Dye sensitized solar cells

Organic PV Symposium
Linz February 2008

Michael Graetzel,
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE
Distinguished Visiting Professor
Department of Material Science and Engineering, NUS

Michael.Graetzel@epfl.ch

Acknowledgement Present LPI Members

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Duriaux Arendse Francine
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Chen Peter
Moon Soo-Jin
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Nazeeruddin Md. Khaja
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Kay Andreas
Kuang Daibin
Lee Hyo Joong
Sivula Kevin
Thorsmolle Verner
Wang Deyu
Wang Mingkui

Professor Jacques E. Moser

Ongoing collaborations

- **PV cells :** **Michael McGehee, (Stanford USA)**
  Brian O'Regan (Imperial College London)
  Nam Gyu Park (KIST, South Korea)
  Paul Dyson
- **Dye Research:** **Jaejung Ko (Korea University)**
  David Officer (Massey University New Zealand)
  Anders Hagfeldt (KTH, Stockholm Sweden)
  Thomas Torre, Autonomous University Madrid
  Guido Viscardi, Claudia Barolo, Turin University
  Frank Nüesch EMPA Switzerland
- **Quntum dots:** **Song-Il Seok KRICT (South Korea)**
- **Electron transfer:** **James Durrant (Imperial College London)**
- **DFT calculations:** **Filippo De Angelis, Simona Fantacci (Perugia), Annabella Selloni (Princeton), Ursula Roethlisberger**
- **Tandem bottom cell:** **A. Tiwari, ETH Zurich**

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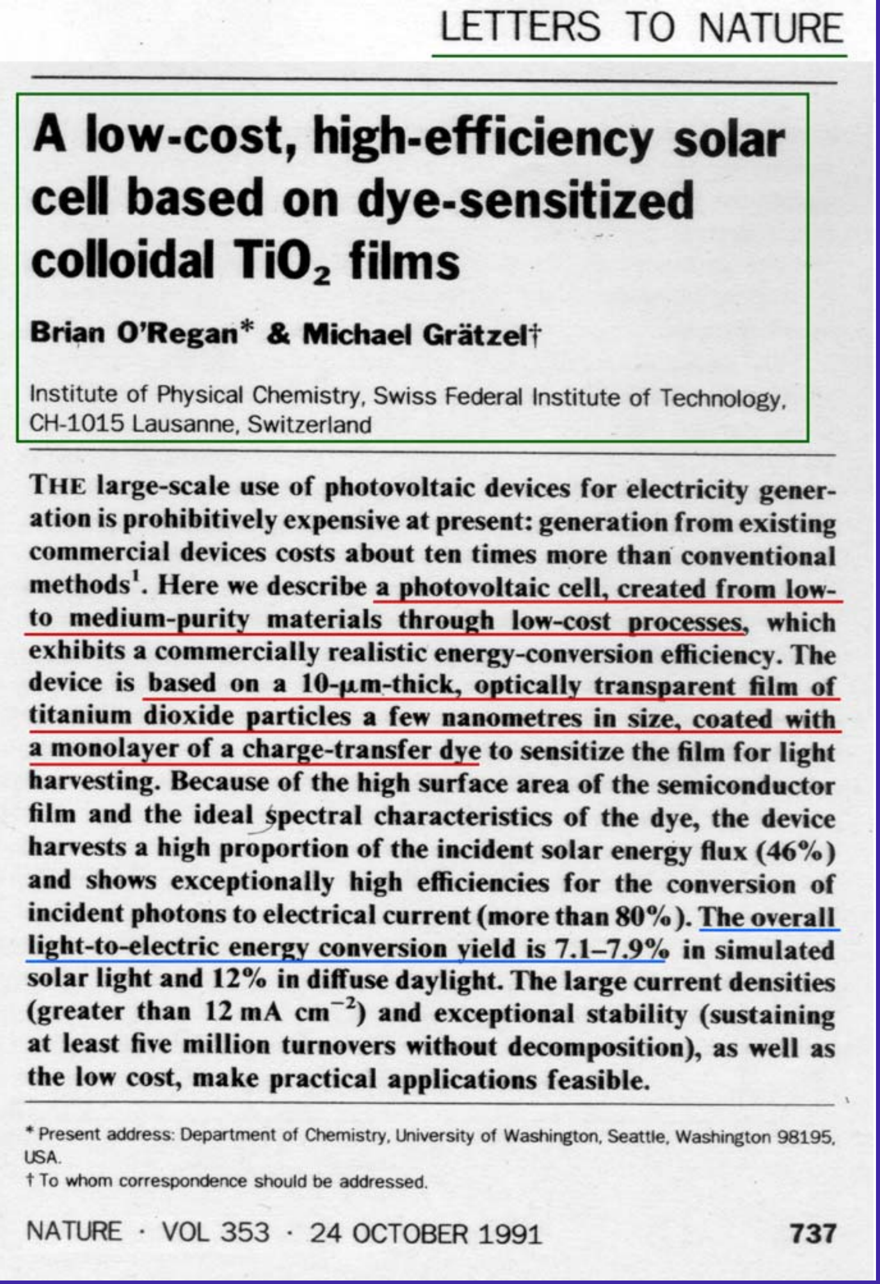
European Joule Projects (NANOMAX, MOLYCELL) , GRLKorea (with KRICT)
Industrial Partners,

Dye sensitized nanocrystalline solar cells lead the new PV generation



LETTERS TO NATURE

A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

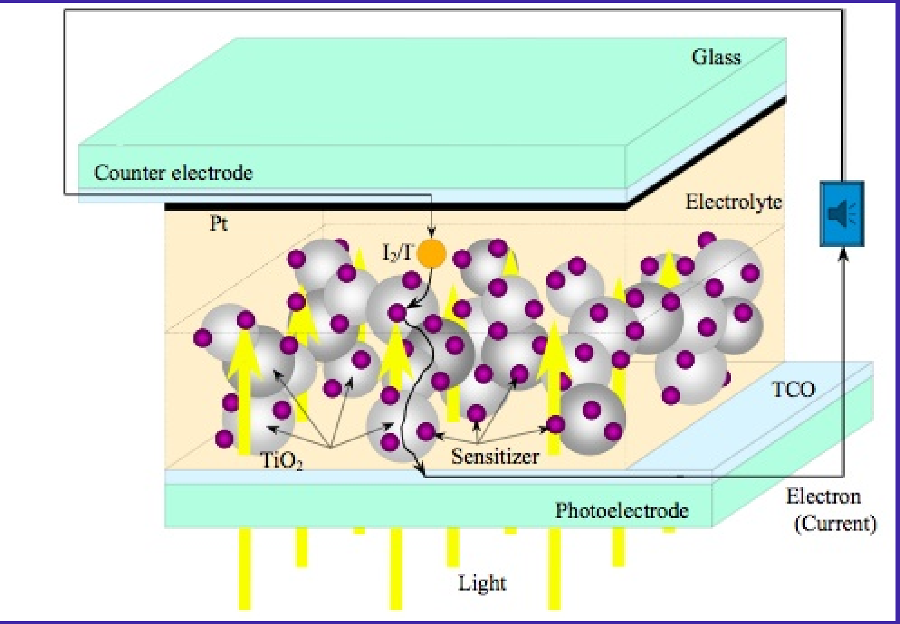
Brian O'Regan* & Michael Grätzel†

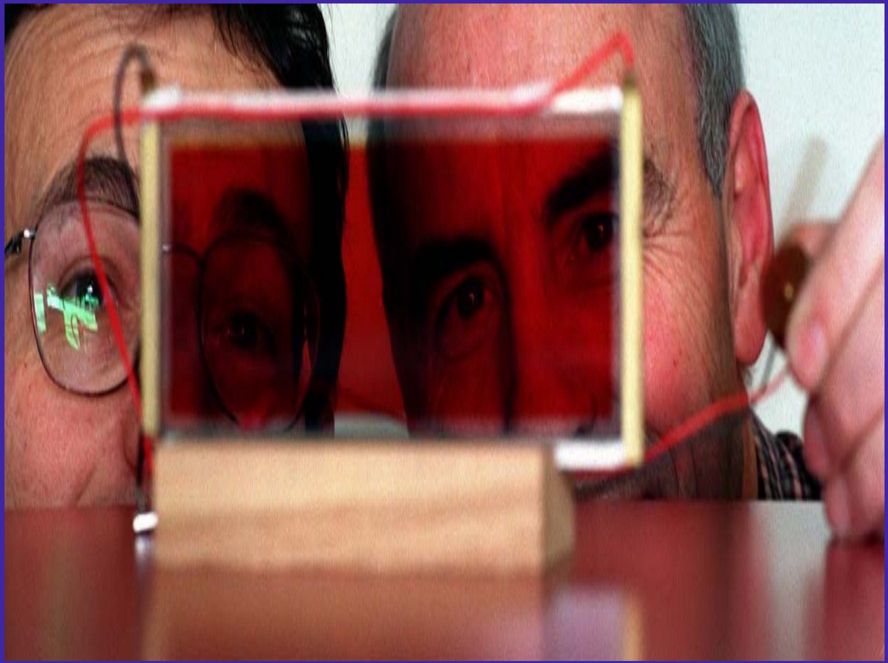
Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

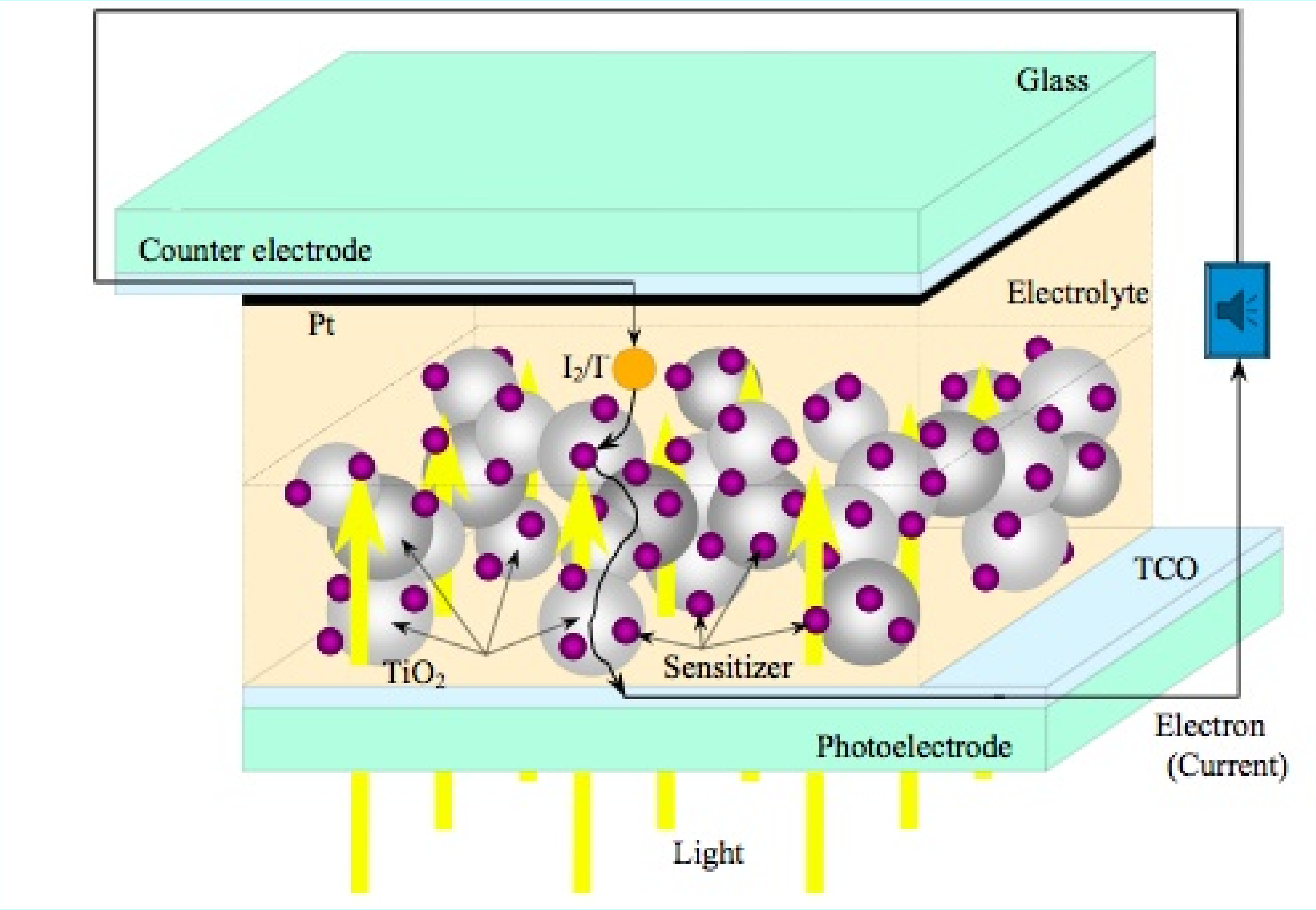
THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

* Present address: Department of Chemistry, University of Washington, Seattle, Washington 98195, USA.
† To whom correspondence should be addressed.

NATURE · VOL 353 · 24 OCTOBER 1991 737



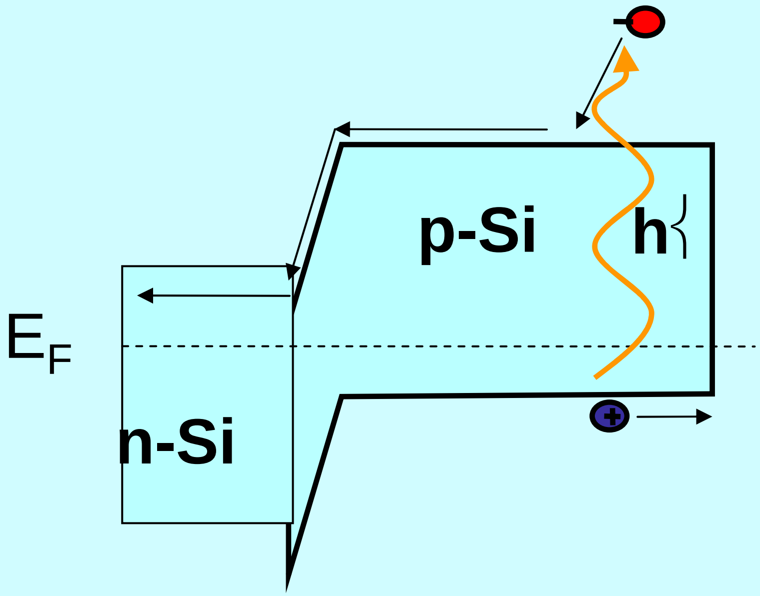


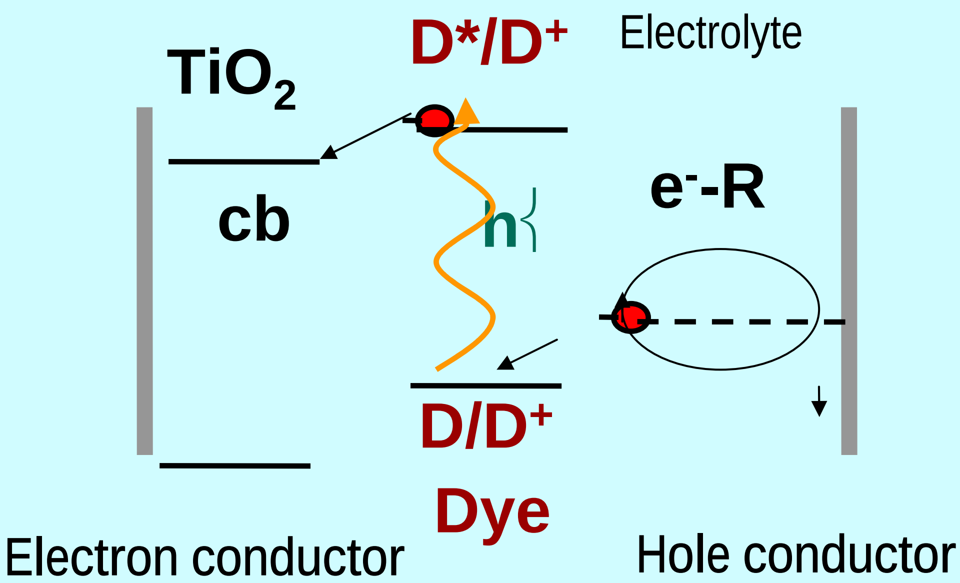

Glass
Counter electrode
Electrolyte
Pt
I_2/I^-
TCO
TiO_2
Sensitizer
Photoelectrode
Electron
(Current)
Light

Dye sensitized solar cells separate light absorption from carrier transport

p-n junction photovoltaic cells

dye sensited solar cells DSC

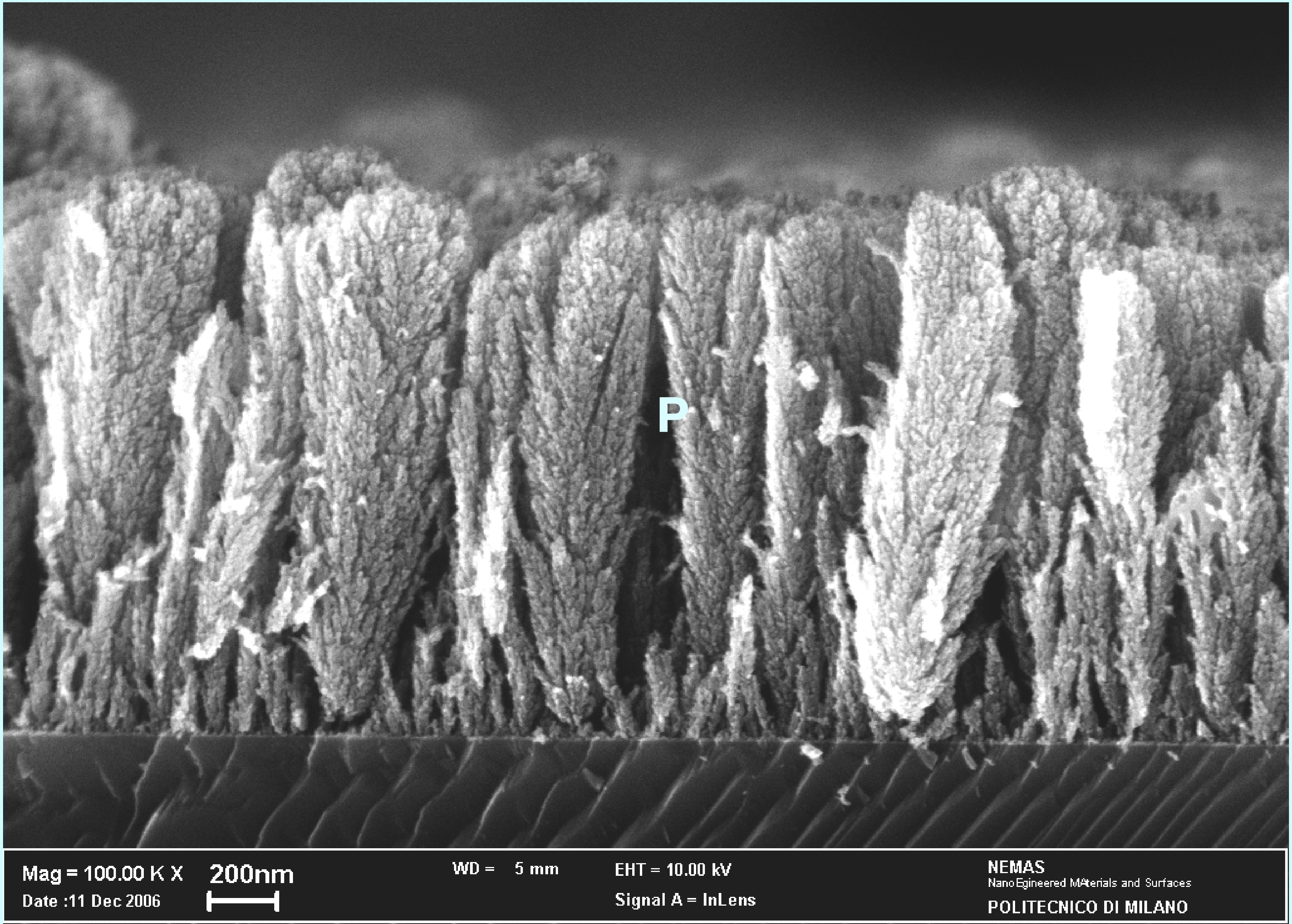




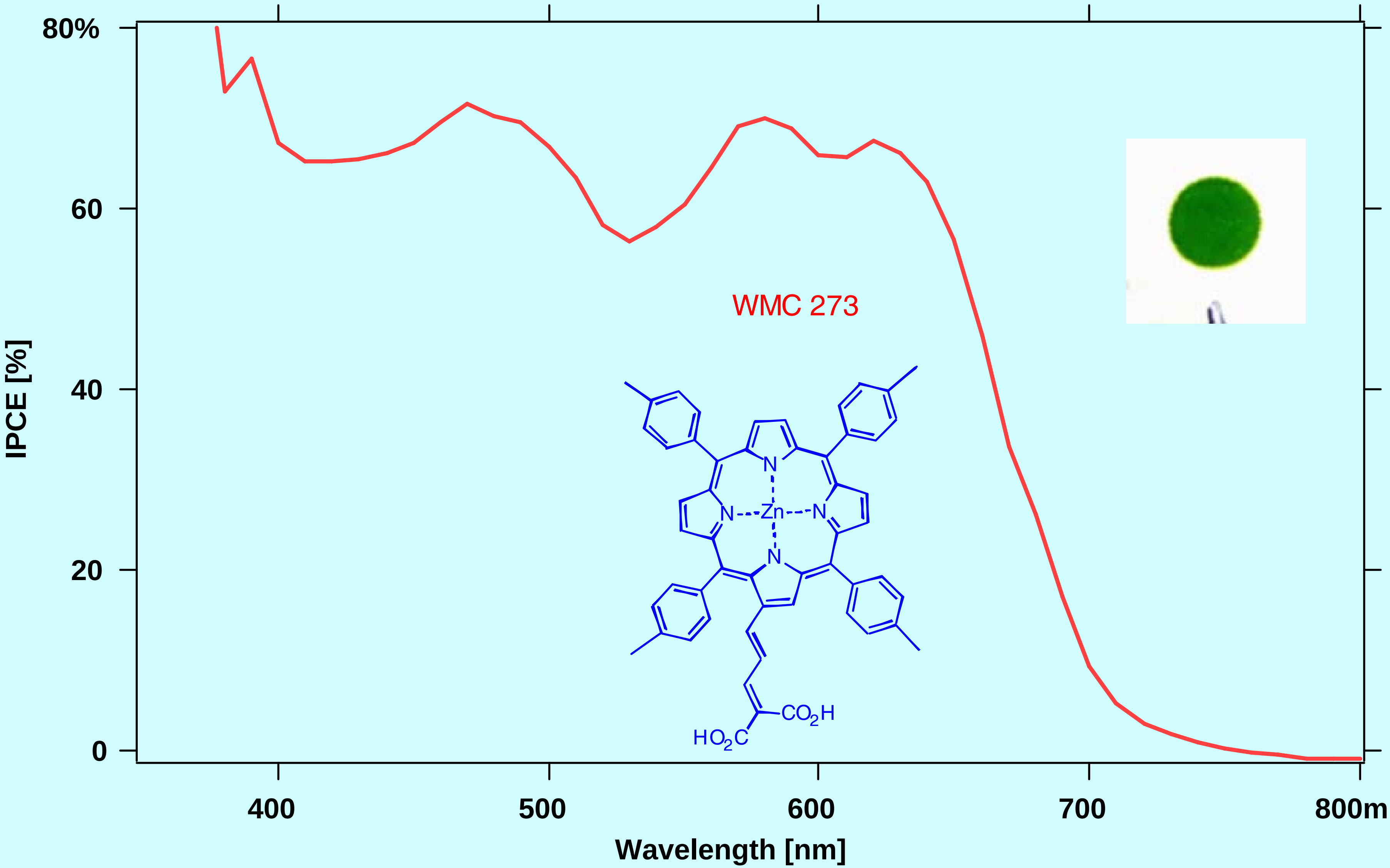
Charge separation by electric field at the p-n junction

Charge separation by kinetic competition as in photosynthesis

inorganic nano-forests mimic their natural counterparts



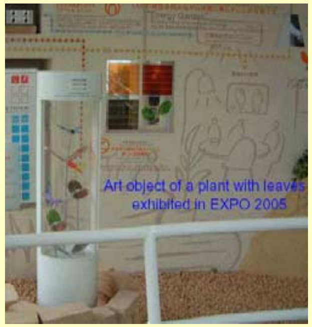
green solar cells mimic the green leave



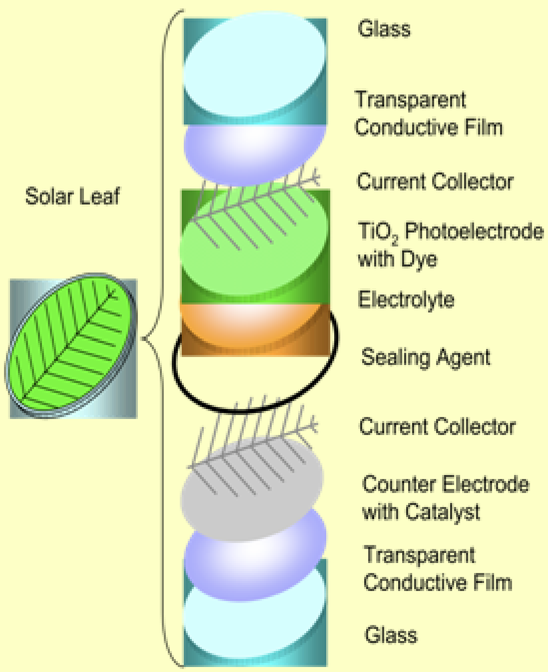
In collaboration with Professor David Officer, Univ.Wollongon,Australia

