
Nanostructured Interfaces and Surfaces
Centre of Excellence
Università di Torino
NIS Colloquium
Classical and new approaches to thin film photovoltaics
Monday, June 23, 2008
Aula Magna, Experimental Physics Department, Via Pietro Giuria 1, Torino
Dye Sensitized Solar Cells
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ENERGY FROM THE SUN

Energy needs: more than **15TW** per year
Sun energy on earth surface: **120000 TW**

Energy delivered from the sun in Italy (centre): 1400 kWh/m^2 per year
Family needs: 2kWp (approximately)
16-20 m^2 of photovoltaic devices with a 12.5-10% efficiency

Lower the photovoltaic module cost per Wp/m^2!

DSSC ADVANTAGES

- *Low cost material*
- *Processes: simple and low cost*

Low cost,
different colors

Transparent, light weight
Flexibility
Easy of integration

- *Efficiency independent from temperature*
- *Can use diffuse light!*

1991: Nanocristalline photovoltaic cells

LOW COST HIGH EFFICIENCY SOLAR CELLS

LETTERS TO NATURE

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

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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.

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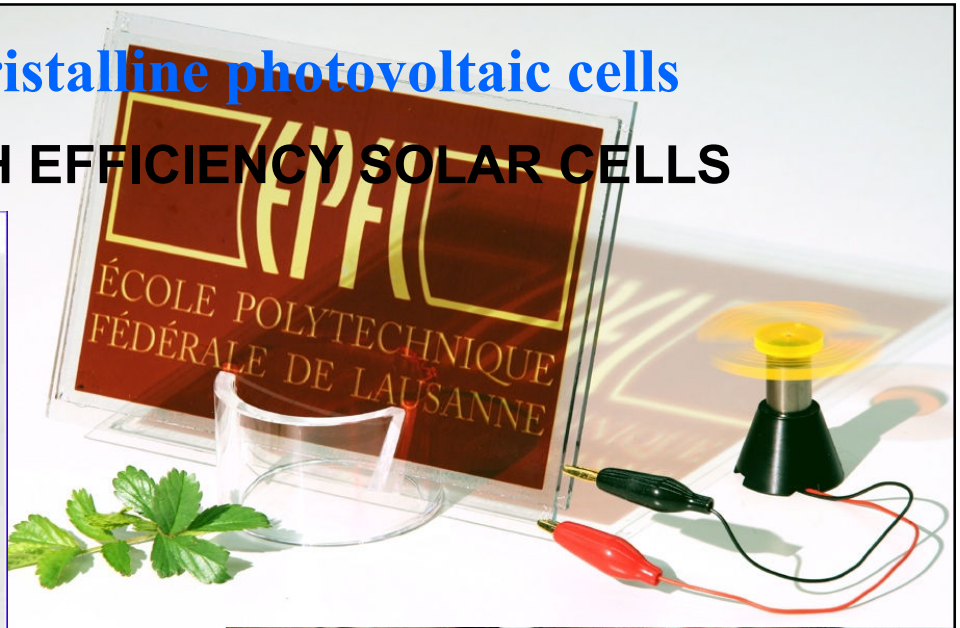
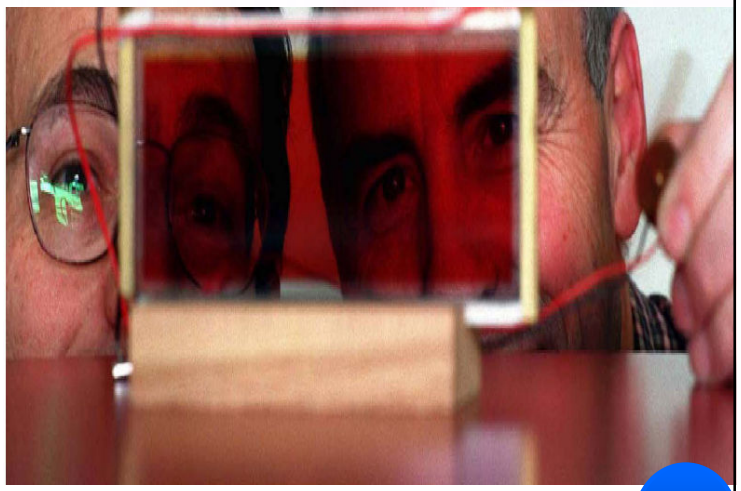
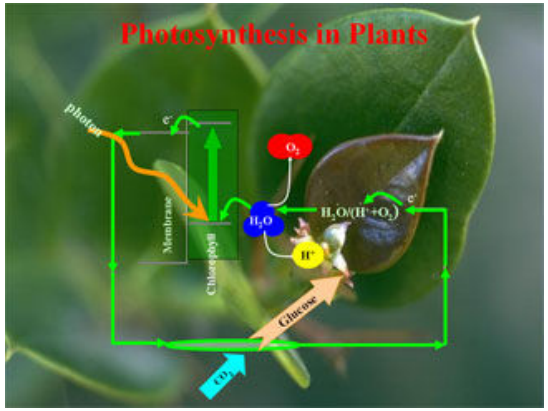
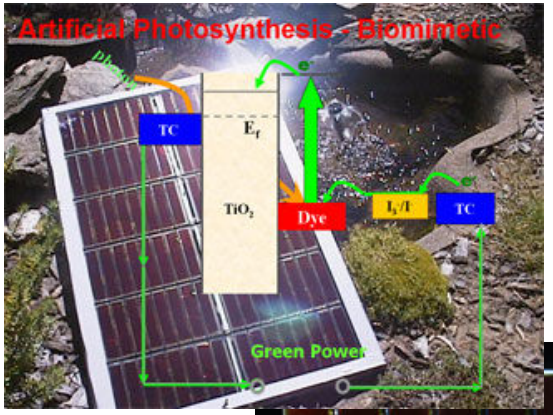
† To whom correspondence should be addressed.

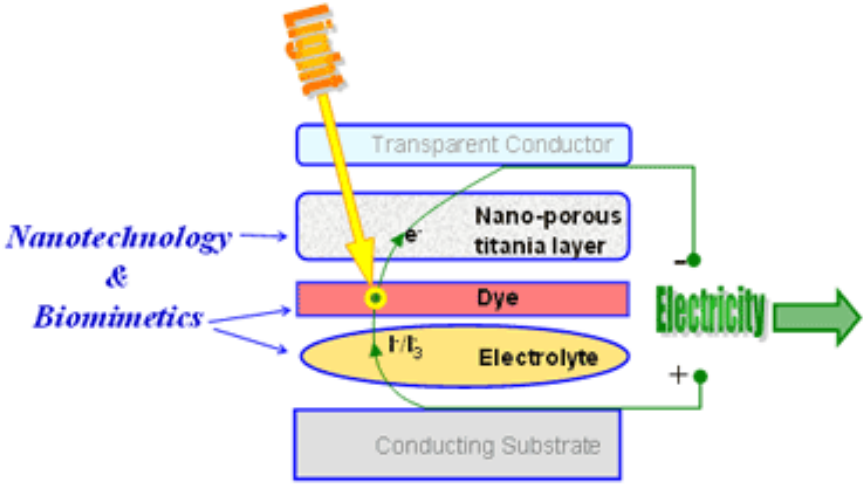




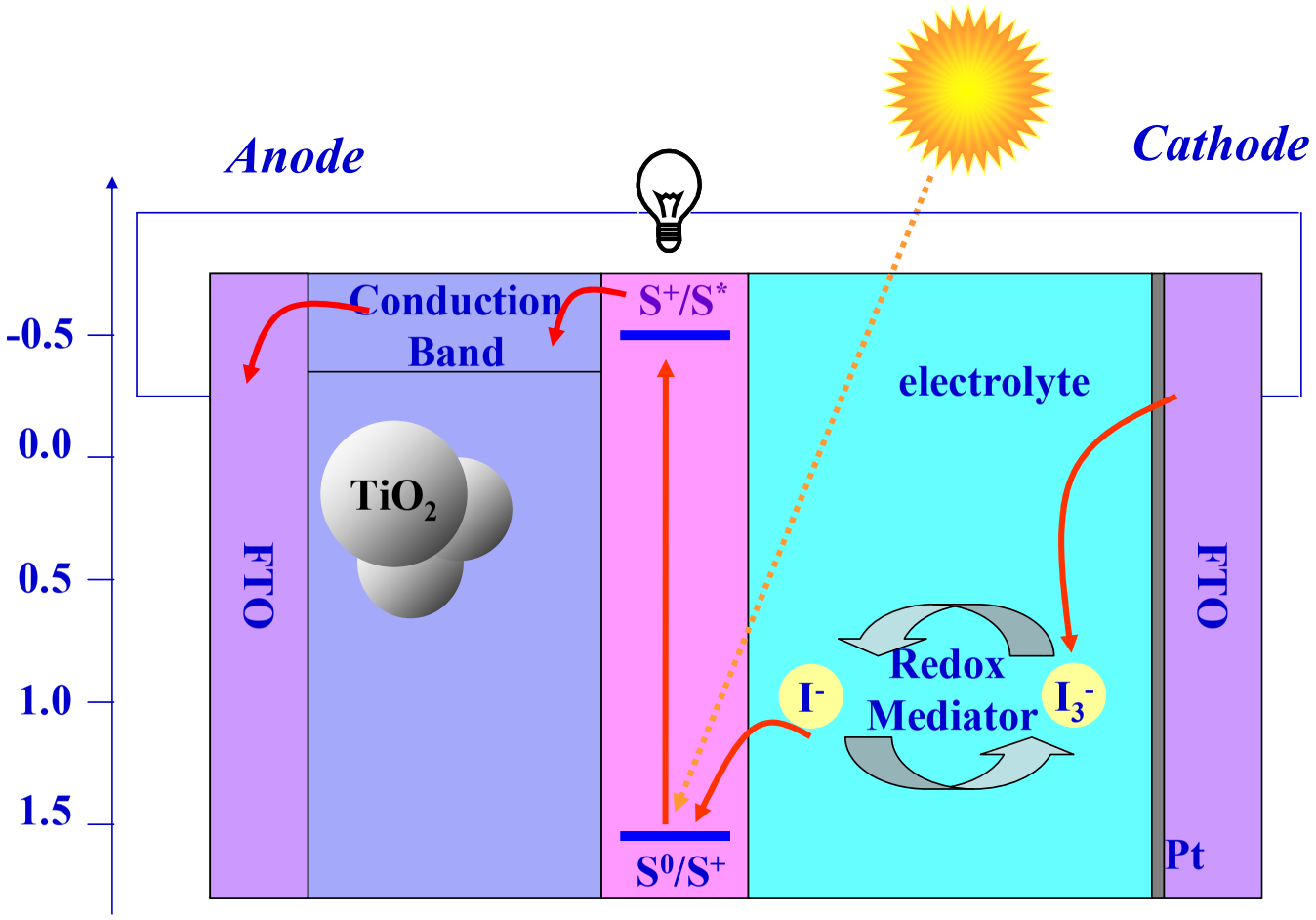
POWER FROM ARTIFICIAL PHOTOSYNTHESIS







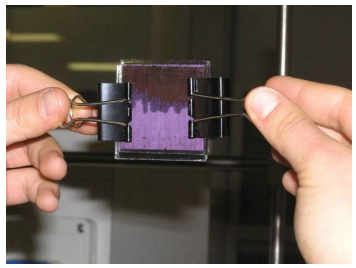
DSC: how does it work?



