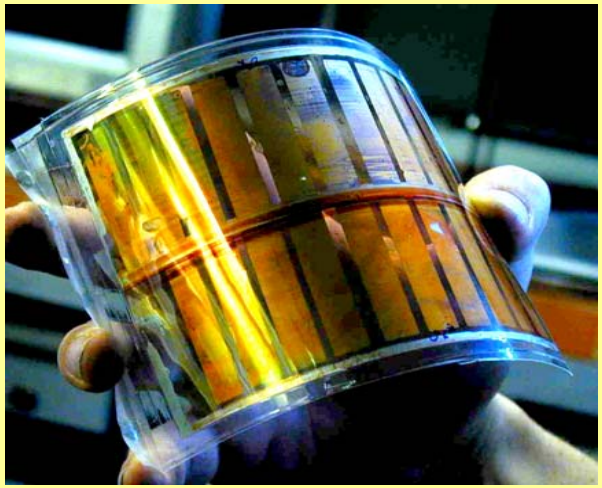
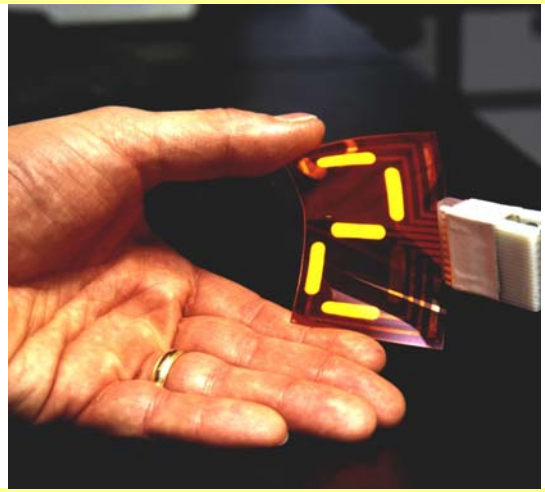
Organic, “Plastic” Solar Cells





Niyazi Serdar SARICIFTCI
Linz Institute for Organic Solar Cells (LIOS),
Institute for Physical Chemistry, Johannes Kepler University Linz
Austria
www.lios.at

Scope

"The electronics of the 20th century is based on semiconductor physics. The electronics of the 21st century will be based on molecular chemistry/physics"

F. L. Carter

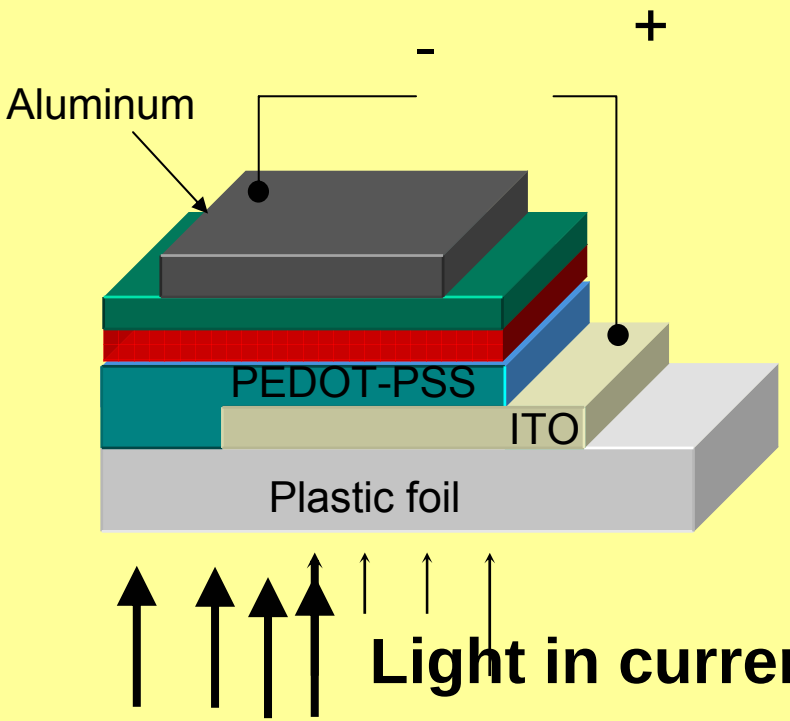
Nobelprize for Chemistry 2000

Alan Heeger, Alan MacDiarmid (†) and Hideki Shirakawa

1974: Discovery of metallic conductivity in iodine doped *trans*-polyacetylene $(CH)_x$

Solar Cells & OLEDs Device Scheme

SOLAR CELLS

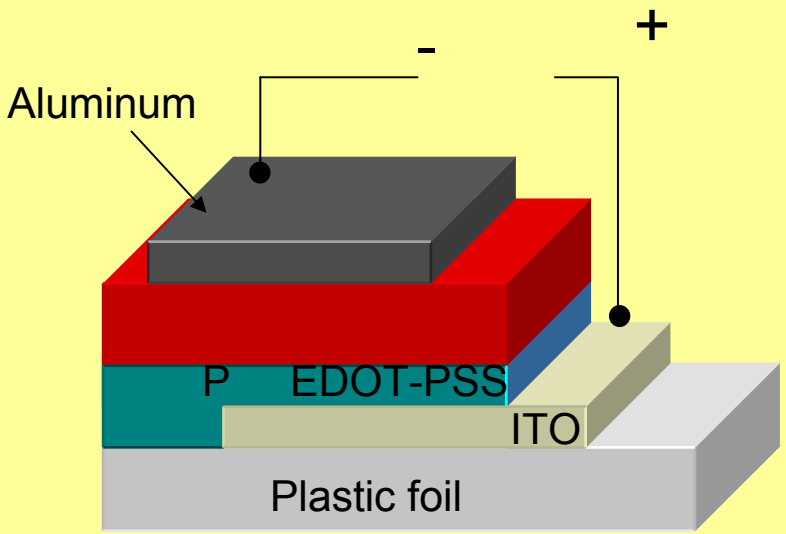


Light in current out

MDMO-PPV

PCBM

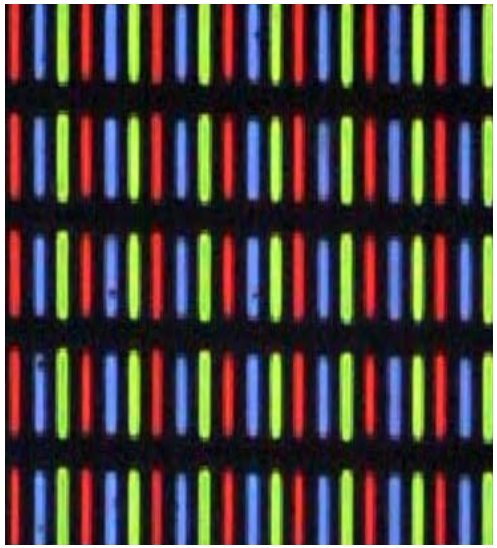
OLEDs

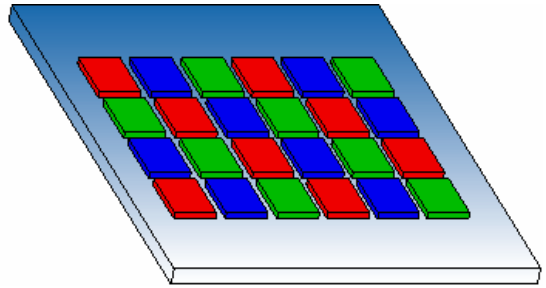


Current in light out

MDMO-PPV

Full Color Plastic Flat Panel Displays

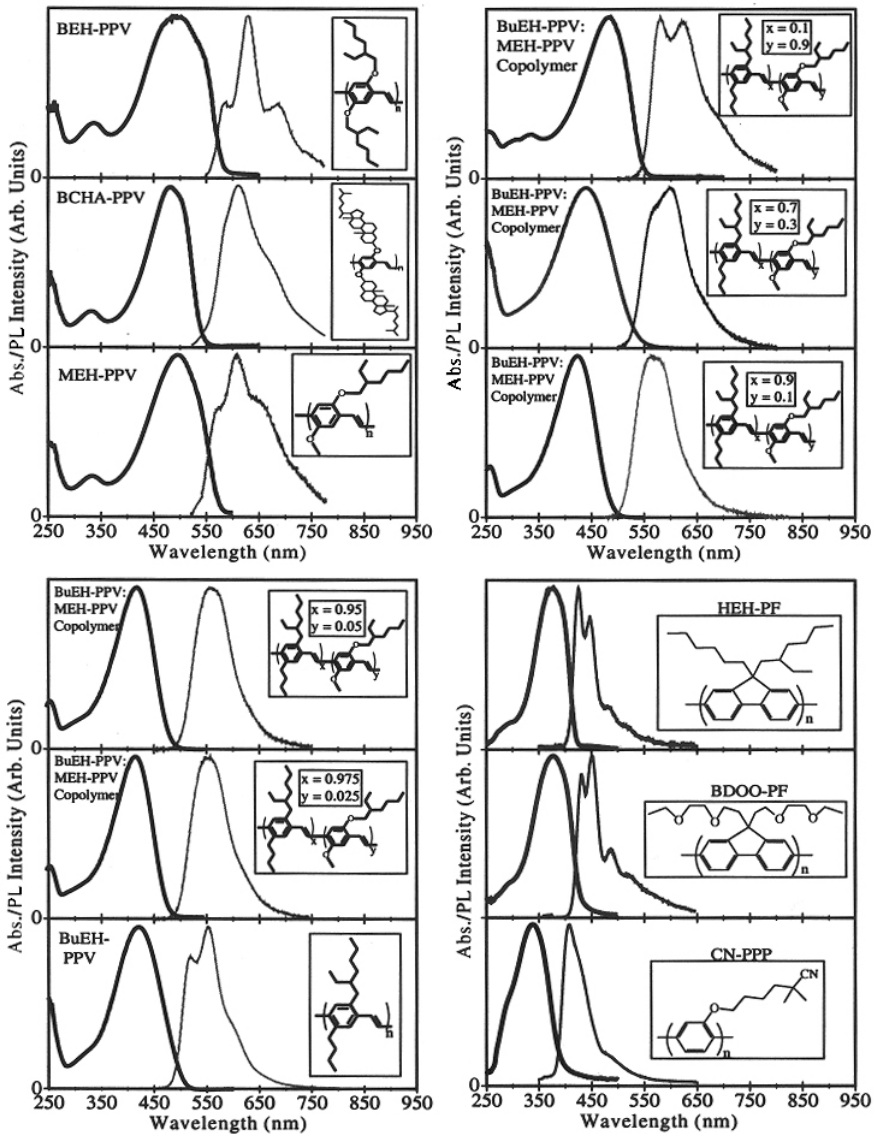


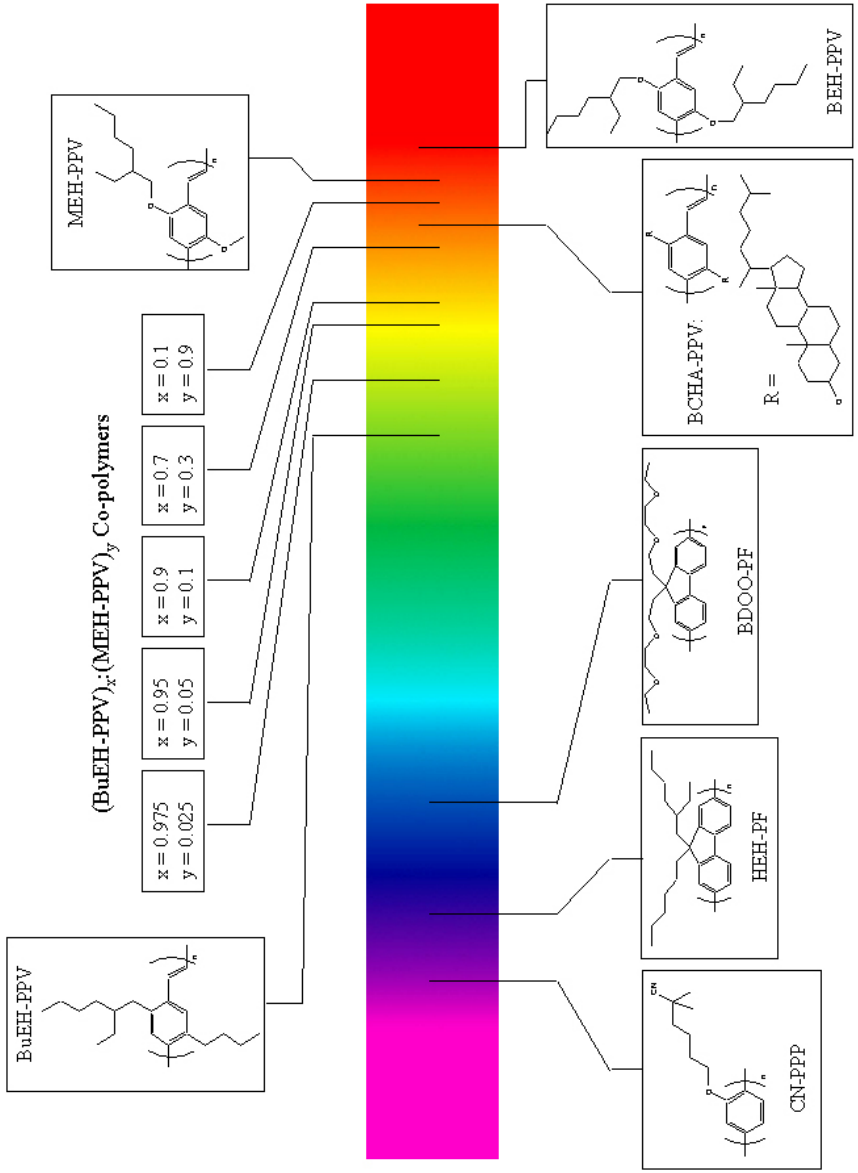


Full Color OLED Flat Panel Displays

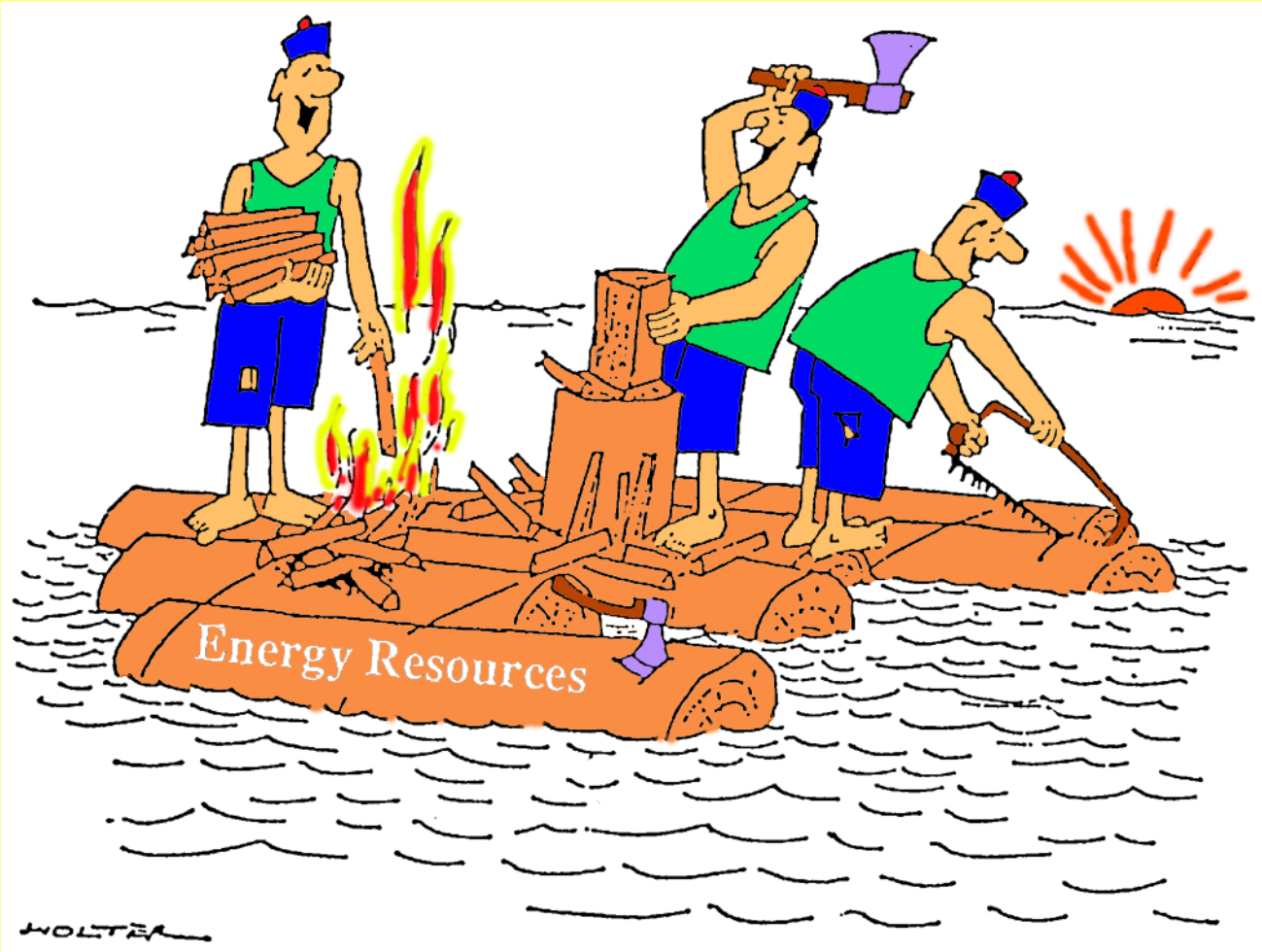
Semiconducting Polymer “Inks”

Color Variations: Band Gap Engineering

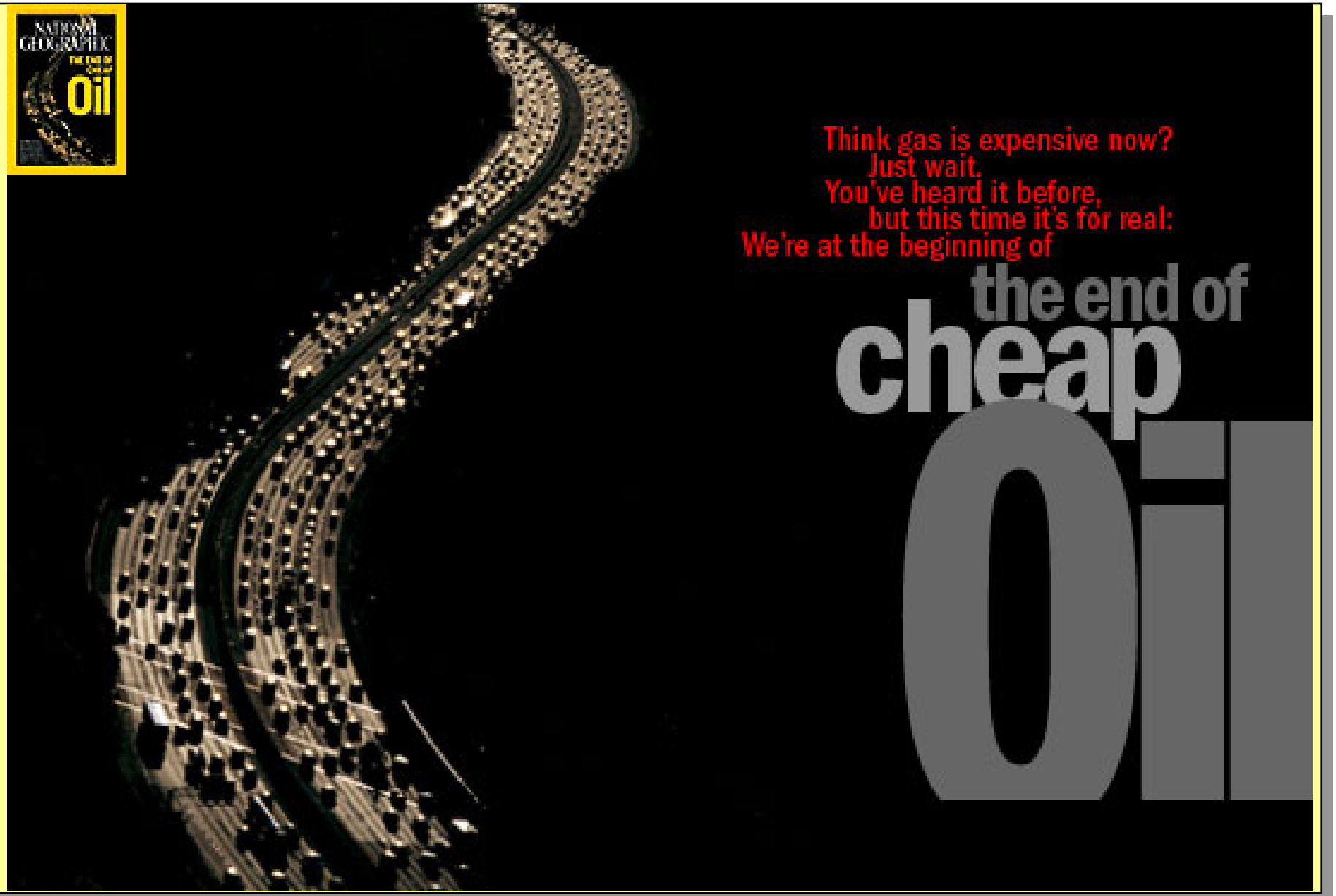




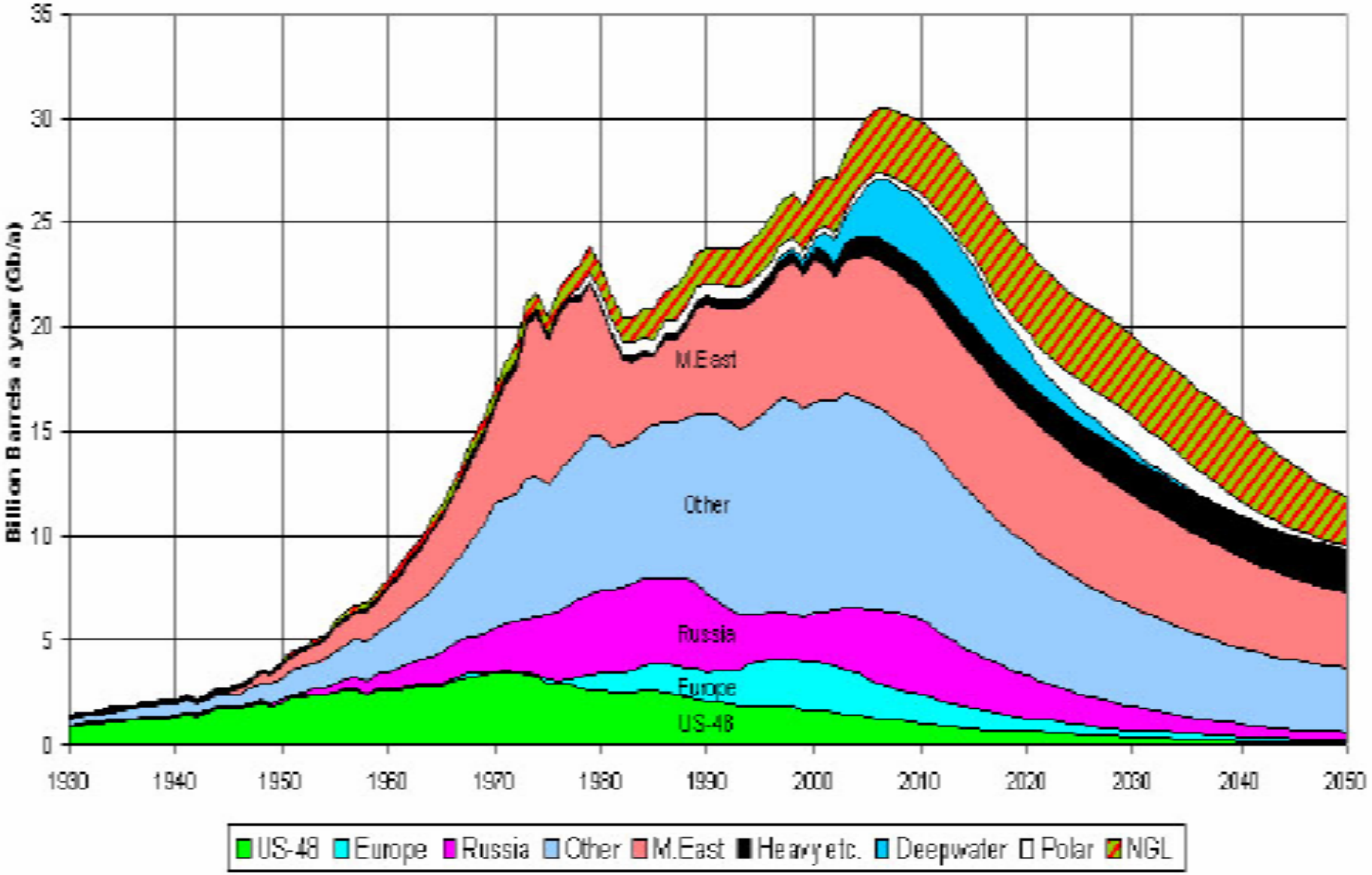
Happy Life



Scope


NATIONAL GEOGRAPHIC
Oil
Think gas is expensive now?
Just wait.
You've heard it before,
but this time it's for real:
We're at the beginning of
the end of
cheap
Oil

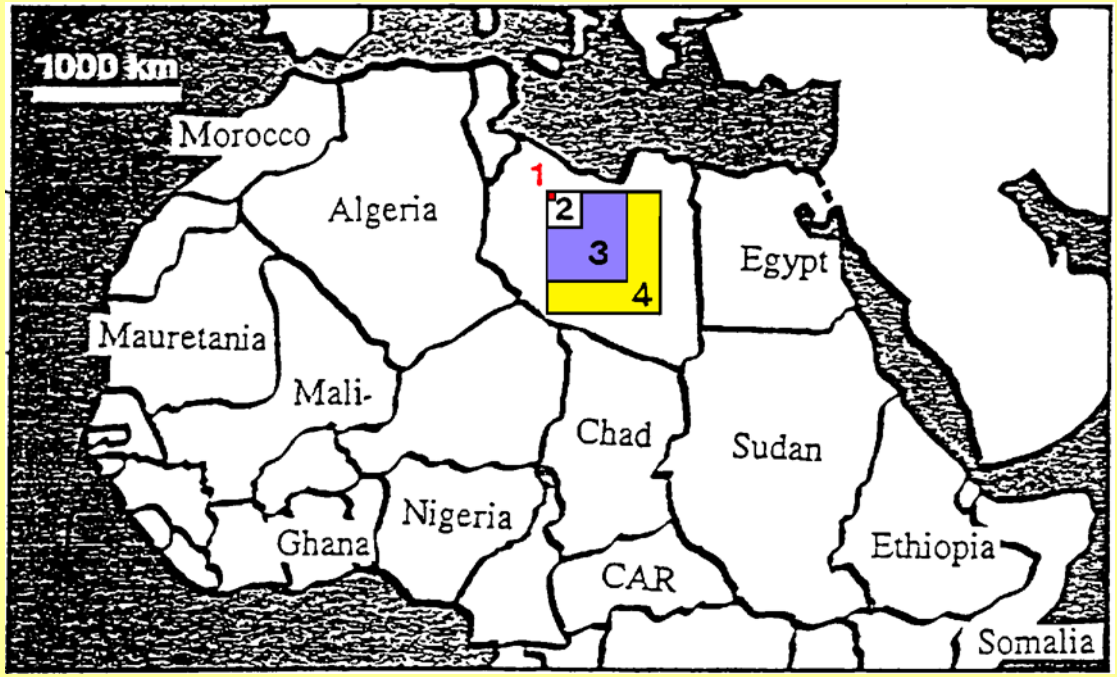
Scope


Billion Barrels a year (Gb/a)
35
30
25
20
15
10
5
0
1930
1940
1950
1960
1970
1980
1990
2000
2010
2020
2030
2040
2050
M.East
Other
Russia
Europe
US-48
US-48
Europe
Russia
Other
M.East
Heavy etc.
Deepwater
Polar
NGL

Photovoltaics

Required Land Areas

using 10 % efficient photovoltaic modules



Percentage of total Sahara area:

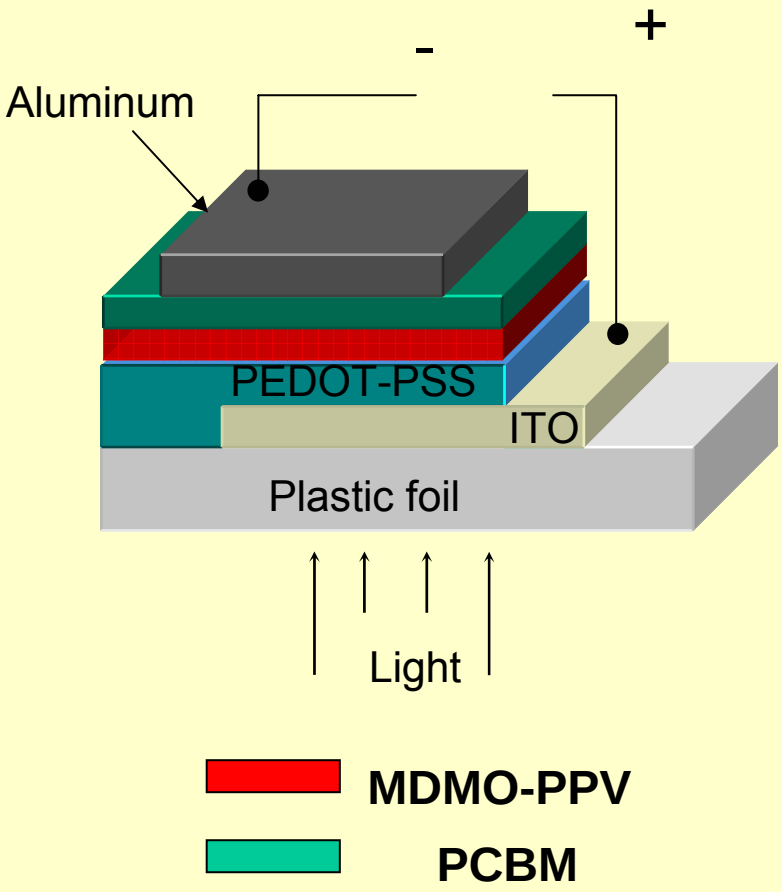
1	0.12 %
2	0.7 %
3	5.4 %
4	7.6 %

1 40 % of present annual end energy consumption of FRG ($3*10^{18}$ J)
2 50% of present end energy use of Western Europe ($1.8 * 10^{19}$ J)
3 50 % of present annual world energy consumption (10^{20} J)
4 50 % of extrapolated annual world energy consumption in 2030 ($2* 10^{19}$ J)

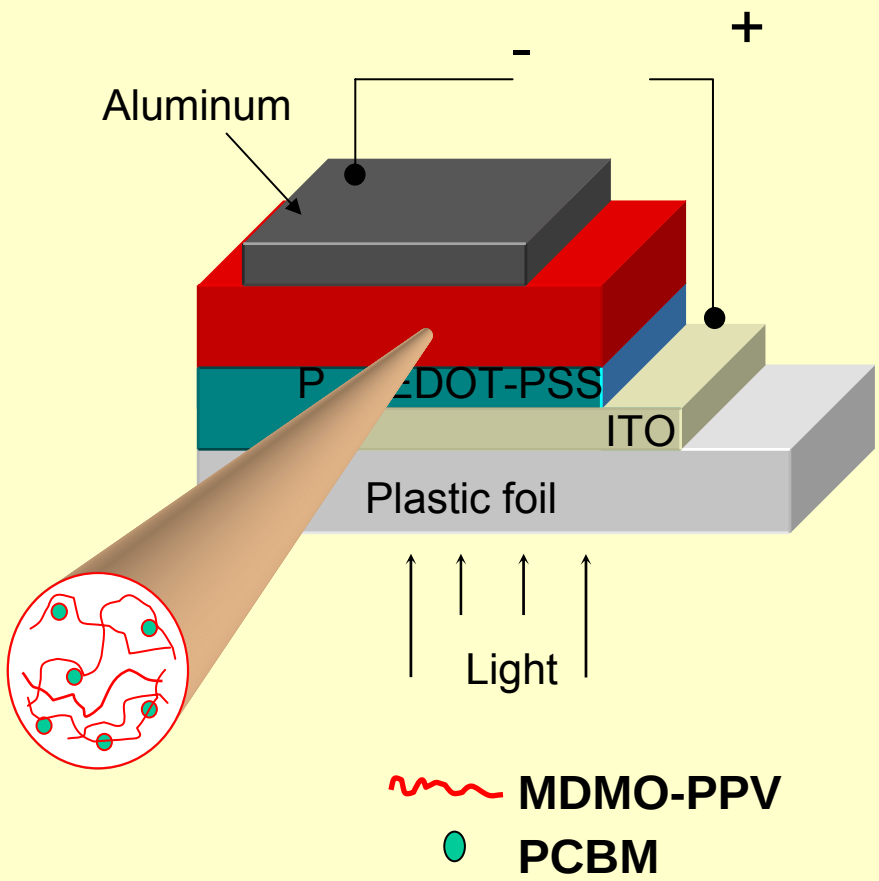
Arbeitskreis Alternativenergie Tübingen (Herausg.): "Energiepolitik vonunten", Fischer, Frankfurt/Main, 1982

