The Abdus Salam International Centre for Theoretical Physics

2269-18

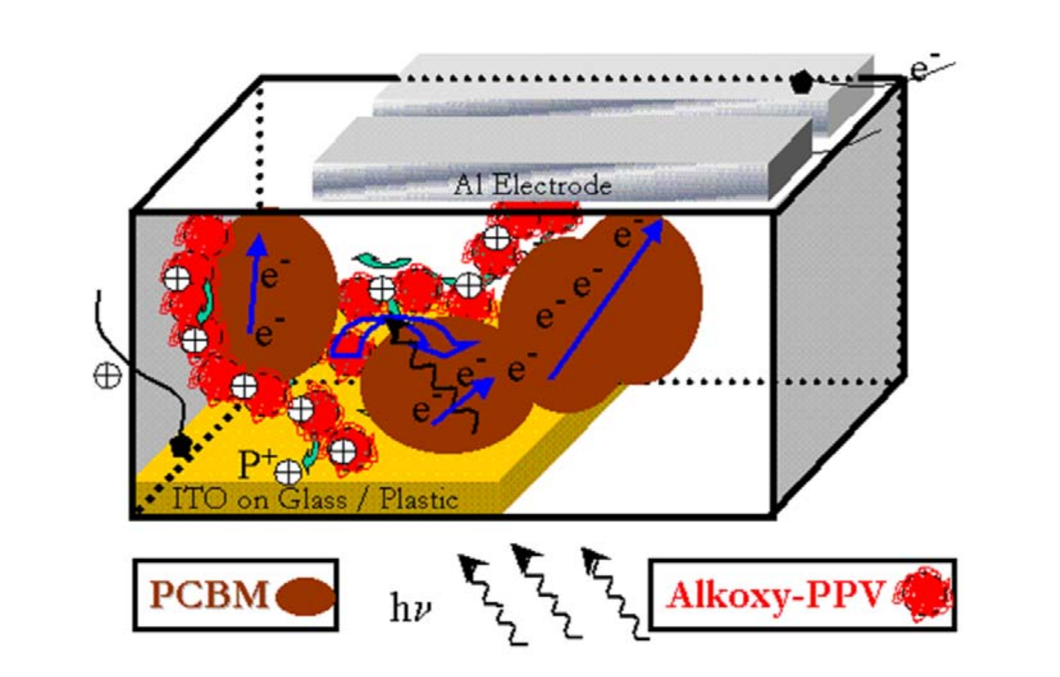
Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Organic and inorganic nanostructures for solar energy conversion

Niyazi Serdar SARICIFTCI
Linz Institute for Organic Solar Cells LIOS
Institute for Physical Chemistry
Johannes Kepler University Linz
Austria

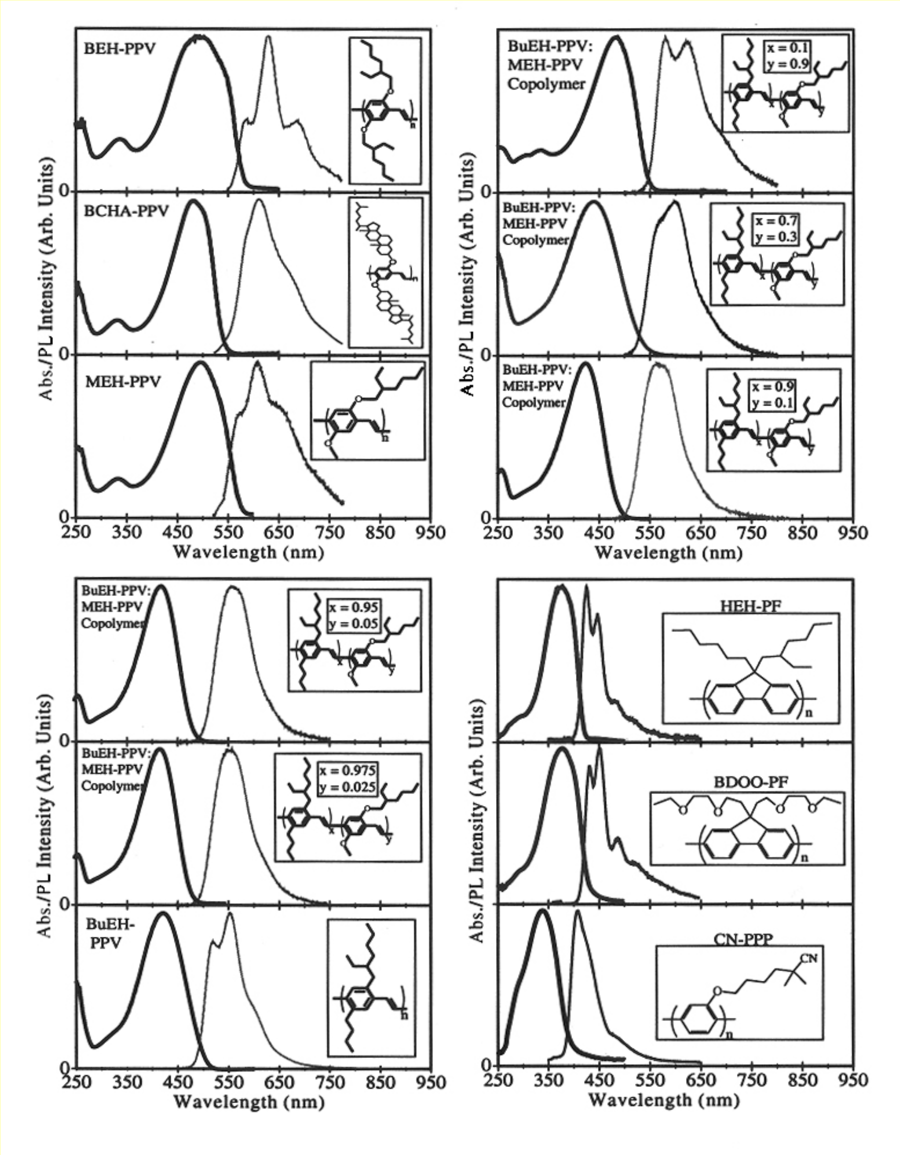
Organic and Inorganic Nanostructures For Solar Energy Conversion

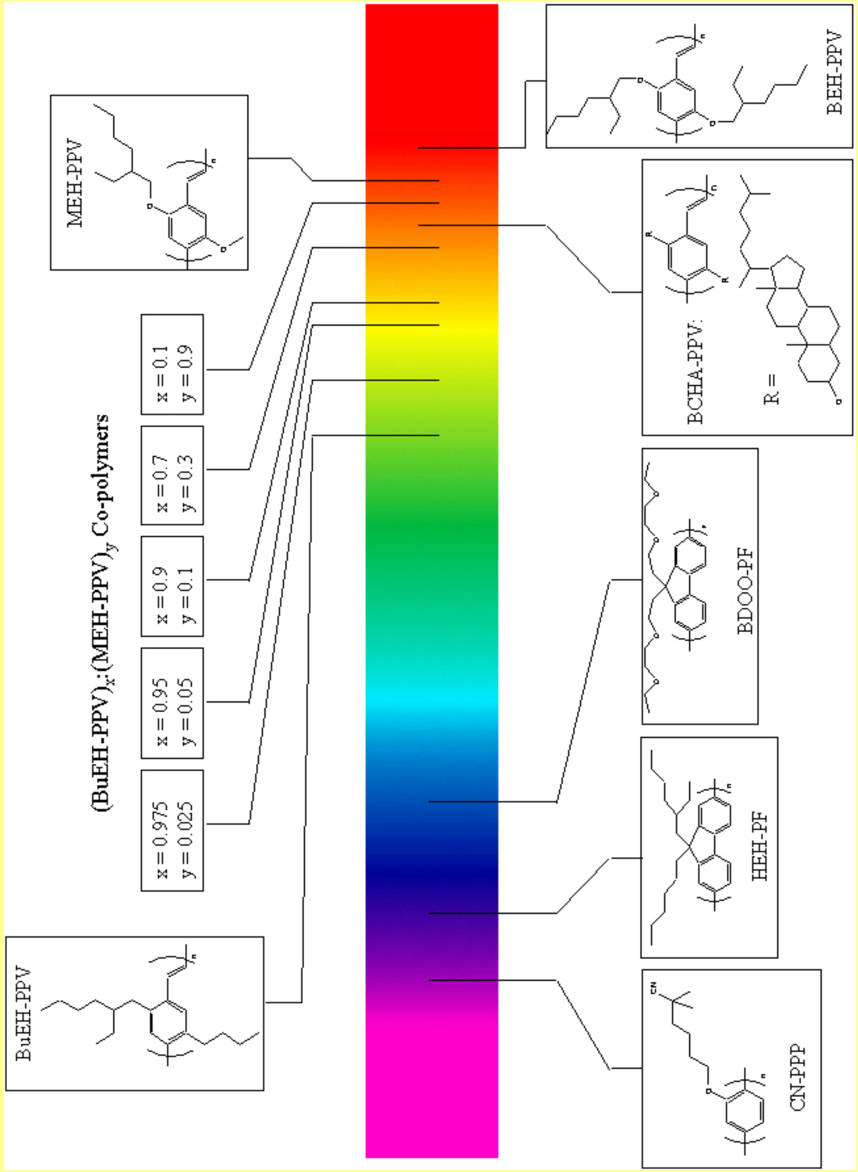


Niyazi Serdar SARICIFTCI
Linz Institute for Organic Solar Cells (LIOS),
Institute for Physical Chemistry, Johannes Kepler University Linz, Austria
www.lios.at

Semiconducting Polymer “Inks”

Color Variations: Band Gap Engineering



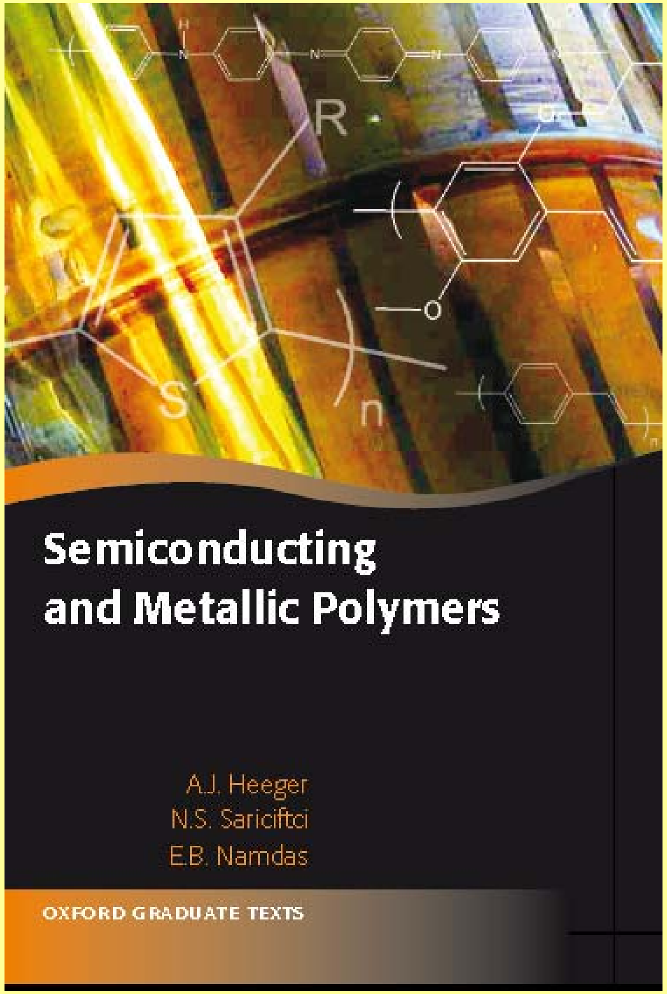


Semiconducting and Metallic Polymers

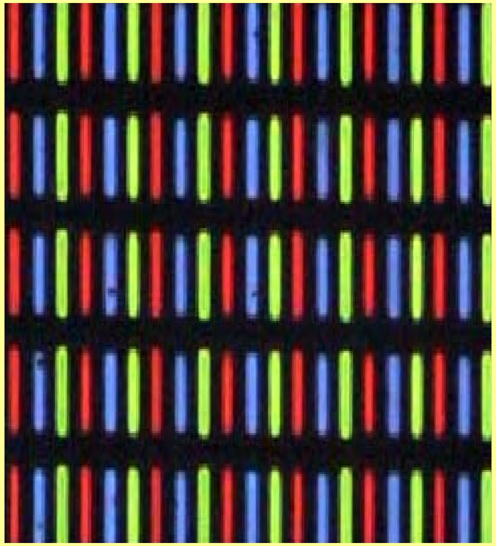
---for they combine the electronic properties of metals and semiconductors

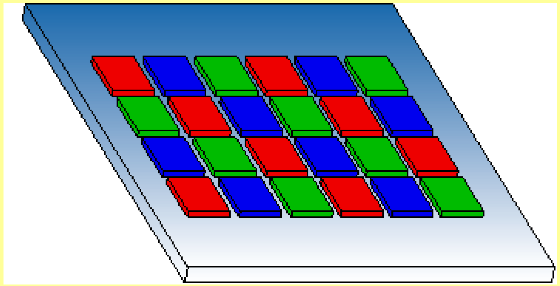
and

the processablity, synthesis advantages and flexibility of polymers..



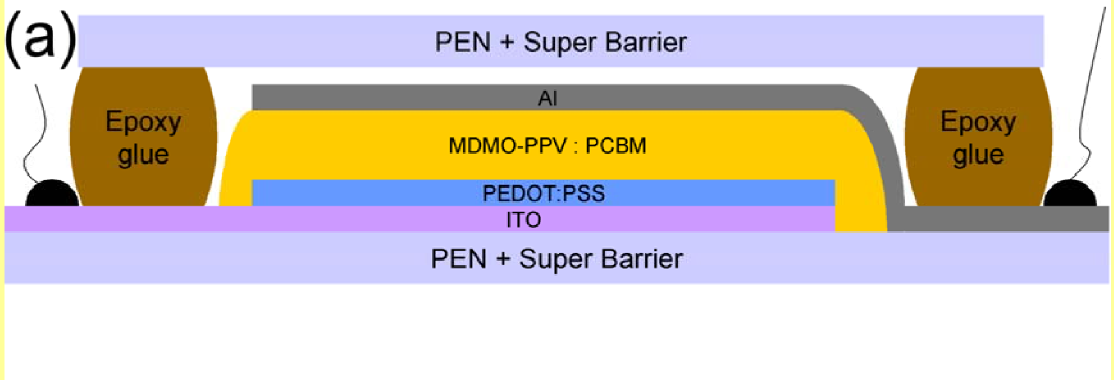
Full Color Plastic Flat Panel Displays





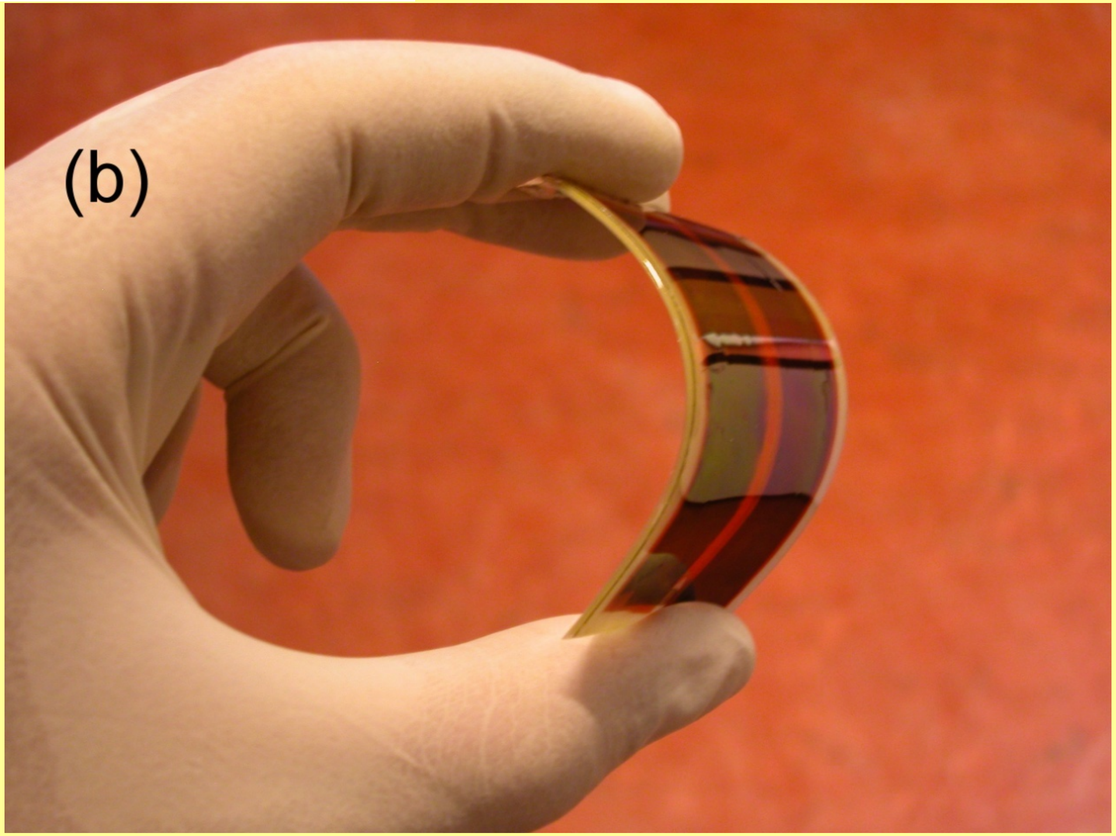
White OLEDs by Lumiotech, Yonezawa

Encapsulation

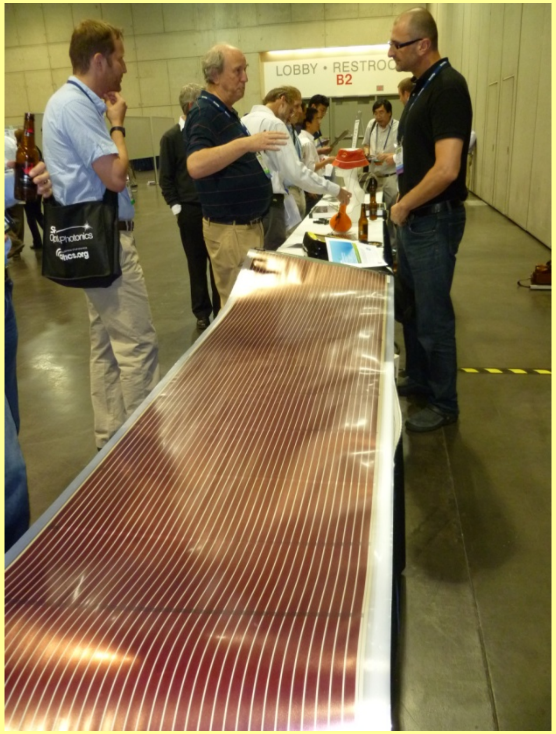


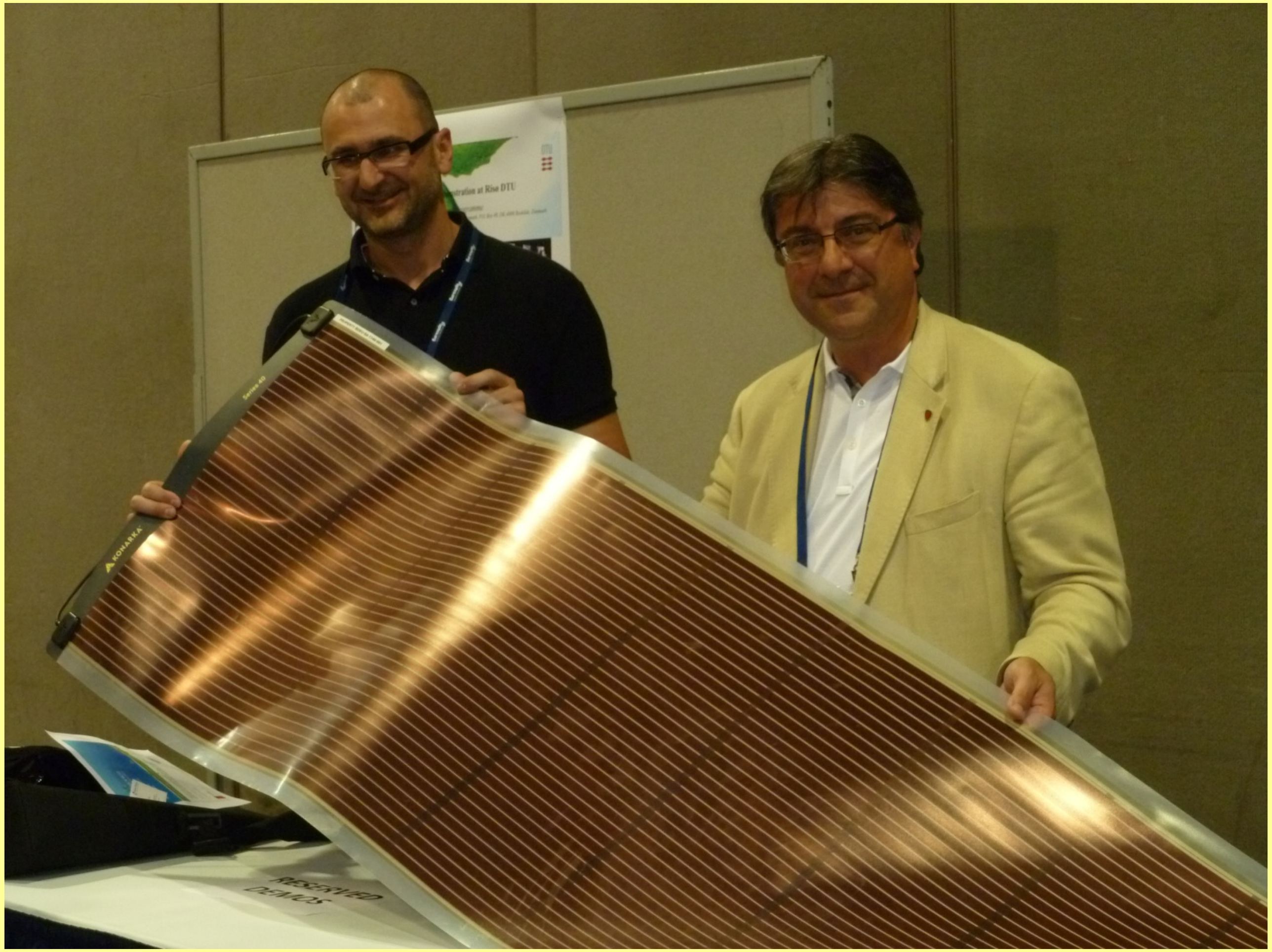
Novaplasma Inc., Montreal, Canada

G. Dennler et al, 2005



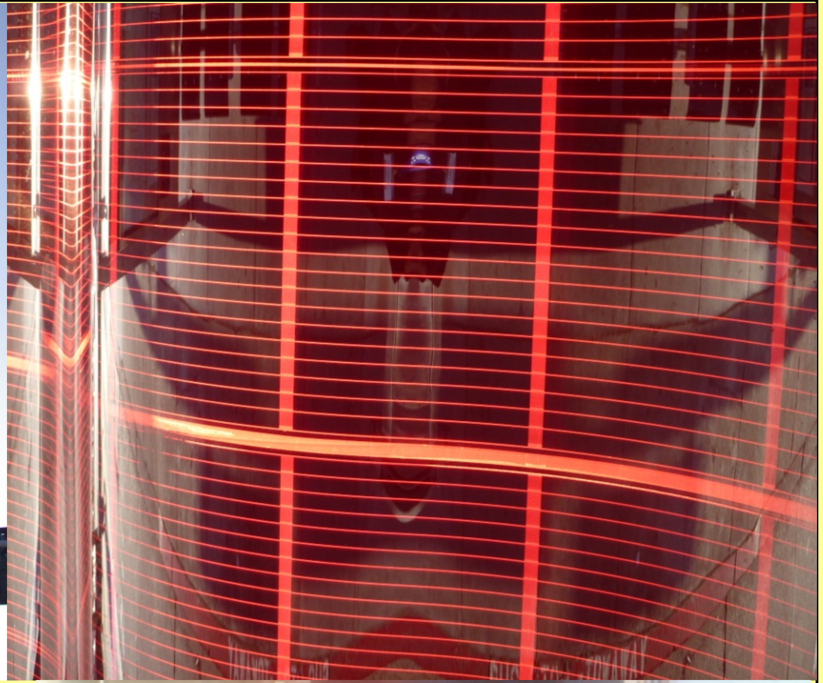
Roll to roll produced solar cells

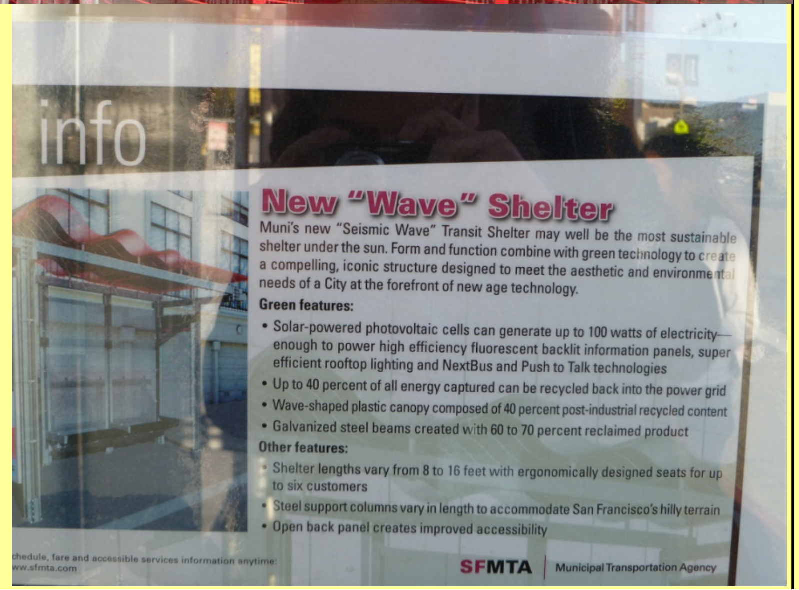




Konarka Inc.

Outdoor Demonstrations



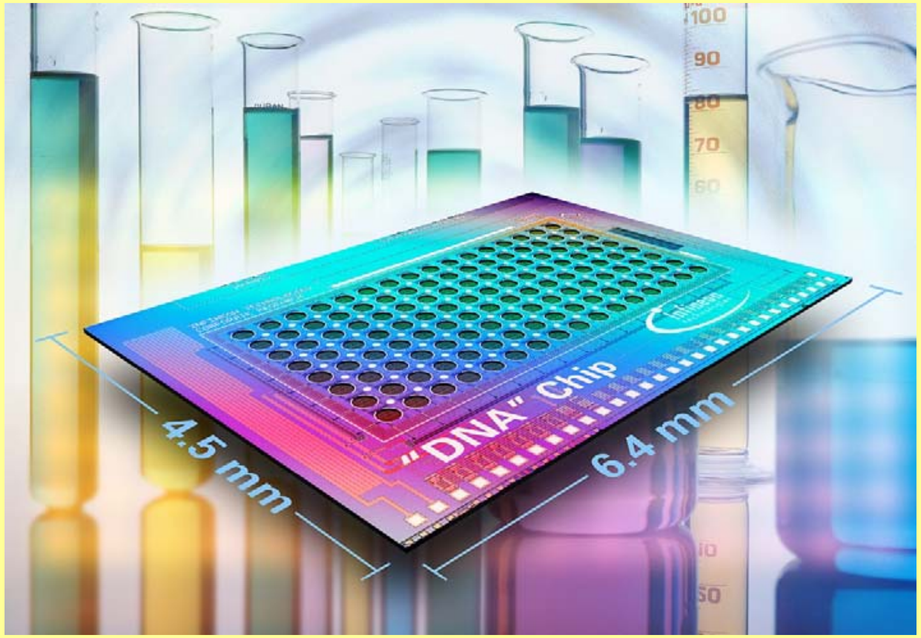


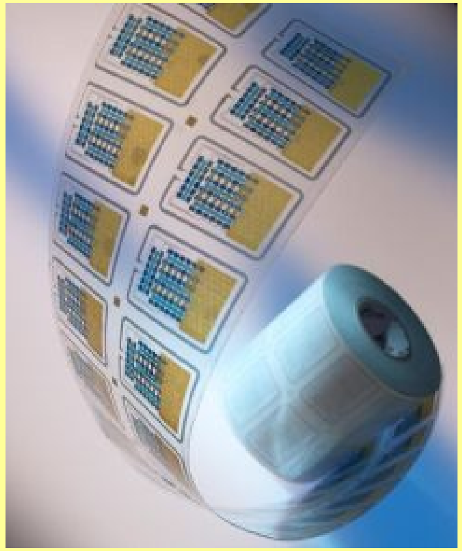
Solar cell integrated textiles

A commercial solar jacket and bag

www.scottevest.com www.neubers.de

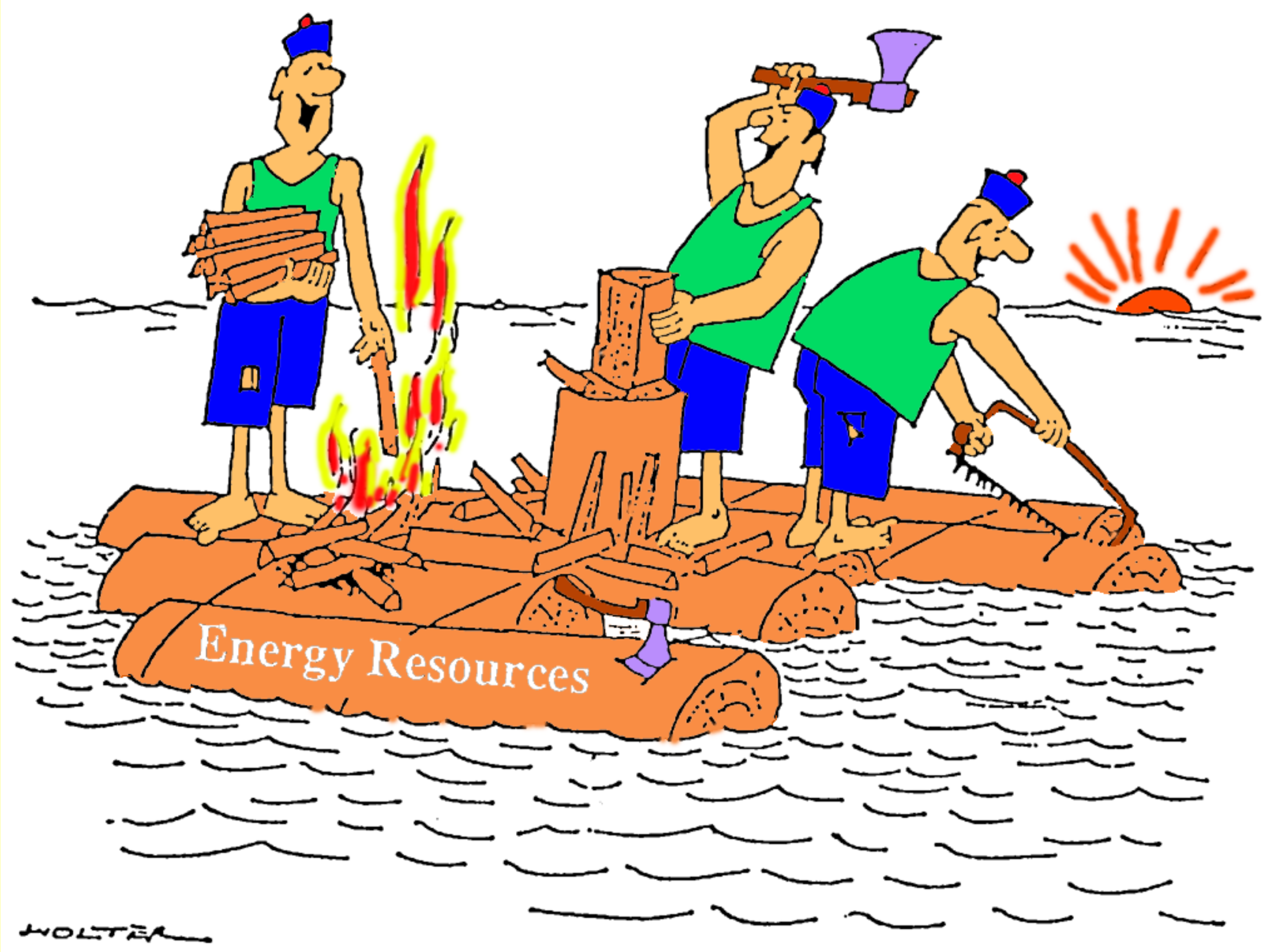
Plastic Electronic Circuits



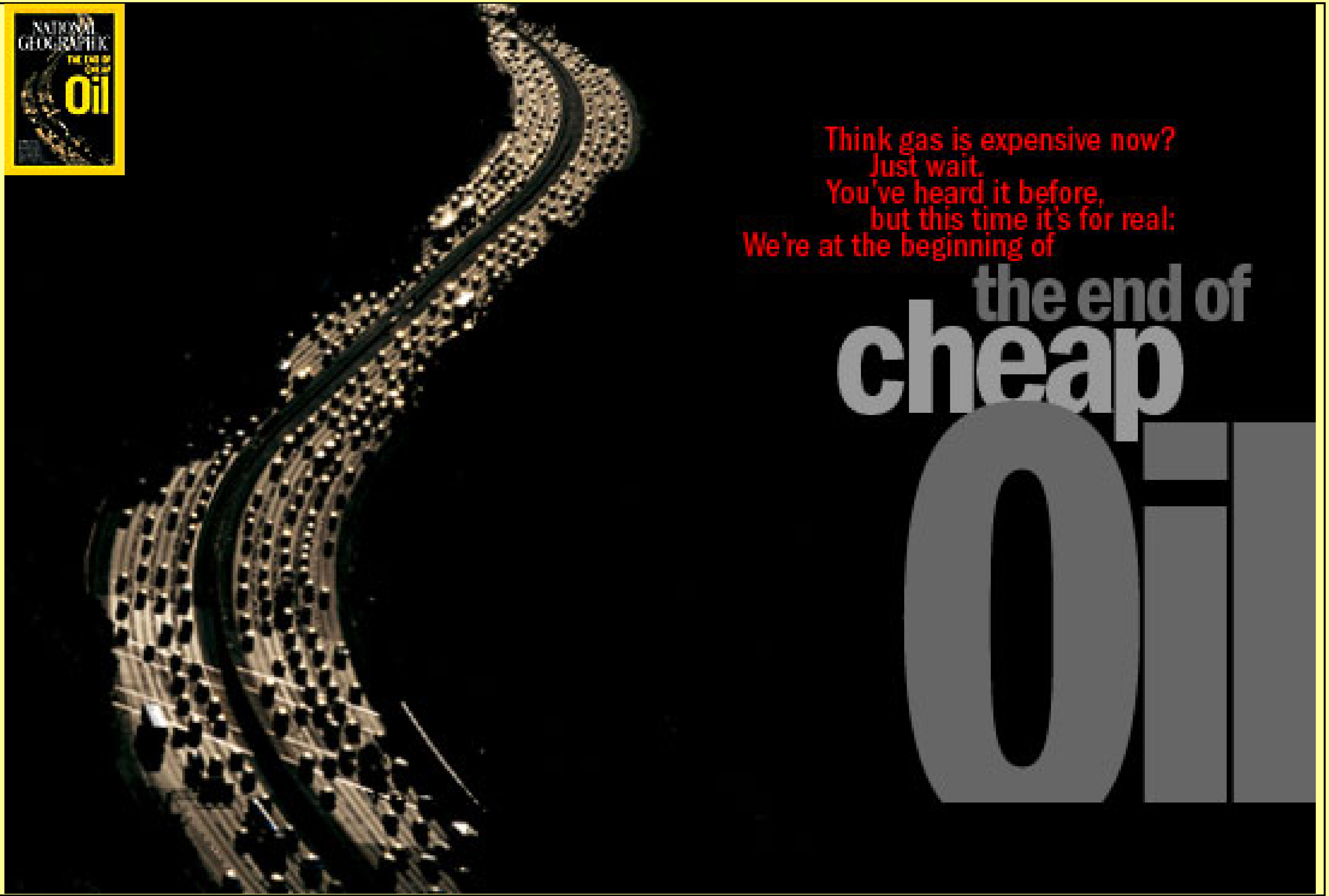


Organic Electronics Association des
Vereins der Deutschen Maschienen- und Anlagenbauer VDMA
www.oe-a.de