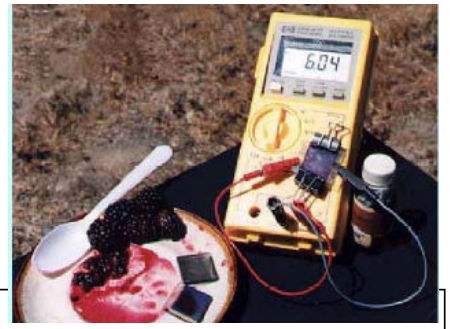
C. Barolo – Dye Sensitized Solar Cells

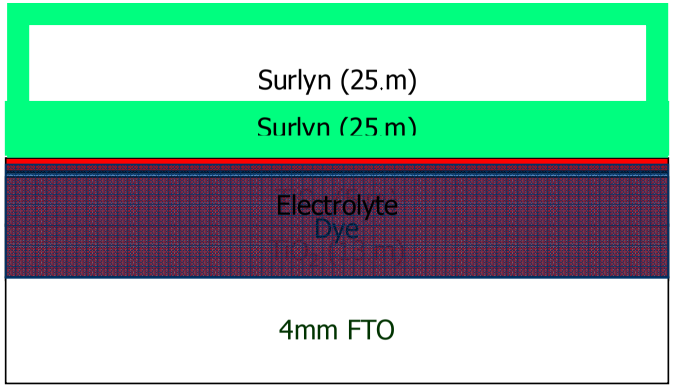
6

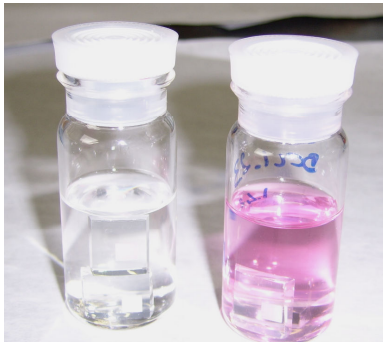
DSC's: cell preparation

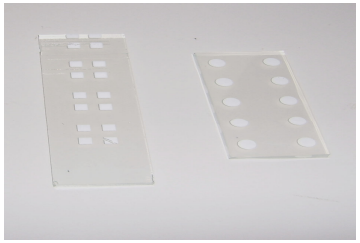


Tenda della scienza 9-11 maggio 2008



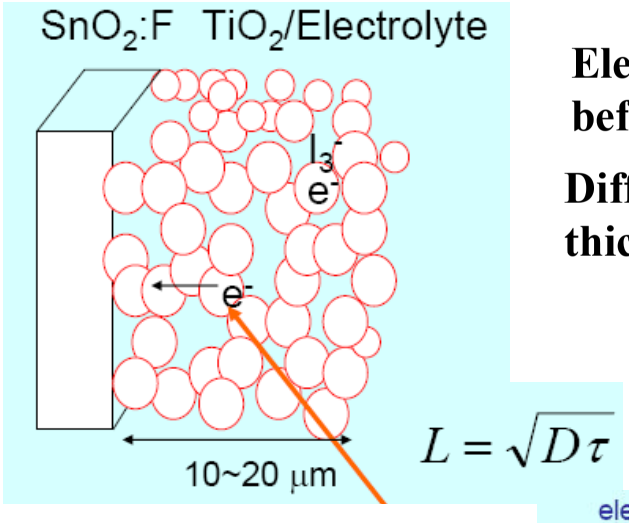






DSC: how does it work?

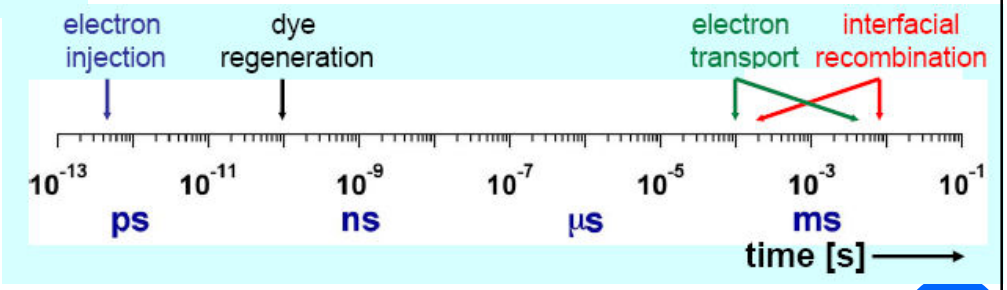
Dye sensitized nanocrystals show quantitative conversion of the photons into electric current



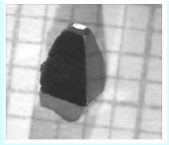
Electrons should travel to the SnO_2 before charge recombination occurs

Diffusion length should exceed the thickness of the mesocopic TiO_2 film

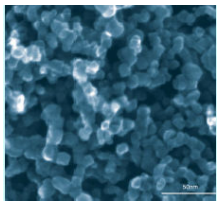
DYNAMIC COMPETITION



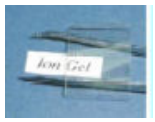
DSSC: components

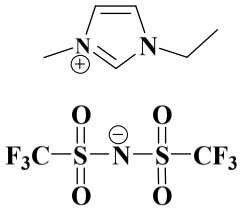


- Doped crystal, (101) surface

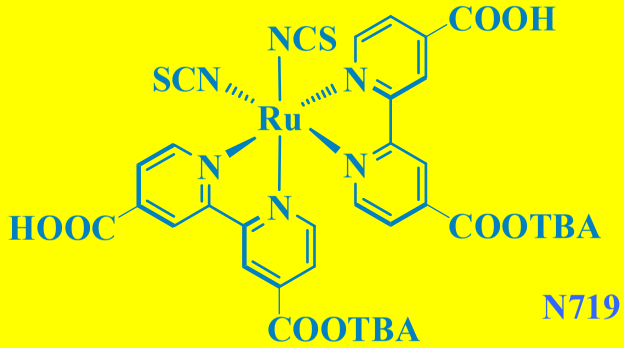


Wide band gap semiconductor ***TiO_2 anatase***





Robust electrolyte ***ionic liquid***

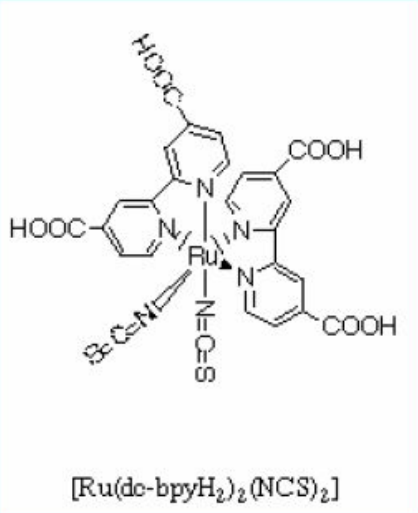


Sensitizer ***Ru oligopyridylic complexes***

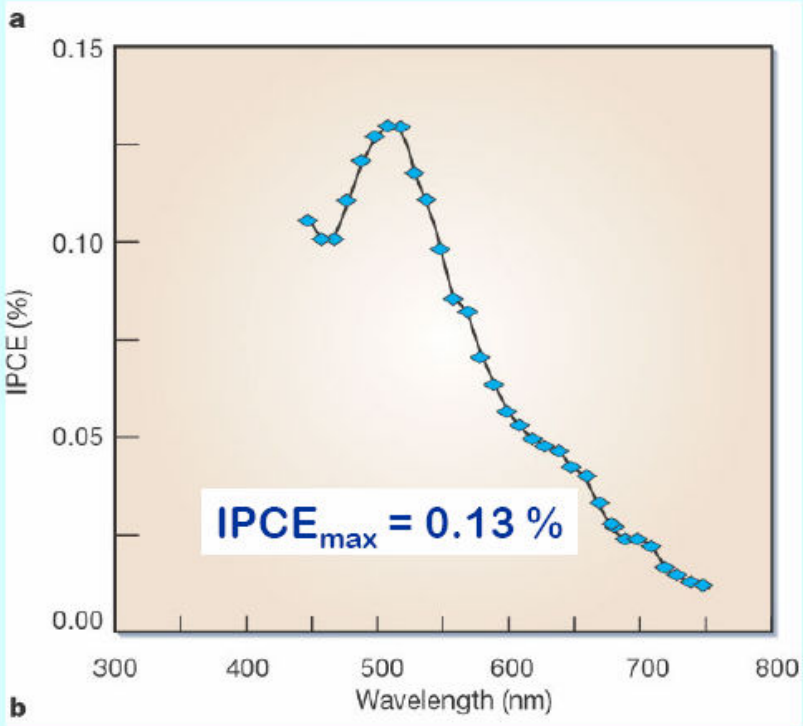
N719 $\eta = 11\%$

Nanostructured TiO_2

Incident photon to electron conversion efficiency (IPCE) of a dye-sensitized TiO_2 (101) single crystal PEC solar cell

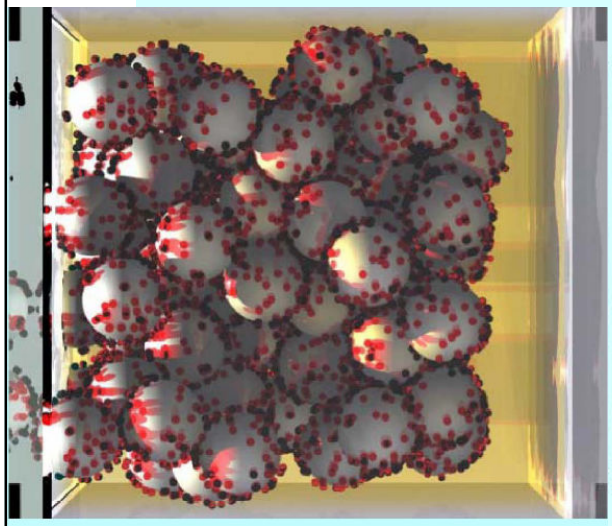


$[Ru(dc\text{-}bpyH_2)_2(NCS)_2]$

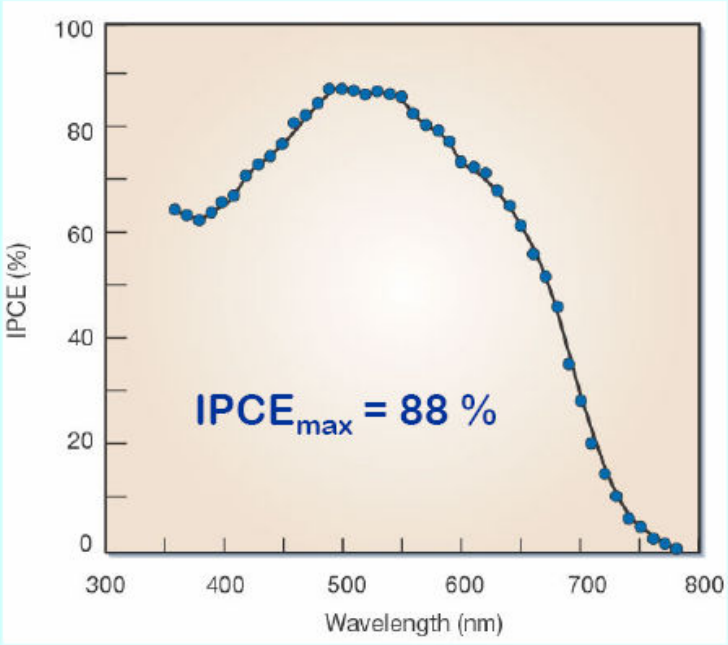


Nanostructured TiO_2

Incident photon to current conversion efficiency of a dye-sensitized solar cell based on a mesoscopic TiO_2electrode



Courtesy of Dr. Arthur J. Frank, NREL, USA



TiO_2 paste

FABRICATION OF SCREEN-PRINTING PASTES

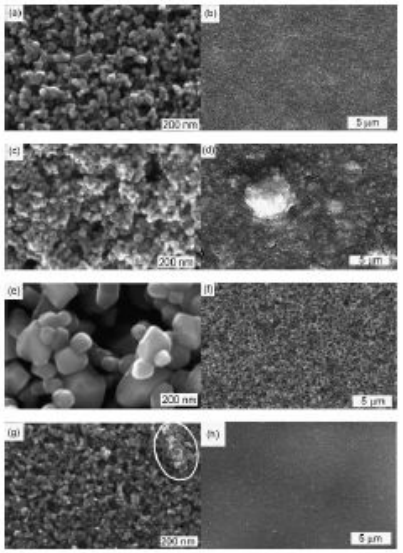


Figure 2. SEM photographs of porous TiO_2 films showing the surface morphology of P25 (a, b), ST21 (c, d), ST41 (e, f) and homemade TiO_2 (d = 20 nm) (g, h) with two types of magnification: 120000× (a, c, e, g) and 5000× (b, d, f, h)

FABRICATION OF SCREEN-PRINTING PASTES

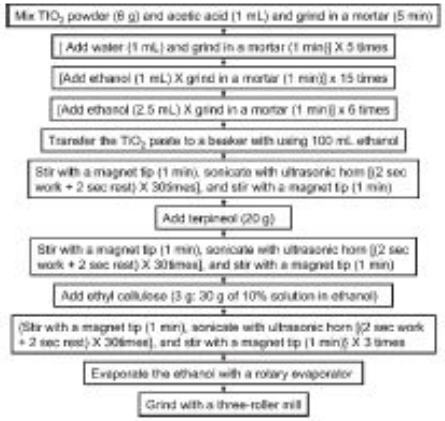


Figure 1. Fabrication scheme of screen-printing paste from a nanocrystalline-TiO_2 powder

