University of Basel

The myth and reality of artificial photosynthesis
-
the dream of free energy

Ed Constable, The 1st Basel Sustainability Forum, 14.10.2016

1	Photosynthesis – the real world model
2	Some facts and figures
3	From „organic“ to „bioinspired and unnatural“
4	Some light in the darkness?
5	Thoughts for the future

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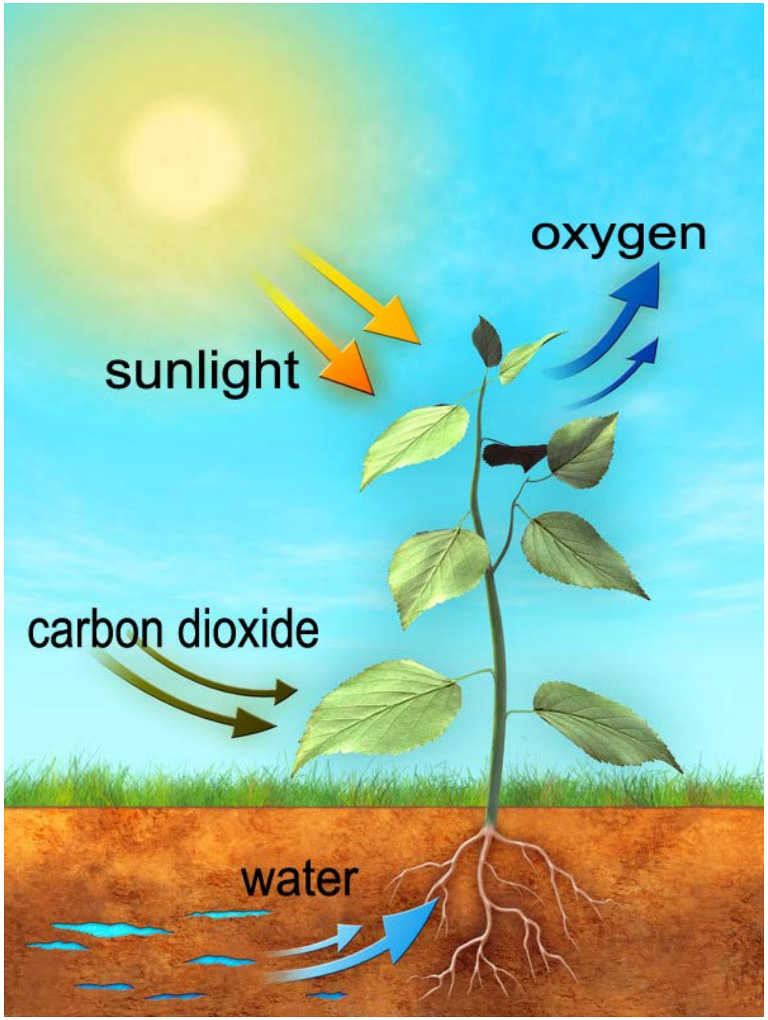
A beginner's guide to photosynthesis

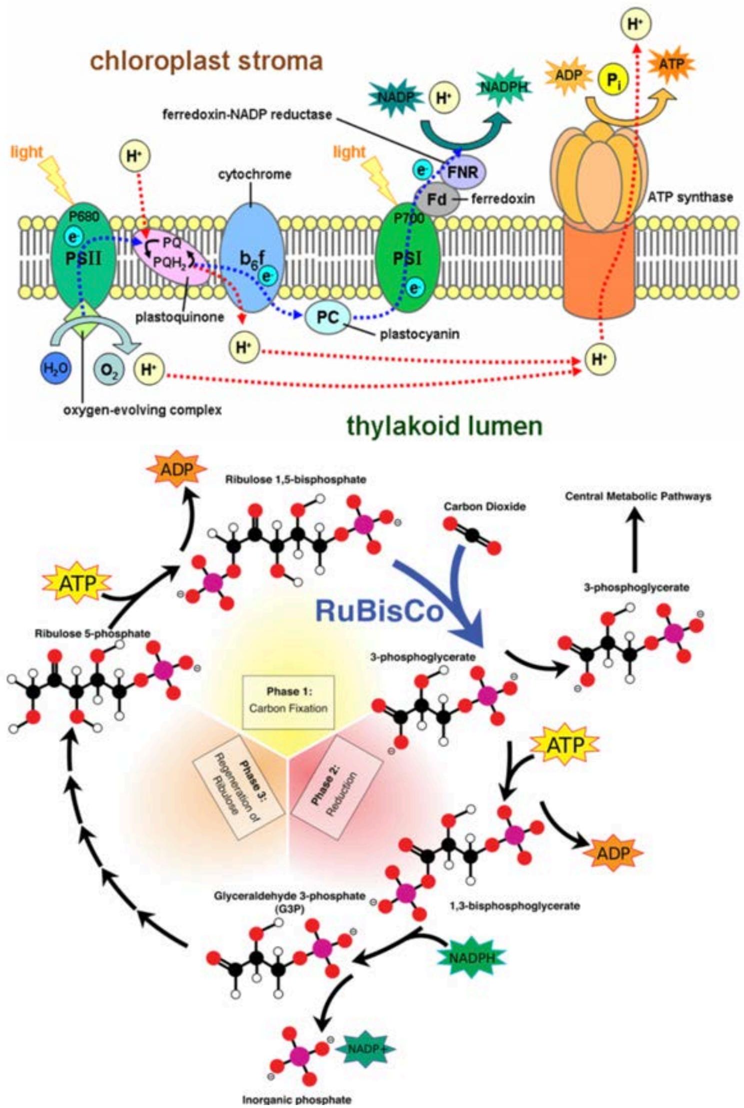


Light energy (free) is used to convert carbon dioxide (a greenhouse gas) and water (free) into oxygen (what we breathe) and carbohydrates (organic fuel).

Inspiration for a whole scientific industry termed "artificial photosynthesis"

Image from http://photosynthesiseducation.com/photosynthesis-in-plants/

Homage to Douglas Adams



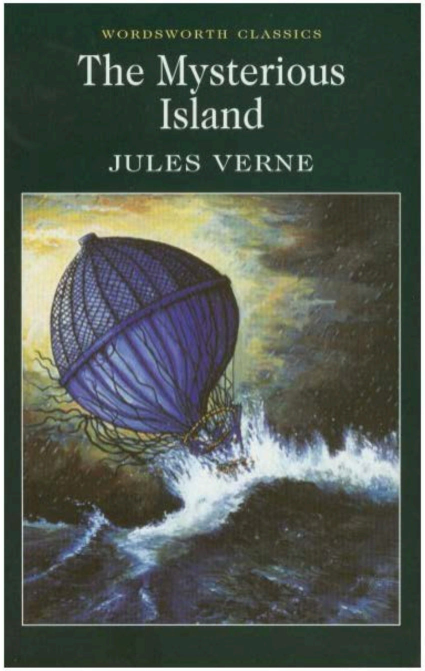
„…the universe is a lot more complicated than you might think, even if you start from a position of thinking it's pretty damn complicated in the first place"

Hitchhikers Guide to the Universe

Two reactions that require light and convert water into oxygen, protons and electrons

"Dark"reactions that convert carbon dioxide to organic compounds

It's a free lunch … what could possibly go wrong?



Convert greenhouse gas into liquid fuel using sunlight

Free stored chemical energy

Oxygen as a by-product

Water as a fuel

I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable … Water will be the coal of the future."

The Mysterious Island, Jules Verne, 1874

TINSTAAFL

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Some facts and figures

Total solar energy absorbed by Earth: ~ 3,850,000 EJ per year

Worldwide primary energy consumption by humanity: ~ 540 EJ per year

EJ = exajoule = 10^{18} joule

How big is 10^{18}?

Alpha centauri is
4.132×10^{16} m distant

Some facts and figures

Net primary productivity by land plants: ~ 45-60 Gt Carbon per year

Humanity carbon emission rate: ~ 6.6 Gt Carbon per year

Global photosynthetic efficiency: ~ 0.3%

Gt = gigatonne = 1 million million kilograms

Weight of an African bush elephant
6000 kg

What have we learnt

Photosynthesis is good for us

We need to do it

Photosynthesis is difficult

We need to learn how to do it

Plants are not efficient

We need to learn how to do it better

Fossil fuels take a long time

We need to learn how to do it faster

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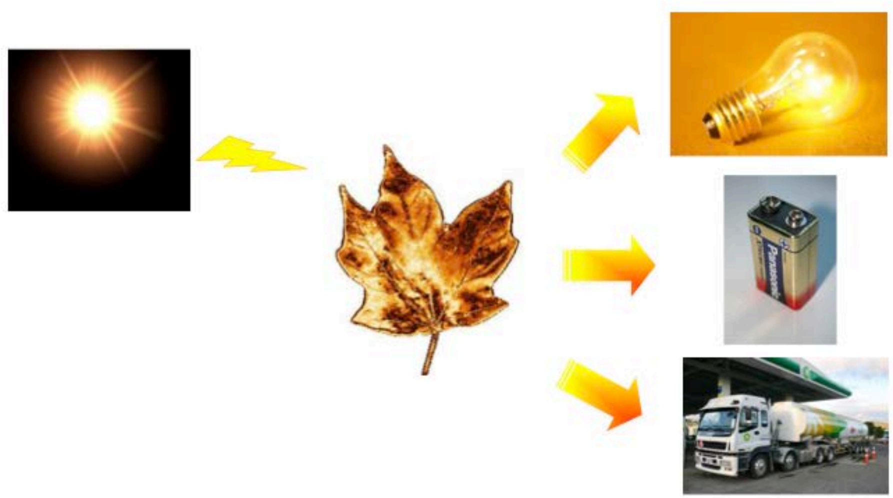
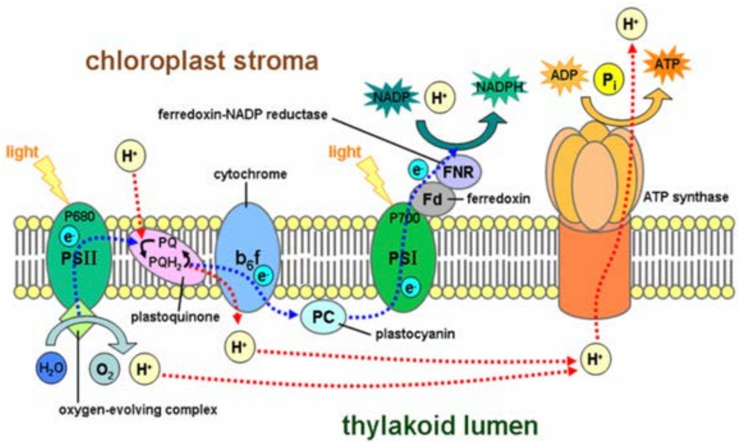
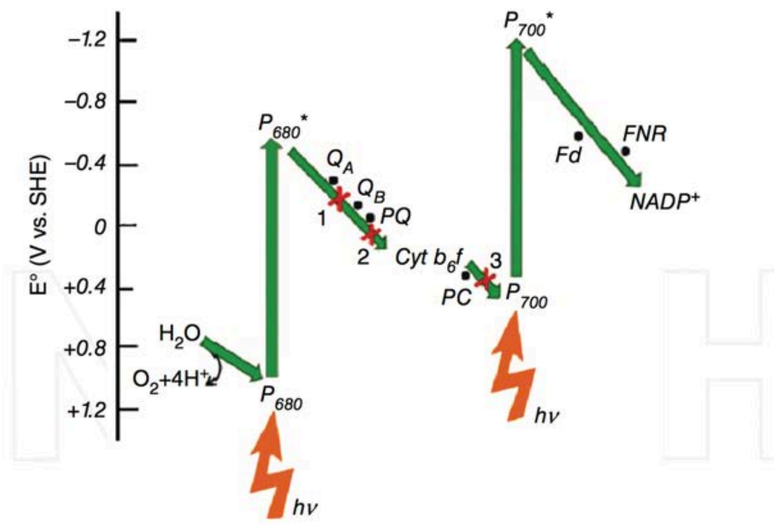
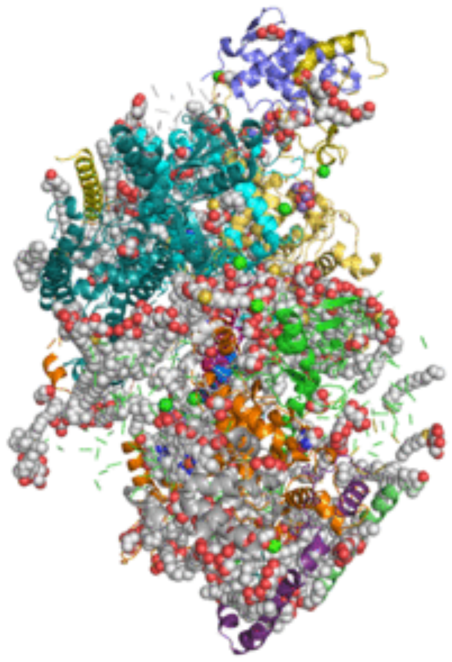