Solar Cell Device Geometries

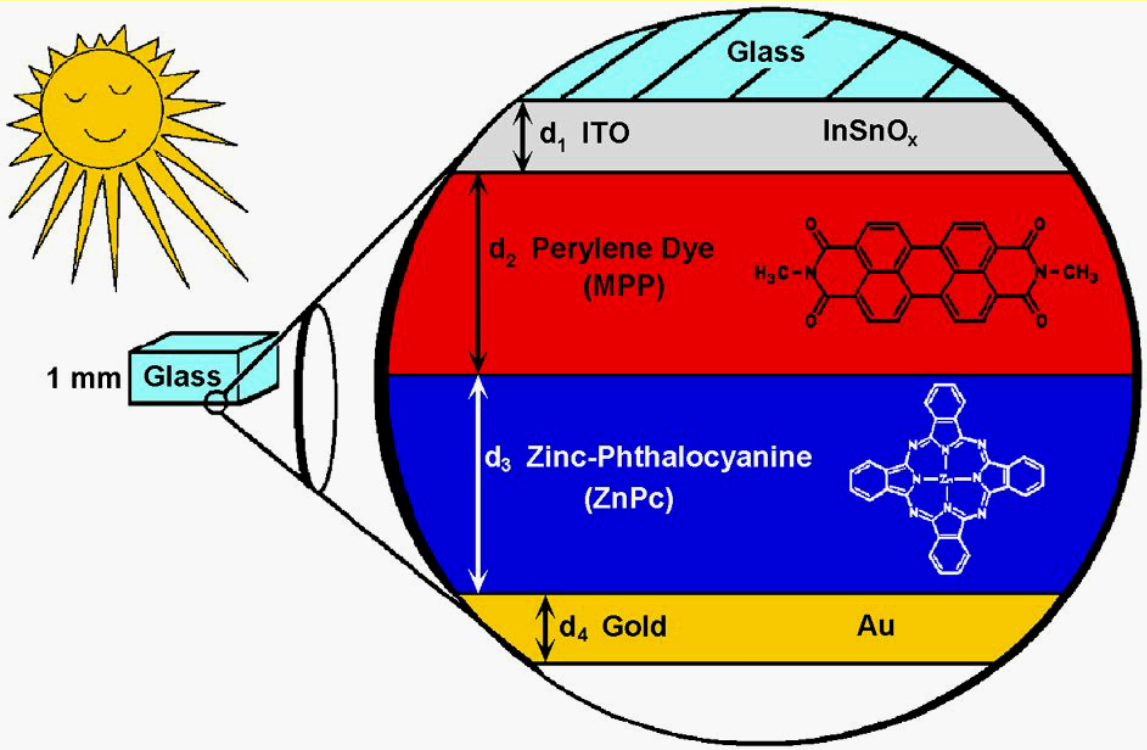
BILAYER



BULK HETEROJUNCTION



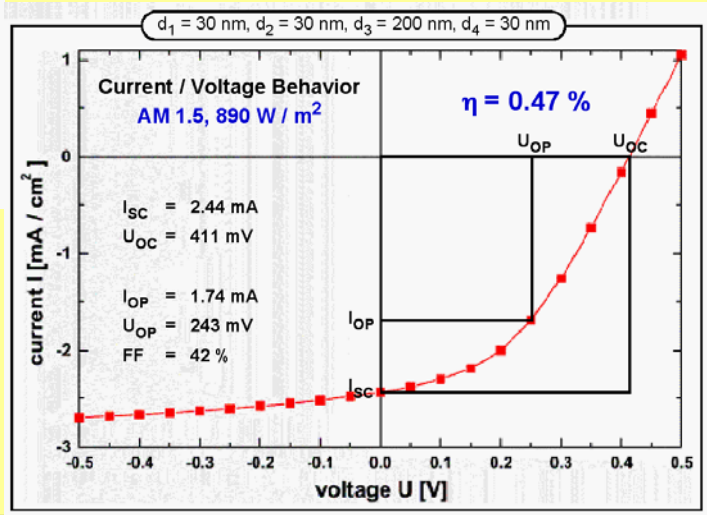
Small Molecular Organic Solar Cells



"Tang- Cell"

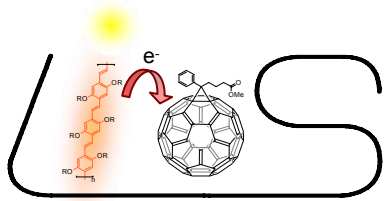
C. W. Tang

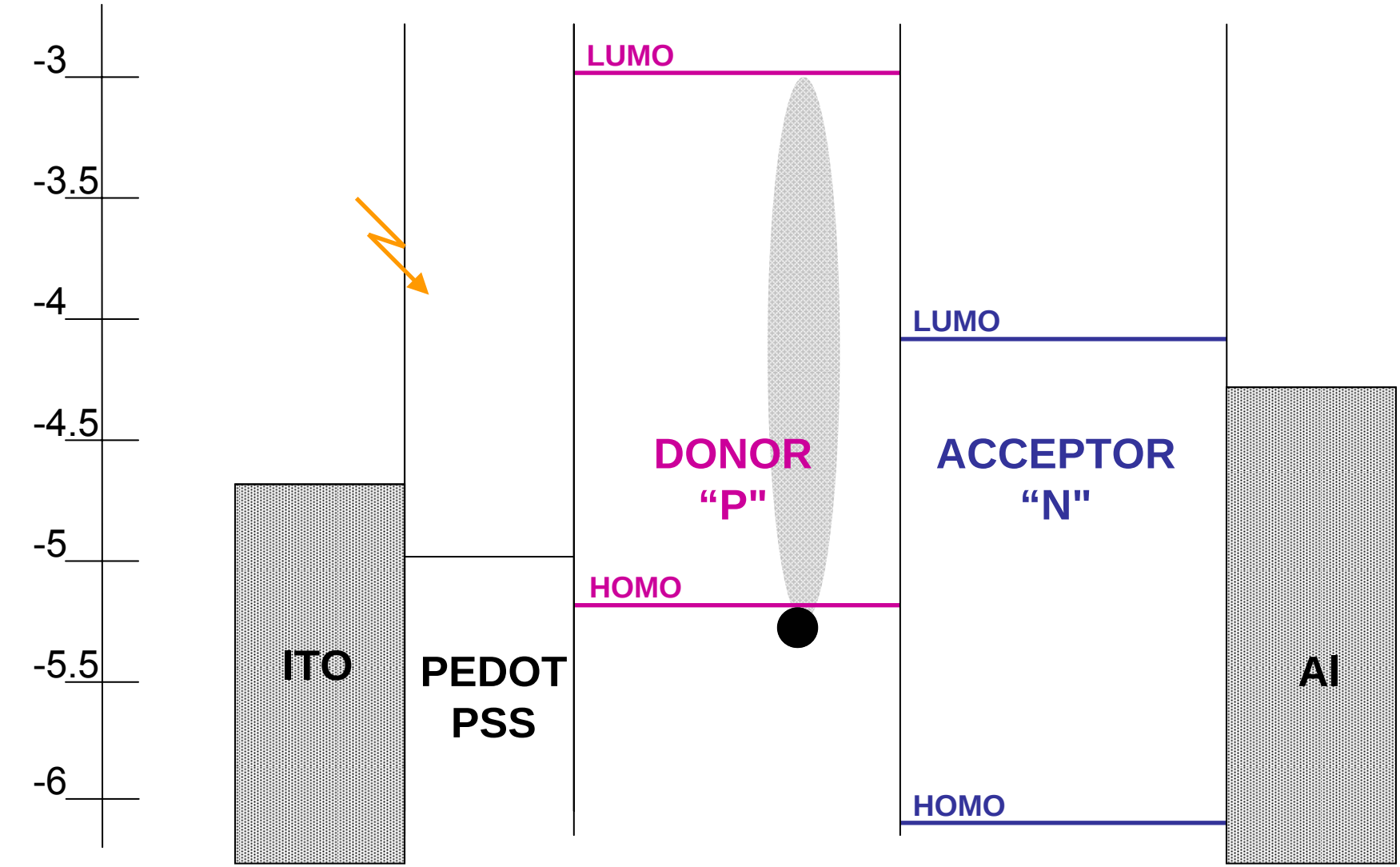
Appl.Phys. Lett. 48(86)183



WORKING PRINCIPLE

Bi-layer polymer solar cells



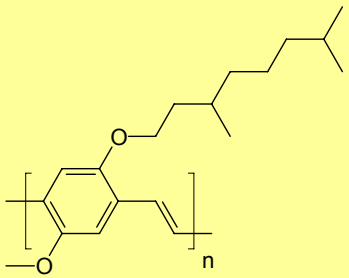


Photoinduced Electron Transfer From Conjugated Polymers onto Fullerenes

Photoinduced Charge Generation

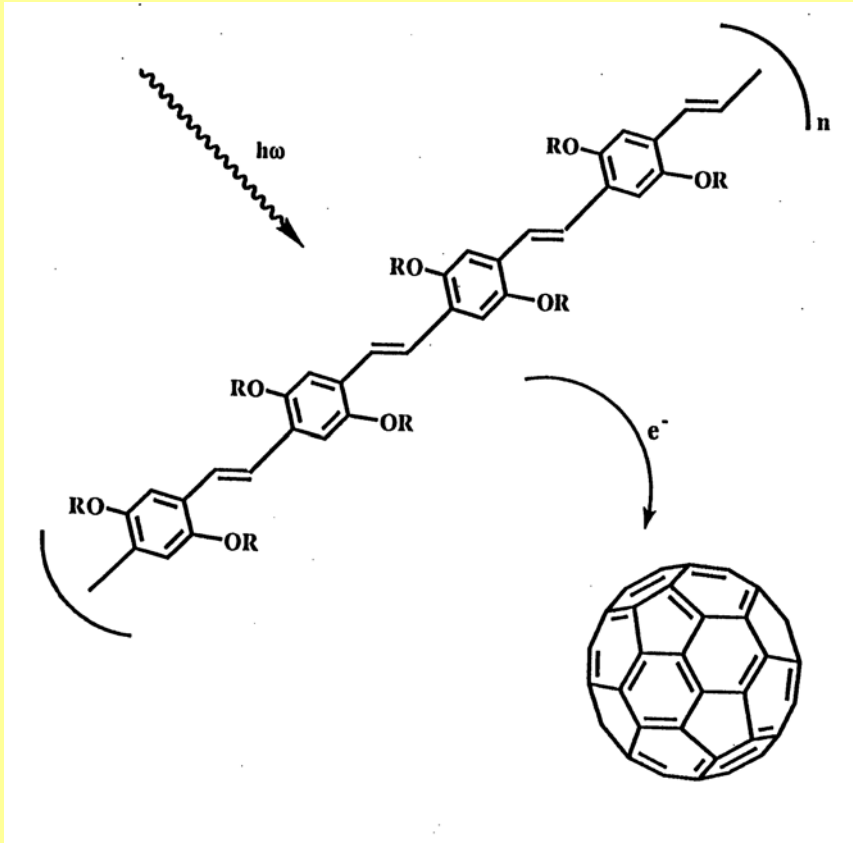
An ultrafast **e$^-$ transfer** occurs between Conjugated Polymer / Fullerene composites upon illumination. The transition time is less than 40 fs. The Internal Quantum efficiency of charge generation is therefore ~100%.

DONOR

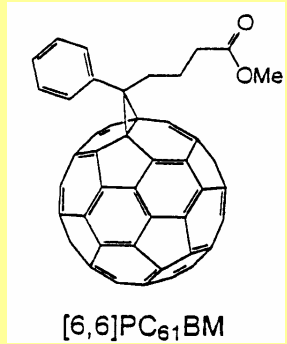


MDMO PPV

3,7 - dimethyloctyloxy methyloxy PPV



ACCEPTOR

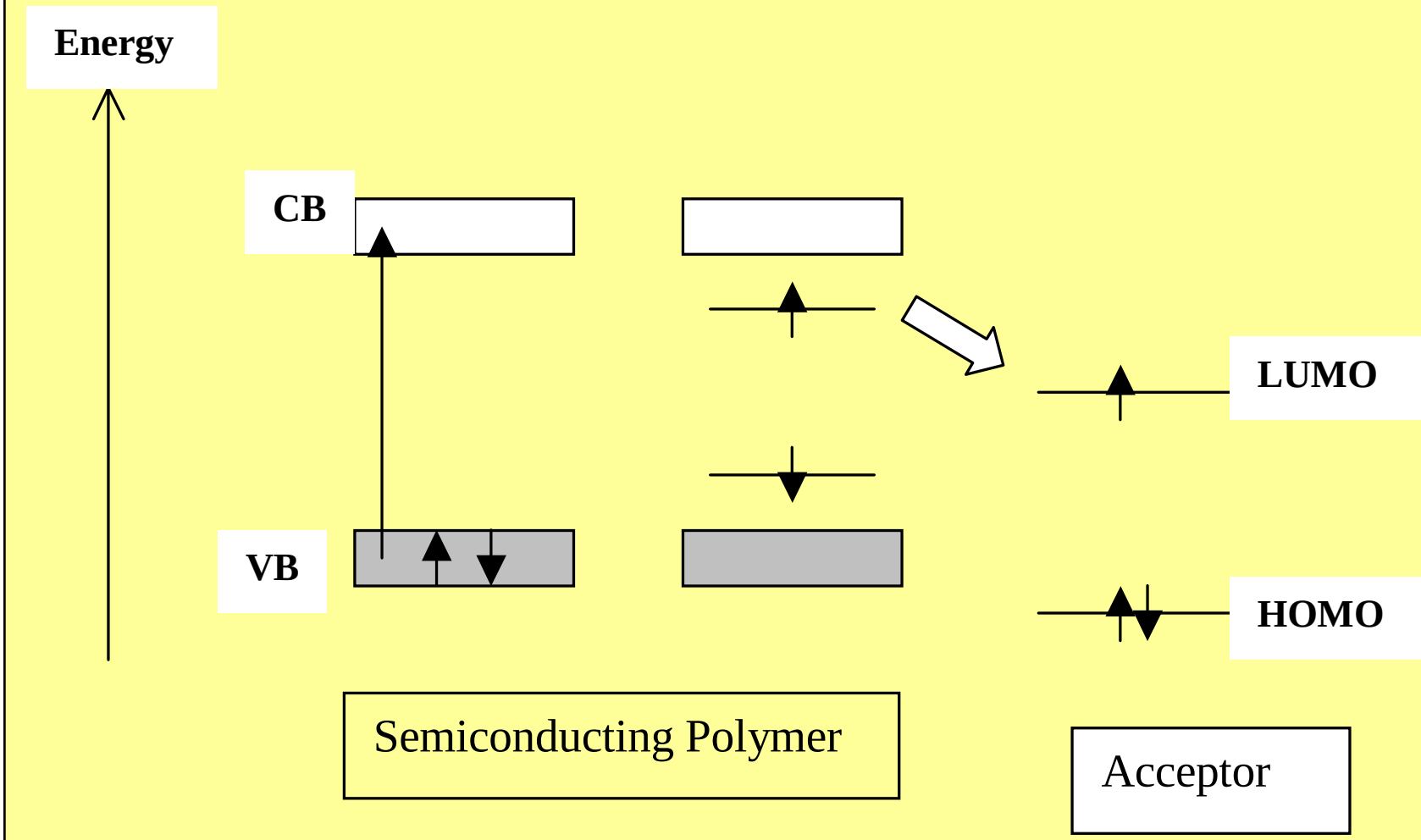


PCBM

1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C_{61}

N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl., *Science* **258**, 1474 (1992)

Photoinduced Charge Generation



N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl., *Science* **258**, 1474 (1992)

Intermediate Steps in Photoinduced Electron Transfer

$D + A + h\upsilon \rightarrow {}^{1,3}D^* + A$ *π- π* excitation of the donor*

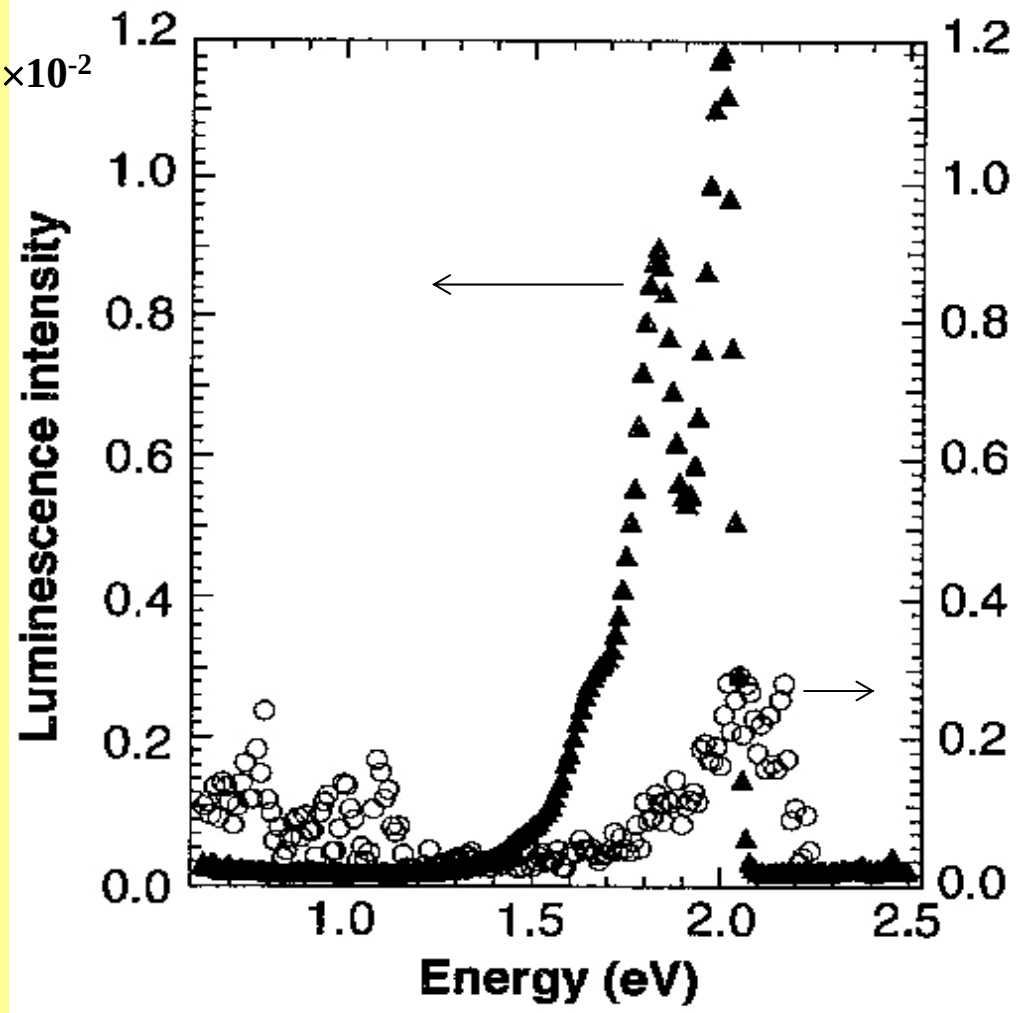
${}^{1,3}D^* + A \rightarrow {}^{1,3}(D\ldots A)^*$ *Excitation delocalised on D-A complex, (exciplex formation)*

${}^{1,3}(D\ldots A)^* \rightarrow {}^{1,3}(D^{\delta+}\ldots A^{\delta-})^*$ *Formation of charge transfer complex (Mulliken type)*

${}^{1,3}(D^{\delta+}\ldots A^{\delta-})^* \rightarrow {}^{1,3}(D^{+}\ldots A^{-})^*$ *Radical pair formation*

${}^{1,3}(D^{+}\ldots A^{-})^* \rightarrow D^{+} + A^{-}$ *Complete charge separation*

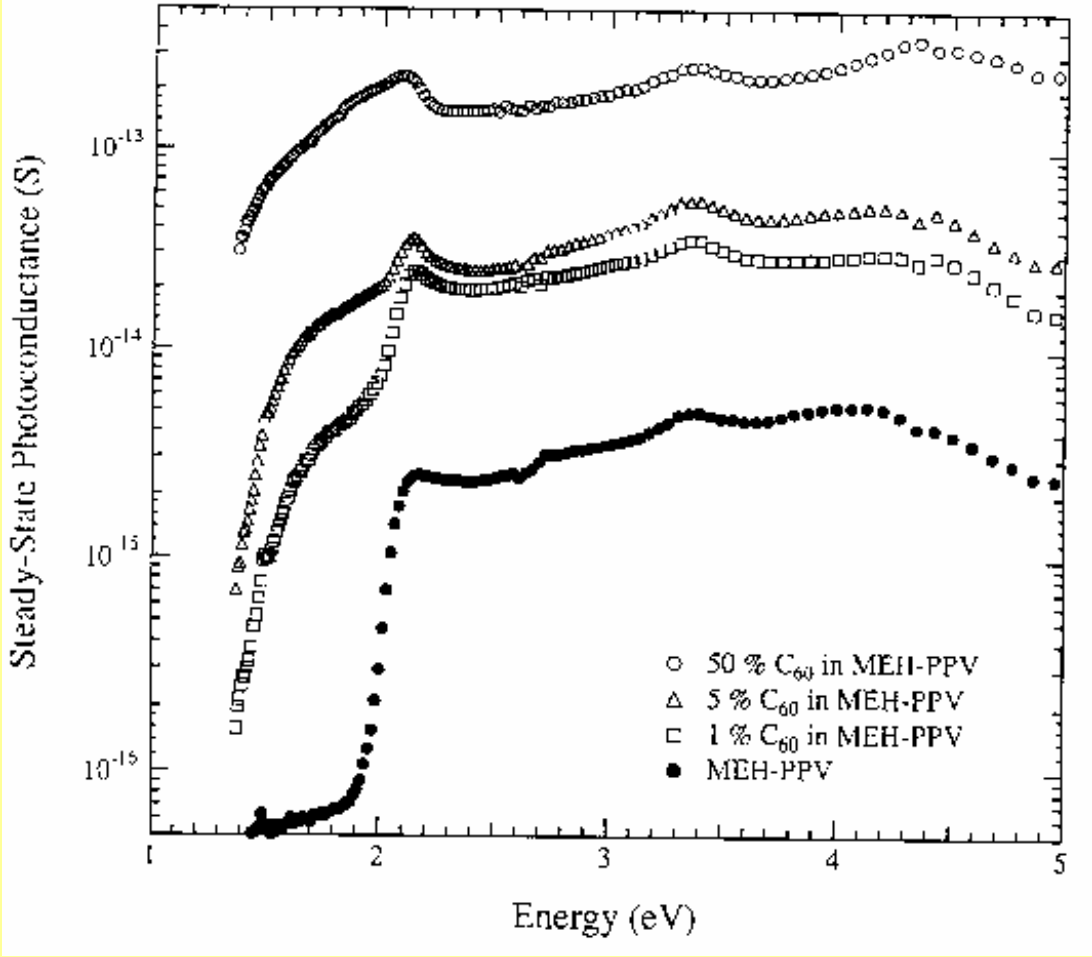
Photoinduced Charge Generation



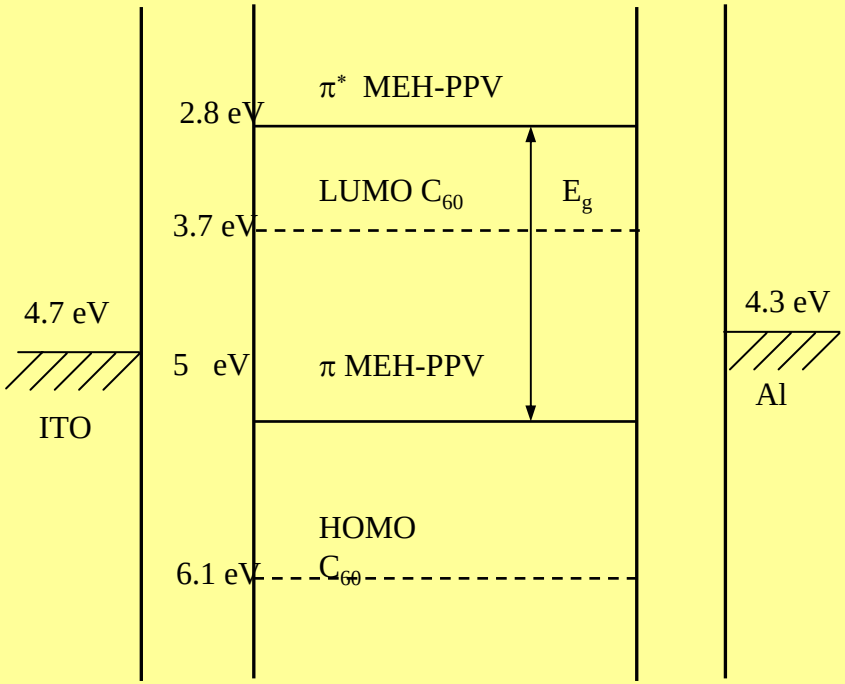
N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl., *Science* **258**, 1474 (1992)

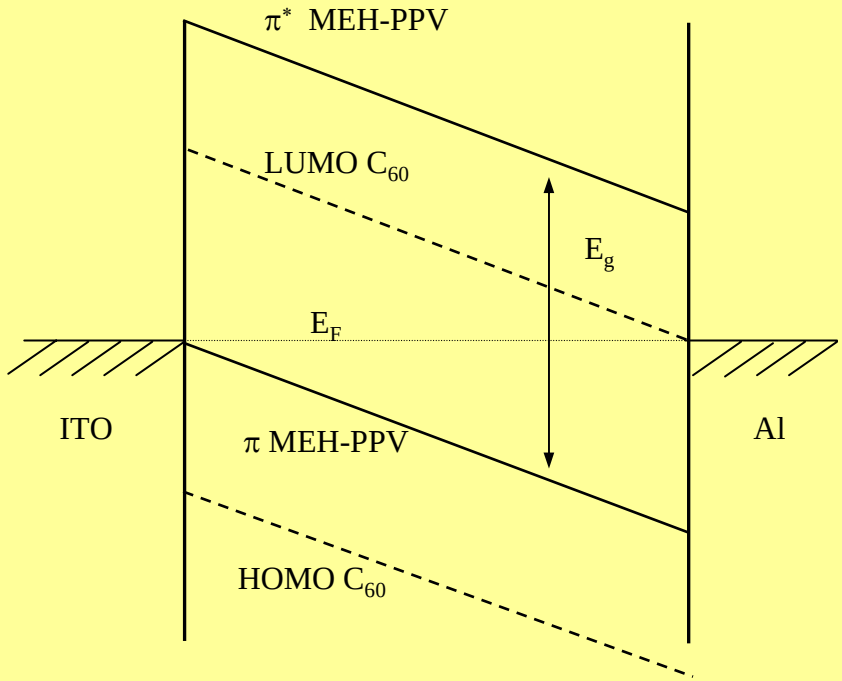
Enhanced Photoconductivity

Steady state photoconductivity of conjugated polymer is enhanced by several orders of magnitude upon adding C60. Changhee Lee *et al.*, *Phys. Rev*. **B 48**, 15425 (1993)



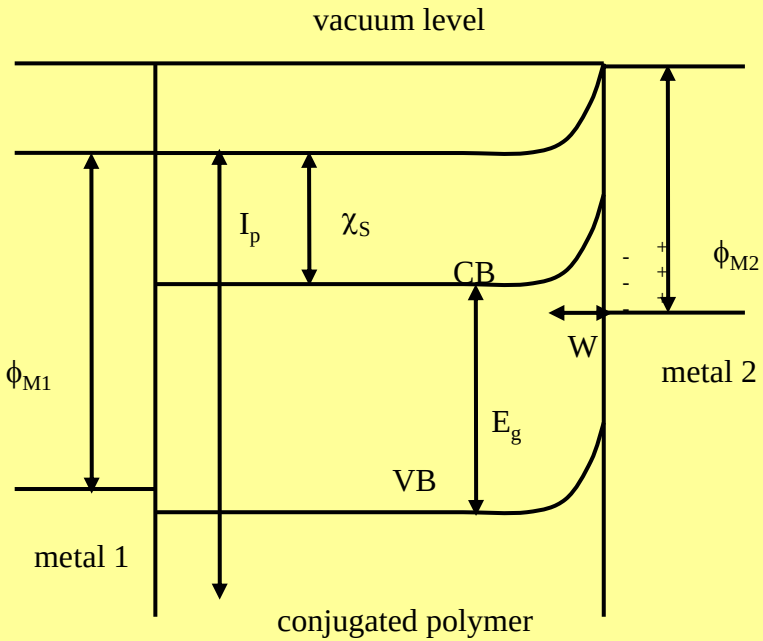
Schematic Band Diagram

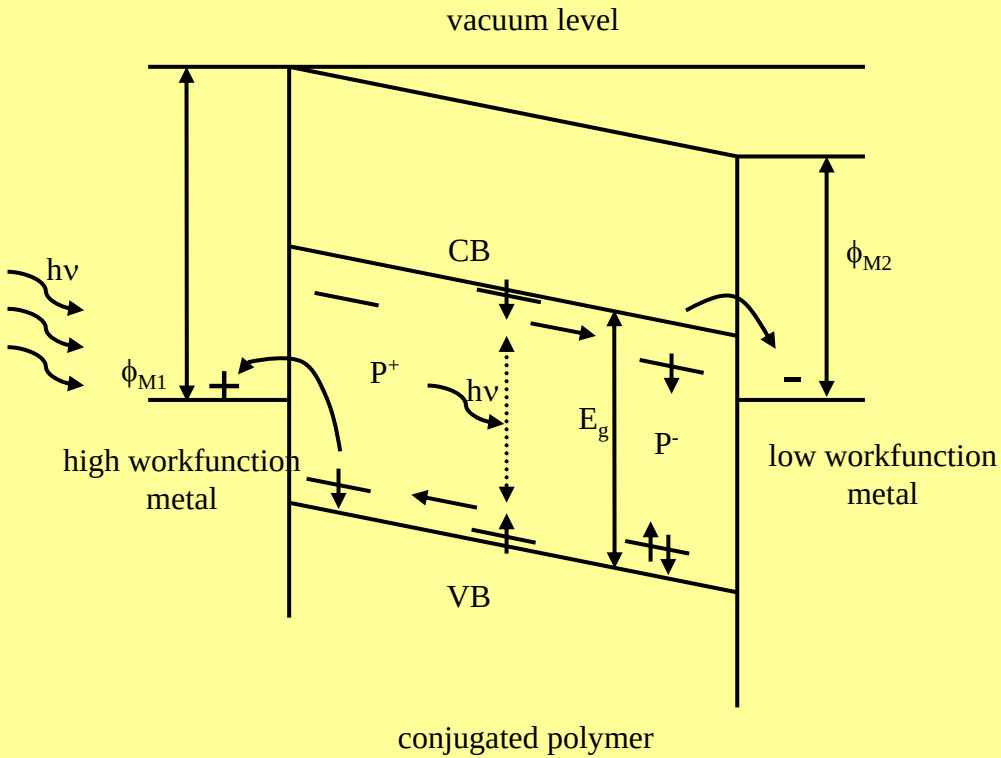




Metal-Insulator-Metal (MIM) picture implies the field of assymetric metal electrodes (All interface effects neglected!)

