Artificial Photosynthesis from Solar Fuels To Solar Chemicals

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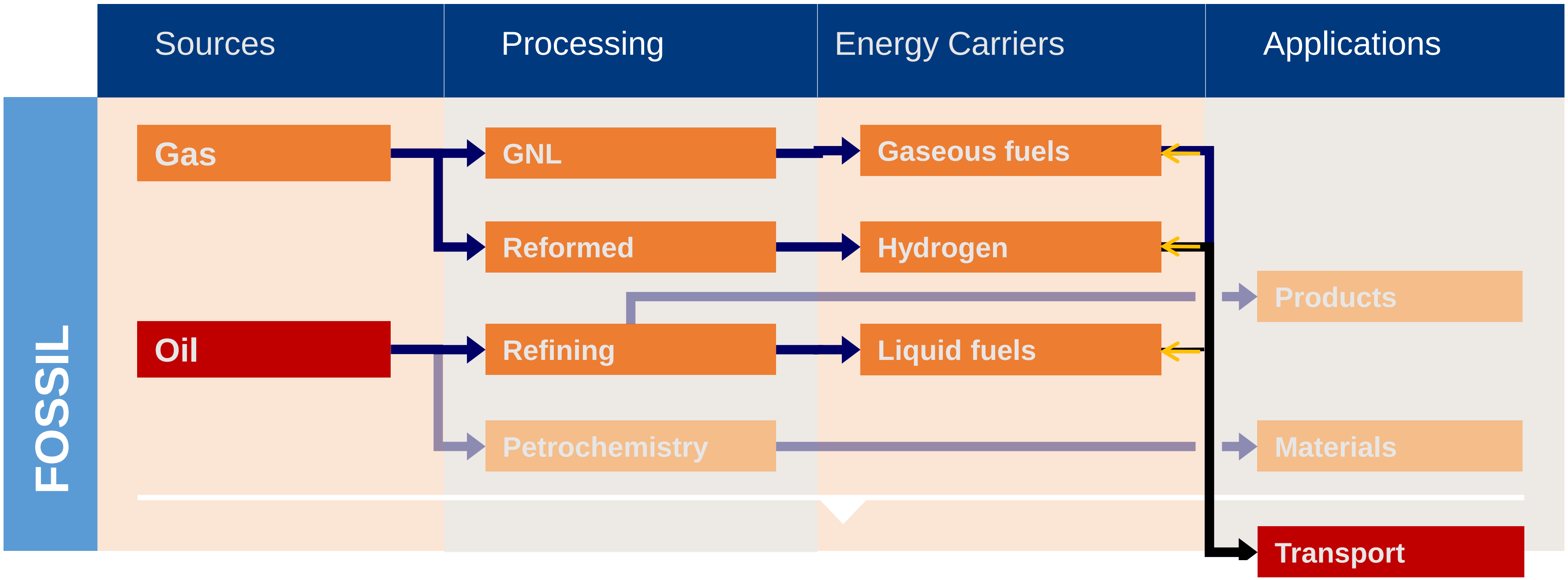
EXCELENCIA SEVERO OCHOA

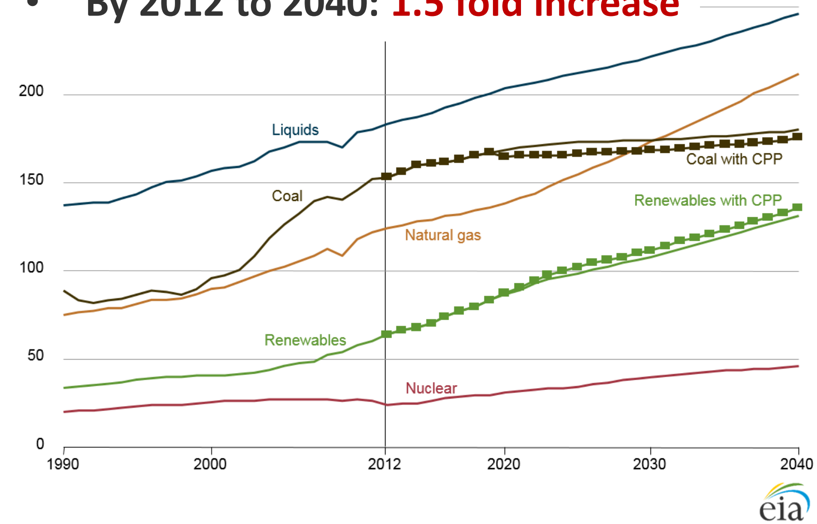
Outline of the tutorial

- **Introduction**
  - The energy challenge (Technological perspective)
- **Artificial Photosynthesis, Water Splitting**
  - Natural and Artificial Photosynthesis
  - Research Tools
  - Water Oxidation
  - Water Reduction
  - CO_2 Reduction
- **Towards Solar Chemicals**
  - Examples of oxidation and reduction reactions

Current technologies



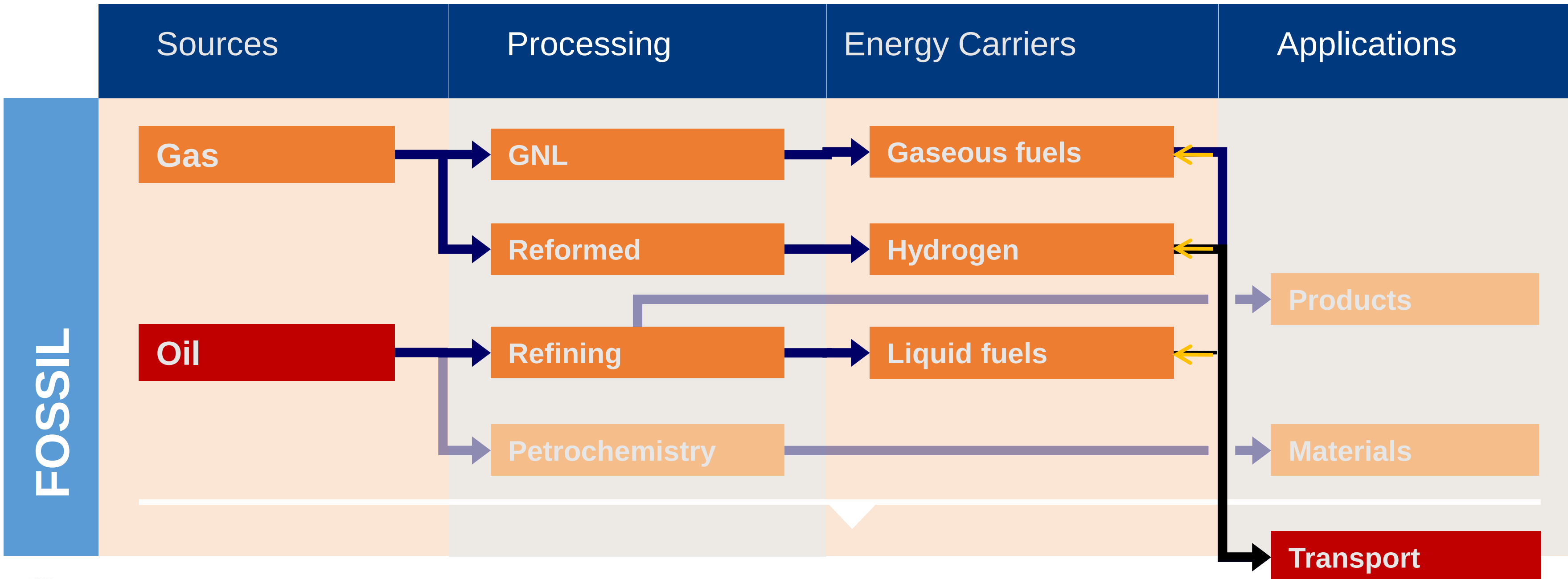
- By 2012 to 2040: **1.5 fold increase**

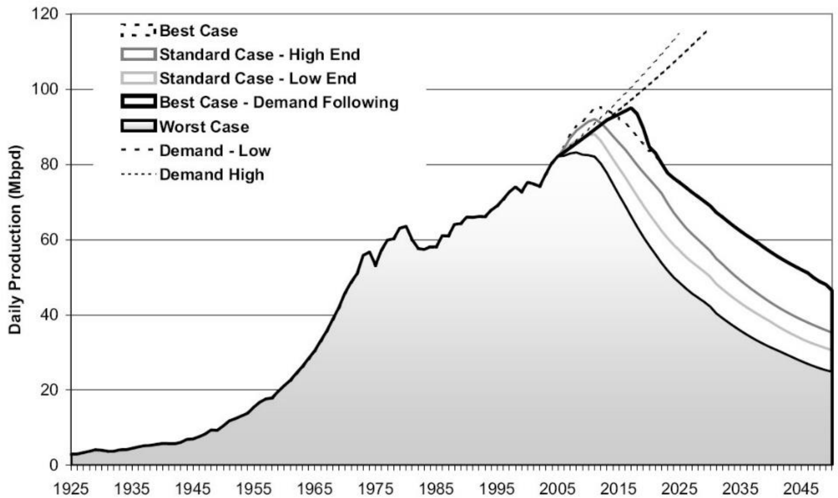


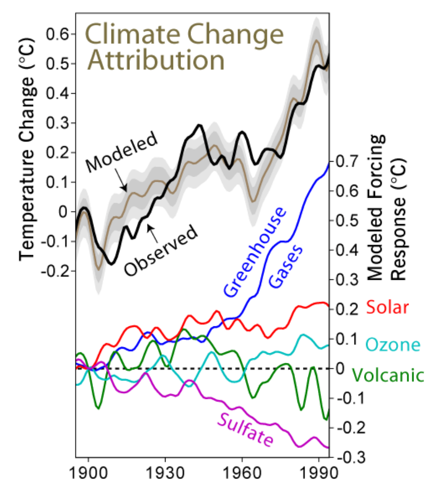
Oil:

- About 40% of world energy (mainly transportation)
- The main source of raw material for the chemical industry.

Current technologies

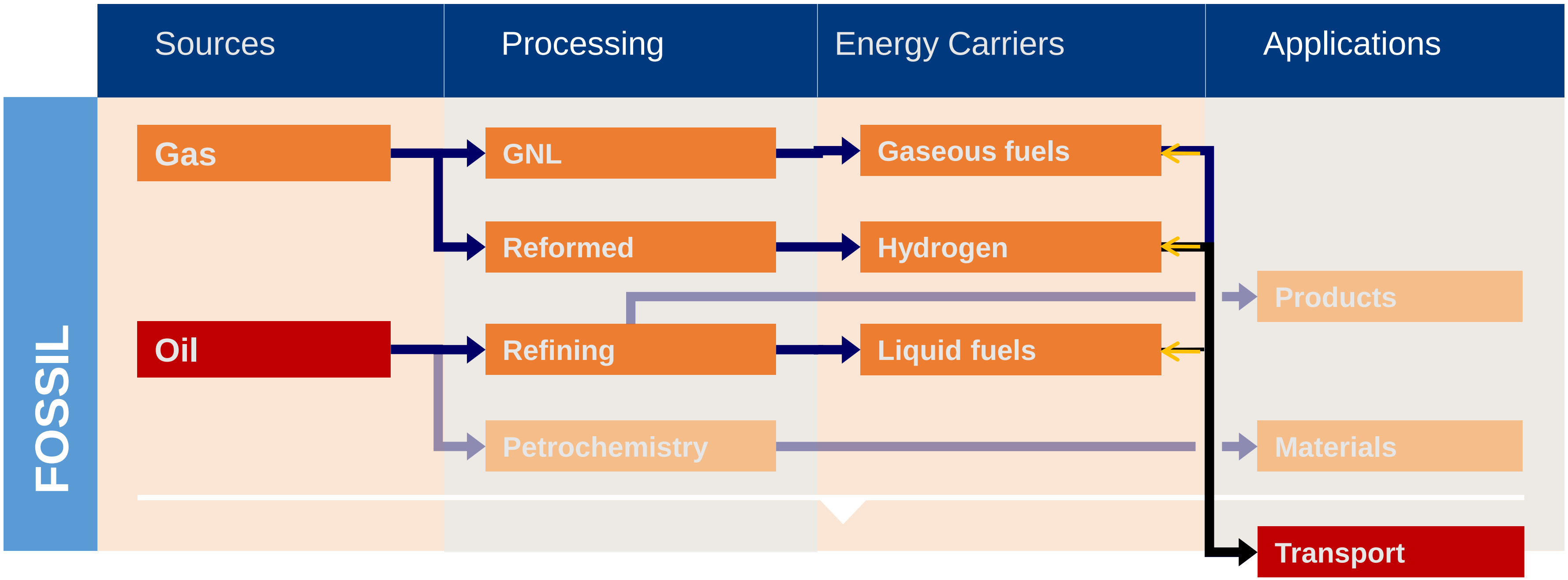






International energy agency, *World energy outlook*, 2011,

Current technologies



H2020-Objectives

2020

- 23% CO_2

+ 20% renovables

+ 20 % eficiencia

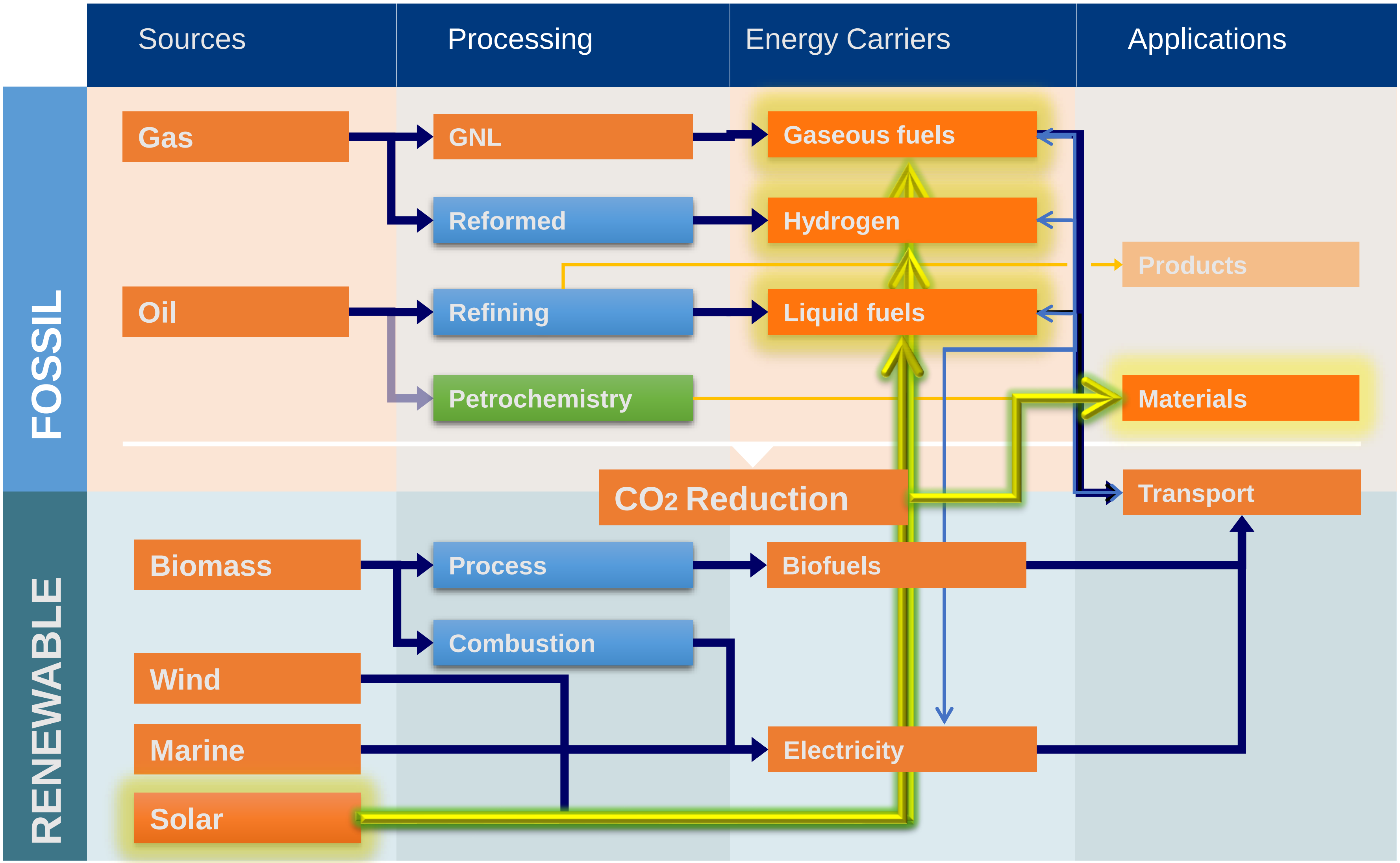
2030

- 40% CO_2

+ 27% renovables

+ 30 % eficiencia

Current technologies



Solar Energy

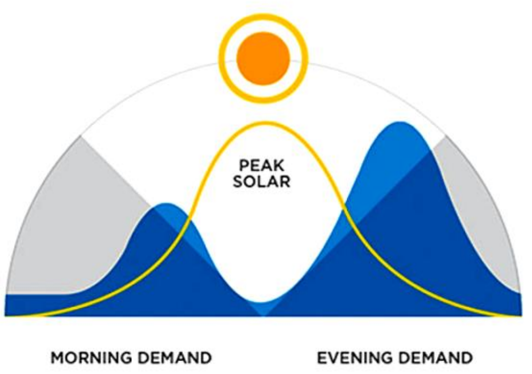
Advantages

- **The most abundant:** 1 h = Consumed in one year
- **RENEWABLE**

Inconvenient

- **DAY – NIGHT CYCLES**
- **Difficult to Store and transport**

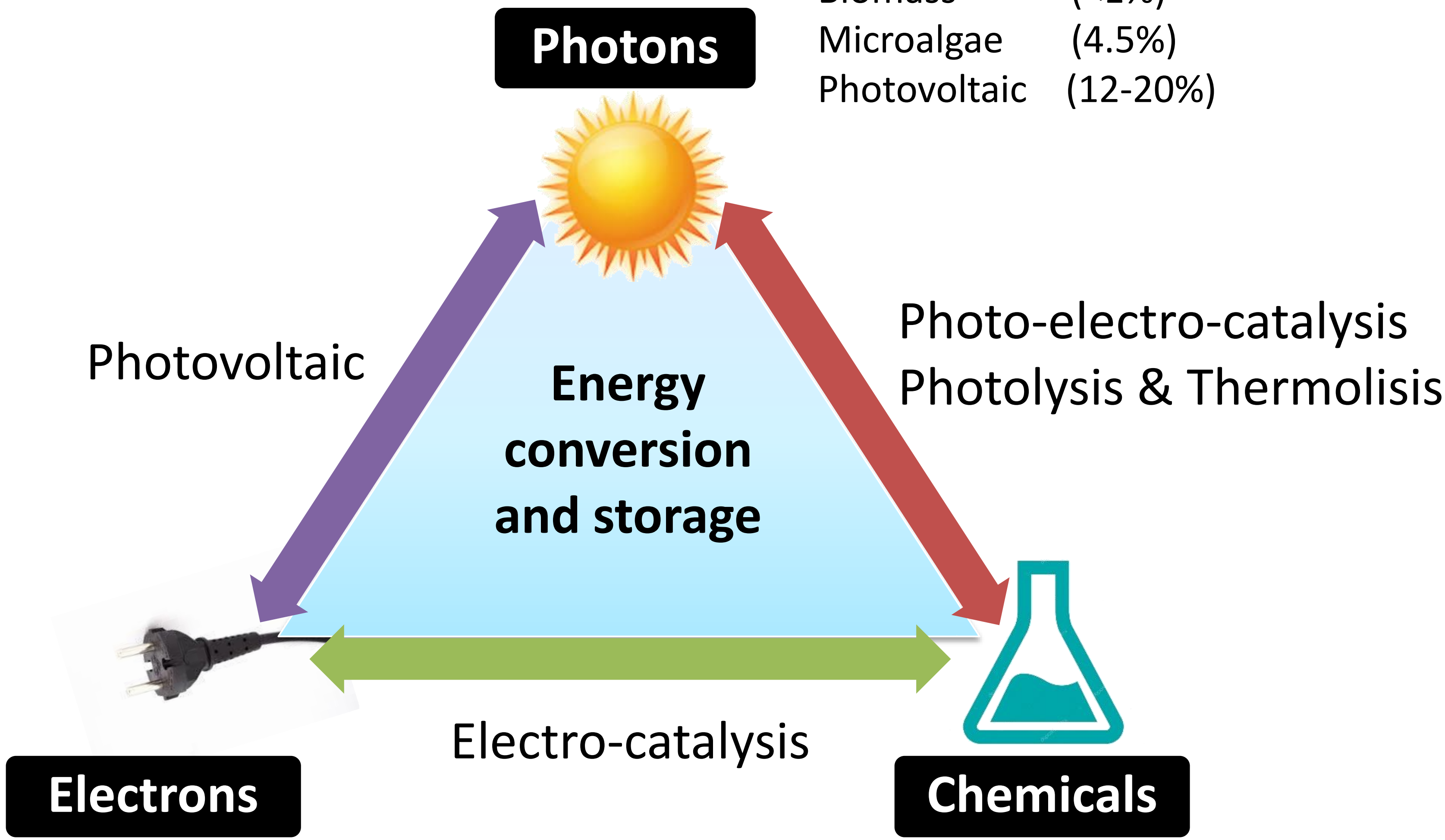
Normalized Energy	
Solar	8000
Biomass	6
Wind	5
Energy used by humans	1



Solar Energy: The most convenient

Efficiencies

Biomass	(<1%)
Microalgae	(4.5%)
Photovoltaic	(12-20%)



The Solar Refinery! CHEMICAL BONDS ≈ 10 · Batteries

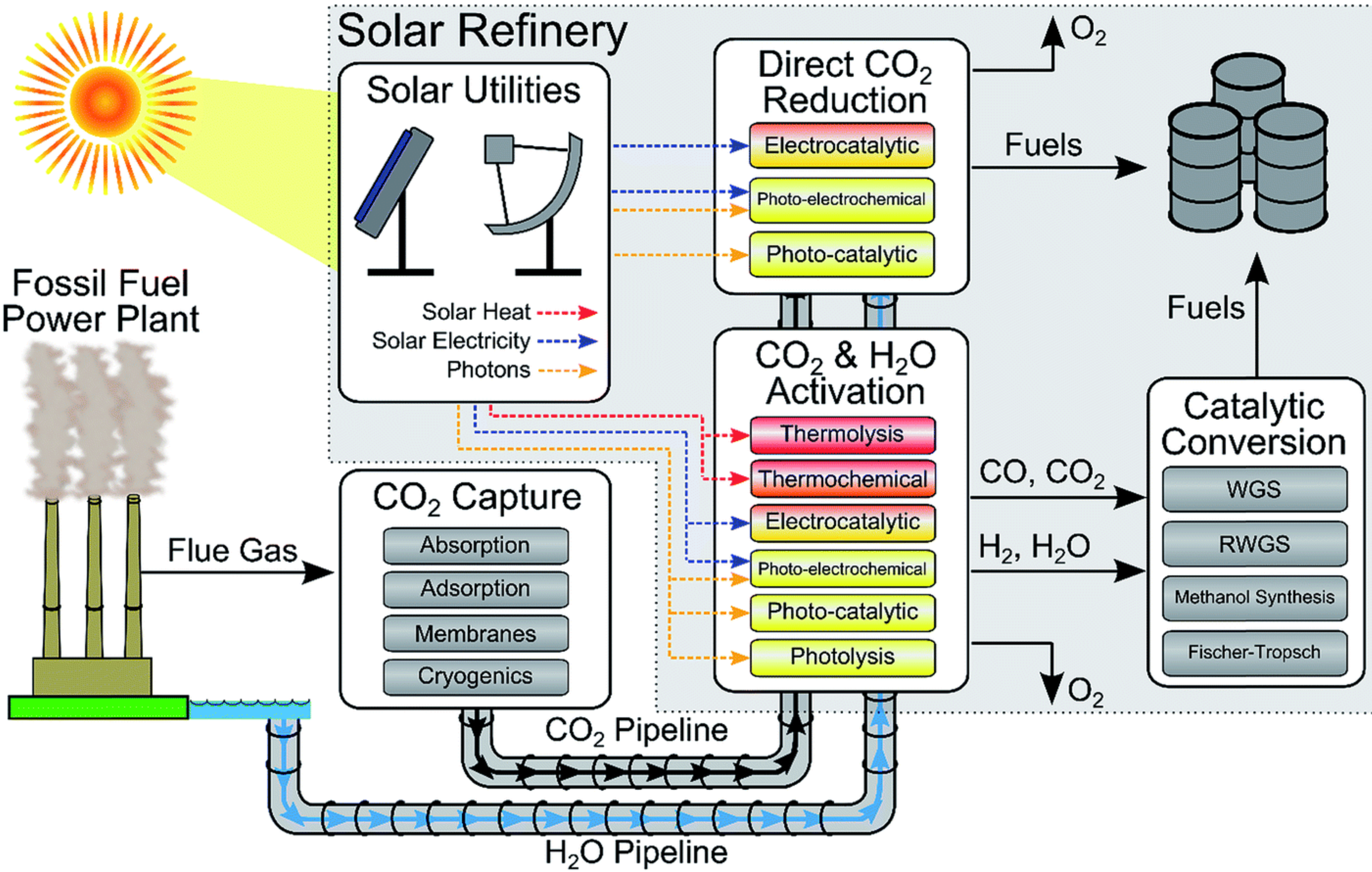
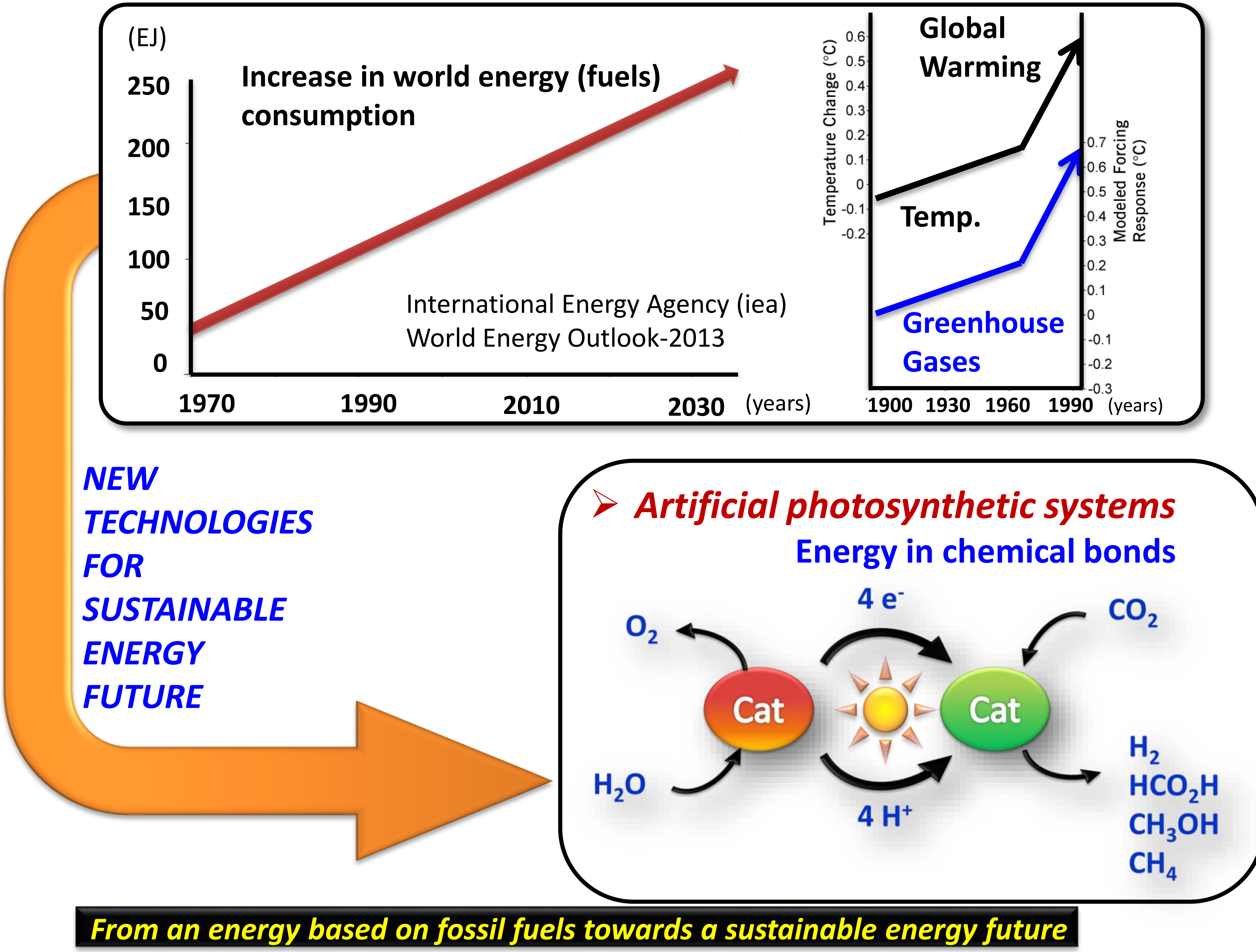


Figure from: *Energy Environ. Sci.*, **2015**, *8*, 126-157


(EJ)
250
200
150
100
50
0
Increase in world energy (fuels) consumption
International Energy Agency (iea)
World Energy Outlook-2013
1970
1990
2010
2030
(years)
Global Warming
Temperature Change (°C)
Temp.
Greenhouse Gases
Modeled Forcing Response (°C)
1900
1930
1960
1990
(years)
NEW TECHNOLOGIES FOR SUSTAINABLE ENERGY FUTURE
Artificial photosynthetic systems
Energy in chemical bonds
4 e-
O_2
CO_2
Cat
Cat
H_2O
4 H+
H_2
HCO_2H
CH_3OH
CH_4
From an energy based on fossil fuels towards a sustainable energy future

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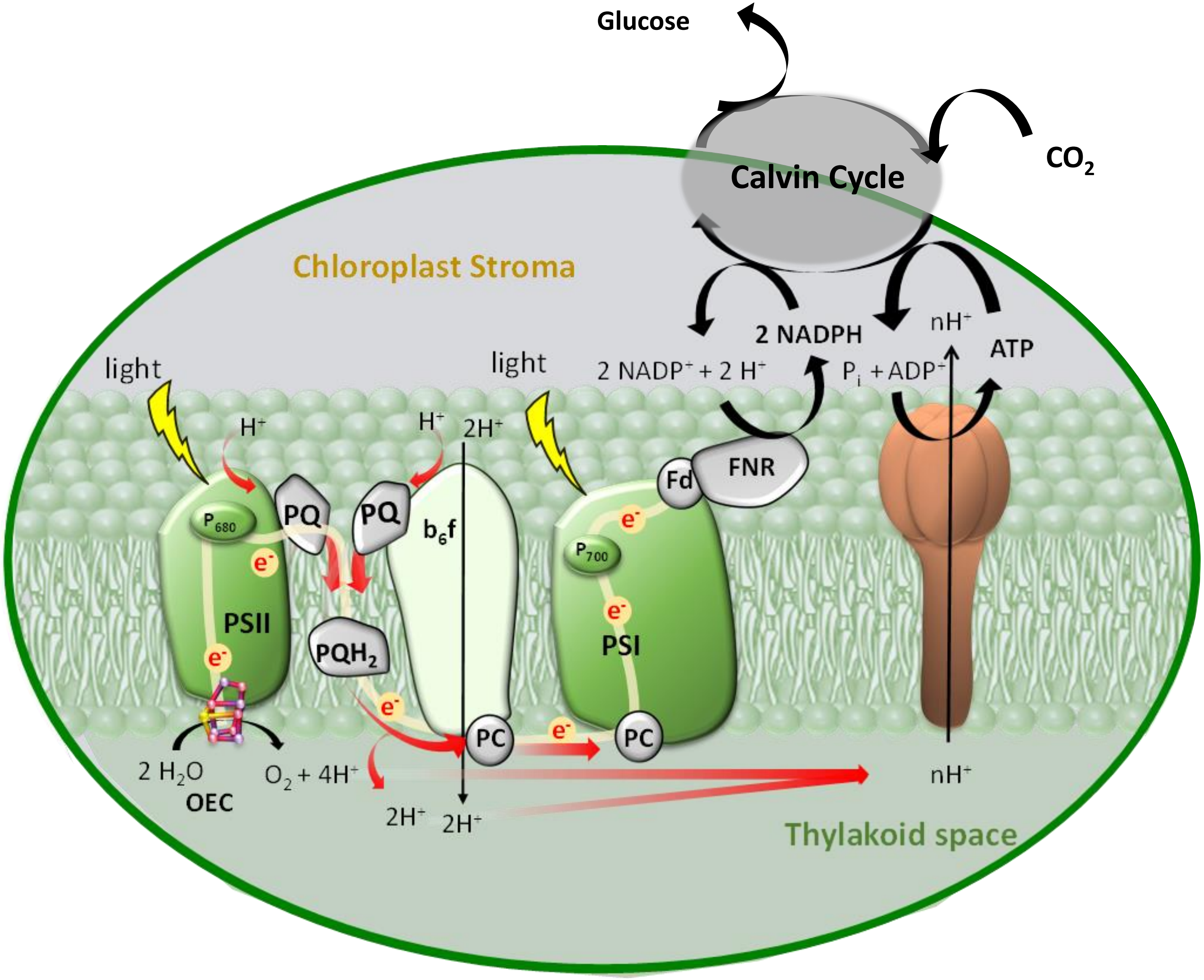
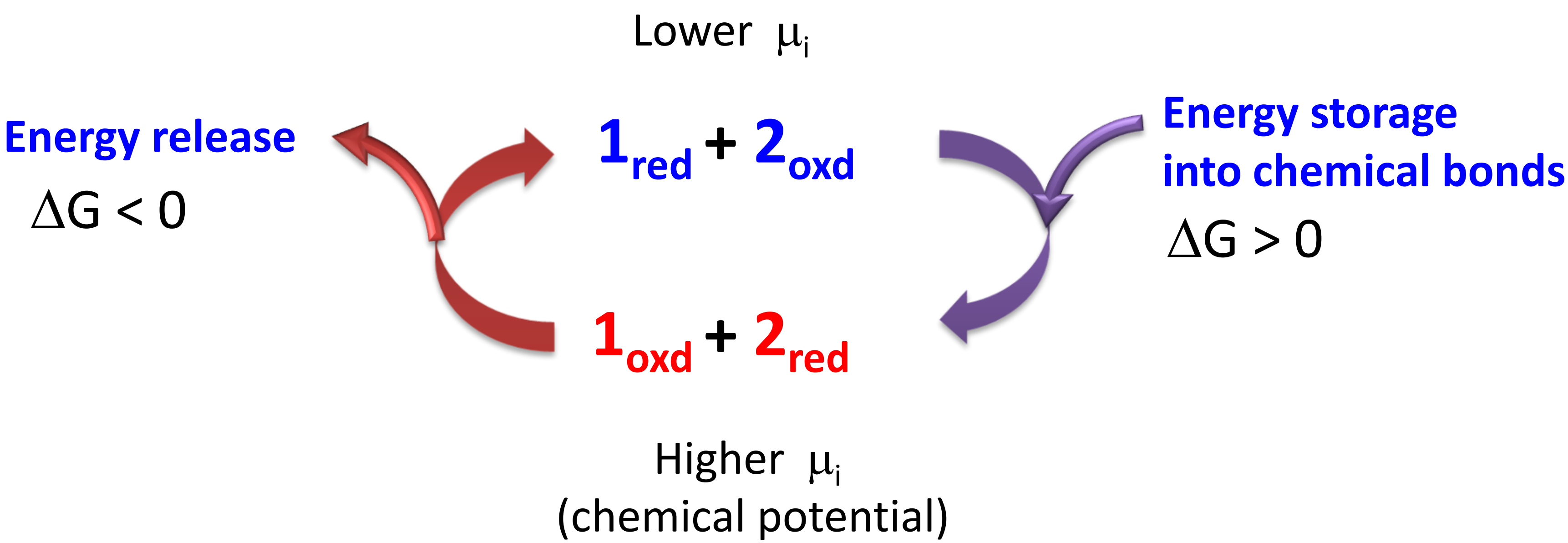
Solar Energy, Natural Photosynthesis



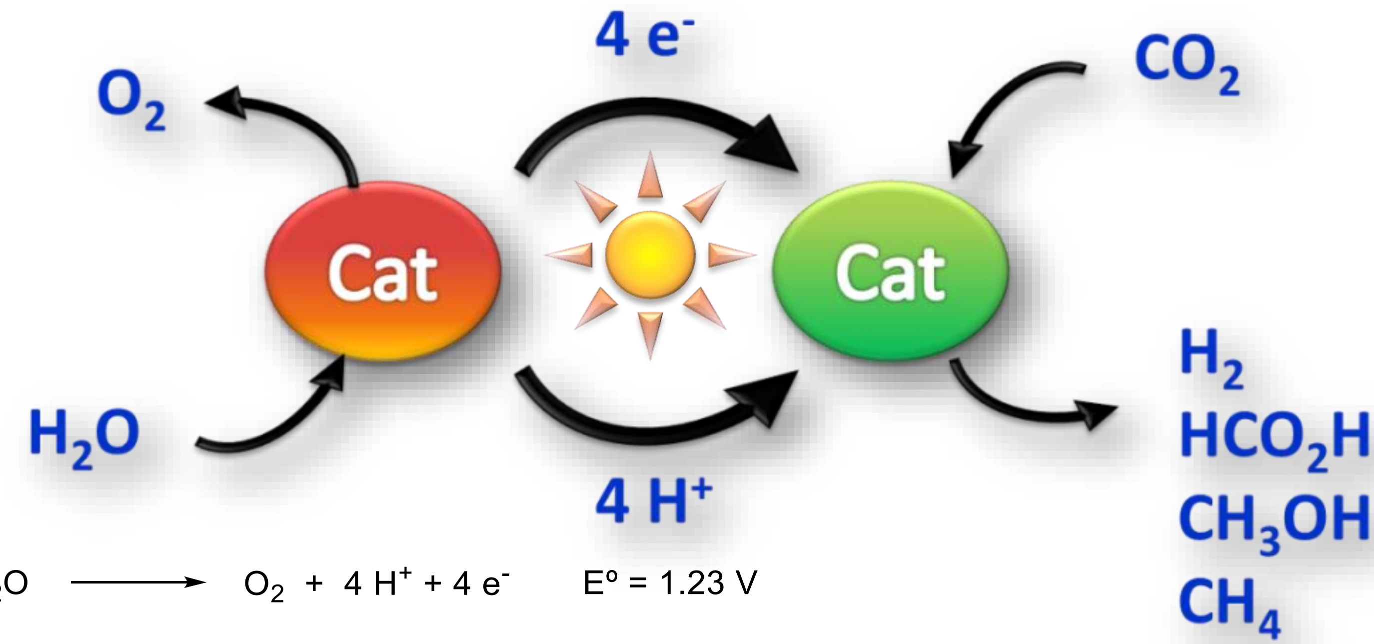
Kamiya *et al*. *Nature* 473, 55–60, 2011

➢ Energy management in chemical entities



➢ *Artificial photosynthetic systems*

Energy in chemical bonds



$2\ H_2O$	$\longrightarrow$	$O_2 + 4\ H^+ + 4\ e^-$	$E^o = 1.23$ V
$4\ H^+ + 4\ e^-$	$\longrightarrow$	$2\ H_2$	$E^o = 0.0$ V
$2\ H_2O$	$\longrightarrow$	$O_2 + 2\ H_2$	$E^o = -1.23$ V

A energetically "up-hill" reaction

$\Delta G^o = 113.4$ kcal/mol

$\Delta H^o = 136.6$ kcal/mol

- **water-splitting**: This process corresponds to split the water in O_2 and H_2. This process must be electro- or photo-catalyzed to be viable. This methodology would be a very safe way to transport hydrogen (as water).