Too complicated to replicate





Photosystem I and II – each contain about 130 components

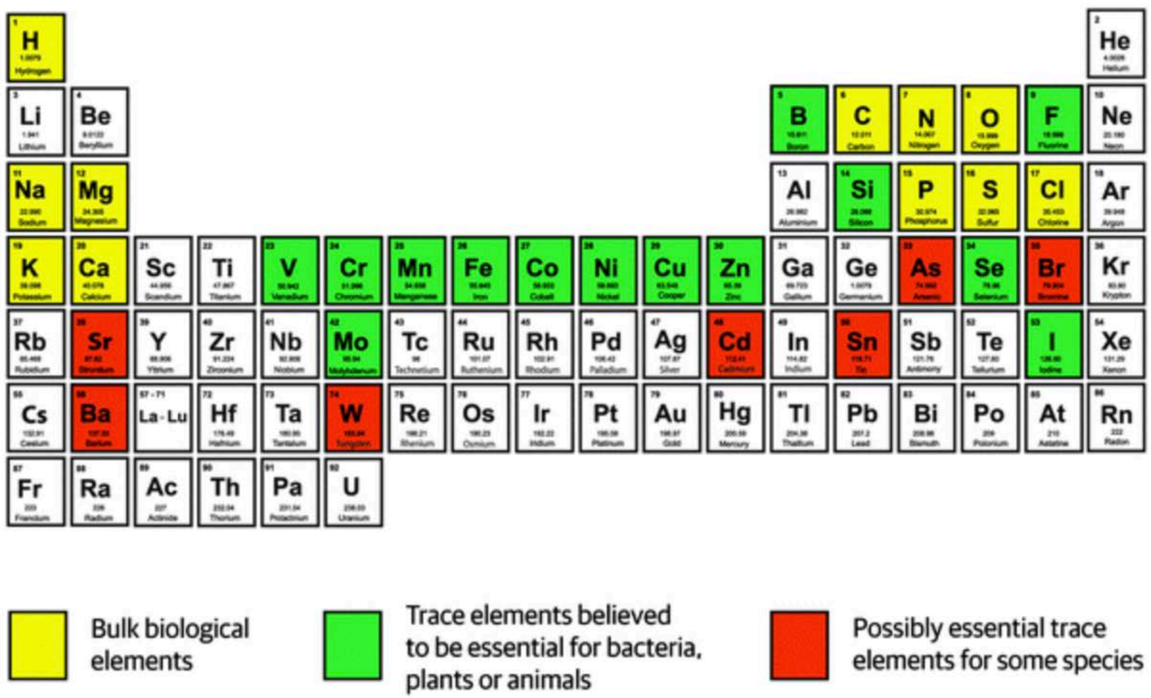


From bio*mimetic* to *bioinspired*

Bio*mimetic* is a strategy to reproduce the biological structures in the hope that this will also replicate function.

In general this is unsuccessful.

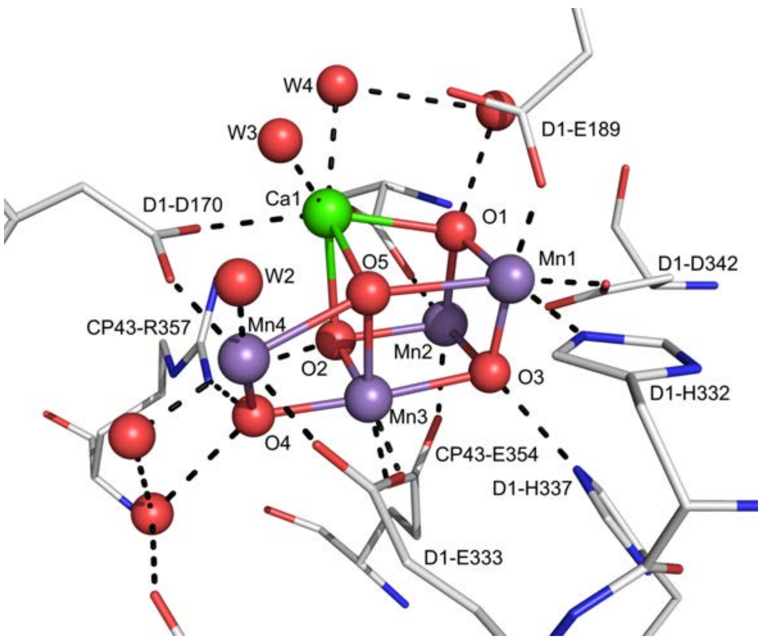
Bio*inspiration* tells you that it *can* be done and gives hints to mechanisms
But we can use elements and motifs that are unknown to biology

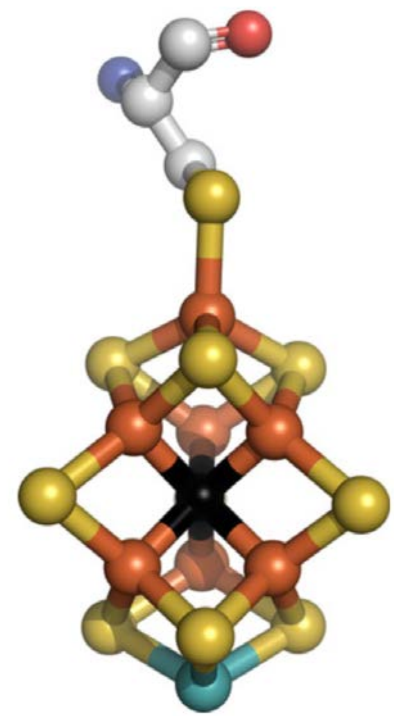


Is bio*mimetic* really unsuccessful

Oxygen evolving centre in PS II
$CaMn_4O_5$ cluster
Hundreds of model compounds
No model compound that
turns over a water-oxygen cycle

Nitrogenase active centre
Fe_7MoSC cluster
Thousands of model compounds
No model compound that
reduce nitrogen





The artificial leaf

Credo:
Learning from, but improving, on nature!

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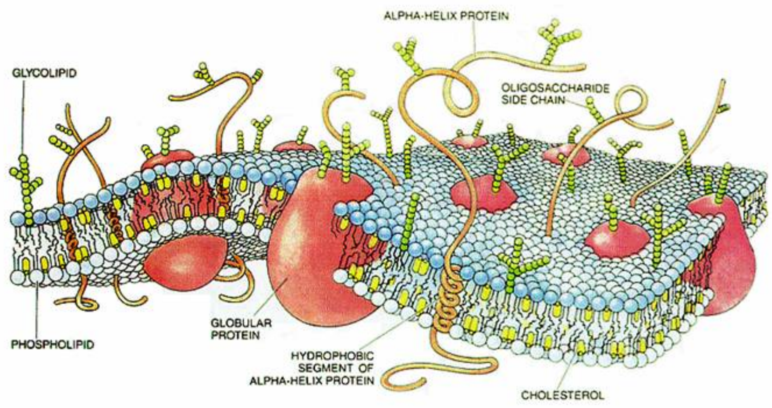
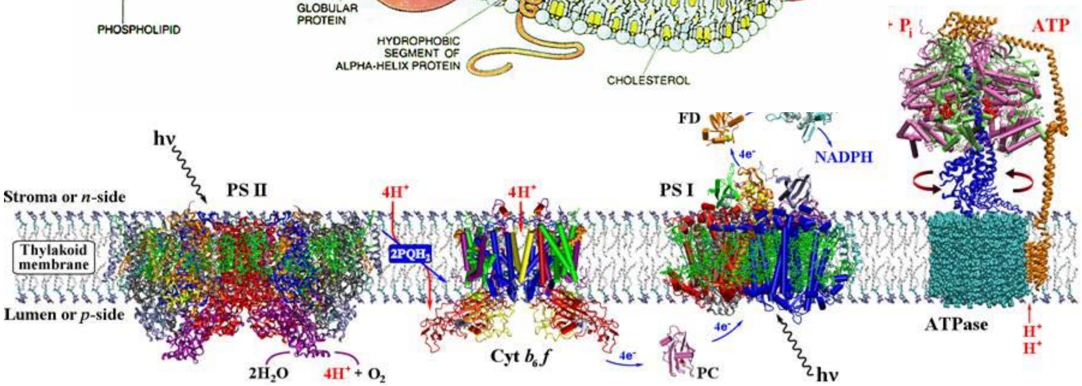
Inspired by biology – but hoping to do better!

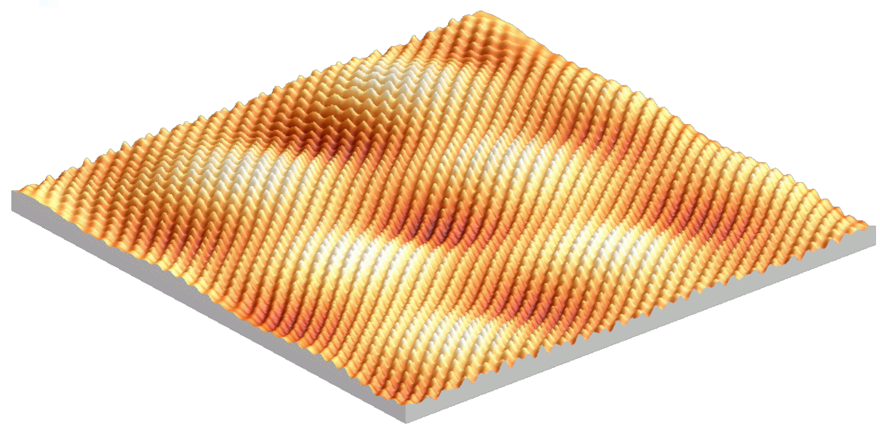


Biological membranes are the Scaffolds that support the machinery

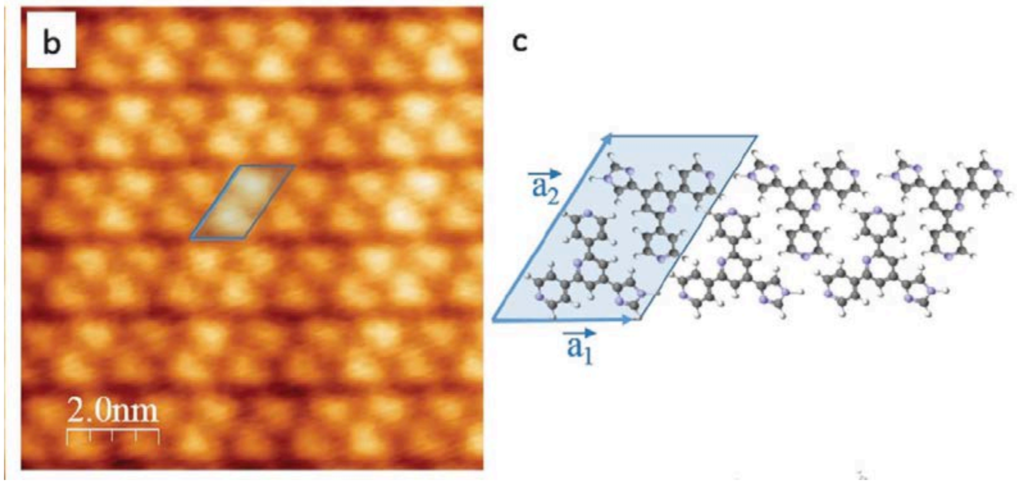


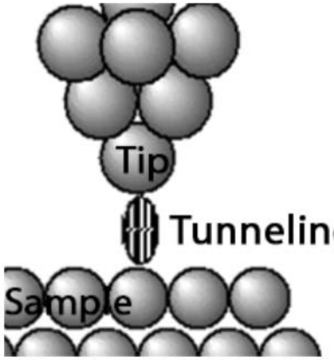
Replace membranes by interfacial surfaces

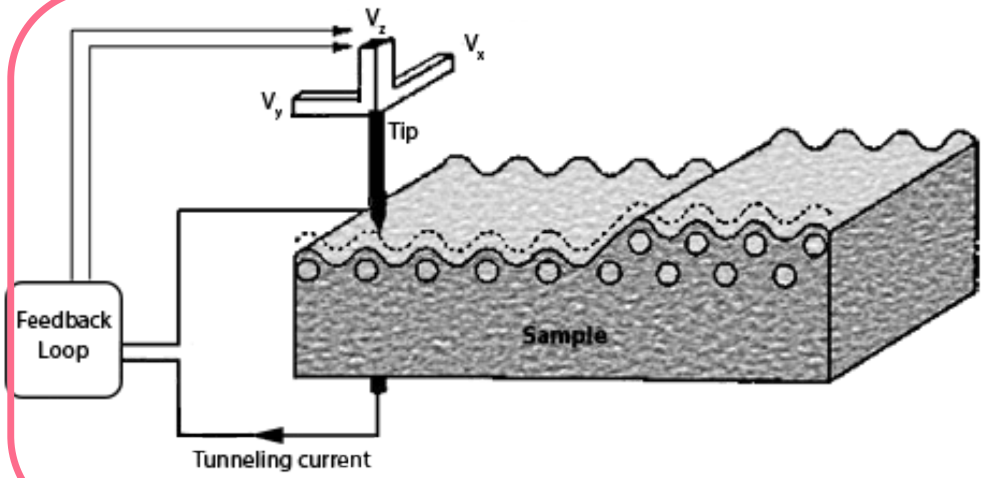
Why? We can make electrical and mechanical contact

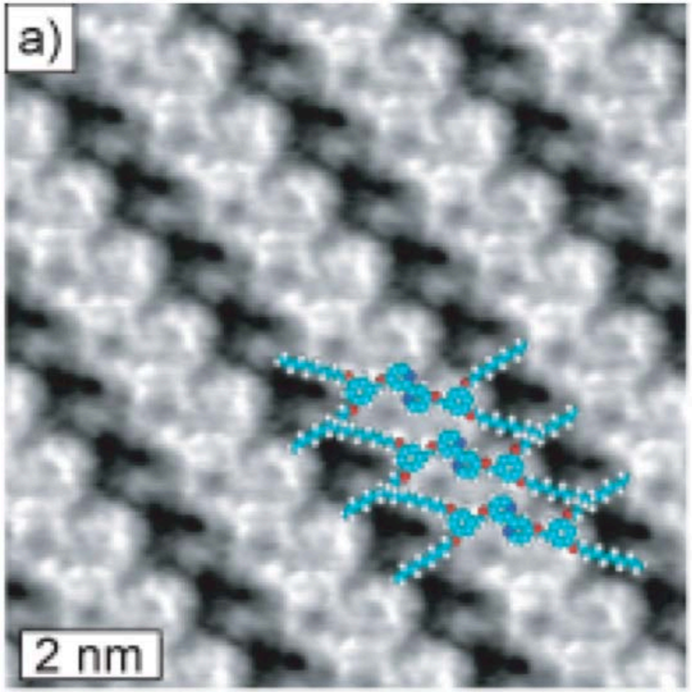


Can we arrange molecules on surfaces?

