



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

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## Organic Photonics Displays, Lighting & Photovoltaics

25th. June 2008

Laboratoire de la photonique  
et des interfaces - EPFL  
Lausanne

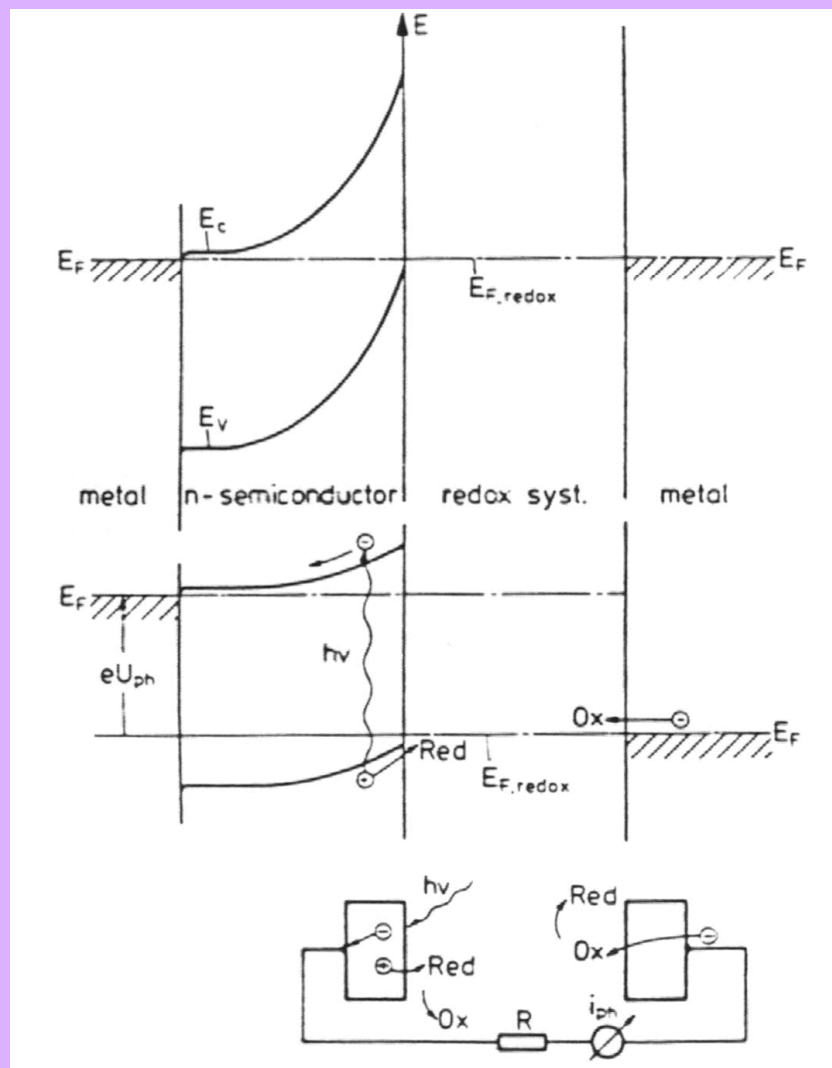
“Electrochemistry for Energy”

**Augustin McEvoy**

[augustin.mcevoy@epfl.ch](mailto:augustin.mcevoy@epfl.ch)



# Photoelectrochemical effect at a semiconductor - redox electrolyte interface.



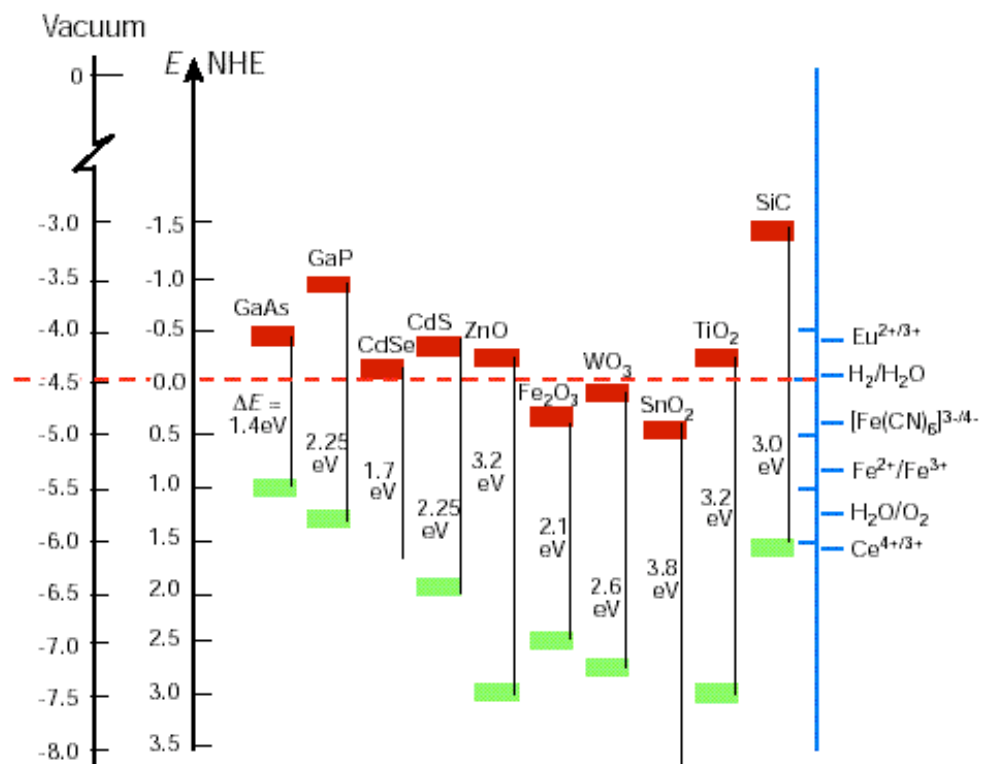
a) On contact the Fermi level of the n-type semiconductor equilibrates with that of the metal and with the redox level of the electrolyte. After charge (electron) transfer a band bending is established as in the case of solid-state junctions.

b) Under light, photoelectrons enter the conduction band; the band bending is reduced and a photovoltage is generated between the semiconductor Fermi level and the redox potential of the electrolyte - equivalent to the potential of the metal counter-electrode. Minority carriers - holes - are then available for an oxidation reaction with the electrolyte at the Semiconductor photoanode. A reduction reaction takes place at the cathode.

The photoelectrochemical interface is functionally identical to a Schottky barrier.

## Semiconductor - electrolyte junctions - photoelectrochemistry

The two materials with different conduction mechanisms - may also be a semiconductor and an electrolyte giving a photoelectrochemical device. The first observation of a photovoltaic effect (Becquerel, 1839) was in fact a photoelectrochemical system using a silver iodide semiconductor.



### Narrow band-gap semi-conductors

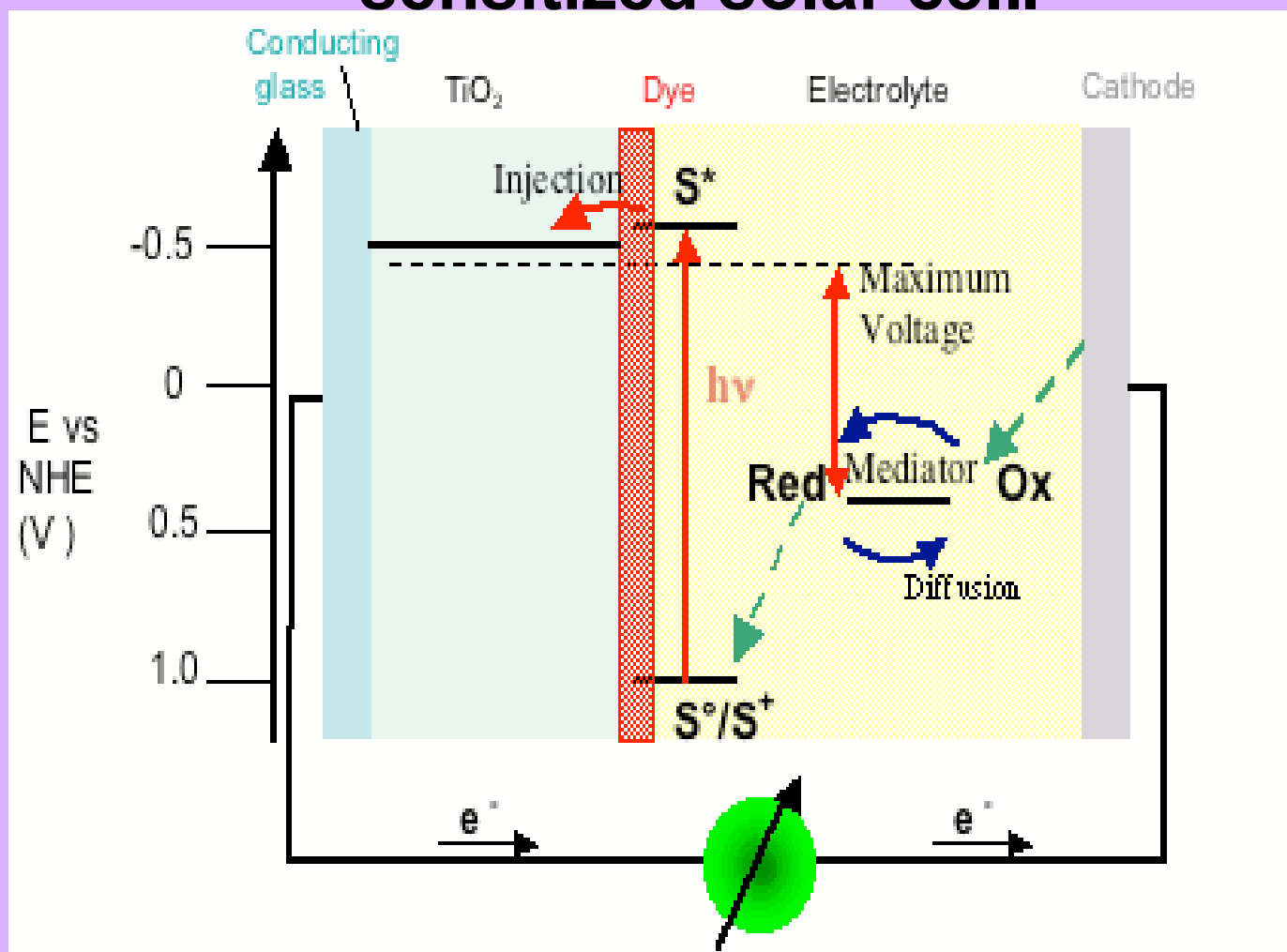
whose photo-response matches the solar spectrum are in general **unstable** in contact with electrolytes. When a hole reaches the interface the most likely object of an oxidation reaction is the material of the semiconductor itself! e.g.  $\text{CdS} + 2\text{h}^+ \rightarrow \text{Cd}^{2+} + \text{S}$ .