Band Models





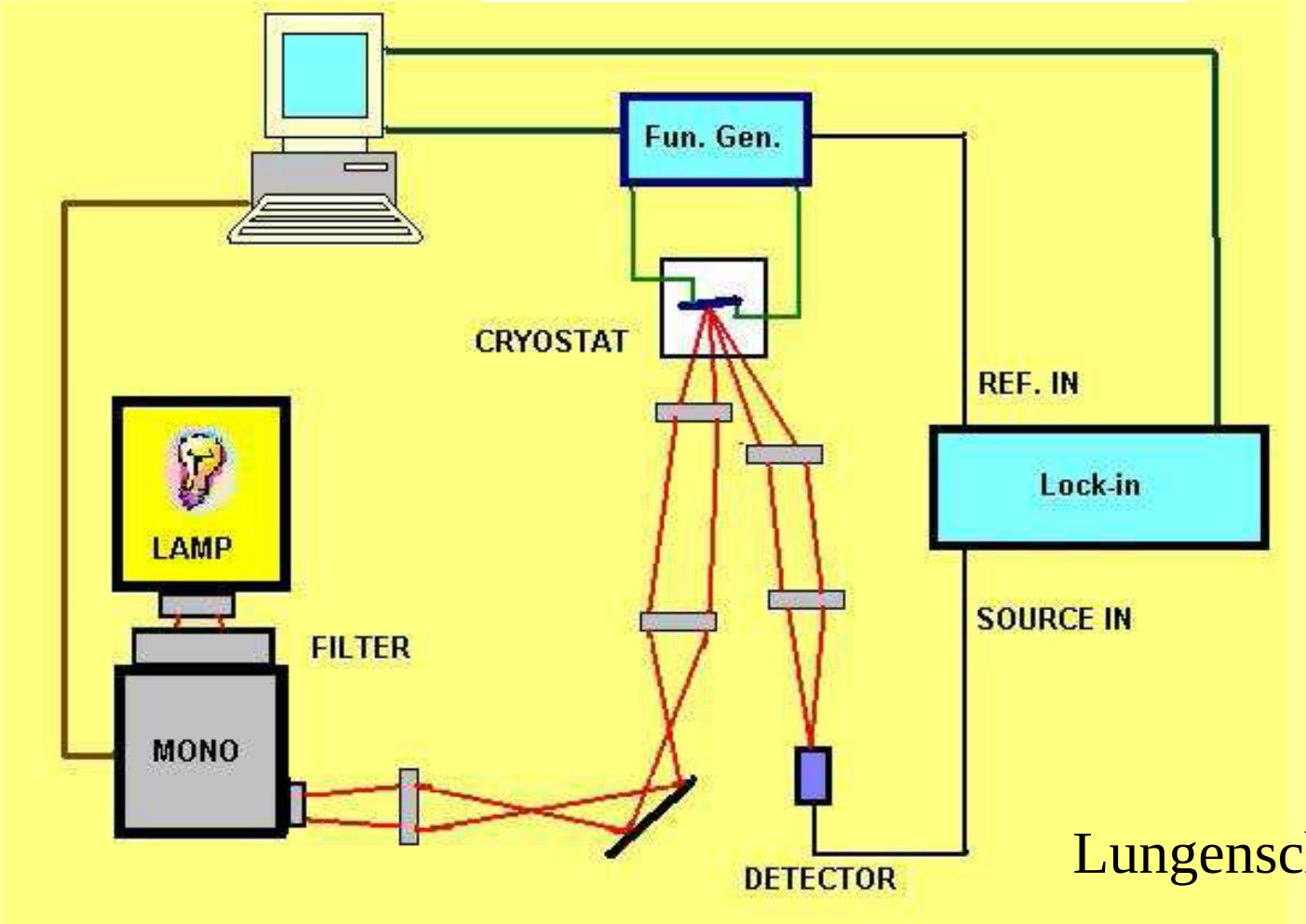
Schottky Contacts for high Impurities
$n >> 10^{16}cm^{-3}$

MIM Picture for low Impurities
$n << 10^{16}cm^{-3}$

Electroabsorption Studies

A measure of the internal electric field in the device

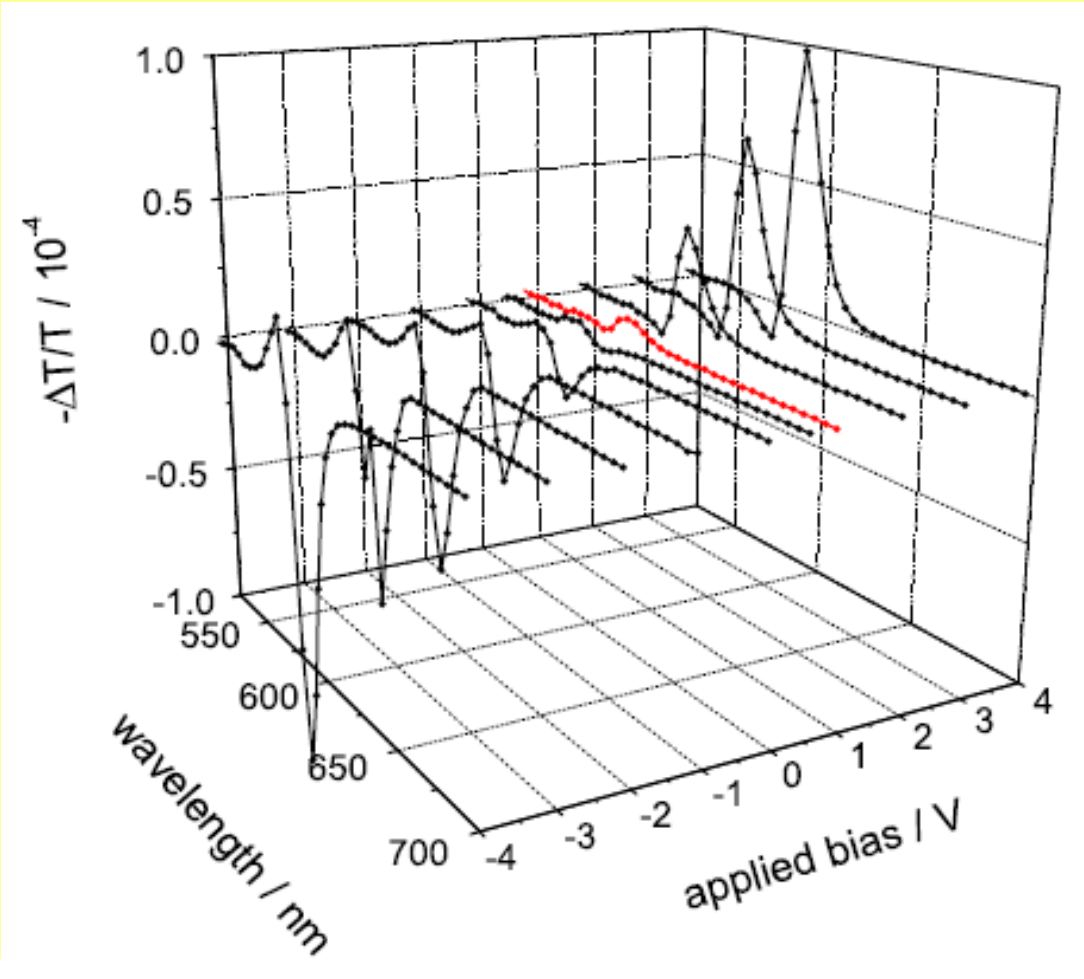
$$\frac{|\Delta T|}{T}(h\nu) \propto (V_{dc} - V_{int}) \cdot V_{ac}$$



Lungenschmied et al., 2006

Electroabsorption Studies

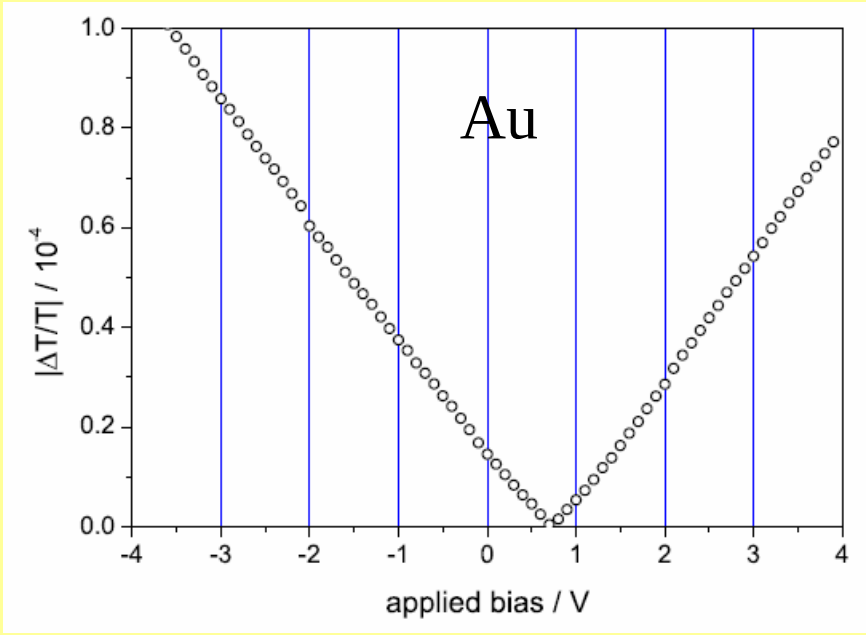
A measure of the internal electric field in the device

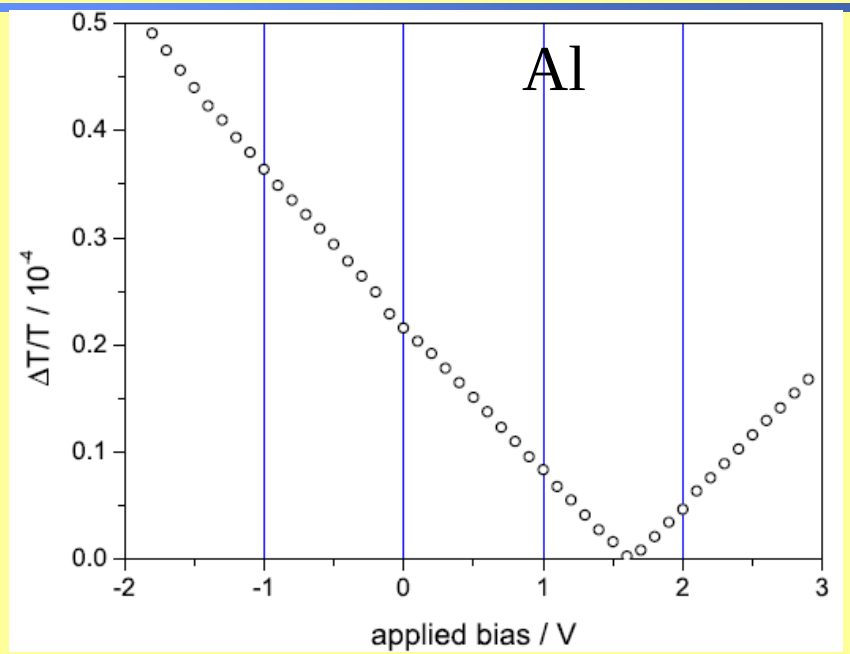


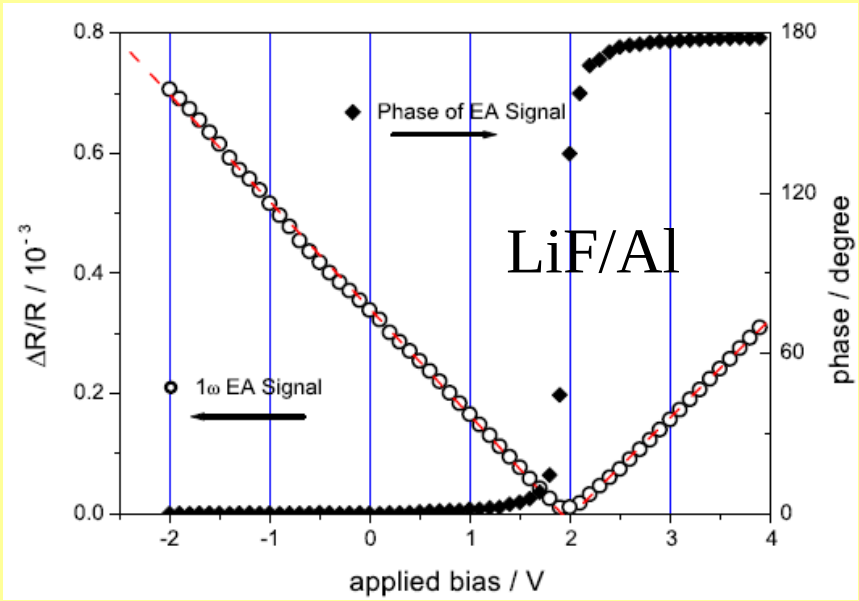
$$\frac{|\Delta T|}{T}(h\nu) \propto (V_{dc} - V_{int}) \cdot V_{ac}$$

Lungenschmied et al., 2006

Electroabsorption Studies





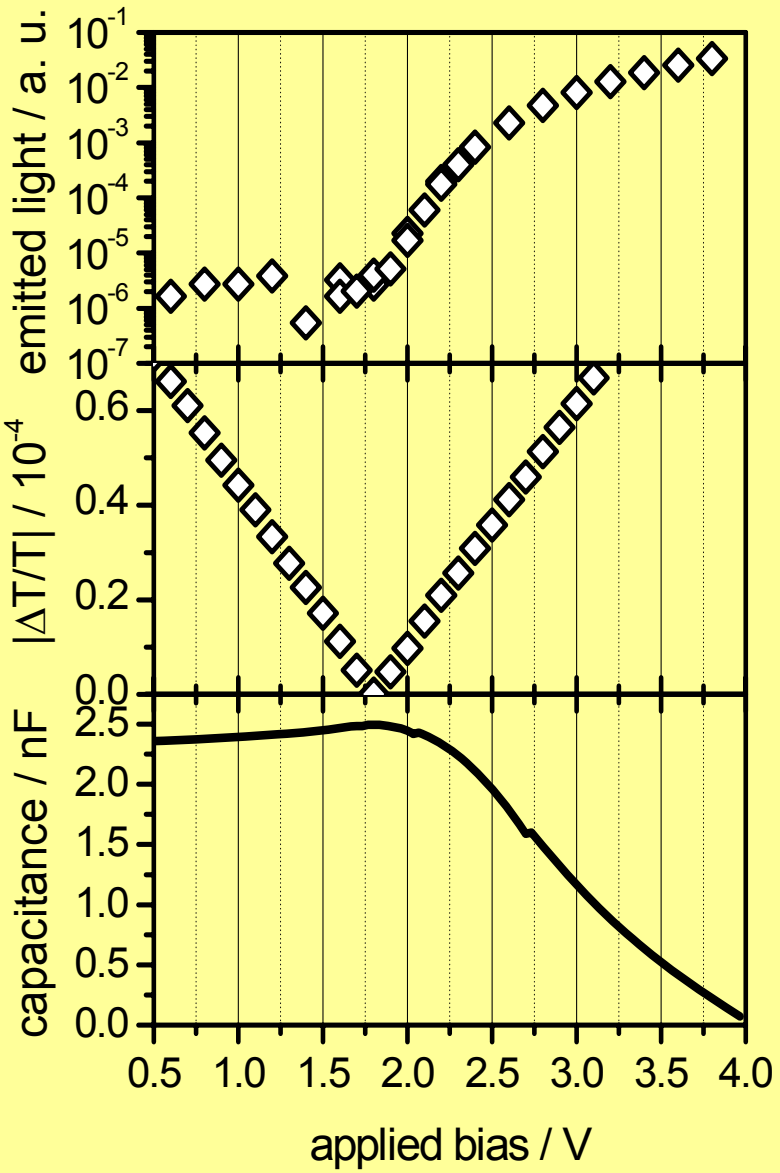


ITO/PEDOT-PSS/MDMO-PPV/Metal

100 K Electroabsorption Vac = 1V
@590nm probed

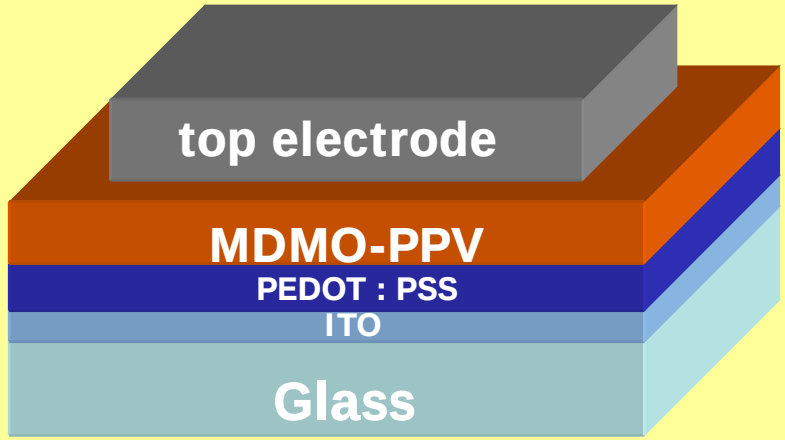
Lungenschmied et al., 2006

Summary for MDMO-PPV



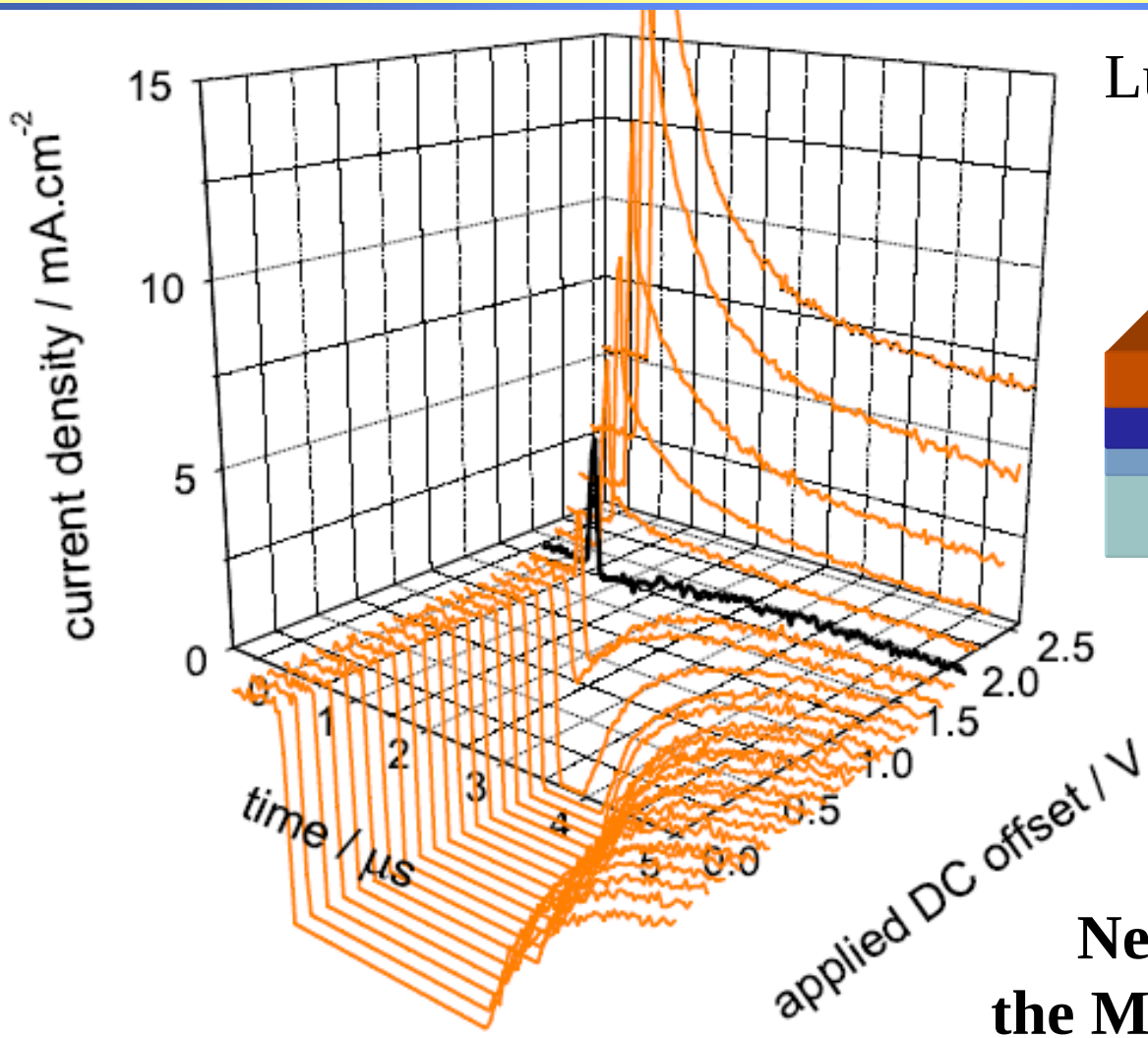
Lungenschmied et al., 2006

ITO/PEDOT-PSS/MDMO-PPV/LiF/Al

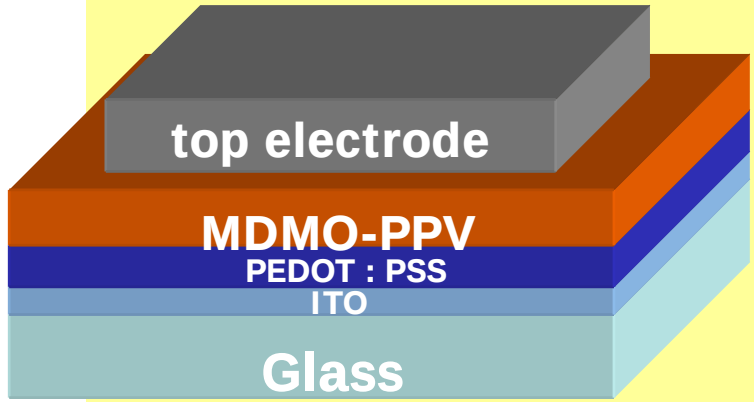


Below the built-in field the MDMO-PPV diodes behave like field driven MIM diodes

Summary for MDMO-PPV



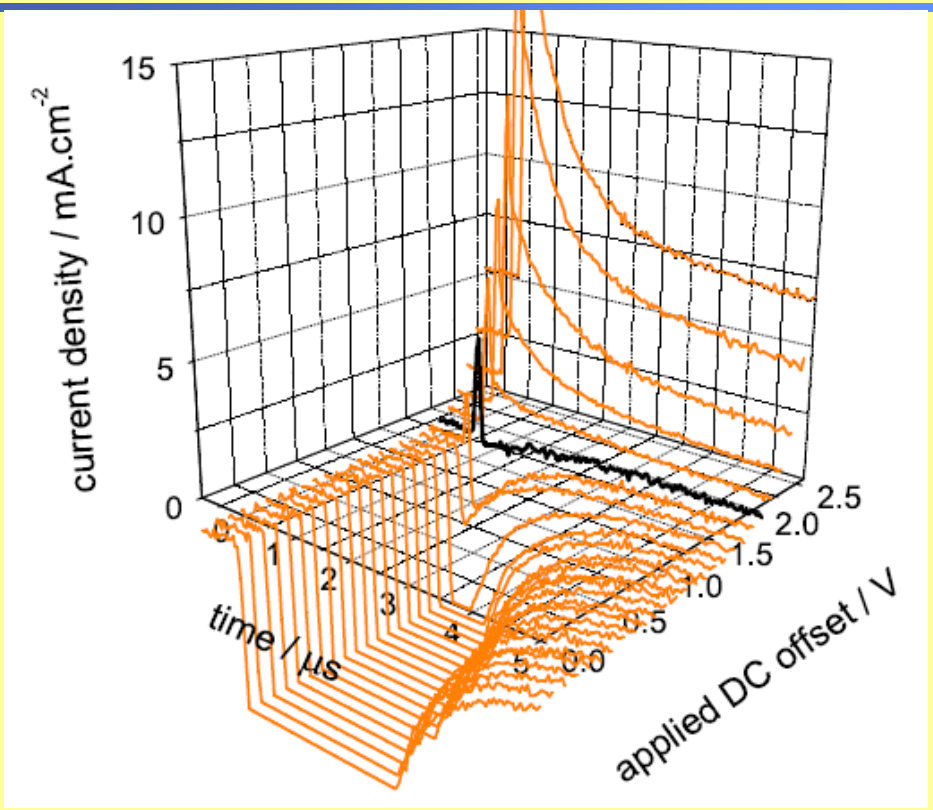
Lungenschmied et al., 2006



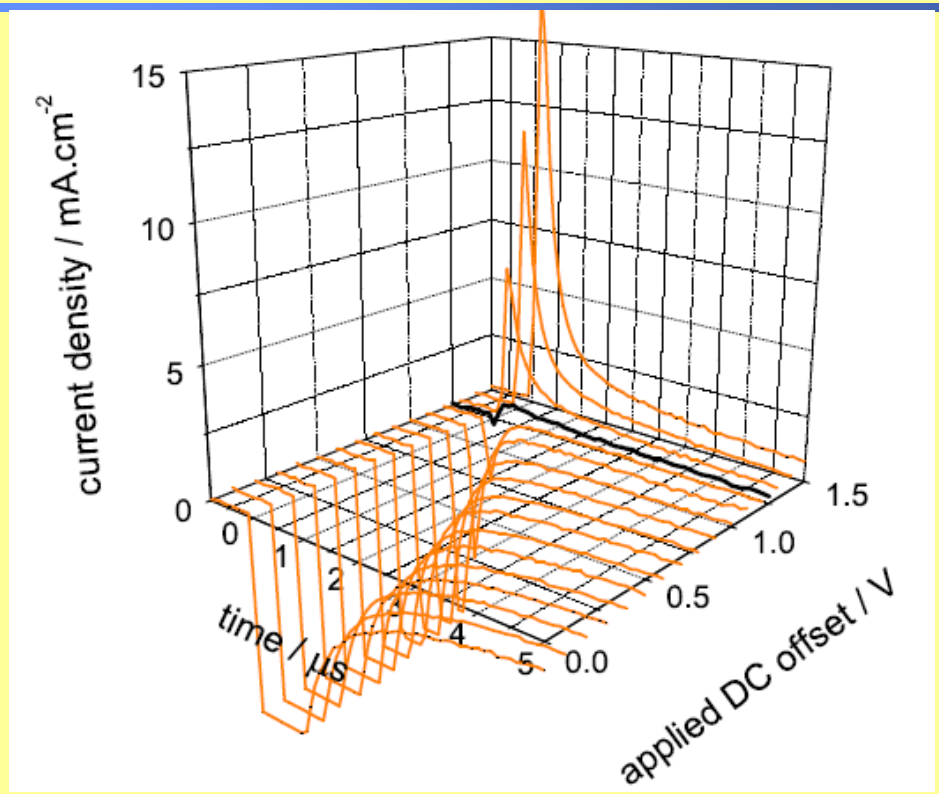
Near the built-in voltage the MDMO-PPV diodes show No photocurrent transients

ITO/PEDOT-PSS/MDMO-PPV/LiF/Al

MDMO-PPV mixed with 1% C60



ITO/PEDOT-PSS/MDMO-PPV/LiF/Al



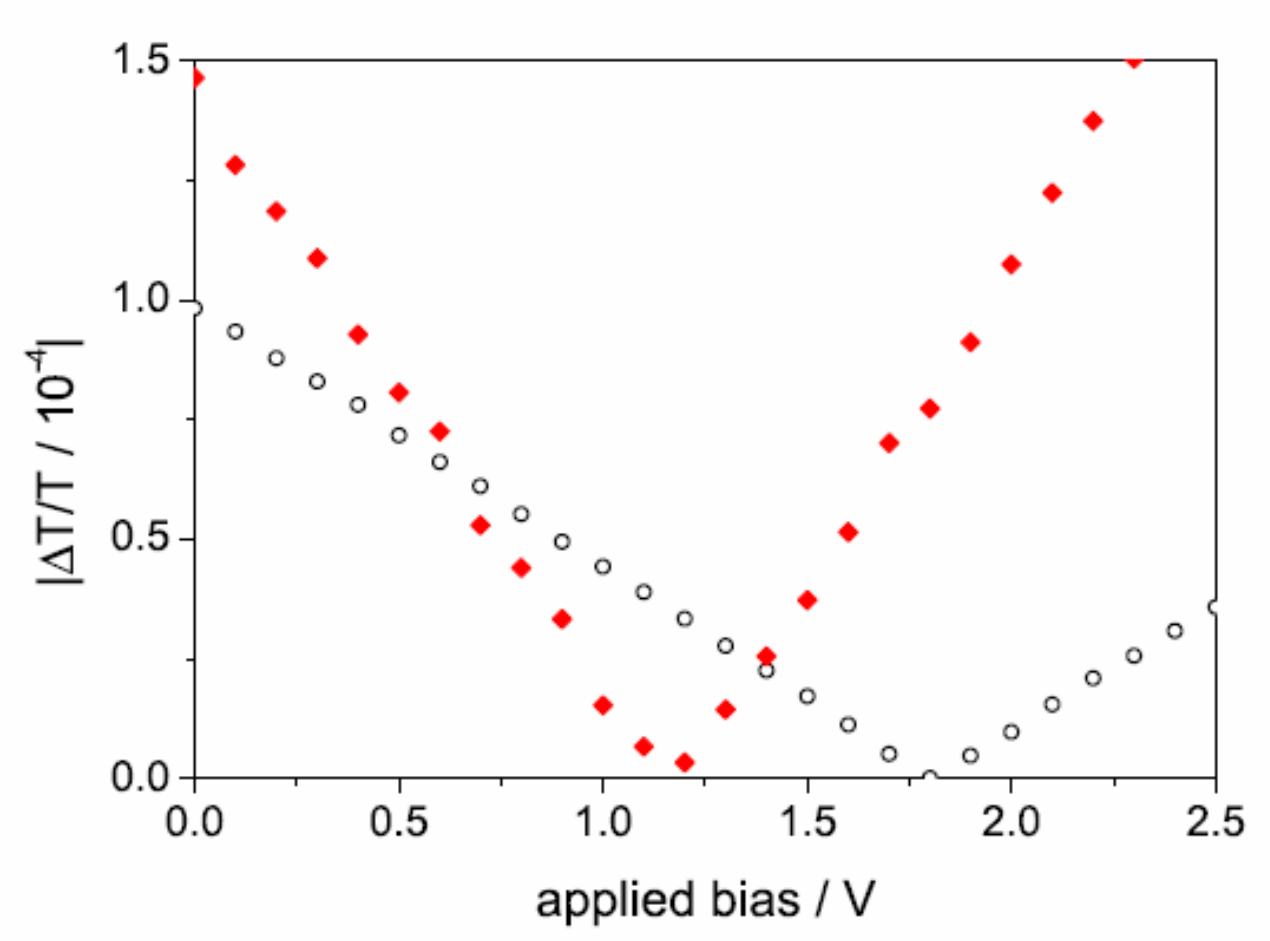
ITO/PEDOT-PSS/MDMO-PPV+1% PCBM/LiF/Al

Built-in field is reduced by nearly 0.8 V
upon addition of 1% PCBM into MDMO-PPV

C. Lungenschmied, G. Dennler, H. Neugebauer, N.S. Sariciftci, E. Ehrenfreund
Applied Physics Letters 89 (2006), 223519

MDMO-PPV mixed with 1% C60

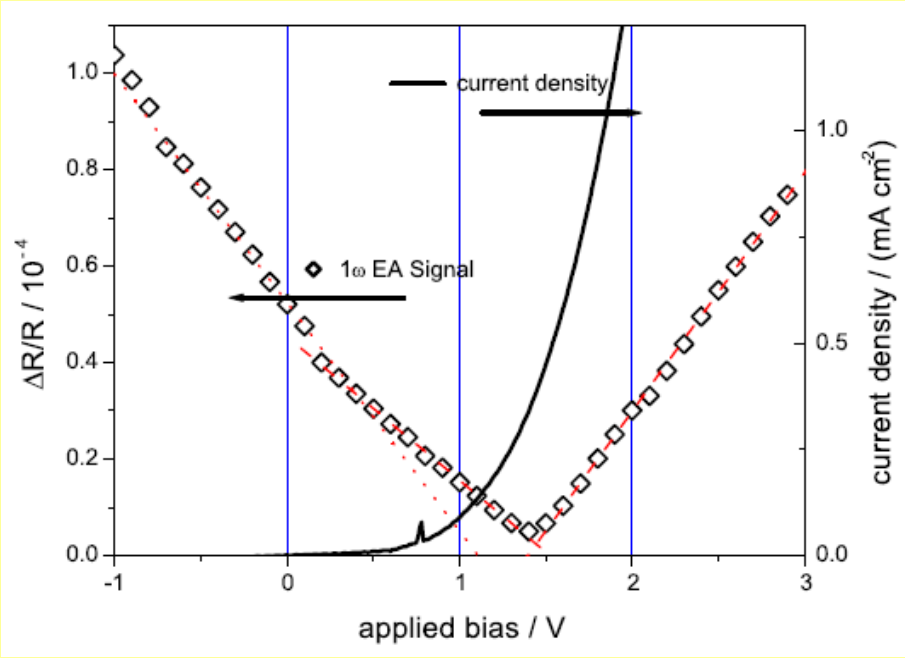
Internal field is reduced by nearly 1 V
upon addition of 1% PCBM into MDMO-PPV

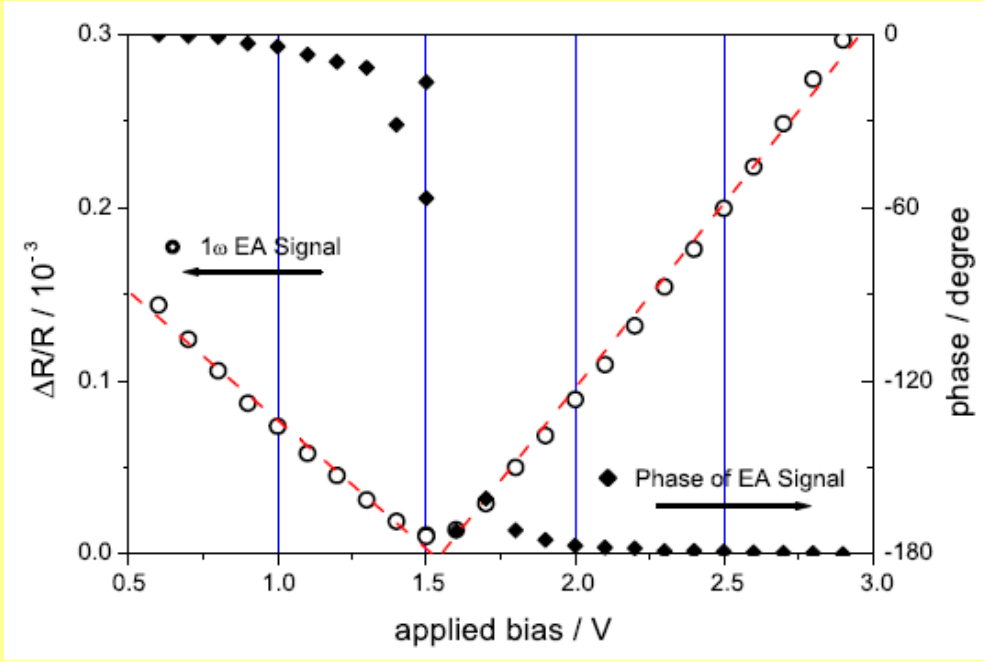


C. Lungenschmied, G. Dennler, H. Neugebauer, N.S. Sariciftci, E. Ehrenfreund
Applied Physics Letters 89 (2006), 223519

What about P3HT ?