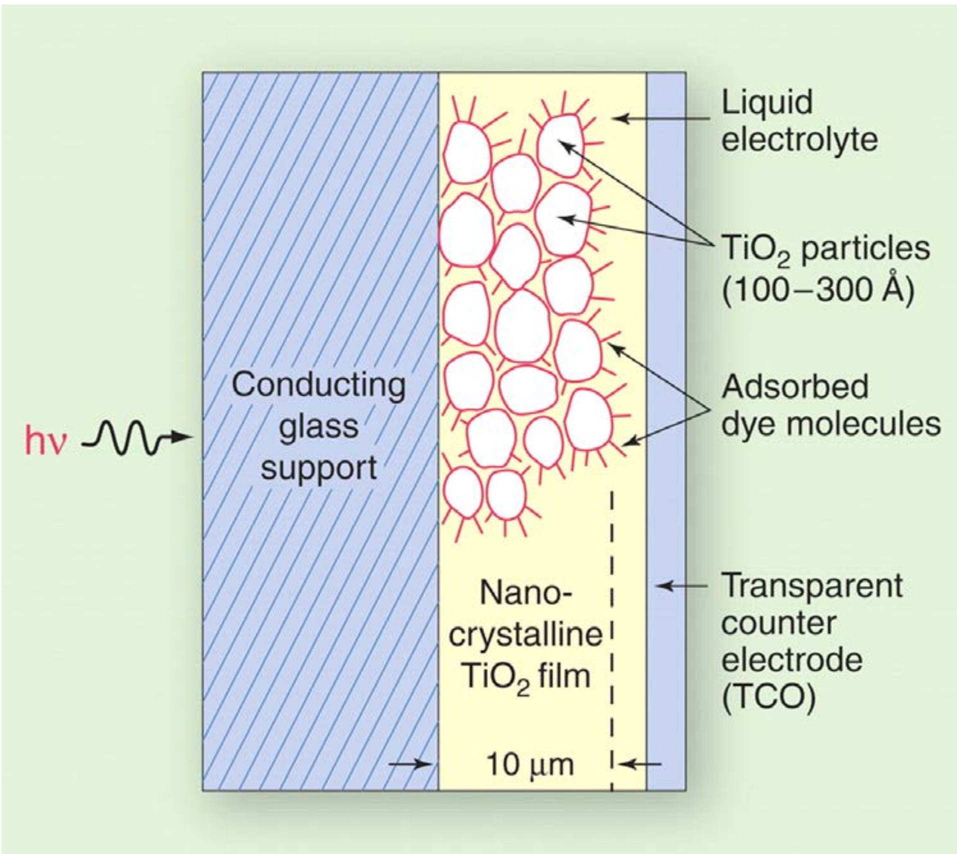


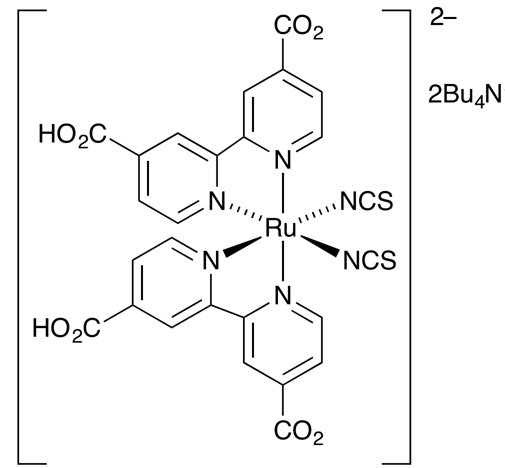




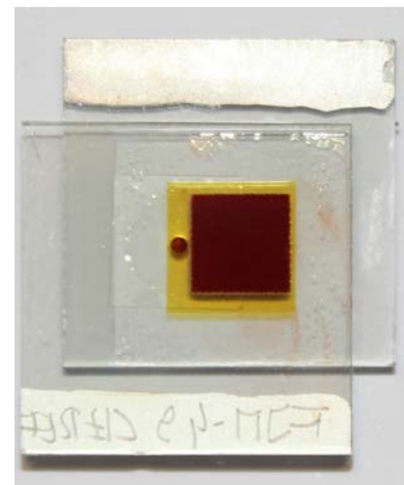


The dye sensitized solar cell





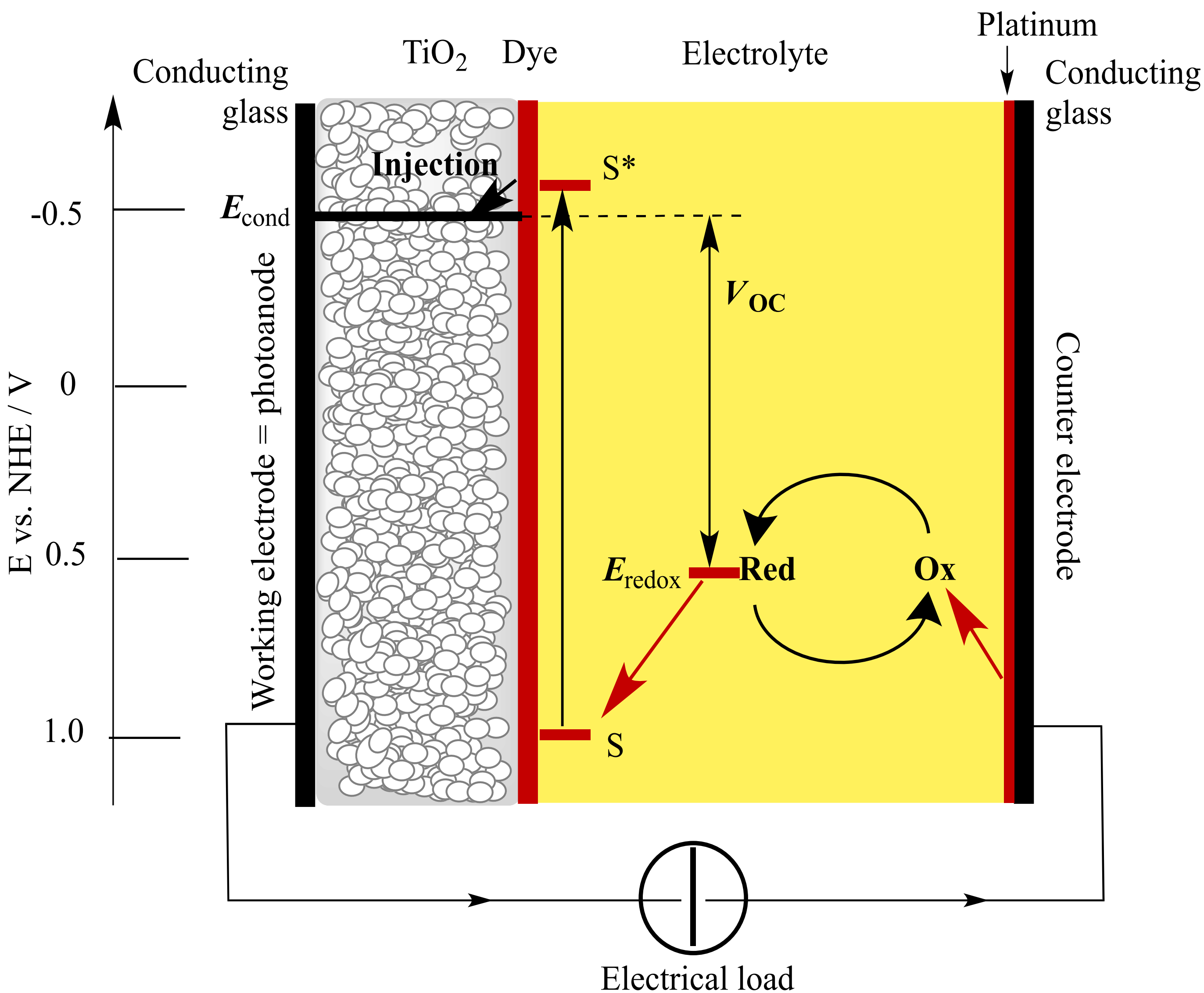
N719



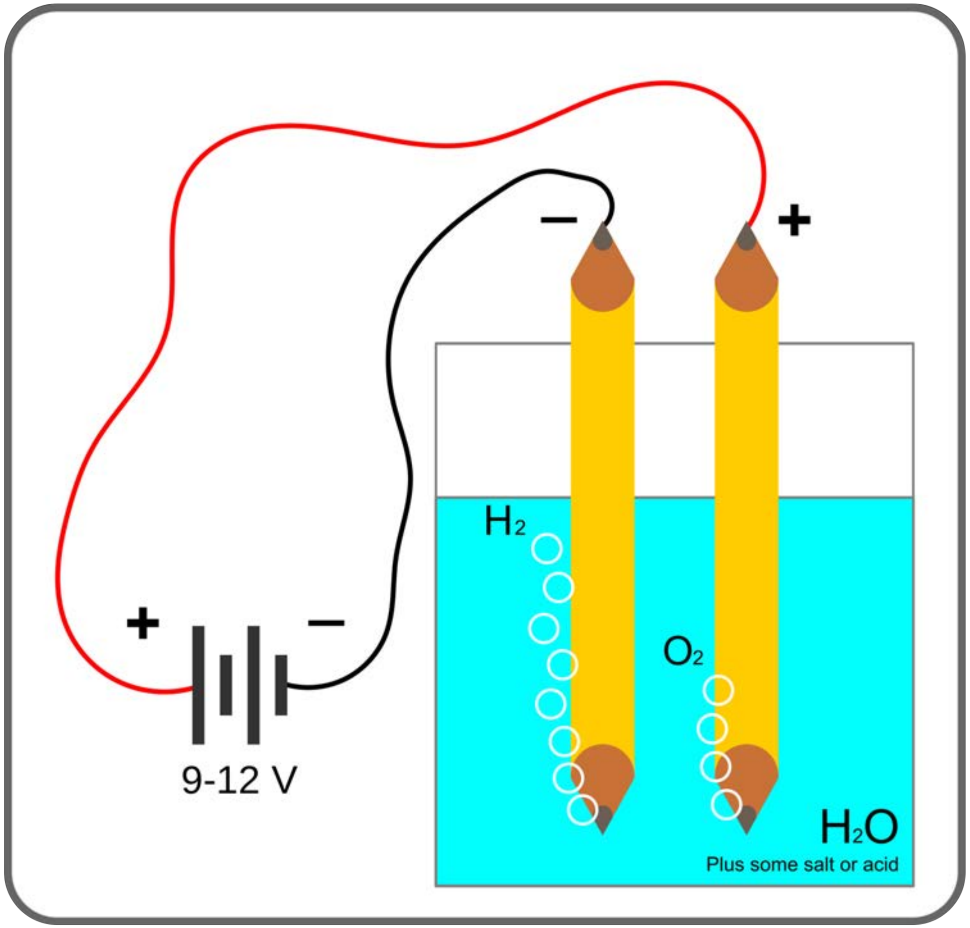
The ruthenium dye N719 and a sealed dye sensitive solar cell

