Dye-sensitized Solar Cells
-
Materials and Interfaces

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Dept. of Chemistry

School of Chemical Sciences & Engineering

KTH Royal Institute of Technology

Stockholm, SWEDEN

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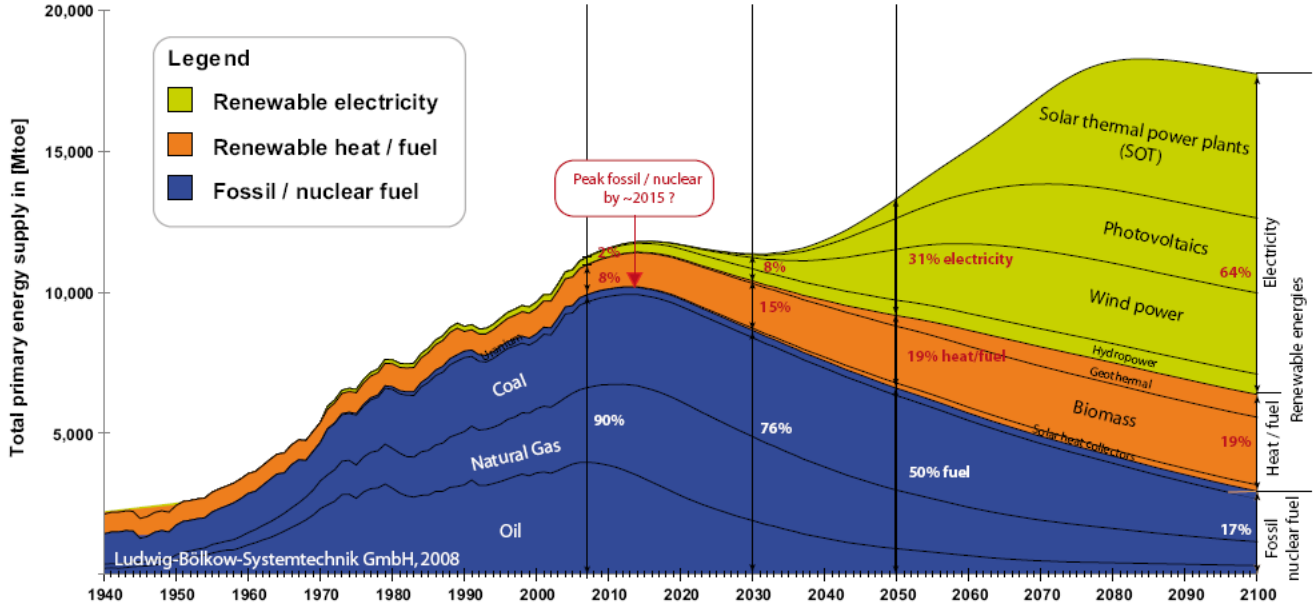
Energy in the future



2009: ca. 16 TW, momentaneous yearly averaged rate of consumption
(*cf.* 4.1 x 10^{20} J/y; 2006 it was 13 TW)

2050: Estimated to 28 TW

Perspective: 1 new 1 GW nuclear reactor *per day* for 30 years…
… BUT, less than *1 hour* of solar light

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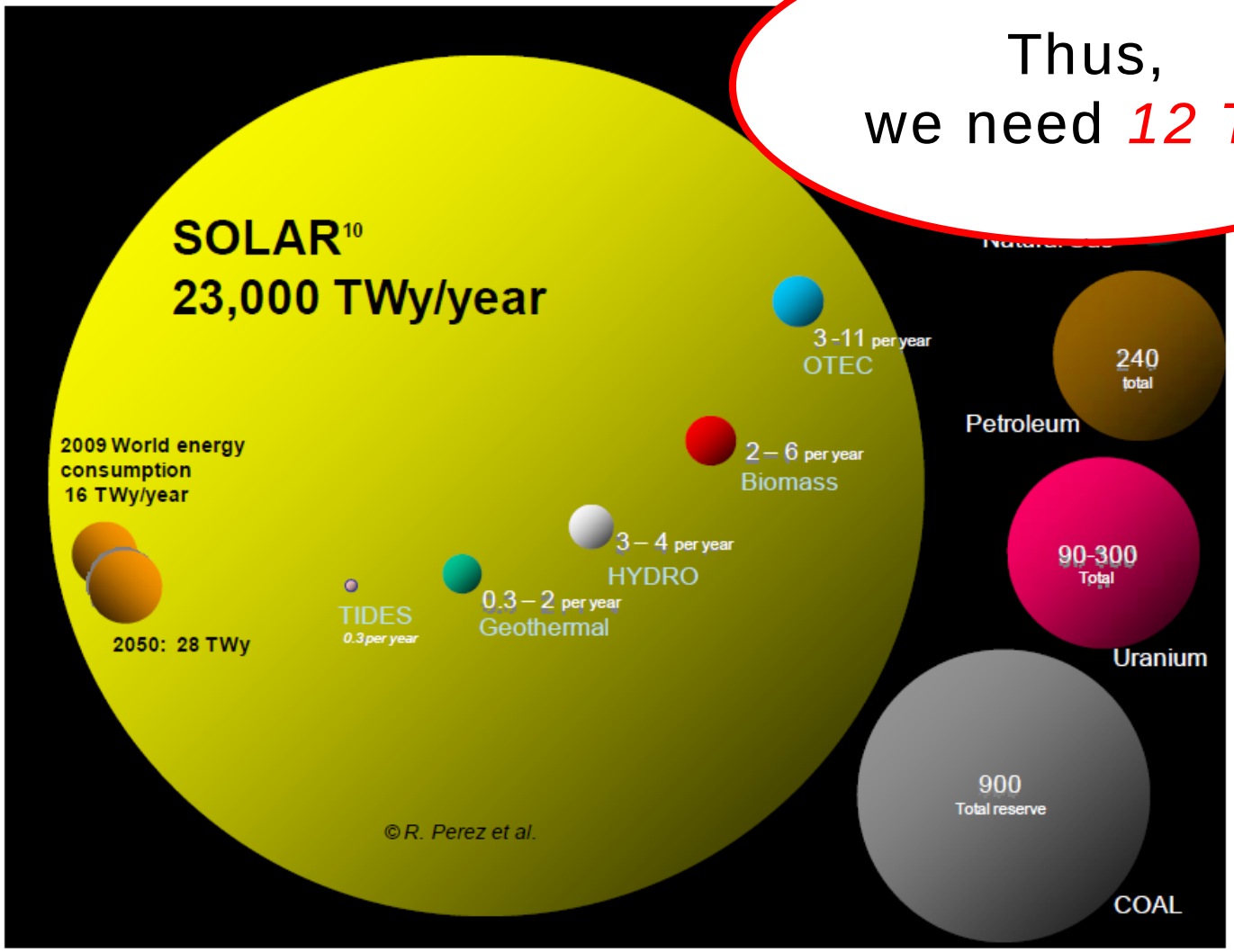
The alternatives



Thus,
we need *12 TW*

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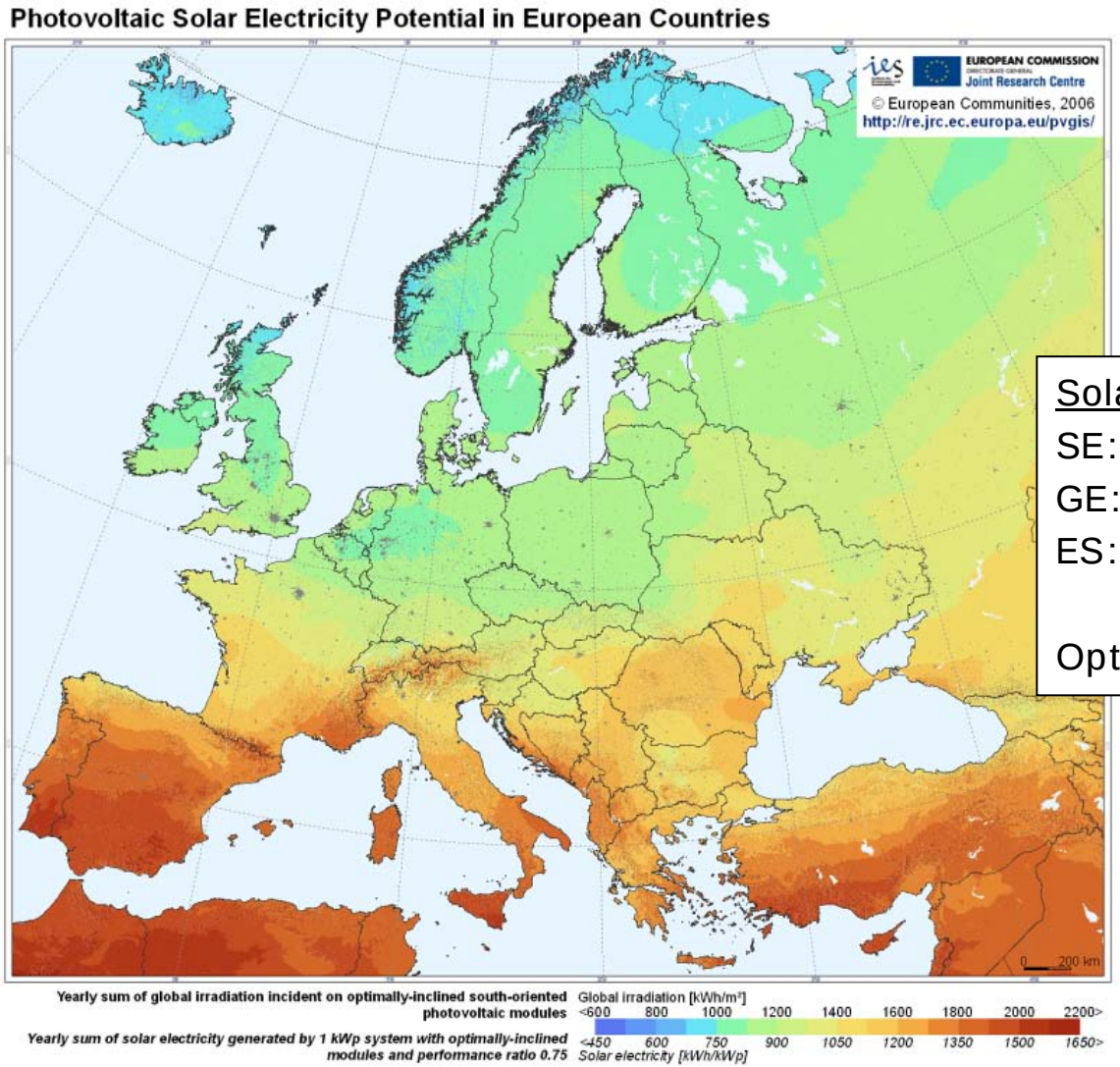
Energy and latitude



Solar light in different regions:

SE: 871 kWh m^{-2} y^{-1} (= 242 W m^{-2})

GE: 1014 kWh m^{-2} y^{-1}

ES: 1586 kWh m^{-2} y^{-1}

Optimal angle in SE: 44°(S): 1079 kWh m^{-2} y^{-1}

Latitude of Moscow ≈ Stockholm

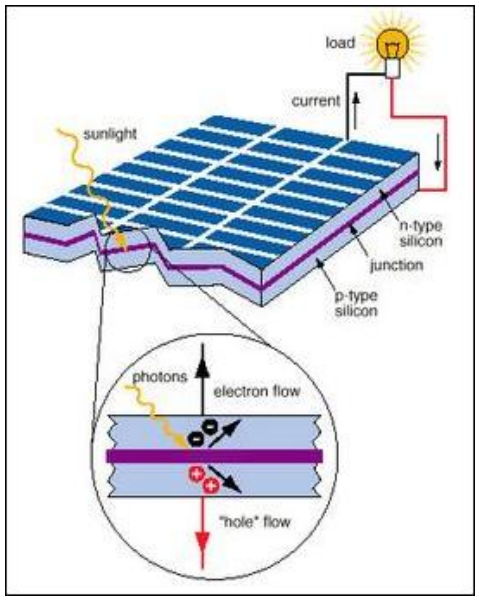
Energy from the Sun

- Photosynthesis → biomass/biofuels
  - Efficiency <1%
- Solar heat:
  - Water heating (domestic): Efficiency ≤70%
  - Elektricity: Conc solar light (CSP), turbines, etc: Efficiency ≤20%

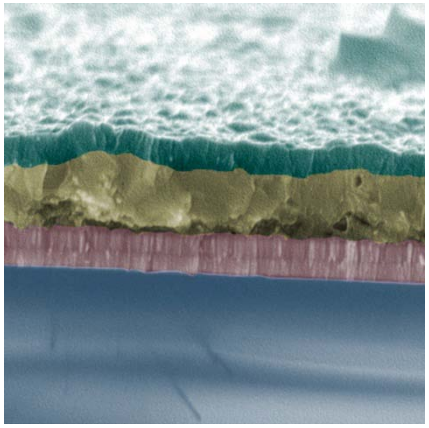
- Solar electricity (solar cells)
  - Direct conversion: Efficiency ≤20%

Common problem: *STORAGE!*

Solar cell technologies



Si
Amorf, polycryst.
or monocryst



p-CIGS – Thin film
Solid solution of
$Cu(In,Ga)Se_2$ (1-3 µm)

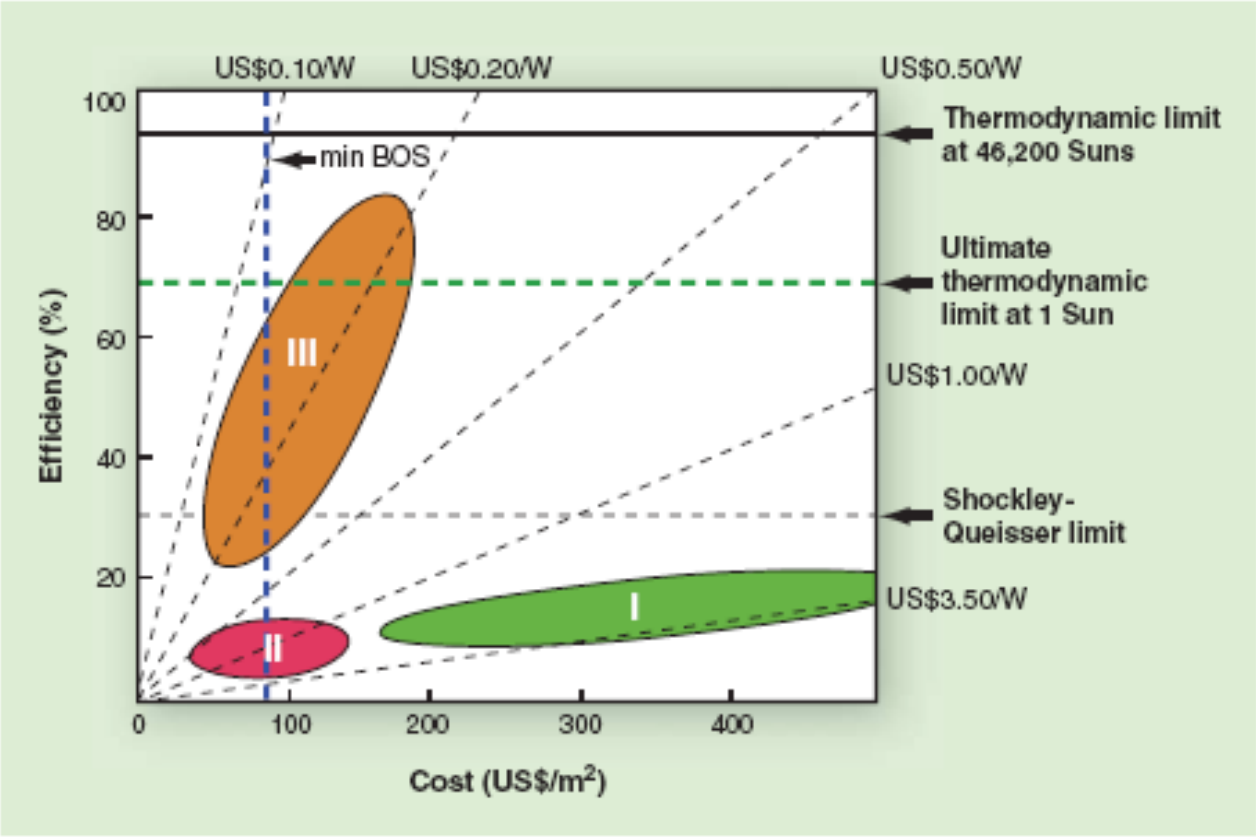
CdTe/CdS – Thin film

Too expensive !!!

Power excellent – Energy not optimal !!!

New and promising technologies ...