Internal field in P3HT diodes is nearly independent to LiF insertion





ITO/PEDOT-PSS/P3HT/Al

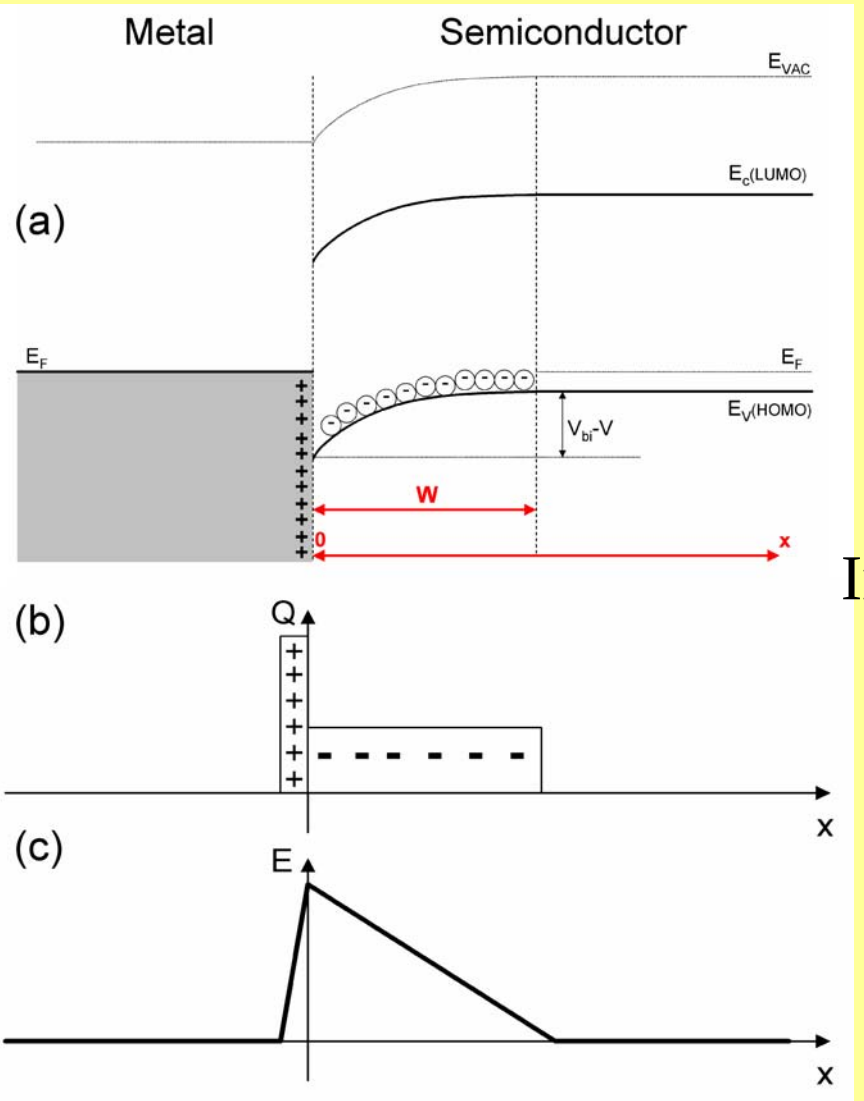
ITO/PEDOT-PSS/P3HT/LiF/Al

Measured @ 640nm and 77 K

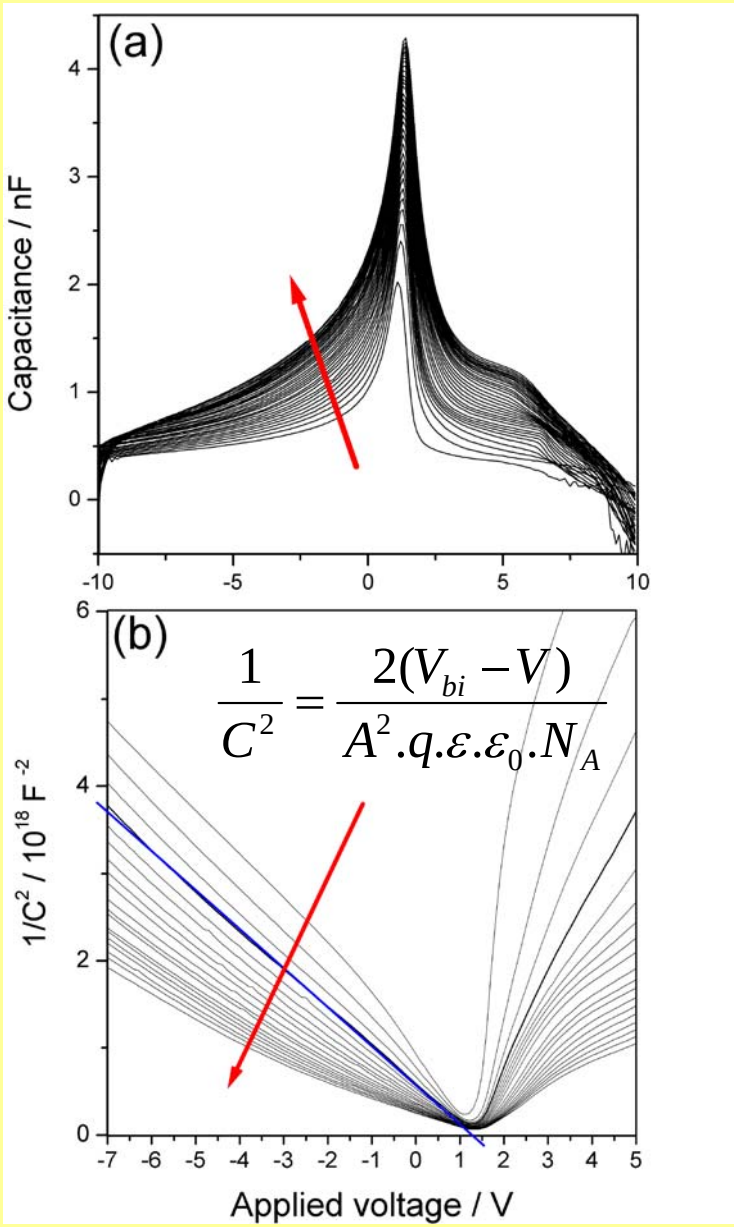
SCHOTTKY JUNCTION FORMATION IS PROBABLE IN P3HT DIODES !

C. Lungenschmied (2006)

Schottky Junction in P3HT Devices ?



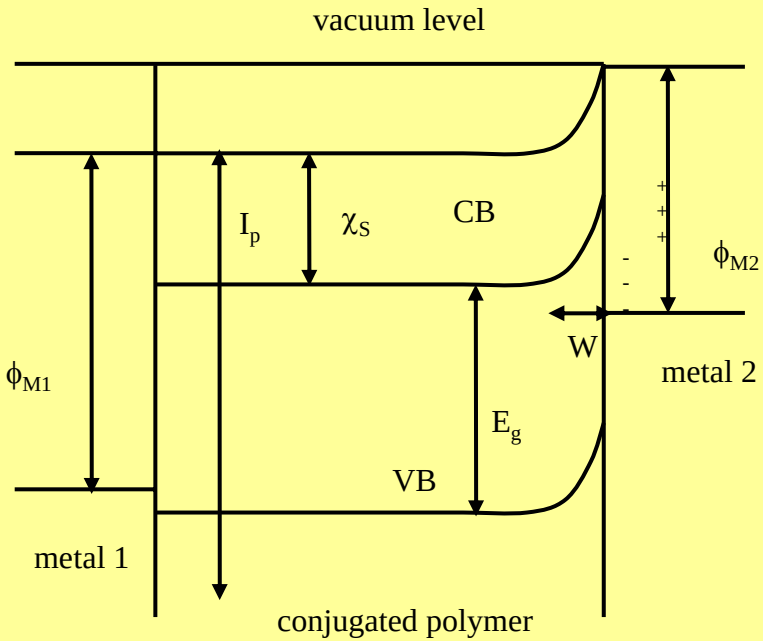
In the dark:
YES !

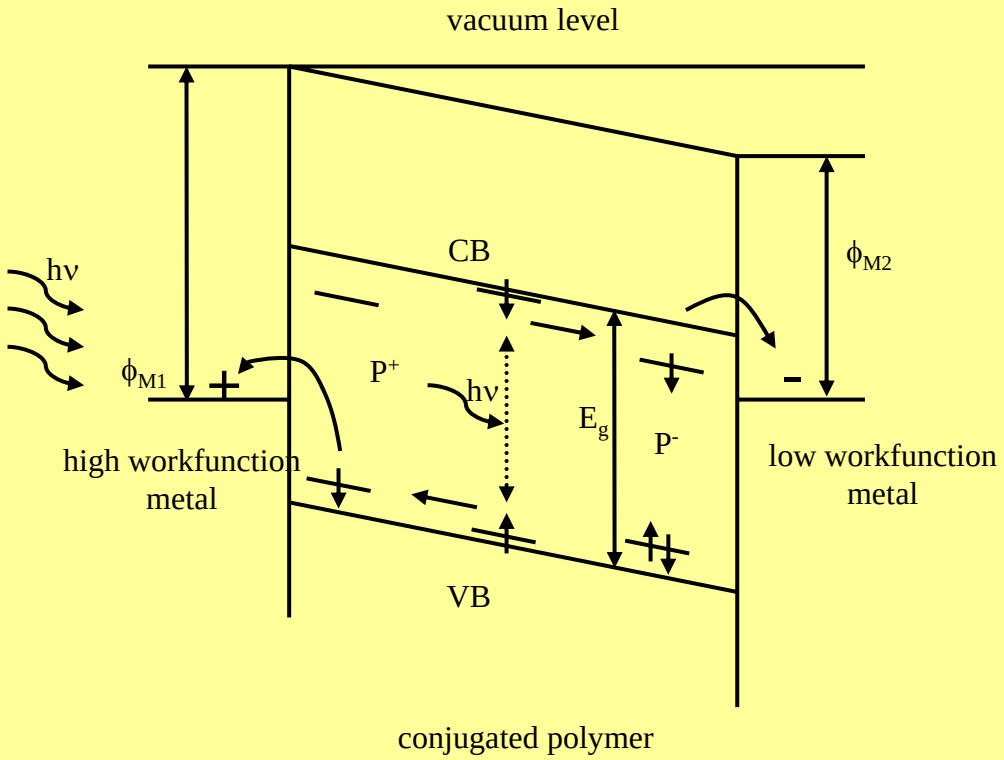


G. Dennler, C. Lungenschmied, N.S. Sariciftci, R. Schwoediauer, S. Bauer, H. Reiss
Applied Physics Letters 87 (2005), 163501

Band Models Revisited

In the dark or at low light intensities!



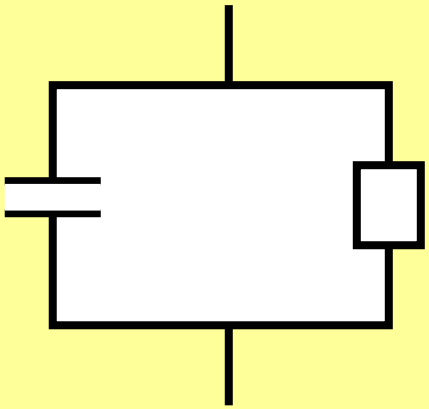


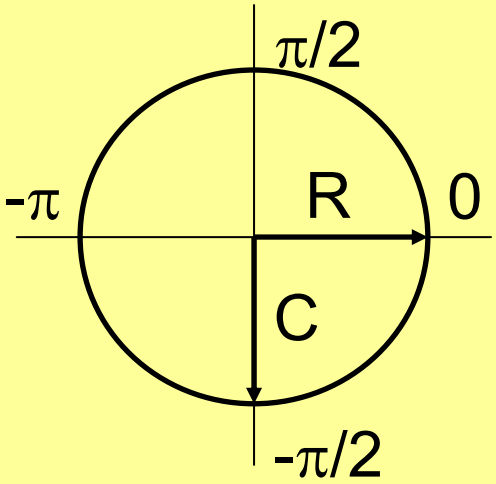
Schottky Contacts for Air Exposed (O_2 doped) ITO/PEDOT/ P3HT/Al

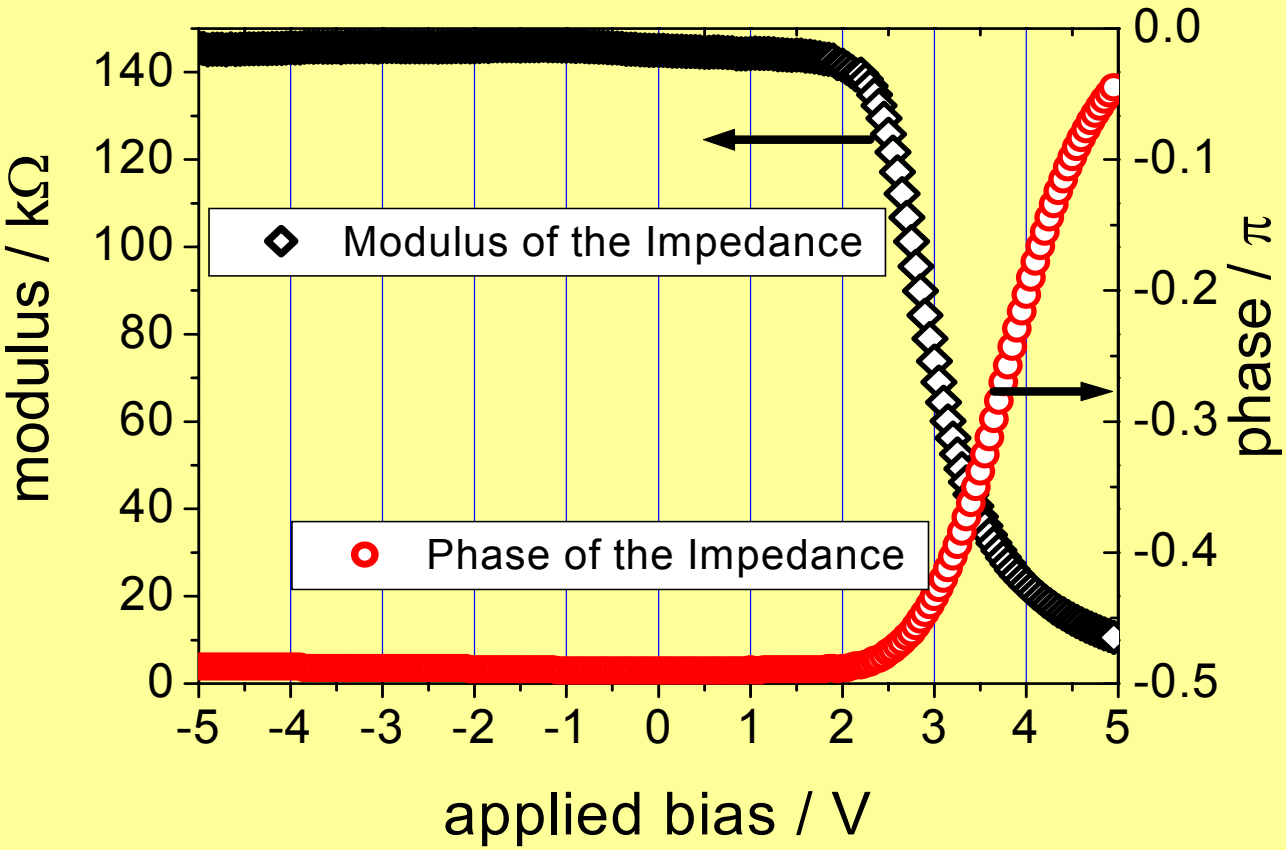
MIM Picture for ITO/PEDOT/MDMO-PPV/Metal System

Impedance spectroscopy

Lungenschmied et al., 2006







Charge injection

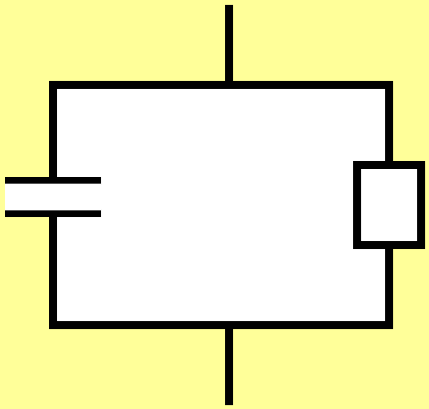
Capacitor (Phase –π/2) ⟶ Resistor (Phase 0)

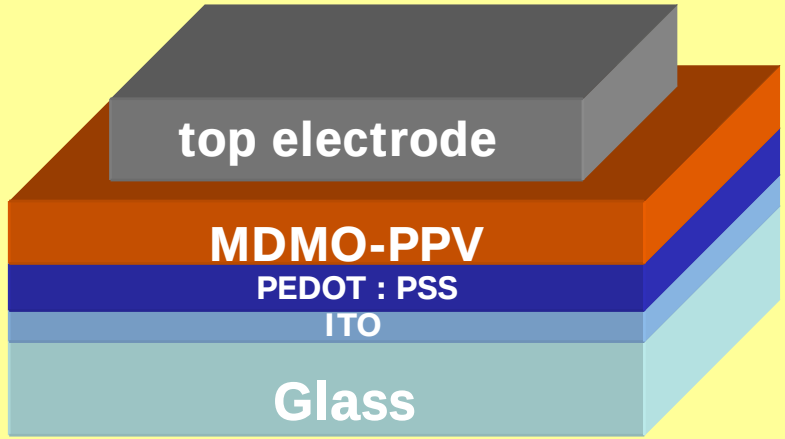
Impedance spectroscopy: Basic Notations

Ehrenfreund, Lungenschmied et al., 2007

Admittance: $$Y(\omega) = \frac{i_{ac}(\omega)}{v_{ac}(\omega)} = \mathrm{Re}\,Y(\omega) + i \cdot \mathrm{Im}\,Y(\omega)$$

Cp –Rp Circuit $$Y(\omega) = \frac{i_{ac}(\omega)}{v_{ac}(\omega)} = G(\omega) + i\omega C(\omega)$$

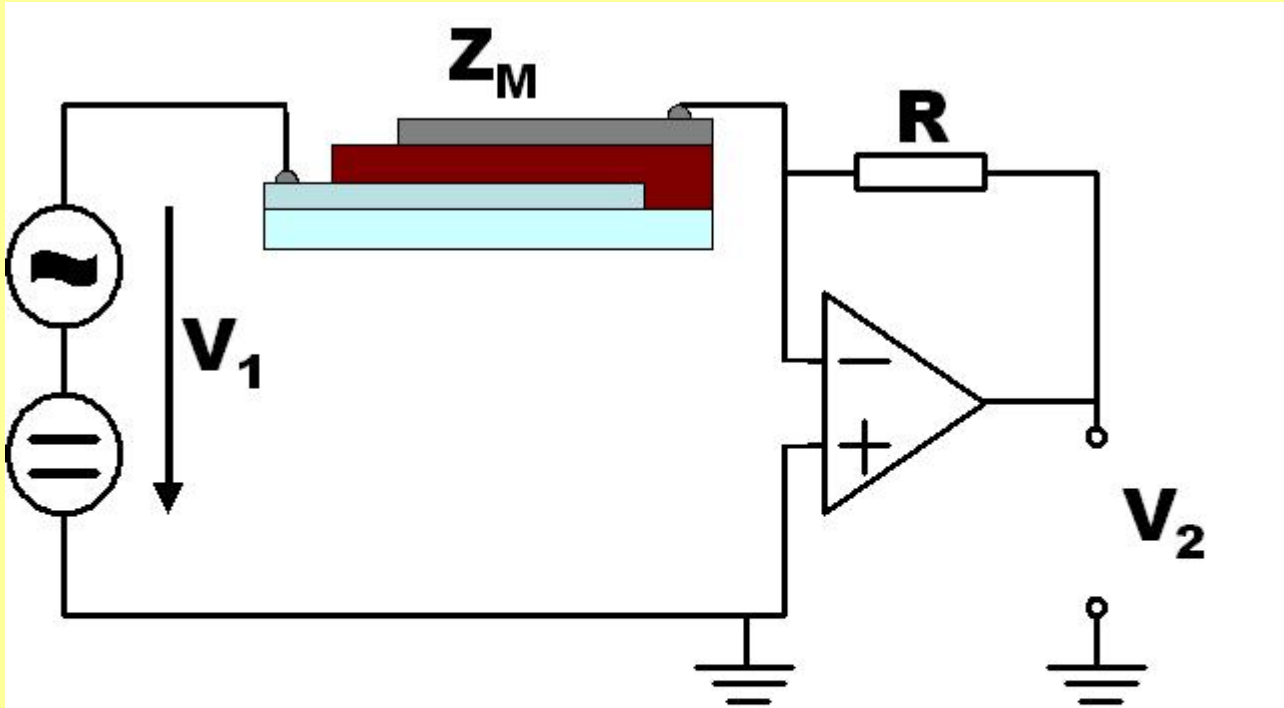




Impedance: Experimental Setup

Ehrenfreund, Lungenschmied et al., 2007

"Autobalance method"

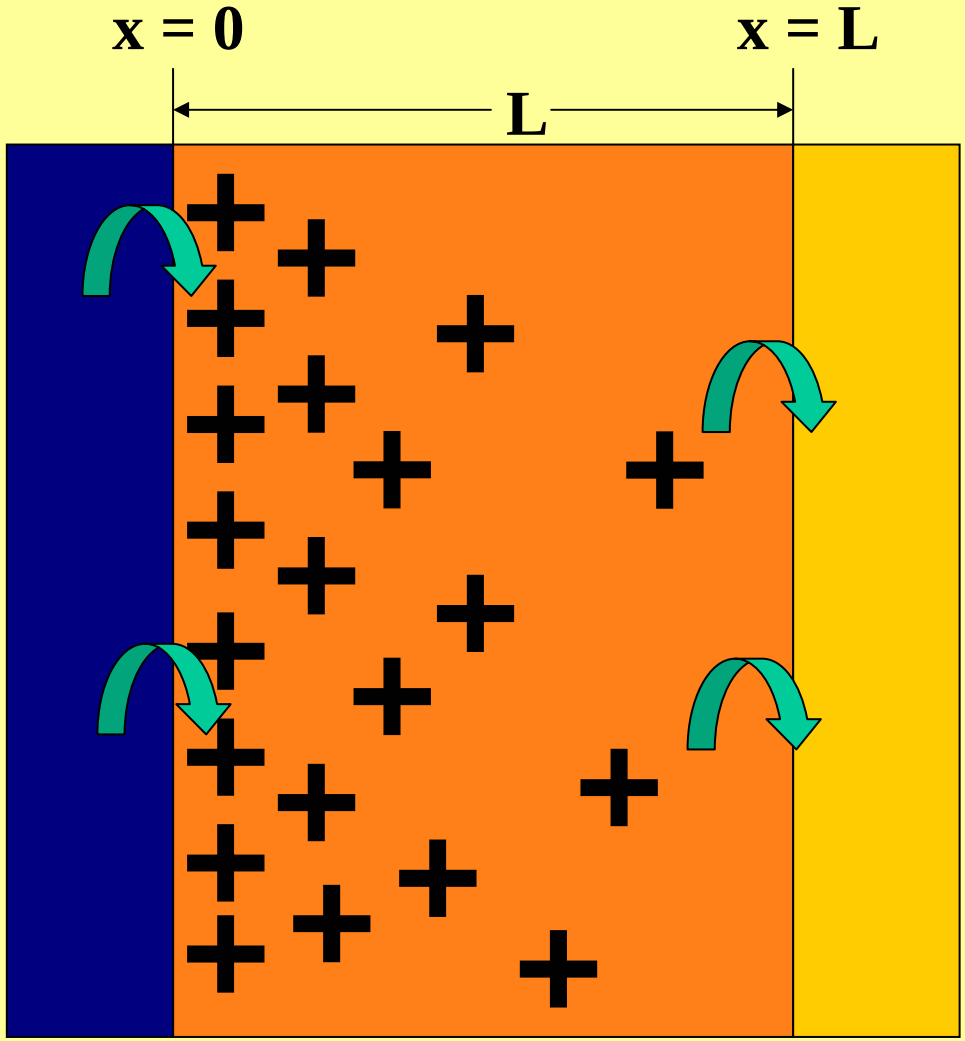


$V_1/Z_M + V_2/R = 0$

ac + dc voltage applied => current and phase shift are measured

Impedance: What to Expect ?

Space charge



Space charge limited current

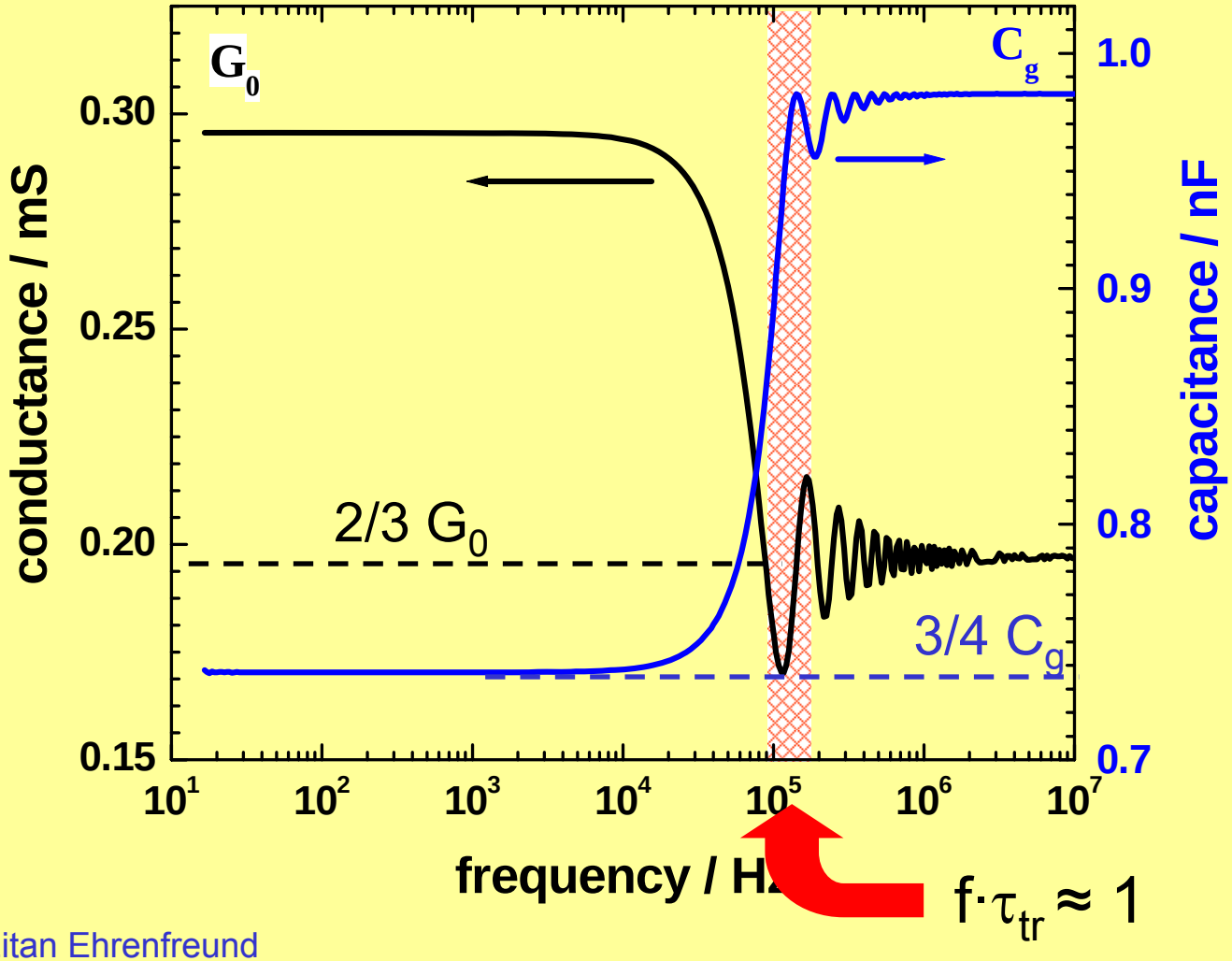
1) Ohm´s law: $J = q \cdot n(x) \cdot \mu \cdot E(x)$

2) Poisson equation: $n(x) = \frac{\varepsilon}{q} \frac{dE}{dx}$

SCLC (dc): $J = \frac{9 \cdot \varepsilon \cdot \mu \cdot V^2}{8 \cdot L^3}$ **(Mott-Gurney law)**

transit time: $t_t = \int_0^L \frac{dx}{v(x)} = \frac{4L^2}{3\mu V}$

SCLC – single carrier, no traps



Simulation by Eitan Ehrenfreund

SCLC – single carrier, with traps

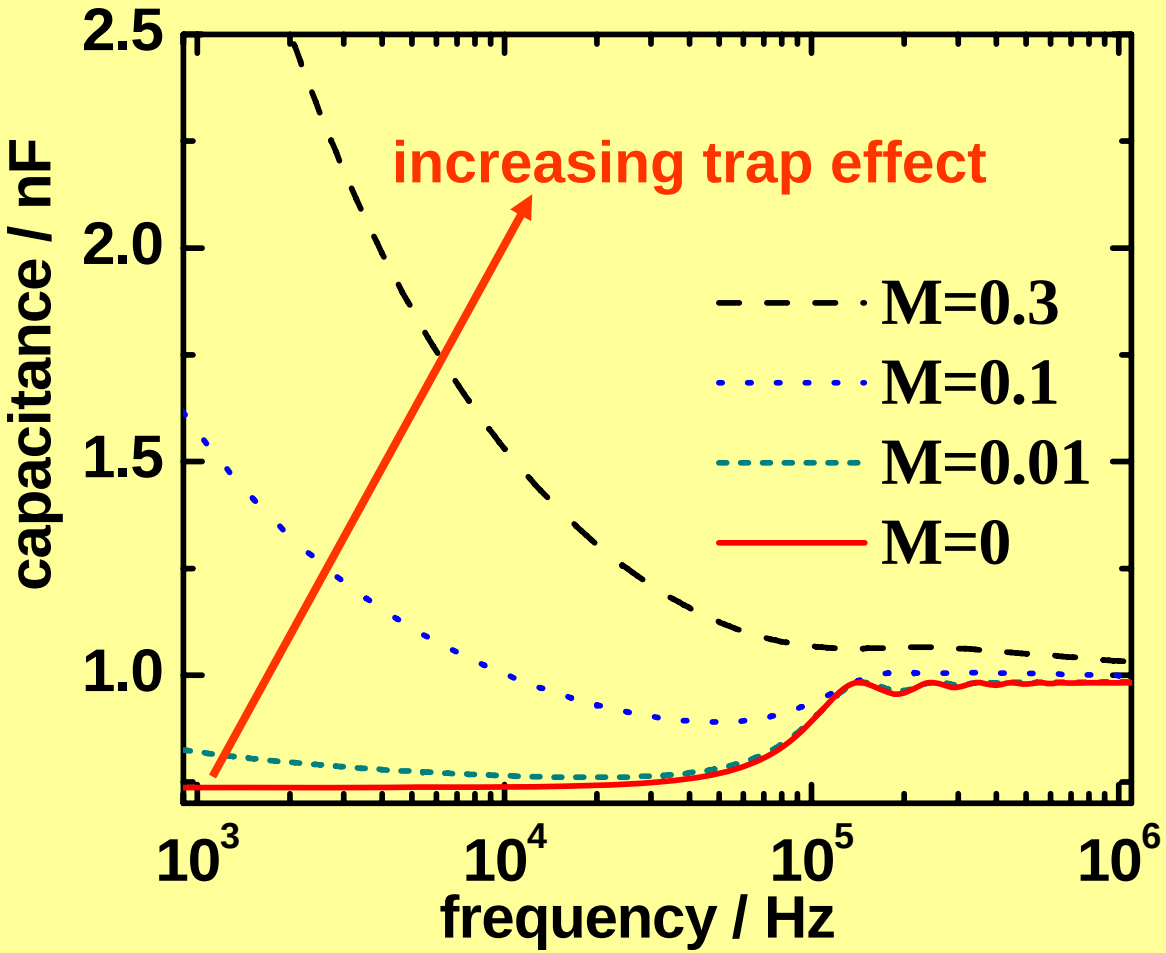
Dispersive transport

$$\tilde{\mu} = \frac{\mu(\omega)}{\mu_{dc}}$$

$$\tilde{\mu} = 1 + M(i\Omega)^{1-\gamma}$$

Proportionality factor

Dispersion coefficient, $\gamma = 0.5$



Martens, Brom, Blom, PRB **60**, 8489 (1999)

Simulation by Eitan Ehrenfreund

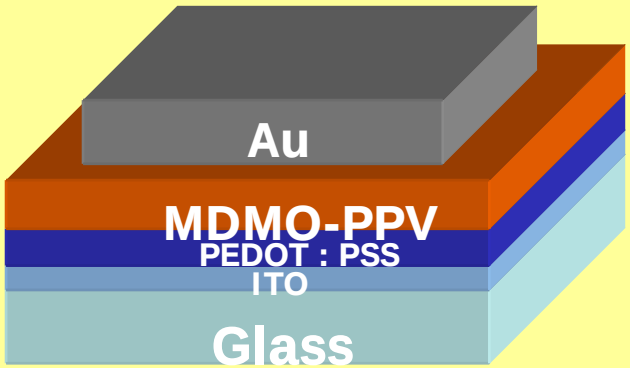
Experiment and fit

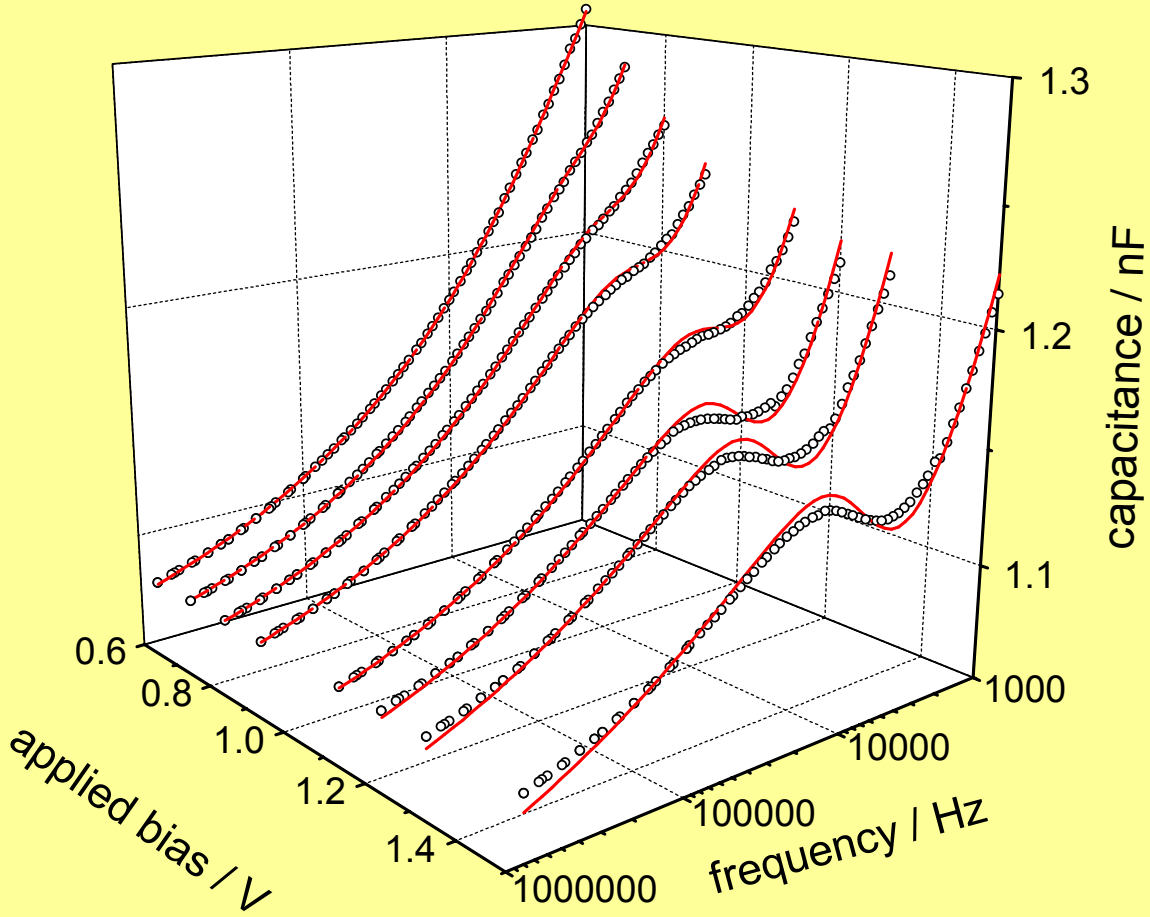
Ehrenfreund, Lungenschmied et al., 2007

Low injection level

$V_{int} \approx 0.8$ V

MDMO-PPV (~220 nm)