This is an example of photocorrosion.

**Wide band-gap semiconductors** have stronger chemical bonding, and are therefore more **stable**, but **do not absorb visible light**.

A **sensitiser** is required - an electrochemically active dye.

# Photoelectrochemical processes in a dye-sensitized solar cell.



In a molecular system such as the dye, the gap between the highest occupied molecular orbital and the lowest unoccupied level (HOMO-LUMO gap) is analogous to the conduction band - valence band gap in a semiconductor. In a sensitised process, the valence band is not involved - only the conduction band; it is a majority-carrier device.

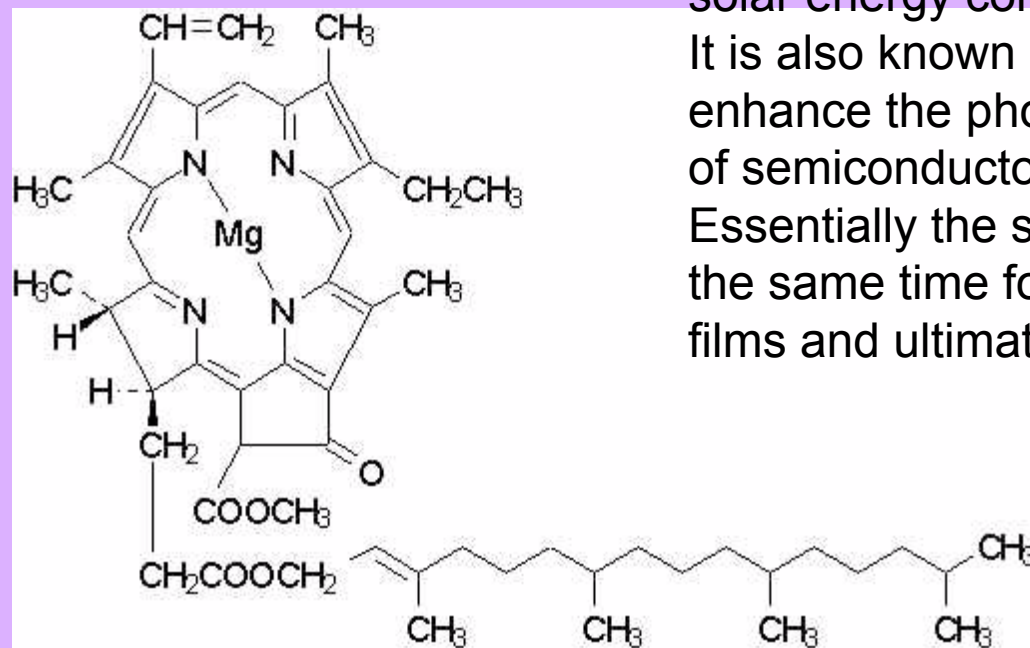
# The natural prototype for a solar energy conversion dye - chlorophyll

There are other systems besides semiconductors which can absorb visible light and store the acquired energy. Photosynthesis - based on chlorophyll - is the primary energy source of the biosphere.

So organometallic porphyrins are a possibility for solar energy conversion.

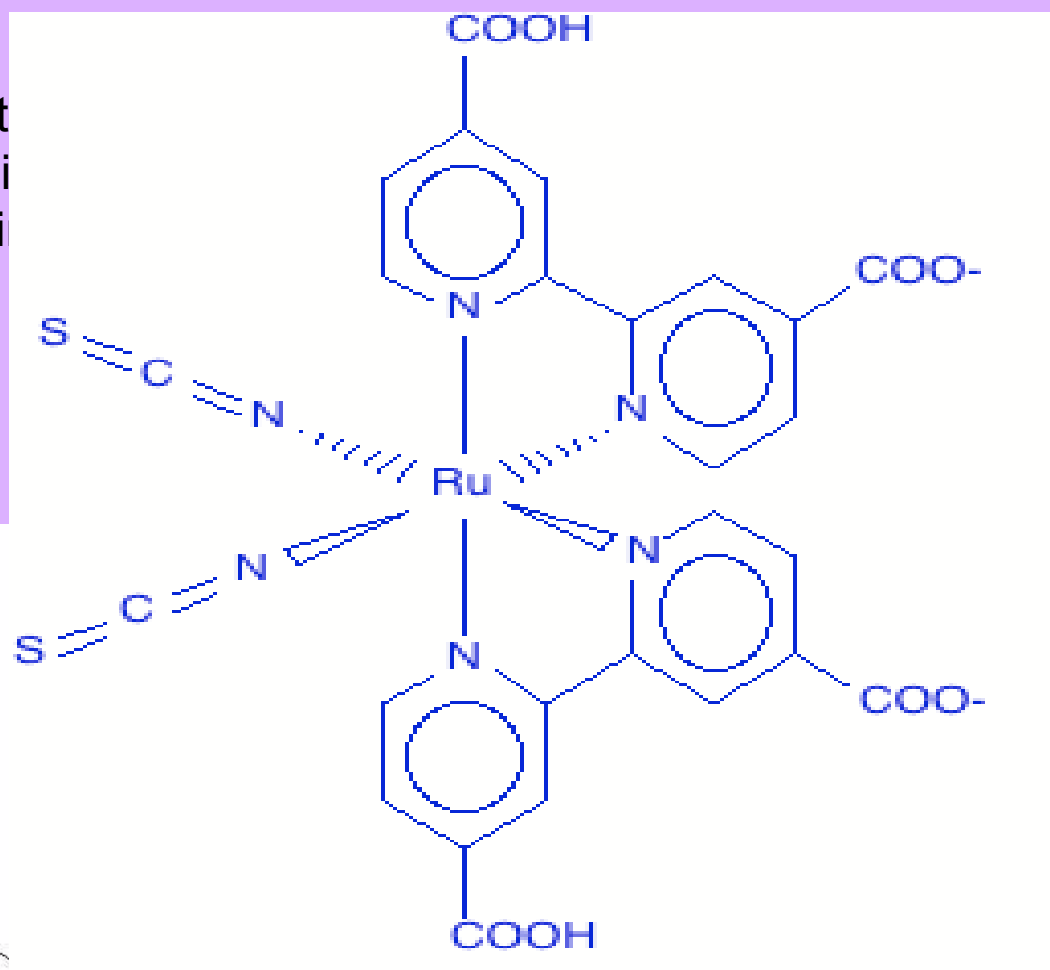
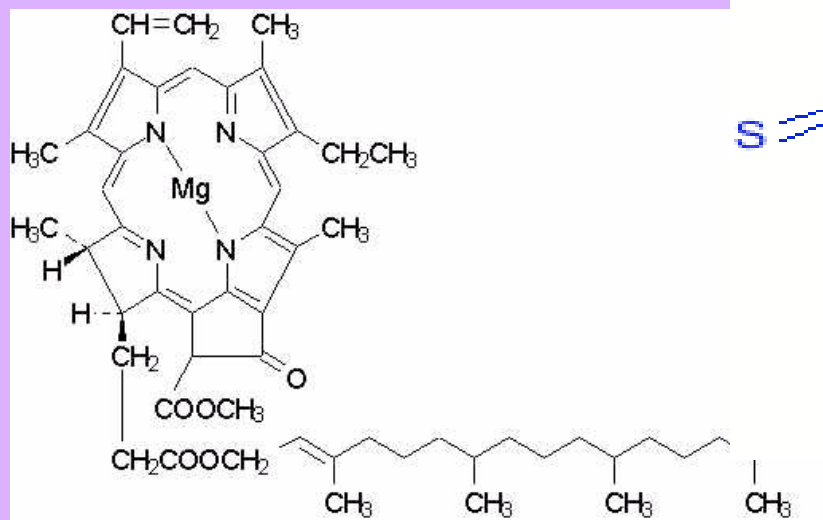
It is also known (Moser, 1987) that dyes can enhance the photoelectrochemical performance of semiconductors.