Cost & efficiency improvmenents



I. Si-based
II. Thin-film
III. ???

Target: <0.5 €/W_p or >20% efficiency at <100 €/m^2

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Grätzel cells ≅ DSC

NATURE · VOL 353 · 24 OCTOBER 1991

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

Brian O'Regan* **& Michael Grätzel†**

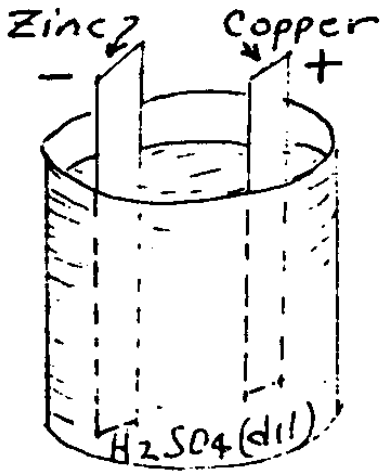
Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

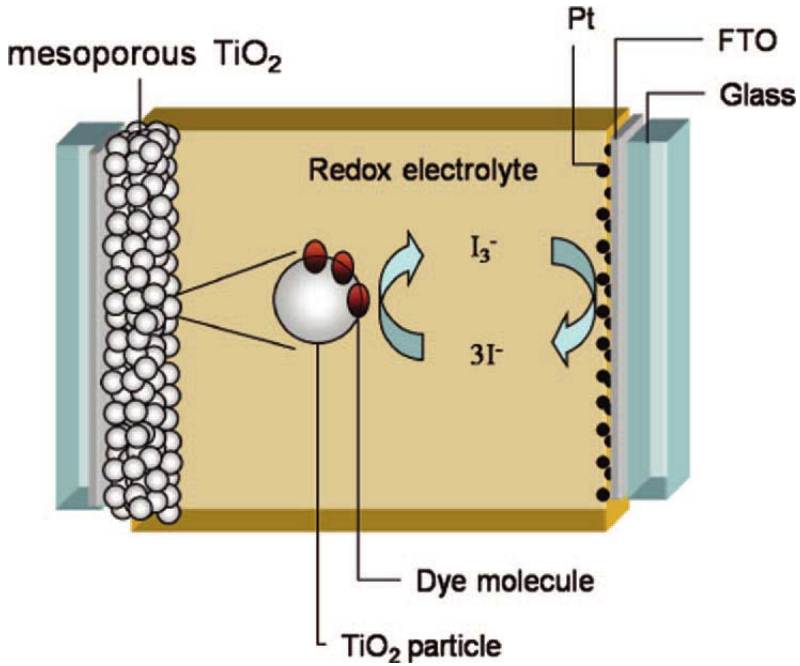
THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low-

Cited 7,800 times; Feb 19, 2012

Current world record (lab cells): ≈13%

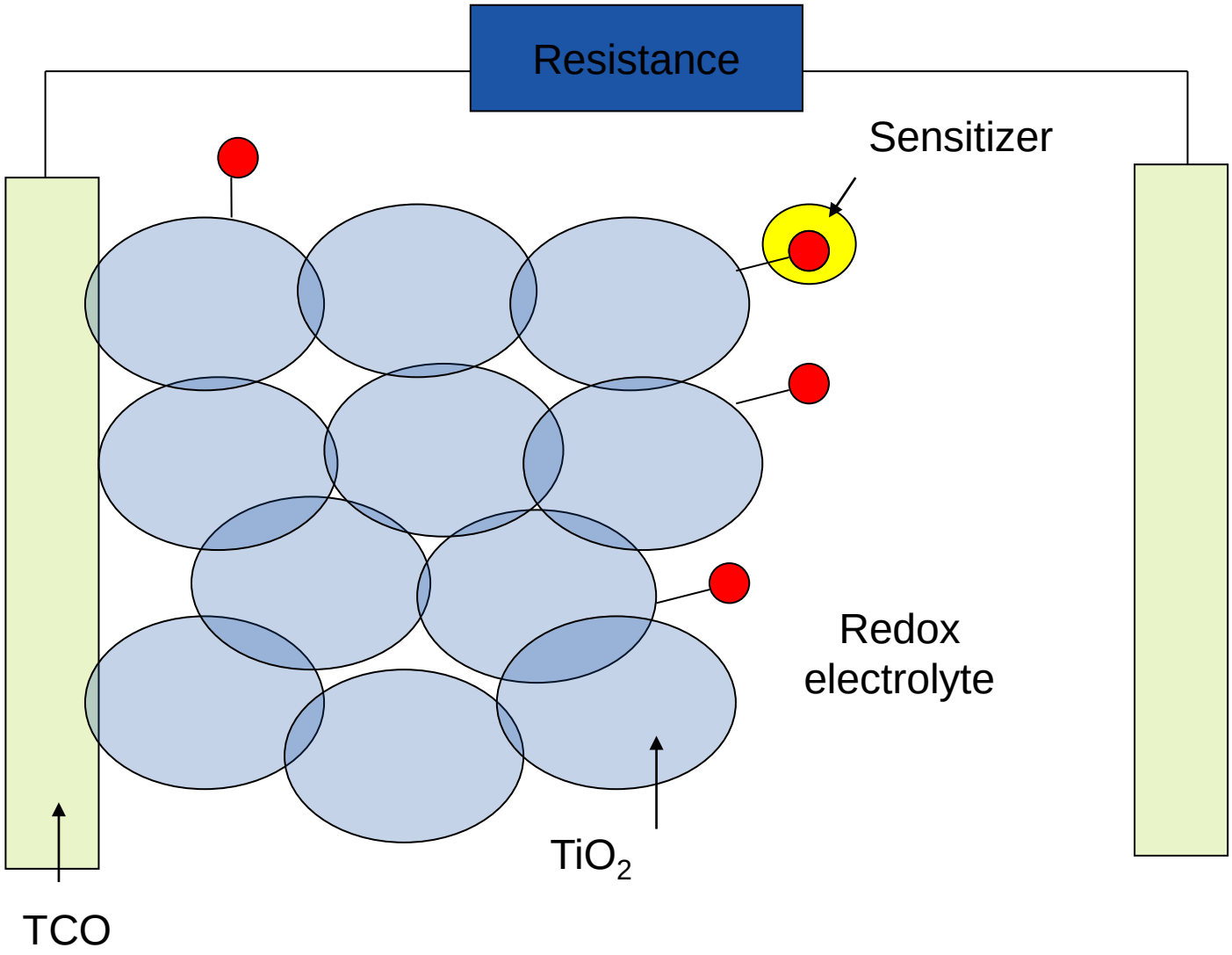
The electrochemical cell



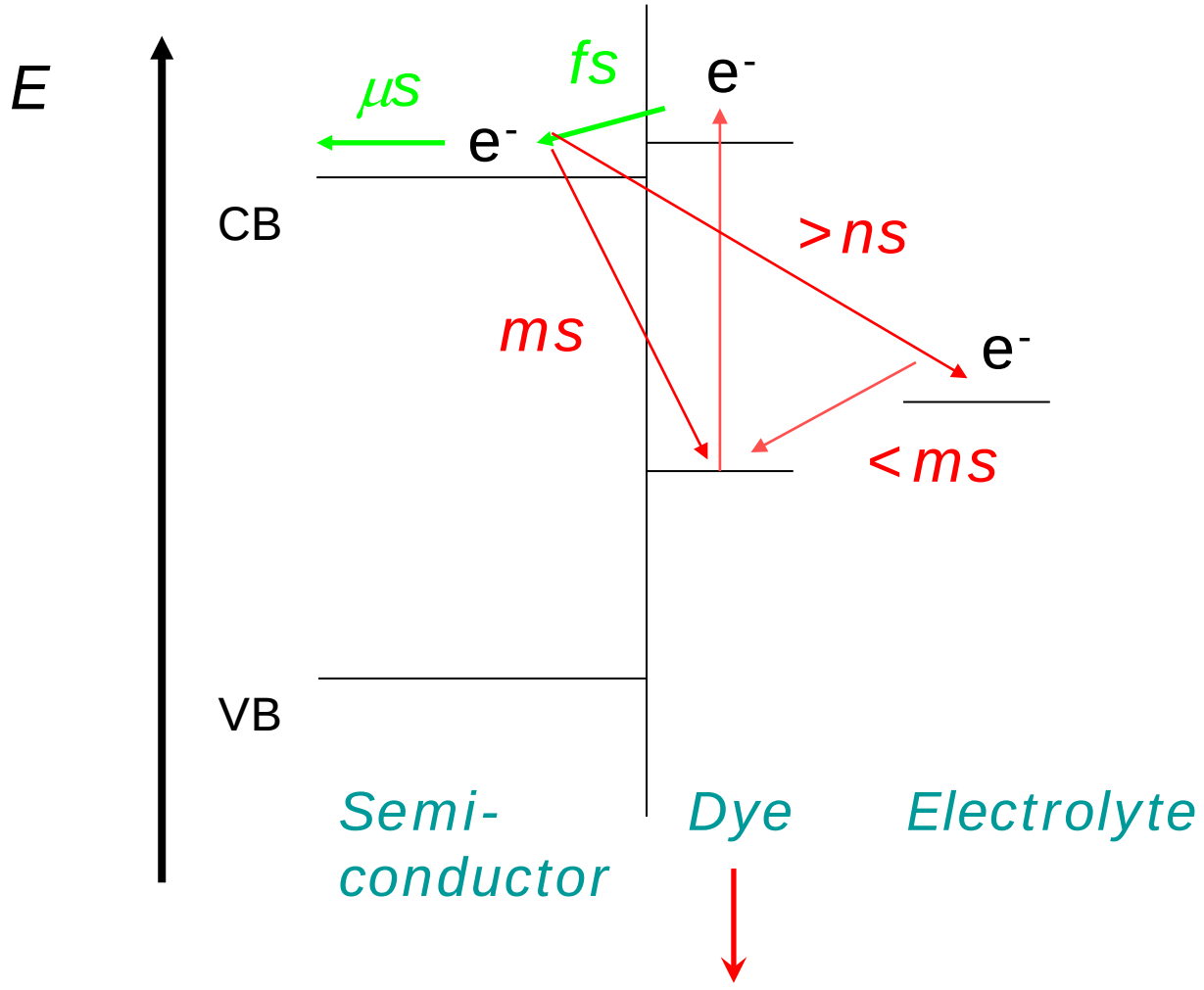


Cell
=
2 electrodes + electrolyte

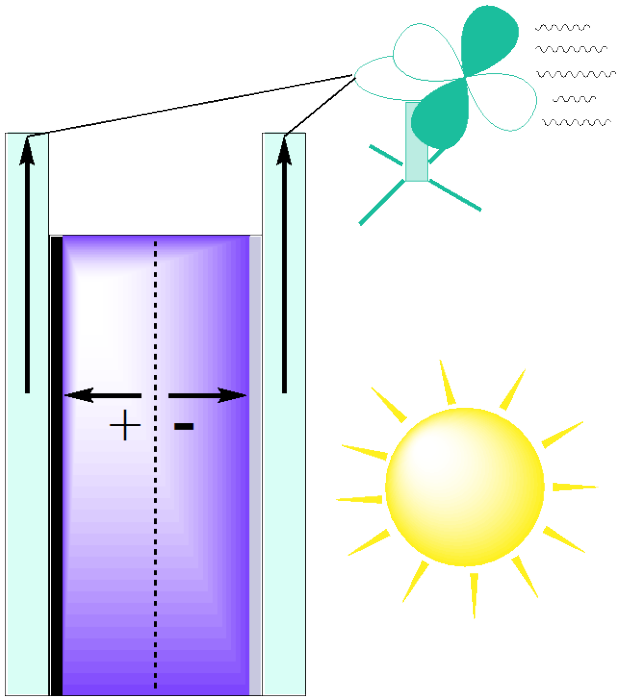
DSC function



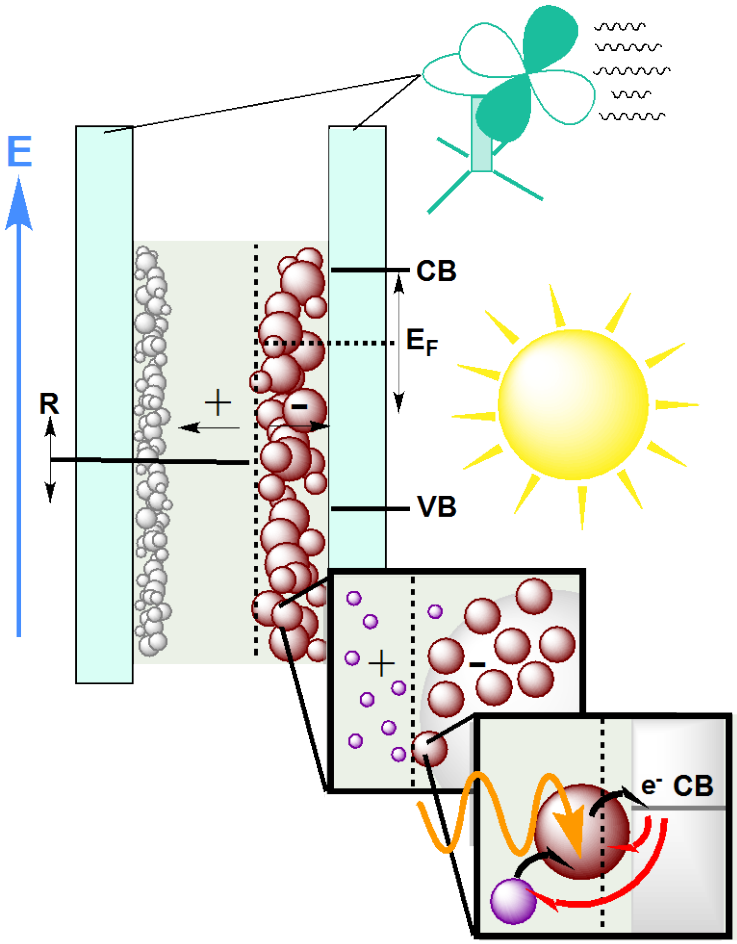
A note on kinetics



Multicomponent cell



Semiconductor-based cell



DSC: Absorption & charge transport separated !!!

Pro's & con's

+

- 'Kitchen chemistry' (*i.e.* easy to make)
- Inexpensive (glass substrate the most expensive)
- Relatively high efficiency
- Also works in *diffuse light* (*i.e.* indoor, cloudy days, *etc.*)

-

- Complex, interlinked reactions (tuning required!)
- Stability
- Competition from other technologies

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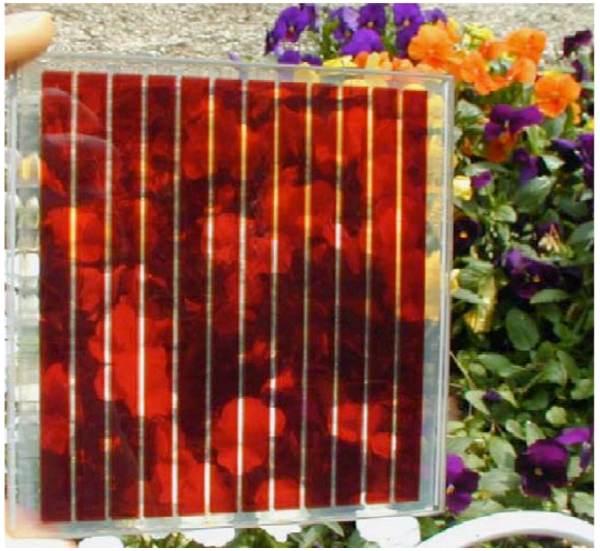
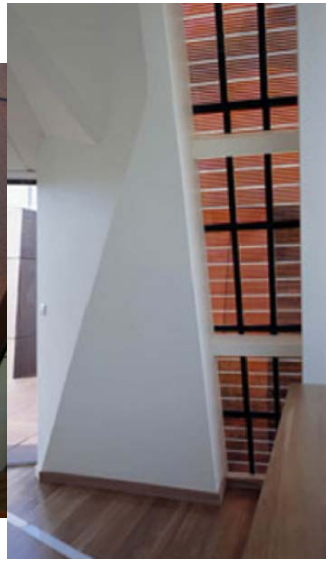
Estetic

Sony (Jpn)

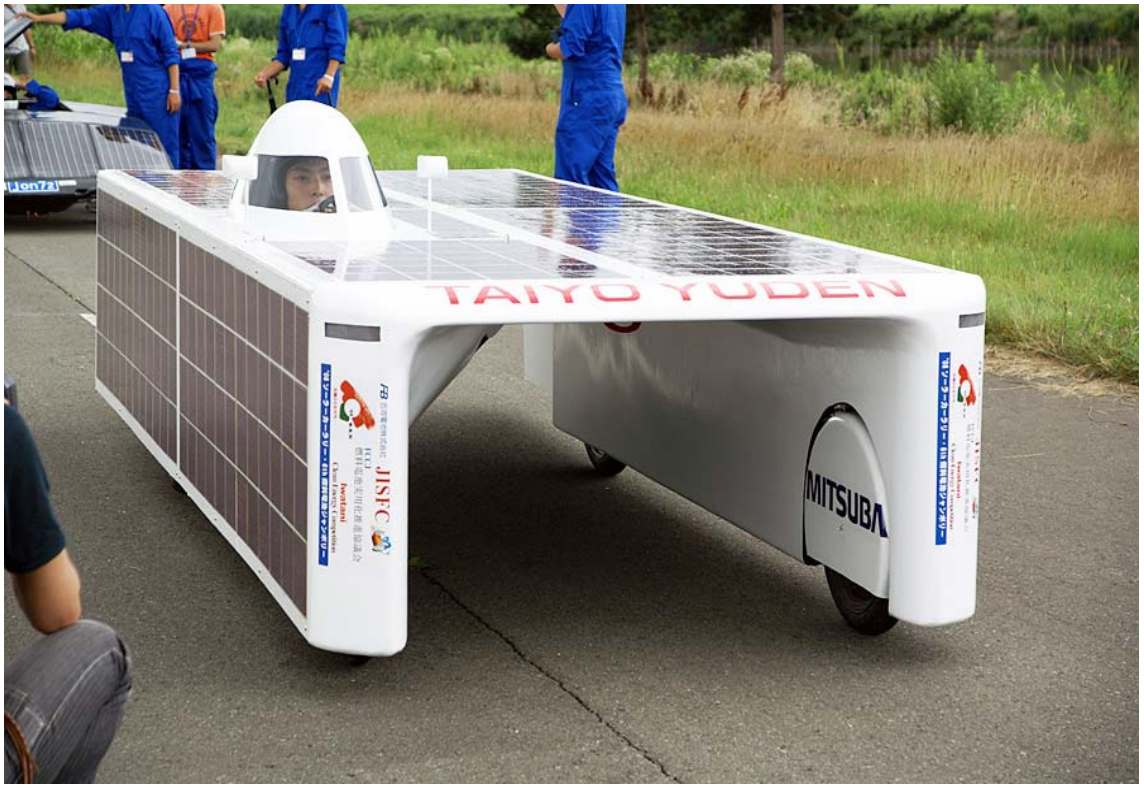


Toyota (Jpn)



Dyesol (Aus)

Useful?



