Artificial Photosynthesis:

From basic concepts to recent developments

Marc Fontecave

Laboratoire de Chimie et Biologie des Métaux, Université Joseph Fourier, CNRS, CEA/DSV/iRTSV
CEA-Grenoble 17 rue des martyrs 38054 Grenoble cedex 9, France
mfontecave@cea.fr; Phone: (0033)438789103 ; Fax: (0033)438789124

Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05

V. Artero
M. Chavarot-Kerlidou
Y. Oudart
S. Canaguier
A. Legoff
B. Fihri
R. Métayé
P. D. Tran
V. Fourmont
P-A. Jacques

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Serge Palacin
Bruno Jousselme

DRT

Laboratoire des composants pour piles à Combustibles
Electrolyse et Modélisation
CEA Grenoble

Nicolas Guillet

DRT

Françoise Vinet
Muriel Matheron
Adeline Leyris

Dalian University of Technology, China:

Prof. Licheng Sun
Prof. Mei Wang
Zhang Pan
Dong Li

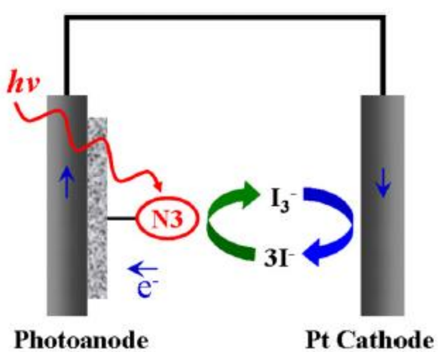
Biomass (natural photosynthesis)
100 TW

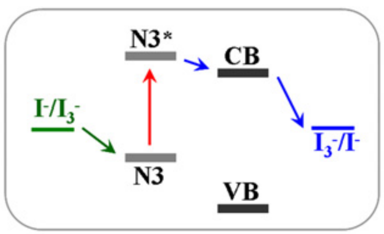
90000 TW

Photovoltaics (Electricity)
Efficiency: 10%

Artificial Photosynthesis

Electricity: DSSC





TiO_2

Efficiency: 11%

Fuels (storage)

- Reduction of CO_2

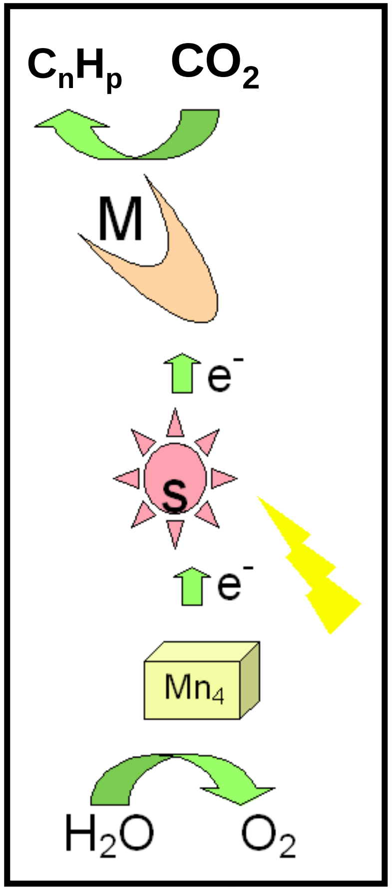
$$H_2O + CO_2 + h\nu \rightarrow O_2 + C_nH_p$$

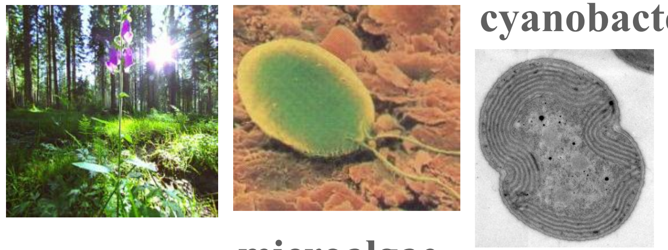
(CO, $HCOOH$, CH_3OH, CH_4,..)

- Water splitting

$$2\,H_2O + h\nu \rightarrow O_2 + 2H_2$$

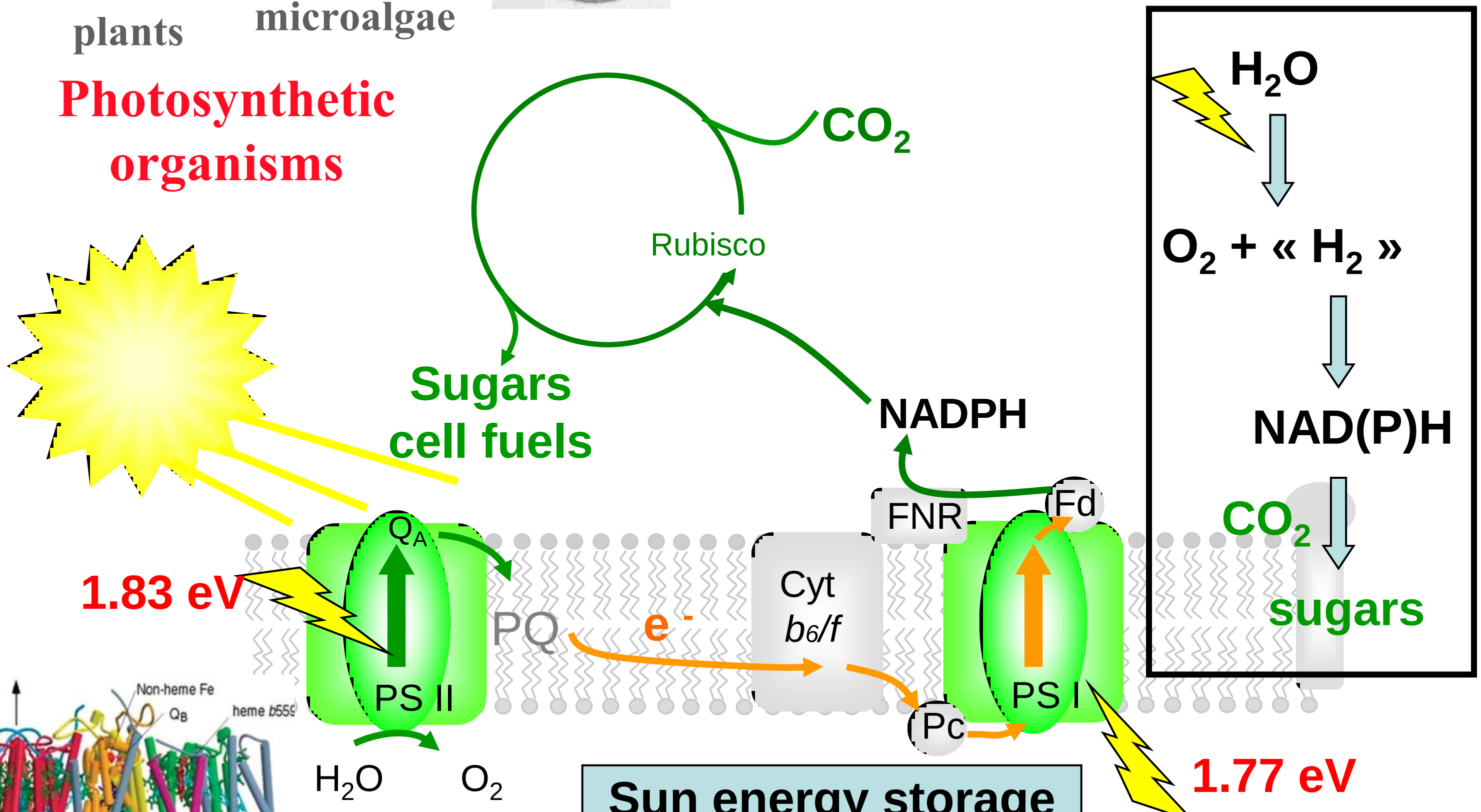
Photosynthesis

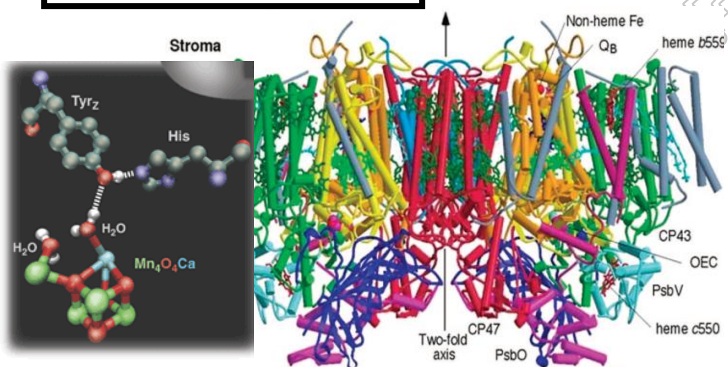




plants microalgae

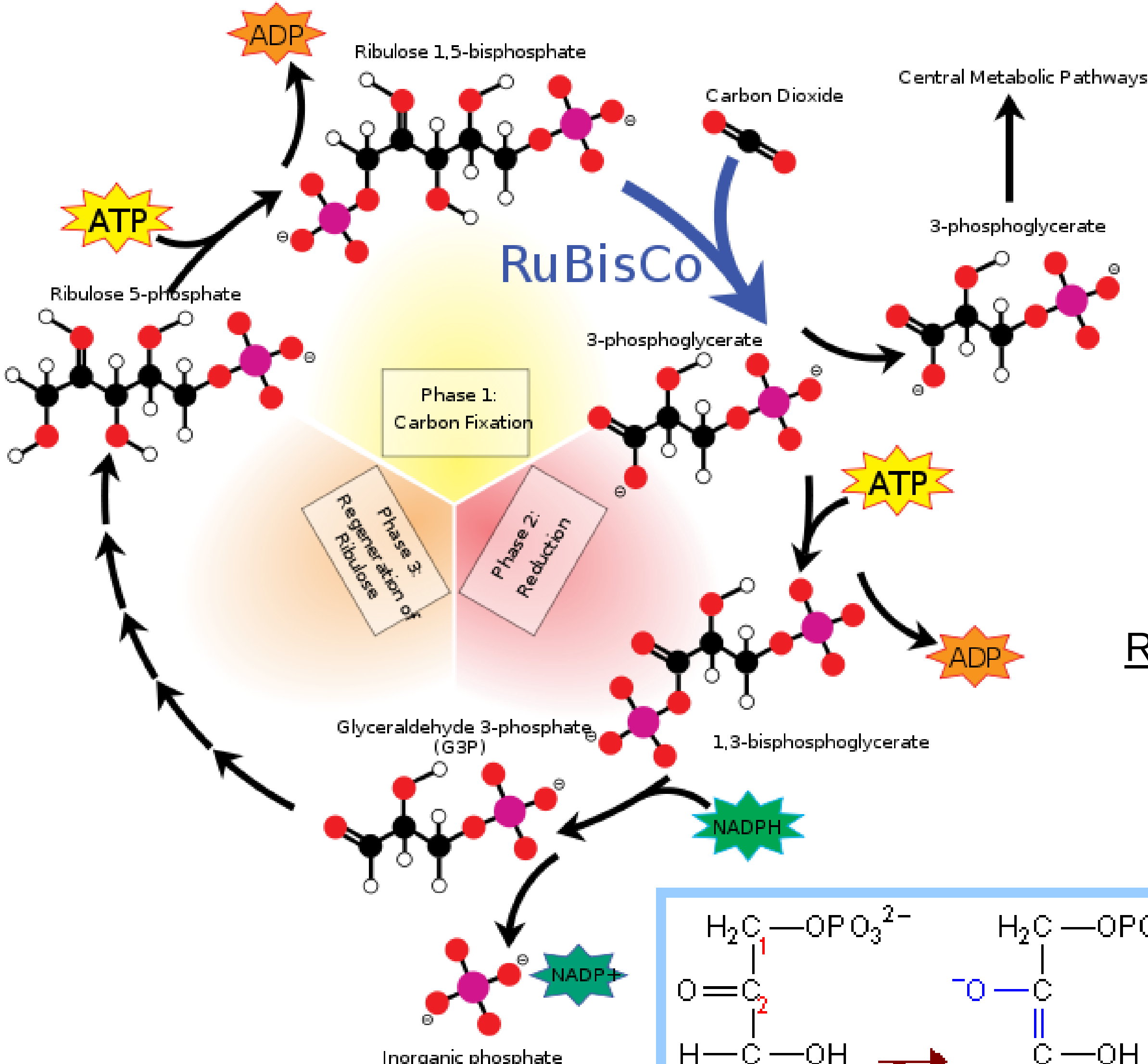
Low efficiecy
- -Plants < 1%
- -Photosynthetic microrganisms 4%
- -Max (theory): 10% (0.34x0.34x0.9)

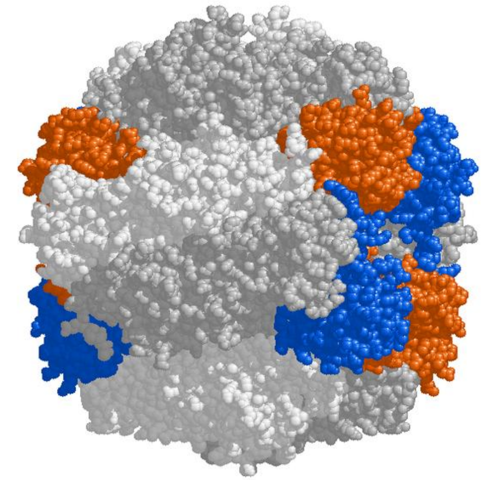




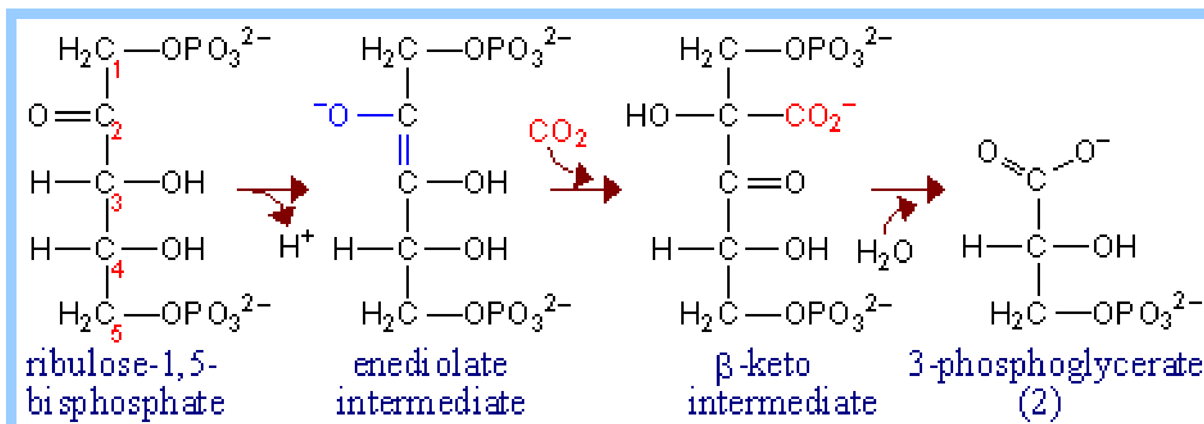
Sun energy storage is in water splitting

$H_2O \rightarrow H_2 + ½ O_2$	ΔE=1.23 V
$CO_2 + H_2O \rightarrow 1/6\ C_6H_{12}O_6 + O_2$	ΔE=1.24V

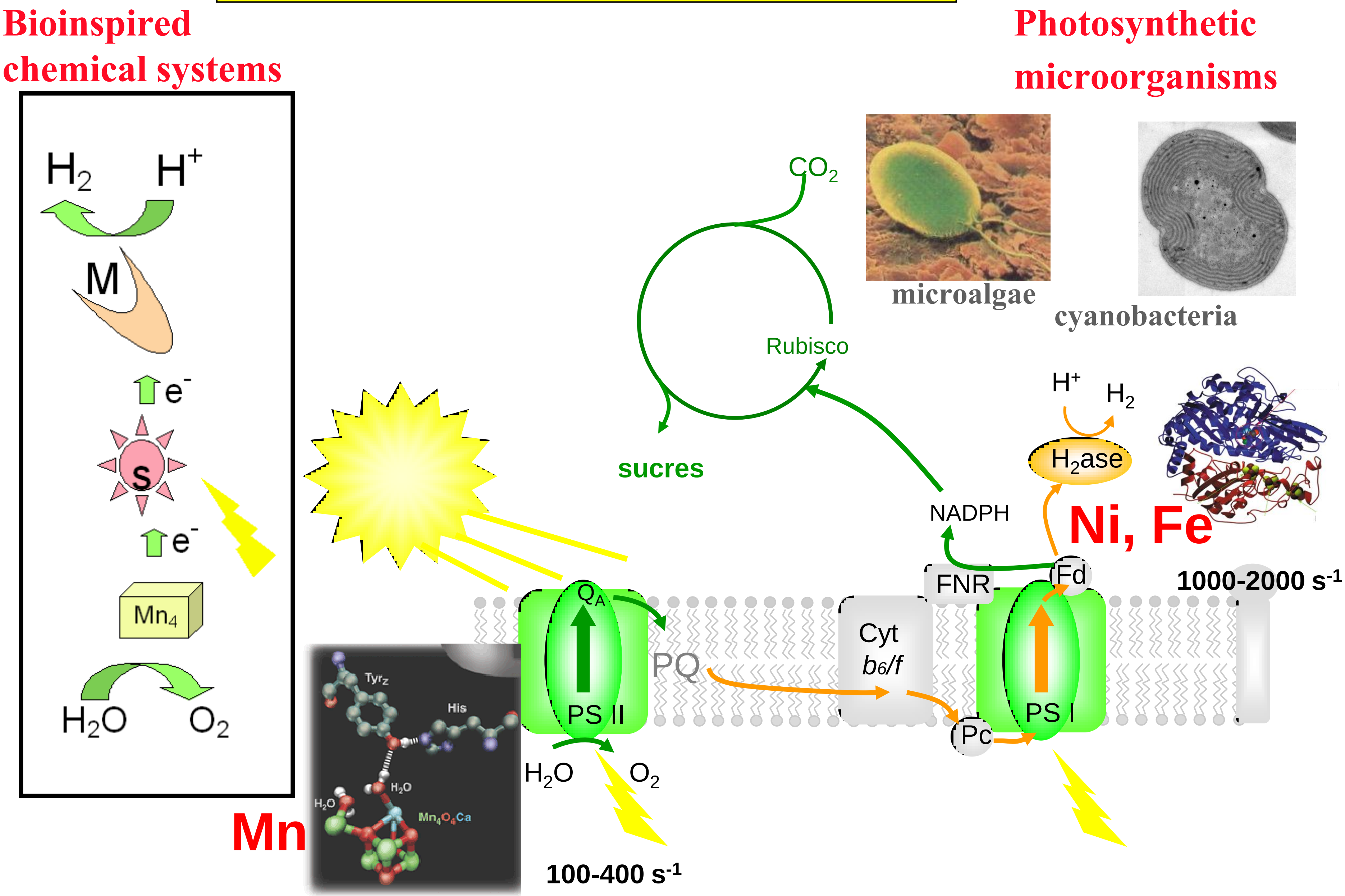




Ribulose1,5-biphosphate carboxylase



Photosynthesis: water splitting

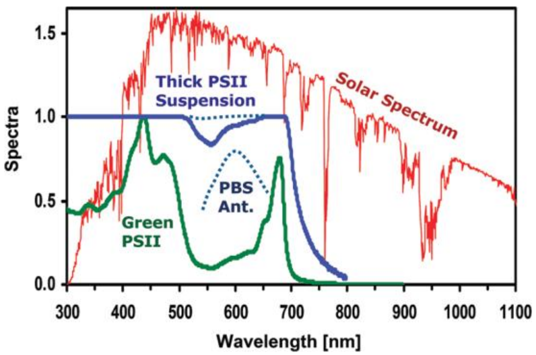


$CO_2 + H_2O + light \rightarrow sugar + 1/2\ O_2$

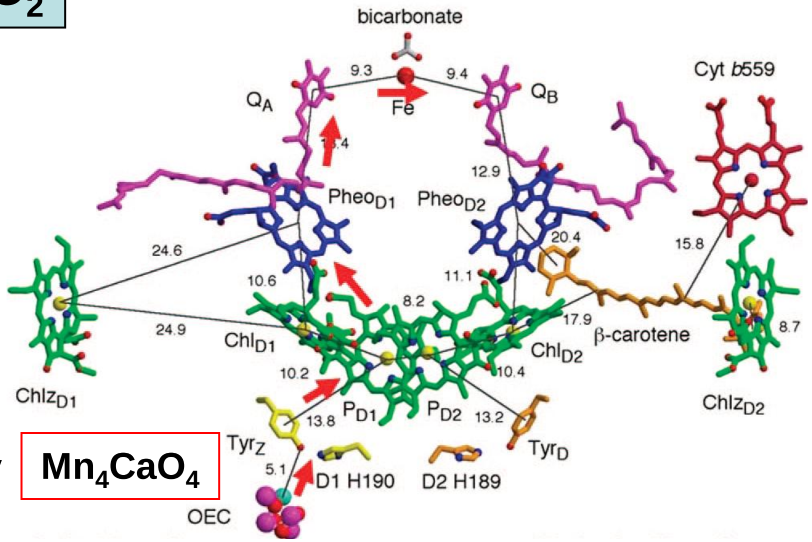
$H_2O + light \rightarrow H_2 + 1/2\ O_2$