S. Ito et al. Prog. Photovolt: Res. Appl. 2007
DOI: 10.1002/pip

ELECTROLYTE

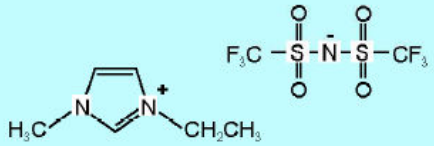
SOLVENT FREE SYSTEM:

- **solid electrolytes (polymer)**
- **solidified ionic liquid**
- **hole conductors**

ION-GEL Electolyte (NEDO)

Features of Ionic Liquids

- Consists of only Ions
- Liquid under wide temp. range ex. -10℃ to 400℃
- non volatile
- Chemically stable and non combustible
- High electronic conductivity



1-Ethyl-3-methylimidazolium - Bis(trifluoromethylsulfonyl) Amide

EMIm-TFSA

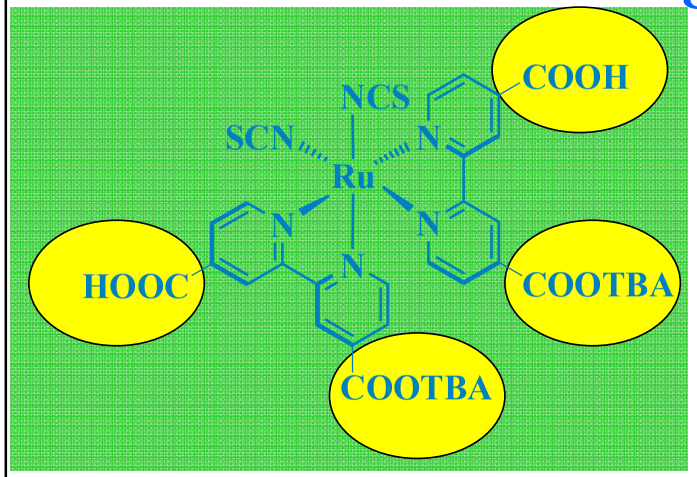
Sensitizers Engineering Approaches

Sensitizers Synthesis

Outlines

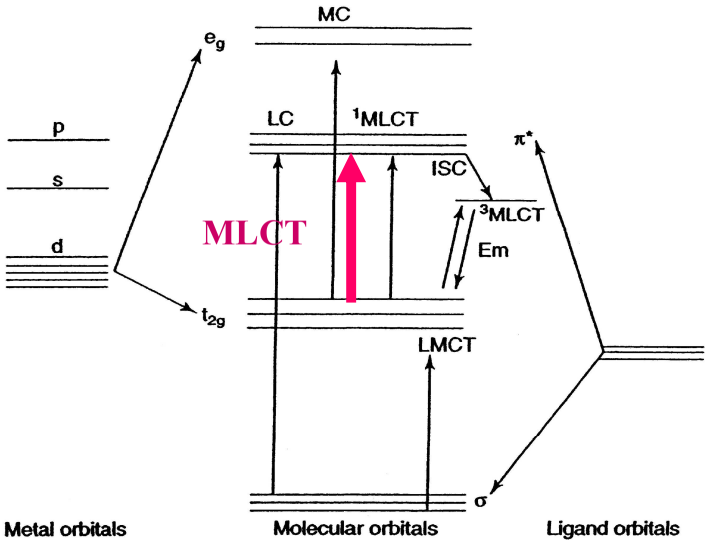
- Classical Organometallic Sensitizers
- Tetradentate Organometallic Sensitizers
- Organic dyes: a new generation of sensitizers?
- *Characterization of the sensitizer absorbing solution*