Profs. Segawa & Uchida, Tokyo Univ., Japan
(among 10 best of 35 …)

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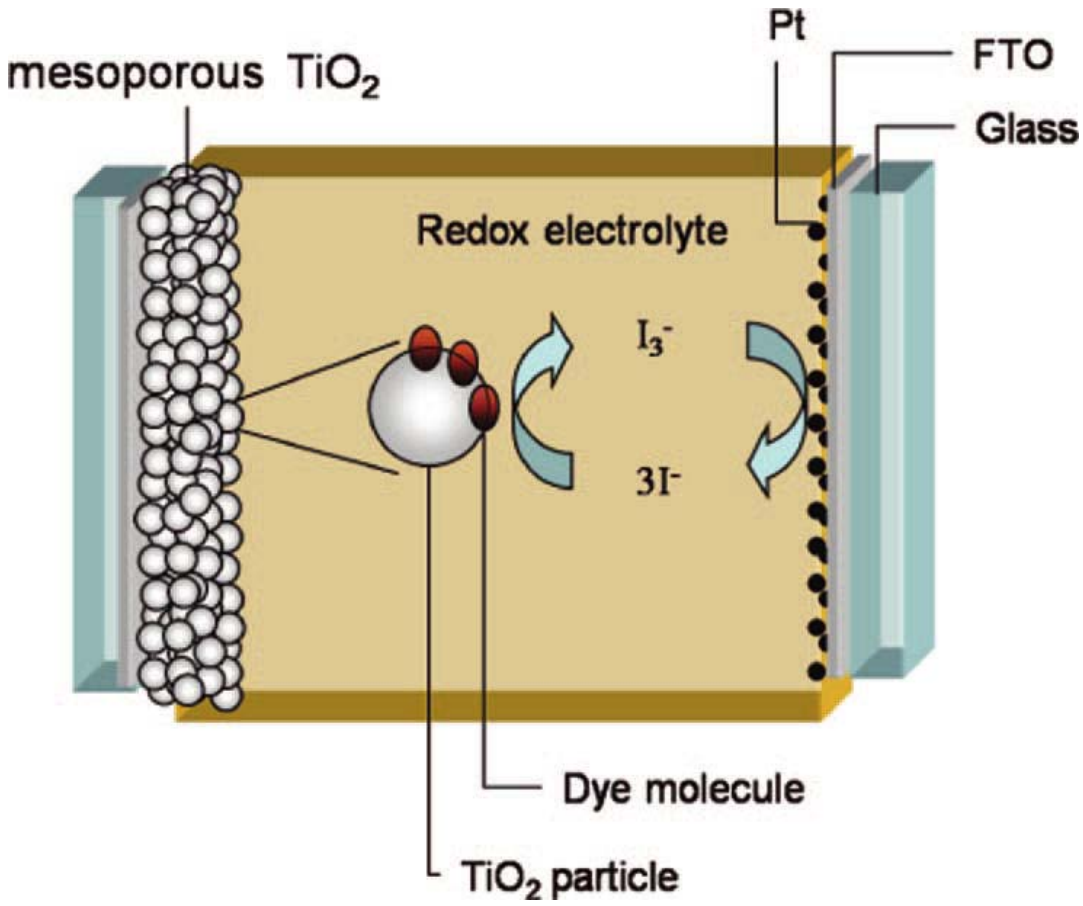
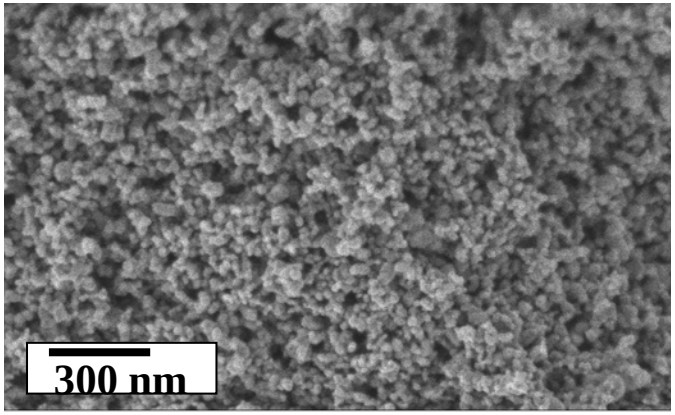
Simple: Three parts only !

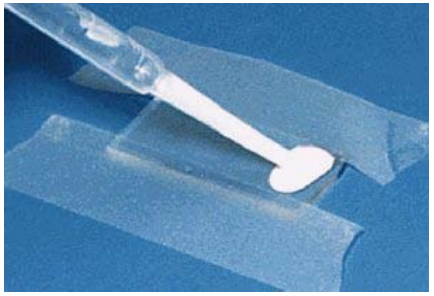


Photoelectrode (Part 1: Semiconductor)



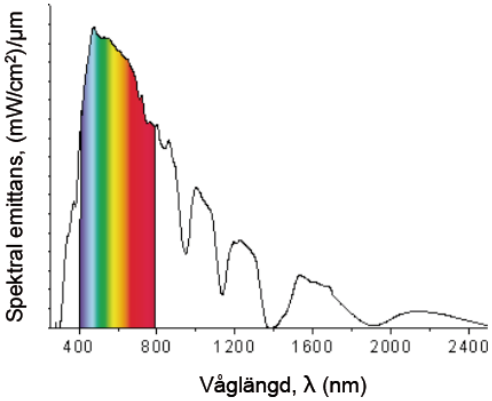
TiO_2-particles, d ≈ 25 nm
1 cm^2 contains ≈ 10^{13} particles
(huge surface – *nano*!)

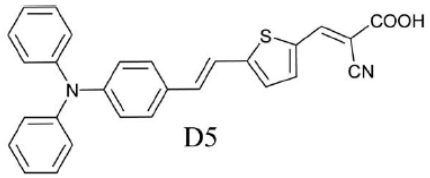
Step 1: Nanostructured semiconductor



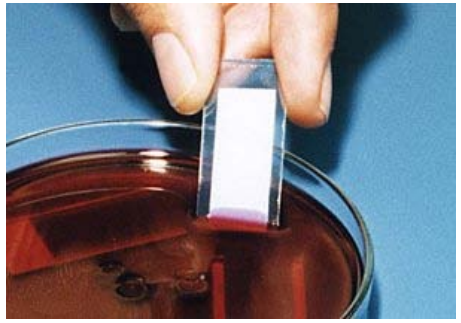
Photoelectrode (Part 2: Sensitizer)

Sensitizing dye



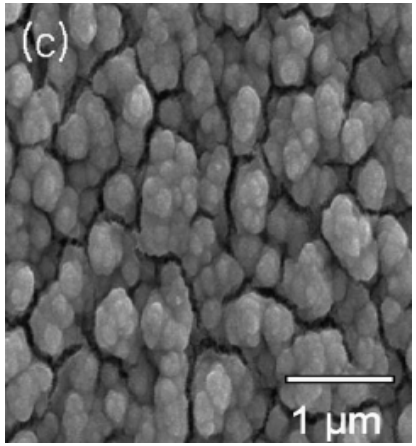


Step 2: The dye



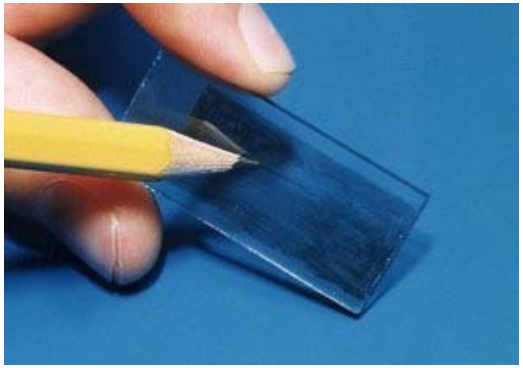
Counter electrode

Catalytical material



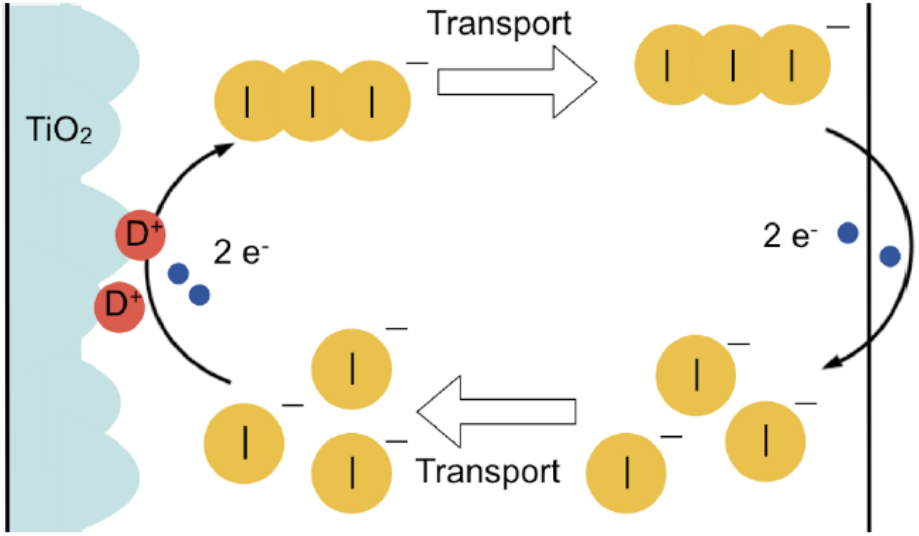
Catalytic platinum (Pt)
Graphite
Conducting polymers
Nanoporous carbon

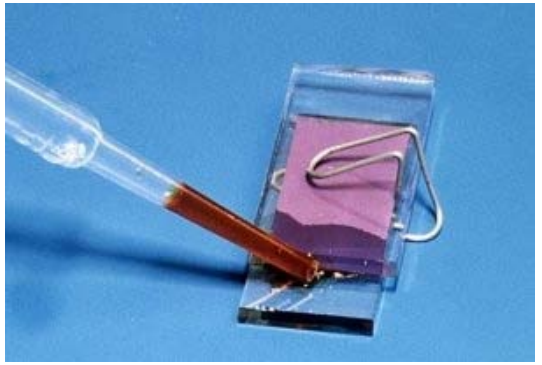
A pencil offers the graphite …



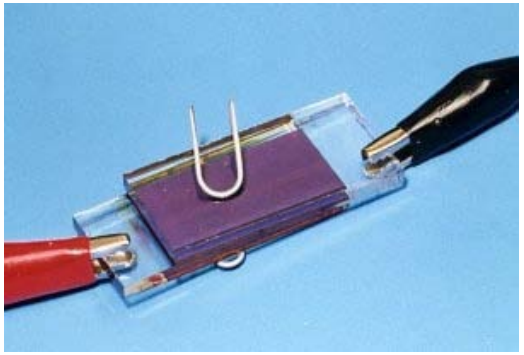
Electrolyte

- Organic solvent (ethanol *etc*.)
- Dissolved redox couple (*eg.* I^-/I_3^-)





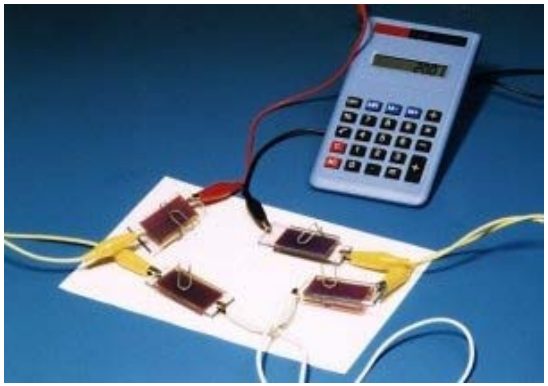
A DSC in about 15 min



The DSC obtained:

- ≈0,5 V photovoltage
- Lousy current
- ≈0.5% efficiency …

Grupp	Färgämne	Voltage V	Current µA
1	Hallon	0,46	335
2	Blåbär	0,44	290
3	Spenat	0,44	170



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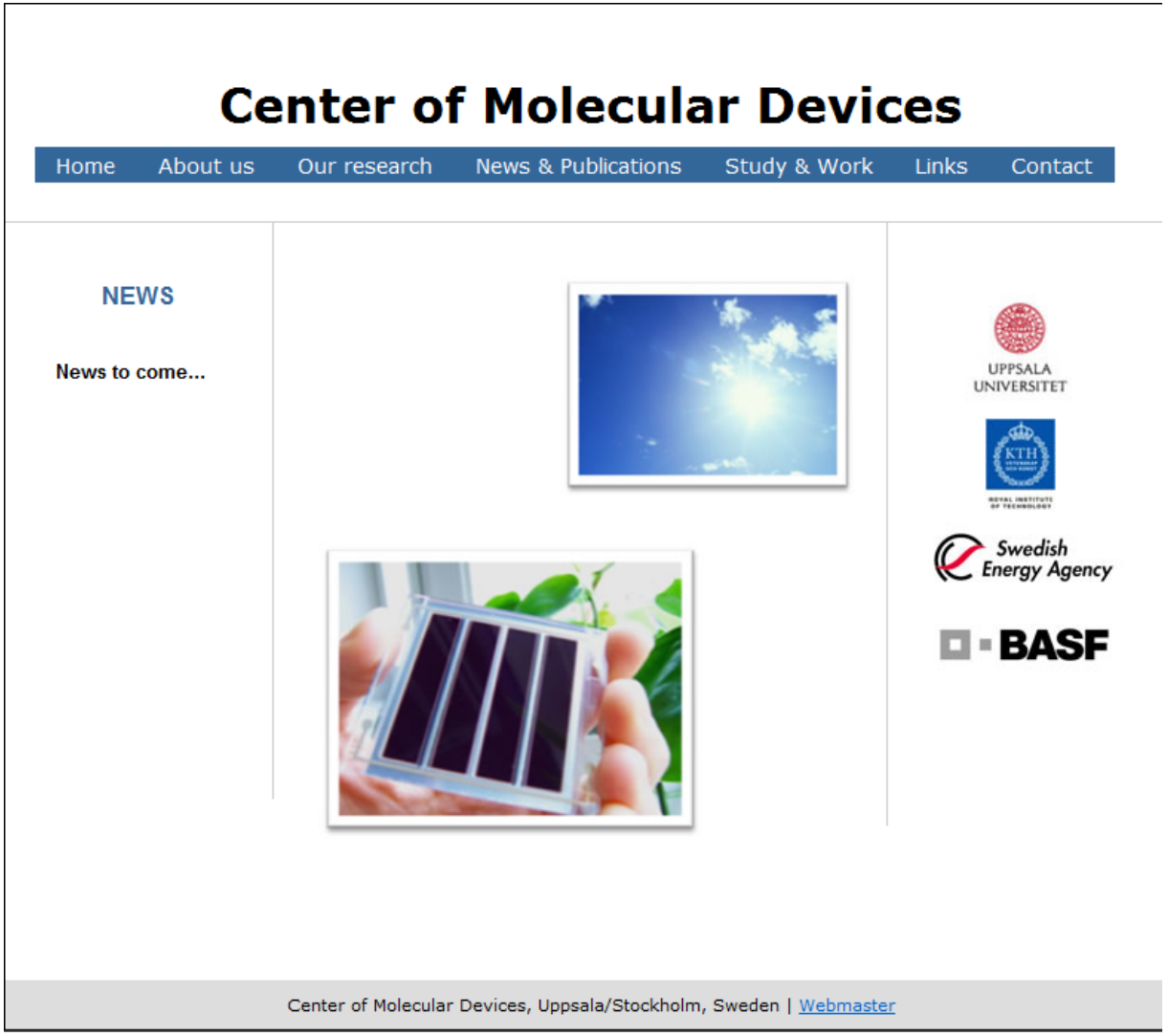
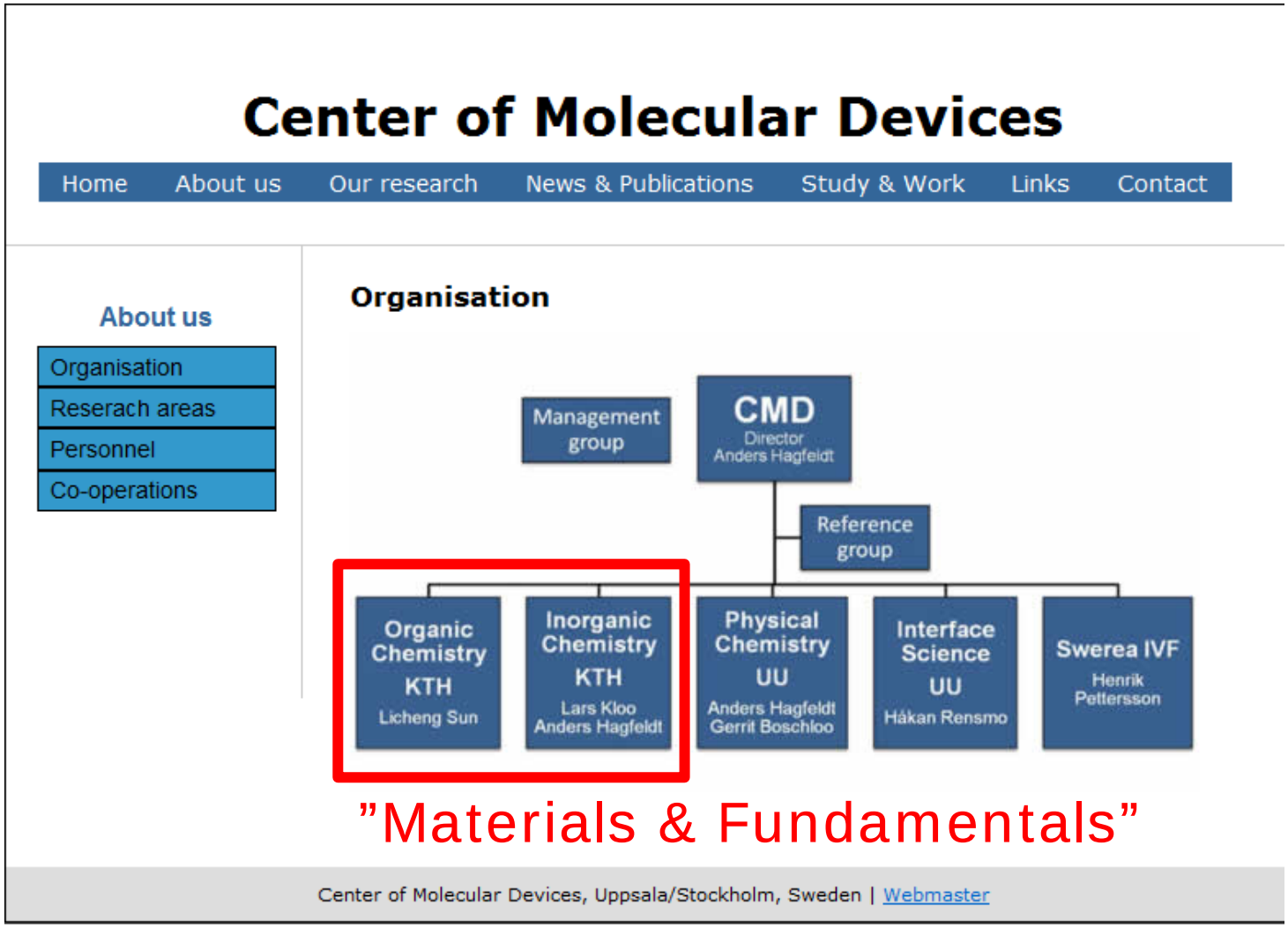
CMD



www.moleculardevices.se

CMD at KTH



CMD: >30 researchers

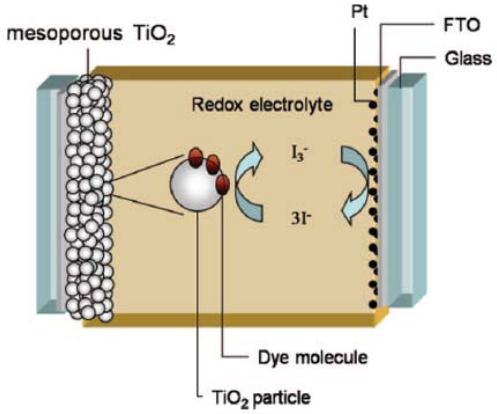
Chem. Rev. **2010**, *110*, 6595–6663

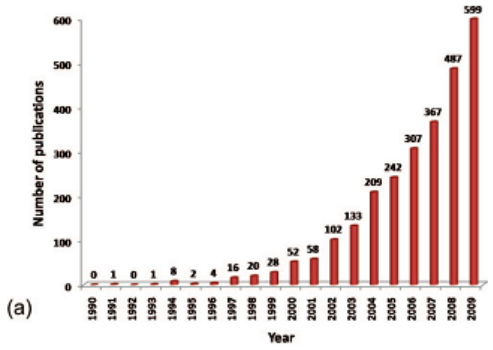
Dye-Sensitized Solar Cells

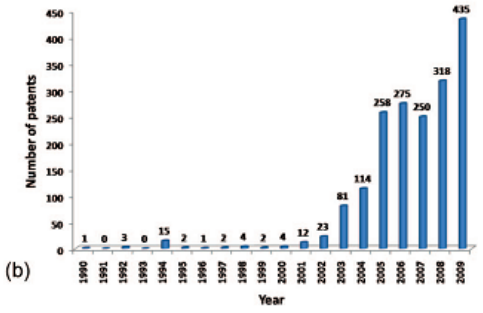
Anders Hagfeldt,*,†,‡,II Gerrit Boschloo,† Licheng Sun,‡,II Lars Kloo,‡ and Henrik Pettersson⊥