Photosystem II: supramolecular

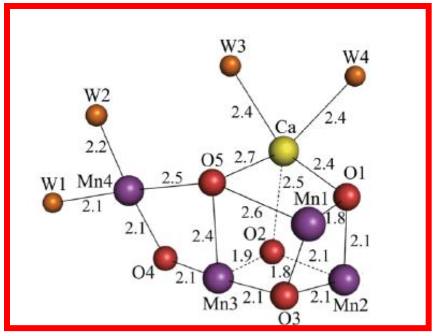
Organization :
- -Space (position)
- -Energy (potentials,…)
- -Time (reaction rates)

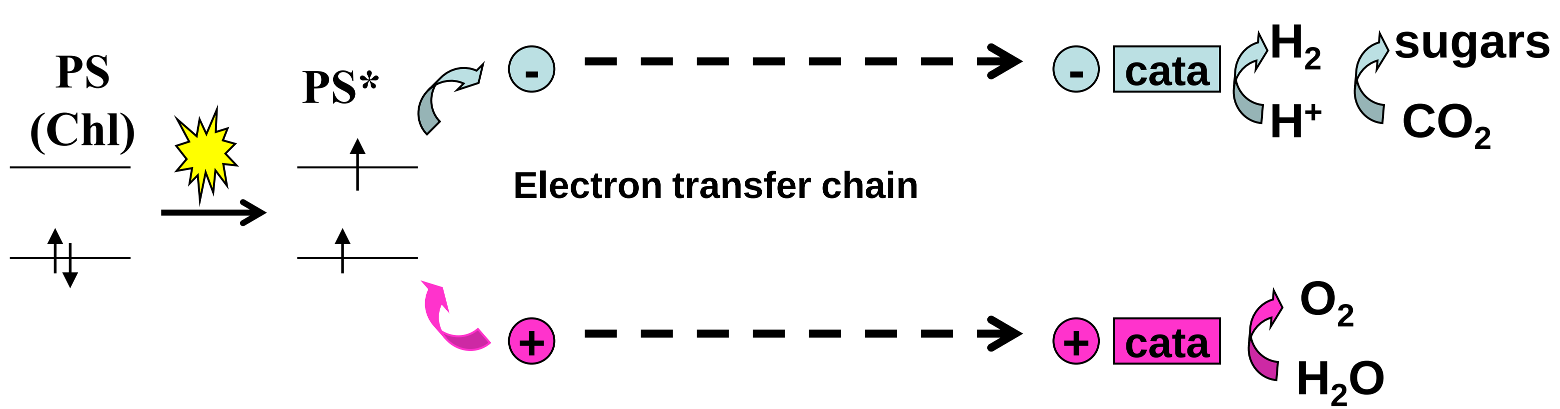


1.56 eV < Visible < 3.12 eV



Mn_4CaO_4





Pb 1: Absorption of 1 photon by a **photosensitizer** PS (H_2O does not absorb light)

-Semiconductor (<1.8eV; visible)
(T_iO2: 3 eV; UV)
- PS inorganic or organic

Pb 2: charge separation (1 hole/1 electron per hν) optimize
→stability of charge separation states
→the **electron transfer chain**

Pb 3: **Catalysts** to quickly accumulate/utilize
4 « holes » (formation O2)
2x2 electrons (formation 2 H2)

Biomass (natural photosynthesis)
100 TW

90000 TW

Photovoltaics (Electricity)
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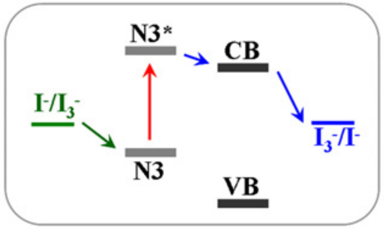
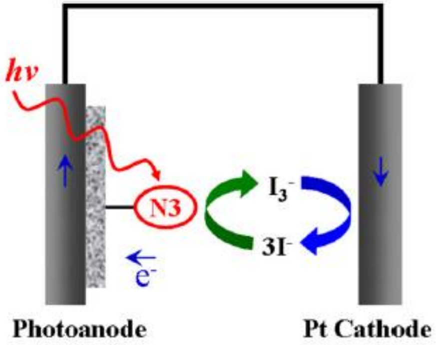
Artificial Photosynthesis

Electricity: DSSC



TiO_2

Rendt: 11%



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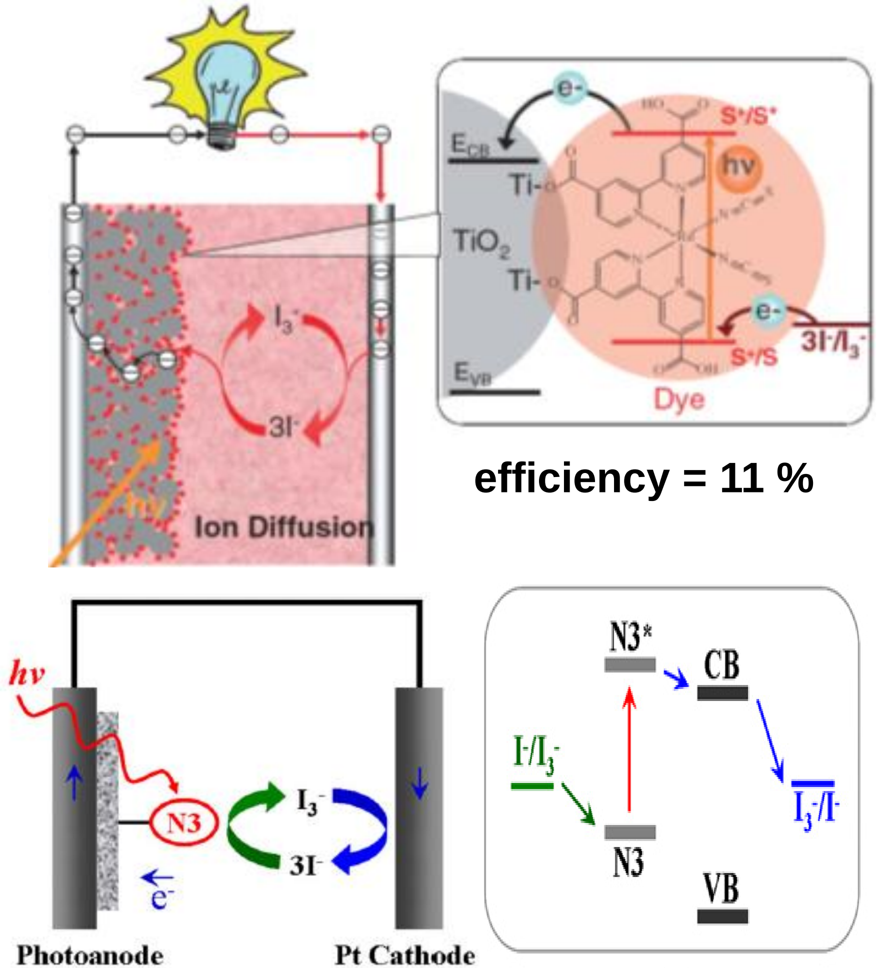
(CO, HCOOH, CH_3OH, CH_4,..)

- Water splitting

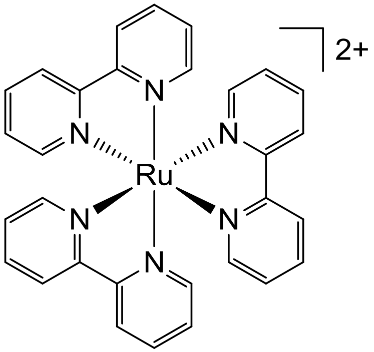
$$2\ H_2O + h\nu \rightarrow O_2 + 2H_2$$

Artificial photosynthesis and electricity: Grätzel cell

M. Grâtzel, EPFL



efficiency = 11 %



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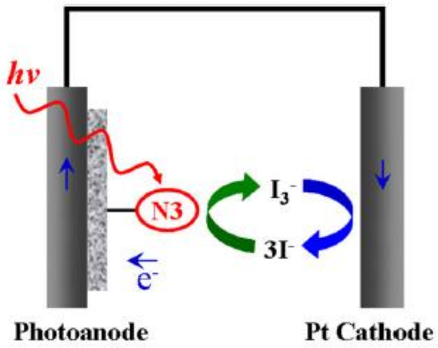

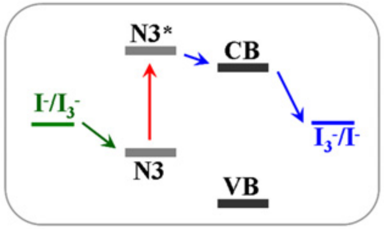

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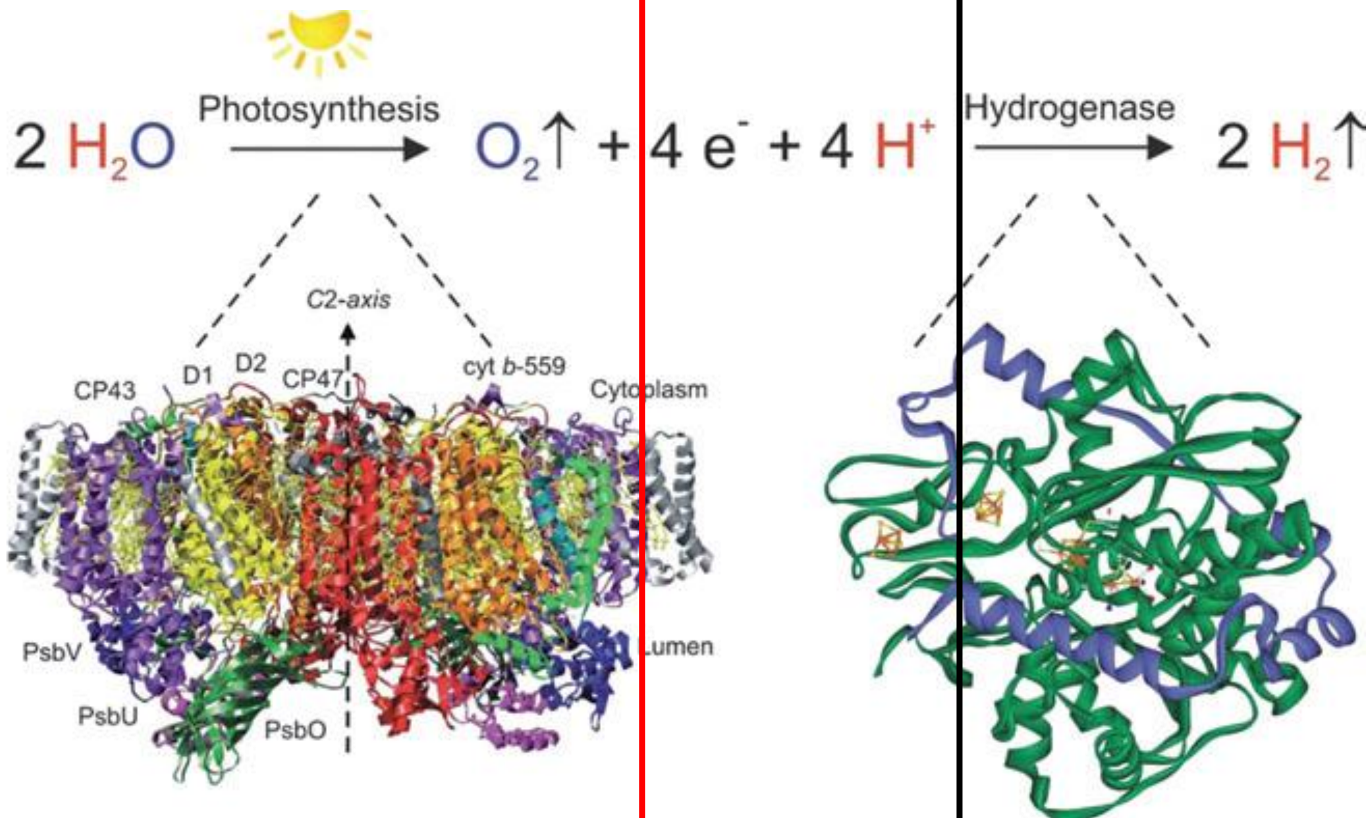
Production of H_2: from sun and water ?



The « tough » part

- $\Delta G >> 0$
- removal of 4 H^+ and four e^- from water
- formation of an O-O bond
- light collection and conversion

The « easy » part (somewhat tough)

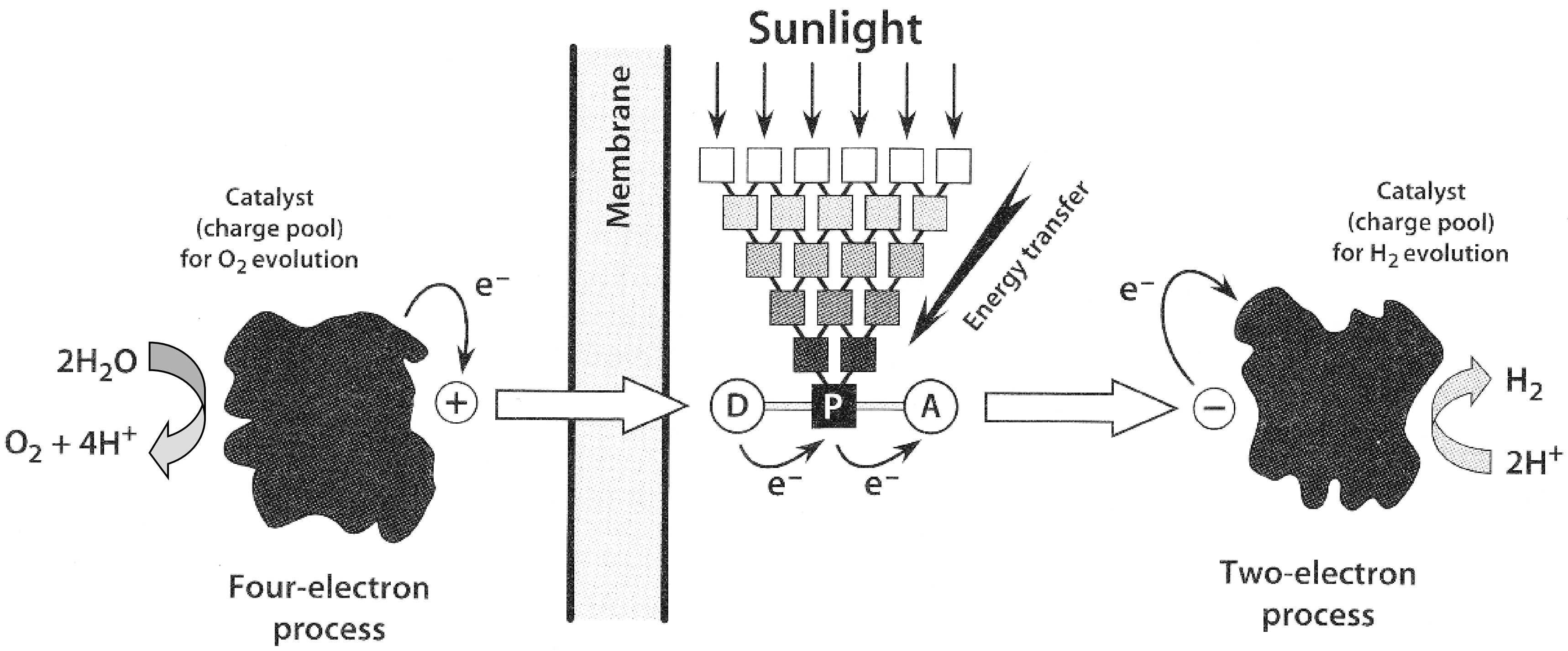
- $\Delta G < 0$
- combining 2 H^+ and 2 e^-
- formation of an H-H bond

From W. Lubitz, En. Env. Sci. 2008

Artificial photosynthesis

Light harvesting: Separation of charges vs recombination

1. semiconductors: TiO_2, WO_3, Fe_2O_3 (hundreds tested)
2. Molecules: phtalocyanins, porphyrins, Ru, Ir, Re complexes