Sensitizers: Engineering Approaches

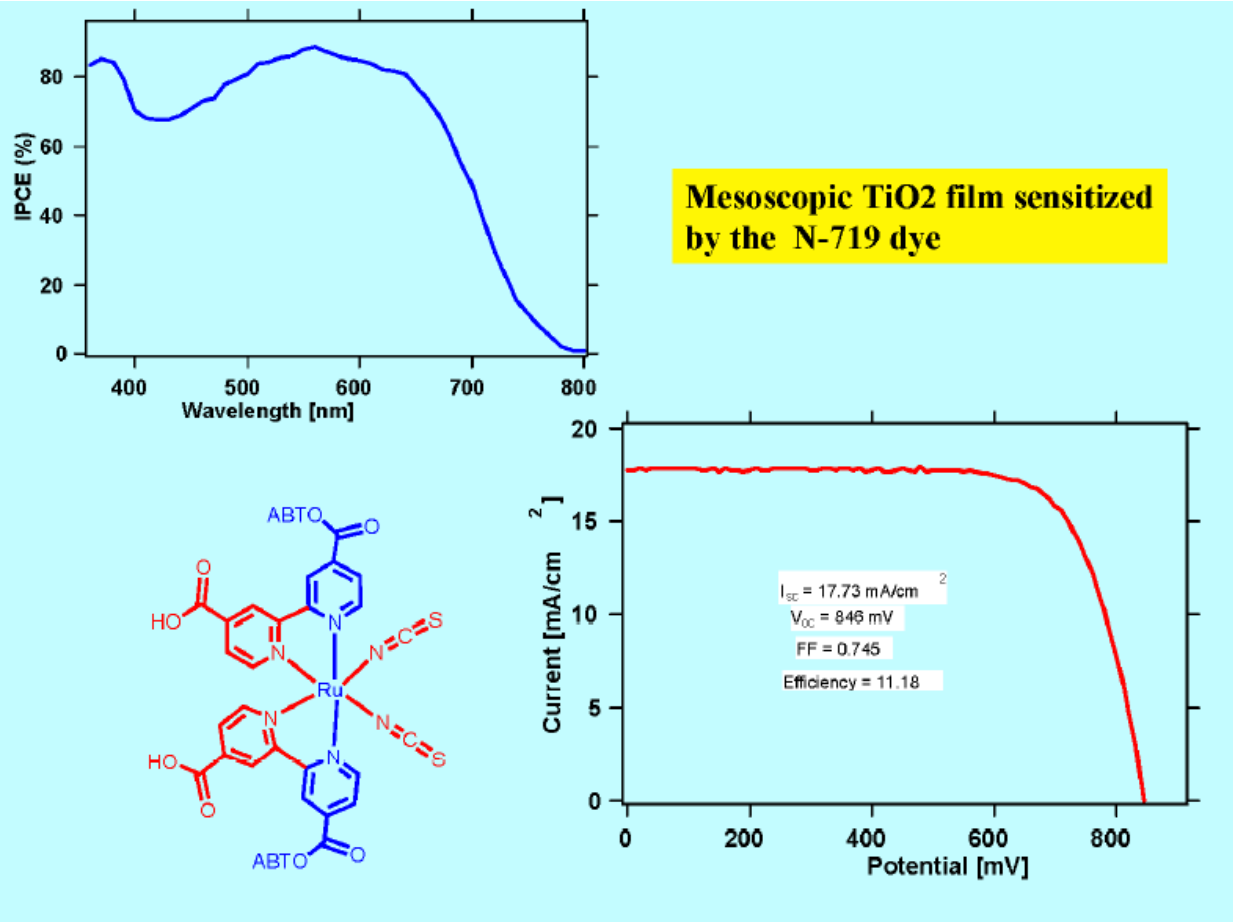


N 719 η=11.2%

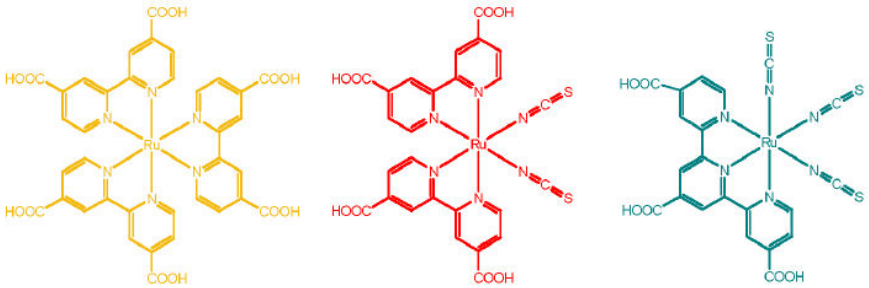
Ru oligopyridylic complexes

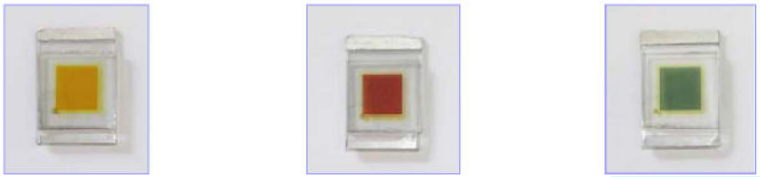


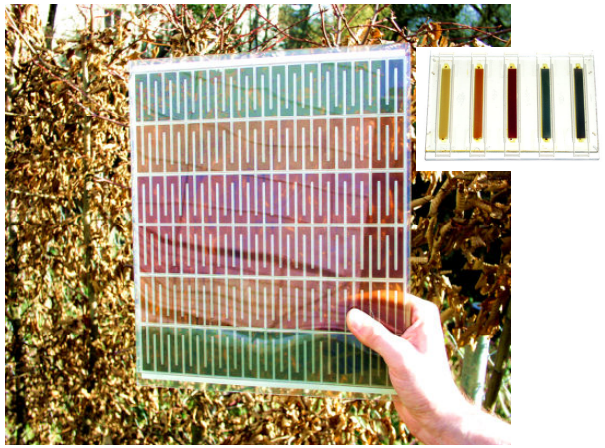
Sensitizers: Engineering Approaches



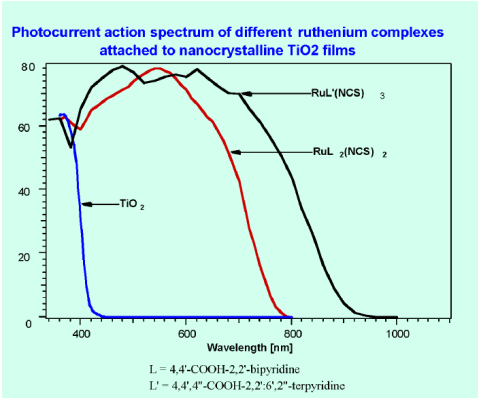
Sensitizers: Engineering Approaches



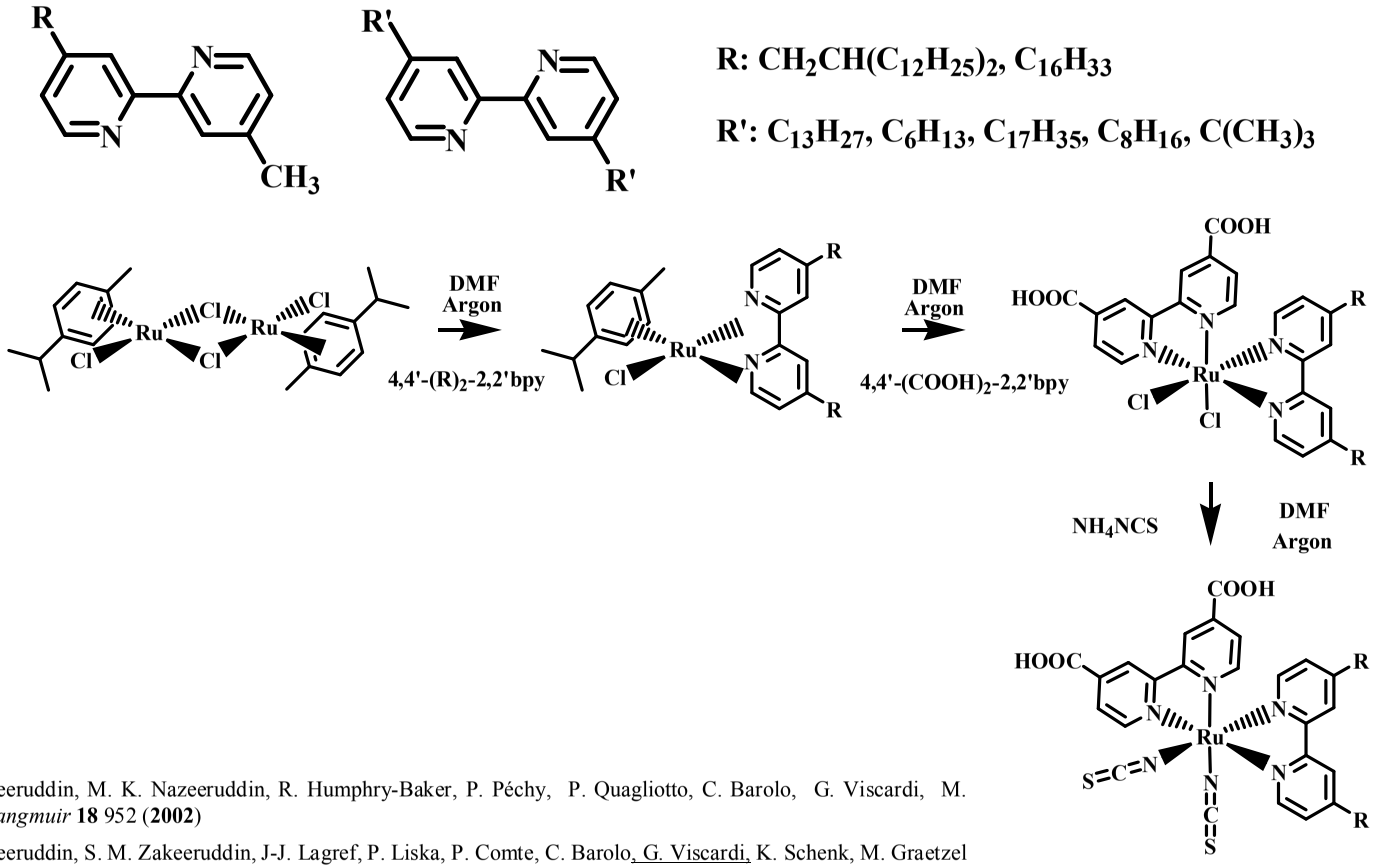




Courtesy of RWE



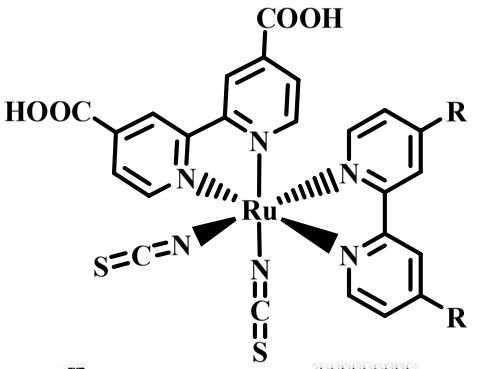
Heteroleptic Hydrophobic Sensitizers

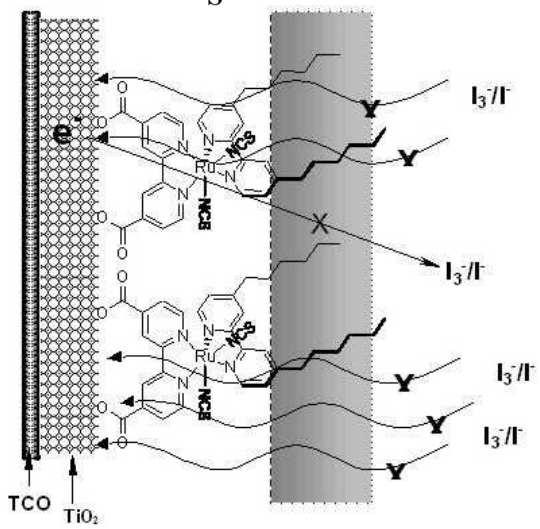


S. M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker, P. Péchy, P. Quagliotto, C. Barolo, G. Viscardi, M. Graetzel *Langmuir* **18** 952 (**2002**)

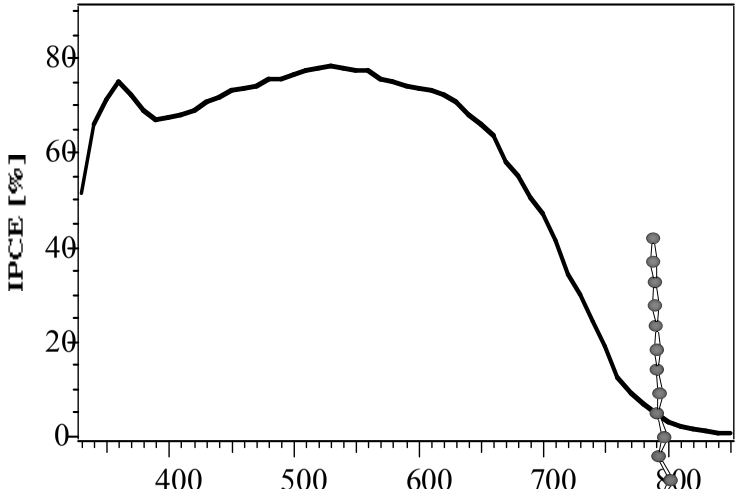
M. K. Nazeeruddin, S. M. Zakeeruddin, J-J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Graetzel *Coord. Chem. Rev.* 248 (13-14): 1317-1328 (**2004**)

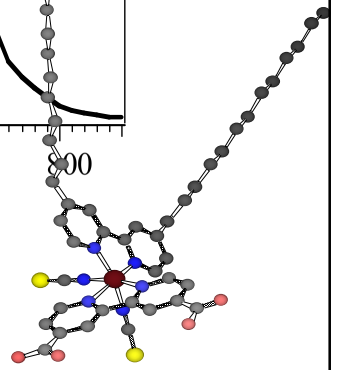
Heteroleptic Hydrophobic Sensitizers





- *long term stability in presence of water*
- *better overall efficiency*





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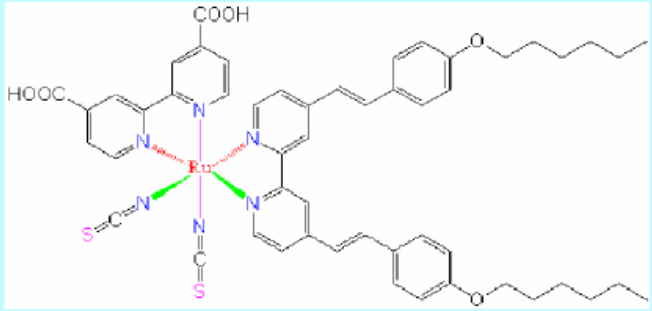
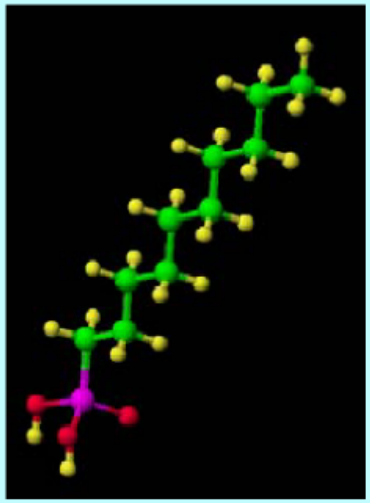
Sensitizers: Engineering Approaches
HIGH STABILITY!

K-19



Photoanode: 8+5

Decylphosphonate



ROBUST Electrolyte

PMII: 0.8 M

I_2: 0.15 M

NMBI: 0.5 M

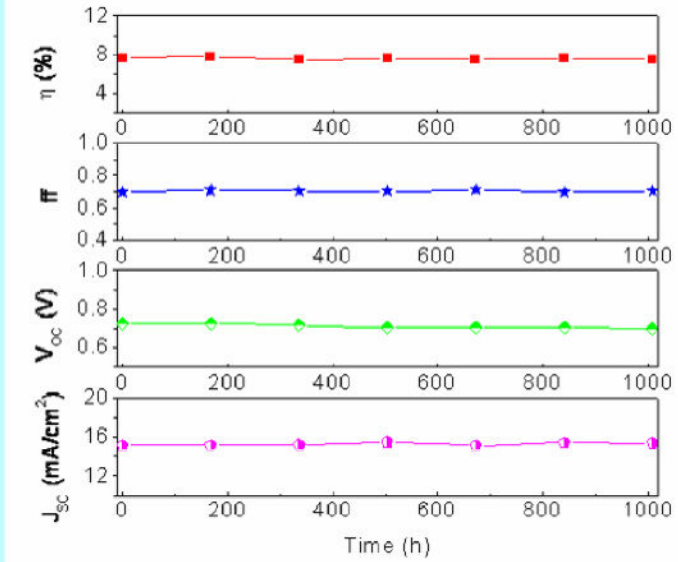
0.1 M GSCN

MPN solvent

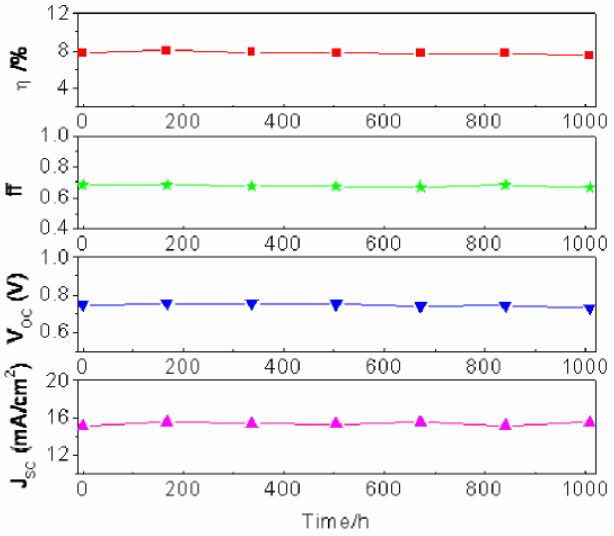
Efficiency: > 8.0%

Sensitizers: Engineering Approaches
HIGH STABILITY!

80 °C evolution of device parameters in the dark



60 °C evolution of device parameters under one sun soaking

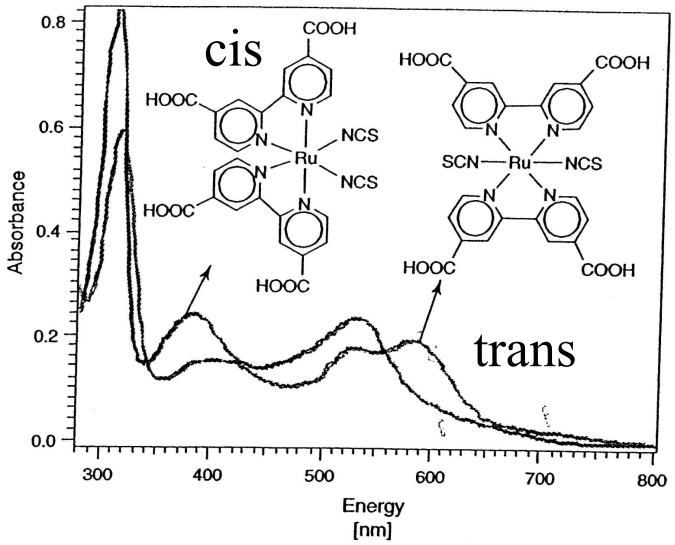


Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. Appl. Phys. Lett. 2005, 86. 123508.