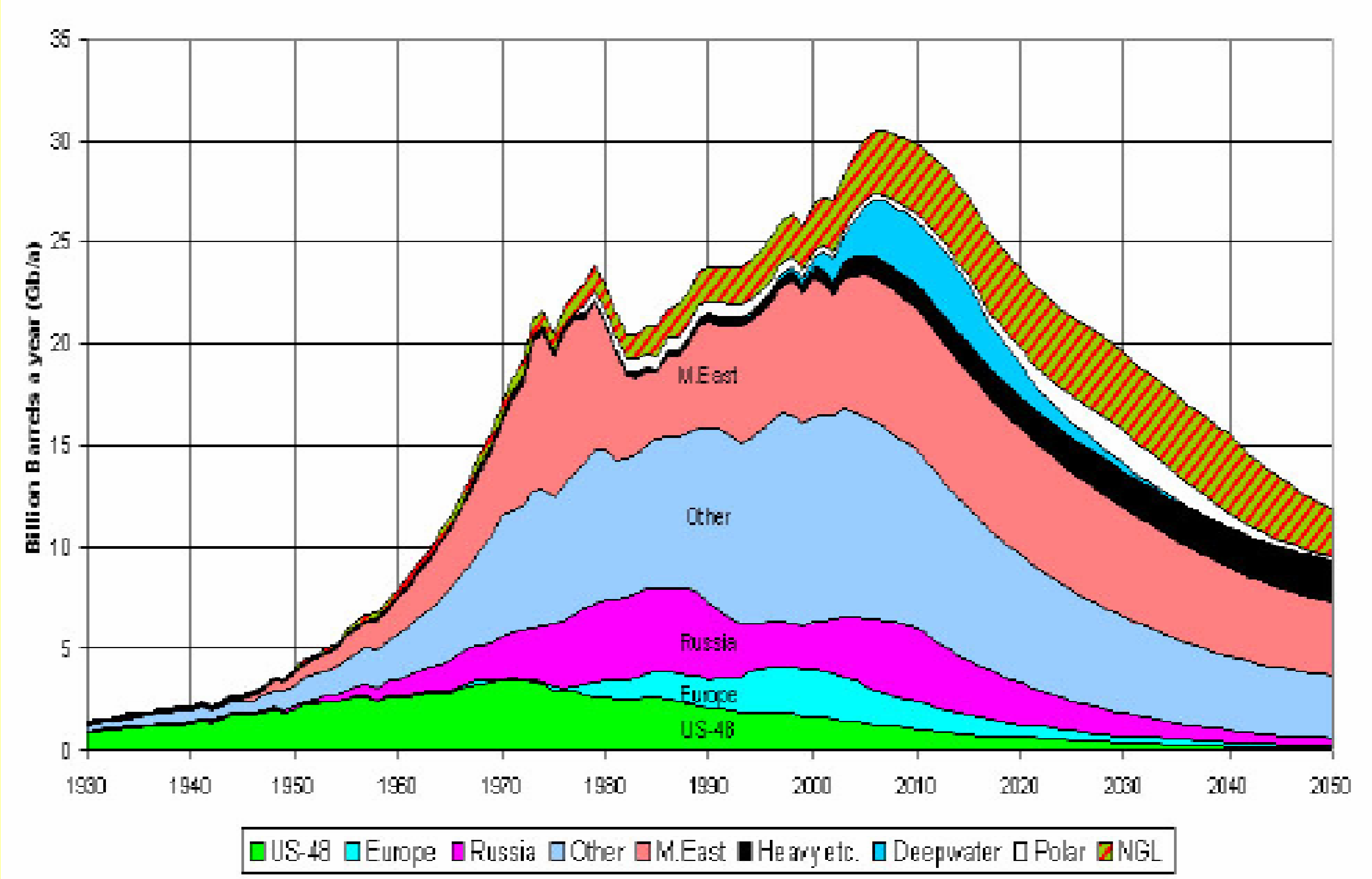
Happy Life



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

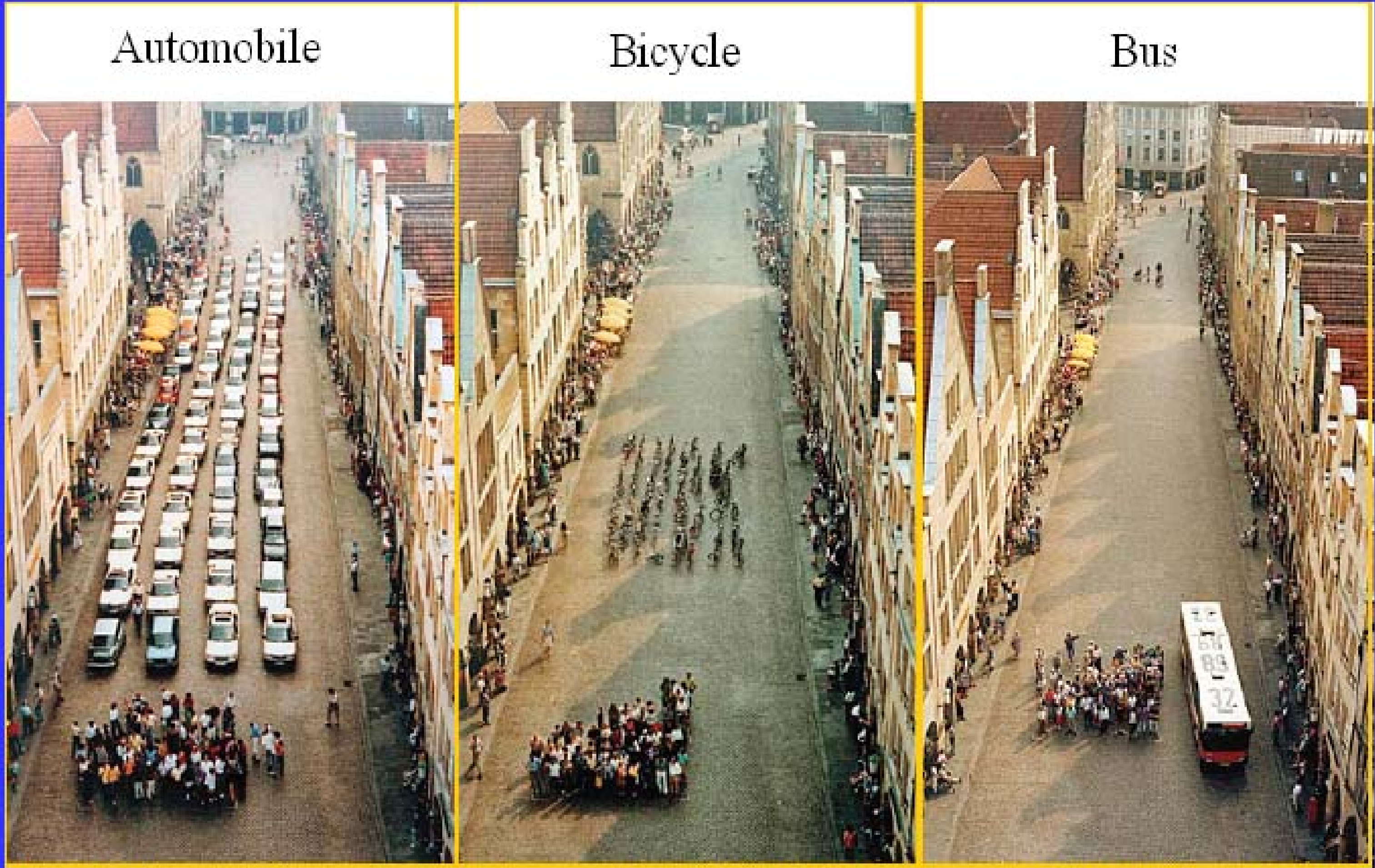
Scope



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

Energy saving

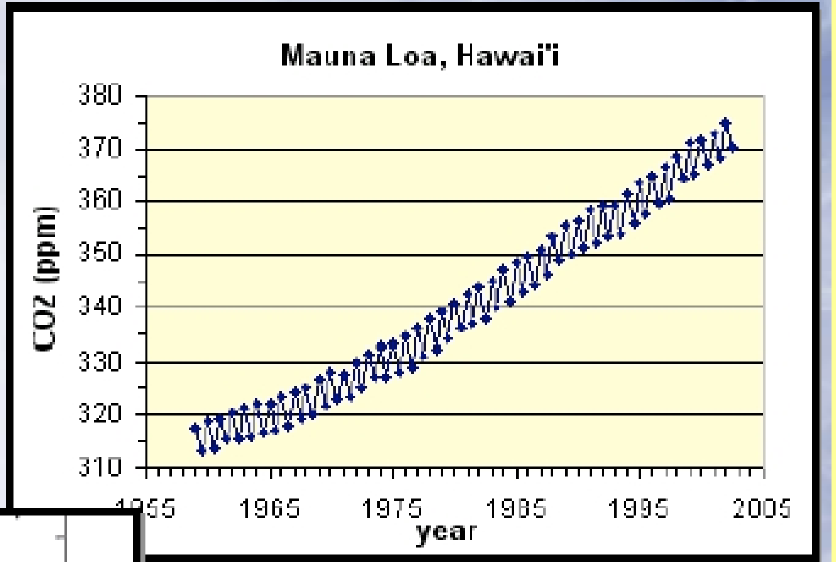
Area Occupied by Various Transport Modes



Nakicenovic Source: WBCSD, 2005 #15 2010

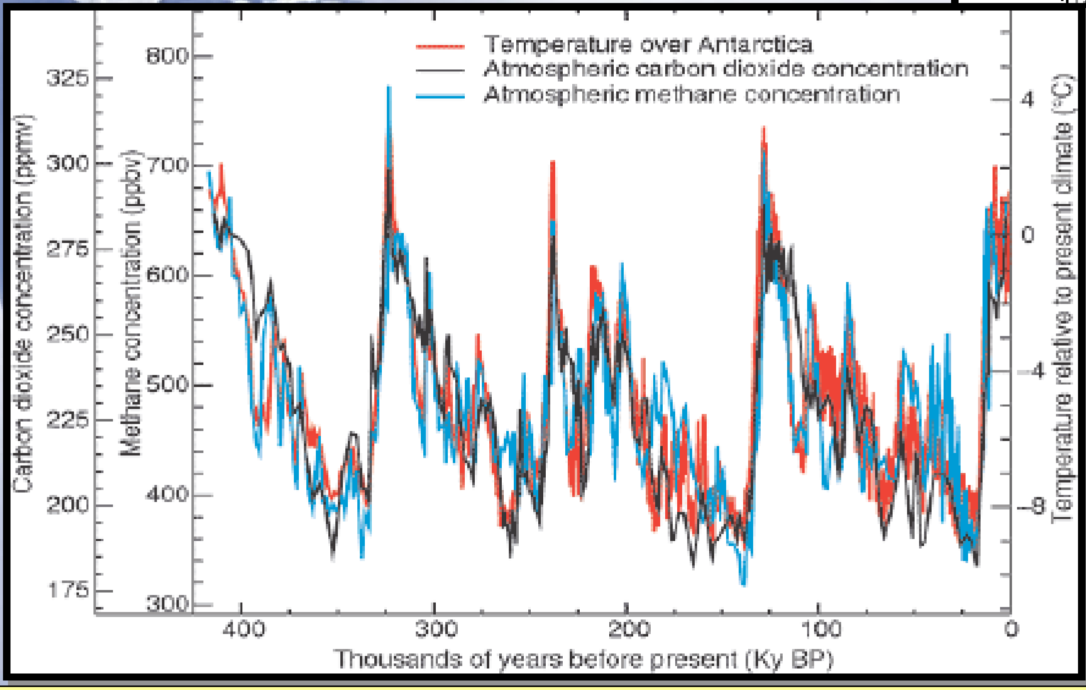
Our planet will be warmer

CO_2 Konzentrationen

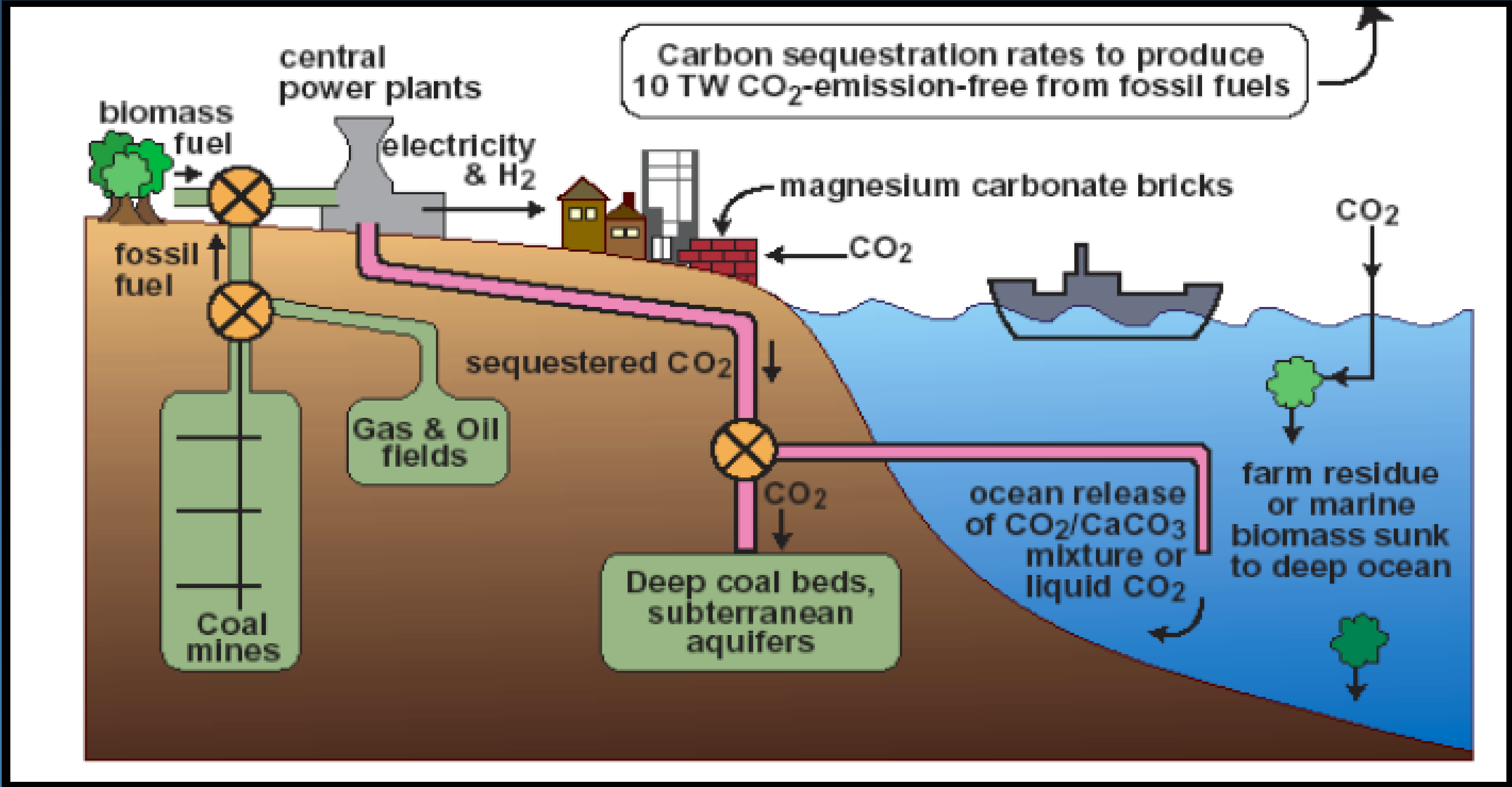


Keeling Atmospheric Data Set

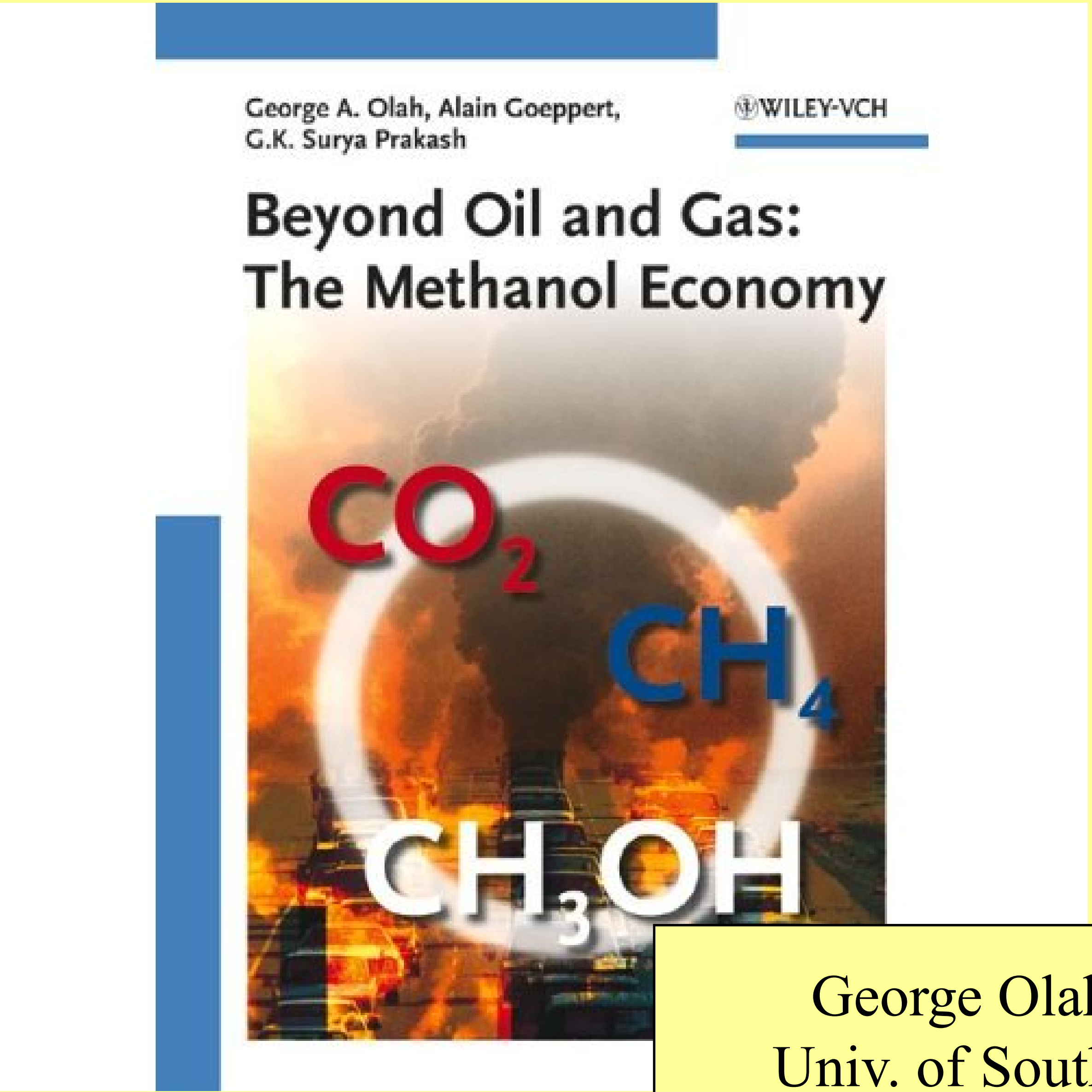
Daten aus Vostok-Eisbohrungen



CO_2-Einlagerung



CO2 Recycling?



George Olah, Nobel Prize 1994
Univ. of Southern California, USA

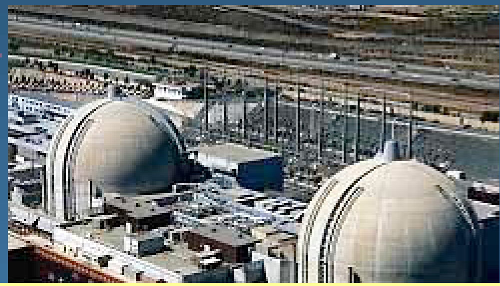
Scope of Nuclear Reactors

- Atomenergie (Spaltung und Fusion)
  - 10 TW = 10,000 neue 1 GW-Reaktoren
  - d.h. 50 Jahre lang alle 2 Tage ein neuer Reaktor

  → 2.3 Mio Tonnen nachgewiesener Reserven; 1 TWh benötigt 22 Tonnes Uran

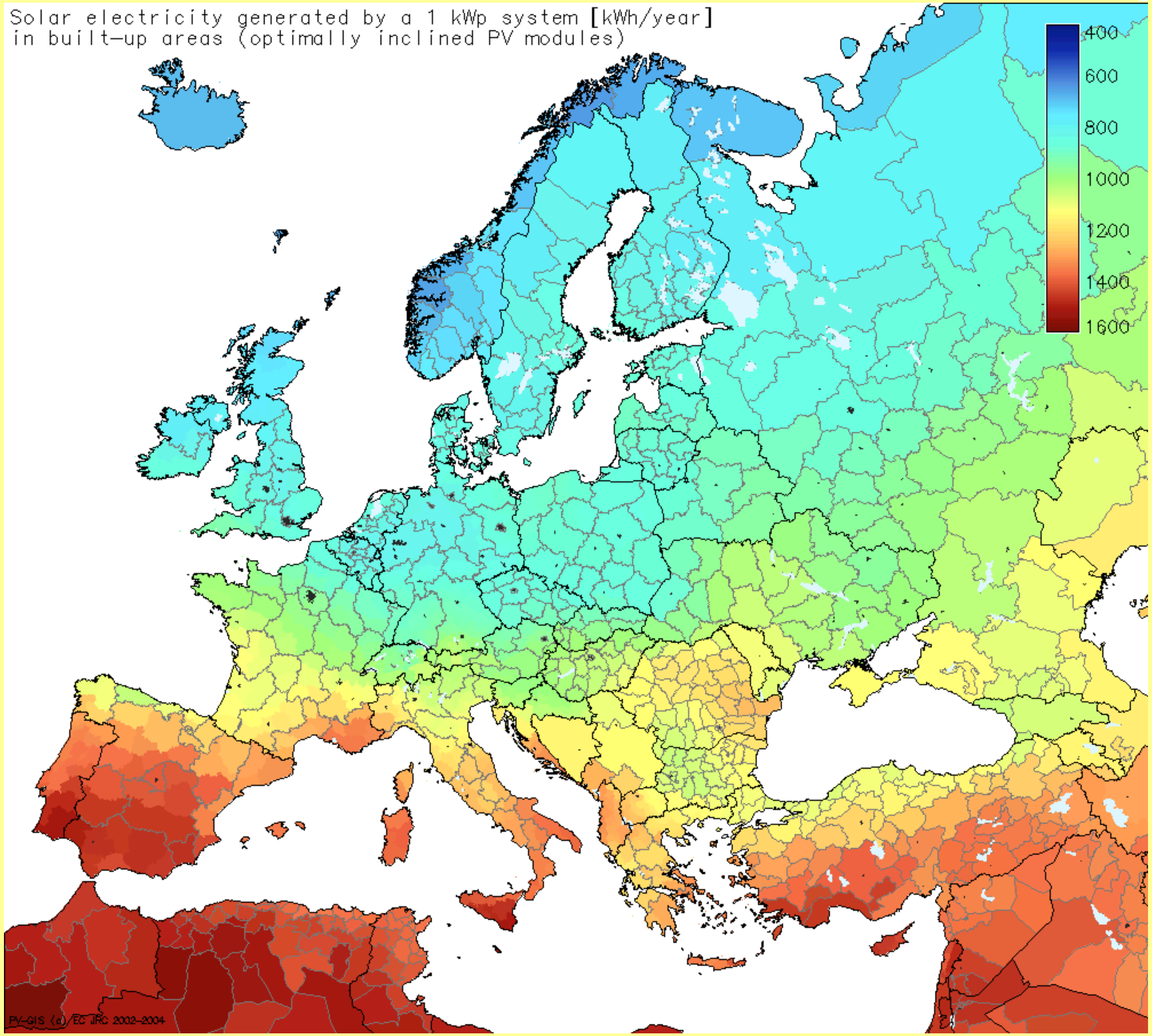
  → entspricht bei 10 TW einem Jahr Energie

  → Alle terrestrischen Ressourcen liefern 10 Jahre Energie

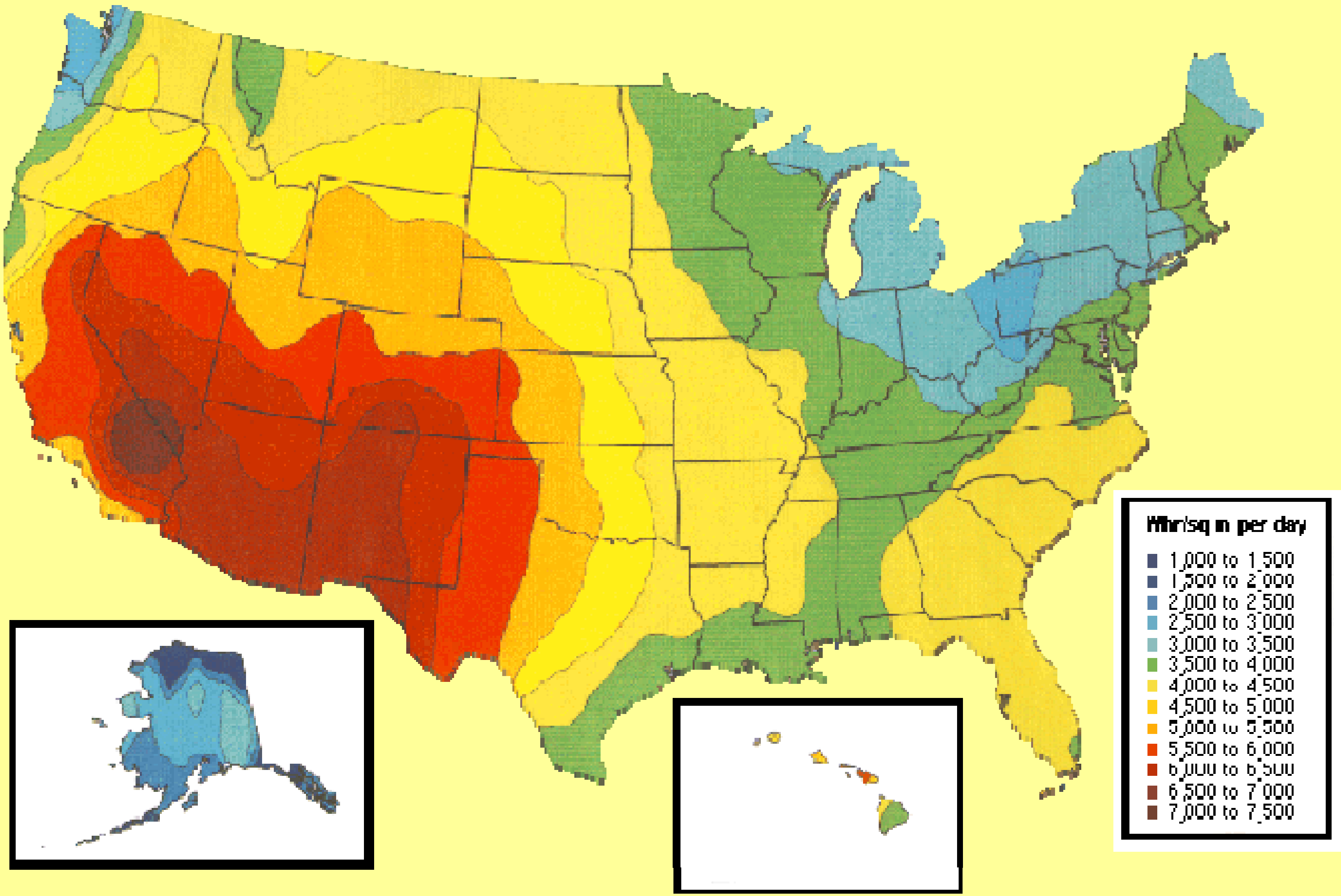


Why no company insures the nuclear power plants?

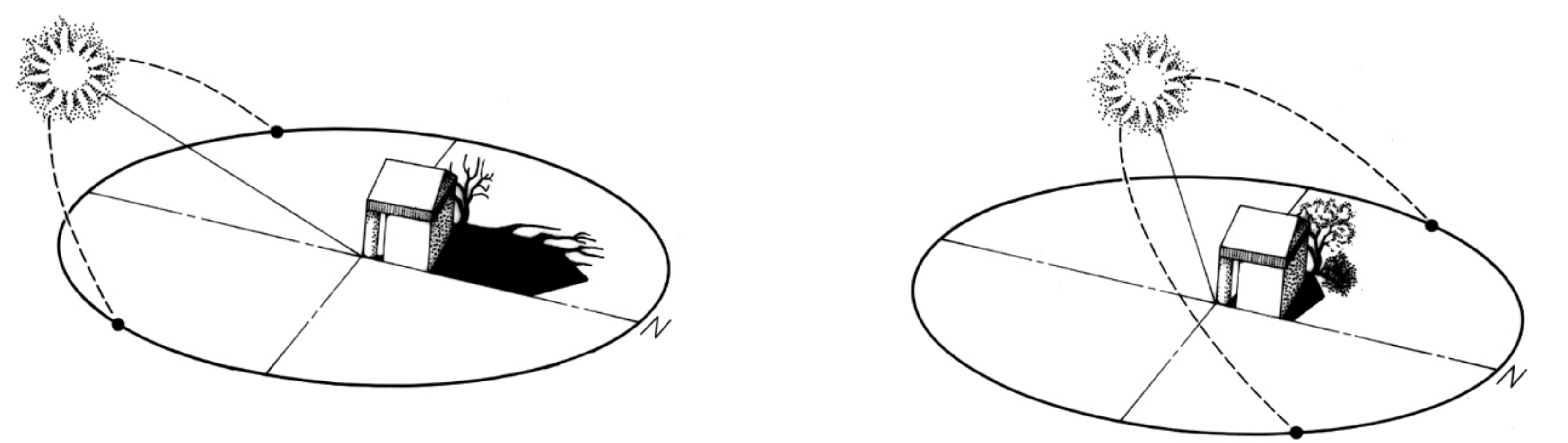
Solar Energy Distribution in Europe

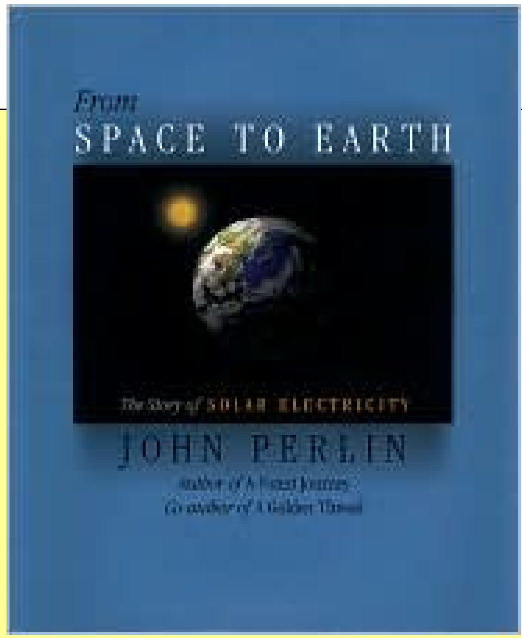


Solar Energy Distribution in USA

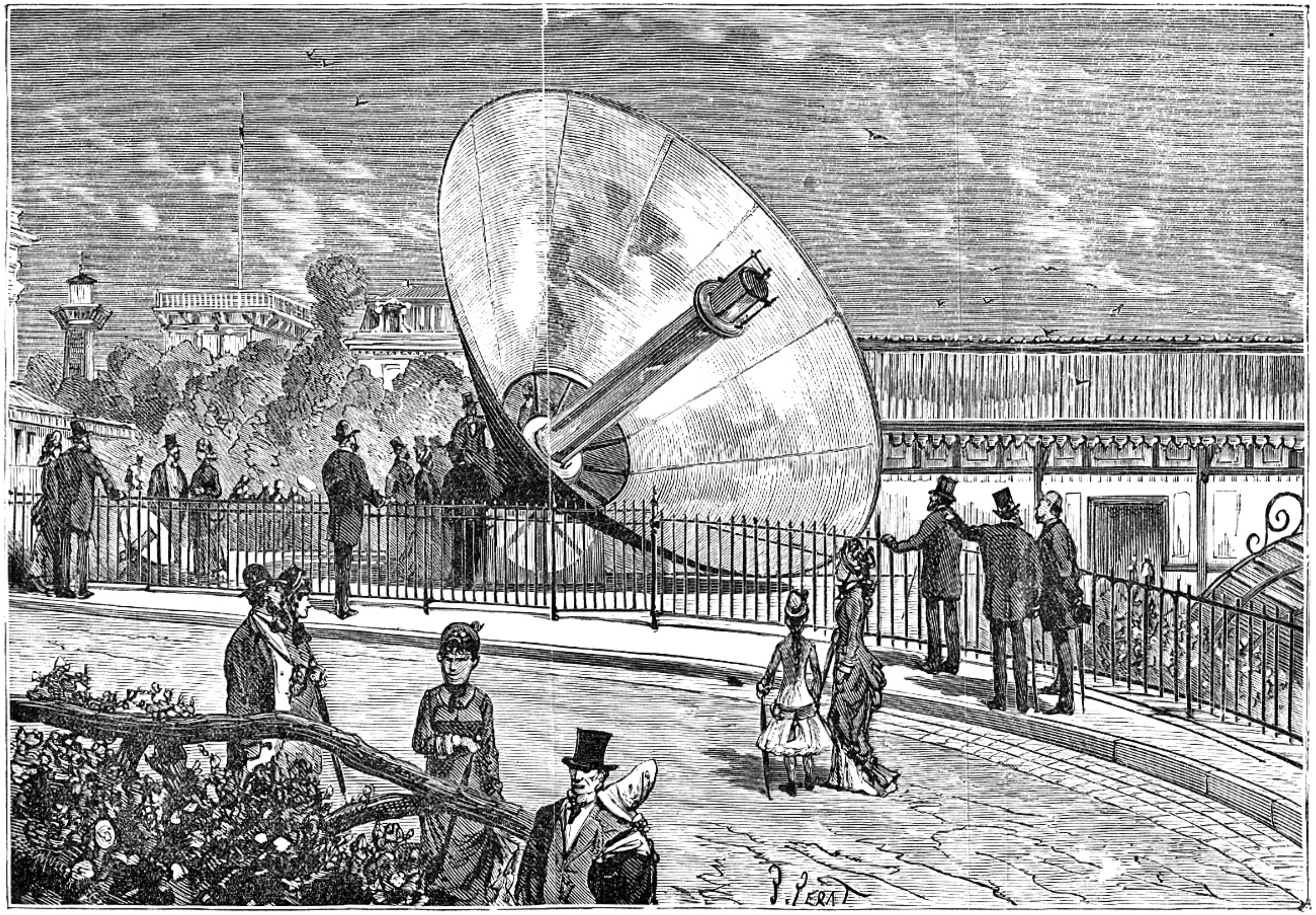


History of Solar Energy by John Perlin

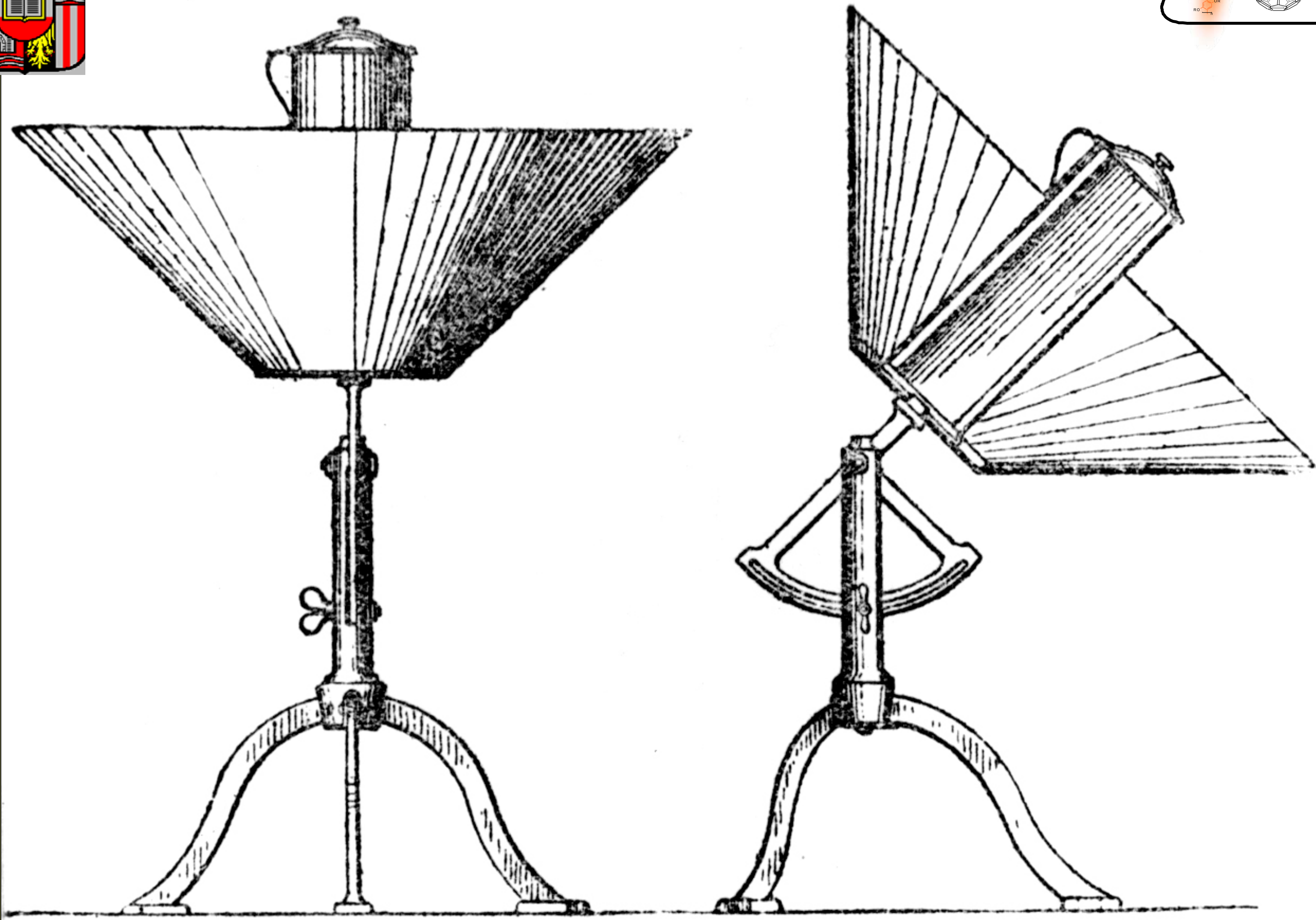




EXPOSITION UNIVERSELLE DE 1878.



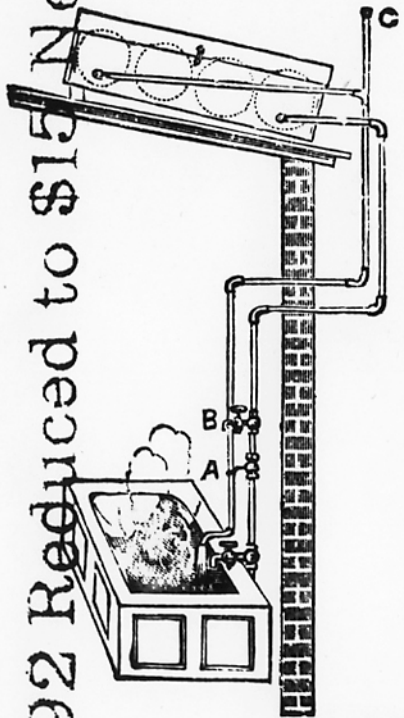
Vue générale de mon grand appareil exposé au Trocadéro, en 1878, (Annexe de l'Exposition Algérienne).



Climax Solar-Water Heater

UTILIZING ONE OF NATURE'S GENEROUS FORCES

THE SUN'S HEAT { Stored up in Hot Water for Baths, Domestic and other Purposes.



Price Of No.1 Heater for 1892 Reduced to $15 Net

GIVES HOT WATER at all HOURS OF THE DAY AND NIGHT.

NO DELAY.

FLOWS INSTANTLY.

NO CARE. NO WORRY.

ALWAYS CHARGED. ALWAYS READY.

THE WATER AT TIMES ALMOST BOILS.

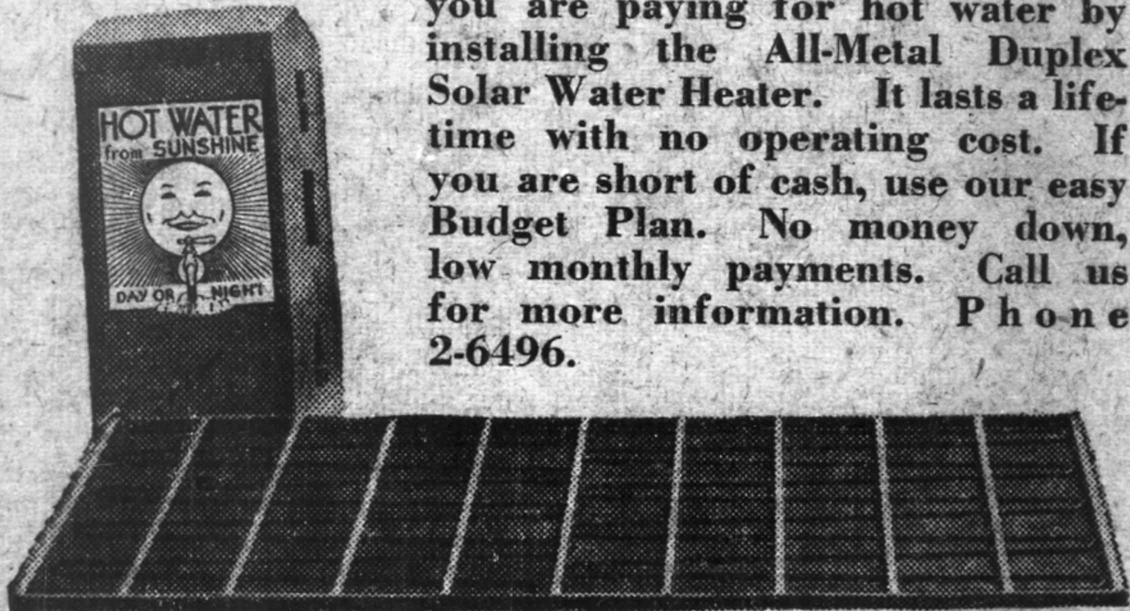
Price, No. 1, $25.00

This Size will Supply sufficient for 3 to 8 Baths.

CLARENCE M. KEMP, BALTIMORE, MD.

¾ MILLION DOLLARS SAVED

It may not seem possible, but it is a fact, 15,000 satisfied owners of the ALL-METAL DUPLEX SOLAR WATER HEATER actually saved ¾ Million Dollars the past year in hot water bills. You too, can save all the money you are paying for hot water by installing the All-Metal Duplex Solar Water Heater. It lasts a lifetime with no operating cost. If you are short of cash, use our easy Budget Plan. No money down, low monthly payments. Call us for more information. Phone 2-6496.



SOLAR WATER HEATER CO.