O2
H2
cogene

Artificial Plant with Leaves exhibited at EXPO 2005

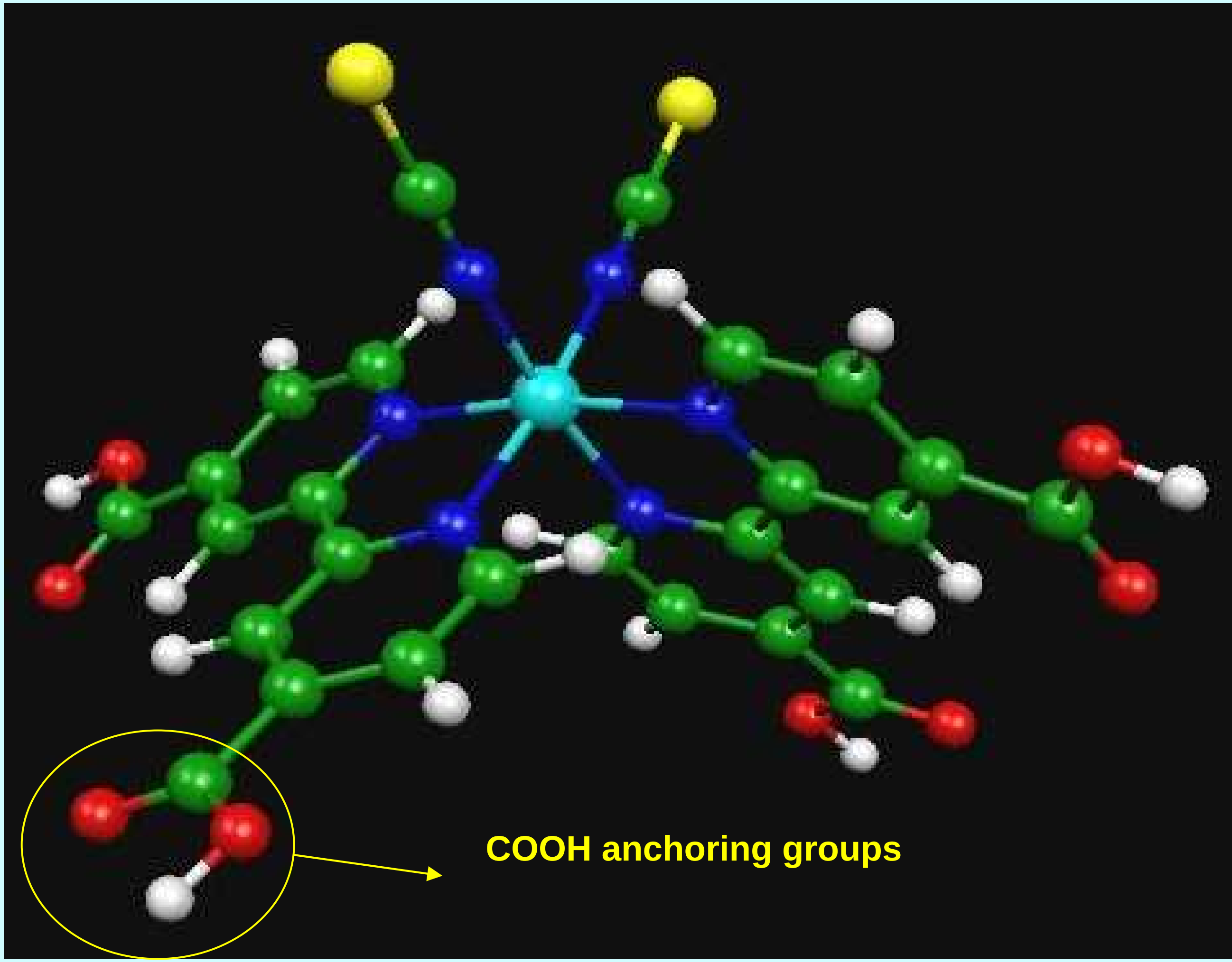


Butterflies flutter and stop using the electricity generated by this plant under the intermittent lightings.



Leaf-shaped transparent DSC with four colors

the work horse of the DSC is the N3 (or N719) ruthenium dye,

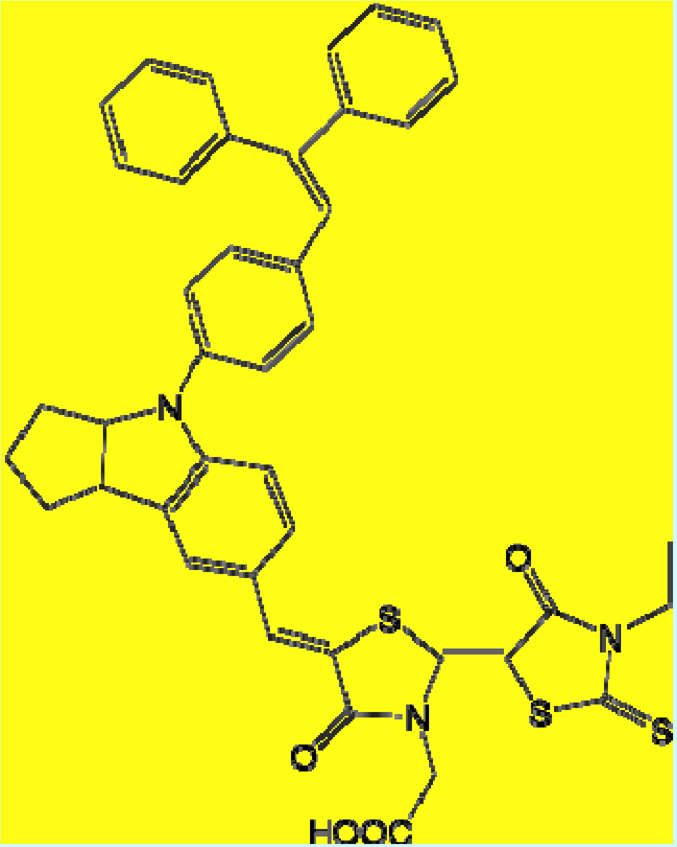


Dr. Md. K. Nazeeruddin
Senior Scientist and
Adjoint scientifique
LPi/EPFL Lausanne

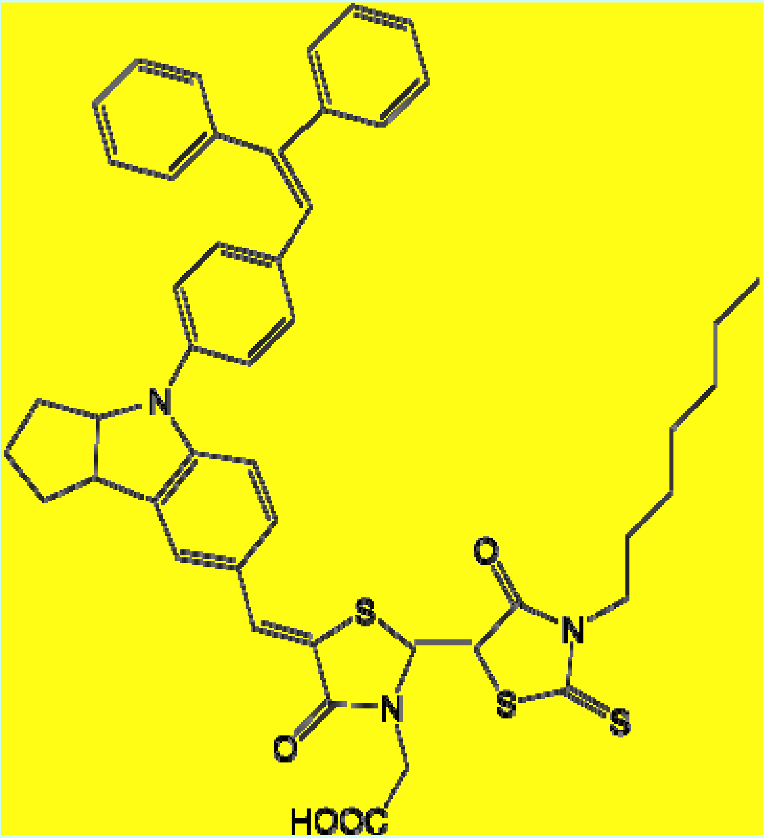
Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. J. American Chemical Society (1993), 115(14), 6382-90.

However organic dyes are catching up

Molecular structures of D149 and D205

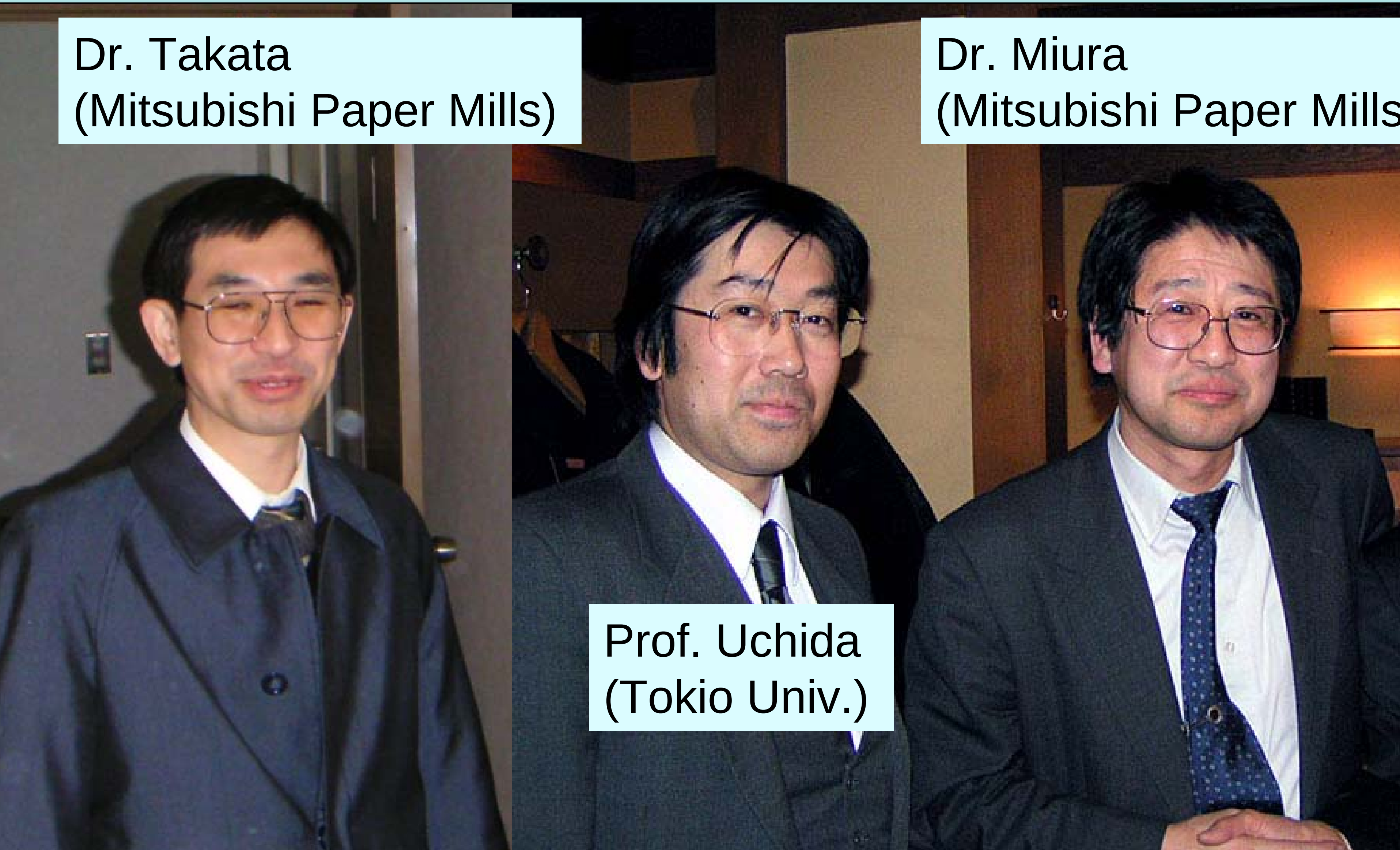


D149

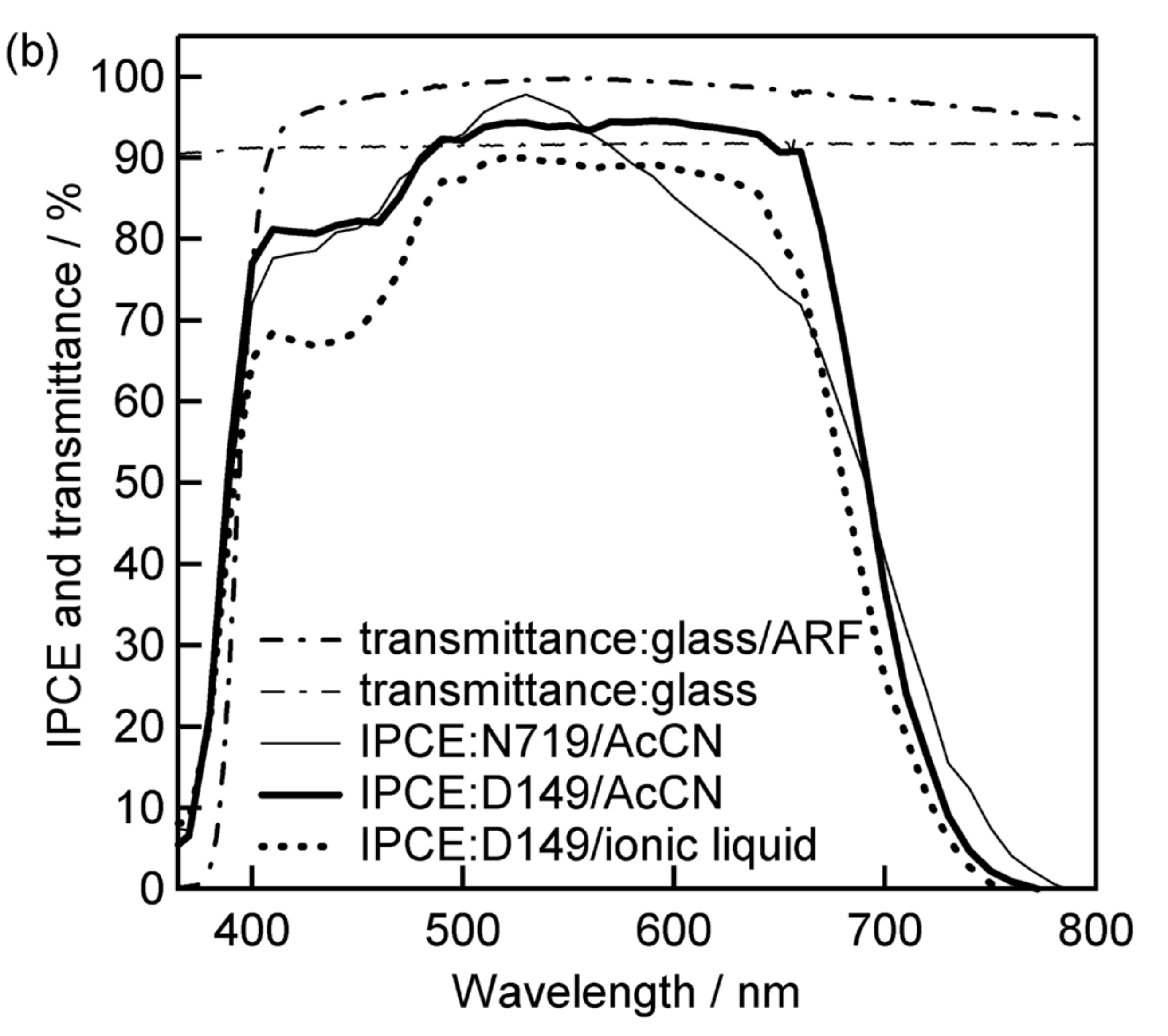


D205

The three inventors of the D-149 dye



The incident photon to current conversion efficiency (IPCE or EQE) attains > 90 % over a broad spectral range in the visible



Dye sensitized nanocrystals achieve quantitative conversion of photons into electric current

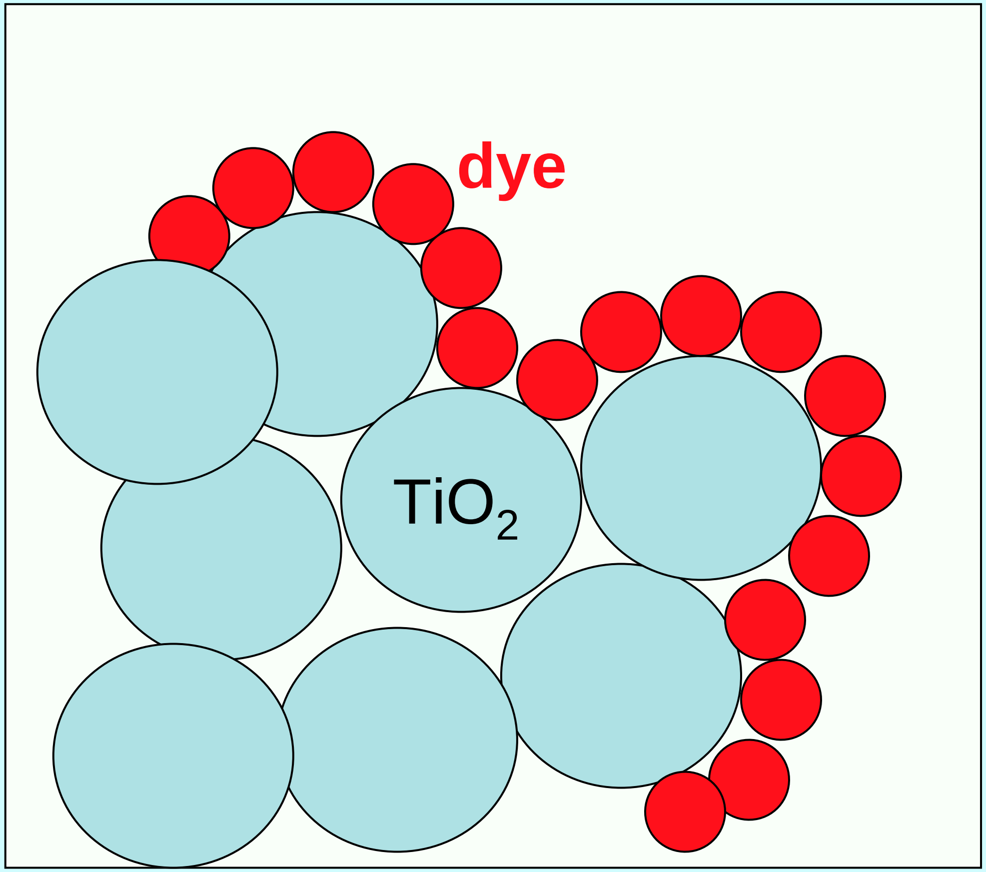
The incident photon to electrical current conversion efficiency (external quantum efficiency) can reach close to 100 %

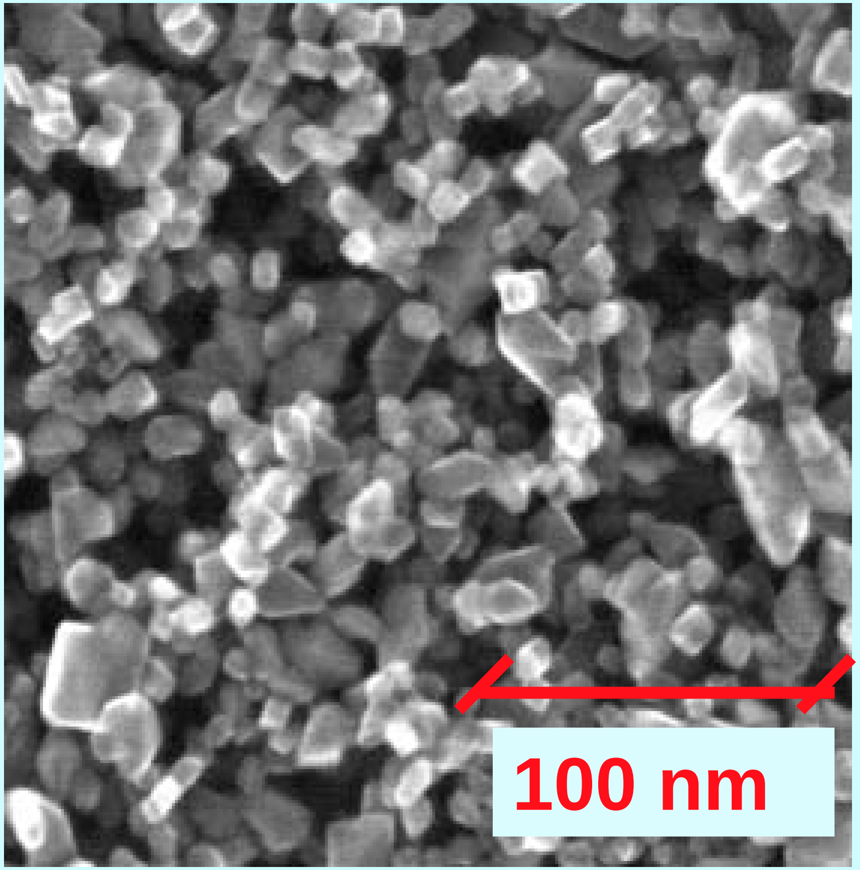
$$\eta = \eta_{abs} * \Phi_{inj} * \eta_{coll}$$

A key question is how electrons are quantitively collected from the disordered network of nanoparticles.

The photocurrent is over 1000 times higher than with a flat junction

The excited dye injects electrons into the network of TiO2 nanocrystals which conduct them to the current collector

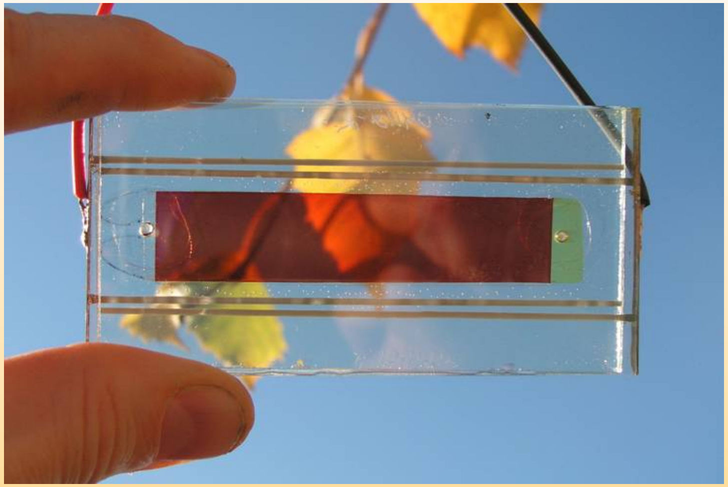


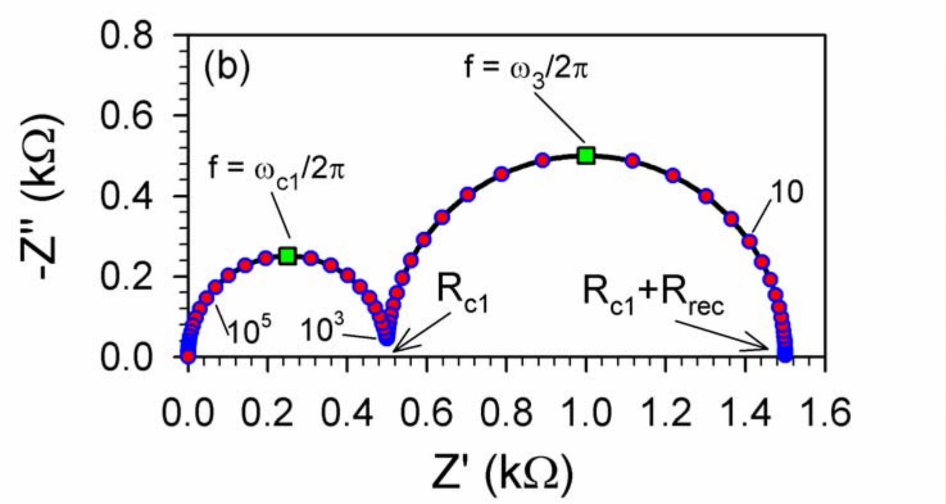


The electrons ad holes move in different phases and are separated by a phase boundary

Impedance studies of mesopic solar cells

Tutorial NUS January 18, 2008





Michael Graetzel,

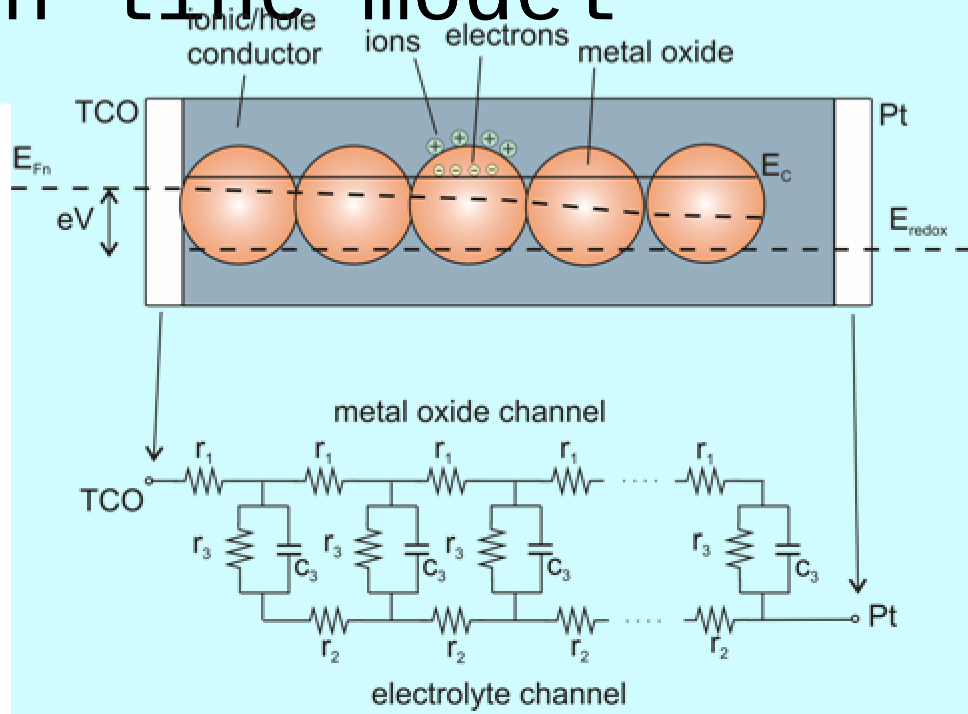
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE

Visiting Professor MSE/NUS

Michael.Graetzel@epfl.ch

Diffusion-recombination transmission line model

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.