Essentially the same process was developed at the same time for photography - panchromatic films and ultimately colour photography:

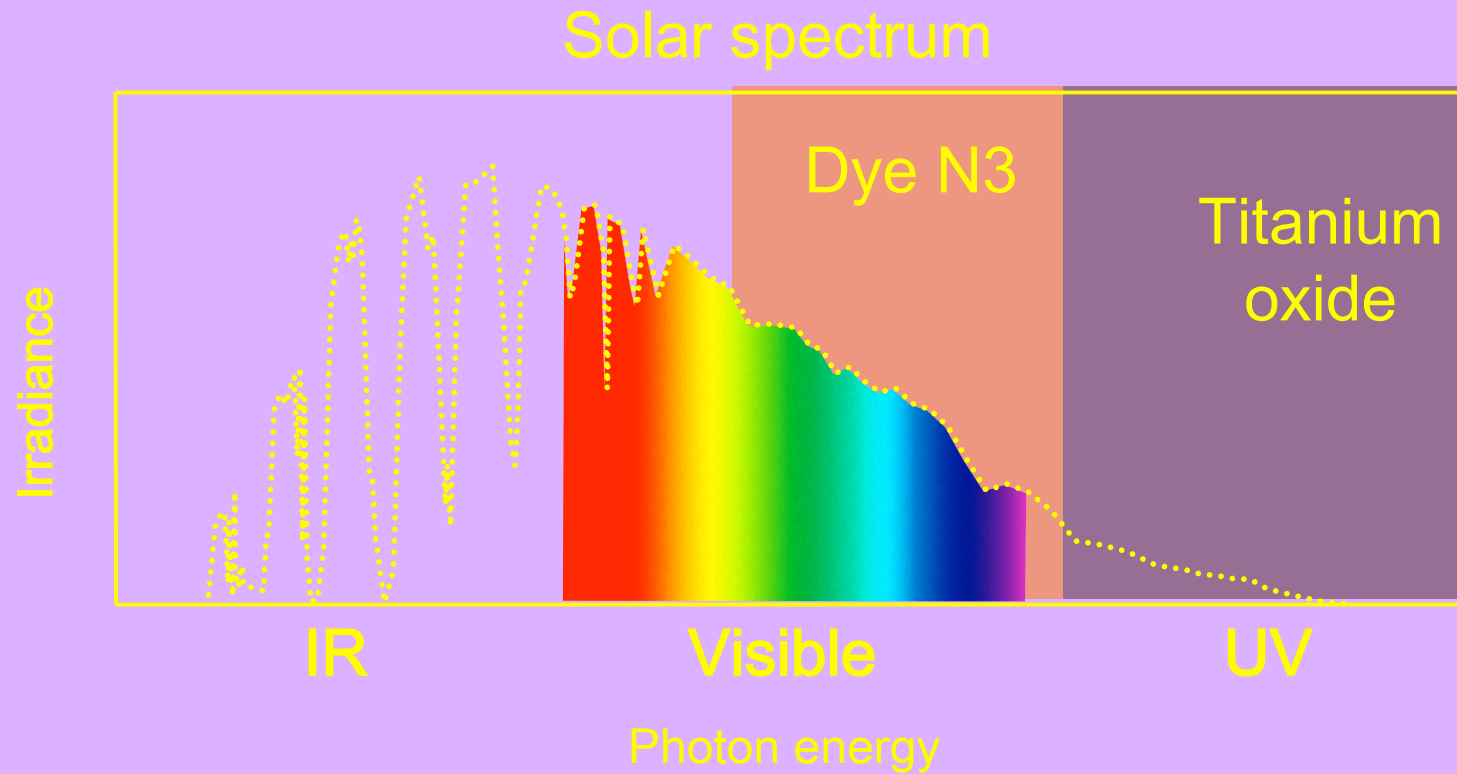


**Standard dye for photoelectrochemical cell development  
- the EPFL « N3 » dye -  
dithiocyanato bis(4,4'-dicarboxylic acid-2,2'-bipyridine) ruthenium(II)**

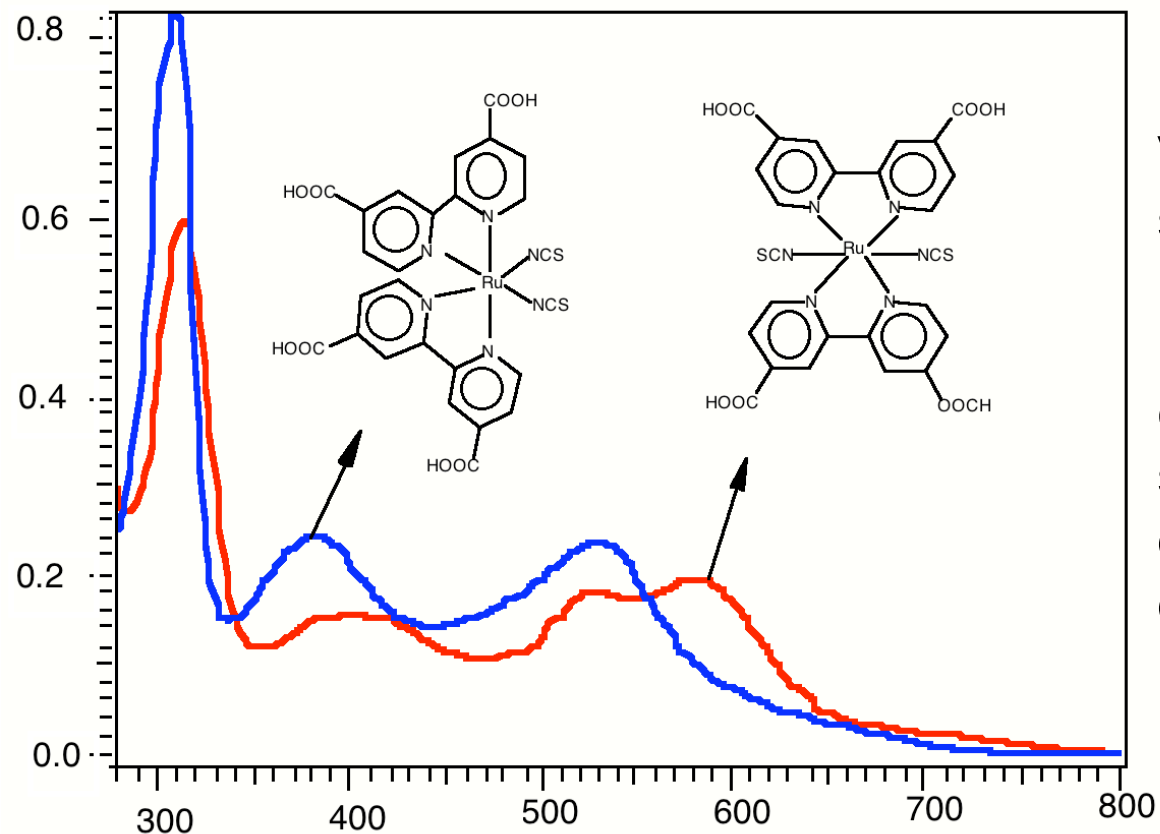
Note the structure and compare with chlorophyll - in both cases a metal in a "cage" of nitrogen atoms, these being heterocyclic aromatic rings.



# Sensitivity to solar spectrum of titanium dioxide and of electroactive dye N3.



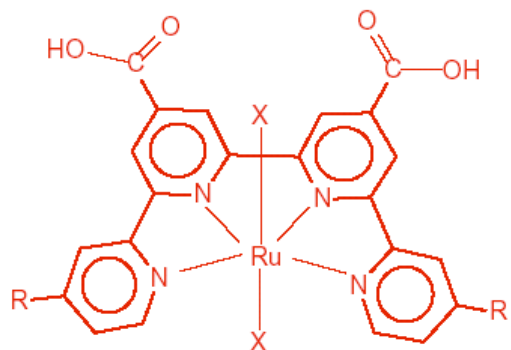
# Molecular engineering of dyes.



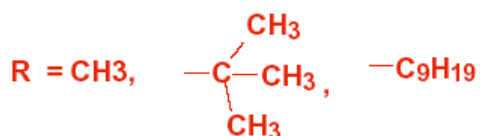
Very small changes to a dye structure can have significant influence on the optical properties. In the present case compare the absorption spectra of two isomers of dithiocyanato bis(4,4'-dicarboxylic acid-2,2'-bipyridine) ruthenium(II) dye.