Chem. Soc. Rev., 2015, **44**, 8386-8398

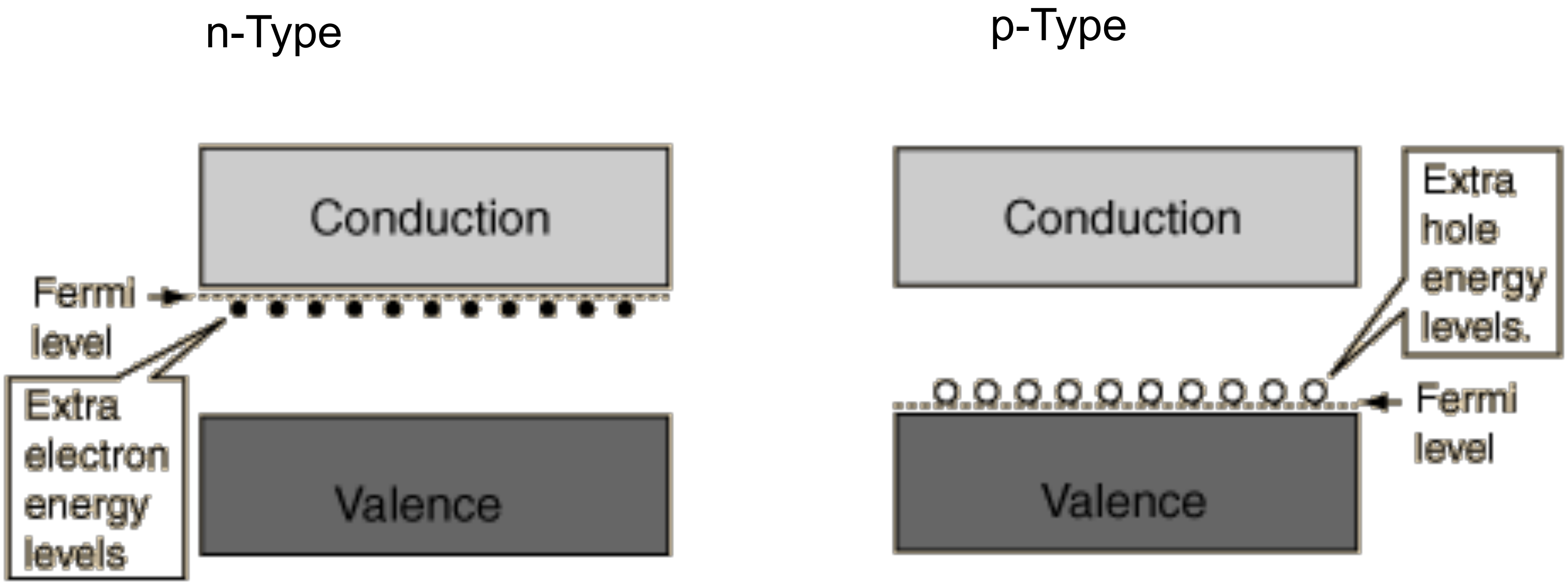
The dye sensitized solar cell - more detail



Separating the electrons and the holes

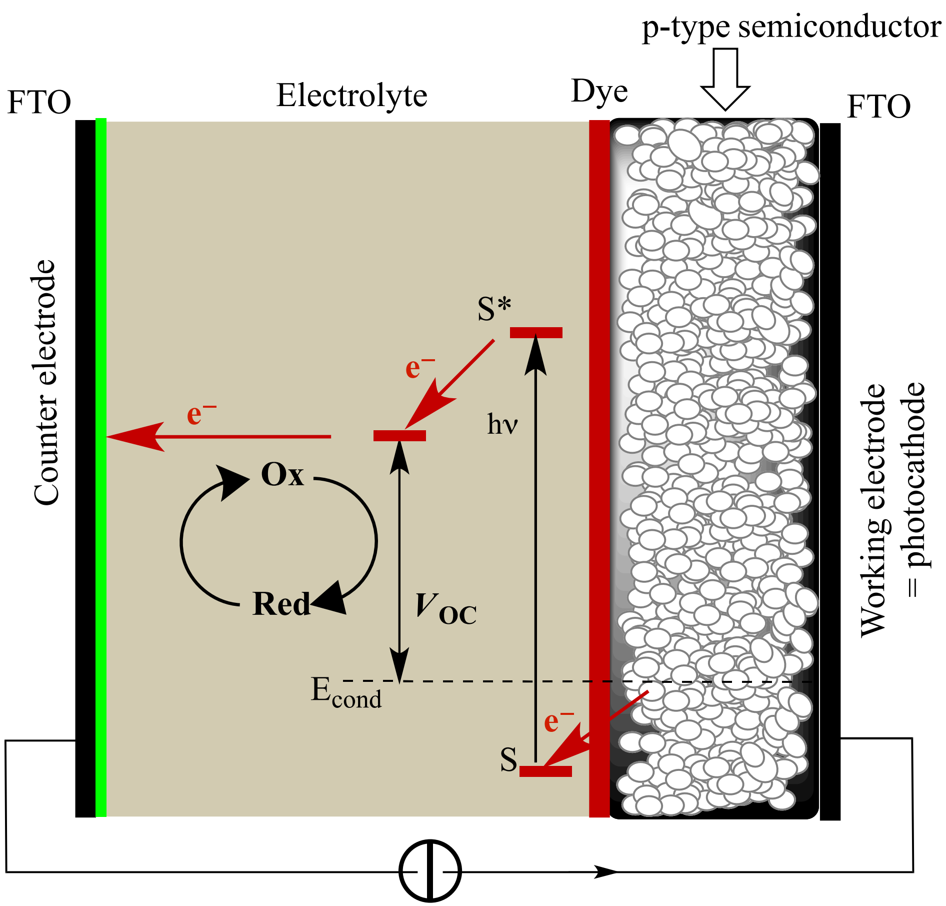


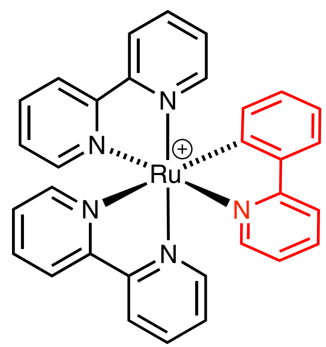
Semiconductors – two types

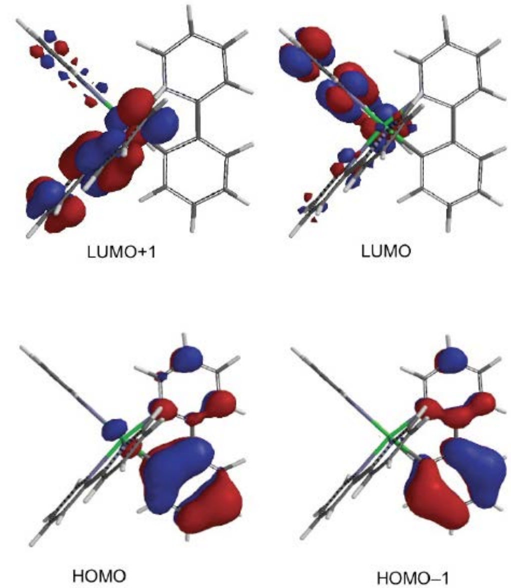


The two types of semiconductor mesh with our need to separate electrons and holes

From n-type semiconductor to p-type

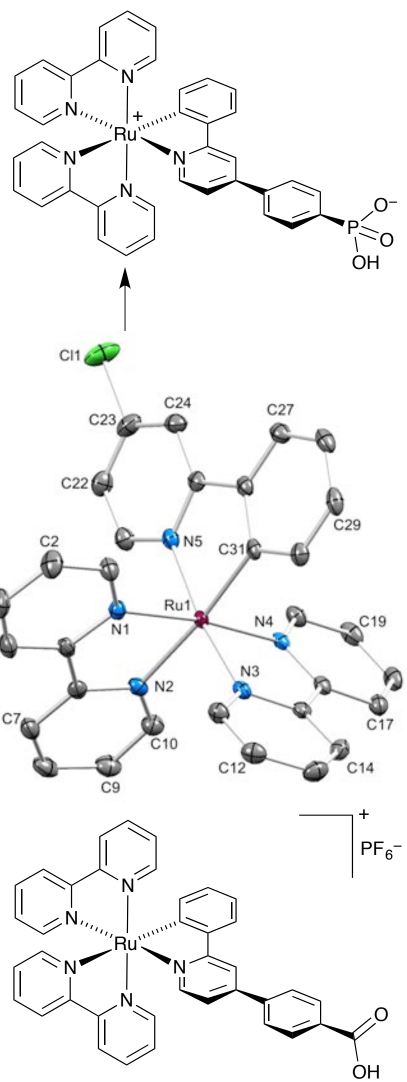




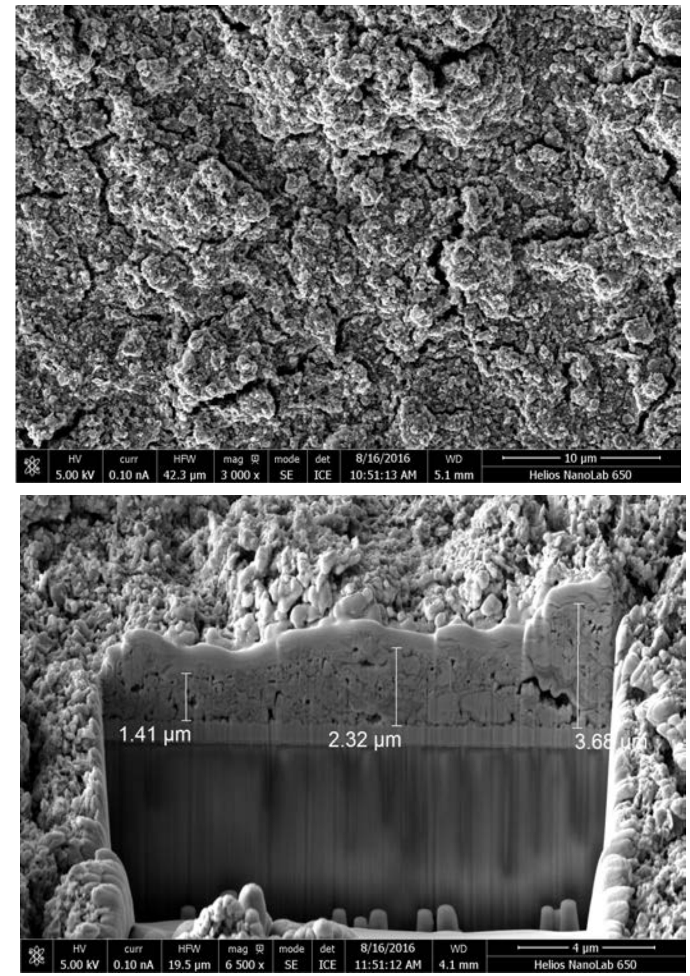


Operating principle of a p-type DSC and the localisation of character in the bpy and ppy domains of cyclometalated $[Ru(bpy)_2(ppy)]^+$ complex cations.

Anchoring cyclometallated complexes to NiO

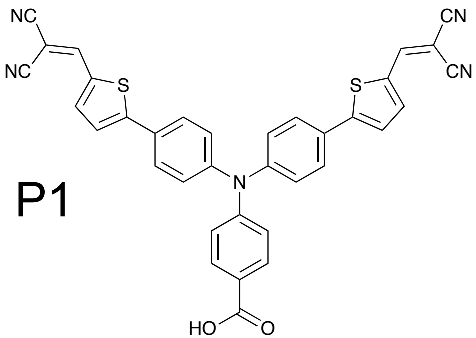


Band-gap of NiO
3.4 - 4.3 eV

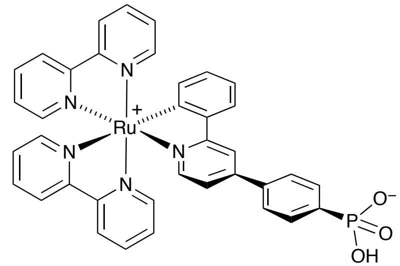


FIB images FTO/NiO electrode ([Ni(acac)$_2$] pre-treatment “screen-printed layers NiO, sintered 350°C): (a) top surface, and (b) Ga beam cut

Comparison of cells with P1

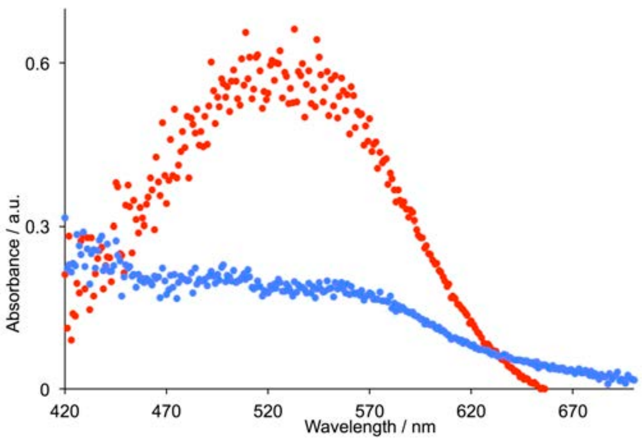


P1

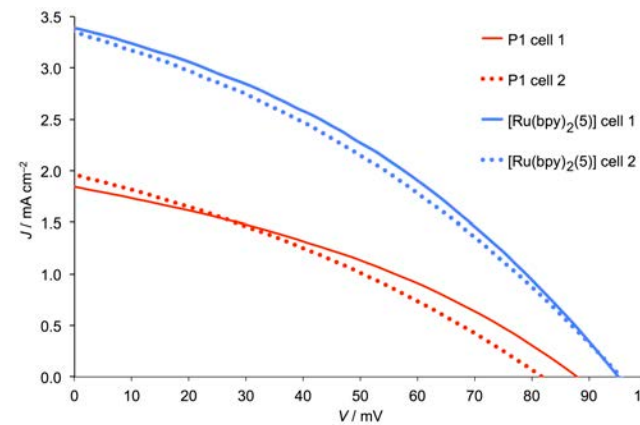


Performance data for DSCs containing dyes Measurementsmade on the day of sealing the DSCs.