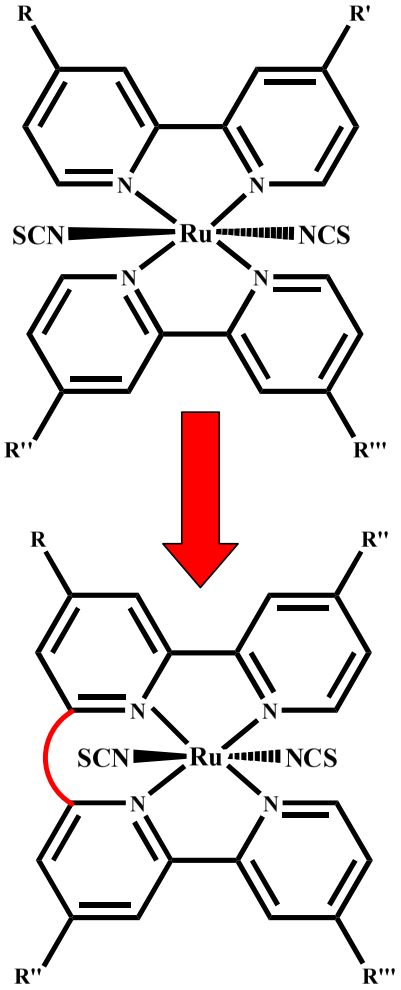
Tetradentate Sensitizers

PURPOSE IN RESEARCH: absorption as large as possible in the visible

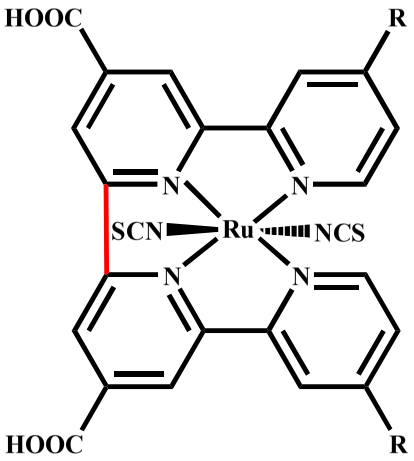
Background



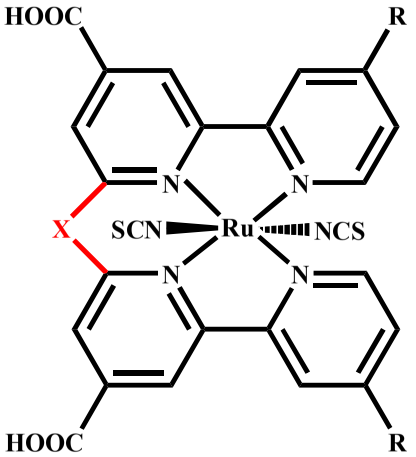
Md. K. Nazeeruddin et al. *Coord. Chem. Rev.* 208 213 (2000)



Tetradentate Sensitizers: the two models

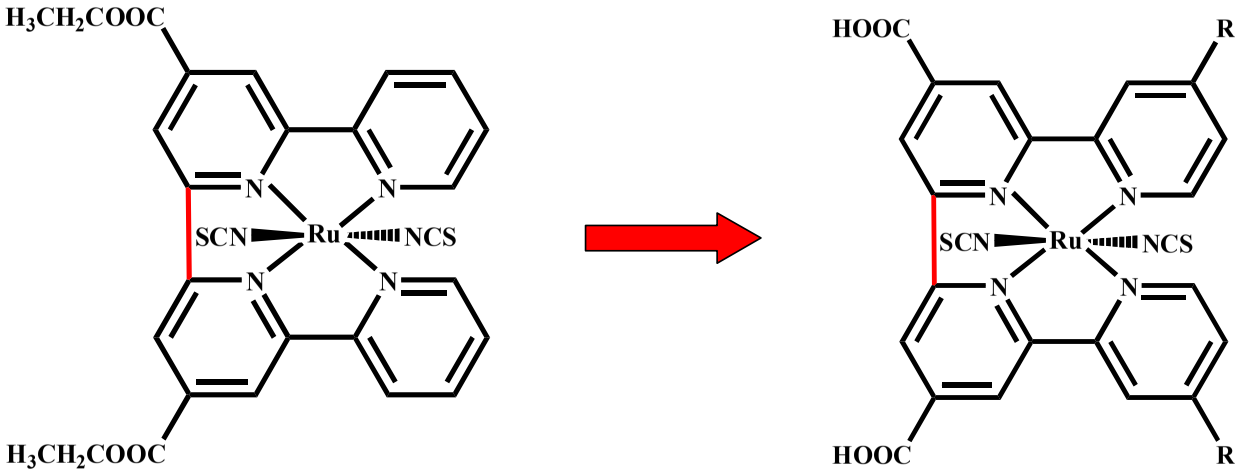


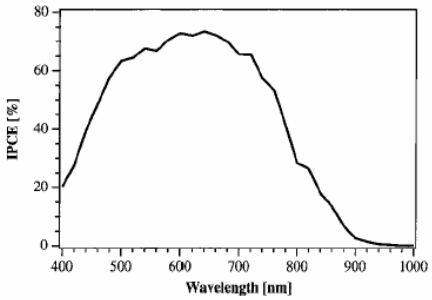
M1



M2 and M3

Tetradentate Sensitizers: direct linking (M 1)

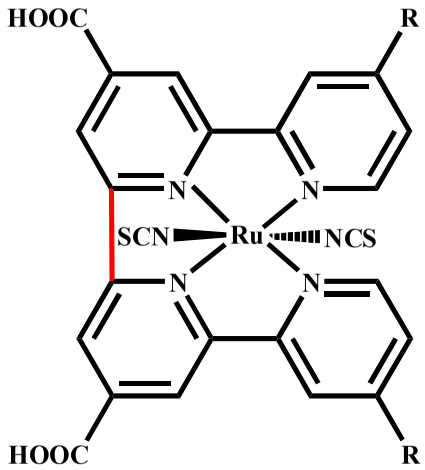




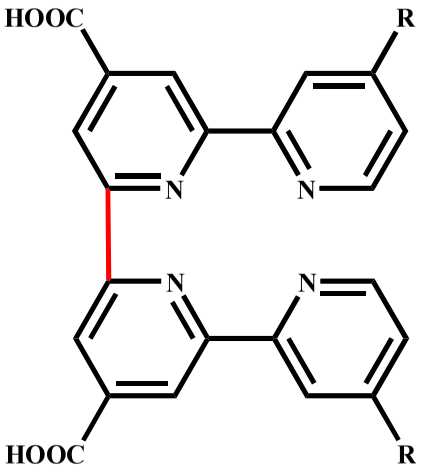
- Anchoring of sensitizer to TiO_2
- Tuning of hydrofobicity to reduce: desorption
  black current

M. Grätzel et al. Tetrahedron 57 8145 (2001)
M. Grätzel et al. *Inorganic Chemistry* 41 367 (2002)

Tetradentate Sensitizers: direct linking (M 1)

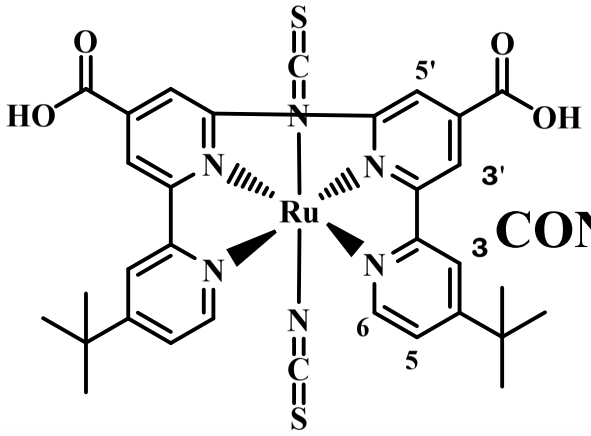


Our synthetic goal

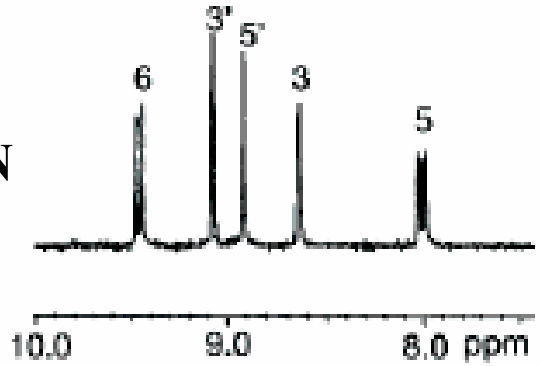


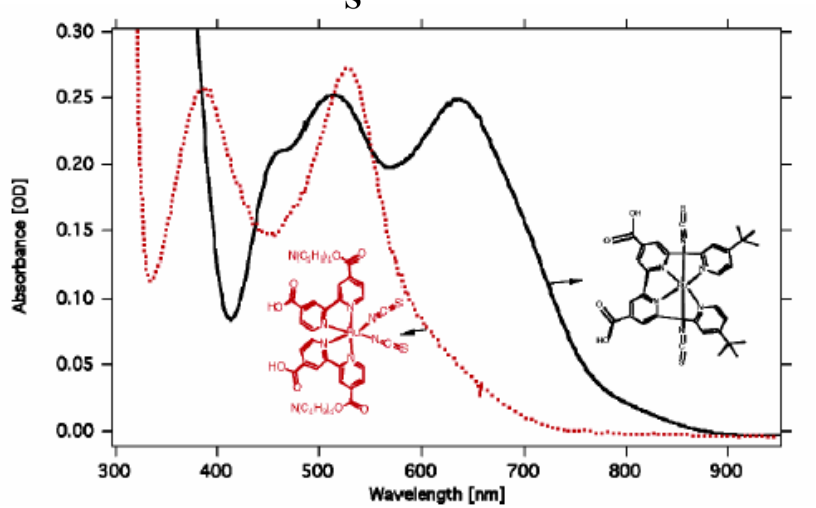
C. Barolo, M. K. Nazeeruddin, S. Fantacci, D. Di Censo, P. Compte, P. Liska, G. Viscardi, P. Quagliotto, F. De Angelis, S. Ito, M. Grätzel **Synthesis, Characterization, and DFT-TDDFT Computational Study of a Ruthenium Complex Containing a Functionalized Tetradentate Ligand** *Inorg. Chem.* **(2006)**

Tetradentate Sensitizers: direct linking (M 1)



TRANS CONFIGURATION

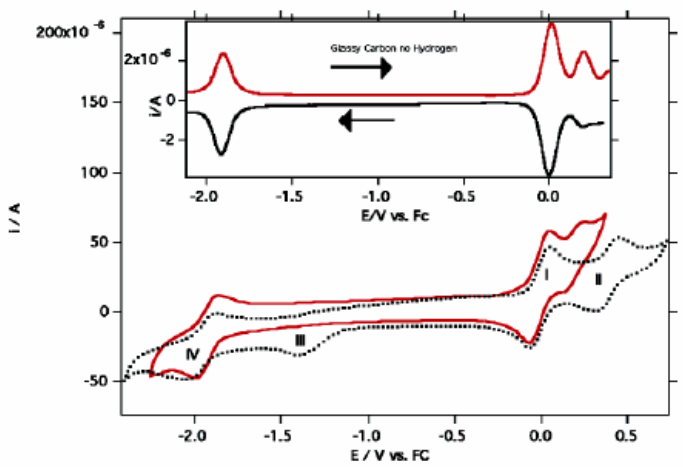




+ 30 nm over the most bathocromic Ru sensitizer MLCT over the entire visible spectrum

Spectral Characterization

Tetradentate Sensitizers: direct linking (M 1)



quasi reversible oxidation and reduction potentials at $E_{1/2}$ = +0.38 e -1,42 vs ferrocene, respectively

Electrochemistry done by Davide Di Censo at EPFL

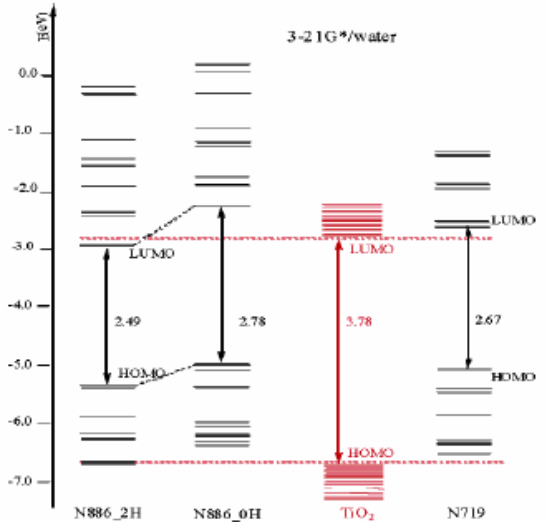
Photovoltaic data

V_{oc} = 680 ± 30 mV (-120 mV vs N786!)