325 N. W. 25TH STREET PHONE 2-6496 MIAMI, FLA.

EAST COAST BRANCHES:

FT. LAUDERDALE, FT. PIERCE, ORLANDO, VERO BEACH, PALM BEACH

SOLAR POWER LIQUID AIR

MECHANICAL POWER, HEAT, LIGHT,
ELECTRICITY, REFRIGERATION
AND FERTILIZERS

FROM SUN HEAT AND AIR

YOU ARE INVITED TO ATTEND AN

EXHIBITION RUN

OF THE

FIRST PRACTICAL SOLAR ENGINE

AT 3400 DISSTON STREET

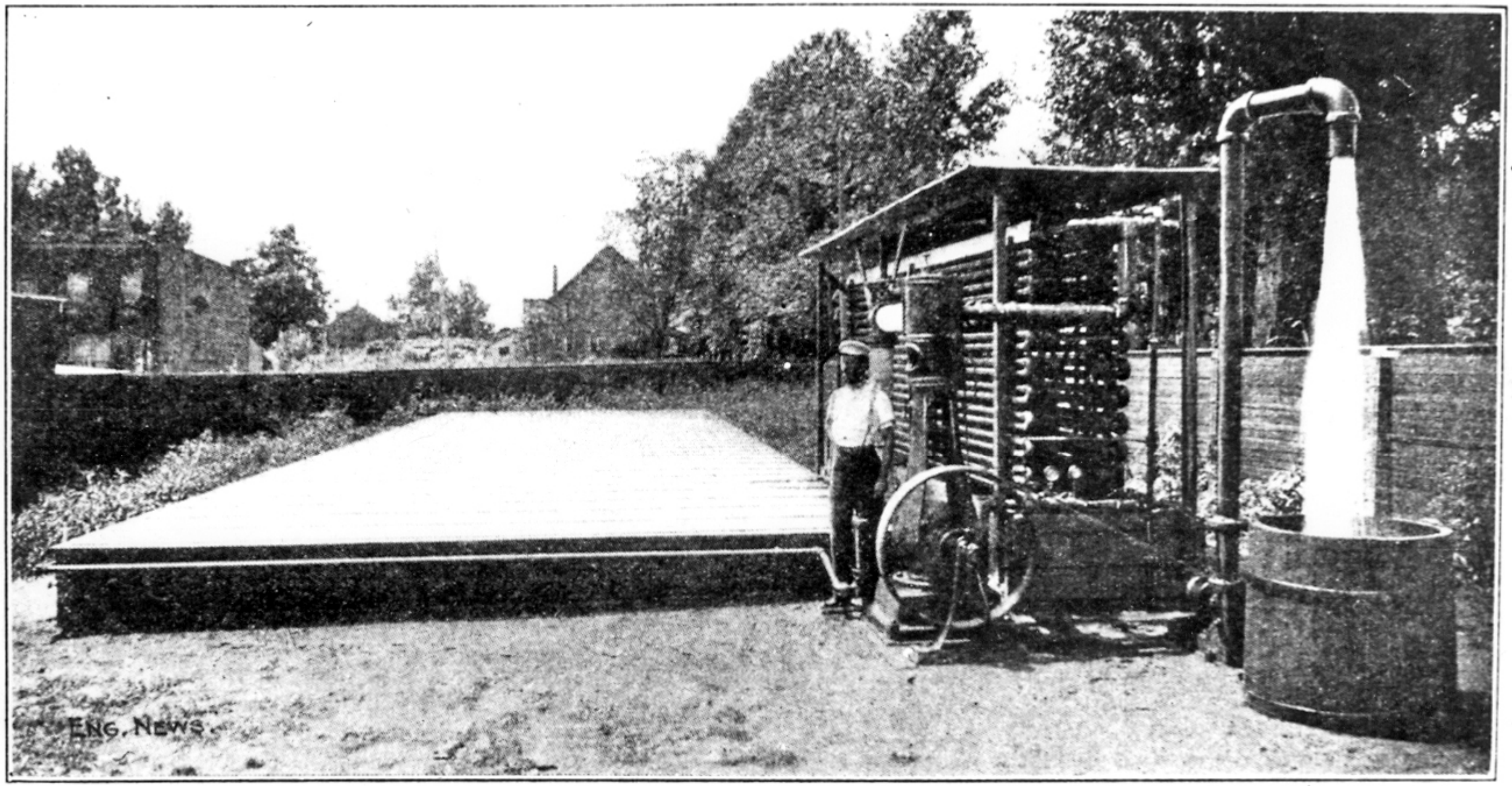
TACONY, PHILADELPHIA, PA.

ANY CLEAR AFTERNOON BETWEEN TWELVE AND THREE P. M.
DURING THE NEXT TWO WEEKS

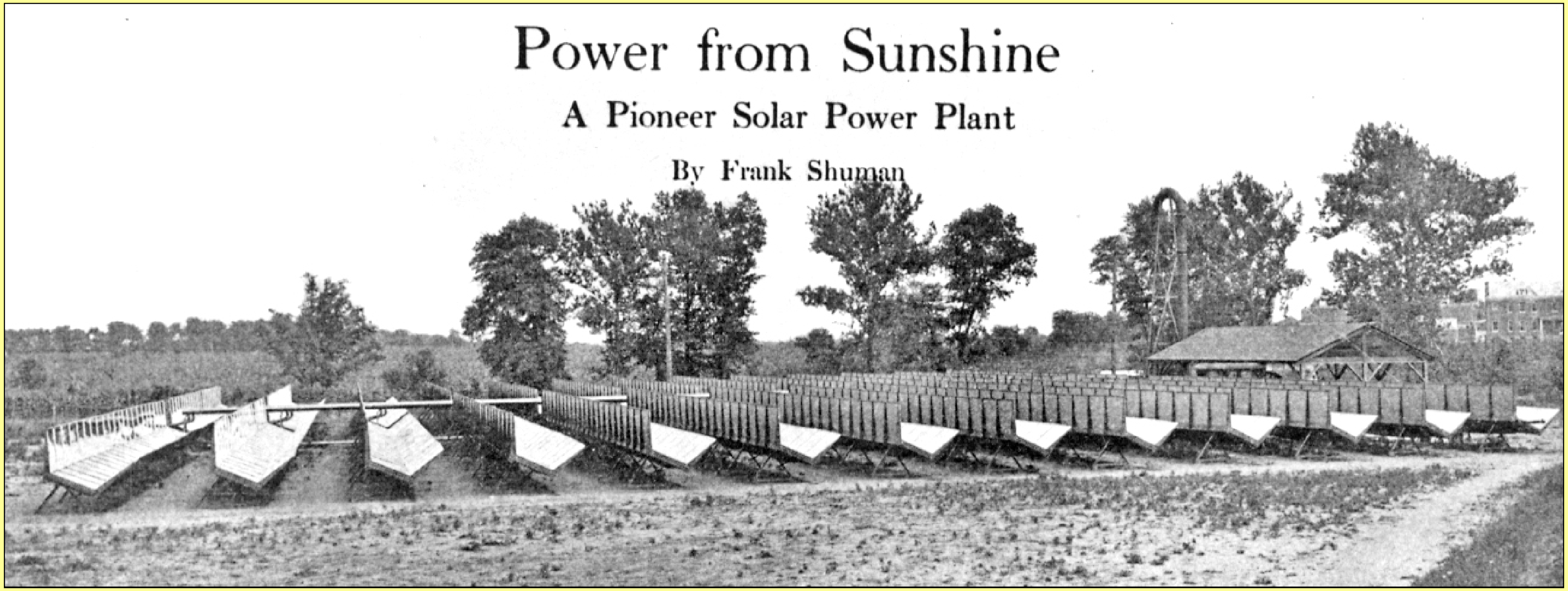
PLEASE ACKNOWLEDGE RECEIPT AND SAY WHEN
YOU WILL COME

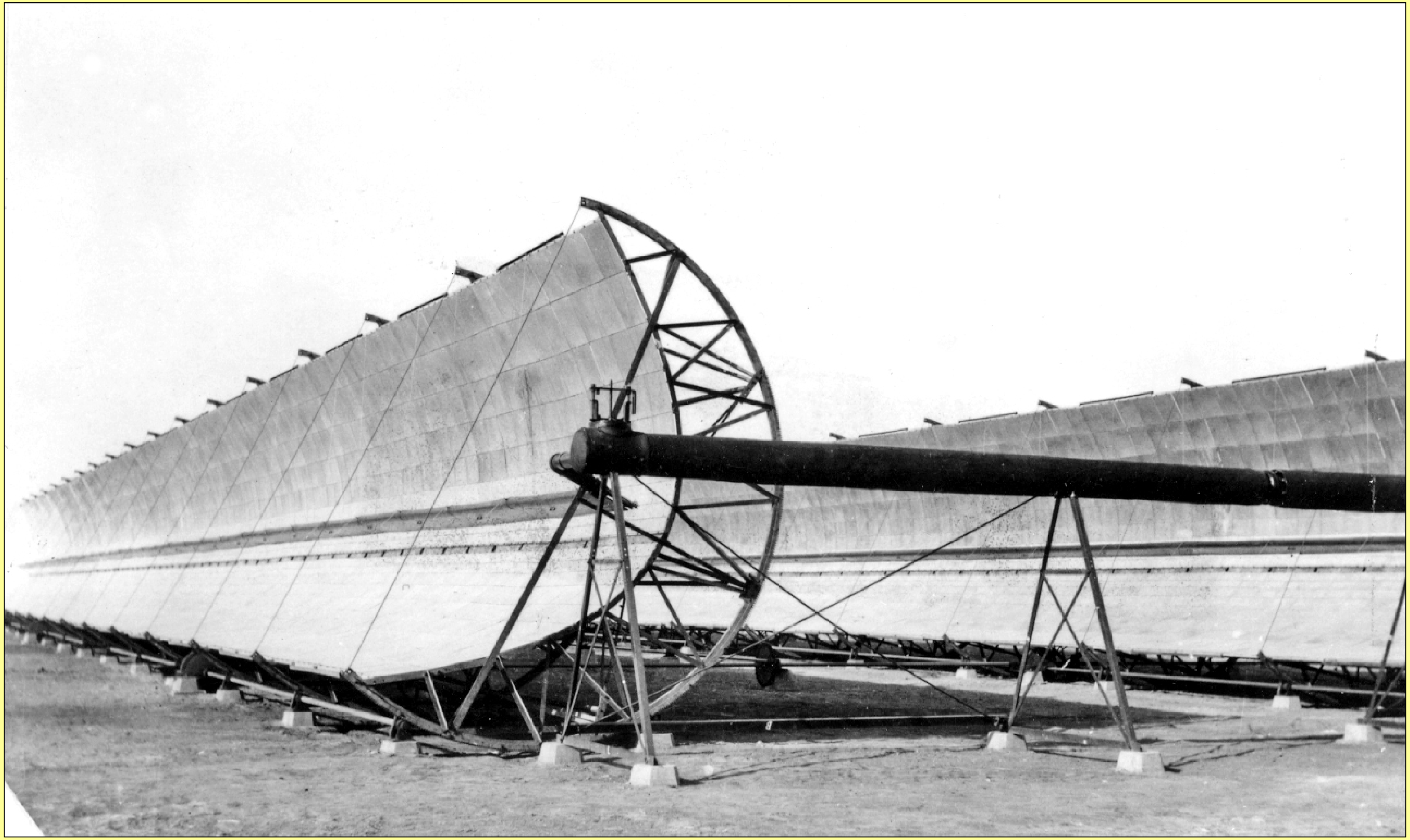
FRANK SHUMAN

TACONY, PHILADELPHIA, AUG. 20TH, 1907



A STEAM ENGINE OPERATED BY THE SUN'S HEAT AT FACTORY, PHILADELPHIA, AUGUST, 1907.
Frank Shuman, Inventor.


Power from Sunshine
A Pioneer Solar Power Plant
By Frank Shuman



Solar Stirling Engines

McDonnell Douglas/Southern of California
California Edison 25 kW dish/Stirling system.
The 944 square foot concentrator consists of 82 spherically curved glass mirrors each 3 foot by 4 foot.
The United Stirling 4-95 Mark II engine
(4 cylinders of 95 cc displacement) uses hydrogen as the working pressure at a maximum gas pressure of 2900psi..
This engine delivered 25kW output at 1000W/m2 insolation.

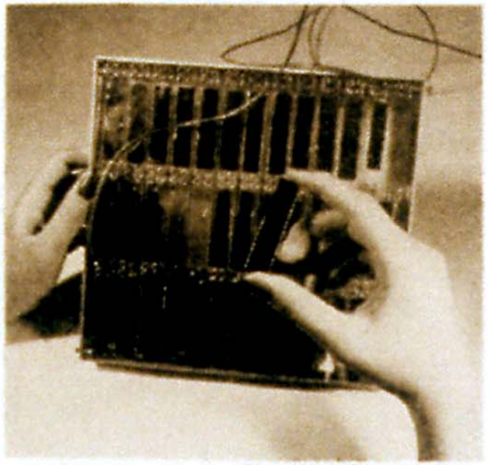
THE SUN'S ENERGY: FUEL UNLIMITED

THREE INVENTORS exhibited last week a small metal box slatted with black, glassy strips. Raw materials for the strips come from sand and borax. But the strips—silicon thinly seeded with boron—turn sunlight into electricity, may provide more power than all the world's coal, oil, uranium. The inventors:

Calvin S. Fuller, 52, chemist.
Daryl M. Chapin, 47, engineer.
Gerald L. Pearson, 49, physicist.

The three men worked as a team at Bell Telephone Laboratories, where all went from college a quarter century ago. Mr. Fuller found how to make the strips, Mr. Pearson put in electronics knowledge, Mr. Chapin put the pieces together.

Secret of the Bell solar battery is electronic activity much like that in a photographer's light meter, but much more powerful. The sun's energy causes rapid movements of electrons in the silicon strips. The

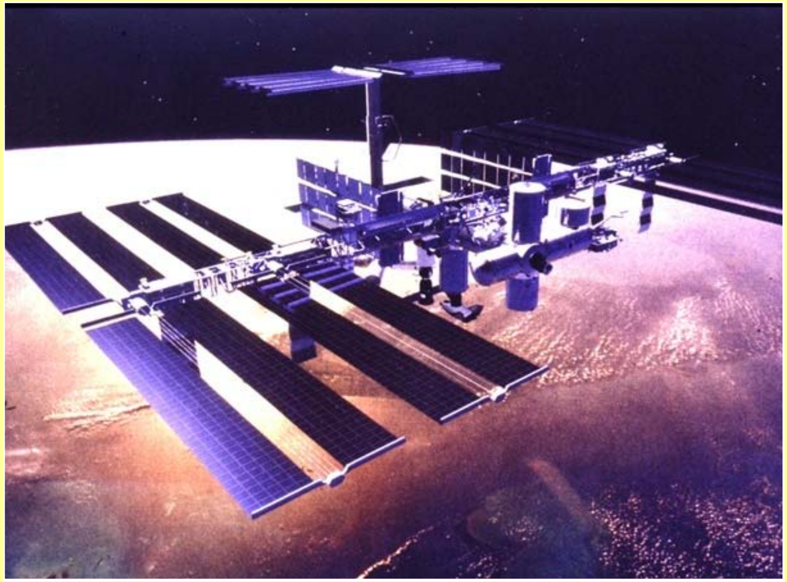


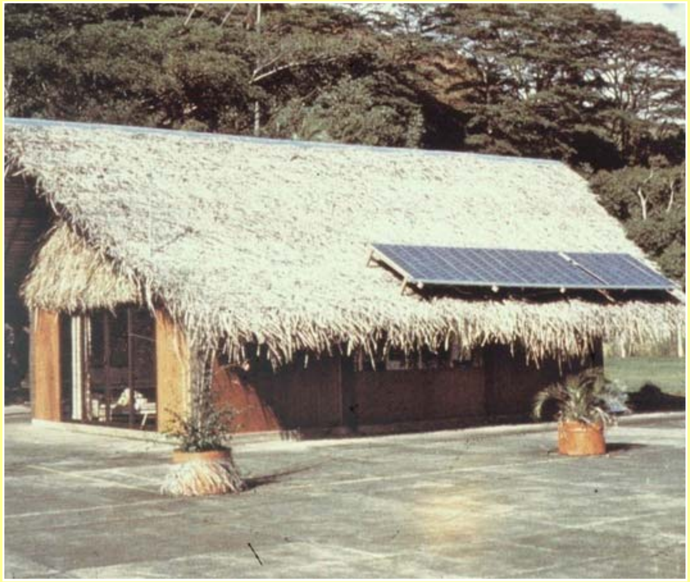
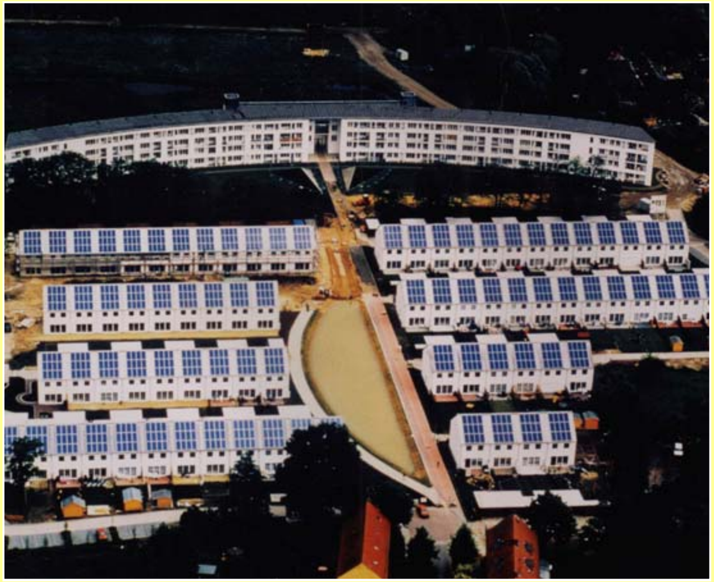
Photos: Bell Laboratories

movements create voltage, become direct-current electricity that can be kept in storage batteries.

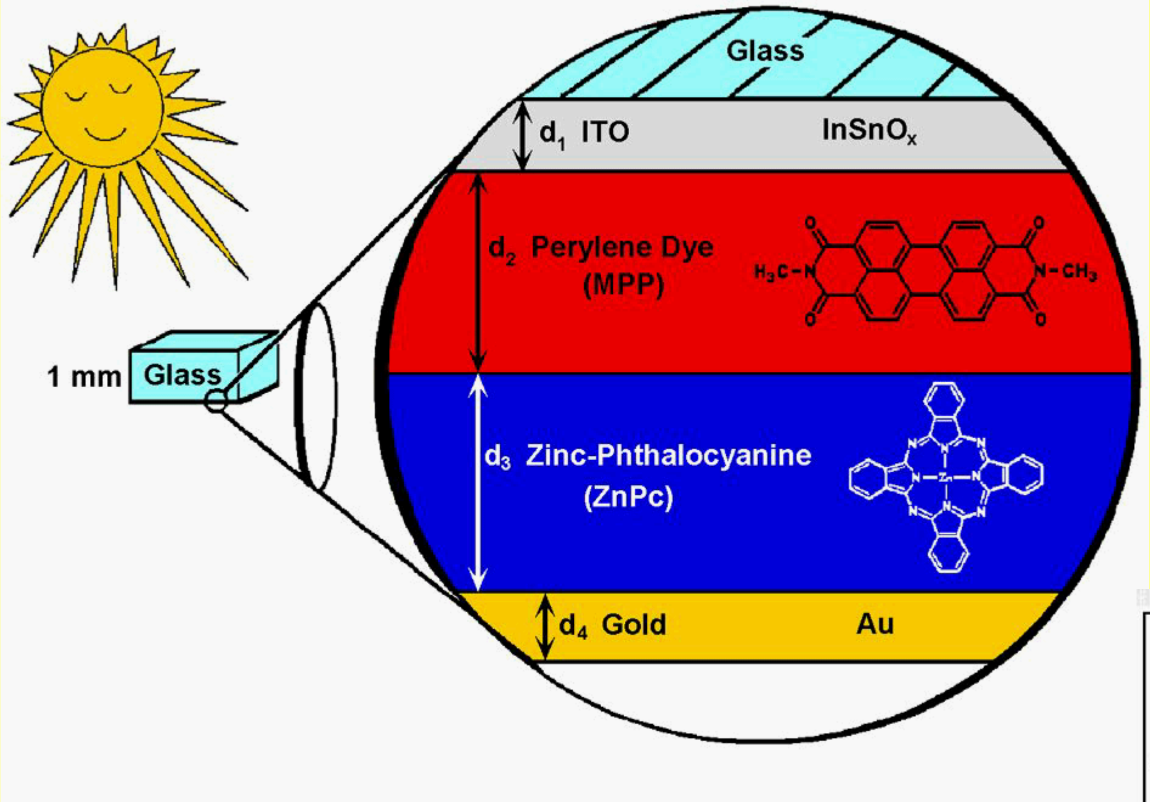
A pocket-size sun battery will send radio signals several miles. The Bell company foresees first uses as power for mobile radio telephones and to charge batteries for rural telephone systems. The Defense Department is highly interested. Engineers are dreaming of silicon-strip powerhouses. The future: limitless.

First press release, 1954



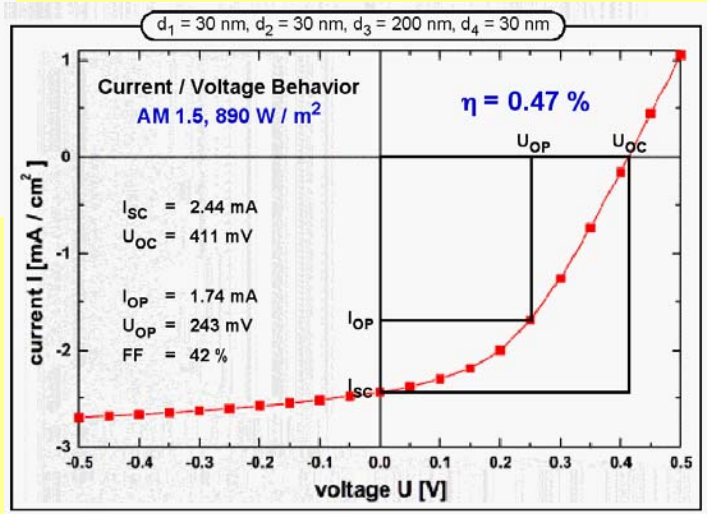





Small Molecular Organic Solar Cells



"Tang- Cell"

C. W. Tang
Appl.Phys. Lett. 48(86)183



Tang Patents in KODAK

United States Patent [19] | [11] **4,125,414**

Tang et al. | [45] **Nov. 14, 1978**

[54] **ORGANIC PHOTOVOLTAIC ELEMENTS**

[75] Inventors: **Ching W. Tang**, Rochester; **Alfred P. Marchetti**, Penfield; **Ralph H. Young**, Rochester, all of N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[21] Appl. No.: **885,926**

[22] Filed: **Mar. 13, 1978**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 821,117, Aug. 2, 1977, abandoned.

[51] **Int. Cl.**[2] **H01L 31/04**

[52] **U.S. Cl.** .... **136/89 NB**; 357/8; 357/30; 250/211 J; 250/212

[58] **Field of Search** .... 136/89 NB; 357/8, 30; 250/211 J, 212; 252/501

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,999,750	9/1961	Miller et al.	96/1
3,009,006	11/1961	Kostelec	136/89
3,038,874	6/1962	Laakso et al.	260/42
3,057,947	10/1962	Calvin et al.	136/89
3,106,544	10/1963	Laakso et al.	260/47
3,106,545	10/1963	Laakso et al.	260/47
3,106,546	10/1963	Laakso et al.	260/47
3,250,615	5/1966	Van Allan et al.	96/1
3,507,706	4/1970	Webb	136/89
3,530,007	9/1970	Golubovic	136/89
3,615,414	10/1971	Light	96/1.6
3,615,415	10/1971	Gramza	96/1.6
3,679,407	7/1972	Stephens	96/1.6
3,706,554	12/1972	Fox et al.	96/1.6
3,732,180	5/1973	Gramzaet al.	260/33.6 R
3,789,216	1/1974	Komp	250/211 R
3,844,843	10/1974	Kay et al.	136/89 X
3,873,312	3/1975	Contois et al.	96/1.6
3,938,994	2/1976	Reynolds et al.	96/1.6

OTHER PUBLICATIONS

R. L. Gamblin, "Solar Cell Utilizing Organic Photoconductor", *IBM Tech. Disc. Bull.*, vol. 18, p. 2442 (1976).
L. W. Davies, "Prospects for the Direct Conversion of Solar Energy to Electricity", *AWA Tech. Rev.*, vol. 15, pp. 139–142 (1974).
T. K. Mukherjee, "Photocurrents and Photopotentials in Organic Solids", *Conf. Record, IEEE Photospecialists Conf.* (1967), pp. 7–21.

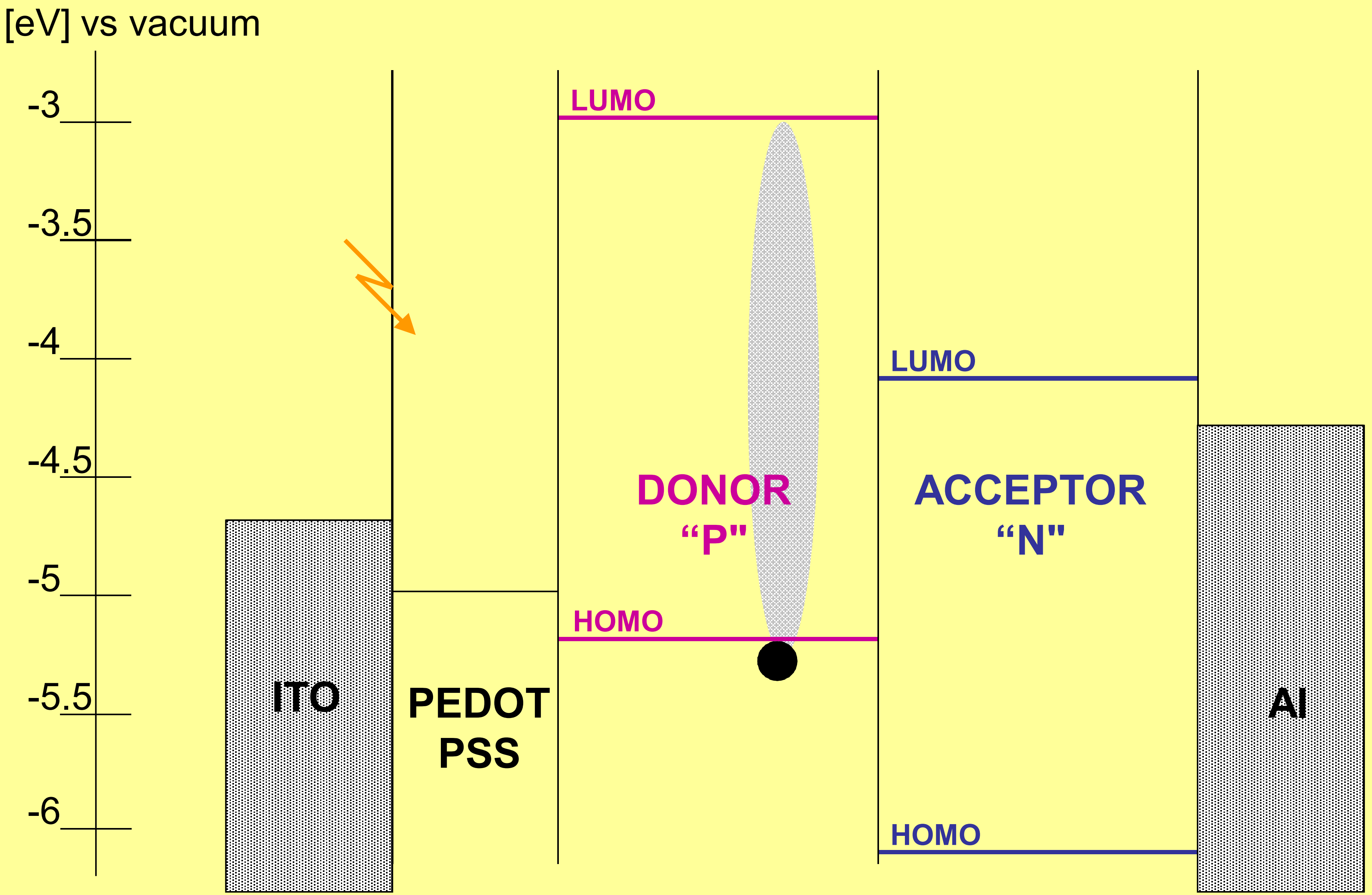
Primary Examiner—John H. Mack
Assistant Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Dana M. Schmidt

[57] **ABSTRACT**

A photovoltaic element featuring a photoconductive composition comprising an electrically insulating binder, an organic dye, and an organic photoconductor is disclosed. The photovoltaic element has superior conversion efficiencies compared to other organic photovoltaic elements.

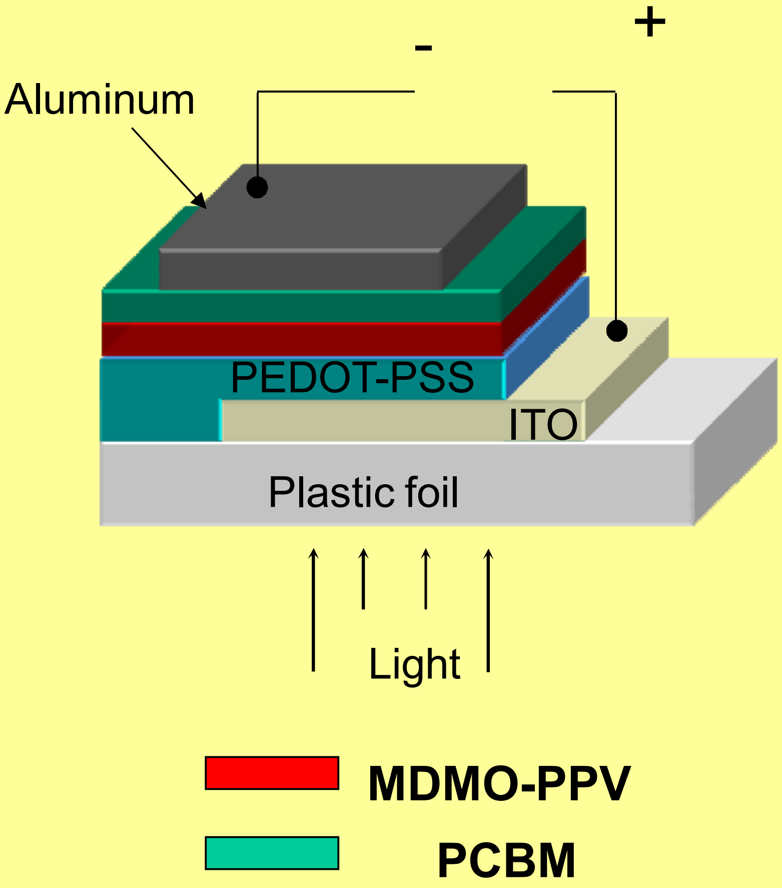
11 Claims, No Drawings

Bi-layer polymer solar cells

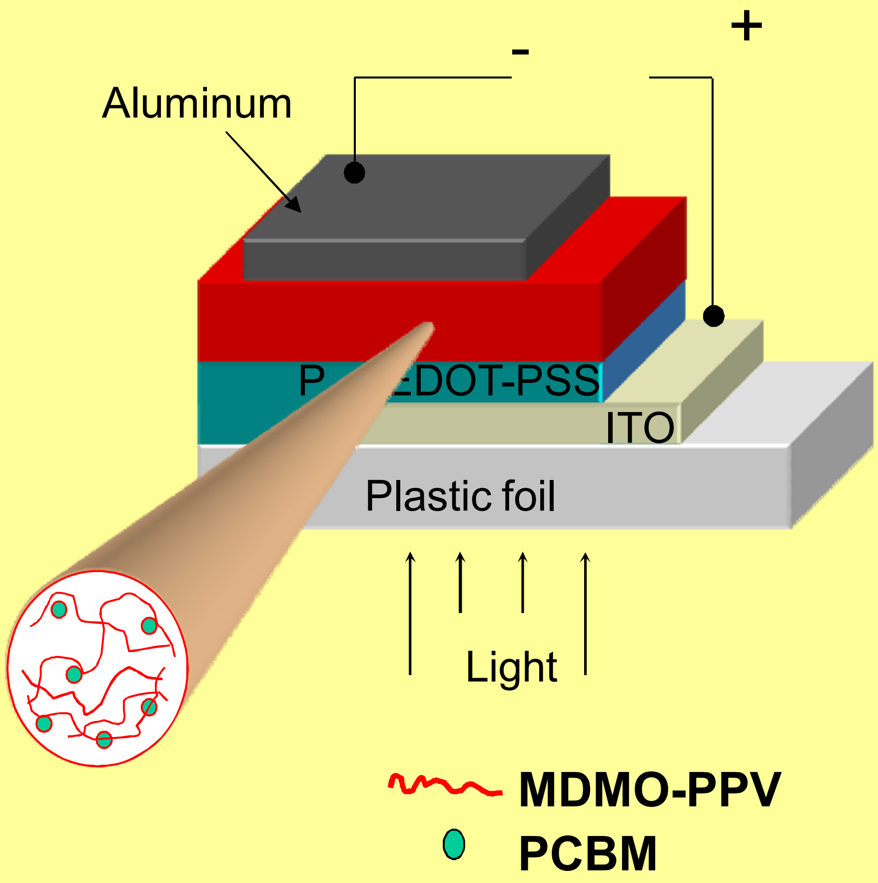


Organic Solar Cell Device Geometries

BILAYER



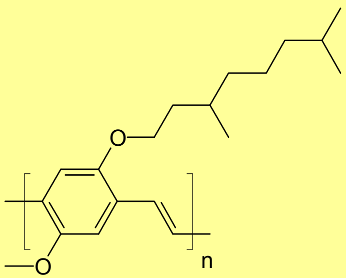
BULK HETEROJUNCTION



Photoinduced Charge Generation

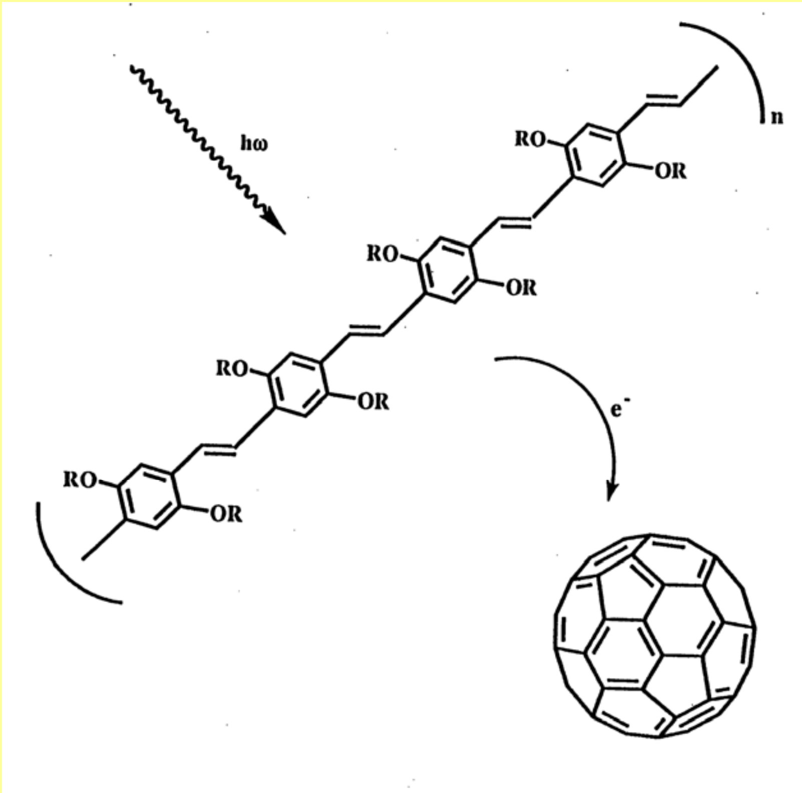
An ultrafast **e⁻ transfer** occurs between Conjugated Polymer / Fullerene composites upon illumination. The transition time is less than 40 fs. The Internal Quantum efficiency of charge generation is therefore ~100%.

DONOR

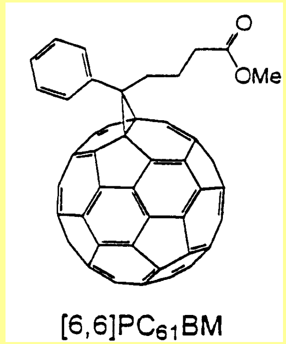


MDMO PPV

3,7 - dimethyloctyloxy methyloxy PPV



ACCEPTOR



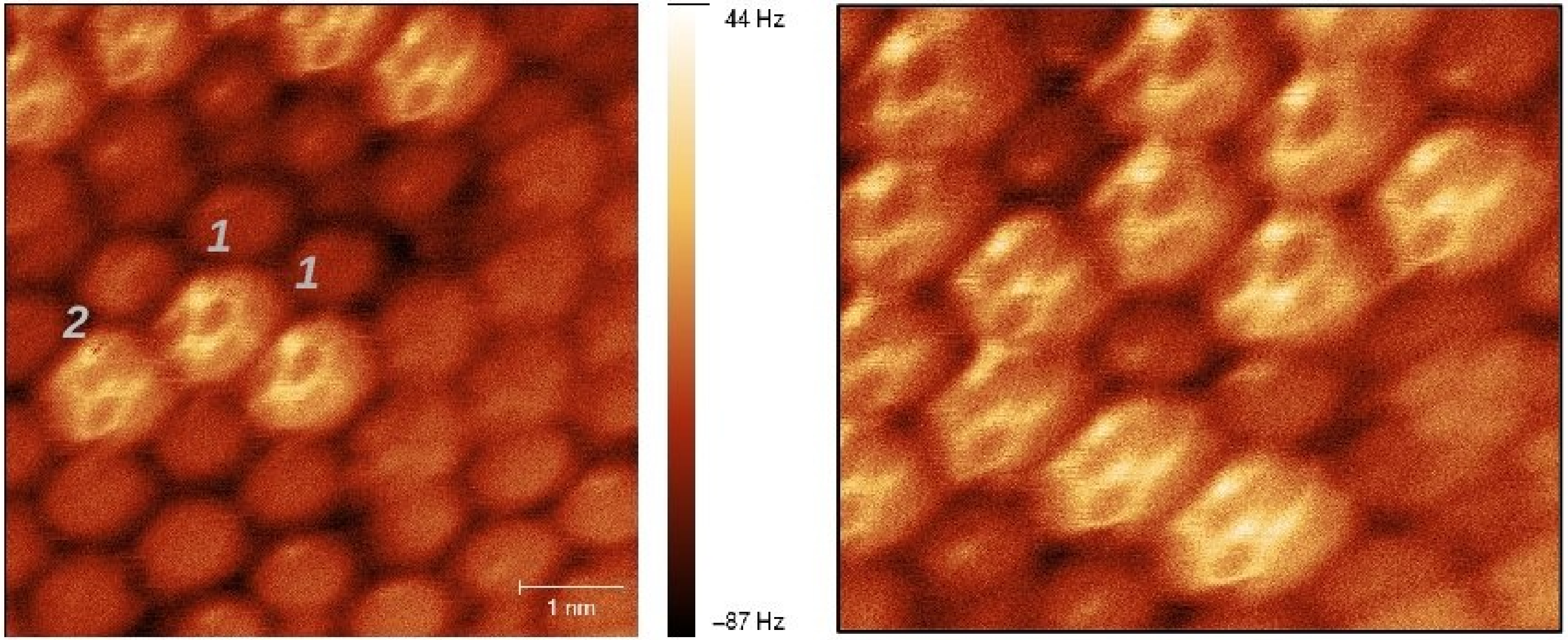
PCBM

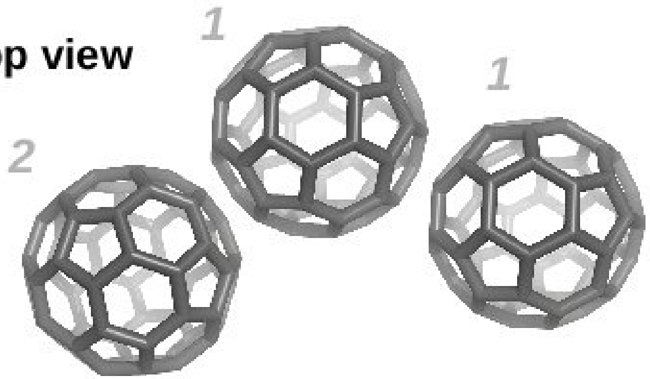
1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C_{61}

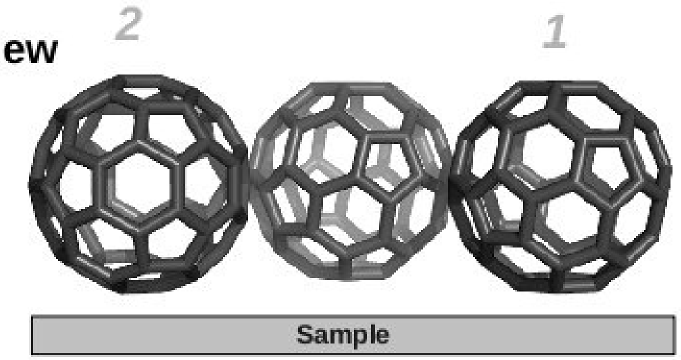
N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl., *Science* **258**, 1474 (1992)

Direct observation of the C_{60} orientations

Frequency shift signal obtained at constant current mode, Ap-p = 48 pm







Courtesy of Thilo Glatzel

UNI BASEL

Sariciftci Heeger Patents at UCSB

US005331183A

United States Patent [19]

Sariciftci et al.

[11] **Patent Number: 5,331,183**

[45] **Date of Patent: Jul. 19, 1994**

[54] **CONJUGATED POLYMER - ACCEPTOR HETEROJUNCTIONS; DIODES, PHOTODIODES, AND PHOTOVOLTAIC CELLS**

[75] Inventors: **N. S. Sariciftci; Alan J. Heeger**, both of Santa Barbara, Calif.

[73] Assignee: **The Regents of the University of California**, Oakland, Calif.

[21] Appl. No.: **930,161**

[22] Filed: **Aug. 17, 1992**

[51] **Int. Cl.^{5}** **H01L 29/28**

[52] **U.S. Cl.** **257/40**; 257/184; 257/461; 136/263

[58] **Field of Search** 257/40, 184, 461; 365/215; 136/263

[56] **References Cited**

U.S. PATENT DOCUMENTS

5,171,373 12/1992 Hebard et al. 257/40

OTHER PUBLICATIONS

Kamat, P. "Photoinduced Charge Transfer Between Fullerenes and Semiconductor ZnO Colloids" J. Am. Chem. Soc., 1991, 113, pp. 9705-9707.