Dye	Number of NiO layers	J_{SC} / mA cm^{-2}	V_{OC} / mV	*ff* / %	η / %
P1	2	1.84	88	35	0.057
P1	2	1.96	82	32	0.051
[Ru(bpy)$_2$(**5**)]	2	3.38	95	36	0.116
[Ru(bpy)$_2$(**5**)]	2	3.34	95	34	0.109



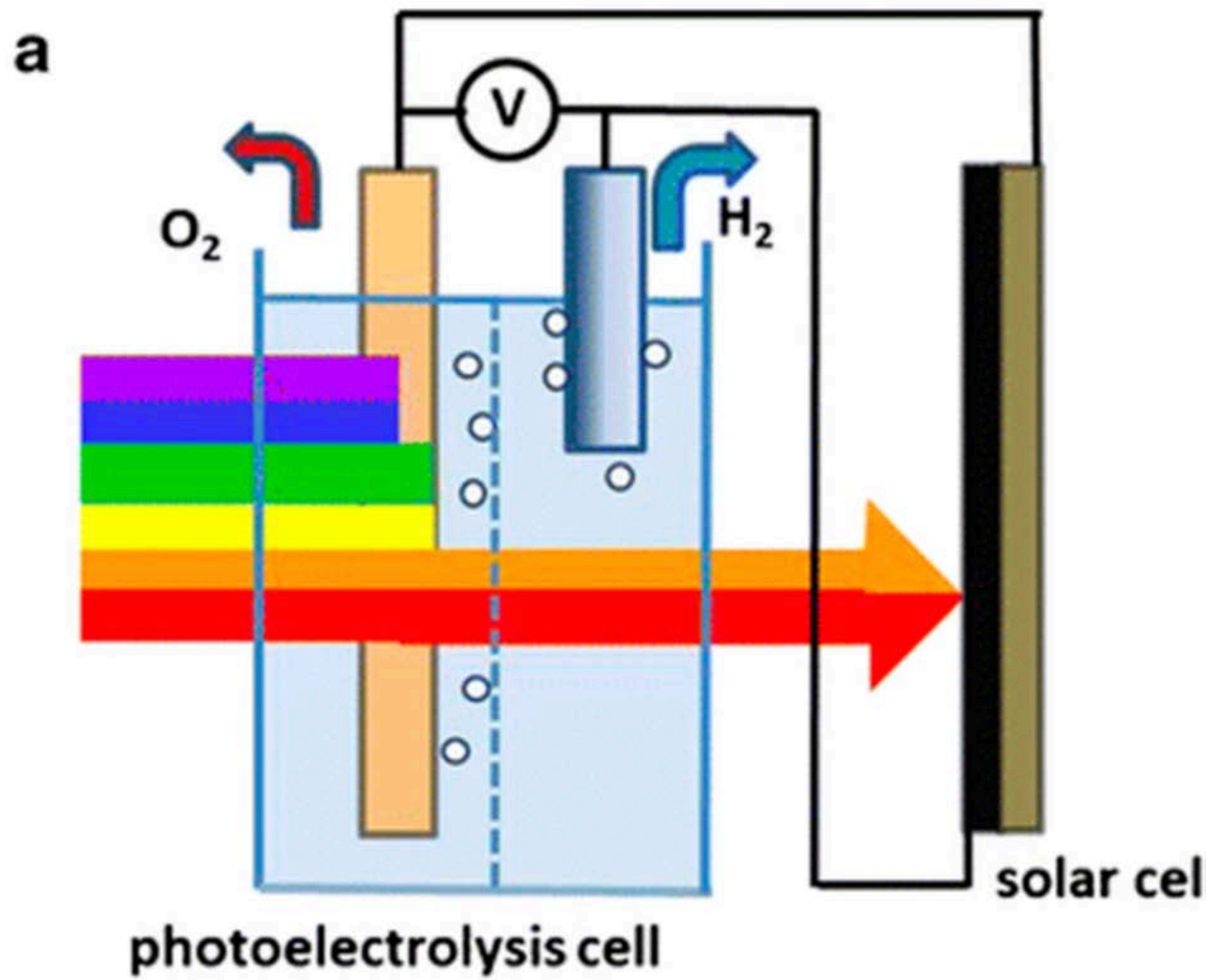
Solid-state absorption spectra of FTO/NiO electrodes with dyes P1 (red) and [Ru(bpy)$_2$(**5**)] (blue).



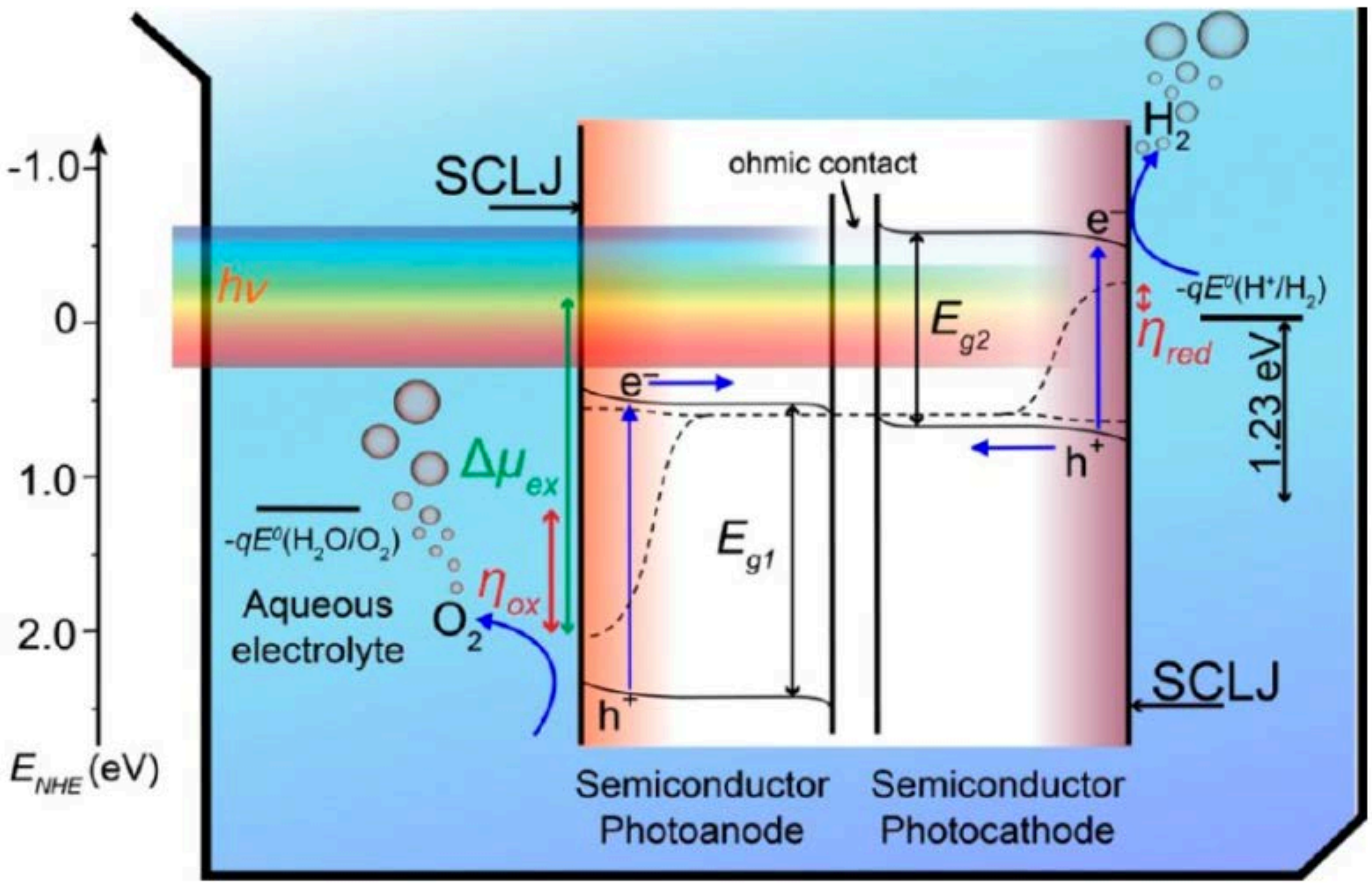
J–V curves for duplicate DSCs containing dye [Ru(bpy)$_2$(**5**)].

J. Mater. Chem. submitted

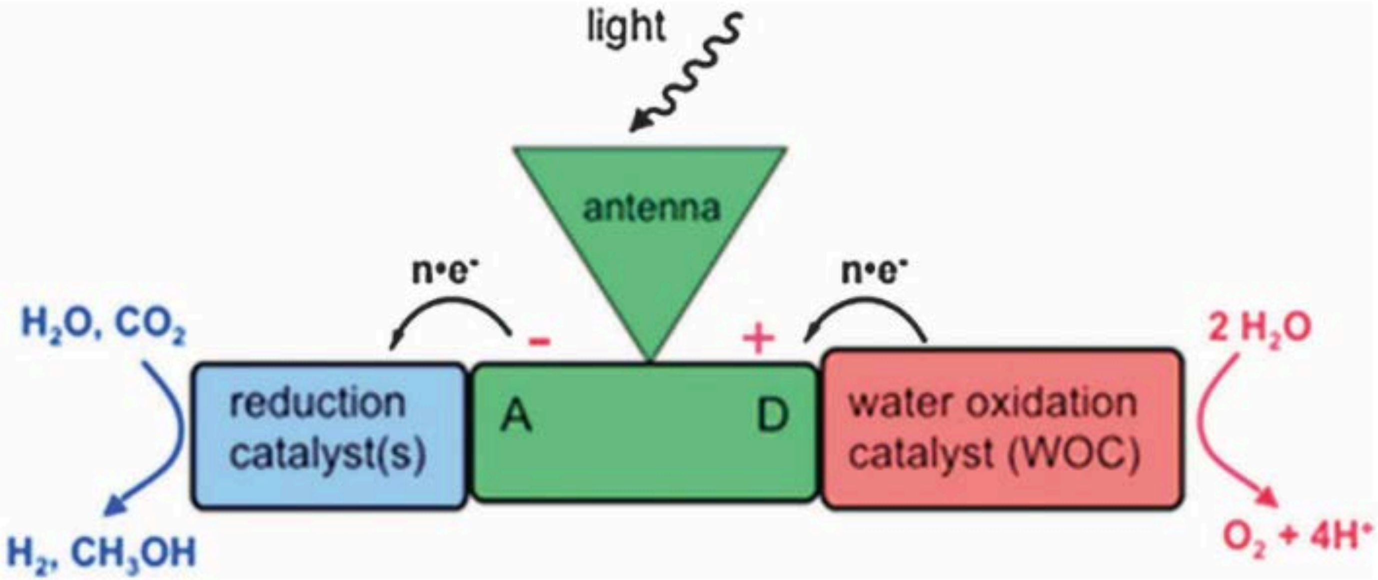
The tandem photcell: two light reactions– one for oxidation and one for reduction



The tandem photcell: two light reactions– one for oxidation and one for reduction