ff = 0.73 ± 0.03

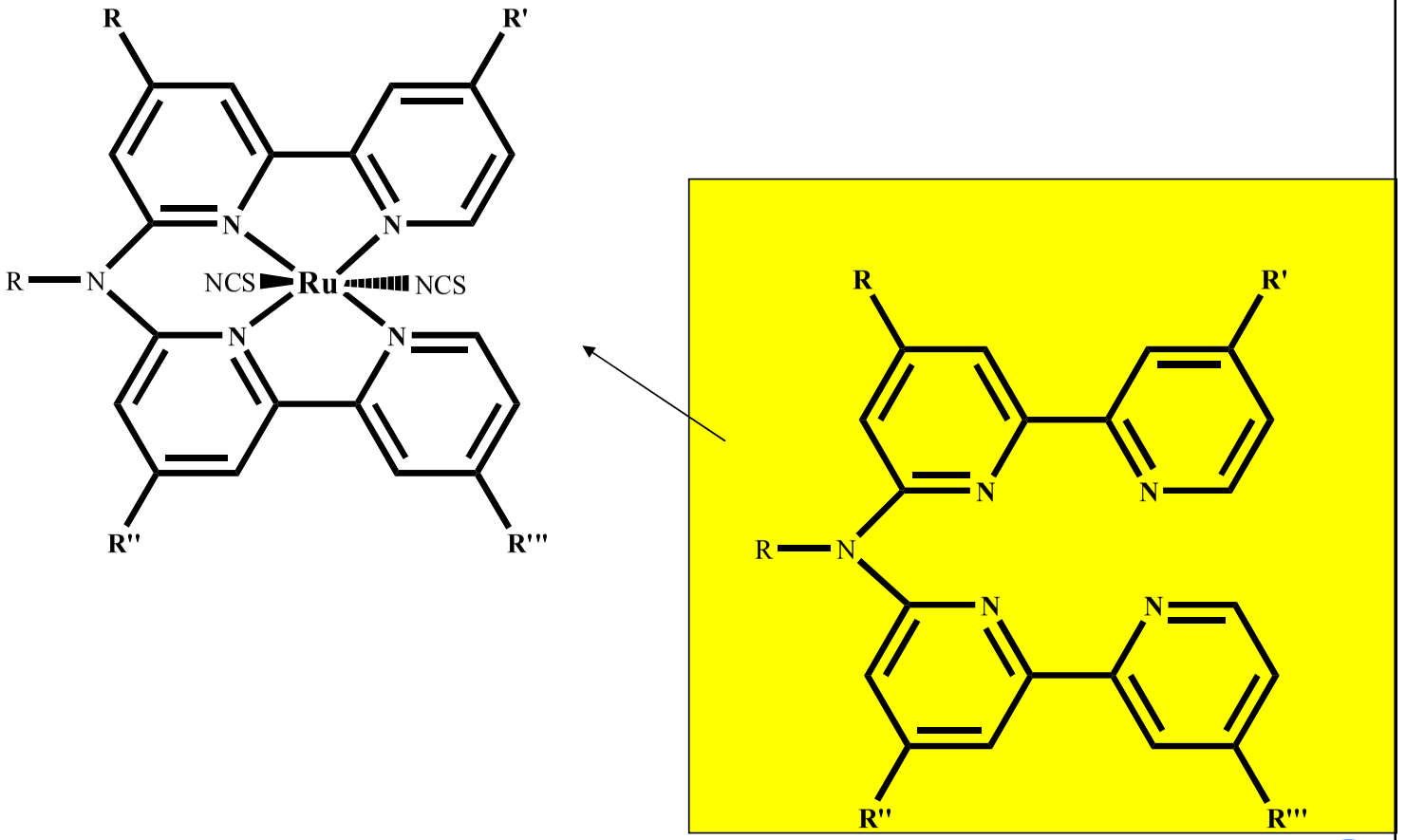
I_{sc} = 11.8 ± 0.20 mA

$\eta = I_{sc} V_{oc}$ ff = 5.85 %



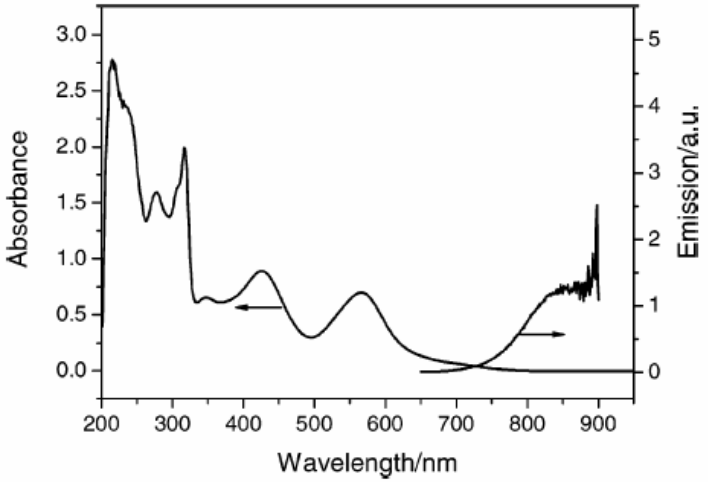
DFT-TDDFT calculations done by Fantacci and De Angelis, Perugia

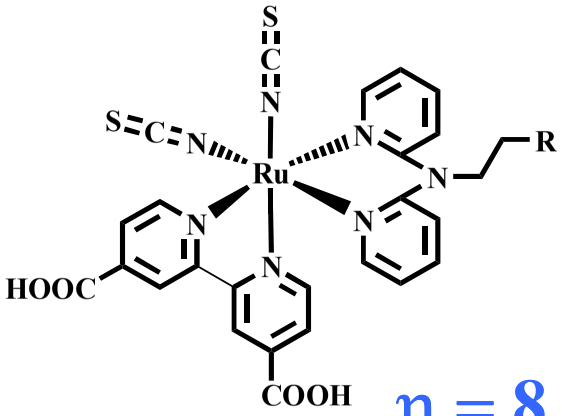
Tetradentate Sensitizers: amino bridge (M 2)



Tetradentate Sensitizers: amino bridge (M 2)

Graetzel et al. *Chem.Mater.* **2004** *16*, 3246-3251





$\eta = 8.2\ \%$

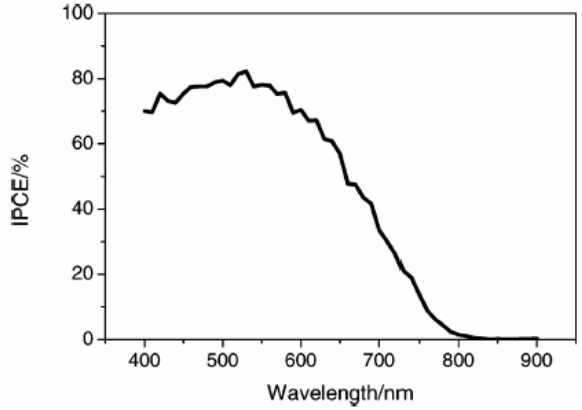
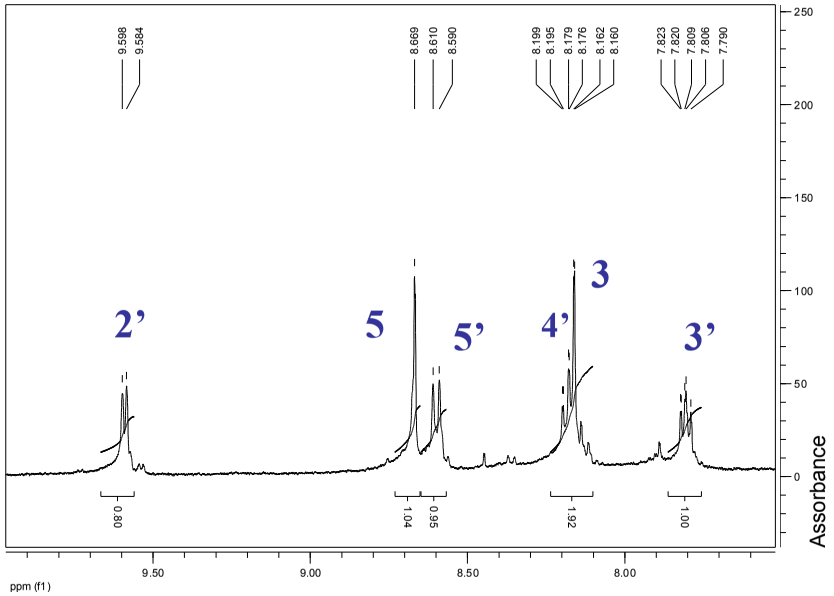


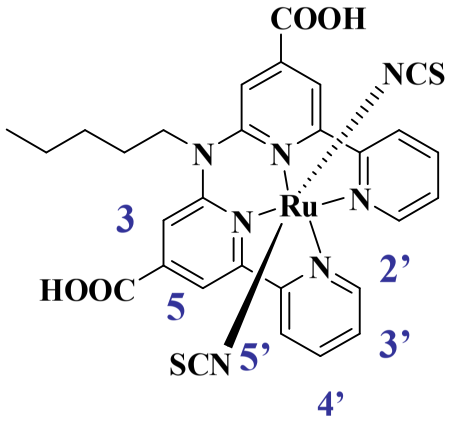
Table 1. Detailed Photovoltaic Parameters of DSCs with Complex I under Different Incident Light Intensities[a]

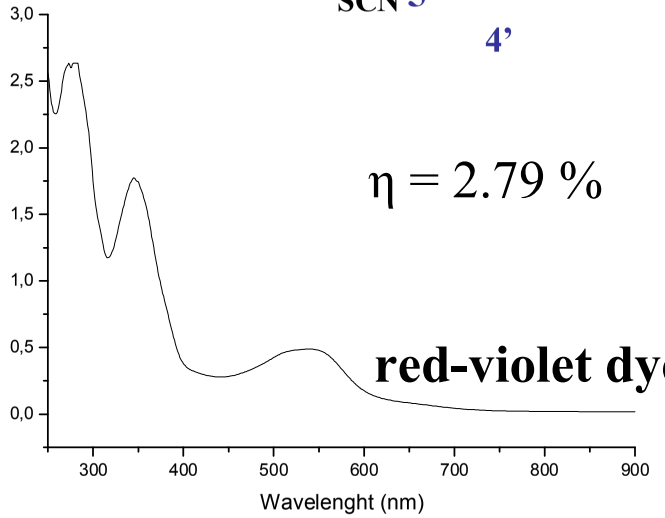
P_{in}/mW cm^{-2}	J_{sc}/mA cm^{-2}	V_{oc}/mV	P_{max}/mW cm^{-2}	*ff*	η/%
9.5	1.54	692	0.84	0.786	8.8
52.1	8.38	740	4.53	0.745	8.7
99.7	15.5	756	8.21	0.702	8.2

[a] The spectral distribution of the lamp simulates air mass 1.5 solar light. Incident power intensity: P_{in}; short-circuit photocurrent density: J_{sc}; open-circuit photovoltage: V_{oc}; maximum electricity output power density: P_{max}; fill factor: $ff = P_{max}/P_{in}$; total power conversion efficiency: η; cell active area: 0.158 cm^2.