Impedance spectroscopy gives all parameters of electronic processes at once:

Conductivity

Chemical capacitance

Recombination resistance

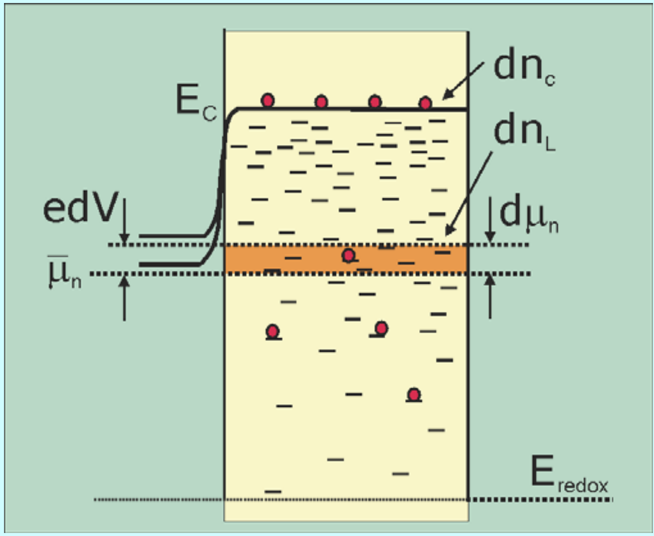
J. Bisquert, J. Phys. Chem. B **106**, 325-333 (2002) F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, A. Hagfeldt *Solar En. Mat. Sol.Cells*, 87, 117-131 (2005).

Chemical Capacitance

Shows the electronic levels for electron or hole (polaron) transport

Shows the energy levels for charge transfer (recombination)

Gives a reference for conduction band position (rules photovoltage and injection from dye)



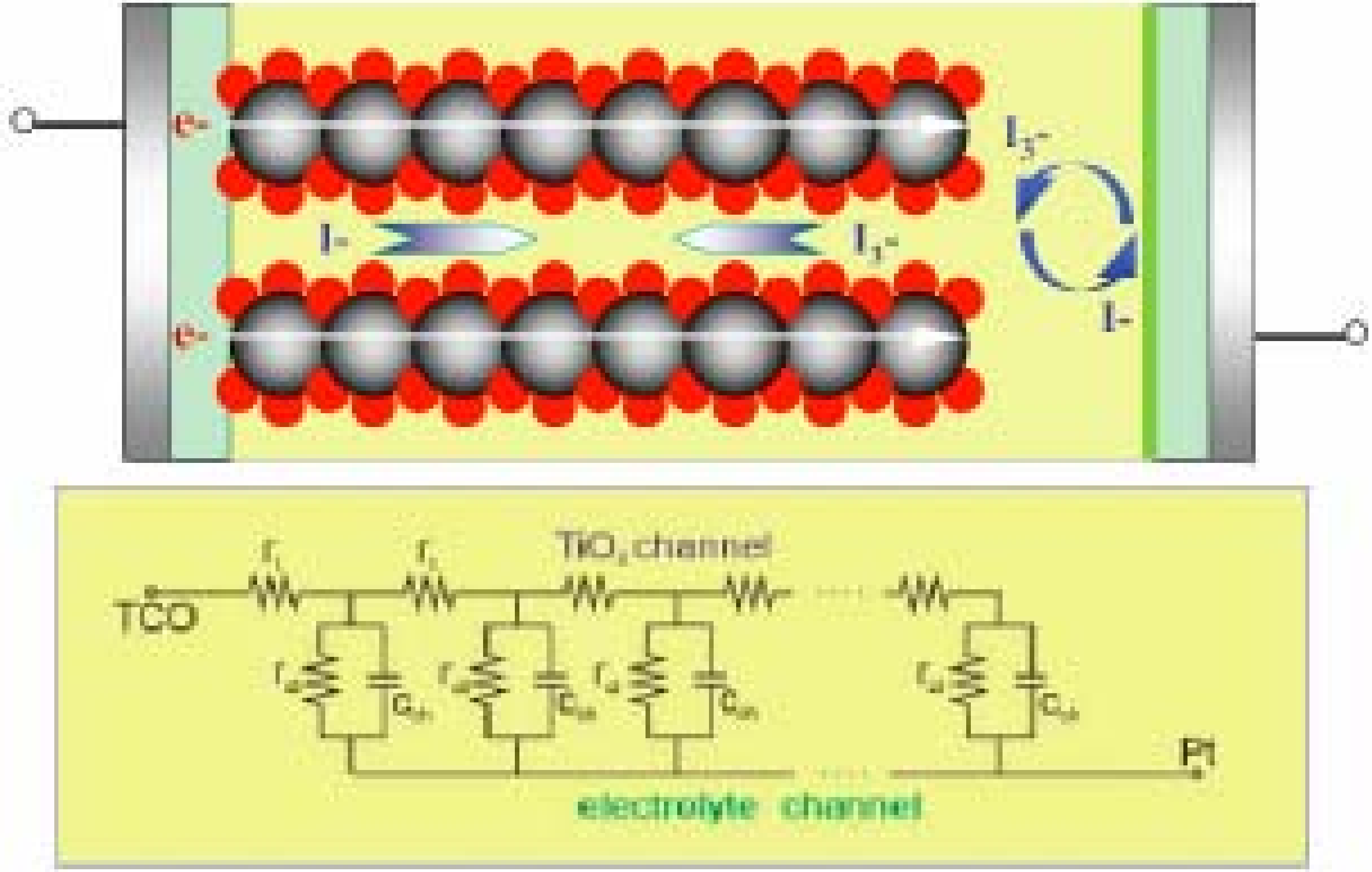
Chemical capacitance

$$C_\mu = q^2 \frac{\partial n}{\partial \mu} = q^2 g(E_F)$$

Density of states:
DOS = C_μ/q

q = e = elementary charge

μ = chemical potential of electron (Fermi level)

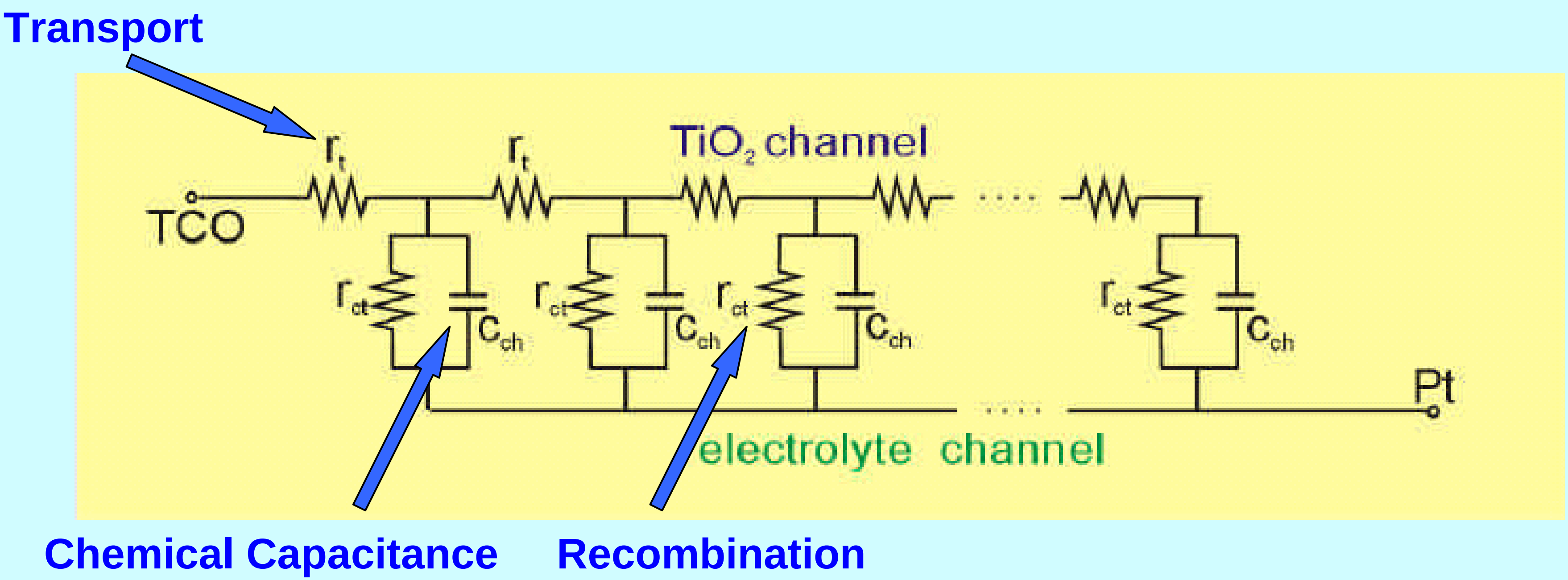


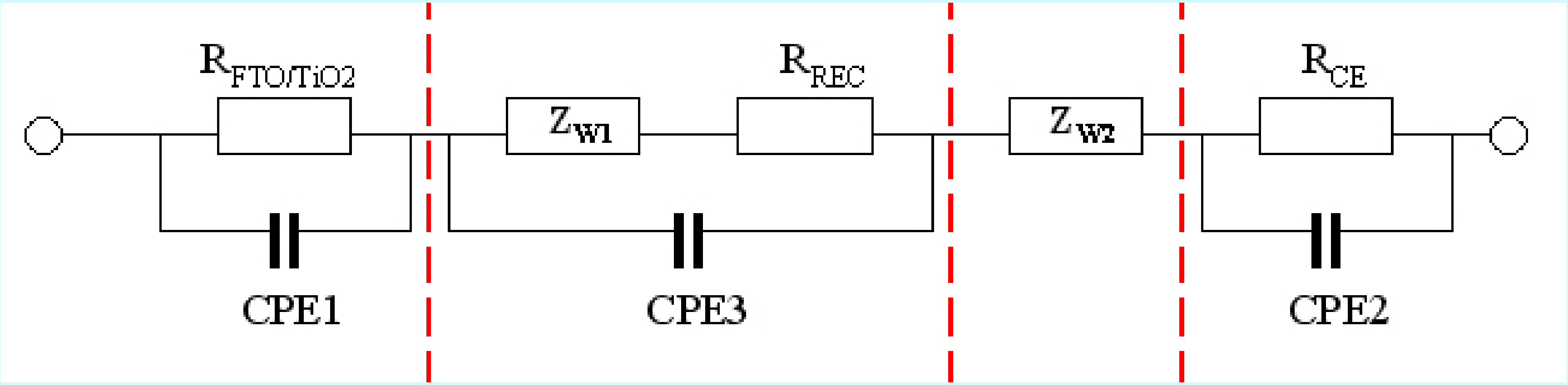
1. FTO/TiO2 interface; 2. TiO2/electrolyte interface; 3. Electrolyte/Pt interface.

Juan Bisquert, Phys.Chem.Chem.Phys 5, 5360 (2003)
Fabregat-Santiago, F. Bisquert, J. Garcia-Belmonte, G. Boschloo, G Hagfeldt, A.

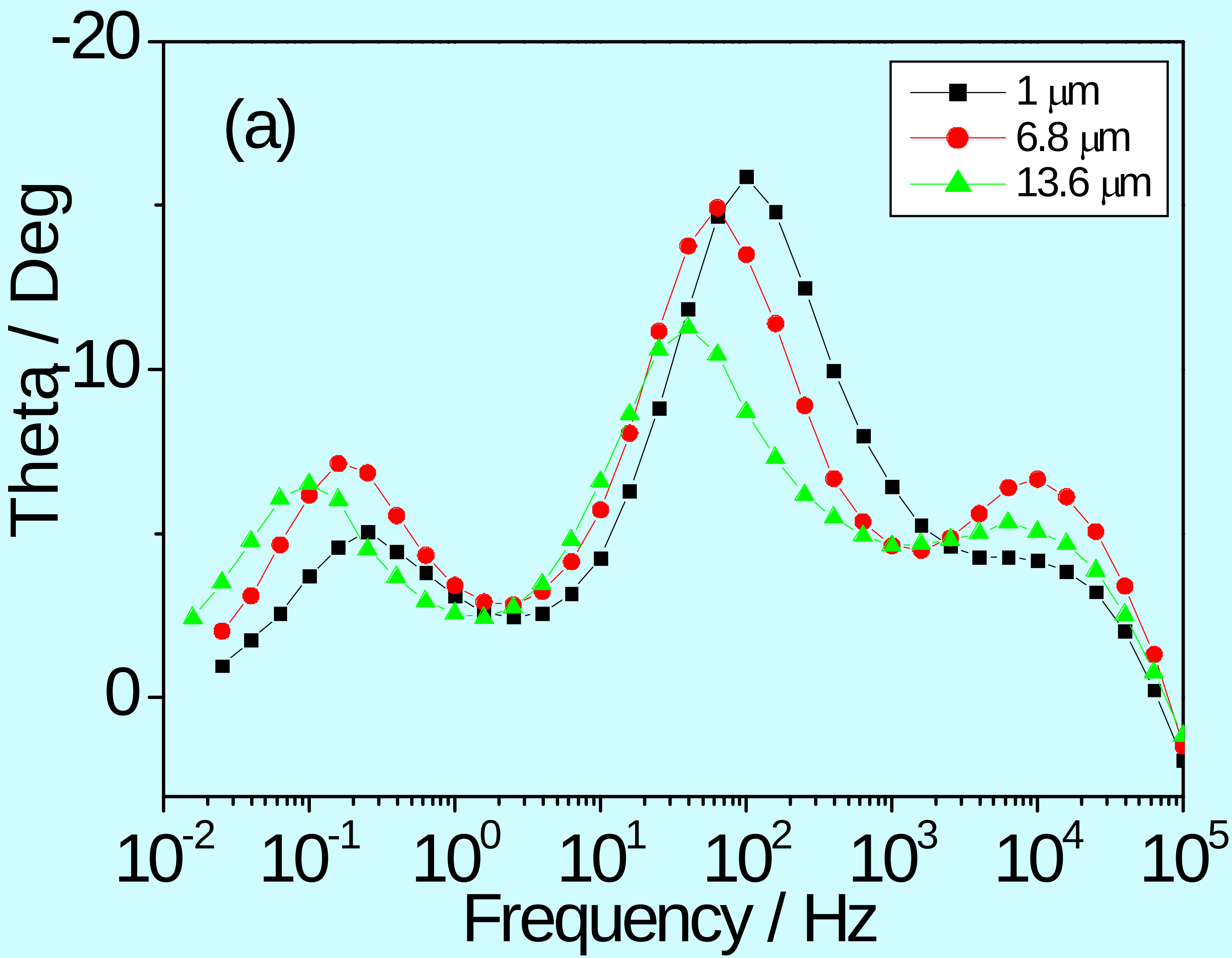
Solar Energy Materials & Solar Cells (2005), 87(1-4), 117-131.

Finite length transmission model (Bisquert)



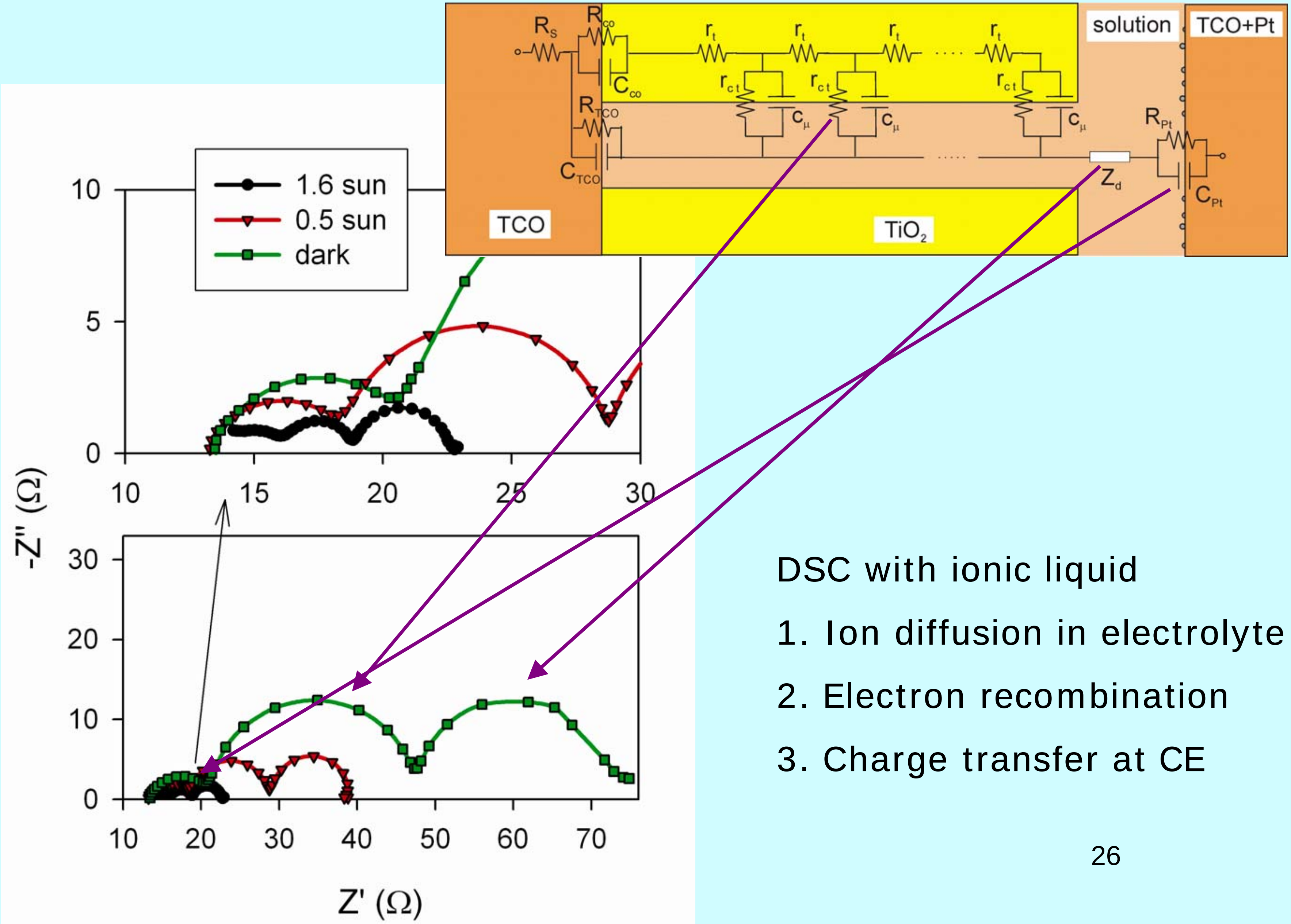


Q Wang, J. Moser and M. Graetzel J.Phys. Chem B 2005



(a)
1 μm
6.8 μm
13.6 μm
Theta / Deg
-20
10
0
10-2
10-1
100
101
102
103
104
105
Frequency / Hz

Impedance characteristics of the DSC



DSC with ionic liquid

1. Ion diffusion in electrolyte
2. Electron recombination
3. Charge transfer at CE

Transmission line for diffusion-recombination

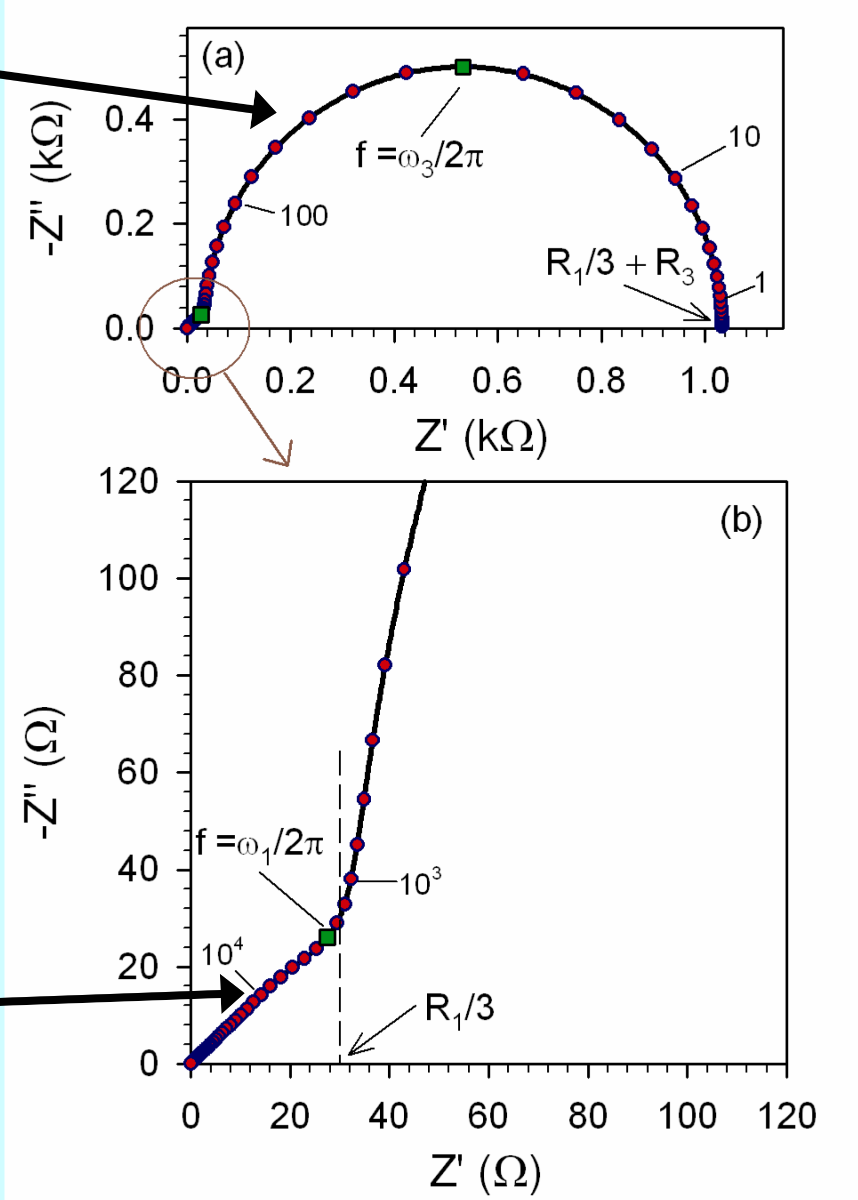
Carrier acumulation and recombination

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

L_D much longer than thickness Ofilm (slow recombination)