The chemistry scheme that drives artificial photosynthesis

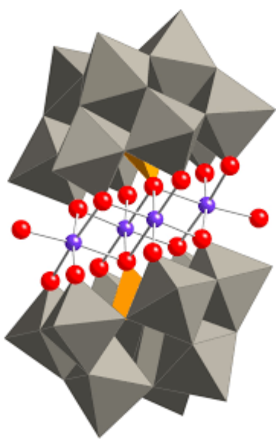


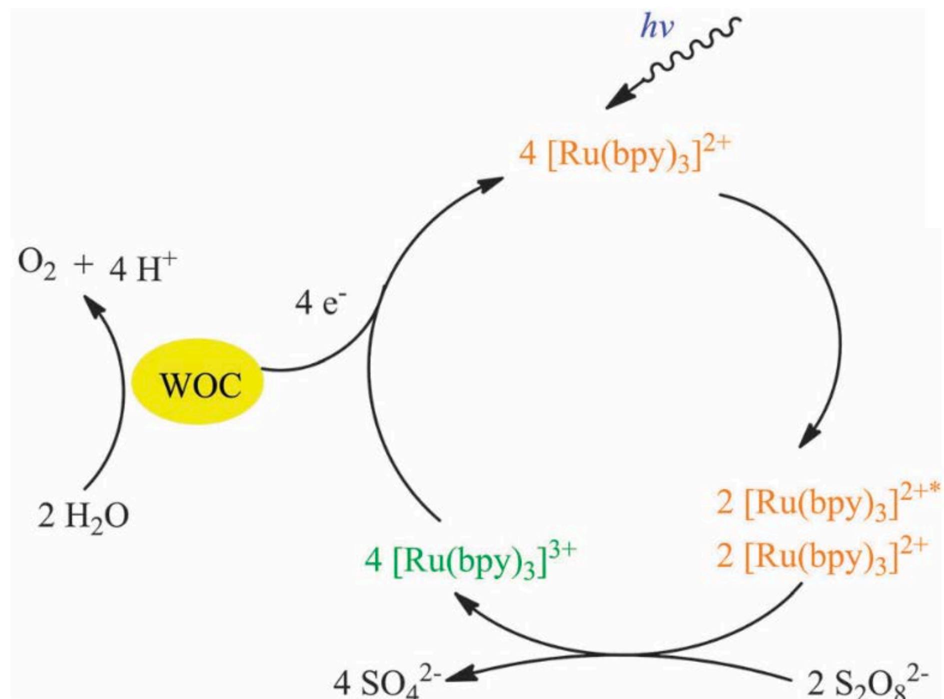
Thoughts about water oxidation

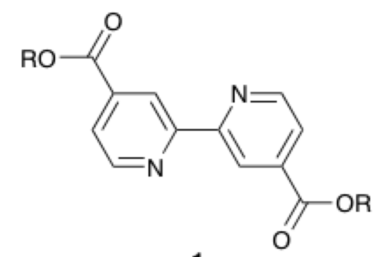
Homogeneous systems studied with Craig Hill
J. Phys. Chem. A, 2010, 114, 6284-6297; RSC Advances, 2013, 3, 20647–20654

$K_{10}[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]$

$[Ru(\mathbf{1})_2(bpy)][PF_6]_2$







1

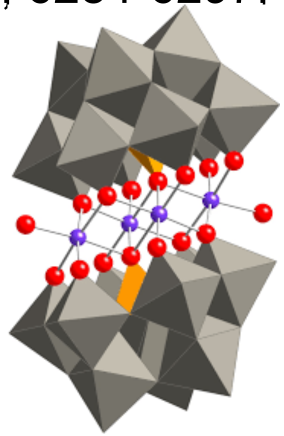
R = $^{n}C_{18}H_{37}$

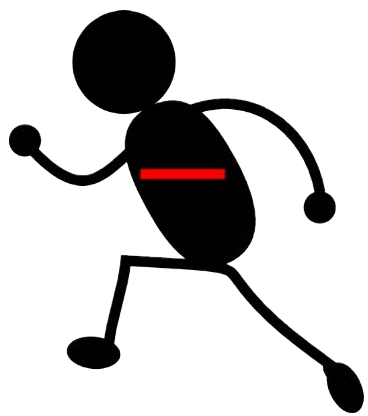
RSC Adv., 2014, **4**, 11766-11775

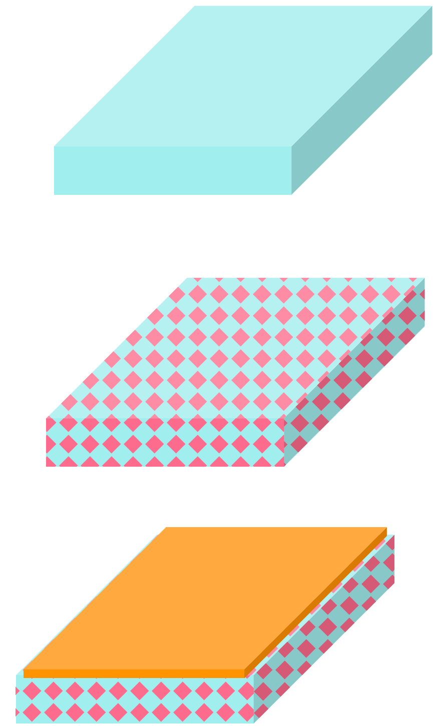
Thoughts about water oxidation

Homogeneous systems studied with Craig Hill
J. Phys. Chem. A, 2010, 114, 6284-6297; RSC Advances, 2013, 3, 20647–20654

$[Ru(\mathbf{1})_2(bpy)]^{2+}$





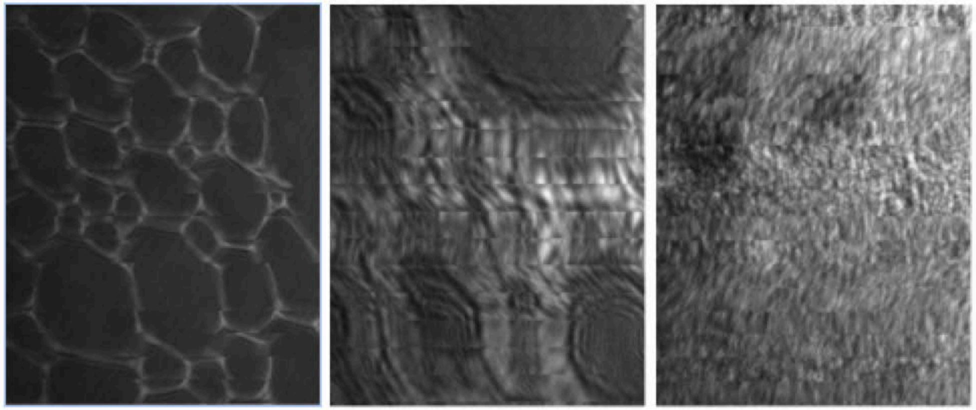


LB trough
Water

LB trough
POM sublayer

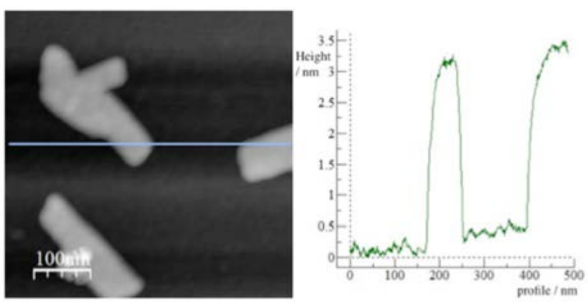
LB trough
POM sublayer
Ru LB layer

And so to WOC



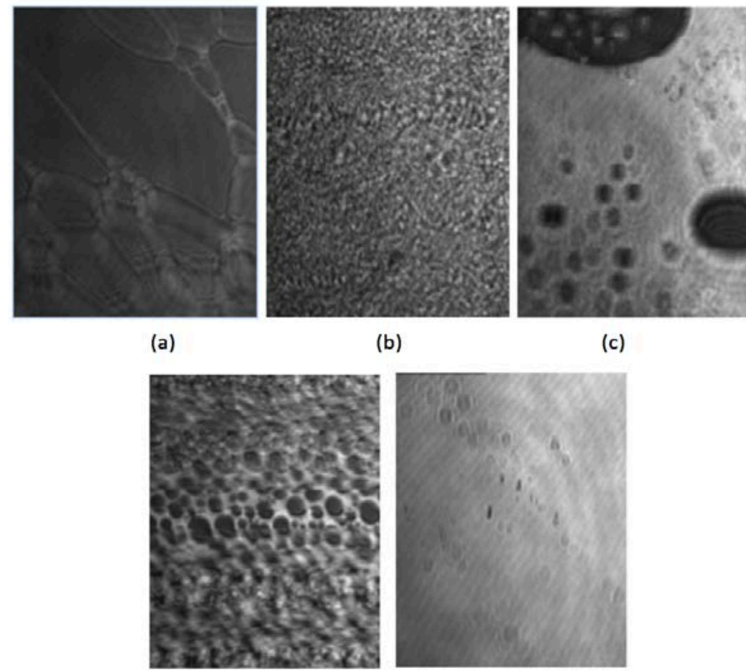
(a) (b) (c)

Fig. 7. Brewster angle microscopy images of [Ru(**1**)$_2$(bpy)][PF$_6$]$_2$ on (a) pure water (0.01 mN/m), (b) aqueous KPF$_6$ (0.02 mN/m) and (c) Co$_4$POM (0.06 mN/m) subphases.



(a) (b)

Fig. 9. (a) AFM height image of *cis*-[Ru(**1**)$_2$Cl$_2$] LB film (one dipping cycle) on mica, transferred from a monolayer formed on pure water subphase. (b) Line profile corresponding to the blue line drawn in (a). The dark area visible between the islands in Fig. 9a is bare mica.



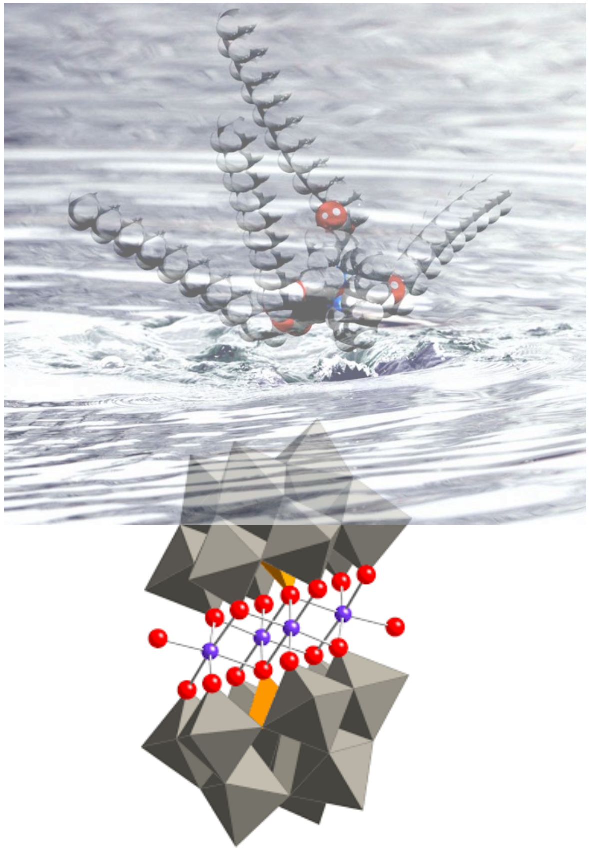
(a) (b) (c)

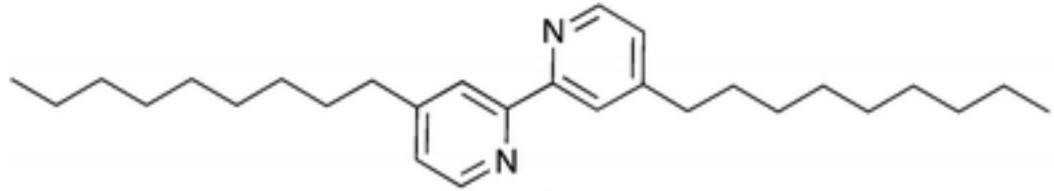
(d) (e)

Fig. 8. Brewster angle microscopy images of [Ru(**1**)$_2$(bpy)][PF$_6$]$_2$/DODA (a) 1 : 0.5 on pure water (0.06 mN/m), (b) 1 : 0.5 on Co$_4$POM subphase (0.04 mN/m), (c) 1 : 5 on Co$_4$POM subphase (0.11 mN/m), (d) 1 : 20 on Co$_4$POM subphase (0.05 mN/m), (e) 1 : 0.5 on Co$_4$POM subphase (0.63 mN/m).

