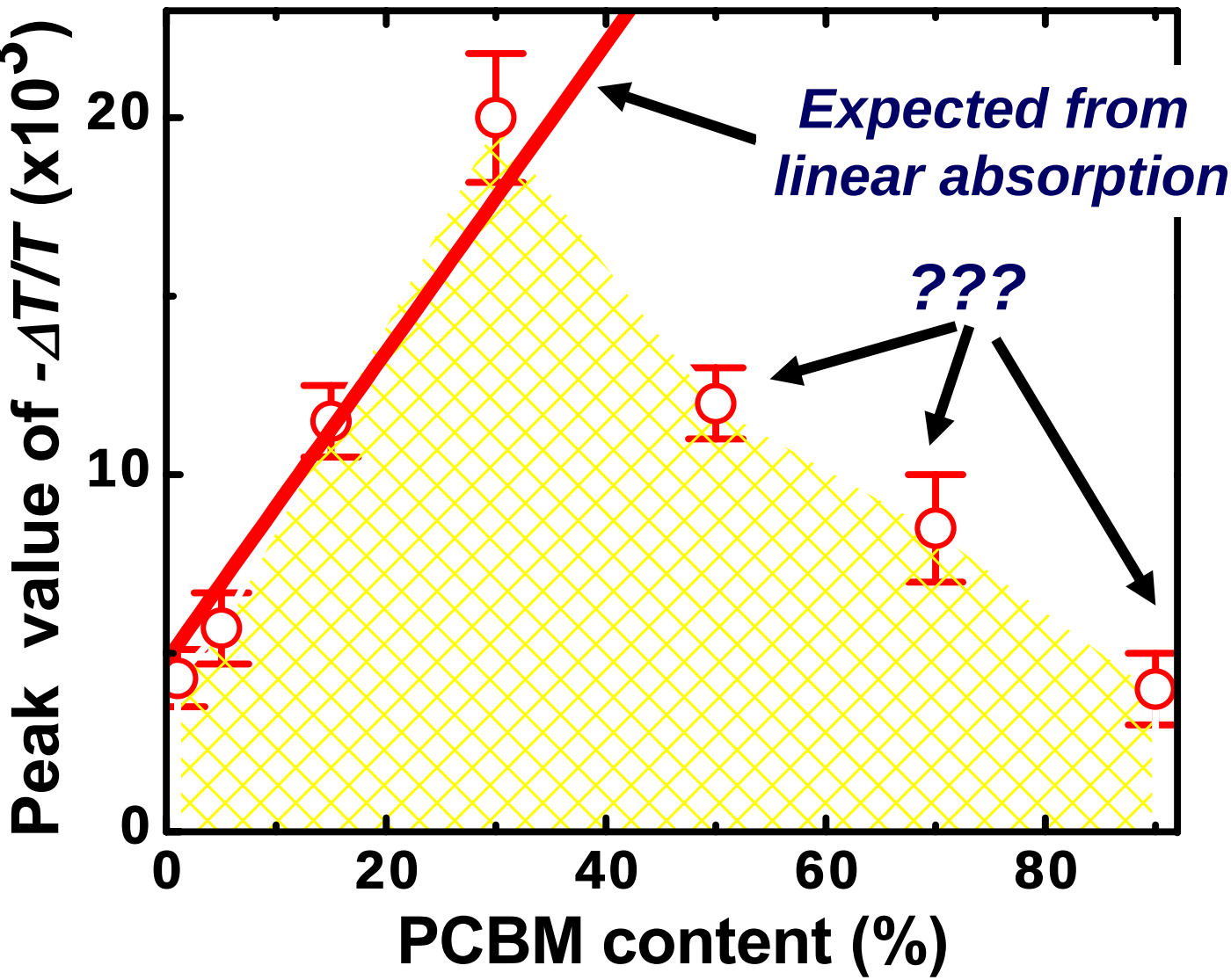
Results II. PIA Amplitudes



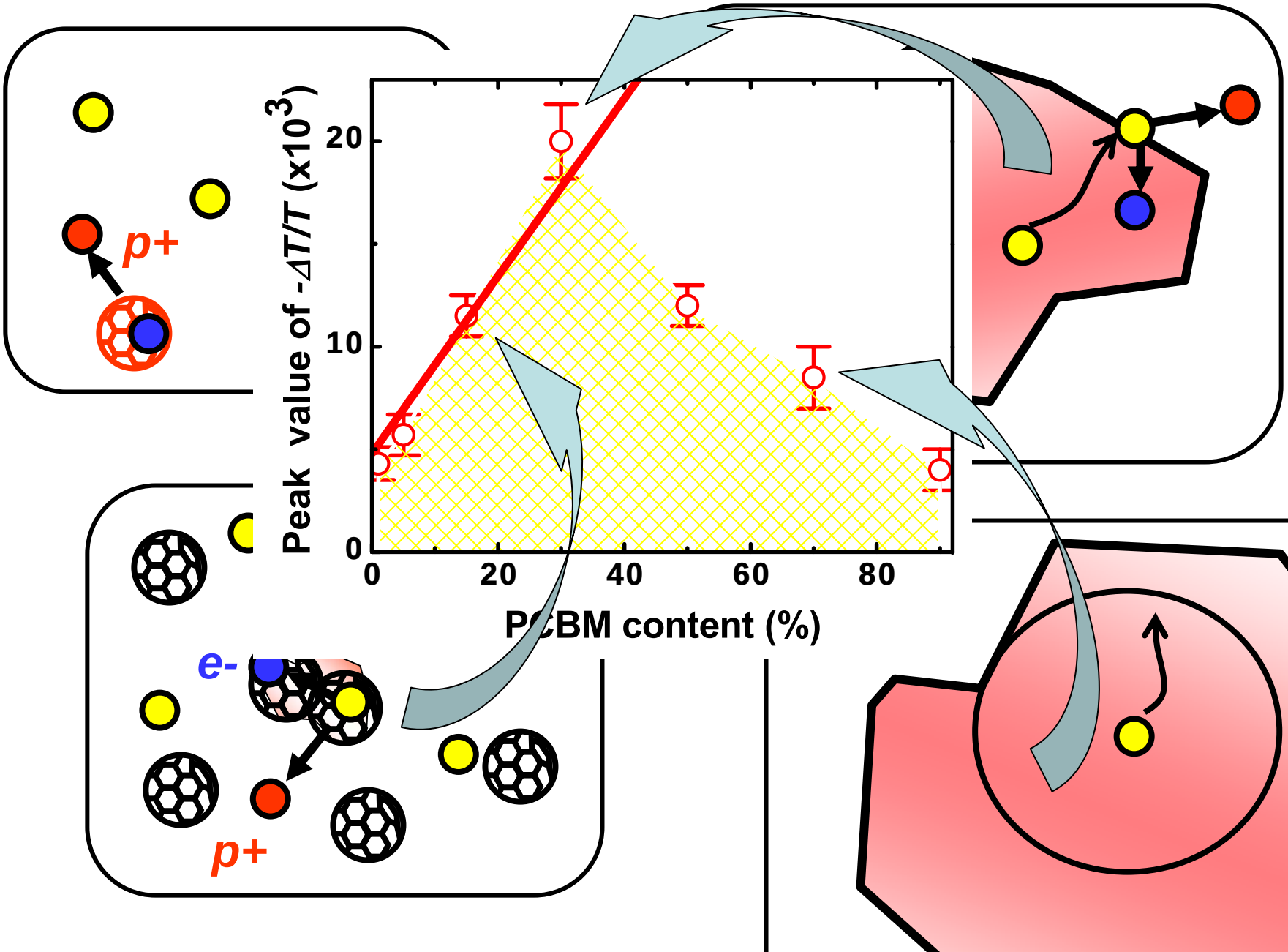
Results II. PIA Amplitudes



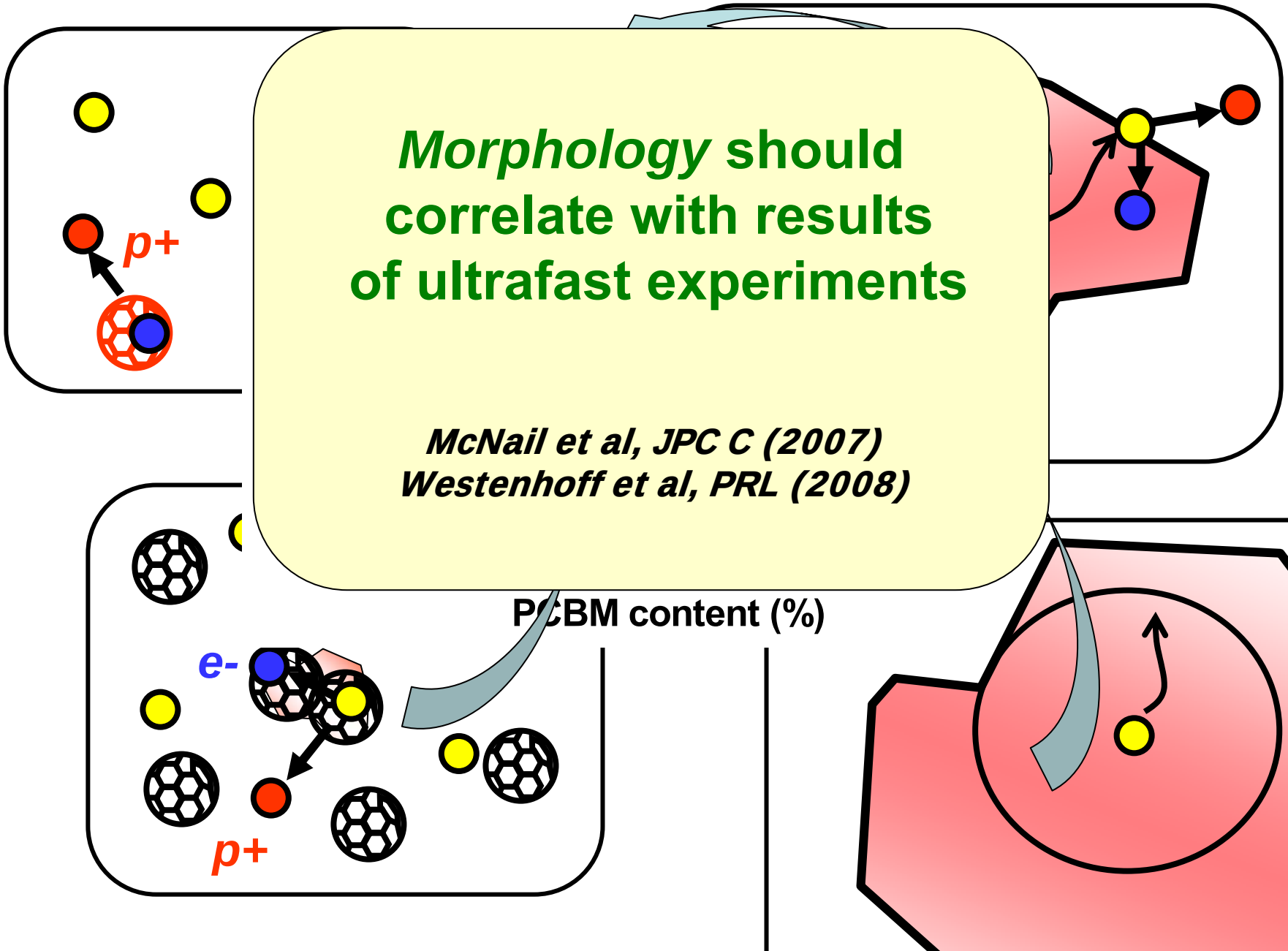
Results II. PIA Amplitudes