Artificial Photosynthesis: Photocatalytic Scheme

$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2$$

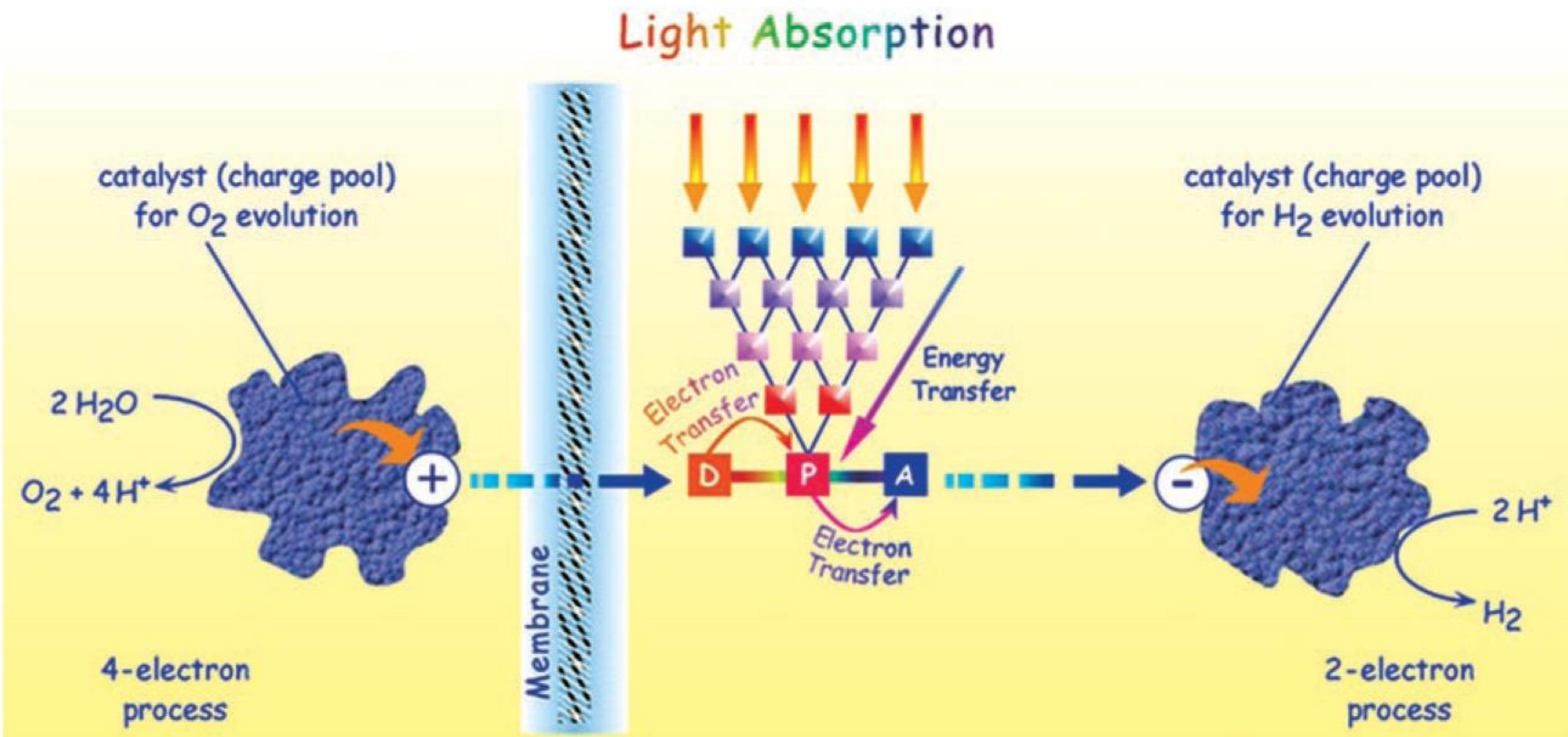


Figure from: Balzani, V.; Credi, A.; Venturi, M. *ChemSusChem* **2008**, *1*, 26-58.

Artificial Photosynthesis: Semiconductor Nanoparticles

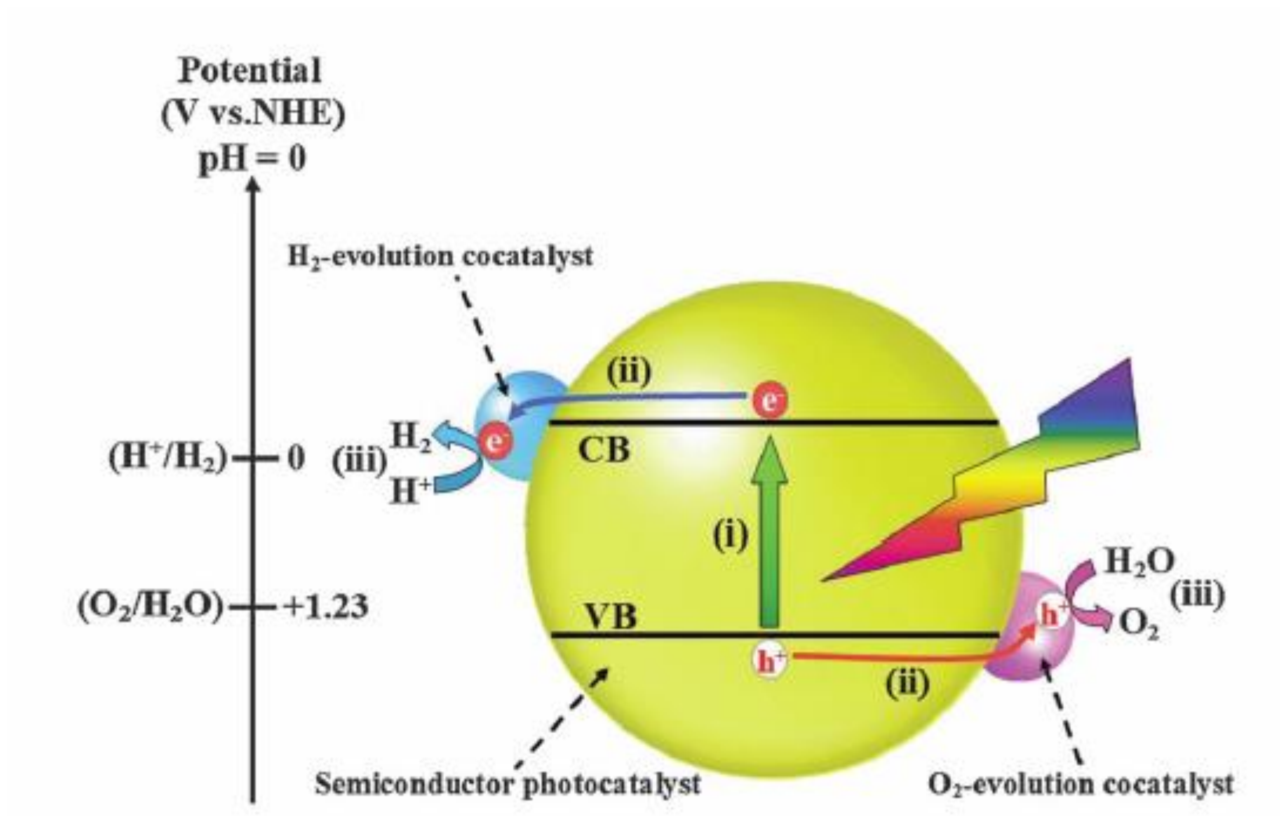


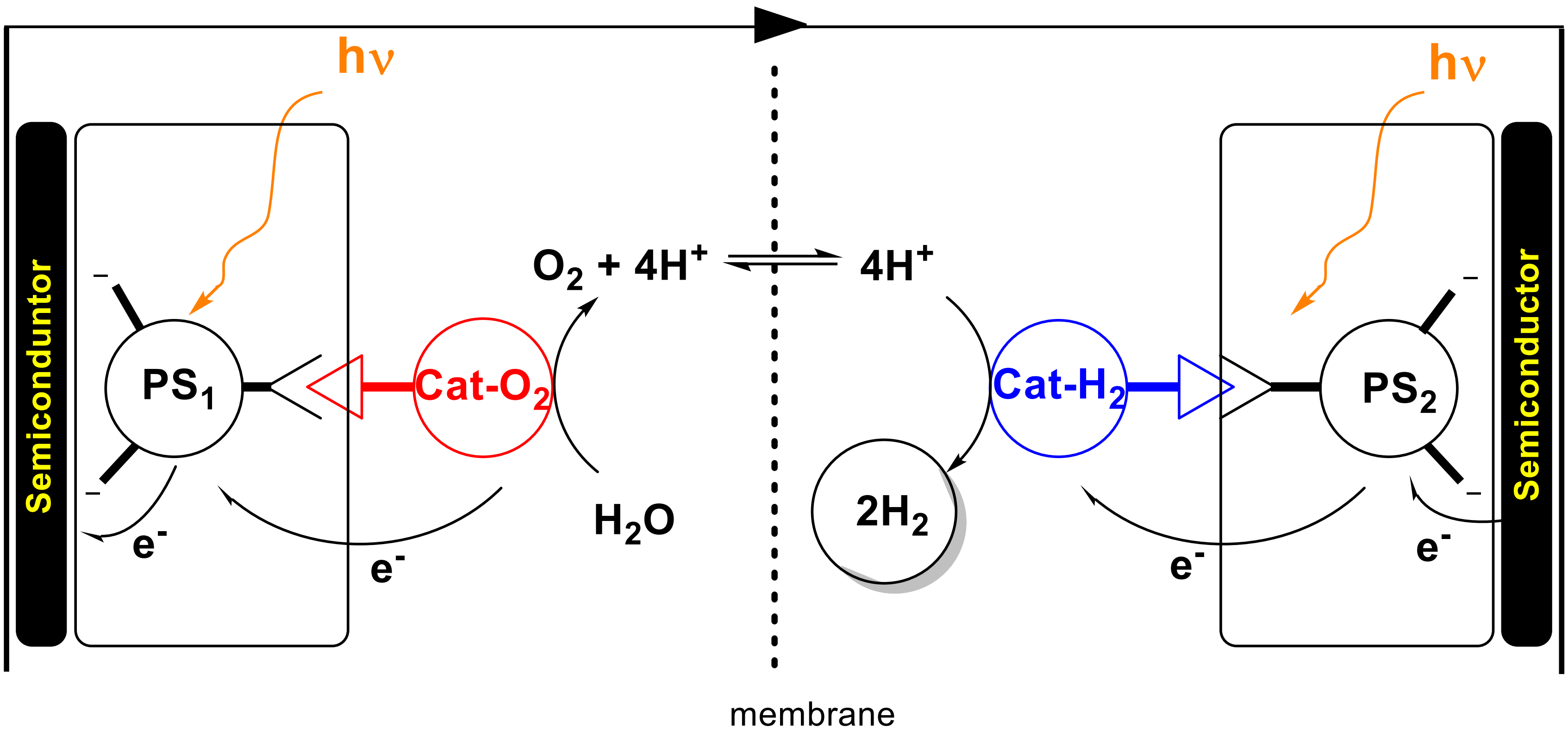
Figure from: S. Z. Qiao ***Chem. Soc. Rev.***, 2014,**43**, 7787-7812

Artificial Photosynthesis: Photoelectrochemical (PEC) cell

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

Photoanode

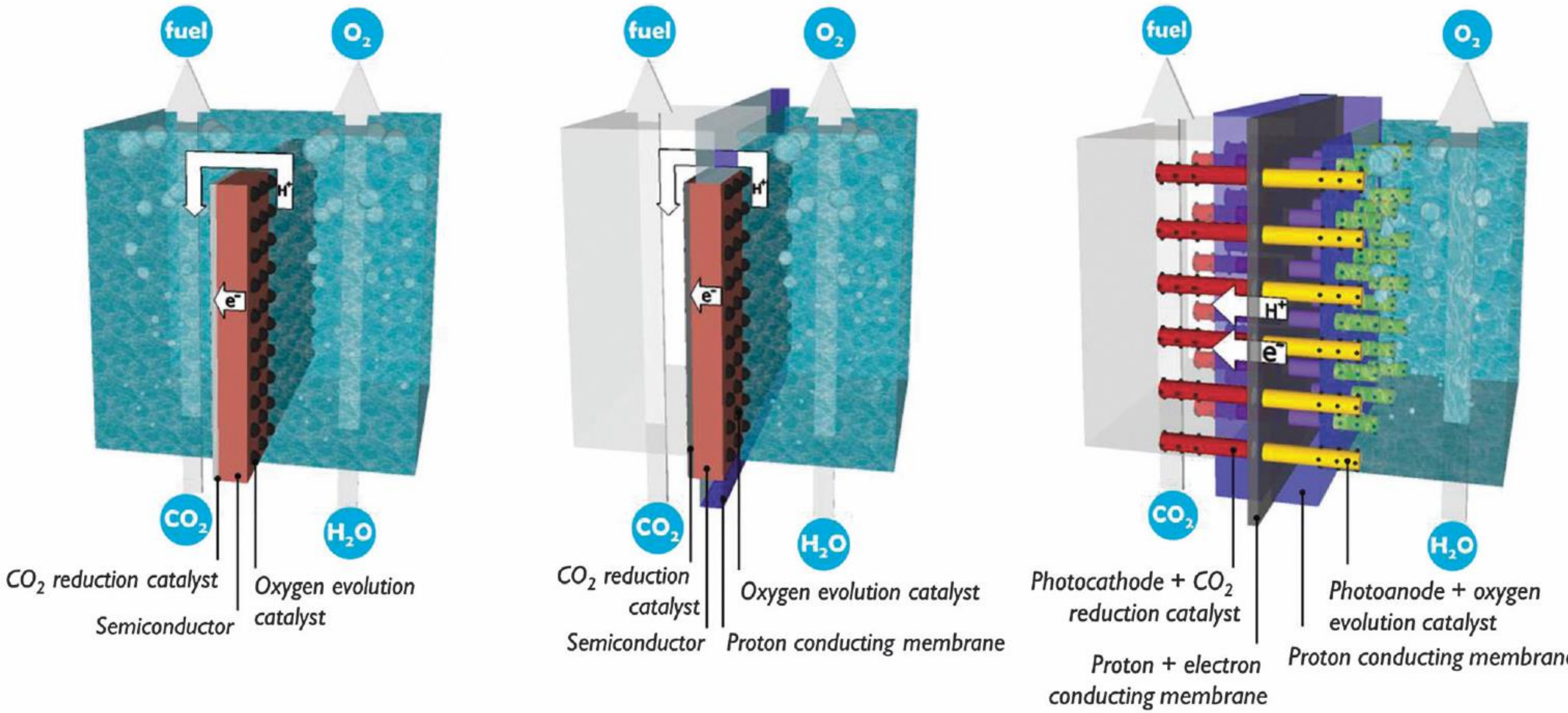
Photocatode



Water oxidation is the energetic demanding half reaction

Water reduction

Artificial Photosynthesis Monolithic devices



	Artificial leaf	Membrane-embedded artificial leaf array	Solar membrane
Compartments	1	2	2
Separated products	(Yes)	Yes	Yes
Gas phase possible	No	Yes	Yes
Proton transport	Around	Around	Through-plane

Nocera and co. *Science,* **2011**, 333, 645
Harry Gray, *Nature Chemistry,* **2009**, *1*, 7
Jan Rongé *et al Chem. Soc. Rev.,* **2014**, *43*, 7963-7981

Devices

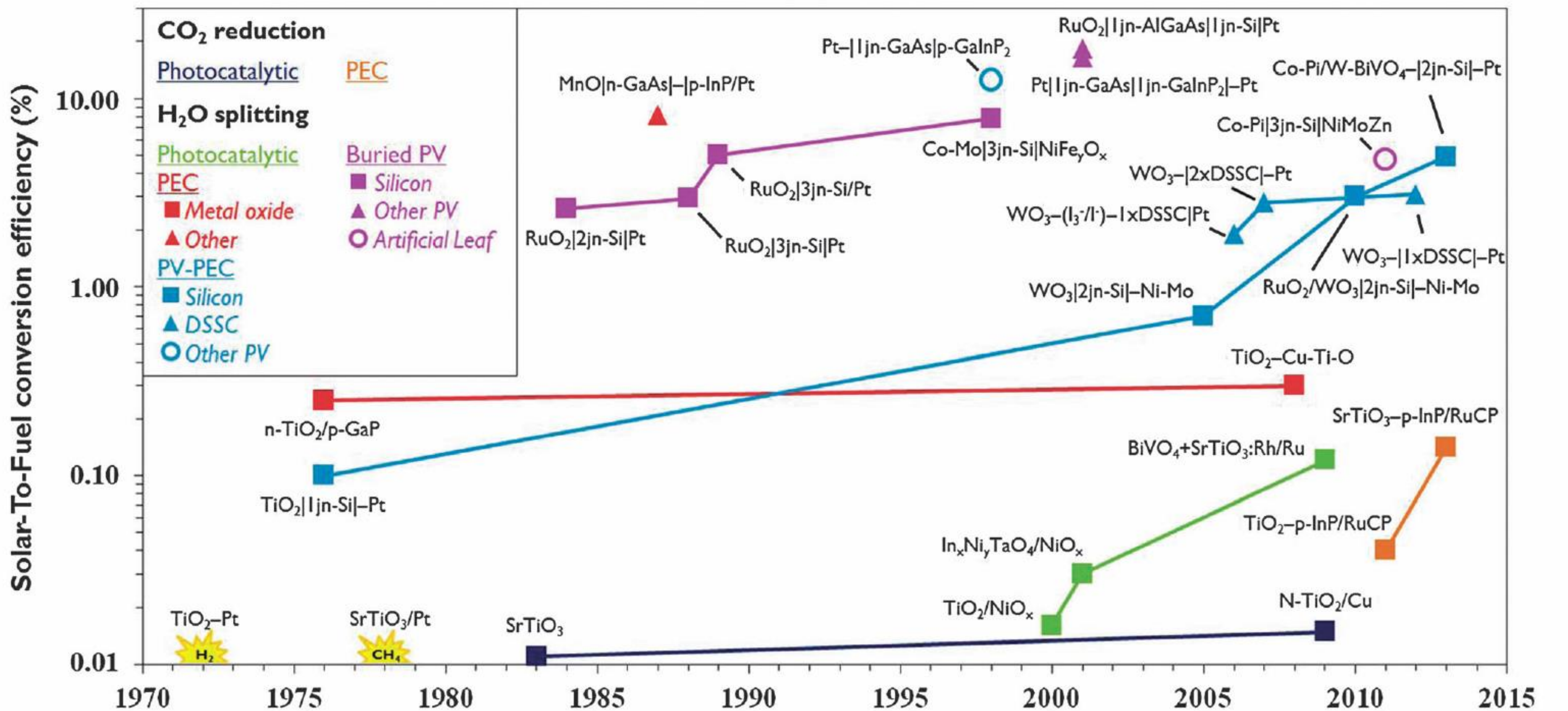


Fig. 1 Evolution of record solar-to-fuel efficiencies of different approaches, reported in the absence of chemical or electrical bias and under (simulated) solar illumination (for additional details, see ESI†). PEC = photoelectrochemical, PV = photovoltaics

Jan Rongé *et al Chem. Soc. Rev.*, **2014**, *43*, 7963-7981

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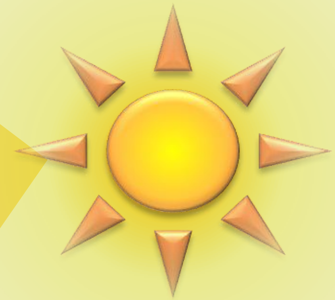
Tools to study the different parts of AP Schemes

Photochemistry

Light harvesting system



Quantum yield

Fast spectroscopy

Applications

Electrochemistry

Electrocatalyst, Electrolyte

Overpotential

TON, TOF, Faraday yield

Mechanism information

Chemicals

Sacrificial Agents

Basic studies

Mechanism

Reaction intermediates

TON, TOF

Chemical Sacrificial Agents:

Chemical oxidants: WO: CAN (1.6 V *vs* NHE, pH 1), $NaIO_4$, Oxone (basic media), $Ru(bpy)_3^{3+}$.

Chemical reductor: WR, CR: Cp_2Co, $Ln^{II}X_2$, almost inexistent

Catalysis: Structure – Activity relationships, yield, TON (n(P)/n(Cat)) and TOF (TON/t).

Kinetics: Reaction order respect of the catalyst and the oxidant. Stop flow.

Spectroscopy: Paramagnetic species. Identification of key intermediates in catalysis (titration with oxidant)

- NMR: No very informative. Purity
- EPR: Basic characterization coord. environment, oxidation and spin state
- UV-Vis: Monitoring kinetics,
- rRaman, IR: M=O, M-O-O-H, M-O-O-M
- IR: M-CO, $M\text{-}CO_2^-$
- EXAFS: Coord environment, oxidation and spin state
- ESI-MS: Identification of speciation in solution

***In situ* spectroscopy:** Under catalytic conditions (i.e. under excess of sacrificial agent)

Labelling studies: D, ^{18}O, ^{13}C. Origin of O_2 , H_2, CO, CH_3OH, CH_4…. and mechanism information.
Kinetic Isotopic Effects of ^{13}C, ^{18}O and D. (PCET).
Mass spectrometry, M=O, M-OH, M-CO, M-H

Heterogeneous vs Homogeneous: DLS, NTA, TEM, kinetics (inductions times, reaction orders). Relation structure activity. Poisoning experiments (Hg). Labelling studies at the ligand …..

Computational Modelling: Spectroscopy of intermediates. Electronic structures. Energy profiles….

Electrochemistry:

half-cell electrochemistry: cyclic votametry, potentiometry and RDE.

CV Electrocatalysis: Structure – Activity relationships, Faraday yield (n(e^-)/n(Cat)), TON and TOF, overpotential. Pourbaix diagrams (E *vs* pH).

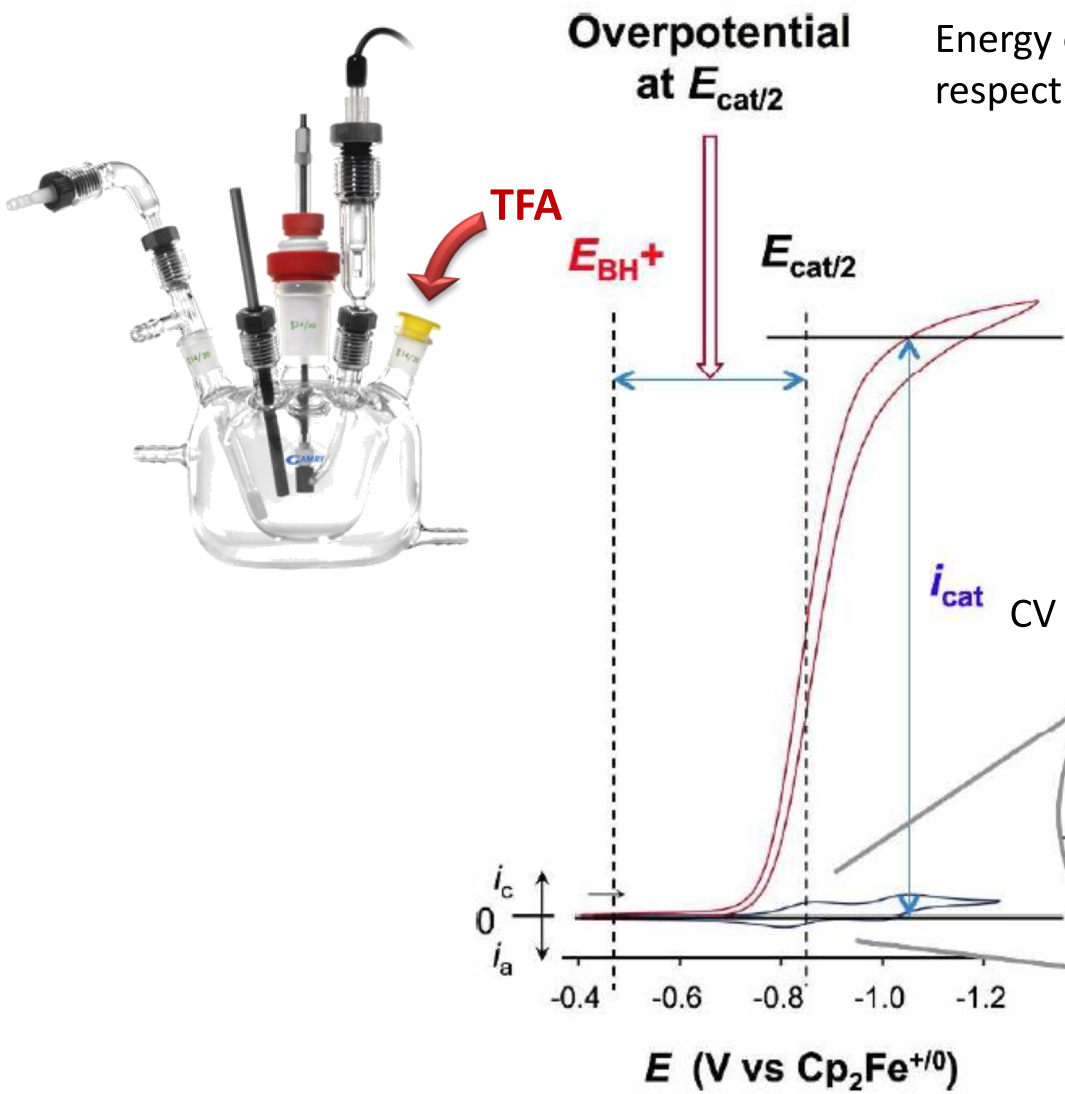
Kinetics: Reaction order respect of the catalyst and the oxidant.

Spectroelectrochemistry: Paramagnetic species. Identification of key intermediates in catalysis
Mainly UV-Vis, IR (CO bonds) and rRaman (M=O bonds)
Also possible: EPR and EXAFS

Labelling studies: Similar to Chemical Agents. Mechanism information. KIE.

Catalytic Phase: Heterogeneous vs homogeneous: Analysis of the surface of the electrode (TEM, SEM, EDX, XPS…..)

Electrochemistry:



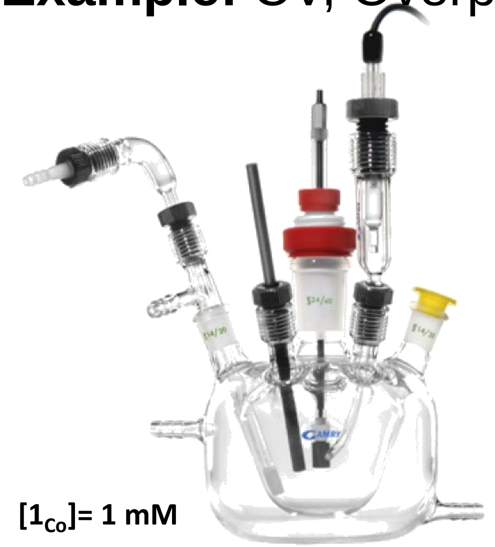
Energy extra needed to produce the electro-catalysis respect to the thermodynamic theoretical value.

When the addition of a substrate produce an increase in current intensity and this is proportional to the substrate concentration we have what is call as electrocatalysis.

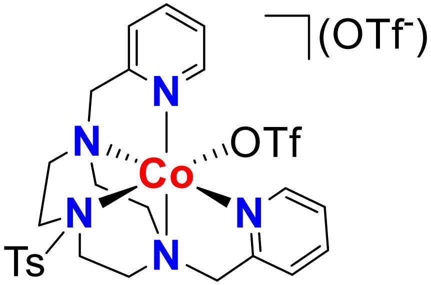
CV in the presence of acid.

From: DuBois, D. L. *Angew. Chemie Int. Ed*. **2012**, *51*, 3152-3155

Example: CV, Overpotential



$[1_{Co}]$= 1 mM

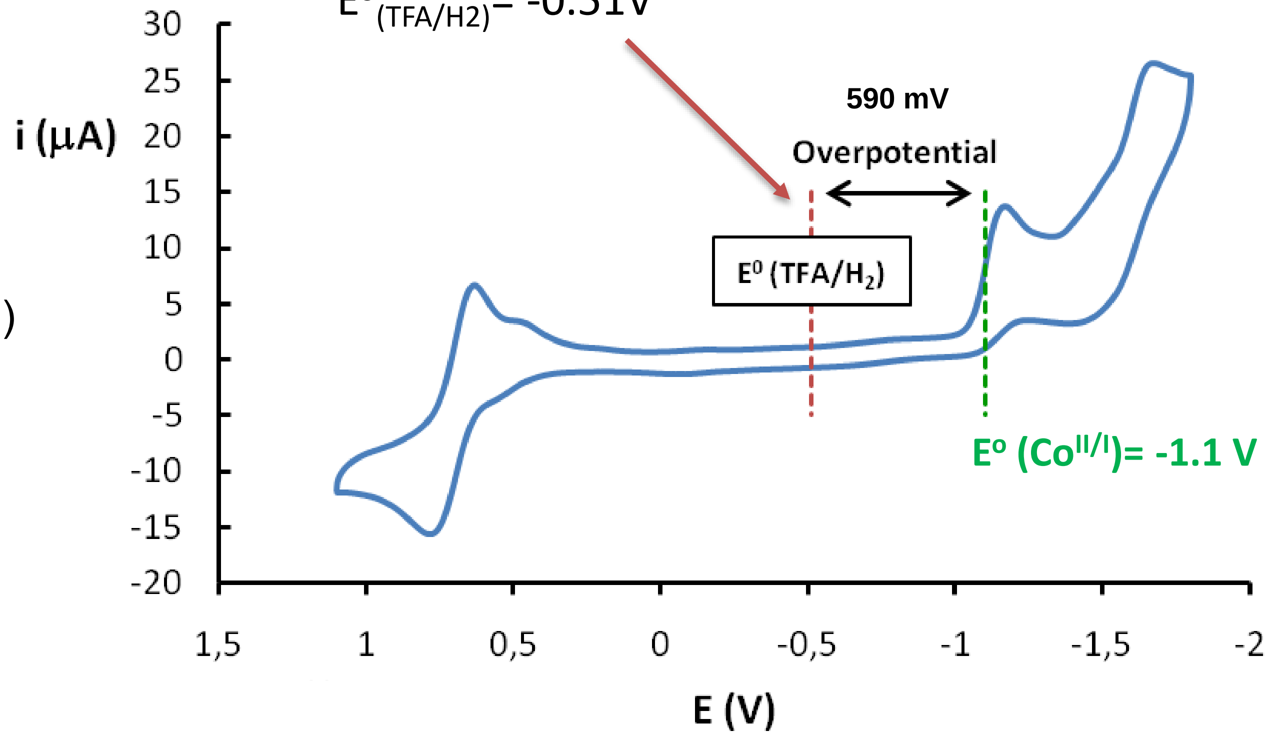


$PK_{a,TFA}$= 12.7

$E^{o\prime}(H^+/H_2)$=**0.24 V** *vs*. SCE in CH_3CN

$E^{o}_{HA} = E^{o\prime}(H^+/H_2) - (2.303RT/F)pK_{a,HA}$

$E^{o}_{(TFA/H2)}$= -0.51V



Chem. Eur. J. **2014**, *20*, 6171

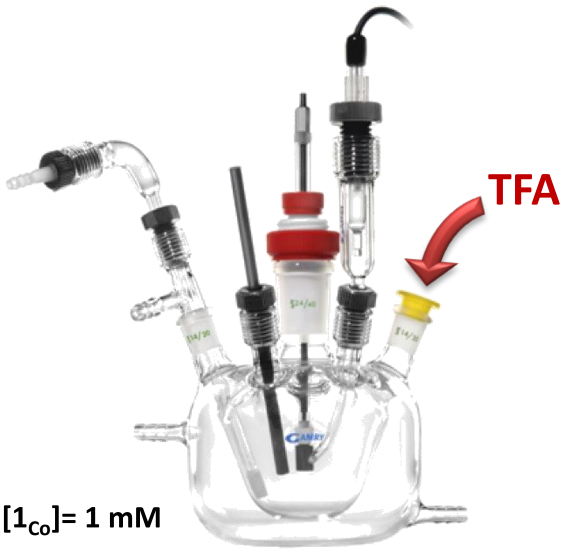
CONDITIONS

100 mM Bu_4NPF_6 in CH_3CN solution (under N_2), Scan rate: 50 mV/s

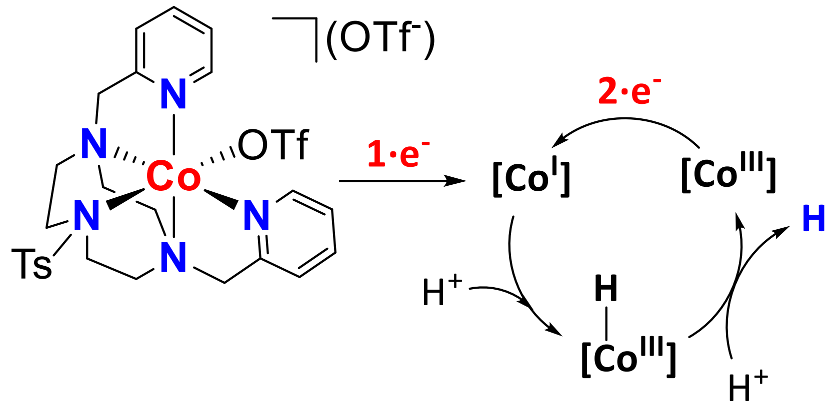
Working electrode: Glassy Carbon; Reference electrode: calomerans electrode; Counter electrode: Pt wire