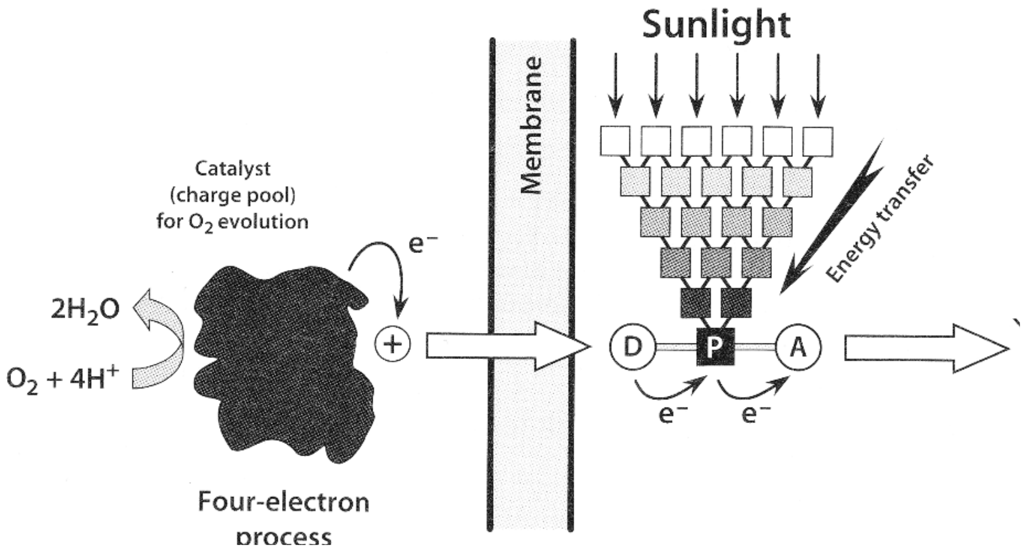


Catalysts:

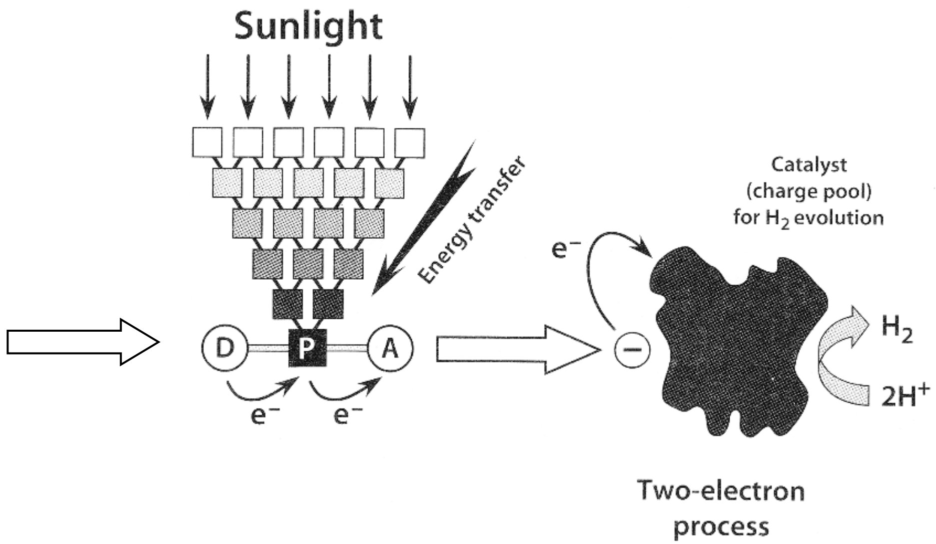
1. Accumulate several electrons (holes) one by one at constant potential close to the thermodynamic potential of the reaction
2. Deliver electrons (holes) to the substrate in a concerted manner

Mechanisms and optimization : sacrificial redox reagents

Large « driving force »
Charge recombination limited



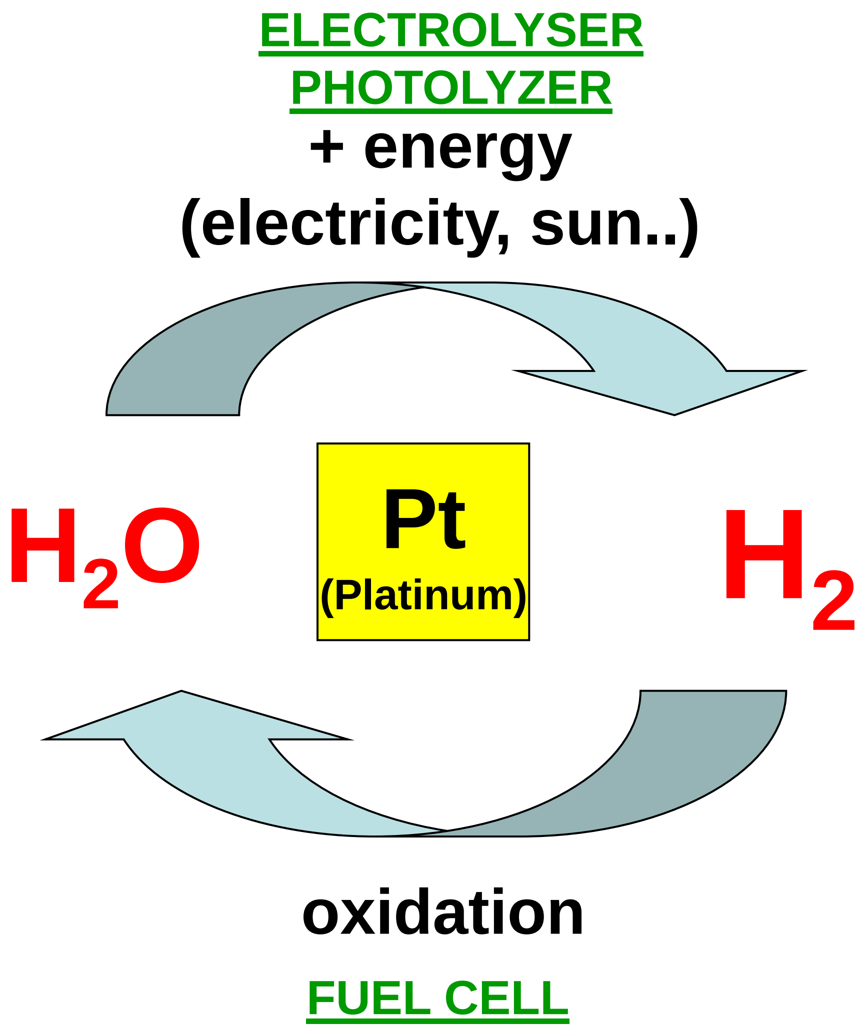
Sacrificial electron acceptor



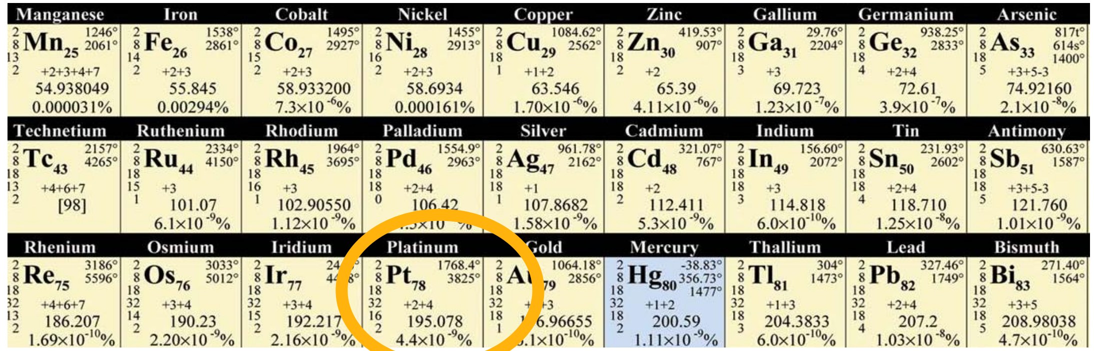
Sacrificial electron donor

The catalysis issue ?

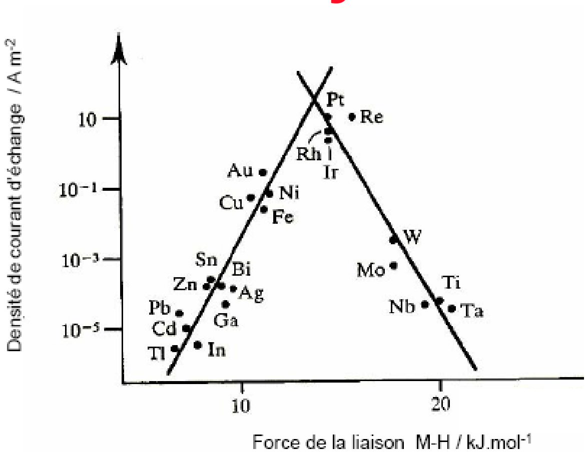
(for hydrogen production and oxidation)



The catalysis issue



Pt: the best catalyst



Pt: an expensive metal

	Abundance (ppm)		Price (€/g)
	terrestrial crust	oceans	
Pt	0,01	/	**50**
Ni	105	0,0005	**0.02**
Ru	0,01	/	**2**
Mn	1400	0,002	**0.002**
Fe	70 700	0,01	**0.0003**
Co	25	/	**0.04**

Pt : an unsustainable metal

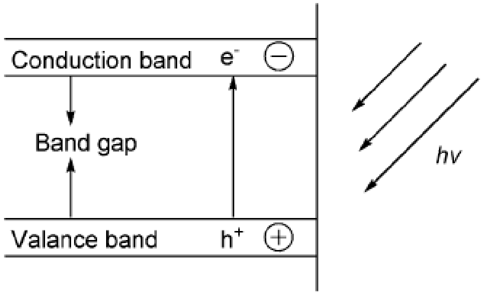
500 millions of vehicles (vehicle power 75 kW)
0.4 g Pt/kW (2010); recycling 50%

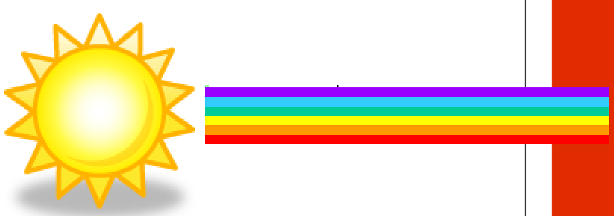
Pt: stocks consumed within 15 years

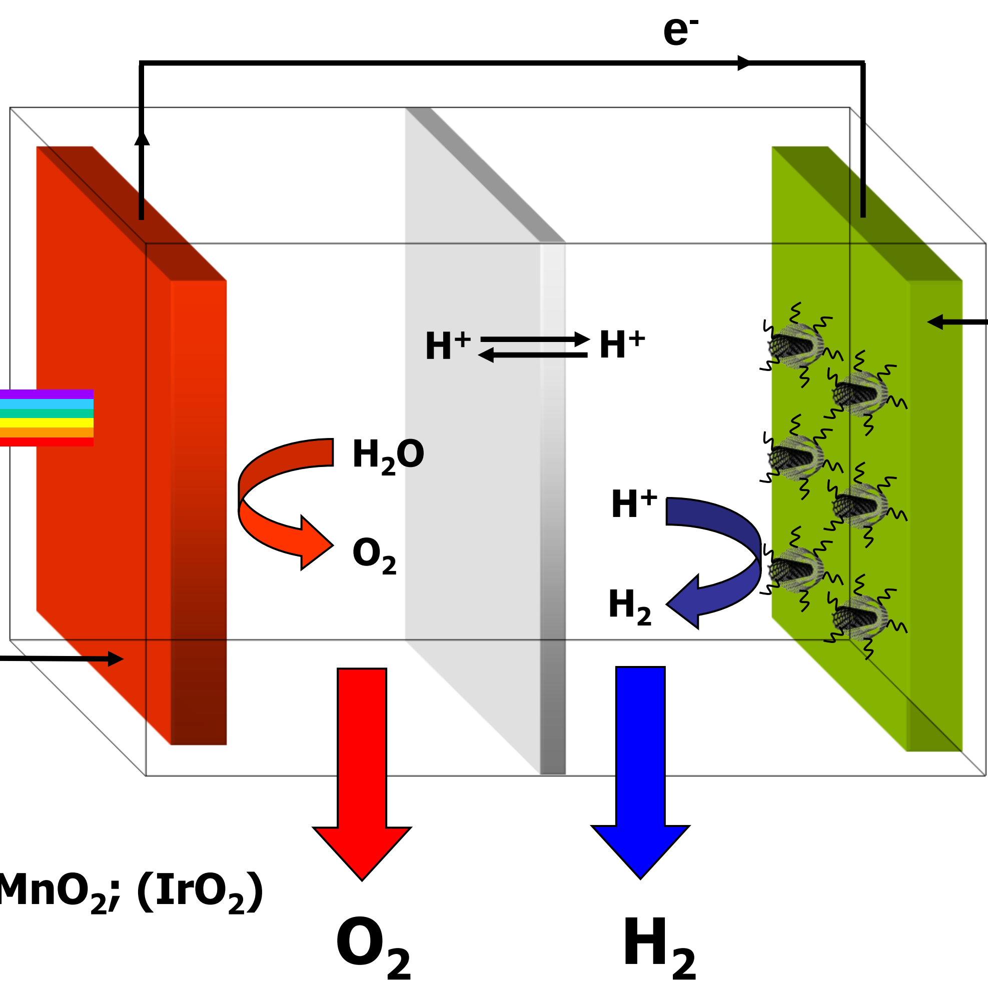
Gordon et al. PNAS 2006
Nature, 2007, 450,334

Water Photolysis: photoelectrochemical cells without noble metals

$$2H_2O = O_2 + 2H_2$$



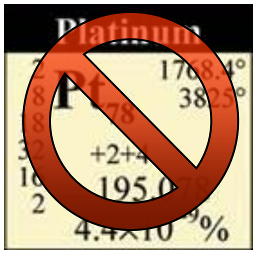




Cathode

or

Photocathode

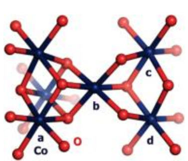


Photoanode

SC-n : Fe_2O_3/WO_3

Catalysts:

CoPi; Co_3O_4; $CaMn_2O_4$; MnO_2; (IrO_2)



D. Nocera, Science 2008 321 1072

Photoanode: Fe_2O_3?

<u>Advantages</u>:

-Fe 2rd element on earth

-Visible light absorption (2,1 eV=539 nm)

-Stability

<u>drawbacks</u>:

-Too weak energy of the CB

-Low efficiency (<5-20%)

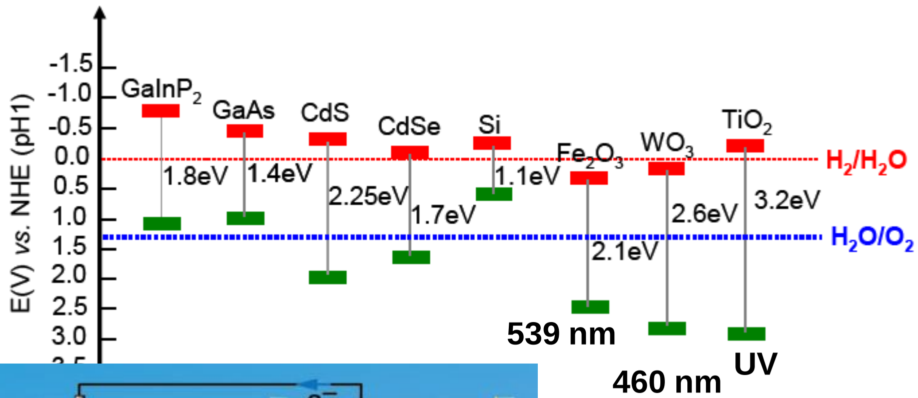
×low reactivity of surface « holes »

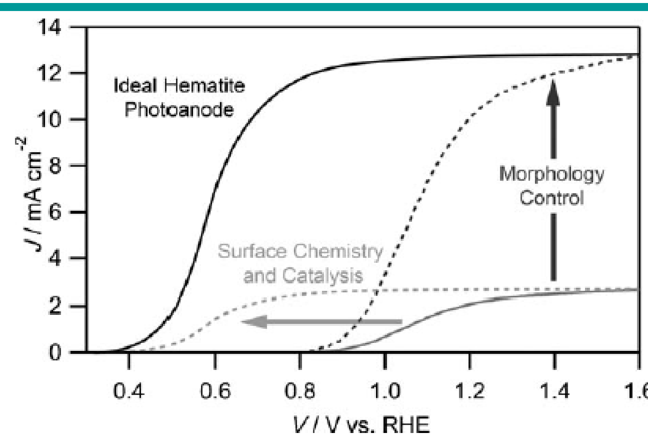
×slow diffusion of « holes »

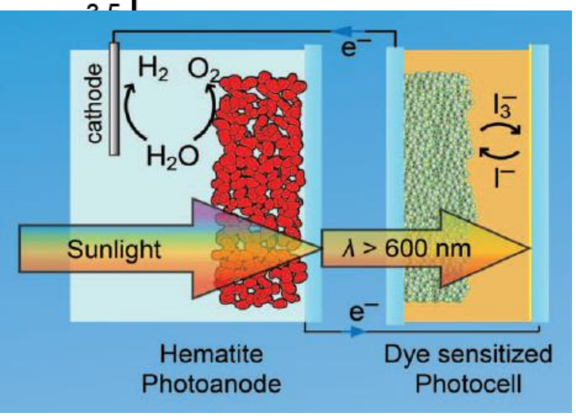
(few nm; $10^{-1} cm^2V^{-1}s^{-1}$)