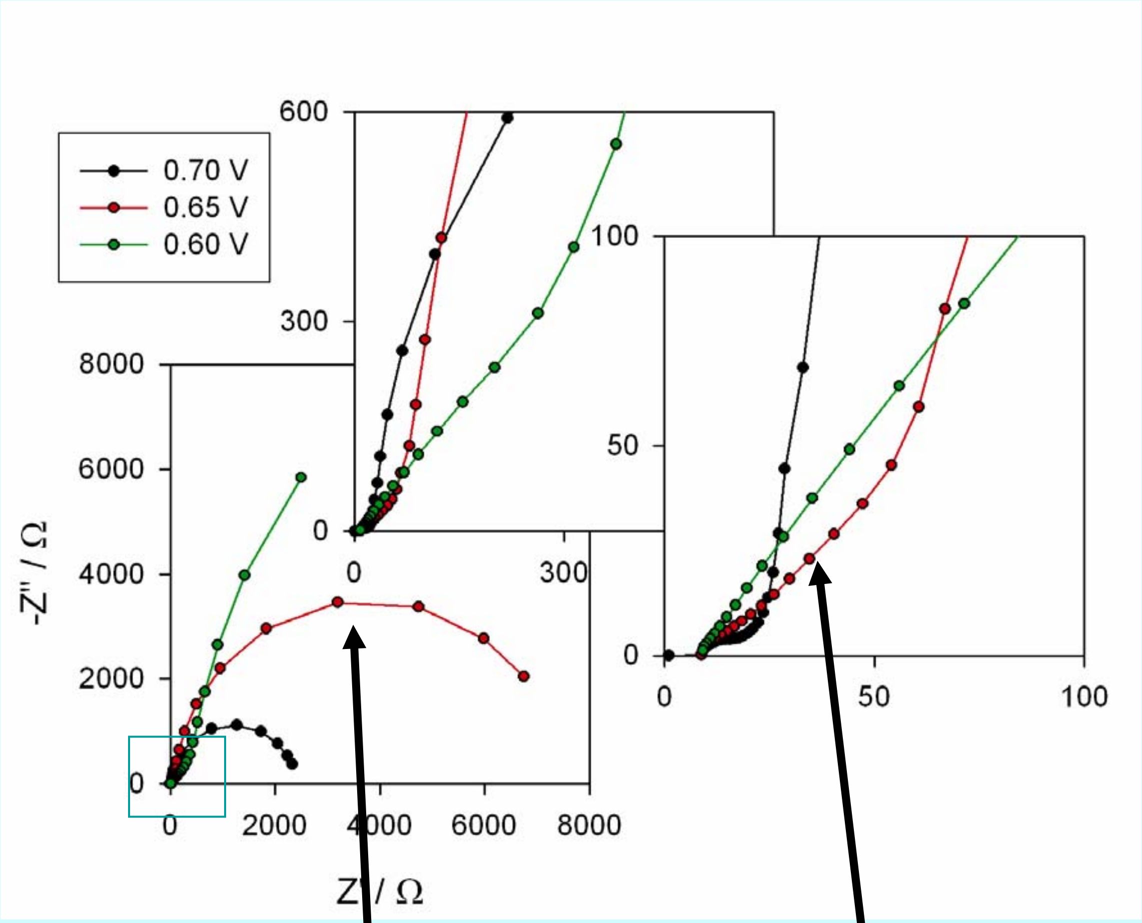
QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

diffusion



Impedance of 11% efficiency dye solar cell

This solar cell shows ideal characteristic of diffusion-recombination model with recombination resistance much larger than transport resistance $R_3 >> R_1$



Recombination arc R_3

Diffusion Warburg $R_1/3$

Michael Grätzel, Francisco Fabregat-Santiago, Juan Bisquert et al.,

J. Phys. Chem. B. **110**, 25210-25221 (2006)

The electron diffusion length exceeds largely the film thickness

$$L_n = \sqrt{D\tau}$$

Typical values for high performance (η >10%) cells at V_{mpp}:

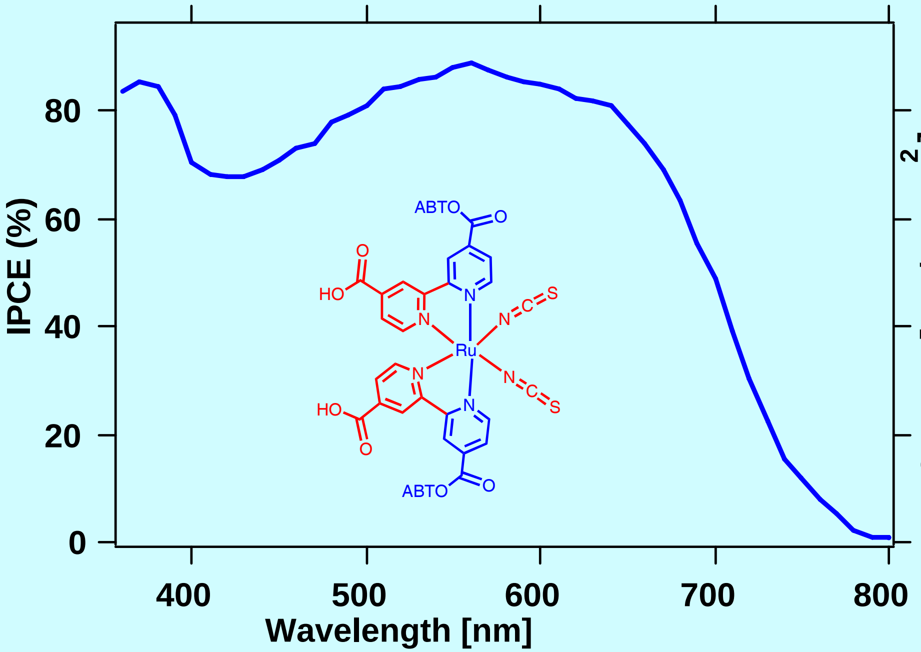
$D = 10^{-4}\ cm^2/s$, $\tau = 1\ s$, $L = 100\ \mu m$

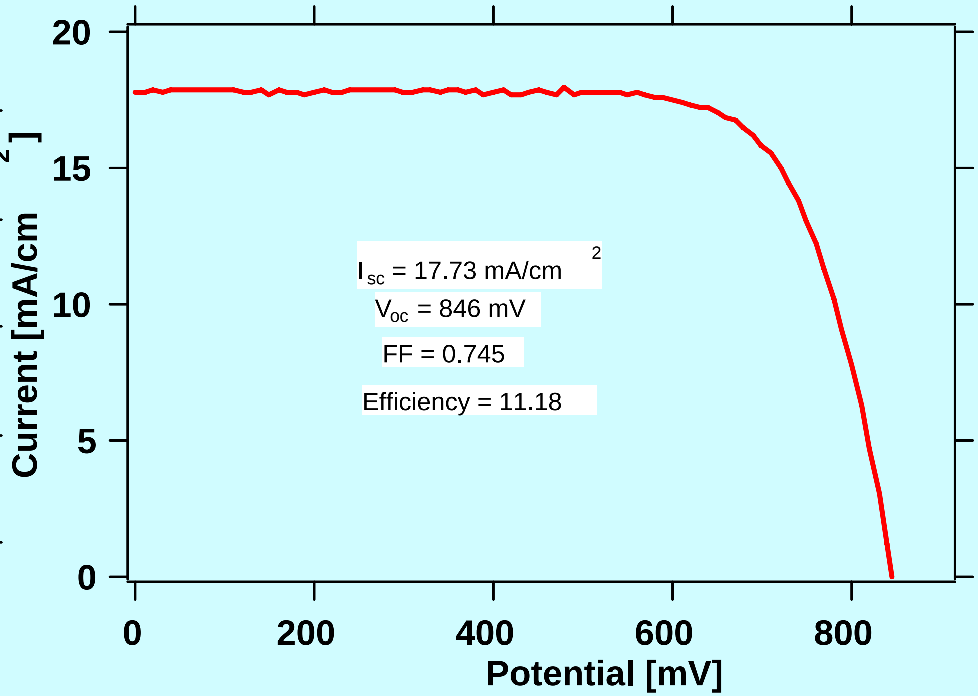
The film thickness is less than 30 micrometer

The solar to electric power conversion efficiency of the DSC in full AM 1.5 sun light validated by accredited PV calibration laboratories has presently reached over 11 %.

Chiba, Y., Islam, A.; Watanabe, Y; Komiya, R.; Koide, N.; Han, L..
Dye-sensitized solar cells with conversion efficiency of 11.1%.
Japanese Journal of Applied Physics, Part 2: Letters & Express Letters (2006), 45(24-28),

Champion cells reach over 11 percent conversion efficiency
However their near IR response is insufficient

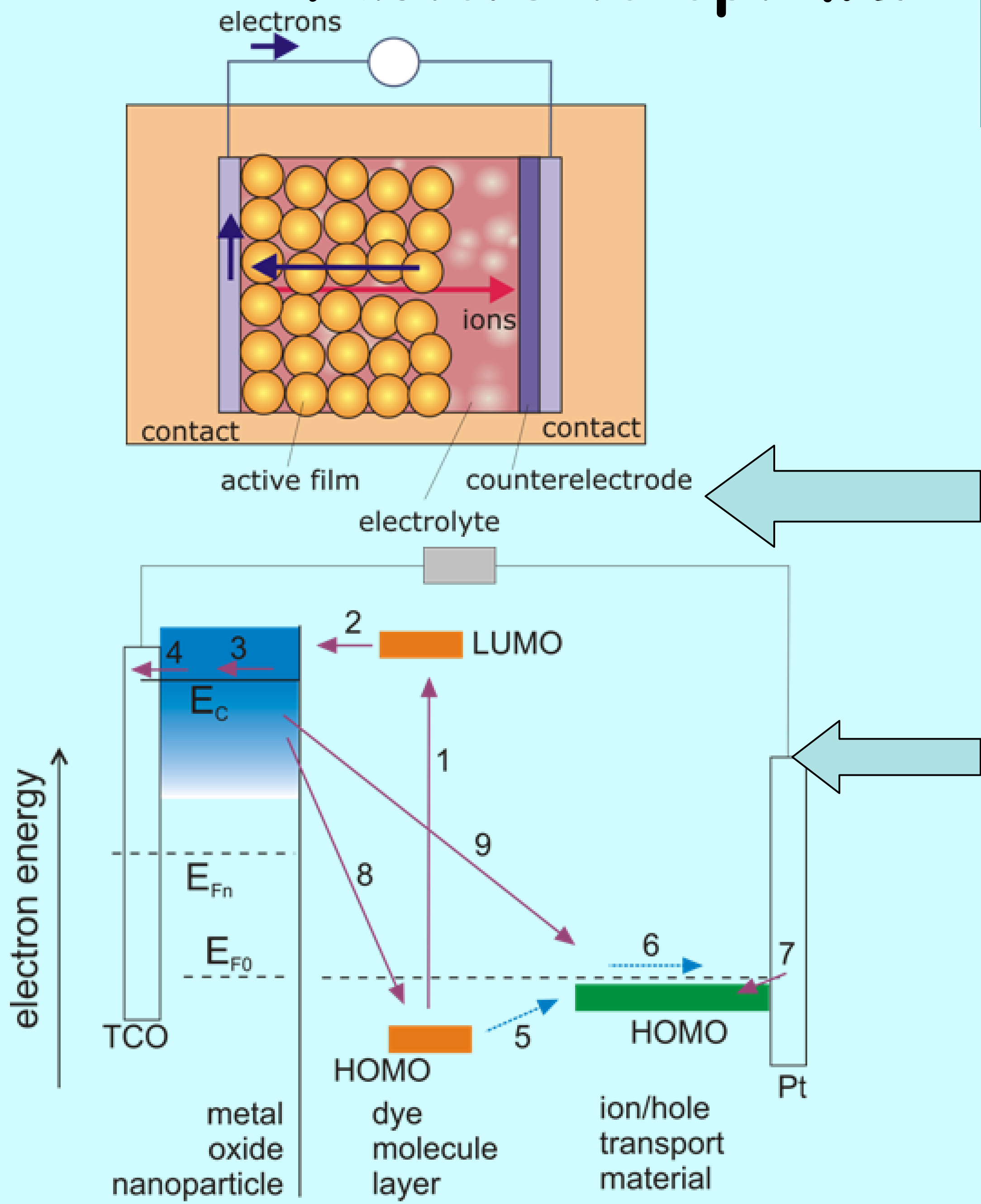




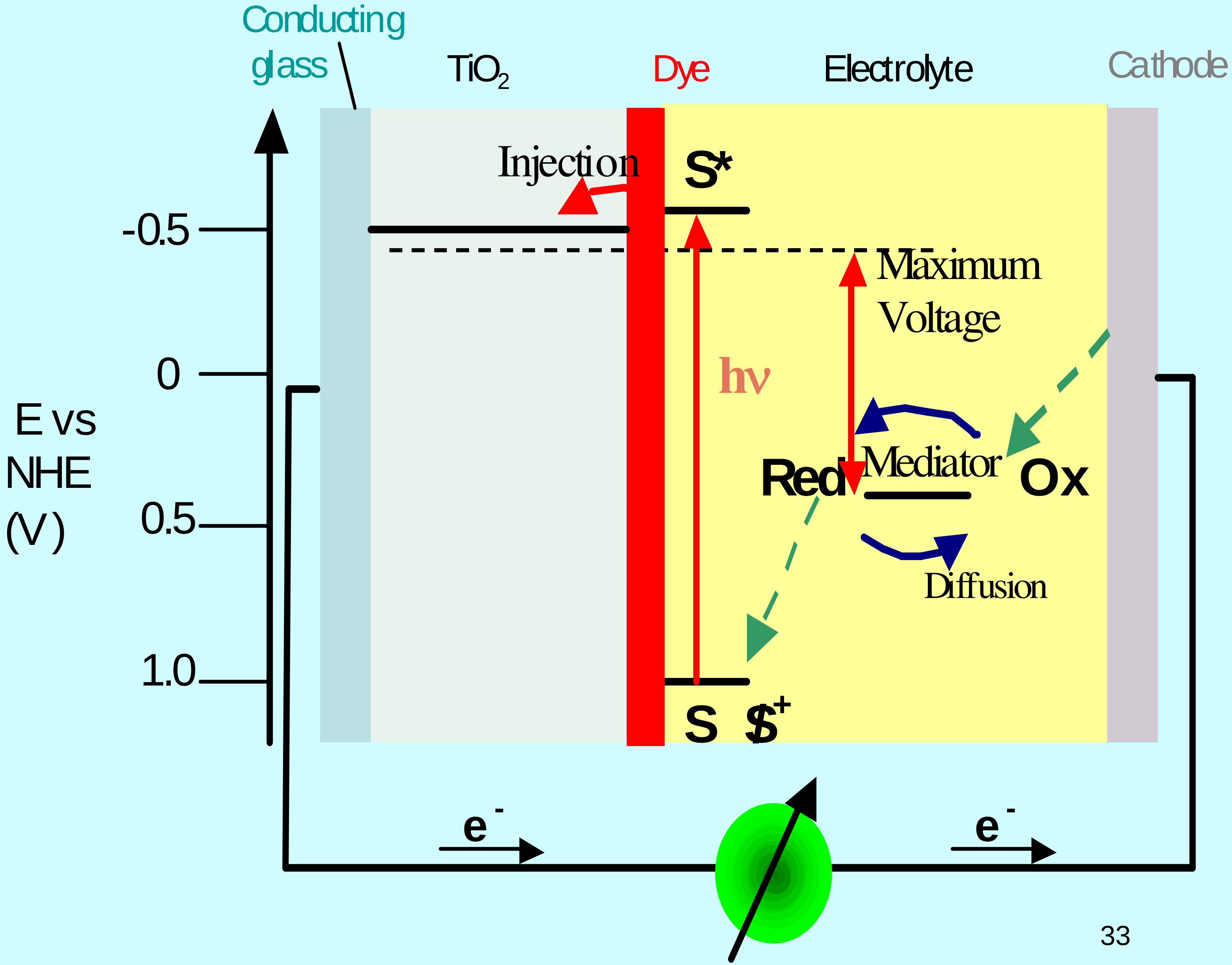
$$\eta = i_{ph} V_{oc} ff / I_s$$

Nazeeruddin, Mohammad K.; De Angelis, Filippo; Fantacci, Simona; Selloni, Annabella; Viscardi, Guido; Liska, Paul; Ito, Seigo; Takeru, Bessho; Graetzel, Michael. JACS (2005), 127(48), 16835-16847.

Factors to optimize



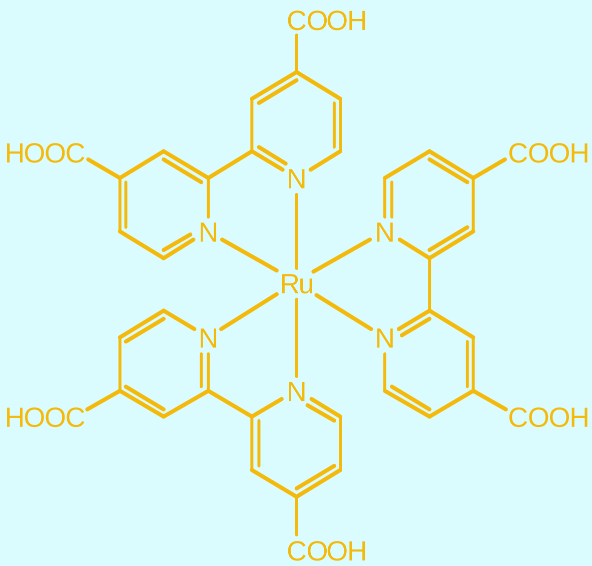
- Light absorption
- Carrier generation
- Electron transport
- Ion/hole transport
- Recombination
- CT at outer contacts
- Series resistance

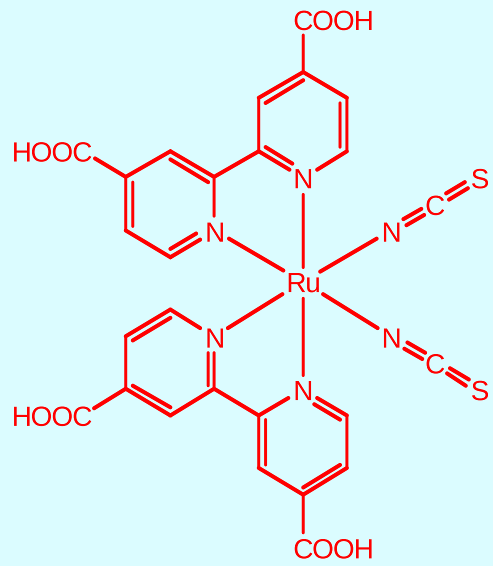


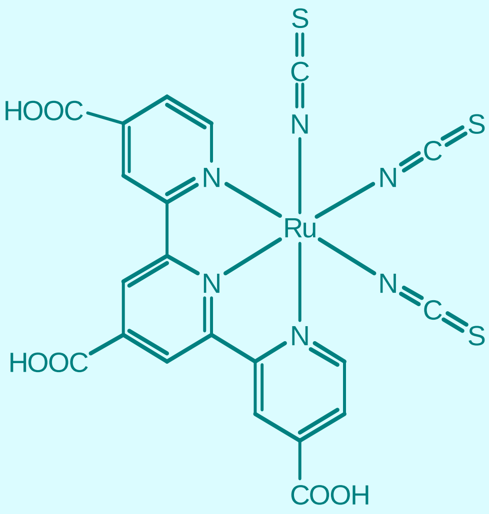
Conducting glass
TiO$_2$
Dye
Electrolyte
Cathode
Injection
S*
-0.5
0
0.5
1.0
E vs NHE (V)
hν
Maximum Voltage
Red
Mediator
Ox
Diffusion
S
S+
e-
e-

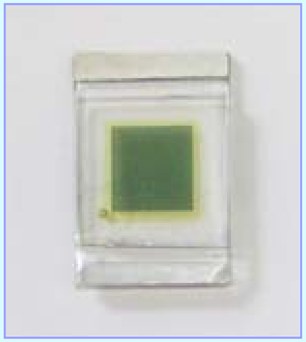
Ongoing research

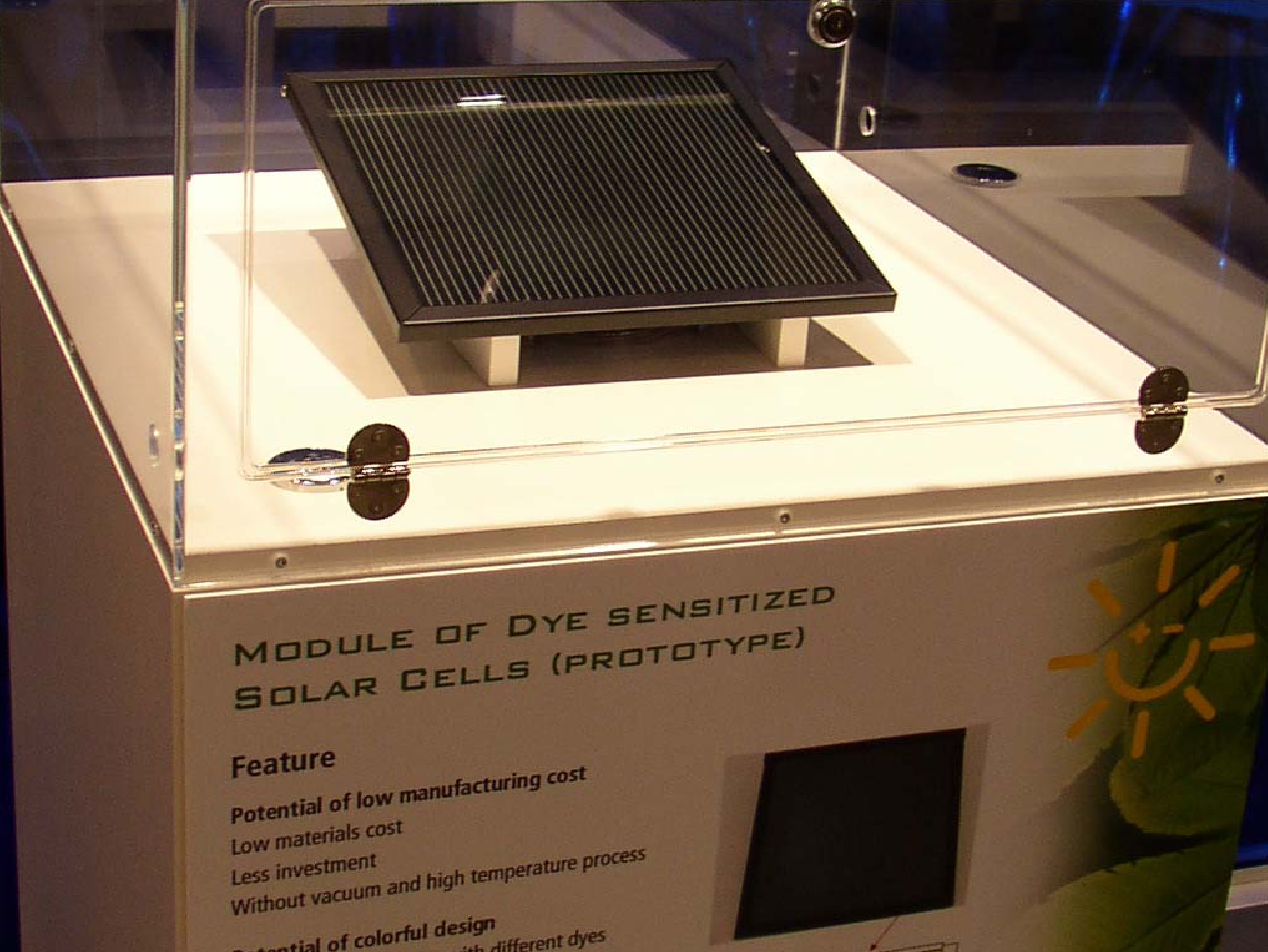
- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- tandem devices
- solar photolysis of water