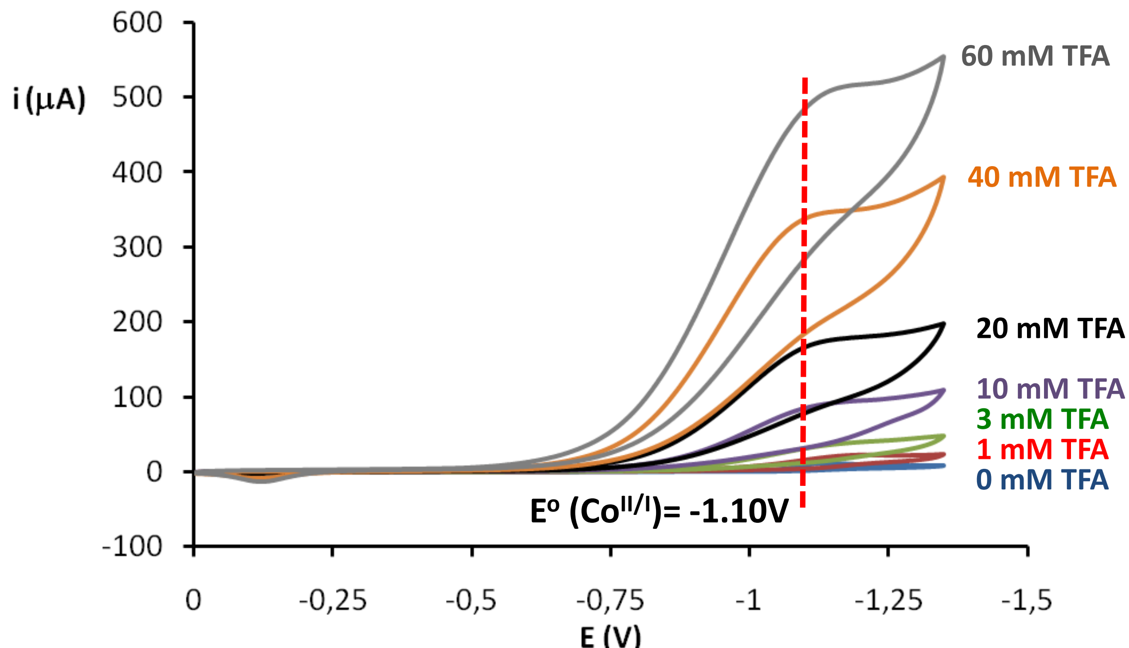
Artificial Photosynthesis, Mechanistic Investigations

Example: CV, TOF



$[1_{Co}]$= 1 mM





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CONDITIONS

100 mM Bu_4NPF_6 in CH_3CN solution (under N_2), Scan rate: 50 mV/s
Working electrode: Glassy Carbon; Reference electrode: calomerans electrode; Counter electrode: Pt wire

Calculation of TOF of the catalyst 1_{Co}

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463}\sqrt{\frac{RT(k[H^+]^2)}{F\nu}}$$

Rate constant

slope

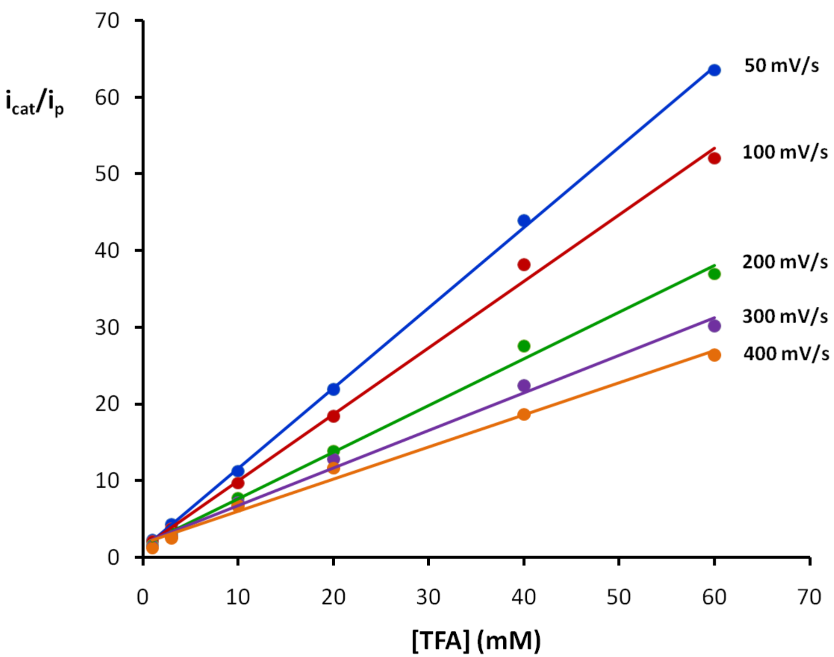
$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463}\sqrt{\frac{RTk}{F\nu}}\,[H^+]$$

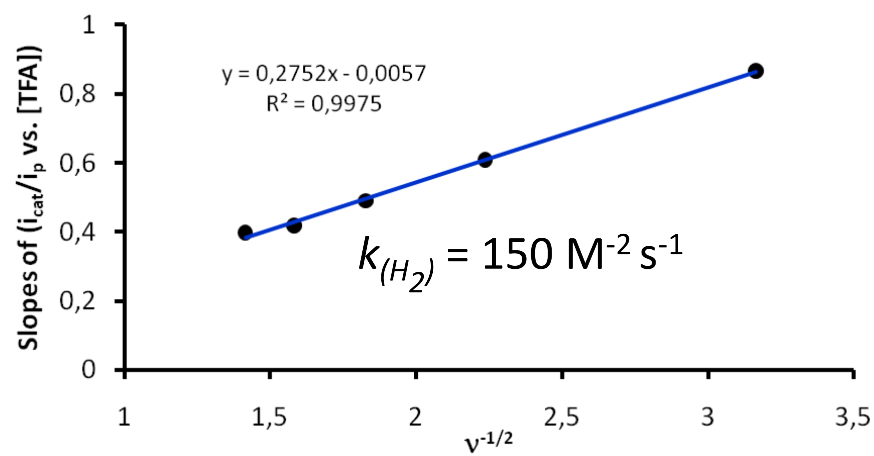
$$y = m \cdot x$$

Rate constant

$$m = \frac{n}{0.4463}\sqrt{\frac{RTk}{F}}\,\nu^{-1/2}$$

$$y' = m' \cdot x'$$





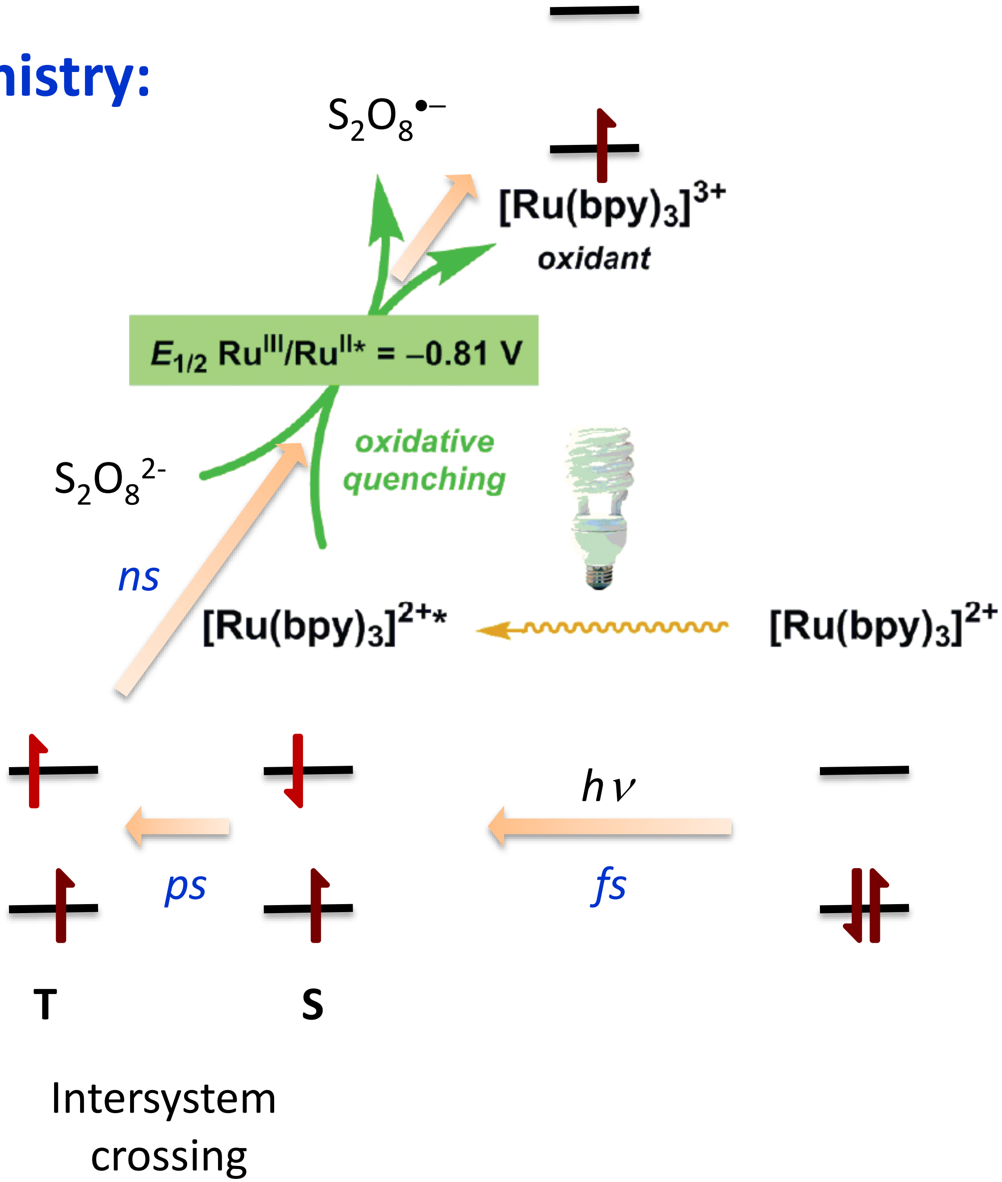
i_{cat}= peak current in the presence of acid
i_p= peak current in the absence of acid

n= number of electrons involved
R= universal gas constant, T= temperature
F= Faraday's constant ν= scan rate

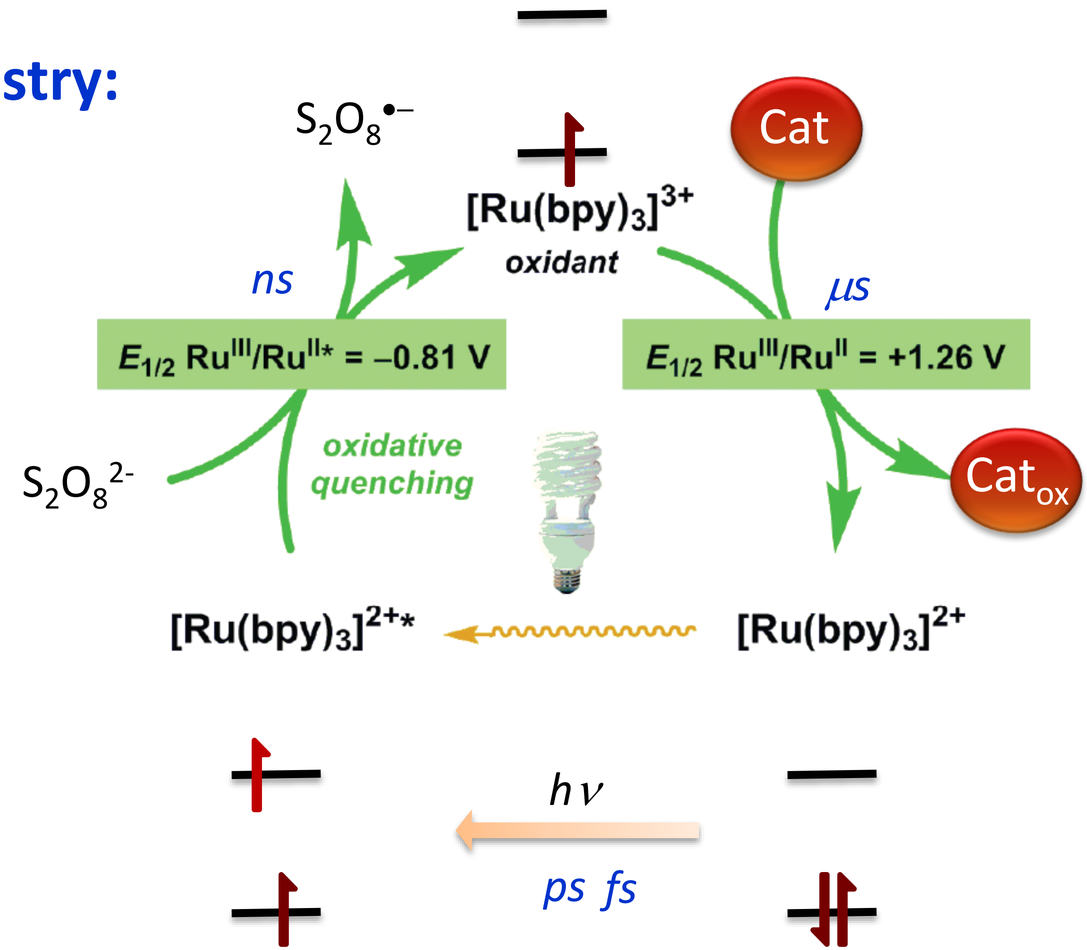
Photochemistry:

Photosensitizer: $Ru(bpy)_3^{2+}$, $Ir(ppy)_2(bpy)$, $Cu(phen)_2$, Organic dyes….
Electron aceptors: Na_2S_2O ; Electron donors: Ascorbic acid, TEOA, terciary amines, etc..

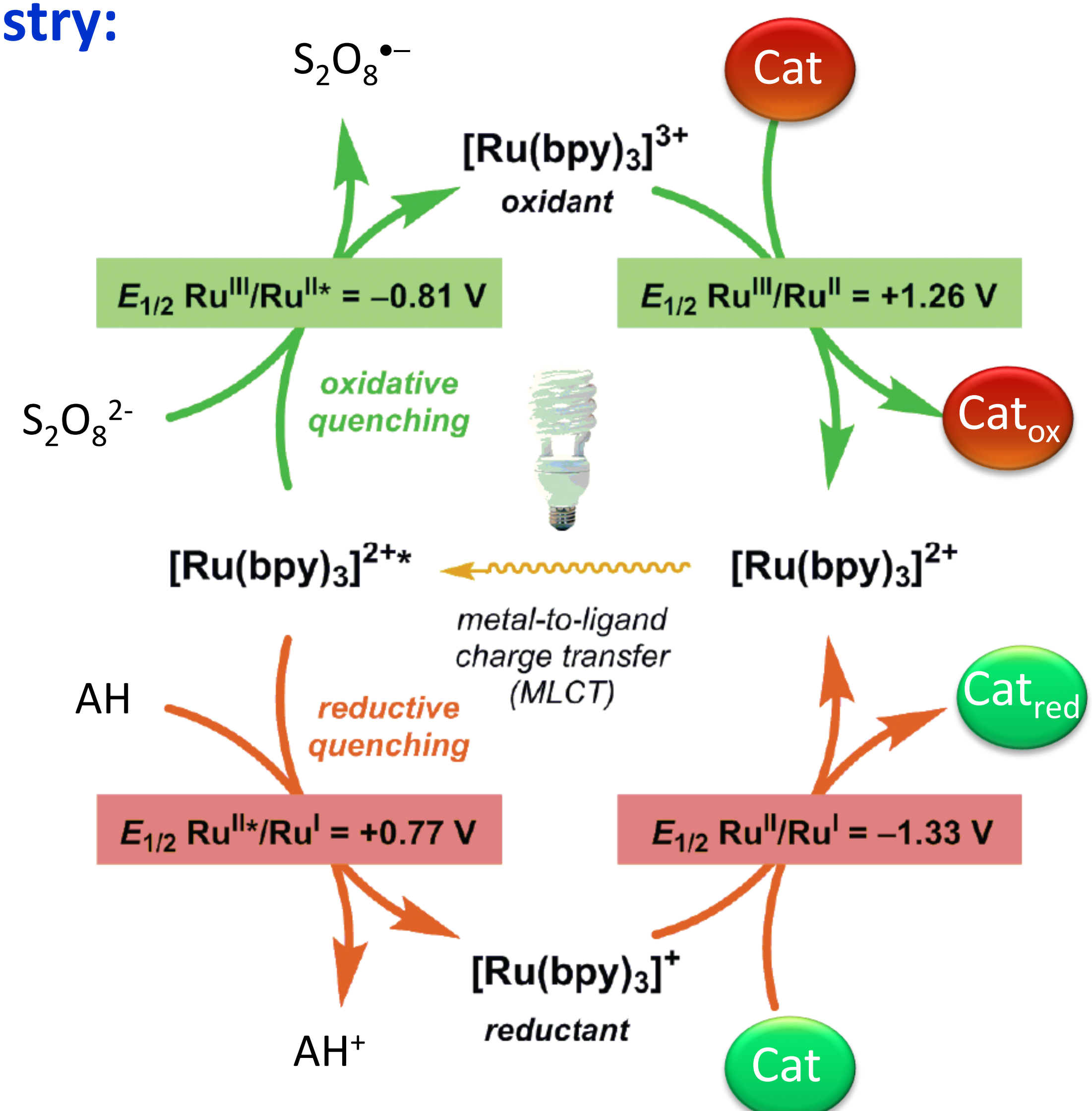
Photochemistry:



Photochemistry:



Photochemistry:

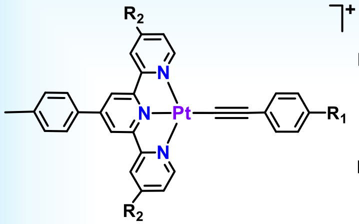


doi:10.5772/62272

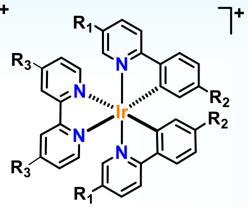
Photochemistry: PS-ED/EA combinations

Reductions

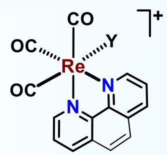
Photoredox catalyst



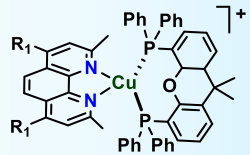
$E_{1/2}$ = [-1.29, -1.40] V



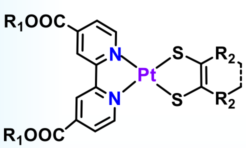
$E_{1/2}$ = [-1.37, -1.61] V



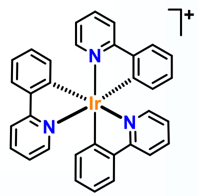
$E_{1/2}$ = -1.01 V



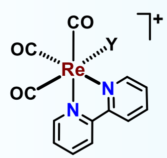
$E_{1/2}$ = -1.53 V



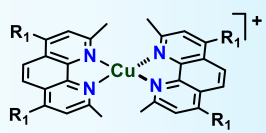
$E_{1/2}$ = [-1.45, -1.55] V



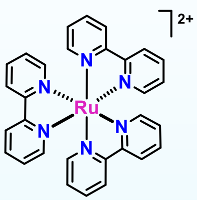
$E_{1/2}$ = -2.16 V



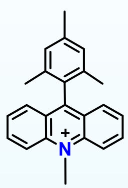
$E_{1/2}$ = -1.66 V



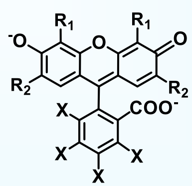
$E_{1/2}$ = -0.55 V



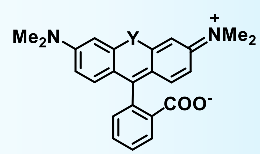
$E_{1/2}$ = -1.54 V



$E_{1/2}$ = -0.57 V



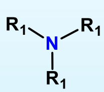
$E_{1/2}$ = -1.05 V

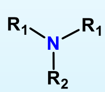


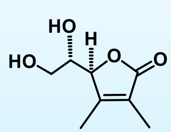
Y = O, S or Se

$E_{1/2}$ = [-0.54, -0.754] V

Electron donors



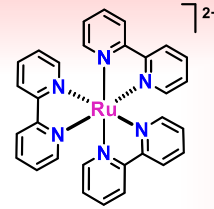




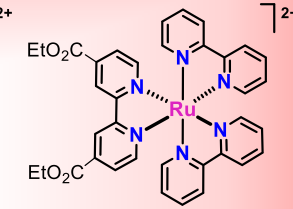
(Potentials vs SCE)

Oxidations

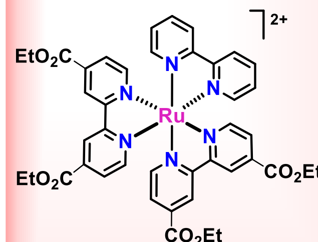
Photoredox catalyst



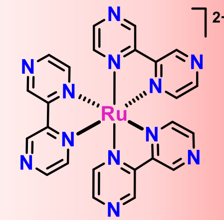
$E_{1/2}$ = 1.02 V



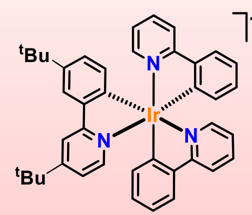
$E_{1/2}$ = 1.16 V



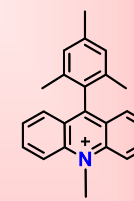
$E_{1/2}$ = 1.30 V



$E_{1/2}$ = 1.69 V



$E_{1/2}$ = 0.9 V



$E_{1/2}$ = 2.06 V

Electron acceptors

$Na_2S_2O_8$

(Potentials vs SCE)

J.I. Goldsmith, W.R. Hudson, M. S. Lowry, *et al.*, *J. Am. Chem. Soc.*, **2005**, 127, 7502; F. Gärtner, A. Boddien, E. Barsch, *et al., Chem. Eur. J.,* **2011**, 17, 6425; ; F. Gärtner, D. Cozzula, S. Losse, *et al., Chem. Eur. J.,* **2011**, 17, 6998; P. Kurz, B. Probst, B. Spingler, R. Alberto, *Eur. J. Inorg. Chem.*, **2006**, 2966; B. Probst, C. Kolano, P. Hamm, R. Alberto, *Inorg. Chem.*, **2009**, 48, 1836; B. Probst, A. Rodenberg, M. Guttentag, *et al.*, *Inorg. Chem.*, **2010**, 49, 6453; P. Du, J. Schneider, P. Jarosz, R. Eisenberg, *J. Am. Chem. Soc.,* **2006**, 128, 7726; J. Zhang, P. Du, J. Schneider, P. Jarosz, R. Eisenberg, *J. Am. Chem. Soc.,* **2007**, 129, 7726; P. Du, J. Schneider, F. Li, W. Zhao, *et al.*, *J. Am. Chem. Soc.,* **2008**, 130, 5056; T. Lazarides, T. McCormick, P. Du, G. Luo, *et al., J. Am. Chem. Soc.,* **2009**, 131, 9192; T. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, *et al.*, *J. Am. Chem. Soc.,* **2010**, 132, 15480; A. Fihri, V. Artero, A. Pereira, M. Fontecave, *Dalton Trans*, **2008**, 5567; S. P. Luo, E. Mejia, A. Friedrich, A. Pazidis, *et al.*, *Angew. Chem. Int. Ed*., **2013**, 52, 419.

Photochemistry:

Photosensitizer: $Ru(bpy)_3^{2+}$, $Ir(ppy)_2(bpy)$, $Cu(phen)_2$, Organic dyes….
Electron aceptors: Na_2S_2O ; Electron donors: Ascorbic acid, TEOA, terciary amines, etc..

Photocatalysis: Structure – Activity relationships, quantum yield, yield, TON and TOF.

Kinetics: Reaction order respect of the catalyst and the oxidant. TAS.

Spectroscopy: Paramagnetic species. Identification of key intermediates in catalysis. Characterization similar to chemical oxidants, but less accessibility to combination of light + spectroscopy and lower control over the reaction. Fluorescence (Life time). F. quenching experiments (reactivity)

***In situ* spectroscopy:** Under catalytic conditions: TAS (UV-Vis, EPR, etc…)

Labelling studies: Similar to Chemical Agents. Mechanism information. Kinetic Isotopic Effects.

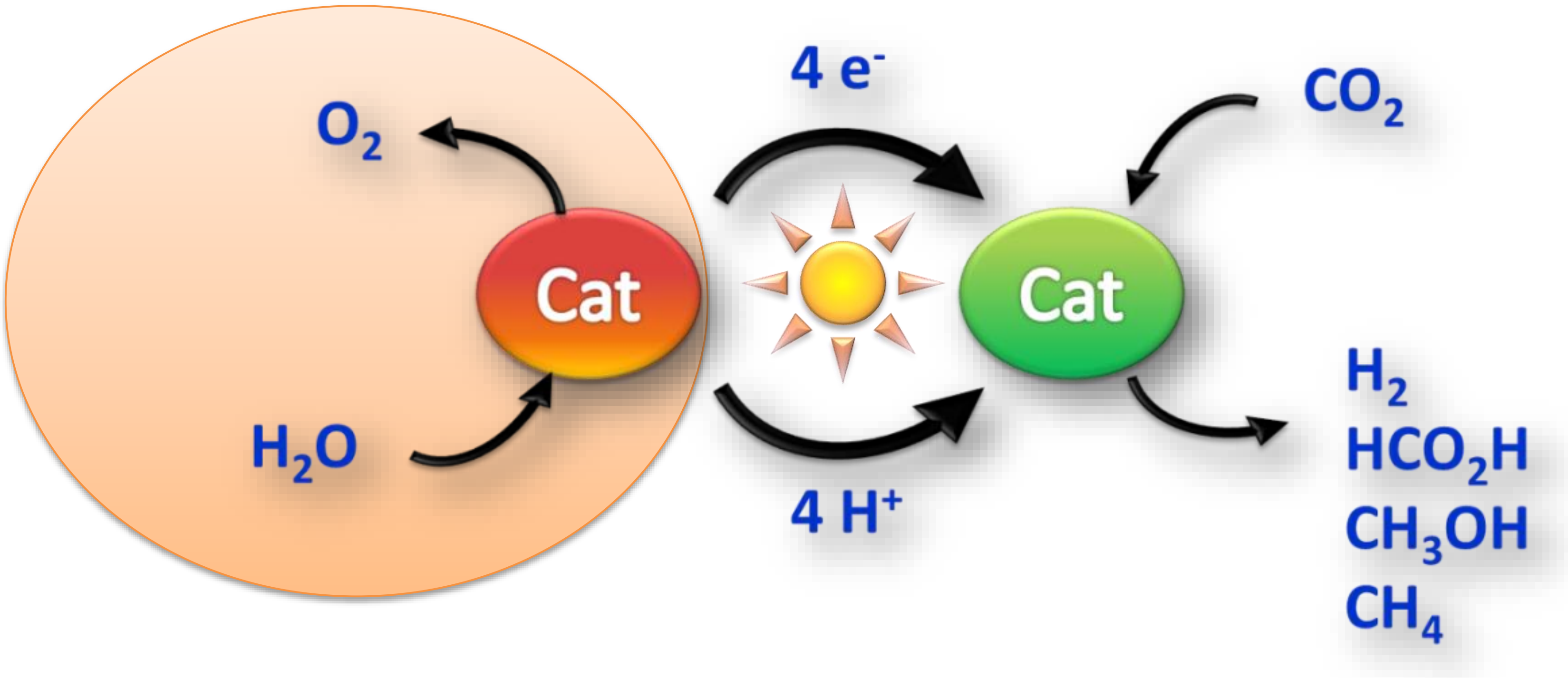
Catalytic Phase: heterogeneous versus homogeneous: DLS, NTA, TEM, kinetics (inductions times, reaction orders). Relation structure activity. Labelling studies at the ligand …..

Outline of the tutorial

- **Introduction**
  - The energy challenge (Technological perspective)
- **Artificial Photosynthesis, Water Splitting**
  - Natural and Artificial Photosynthesis
  - Research Tools
  - **Water Oxidation**
  - Water Reduction
  - CO_2 Reduction
- **Towards Solar Chemicals**
  - Examples of oxidation and reduction reactions

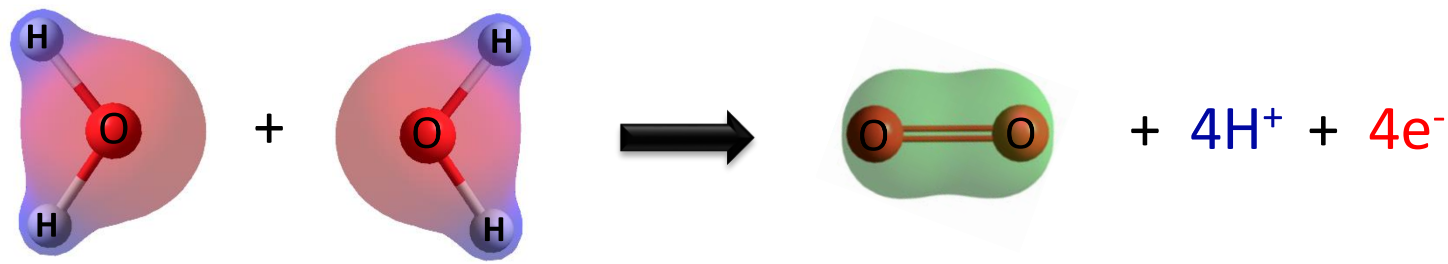
➢ *Artificial photosynthetic systems*

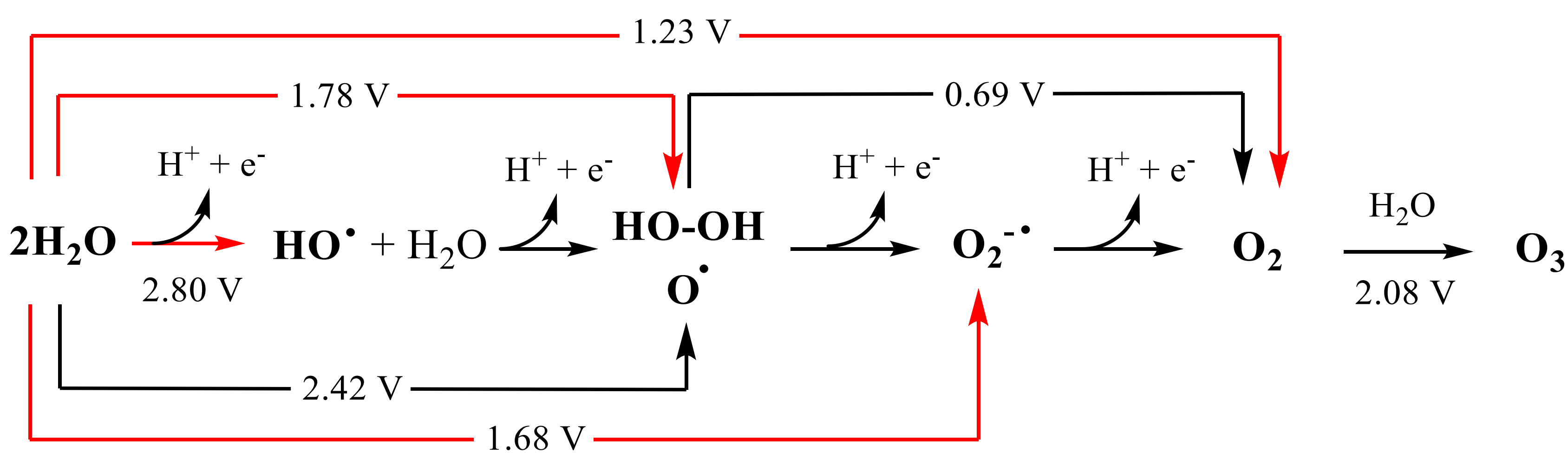
Energy in chemical bonds



- **Water Oxidation** is considered as the bottleneck of water splitting

Water Oxidation fundamental requirements





Potential diagram for the water molecule

Needs to be catalyzed

Artificial Photosynthesis

Crabtree, Brudvig, Dismukes

Bernhard Lloret & Costas

Gupta & Dhar

Hill Nocera

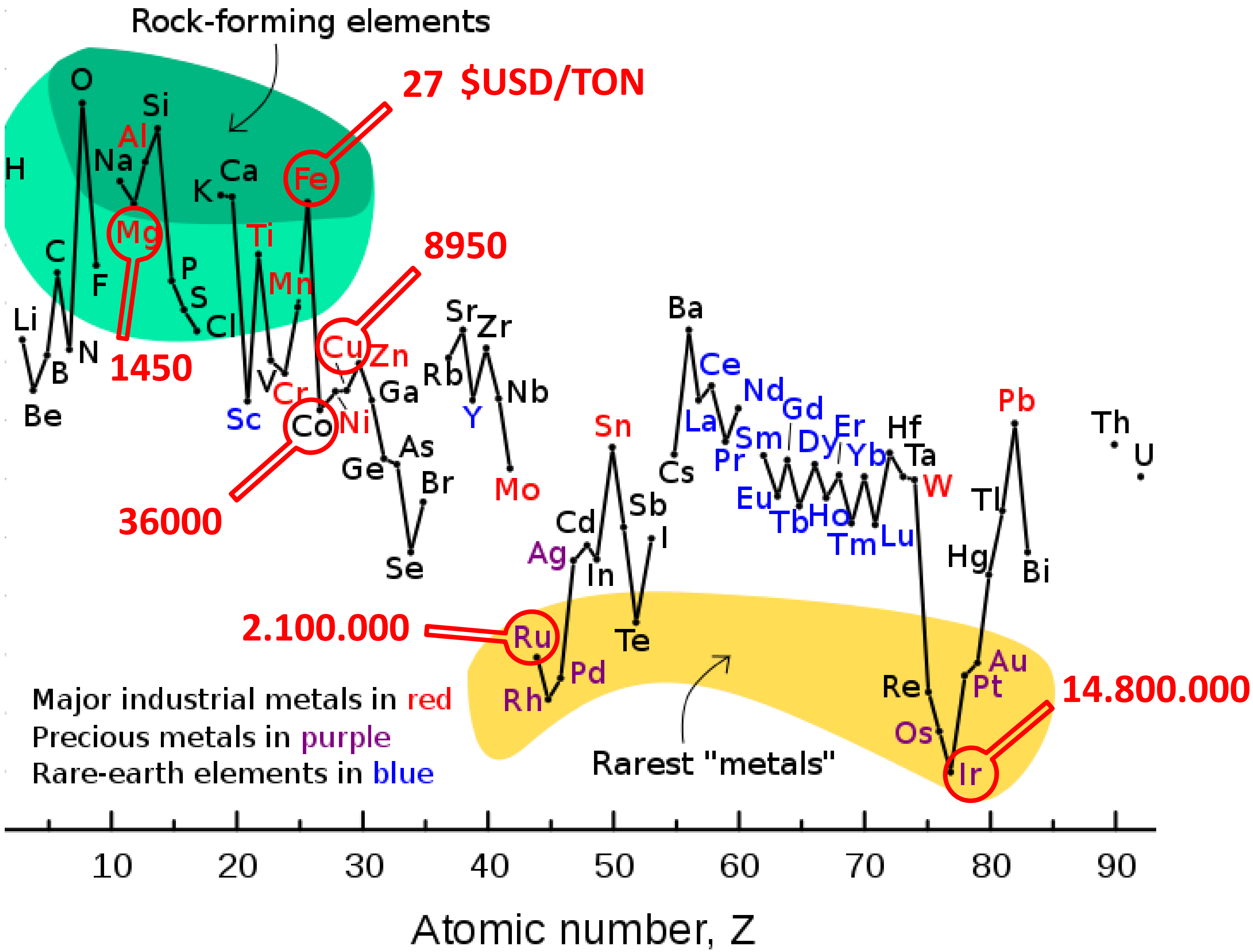
Hill

Meyer Mayer Llobet

21 Sc 44.9559 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	**25 Mn 54.938 Manganese**	**26 Fe 55.845 Iron**	**27 Co 58.9332 Cobalt**	**28 Ni 58.6934 Nickel**	**29 Cu 63.546 Copper**	30 Zn 65.4089 Zinc
39 Y 88.9058 Yitrium	40 Zr 91.224 Zirconium	41 Nb 92.9064 Niobium	42 Mo 85.94 Molybdenum	43 Tc 98 Technetium	**44 Ru 101.07 Ruthenium**	45 Rh 102.9055 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium
71 Lu 174.967 Lutetium	72 Hf 178.49 Hafnium	73 Ta 180.9497 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	**77 Ir 192.217 Iridium**	78 Pt 195.084 Platinum	79 Au 196.9666 Gold	80 Hg 200.59 Mercury

Meyer, Sun, Llobet, Thummel

Bernhard, Albretch Crabtree, Brudvig, Beller Machioni



Rock-forming elements
27 $USD/TON
8950
1450
36000
2.100.000
14.800.000
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
Major industrial metals in red
Precious metals in purple
Rare-earth elements in blue
Rarest "metals"
10
20
30
40
50
60
70
80
90
Atomic number, Z

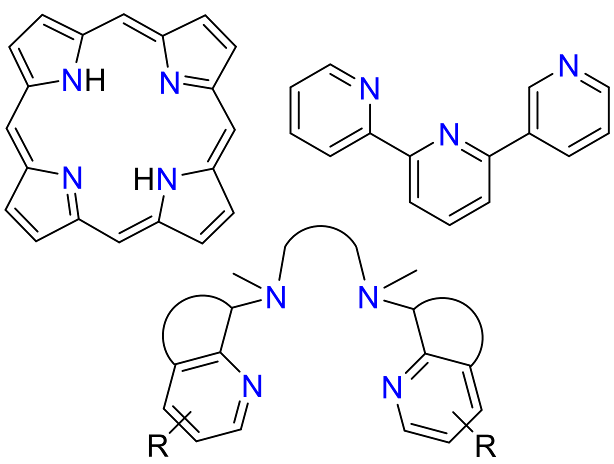
a) Stabilization of High Oxidation States

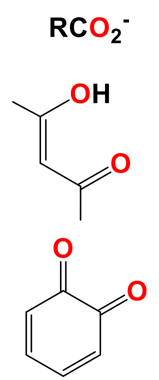
Basic and strong chelating multidentante ligands: N-ligands, anions.