RSC Adv., 2014, **4**, 11766-11775

And so to WOC





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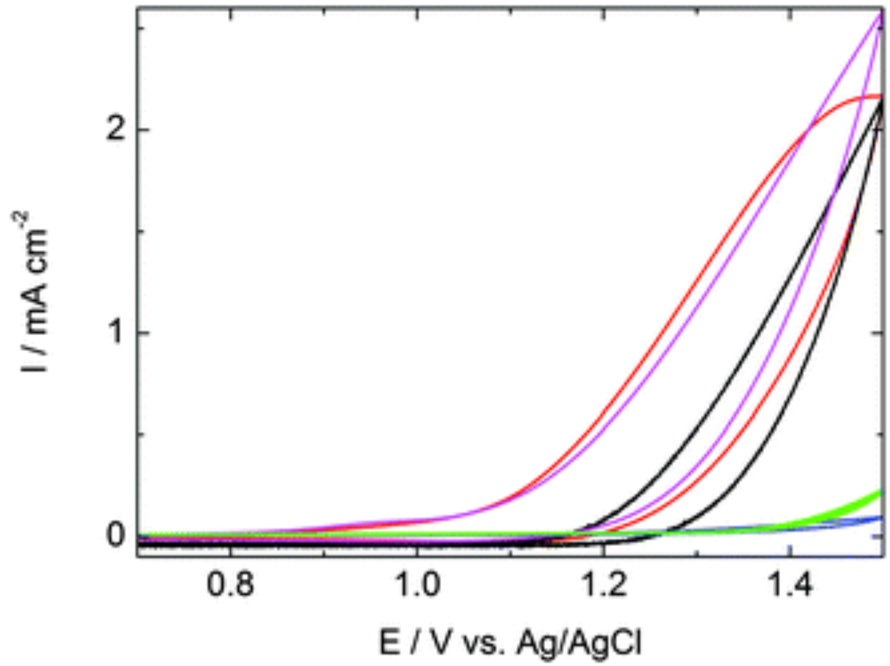
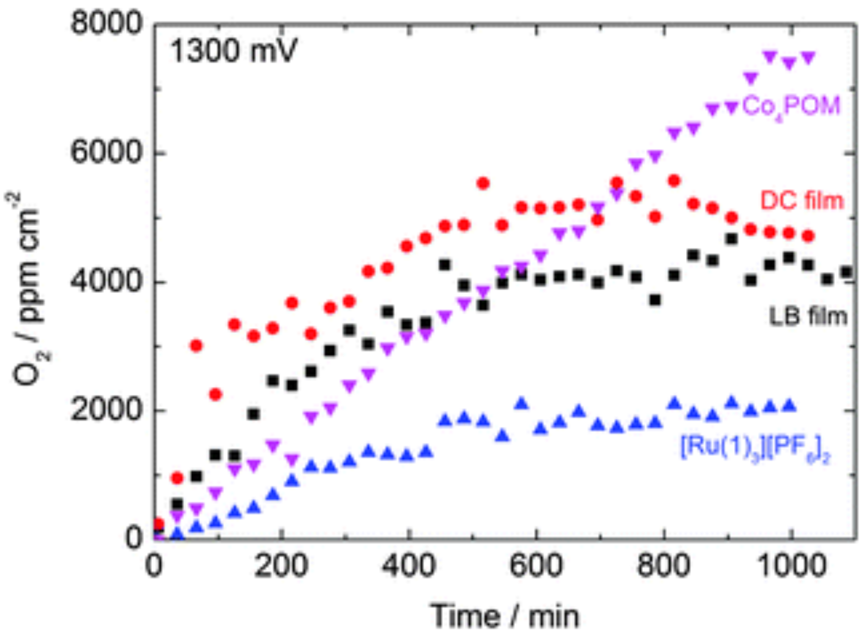
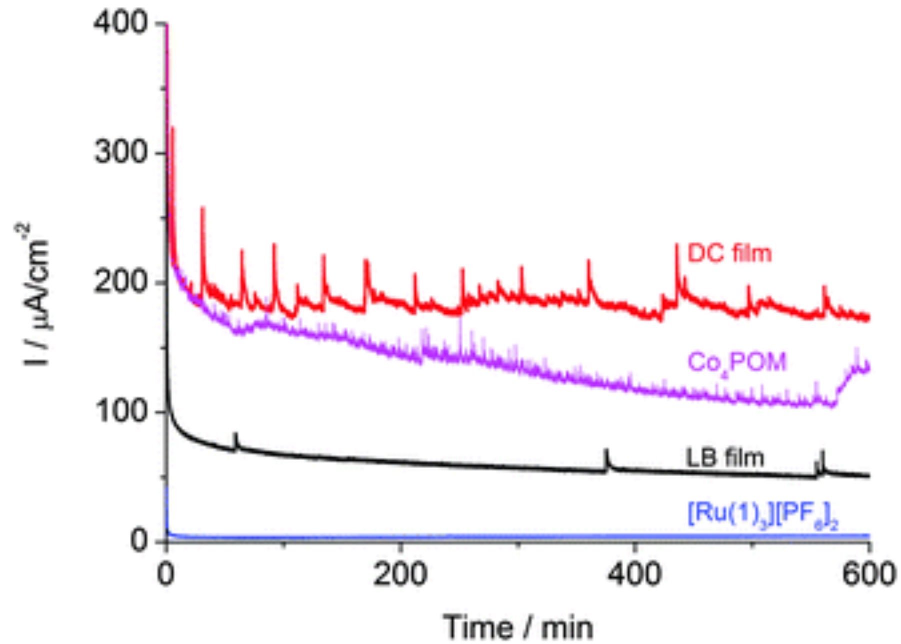


CVs of 50-layer LB and DC films of $[Ru(\mathbf{1})_3][PF_6]_2/Co_4POM$ on FTO (black and red curves)
DC films of $[Ru(\mathbf{1})_3][PF_6]_2$ (blue) and Co_4POM (magenta) on FTO, and bare FTO (green)

Chem. Commun., 2016, **52**, 2940-2943

And so to WOC





O_2 evolution vs. time at +1.3 V

Current densities of LB and DC films, and DC Co_4POM and $[Ru(\mathbf{1})_3][PF_6]_2$ films chronoamperometry (+1.3 V)

Chem. Commun., 2016, **52**, 2940-2943

Is the Emperor naked?

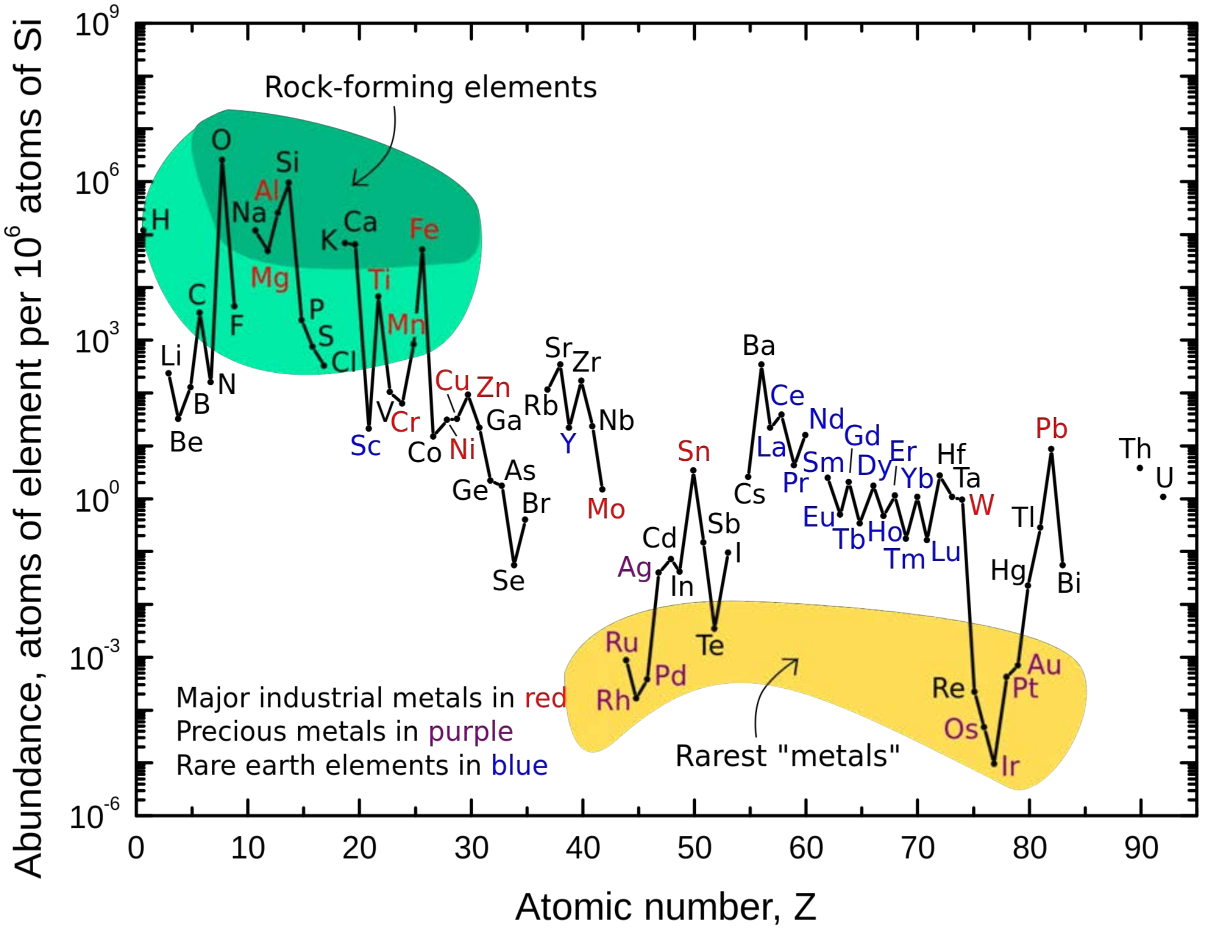
Have we made fuels?

We are socially conditioned for liguid organic fuels (petroleum) rather than gas-phase fuels (hydrogen)

Is the technology sustainable?

We use elements such as platinum and ruthenium which are amongst the rarest on our planet.

Why do we need a sustainable materials chemistry?



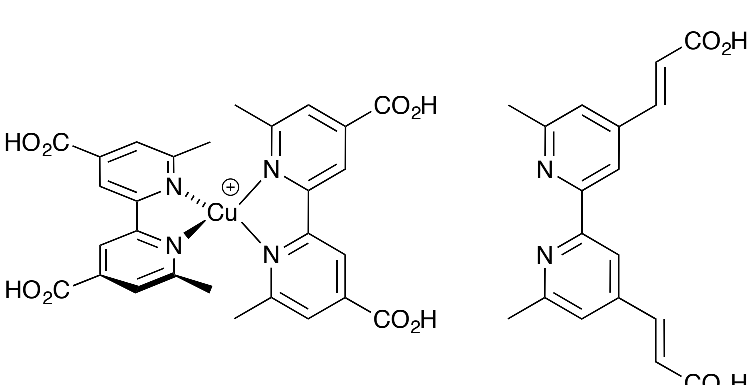
Coord. Chem. Rev., 2013, 257, 3089

From ruthenium to copper (prices 29.08.2016)

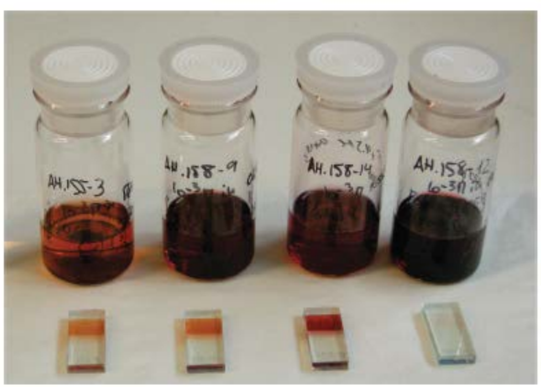
Ruthenium	Price: 1,350 \$ kg^{-1}	Abundance:	0.001 ppm
Copper	Price: 4.6 \$ kg^{-1}	Abundance:	68 ppm

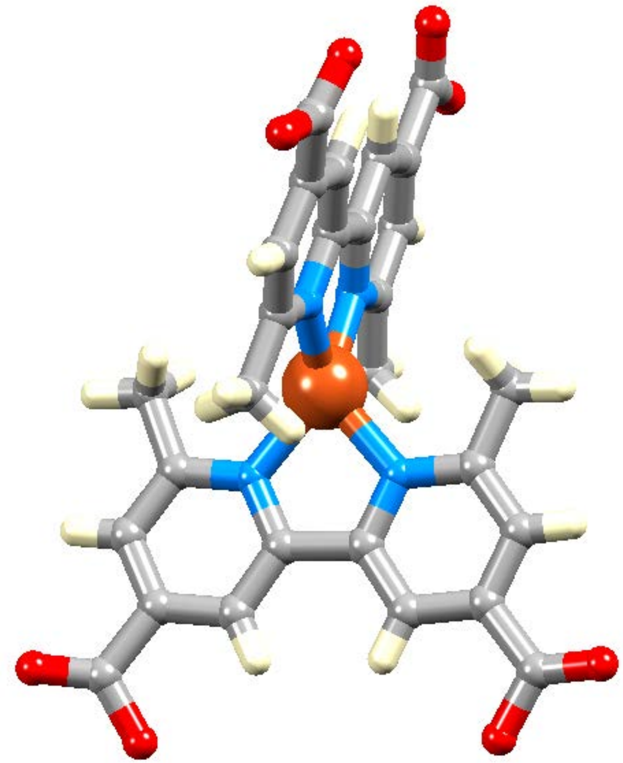
$[RuL_3]^{2+}$ and $[CuL_2]^+$ (L = diimine ligand) are orange, λ_{max} 400 - 550 nm, although the copper complexes are less absorptive ($\varepsilon \approx 5{,}000\ M^{-1}\ cm^{-1}$) than ruthenium ($\varepsilon \approx 15{,}000\ M^{-1}\ cm^{-1}$).