Department of Physical and Analytical Chemistry, Uppsala University, Box 259, SE-751 05 Uppsala, Sweden, Department of Chemistry, KTH - Royal Institute of Technology, Teknikringen 30, SE-100 44 Stockholm, Sweden, State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Centre on Molecular Devices, Dalian University of Technology (DUT), Dalian 116012, China, and Swerea IVF AB, Box 104, SE-431 22 Mölndal, Sweden

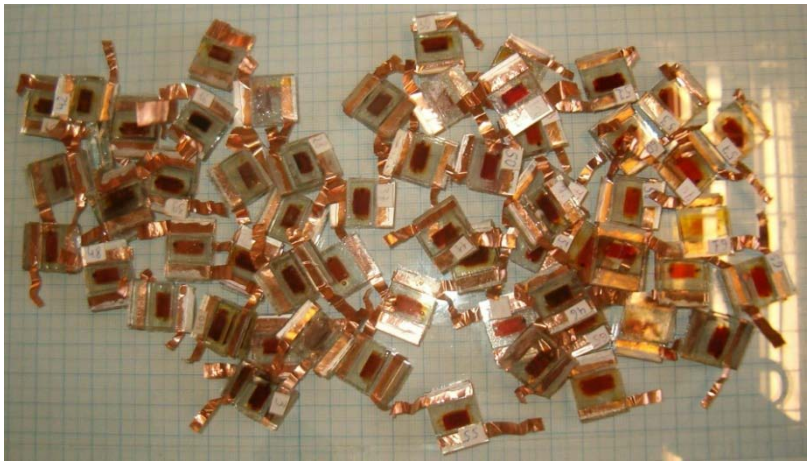
Cited >300 times in a year



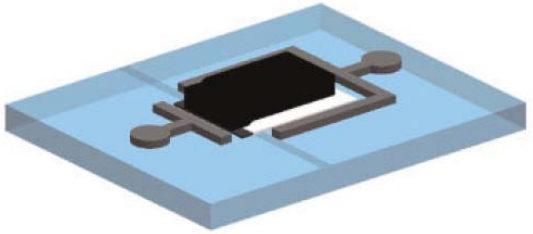


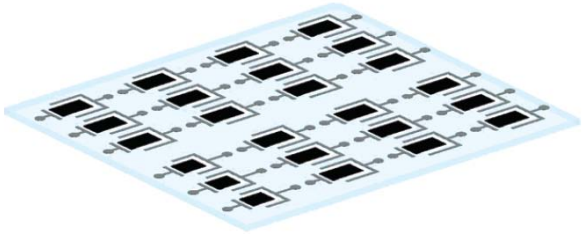


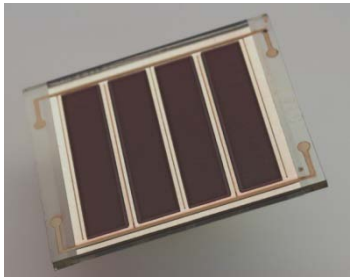
The cells



Lab cells







Monolithic cells
(Swerea IVF AB)

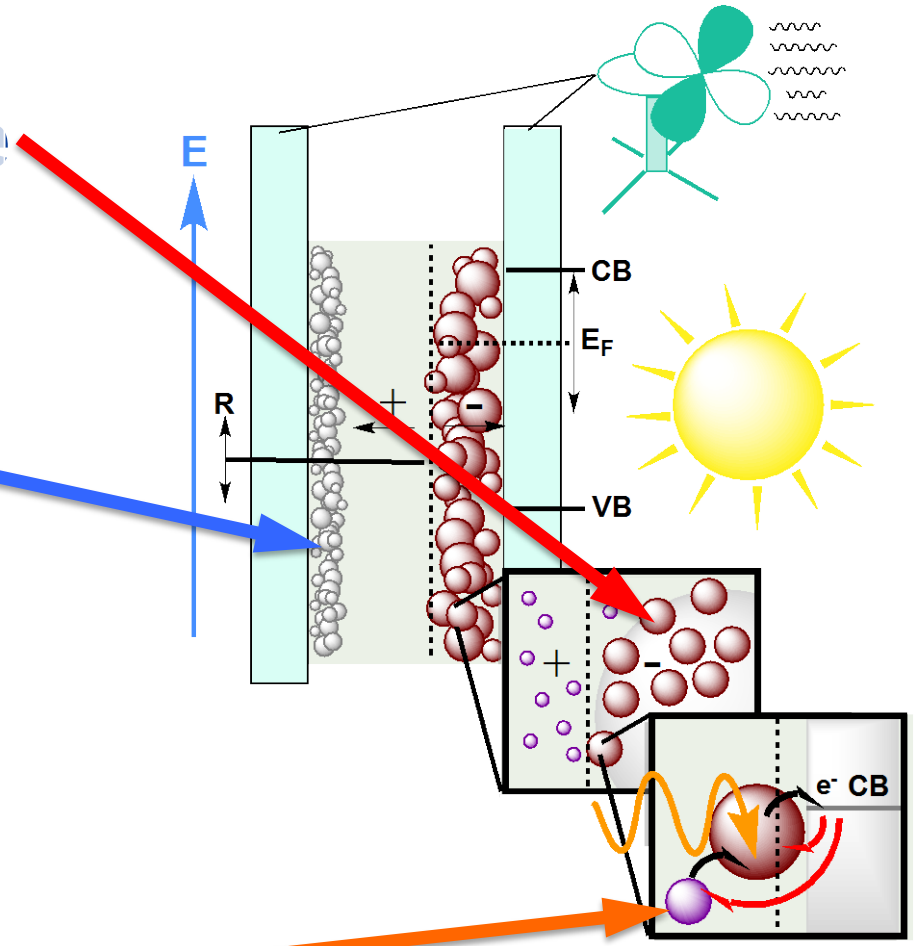
CMD: Electrode materials

Working Electrode

- Metal oxide semiconductors

Counter Electrode

- Metals
- Carbon materials
- Semiconductors
- Polymers

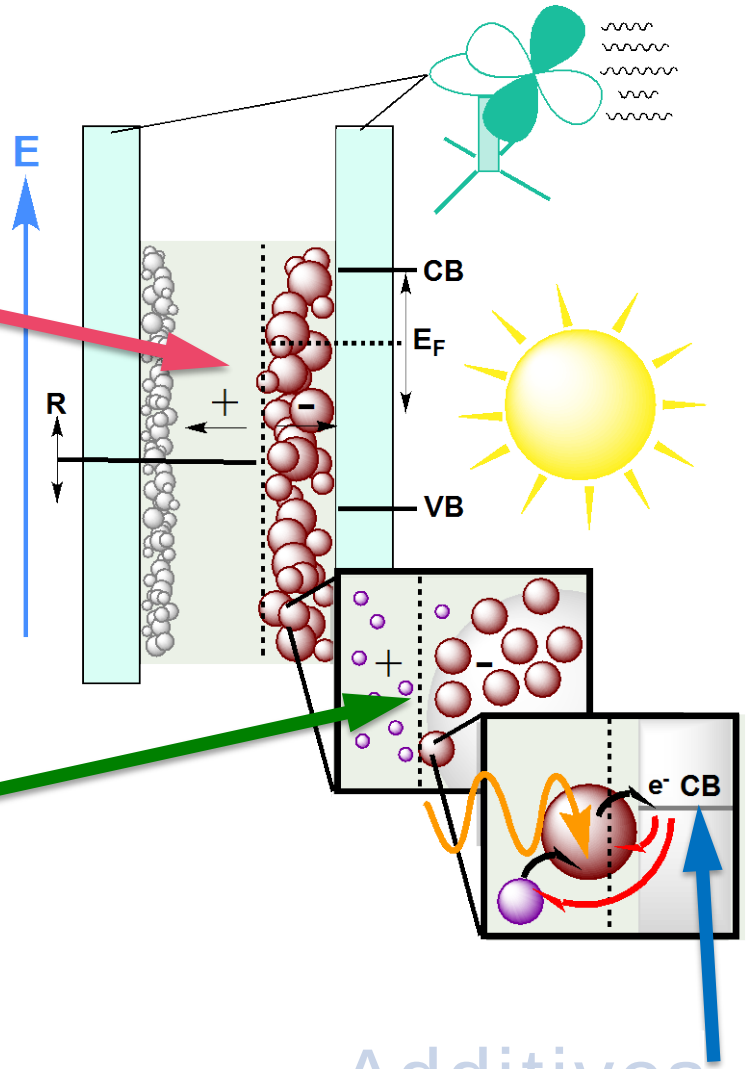


Sensitizer

- Metal coordination complexes
- Organic dyes
- Semiconductor Quantum-Dots

CMD: Electrolyte

Solvents
- Ionic liquids
- ISILs

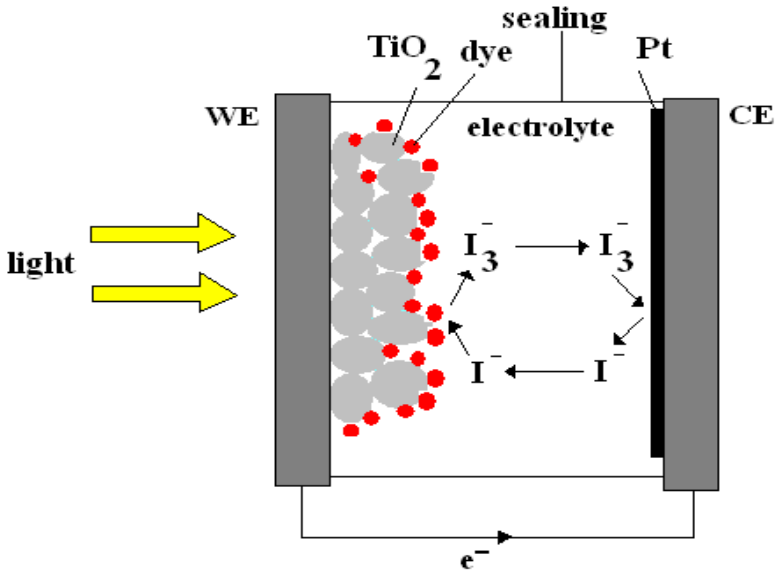


Redox Couple
- Halogens
- Organic molecules
- Solid-state mediators

Additives
- Cations
- Lewis bases

The electrolyte

An electrolyte is a chemical system that provides an electrolytic contact between the solar cell electrodes



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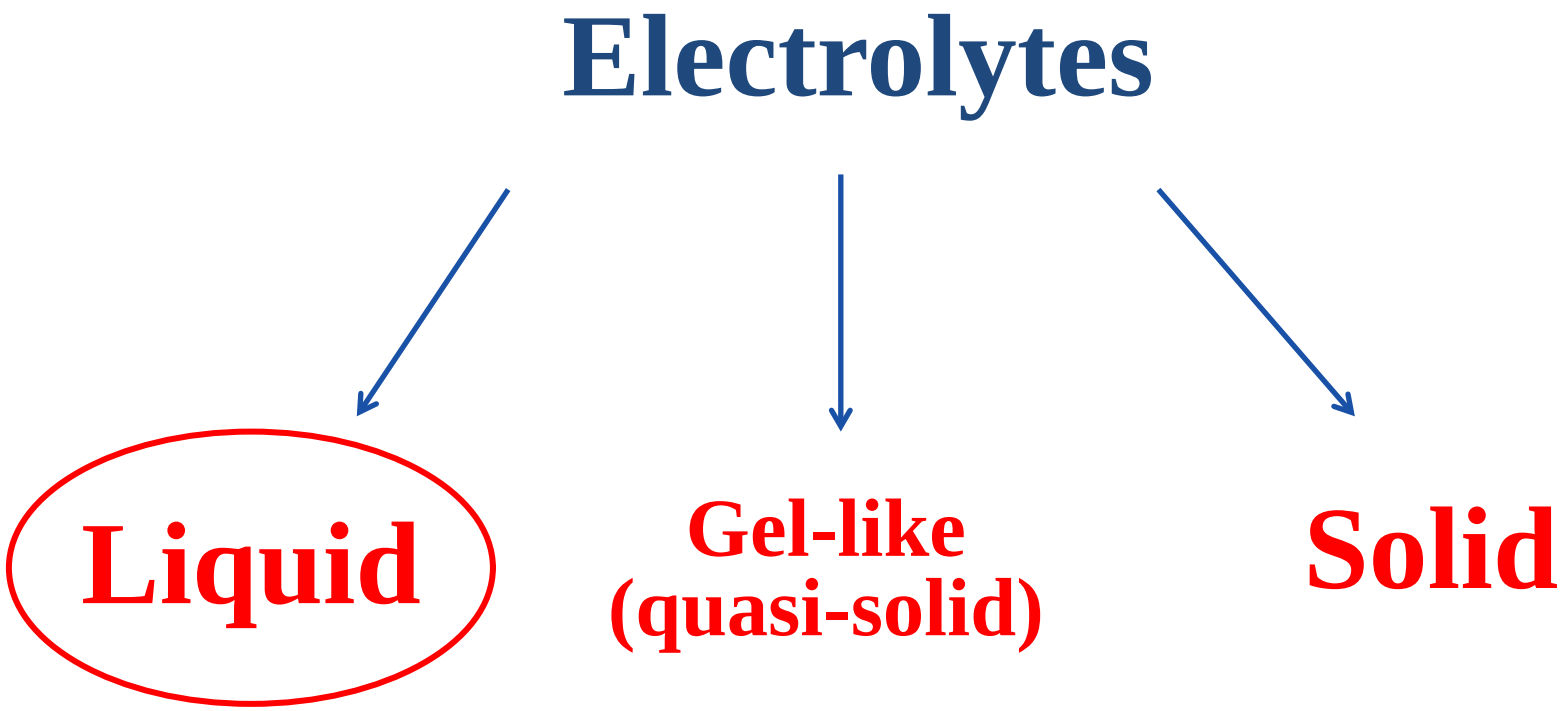
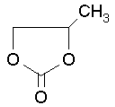
Types



Organic solvents

Name	Formula	Melting Point °C	Boiling Point, °C	Viscosity, cp
Water	H_2O	0	100	0.89
Ethanol	CH_3CH_2OH	-114	78	1.08
Acetonitrile	CH_3CN	-44	82	0.33(30°C)
Valeronitrile	$CH_3(CH_2)_3CN$	-96	139	0.78(19°C)
Glutaronitrile		-29	287	5.3
3-Methoxy-propionitrile	$CH_3OCH_2CH_2CN$	-63	164	1.1
Propylene carbonate		-49	241	2.5
γ-Butyrolactone		-44	204	1.7

Problems:
- Evaporation
- Chemical stability
- Electrochemical stability
- Temperatur range
- Toxicity
- ...

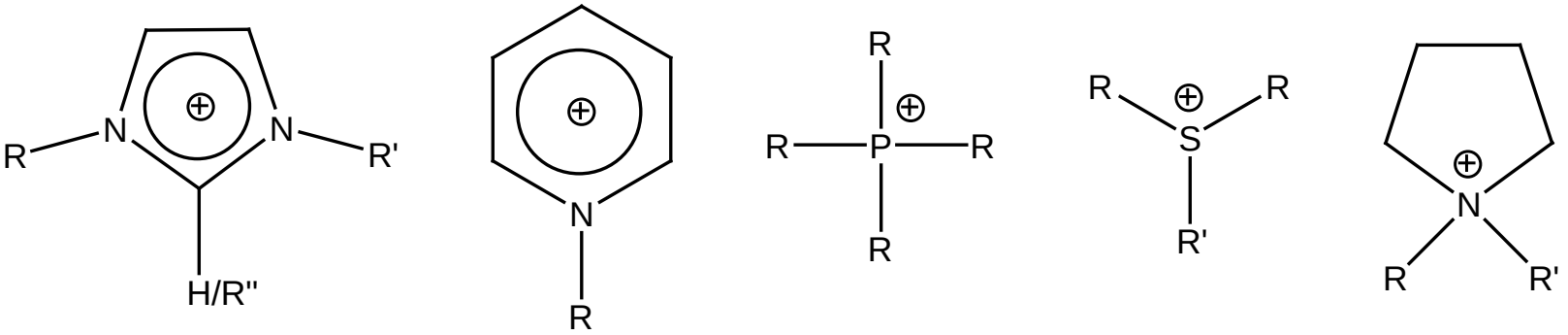
L. Kloo *et* al., Dalton Trans. **2011**, *40*, 10289 (Perspective)

Ionic liquids

Definition:

”Liquid consisting of *only* ions and with a melting point <100 °C”

a) cations



b) anions Hal^-, PF_6^-, BF_4^-, OTf^-, NO_3^-, $N(CN)_2^-$, SCN^-, $Co(CO)_4^-$

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Ionic liquids

Advantages:

- No vapour pressurs (almost)
- Non-explosive / non-flammable
- Thermally & electrochemically very stable
- Good solvent for both salts and organics
- ... not yet toxic ...