→overvoltages

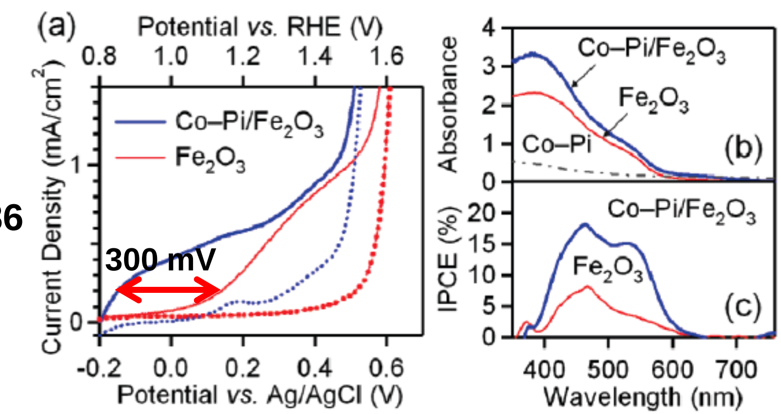
→catalysts

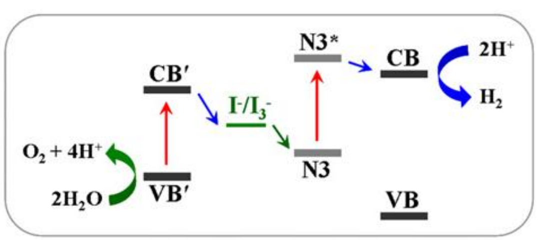






JACS 2009 <u>131</u> 6086

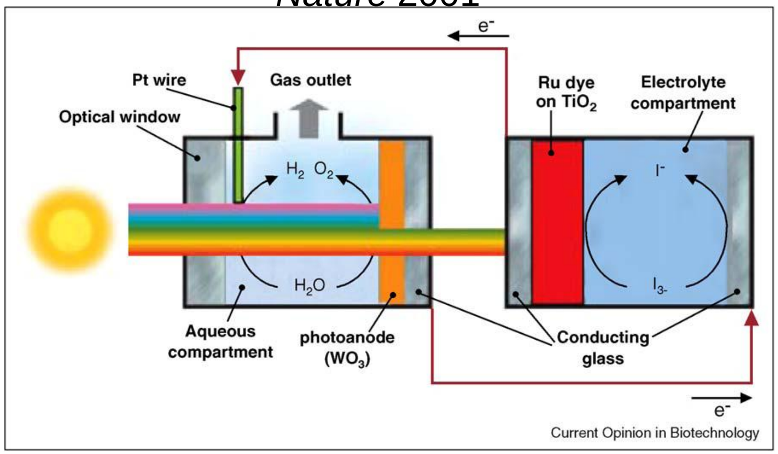


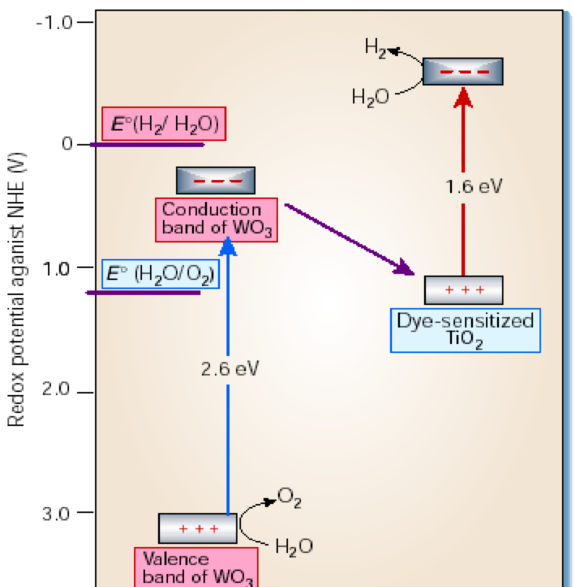


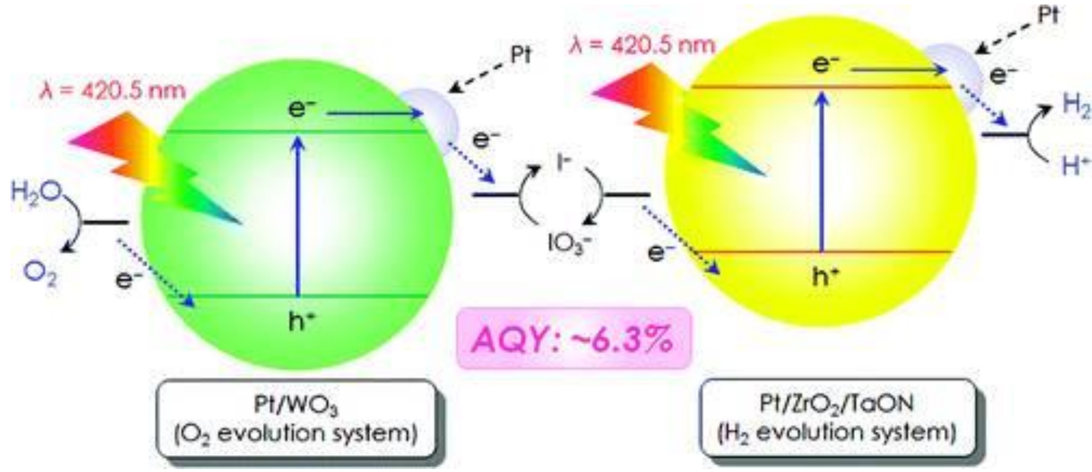
M. Grätzel: JACS 2006, Curr Op Biotech 2010; ChemSusChem 2011

Photoanode: WO_3

M. Grätzel *J. Phys Chem* 2005; 2009
Nature 2001







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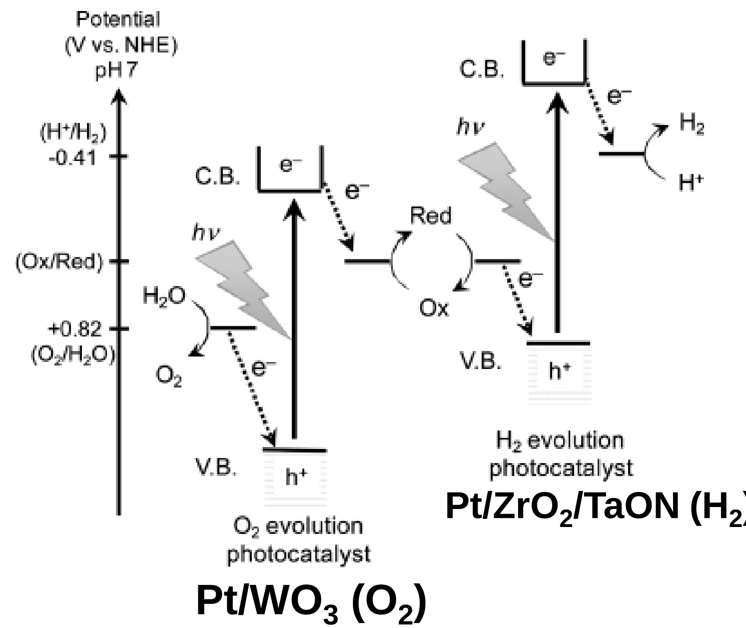


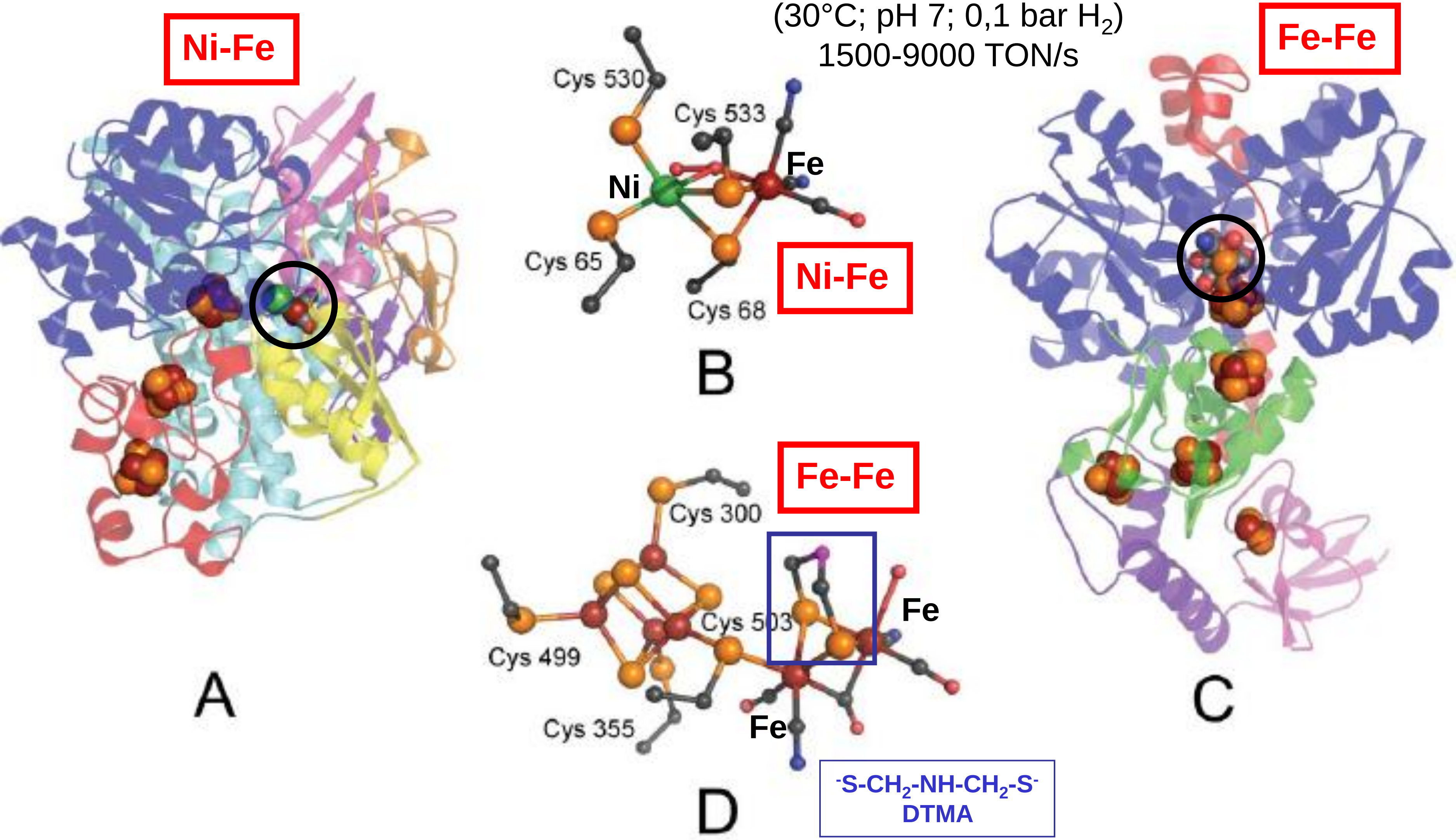
For the cathode ?

The bioinspired approach

Hydrogenases

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2$$

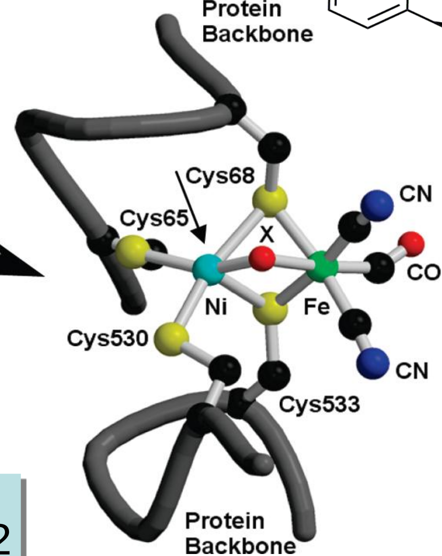
E = -400 mV vs SHE
(30°C; pH 7; 0,1 bar H_2)
1500-9000 TON/s

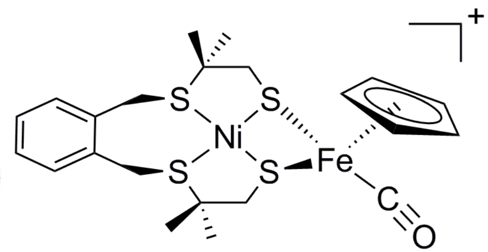


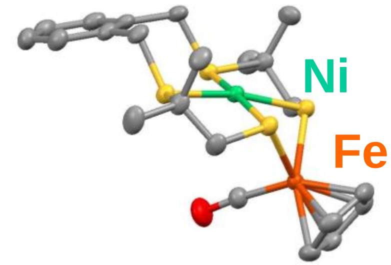
Volbeda, A. et al., *Nature* (1995), **373**, 580-587.
Volbeda, A. et al., *J. Am. Chem. Soc.* (1996), **118**, 12989-12996.

JW Peters et al *Science* (1998) 282, 1853
Y Nicolet et al *Structure* (1999) 7, 13

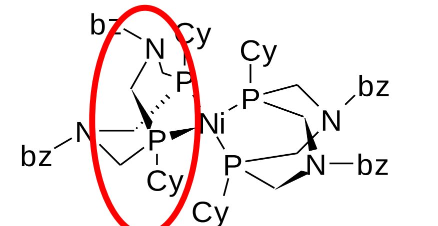
Hydrogenases and bioinspired catalysts



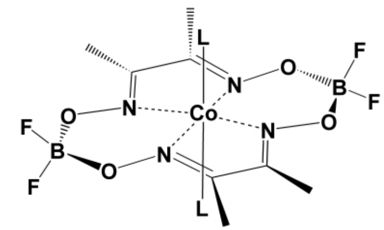




V. Artero, M. Fontecave, *Chem Commun* 2010



Dubois et al. *J. Am. Chem. Soc.*, 2006 and 2007.



V. Artero, M. Fontecave, Angew. Chem. 2008

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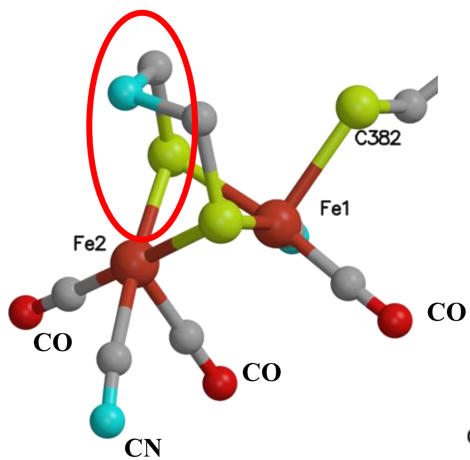
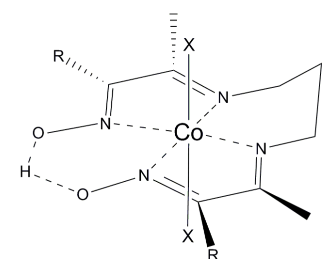
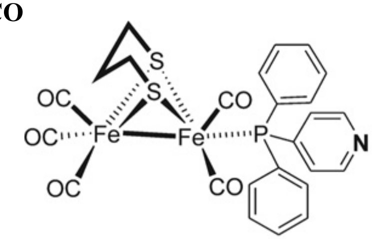
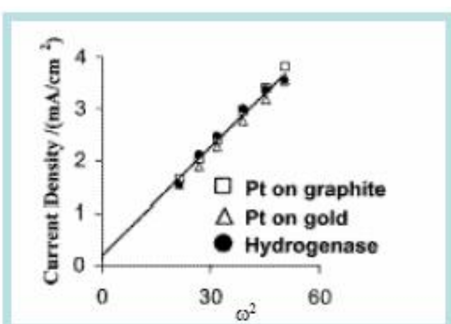


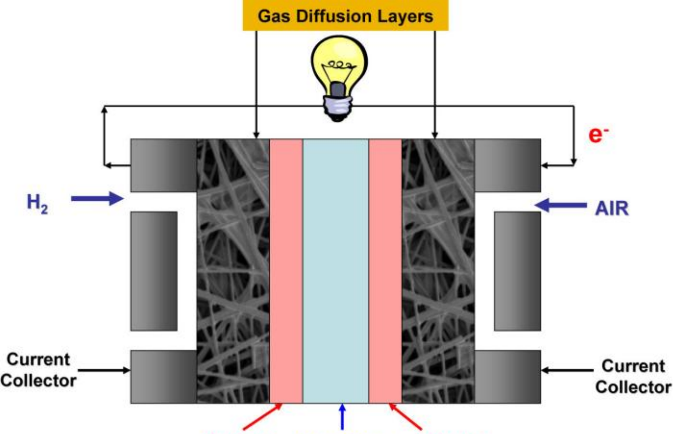


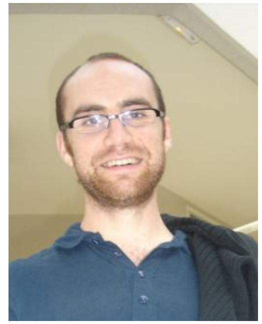
V. Artero, M. Fontecave, PNAS (2009) *106*,20627





Armstrong. et al. *Chem. Commun.* 2002.





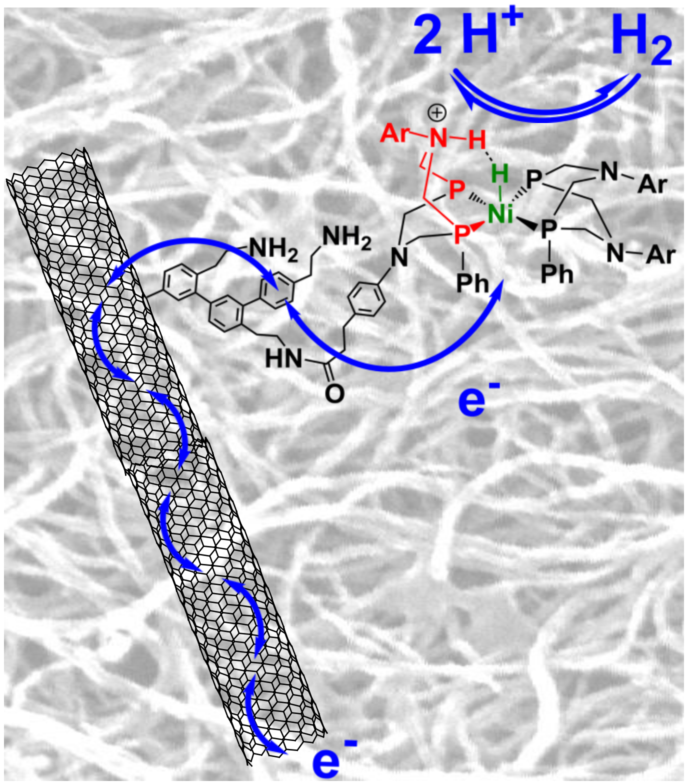
A. Le Goff

From Hydrogenases to Noble Metal–Free Catalytic Nanomaterials for H_2 Production and Uptake

Alan Le Goff,[1] Vincent Artero,[2*] Bruno Jousselme,[1] Phong Dinh Tran,[2] Nicolas Guillet,[3] Romain Métayé,[1] Aziz Fihri,[2] Serge Palacin,[1*] Marc Fontecave[2,4]

4 DECEMBER 2009 VOL 326 SCIENCE

European patent application **EP-08 290 988.8**



A bioinspired Ni complex grafted on NTCs deposited on an electrode

+++

A catalyst for oxidation and production of H_2

>100.000 cat cycles !!

Stability

Compatible with PEM technology

Overvoltage= 20 mV !!