Tetradentate Sensitizers: amino bridge (M 2)







$\eta = 2.79\ \%$

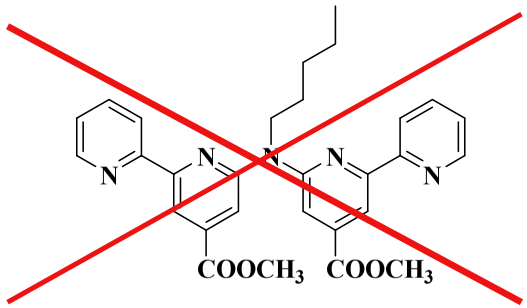
red-violet dye

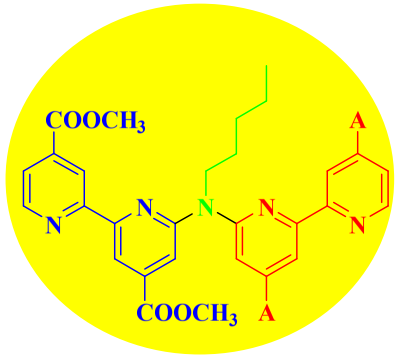
^{1}H-NMR:

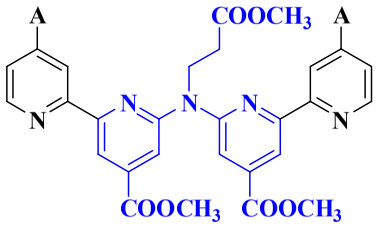
7.81 ppm (2H, dd, H3')
8.20 ppm (2H, dd, H4') } **merged**
8.16 ppm (2H, s, H3) }
8.60 ppm (2H, d, H5')
8.67 ppm (2H, s, H5)
9.59 ppm (2H, d, H2')

TRANS CONFIGURATION

Tetradentate Sensitizers: amino bridge (M 2)

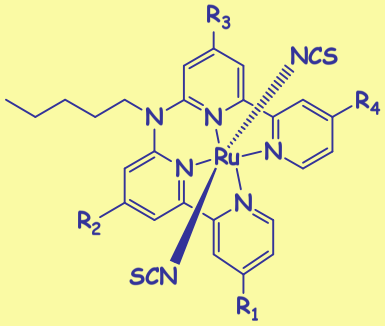


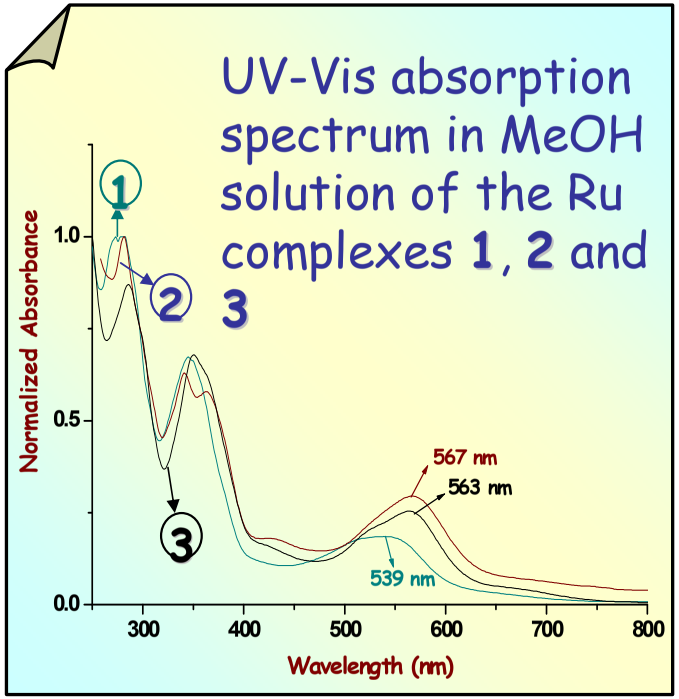




Tetradentate Sensitizers: amino bridge (M 2)

1. DMF, reflux, 24 h , in darkness
2. NH_4SCN, DMF, reflux, 12 h
3. NEt_3, H_2O, 48 h





Complex 1: 2 COOH centered **η = 2.79 %**
Complex 2: 2 COOH one side **η = 4.30 %**

Complex 3: 4 COOH **η = 7.22 %**

Organic dyes

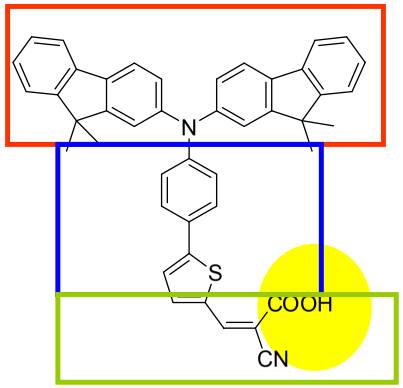
Background in solar cell

Metal free sensitizers in DSSC's since 2003

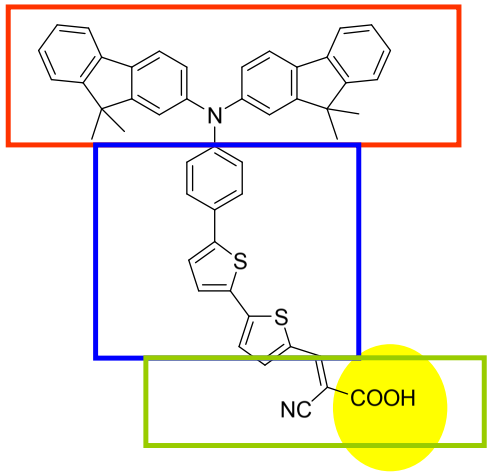
Efficiency range: 5-8%

Hagfeldt et al. *Chem.Commun.* 2006 2245-2247

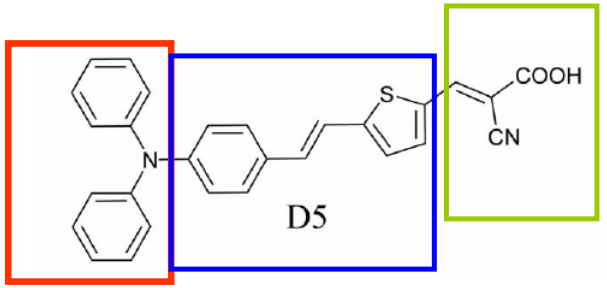
Graetzel et al. *JACS* 2006 **128** 16701-16707



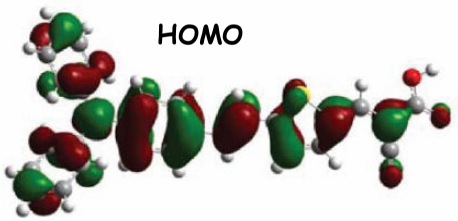
η = 7.2 %



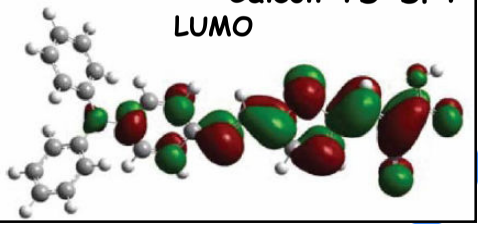
η = 8.01 %



η= 4–5 %



Calcoli TD-DFT



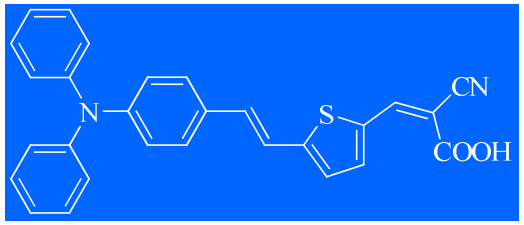
DONOR — π bridge — ACCEPTOR

Push → **Pull**

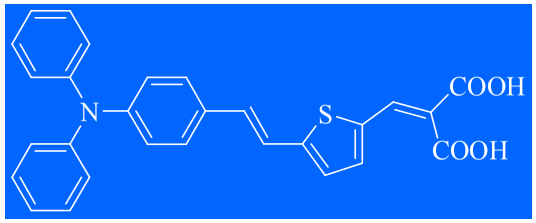
e^-

C. Barolo – Dye Sensitized Solar Cells

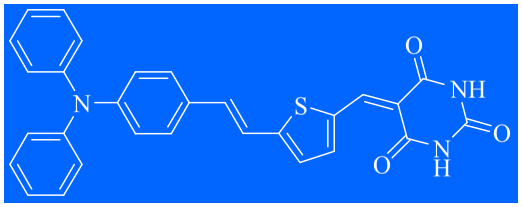
Organic dyes



η @1Sun	J_{sc} (mA/cm²)	V_{oc} (mV)	ff
5.55 %	11.21	664.2	0.75

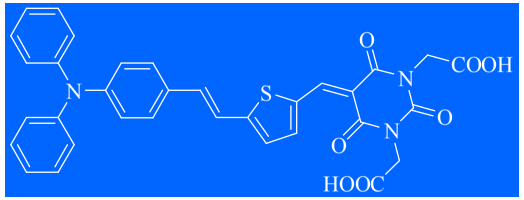


η @1Sun	J_{sc} (mA/cm²)	V_{oc} (mV)	ff
4.5 %	9.83	636.38	0.72



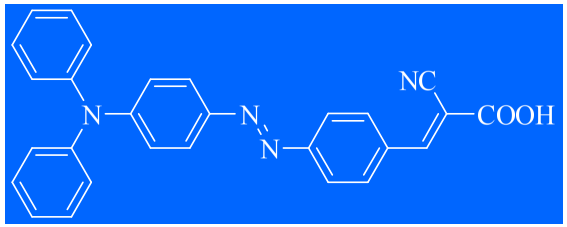
η @1Sun	J_{sc} (mA/cm²)	V_{oc} (mV)	ff
0.81 %	2.25	480.34	0.75

AGGREGATION!



η @1Sun	J_{sc} (mA/cm²)	V_{oc} (mV)	ff
0.15 %	0.44	466.22	0.75

Organic dyes



η @ 1 Sun	J_{sc} (mA/cm²)	V_{oc} (mV)	FF
0,35%	0,83	549,06	0,78

- No aggregation problems!
- LUMO at the right level (from CV point of view)
- excitation state life-time too short (azo isomerization process?)

NOT ONLY SYNTHESIS …

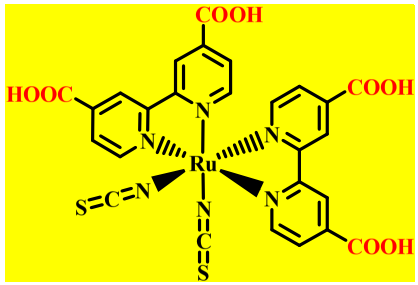
PRODUCT PURIFICATION

NOT ONLY SYNTHESIS …

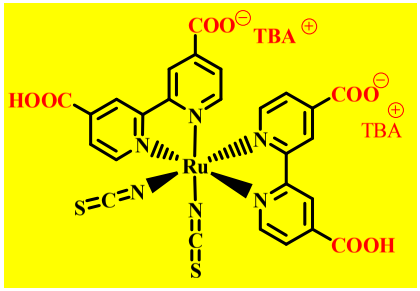
PRODUCT CHARACTERISATION

A Mass Spectrometric Analysis of N-719 Sensitizer Solution used for Dye-Sensitized Solar Cell

WHY?



N3



N719

The high performance achieved using (N719) sensitized TiO_2 solar cell can be related to several factors:

- broad range of visible light absorption,
- relatively long-lived excited states,
- its excited energy almost matching those of TiO_2 conduction band
- **the effect of protons and the cations carried by the sensitizer**

G. Viscardi et al. *Inorganica Chimica Acta*, **2008**

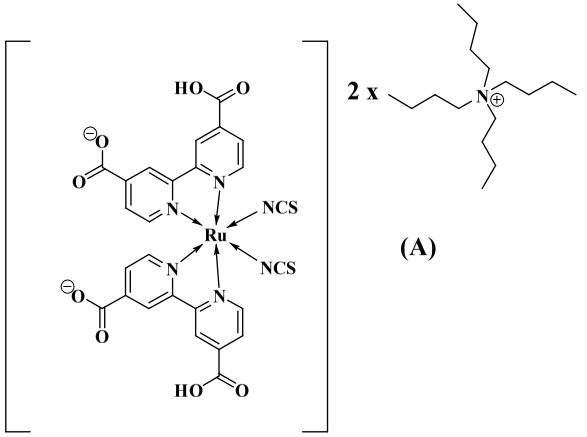
NOT ONLY SYNTHESIS …

PRODUCT CHARACTERISATION

First Mass Spectrometric Study with a ESI interface

ANALYZE THE SENSITIZER STRUCTURE DIRECTLY FROM ADSORBING SOLUTION in order to design and develop new tailored sensitizers

- ✓ it can directly detect mono and multi-charged ion
- ✓ does not alter the connectivity of the complex through disassembly/reassembly sequences
- ✓ causes essentially no or very little fragmentation.