Academically interesting but useless ...

1988

EUCHEM CONFERENCE ON MOLTEN SALTS

St. ANDREWS, SCOTLAND. July. 3rd. – 8th.

Last lecture ...

SOME STRUCTURAL STUDIES UPON
ROOM-TEMPERATURE CHLOROALUMINATE(III)
IONIC LIQUIDS

Kenneth R. Seddon
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ (UK)

To date, the majority of the studies relating to the eponymous ionic liquids [1,2] have centred upon the following anionic equilibrium:

$$2[AlX_4]^- \rightleftharpoons [Al_2X_7]^- + X^- \qquad (1)$$

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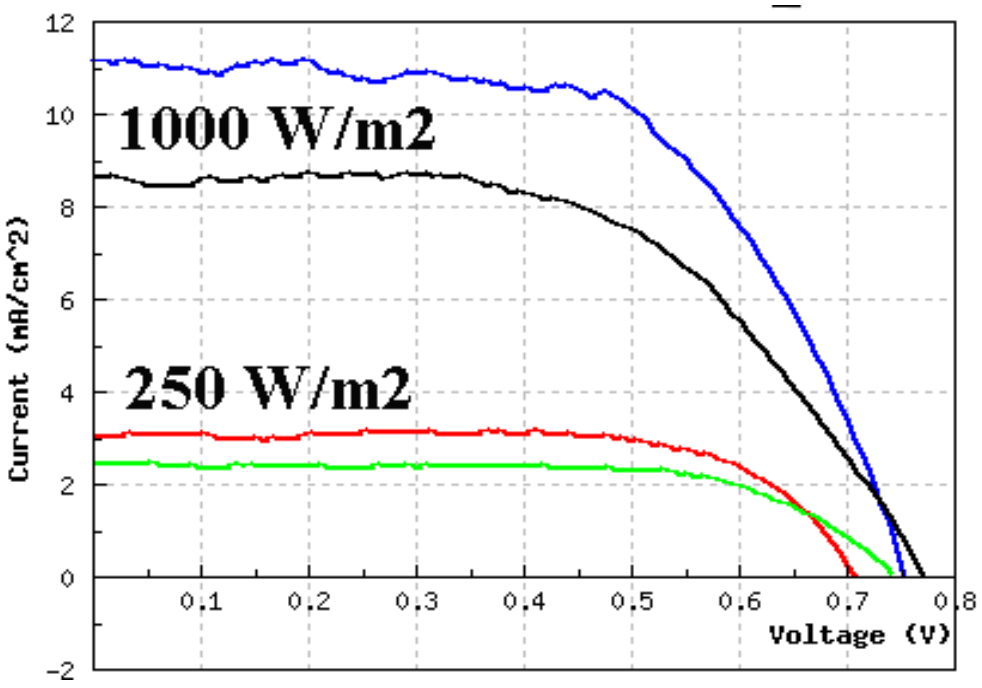
Murky crystal ball ...

Reasonable performance

Intensity (W/m^2)	I_{sc} (mA/cm^2)	V_{oc} (V)	Fillfactor	Efficiency (%)
250	3.0	0.70	0.69	6.0
250	2.5	0.74	0.66	4.9
1000	11.1	0.75	0.60	5.0
1000	8.6	0.77	0.56	3.7

Composition of electrolyte

0.2 M I_2
0.1 M GuanSCN
0.5 M NMBI
2 M *n*-BuMeIm$^+$ I$^-$
BuMeIm$^+$ N(CN)$_2^-$



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The world record for ILs

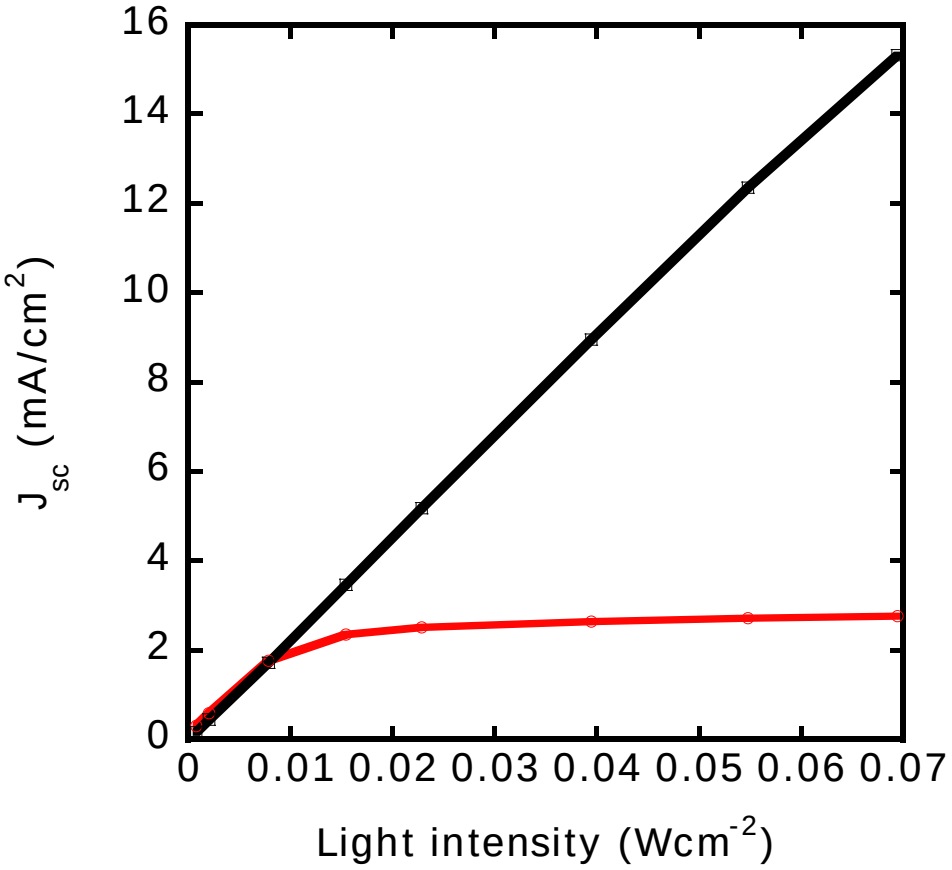
High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts

YU BAI[1]*, YIMING CAO[1]*, JING ZHANG[1], MINGKUI WANG[2], RENZHI LI[1], PENG WANG[1]†, SHAIK M. ZAKEERUDDIN[2] AND MICHAEL GRÄTZEL[2]†

nature materials | VOL 7 | AUGUST 2008 |

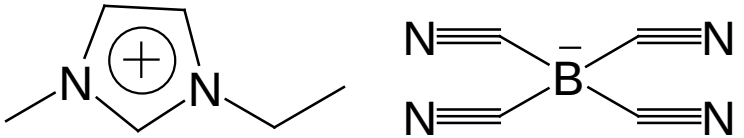
the discovery of solvent-free electrolytes for DSCs showing unprecedented efficiency and excellent stability. An efficiency of 8.2% achieved in full sunlight sets a benchmark for

Does not solve all problems



AN (0.03 M I_2)

IL_{low} (0.03 M I_2)

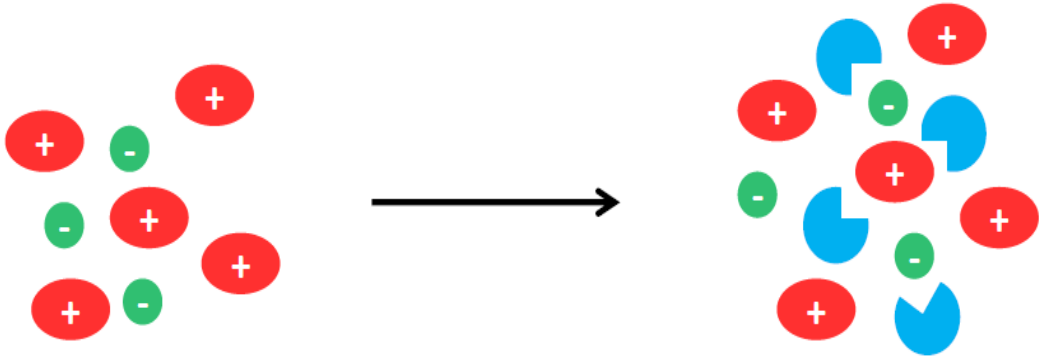


EMITCB

Mass-transport problems already at 1/5 Sun

L. Kloo *et al.*, Dalton Trans. **2008**, *38*, 2655 (Perspective)

ISILs



- ✓ Low viscosity
- ✓ Low vapor pressure
- ✓ High chemical and electrochemical stability

→

High ion mobility

High long-term durability

New redox systems

I^-/I_3^-

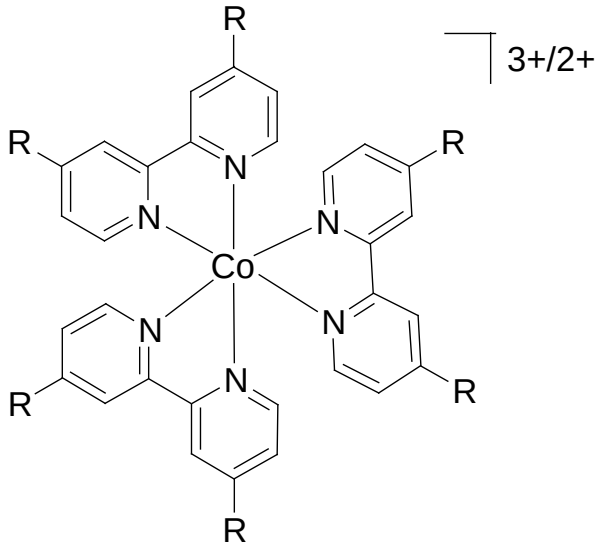
Br^-/Br_3^-

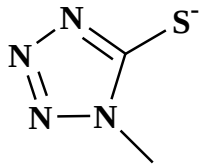
Pseudohalogens

Interhalogens

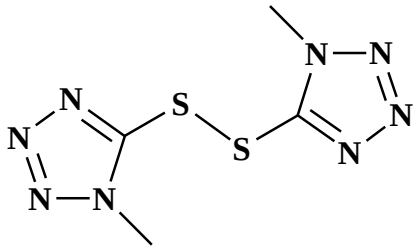
Sulfur-based systems

Metal complexes



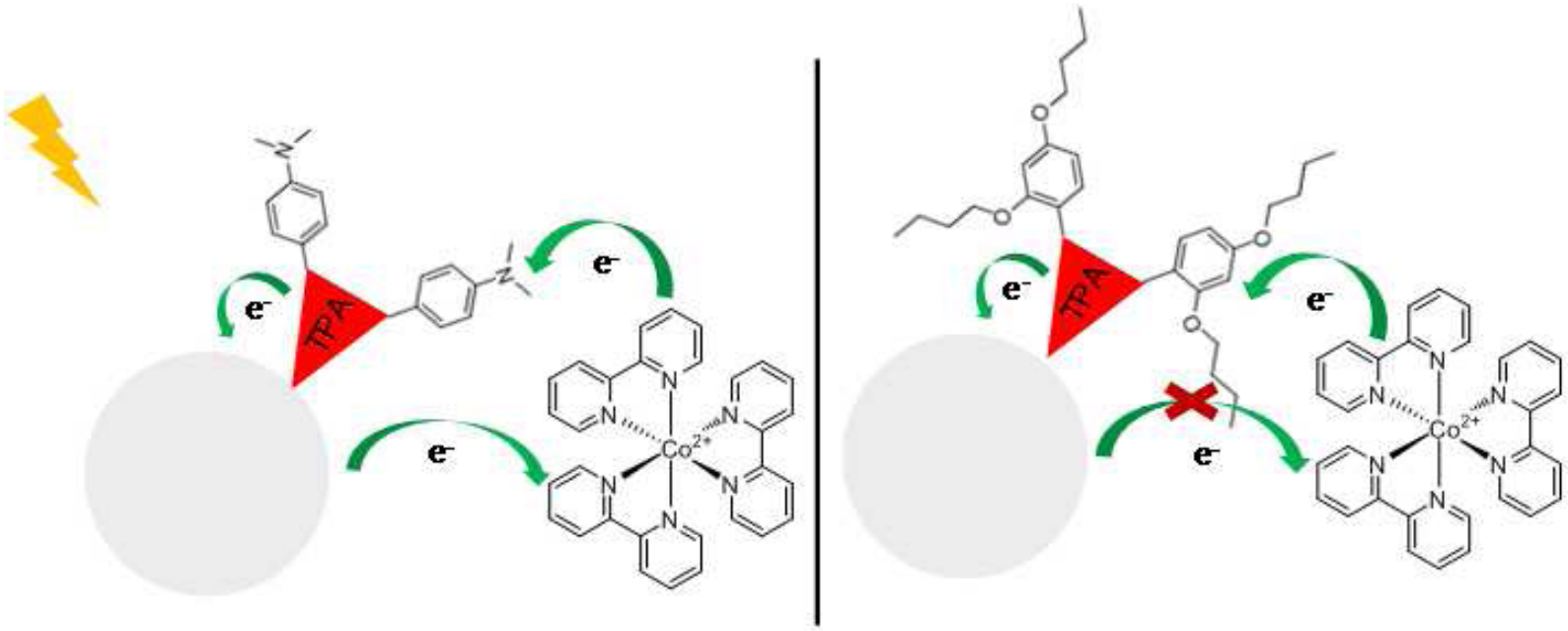


T^-



T_2

D35 Dye + Co-based redox system

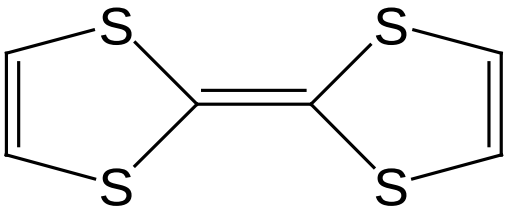


A. Hagfeldt, L. Sun *et al*., *JACS* **2010**, *132,* 16714

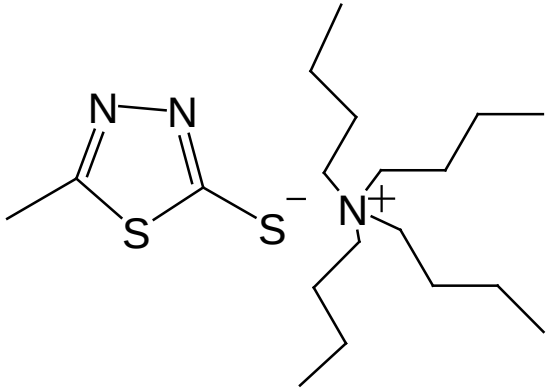
Later: M. Grätzel *et al.* made the current 13% world record using a similar system (Science 2011)

N.B. Not *one single* component can be changed at a time !!!