Experiment and fit

Ehrenfreund, Lungenschmied et al., 2007

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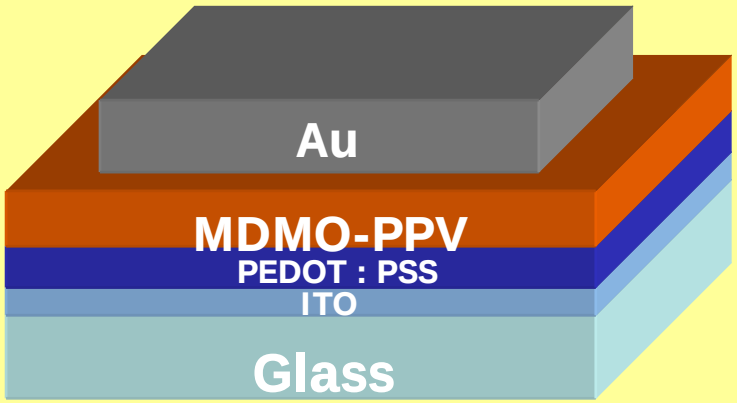
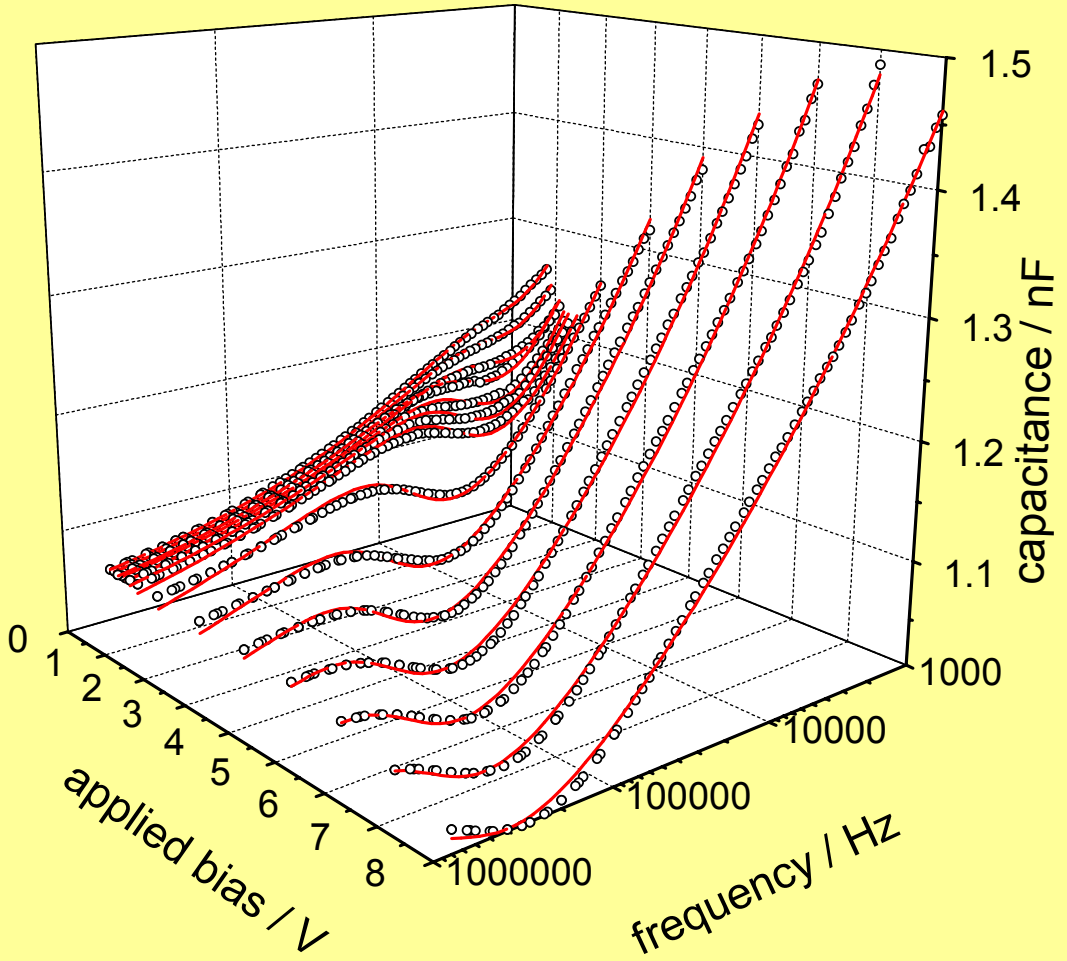




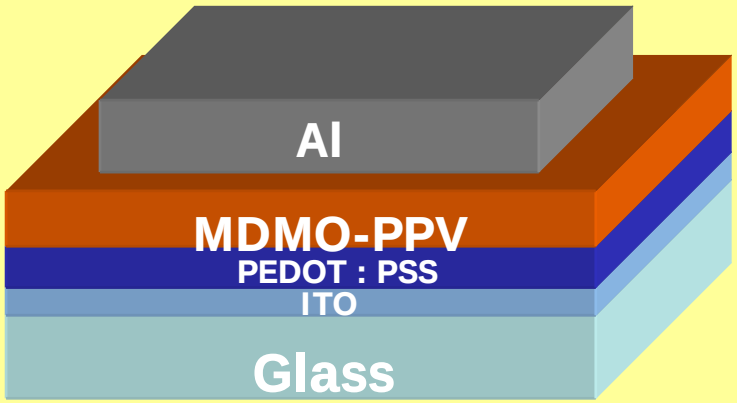
Anomaly at Low Frequencies

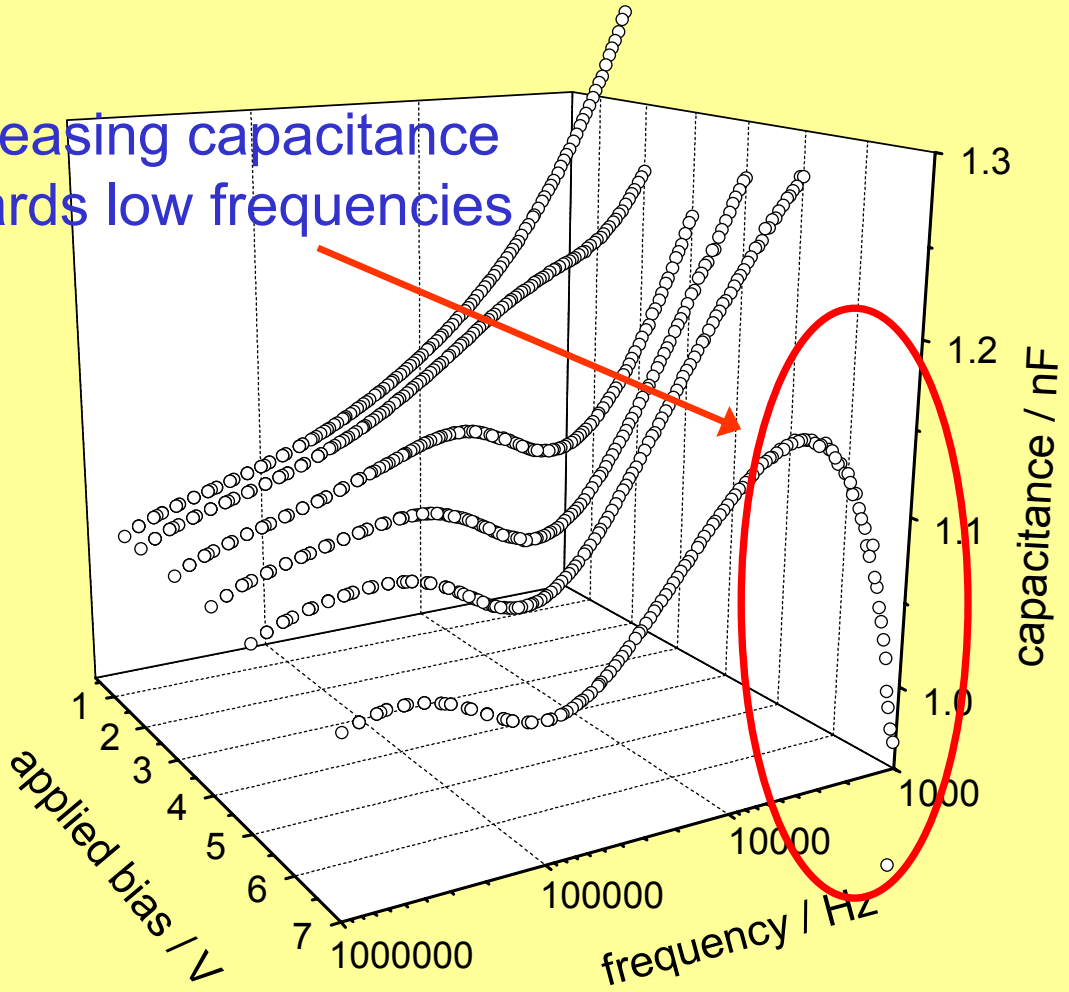
Ehrenfreund, Lungenschmied et al., 2007

Al top electrode

$V_{int} \approx 1.6$ V

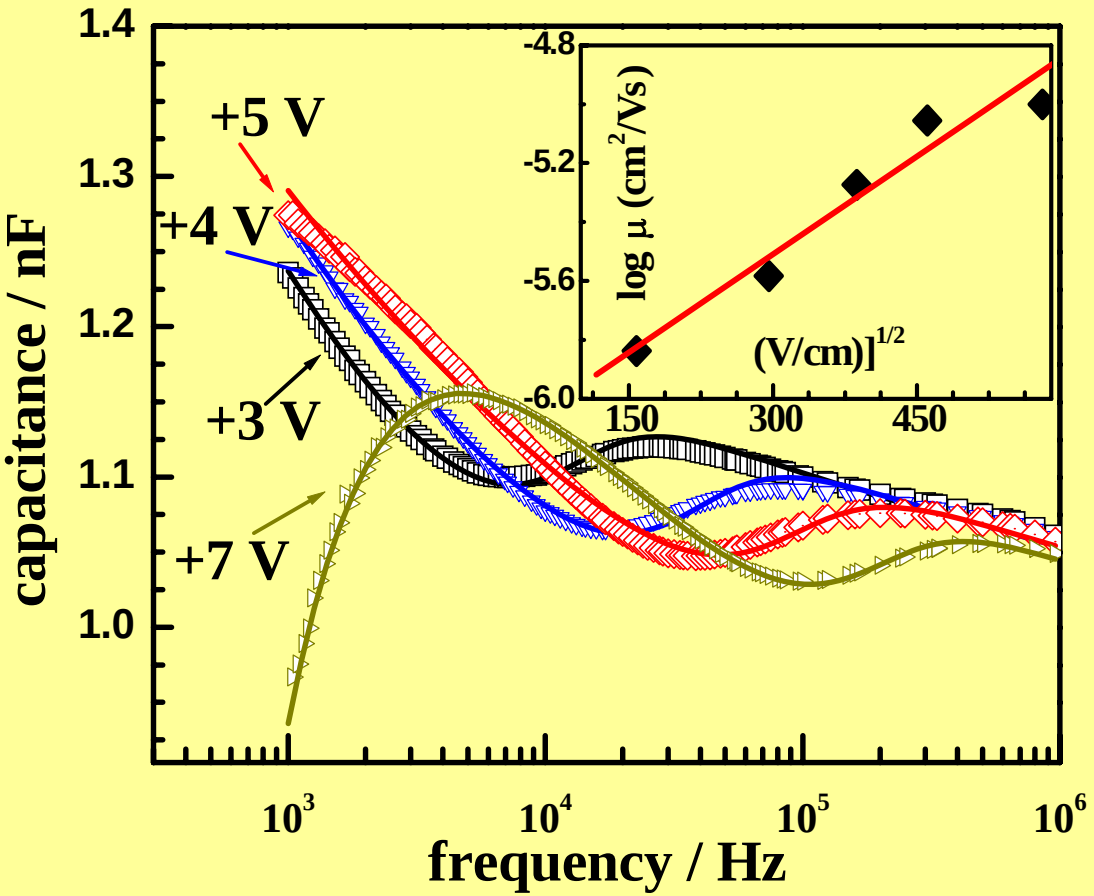
MDMO-PPV (~130 nm)





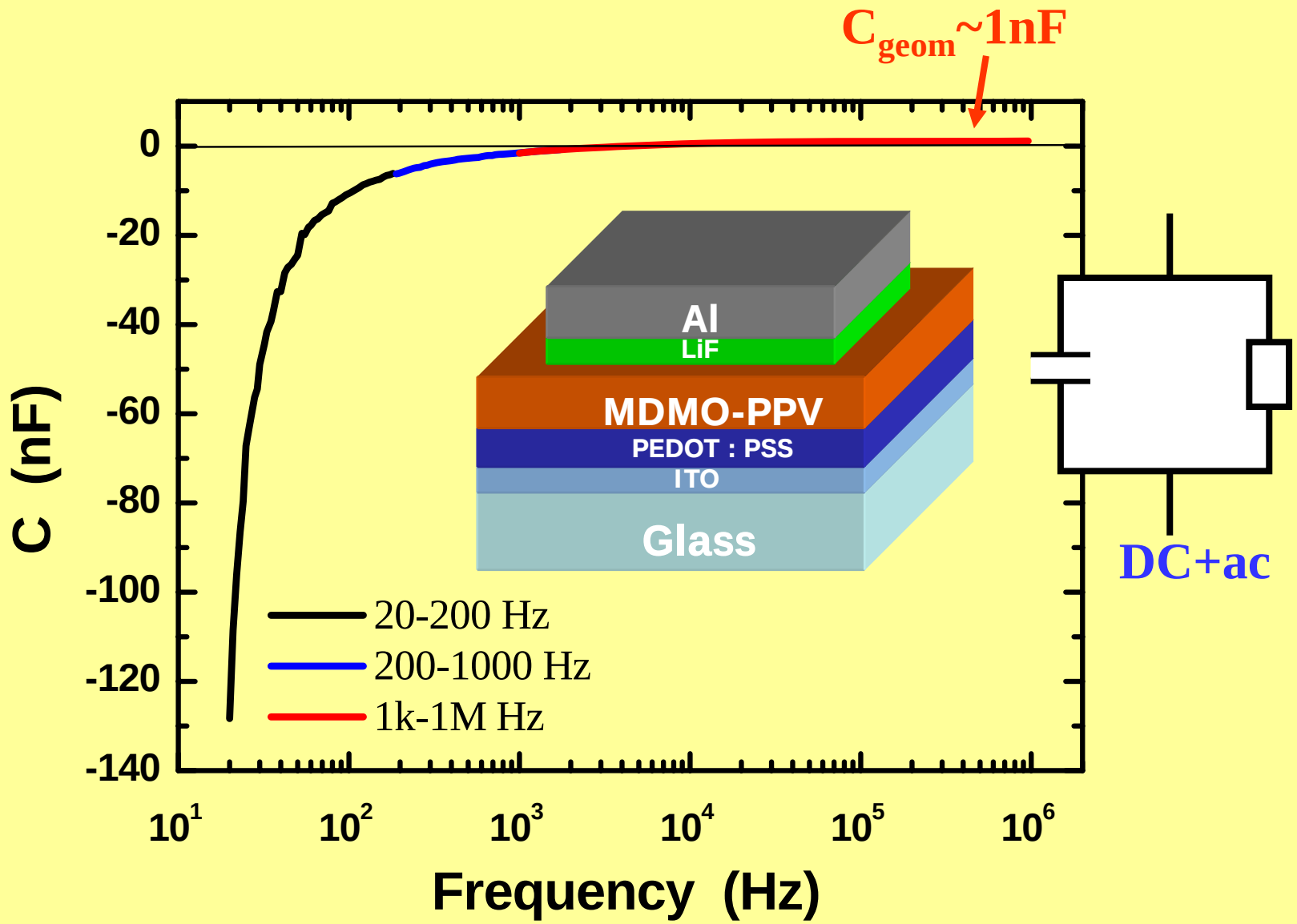
Bipolar Injection Gives Negative Capacitance

Ehrenfreund, Lungenschmied et al., 2007



ITO – PEDOT:PSS - MDMO-PPV - Al

Negative Capacitance at Low Frequencies



Ehrenfreund Formalism
Fit to the Negative Capacitance

$$Y(\omega) = \frac{C_g}{t_t} \frac{\Omega^3}{2i\tilde{\mu}^2[1-e^{-i\Omega/\tilde{\mu}}] + 2\tilde{\mu}\Omega - i\Omega^2}$$

SCLC – single carrier with traps

$$\Omega = \omega t_t \qquad ; \quad \tilde{\mu} = 1 + M(i\Omega)^{1-\alpha}$$

$$\Delta C_r(\omega) = -\frac{\Delta G_r}{1 + (\omega^2 \tau_r^2)^{\delta}}$$

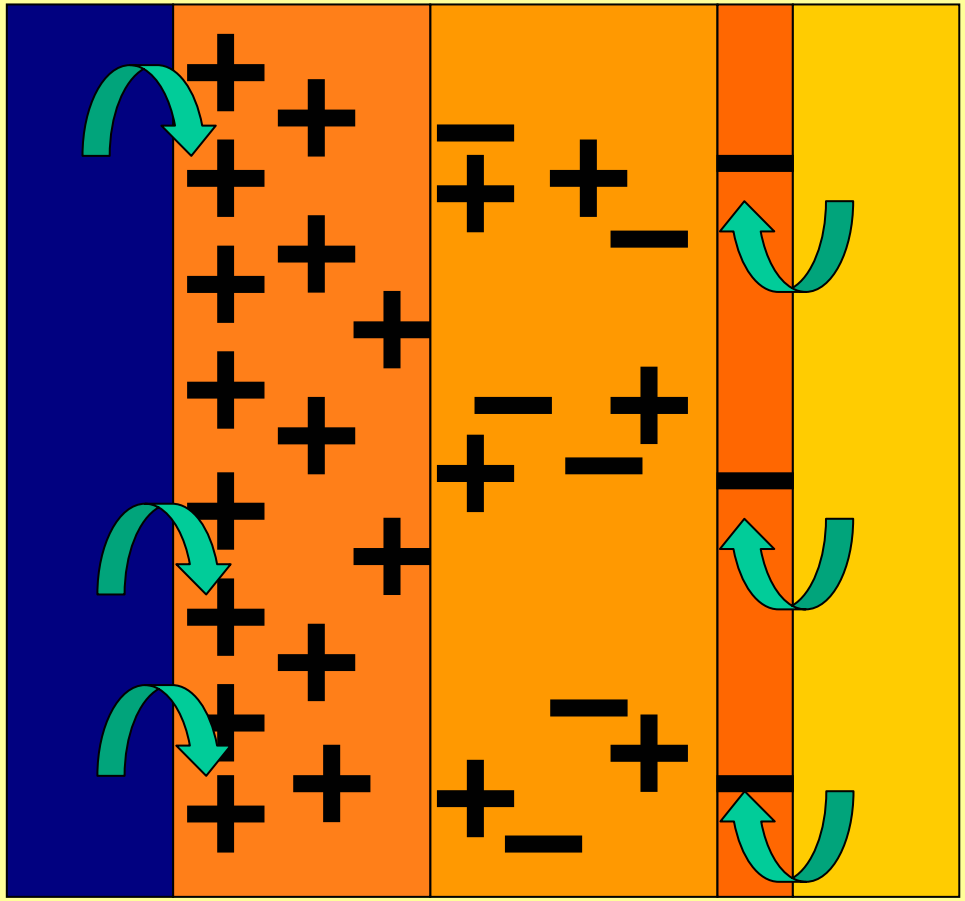
Negative contribution to C

Ehrenfreund, Lungenschmied et al., *Appl. Phys. Lett.* **91**, 12112 (2007)

Double injection device

Ehrenfreund, Lungenschmied et al., *Appl. Phys. Lett.* **91**, 12112 (2007)

PEDOT:PSS



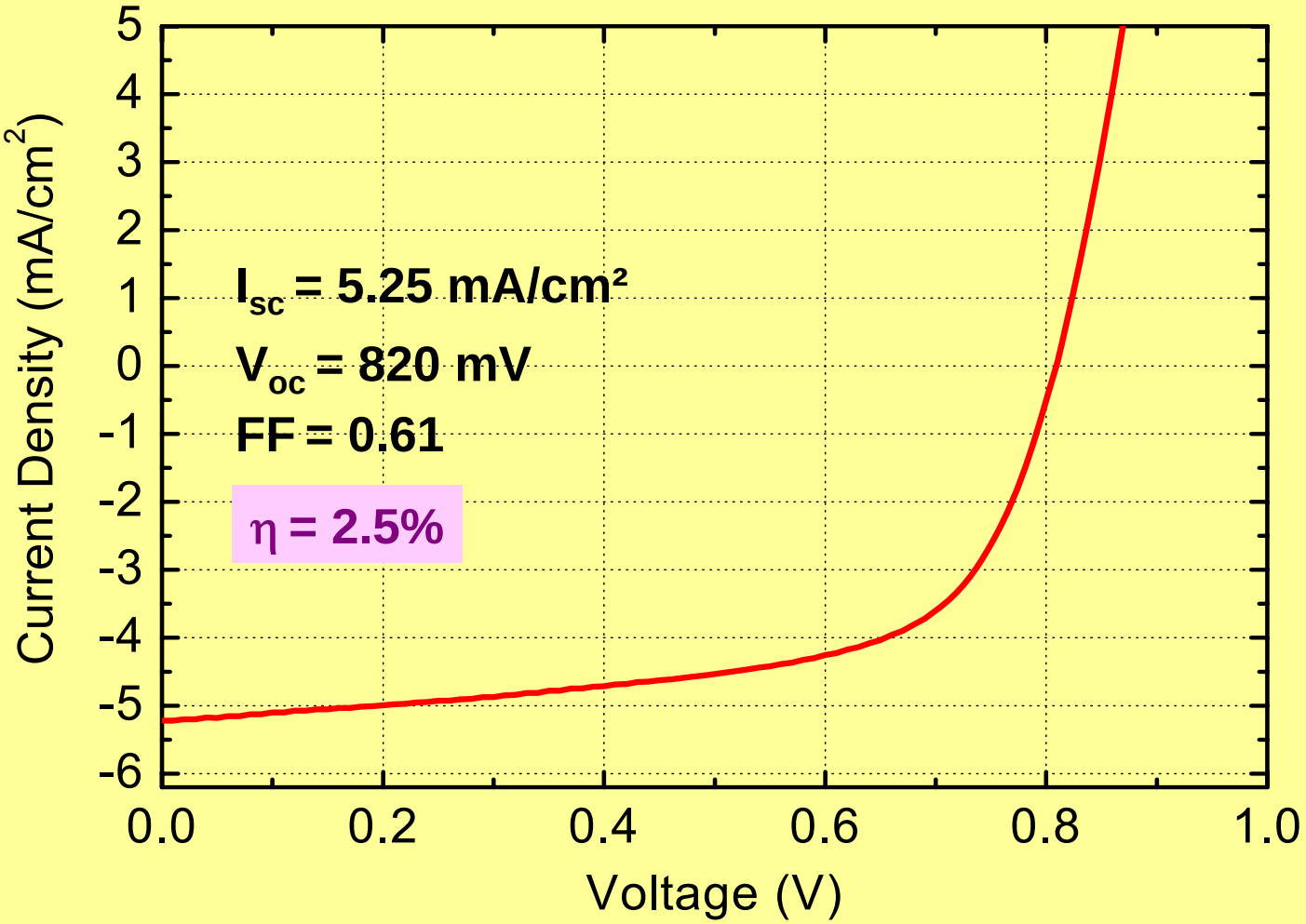
LiF/Al

Back to the Photovoltaic Diodes

Bulk-heterojunction

"Bulk Heterojunction "

MDMO-PPV / PCBM 1:4



Bulk-heterojunction

"Bulk Heterojunction "

P3HT / PCBM Dyakonov et al.

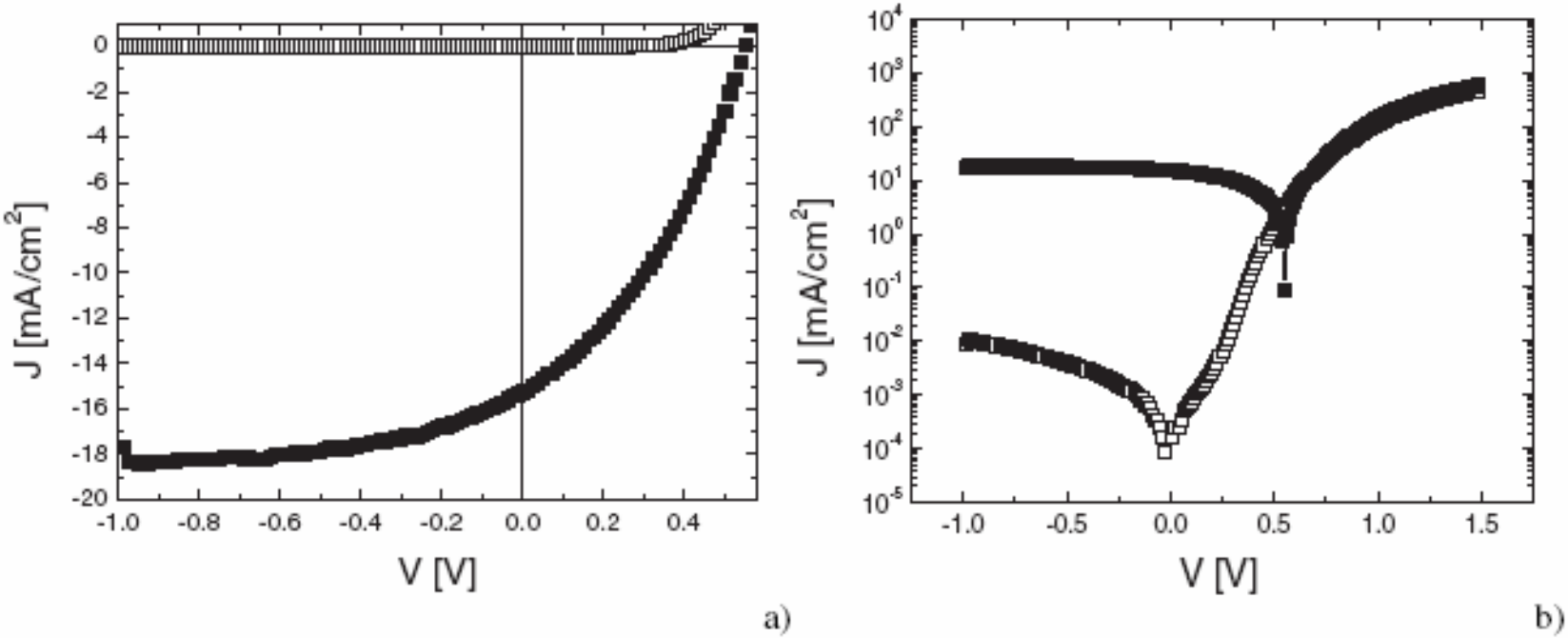
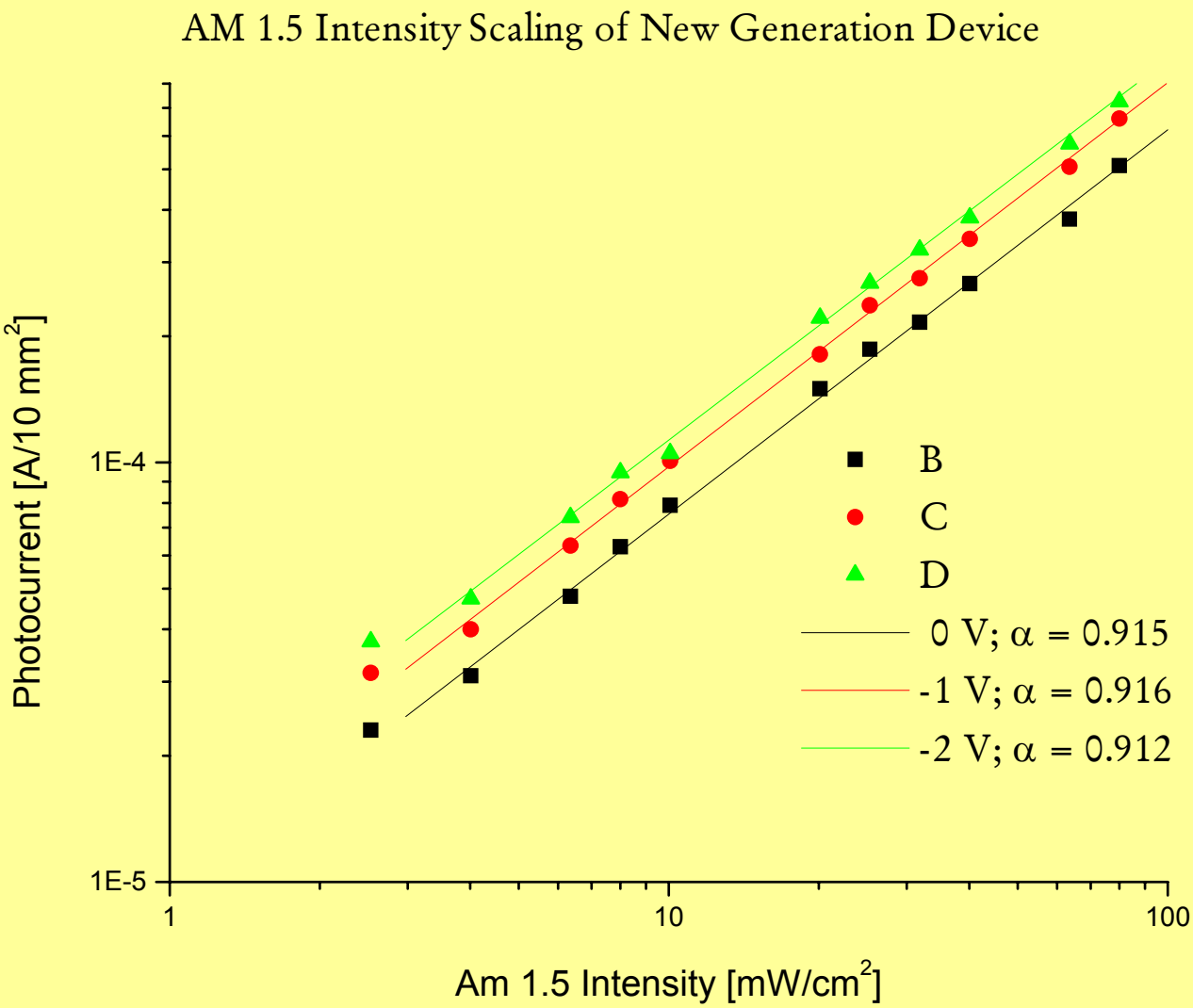


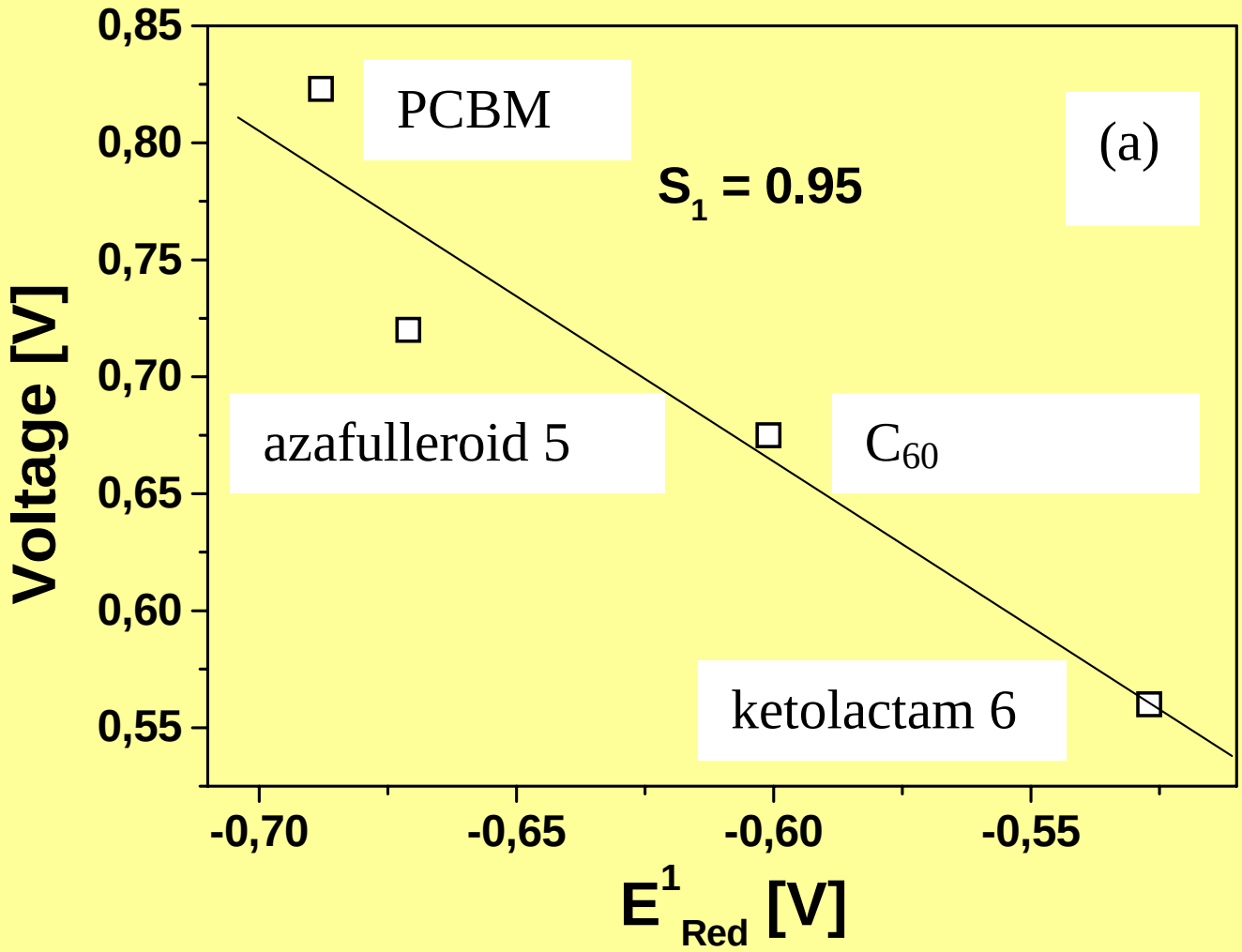
Fig. 8 Current density–voltage characteristics for an annealed ITO/PEDOT:PSS/P3HT:PCBM/Al solar cell with 350 nm active layer thickness under illumination with $P_{Light} = 100$ mW/cm^2 (full symbols) and in the dark (open symbols). (a) $J-V$ profiles in third and fourth quadrants, (b) semi-logarithmic representation in the full voltage range.