N donor ligands: Amino-pyridine ligands, porphyrinic ligands, amidates

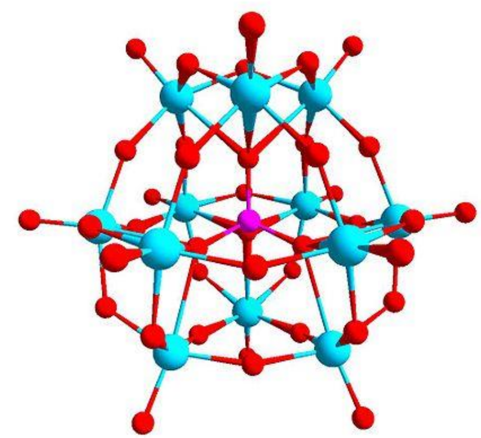
O donor ligands: Carboxylates, “alcohols”, acetyl acetonates, ortho quinones…

Polyoxometalates (POM): Is a transition metal polyoxoanion. Usually, the metal ions are group 5 or 6 in high oxidation state. TM = V(V), Nb(V), Ta(V), Mo(IV) and W(IV). Additional heteroatoms such as Si, P Se or Ge are presence in the core.





o-benzoquinone



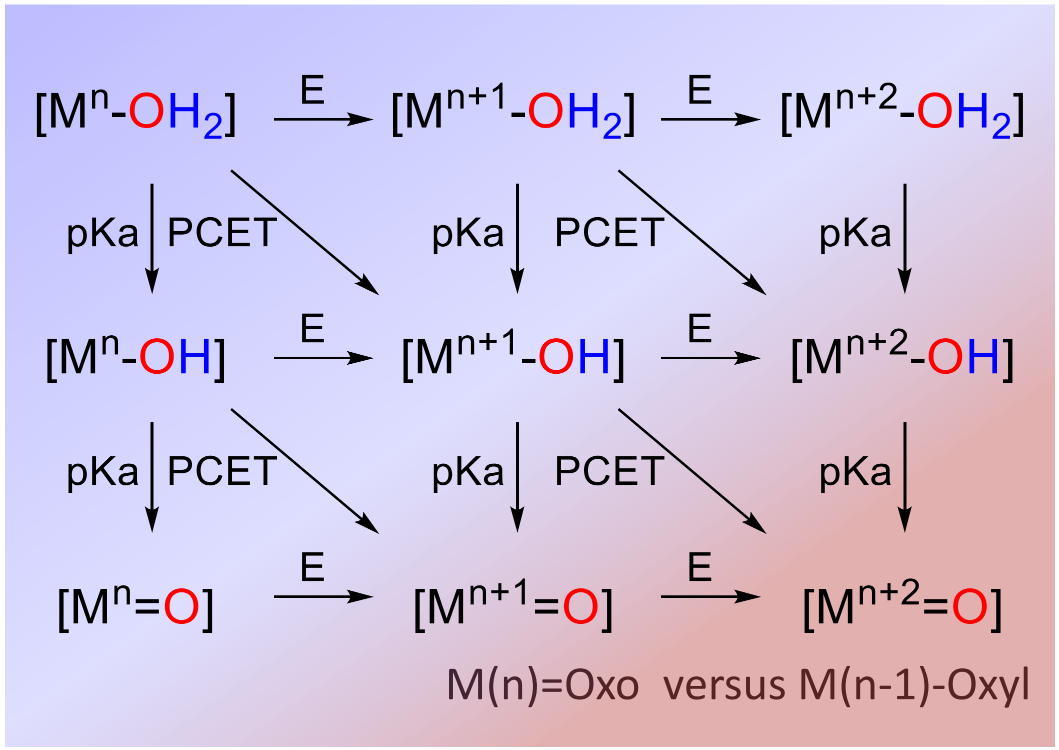
$[PW_{12}O_{40}]^{3-}$

Strategies to Improve the WOR

a) Stabilization of High Oxidation States

Basic and strong chelating multidentante ligands: N-ligands, anions.

PCET



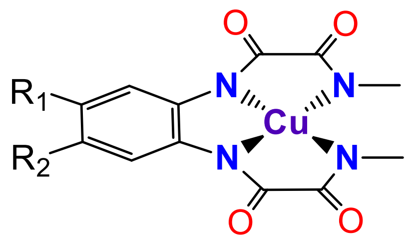
Most common oxidation states active for water oxidation

Mn(V) / Fe(V) / Co (IV) / Ni(IV) ? / Cu (III)
Ru(V) / Ir(V) ?

a) Stabilization of High Oxidation States

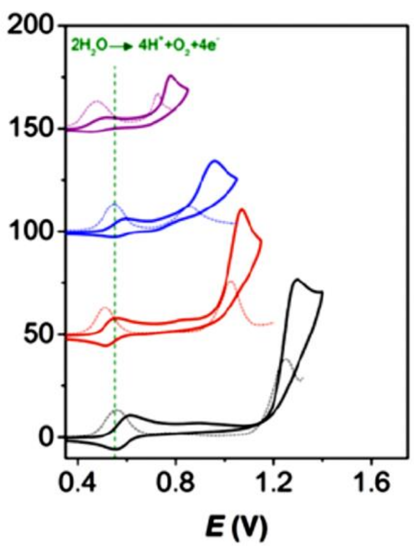
Basic and strong chelating multidentante ligands: N-ligands, anions.

Change delocalization: Non-innocent ligands. Multimetalic catalytic centers



R_1	R_2
OMe	OMe
H	OMe
Me	Me
H	H

Thermodynamic potential



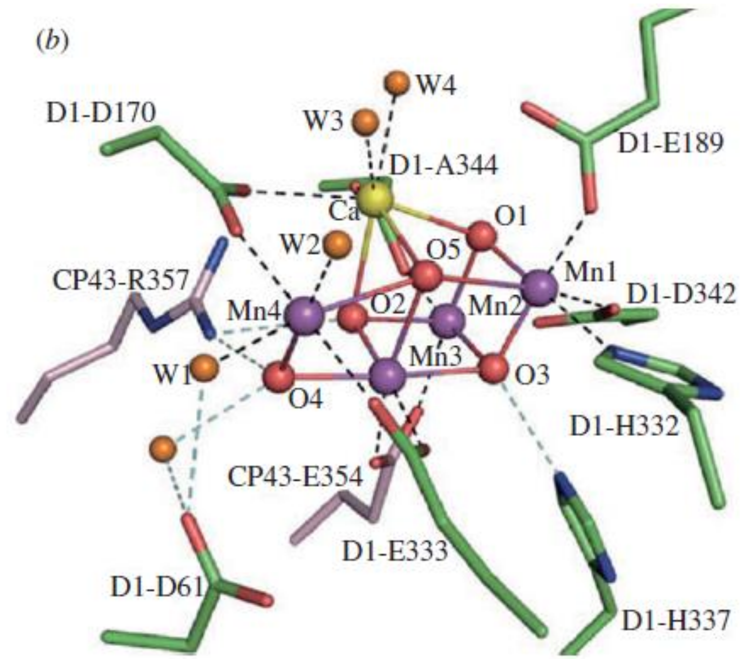


Figure 4. (*a*) Structure of the Mn_4CaO_5 cluster and (*b*) its ligand environment as determined at a resolution of 1.9 Å by Umena *et al.* [32].

J. Am. Chem. Soc., **2015**, *137*, 6758

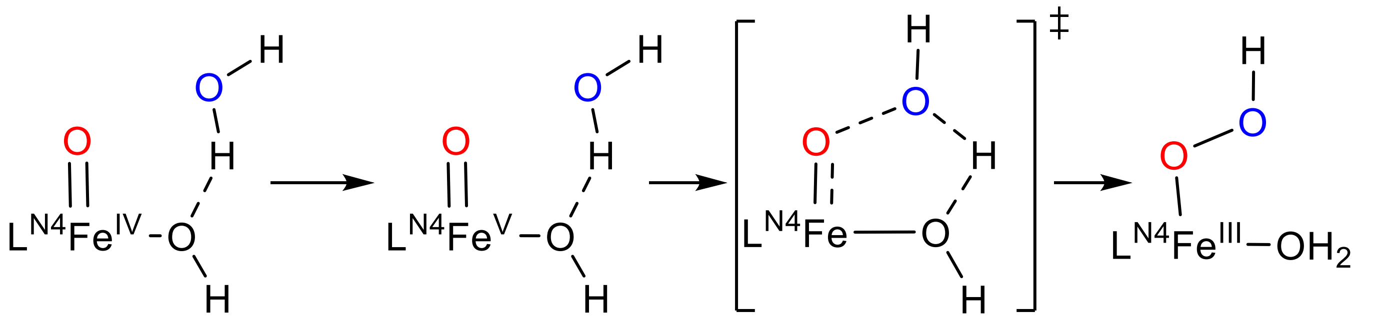
Strategies to Improve the WOR

a) Stabilization of High Oxidation States

Basic and strong chelating multidentante ligands: N-ligands, anions.

Change delocalization: Non-innocent ligands. Multimetalic catalytic centers

b) Activation of the water molecule: internal base or Lewis acid.



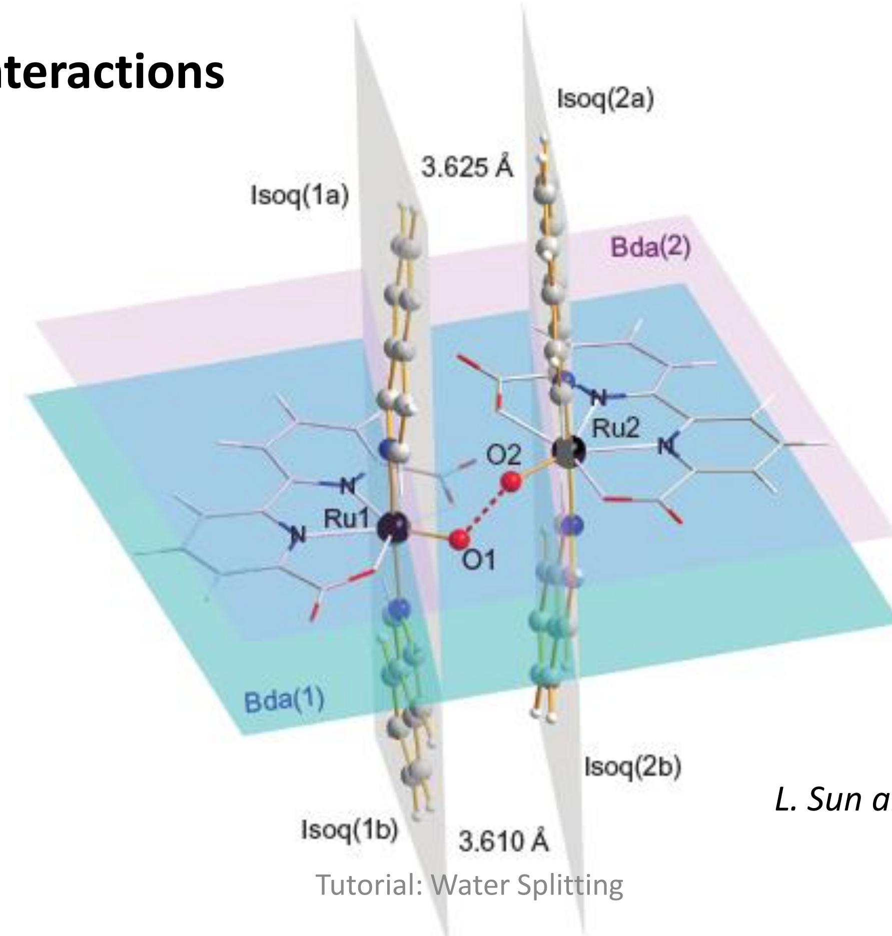
a) Stabilization of High Oxidation States

Basic and strong chelating multidentante ligands: N-ligands, anions.

Change delocalization: Non-innocent ligands. Multimetalic catalytic centers

b) Activation of the water molecule: internal base or Lewis acid.

c) Supramolecular interactions

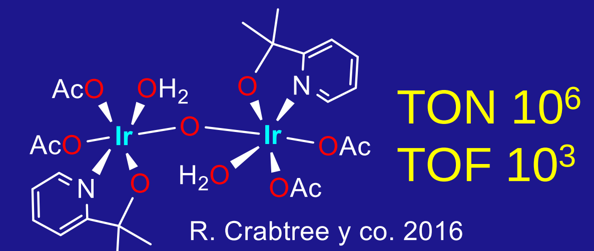


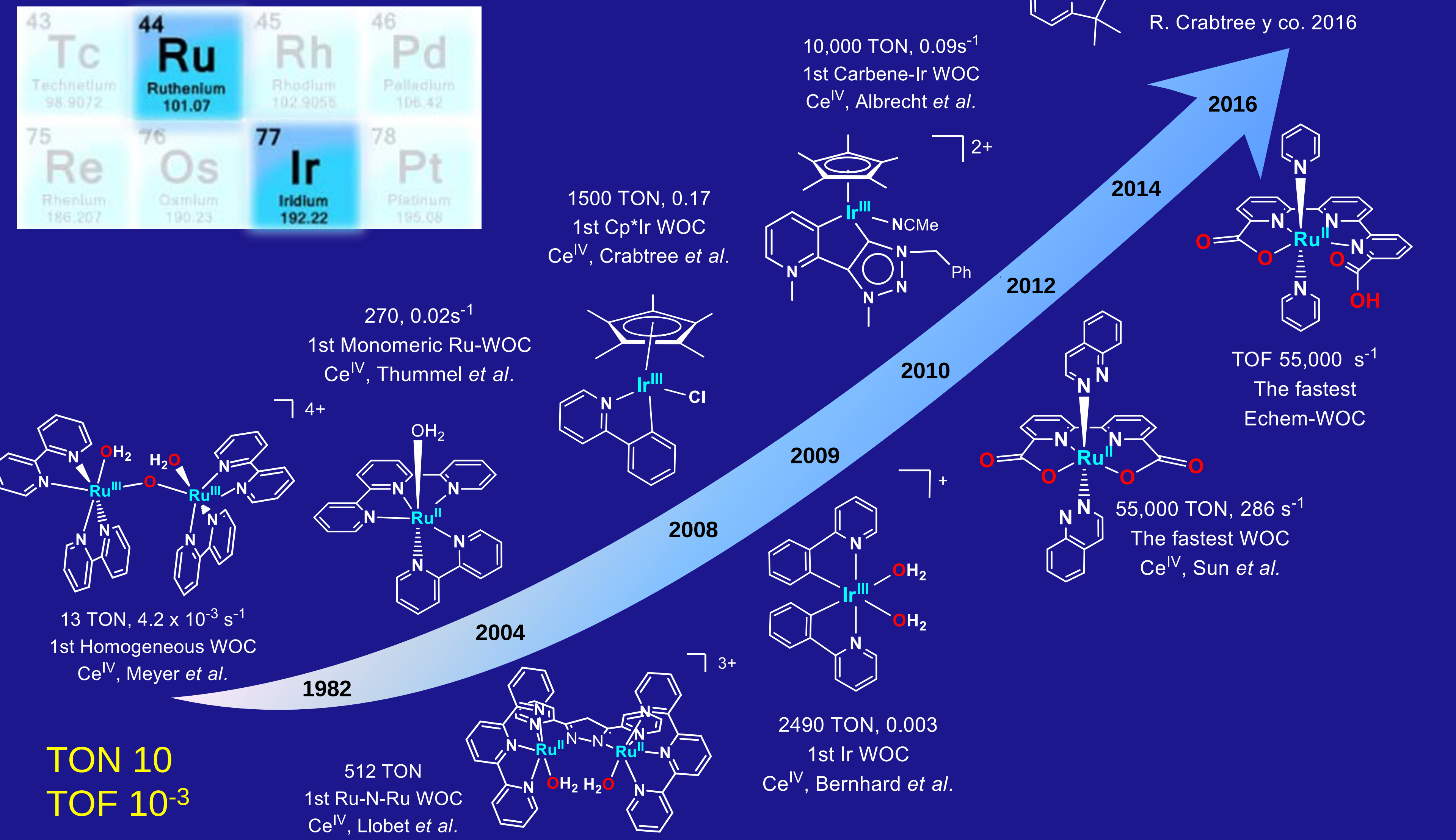
L. Sun and co. Nat Chem, **2012,** *4*, 418

Examples for Water Oxidation Catalysts

References:

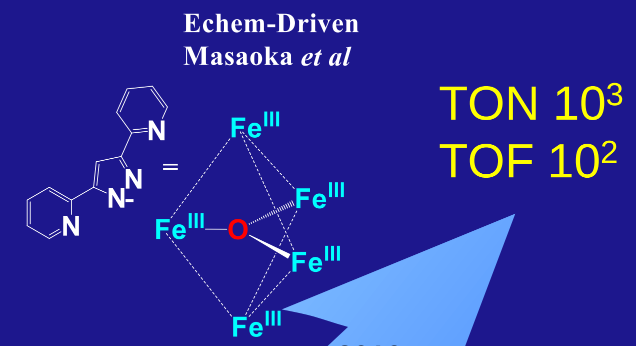
Meyer *et al. JACS*, **1982**, *104*, 4029 / Llobet *et al. JACS*, **2004**, *126*, 7798 / Thummel *et al. JACS*, **2005**, *127*, 12802 / Bernhard *et al. JACS*, **2008**, *130*, 210 / Crabtree *et al. JACS*, **2009**, *131*, 8730 / Albrecht *et al. Angew. Chem. IE*, **2010**, *49*, 9765 / Sun *et al. Angew. Chem. Int. Ed.* **2010,** *49*, 8934 and *Nat Chem*, **2012,** *4*, 418; Llobet *et al JACS* **2015**, *137*, 10786; Batista *et al. JACS* **2016**, *138*, 5511

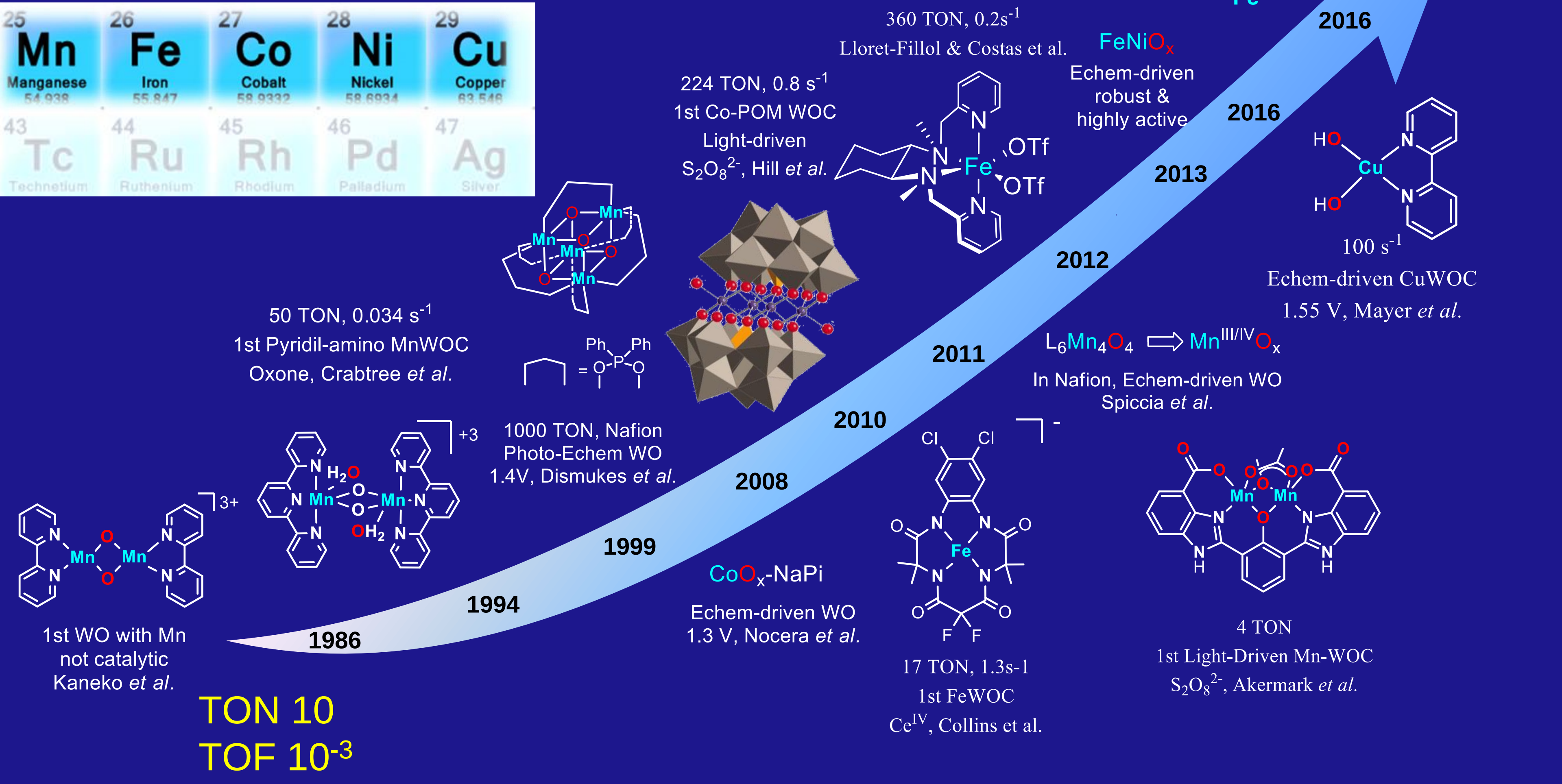




Examples for Water Oxidation Catalysts

References:
Lloret-Fillol, Costas *Coord. Chem. Rev.* **2017**, *334*, 2, Cao, Lai and Du EES **2012**, *5*, 8134-8157**;** Liu and Wang *Coord. Chem. Rev.* **2012**, *256*, 1115; D. G. Nocera *et al Science* **2008**, *321,* 1027; G. C. Dismukes *et al Acc. Chem. Res.,* **2009**, *42*, 1935; T. J. Collins, S. Bernhard *et al JACS,* **2010**, *132,* 10990; C. L. Hill *et al Science* **2010**, *328,* 342; Lloret-Fillol, Costas *Nat. Chem.* **2011**, *3*, 807; L. Spiccia *et al Nat. Chem.* **2011**, *3*, 462. J. M. Mayer *Nat. Chem.* **2012**, *4*, 498-502. Okamura, M. et *al. Nature* **2016**, *530*, 465

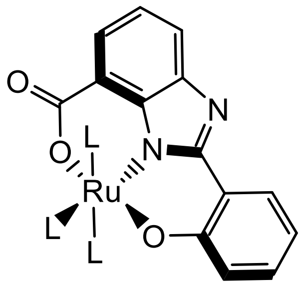


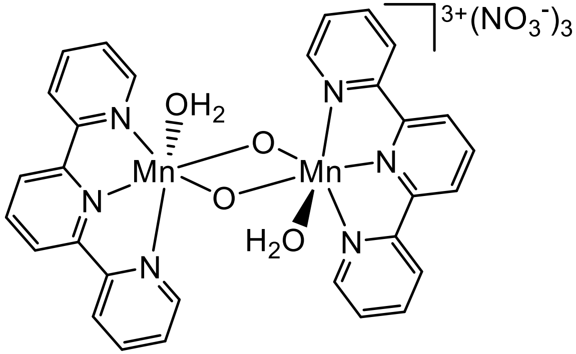


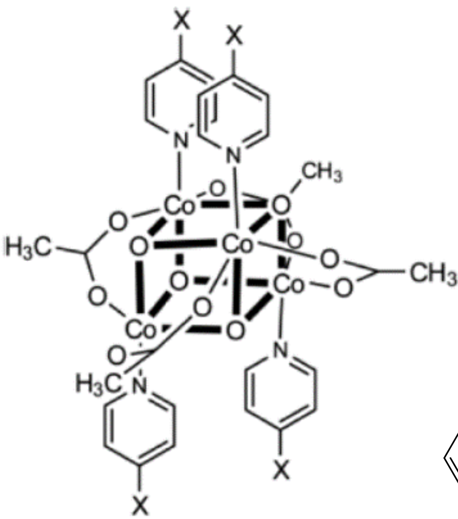
Introduction: Homogeneous vs Heterogeneous systems

It is difficult to distinguish the nature of the active species in solution

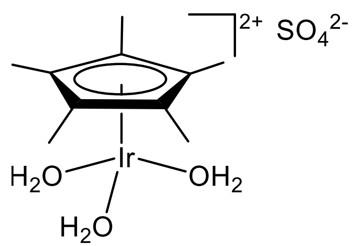
- WO molecular catalysts

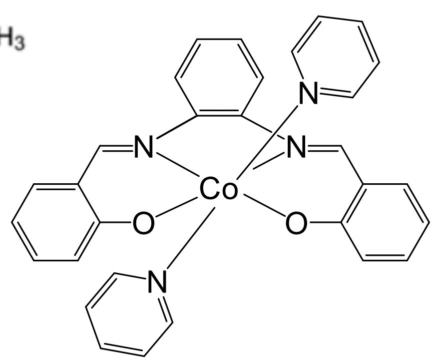






X = H , **1**
X = COOMe , **1-COOMe**



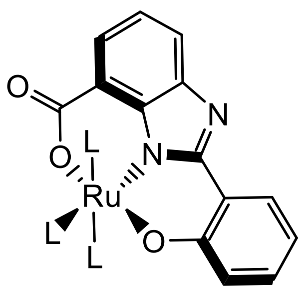


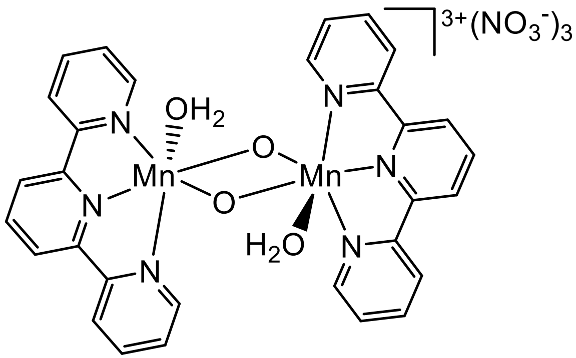
J. D. Blakemore, R. H. Crabtree, and G. W. Brudvig *Chem. Rev.* **2015**, 115, 12974; M. A. Asraf, H. A. Younus, C. I. Ezugwu, A. Mehta and F. Verpoort *Catal. Sci. Technol.*, **2016**, 6, 4271.

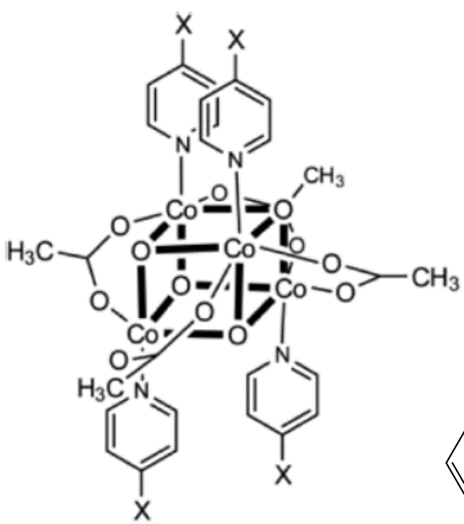
Introduction: Homogeneous vs Heterogeneous systems

It is difficult to distinguish the nature of the active species in solution

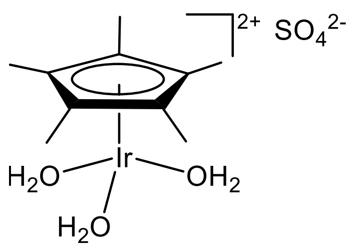
– WO molecular catalysts

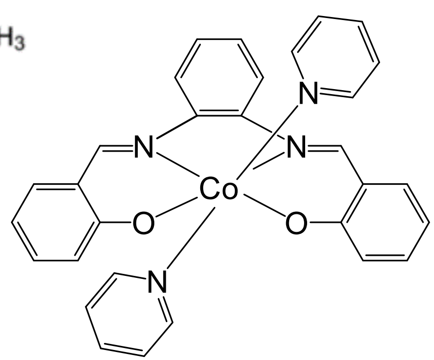






X = H , **1**
X = COOMe , **1-COOMe**





– M oxides stable at low pHs → Ru, Ir, Co, Mn …

$RuO_2 \cdot 2H_2O$

MnO_2 } colloids

$IrO_2 \cdot xH_2O$ and Ir

RuO_2, IrO_2, Co_3O_4, $NiCo_2O_4$, Mn_2O_3

✓ Photocatalytic and chemical WO

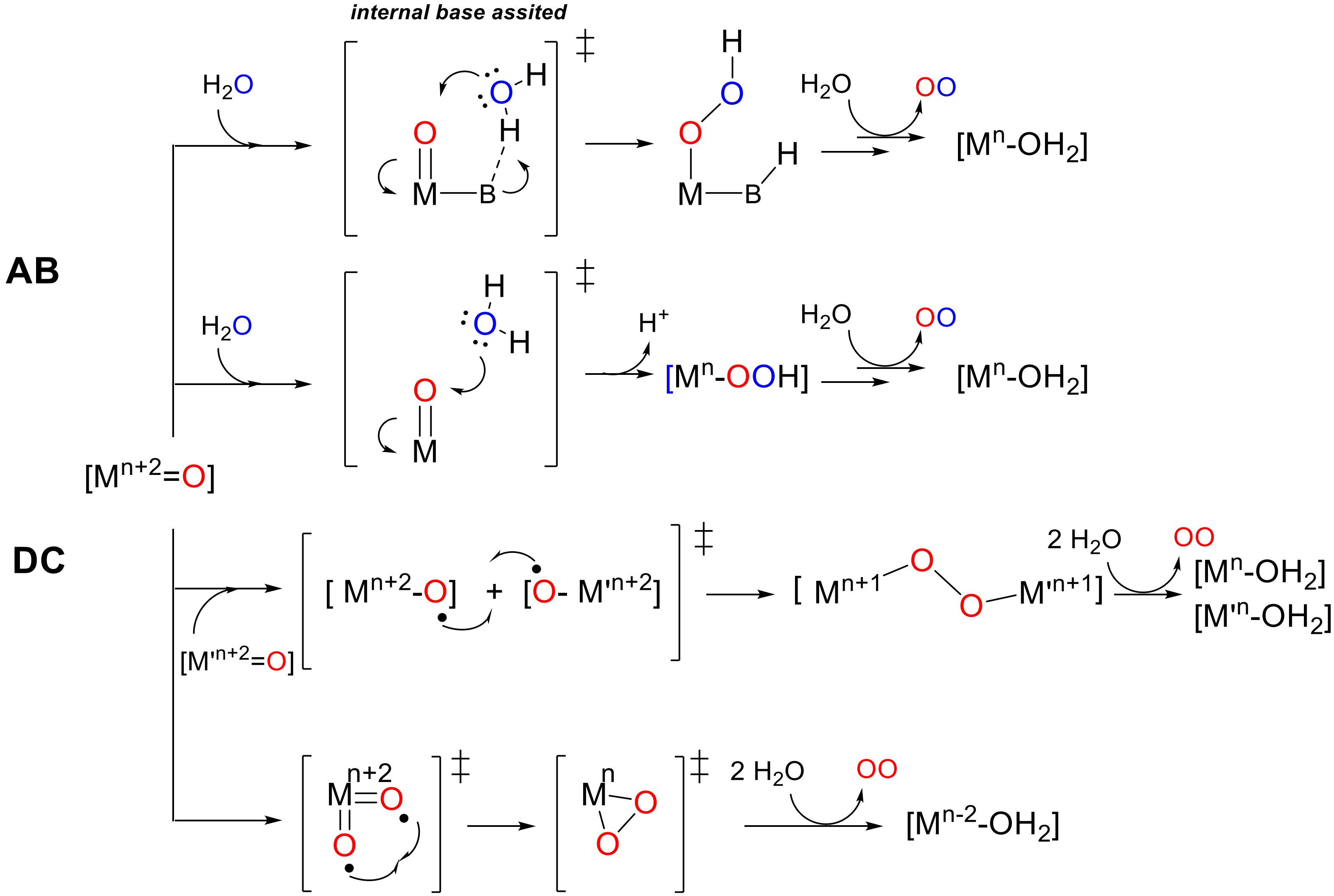
$NiFeAlO_4$, $NiFeGaO_4$, $NiFeCrO_4$, Co_3O_4

✓ Electrochemical WO

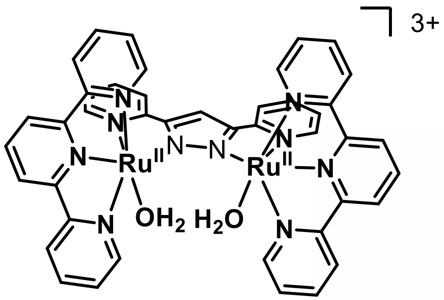
J. D. Blakemore, R. H. Crabtree, and G. W. Brudvig *Chem. Rev.* **2015**, 115, 12974; M. A. Asraf, H. A. Younus, C. I. Ezugwu, A. Mehta and F. Verpoort *Catal. Sci. Technol.*, **2016**, 6, 4271.

Water Oxidation Mechanism

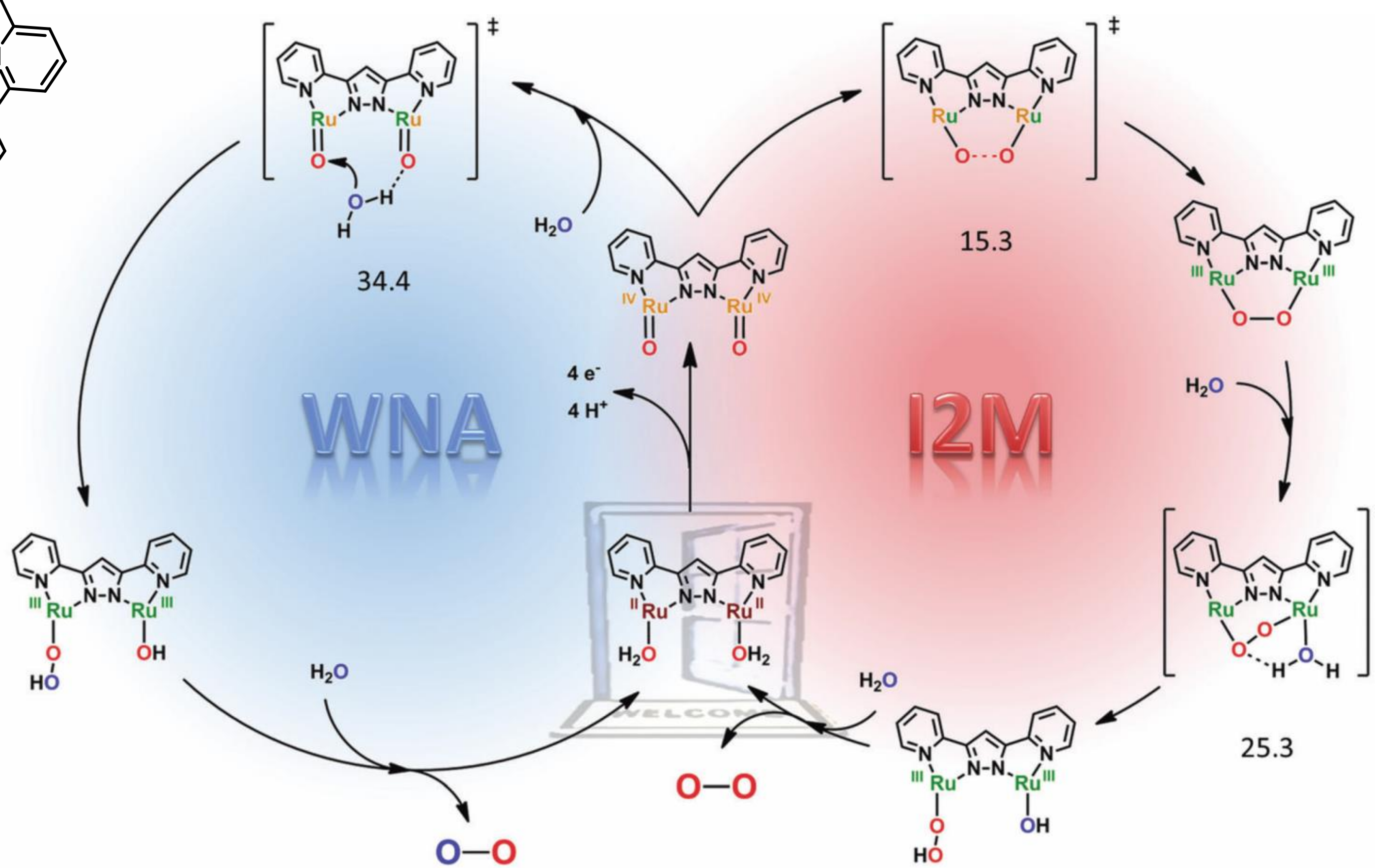
Mechanistic proposals for the O-O bond formation in the Acid based and direct coupling water oxidation.