# Tetradentate polypyridyl and other ligands

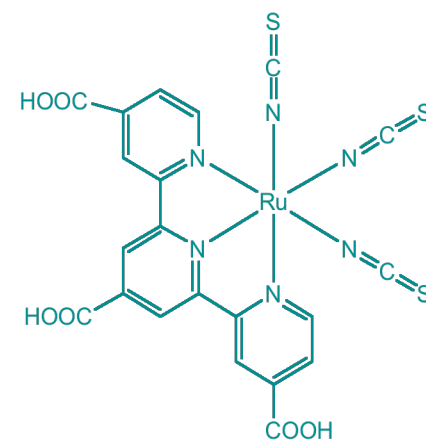
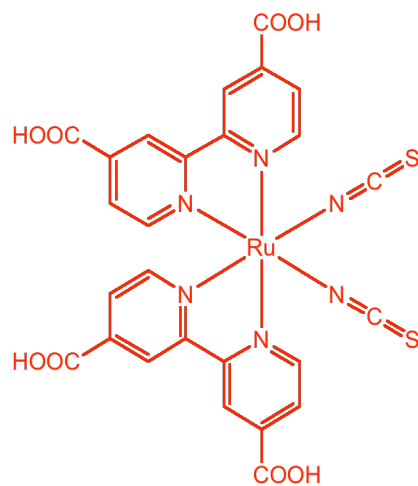
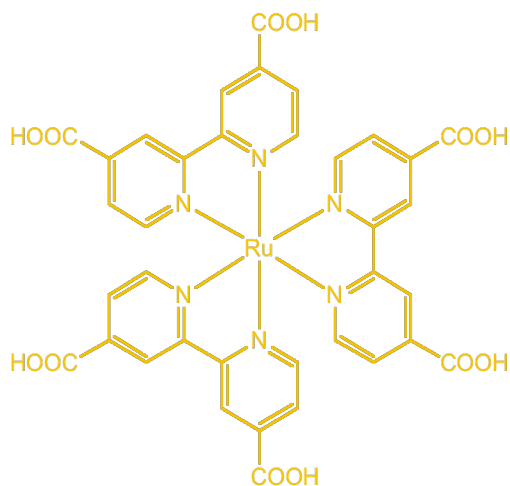


$X = \text{Cl}^-, \text{NCS}^- \text{ and } \text{CN}^-$

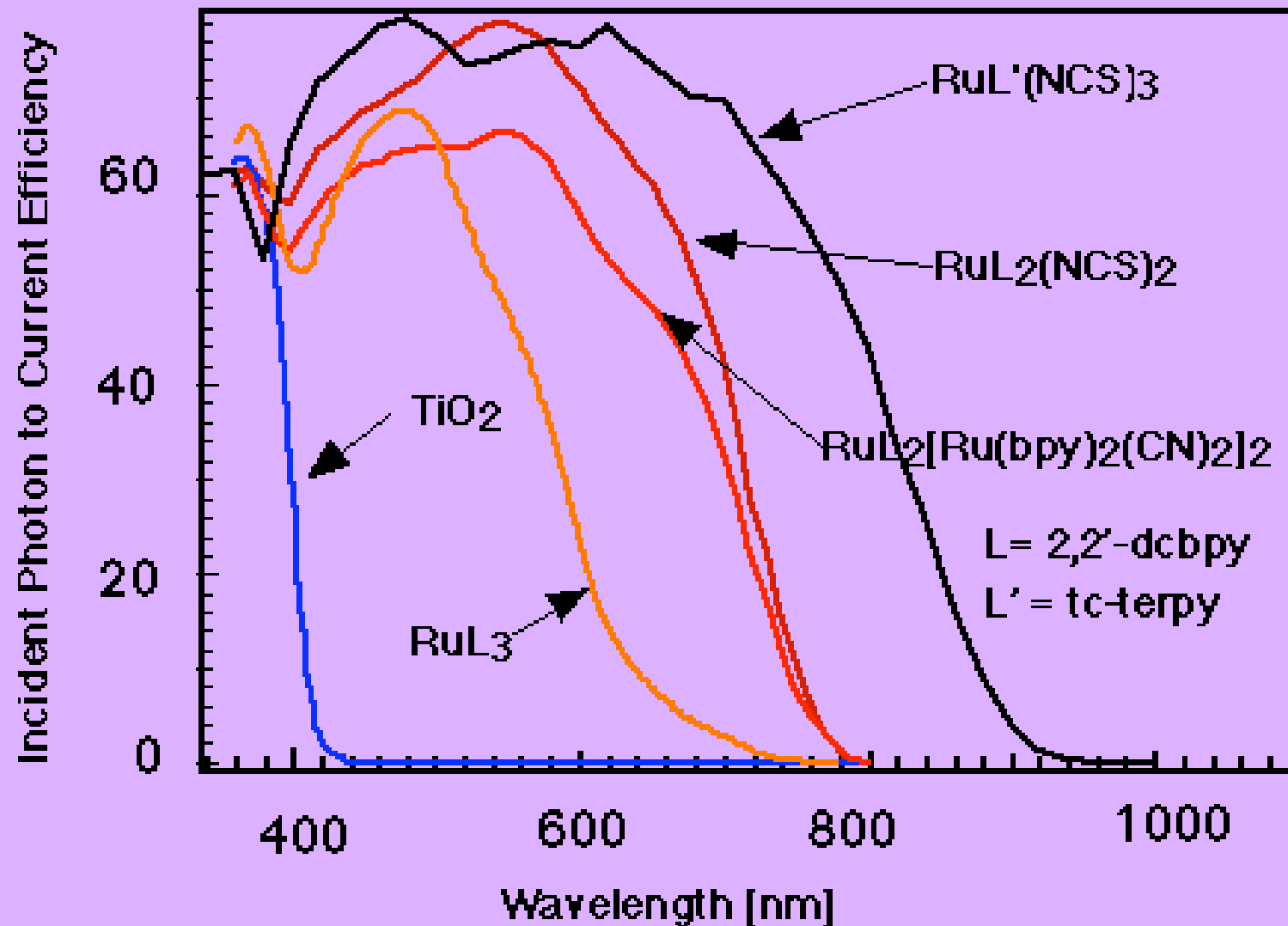


More molecular engineering:  
the bis-bipyridyl trans- isomer with the improved absorption characteristics tends to revert to the cis- structure with time. To stabilise the trans- form, the two bipyridyl components can be chemically linked to provide a tetra-pyridyl ligand.

The dye colour can be chosen - for example for architectural or esthetic reasons.



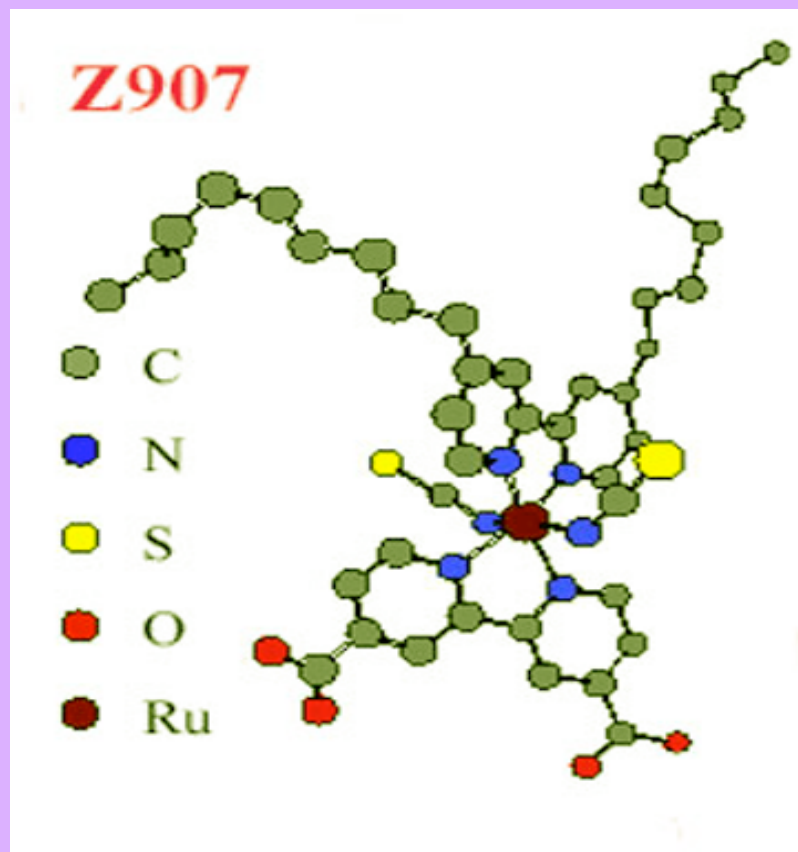
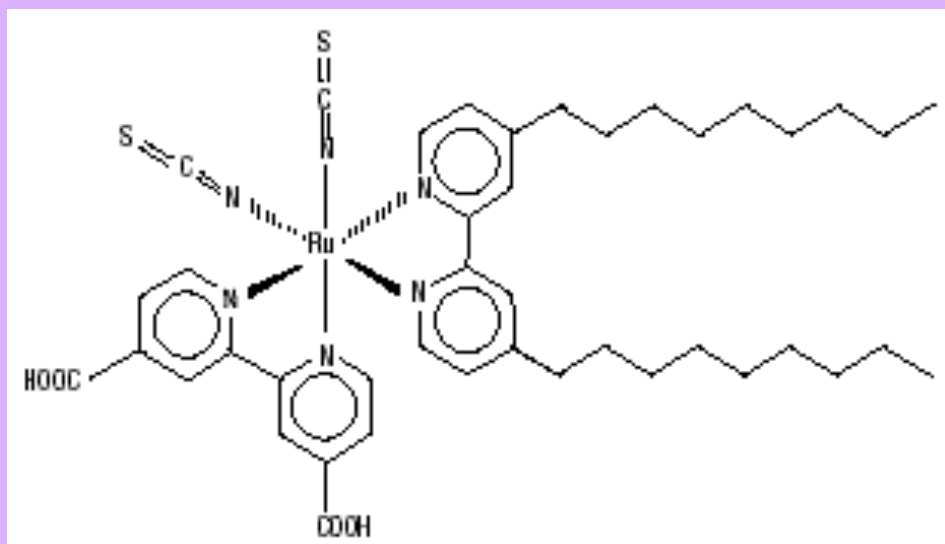
# Optical absorption of titania - development of sensitising dyes.