Intensity Dependence of Photocurrent

Scaling Coefficient α ~ 0.92

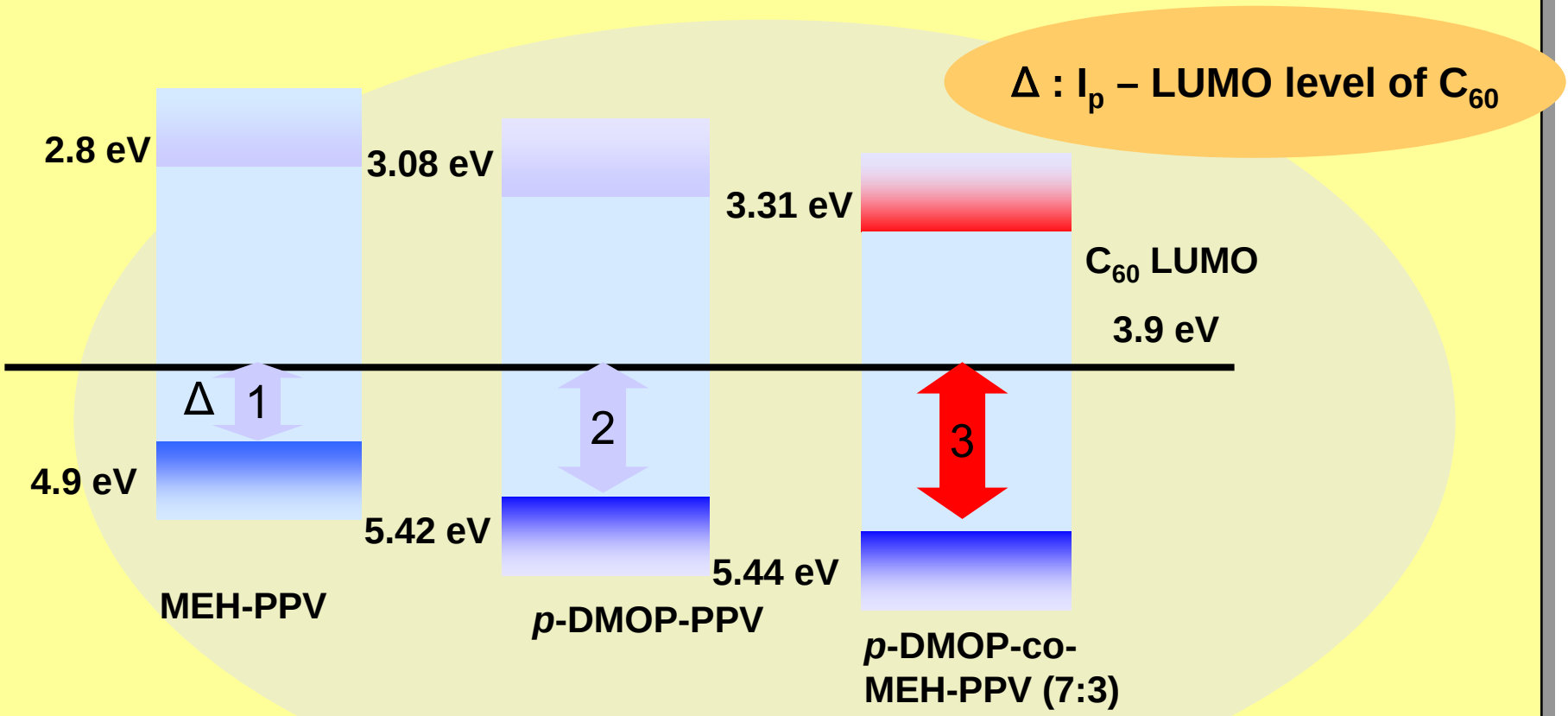


Voc vs LUMO of Acceptor



*Brabec et al., Advanced Functional Materials (2001), **11**, No.5, 374-380*

Voc vs HOMO of the Polymer Donor

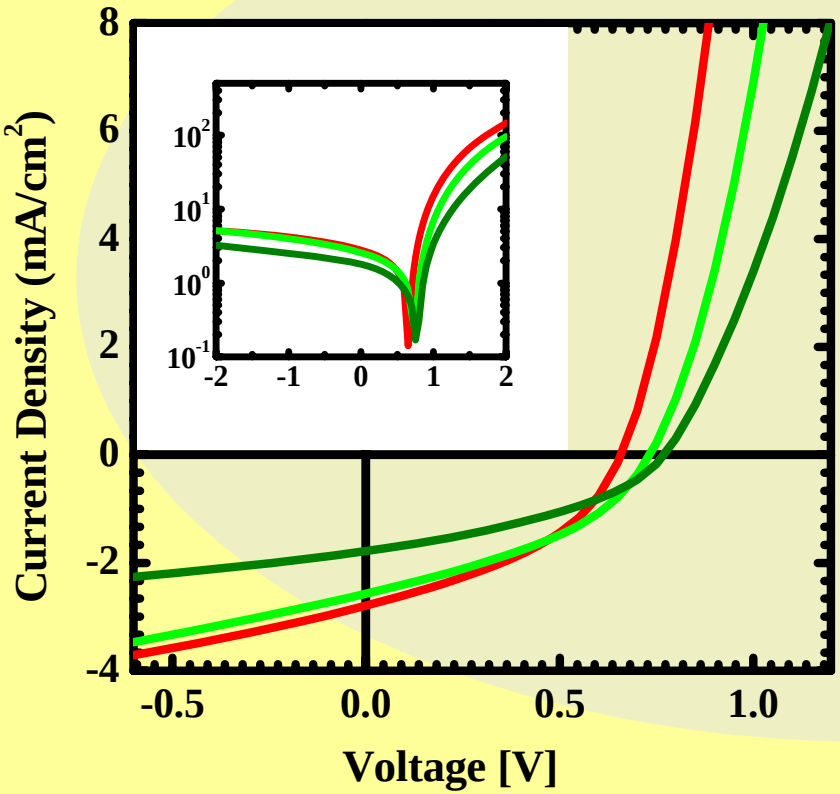


- High PL Quantum Efficiency Materials
- High Ionization Potential Materials

	1	2	3
Q.E.	10%	40%	23%

Voc vs HOMO of the Polymer Donor

PCBM + Conjugated polymer (1,2,3) ➡ 3:1 weight ratio



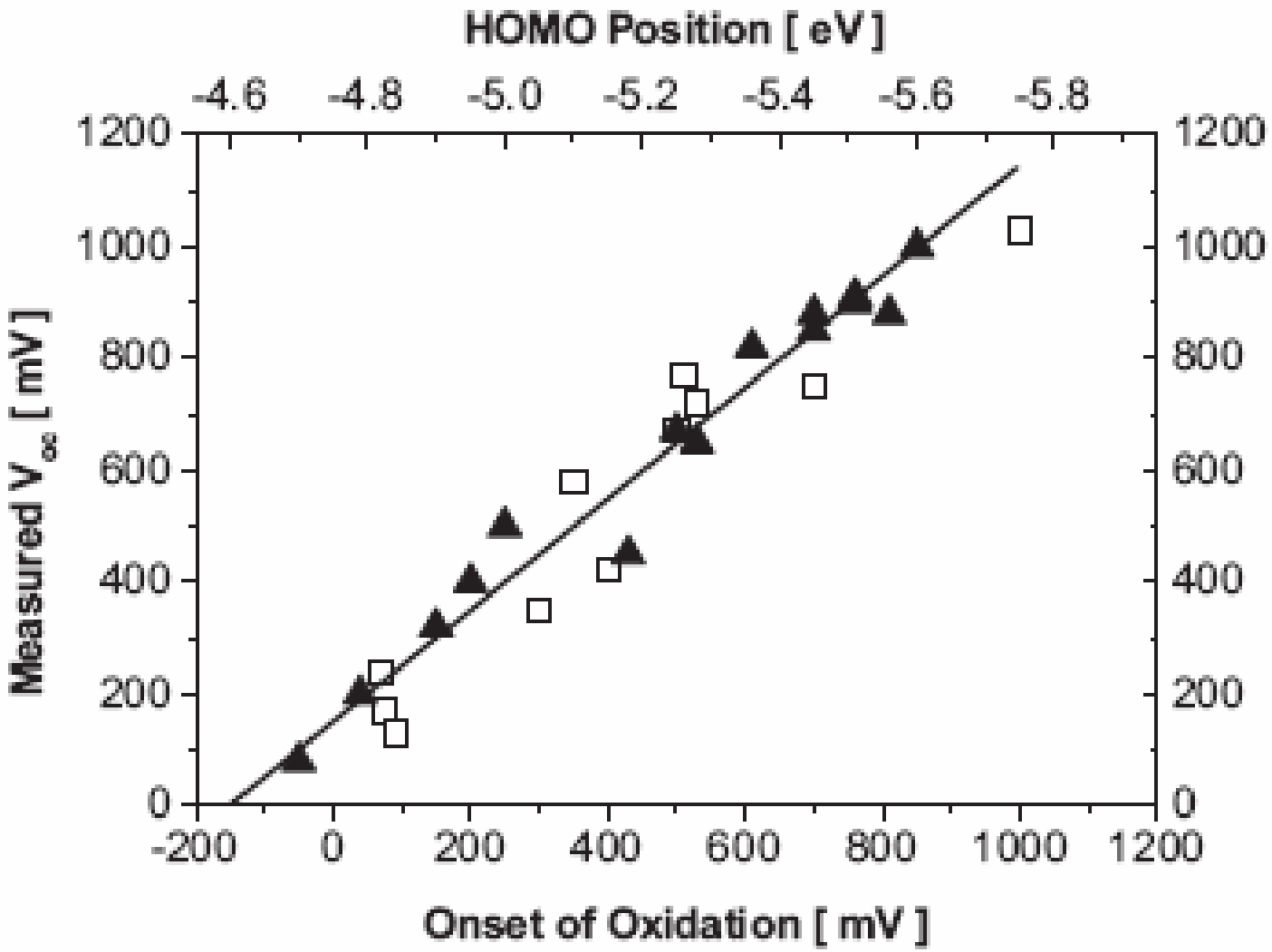
Sample	I_{sc}	V_{oc}	FF
1	2.79	0.66	0.40
2	2.57	0.73	0.40
3	1.64	0.77	0.39

1. MEH-PPV+PCBM
2. *p*-DMOP-PPV+PCBM
3. *p*-DMOP-co-MEH-PPV+PCBM

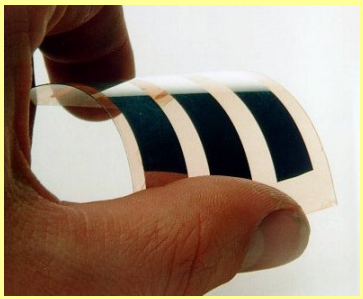
Sample	V_{oc}	I_p
1	0.66	4.90
2	0.73	5.42
3	0.77	5.44

Kwanghee Lee et al, Pusan Univ. Korea

Voc vs HOMO of the Polymer Donor



Markus Scharber *et al*, *Adv. Mater*. **18** (2006) 789



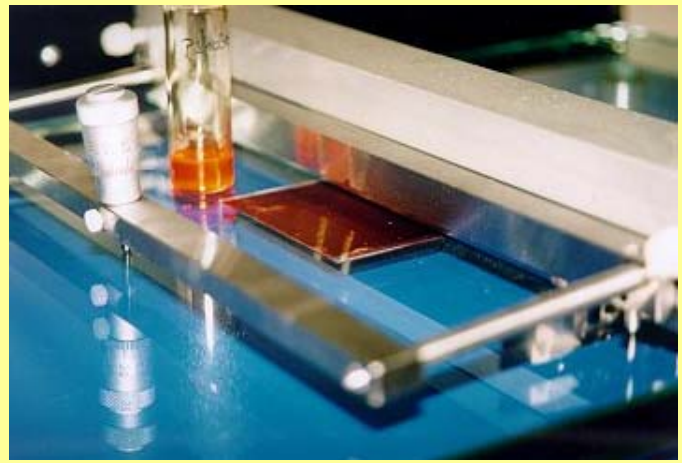
Production Scheme

THIN FILM PREPARATION

Spin Casting is a easy coating technique for small areas. Material loss is very high.

Doctor Blade Technique was developed for large area coating

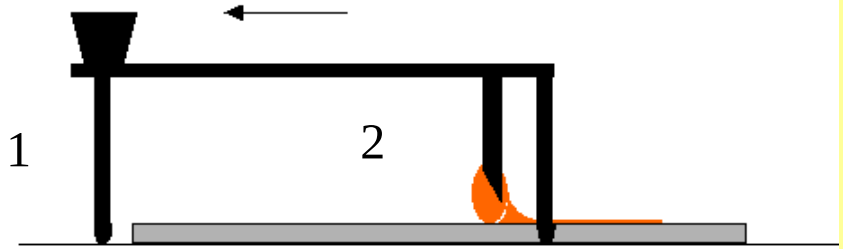
Doctor Blade Technique has no material loss



FILM THICKNESS IS ~ 100 nm

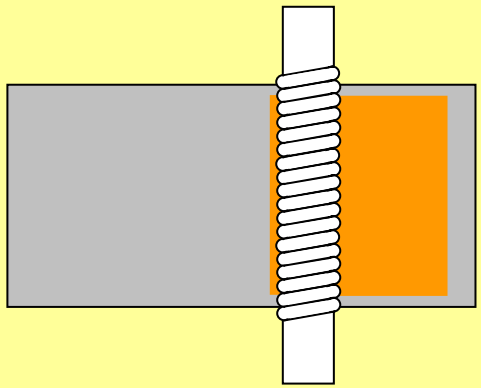
Production - Large Area

Large Area Thin Film Production using Doctor/Wire Blading



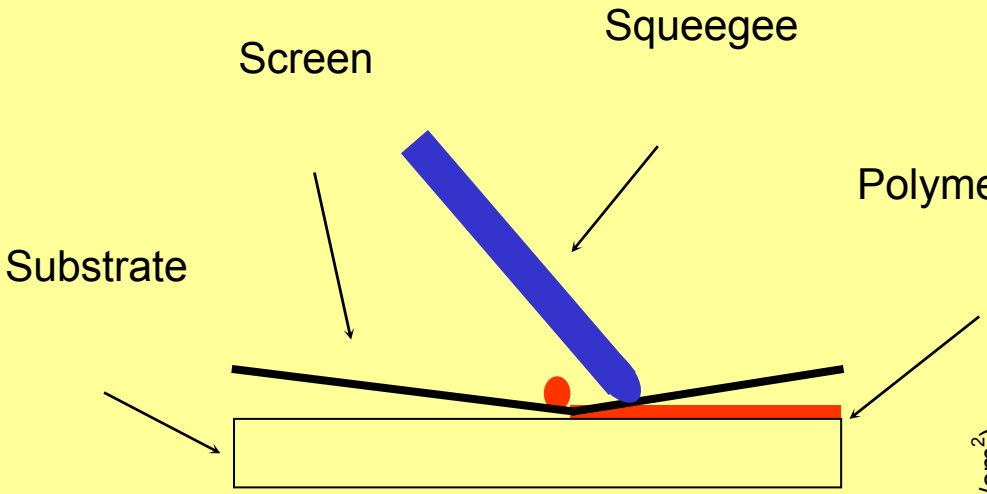
a)

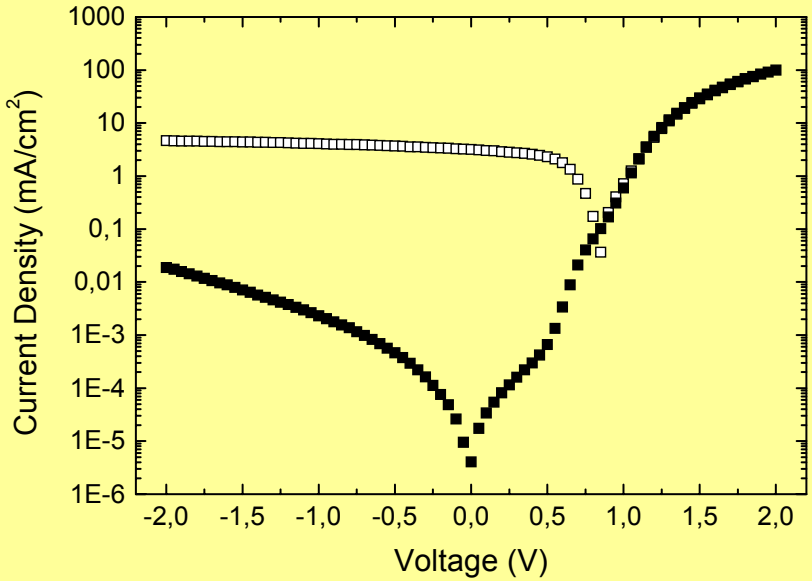
b)



Production - Large Area

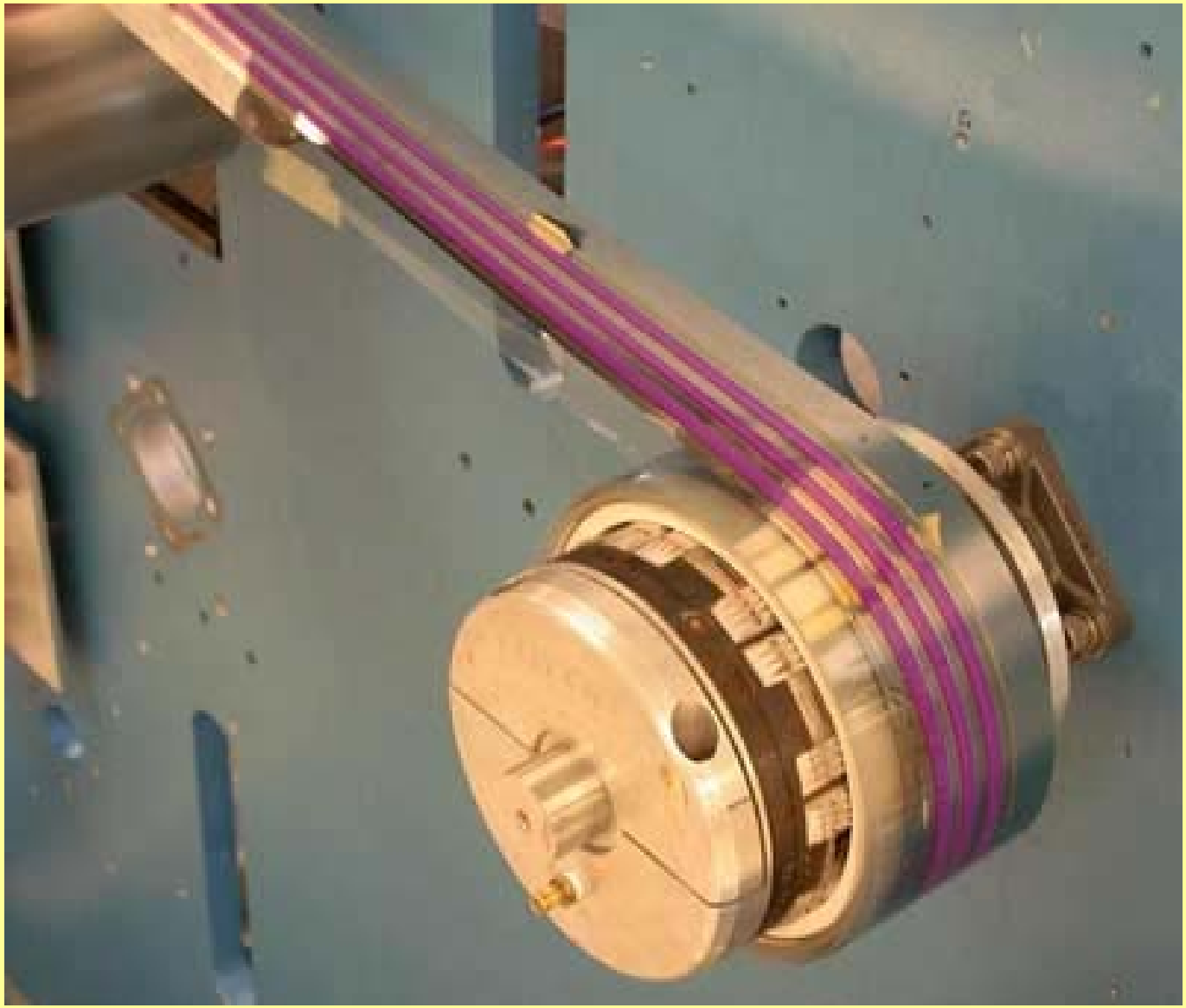
Large Area Thin Film Production Using Screen Printing





S. Shaheen, R. Radspinner, N. Peygambarian, G. Jabbour, *Appl. Phys. Lett.* **79**, 2996 (2001)

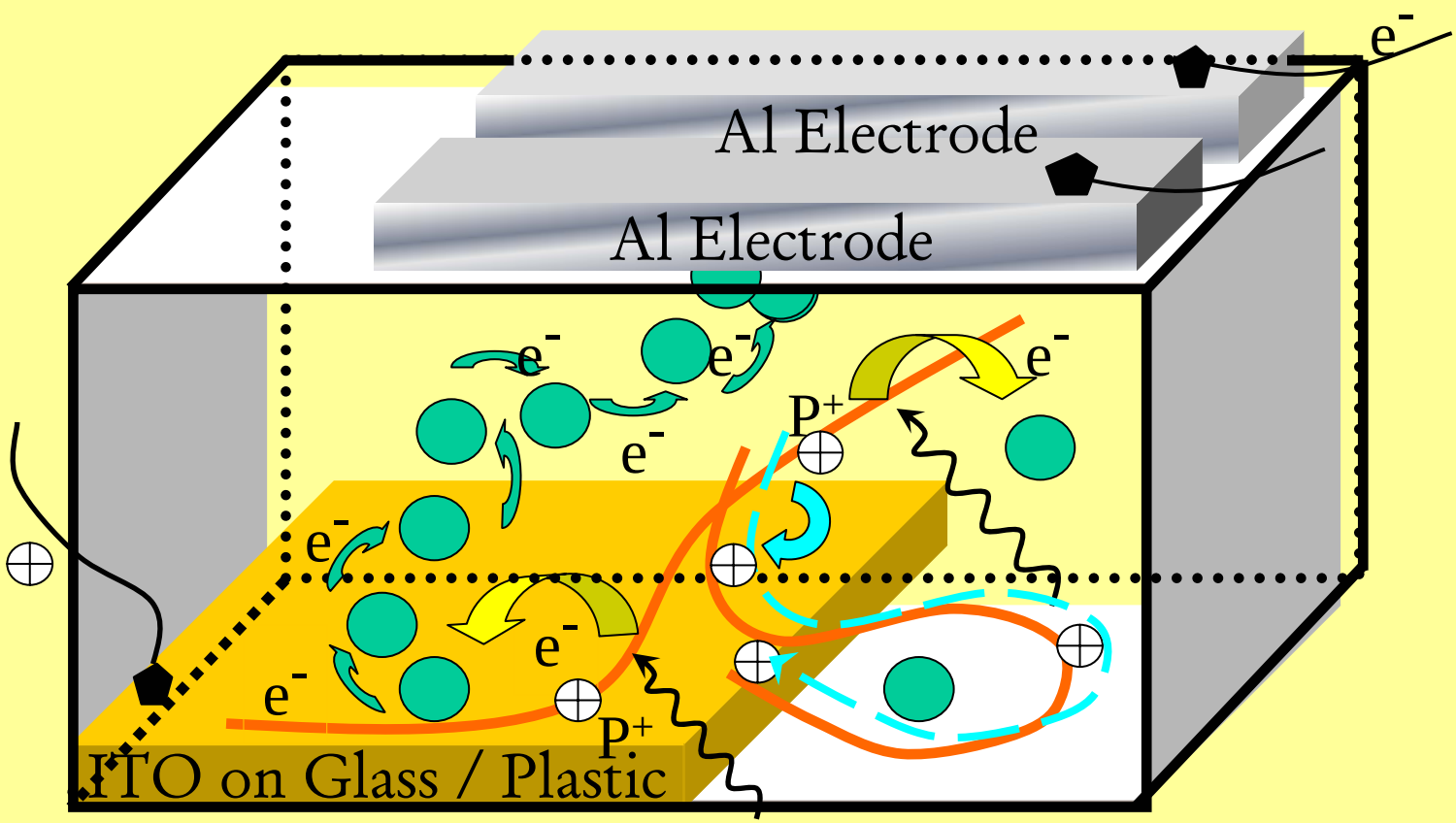
Production – Roll to Roll



Konarka Technologies Inc., www.konarka.com

Nanomorphology of the donor-acceptor composites

Bulk Heterojunctions



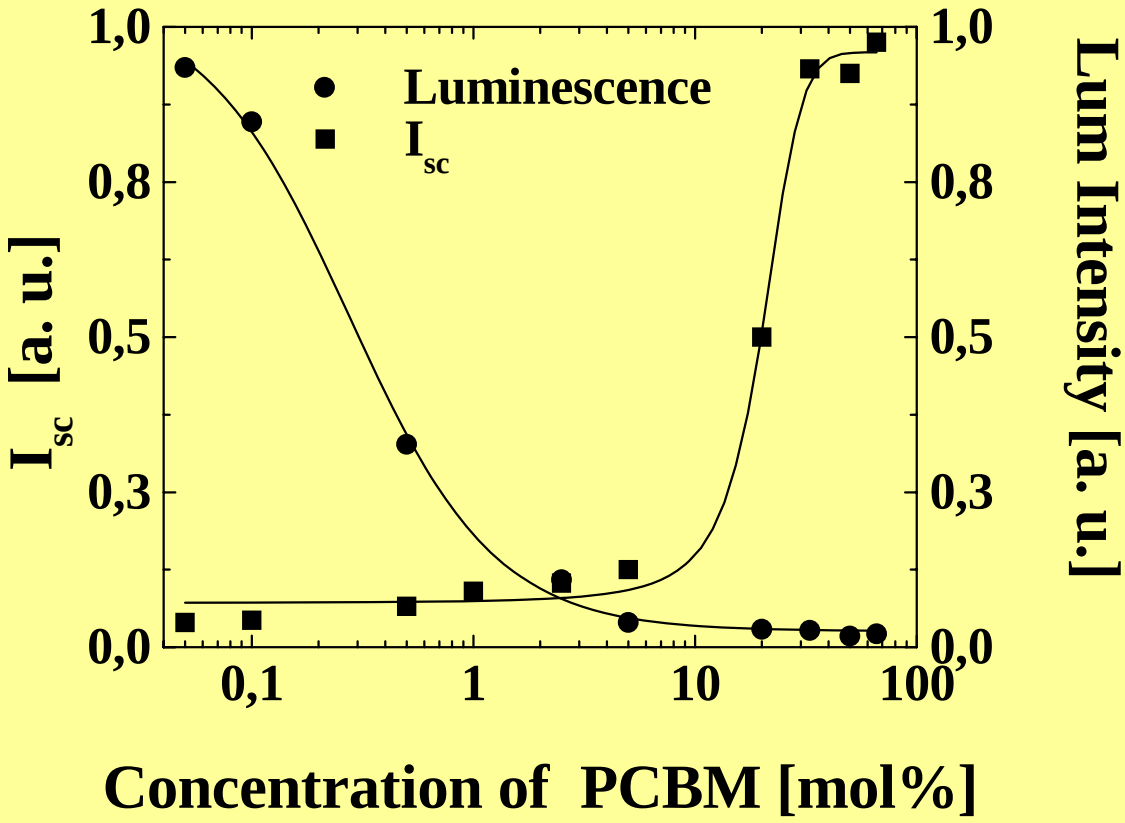
PCBM

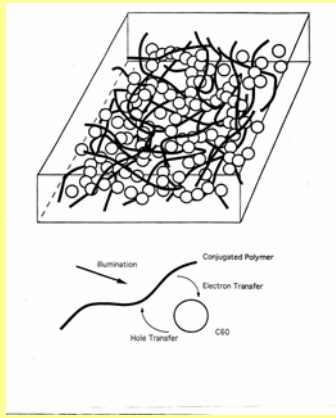
hν

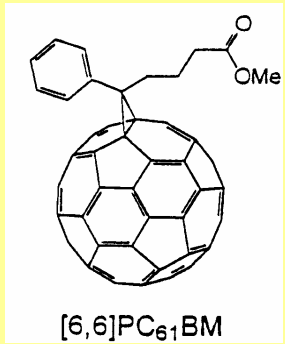
Alkoxy-PPV

3-D Percolation

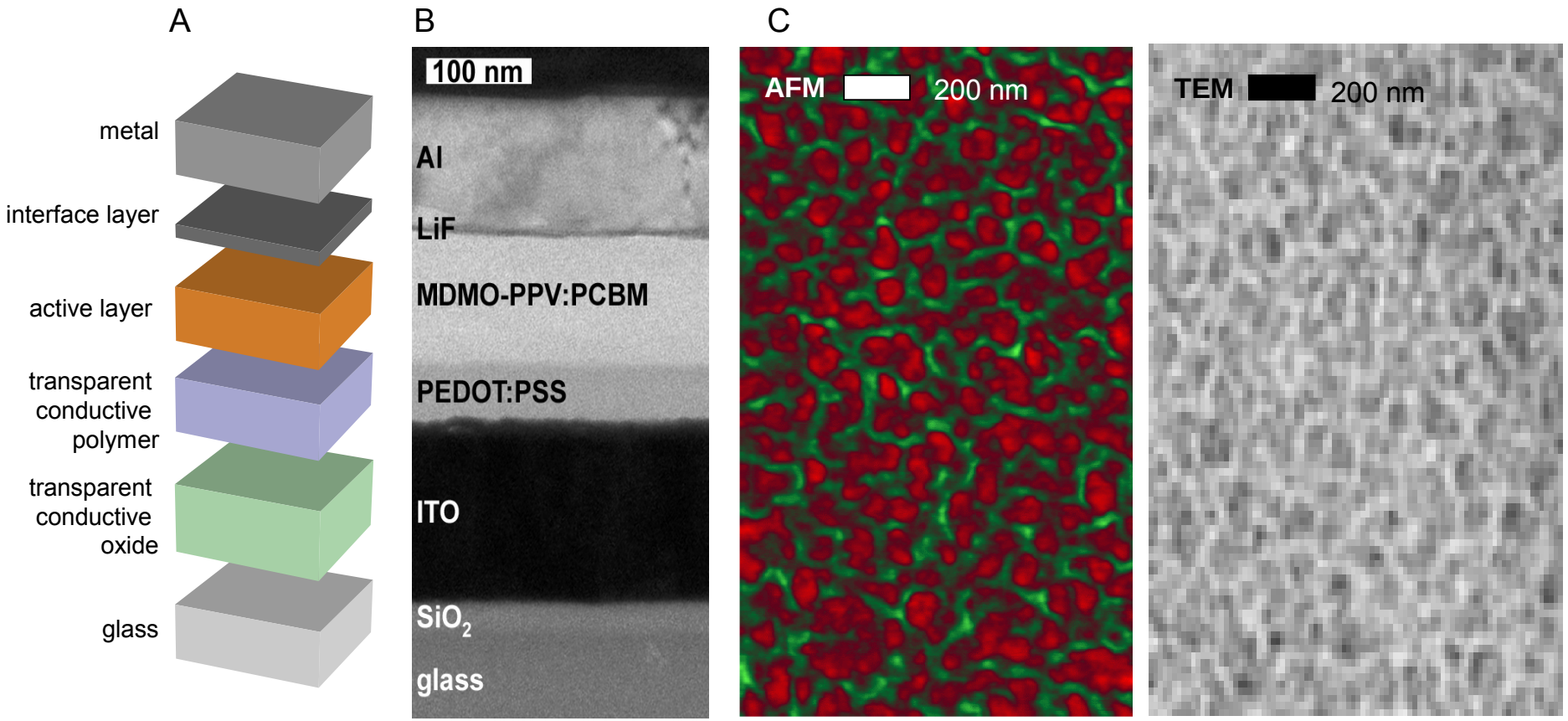
Strong luminescence quenching occurs at appr. 1 mol% of PCBM in alkoxy-PPV. Photocurrent onset at appr. 17 mol% PCBM, in accordance with percolation theory.