Water Oxidation Mechanism



512 TON
1st Ru-N-Ru WOC
Ce^{IV}, Llobet *et al.*



J. Am. Chem. Soc., **2008**, *130*, 16231

Proc. Natl. Acad. Sci. U. S. A., **2015**, *112*, 4935

Background

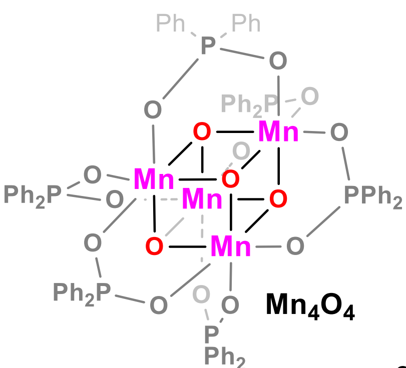
Molecular complexes

- Mechanistic understanding
- Catalyst design

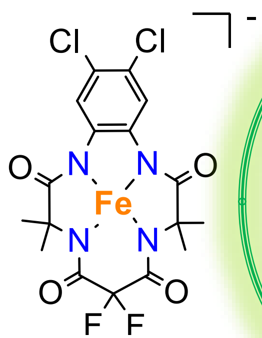
Iron

- Beyond the state of the art
- Biocompatible
- Earth abundant

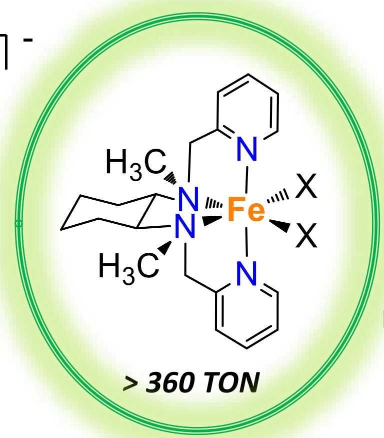
5	6	7	8	9	10	11
23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55
41 Nb niobium 92.91	42 Mo molybdenum 95.96(2)	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9
73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0



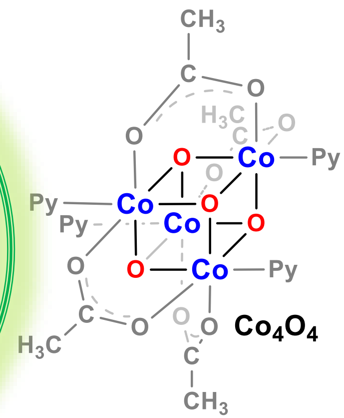
Mn_4O_4 Nafion
Dismukes, Spiccia,
G. F. Swiegers *et al*



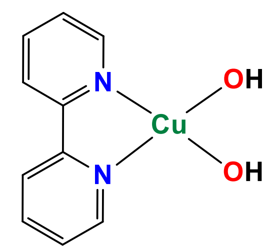
Collins , Bernhard *et al*
16 TON



Molecular iron Catalysts



Molecular Co_4O_4
M. Brochio, G. Hill, D.
Nocera, C. Dismukes .....



Cu-OH

Copper Cu
J. Mayer *et al.*
≈ 100 TON/s
~30 TON

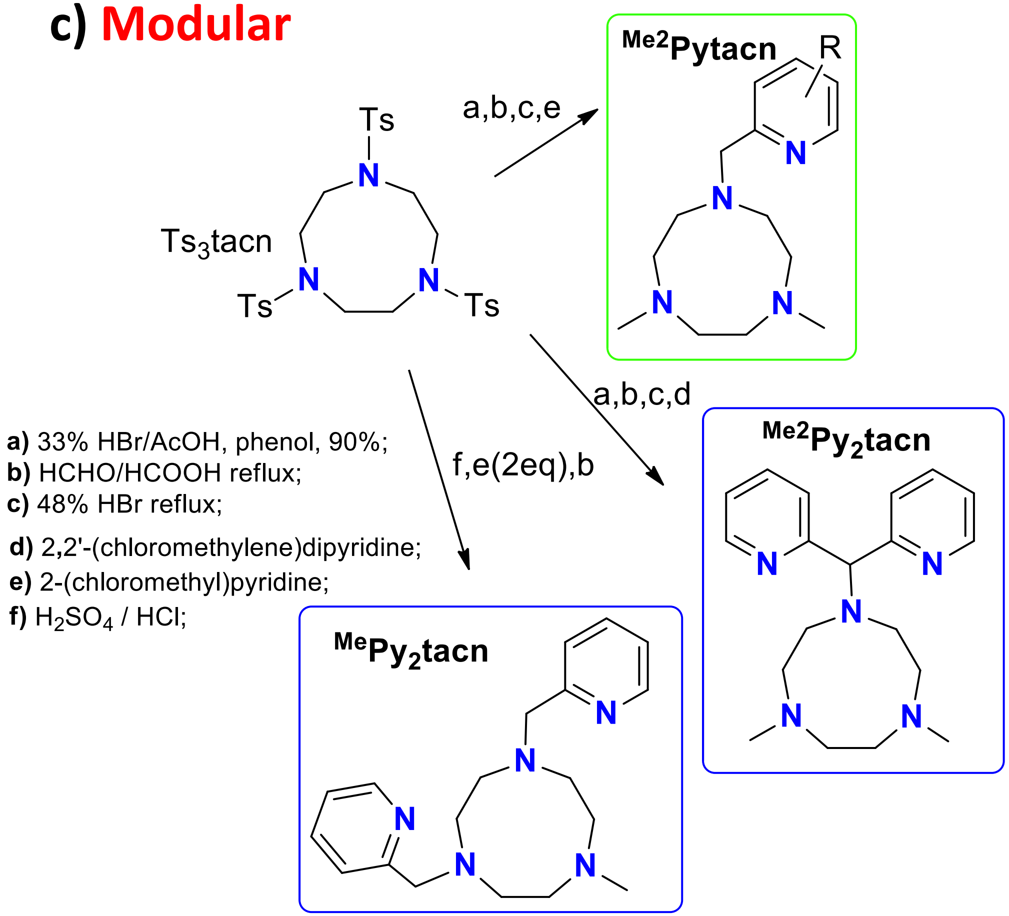
Selected References: Cao, Lai and Du EES **2012**, *5*, 8134-8157**;** Liu and Wang *Coord. Chem. Rev.* **2012**, *256*, 1115; Bonnet et al. *Coord. Chem. Rev.* **2012**, *256*, 1451; A. Sartorel, F. Scandola, S. Campagna *et al JACS* **2012**, *134*, 11104; D. G. Nocera *et al Science* **2008**, *321*, 1027; Llobet *et al Angew. Chem. IE.*, **2009**, *48*, 2842; G. C. Dismukes *et al Acc. Chem. Res.*, **2009**, *42*, 1935; T. J. Collins, S. Bernhard *et al JACS,* **2010**, *132,* 10990; C. L. Hill *et al Science* **2010**, *328,* 342; L. Spiccia *et al Nat. Chem.* **2011**, *3*, 462. J. M. Mayer *Nat. Chem.* **2012**, *4*, 498-502

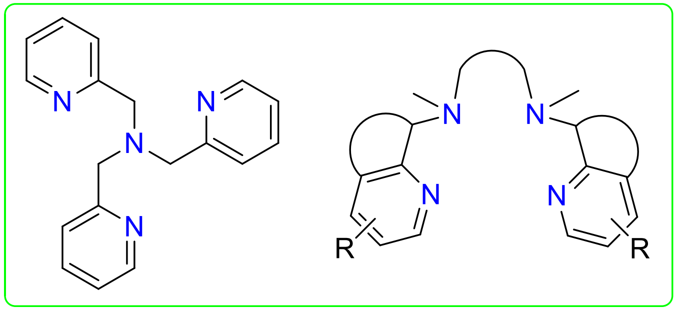
Homogeneous Water Oxidation Catalysts Based on First Row Transition Metals

a) Strongly Chelating and Robust Ligands

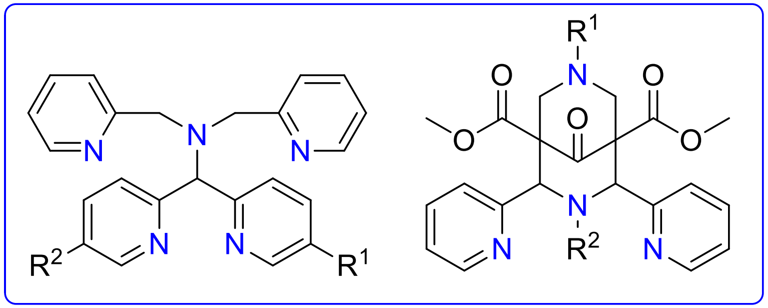
b) Stabilization of High Oxidation States

c) Modular



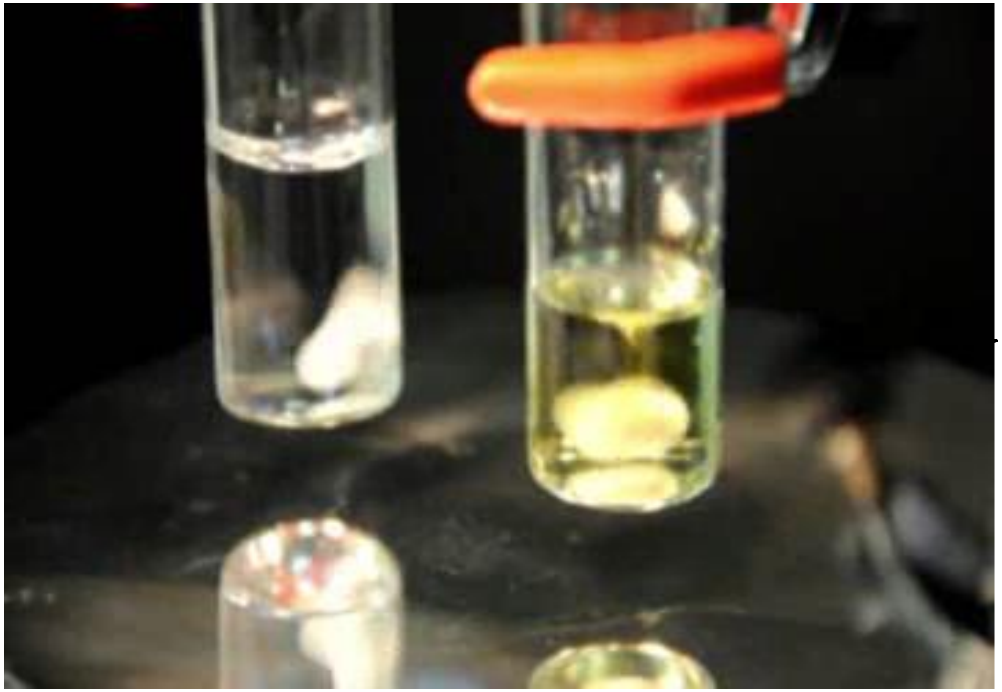


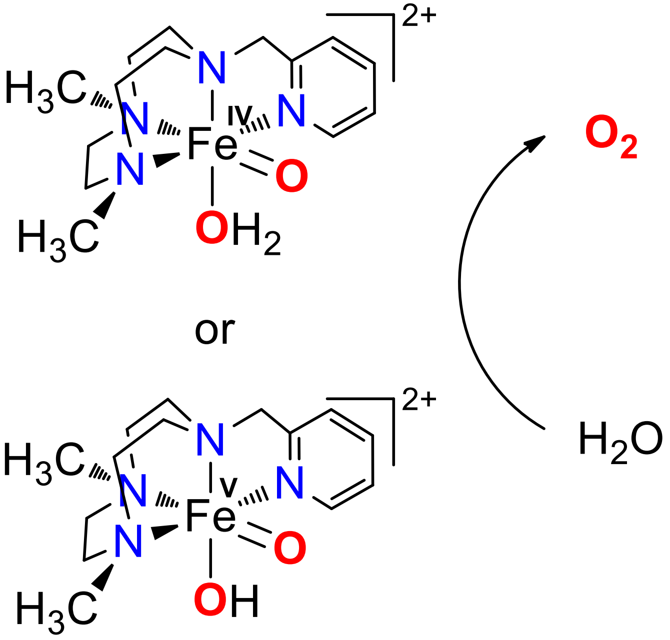
Among many other



b) Stabilization of High Oxidation States

Model system





Oxidant: **Cerium (IV) amonium nitrate (CAN), $NaIO_4$…**

C. A. Grapperhaus, B. Mienert, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 5306-5317

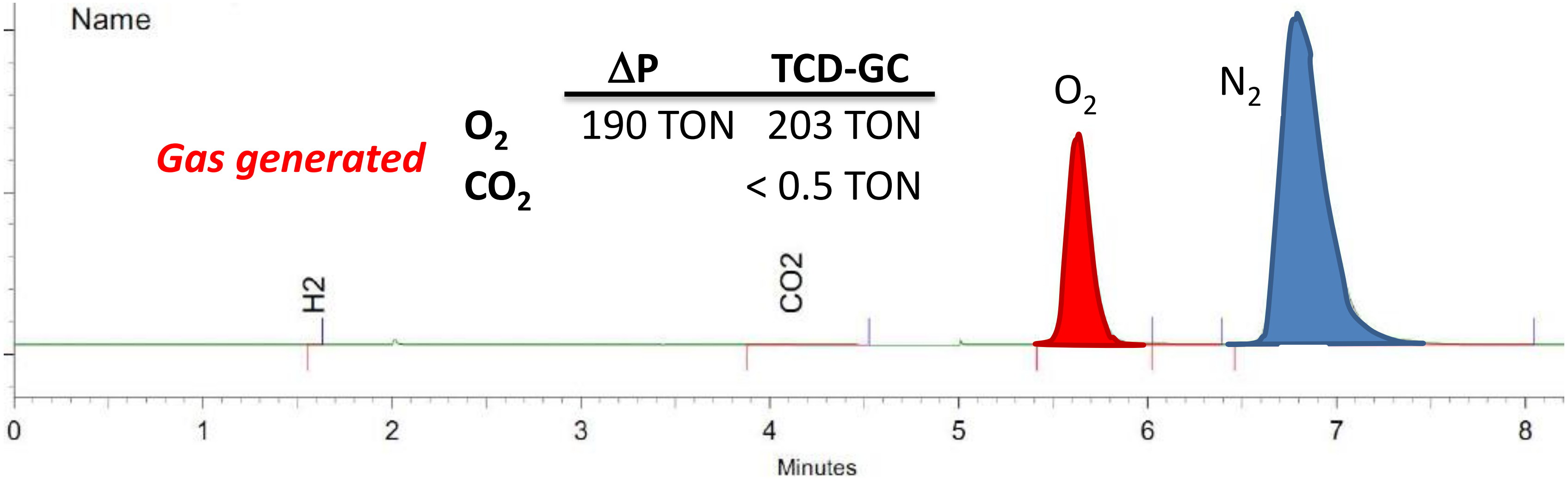
J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam, L. Que, *Science* **2003**, *299*, 1037-1039.

A. Thibon, J. England, M. Martinho, V. G. Young, J. R. Frisch, R. Guillot, J.-J. Girerd, E. Münck, L. Que, F. Banse, *Angew. Chem. Int. Ed.* **2008**, *47*, 7064-7067

A. Company, I. Prat, J. R. Frisch, R. Mas-Ballesté, M. Güell, G. Juhász, X. Ribas, E. Münck, J. M. Luis, L. Que, M. Costas, *Chem. Eur. J.* **2011**, *17*, 1622-1634.

I. Prat, J. S. Mathieson, M. Güell, X. Ribas, J. M. Luis, L. Cronin, M. Costas, *Nat. Chem.* **2011**, *3*, 788/793.

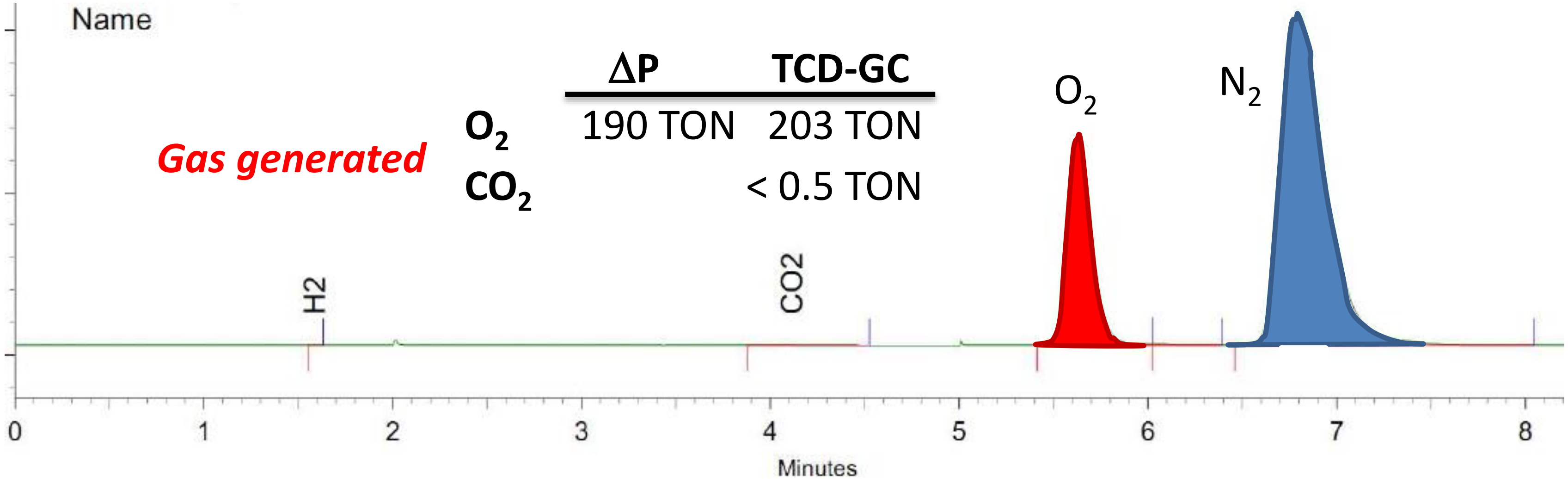
Gas evolution: (on-line pressure monitoring) / (TCD-GC) / (GC-MS)



Gas generated

	ΔP	TCD-GC
O_2	190 TON	203 TON
CO_2		< 0.5 TON

Gas evolution: (on-line pressure monitoring) / (TCD-GC) / (GC-MS)



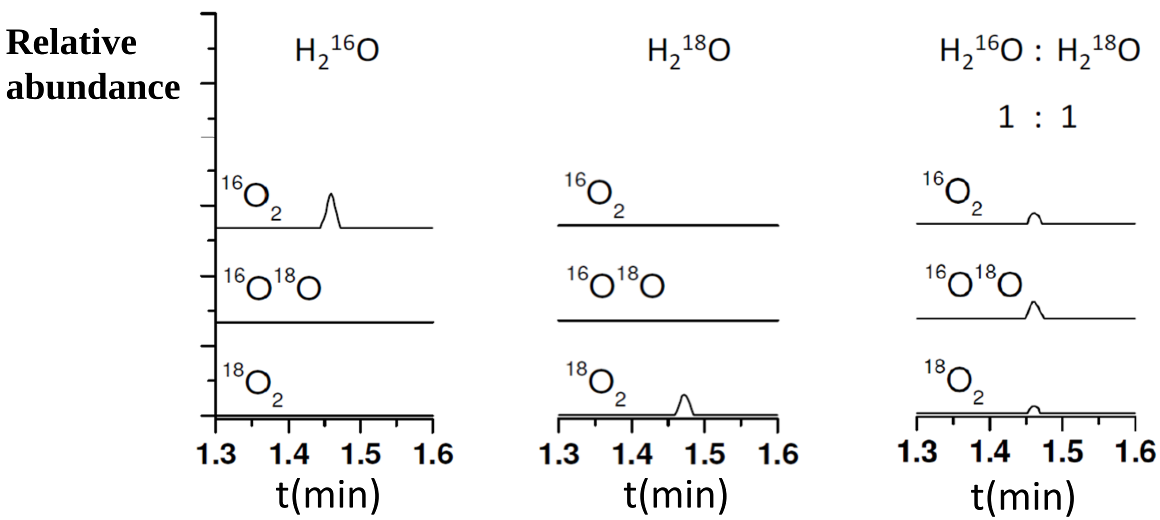
Gas generated

	ΔP	TCD-GC
O_2	190 TON	203 TON
CO_2		< 0.5 TON

Source of Oxygen: Isotopic O_2 Distribution (GC-MS)

$$\textbf{1Fe} + \text{CAN} + 50\%\ H_2{}^{18}O \rightarrow 2({}^{16}O{=}{}^{18}O) + {}^{16}O_2 + {}^{18}O_2$$

H_2O is the source of O_2



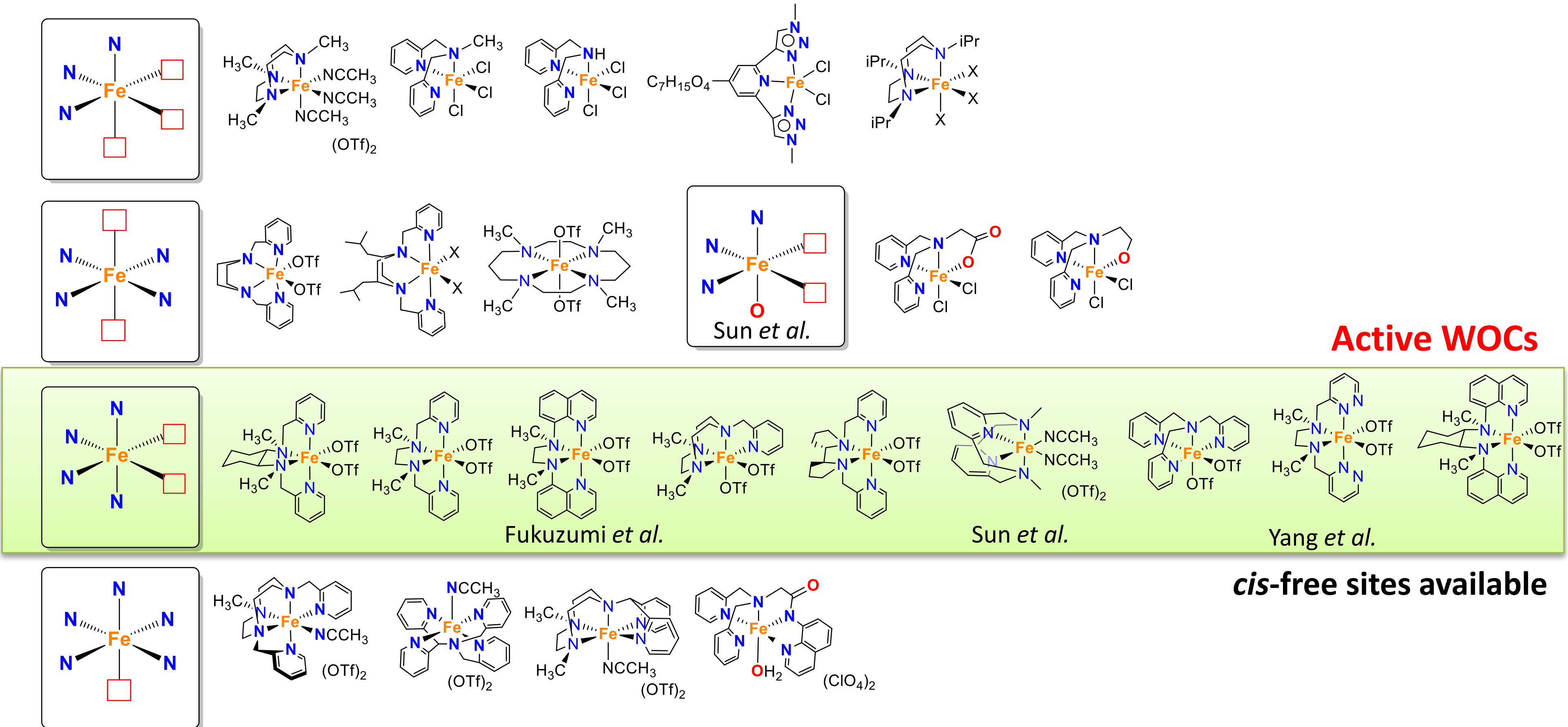
Isotopic Distribution (6% of $H_2{}^{18}O$)

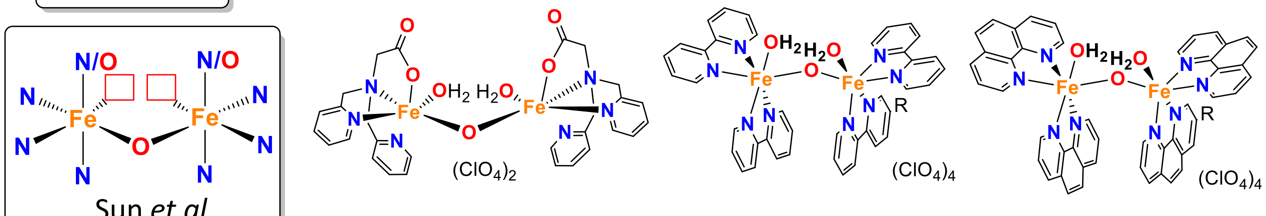
c

	Relative abundance (%)		
	${}^{16}O_2$	${}^{16}O{}^{18}O$	${}^{18}O_2$
Observed	88.40	11.23	0.37
Theoretical	88.36	11.28	0.36

Extension to selected tetra- and pentadentate iron complexes

Effect of ligand environment and coordination number

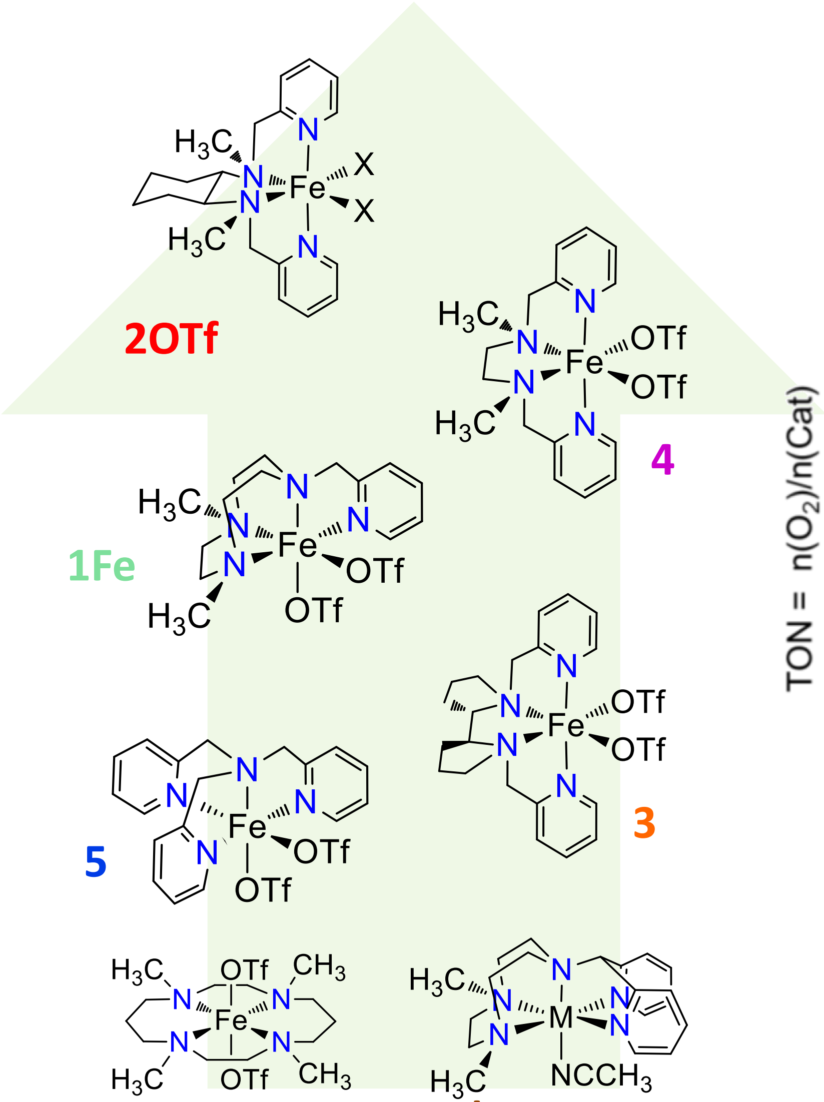




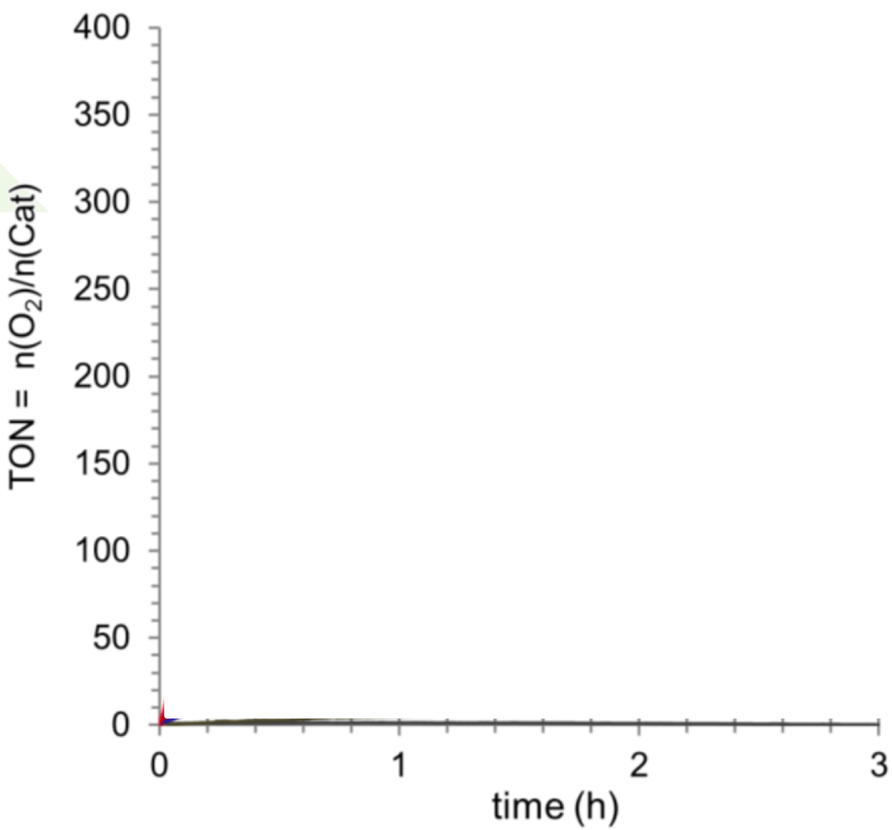
Lloret-Fillol *et al. Nat. Chem.* **2011**, 3, 807
Fukuzumi *et al. Inorg. Chem.* **2013**, 52, 9522
Yang *et al. EJIC*. 2013, 3846
Sun *et al. Asian J. Chem.* **2014**, DOI: 10.1002/asia.201400066

Extension to selected tetra- and pentadentate iron complexes

Effect of coordination environment and coordination number

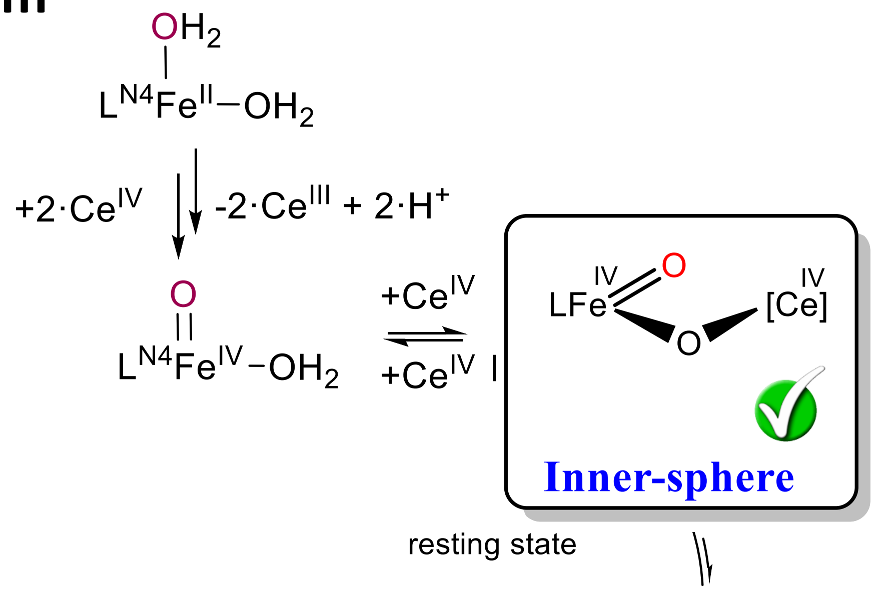


$$2\cdot H_2O \rightarrow O{=}O + 4H^+ + 4e^-$$



J. Lloret Fillol,* Z. Codolà, I. Garcia-Bosch, J. J. Pla, L. Gomez, M. Costas*
Nat. Chem. **2011**, *3*, 807 – 813.

Tentative mechanism



by kinetics

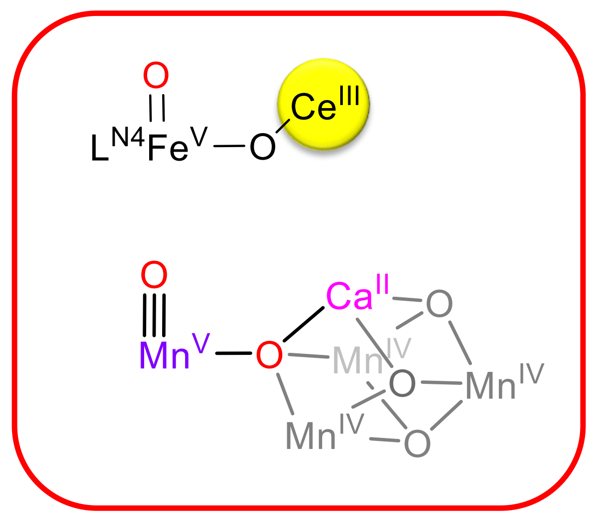
effect of [Ce(III)]

by ESI-MS (25ºC)

$LFe^{IV}O_2Ce^{IV}(NO_3)_3$

by rRaman

LFe^{IV}=O and LFe^{IV}-O-Ce



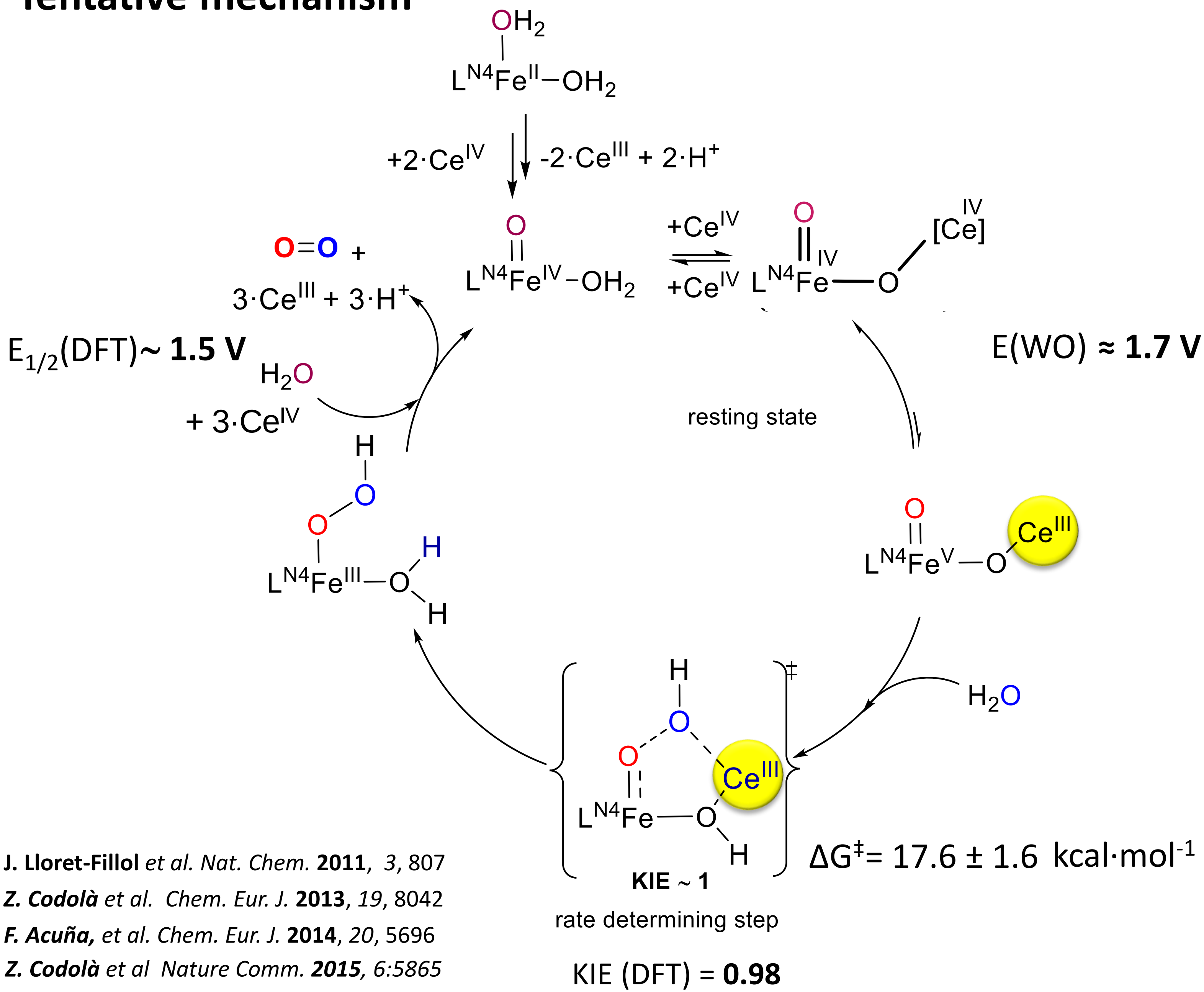
J. Lloret-Fillol *et al. Nat. Chem.* **2011**, *3*, 807