# Advanced ruthenium complex dye structure - the amphiphilic dye Z-907

(cis-Ru(H<sub>2</sub>dcbpy)(dnbpy)(NCS)<sub>2</sub>,

where H<sub>2</sub>dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine  
and dnbpy = 4,4'-dinonyl-2,2'-bipyridine.



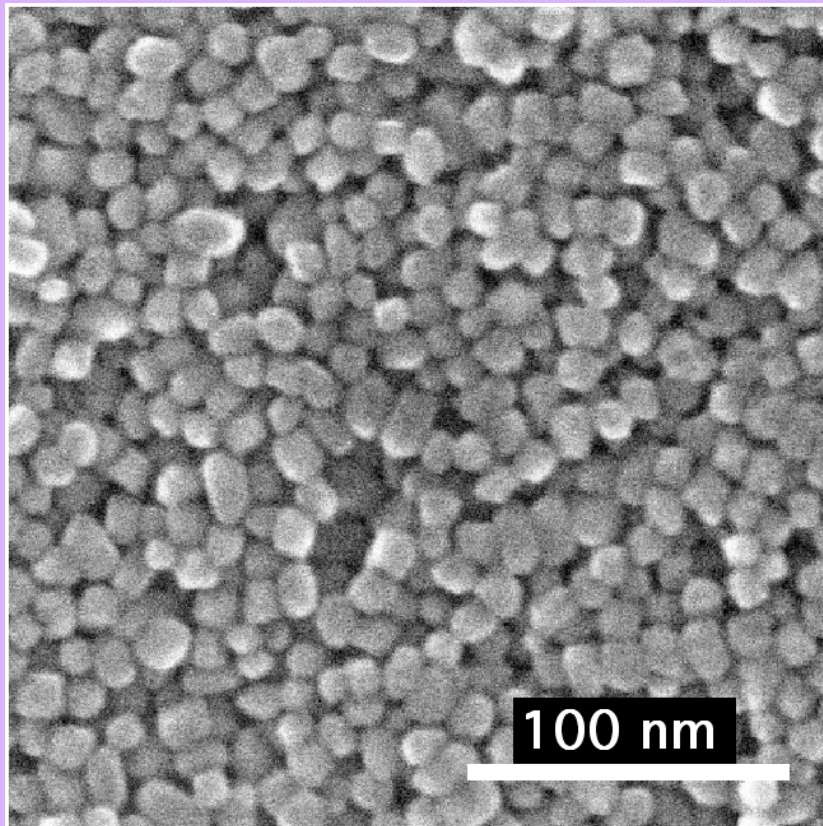
## Design features of the EPFL dye Z-907:

1. Chromophore provided by polypyridyl complex of ruthenium - the prototype dye of this series is the trisbipyridyl compound.
2. Energetics - HOMO-LUMO gap and hence spectral response - modified by substitution of thiocyanide groups.
3. Chemisorption to titanium dioxide surface through carboxylate groups.
4. Layer self-organisation and surface characteristics determined by hydrocarbon « tail » with suppression of redox capture of injected electrons by the electrolyte.
5. Particularly suitable with ionic liquid and gel electrolytes.

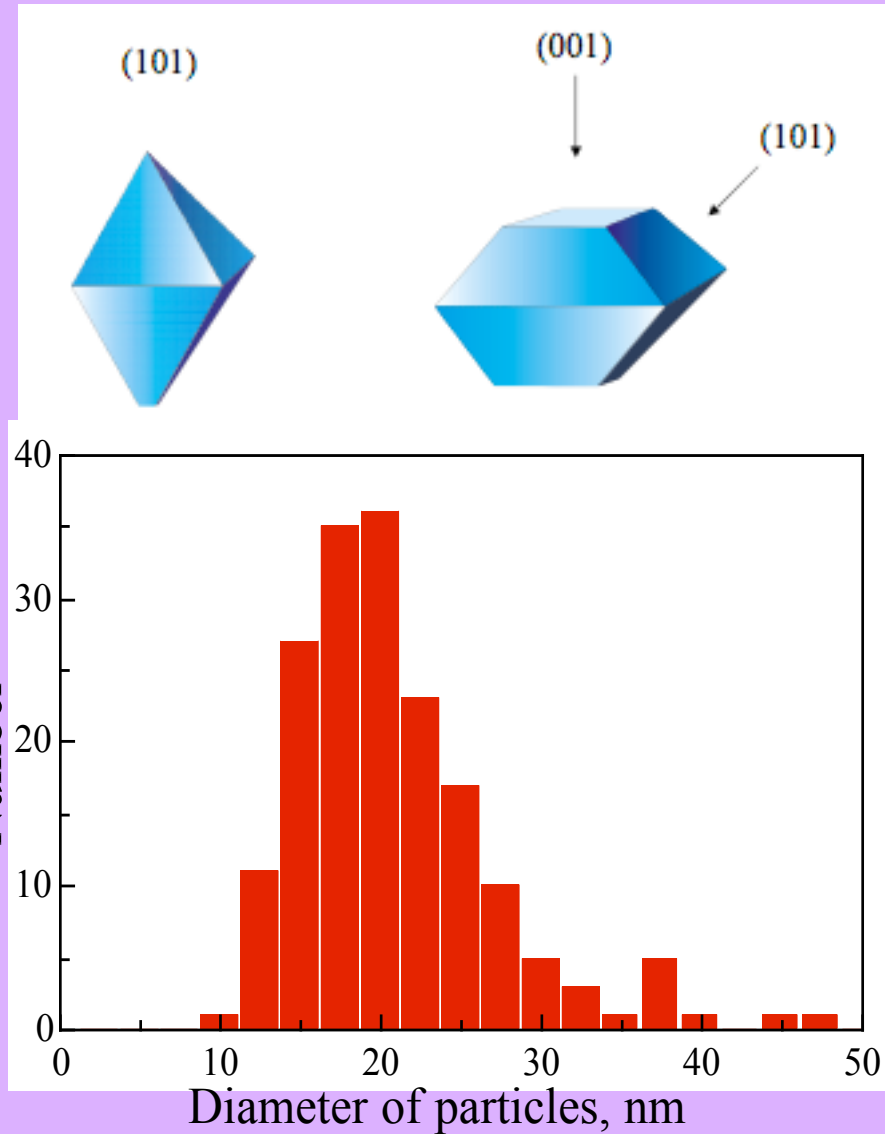
# Nanocrystalline oxide films exhibit extraordinary properties

- surface extension by a factor of over 1000 for a 10  $\mu$  film, huge junction contact area.
- ease of electron percolation through the particle network
- high photocatalytic activity
- high sensitivity for detecting ambients
- efficient photovoltaic energy conversion by dye sensitization

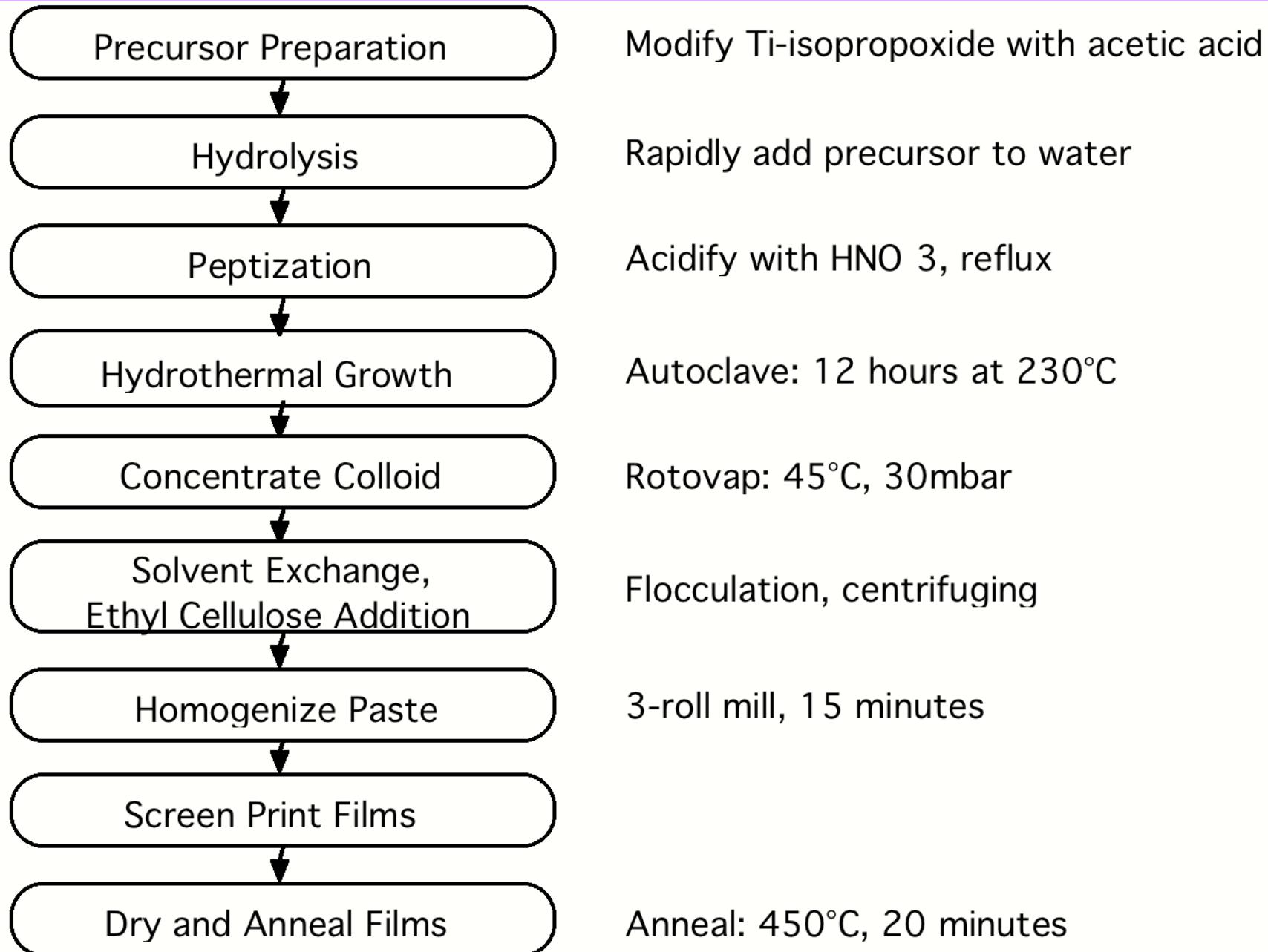
# SEM image of a mesoporous titania film.