Wang, Y. "Photoconductivity of Fullurene-Doped Polymers" Nature, Apr. 16, 1992, pp. 585-587.

Arbogast, J. W., et al., "Photophysical Properties of C_{60}" J. Phys. Chem., Jan. 10, 1991, pp. 11-12.

Sze, M. S., *Physics of Semiconductor Laser Devices*, (1981) Wiley-Interscience, New York, Chapter 13, "Photodetectors" pp. 743-789.

Sze, M. S., *Physics of Semiconductor Laser Devices*, (1981) Wiley-Interscience, New York, Chapter 14, "Solar Cells" pp. 790-838.

Primary Examiner—Sara W. Crane

Attorney, Agent, or Firm—Morrison & Foerster

[57] **ABSTRACT**

This invention relates generally to the fabrication of heterojunction diodes from semiconducting (conjugated) polymers and acceptors such as, for example, fullerenes, particularly Buckminsterfullerenes, C_{60}, and more particularly to the use of such heterojunction structures as photodiodes and as photovoltaic cells.

15 Claims, 3 Drawing Sheets

Sariciftci Heeger Patents at UCSB

We claim as our Invention:

1. A heterojunction device comprising
a. a layer of a conjugated polymer which serves as a donor, and adjacent thereto, a
b. layer of an acceptor material comprising an acceptor selected from the group consisting of the group of fullerenes, substituted fullerenes, fullerene derivatives, polymers comprising fullerenes or substituted fullerenes or of organic or polymeric acceptors having electronegativity in the range to enable a photoinitiated charge separation process defined

3. A heterojunction device comprising
a. a conjugated polymer which serves as a donor, and adjacent thereto,
b. an acceptor material comprising an acceptor selected from the group consisting of fullerenes or fullerene derivatives, polymers comprising fullerenes or fullerene derivatives, organic and or polymeric acceptors having electronegativity in the range to enable a photoinitiated charge separation

where

donor (D) and acceptor (A) units are either covalently bound (intramolecular), or spatially close but not covalently bonded (intermolecular);

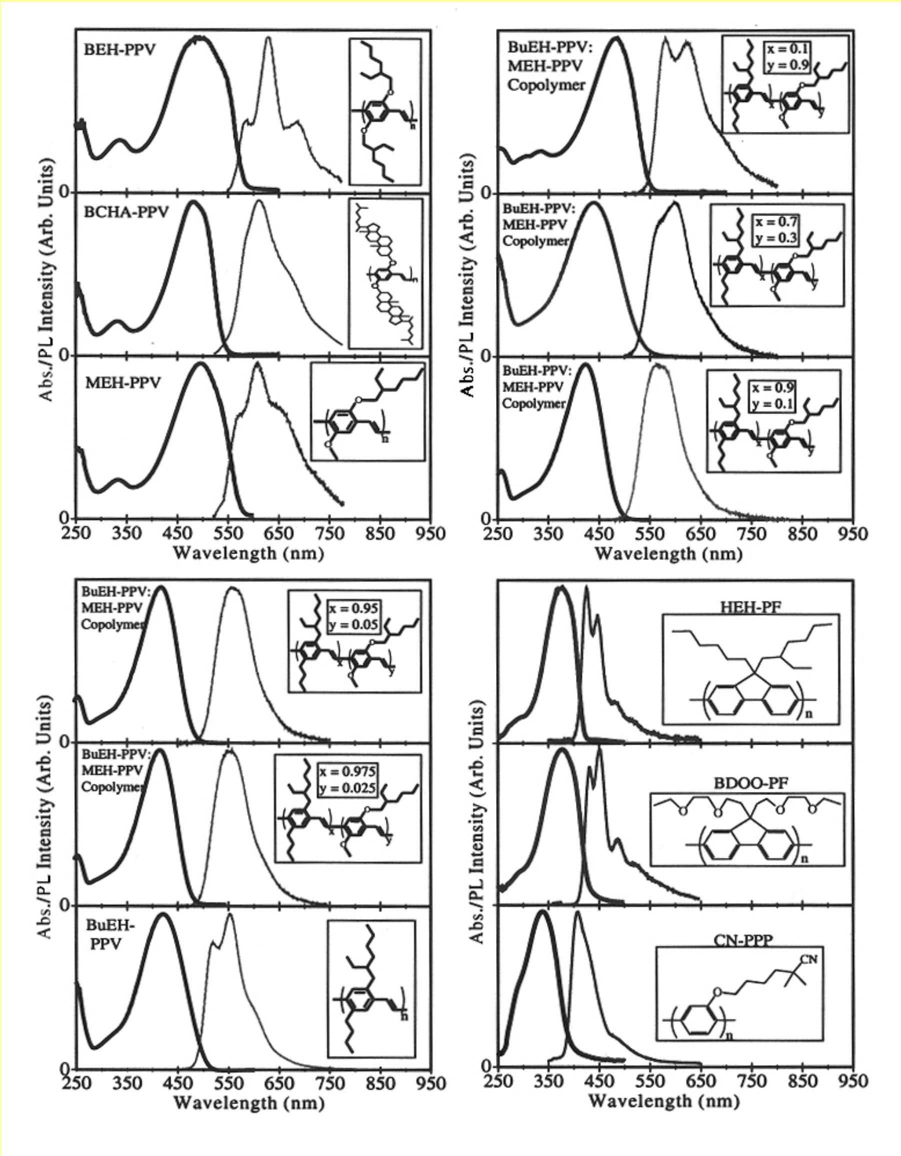
"1,3" denotes singlet or triplet excited states, respectively,

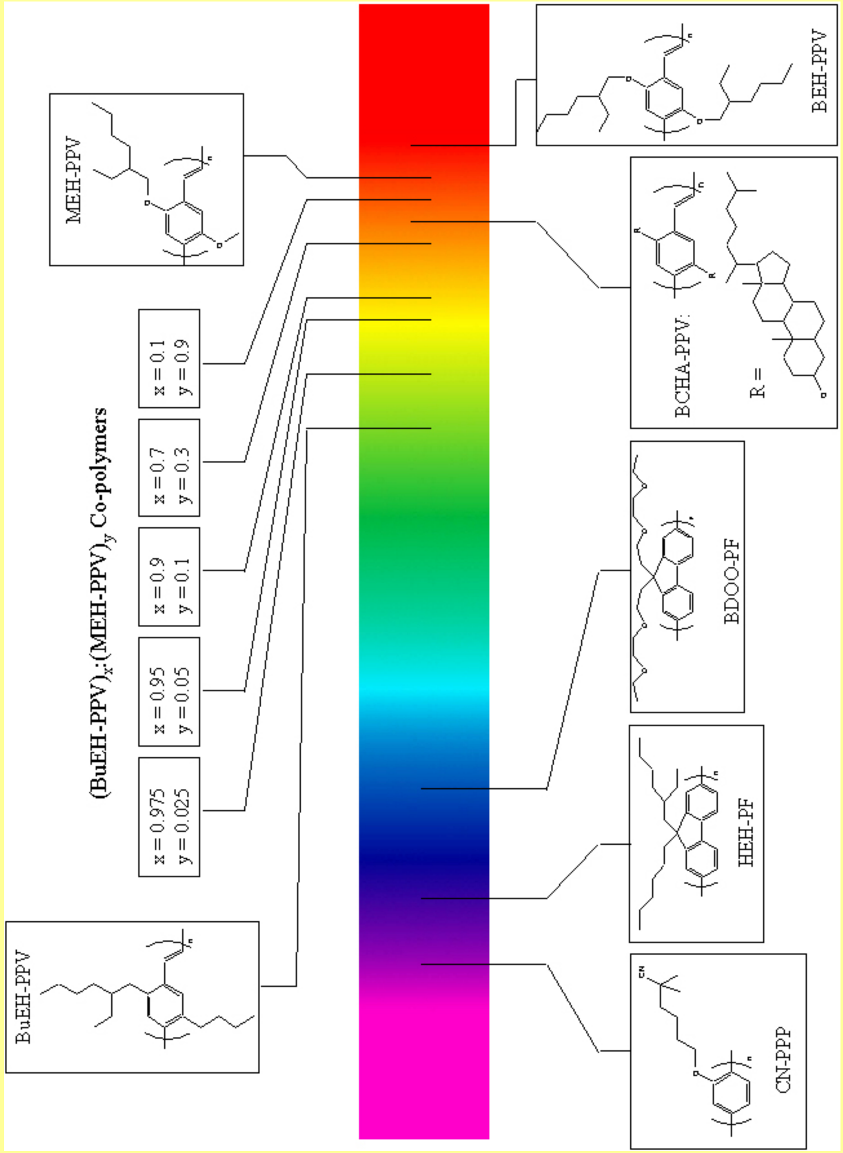
and where a heterojunction between the conjugated polymer and acceptor material is formed in situ by controlled segregation during solidification from a solution containing both the donor and the acceptor moieties.

Definition →

Birth of Bulk Heterojunction, 1992

Color Variations: Band Gap Engineering





Are our concepts working?

1.) Light absorption

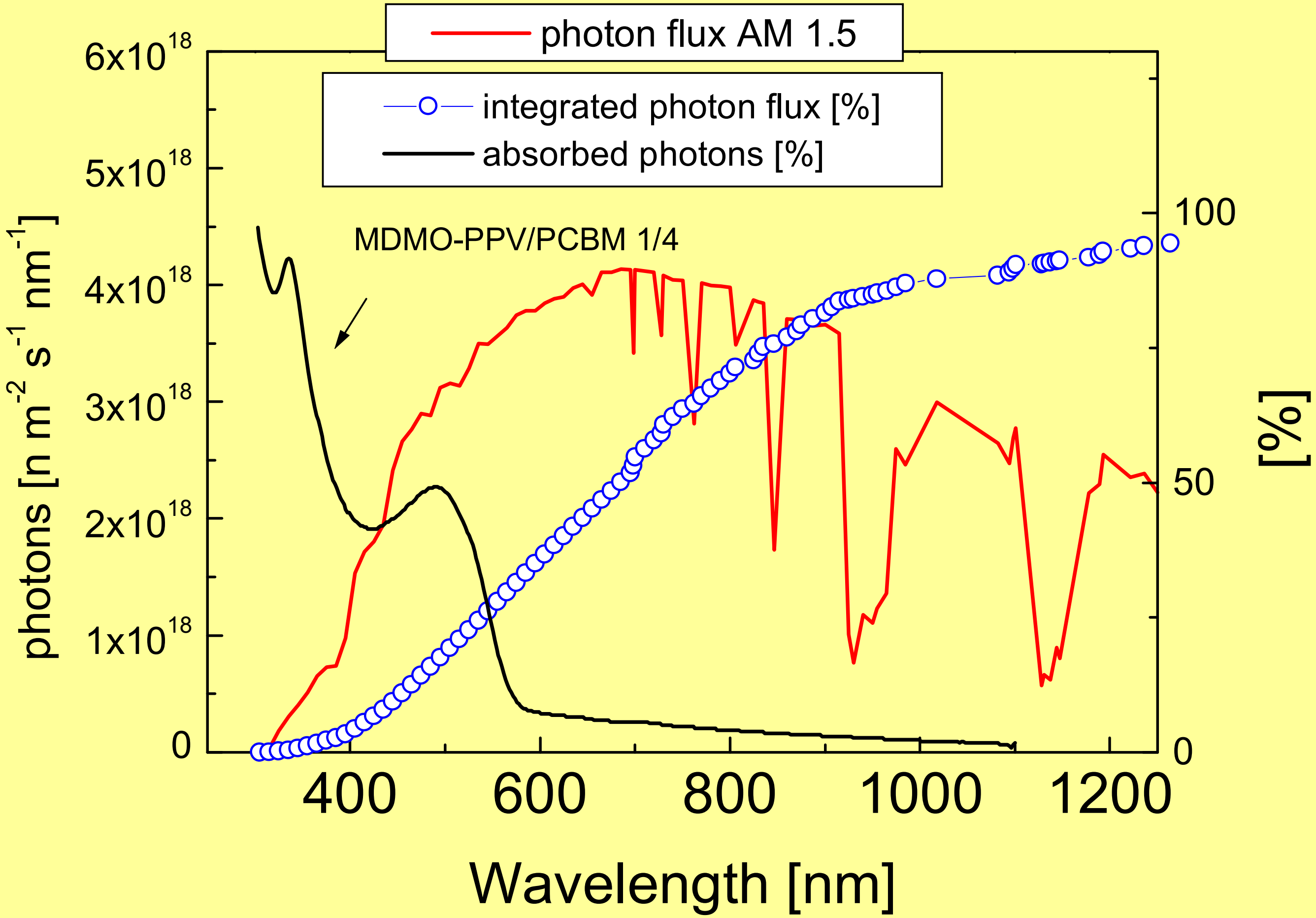
2.) Exciton diffusion

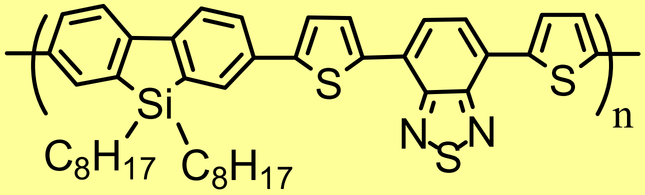
3.) Photoinduced electron transfer (exciton dissociation)

4.) Charge carrier transport (charge carrier recombination)

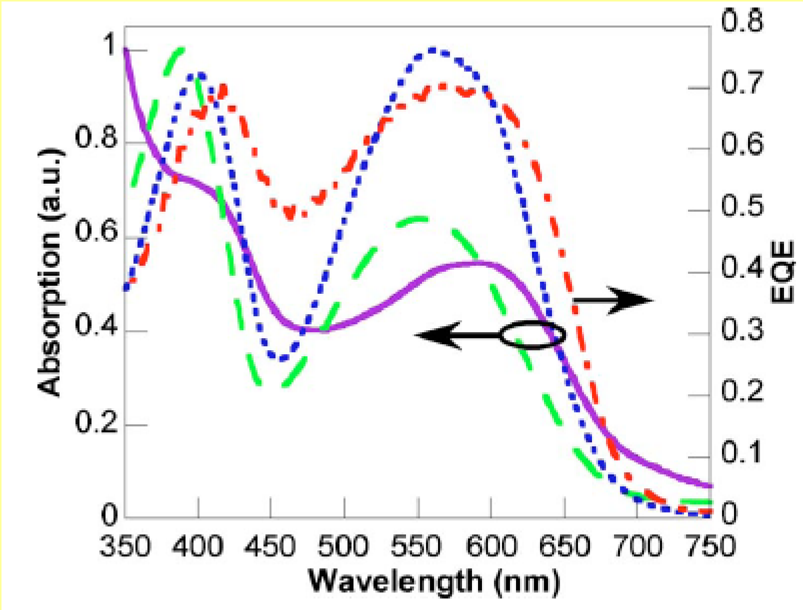
5.)Charge carrier collection at the electrodes (interface engineering)

Photon Harvesting

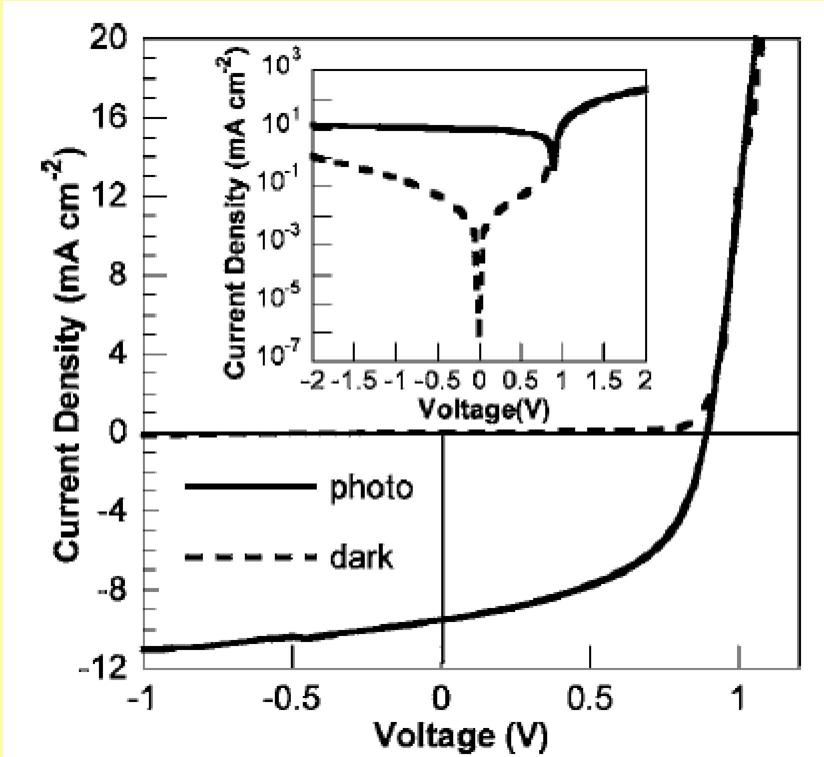




PSiF-DBT



Absorption spectra of PSiF-DBTfilm (dot), solution (broken) and PSiF-DBT:PC60BM 1:2, *w/w* blend film (solid) and the EQE of the PSC.



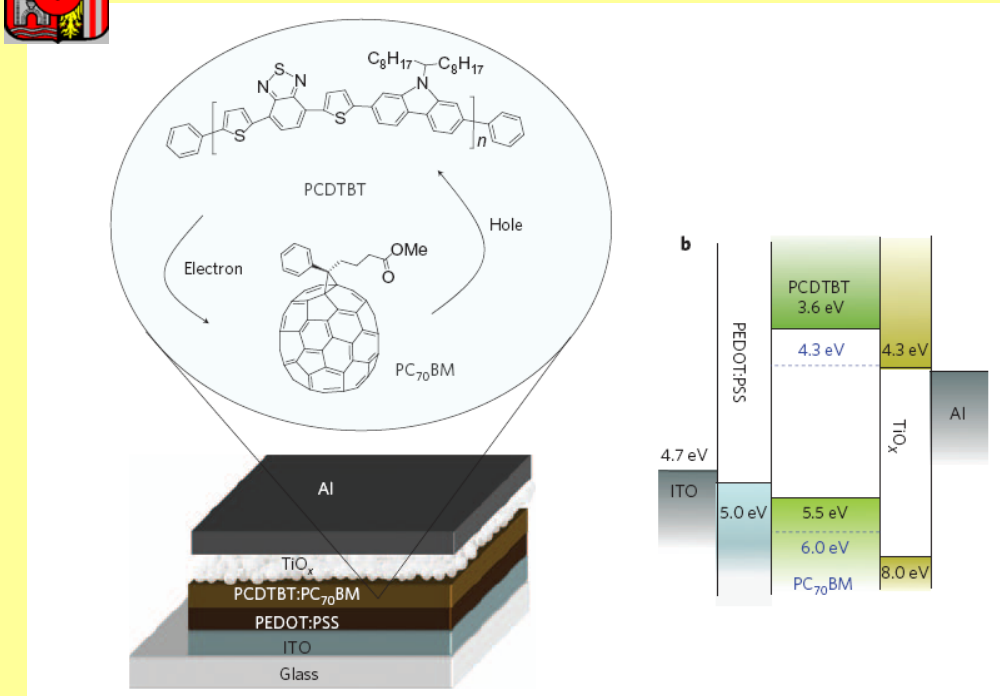
I-V curve of the device *ITO/*PEDOT:PSS/PSiF-DBT:PC60BM 1:2, *w/w/Al*, AM 1.5 G 800 Wm−2.

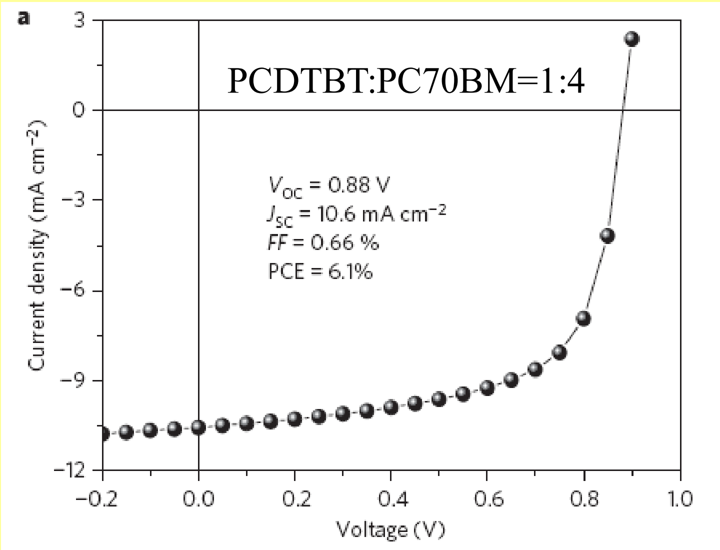
Voc =*0.90 V, Jsc* =9.5 mA cm−2

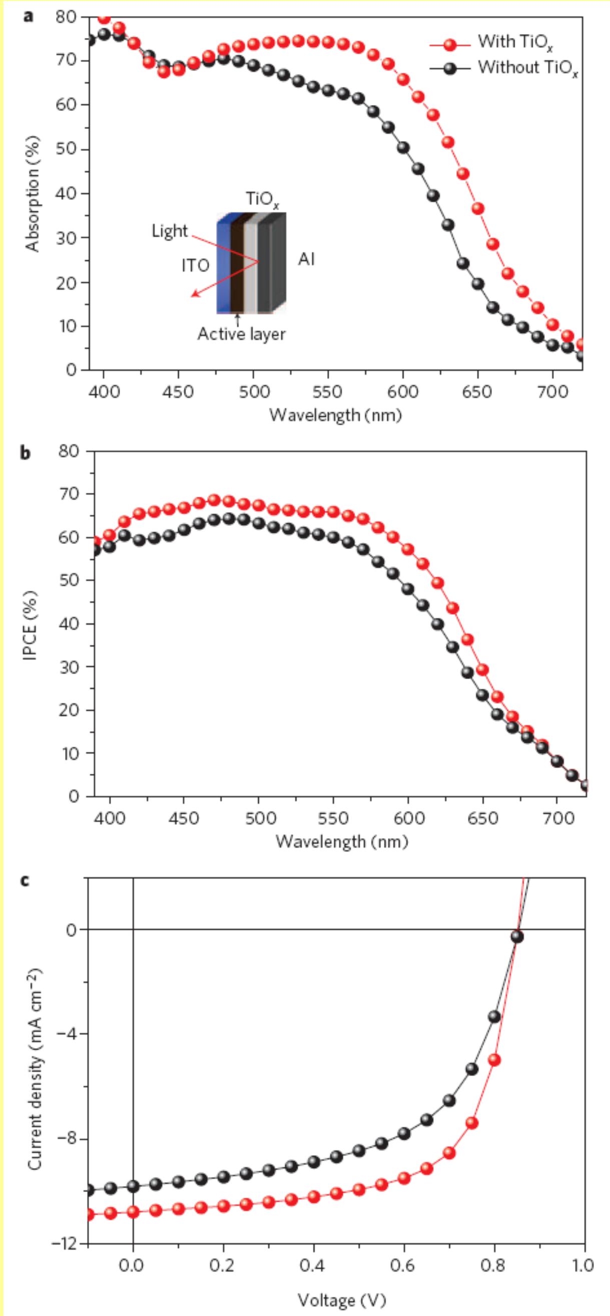
FF = 50.7%,

η: 5.4%

E.G. Wang,et al., *Appl. Phys. Lett.* **2008,** *92*, 033307.

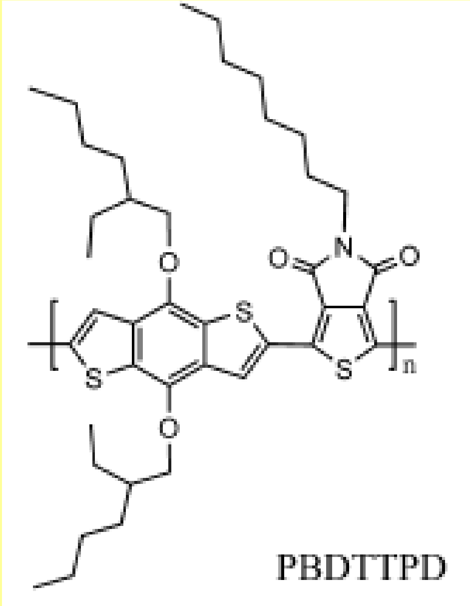


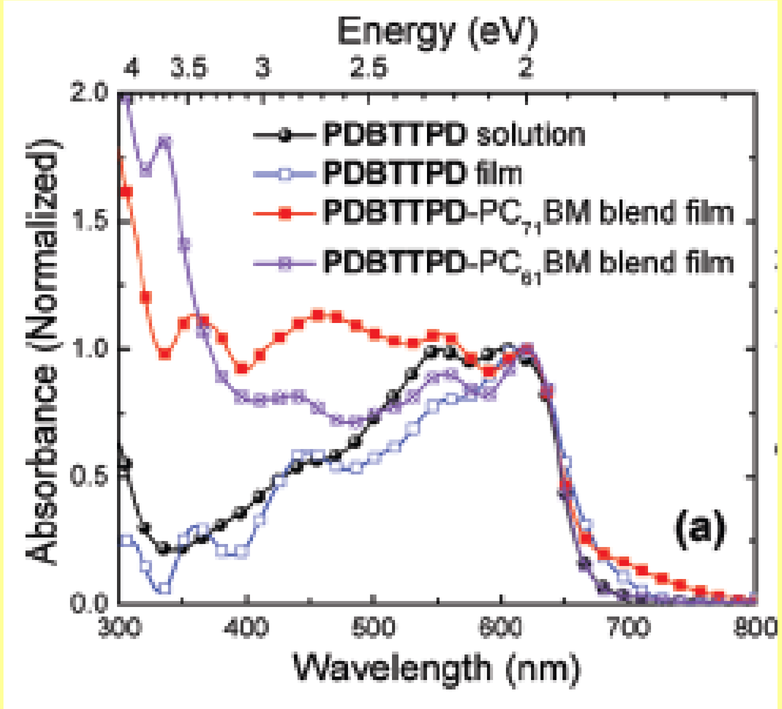


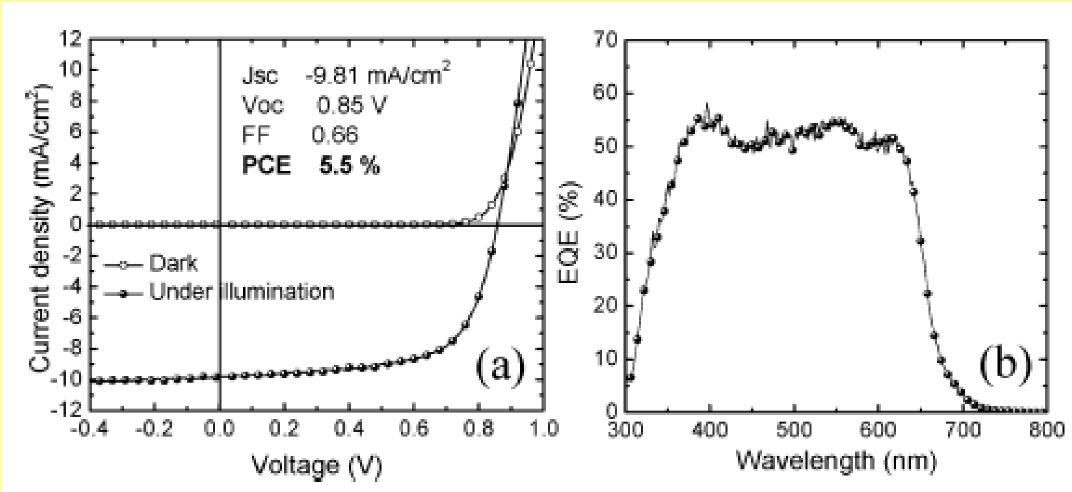


A. J. Heeger, M. Leclerc, et al. *Nature Photonics*, 2009, 3, 297 (**η: 6.1%**)

Narrow bandgap D-A copolymers



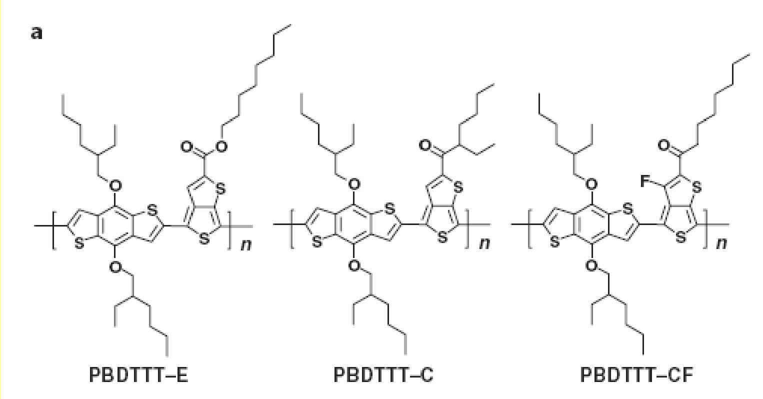


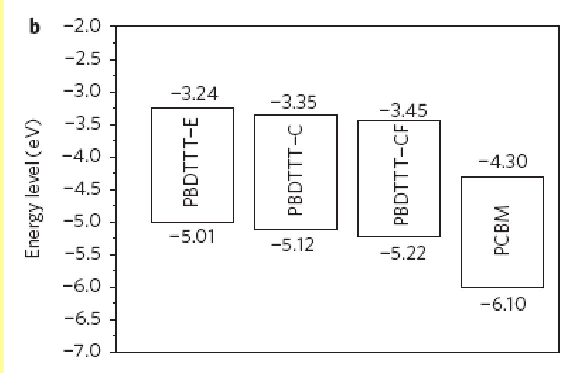


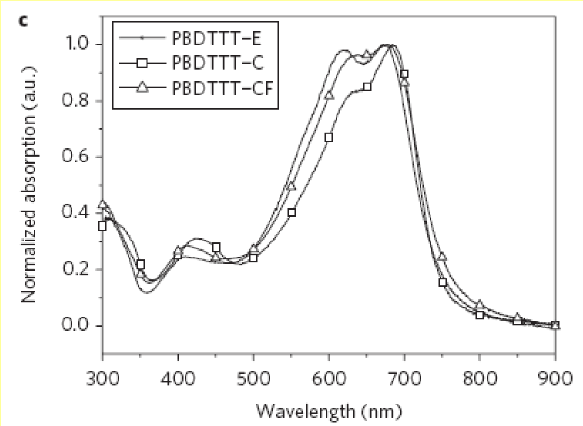
Device area:1 cm2

PCE: 5.5%

[Yingping Zou, M. Leclerc*, et al., *J. Am. Chem. Soc.*, 2010, DOI: 10.1021/ja101888b]







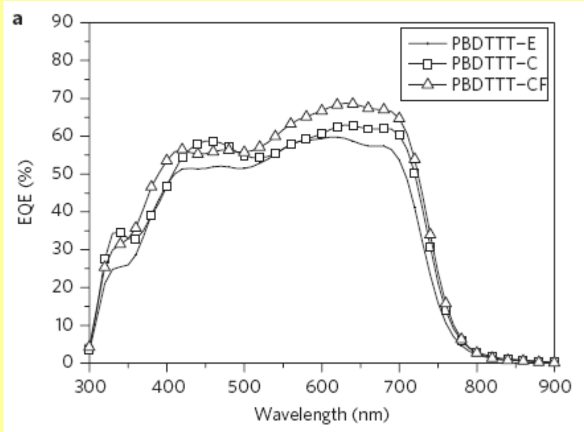


Table 1 | Solar cell parameters of devices based on the three different polymers.

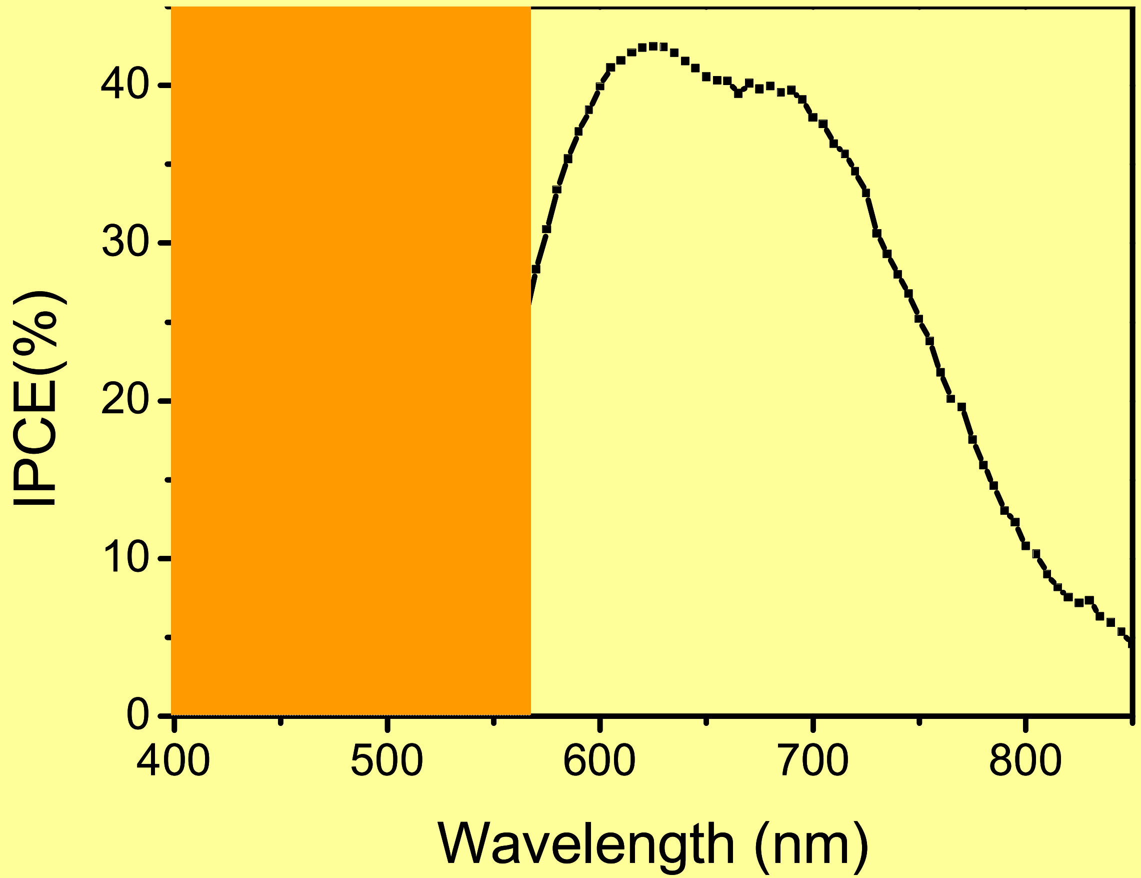
	LUMO	HOMO	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	
						Best	Ave
PBDTTT-E	−3.24	−5.01	0.62	−13.2	63	5.15	4.8
PBDTTT-C	−3.35	−5.12	0.7	−14.7	64.1	6.58	6.3
PBDTTT-CF	−3.45	−5.22	0.76	−15.2	66.9	7.73	7.4

LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital; FF, fill factor; PCE, power conversion efficiency.

H. Y. Chen, J. H. Hou, et al., *Nature Photonics*, 2009, *3*, 649-653.
J. H. Hou, et al., *J. Am. Chem. Soc.*, 2009, *131*, 15586–15587.
Yongye Liang, et al., *J. Am. Chem. Soc.*, 2009, *131, 56–57*
Yongye Liang, et al., *J. Am. Chem. Soc*. 2009, 131, 7792-7799

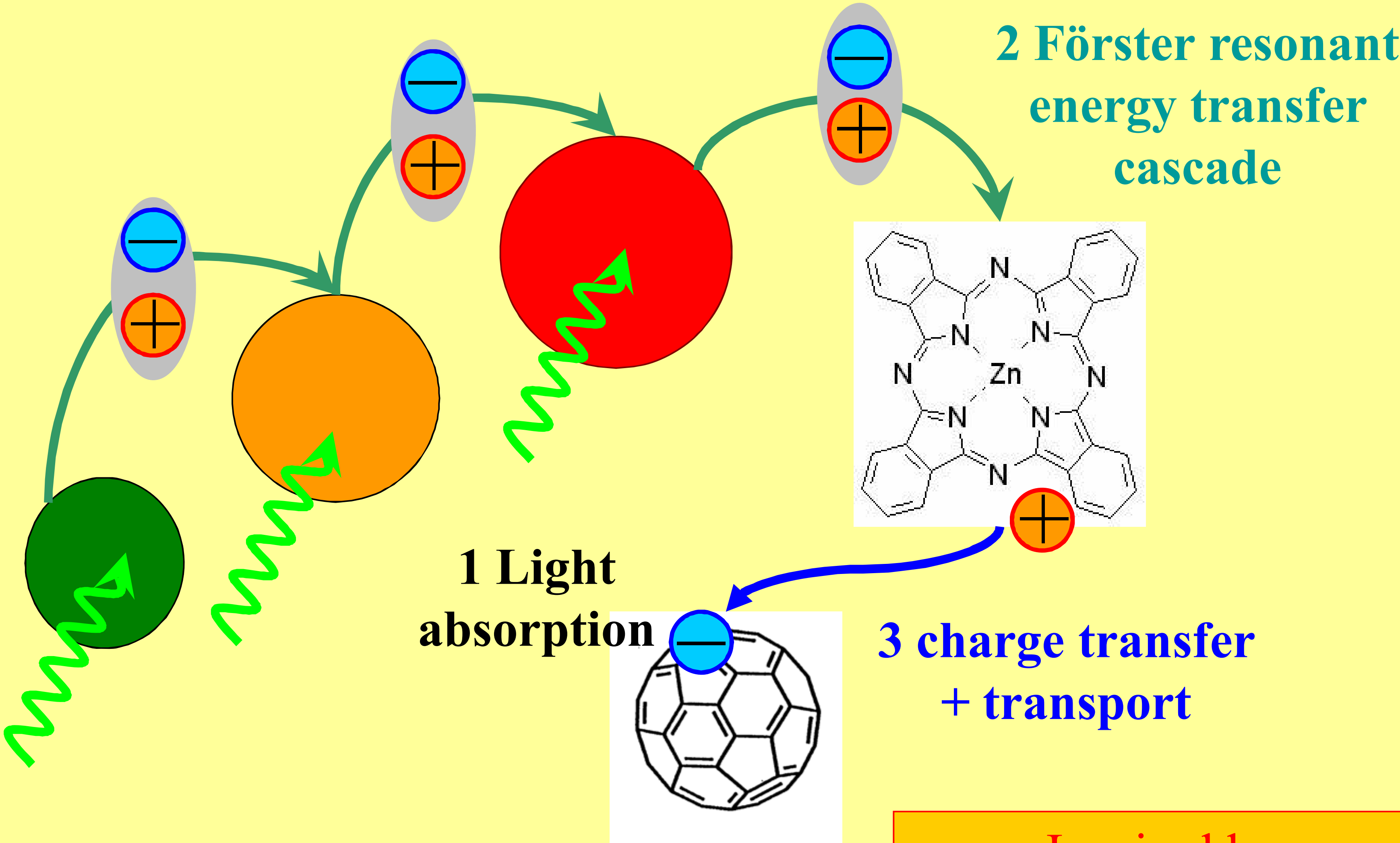
Photon Harvesting Problem

Incident Photon to Electron Conversion efficiency:



By low band gap materials we are loosing the green-blue region

Energy Transfer Cascades

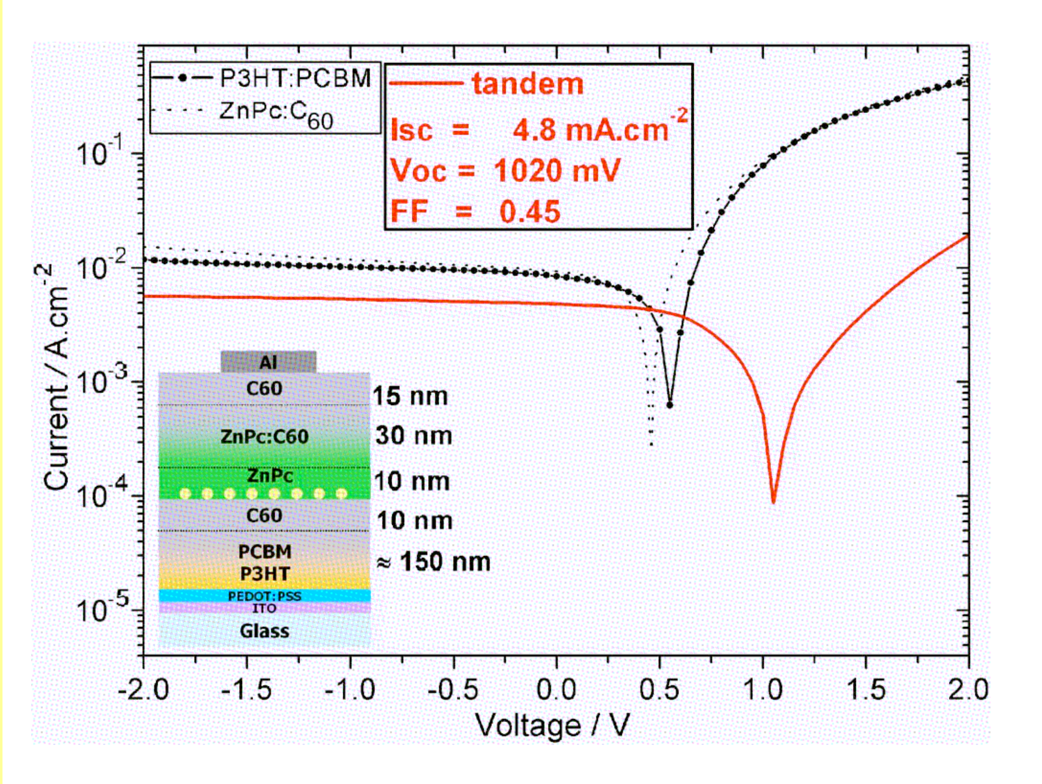


- R. Koeppe, O. Bossart, G. Calzaferri, and N.S. Sariciftci, Sol. Energ. Mater. Sol. Cells. 91(11); 986-995 (2007)

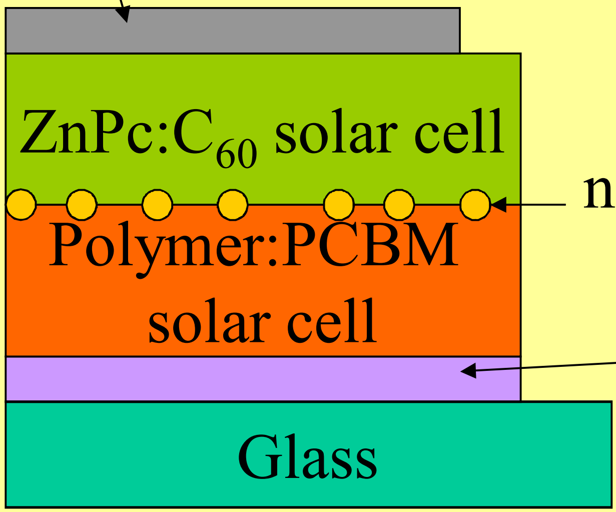
Inspired by photosynthesis

Tandem Solar Cells

Organic tandem solar cells:



Aluminium electrode



noncontinuous recombination layer

transparent ITO electrode

G. Dennler, H.-J. Prall, R. Koeppe, M. Egginger, R. Autengruber, N.S. Sariciftci, *APL* **89** (2006), 073502-1

Critical Steps for the Organic Photovoltaic Devices

1.) Light absorption (interface effects !)