Z. Codolà *et al. Chem. Eur. J.* **2013**, *19*, 8042

F. Acuña, *et al. Chem. Eur. J.* **2014**, *20*, 5696

Z. Codolà *et al Nature Comm.* ***2015***, *6:5865*

Tentative mechanism



J. Lloret-Fillol *et al. Nat. Chem.* **2011**, *3*, 807

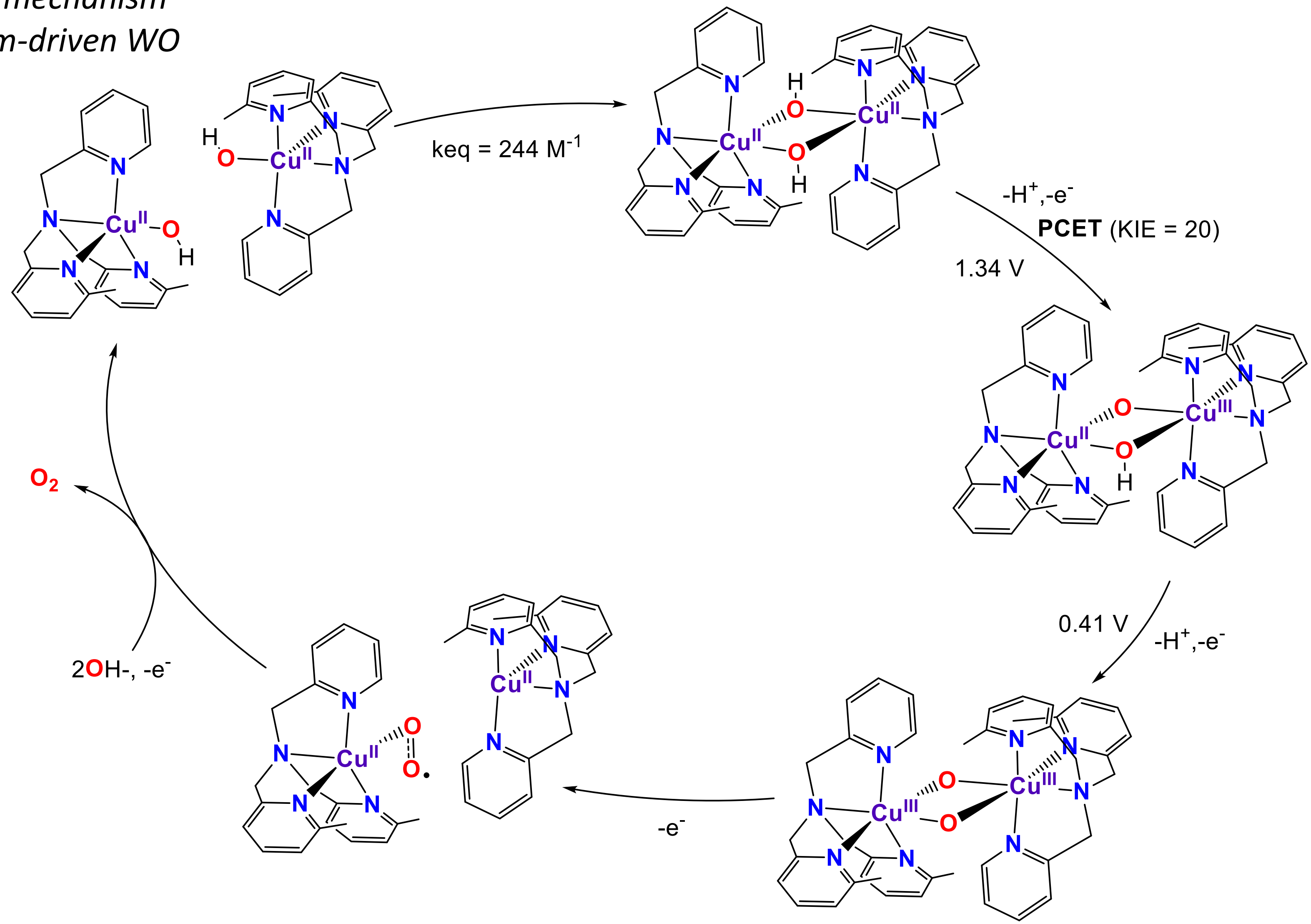
Z. Codolà *et al. Chem. Eur. J.* **2013**, *19*, 8042

F. Acuña, *et al. Chem. Eur. J.* **2014**, *20*, 5696

Z. Codolà *et al Nature Comm.* ***2015***, *6:5865*

Water Oxidation Mechanism

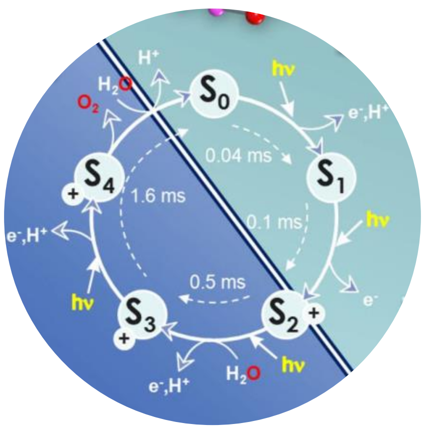
Proposed mechanism electrochem-driven WO



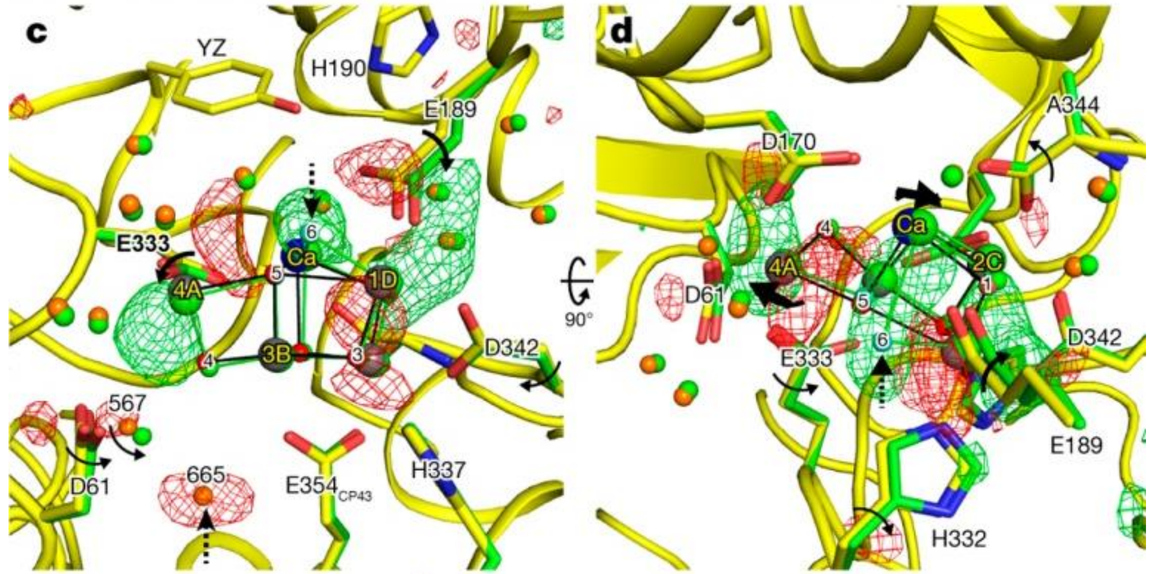
J. M. Mayer, *Nat Chem* **2012**, *4*, 498.

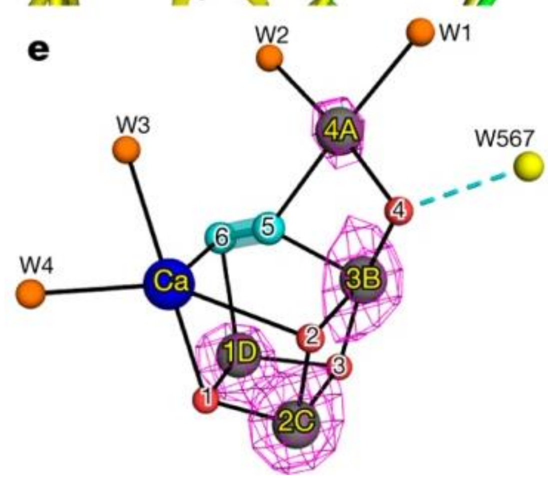
M. T. Kieber-Emmons, *JACS*, **2017**, *139*, 8586.

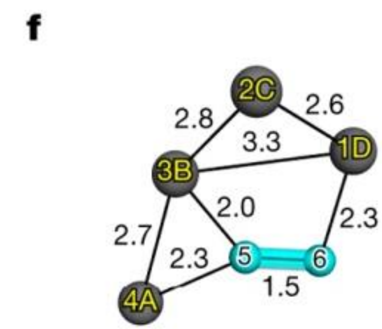
S3 state obtained after two-flash illumination at a resolution of 2.35 Å using a time-resolved femtosecond crystallography with a femtosecond X-ray free electron lasers (XFEL)



Kok cycle







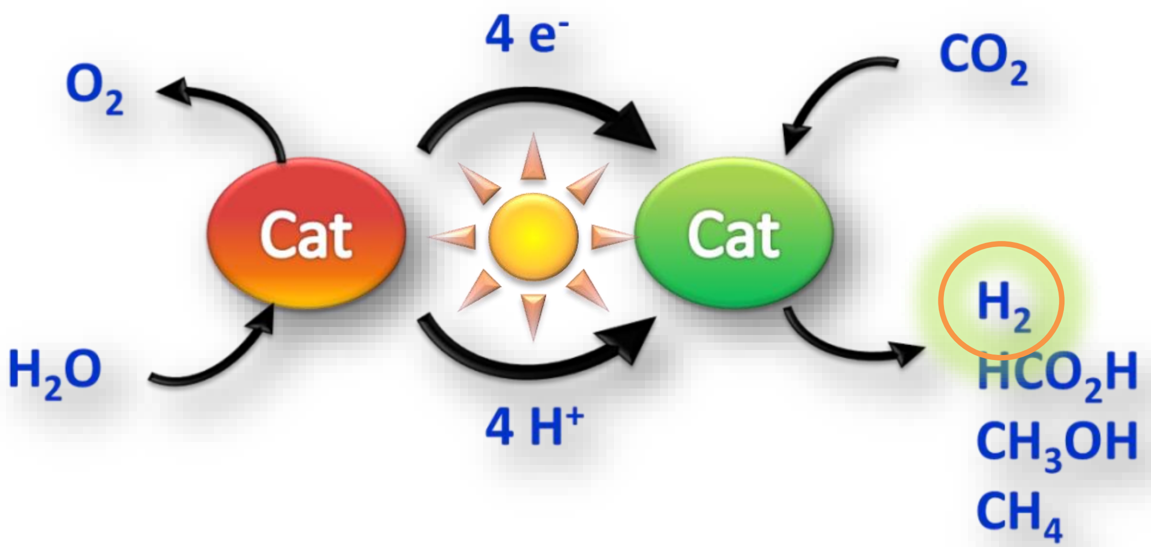
M Suga *et al.* *Nature* 1–5 (2017)
doi:10.1038/nature21400

nature

Outline of the tutorial

- **Introduction**
  - The energy challenge (Technological perspective)
- **Artificial Photosynthesis, Water Splitting**
  - Natural and Artificial Photosynthesis
  - Research Tools
  - Water Oxidation
  - **Water Reduction**
  - CO_2 Reduction
- **Towards Solar Chemicals**
  - Examples of oxidation and reduction reactions

Water Reduction



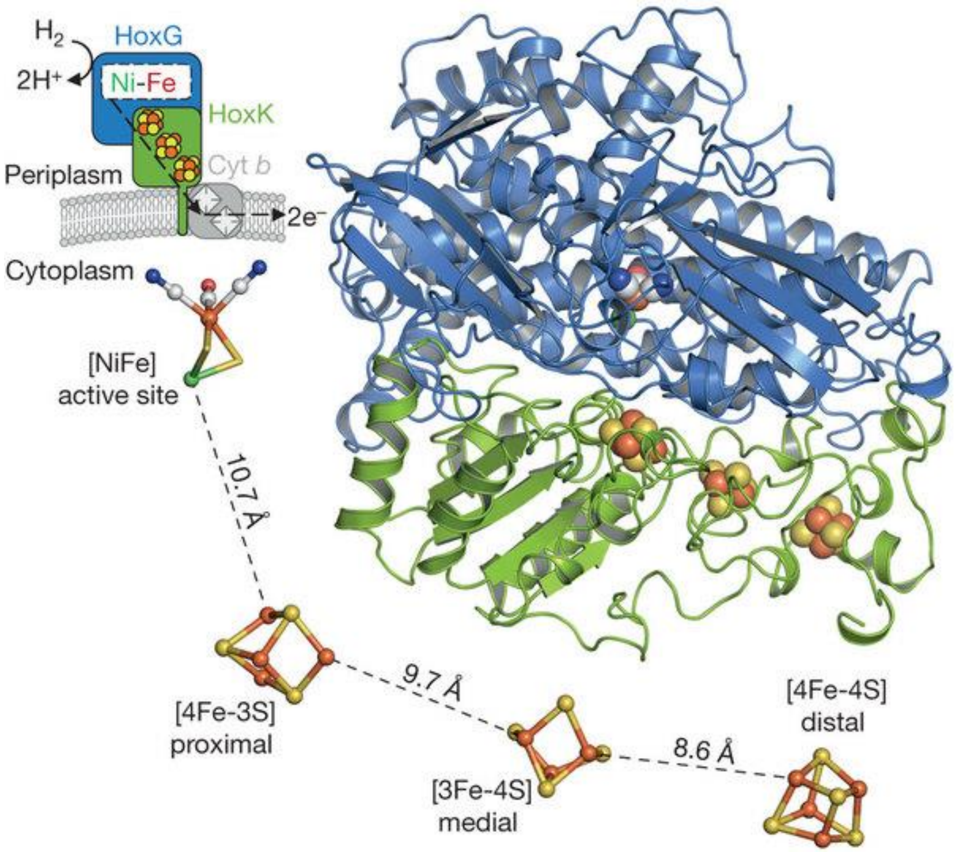
- Development of alternative fuels which are clean, sustainable and renewable.
- Hydrogen produced from solar energy through the catalyzed decomposition of water is an ultimate clean fuel and its use as a primary energy source desirable.
- Current electrochemical catalysts for H_2 production suffer from large overpotentials, short live times and they are based on expensive metals (platinum).
- A water reduction catalyst (WRC) based on “Earth abundant elements” (first row transition metal) is required.

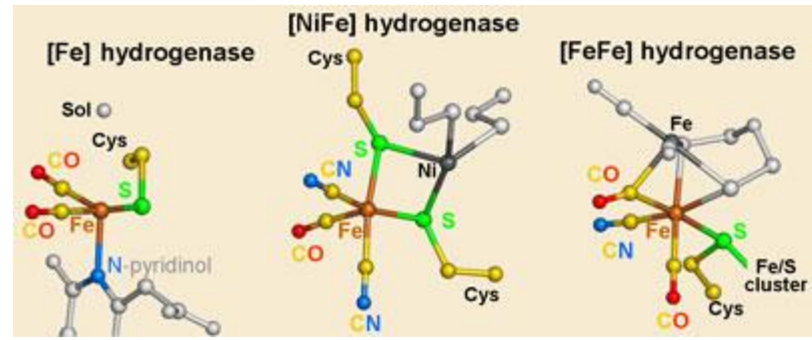
Toward a Hydrogen Economy (special issue). *Science* **2004**, *305*, 957

Vincent, K. A.; Cracknell, J. A.; Parkin, A.; Armstrong, F. A. *Dalton Trans*. **2005**, *21*, 3397-3403.

Turner, J. A. Science **2004**, *305*, 972-974.

Natural molecular hydrogen generation: Hydrogenases





$$2H_2 \leftrightarrow 2H^+ + 2e^-$$

- The **hydrogenase** enzyme catalyses the reversible oxidation of molecular H_2.
- Hydrogenases are classified based on metal atoms composing the active site: [NiFe], [FeFe], and [Fe]-only.
- Understanding its catalytic mechanism might help to design catalyst for H_2 production.

Vignais, P.M.; Billoud, B.; Meyer, J. *FEMS Microbiol. Rev.* **2001**, *25* (4), 455–501

Fontecilla-Camps, J.C.; Volbeda, A.; Cavazza, C<.; Nicolet ,Y. *Chem. Rev.* **2007**, *107* (10), 4273–4303.

Water Reduction

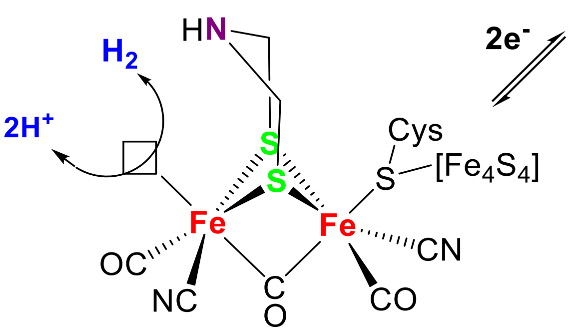
H**ydrogenases** catalyzes the reversible oxidation of molecular hydrogen:

Hydrogen Production

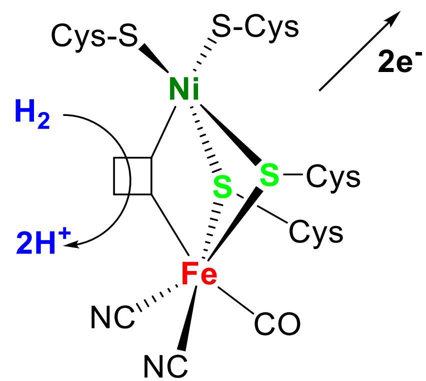
$$2\,e^- + 2\,H^+ \rightleftharpoons H_2$$

Hydrogen Oxidation

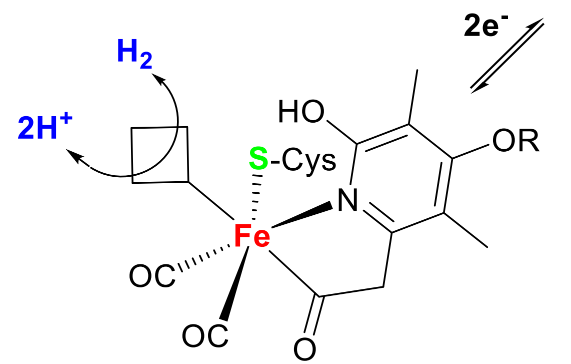
Two-proton, two-electron production and oxidation



[FeFe]-Hydrogenase



[NiFe]-Hydrogenase



[Fe]-Hydrogenase

Vignais, P.M. *et al. FEMS Microbiol. Rev.* **2001**, *25*, 455.

Fontecilla-Camps, J.C. *et al. Chem. Rev.* **2007**, *107*, 4273.

Water Reduction

21 Sc 44.9559 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938 Manganese	26 Fe 55.845 Iron	27 Co 58.9332 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.4089 Zinc
39 Y 88.9058 Yitrium	40 Zr 91.224 Zirconium	41 Nb 92.9064 Niobium	42 Mo 85.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.9055 Rbodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium
71 Lu 174.967 Lutetium	72 Hf 178.49 Hafnium	73 Ta 180.9497 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.9666 Gold	80 Hg 200.59 Mercury

a) Stabilization of Low Oxidation States

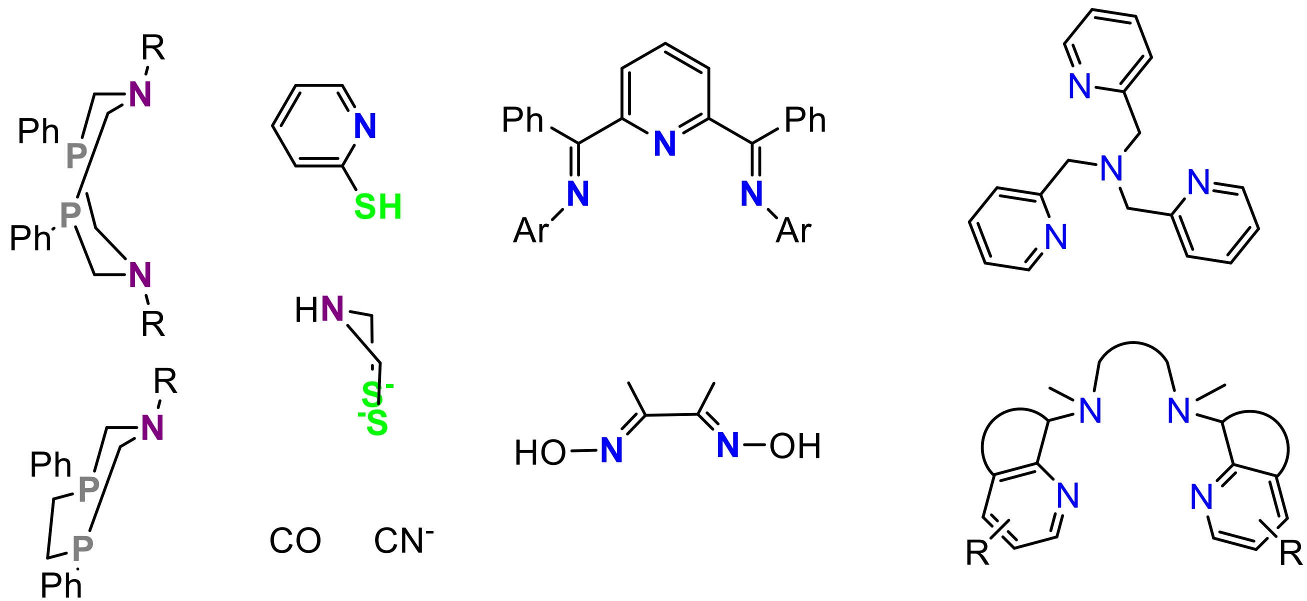
Strong chelating multidentante ligands, which stabilize complexes in low oxidation states

TYPES of Ligands:

Soft ligands such as di-phophines (P donor), thiols (S donor), CO (Organometallic)

N donor: polypiridin aminoligands, imines, glioxime, porphyrins,

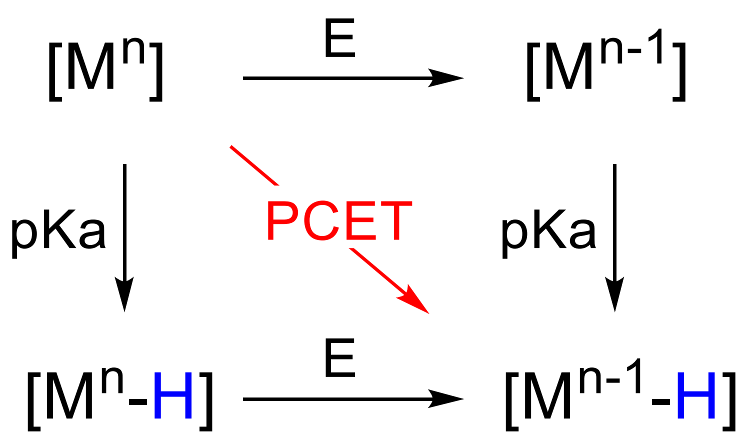
Polyoxometalates (POM): Rare examples.



a) Stabilization of Low Oxidation States

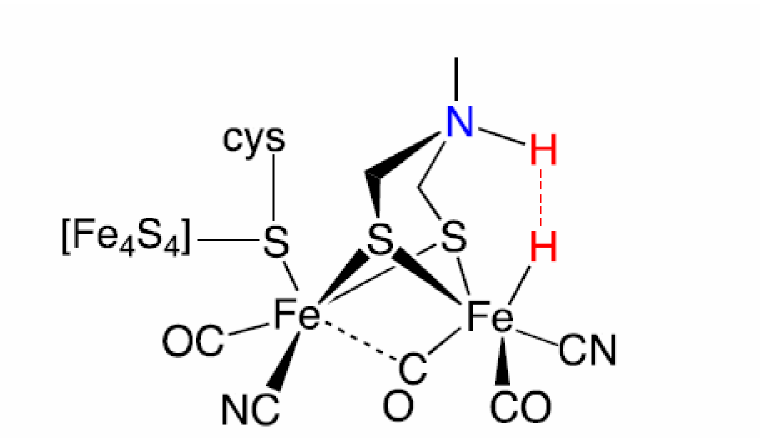
Strong chelating multidentante ligands, which stabilize complexes in low oxidation states

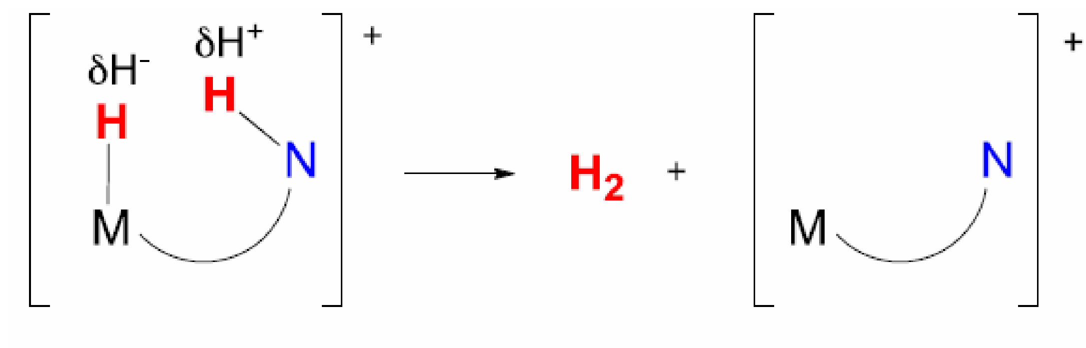
PCET



a) Stabilization of Low Oxidation States

b) Pendan base



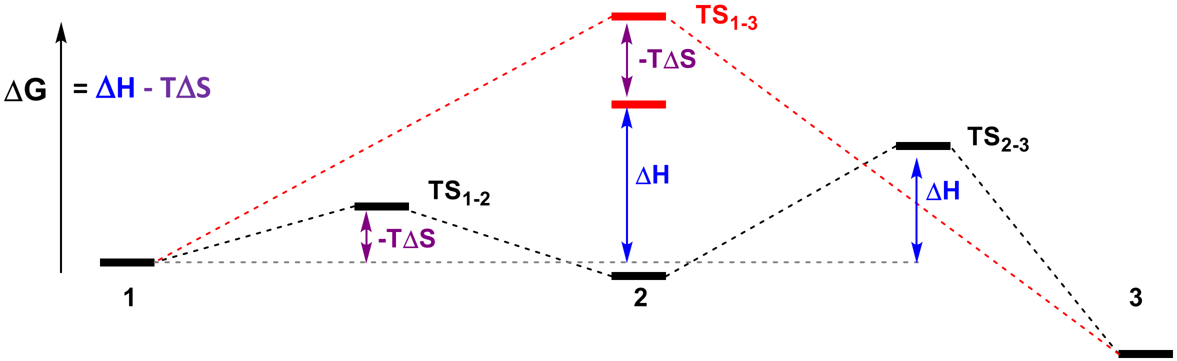


- The active site of the [FeFe] hydrogenase, presents a pendant base that facilitate the proton delivery into the iron.

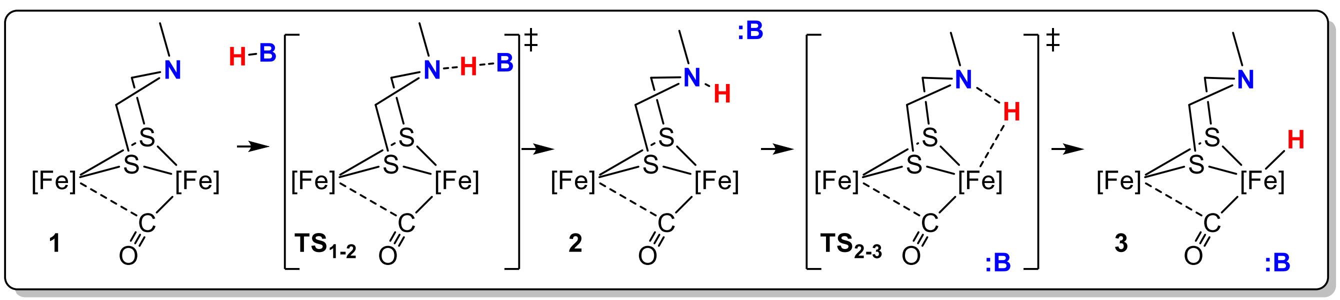
Water Reduction

a) Stabilization of Low Oxidation States

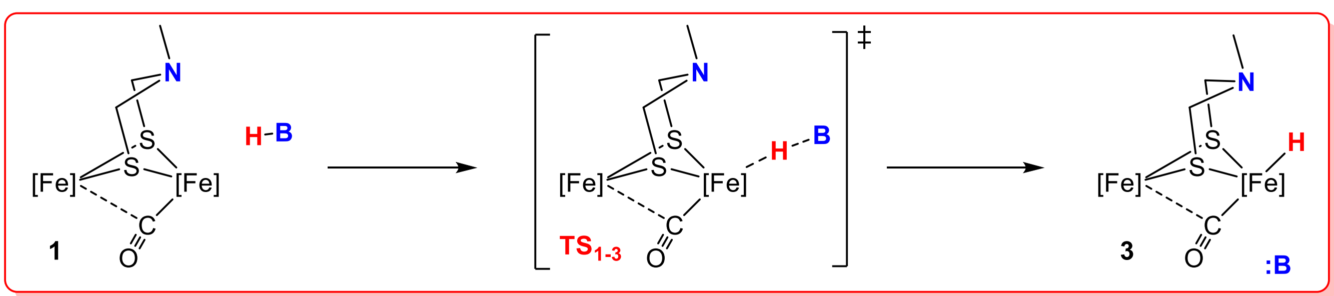
b) Pendan base Hydride formation at the active site of the [Fe-Fe] hydrogenase's type



Notice that we did not discussed the electron reduction events at the catalytic center.



Split of the ΔH and ΔS terms

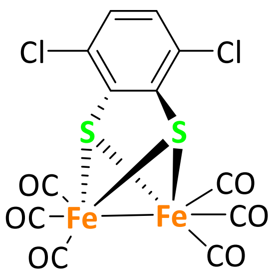


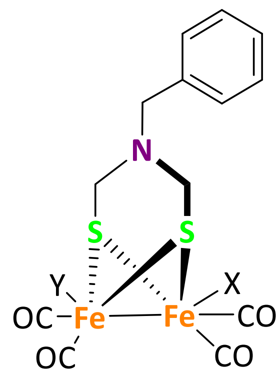
The two terms contribute in the same TS producing a higher energy barrier.

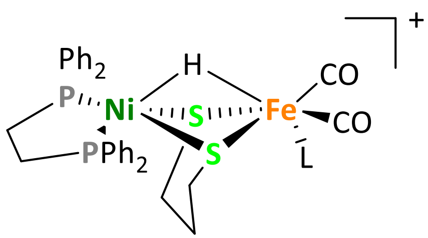
M. Ahlquist *et al Chem. Commun.*, **2012**, *48*, 4450-4452 and *Dalton Trans.*, **2013**, *42*, 7816

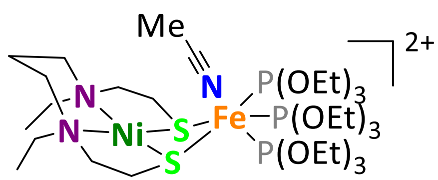
Water Reduction: Selected Examples

Biomimetic complexes







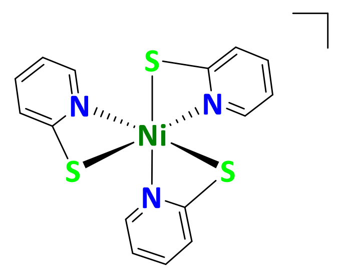


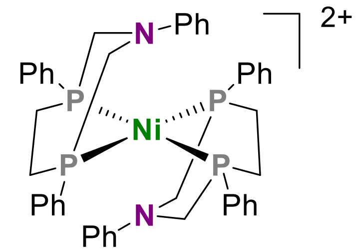
Ohhara, T. *et al. Science* **2013**, *339*, 682

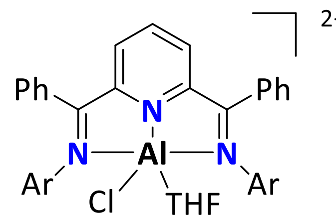
Ott, S. *et al. Chem. Eur. J.* **2010**, *16*, 60

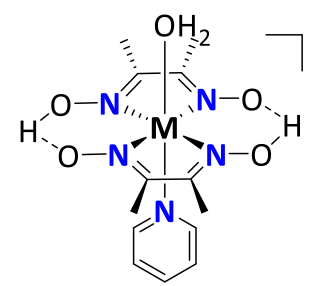
Gray, D. L. *et al. J. Am. Chem. Soc.* **2009**, *131*, 6942

Bioinspired complexes









M = **Co**, **Ni**

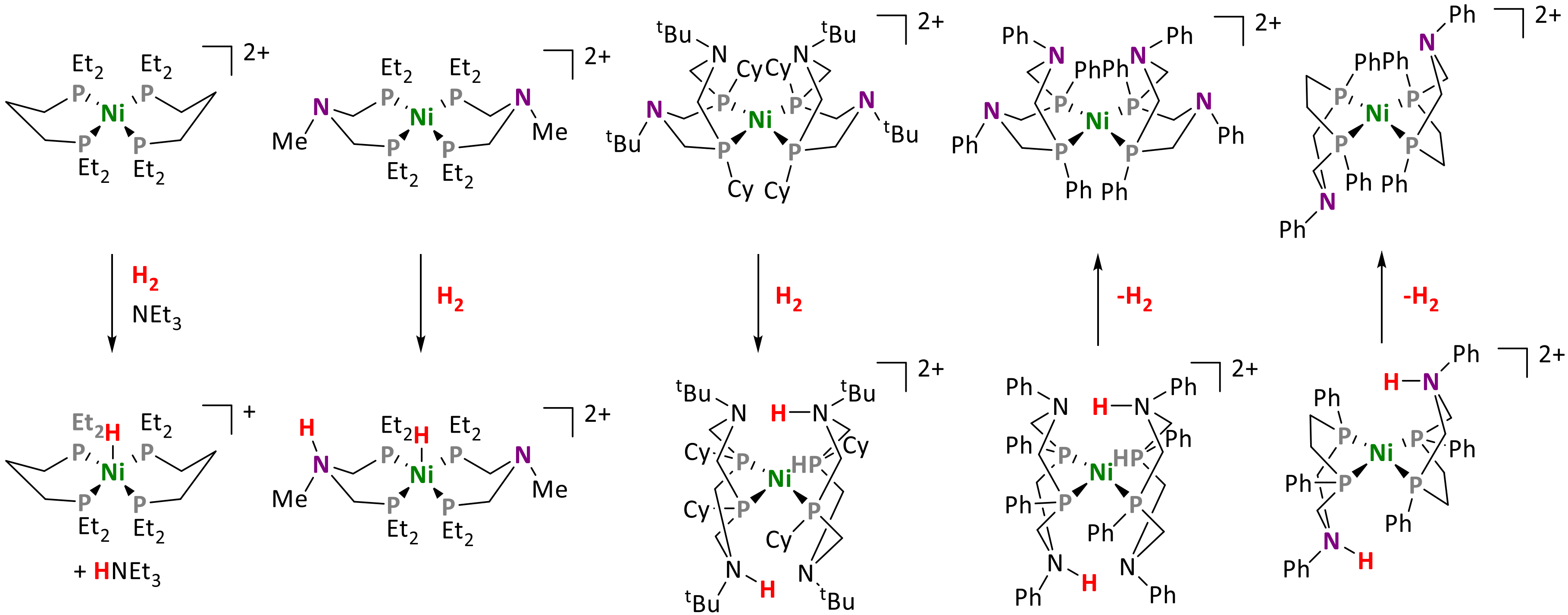
Berben, L. A. *et al. Angew. Chem. Int. Ed.* **2015**, *127*, 11808

Eisenberg, R. *et al. Angew. Chem. Int. Ed.* **2012**, *51*, 1667

Peters, J. C. *et al. J. Am. Chem. Soc.* **2012**, *134*, 3164

Dubois, D. L.. *et al. Science.* **2011**, *133*, 863

Water Reduction: Selected Examples



TOF < 0.2 s^{-1}
Overpotential = 1.2 V

TOF < 0.2 s^{-1}
Overpotential = 0.5 V

TOF = 50 s^{-1}
Overpotential = 0.4 V

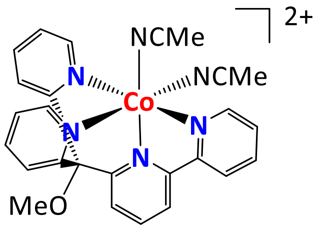
TOF = 720 s^{-1}
Overpotential = 0.3 V

TOF = 1.1 x 10^5 s^{-1}
Overpotential = 0.6 V

DuBois, M. R.; DuBois, D. L. *Inorg. Chem.* **2003**, *42*, 216; Helm, M. L. *ACS Catal.* **2015**, *5*, 2116; R. D.; DuBois, D. L. *J. Am. Chem. Soc.* **2006**, *128*, 358–366; Bullock, R. M.; DuBois, D. L. *J. Am. Chem. Soc.* **2011**, *133*, 5861; DuBois, D. L.; Bullock, R. M. *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 3152; DuBois, M. R.; DuBois, D. L. *Science* **2011**, *333*, 863; M.; DuBois, D. L.; Bullock, R. M. *J. Am. Chem. Soc.* **2013**, *135*, 9700;

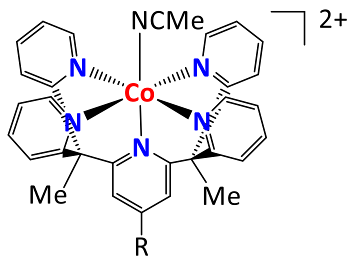
Water Reduction: Selected Examples

η: 400 mV
-, $1.1 \cdot 10^{-2}\ s^{-1}$



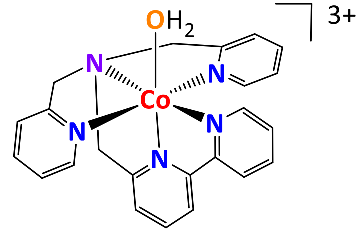
Chang, C. J. *et al.*
Chem. Commun. **2010**, *46*, 958

η: 660 mV
5.5×10^4, 0,3 s^{-1}

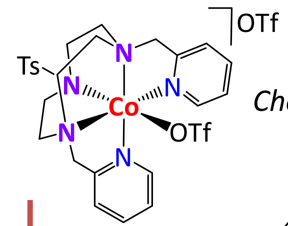


R = CF_3, H, NMe_2
Chang, C. J. *et al.*
JACS **2011**, *133*, 9212

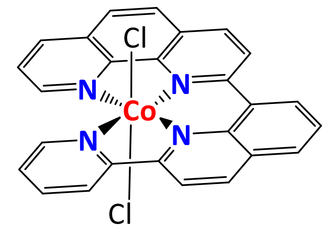
4400 TON,
Ascorbic acid, $[Ru(bpy)_3]^{2+}$



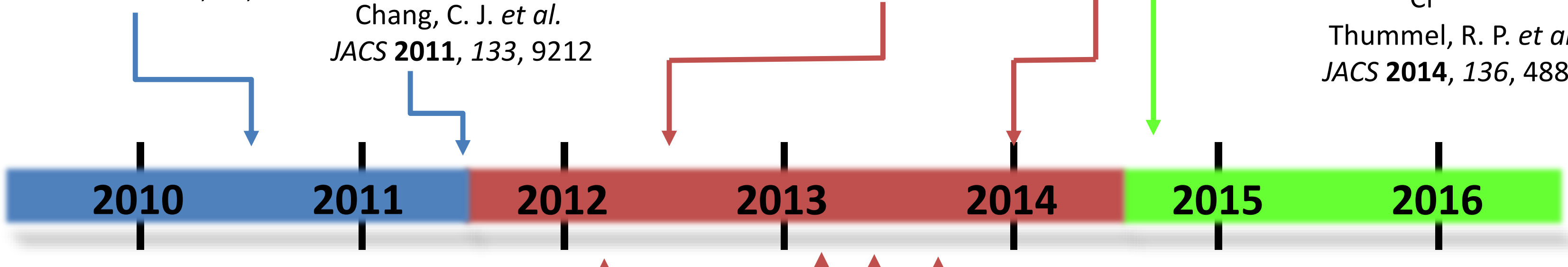
Zhao, X. *et al.*
ACIE **2012**, *51*, 5941

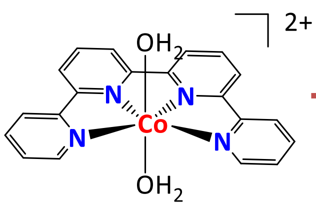


1000 TON,
Et_3N, $[Ir(bpy)(ppy)_2]^{+}$
Lloret, *et al.*
Chem.Eur.J. **2014**, *20*, 6171



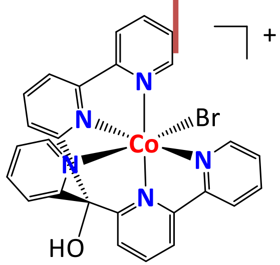
Thummel, R. P. *et al.*
JACS **2014**, *136*, 4881.