Resistance to CO

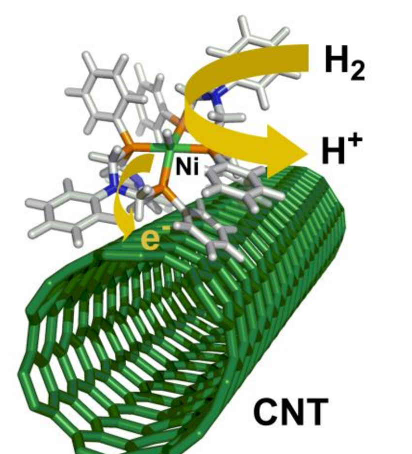
Cost: Ni 20 euros/kg (Pt: 20000 euros/kg)

- - -

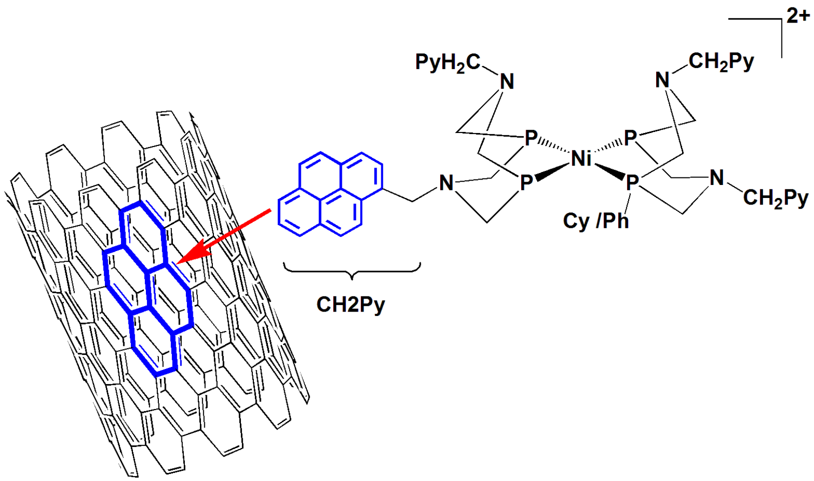
Weak current densities

~4-5 mA.cm^{-2}

(1/100 vs Pt)



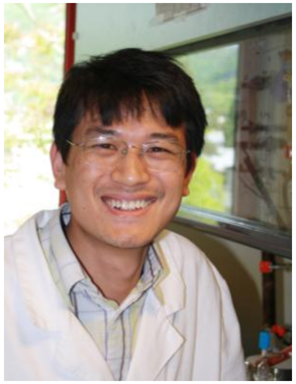
Optimization: new ligands/new immobilization methods

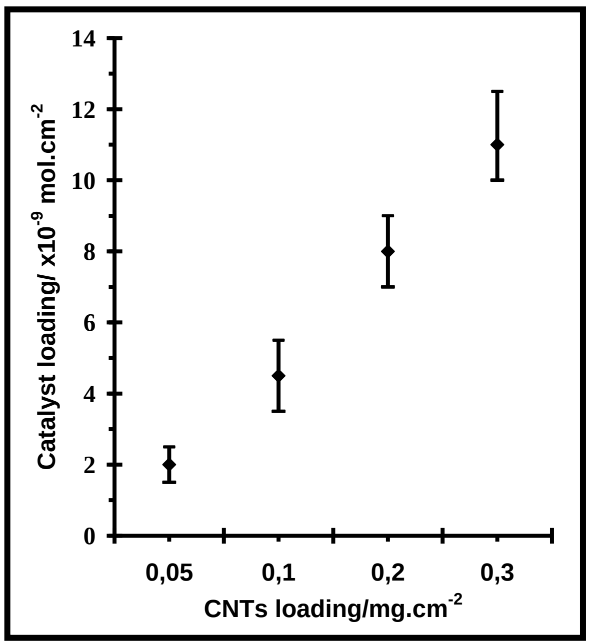


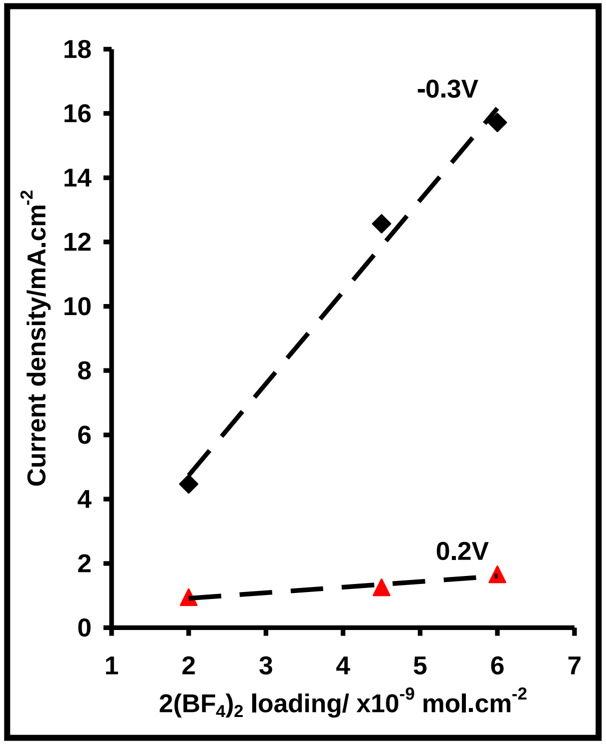
MWCNTs

PD Tran, V Artero, M Fontecave et al.
Angew Chem 2011

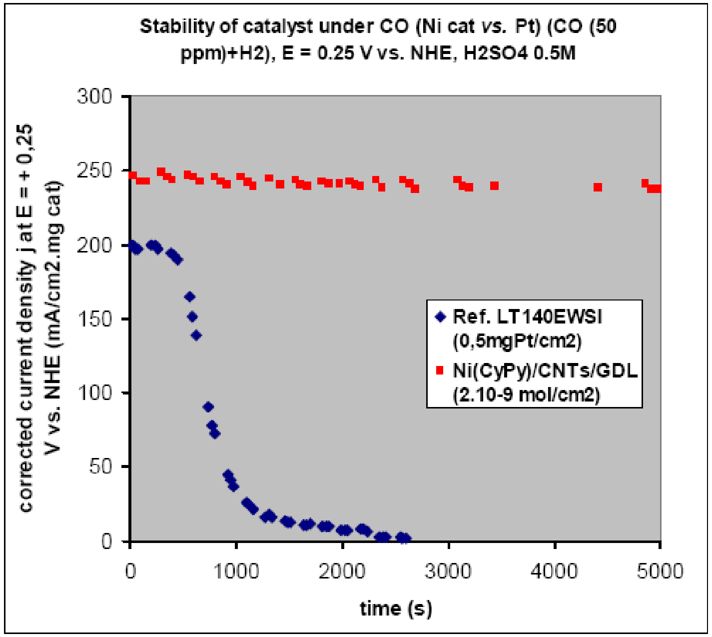
- Simplified preparation
- Catalyst loading ↑
- Current densities ↑



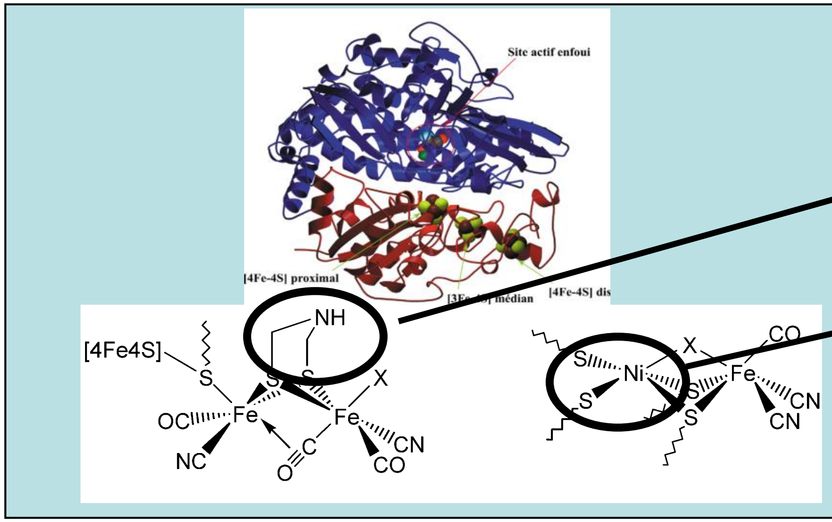


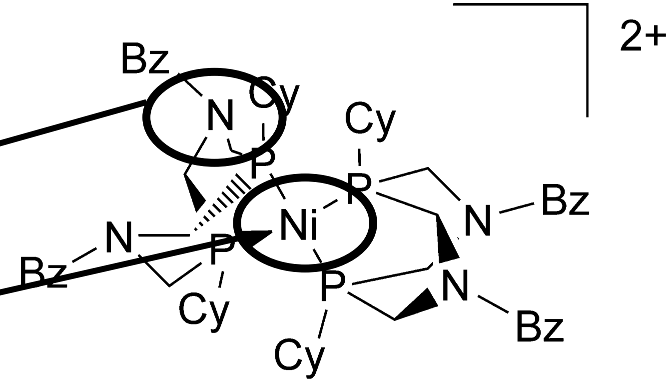


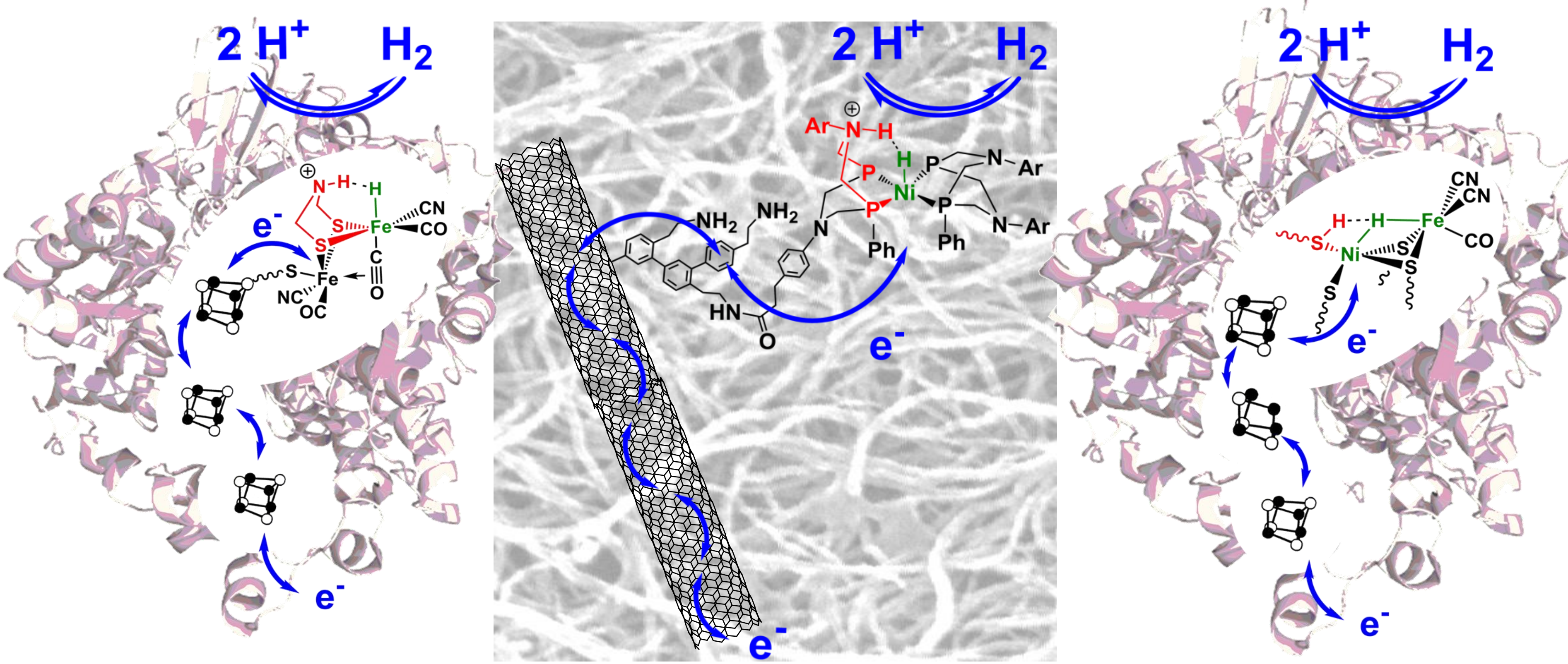
Resistance to CO



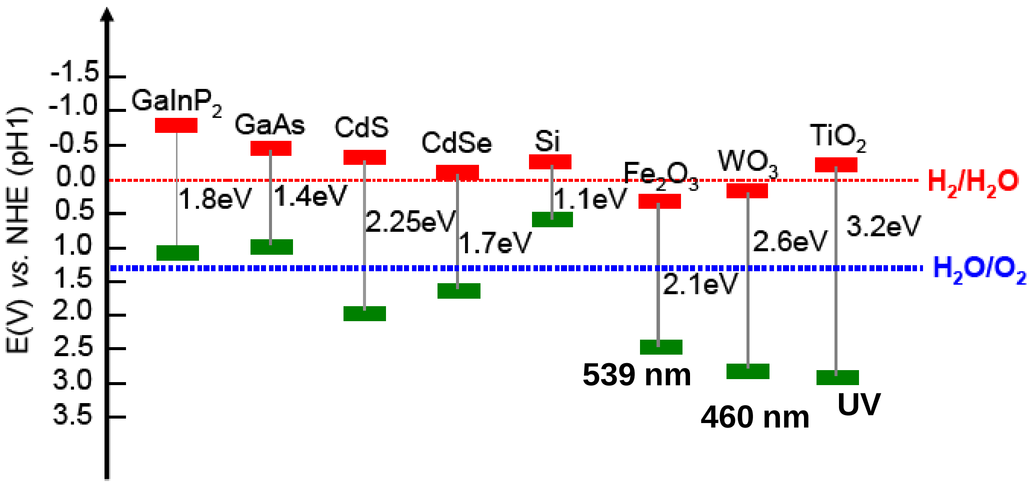
From enzymes to bio-inspired nanocatalysts



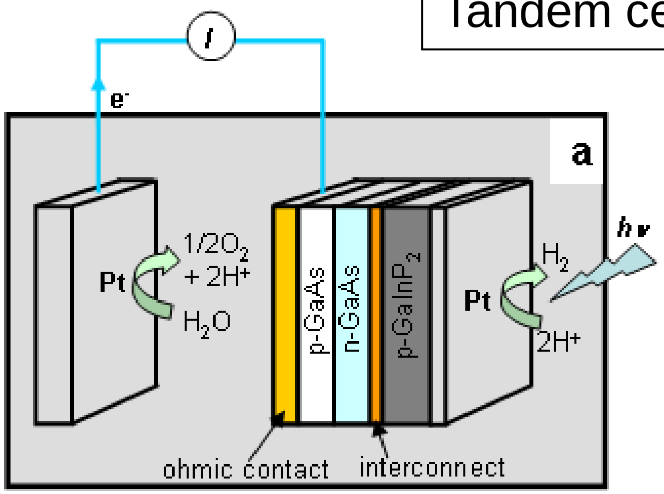




A photocathode ?



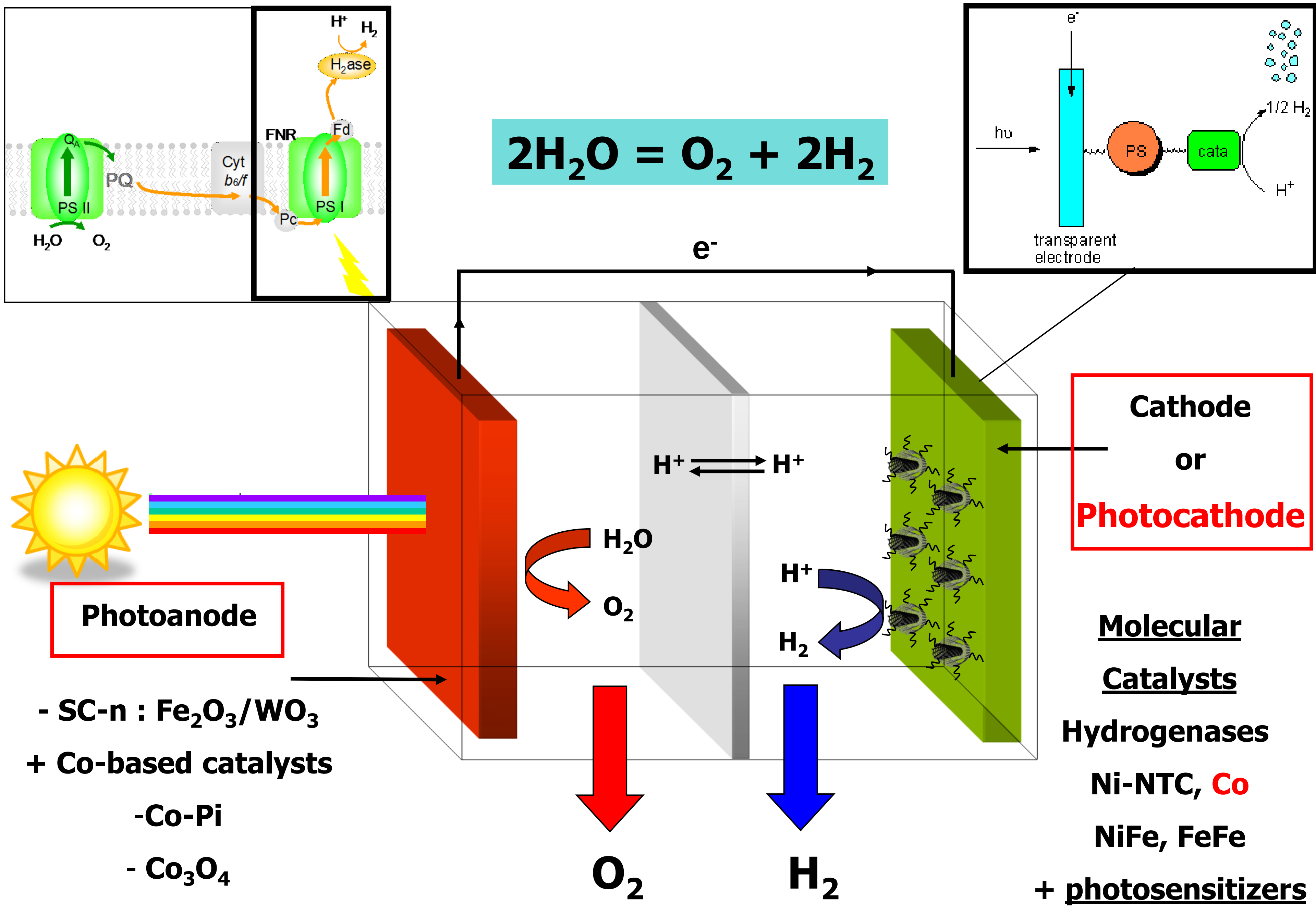
Tandem cell PEC/PV



Solar-to-H_2 = 12.4%
(theor= 34%)
Cost = \$100,000/m^2

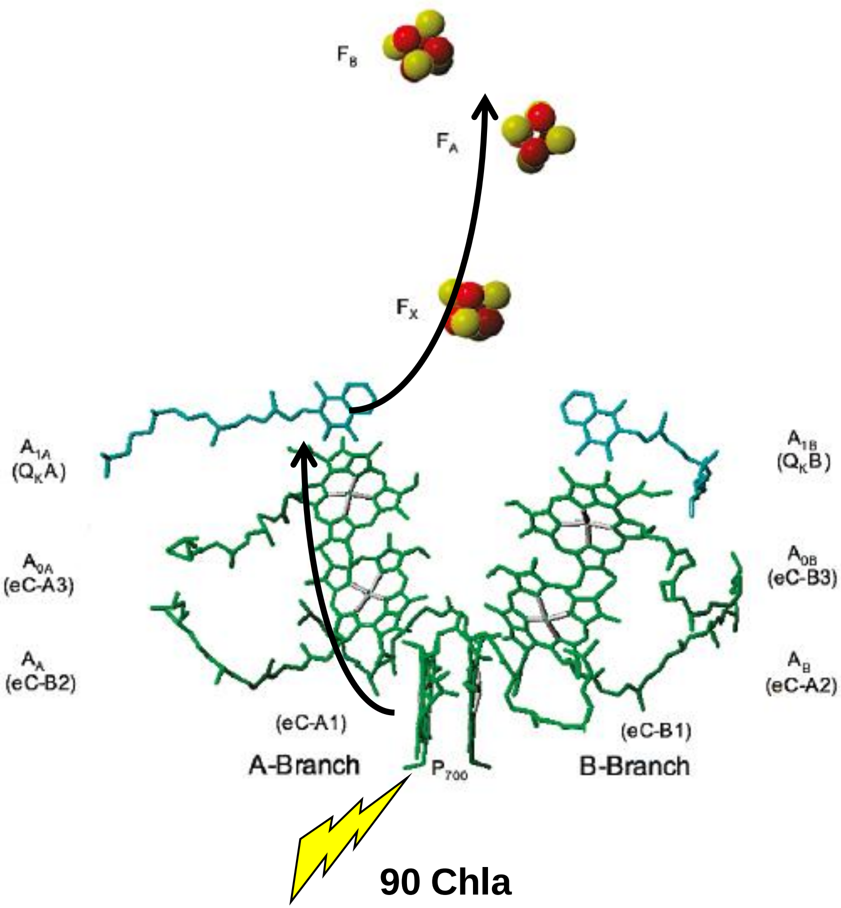
SC: p-type In and Ga phosphide
BG= 1.83 eV; bias= 300 mV
SC: p/n junction GaAs BG=1.42 eV (IR)