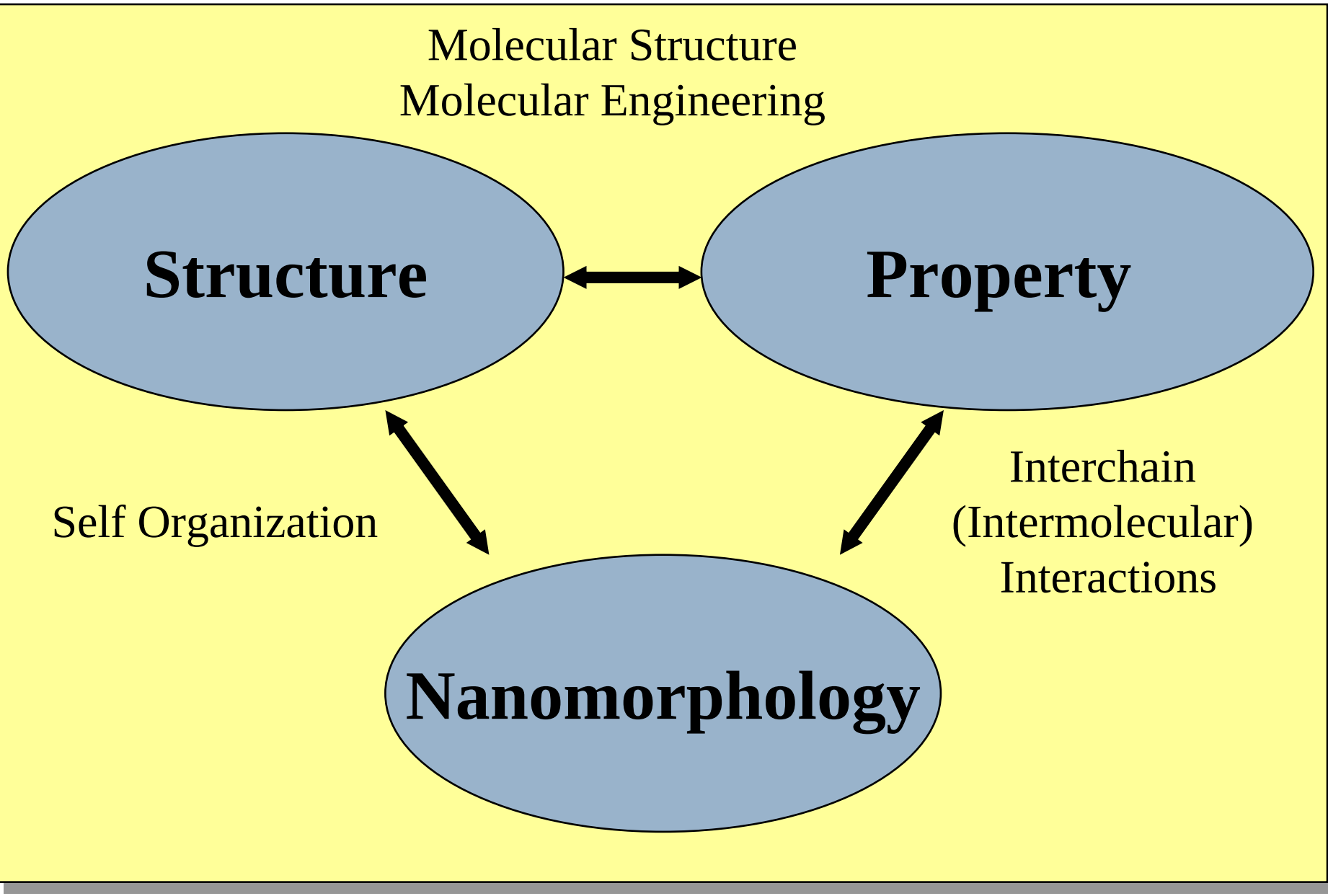


Bulk Heterojunction Device Structure



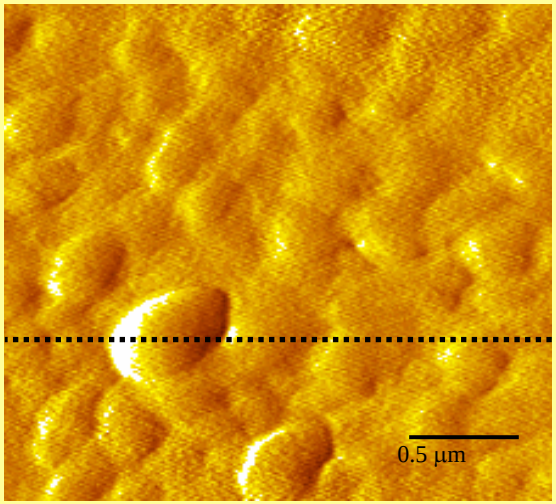
Rene Janssen *et al*, 2004

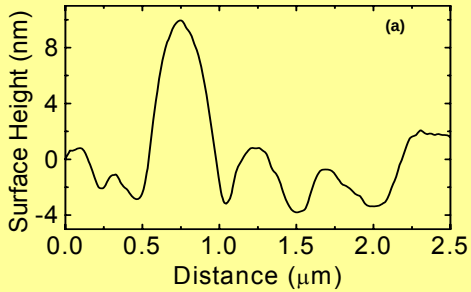
Property Optimization



Nanomorphology: Solvent Effects

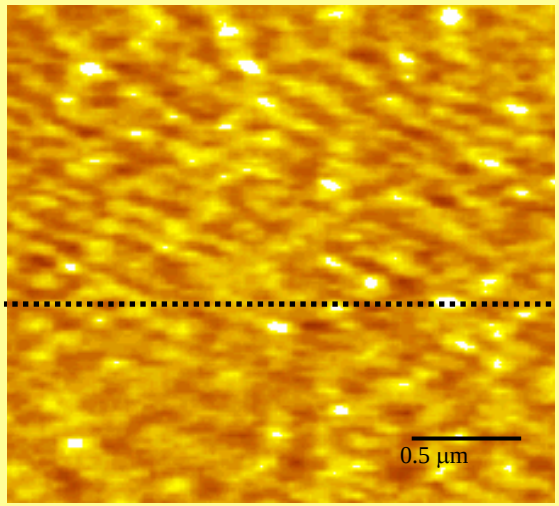
a

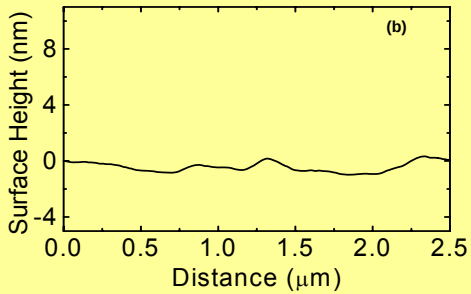




Toluene cast film

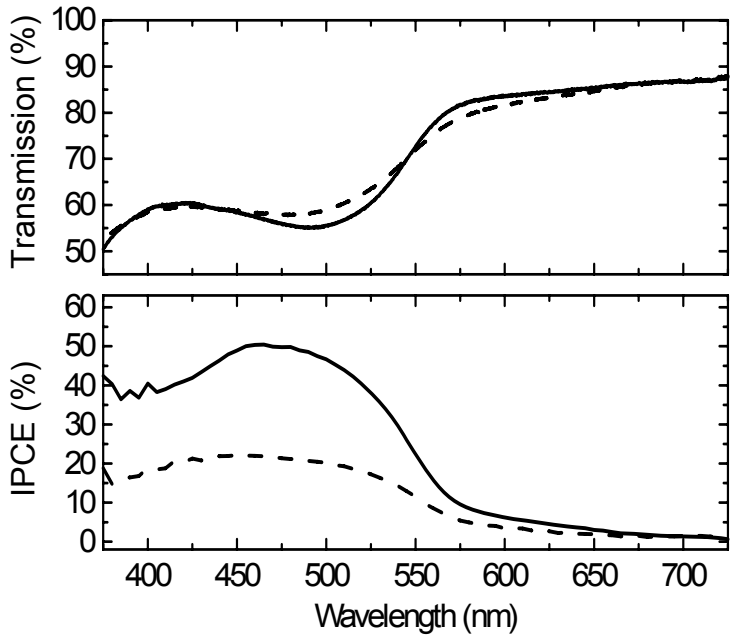
b

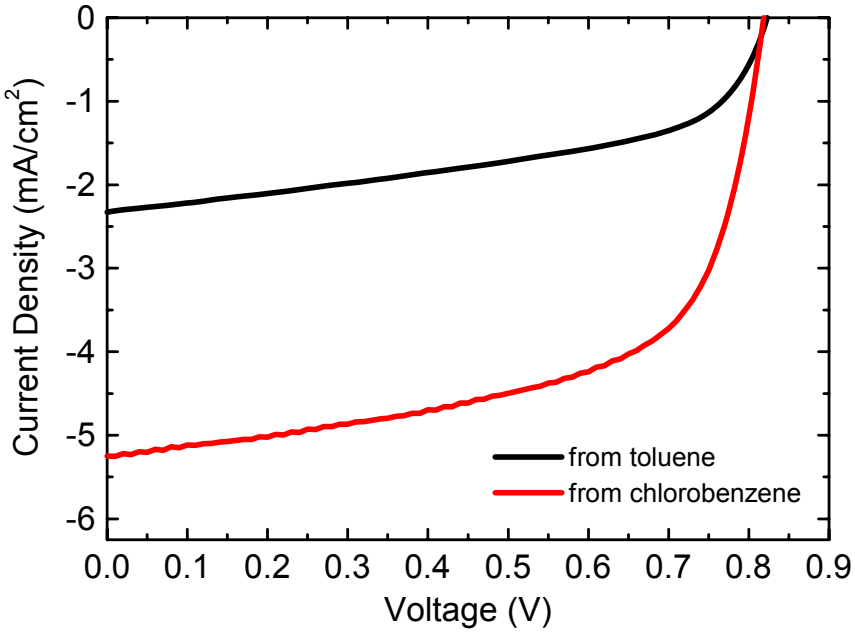




Cholorobenzene cast film

Morphology: Solvent effects

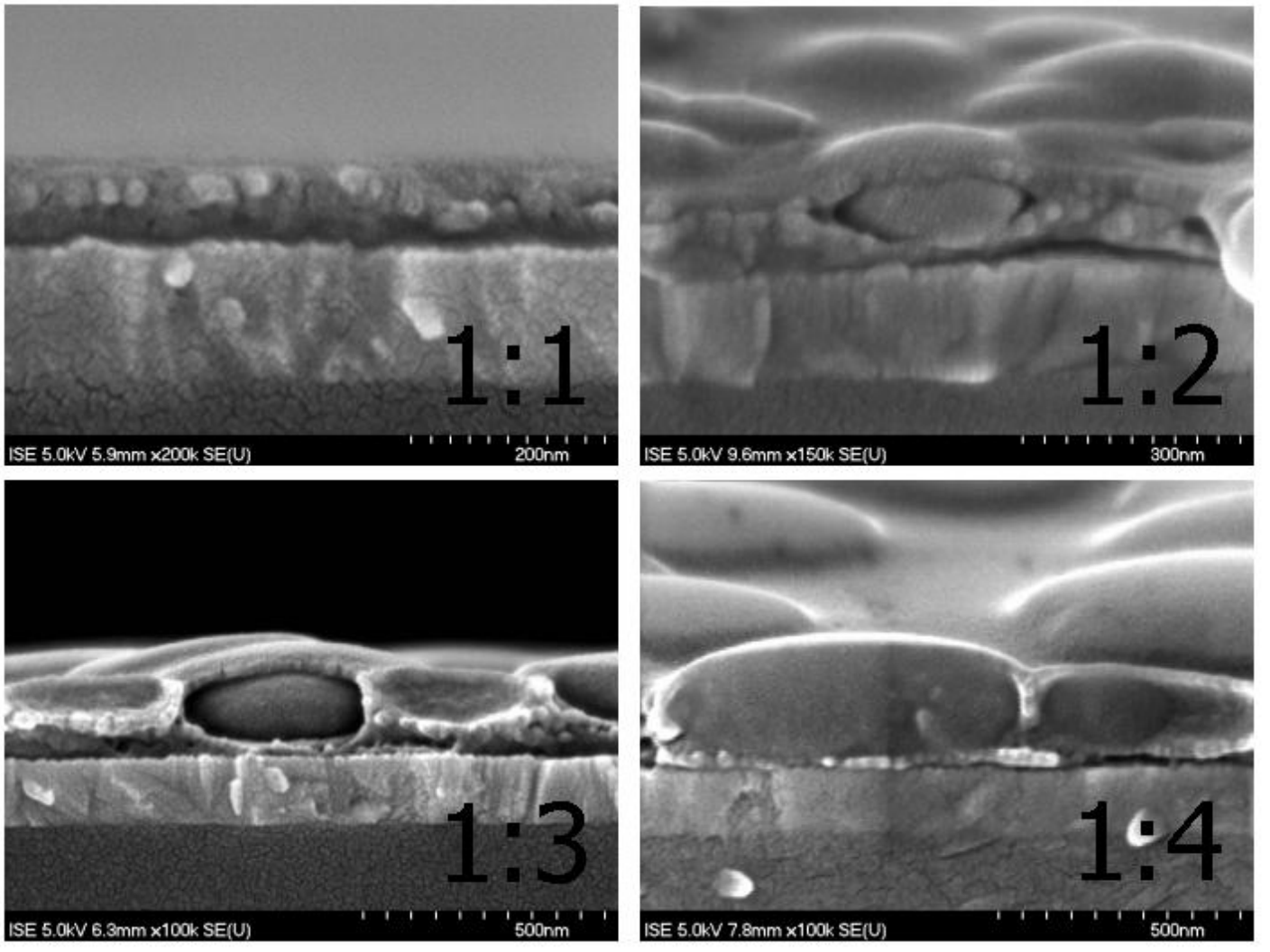




A 2-3 fold increase of the IPCE and short circuit current was observed by S.E. Shaheen et al.* due to the change from toluene to chlorobenzene as solvent, while by AFM measurements a decrease in the surface roughness was detected.

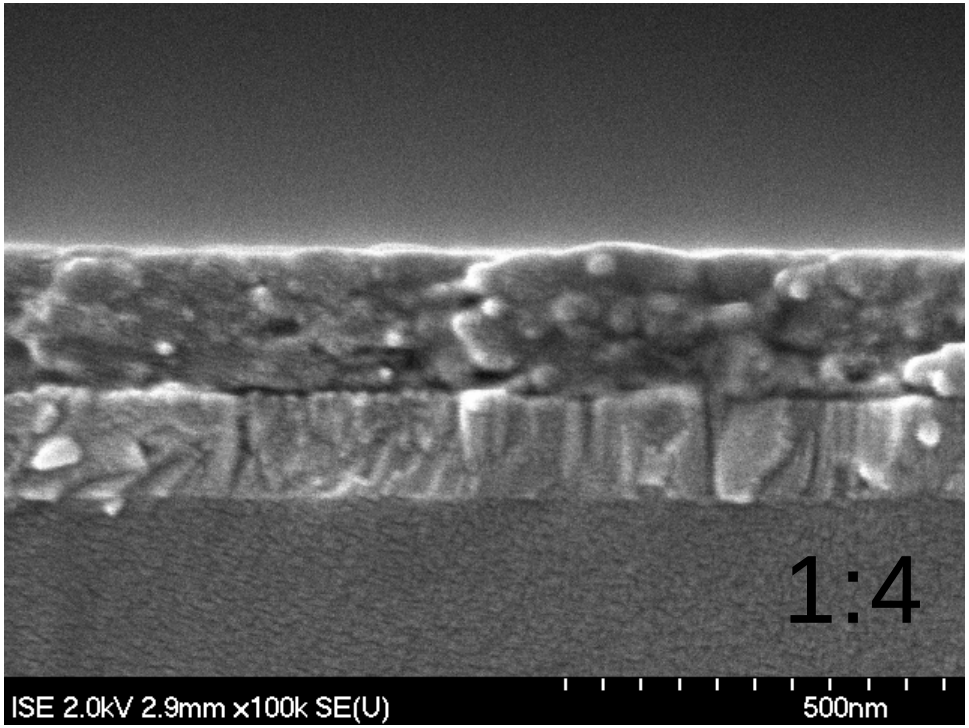
*S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, *Appl. Phys. Lett.* **78**, 841 (2001)

Nanomorphology Effects-SEM Studies



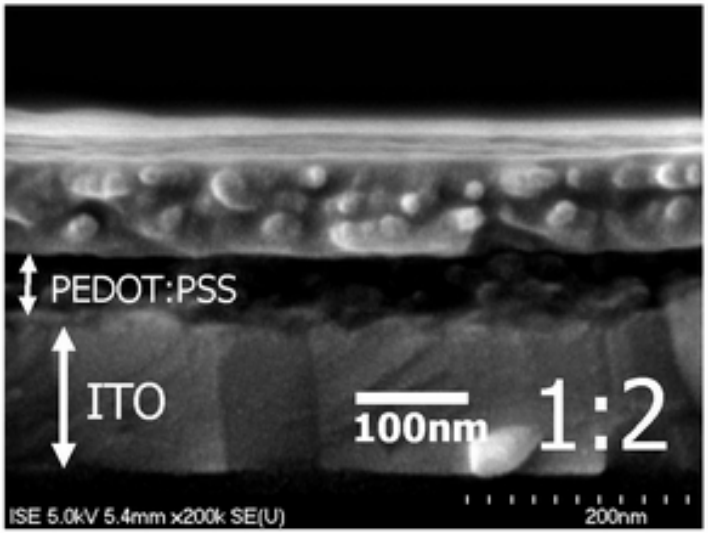
Harald Hoppe *et al*. *Adv*. *Func*. *Mater*. **14**, (2004) 1005,

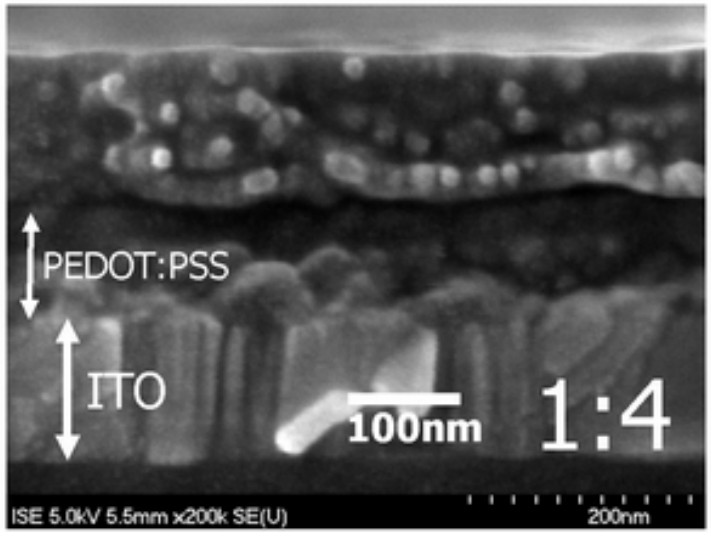
...and from Chlorobenzene?

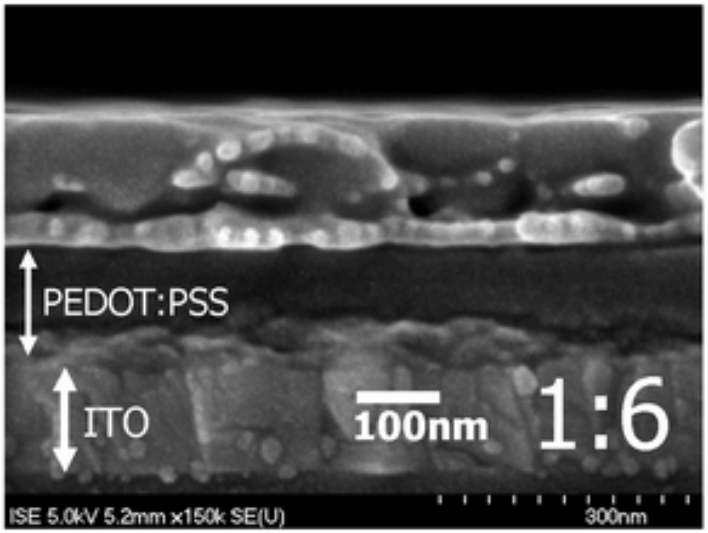


Harald Hoppe *et al*. *Adv*. *Func*. *Mater*. **14**, (2004) 1005,

Nanomorphology Effects-SEM Studies



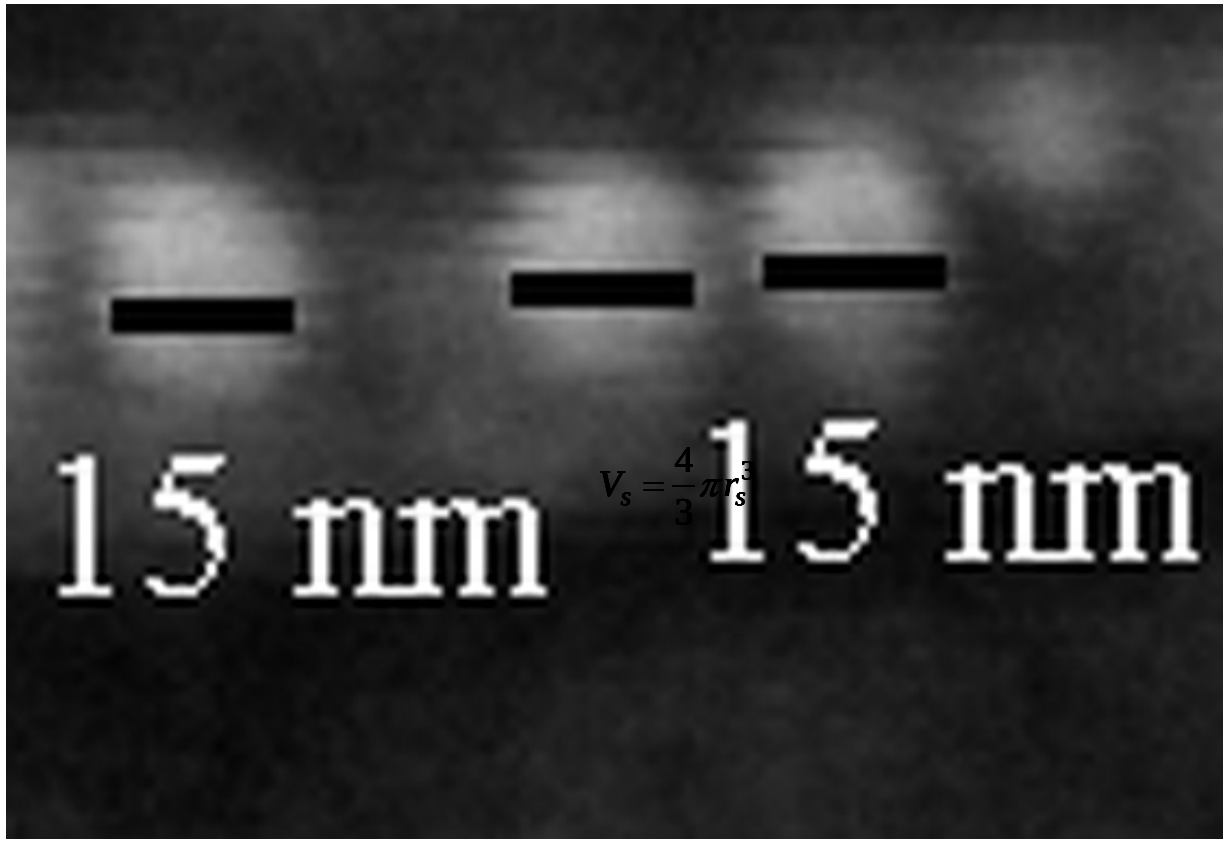




Chlorobenzene cast films
have
much smoother and
more homogenous
nanostrcuture

Harald Hoppe, et al. *Adv. Func. Mater*. **14**, 1005 (2004)

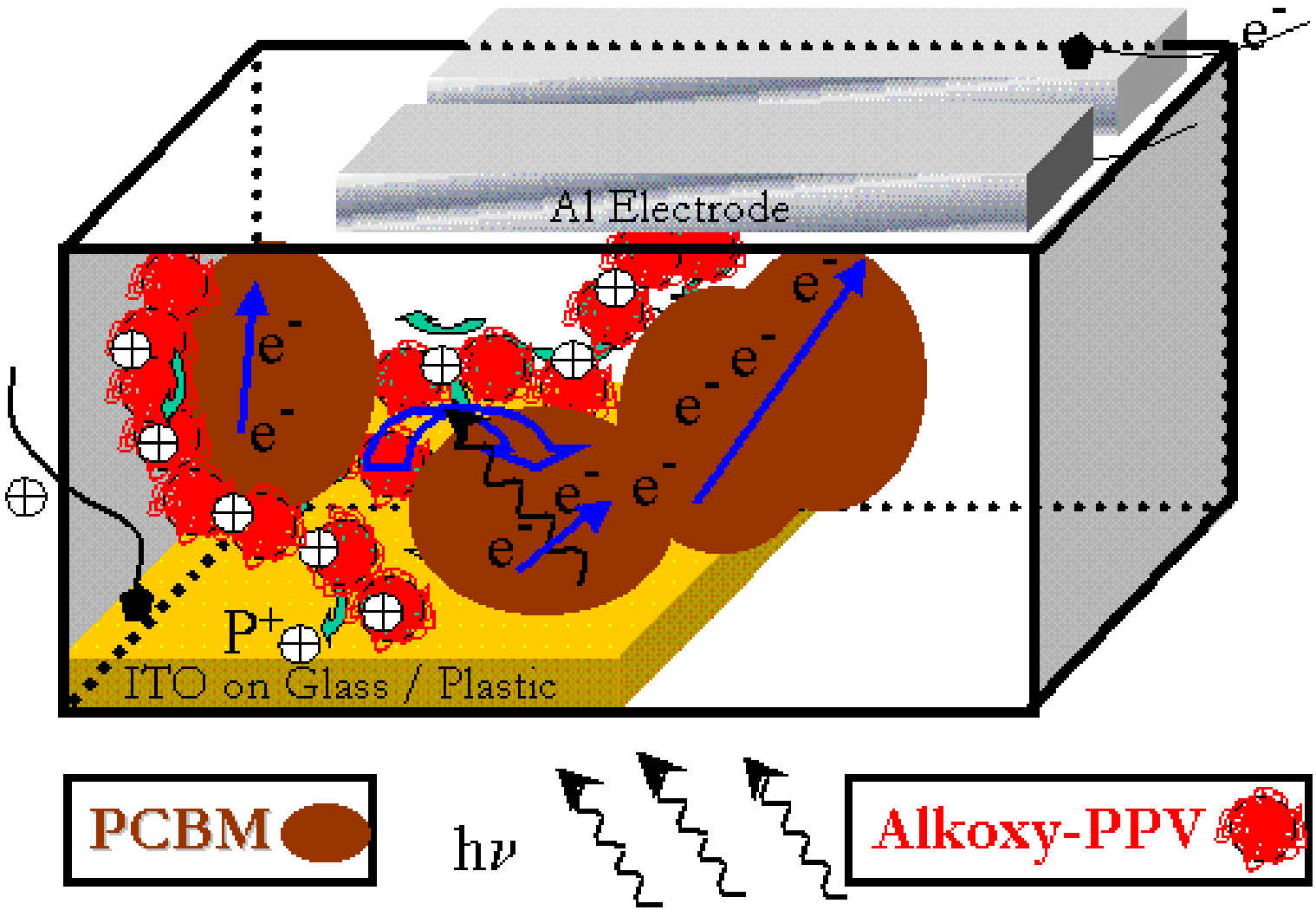
Wessling Nanospheres



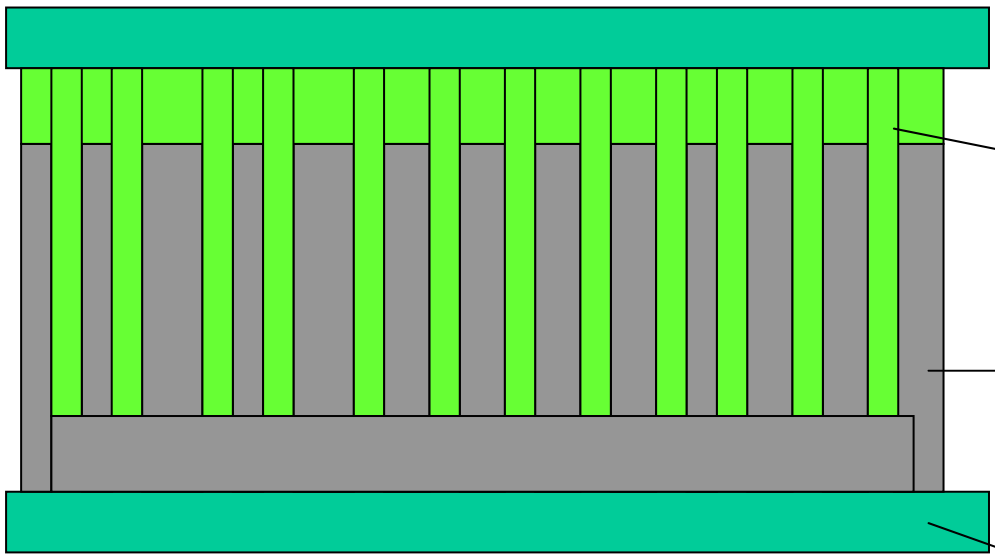
$\Rightarrow$ Diameter of MDMO-PPV Nanospheres $\approx$ 15-20 nm

Harald Hoppe, PhD Thesis (2004)

Bulk Heterojunctions: Revised



„Optimum“ Geometry for Organic and Hybrid Solar Cells



High workfunction electrode

Organic p-type conductor (donor)

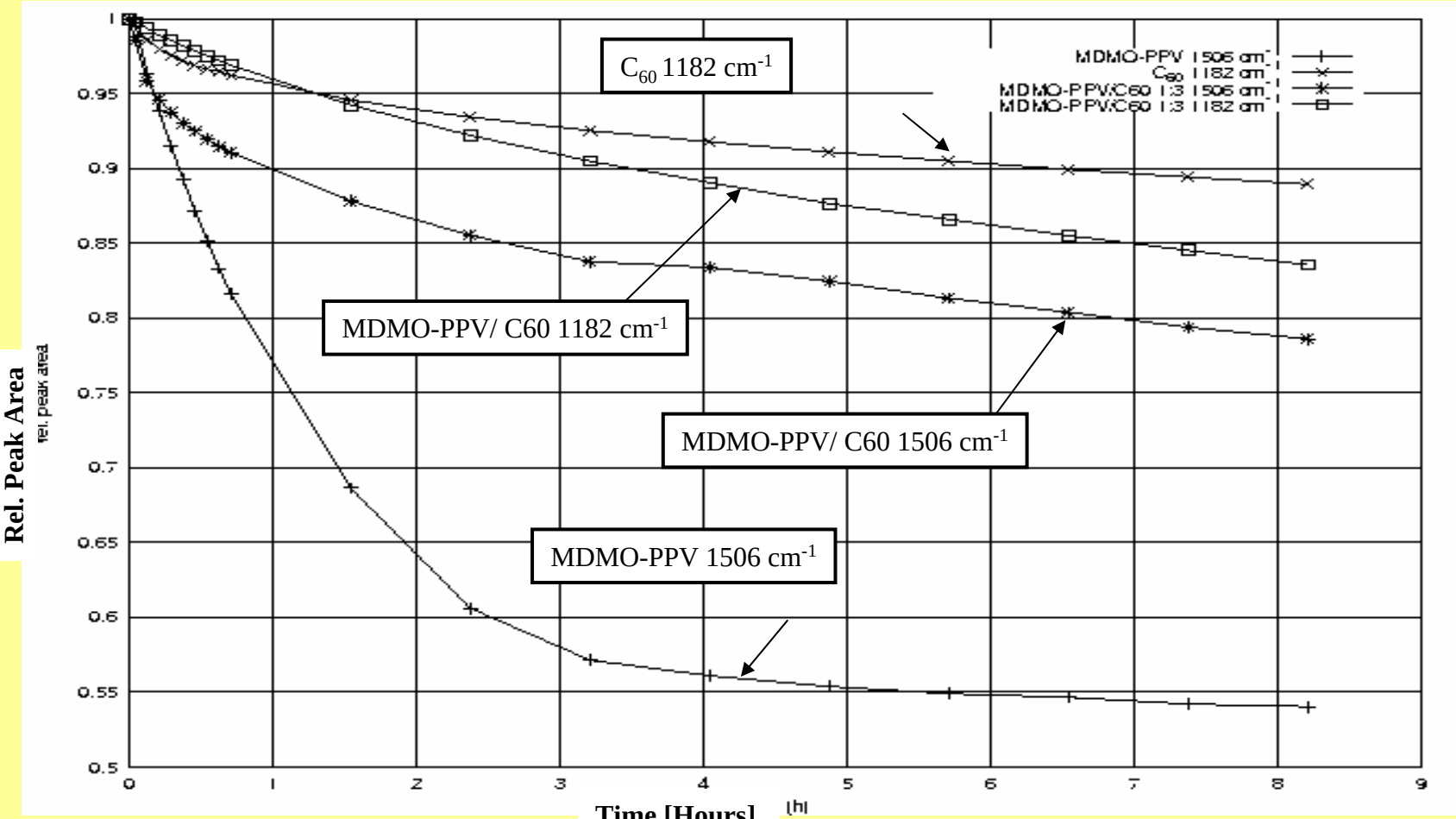
Organic n-type conductor (acceptor)