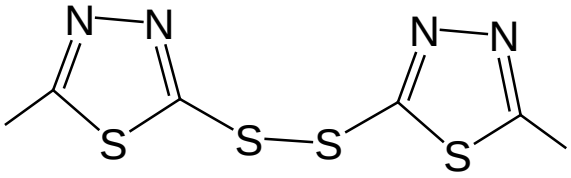
Sulfur-based alternatives



TTF

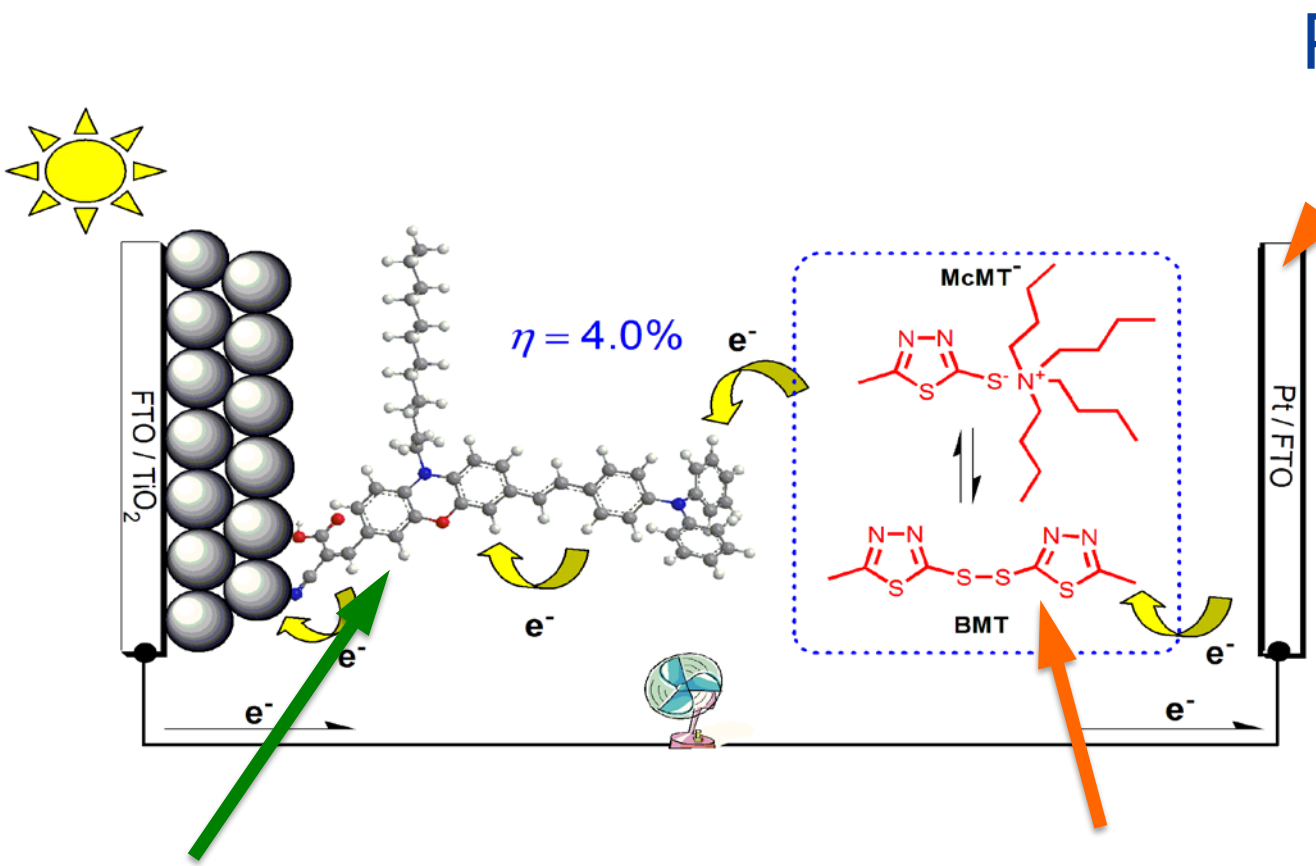


McMT$^-$



BMT

Energy in the Future



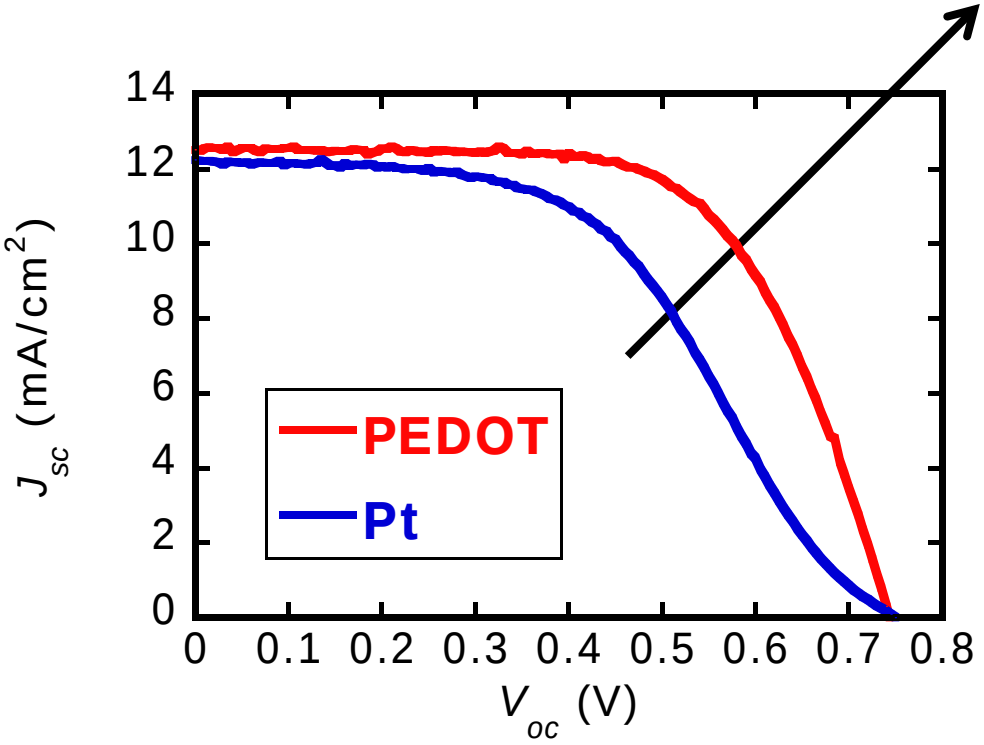
H. Tian, L. Sun, L. Kloo *et al.*, *Angew. Chem. Int. Ed.* **2010**, *49*, 7328 & JACS **2011**, *133*, 9413

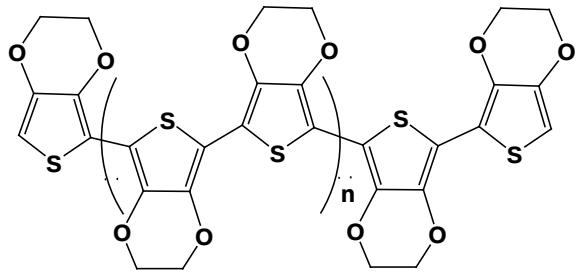
N.B. Not *one single* component can be changed at a time !!!

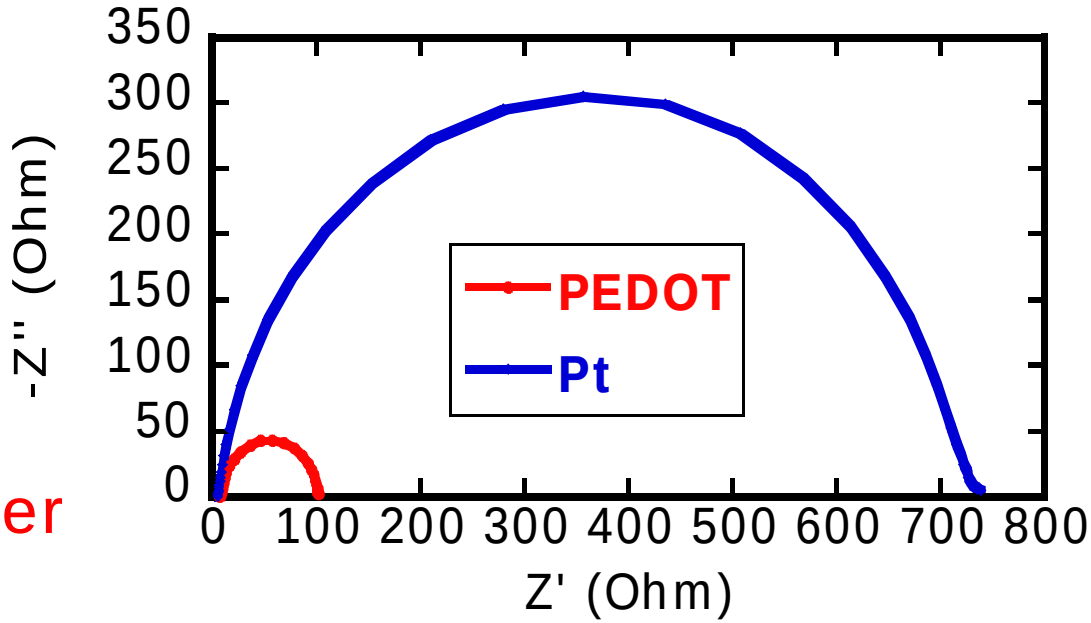
Counter electrode effect

FF: 0.50 → 0.65

η = 6.0%

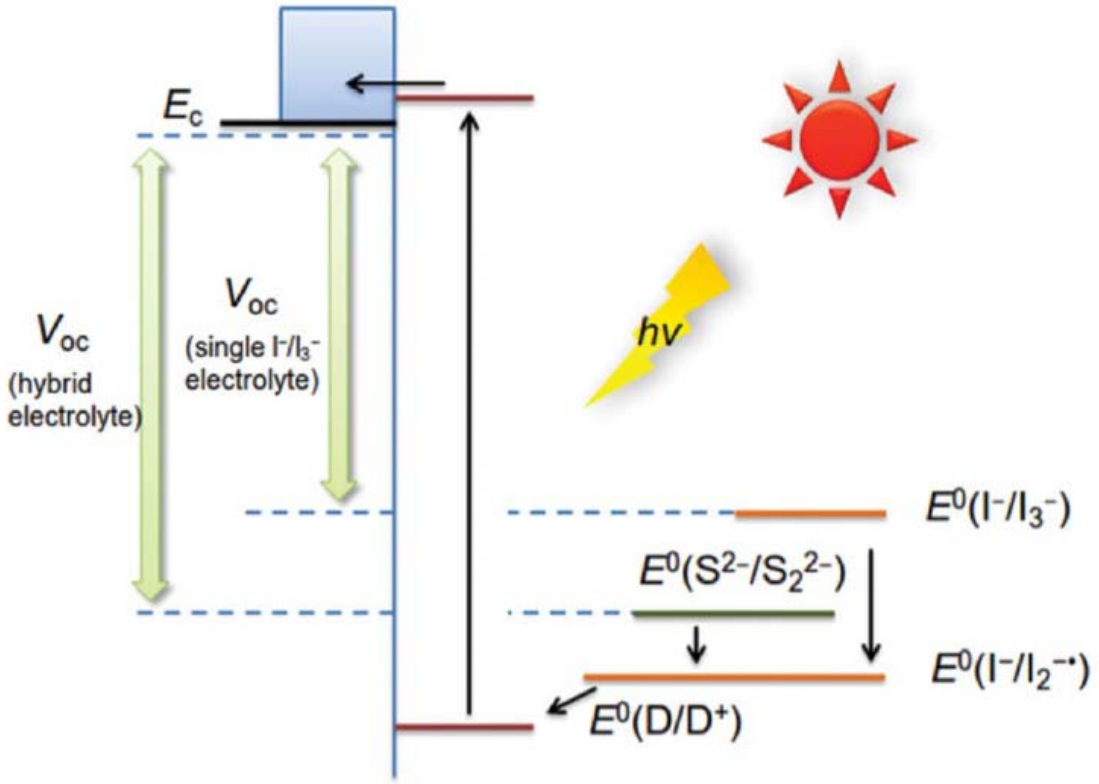


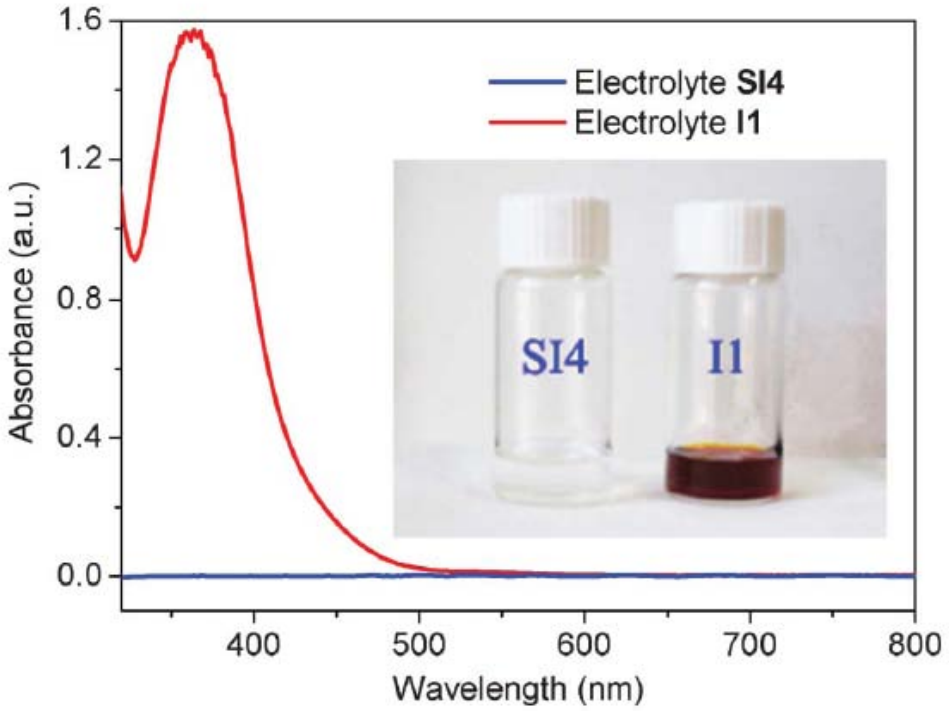




PEDOT CE shows considerably lower charge-transfer resistance

Hybrid systems





X.Yang, L. Sun, L. Kloo *et al*., *RSC Advances* **2012**, *in print*

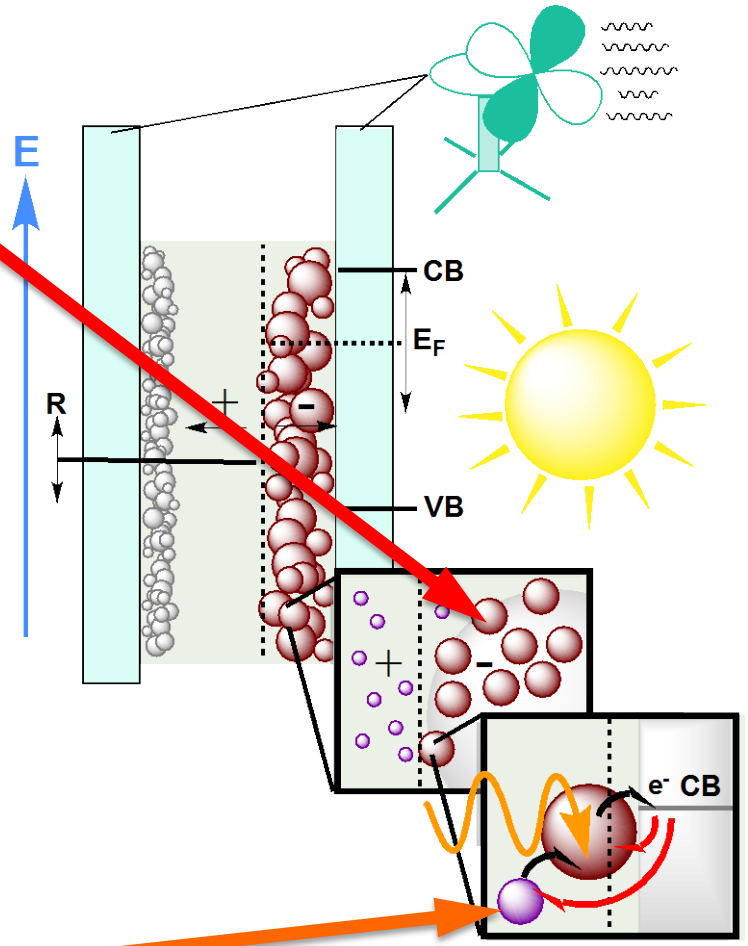
Presence of S^{2-} suppresses the formation of coloured I_3^-

Efficiency > 9%

CMD: Fundamentals

Working Electrode

- Dye coordination
- Dye organization



Regeneration

- Mechanism of regeneration

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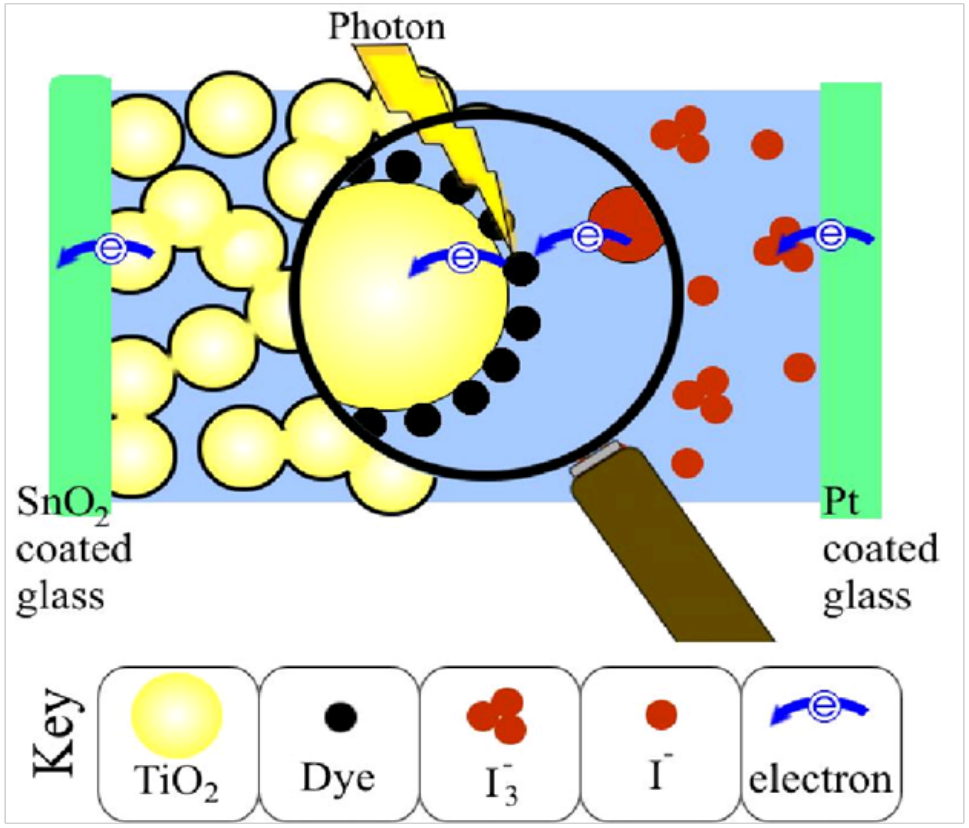
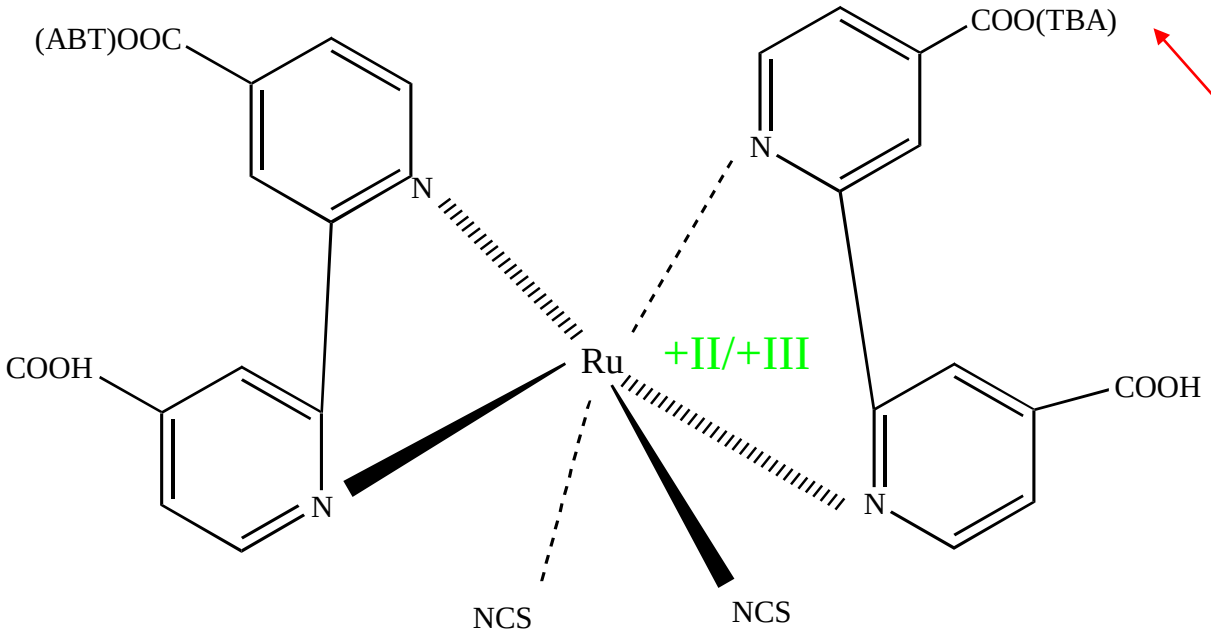
On the myth about SAM