COOH
HOOC
COOH
N
N
N
Ru
N
N
N
HOOC
COOH
COOH

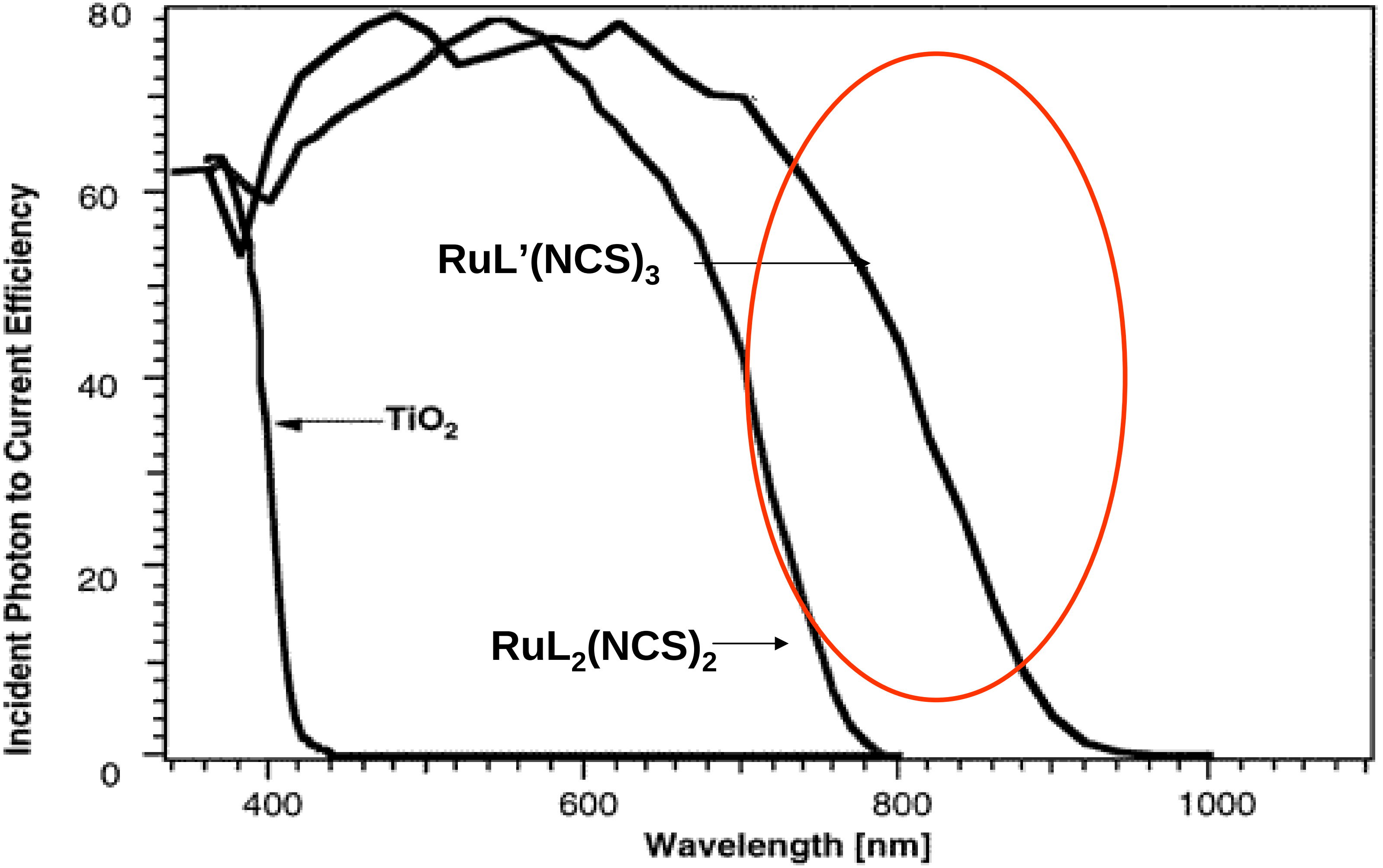

COOH
HOOC
N
N
Ru
N=C=S
N
N
N=C=S
HOOC
COOH


S=C=N
HOOC
N
Ru
N=C=S
N
N=C=S
N
HOOC
COOH




MODULE OF DYE SENSITIZED
SOLAR CELLS (PROTOTYPE)
Feature
Potential of low manufacturing cost
Low materials cost
Less investment
Without vacuum and high temperature process
Potential of colorful design

Development of near IR sensitizers is critical to reach 15 % efficiency goal

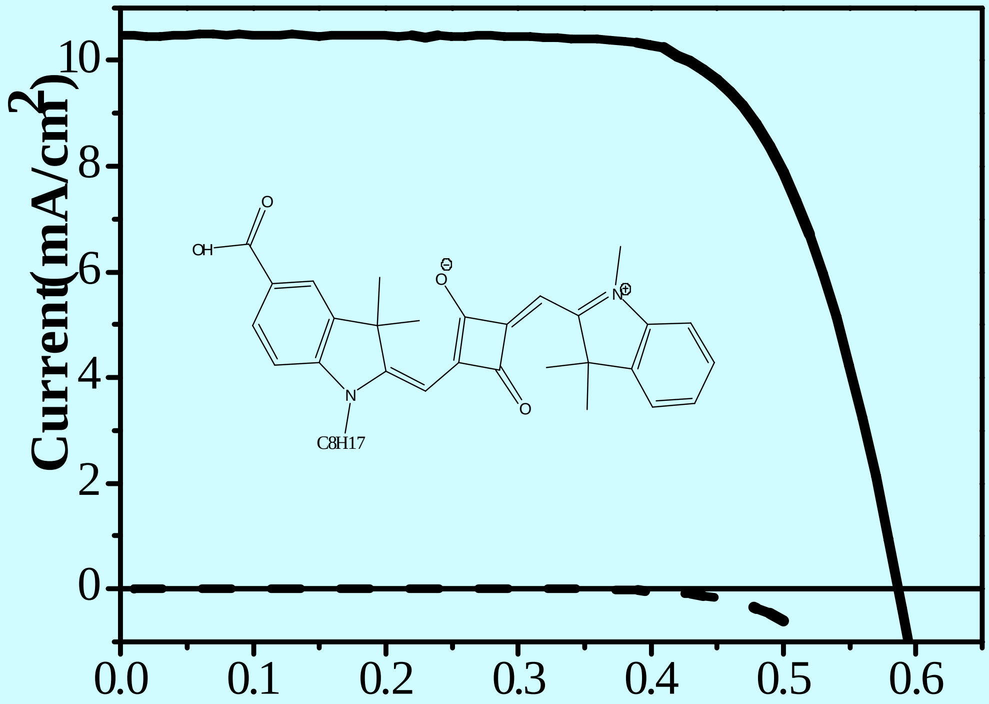


L = 4,4'-COOH-2,2'-bipyridine

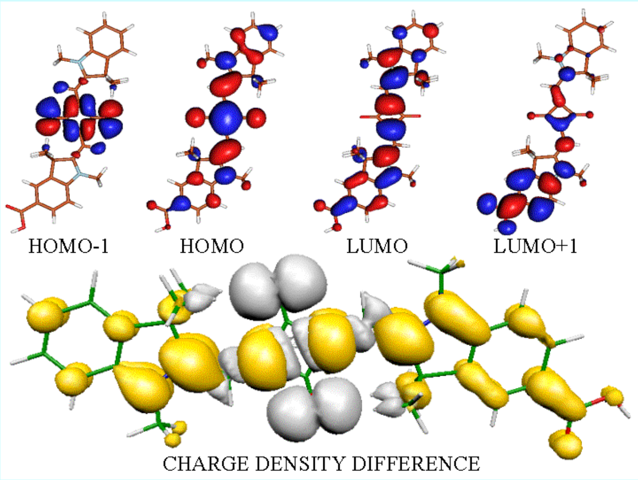
L' = 4,4',4"-COOH-2,2':6',2"-terpyridine

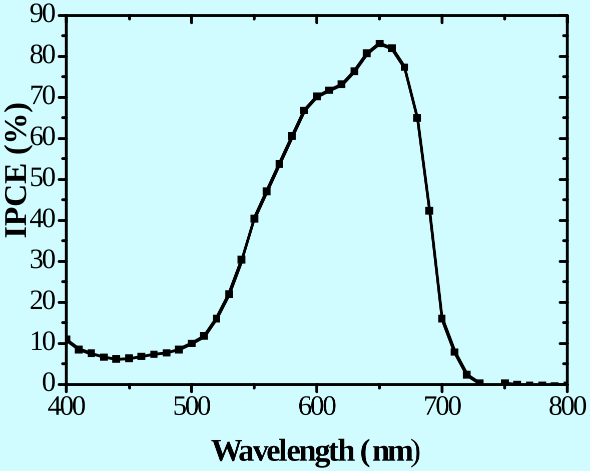
Near IR dyes

Squaraine dyes look very promising !



J.H.Yum et a JACS 1007 12, 1032

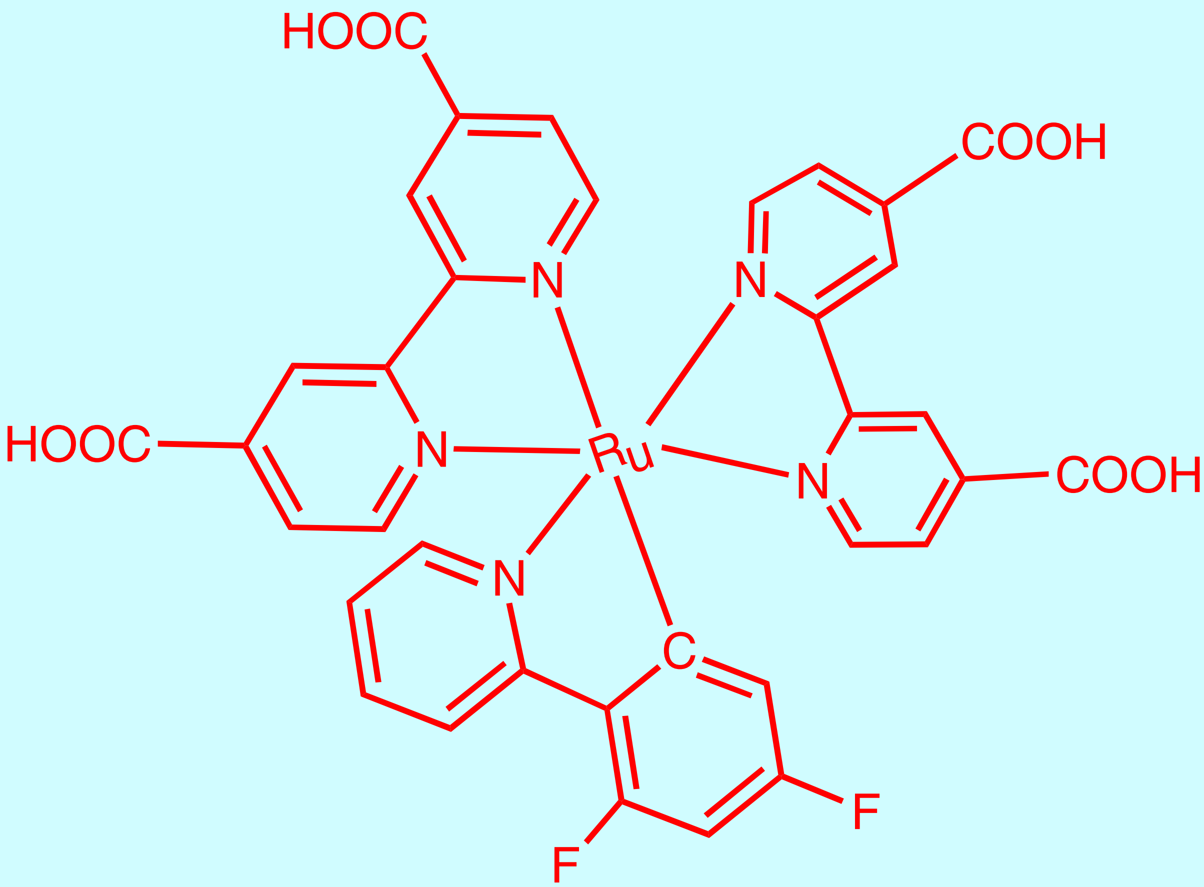




Dr. Jun-Ho Yum

ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

New cyclometallated ruthenium complexes show enhanced red response



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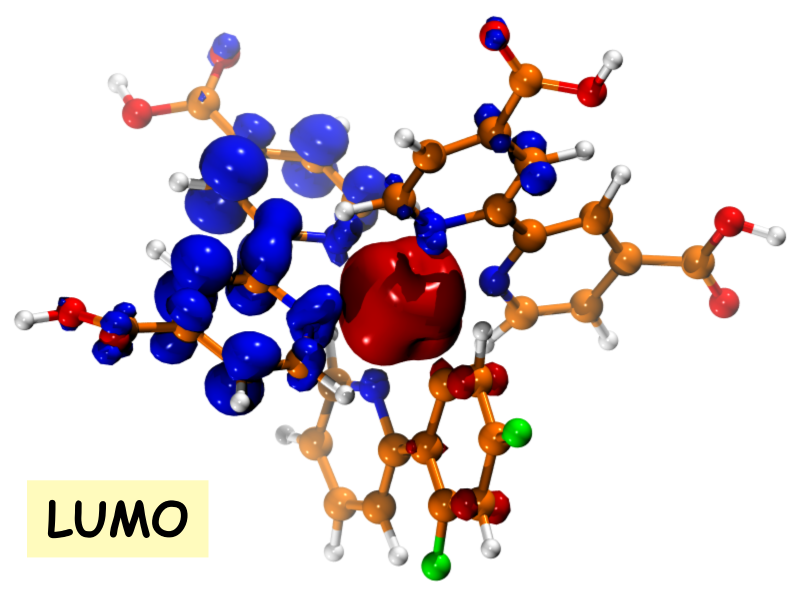
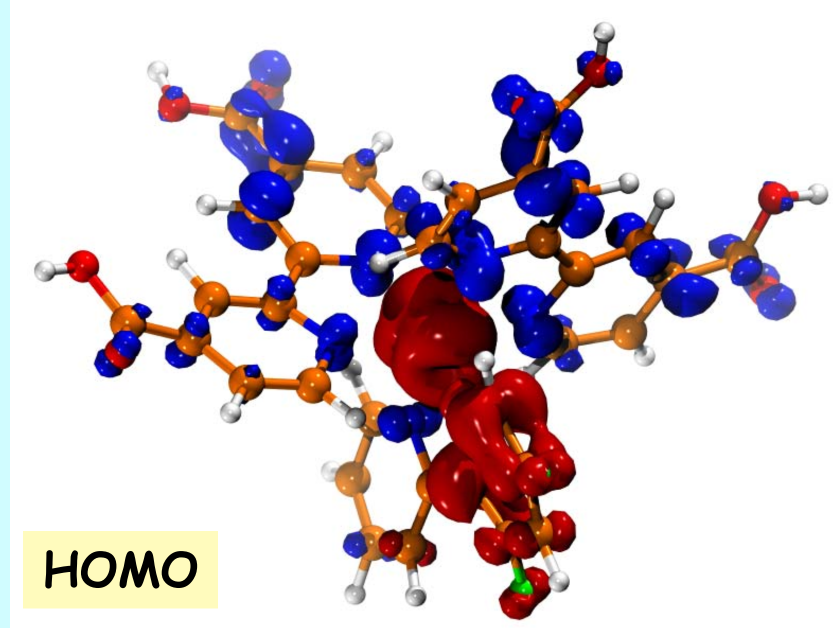
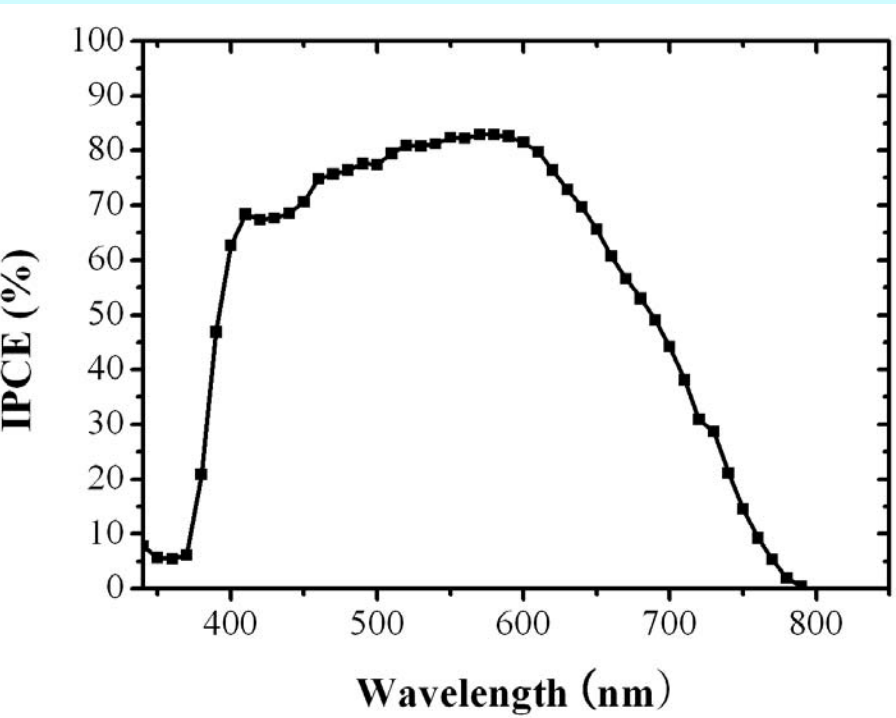
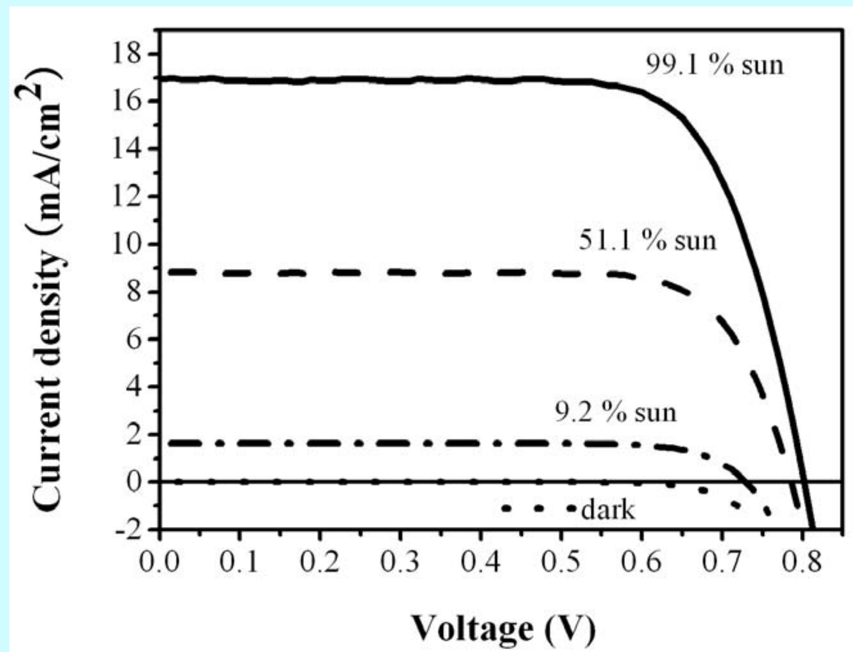


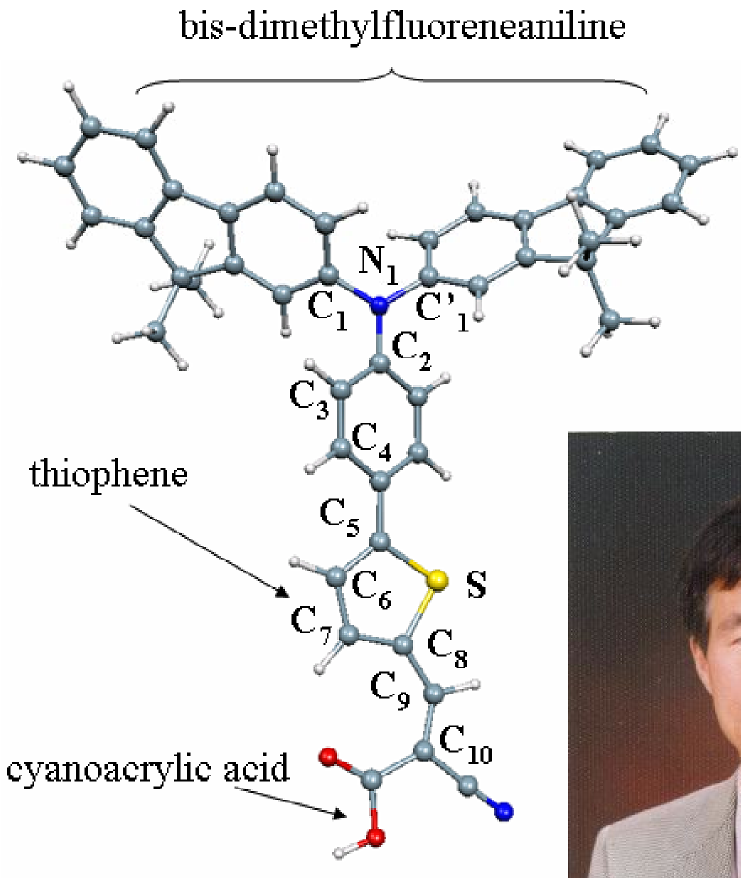




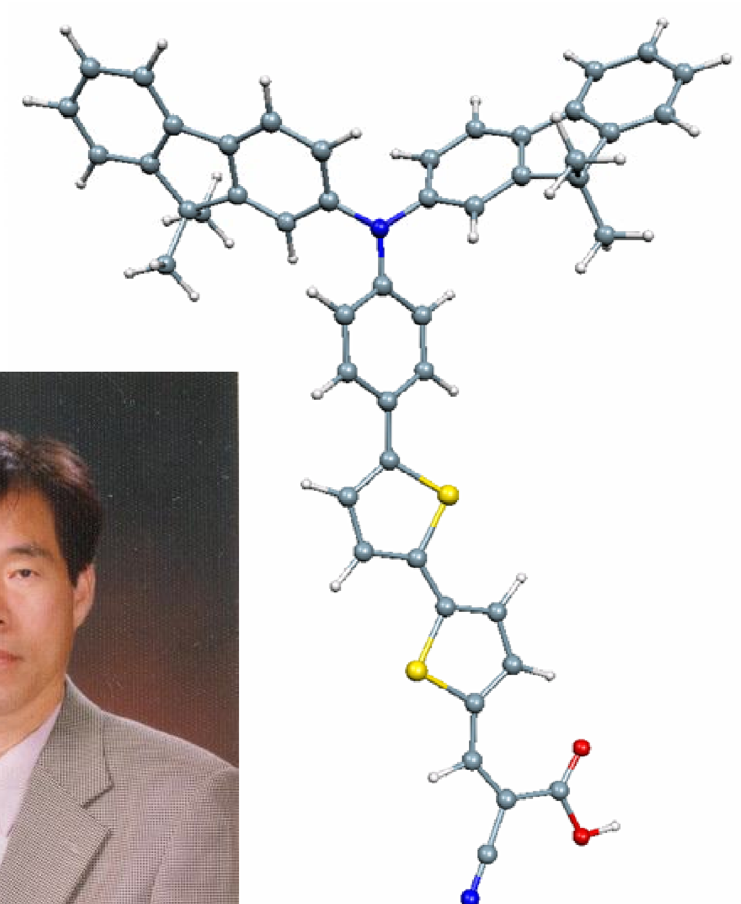


In collaboration with Matteo Guglielmi, Ivano Tavernelli and Ursula Rothlisberger

The race is on !
Molecular engineering of efficient and stable organic sensitizers



JK-1

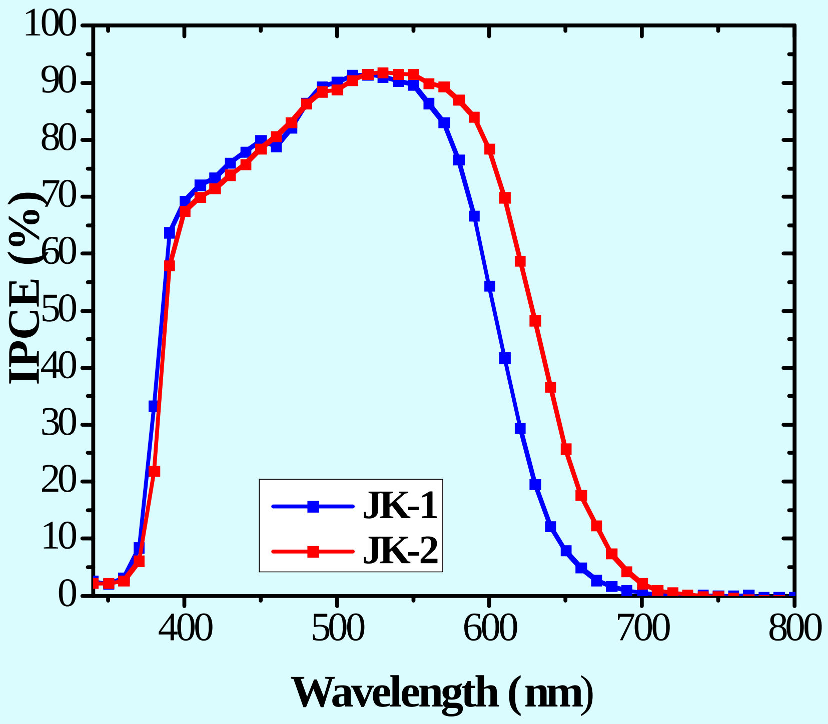


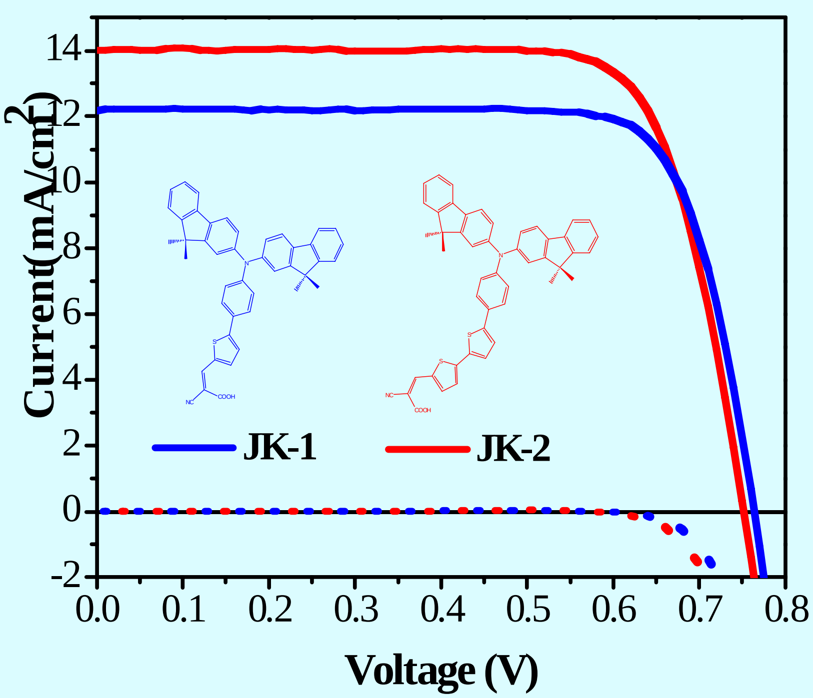
JK-2

Prof. Jaejung Ko

Electronic structure calculations by DFT calculations: Gaussian 03 program package, B3LYP exchange-correlation functional 6-31g* basis set; solvation effects included by using the Polarizable Continuum Model.