Preferred (101) orientation  
of surface planes visible

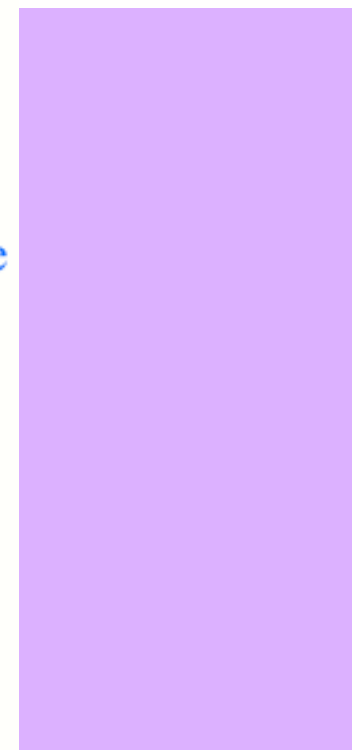
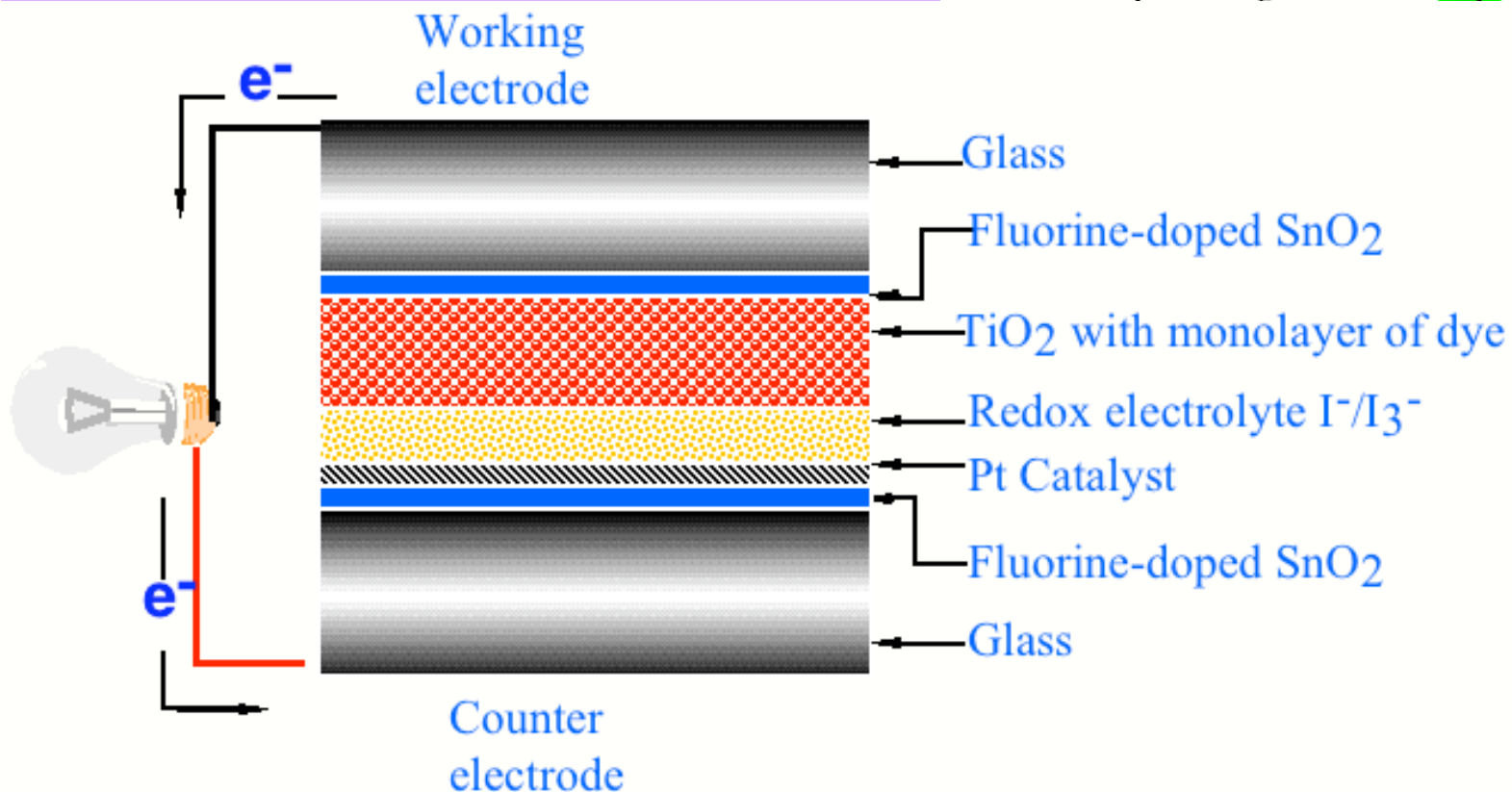
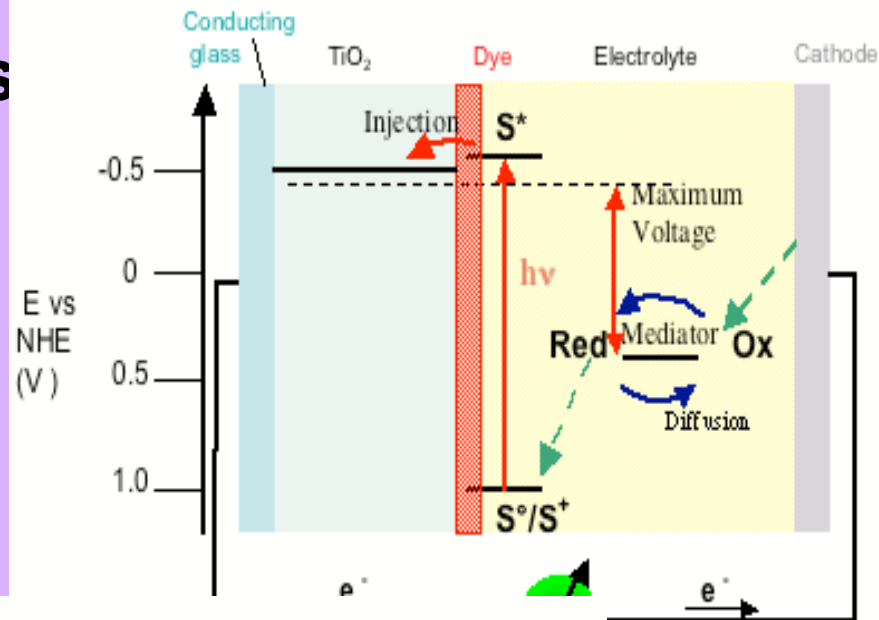