O. Khaselev, J. Turner. *Science*, **1998**, 280, 425.

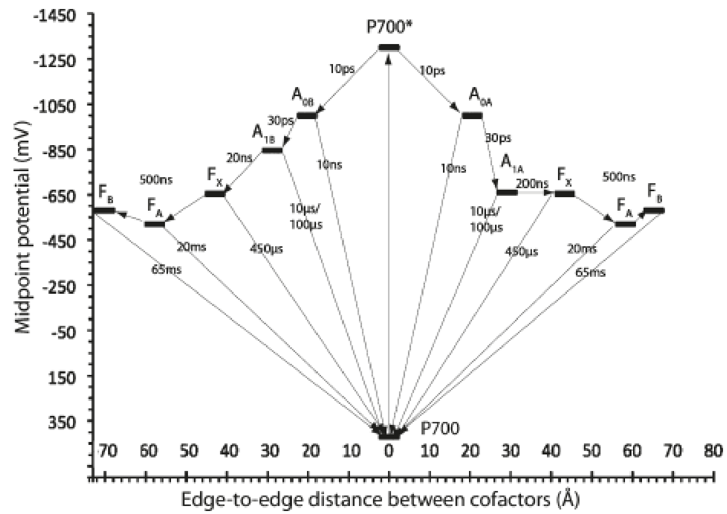


$2H_2O = O_2 + 2H_2$
H+
H2
H2ase
FNR
Fd
QA
PQ
Cyt b6/f
PS II
PS I
Pc
H2O
O2
e-
hυ
PS
cata
1/2 H2
H+
transparent electrode
e-
H+ ⇄ H+
H2O
O2
H+
H2
Cathode
or
Photocathode
Photoanode
- SC-n : Fe2O3/WO3
+ Co-based catalysts
-Co-Pi
- Co3O4
O2
H2
Molecular
Catalysts
Hydrogenases
Ni-NTC, Co
NiFe, FeFe
+ photosensitizers

A « biological semiconductor »: PS1



90 Chla
22 β-carotene



◆ PSI absorbs λ < 700 nm (45% solar spectrum; 1000 e^-/s)

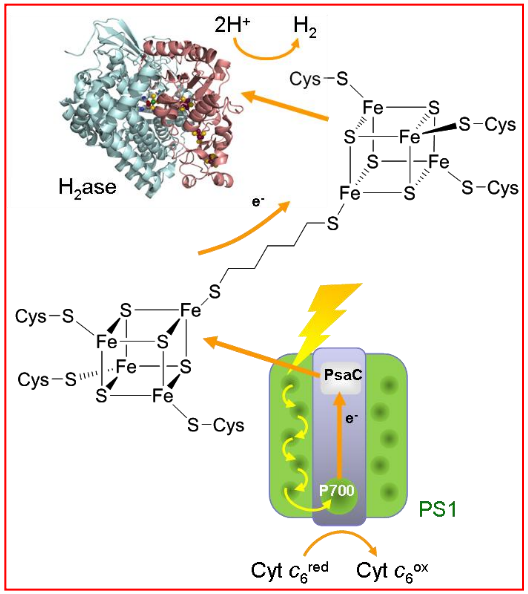
◆Quantum yield= 1

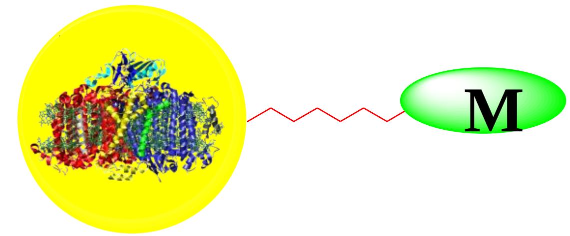
◆ half life P_{700}^+/F_B^- τ= 60 ms

◆Potential F_B E= - 580 mV (< H^+/H_2 by 166 mV)

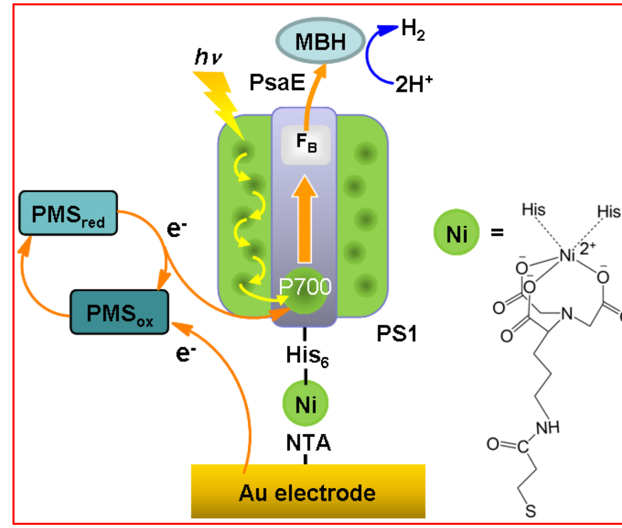
◆ robust

« Biological » photocathodes: PS1 et hydrogenases





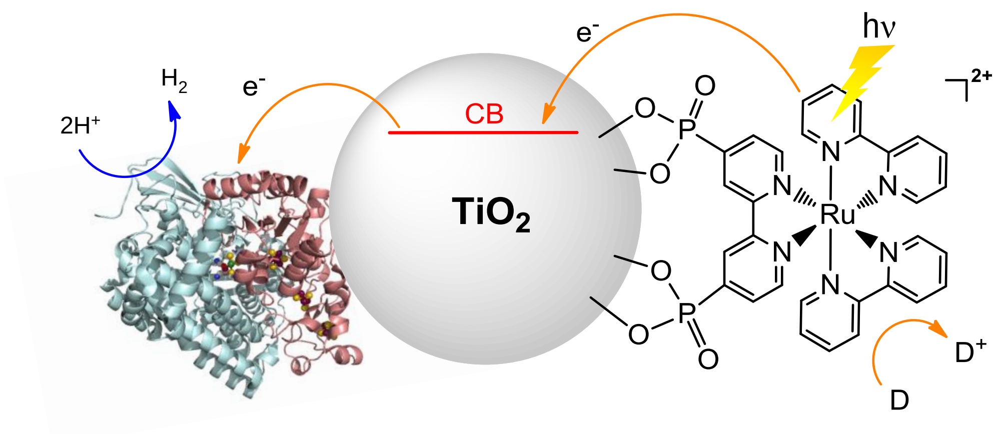
B. Friedrich, O. Lenz, et al. 2009. ACS Nano 3:4055



JH Golbeck JACS 2008 130 6308
Dalton Trans 2009 10106, Biochemistry 2010 49 404

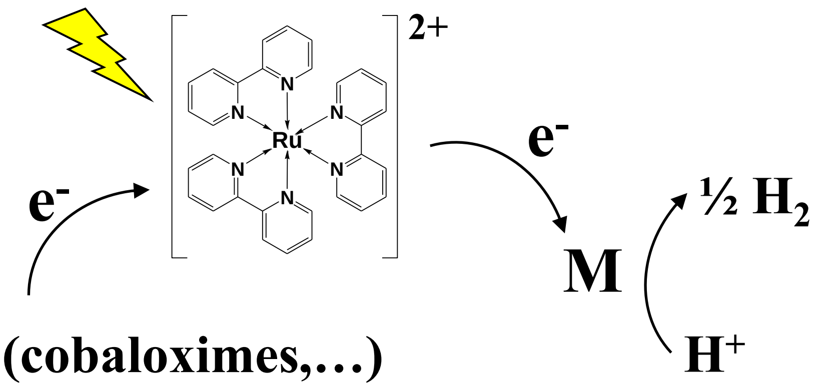
PMS= methylphenazonium methyl sulfate

4500 ± 1125 mol H_2 min^{-1} mol^{-1}
$PSI_{\Delta PsaE}$-MBH_{PsaE} hybride

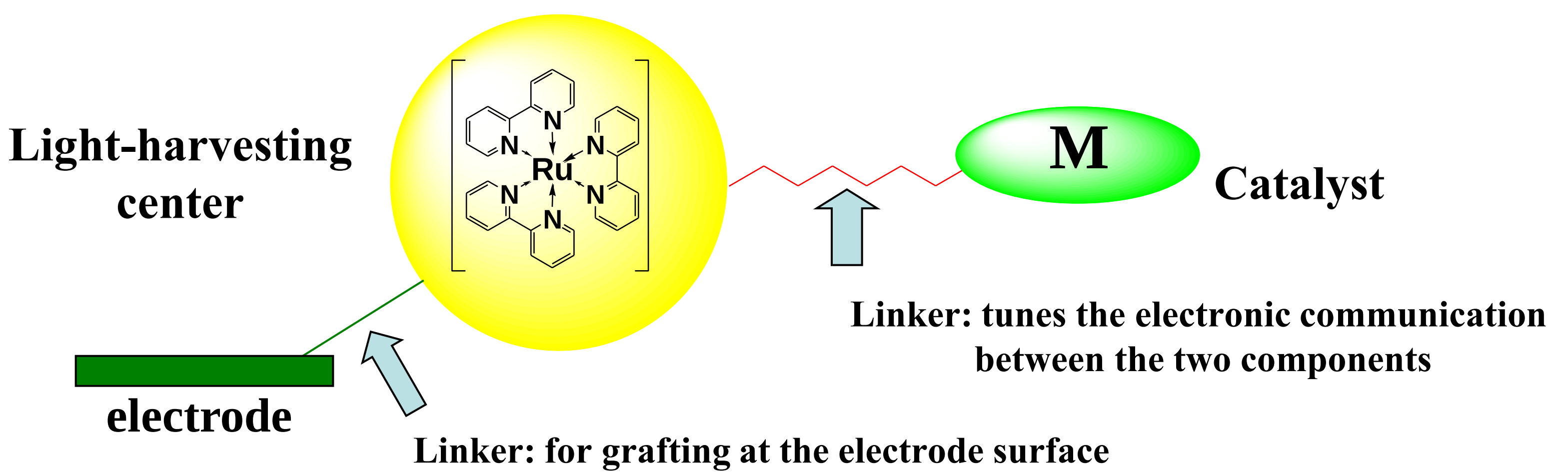


FA Armstrong, *Chem. Commun.* 2009, 550;
JACS 2009, 18467

Towards a photocathodic molecular material

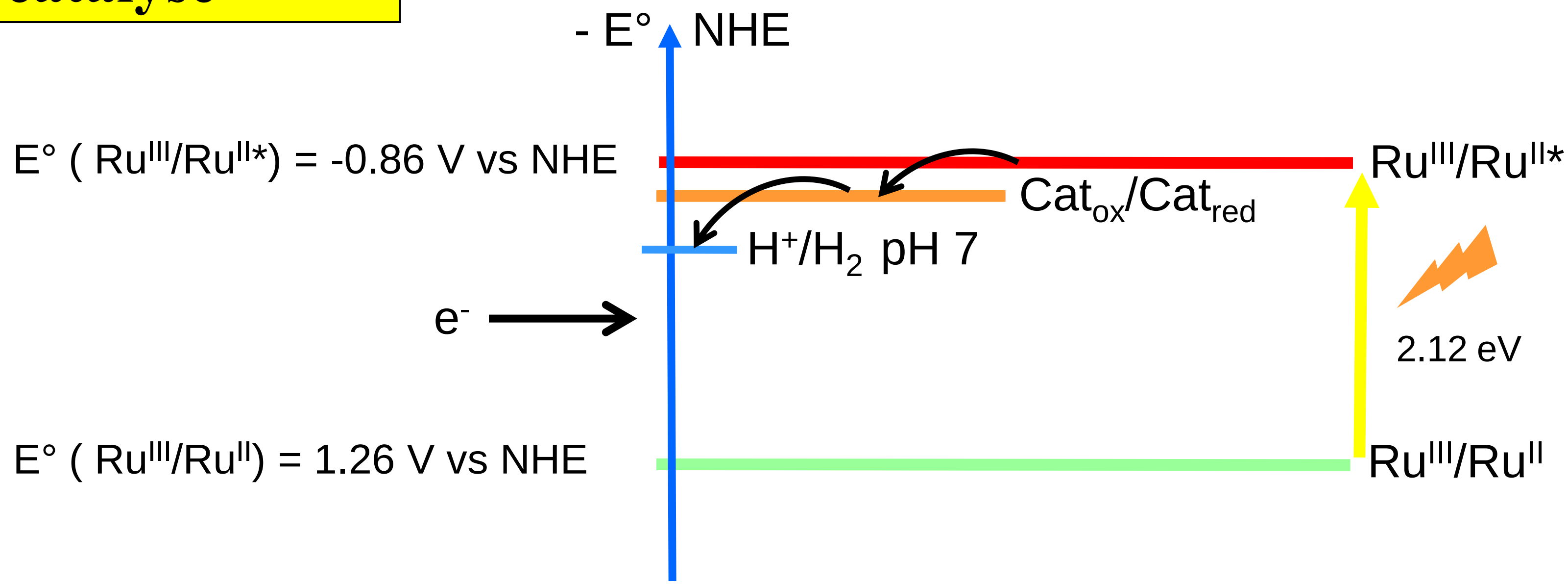


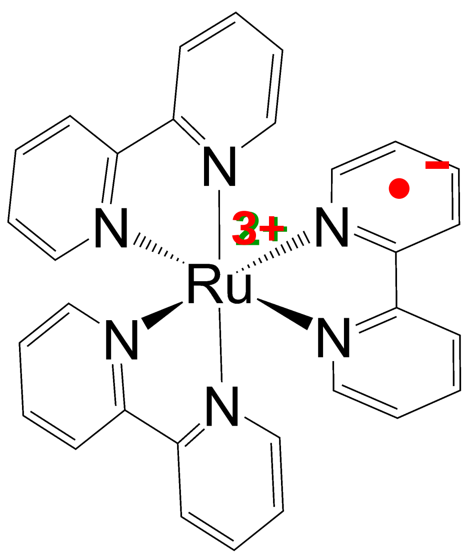
- ⇨ Find the good catalyst M (cobaloximes,…)
- ⇨ Find the good photosensitizer (high extinction coefficients, long-lived triplet excited state, photostability)
- ⇨ Make a multi-functional (supramolecular) system
- ⇨ Graft the compound on the electrode surface