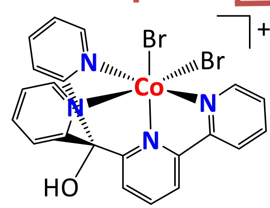


Lau, T.C. *et al.*
Energy Environ. Sci. **2012**, *5*, 7903.

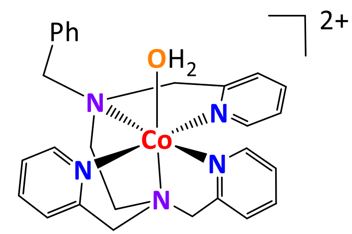
1730 TON,
TEOA, $[Ir^{III}(dF(CF_3)ppy)_2(dtbbpy)]^{+}$



Alberto, R. *et al.*
Inorg. Chem.
2013, *52*, 6055

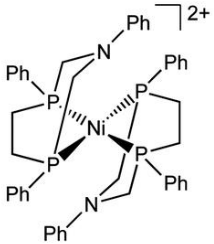


Dalton Trans.,
2013, *42*, 334
9000 TON,
Ascorbic acid, $[Ru(bpy)_3]^{2+}$

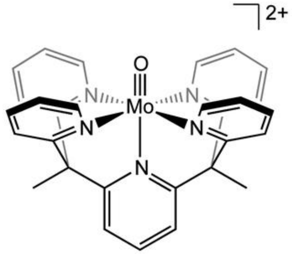


Sun, L. *et al.*
Chem. Commun. **2013**, *49*, 9455

Water Reduction: Selected Examples

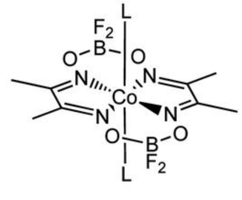


1



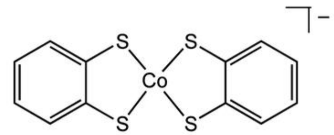
$[Py_5MoO]^{2+}$ (**2**)

3 = $[Py_5MoS_2]^{2+}$

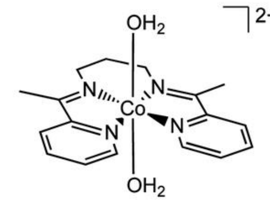


L = MeCN

4



5



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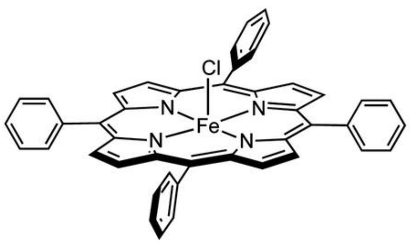
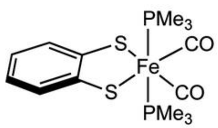


7



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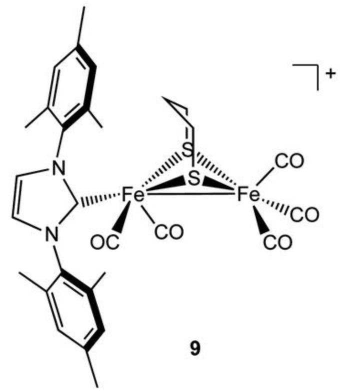
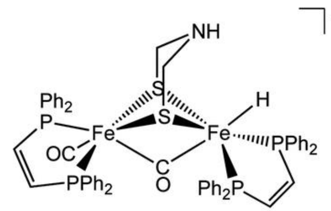
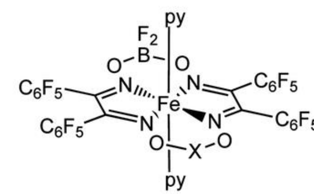


9

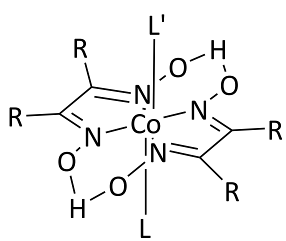


10



X = H, BF_2

11

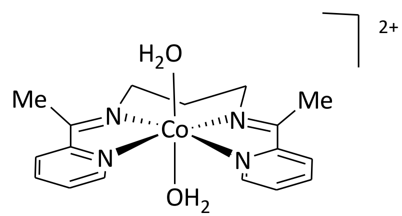


Espenson

Inorg. Chem. **1986**, *25*, 2684

Overpotentials: 100-300 mV

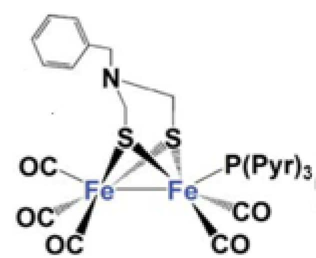
TOF: 1400 s^{-1}



Peters

JACS **2011**, *133*, 18070

k_{app}: < 10^7 s^{-1}



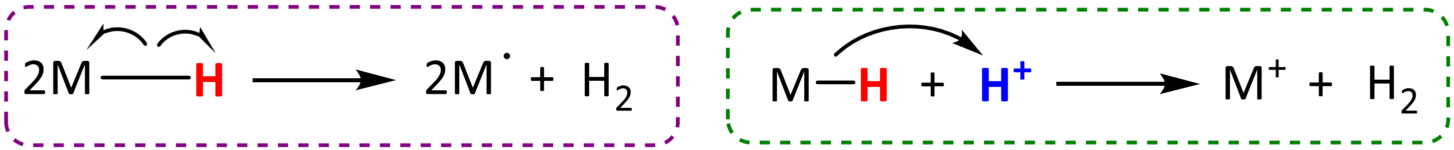
Sun *et al.*

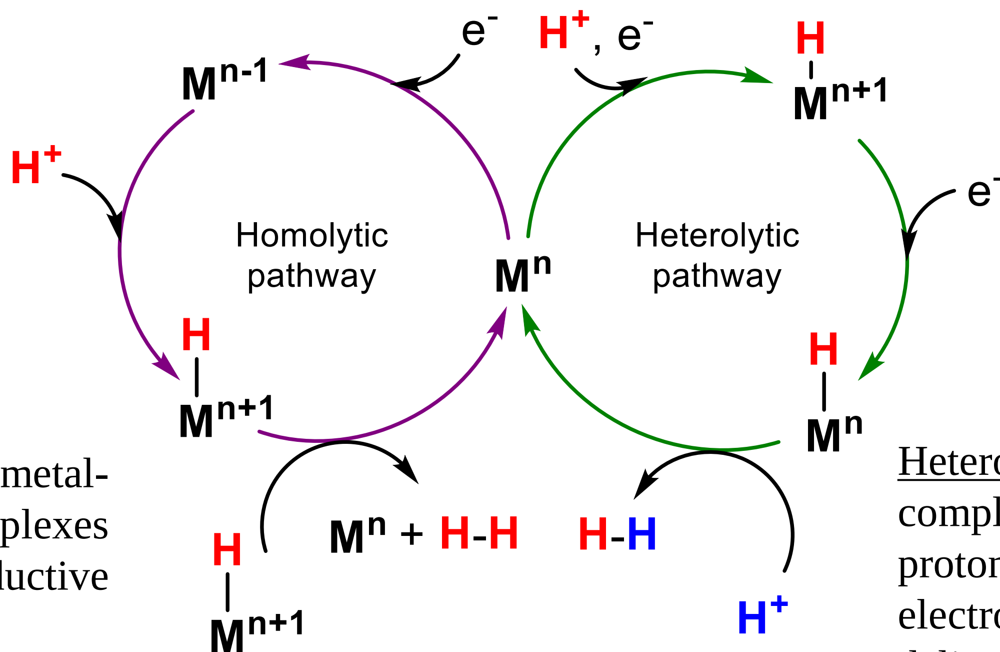
Inorg. Chem**, 2008**, *47*, 2805

660 TON,

Et_3N, $Ir(ppy)_2(bpy)$

Water Reduction: Mechanisms





<u>Homolytic:</u> Two metal-hydride complexes generate H_2 *via* reductive elimination.

<u>Heterolytic:</u> The metal-hydride complex is further reduced and protonated to evolve H_2. Two electrons and two protons are delivered to a single metal center and a putative $[M^n]$-H is formed.

Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42*, 2388-2400

Hamm, P. *et al. Inorg. Chem.* **2015**, *54*, 646

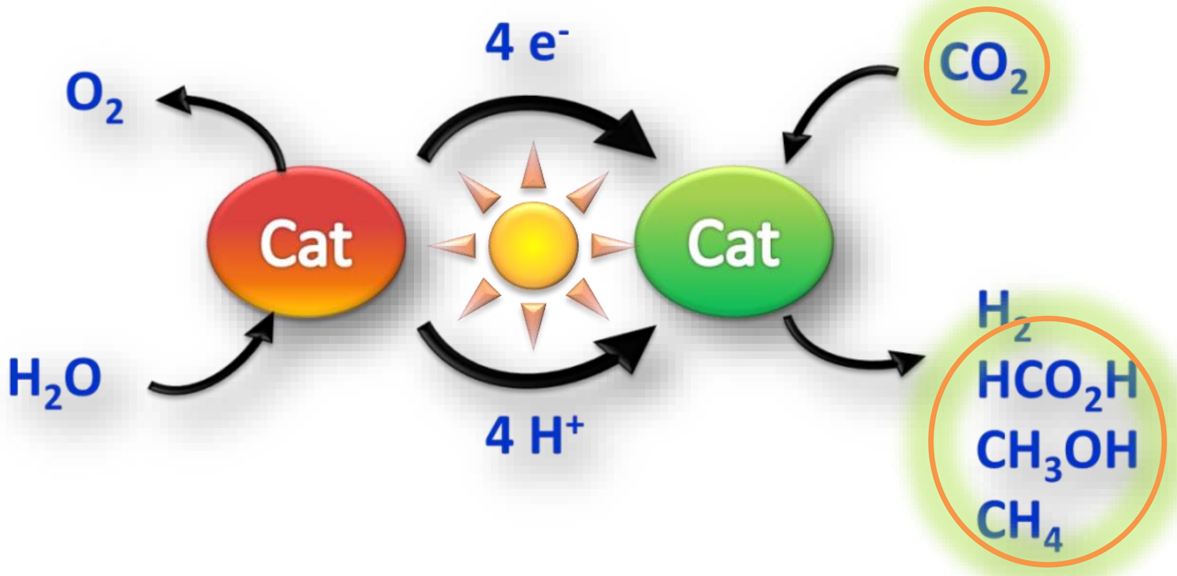
Alberto, R. *et al. Chem. Commun.* **2014**, *50*, 6737

Chavarot-Kerlidou, M. *et al. Coord. Chem. Rev.* **2015**, *304*, 3

Outline of the tutorial

- **Introduction**
  - The energy challenge (Technological perspective)
- **Artificial Photosynthesis, Water Splitting**
  - Natural and Artificial Photosynthesis
  - Research Tools
  - Water Oxidation
  - Water Reduction
  - **CO_2 Reduction**
- **Towards Solar Chemicals**
  - Examples of oxidation and reduction reactions

Water Reduction



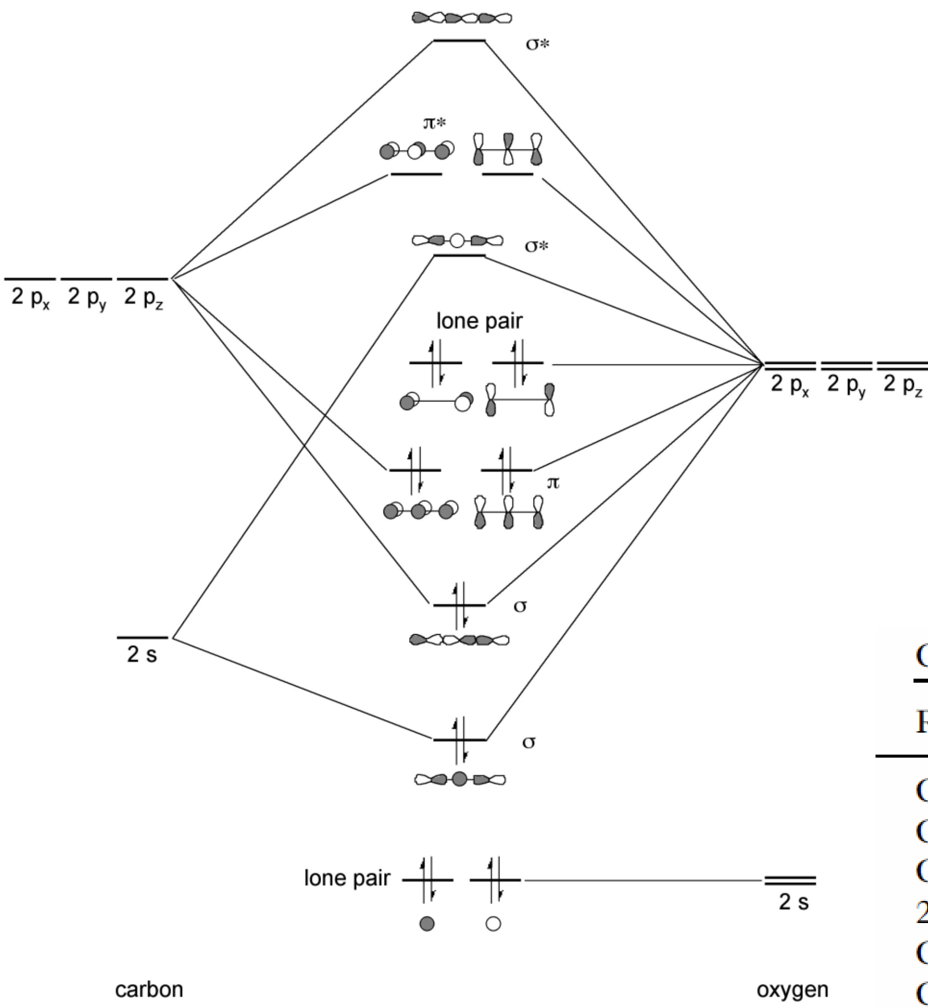
Solar Fuels:

· CO_2 (Photo)reduction to formic acid, methanol or methane:

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH$$

Lewis and Nocera *PNAS* **2006**, *103*, 15729-15735
Meyer and co-workers *Inorg. Chem.* **2005**, *44*, 6802-6827
Moore and co-workers *Acc. Chem. Res.* **2009**, *42*, 1890-1898

CO2 Reduction to CO, HCO_2H and hydrocarbons



CO_2 reduction

Reaction	$E^{0\prime}$
$CO_2 + 1e^- \rightarrow CO_2^{\bullet -}$	−1.9
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	−0.61
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.53
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.49
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.48
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24

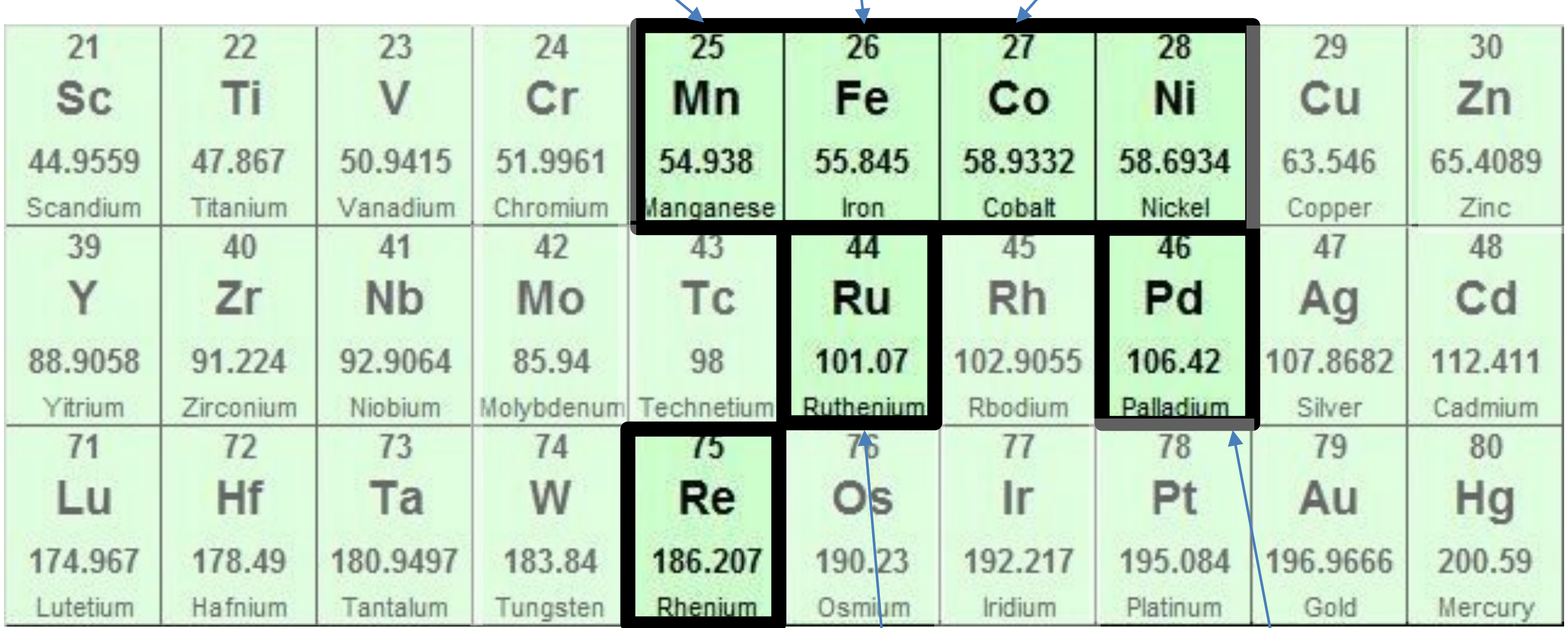
Molecular complexes for CO_2 Reduction

Since 2011
C.P. Kubiak,
A. Deronzier
R. Gobetto

J-M. Saveant
C. costentin
M. Robert

M. Robert
M. Koper
C. Chang
E. Fujita

C. Chang
J-P Sauvage



80's
J.-M. Lehn
C.P. Kubiat
E. Fujita

80's
Tanaka
C.P. Kubiak
A. Deronzier

90's
D. Dubois

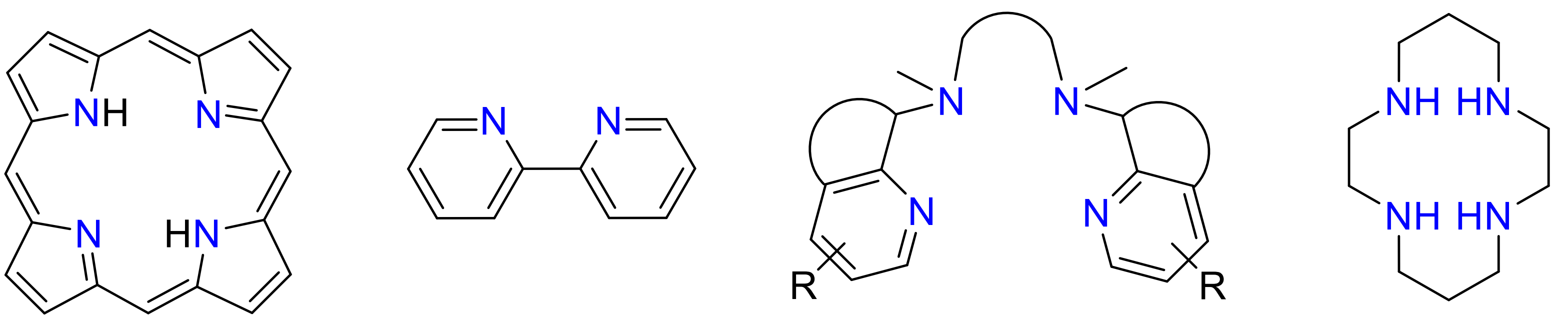
a) Stabilization of Low Oxidation States

Strong chelating multidentante ligands

TYPES of Ligands:

Soft ligands such as di-phophines (P donor), thiols (S donor), CO (Organometallic)

N donor: polypiridine, bipyridines, amine based macrocycle ligands, porphyrins,



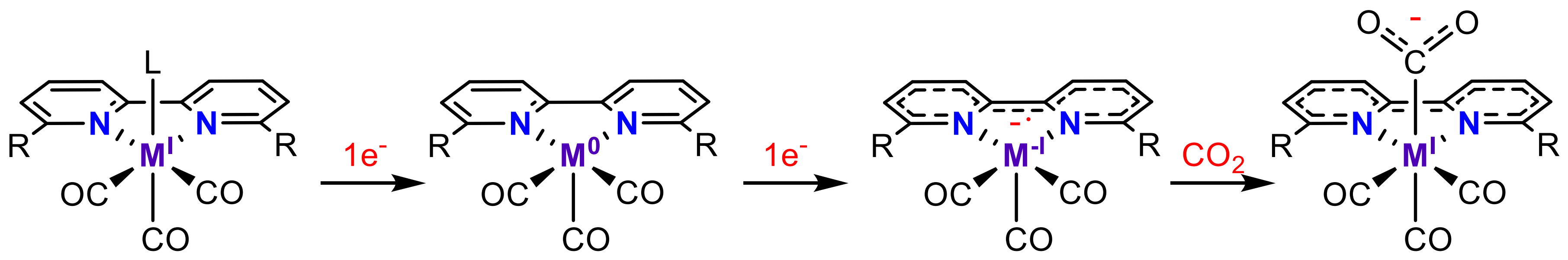
O. Ishitani, M. Robert and co. *ACS Catal.* **2017**, *7*, 70

Strategies to Improve the CO_2 Reduction

a) Stabilization of Low Oxidation States

Strong chelating multidentante pi-acceptor ligands

Change delocalization: Non-innocent ligands.



M = Mn, Re

Reduction
of the overpotential

D. C. Grills, M. Z. Ertem, J Rochford and co. *J. Am. Chem. Soc.* **2017**, *139*, 2604

Strategies to Improve the CO_2 Reduction

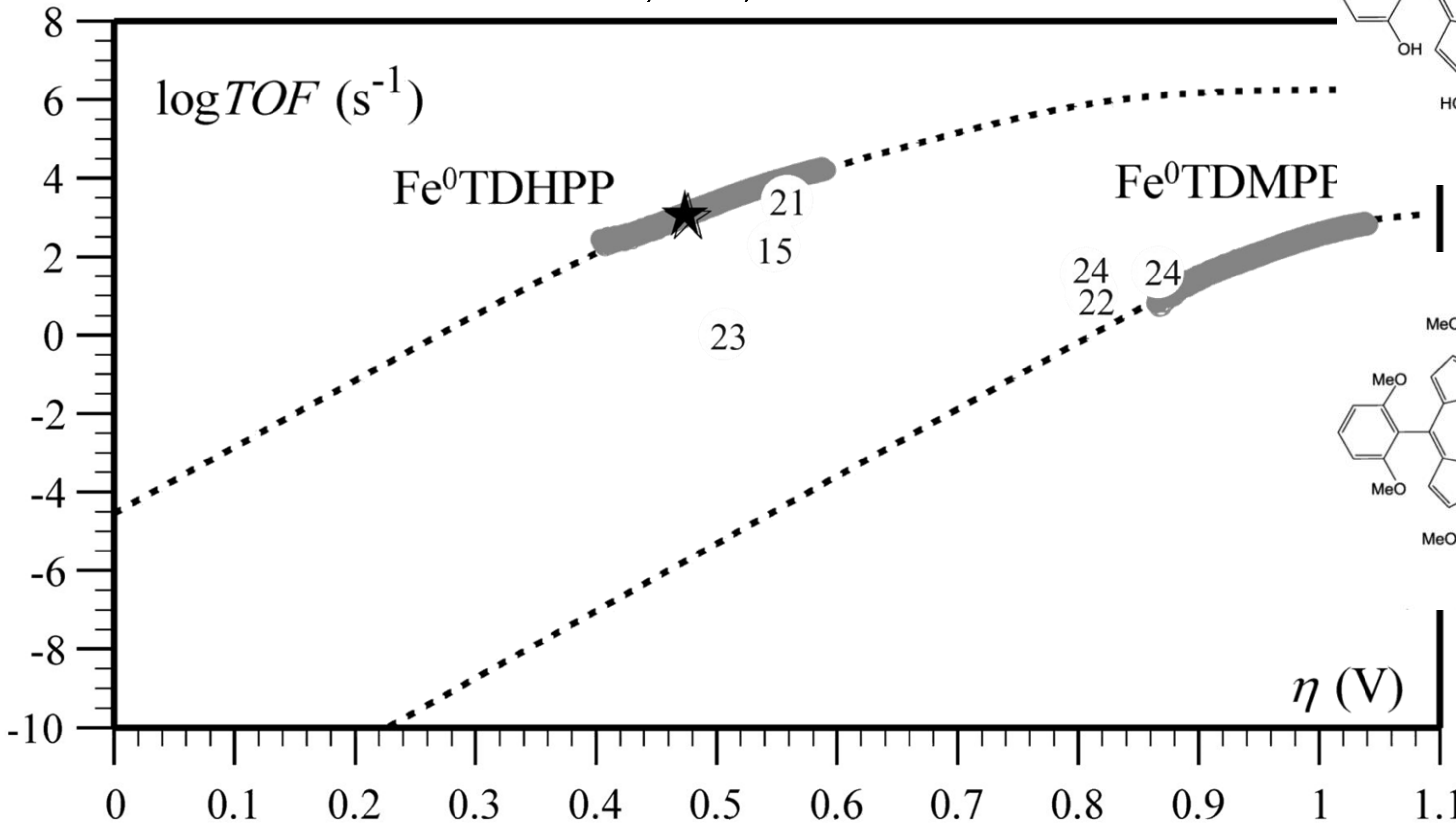
a) Stabilization of Low Oxidation States

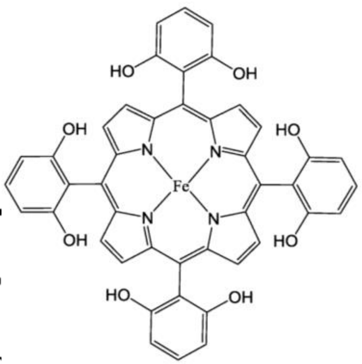
Strong chelating multidentante pi-acceptor ligands

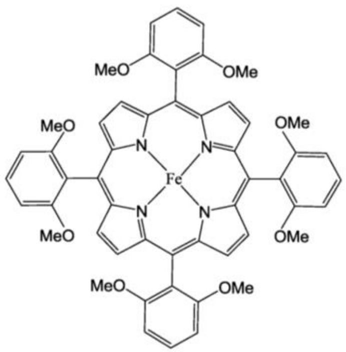
Change delocalization: Non-innocent ligands.

b) Activation of the CO_2 molecule: internal brønsted or Lewis acid.