2.) Exciton diffusion

3.) Photoinduced electron transfer (exciton dissociation)

4.) Charge carrier transport / recombination

5.)Charge carrier collection at the electrodes (interface engineering)

Diffusion versus Drift Effects

JOURNAL OF APPLIED PHYSICS VOLUME 93, NUMBER 6 15 MARCH 2003

Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation

Brian A. Gregg[a)] and Mark C. Hanna
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

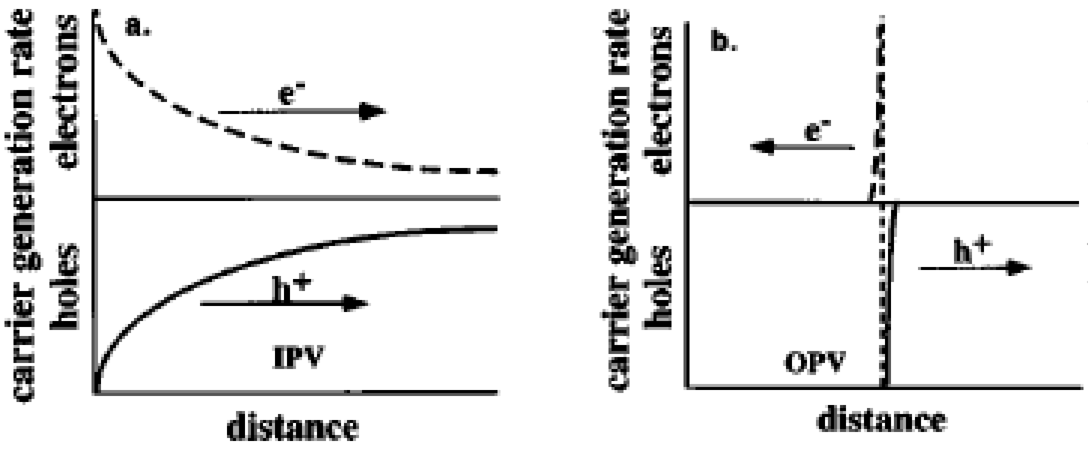


FIG. 3. A cartoon illustrating the difference in charge-carrier generation mechanisms in conventional (a) and excitonic (b) solar cells. In conventional solar cells (a), electrons and holes are photogenerated together wherever light is absorbed. Therefore, the photoinduced chemical-potential-energy gradient $\nabla\mu_{h\nu}$ (represented by arrows) drives both carrier types in the same direction. In the excitonic cell (b), however, electrons are photogenerated in one phase while holes are generated in the other via interfacial exciton dissociation. Carrier generation is simultaneous to, and identical with, carrier separation across the interface in OPV cells; $\nabla\mu_{h\nu}$ therefore drives electrons and holes in opposite directions.

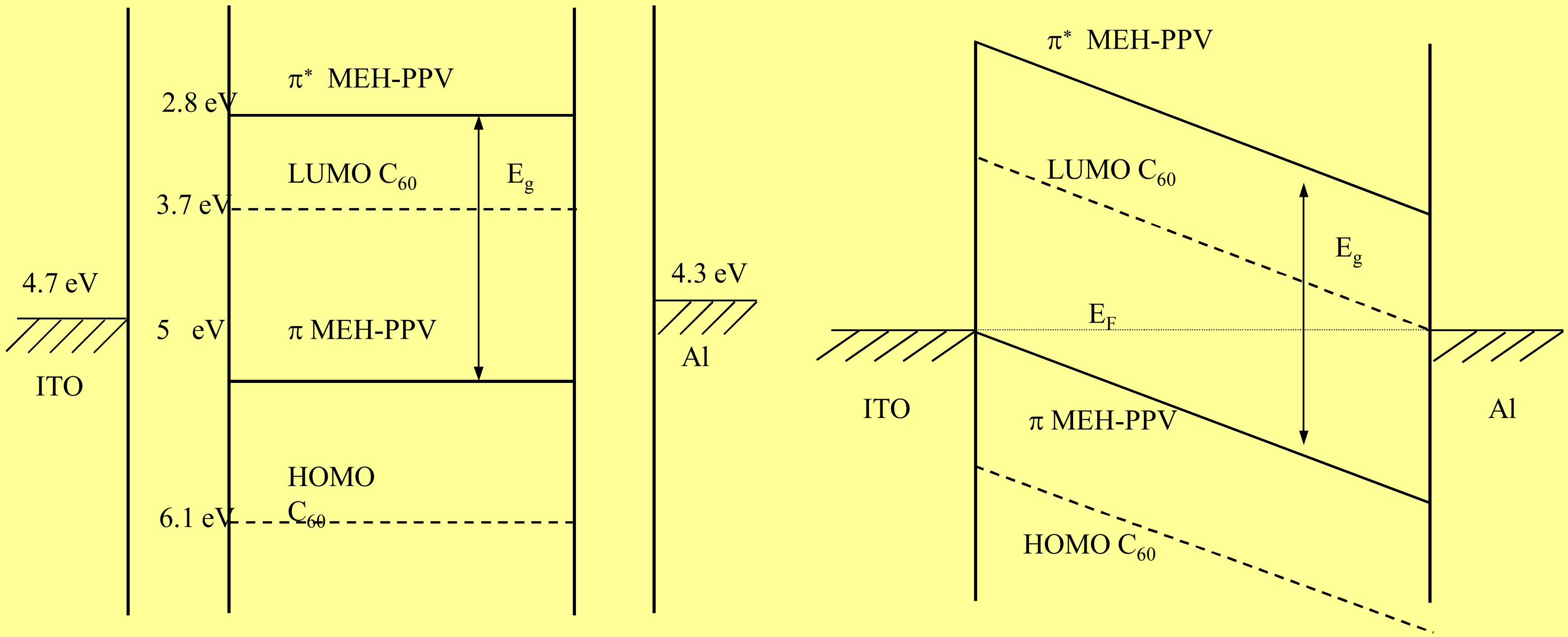
The general kinetic expression for the one-dimensional current density of electrons $J_n(x)$ through any device is usually expressed as[1]

$$J_n(x) = n(x)\mu_n \nabla U(x) + kT\mu_n \nabla n(x), \quad (1)$$

where $n(x)$ is the concentration of electrons, μ_n is the electron mobility (not to be confused with the chemical potential energy μ), and k and T are Boltzmann's constant and the

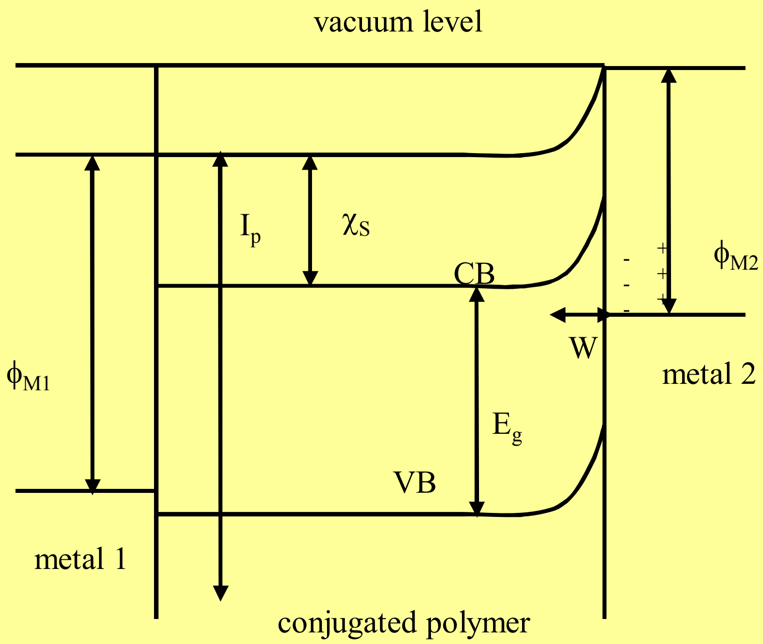
ing force. Thus, ∇U can be ≈ 0, for example, and a highly efficient solar cell can be made based wholly on $\nabla\mu_{h\nu}$. This is how dye-sensitized solar cells (DSSCs) function,[19,32] in which the mobile electrolyte permeating the cell eliminates the internal electric fields (see below). In solid-state OPV cells without mobile electrolyte, both ∇U and $\nabla\mu$ must be taken into account.

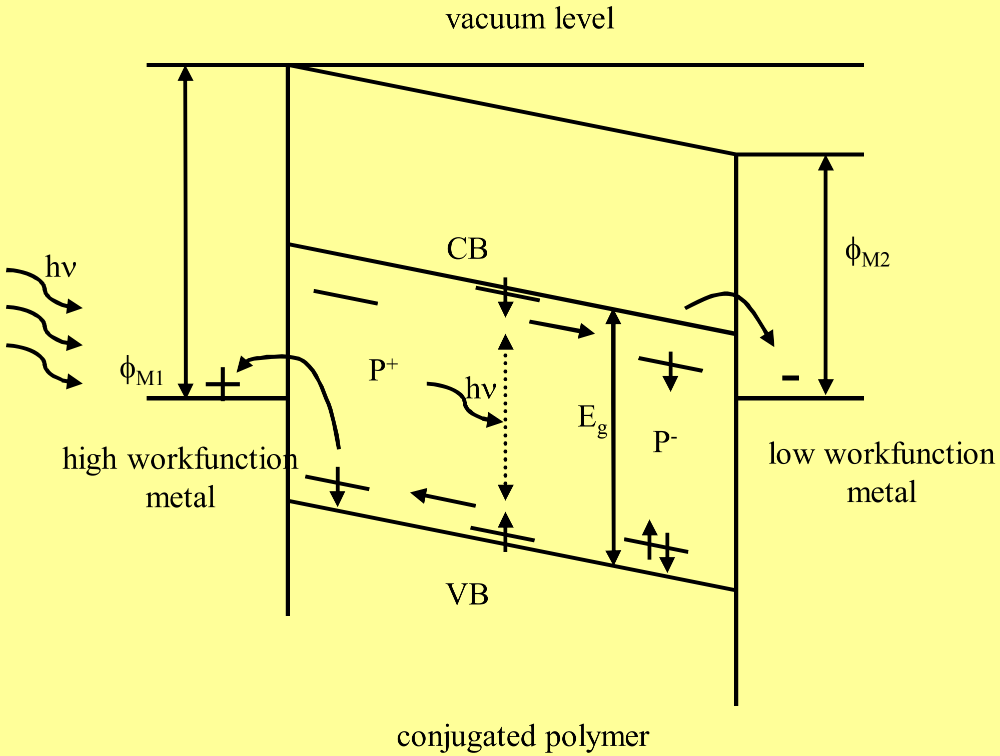
Schematic Band Diagram



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

Band Models





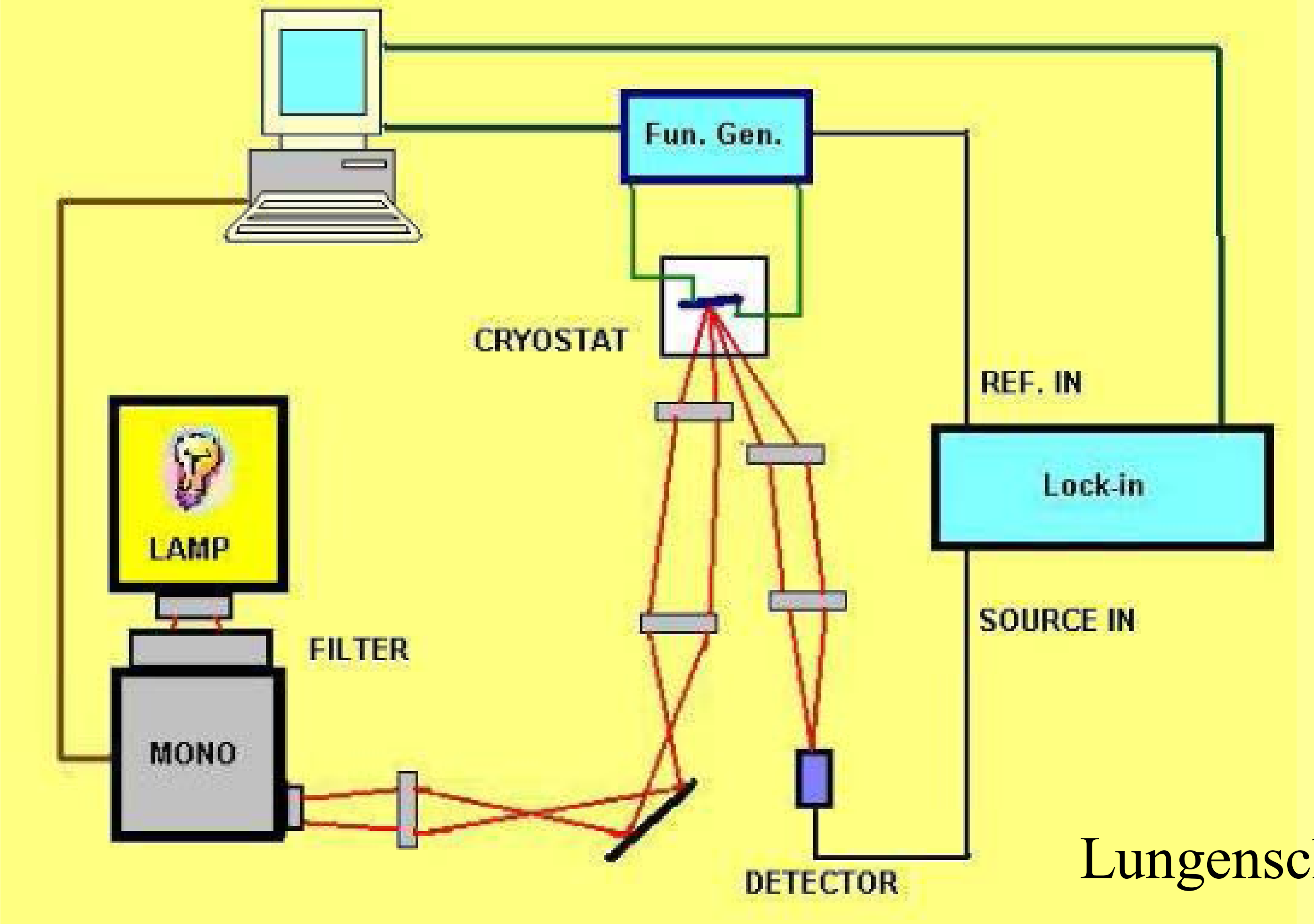
Schottky Contacts for
high Impurities
$n >> 10^{16} cm^{-3}$

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

Electroabsorption Studies

A measure of the internal electric field in the device

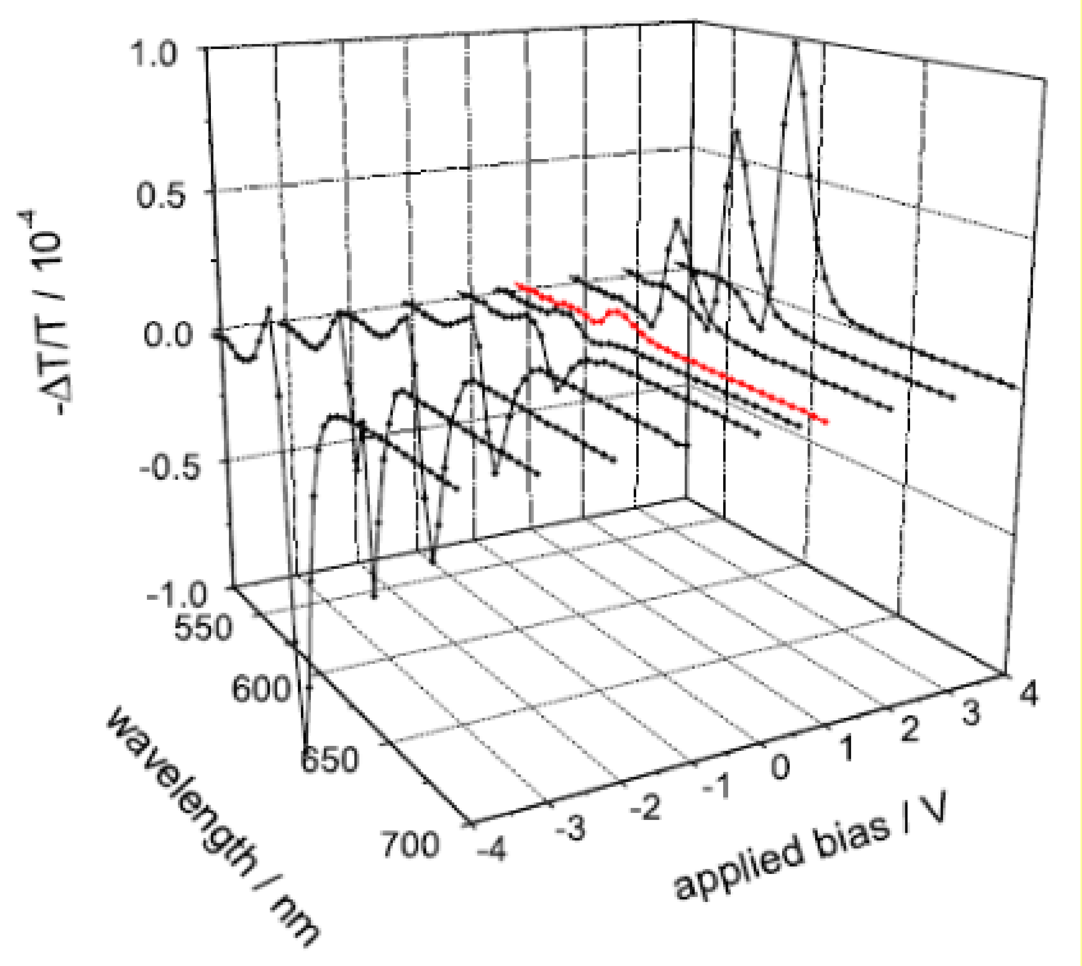
$$\frac{|\Delta T|}{T}(h\nu) \propto (V_{dc} - V_{int}) \cdot V_{ac}$$



Lungenschmied et al., 2006

Electroabsorption Studies

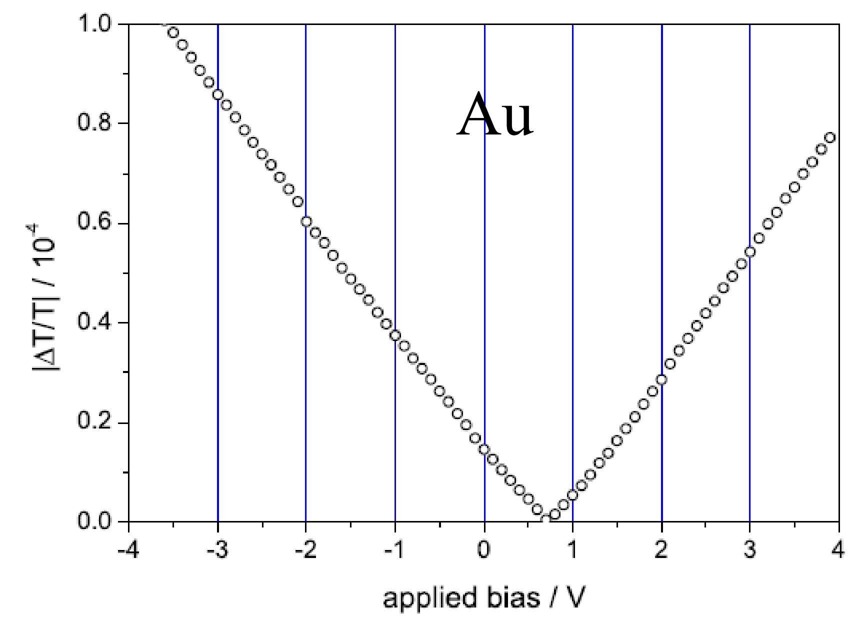
A measure of the internal electric field in the device

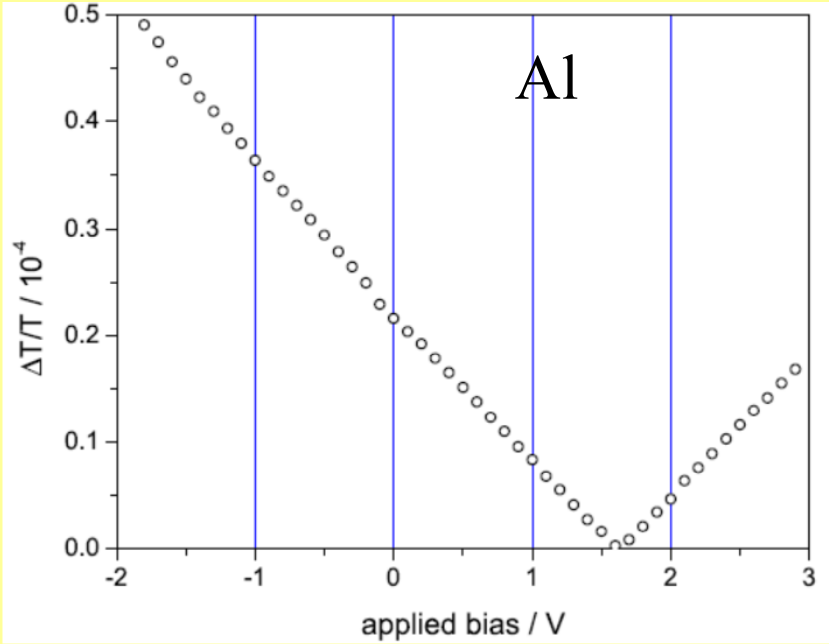


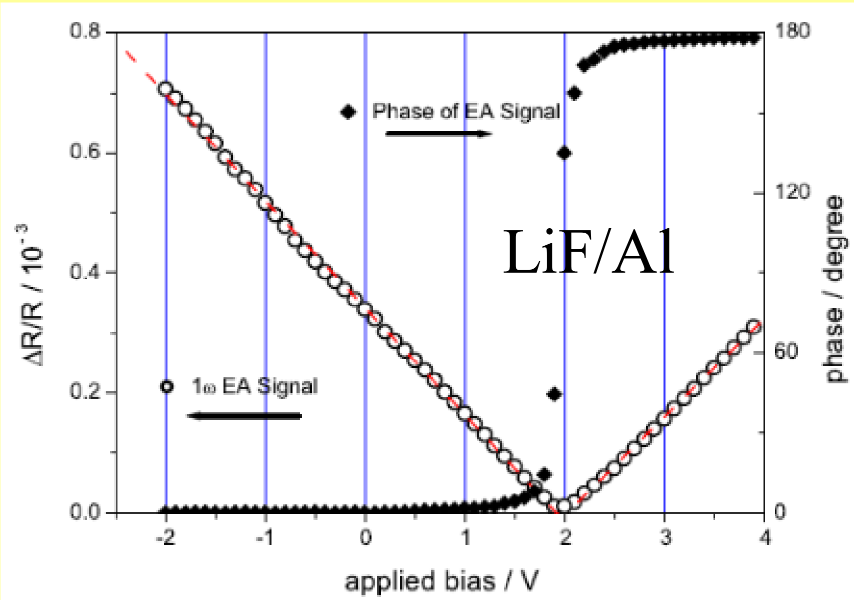
$$\frac{|\Delta T|}{T}(h\nu) \propto (V_{dc} - V_{int}) \cdot V_{ac}$$

Lungenschmied et al., 2006

Electroabsorption Studies







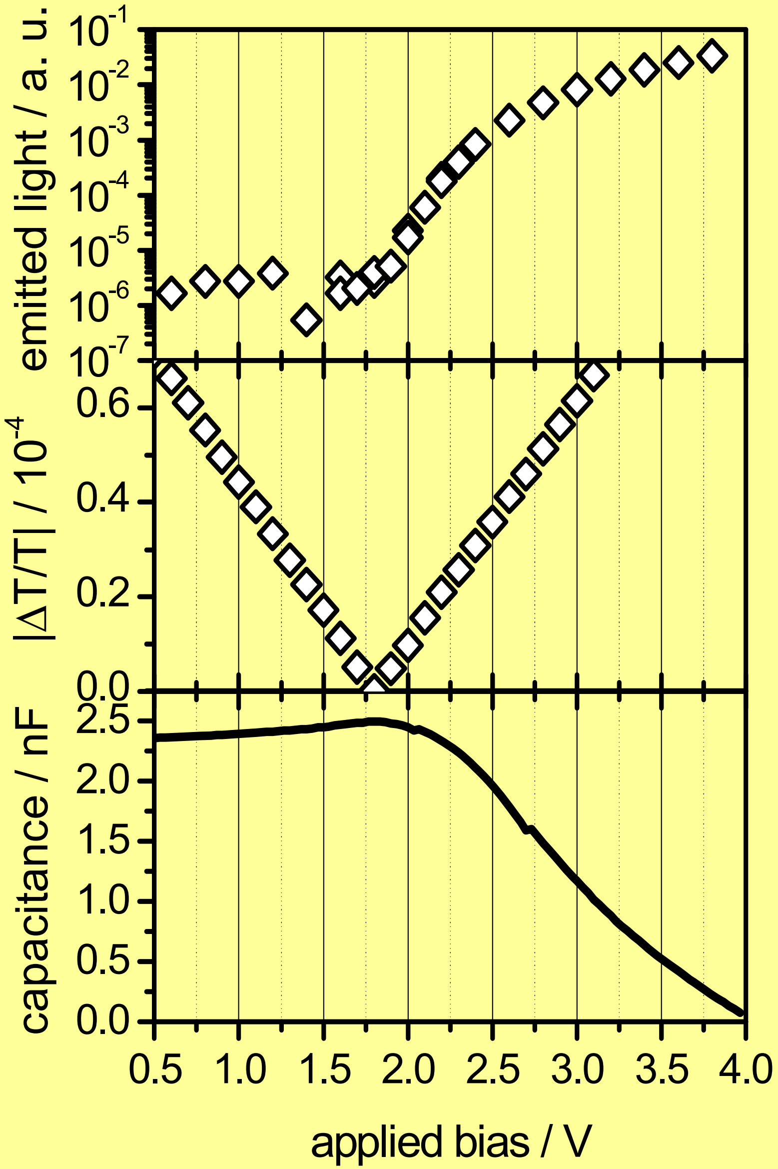
ITO/PEDOT-PSS/MDMO-PPV/Metal

100 K Electroabsorption Vac = 1V
@590nm probed

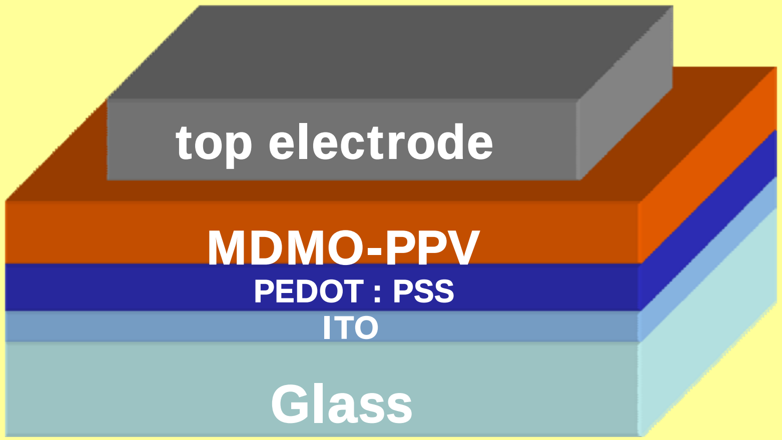
Lungenschmied et al., 2006

Summary for MDMO-PPV

Lungenschmied et al., 2006

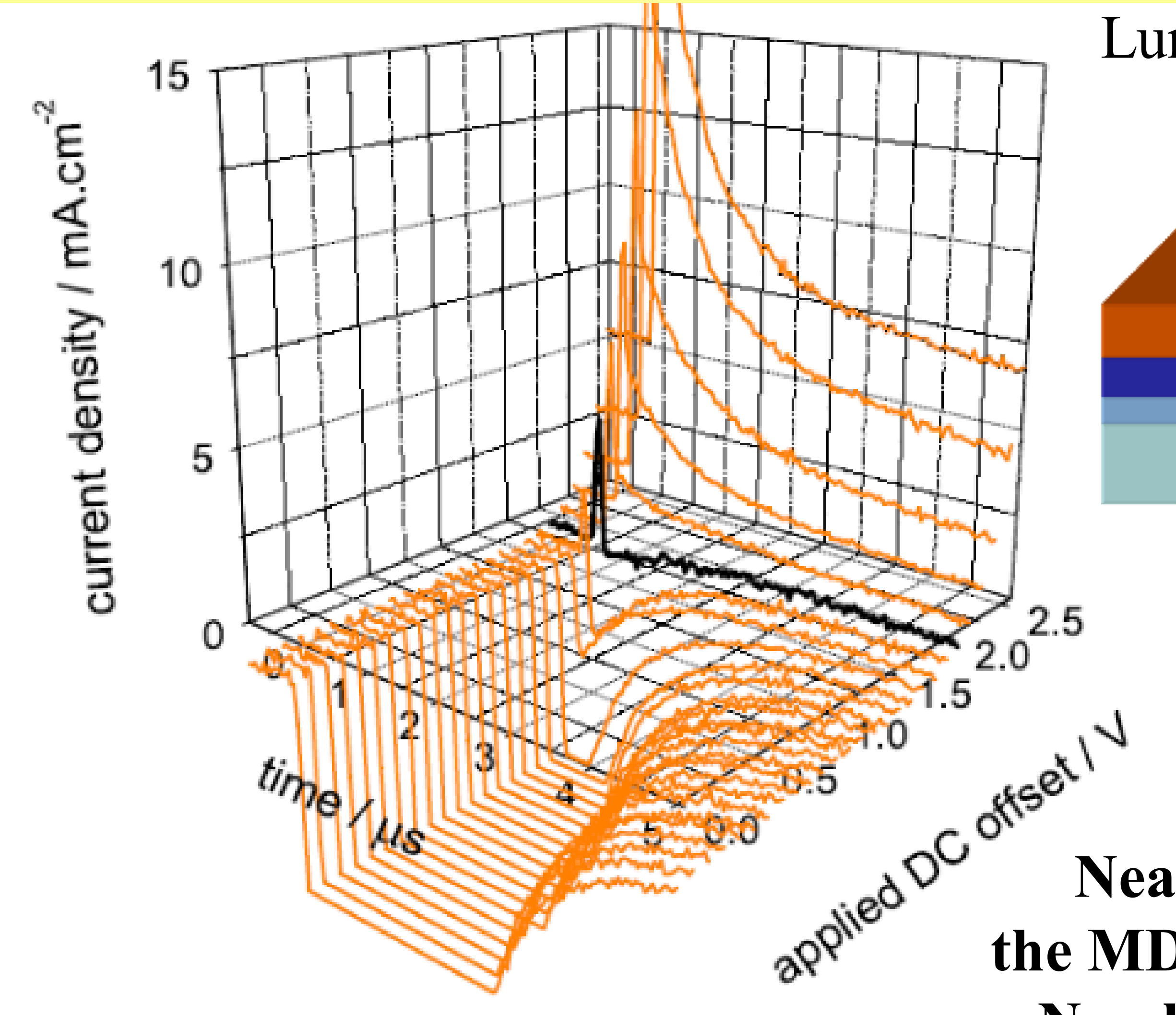


ITO/PEDOT-PSS/MDMO-PPV/LiF/Al

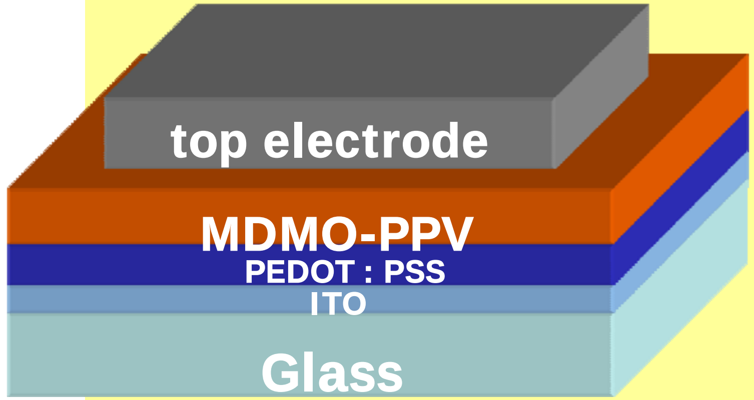


Below the built-in field the MDMO-PPV diodes behave like field driven devices but built-in field is higher than MIM model prediction

Summary for MDMO-PPV



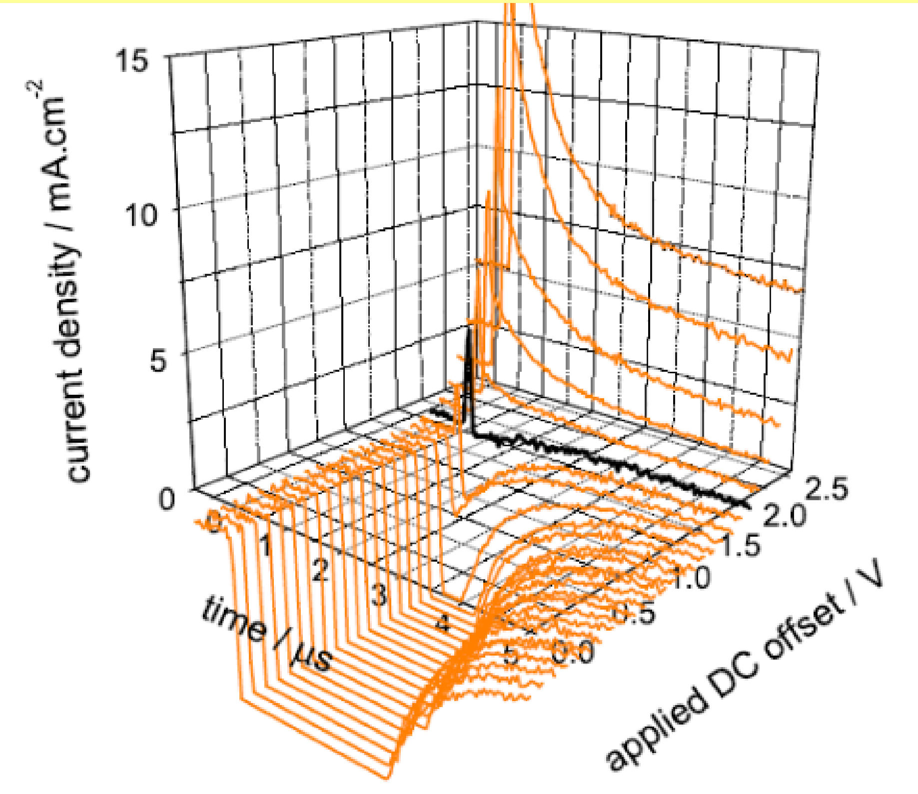
Lungenschmied et al., 2006



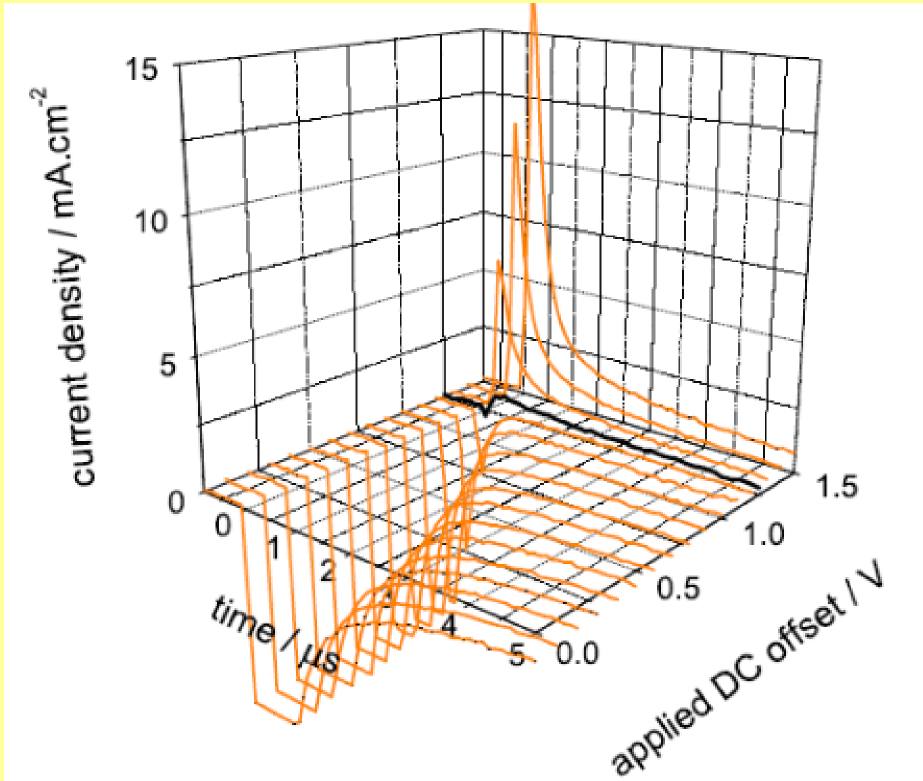
Near the built-in voltage the MDMO-PPV diodes show No photocurrent transients