Low workfunction electrode

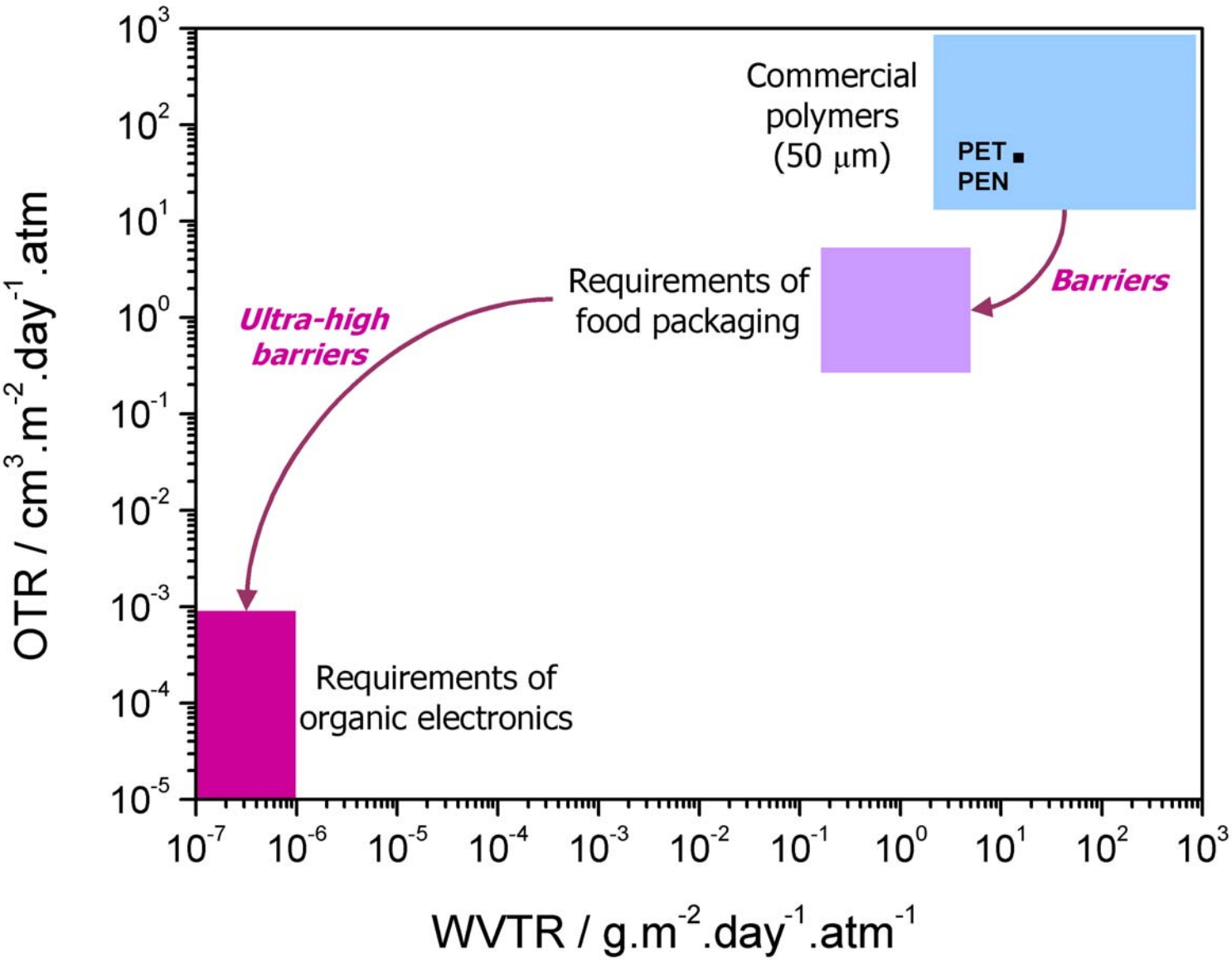
Stability

OUTLOOK - Stability

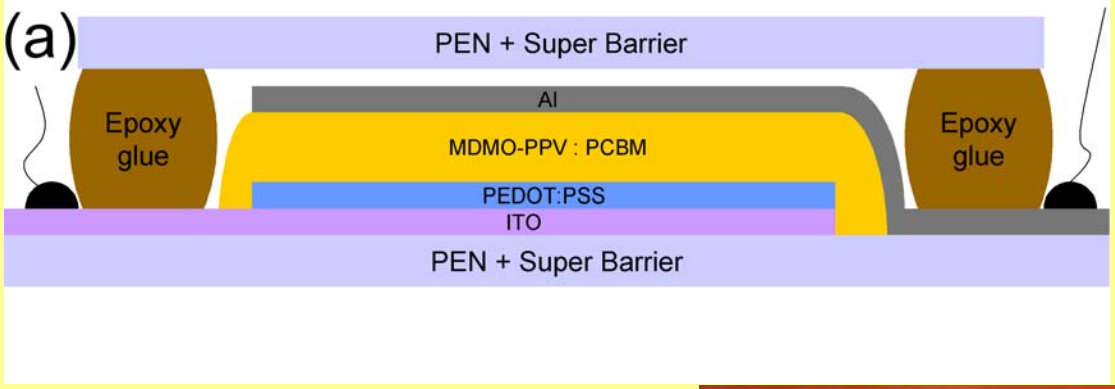
C_{60} slows down degradation of the Conj. Polymer



Encapsulation

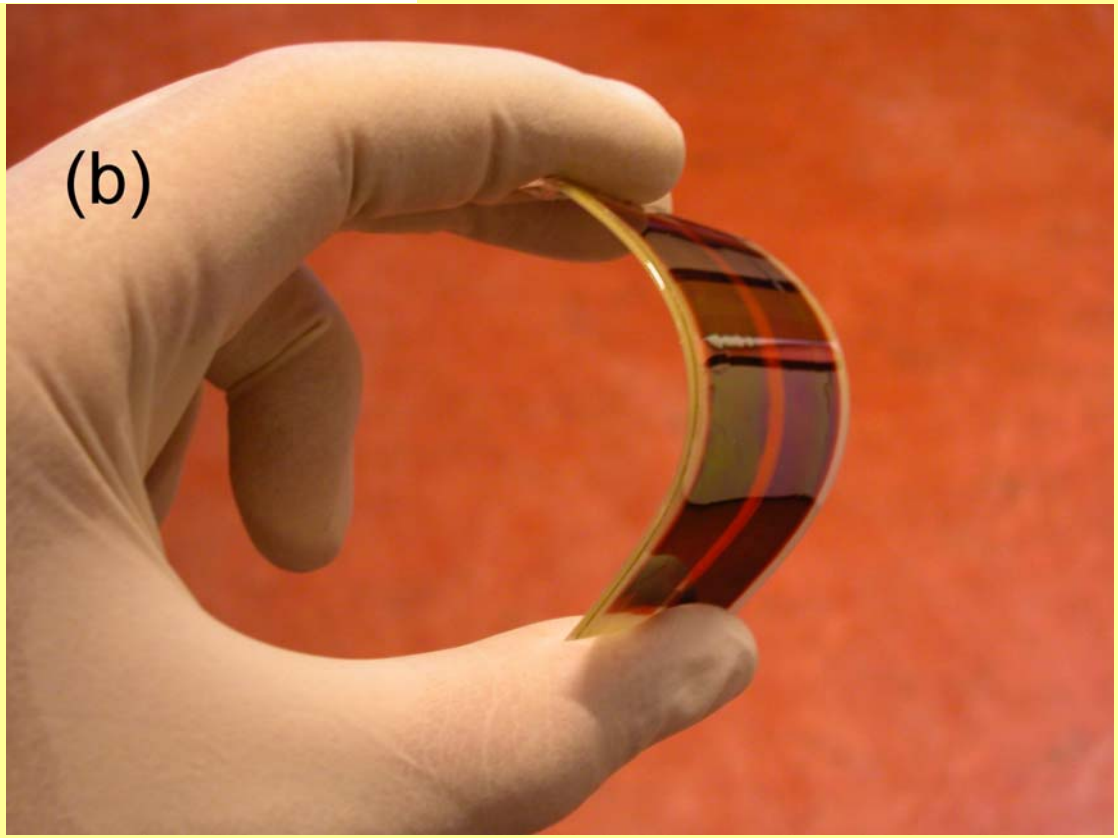


Encapsulation

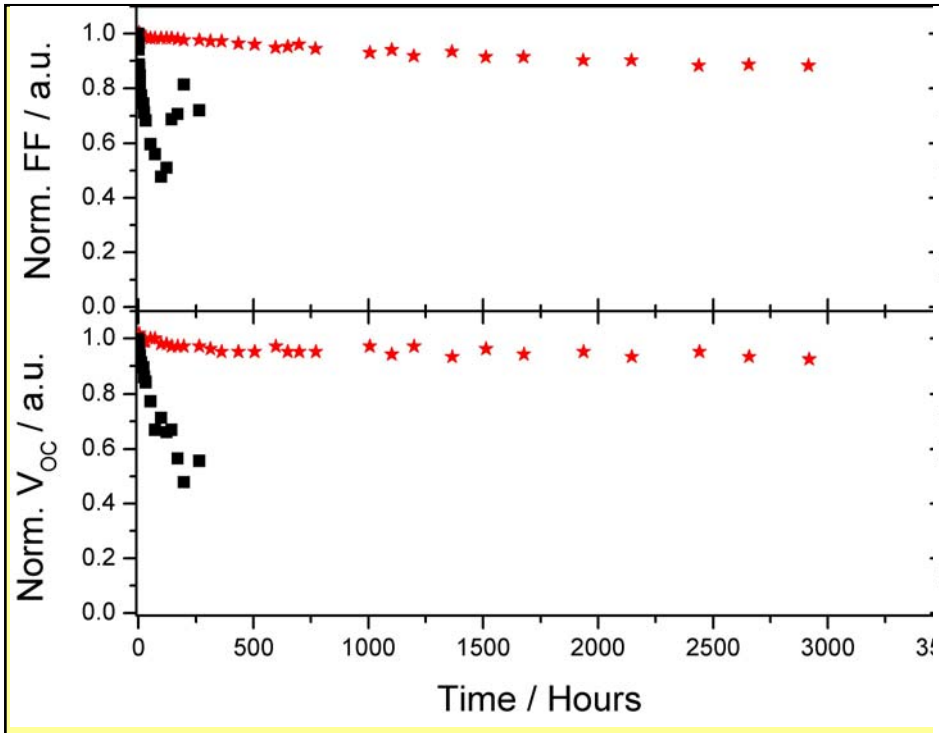


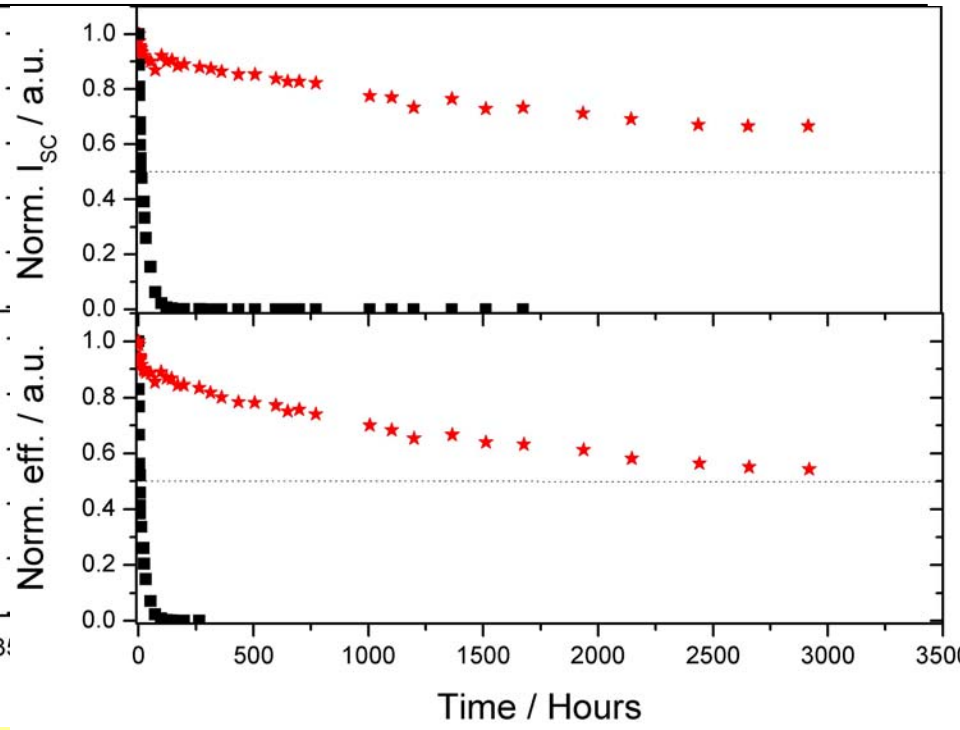
Novaplasma Inc., Montreal, Canada

G. Dennler et al, 2005



Encapsulation



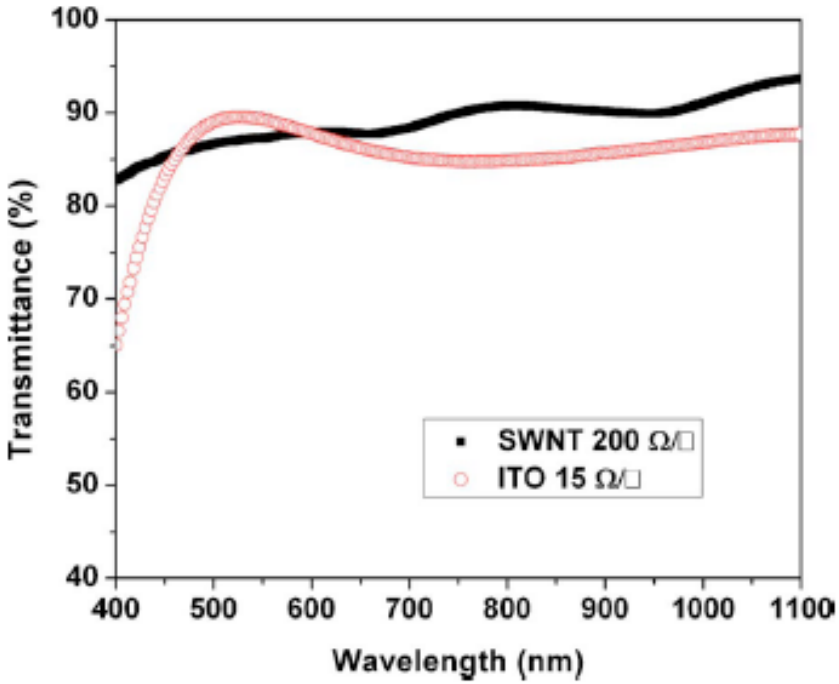


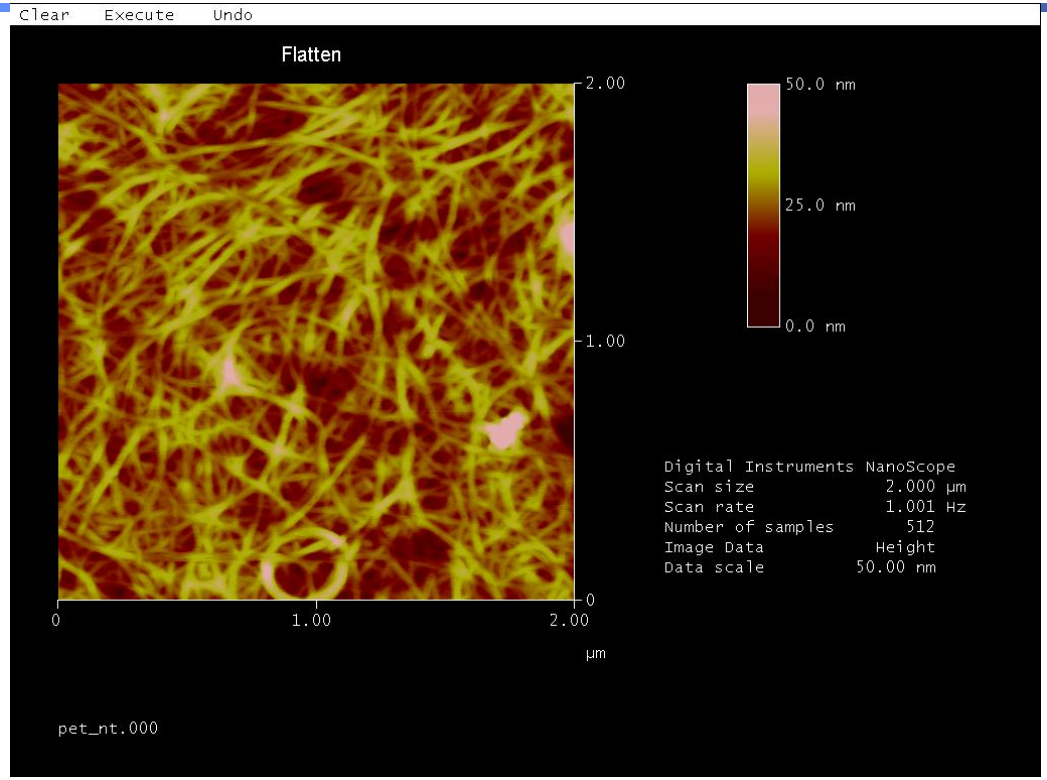
NOVAPLASMA Encapsulation Foils

G. Dennler et al, 2005

Can we get rid of ITO As Substrate?

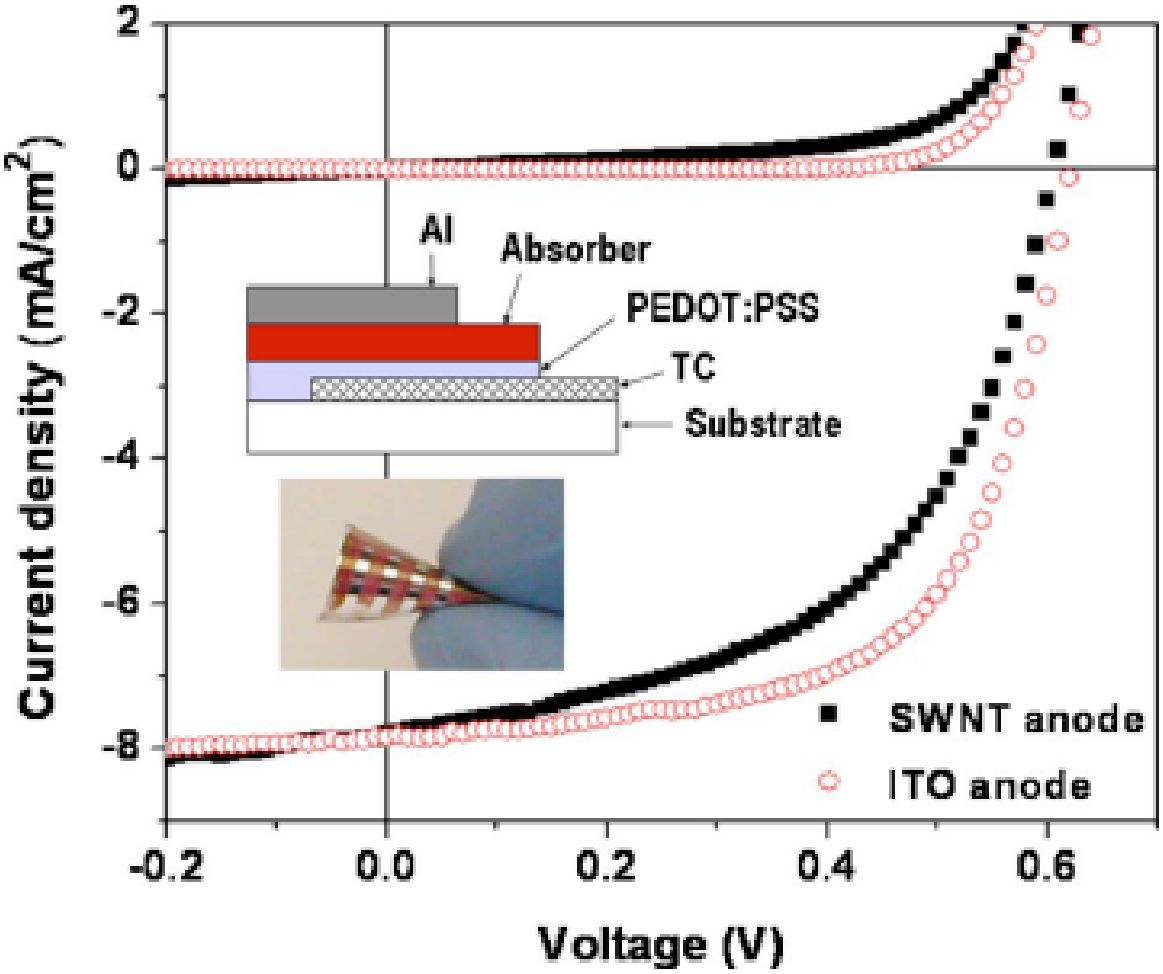
NANOTUBE ELECTRODE ?





Rowell *et al*, *Appl. Phys. Lett.* **88** (2006) 233506

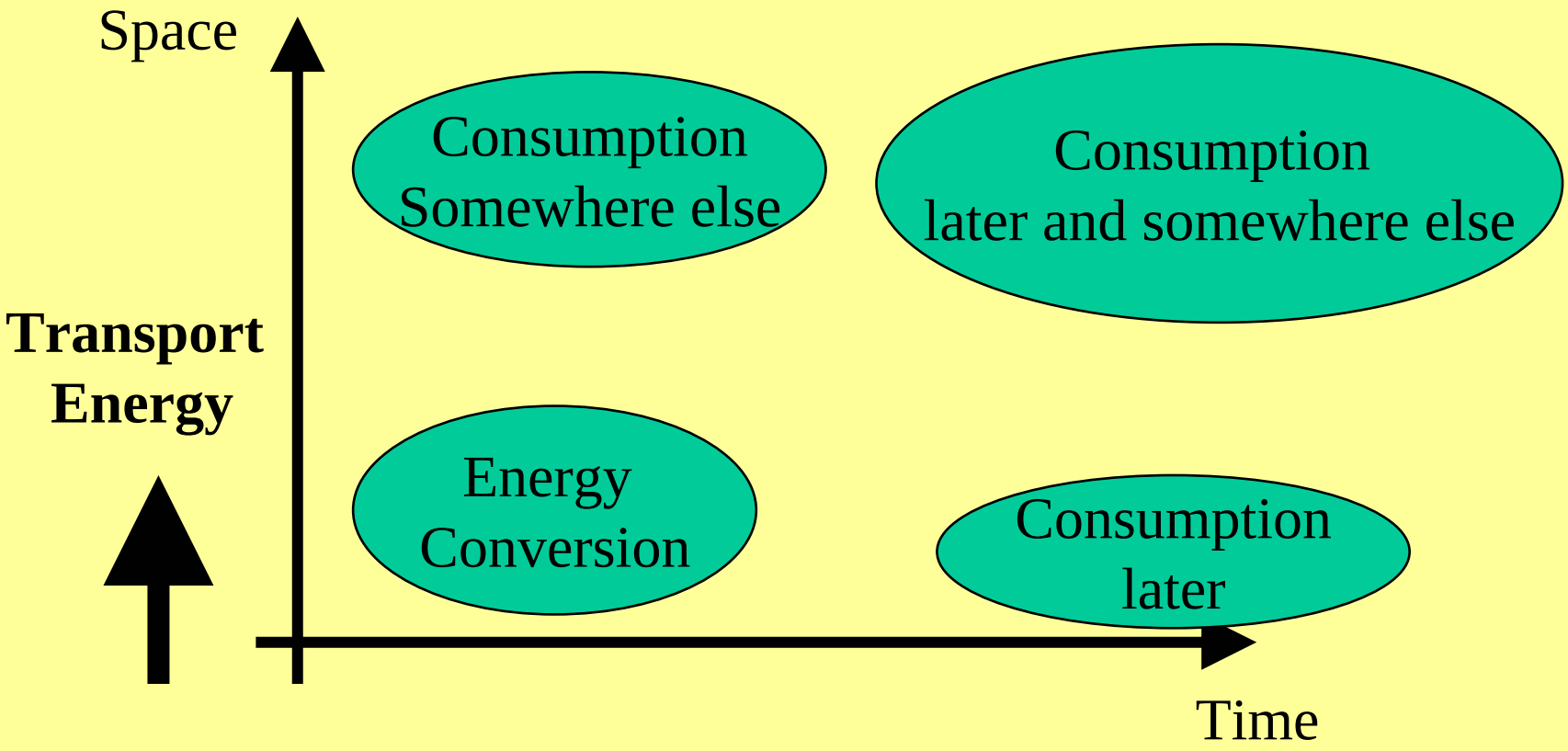
NANOTUBE ELECTRODE ?



It works !!!

Rowell *et al*, *Appl. Phys. Lett.* **88** (2006) 233506

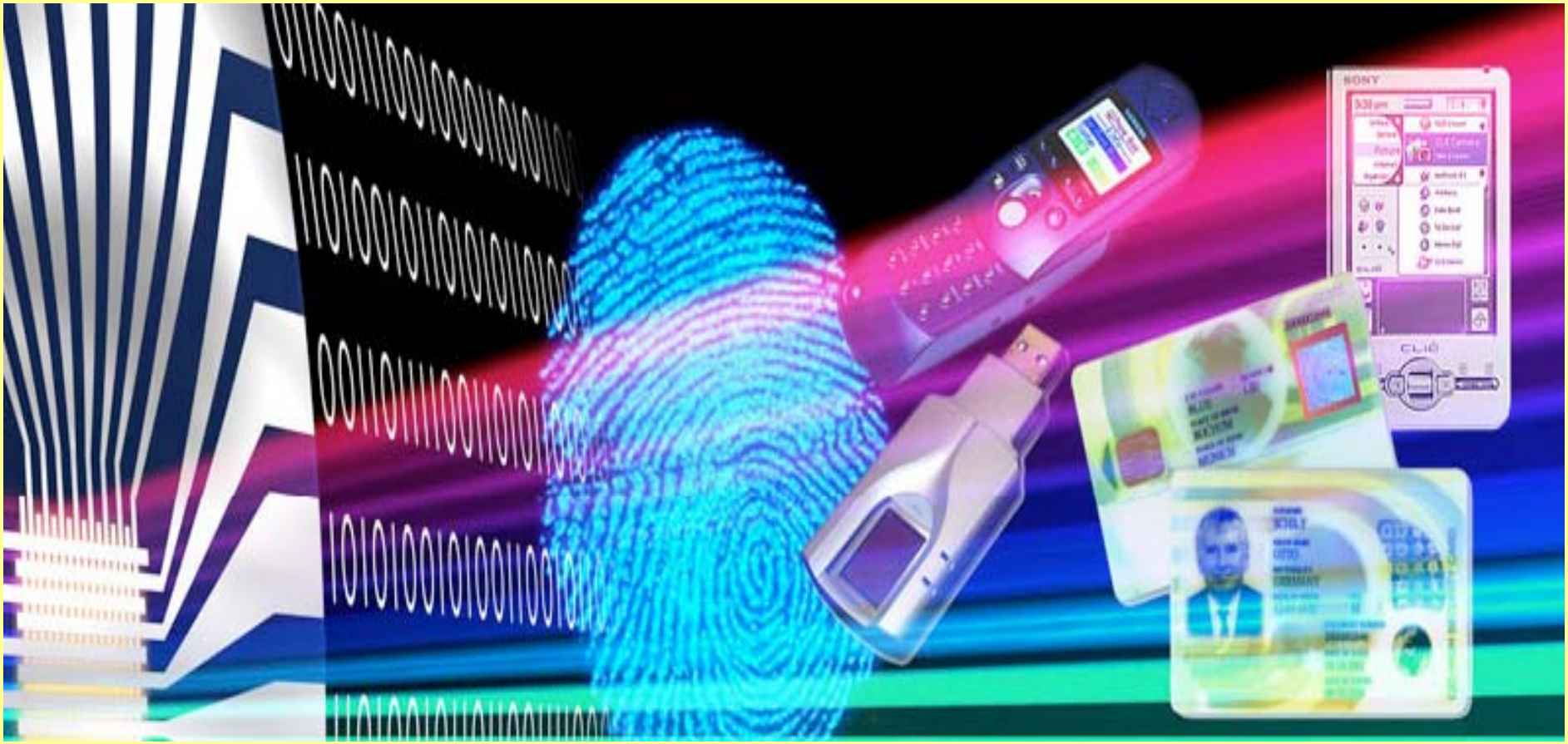
Storage-Transport Problem



Storage of Energy

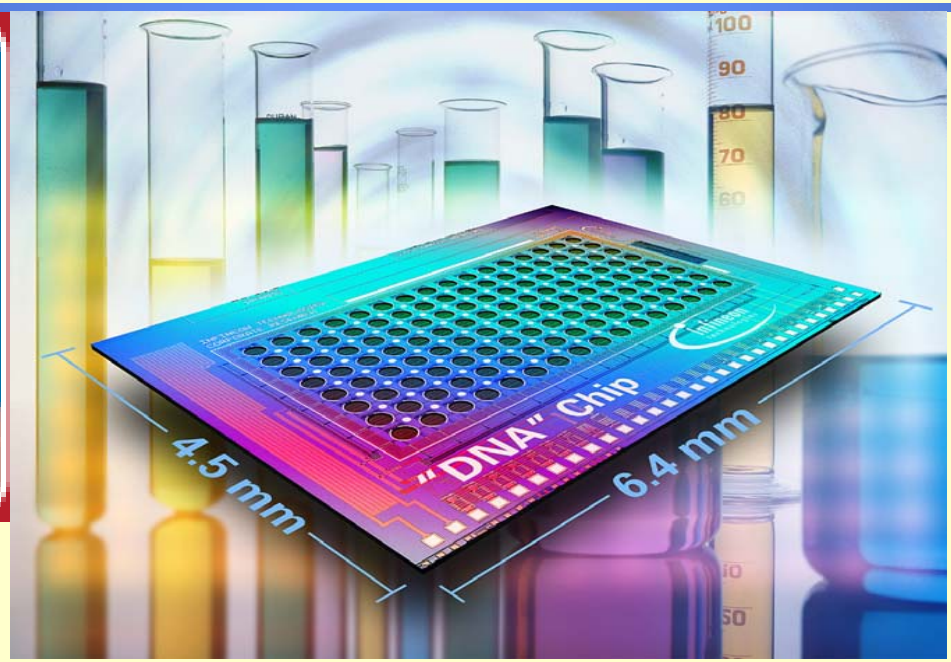
Transportable fuel created by solar energy conversion !!!

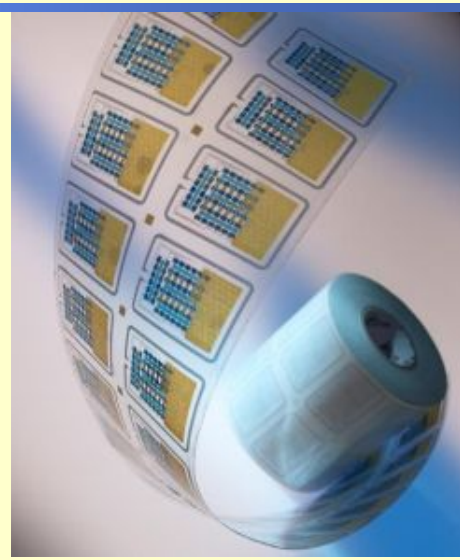
Optoelectronic Detector Arrays



www.nanoident.com
www.bioident.com

Plastic Electronic Circuits



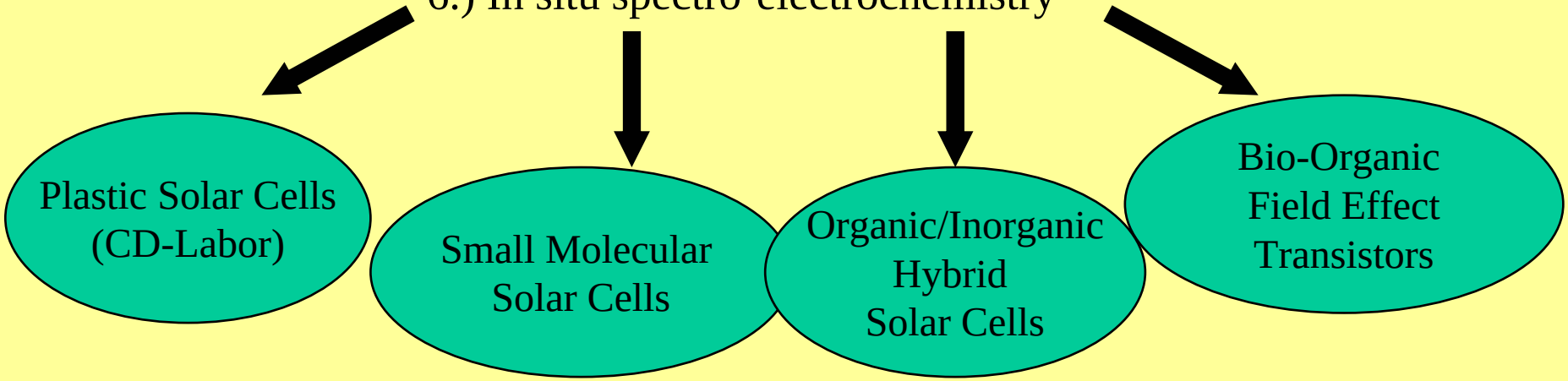


Organic Electronics Association des
Vereins der Deutschen Maschienen- und Anlagenbauer VDMA
www.oe-a.de
New spin off from LIOS:
www.plastic-electronic.com

Linz Institute for Organic Solar Cells

Physics of Organic Semiconductors:

1.) Photoexcited spectroscopy
2.) Photoconductivity
3.) Thin film characterization
4.) Nanoscale engineering
5.) Nanoscale microscopy (AFM, STM...)
6.) In situ spectro-electrochemistry



„Incubator“ for small high tech spin-off companies:
Konarka Austria (former QSEL), NanoIdent AG,
Plastic Electronic GesmbH, Prelonic,…

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NanoIdent Technologies (Bioidentification photodetector arrays)
Plastic Electronic (Organic circuits and chips)

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