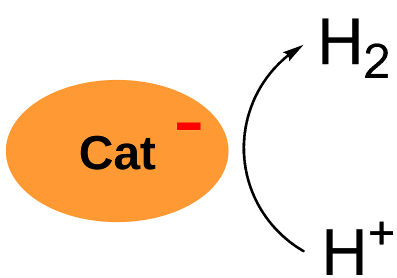


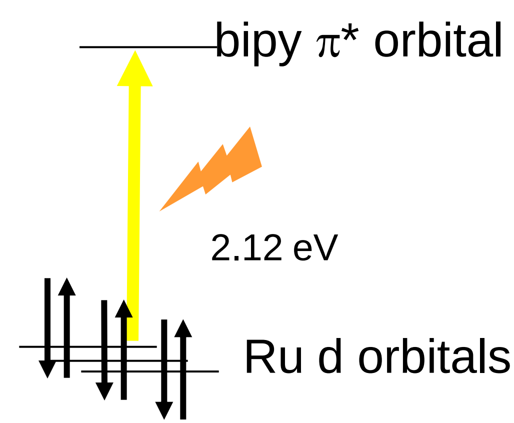
Photosensibilisation: catalyse

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2$$



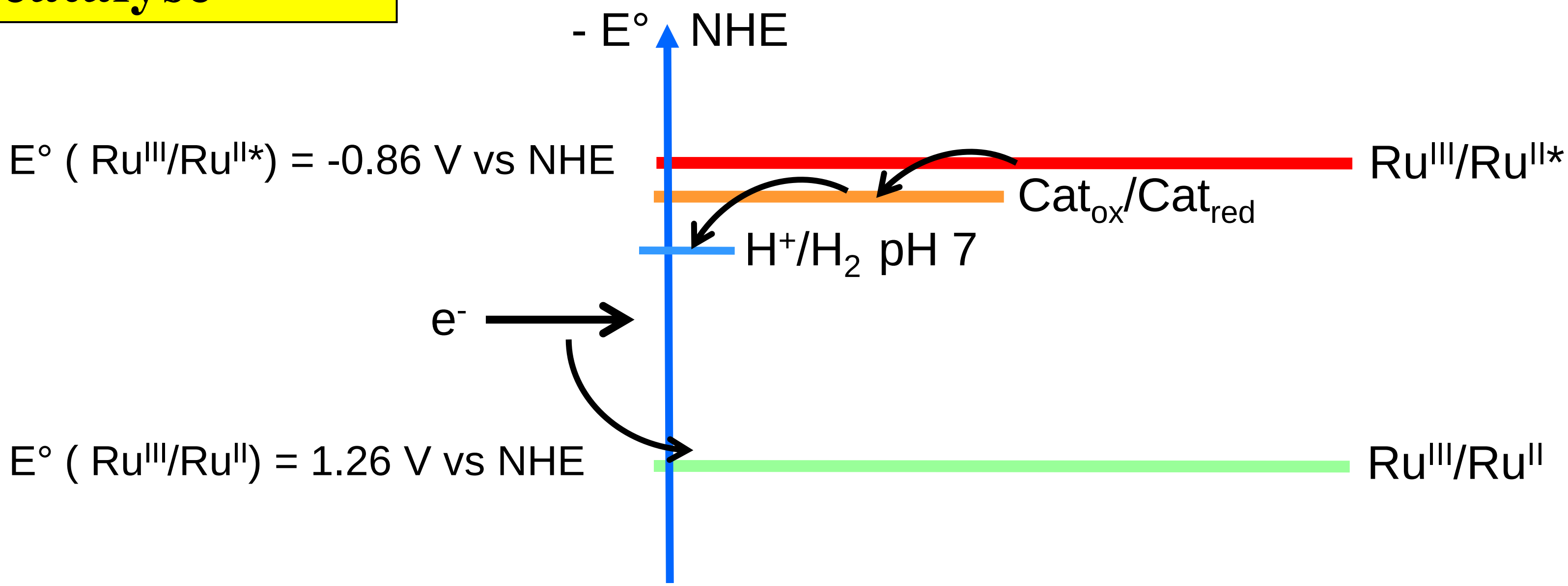


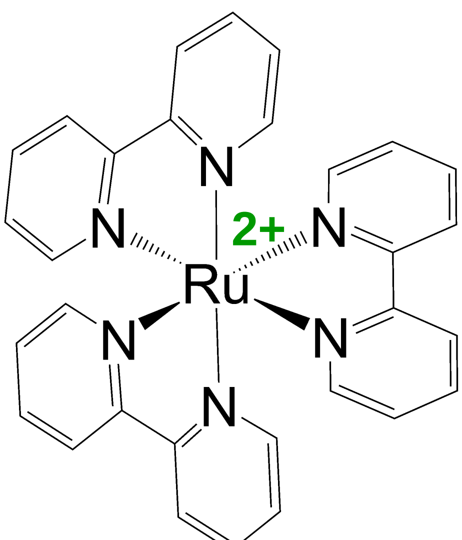


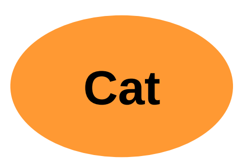


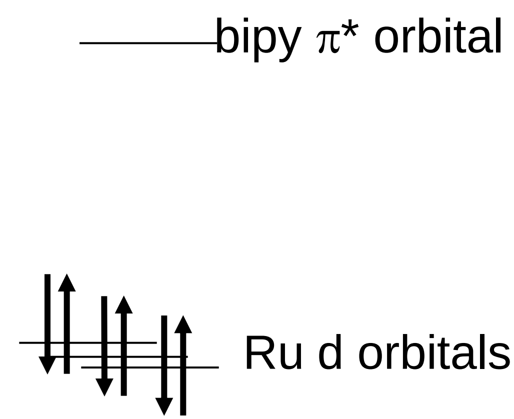
Photosensibilisation: catalyse

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2$$

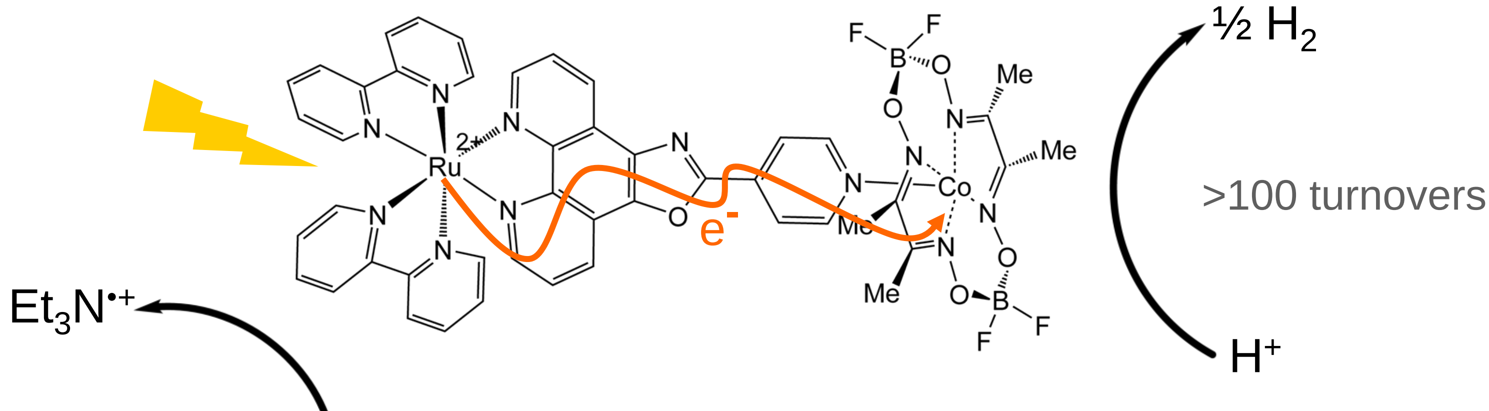




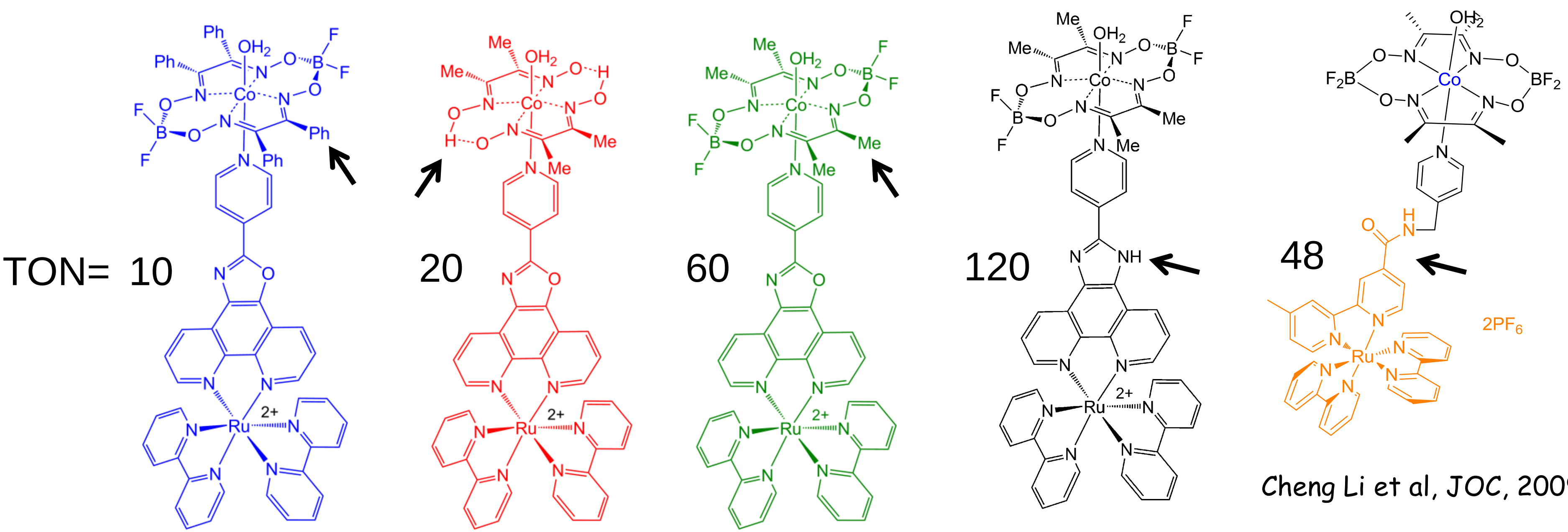




The first cobalt-based supra-molecular photocatalyst: cobaloximes

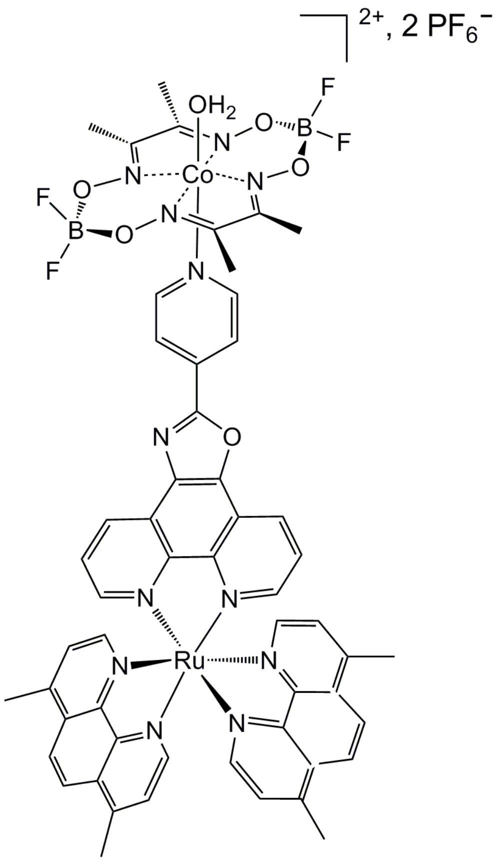


Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M., Cobaloxime-Based Photocatalytic devices for Hydrogen Production. *Angewandte Chemie, International Edition* **2008**

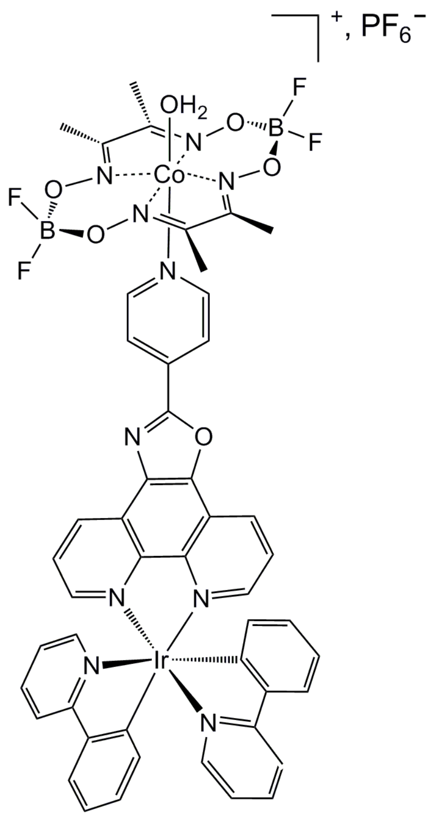


Cheng Li et al, JOC, 2009

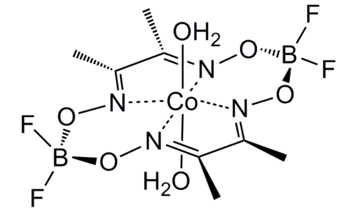
A tunable supramolecular complex: the photosensitizer



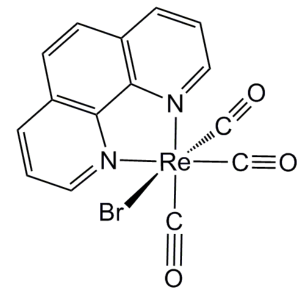
1



2



$[Co(dmgBF_2)_2(OH_2)_2]$



$[ReBr(CO)_3(phen)]$

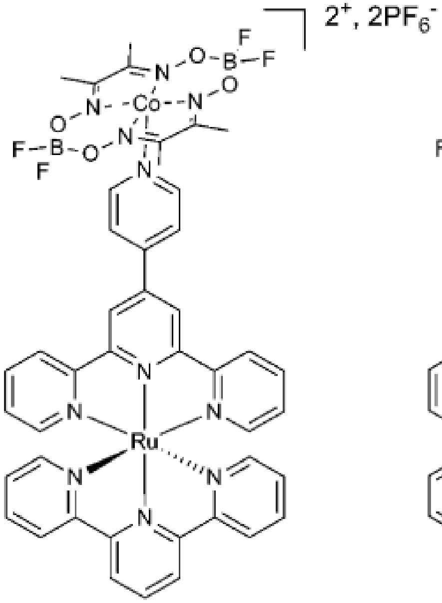
Turnovers	9	210	273

Quantum yields: 16-18%

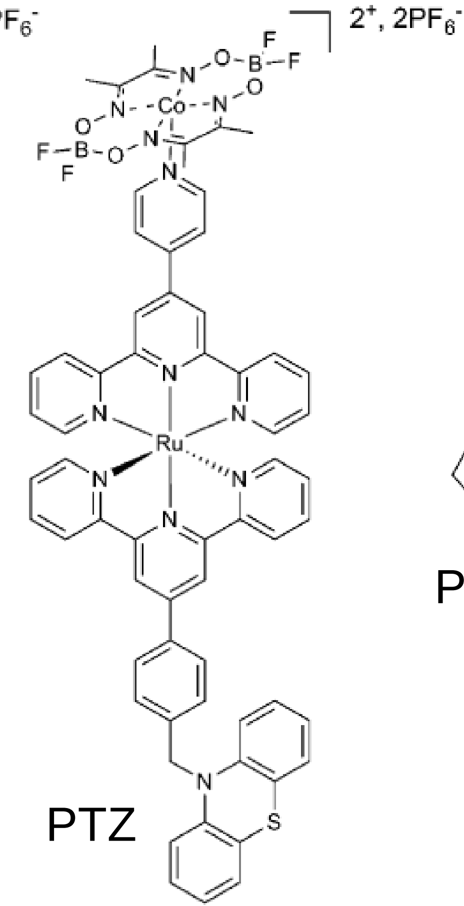
Visible light
Organic solvents

Fihri, Artero, Fontecave, Dalton Trans 2008

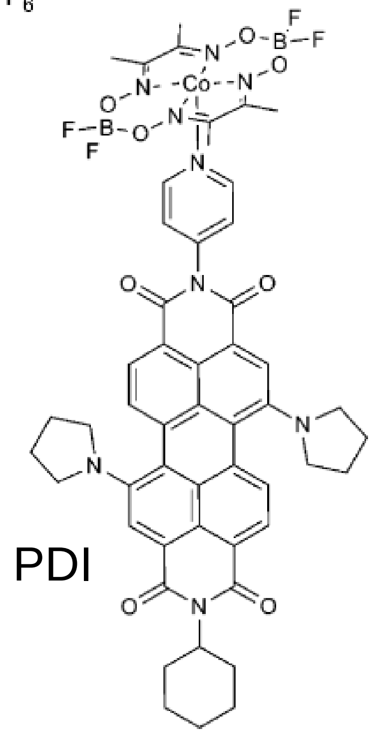
Further extensions



2



3



4

PDI= perylene-bis(dicarboximide)

DM Tiede, J. Phys Chem B 2010

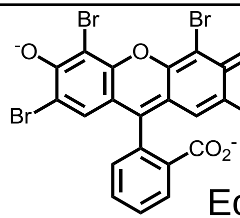
<u>Conclusion 1</u>:

3, with a phenothiazine (PTZ) secondary donor group, exhibits the largest excited state quenching (org solv)

<u>Conclusion 2 (drawbacks)</u>:

- Significant disassociation of the cobaloxime and PS fragments
- Performances limited by cobaloxime decomposition (R. Alberto, Inorg Chem 2010)

Further extensions: recent systems without noble metals

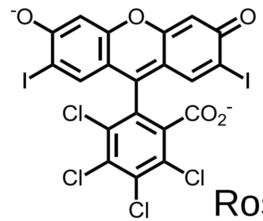


Eosin Y

$Co(dmgH)_2(py)Cl$
+ excess dmgH

TON = 180 (12h)

Eisenberg et al. *J. Am. Chem. Soc*. **2009**, *131*, 9192.

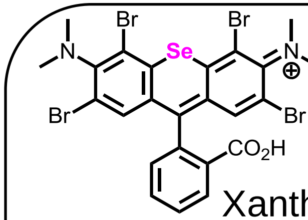


Rose Bengal

$Co(dmgBF_2)_2$

TON = 327 (5h)

Sun, Wang, et al. *J. Phys. Chem. C*. **2010** in press.

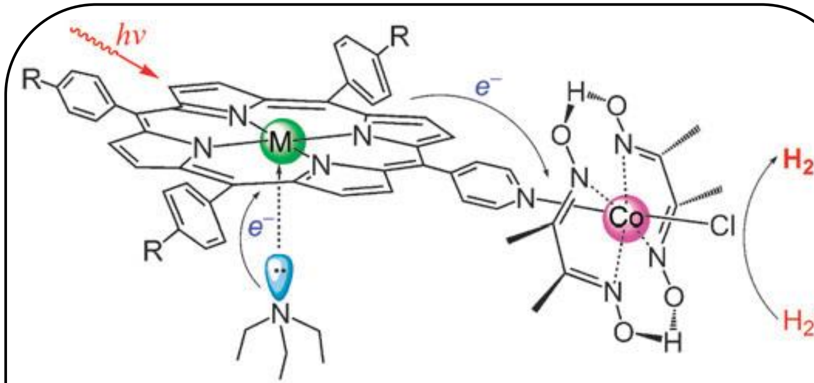


Xanthene Se

$Co(dmgH)_2(py)Cl$
+ excess dmgH

TON = 127 (24h)

Eisenberg et al. *J. Am. Chem. Soc*. **2010**, in press.

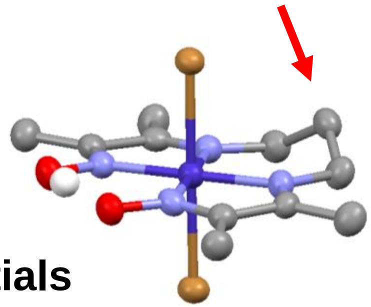


TON = 22 (3h)

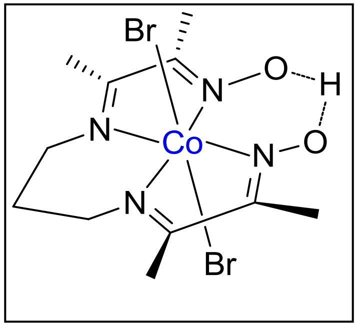
Sun et al. *Chem. Commun*. **2010** in press.