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

MDMO-PPV mixed with 1% C60



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



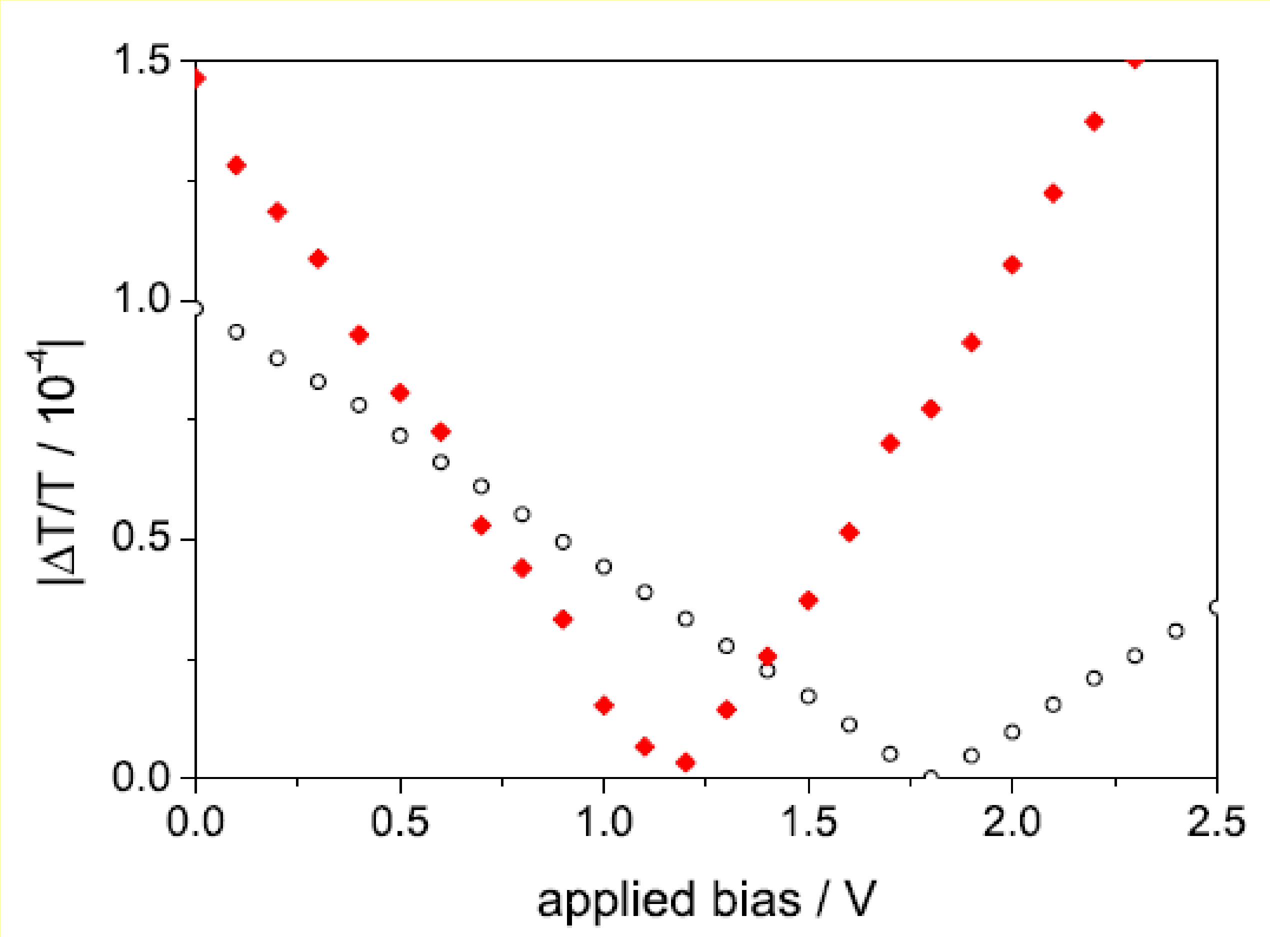
ITO/PEDOT-PSS/MDMO-PPV+1% PCBM/LiF/Al

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

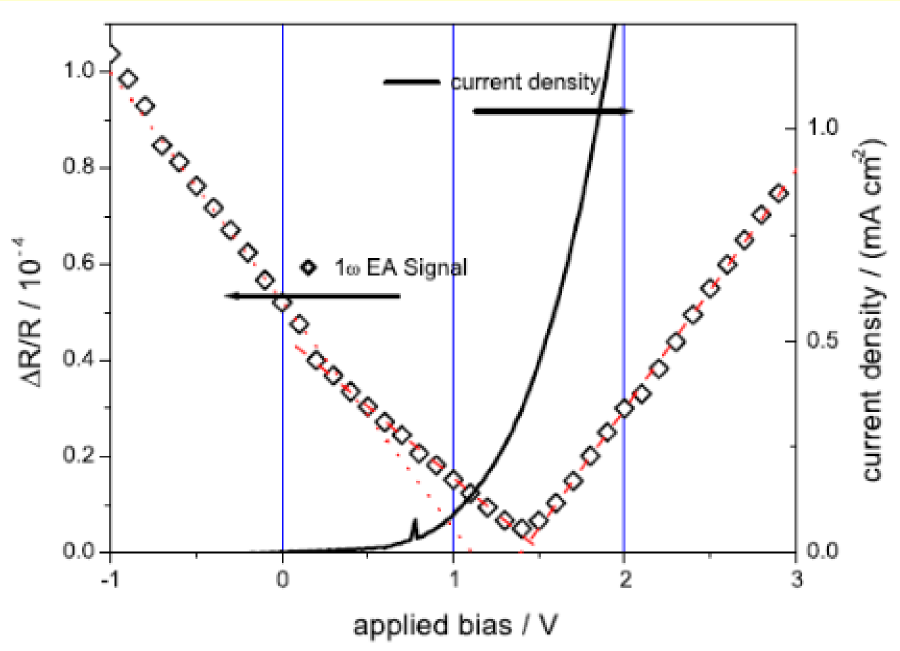
Internal field is reduced by nearly 1 V
upon addition of 1% PCBM into MDMO-PPV



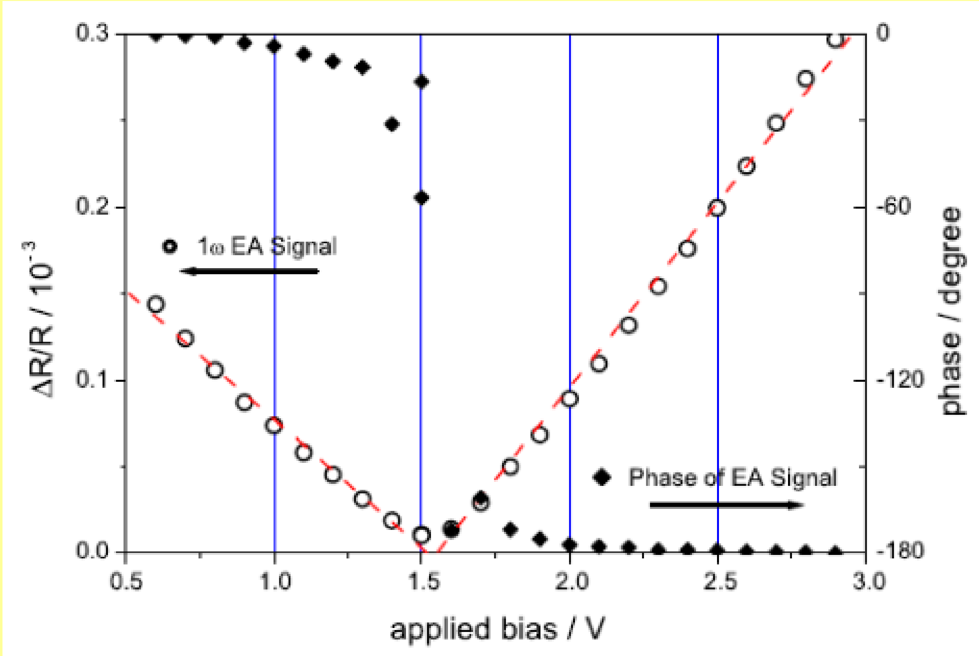
C. Lungenschmied, G. Dennler, H. Neugebauer, N.S. Sariciftci, E. Ehrenfreund
Applied Physics Letters 89 (2006), 223519

What about P3HT ?

Internal field in P3HT diodes is nearly independent to LiF insertion



ITO/PEDOT-PSS/P3HT/Al



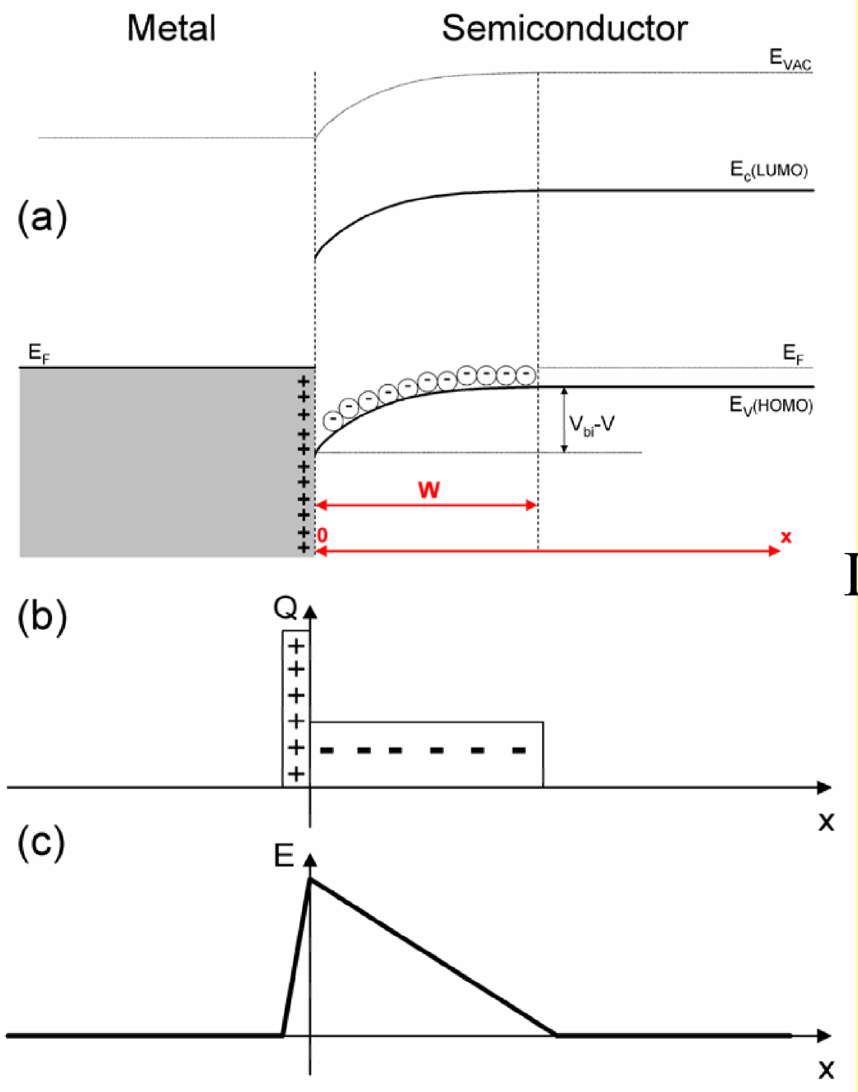
ITO/PEDOT-PSS/P3HT/LiF/Al

Measured @ 640nm and 77 K

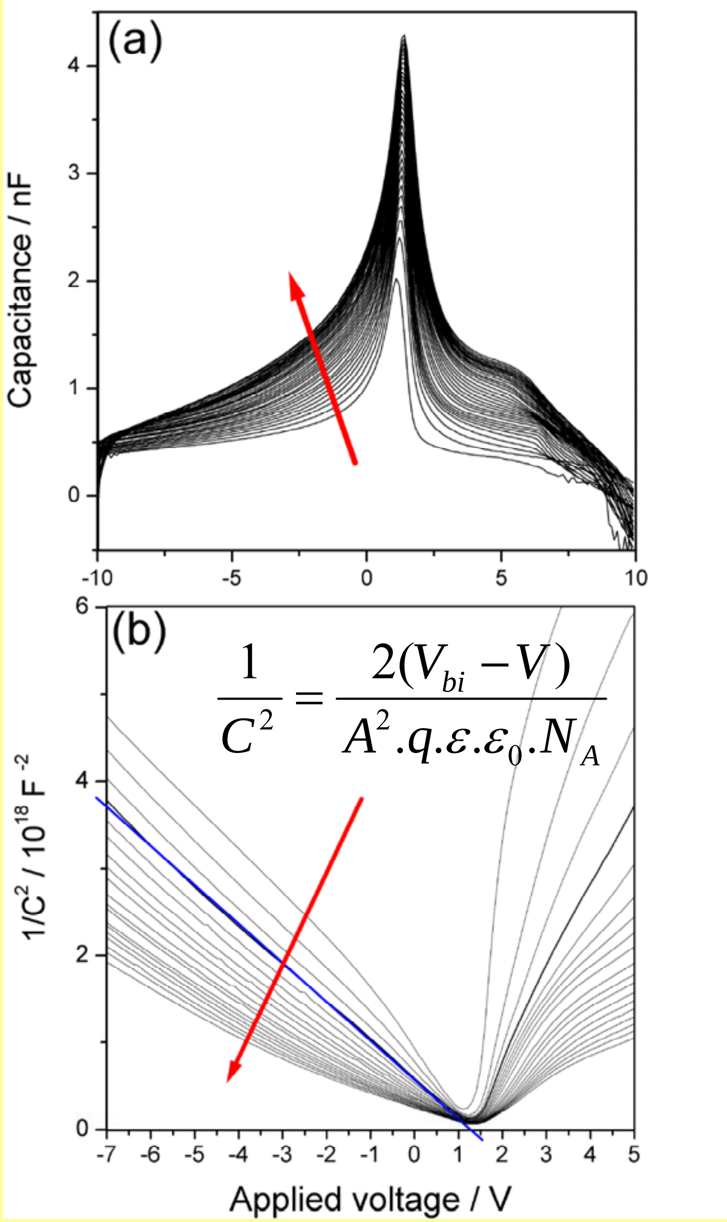
SCHOTTKY JUNCTION FORMATION IS PROBABLE IN P3HT DIODES !

C. Lungenschmied (2006)

Schottky Junction in P3HT Devices ?

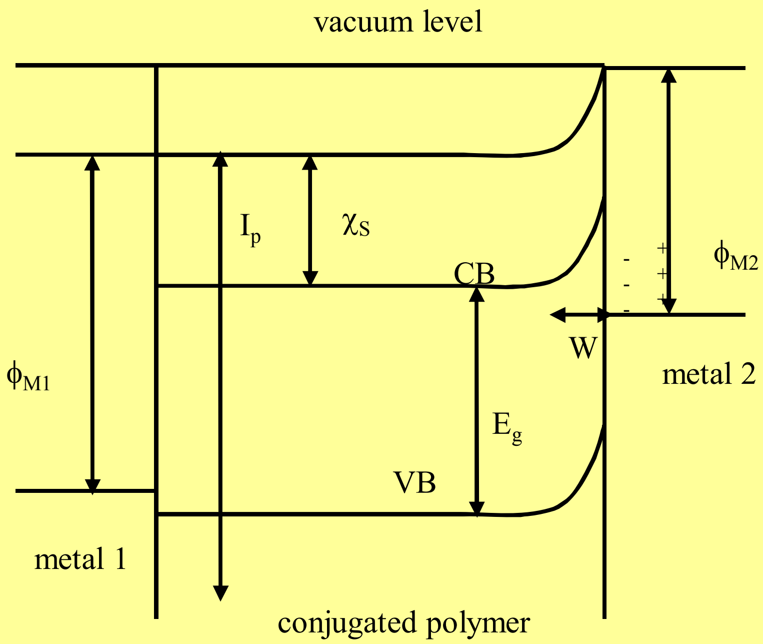


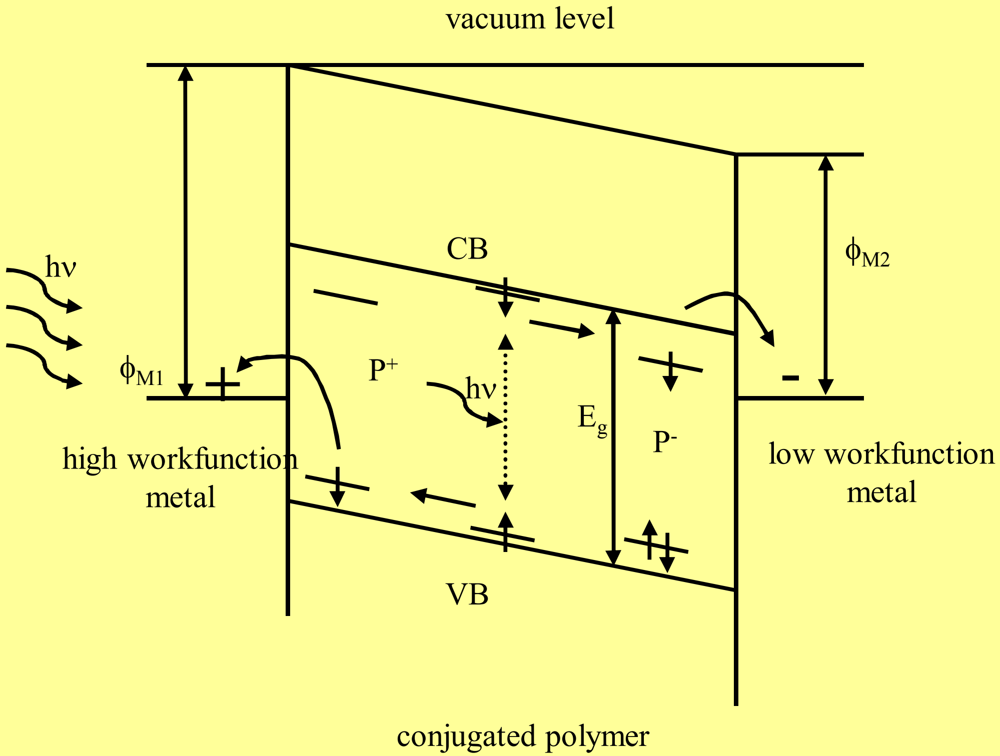
In the dark:
YES !



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

Band Models



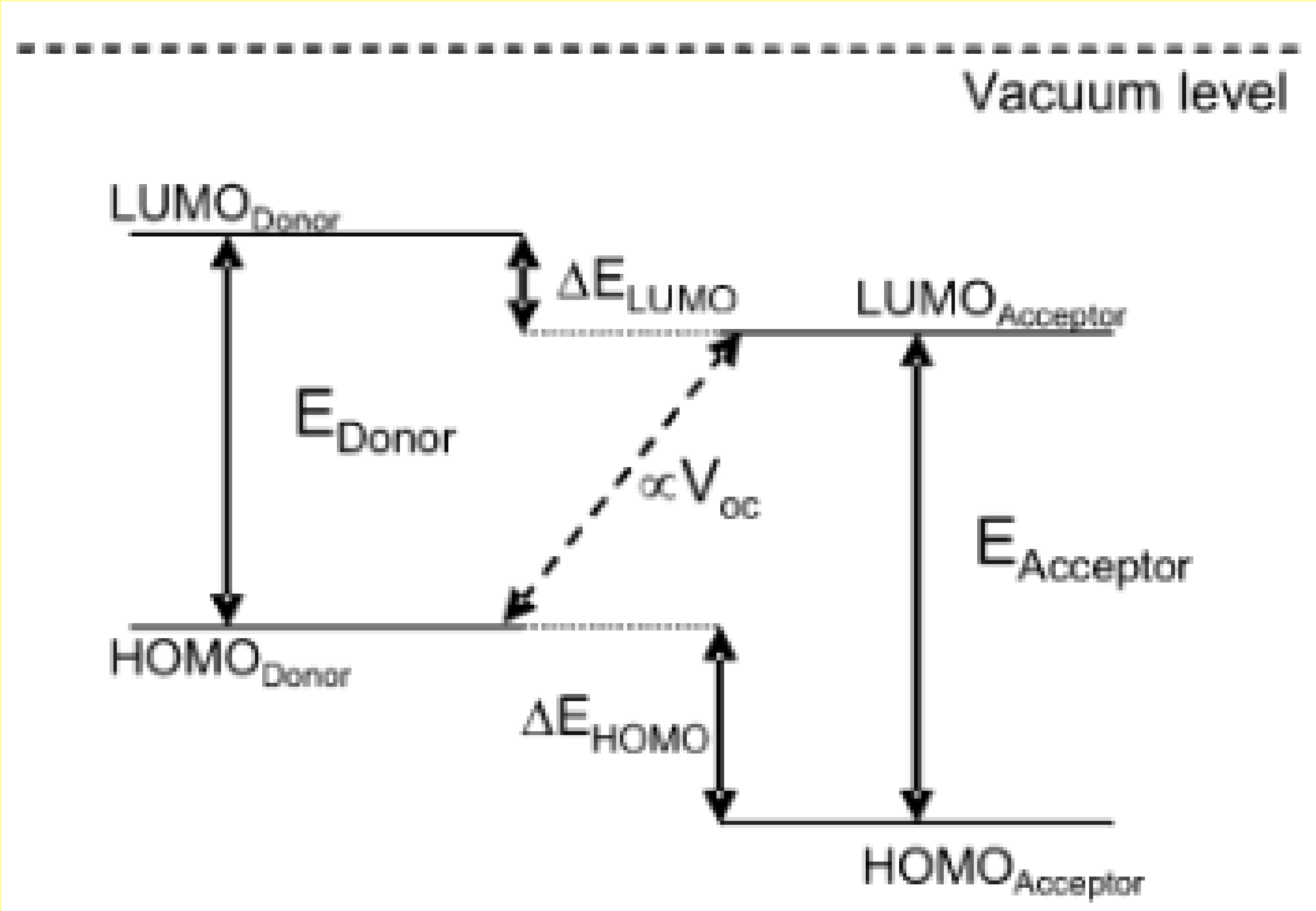


Schottky Contacts for
high Impurities
$n >> 10^{16} cm^{-3}$

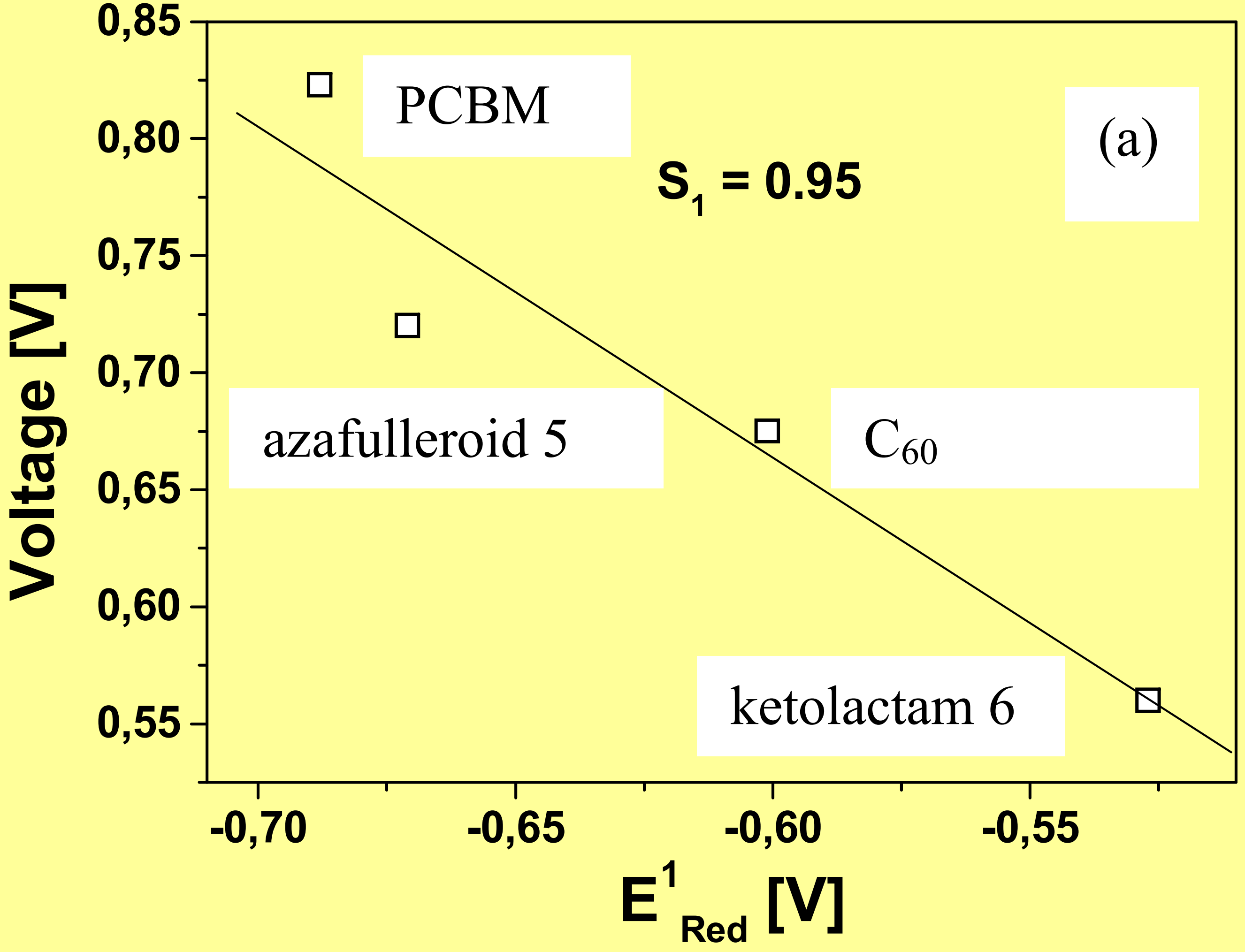
MIM Picture for
low Impurities
$n << 10^{16} cm^{-3}$

Origin of the Open Circuit Voltage Voc

Voc of Organic Solar Cells

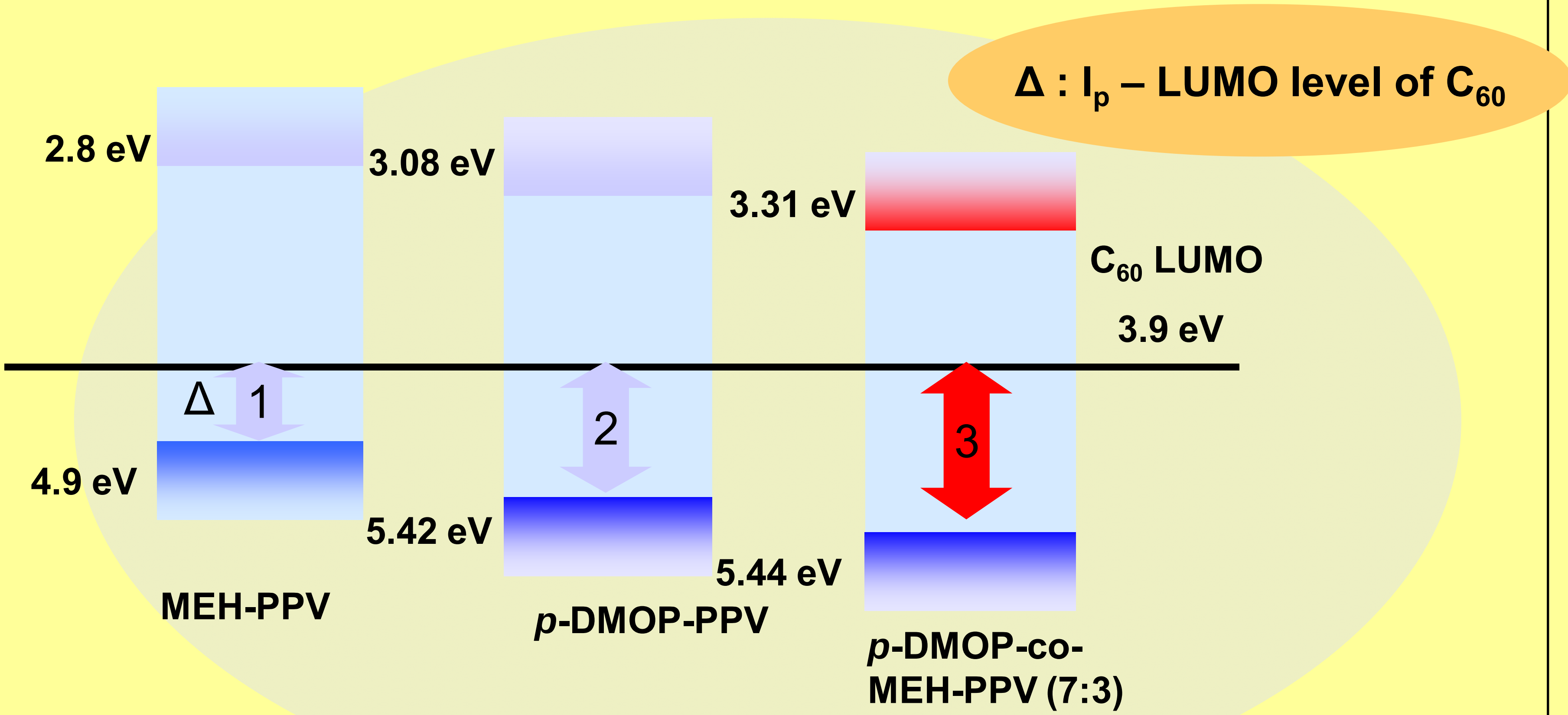


Voc vs LUMO of Acceptor



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

Voc vs HOMO of the Polymer Donor

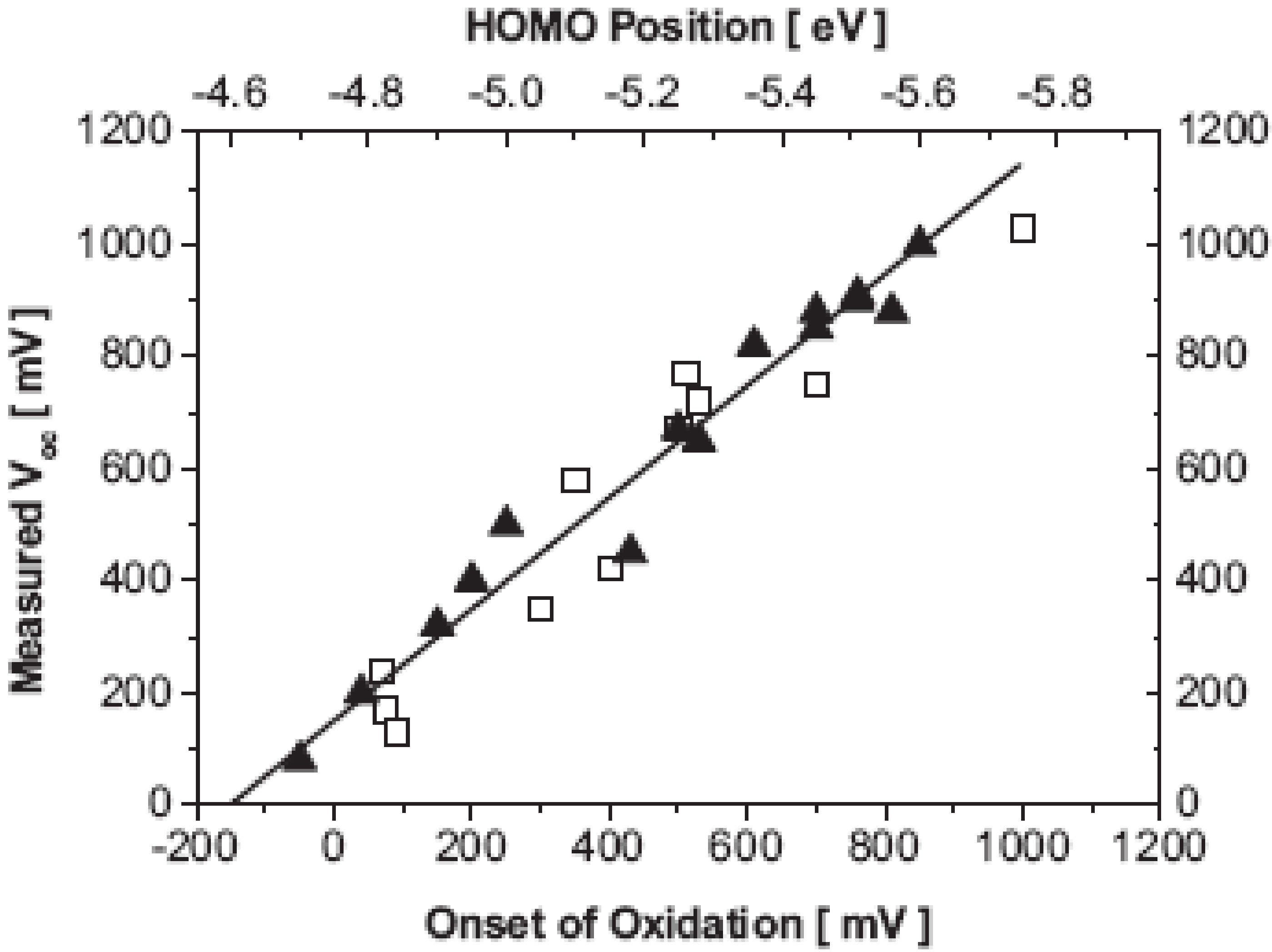


- High PL Quantum Efficiency Materials
- High Ionization Potential Materials

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

Kwanghee Lee et al, Pusan Univ. Korea

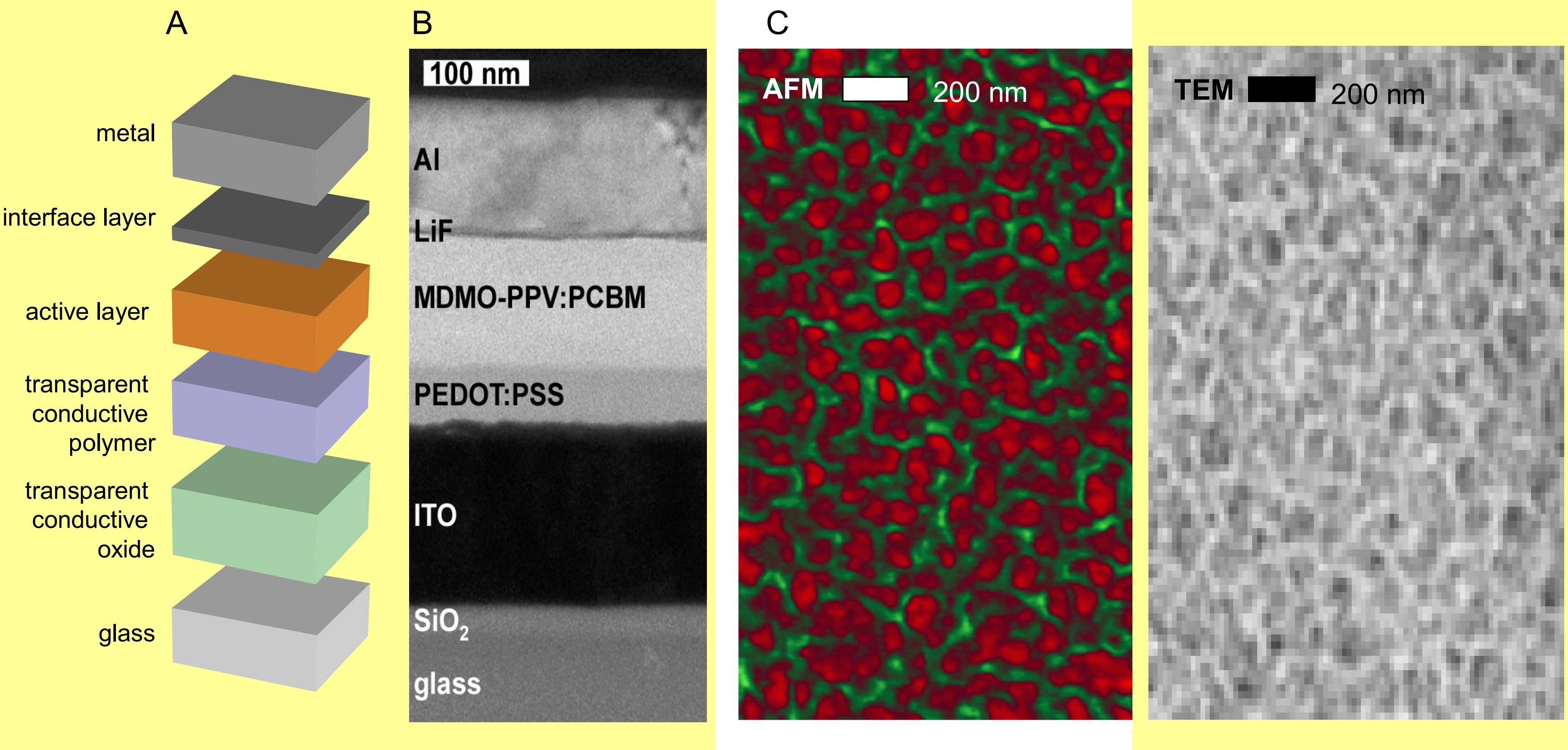
Voc vs HOMO of the Polymer Donor



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

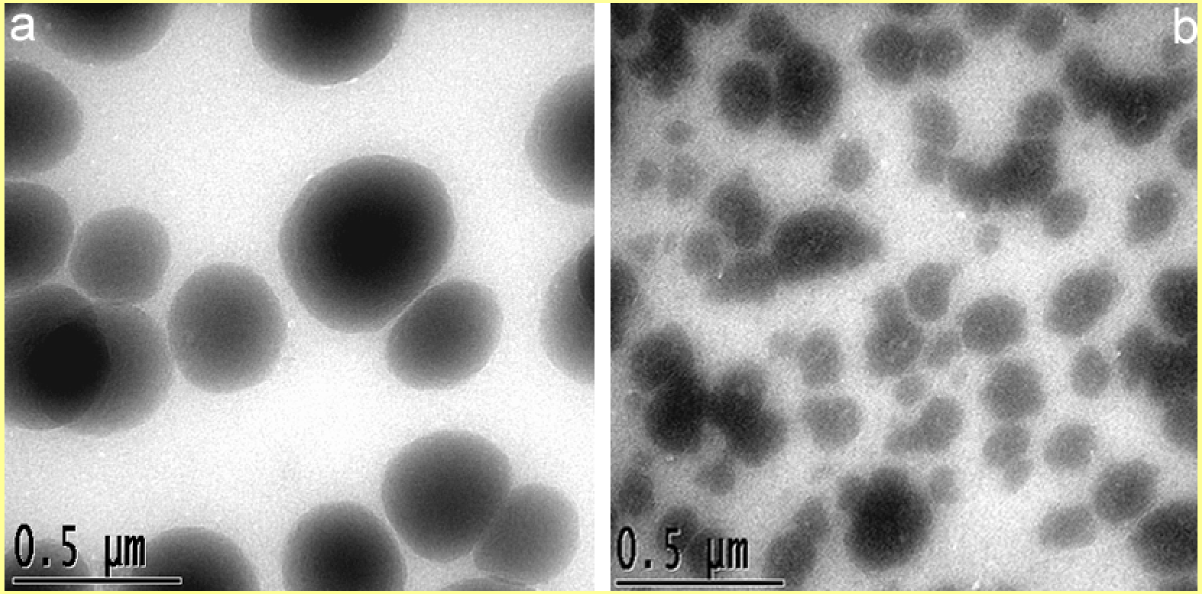
Nanomorphology of the donor-acceptor composites