The JK-2 dye gives over 8 % conversion efficiency





S.Kim, J.K. Lee, S.O.Kang, J.J. Ko, J.H. Yum, S. Fantacci, F.De Angelis, D. Di Censo, Md.K. Nazeeruddin and M Graetzel

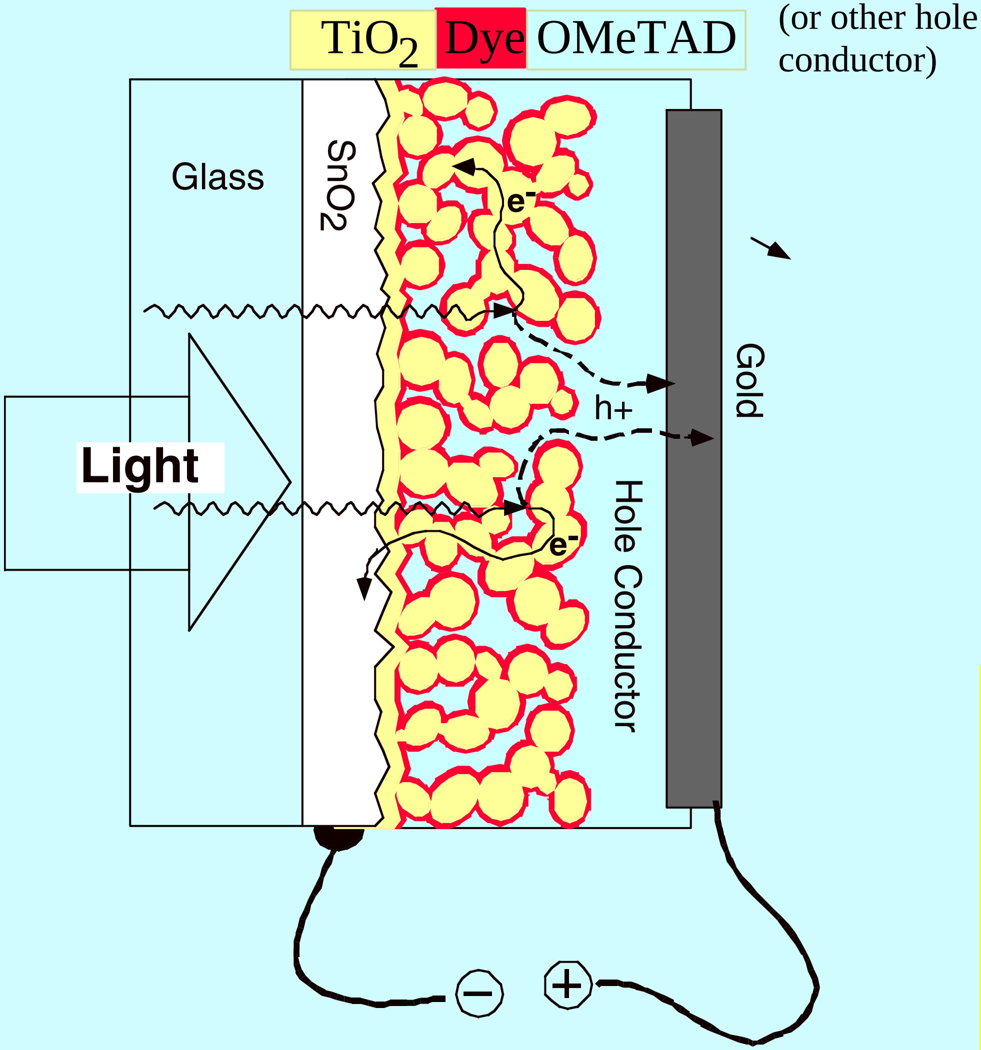
Molecular Engineering of Organic Sensitizers for Solar Cell Applications.

J. Am. Chem, Soc (2006), 128,16701

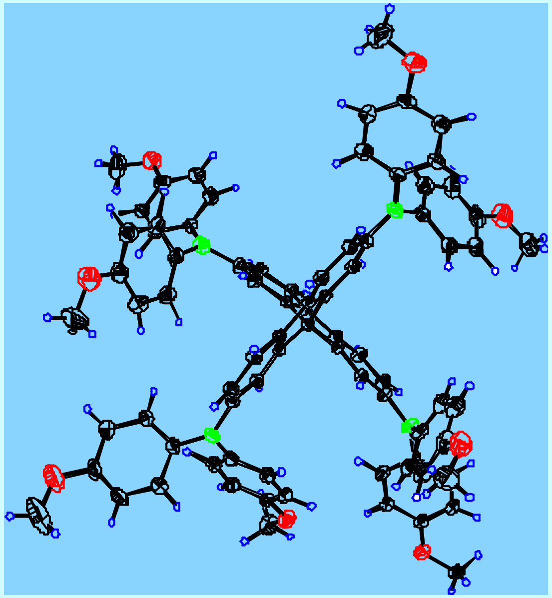
Ongoing research

- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- tandem devices
- solar photolysis of water

Solid State Dye Sensitized PV cell



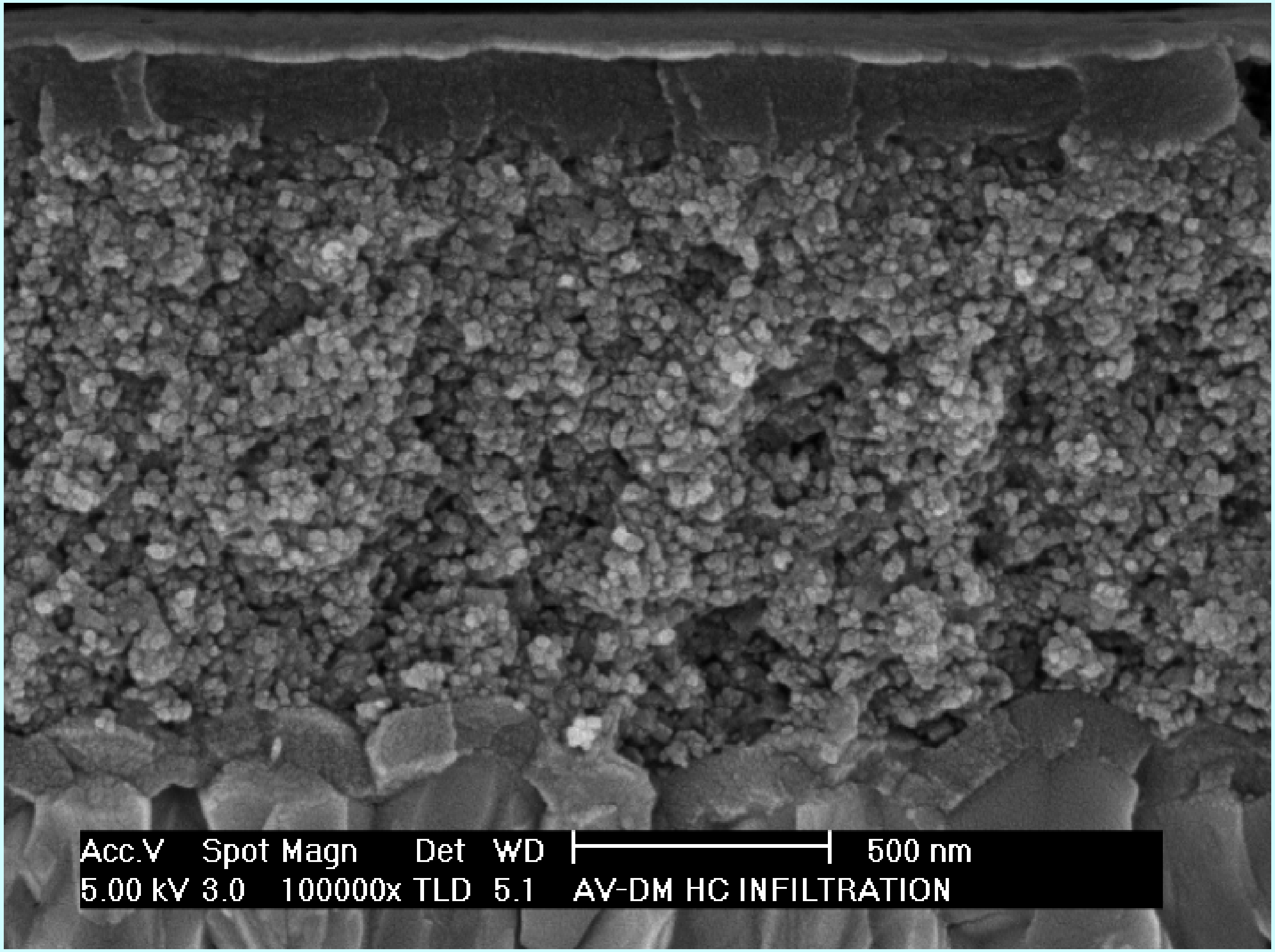
Spiro-OMeTAD



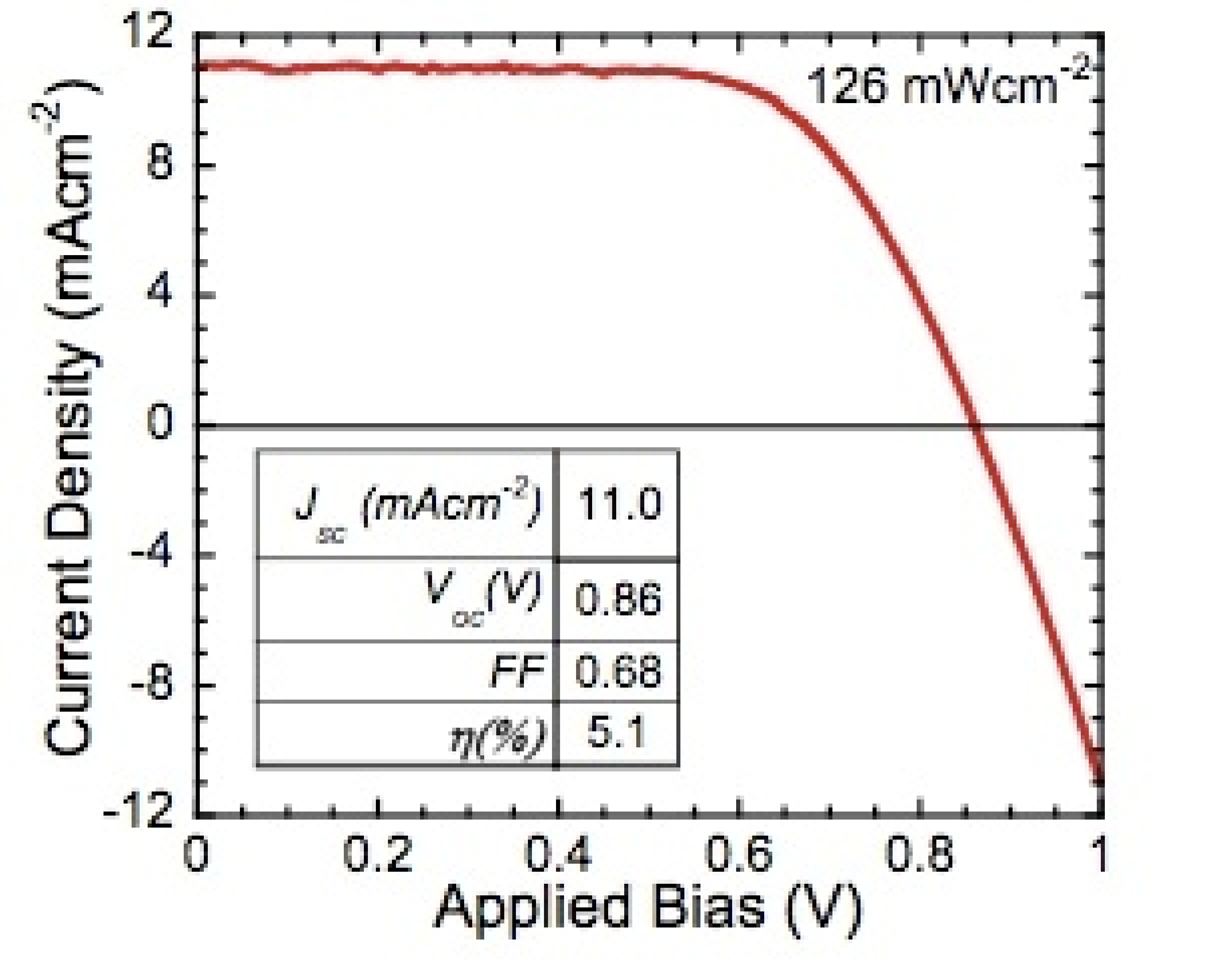
Glass transition temperature: *121 °C*
Melting Point: *246 °C*
Work function: *4.9 eV*
(CV in CH_2Cl_2. *110 mV* vs. Fc/Fc^+)
Absorption maximum neutral:
λ_{max}=*372 nm* (ε=*40100*)
Radical cation:
λ_{max}=*511 nm* (ε=*37400*)

Mobility ~ 1 x10^{-4} V/cm

Courtesy Brian O'Regan



Acc.V Spot Magn Det WD 500 nm
5.00 kV 3.0 100000x TLD 5.1 AV-DM HC INFILTRATION


126 mWcm-2
Current Density (mAcm-2)
Applied Bias (V)
12
8
4
0
-4
-8
-12
0
0.2
0.4
0.6
0.8
1
Jsc (mAcm-2) 11.0
Voc(V) 0.86
FF 0.68
η(%) 5.1

STABILITY

Requirements for outdoor use according to international PV standards applied to single crystal silicon but so far not to thin film PV cells

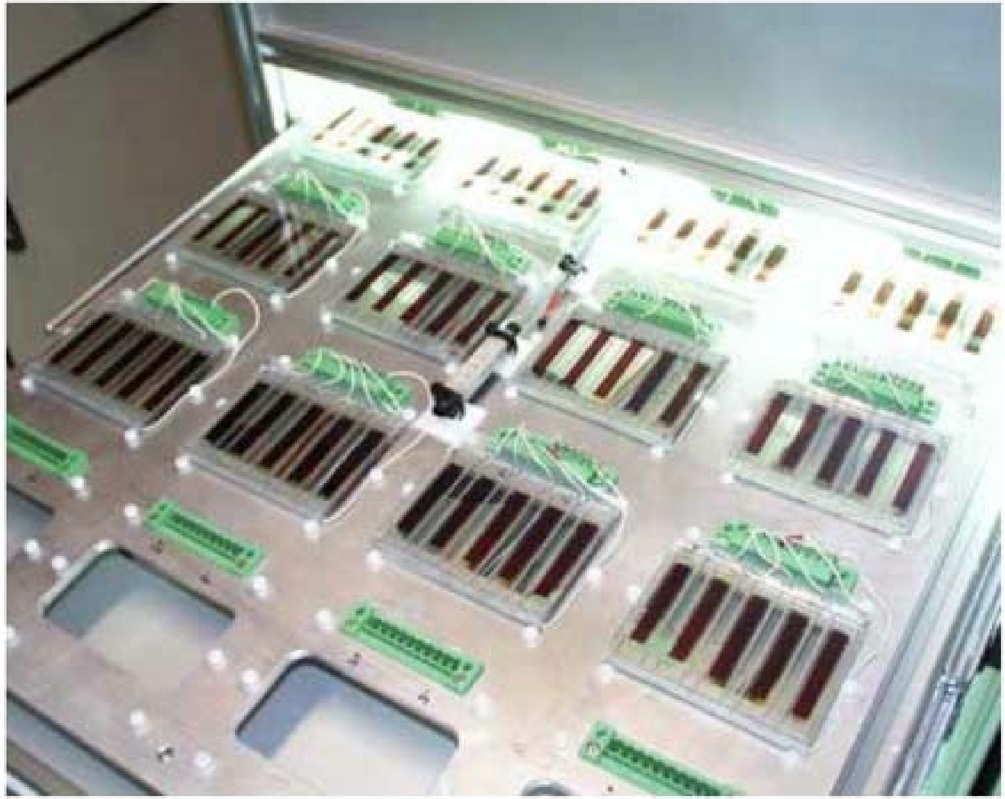
UV plus heat (55-60 C): 1000 hours

Accelerated thermal test at 85 C: 1000 h

Humidity test and temperature cycling (sealing issues)

Light soaking at 2.5 suns (2.5kW/m2)

DSC masterplates



LONG-TERM STABILITY OF DYE SENSITIZED SOLAR CELLS FOR LARGE AREA POWER APPLICATIONS (LOTS-DSC)

[1] : A. Hinsch*, J.M. Kroon, M. Späth , J.A.M. van Roosmalen, N.J. Bakker, P. Sommeling, N. van der Burg, R. Kinderman,
[2] : R. Kern, J. Ferber, C. Schill, M. Schubert [3] : A. Meyer, T. Meyer, [4] : I. Uhlendorf, J. Holzbock, R. Niepmann
[1] ECN Solar Energy, PO Box 1, 1755 ZG Petten, The Netherlands
*phone: (+31) 224 56 4703, fax: (+31) 224 56 3214, e-mail: hinsch@ecn.nl
[2] Freiburg Materials Research Center FMF, Stefan Meier Strasse 21, D 79104 Freiburg Germany
[3] Solaronix S.A., Rue de L'Ouriette 129, CH 1170 Aubonne, Switzerland
[4] Institut fur Angewandte Photovoltaik, Munscheidstrasse 14, D45886 Gelsenkirchen, Germany

4. DISCUSSION

4.1 Photo-electrochemical stability

Intense visible light soaking ("2.5 sun" sulphur lamp) alone is not a dominant stress factor for dye sensitised solar cells (figure 3) . Remarkably, as predicted already in the "early" days [1] and doubted by many, the system is very regenerative in terms of photo-electrochemical stability (amount of turnovers). As explanation, the following hypothesis has been proposed [6]; the photo-excited state of the dye is very rapidly (sub pico-seconds) quenched by electron transfer to the titanium dioxide. The oxidised dye molecules (Ruthenium (III) centre) are then quickly enough regenerated (reduced) by iodide from the redox couple in the electrolyte to prevent non-regenerative side reactions.

5. CONCLUSIONS

Our accelerated ageing tests on large numbers of dye sensitised solar cells show, that to first order a separation between the effects of the stresses visible light soaking, UV-illumination and thermal treatment on long-term stability can be made. The corresponding mechanisms are of electrochemical, photochemical and pure chemical nature respectively.

Intense visible light soaking with "2.5 sun" equivalent intensity is not a dominant stress factor. Cell stability up to 8300 h has been demonstrated under these conditions corresponding to at least 10 years outdoor equivalent operation.

Very successful are our results on UV-stabilisation. A dramatic improvement in stability under strong UV-light illumination has been reached by using MgI_2 as additive to the electrolyte. 1600 h under this condition have been demonstrated corresponding to at least 2 year outdoor equivalent operation without (!) additional UV-filter. In combination with a simple UV-filtering top-layer, dye sensitised solar cells can therefore be UV-stabilised for real (10 year) long-term outdoor operation.

The long-term extrapolation of the thermal stability achieved so far is still most critical. Experiments at higher temperatures (80 °C to 100 °C) have still to be made t learn more about thermal activation energies. Also, th upper module temperatures in outdoor condition of DSC depending on location and module mounting (roof, stan alone, facade) have to be determined. Nevertheless, th results (minor decrease from 5% solar efficient cells aft 2000 h at 60 °C in the dark) are very promising.

For cells under combined thermal stress and ligl soaking (3400 h, 45 °C) so far good stability with 15 % degrease in maximum power could be demonstrated. Unde certain outdoor conditions a first extrapolation to 5 yea stability can be drawn from these results.

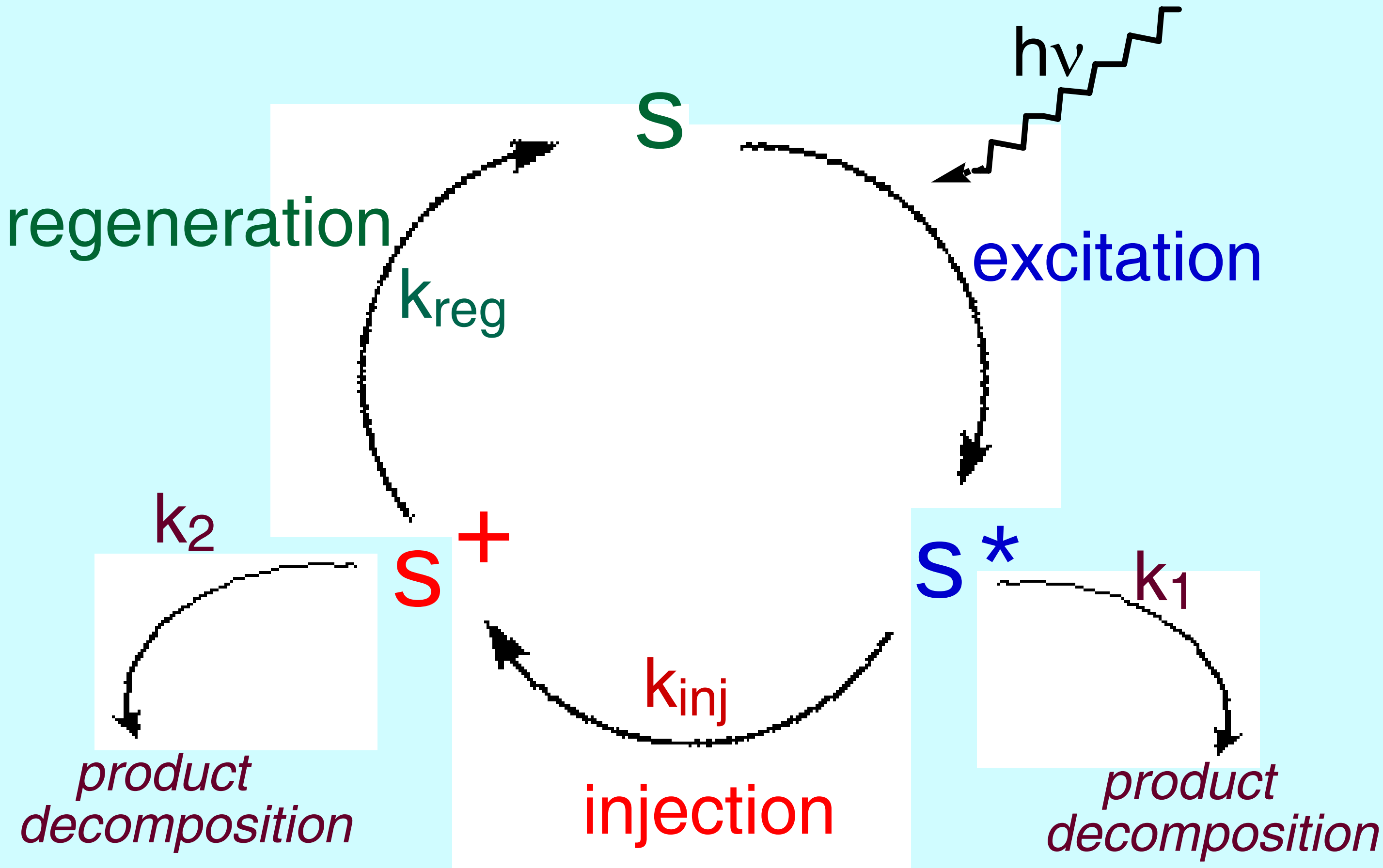
Not studied so far has been the effect of applyin periodic stresses. Physical failures but also healing effect are expected then.

In general, the authors have the impression, tha long-term stability of dye sensitised solar cells is not a intrinsic problem of the technology but can be improve further by better understanding of the degradatio mechanisms and the chemical balancing of the electrolyt components. The on-going work will therefore focu especially on the chemical part on a device level.