SAM = Self-assembled monolayer



http://people.bath.ac.uk/pysabw/research/scell/dssc.htm

The sensitizing dye



Anchoring groups
(e^- injection)

Site(?) of re-generation
(reduction)

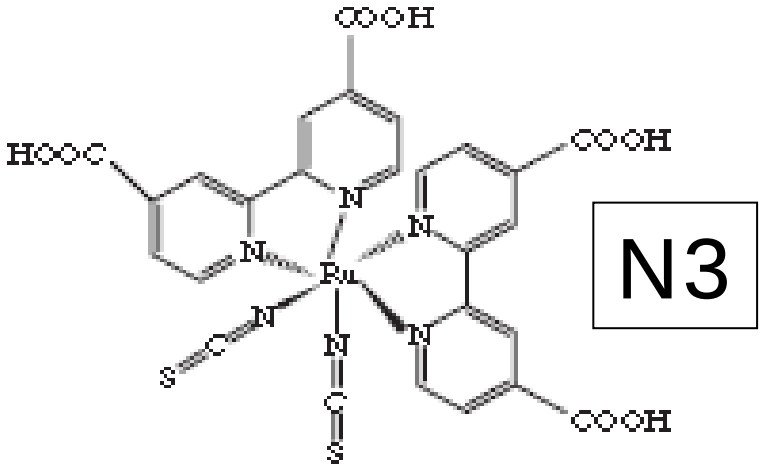
N 719

(*cf*. Kodak)

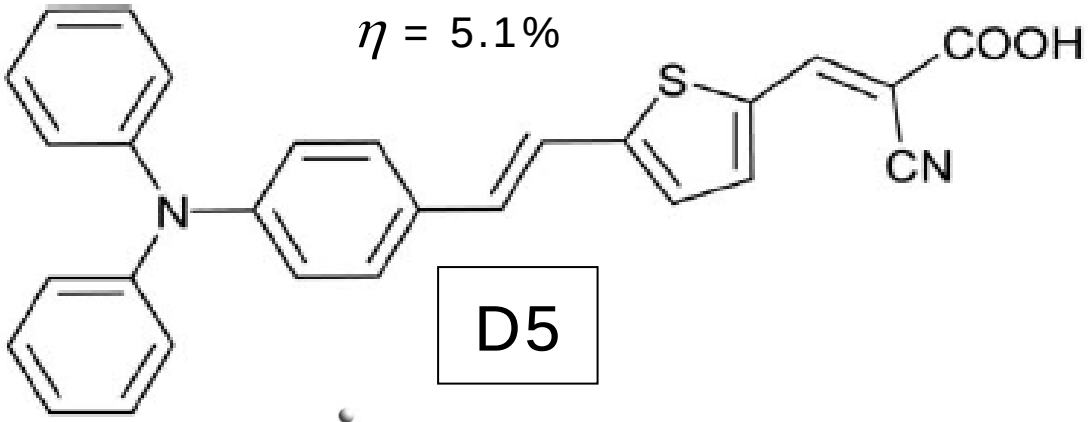
Good dyes have:

- match energetic condition
- broad absorption
- high extinction coefficient
- good charge separation

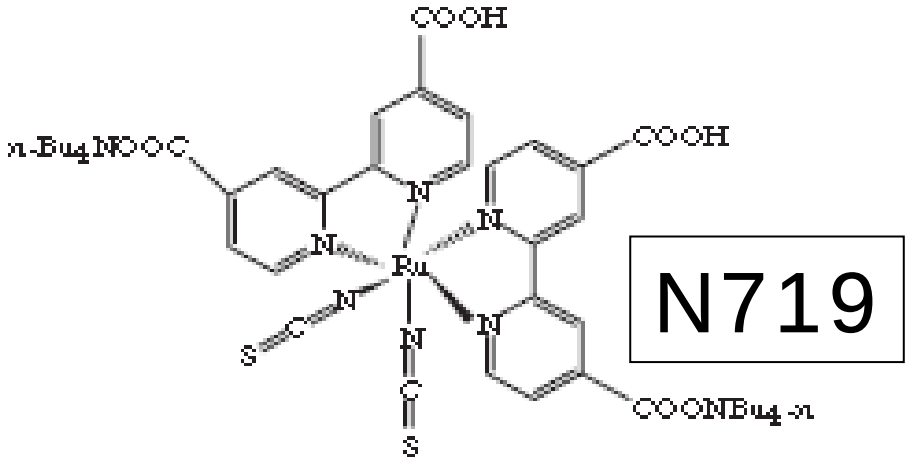
Towards organic dyes



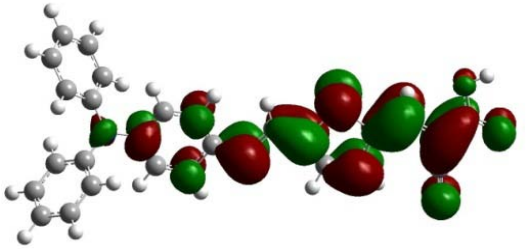
N3



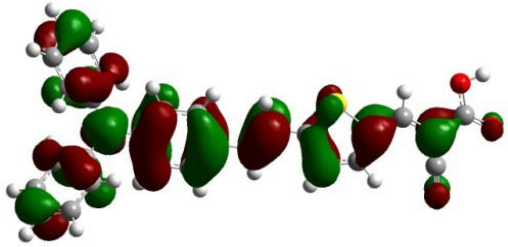
D5



N719



LUMO



HOMO

From Organometallic to Organic

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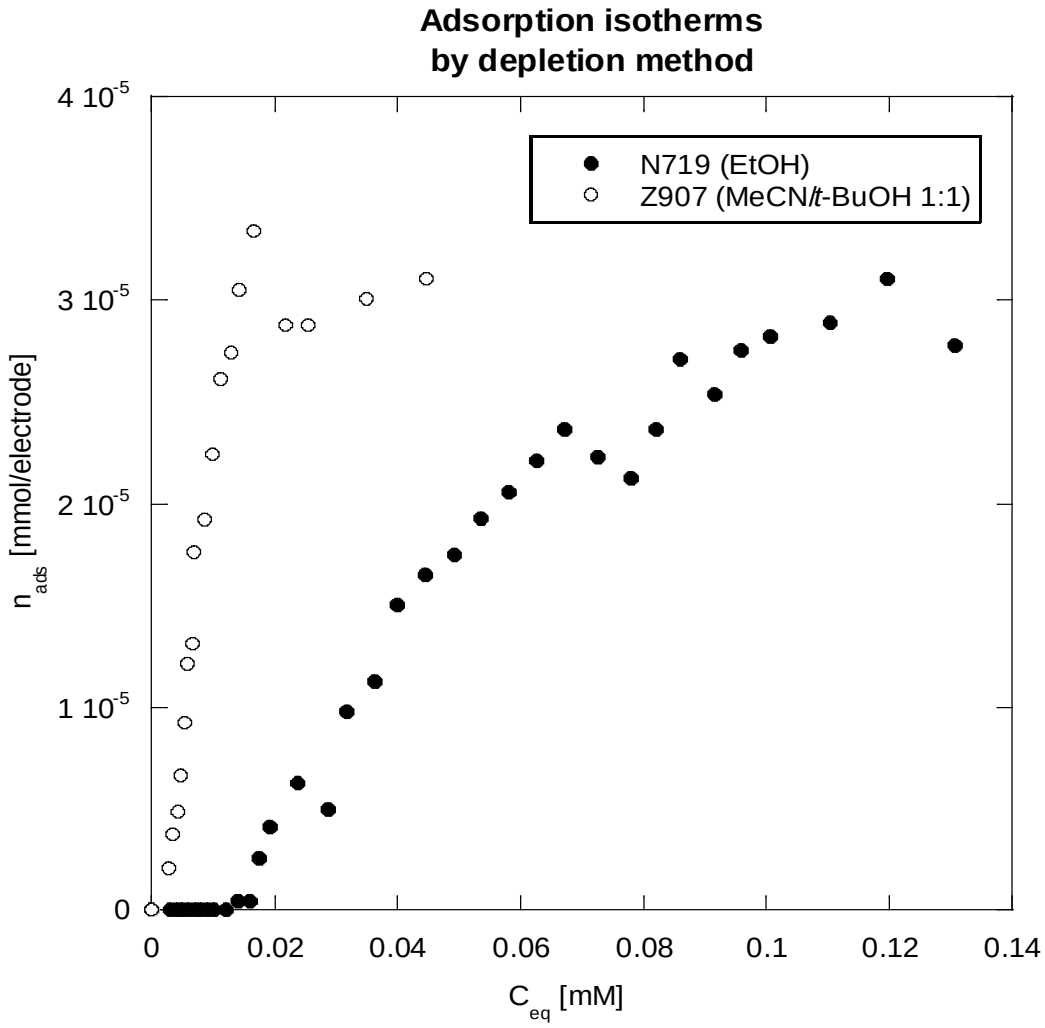
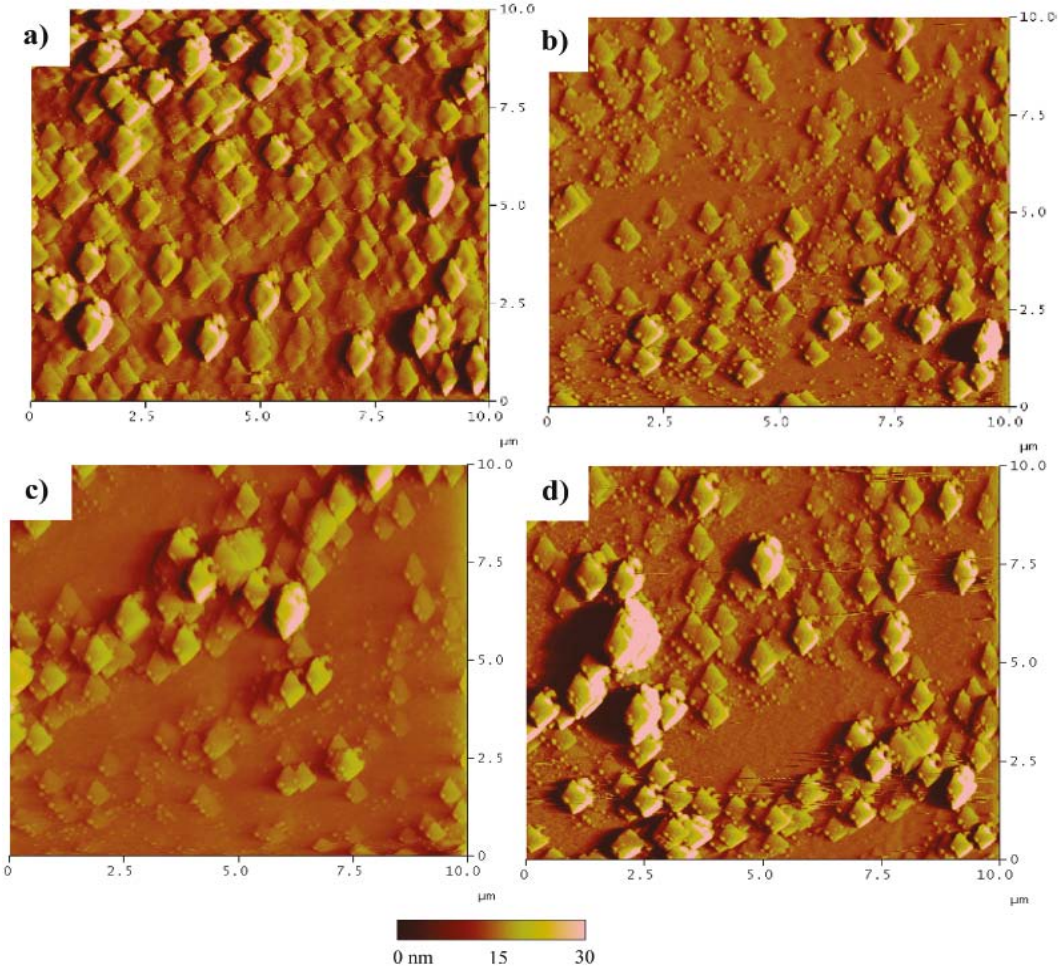
Adsorption isotherms



AFM: A problem indicator



AFM (in electrolyte)
100 µm²
TiO_2 under 24h:

a) t = 0h

b) t = 3h

c) t= 24h

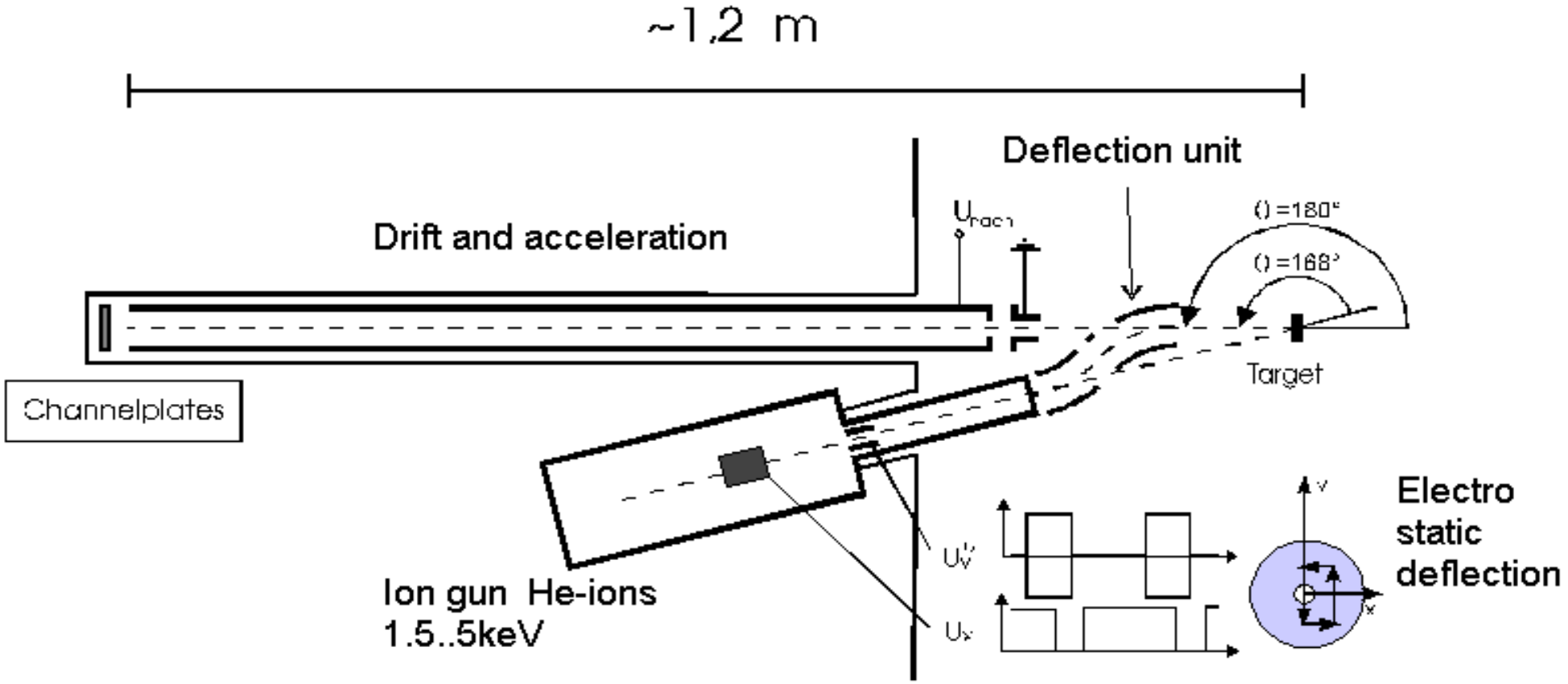
d) After rinsing

Aggregation / Precipitation

Langmuir (**2010**)

Collaboration: Rob Atkin, Univ. of Newcastle

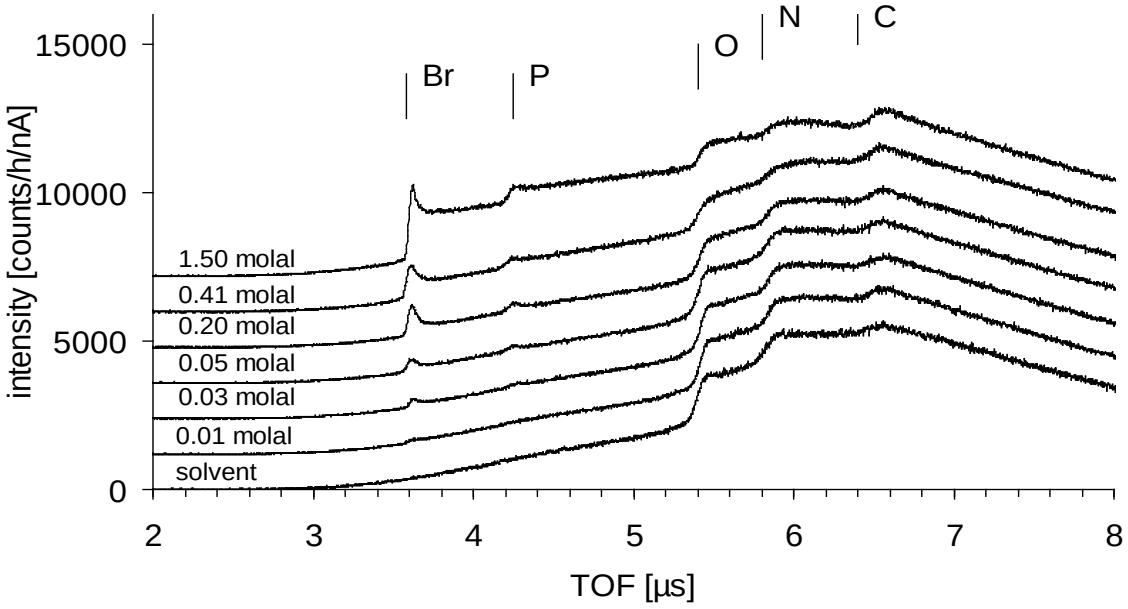
The NICISS technique

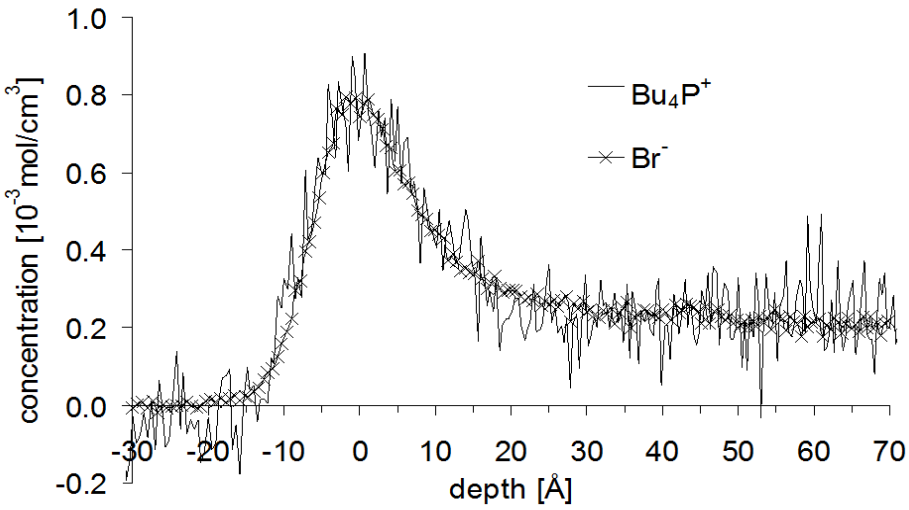


NICISS = Neutral Impact Collision Ion Scattering Spectroscopy

Collaboration: Gunther Andersson, Flinders Univ.