Bulk Heterojunction Device Structure

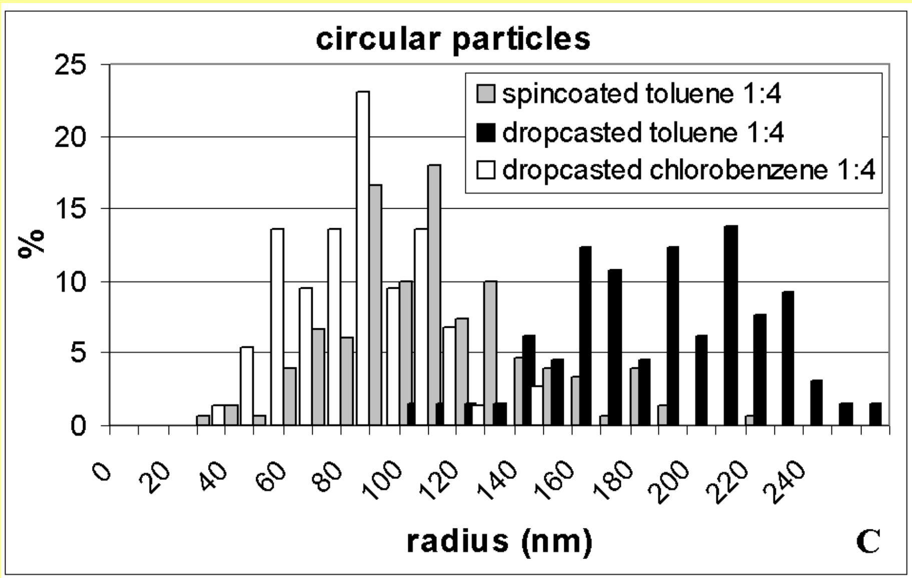


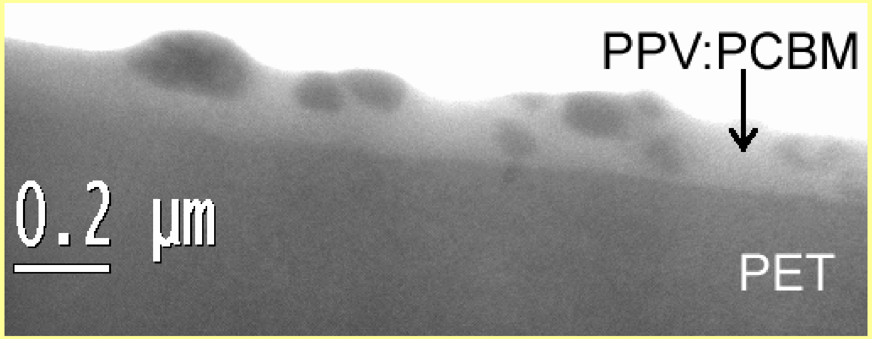
Rene Janssen *et al*, 2004

Morphology Effects-TEM Studies



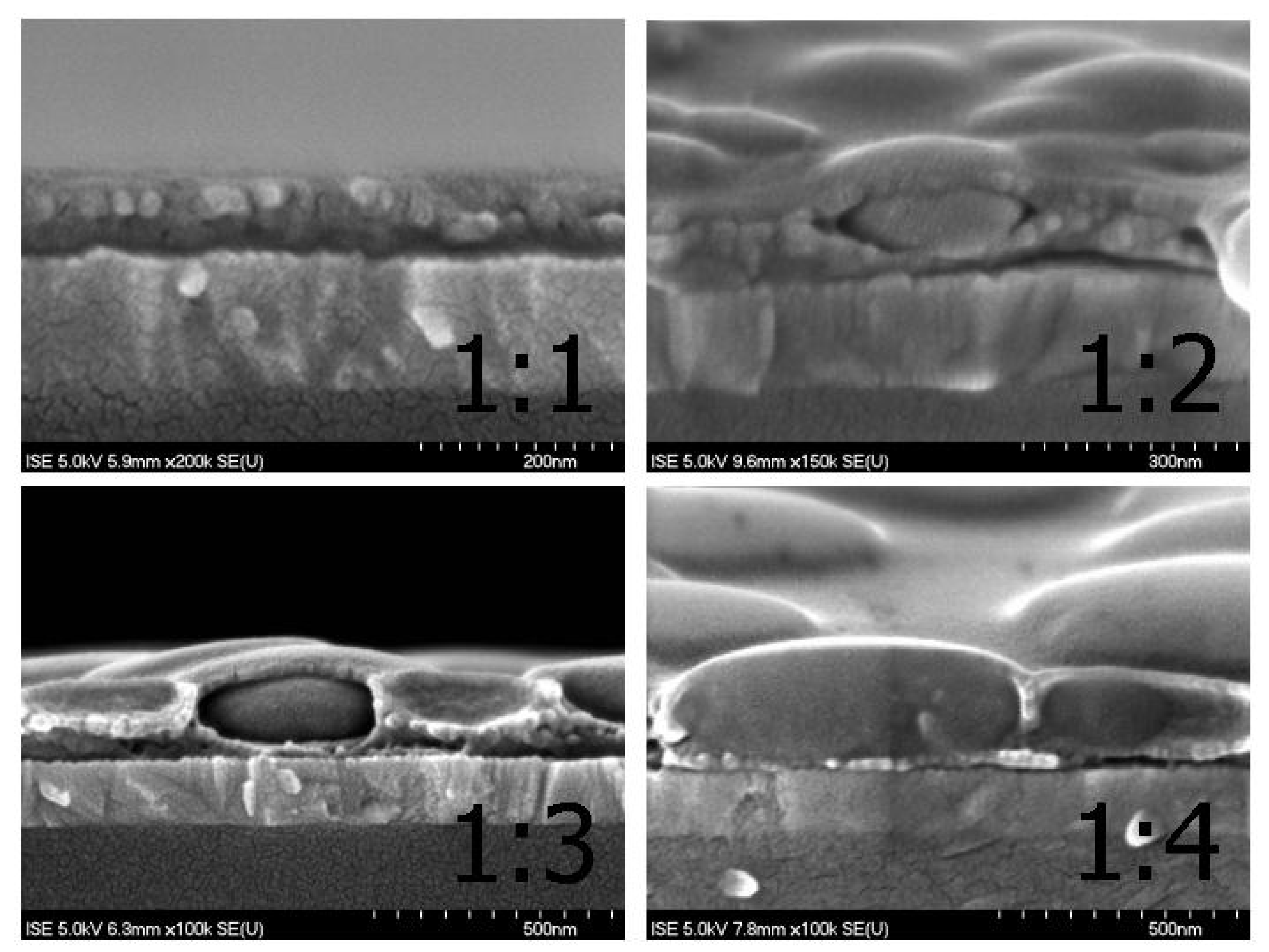
Solvent effects on the nanoparticle dimensions





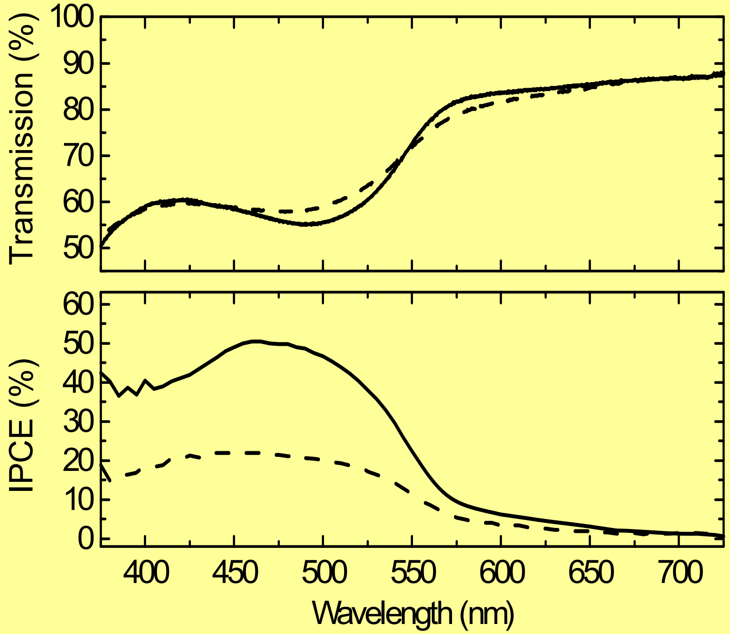
Tom Martens, Jean Manca *et al*, 2003.

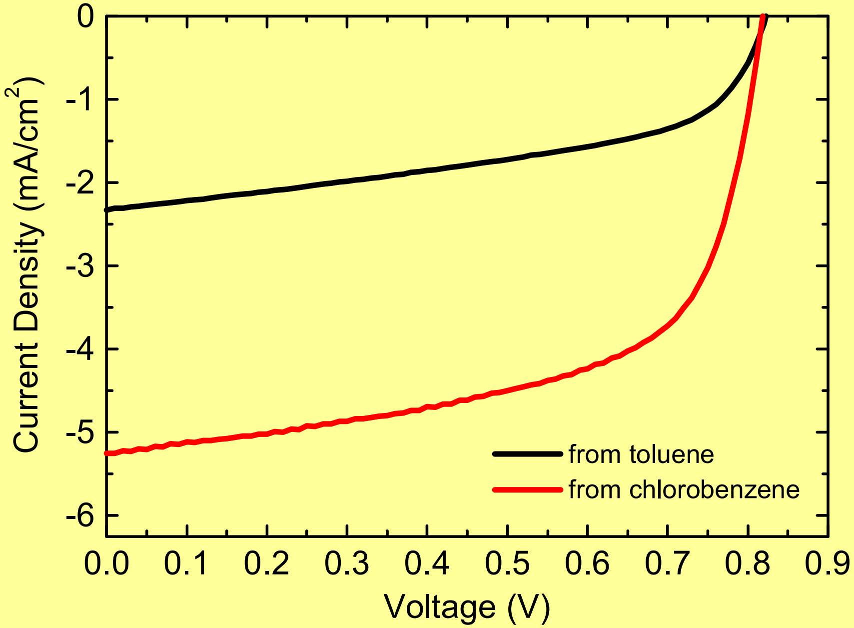
Nanomorphology Effects-SEM Studies



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

Morphology: Solvent effects

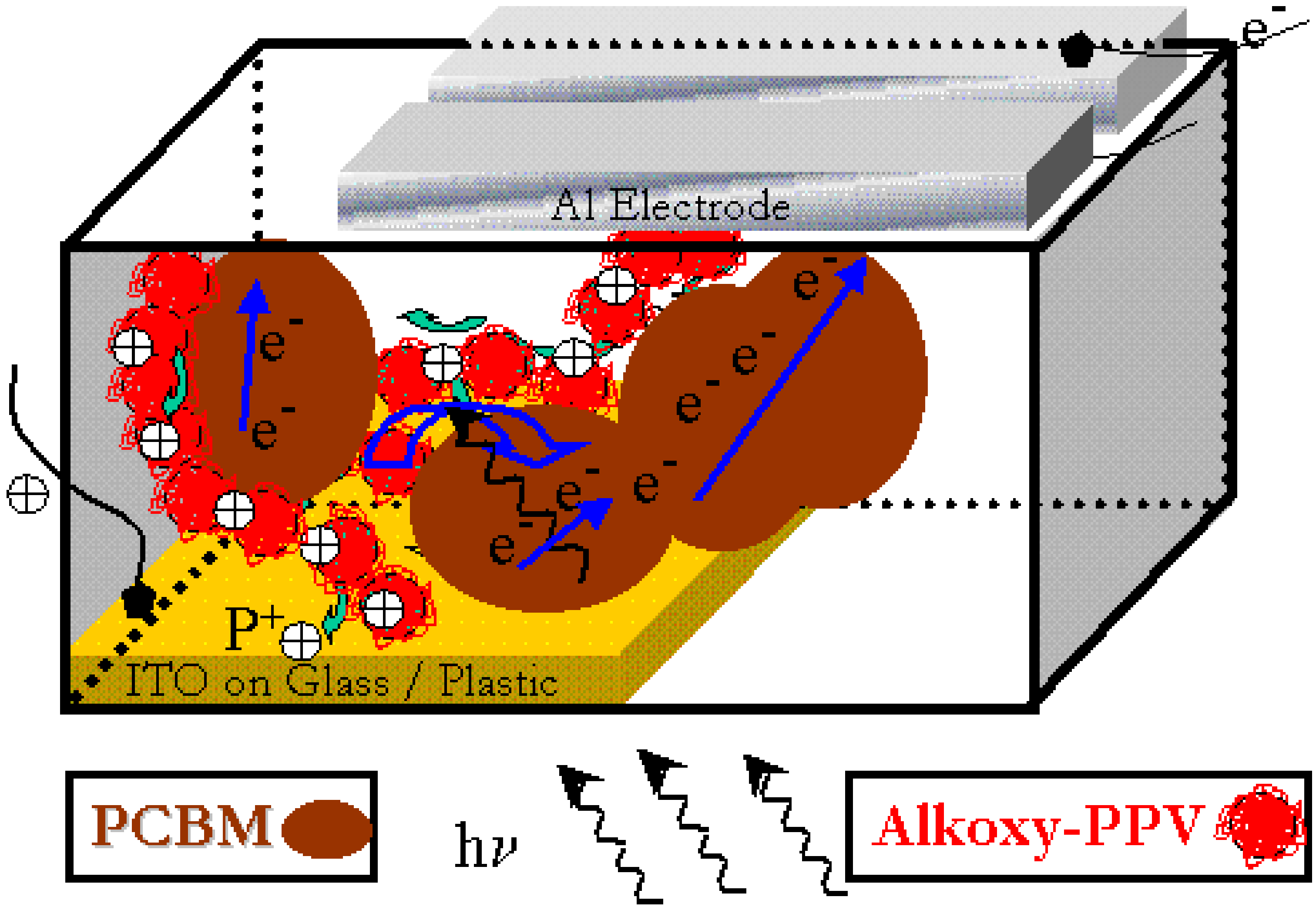




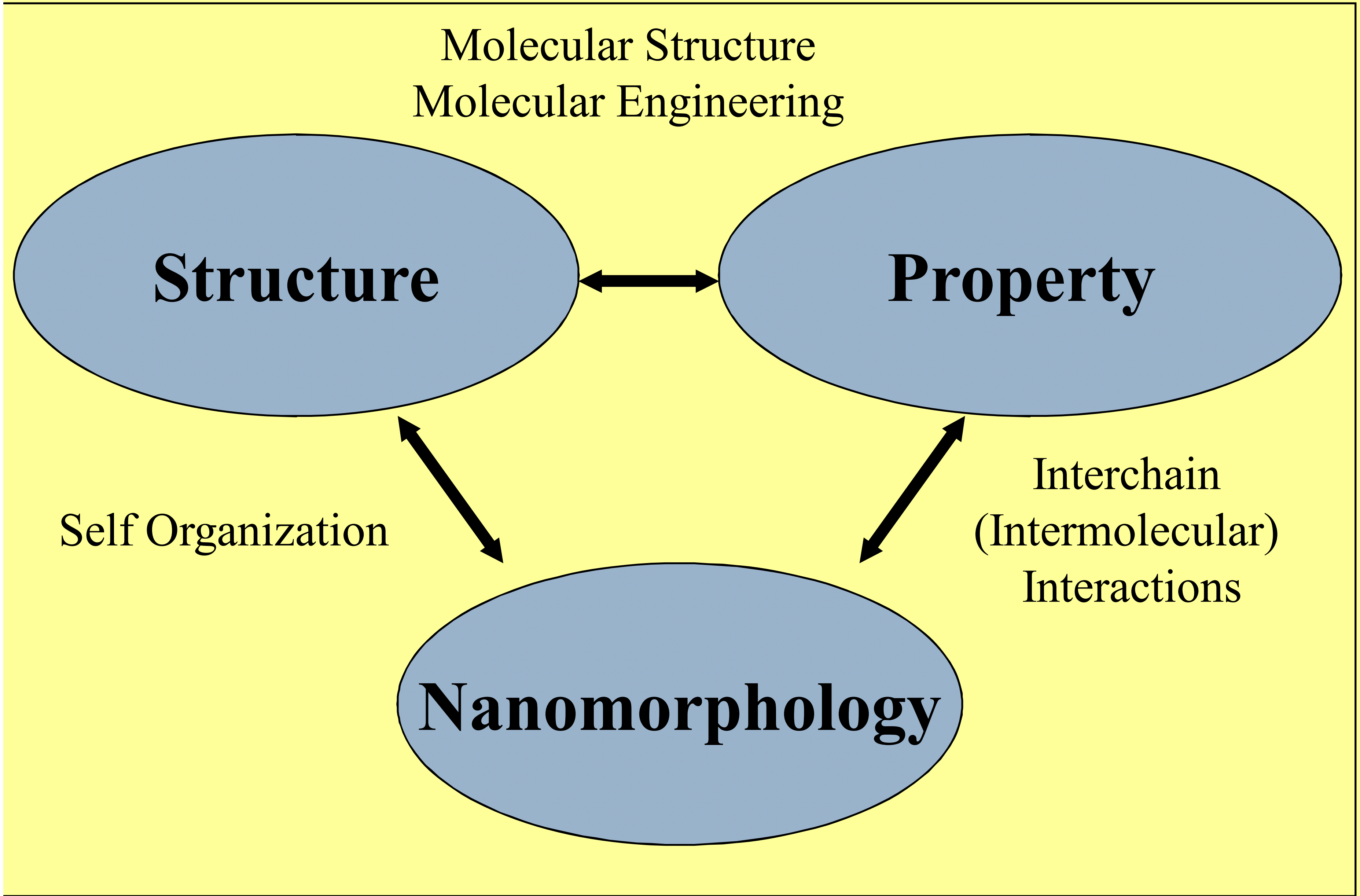
A 2-3 fold increase of the IPCE and short circuit current was observed by S.E. Shaheen et al.* due to the change from toluene to chlorobenzene as solvent, while by AFM measurements a decrease in the surface roughness was detected.

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

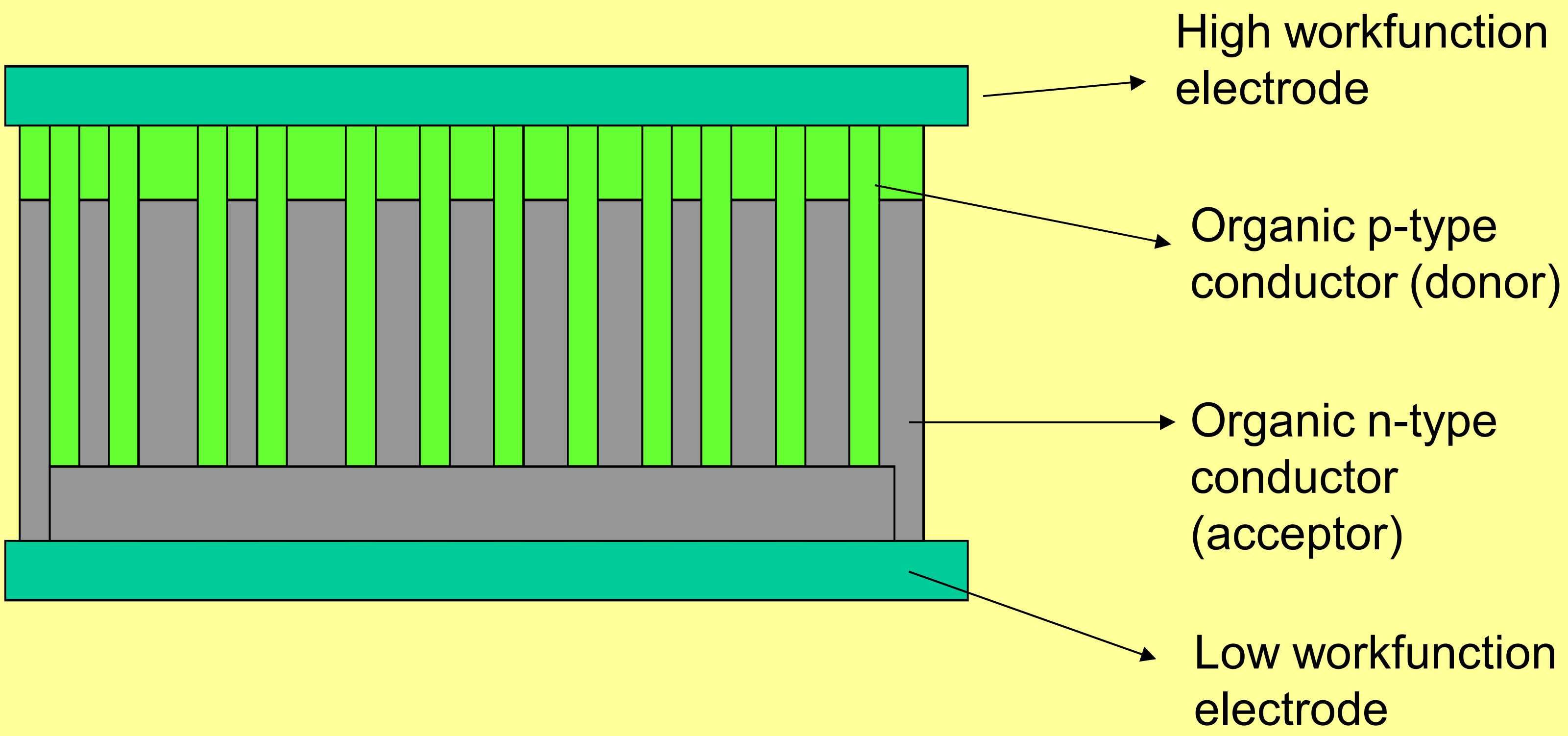
Bulk Heterojunctions: Revised



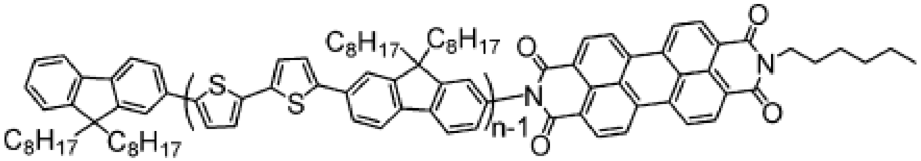
Property Optimization



„Optimum“ Geometry for Organic and Hybrid Solar Cells

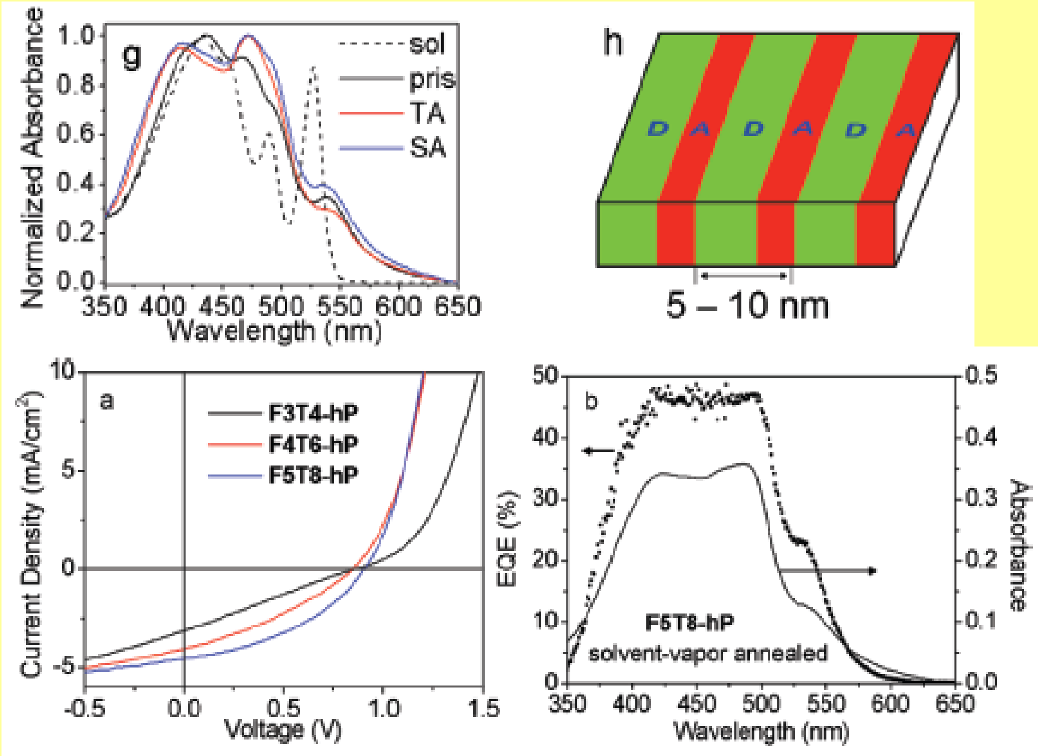


D-A block copolymers



n = 3, **F3T4-hP** G 66.4 S_{X2} 212.3 S_{X1} 215.7 I
4, **F4T6-hP** G 83.4 S_{X3} 194.8 S_{X2} 204.7 S_{X1} 233.5 I
5, **F5T8-hP** G 90.4 S_X 189.5 N 248.5 I

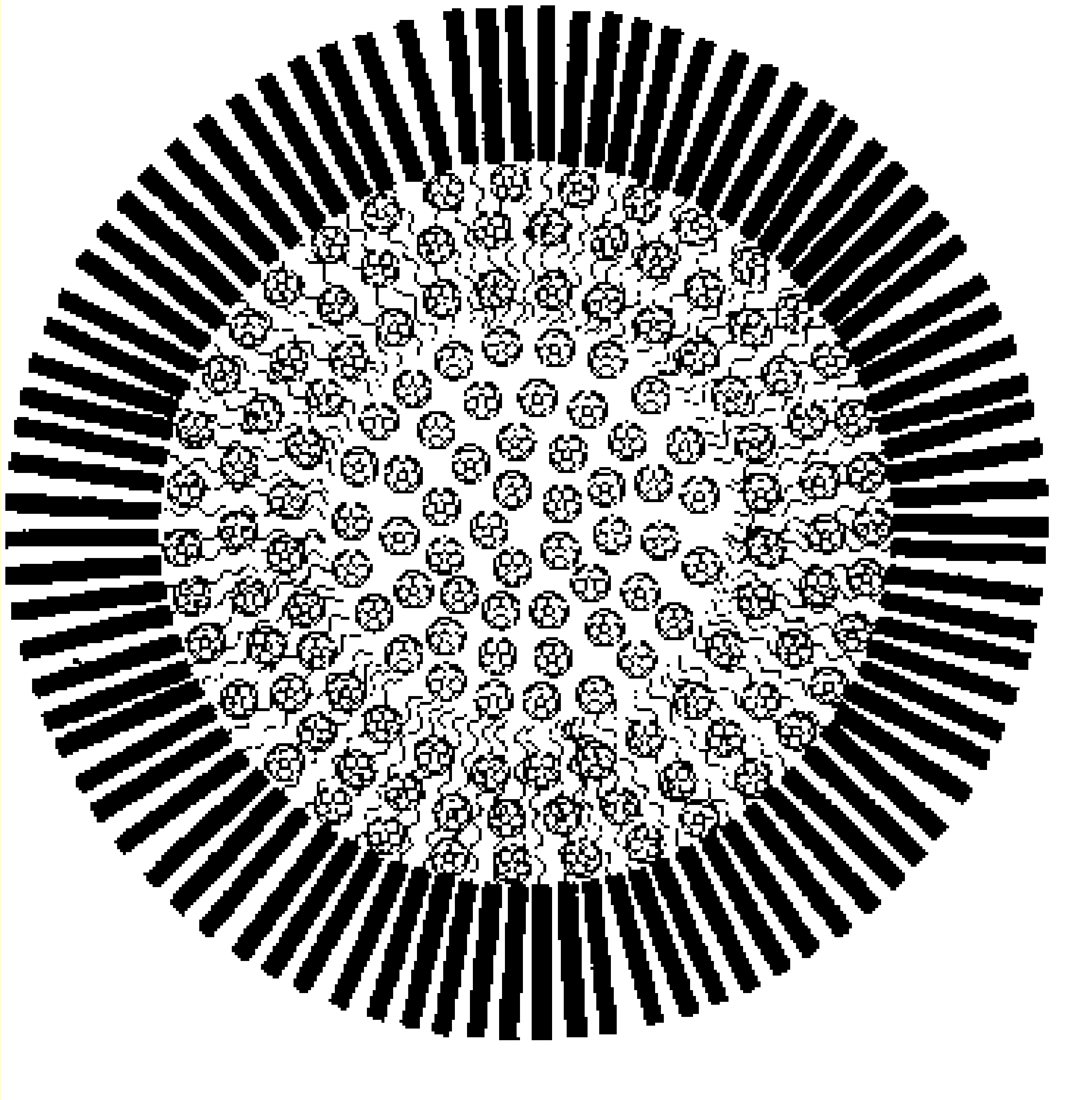
[a] Symbols: G, glassy; S, smectic; N, nematic; I, isotropic.



PCE ＝1.50%
Voc = 0.87 V;
Isc = 4.49 mA/cm2;
FF = 0.38

[Y. H. Geng, et al., *J. Am. Chem. Soc.*, 2009, *131*, 13242–13243]

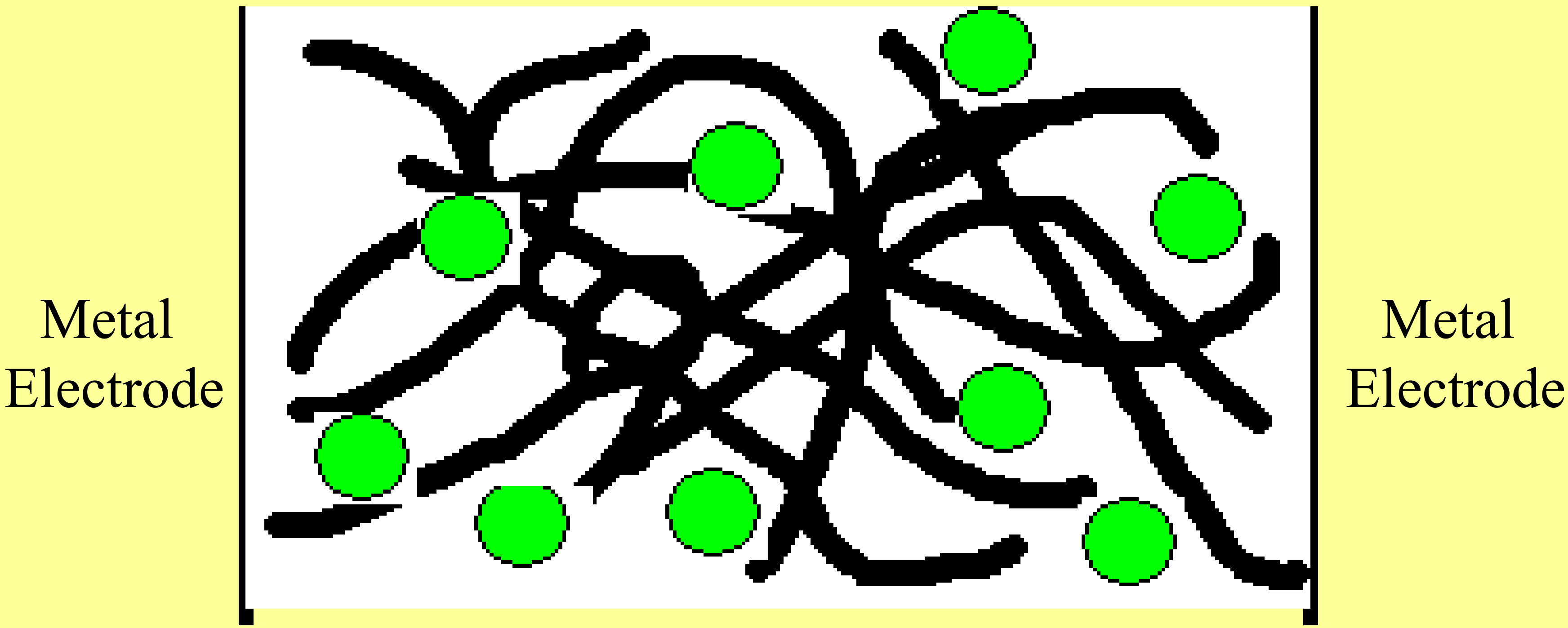
Supramolecular Ordering

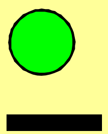


Di-block copolymer miscelle formation encapsulating fullerenes.

S. Jenekhe, & Chen, *Science* **279**, 1903 (1998)

Percolation Problem in Composites

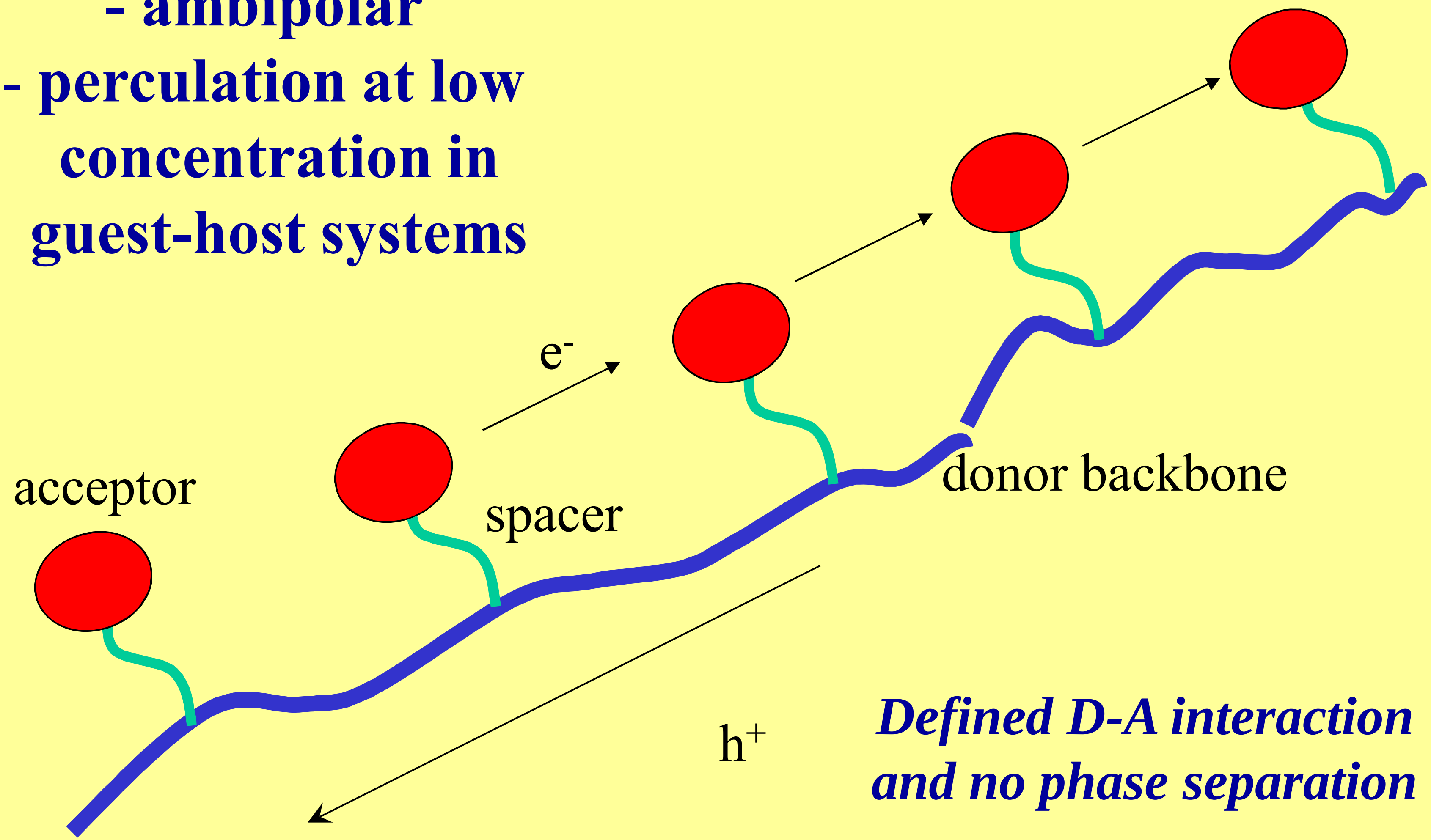




Both donor ***and*** acceptor phases have to be percolated !!!

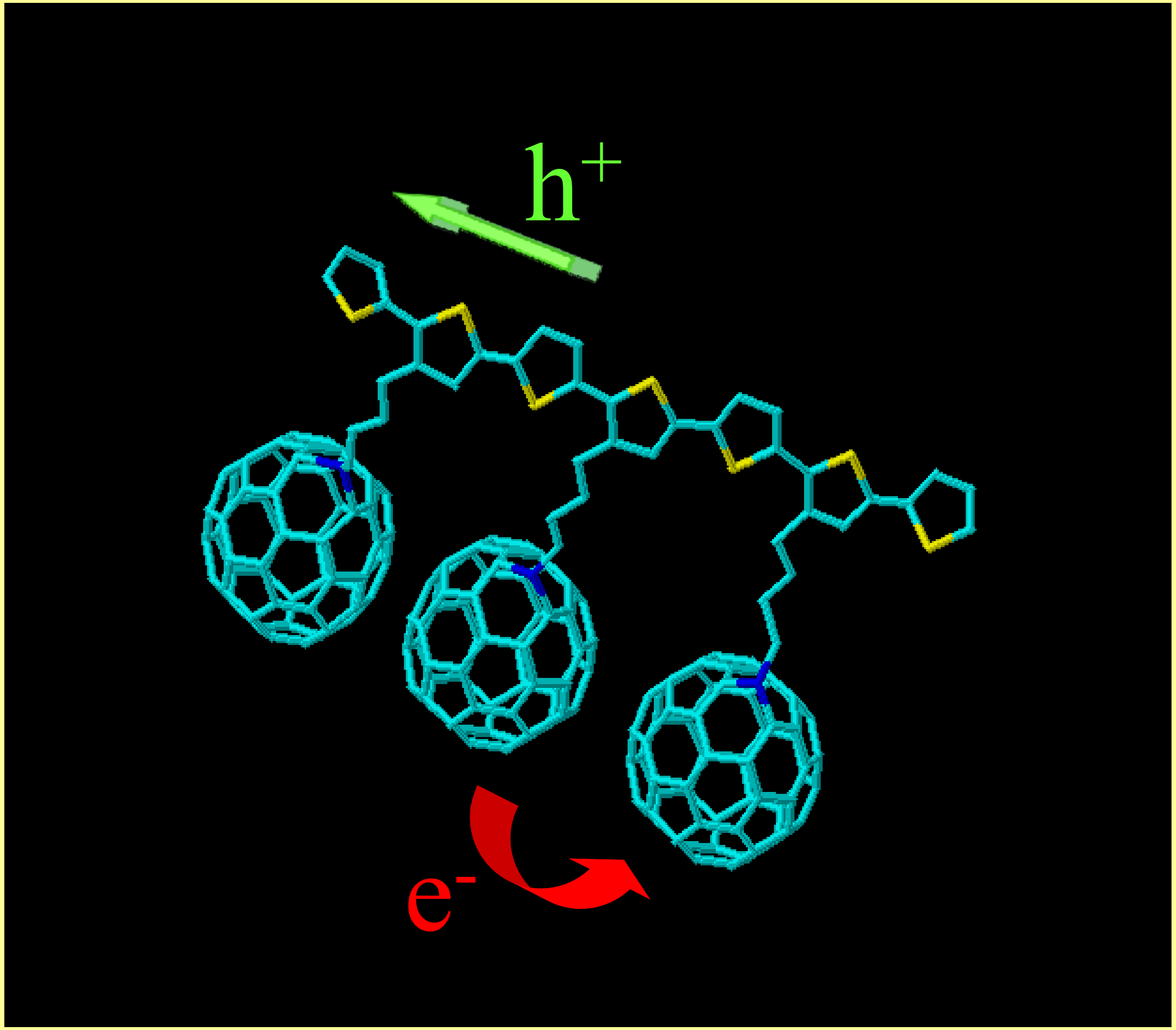
The ideal double-cable polymers…

- ambipolar
- perculation at low concentration in guest-host systems



Defined D-A interaction and no phase separation

The double-cable concept

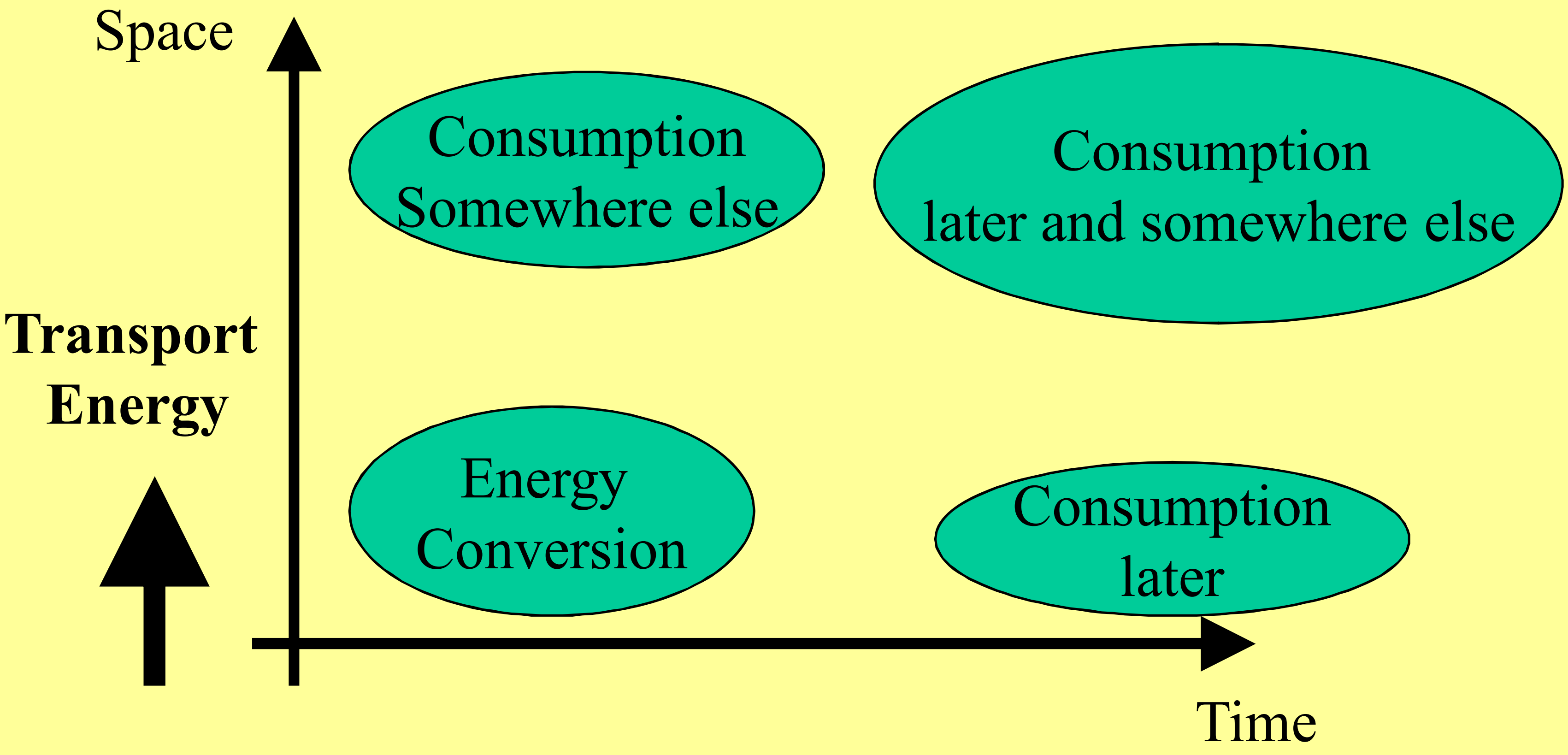


What is the next challenge in

Organic Solar Energy Conversion?