6. REFERENCES

[1] B. O'Regan, M. Grätzel, Nature, **353**, 1991, 737

The sensitizer has to sustain 100 million cycles during 20 years of outdoor cell operation



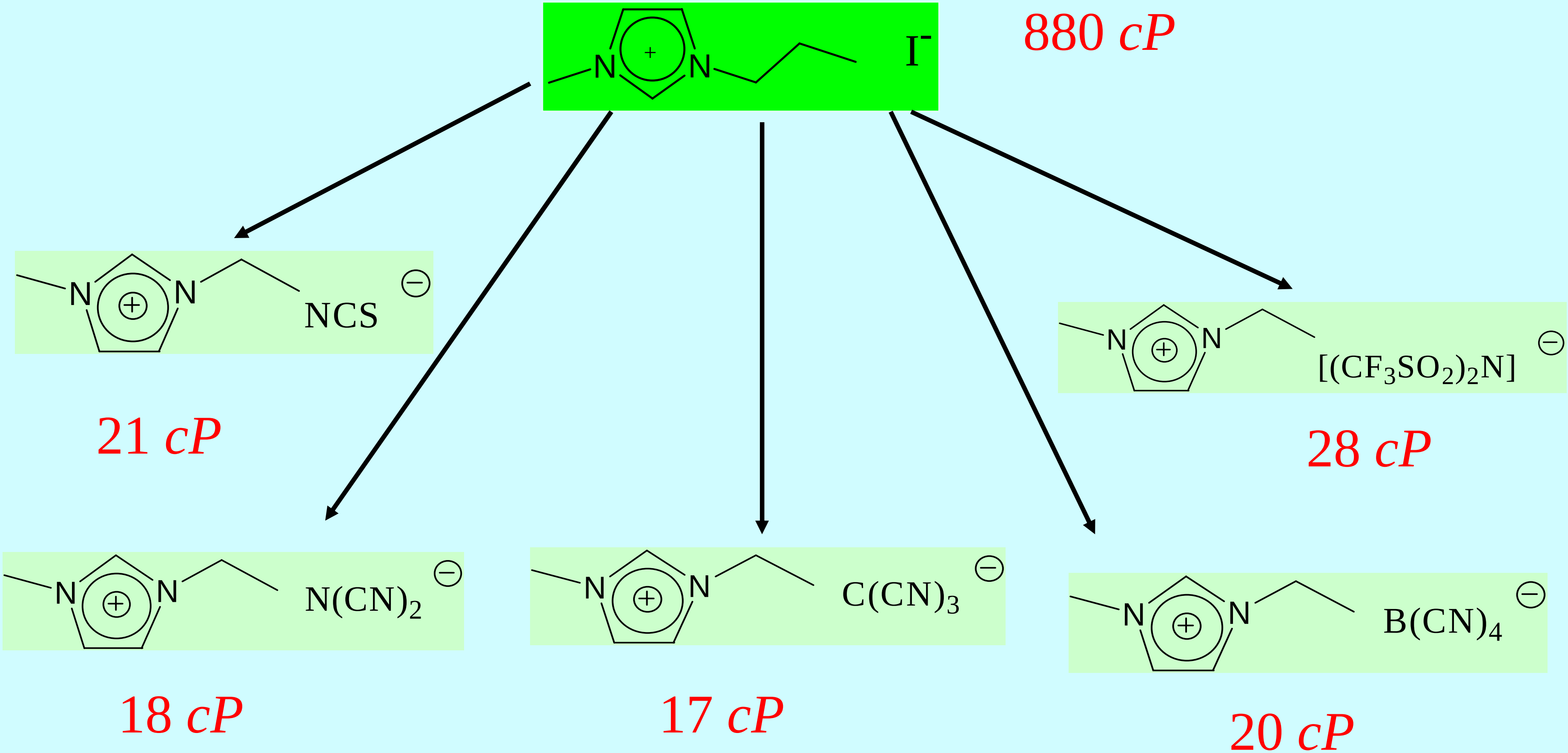
To reach 100 million turnovers branching ratios of k_{Inj}/k_1 and $k_{reg}/k_2 > 10^8$ are required

Ionic Liquids (Ils)have attractive features

- *Thermal Stability;*
- *Non Flammability;*
- *High Ionic Conductivity;*
- *Negligible Vapor Pressure;*
- *Wide Electrochemical Window;*
- *Non-toxic*

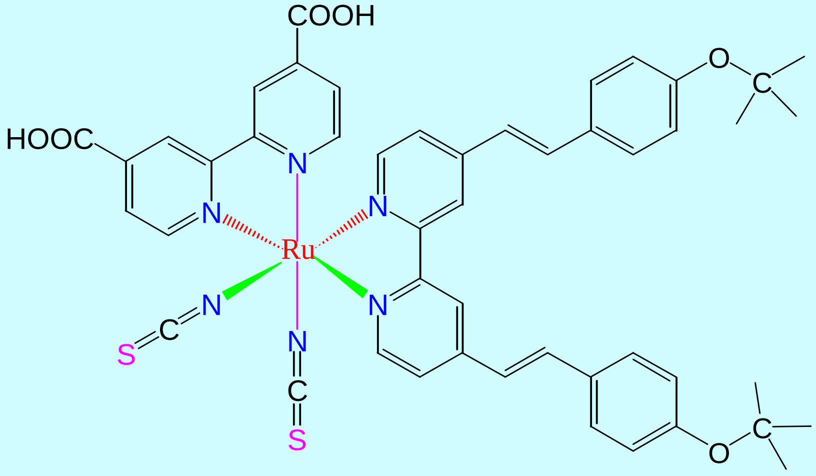
Solid polymer/IL gels are formed by the addition of poly-(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF–HFP)

Wang, P; Zakeeruddin, S. M.; Exnar, I.; Graetzel, M..
High efficiency dye-sensitized nanocrystalline solar cells
based on ionic liquid polymer gel electrolyte.
Chemical Communications (Cambridge, United Kingdom) 2002, 24, 2972-2973.

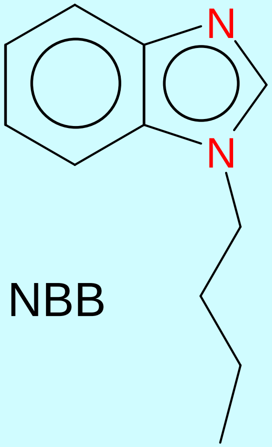

N N I-
880 cP
N N NCS
21 cP
N N [(CF3SO2)2N]
28 cP
N N N(CN)2
18 cP
N N C(CN)3
17 cP
N N B(CN)4
20 cP

K77+Ionic liquid based electrolyte

K77 sensitzer

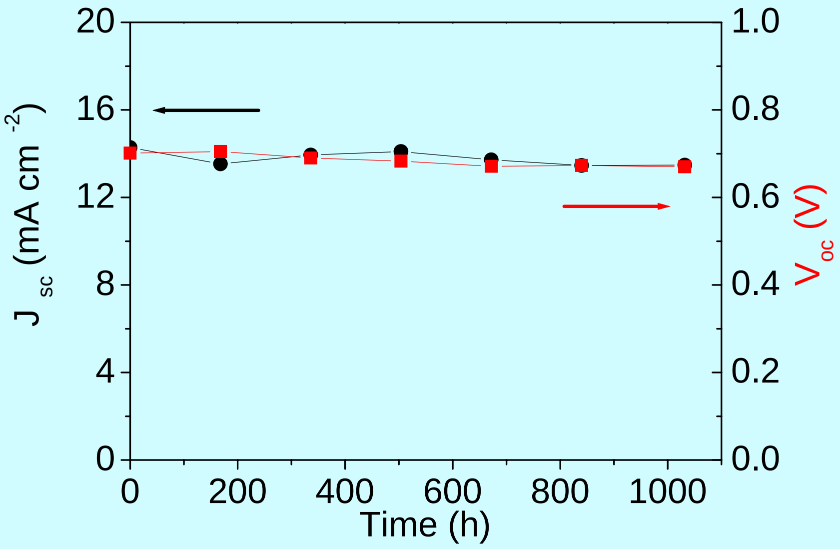


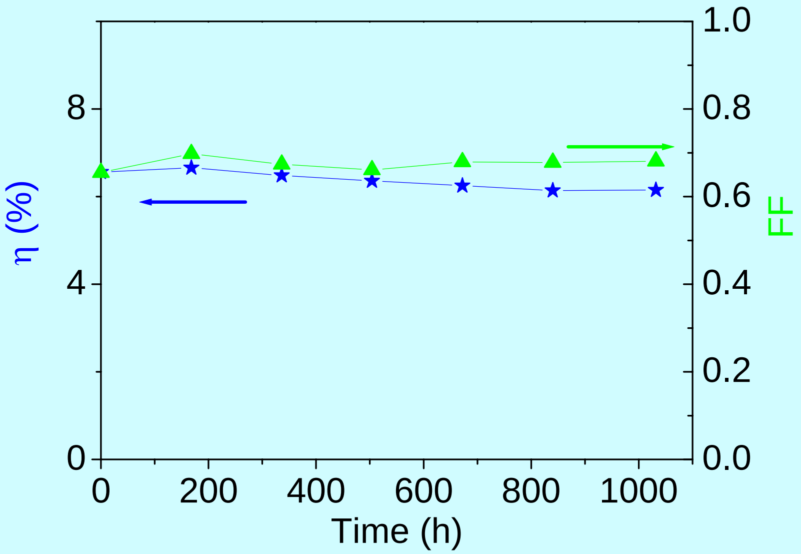
PMII/EMIB(CN)4
: 65:35 %
I_2 : 0.15 M
NBB: 0.5 M
GuNCS: 0.1 M



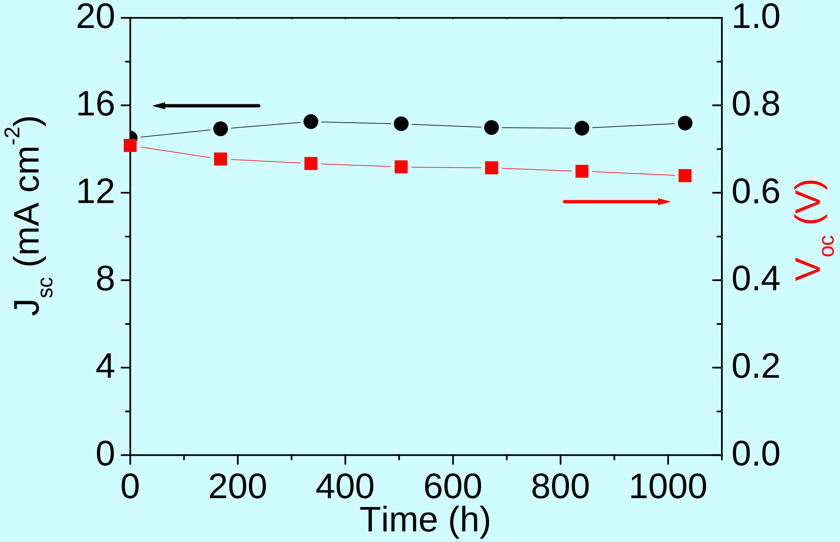
NBB

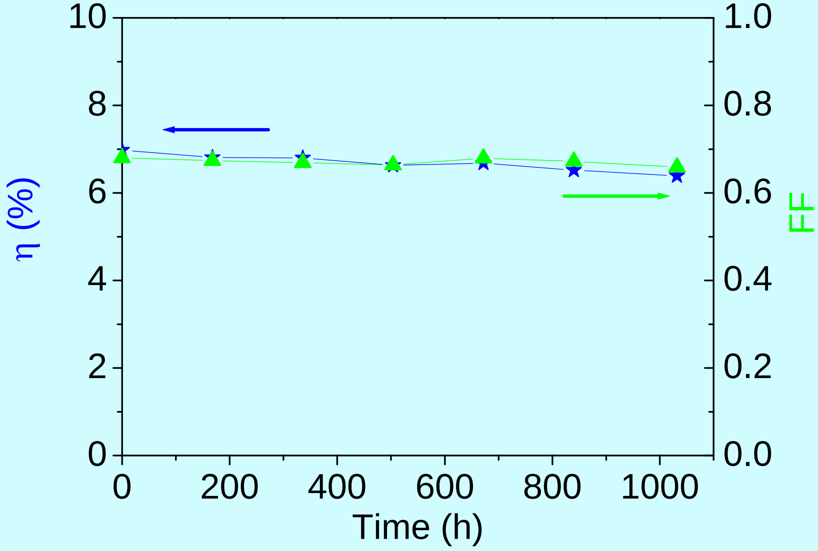
Stability, 80 degrees in dark



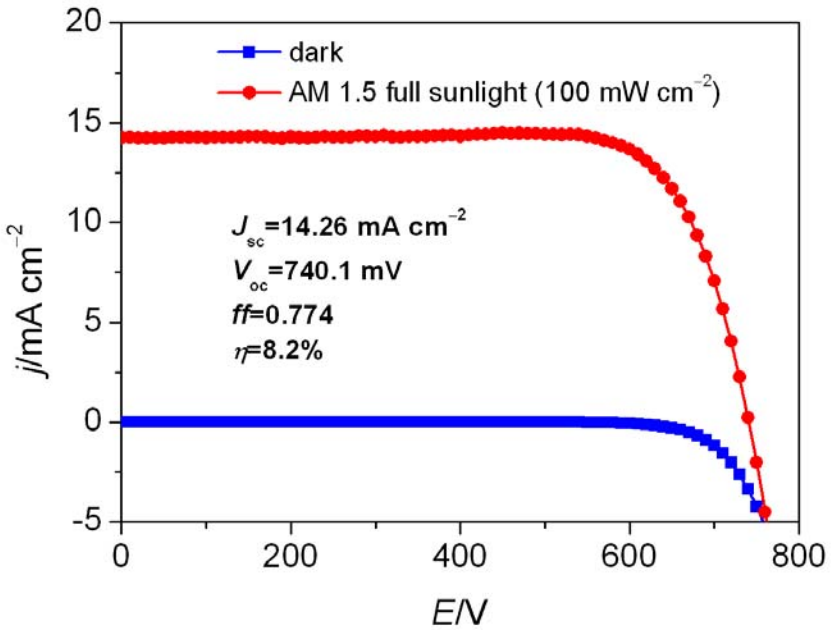


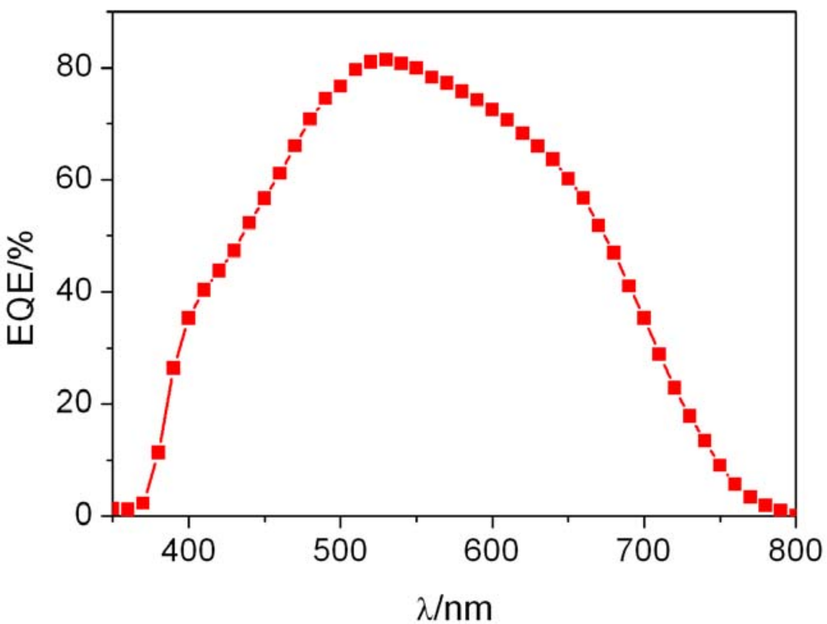
Stability, Light soaking at 60 degrees





Eutectic ionic liquids: a new efficiency record of 8.2%





Z907 Dye

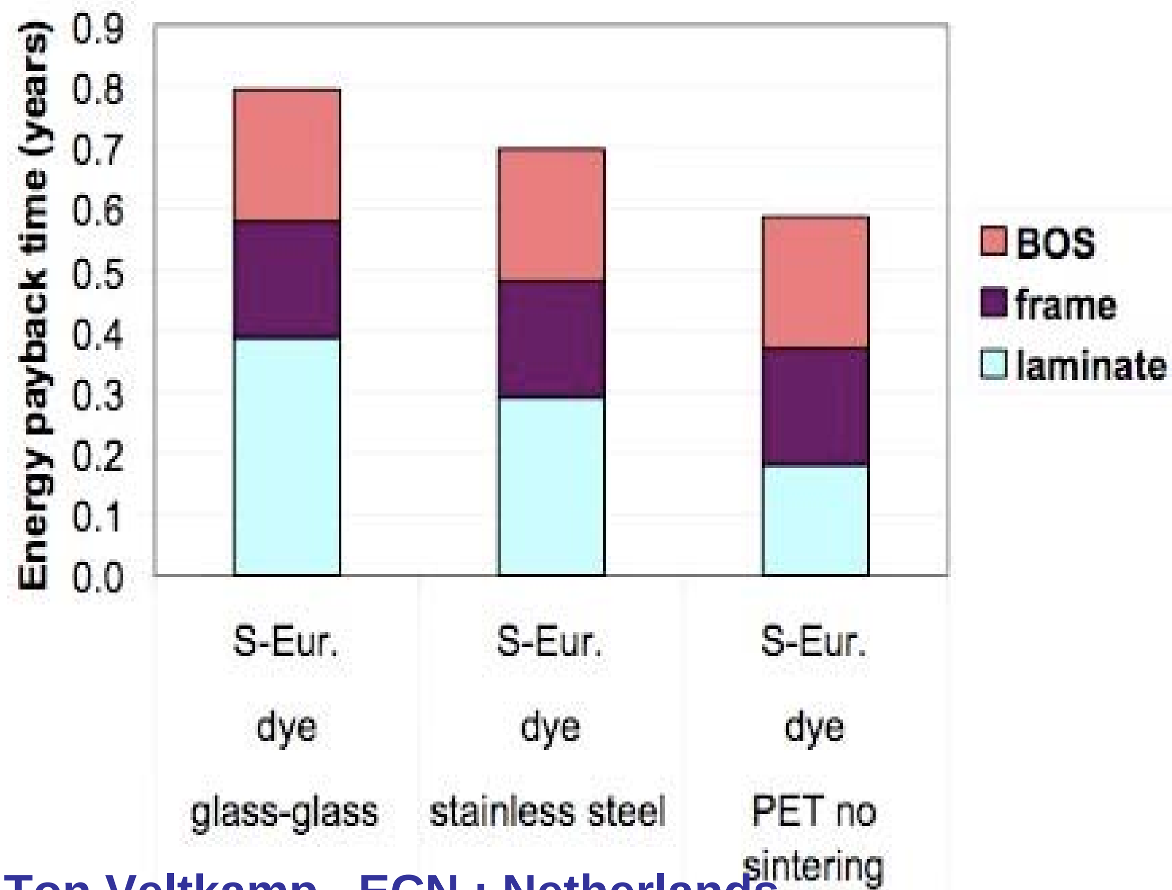
In collaboration with Prof. Peng Wang, CAS China

Our previous data: **7.4%** efficiency in **JACS 127 (2005) 6850**

Life cycle analysis

Dye sensitized cells have short energy payback times

Energy payback time with different substrates



Courtesy Dr. Ton Veltkamp , ECN ; Netherlands

Emerging and new applications call for:

- Ease of integration
- color
- flexibility
- light weight
- many more,,,

- **... further development and new technologies in order to meet optimally the customer demands and needs**

Courtesy Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

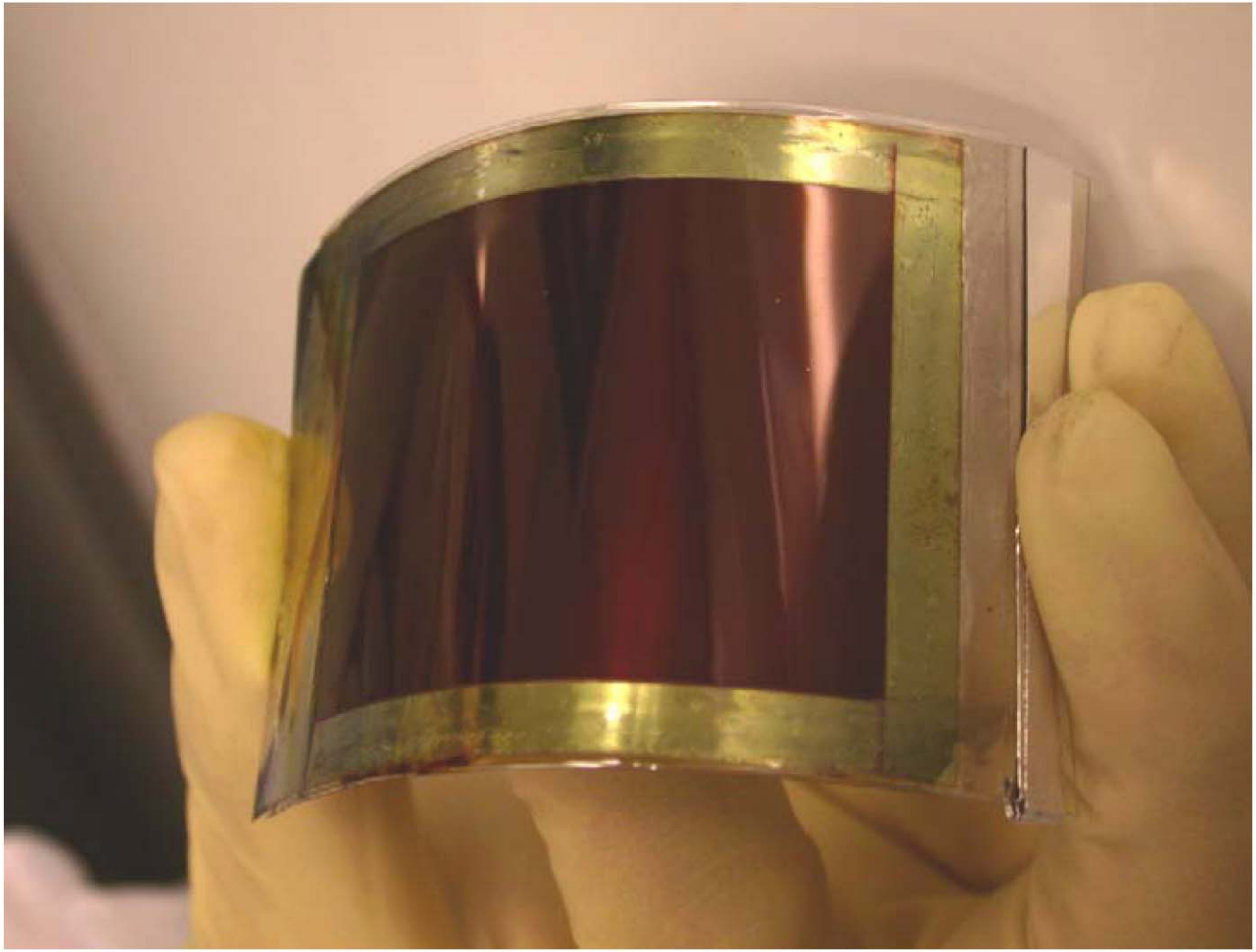
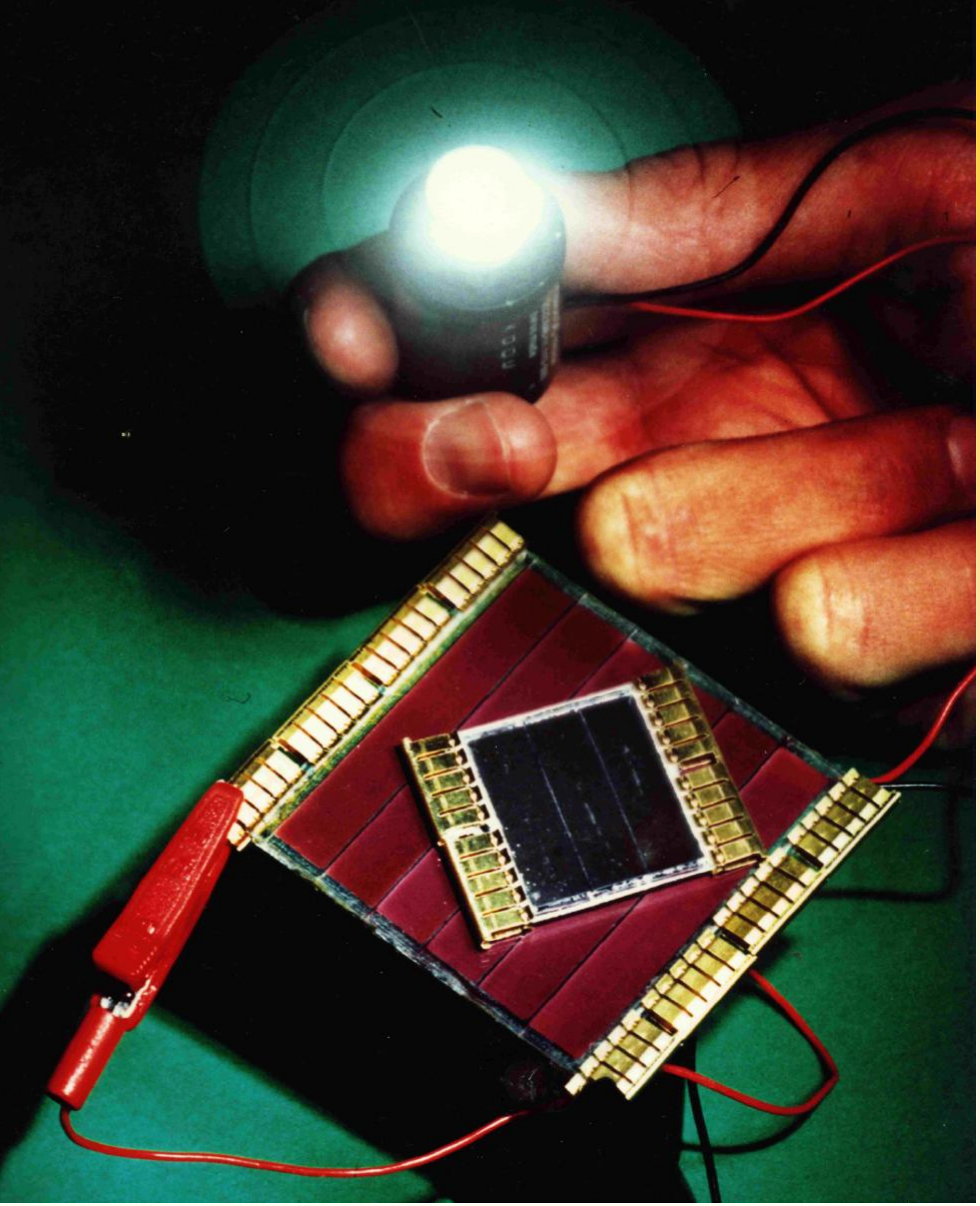
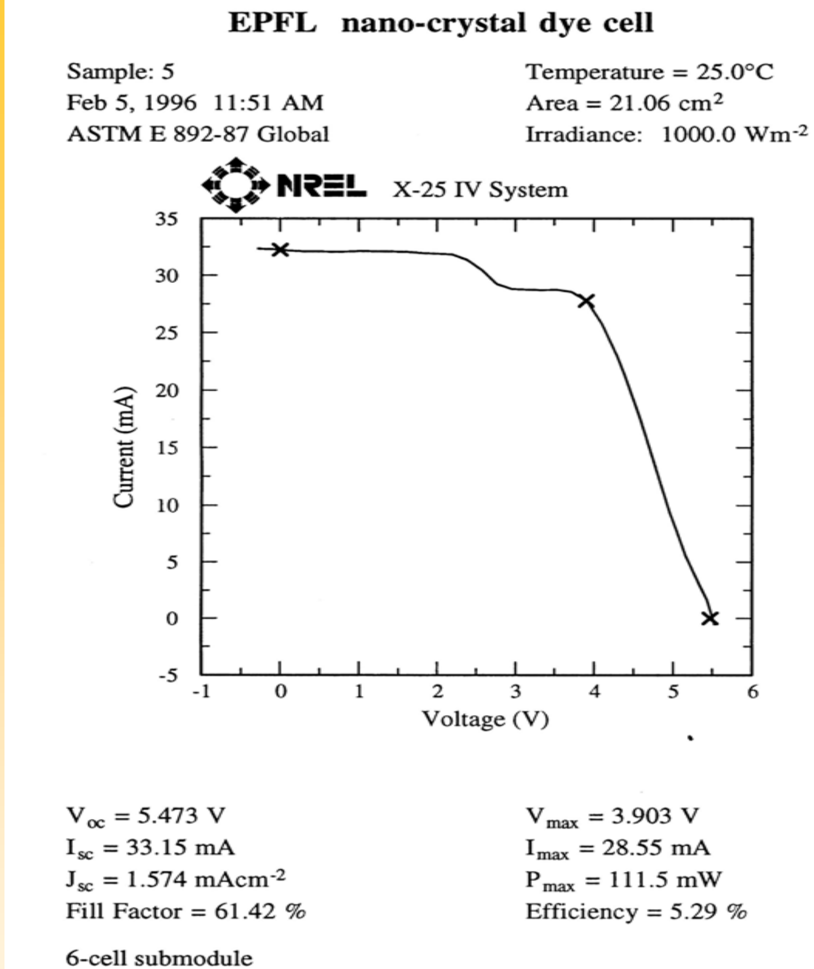


Fig. 1. A prototype of a stainless steel supported, flexible cell.