# Hydrothermal growth of nanostructured titania



# Photochemical energetics and structure of DSC

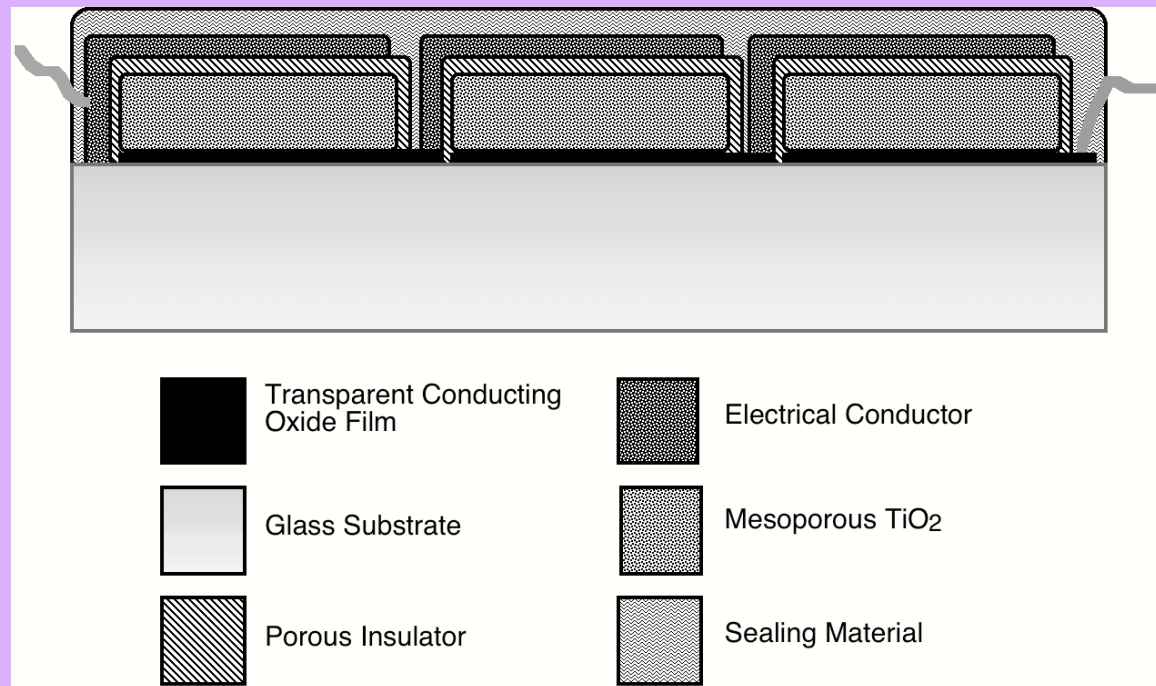
The valence band is not involved in the carrier excitation process - this is a majority carrier Device. As a result there is no charge carrier loss by recombination within the semiconductor. A nanocrystalline semiconductor can be used.





# Choice of electrolyte

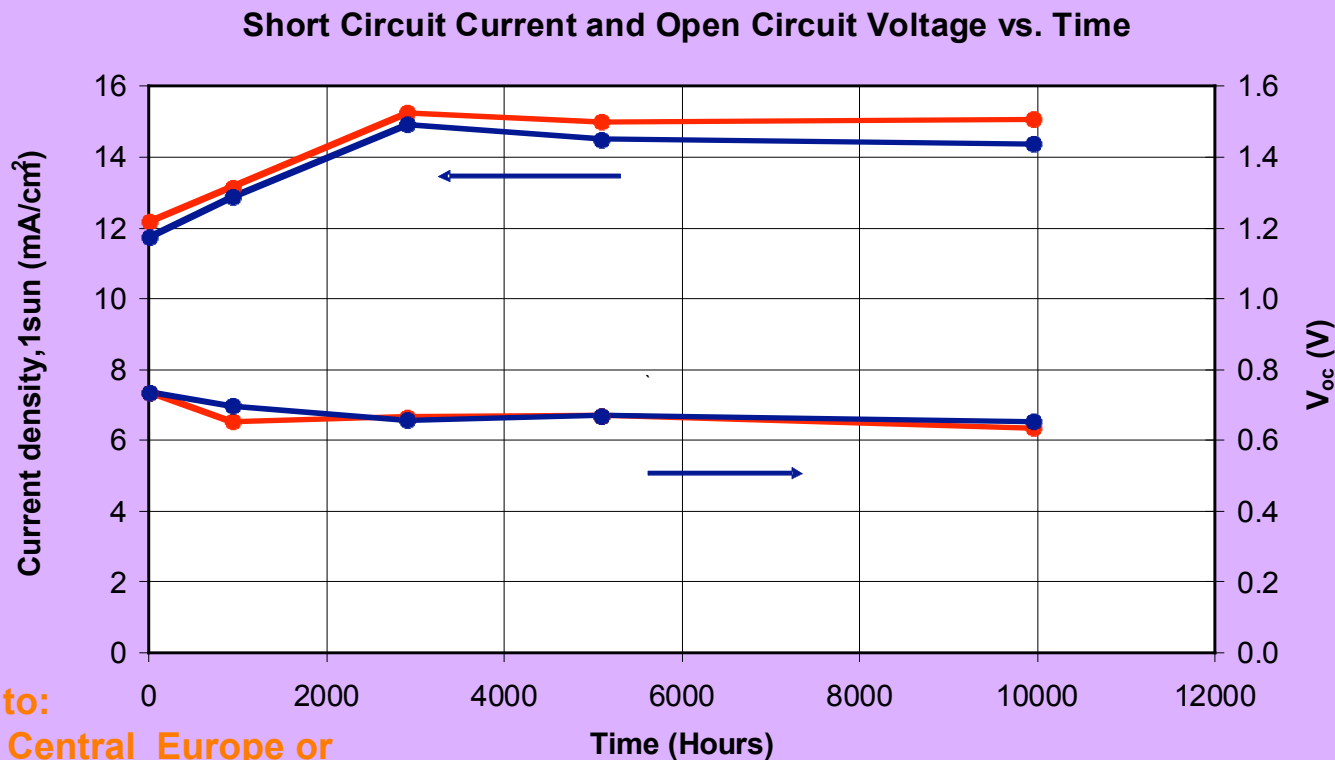
1. Efficiency is a compromise between electrolyte viscosity and ionic mobility.
2. Particularly for monolithic arrays inter-cell sealing is a critical consideration.
3. Gelled ionic liquids have an anomalously high ionic mobility despite their high viscosity.



**Interconnected monolithic 3-cell module.**

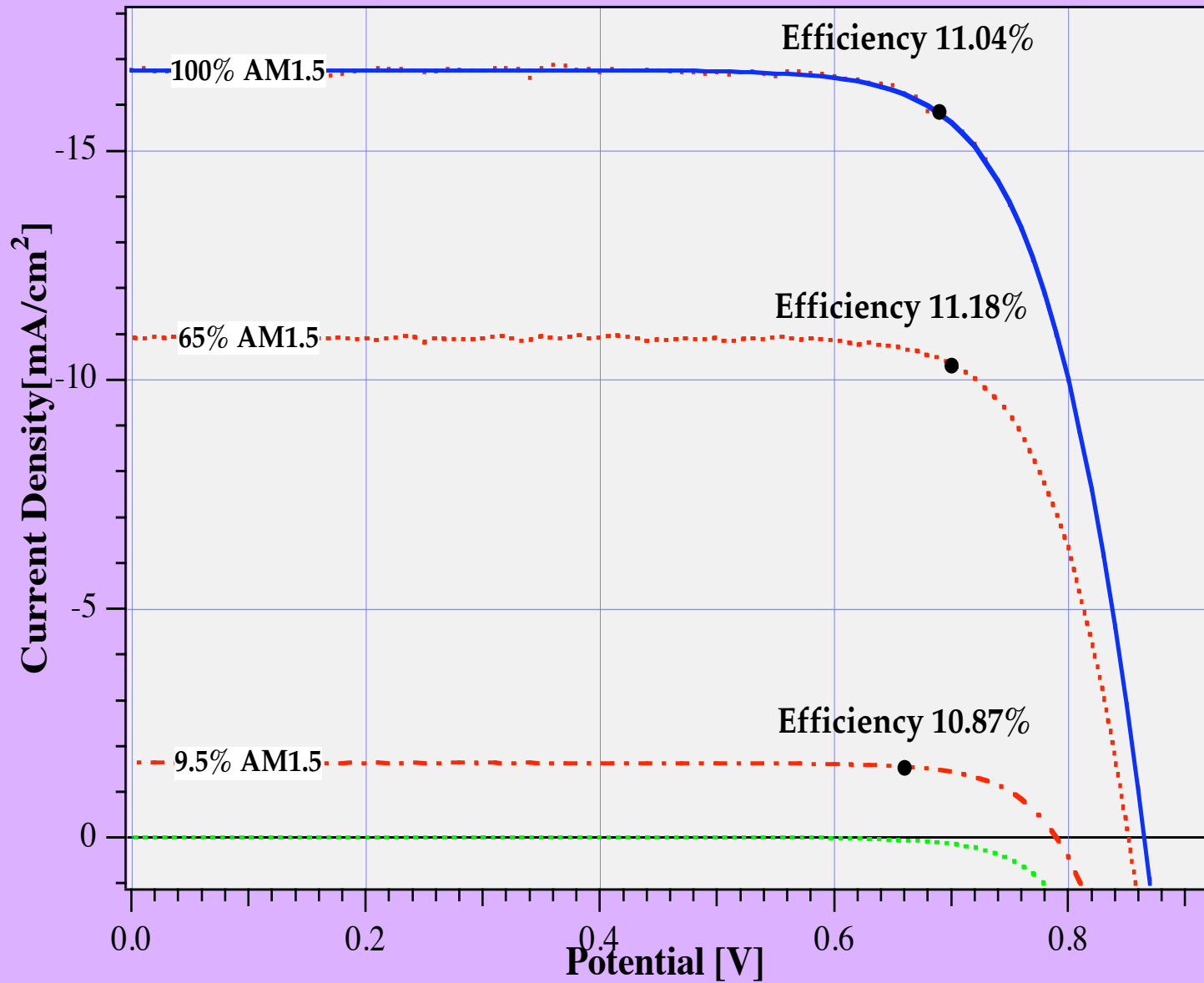
# Advantages of gel electrolyte DSC

1. Stability over an extended temperature range.
2. Ease of assembly and interconnection, due to high viscosity of the electrolyte.