Solar energy into chemical energy

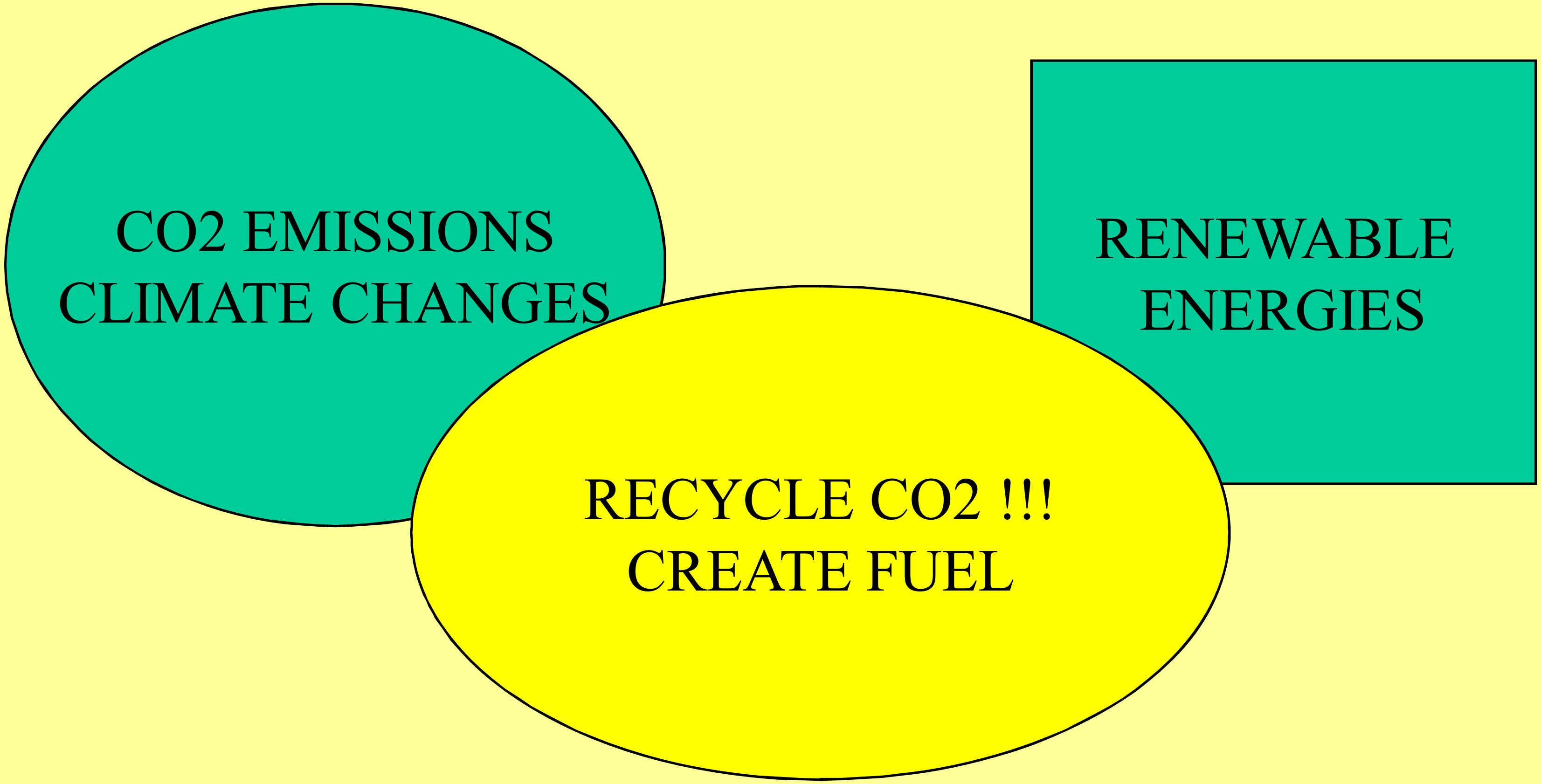
Storage-Transport Problem



→ **Storage of Energy**

Transportable fuel created by solar energy conversion !!!

INTERFACE BETWEEN CO2 REDUCTION AND RENEWABLE ENERGY CREATION



Future recycling of CO_2 as important mission of renewable energies

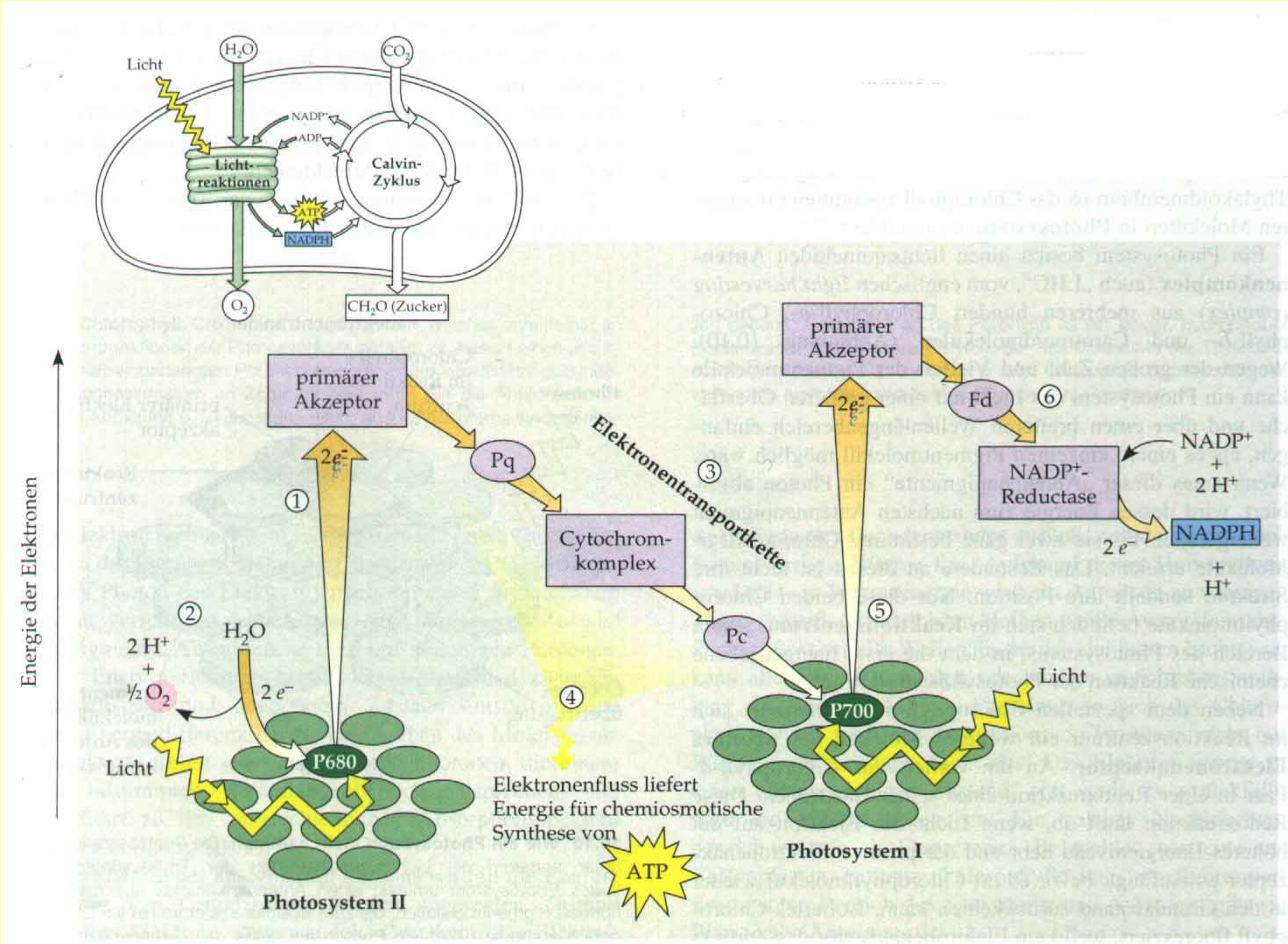
INTERFACE BETWEEN CO2 REDUCTION AND RENEWABLE ENERGY CREATION

Renewable energies such as solar photovoltaic or wind energy have instabilities that can not be controlled in time domain.
► creating synthetic fuels will solve this problem

10-20 billion tons of CO2 is coming from burning fossil fuels including coal for making electricity.
► Local high sources of CO2
► Can be combined with renewable energy for recycling
► CO2 can be much easier transported in gas pipelines than H2

Binding CO2 away from emissions will bring increasingly more macroeceonomic load (Kyoto, Seweso etc, payments)
► Recycling CO2 will be ecenomically attractive

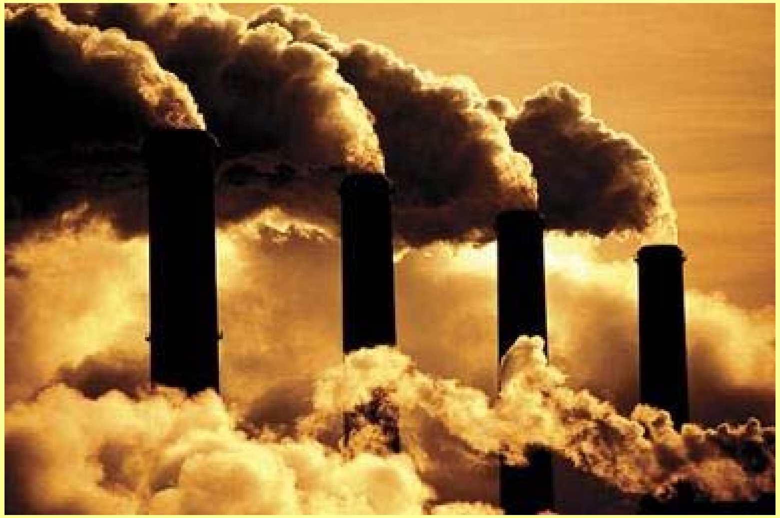
Natural Photosynthesis



Recycling of CO_2

Over 90 % of emitted CO_2 is generated by energy products.

To convert back CO_2 to fuels hydrogen or energy is required.



One promising field in this direction is the **photochemical**

Or electrochemical reduction of carbon dioxide using solar light

IS IT POSSIBLE TO RECYCLE CO_2? The answer is yes!

$$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH \qquad (1)$$

$$HCOOH + 2e^- + 2H^+ \rightarrow CH_2O + H_2O \qquad (2)$$

$$CH_2O + 2e^- + 2H^+ \rightarrow CH_3OH \qquad (3)$$

$$CH_3OH + 2e^- + 2H^+ \rightarrow CH_4 + H_2O \qquad (4)$$

Steps in methanol oxidation/production.

Overall: 6e- process

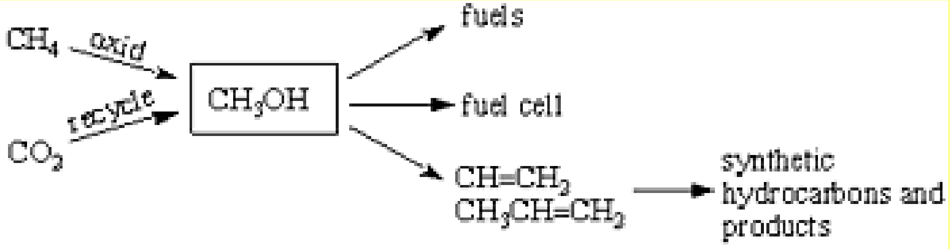
CH3OH + H2O → CO2 + 6H+ + 6e-

Biocatalysis

Photocatalysis

Electrocatalysis

RECYCLING CO2



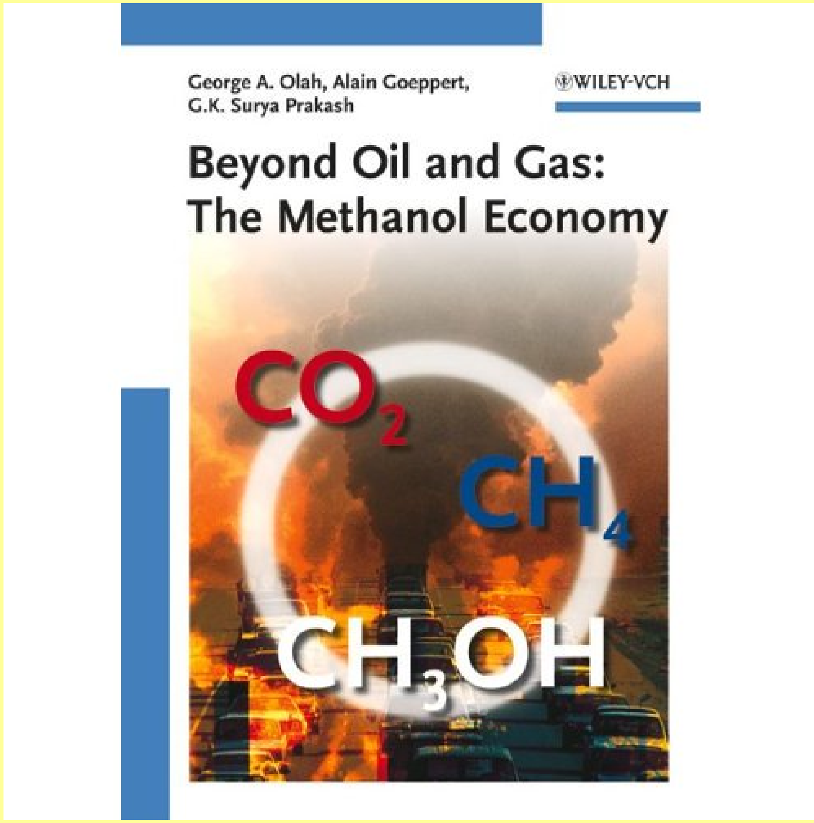
Methanol as carrier and storage of energy

a.) Methanol can be mixed to gasoline

b.) Methanol is used in fuel cells

c.) Methanol is starting chemical for
Many other derivatives

George Olah, Nobel Prize 1994
Univ. of Southern California, USA



Electrochemical reduction of CO_2

- Excess electric energy can be conveniently used for the catalysed reduction of CO_2 in water to afford alcohols and/or C_n-hydrocarbons :

  storage of electricity!
- Such use of excess electric energy can play a key role in the short term for the conversion of CO_2 into fuels implementing a significant recycling of carbon.
- The use of **solar energy** for CO_2 reduction in water is a key issue for the medium term: a substantial recycling of carbon could be performed.

Photocatalytic reduction of CO_2

1.$Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) as both photosensitizer and catalyst

2. $Ru(bpy)_3^{2+}$ as the photosensitizer and another metal complex as the catalyst

3. $ReX(CO)_3(bpy)$ (X = halide or phosphine-type ligand) or a similar complex as both photosensitizer and catalyst

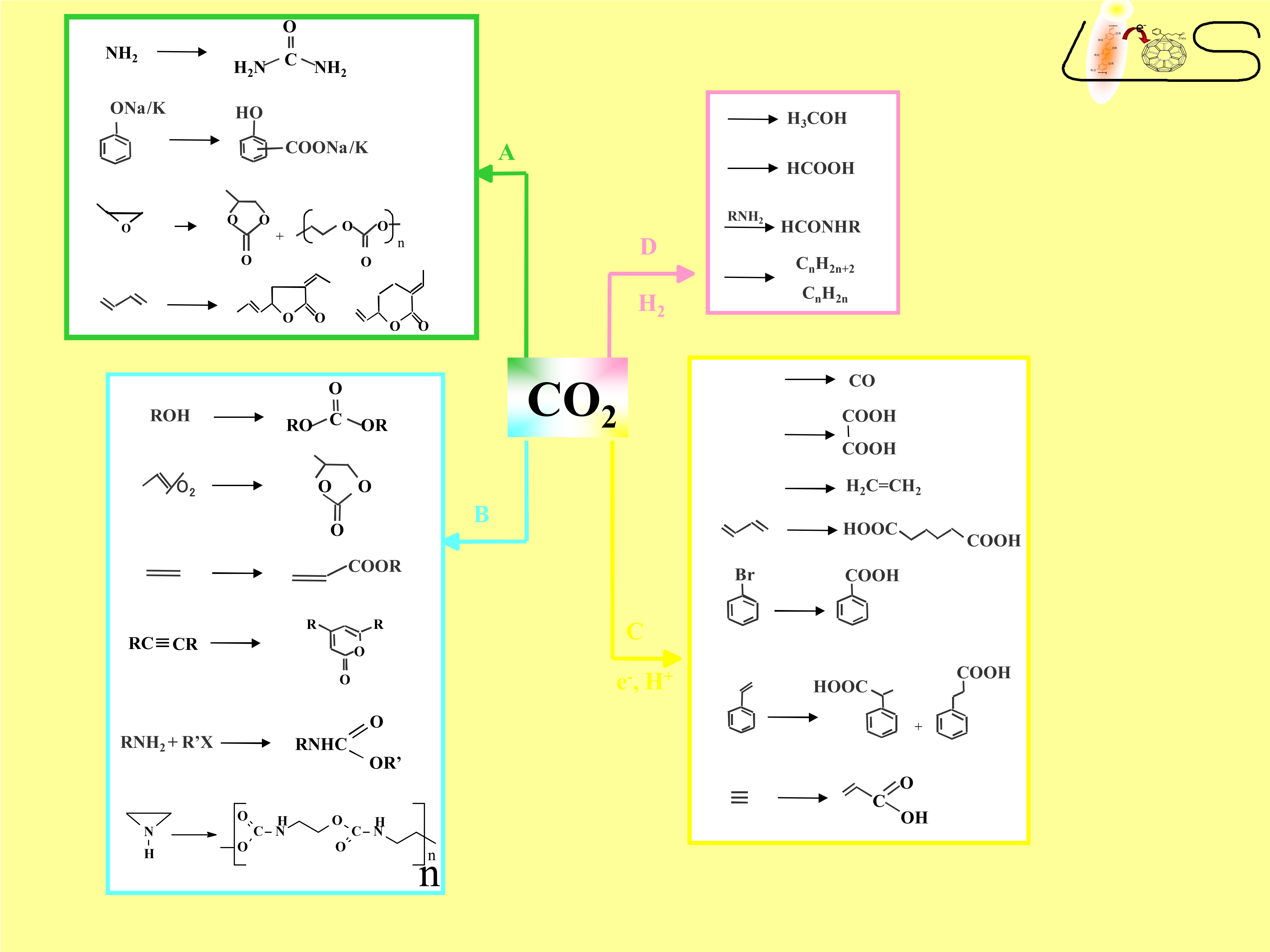
4. $Ru(bpy)_3^{2+}$ or $Ru(bpy)_3^{2+}$-type complex as the photosensitizer in micro-heterogeneous systems

5. A metalloporphyrin as both the photosensitizer and the catalyst

6. Organic photosensitizers with transition-metal complexes as catalysts

---

1."*Photochemical carbon dioxide reduction with metal complexes*" E. Fujita, *Coord. Chem. Rev.* 1999



CO2
A
B
C
e-, H+
D
H2
NH2
H2N C NH2
O
ONa/K
HO
COONa/K
ROH
RO C OR
RC≡CR
R
RNH2 + R'X
RNHC
OR'
N
H
n
H3COH
HCOOH
RNH2
HCONHR
CnH2n+2
CnH2n
CO
COOH
COOH
H2C=CH2
HOOC
COOH
Br
OH

Coupling Chemistry and Biotechnology

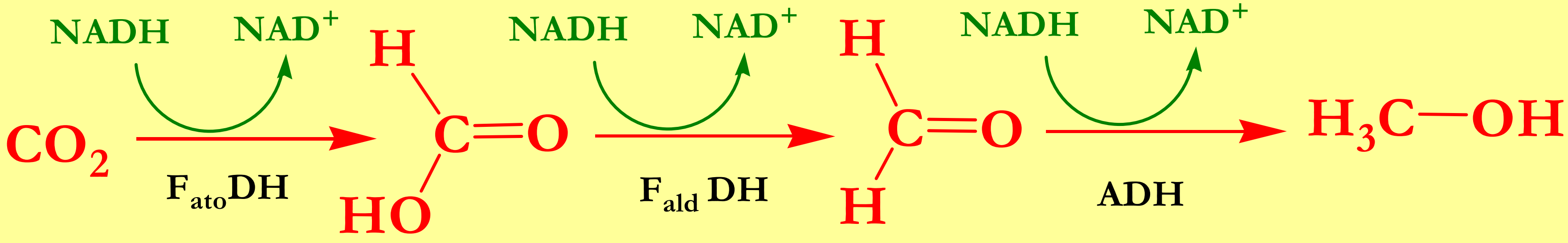
- $CO_{2\,aq}$ → $HCOO^-$ **Formate dehydrogenase**

- $HCOO^-$ → H_2CO **Formaldehydedehydrogenase**

- H_2CO → CH_3OH **Methanoldehydrogenase**

- **$NAD^+/NADH$ is the source of energy .**
- **Key issue : how to reverse the $NAD^+/NADH$ couple after oxidation ?**
- **Use of chemical systems for solar light harvesting and conversion**

Scheme of the enzymatic reduction of CO_2



Reaction conditions

Solution buffered at pH 7

T = 37 °C

P = 1 atm

4 mL of solution of
Sodium Alginate 2% (m/v)
In deionized water

1.6 mL TEOS

1 mL solution

$F_{ato}DH$ (10.0 mg)
$F_{ide}DH$ (10.0 mg)
ADH (10.0 mg)

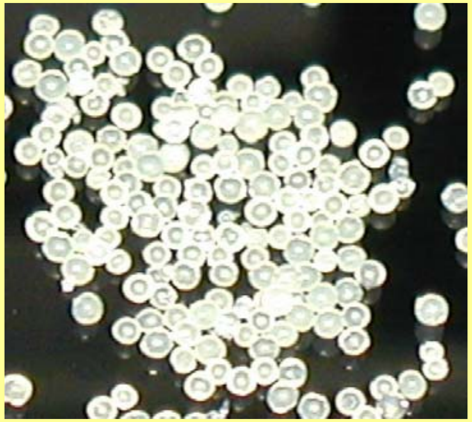
In buffer TRIS-HCl 0.1 M (pH 7)

Drop by drop addition in
20 mL $CaCl_2$ 0.2 M+TESO

Sol-gel-formation time 30 min

Filtration

Washing with water

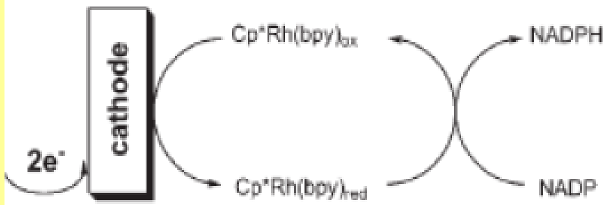


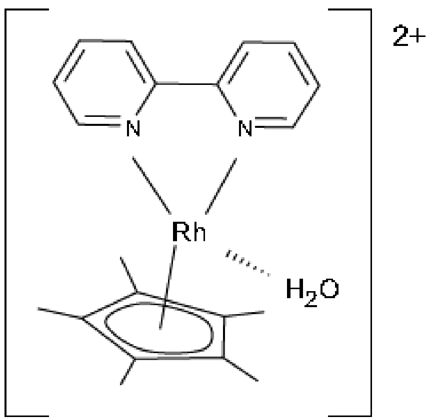
Michele Aresta, Bari, Italy

Reduction of NAD+ to NADH

1.) Electrochemical Reduction: Use of „mediators“ needed

Process	U/ V	ΔG_{0}/ kJ mol-1	Energy for 1 mol of MeOH/ kJ mol-1
NADH Electrolysis	-1,136	219,2	657,6
Water Electrolysis	-1,23	237,5	712,5





Cp*Rh(bpy)$_{ox}$

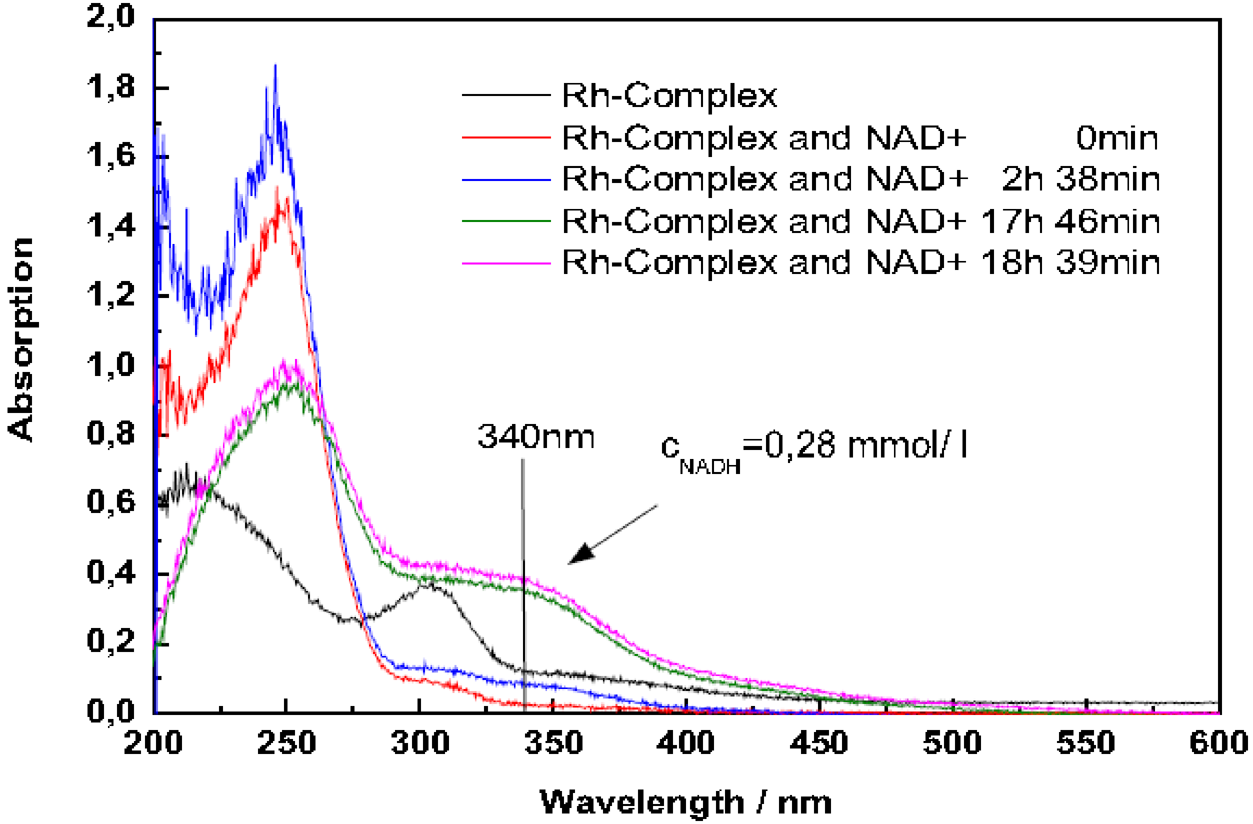
- Mediator: Rh-Complex ($0{,}024 mmol\ l^{-1}$)
- 50 mmol Phosphate buffer pH=7 (100ml total volume)
- Potentiostatic
- -750 mV on a graphite electrode (A= $3{,}11 cm^2$)
- approximately 18h
- NAD+ at start: $0{,}4 mmol\ l^{-1}$

Trefflinger, Oppelt, 2009

erature: Hildebrandt et al., Adv.Synth.Cat. **2008**, 350, 909-918

Reduction of NAD+ to NADH

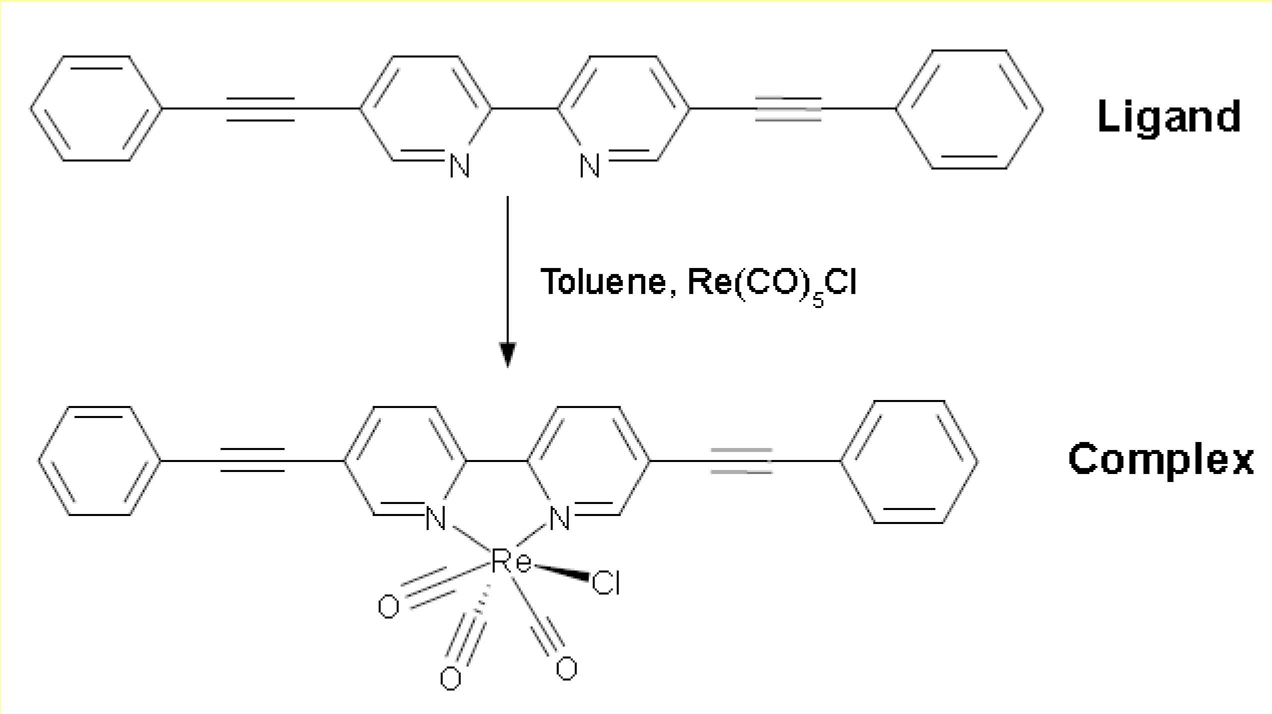
Electrochemical Reduction of NAD+ with $[Cp^*Rh(bpy)H_2O]^{2+}$



Trefflinger, Oppelt, 2009

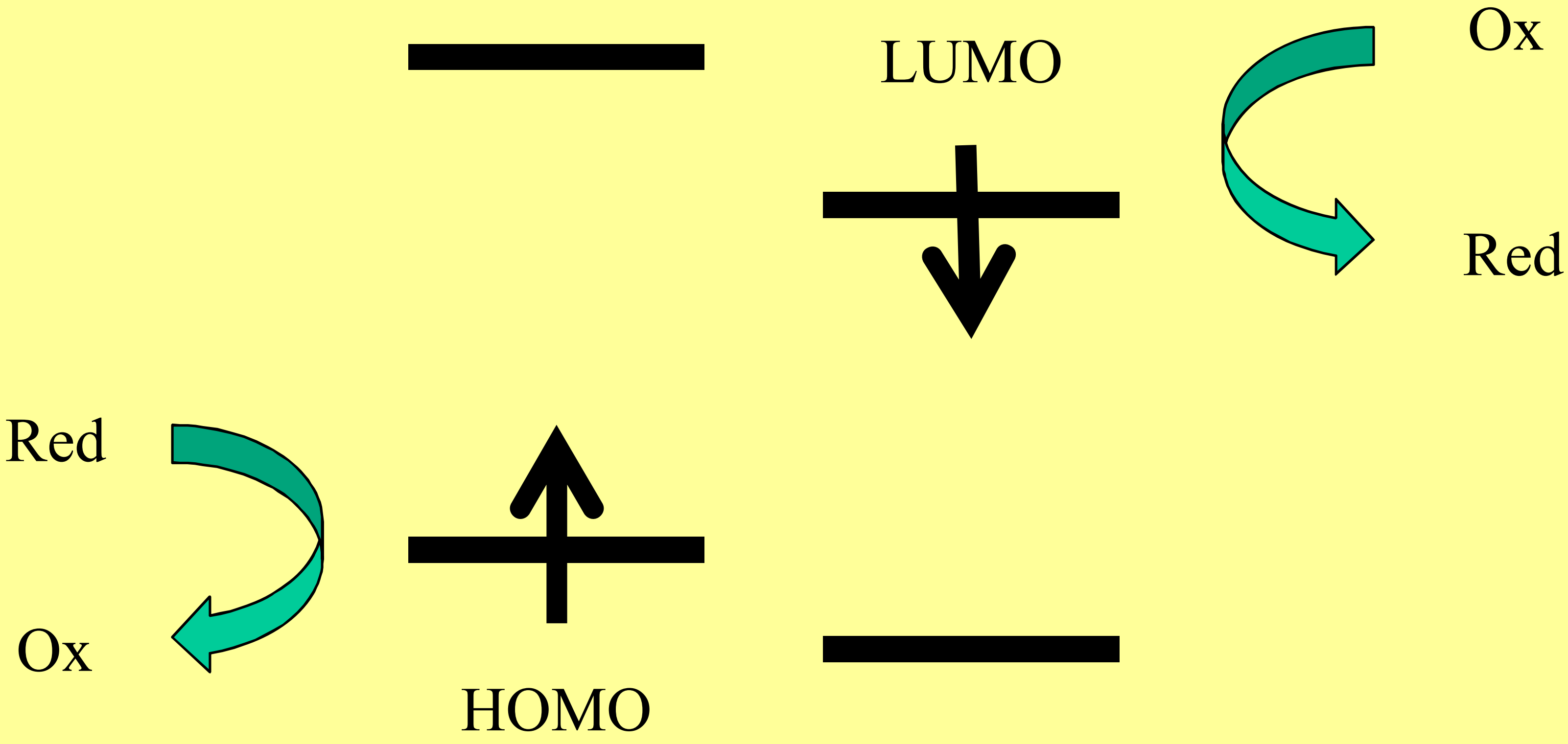
Photochemical Reduction of NAD+ to NADH

Homogeneous photocatalysts



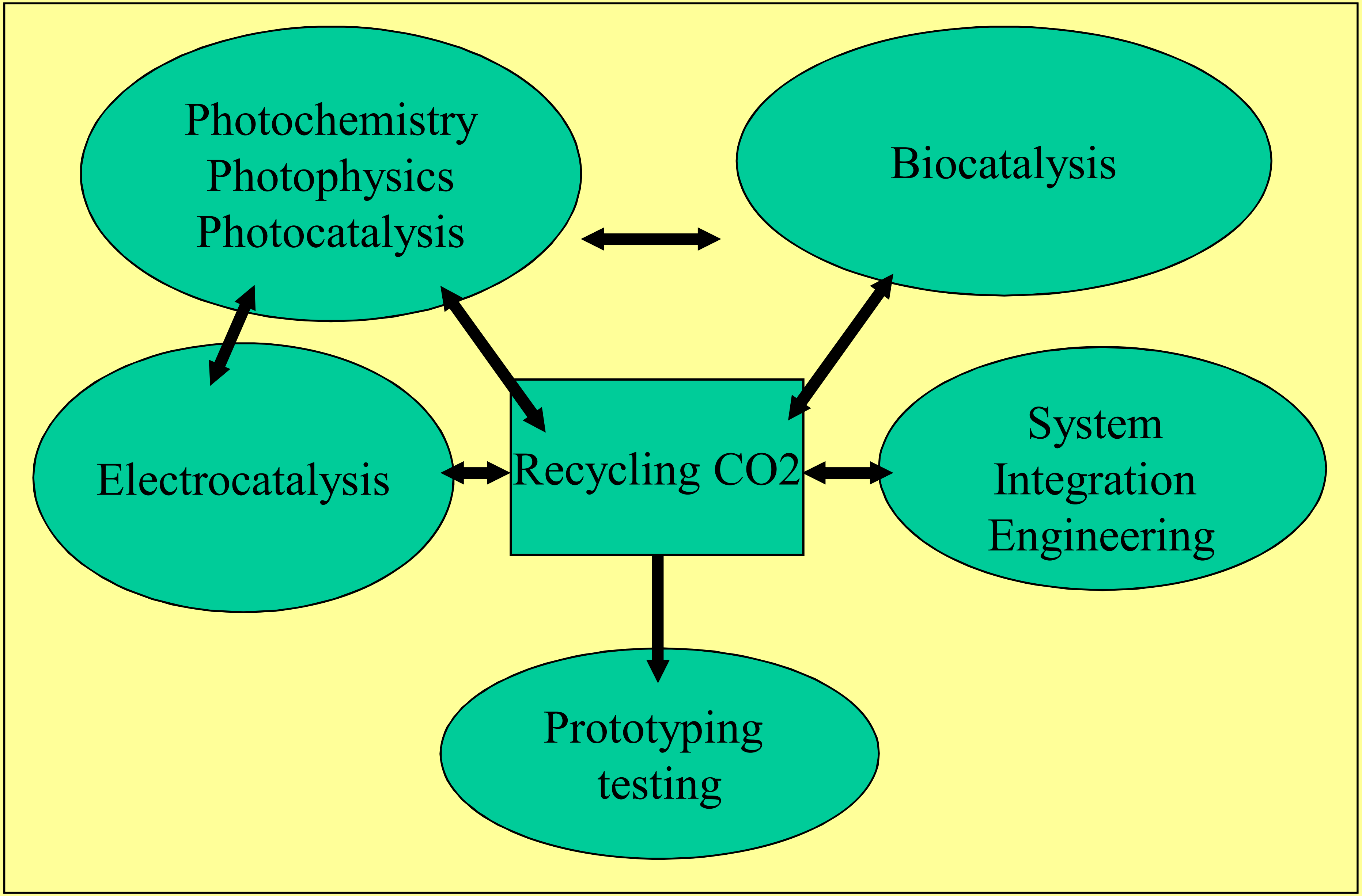
Oppelt, Knör, 2010 unpublished

Photoinduced Charge Generation



Photoinduced Redox Chemistry

Interdisciplinary R & D



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

- Plastic Solar Cells (CD-Labor)
- Small Molecular Solar Cells
- Organic/Inorganic Hybrid Solar Cells
- Bio-Organic Field Effect Transistors

„Incubator" for small high tech spin-off companies:
Konarka Austria (former QSEL), ~~NanoIdent AG~~, Botest,
Plastic Electronic GesmbH, Prelonic OHG, Isiqiri, Solar Fuel GesmbH

Acknowledgements

Members of LIOS:
Helmut Neugebauer, Mihai Irimia-Vladu, Elif Arici, Anita Fuchsbauer, Martin Egginger, Philipp Stadler, Alberto Montaign, Jacek Gasiorovski, Patchanita Thamyongkit, Almantas Pivrikas, Gebi Matt, Martin Kruijen, Gerda Kalab, Edina Mujcinovic, Beatrice Esteban-Meana, Kerstin Oppelt, Daniel Egbe, Serpil Tekoglu, Stefan Schaur, Doris Sinwel, Sandra Kogler, Christoph Ulbricht, Matthew White, Mamatimin Abbasi, Stefanie Schlager, Stefan Kraner, Valery Bliznyuk and many many more…

Uni. Linz, Collaborators.: Helmut Sitter, Thomas Fromherz, Siegfried Bauer, Reinhard Schwödiauer, Günther Knör

Spin-off companies:

Konarka Austria (plastic solar cells)
(**NanoIdent)** (insolv.)
Botest (plastic detector arrays)
Plastic Electronic (plastic pressure sensors)
Prelonic (printed batteries)
Isiqiri (intelligent display boards)
Solar Fuel (artificial fuels)

Funded by:
Solar Fuel Company
Austrian Foundation of Science (FWF)
European Commission