4.2% flexible DSC: M.G. Kang et al. / Sol. En. Mat. Sol. Cells, 90 (2006) 574.

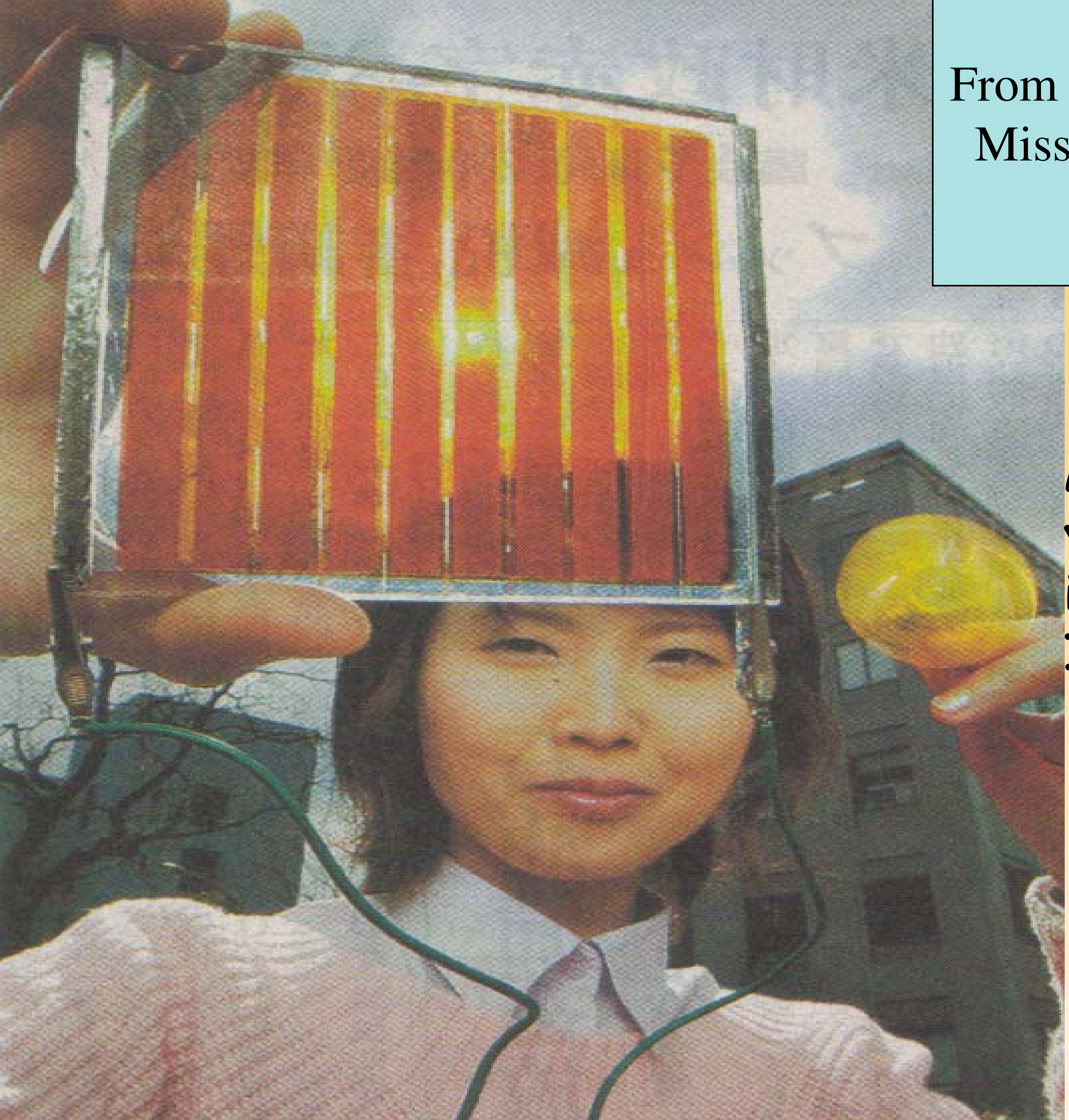
Scale-up and production





A.Kay, M.Graetzel, Low cost PV modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder.
Solar En. Mat. Solar Cells 1996), 44(1), 99- 17.

The first monolithic in series connected DSC modules showed a validated standard AM 1.5 G conversion efficiency of 5.3 %

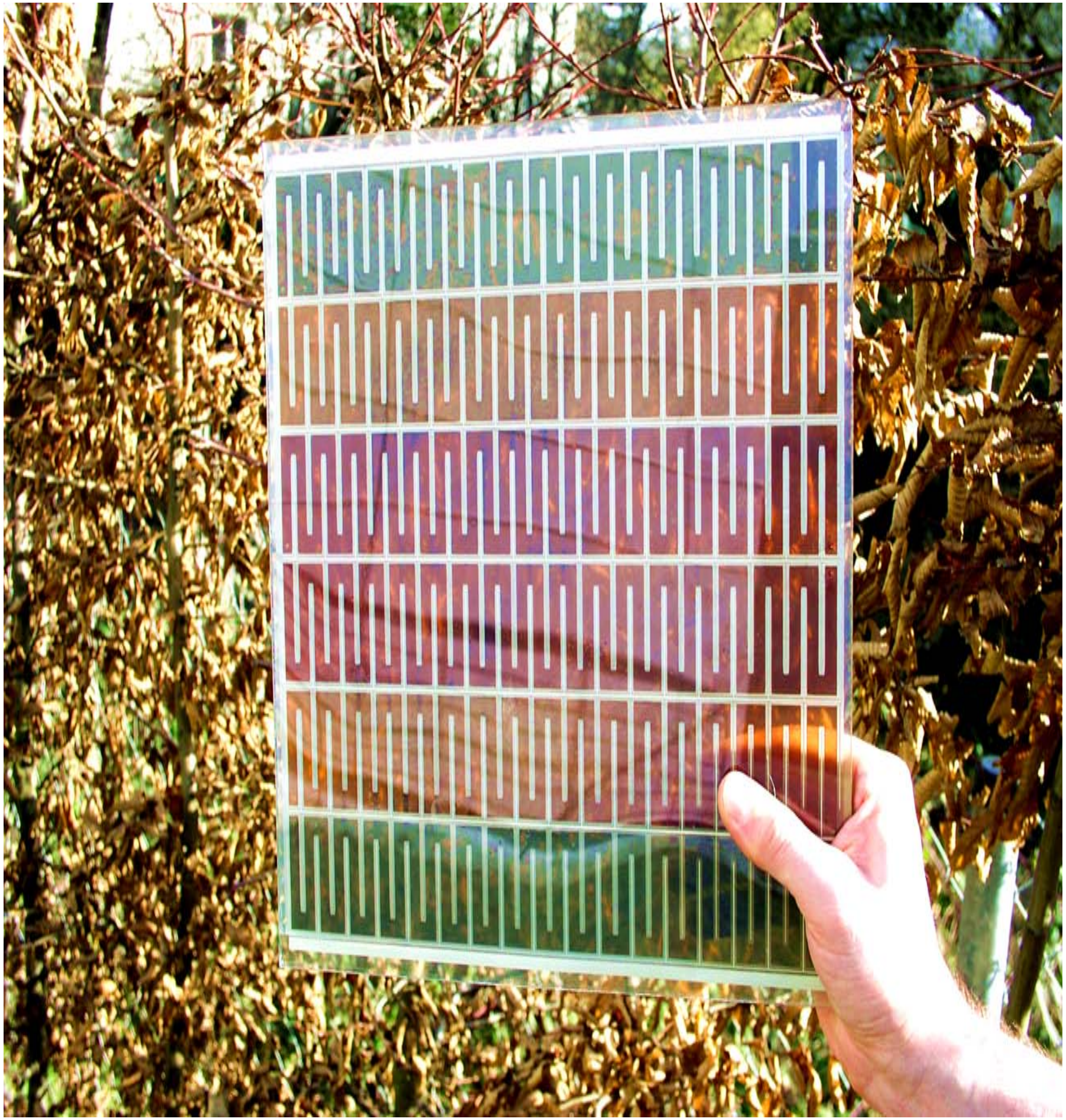


From Nikkei（日本経済新聞）
Miss Noriyo Yamanaka
Nippon Oil

Motivating the young generation is of paramount Importance !


色素増感型太陽電池
AISIN
消火器

Various colours in a series-connected dye solar cell module



Courtesy Dr. Andreas Hinsch, FHI, ISE Freiburg Germany


KYOCERA
TDK
TDK
TDK
TDK
STAF

10 m² of Dyesol DSC facade panels have been integrated to form a magenta »stripe« across the undulating wall floor-roof of one of the Houses of the Future on display at the Sydney Olympic Park.


QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.
HOUSE
OF THE
FUTURE

Courtesy Dr. Nam Gyu Park KIST

transparent, colorful, beautiful

Transparency: due to nano-sized (~20 nm) TiO_2 particle film

Color: due to visible light absorption by dye

* DSC costs lower than Si solar cell; 1/4 -1/5 of Si solar cell

Real Outdoor Test of DSC Modules

- Module Unit

Series connected
64 DSC cells

- Outdoor Test

Kariya City at lat. 35°10'N,
Asimuthal angle: 0°
Facing due south, Tilted at 30°

The Toyota Dream House

３）モジュール設置固定

8）バイオトイレ正面

G24I builds 120 MeW capacity plant for flexible DSC production in Wales

Adran Menter, Arloesi a Rhwyd
Department for Enterprise Inn
and Networks

Llywodraeth Cynulliad Cymru
Welsh Assembly Government

yddion News

Tuesday, 17th October 2

WORLD-LEADING SOLAR TECHNOLOGY FIRM TO INVEST IN WALES

A multi-million pound investment into a unique world-leading renewable energy technology is to create up to 300 jobs in South Wales, it was announced today **(Tuesday, 17th October 2006).**

G24 Innovations Ltd (G24i), a new UK registered company (whose major shareholder is Renewable Capital LP of the United States), is to manufacture dye sensitised solar cells – one of the latest, lightest, most efficient and least costly solar technologies in the world – at a 187,000 sq ft facility at Wentloog Park, Cardiff and plans to begin manufacturing early in 2007.

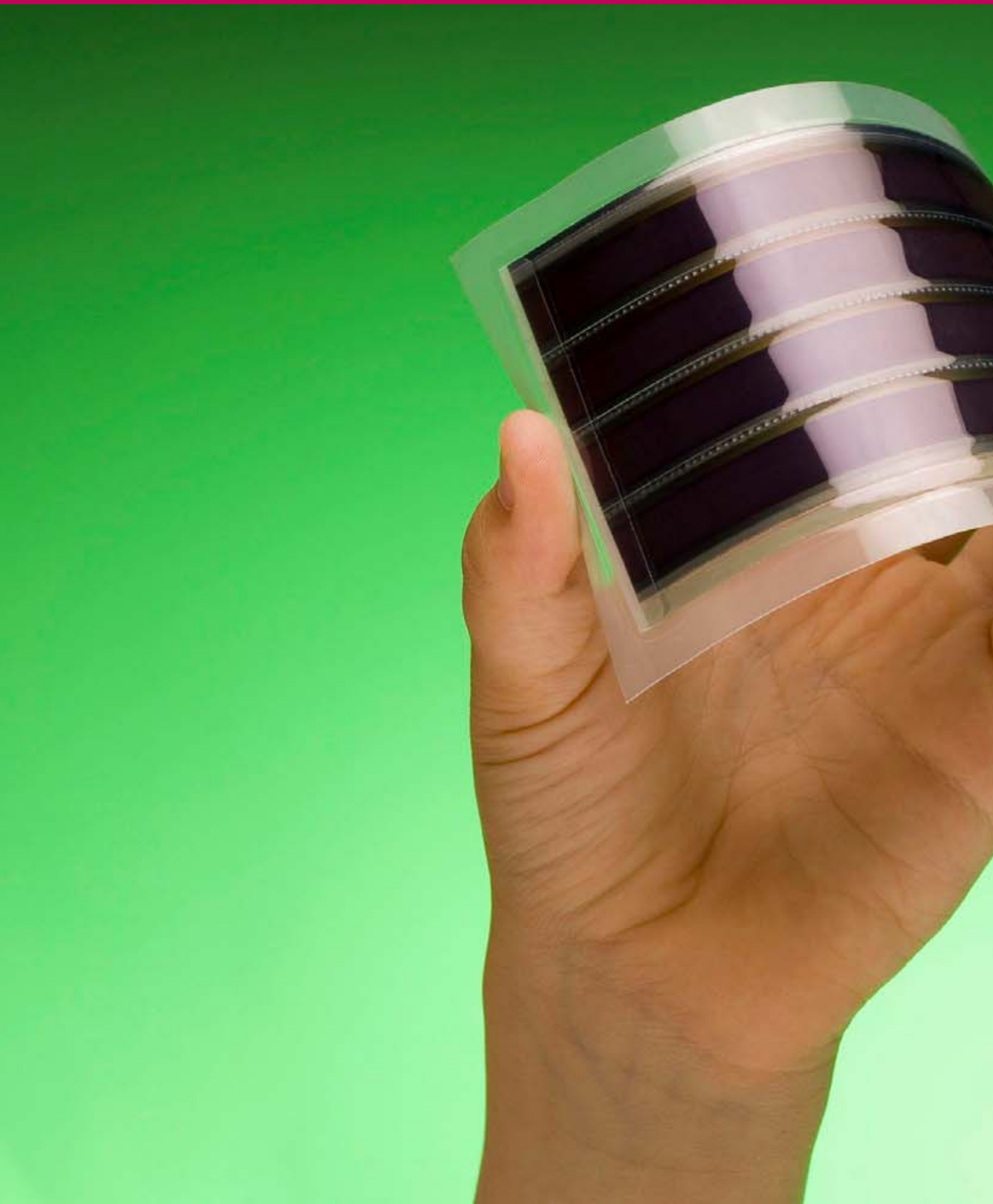
G24i's new cells will have potential application in a wide range of products although the initial market is expected to be for mobile consumer led products such as mobile phone chargers, smart textiles (incorporating the technology into fabrics), emergency and homeland security applications, MP3 players, laptop computers and handheld game consoles.

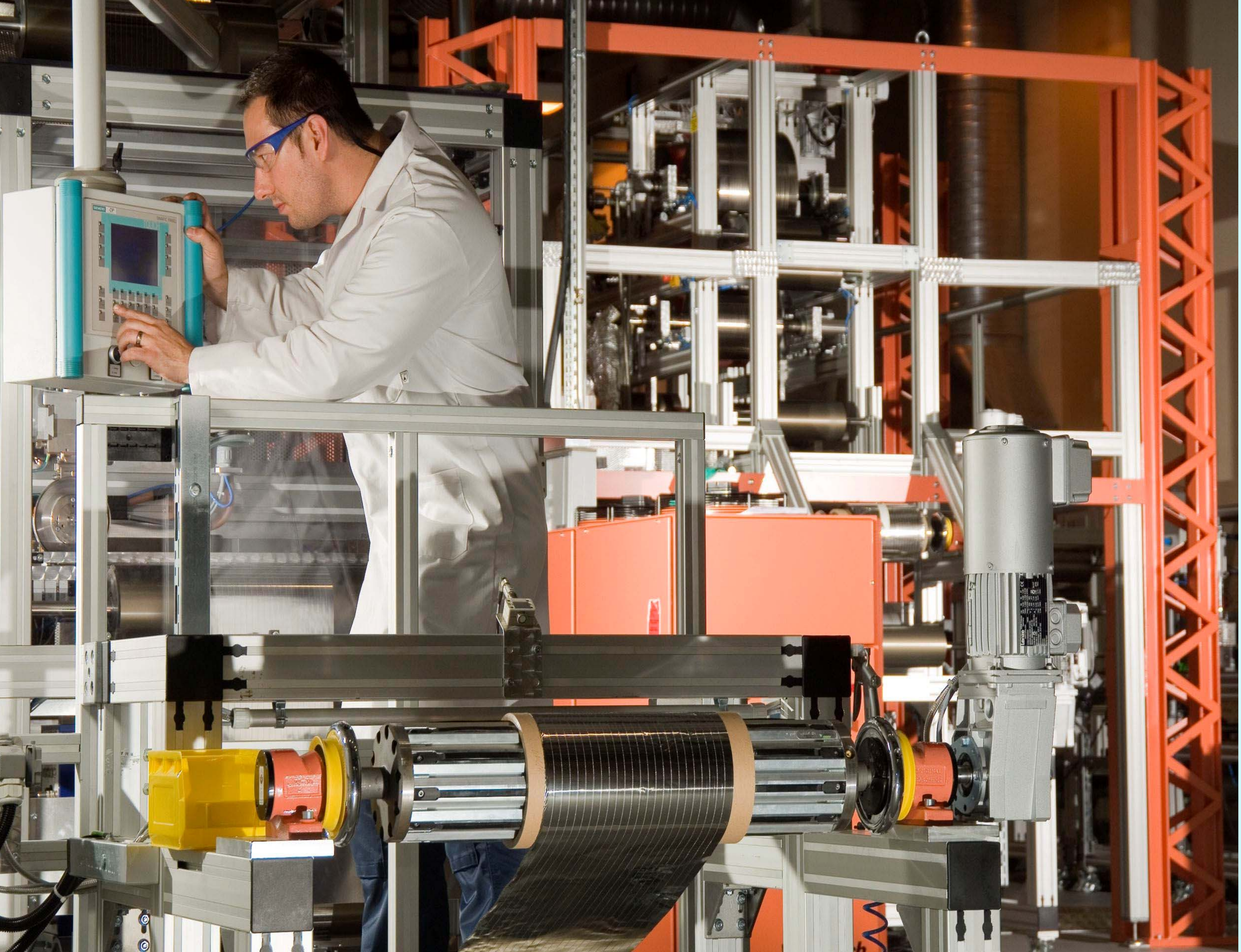
The company also believes there is an opportunity to integrate the cells in building products that can meet part of a building's energy requirements and further reduce carbon emissions.

Founders of G24I: Ed Stevenson and Robert Hertzberg (64th speaker of Californian State Assembly)

The G24I plant in Cardiff has started production on June 21 (solstice),2007

The first G24I product is a light weight flexible power supply for mobile telephones



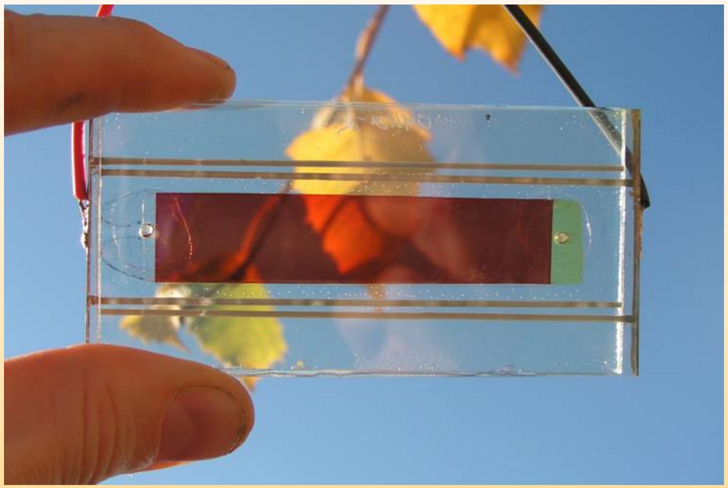


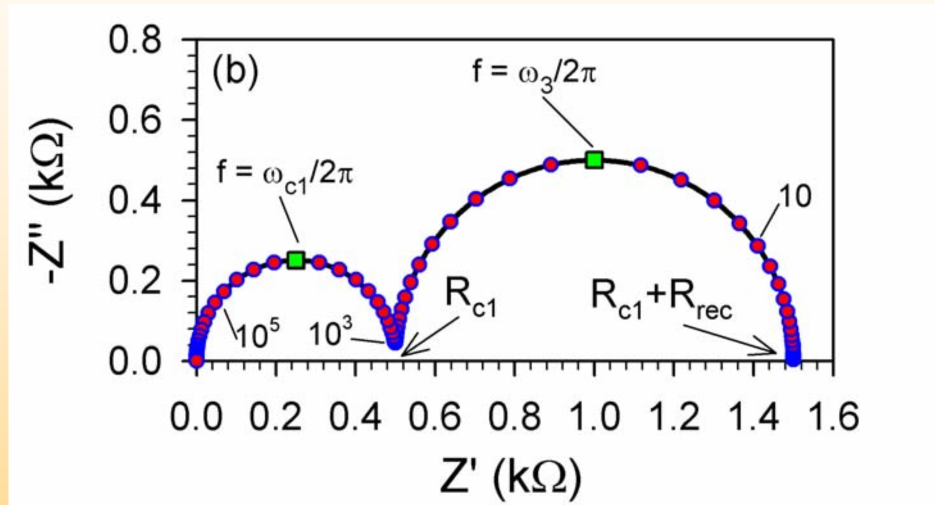
The attractive features of dye sensitized nanocrystalline solar cells

- current efficiency of > 11 percent is already competitive with conventional PV devices.
- multijunction and multiexciton devices offer path to efficiencies of > 30 %.
- Short energy pay back time of (< 1 year)
- unique light weight, flexibility transparency, and color options facilitate market entry
- Low materials and manufacturing cost, roll to roll 35 megawatt production of flexible foil cells started in Wales (www.g24i.com).

Impedance studies of mesopic solar cells

Tutorial NUS January 18, 2008





Michael Graetzel,
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE
Visiting Professor MSE/NUS

Michael.Graetzel@epfl.ch