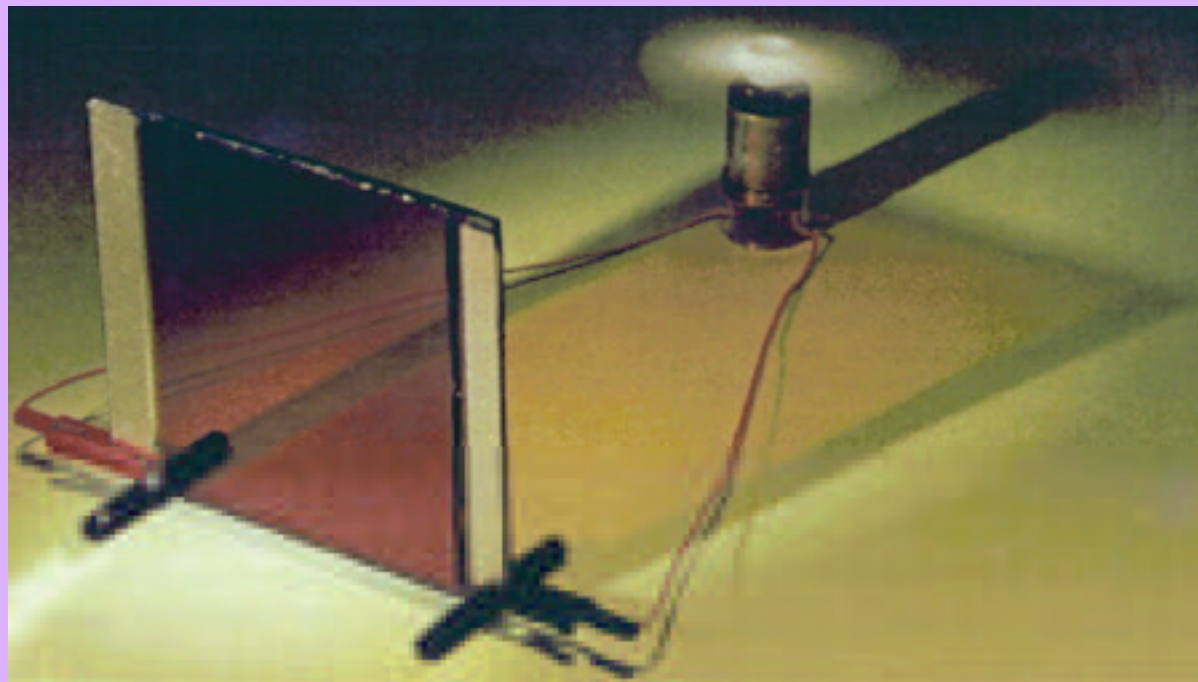


Equivalent to:  
16 years in Central Europe or  
London  
9 years in Southern Europe or  
Australia

# Characteristics of a dye-sensitised cell under light



What it looks like - prototype 1996.



# Product concept - flexible cells

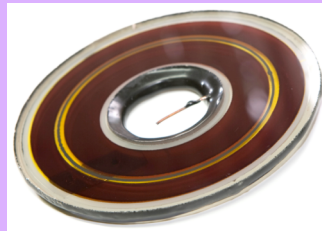
(Hitachi-Maxell, Japan)



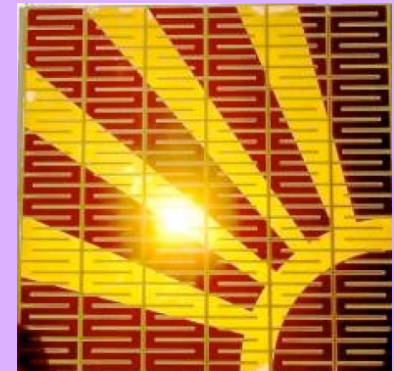
# Examples of industrial DSC development



Dyesol



Dyesol



Fraunhofer ISE



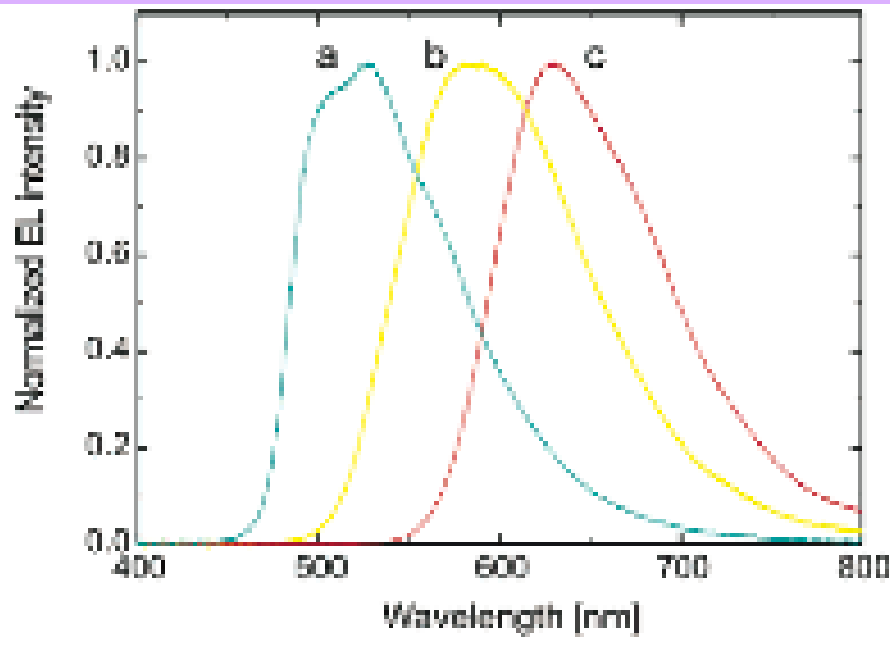
Dyesol



G24i

# OLEDs - the lighting of the future - contributing to energy efficiency. The photovoltaic effect reversed!

## Selection of luminescent material for required emission spectrum.



Electroluminescence spectra of ITO/electroluminescence (EL) layer/Ag devices, where the EL layer consists of:

- (a)  $[\text{Ir}(\text{ppy})_2(\text{dma-bpy})]\text{PF}_6$ ;
- (b)  $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6 + \text{PMMA}$ ;
- (c)  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2 + \text{PMMA}$ .

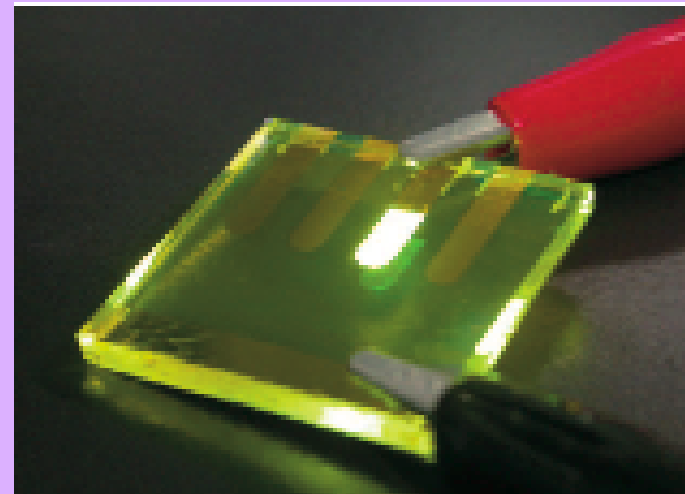
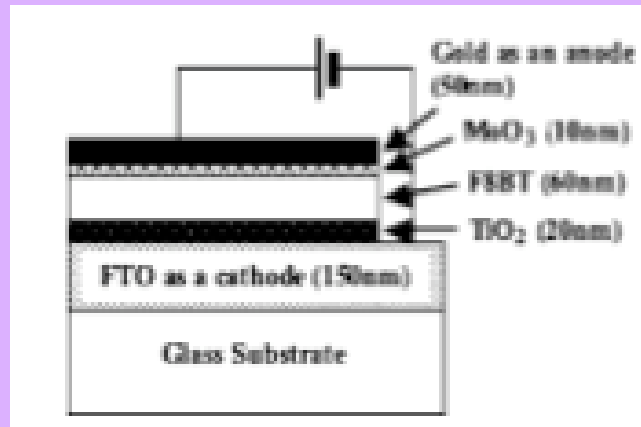
The EL intensities are in arbitrary units.  
ppy = 2-phenylpyridyl.  
bpy = bipyridyl.

# HOLEDs - hybrid organic-inorganic LEDs - increased stability against oxidation

**Economy = efficiency + reliability/stability - for LEDs as for PV!**

LPI/EPFL is in cooperation with EPSON for HOLED R&D.

APPL. PHYS. LETT. **89**, 183510 (2006).6



The green emitter material “F8BT” is poly(di-octylfluorene-benzothiadiazole)



# Acknowledgements

Members of the EPFL development team, past and present.

Industrial partners who have shown their interest in this technology by licensing EPFL patents and cooperating in research and development.

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