Towards optimized photocatalysts

catalyst

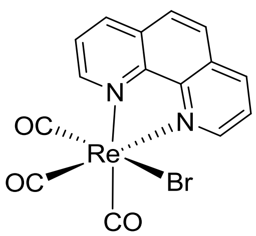


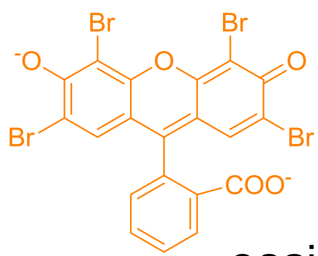
More robust
Low overpotentials
functionalizable



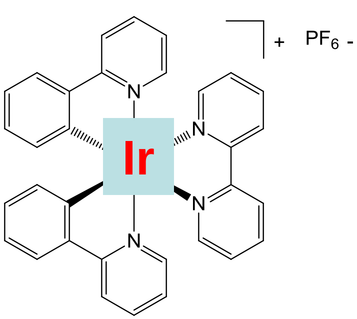
V. Artero, M. Fontecave, PNAS (2009) *106*,20627

photosensitizer

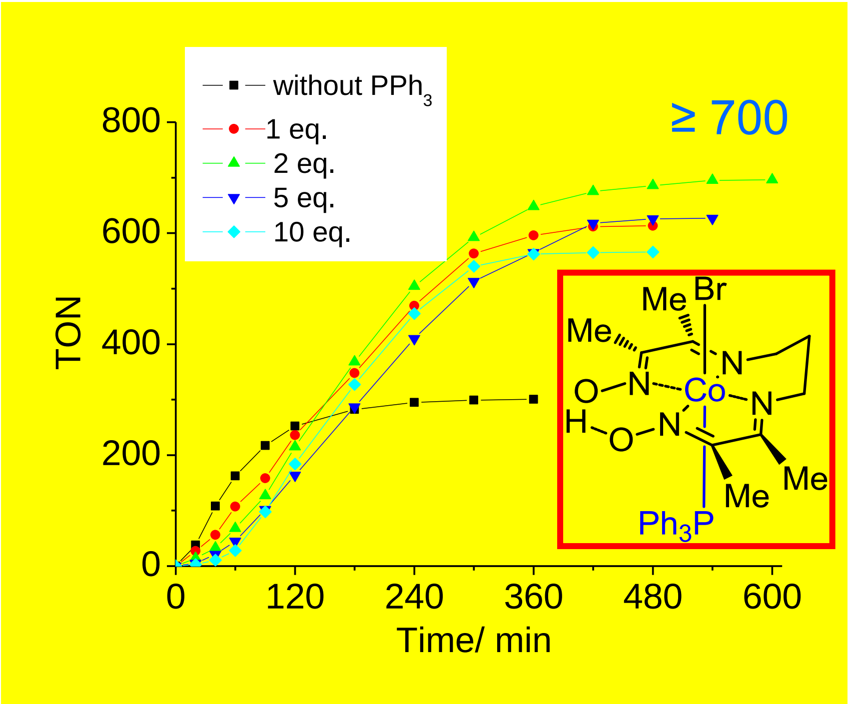




eosinY



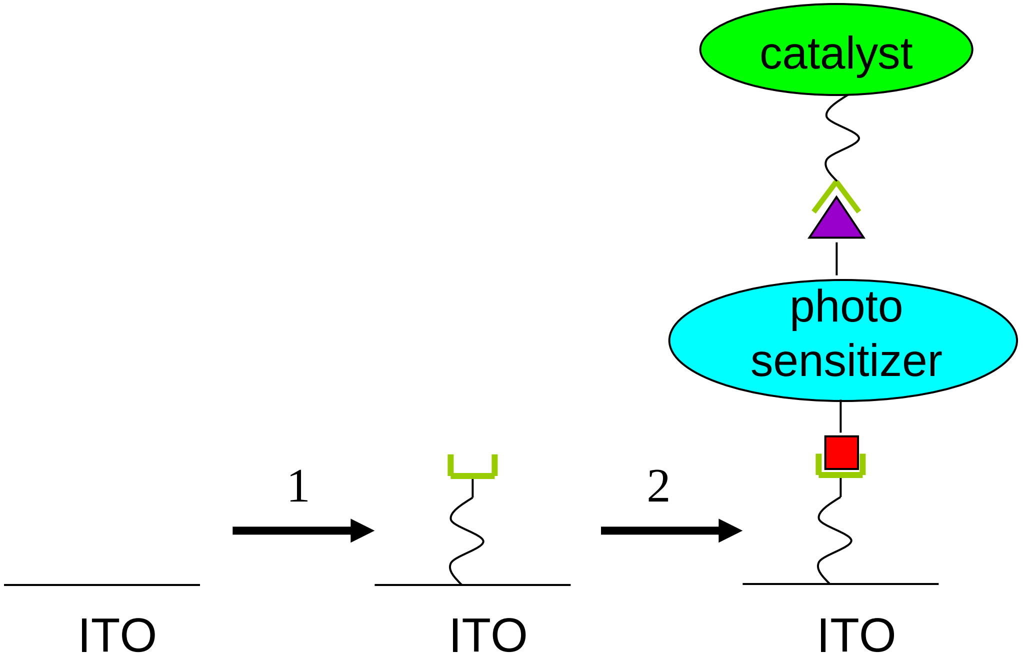
The highest
TON value so far !
ChemSusChem **2011**



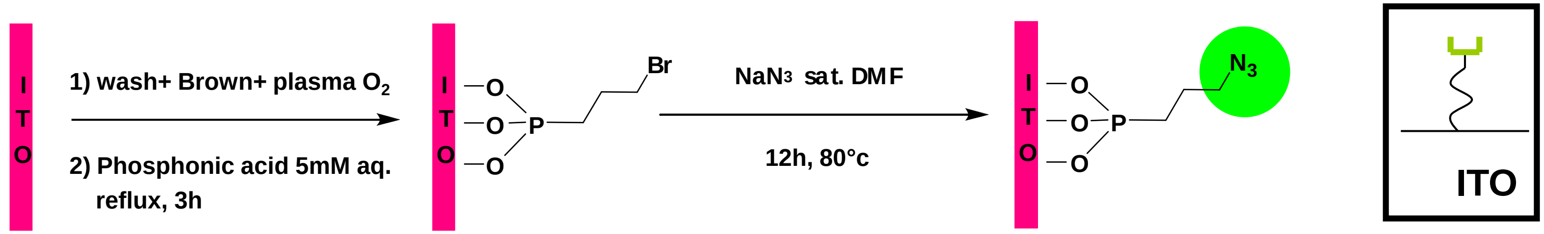
<u>Conditions</u>: Co(DO)(DOH)pnBr_2, 0.1mM; Ir complex, 0.1 mM; CH_3CN/H_2O, 1:1; sacrificial electron donor; irradiation with a Xe lamp (500W) using a Pyrex-glass filter (λ > 400 nm).

Towards the photocathode

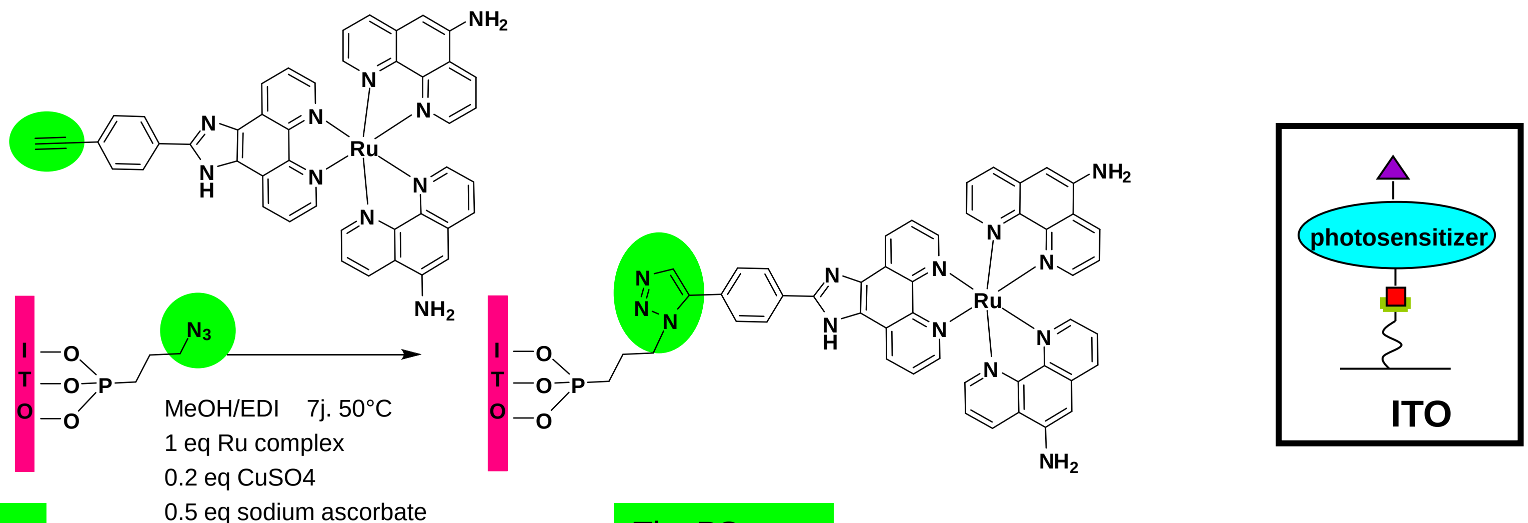
(unpublished)



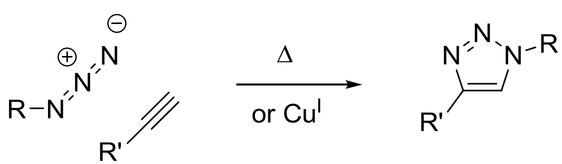
1. Phosphonate/azide link to ITO



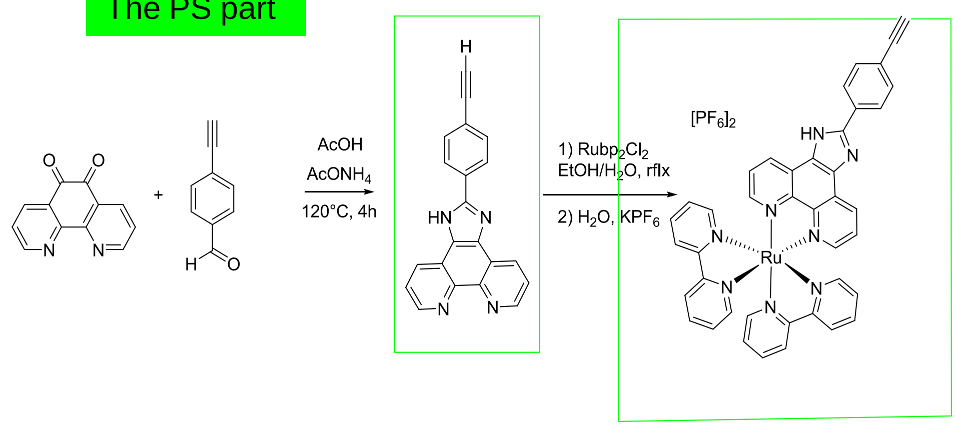
2. Click chemistry

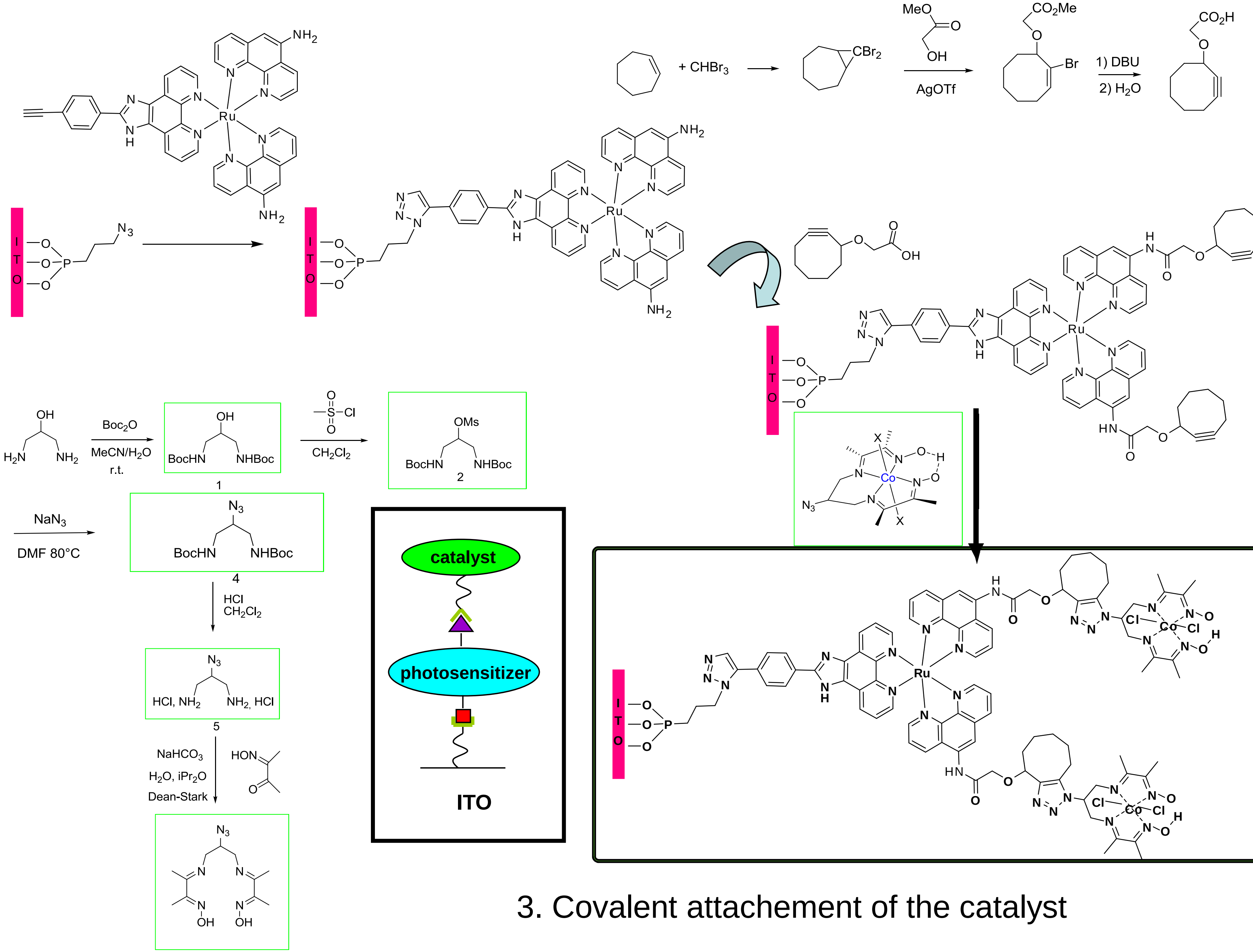


Click chemistry



The PS part

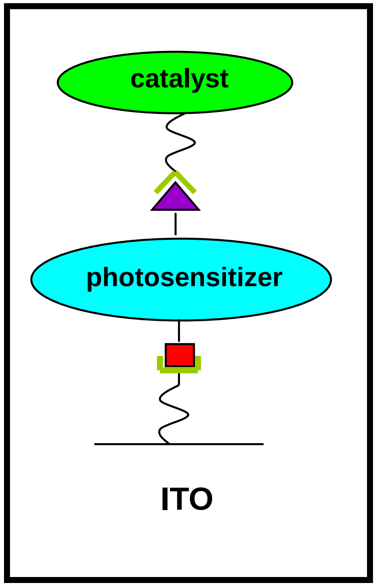


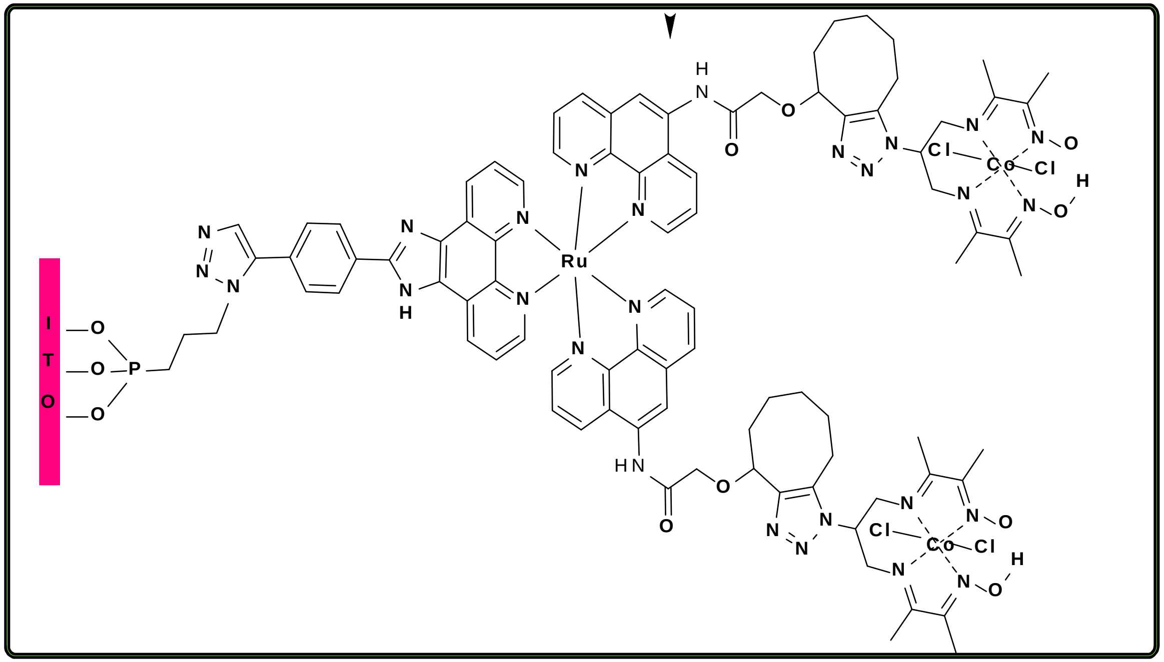


3. Covalent attachement of the catalyst

Towards the photocathode

(unpublished)





Artificial Photosynthesis:

From basic concepts to recent developments

Marc Fontecave

Laboratoire de Chimie et Biologie des Métaux, Université Joseph Fourier, CNRS, CEA/DSV/iRTSV
CEA-Grenoble 17 rue des martyrs 38054 Grenoble cedex 9, France
mfontecave@cea.fr; Phone: (0033)438789103 ; Fax: (0033)438789124

Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05

V. Artero
M. Chavarot-Kerlidou
Y. Oudart
S. Canaguier
A. Legoff
B. Fihri
R. Métayé
P. D. Tran
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cnrs advancing the frontiers

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