Microscopic Picture of Charge Dynamics



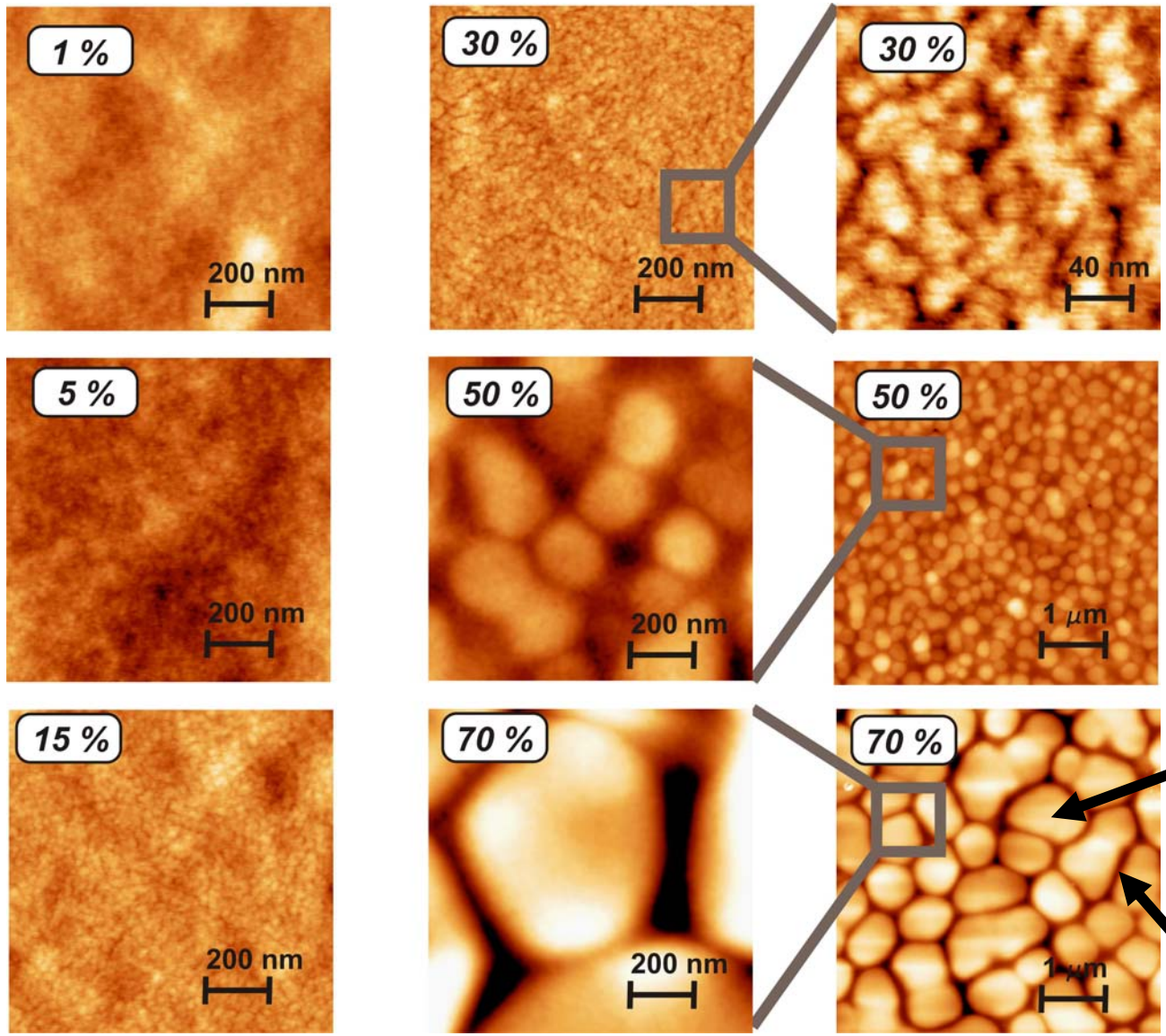
Microscopic Picture of Charge Dynamics



***Morphology* should correlate with results of ultrafast experiments**

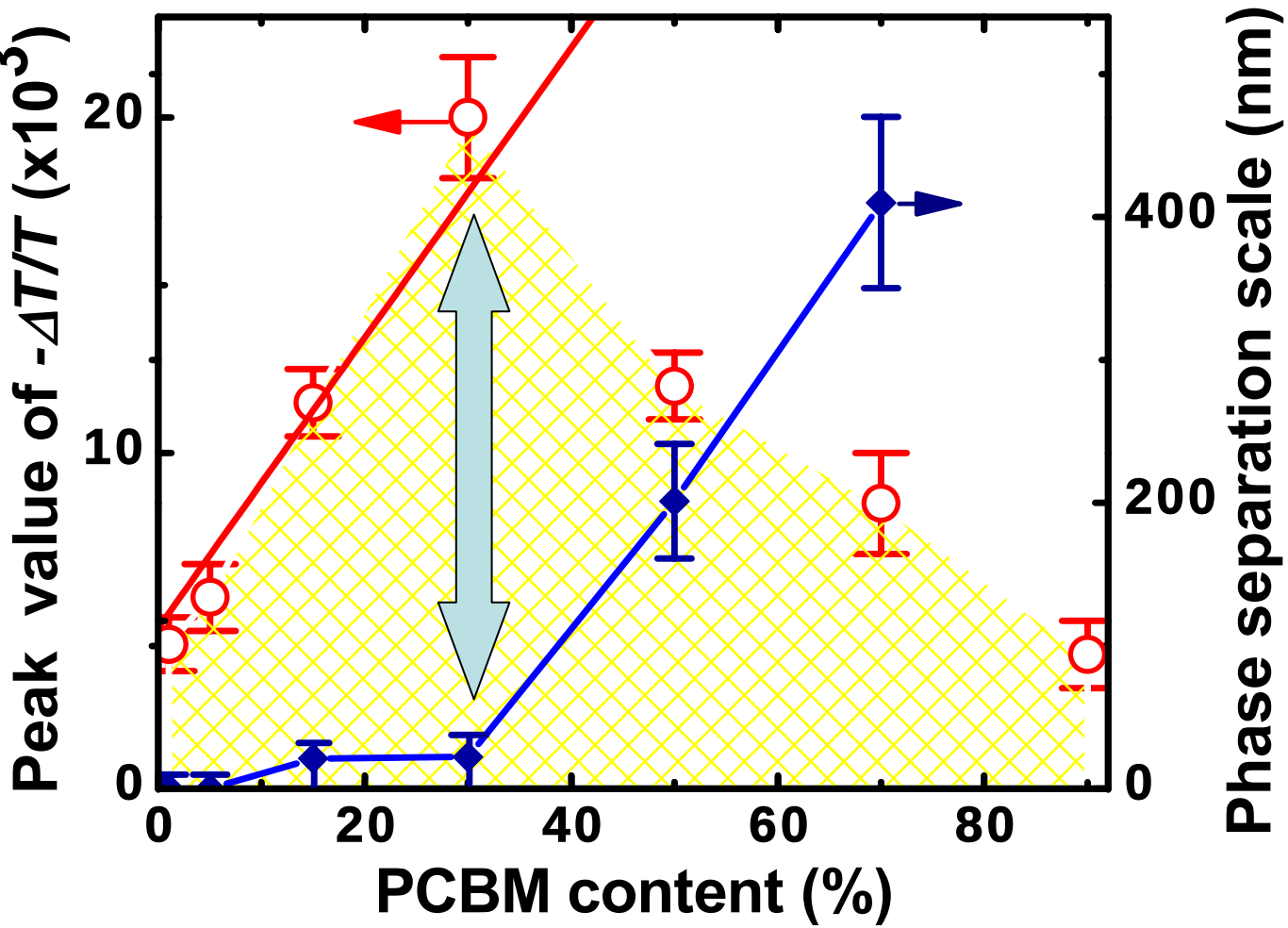
McNail et al, JPC C (2007)
Westenhoff et al, PRL (2008)

From Cartoons to AFM Images



Spatial correlation analysis: $\varphi(a,b) = \iint f(x,y) \cdot f(x+a, y+b) \cdot dxdy$

Phase Separation and Charge Generation



Correlation between the amount of charges and domain size

Conclusions

- Hole transfer time of ~30 fs
- …is very close to the electron-transfer time of 45 fs
- …so the two processes very efficient
- … and act literally in concert !

- Blend morphology strongly influences the hole transfer process

- PCBM domain size of 10 nm seems the largest for the efficiency

- …more experiments to come!