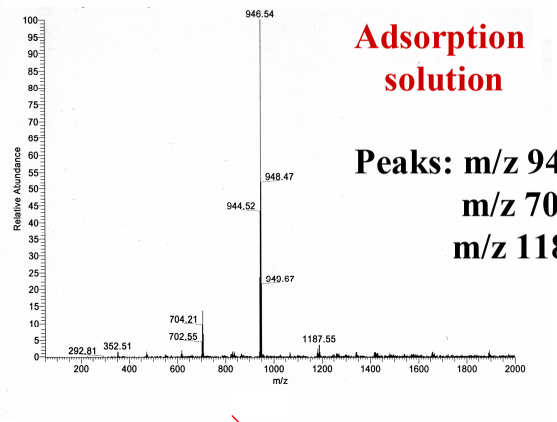


N719
$C_{58}H_{86}N_8O_8RuS_2$
Exact Mass: 1188,51

NOT ONLY SYNTHESIS …

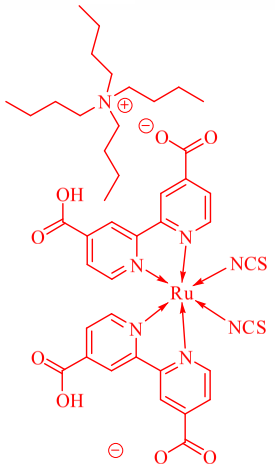
PRODUCT CHARACTERISATION

Solvent effect



Adsorption solution

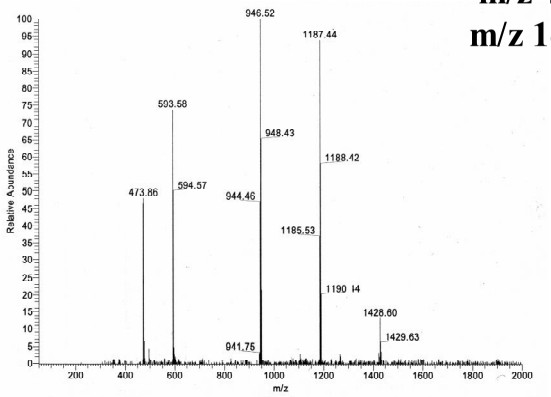
Peaks: m/z 946,1, (E)
m/z 704,9, (B)
m/z 1187,5 (D)



m/z 946,1

H_2O+5%CH_3OH

Peaks: m/z 1187,5 (F)
m/z 593,2 (D)
m/z 473,9 (C)
m/z 1428,8 (G)



DSC INDUSTRIALIZATION

Advantages *vs.* Silicon Cells

- No feedstock supply problems, low cost and ease of production,
- Performance insensitive to temperature
- Bifacial configuration - advantage for diffuse light and albedo
- Efficiency less sensitive to angle of incidence,
- 10 -30 percent higher energy output than silicon cells at equal SRC rating
- Transparency for power windows
- Color can be varied by selection of the dye, invisible PV-cells based on near-IR sensitizers are feasable
- Low energy content (for silicon this is 5 GJ/m2 !), payback time is only a few months as compared to years for silicon.
- Outperforms single junction amorphous Si

DSC INDUSTRIALIZATION

INDUSTRIALISATION OF DSC
FROM RESEARCH TO PRODUCT
9 &10 FEBRUARY 2006

INVITATION

The inaugural conference "Industrialisation of DSC—from Research to Product"
is being held in Canberra, Australia 9 & 10 February 2006.

DYESOL
Organiser

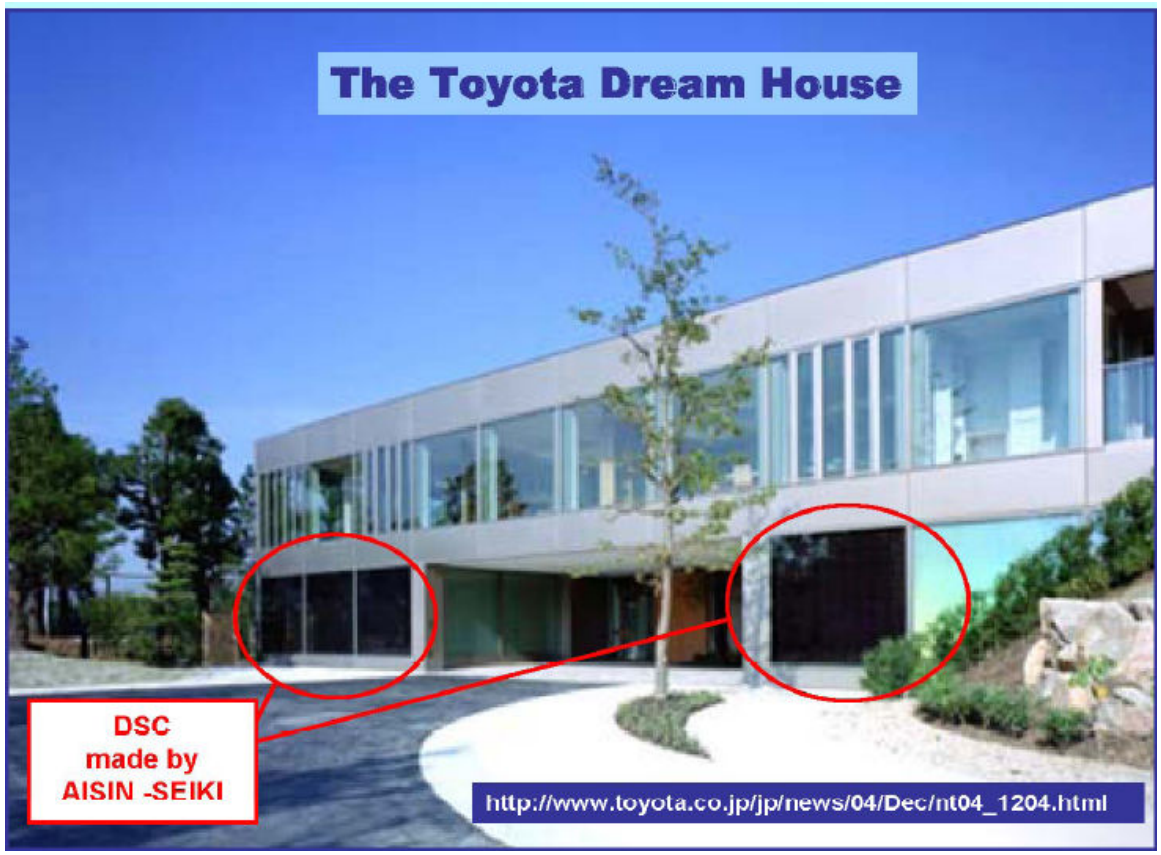
Greatcell SOLAR S.A.
Co-Organiser

2nd INTERNATIONAL CONFERENCE
on the INDUSTRIALISATION of DSC

DSC-IC 2007
St Gallen, Switzerland, 11-13 September 2007

rogram Overview | Speakers | Registration | DSC Network | Sponsors | Hotel and Travel | See & Do

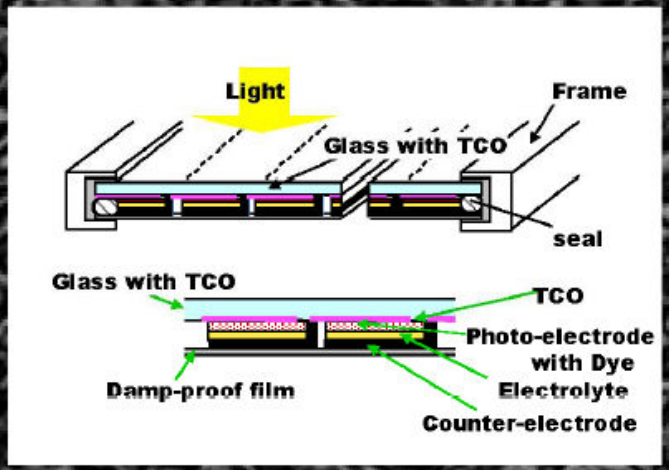
DSC INDUSTRIALIZATION



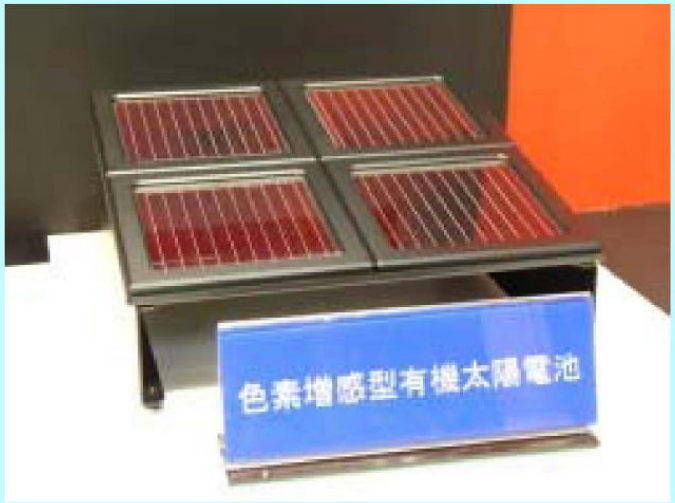
DSC INDUSTRIALIZATION

AISIN Prototype production

- Search of new module design from industrial point of view
  < performance, durability, number of parts, production time, cost >

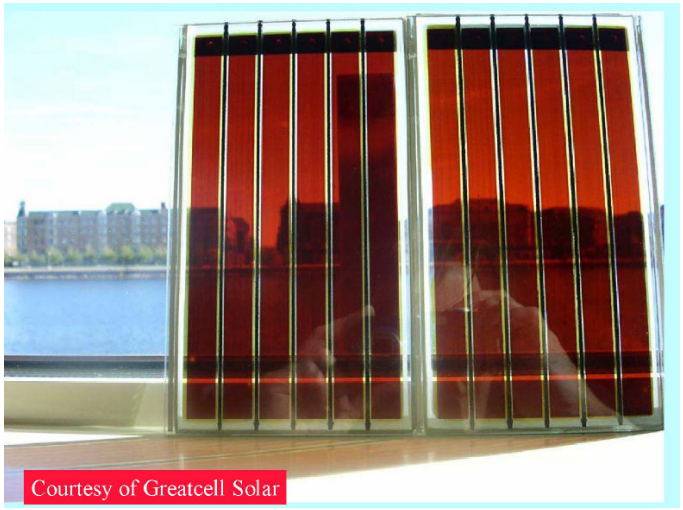


DSC INDUSTRIALIZATION



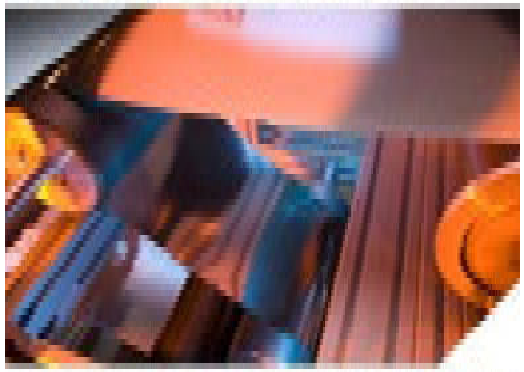
Hitachi's new dye sensitized cell achieves 9.3 percent efficiency

DSC INDUSTRIALIZATION

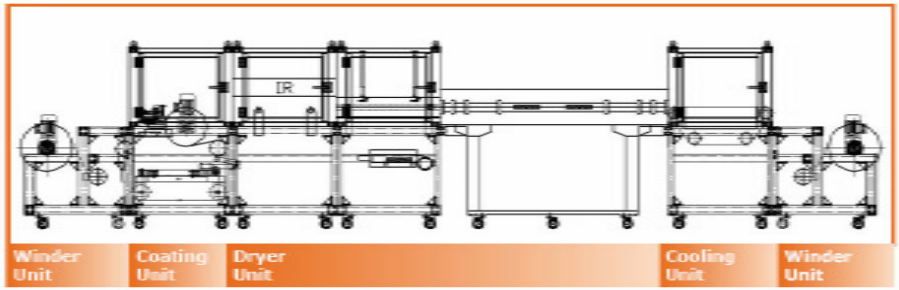


10 m² of Dyesol DSC facade panels have been integrated to form a magenta »stripe« across the undulating wall floor-roof of one of the Houses of the Future on display at the Sydney Olympic Park.

DSC INDUSTRIALIZATION



G24i
First production plant: Cardiff, Galles
roll to roll



ACKNOWLEDGMENTS

Prof. Ermanno Barni and Prof. Guido Viscardi
Chimica Organica Applicata

Prof. Michael Graetzel
LPI group at EPFL

This work was supported by a contribution from the University of Torino (ex-60% funds), NANOMAT Project, ASP, Swiss Federal Office for Energy (OFEN) and EU COST action D35/0007/05.

We thank Compagnia di San Paolo and Fondazione CRT, Torino Italy for continuous equipment supplied.

AND NOW?

NIS Colloquium
Classical and new approaches to thin film photovoltaics

Monday, June 23, 2008

Aula Magna, Experimental Physics Department, Via Pietro Giuria 1, Torino

DYE SENSITIZED SOLAR CELLS

Claudia Barolo

claudia.barolo@unito.it, +390116707596

Dipartimento di Chimica Generale e Chimica Organica
Centro di Eccellenza Interdipartimentale NIS (Superfici ed Interfasi Nanostrutturate)
Università degli Studi di Torino

THANK YOU FOR YOUR ATTENTION !