Birth of copper(I)-based DSCs



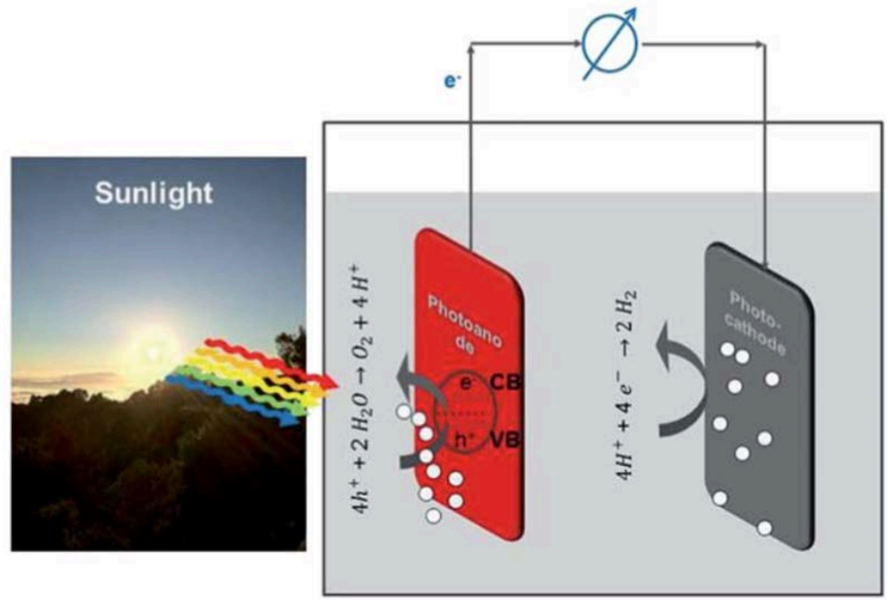
$[Cu(\mathbf{1})_2]^+$ **2**

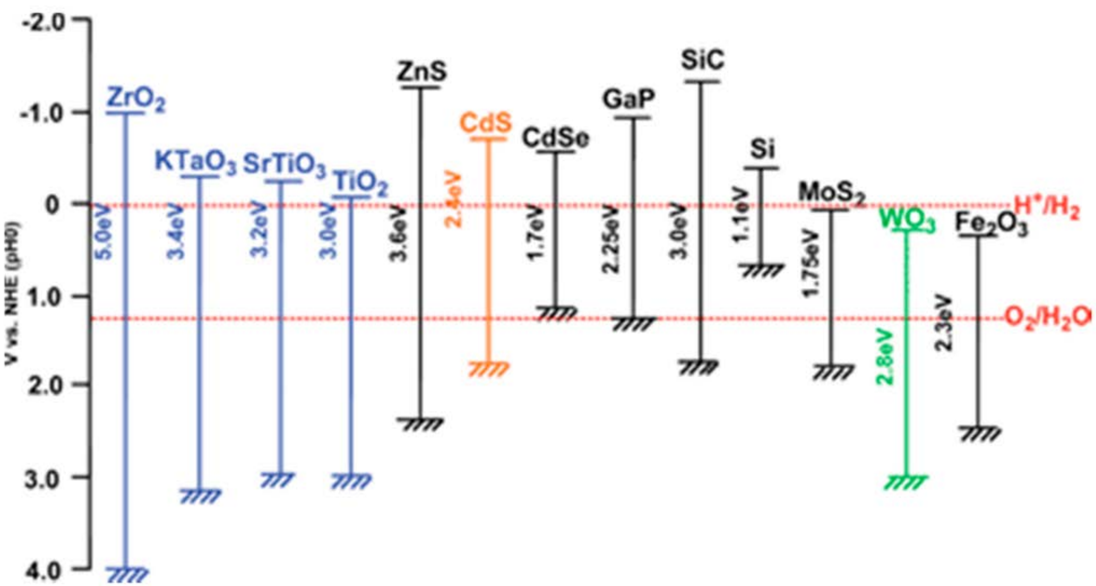




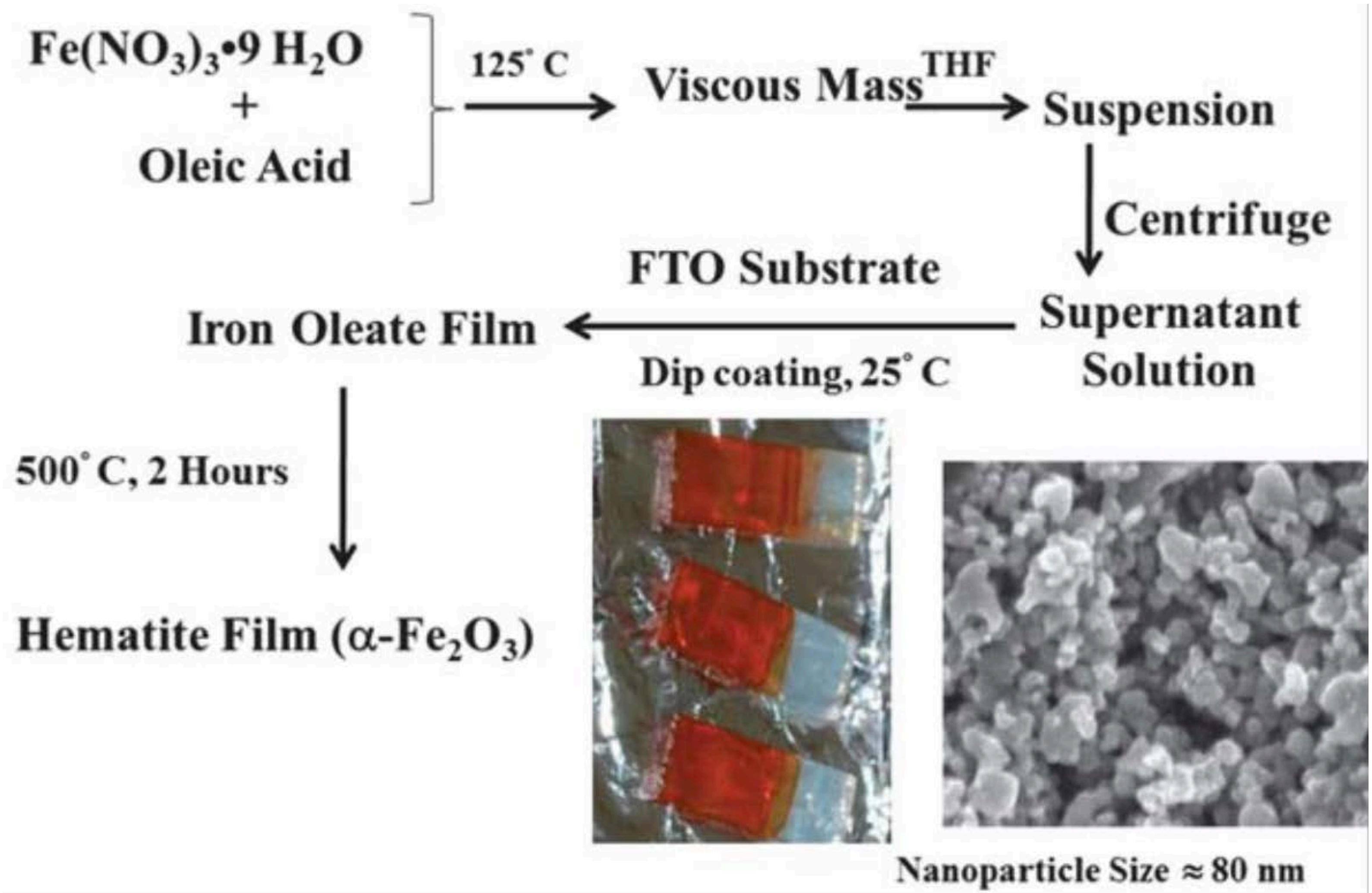
Chem. Commun., 2008, 3717-3719

In rust we trust!

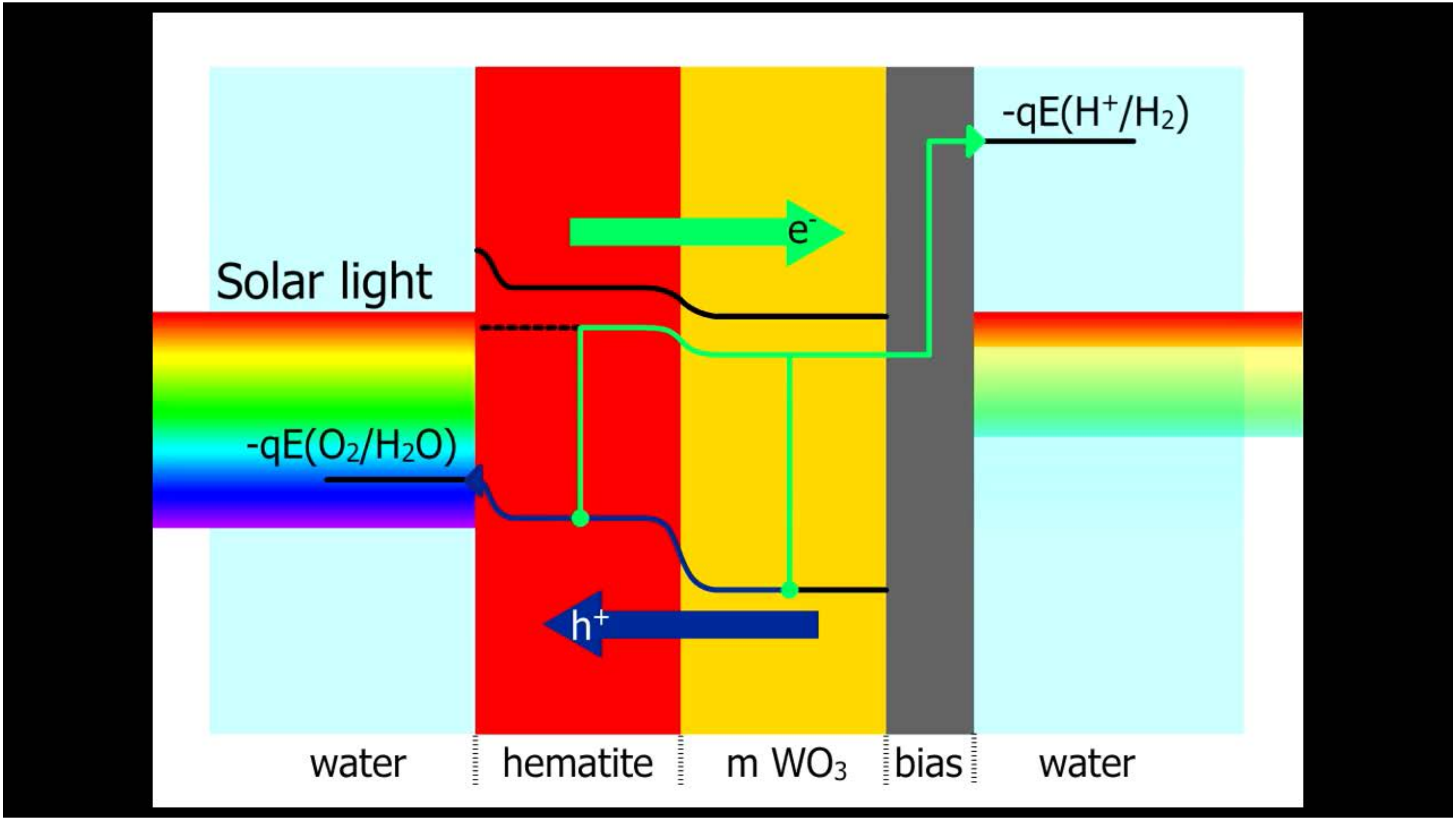




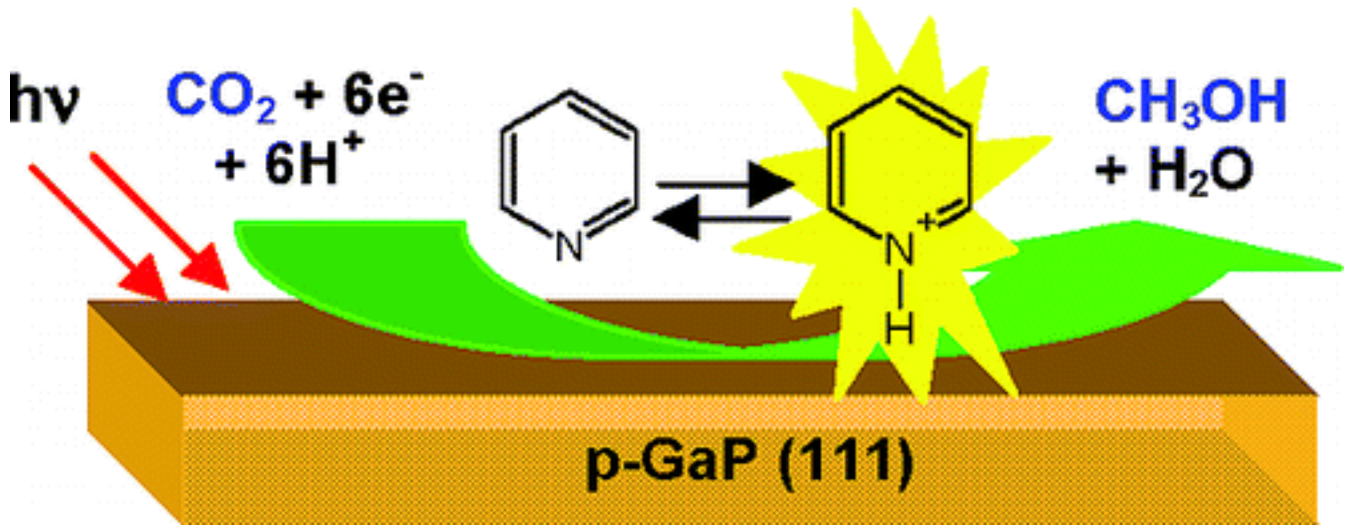
In rust we trust!



In rust we trust!



From hydrogen to more conventional fuels



Selective Solar-Driven Reduction of CO_2 to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell

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Towards a green (and rusty) future

University of Basel

Thank you
for your attention.