The NICISS technique

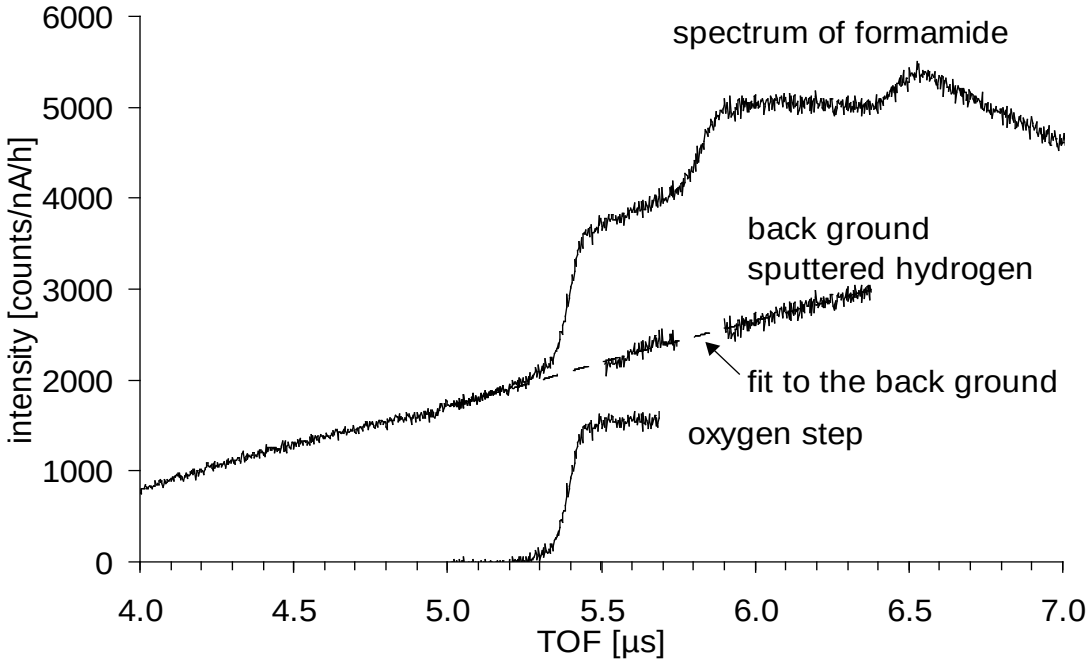




Allows element-specific depth profiling at interfaces

Depths up to ~20 nm with a few Å resolution

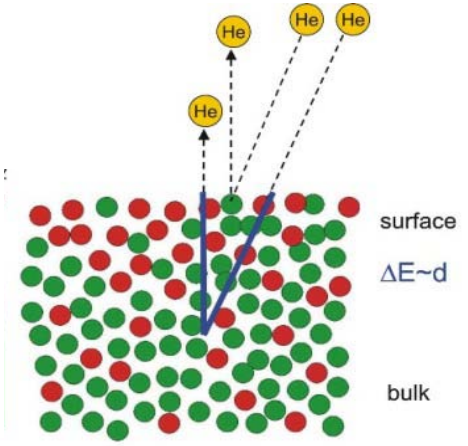
The NICISS technique



Backscattering process
mass dependent
(element identity)

He^+, 3 keV - E_{loss} - ΔE

Trajectory loss
SA scattering & excitations
(depth profile)



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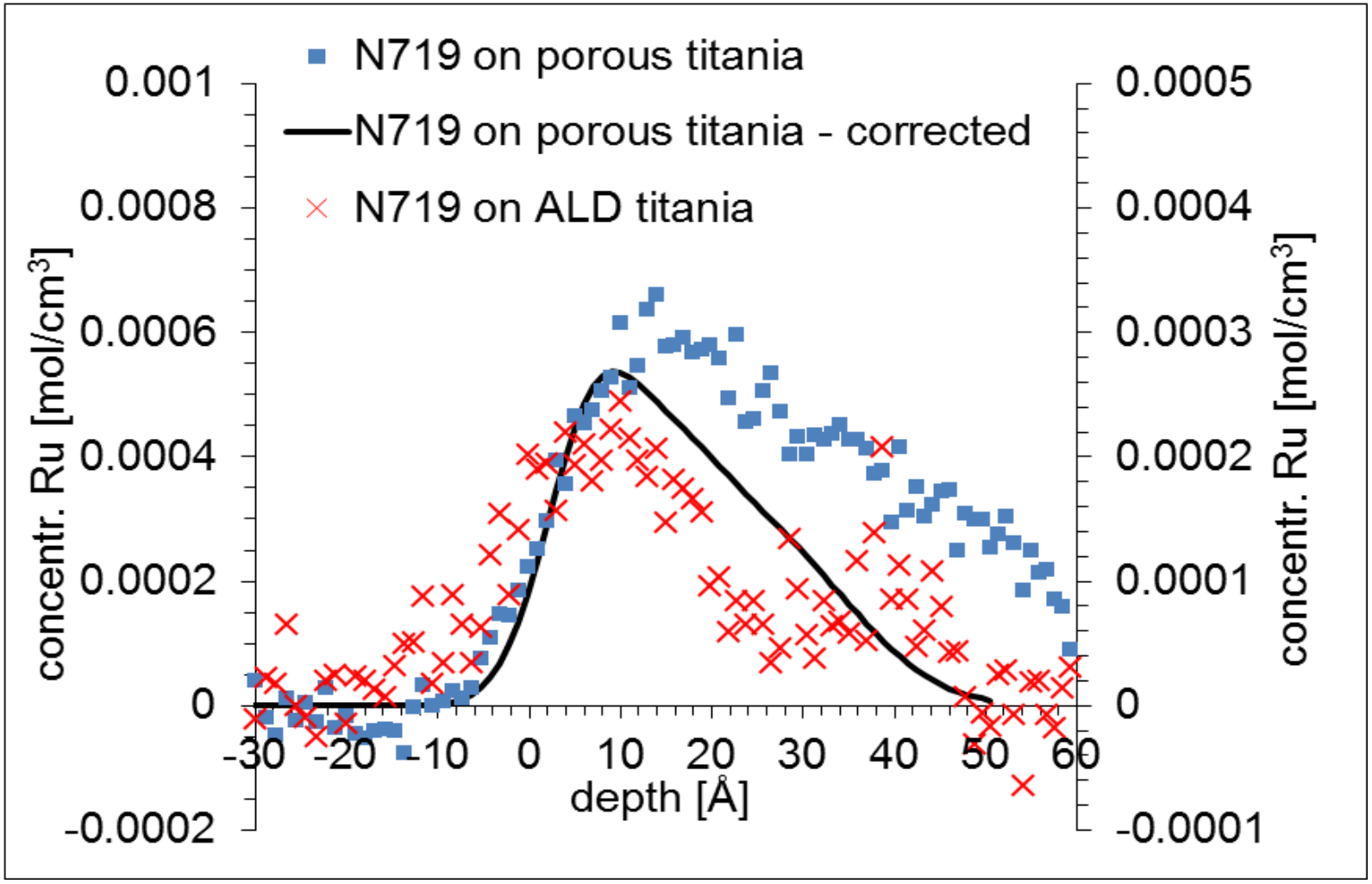
Depth profile of Ru (N719)



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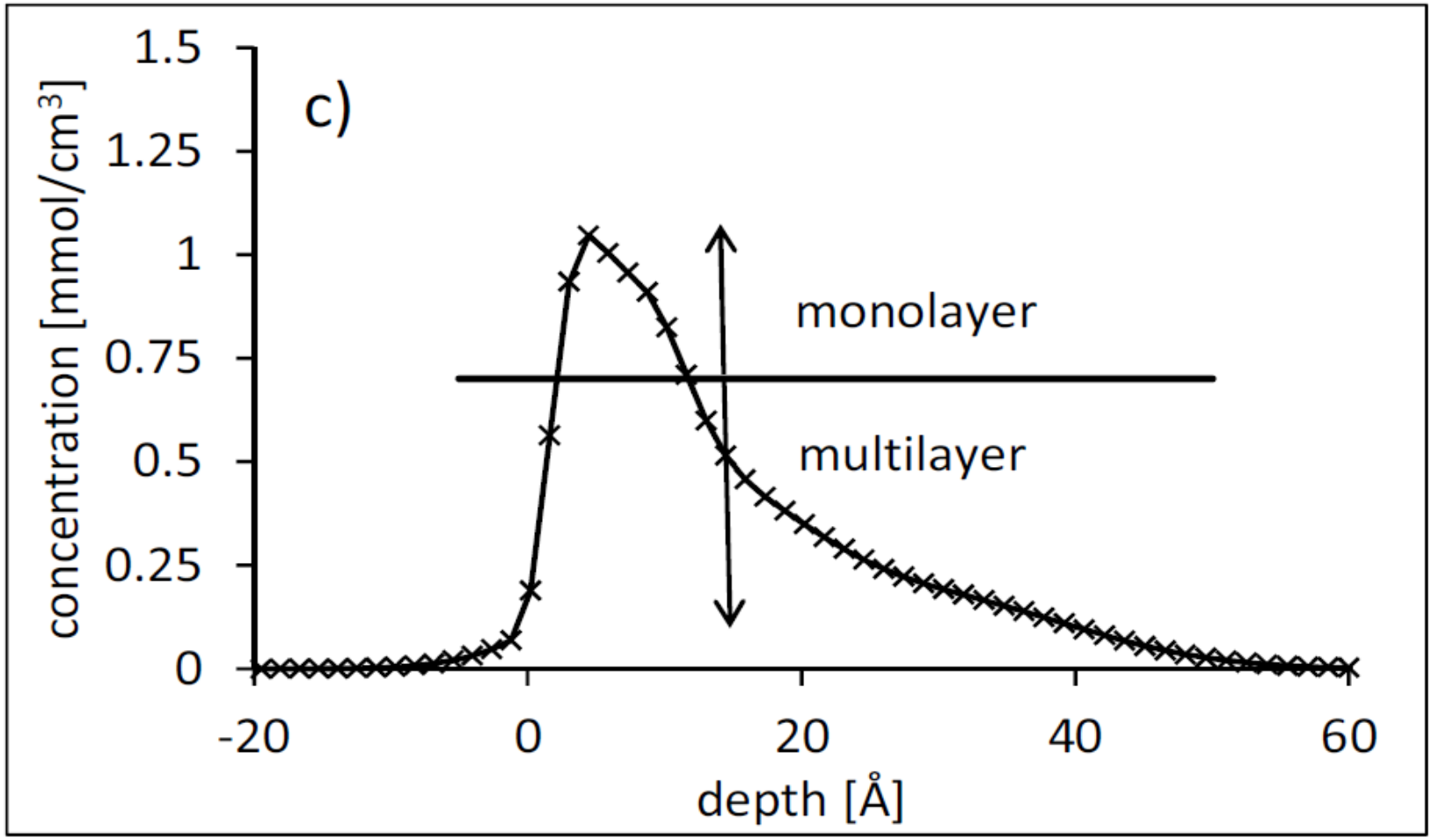
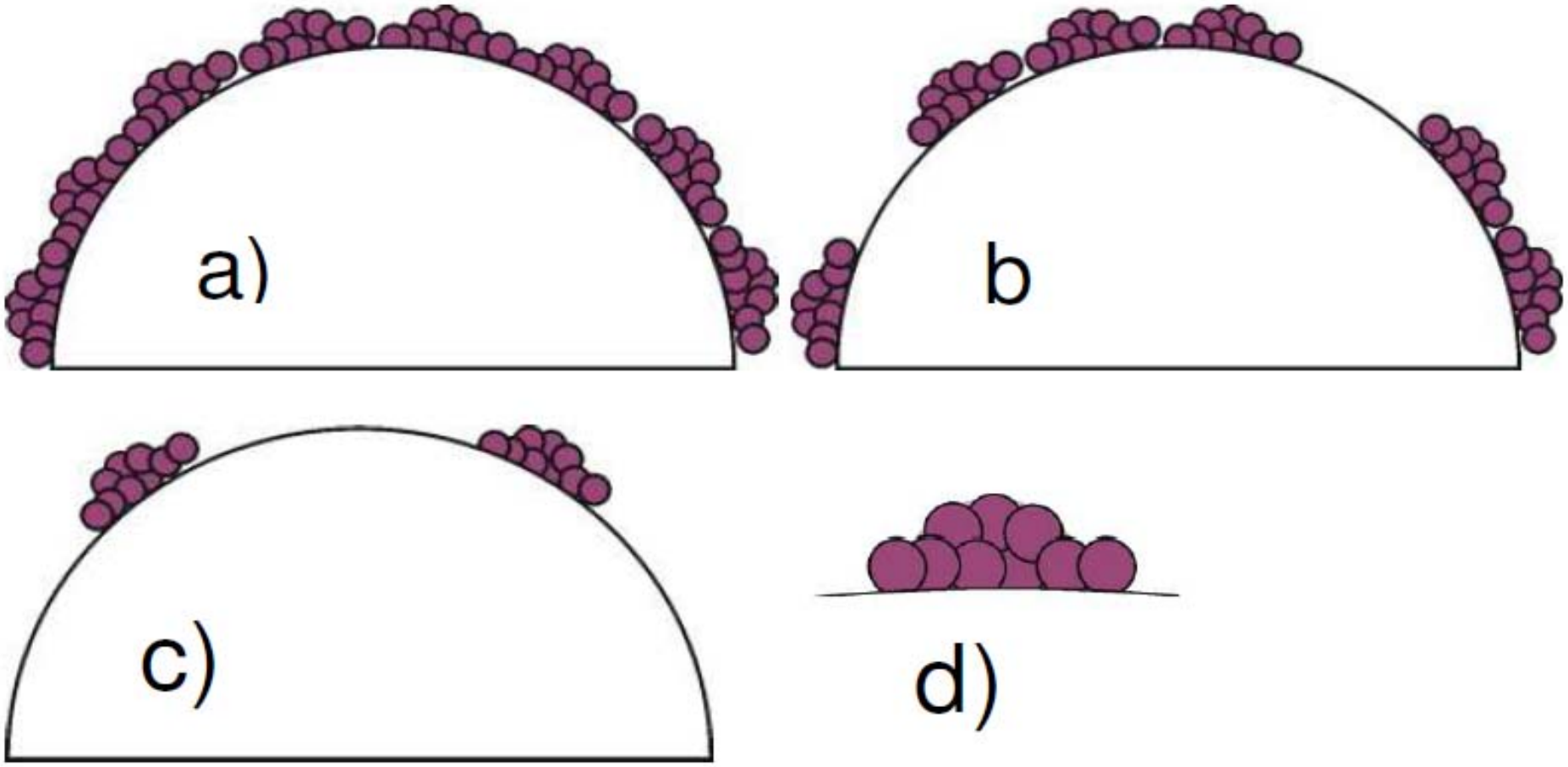
Mono- *vs.* multilayers



Multilayer = 2-3 dye layers thick

Growth echanism



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The main conclusion

Forget SAMs !

Ongoing work:

- Other dyes
- Correlation to photovoltaic performance
- Adsorption isotherm resolution

A materials challenge

Long-term goal: Mass production of solar cells
requires "solid-state" devices using inexpensive materials

Electrolytes: Combine non-volatile systems with good mass transport properties, ionic liquids, hole conductors

Dyes: Organic dyes with high extinction coefficients, water/O_2 tolerant, easy to recycle

Mesoporous oxide: Larger pores, thinner films, nanowires, electrolyte interaction

Device performance is not improved by optimizing components single-handledly !!!

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.com

Using (tele)communication as a model example looking back from 2008 to 1988, the energy sector is the next to face a paradigm in terms of product and company diversification until 2028
(F. Härén, 2008)

DYESOL

Konarka technologies

AISIN Geared up for the future

SOLARONIX "in sun we trust"

G24i

heliatek

... and many more

Dye sensitised (submodule)††	8·2 ± 0·3	25·45 (ap)	Sharp, nine serial cells[7]
Dye sensitised (submodule)††	8·2 ± 0·3	18·50 (ap)	Sony, eight serial cells[8]

ProgPhotovolt, 2008

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NEW RECORD SET FOR RECYCLING INDOOR LIGHT TO ELECTRICITY

Cardiff, Wales. April 5, 2012: G24 Innovations, a pioneer of light energy harvesting – the recycling of ambient indoor light to electricity - has achieved ground-breaking efficiency rates for the indoor performance of its Dye-Sensitised Cells . At an average of 26% conversion efficiency, a new cell composition has broken the company's previous record of 15%, already recognised by Texas Instruments' Solar Lab as the most efficient indoor light energy harvesting technology on the market.

The breakthrough, which rates G24i's new PV cell as almost five times more powerful than its nearest commercial competitor, is based on recent work by Professor Michael Graetzel and colleagues at the Laboratory of Photonics and Interfaces , Ecole Polytechnique Fédérale de Lausanne. Professor Graetzel's dye-sensitised cell invention is recognised as coming close to mimicking the light reaction in nature's photosynthesis.

WWW: April 5, 2012

Acknowledgements

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- Muthuraaman BhagavaThiachiari (post-doc)
- Himanshu Jain (post-doc)
- Erik Gabrielsson (PhD, LS group)
- Haining Tian (post-doc, LS group)

CMD
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- Gerrit Boschloo (UU)
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- Henrik Pettersson (IVF AB)
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