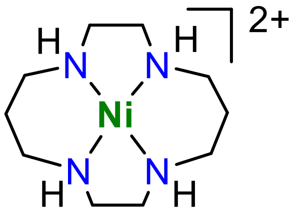
J.-M. Saveant *Science* **2012**, *338*, 90



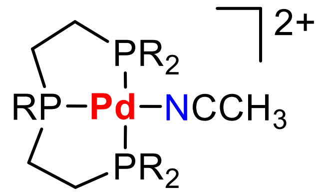




Selection of Catalysts of CO_2 Reduction

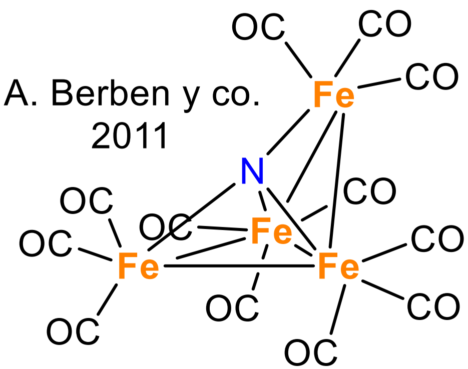


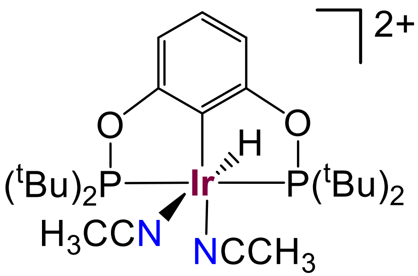
J. P. Sauvage y co.
1984



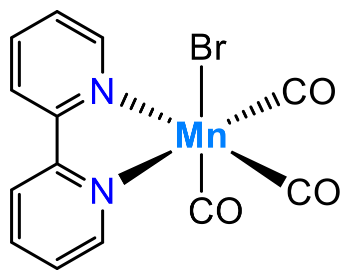
D. L. DuBois y co.
1991

A. Berben y co.
2011

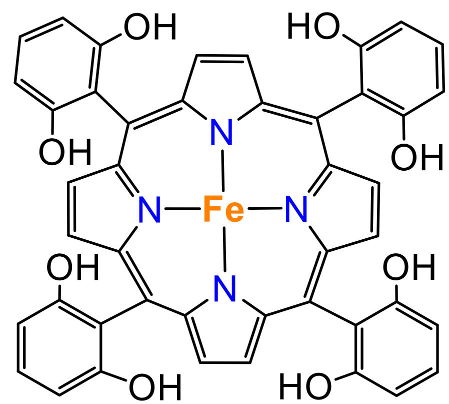




T. Meyer, M. Brookhart y co. 2012

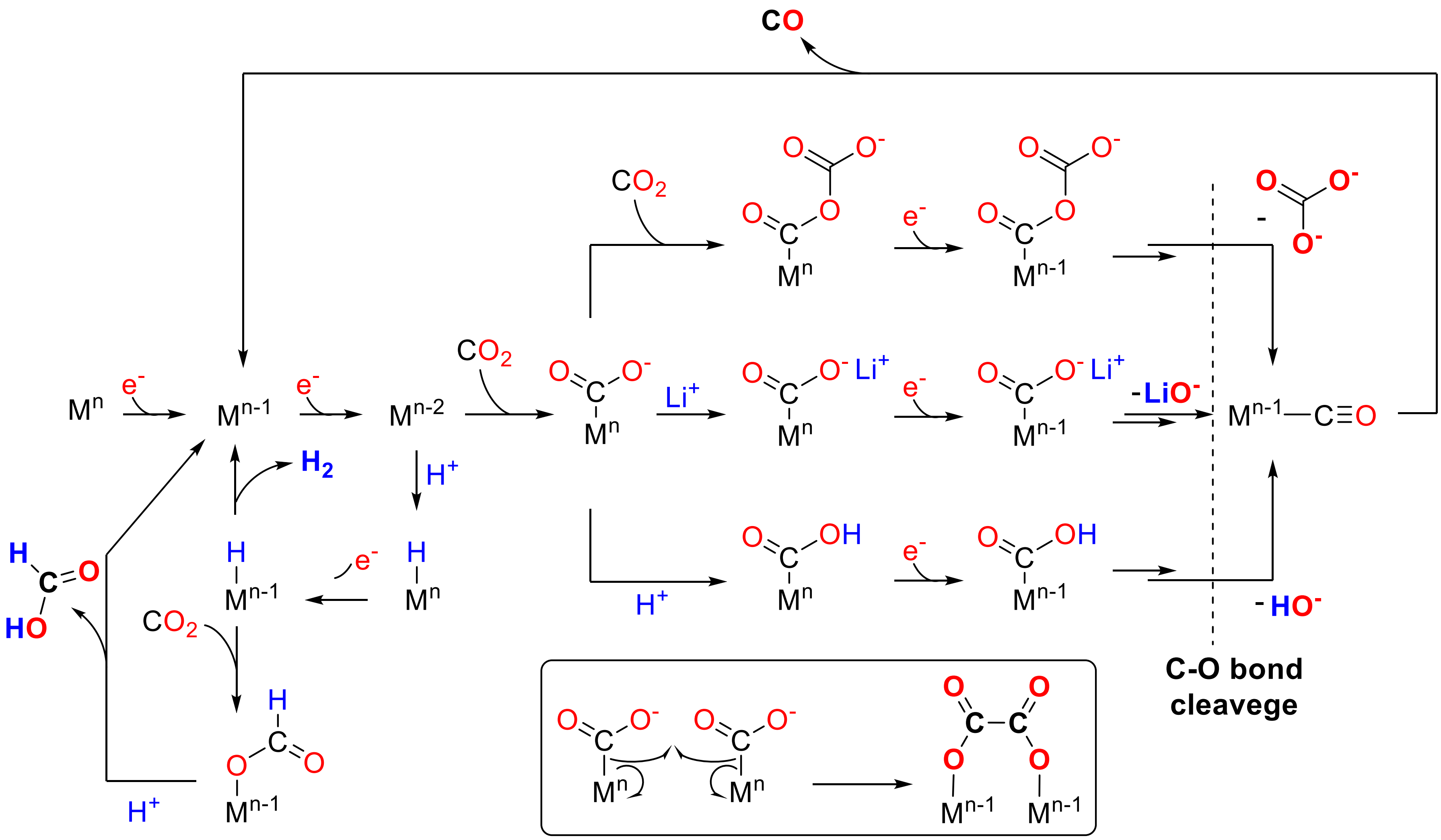


S. Chardon-Noblat,
A. Deronzier y co. 2014



C. Costetin, J. M. Savéant y co. 2012

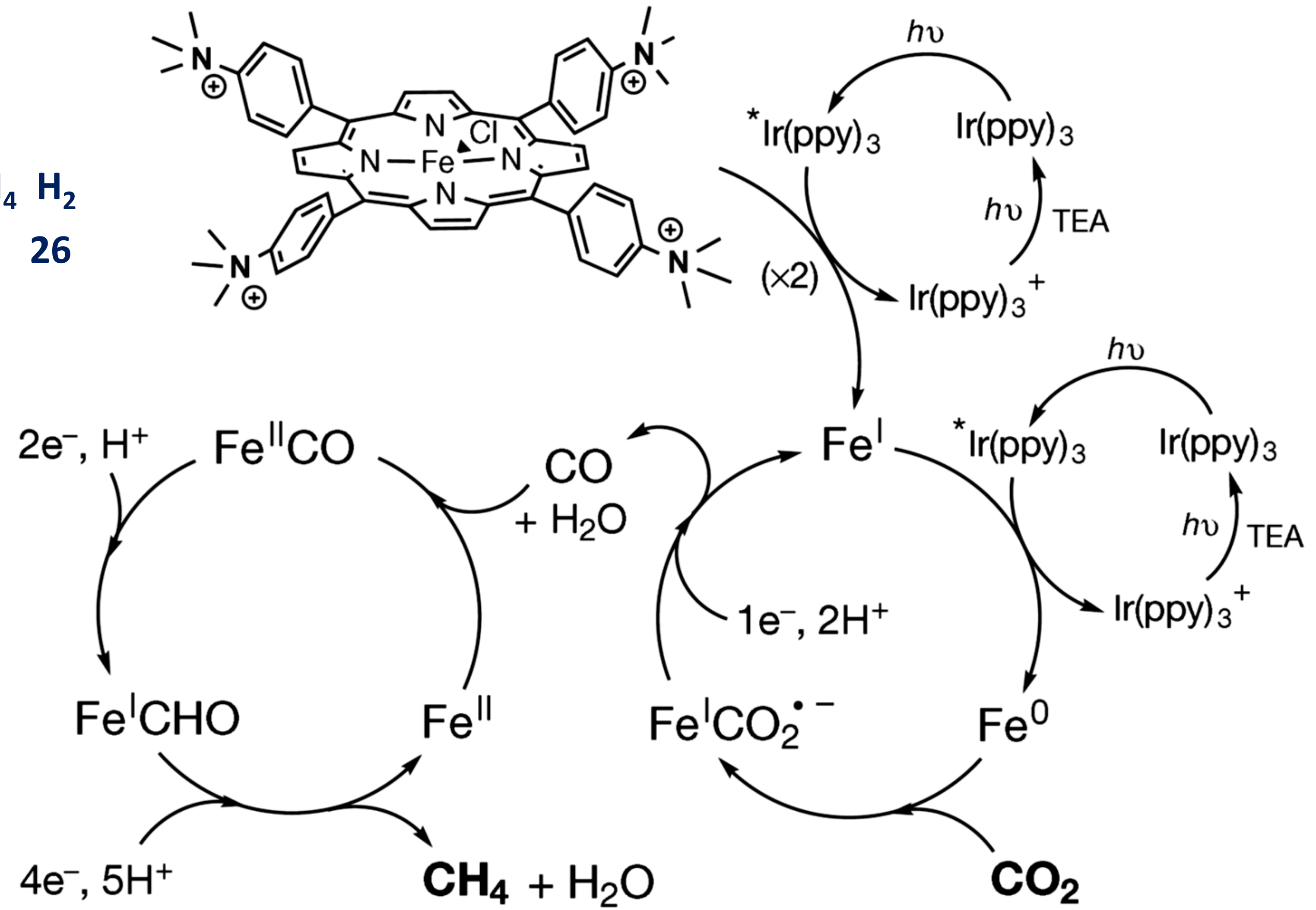
Mechanisms of CO_2 Reduction



Selected examples of CO_2 Reduction

CO_2 reduction or CO reduction to CH_4

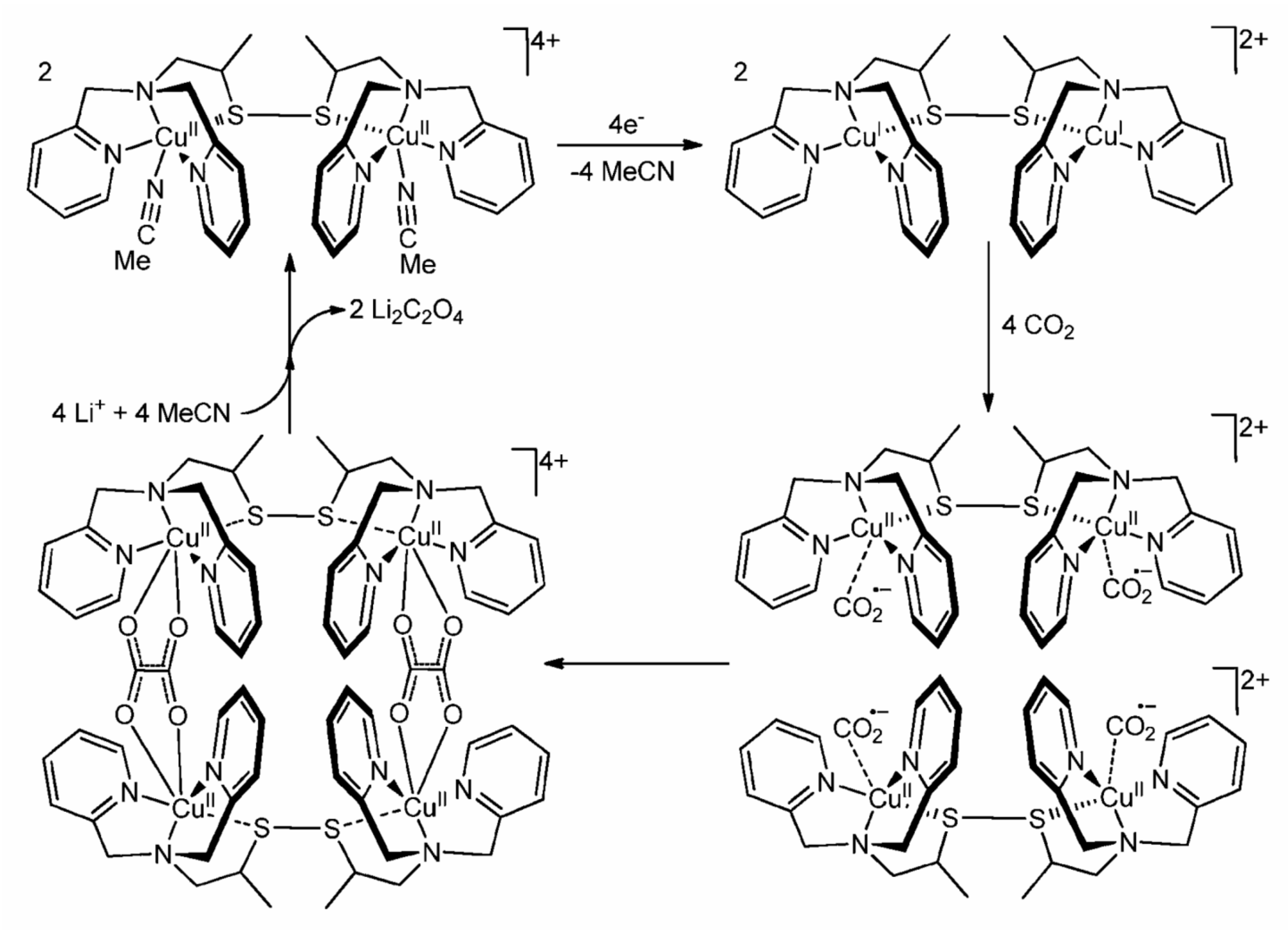
	CO	CH_4	H_2
TON	367	79	26



M. Robert and co. *Nature* **2017**, *548*, 74

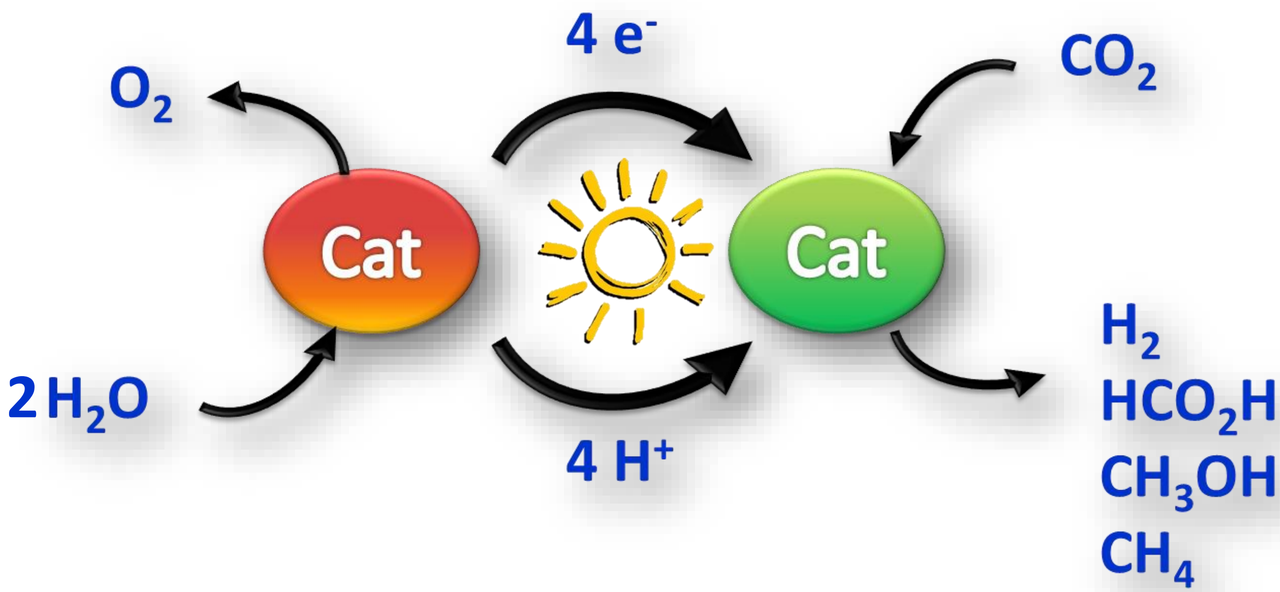
Selected examples of CO_2 Reduction

Selective formation of oxalate, Low overpotential
Prior the reduction O_2 allows for capturing the CO_2 from air



E. Bouwman, and co. *Science,* **2010**, *327*, 313.

Water Splitting



Water Oxidation:
source of electrons

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

E = 1.23 V at pH 1

$\Delta G = 113.4\ \text{kcal}\cdot\text{mol}^{-1}$

Solar Fuels:

· (Photo)chemical Water Splitting:

$$2H^+ + 2e^- \rightarrow H_2$$

· CO_2 (Photo)reduction to formic acid, methanol or methane:

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH$$

Lewis and Nocera *PNAS* **2006**, *103*, 15729-15735
Meyer and co-workers *Inorg. Chem.* **2005**, *44*, 6802-6827
Moore and co-workers *Acc. Chem. Res.* **2009**, *42*, 1890-1898

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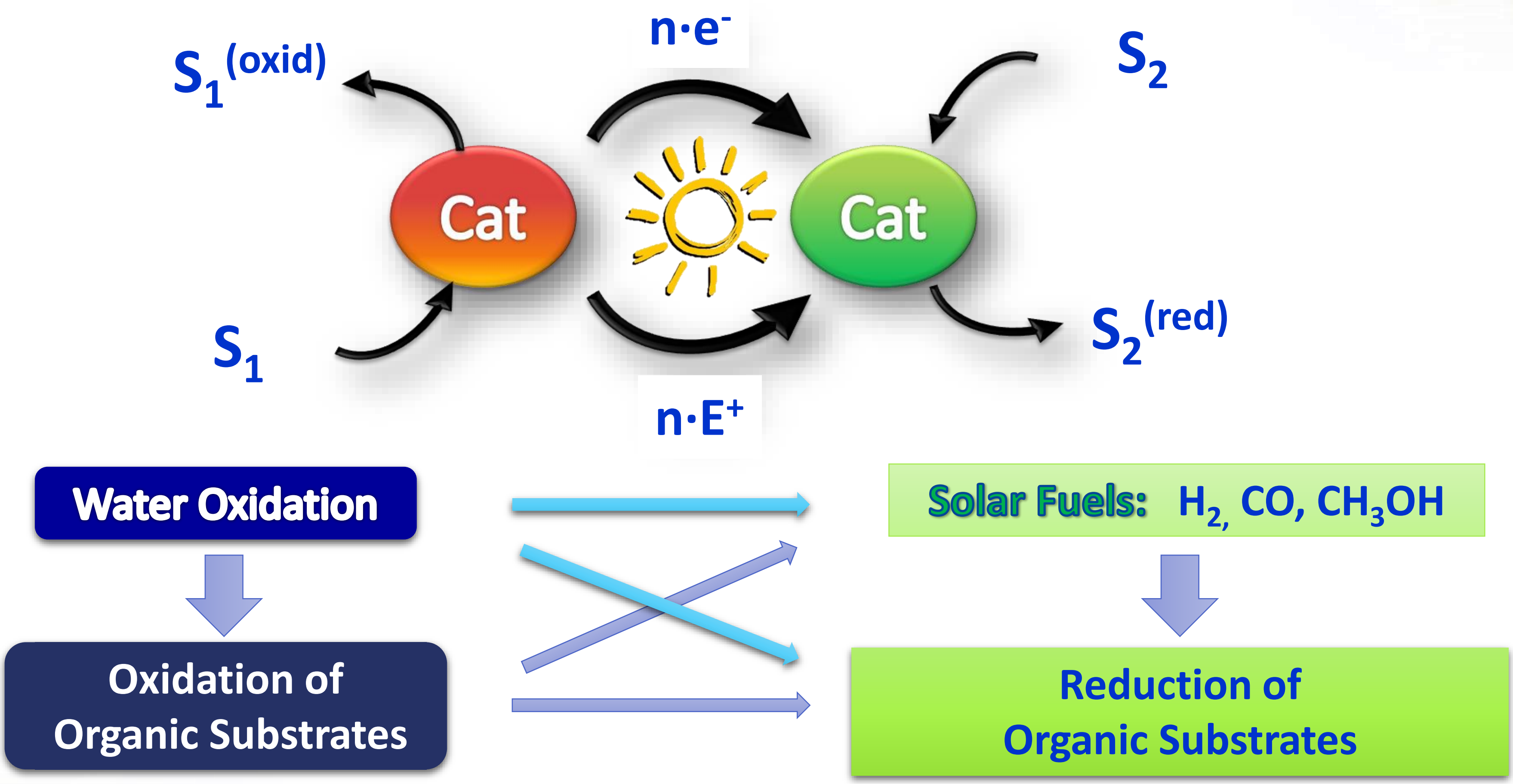
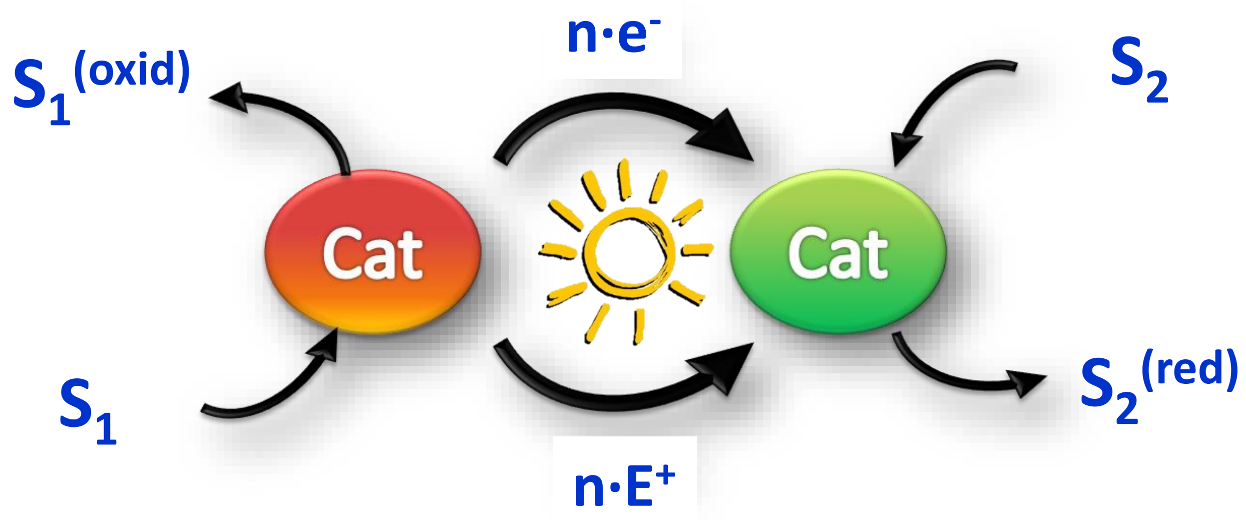
  - **Examples of oxidation and reduction reactions**

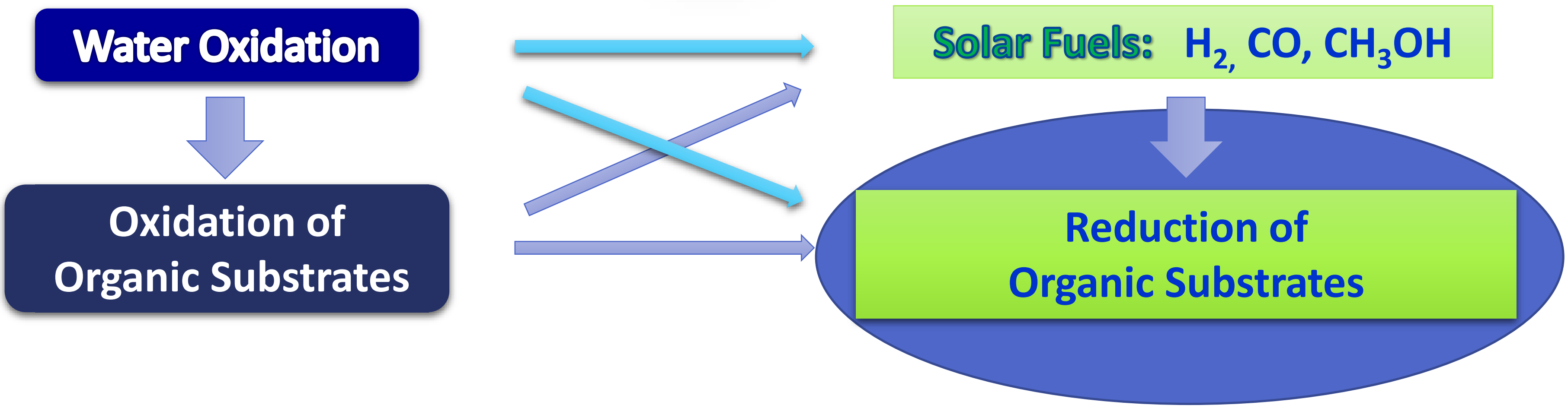
General Scheme



Light as energy source to carry out energetically up hill transformations

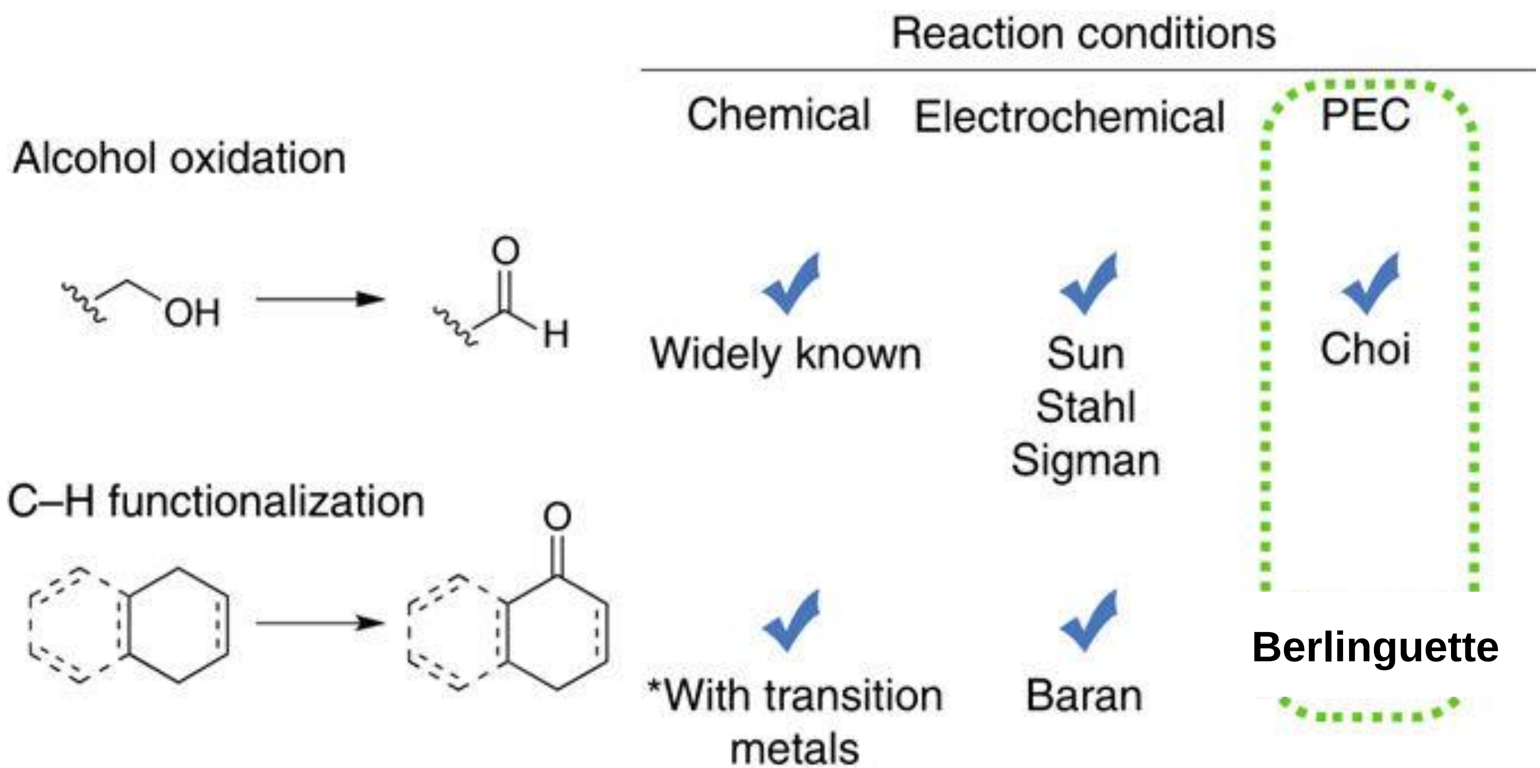
Light as energy source to carry out transformations





$CO_2 \rightarrow HCO_2H$	*J. Am. Chem. Soc.*, **2012**, *134*, 11455	Jin-Ook Beak, C.B. Park
L-Glutamate dehydrogenase	*ACS Appl. Mater. Interf.*, **2014**, *6*, 8434	A. Corma, F. Hollmann
Ketone reductions	*Angew. Chem.*, **2012**, *124*, 11792	Fraser A. Armstrong….
Hydrogenation	*Nature Commun.*, **2014**, *5*, 3145	

OXIDATIONS: Selected electrocatalytic and PEC processes



T. Meyer, *J. Am. Chem. Soc.*, **2014**, *136*, 9773

M. Sigma, *J. Am. Chem. Soc.* **2015**, *137*, 16179

K.-S. Choi, *Nat. Chem.* **2015**, *7*, 328

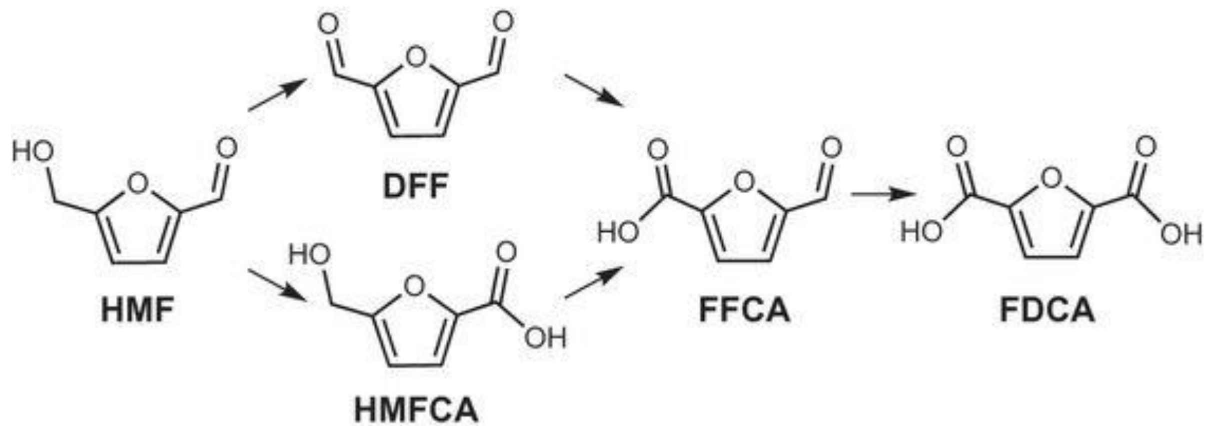
Y. Sun, *J. Am. Chem. Soc.* **2016***, 138*, 13639

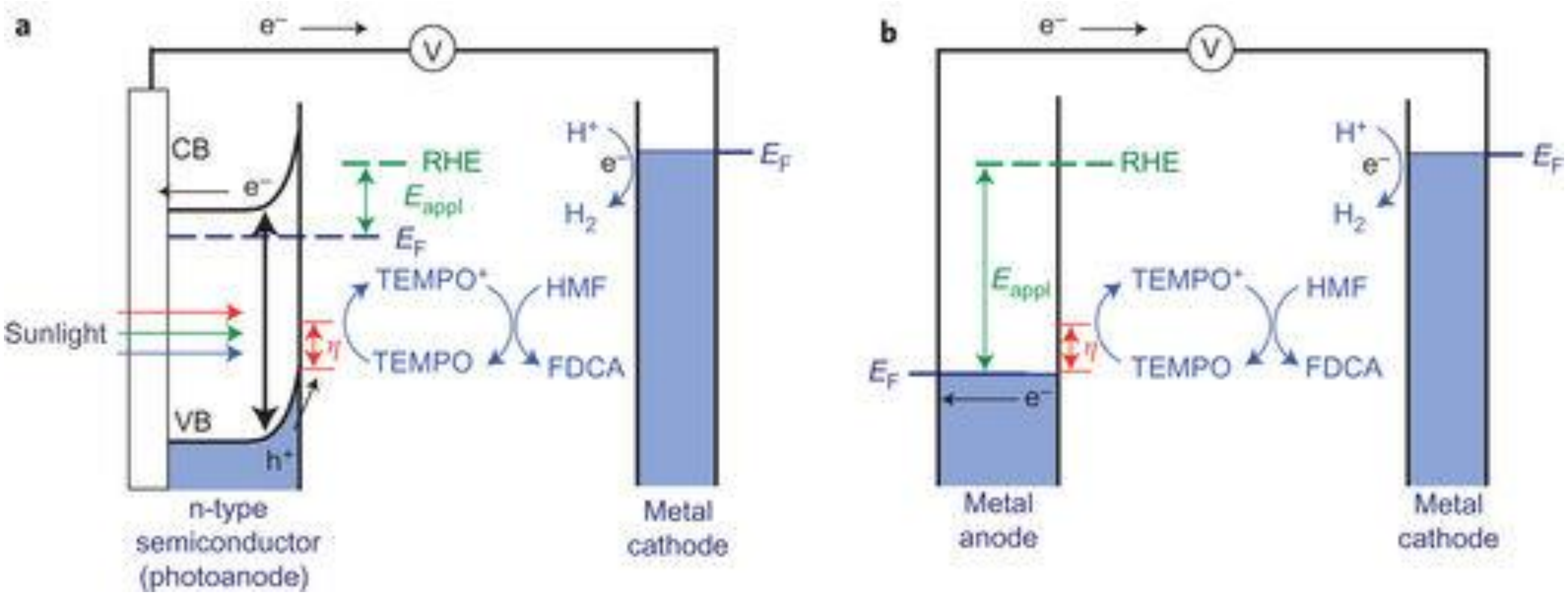
S.S. Stahl, *Nature* **2016**, *535*, 406

P. Baran *Nature* **2016**, *533*, 77

C. P. Berlinguette *Nat. Commun* **2017**, *8*, *390*

OXIDATIONS: Selected electrocatalytic and PEC processes



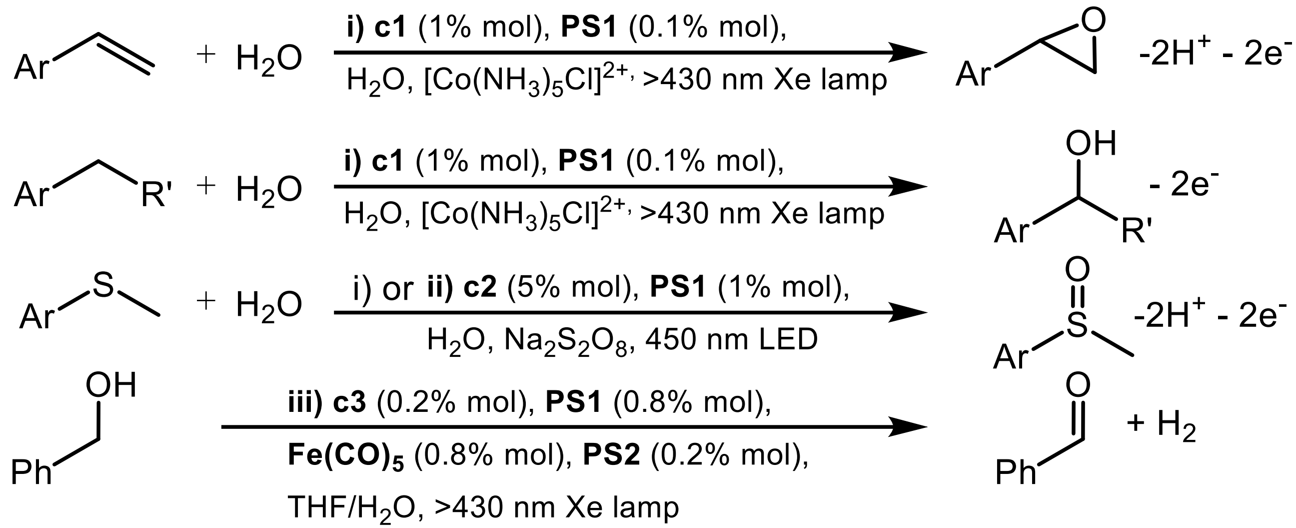


$BiVO_4$ photoanode

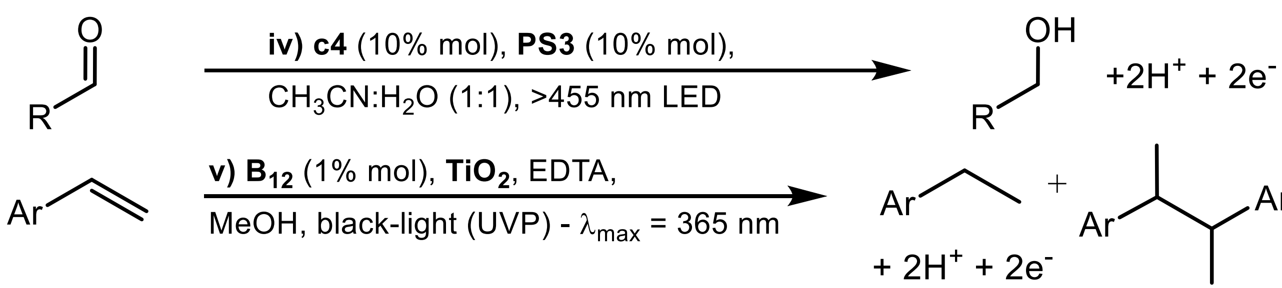
K.-S. Choi, *Nat. Chem.* **2015**, *7*, 328

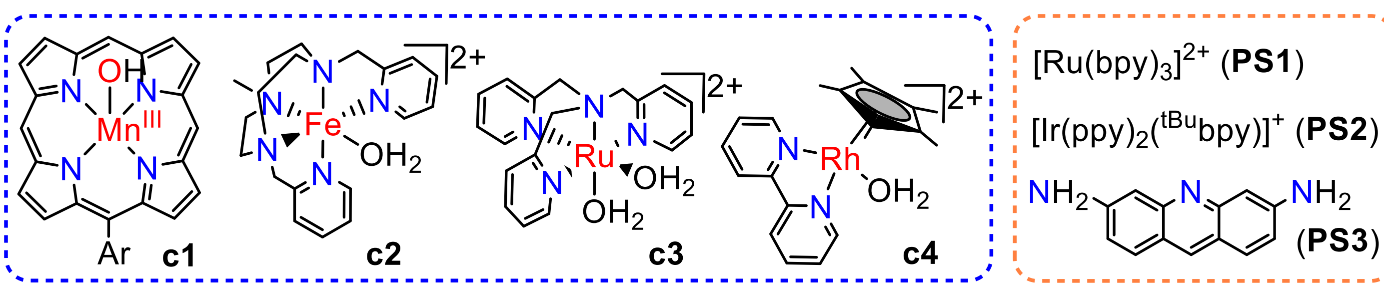
OXIDATIONS AND REDUCTIONS: Photochemical

Oxidación



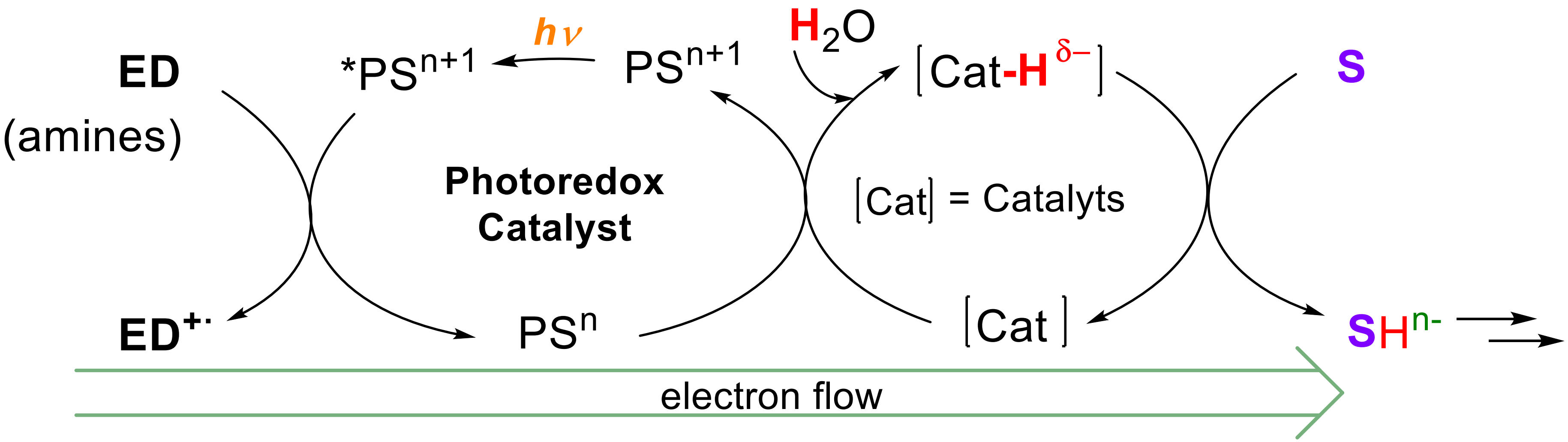
Reducción





J. Lloret et al. *An. Quím.* **2016**, *112*, 133

Metal-catalyzed Light-driven Reductions

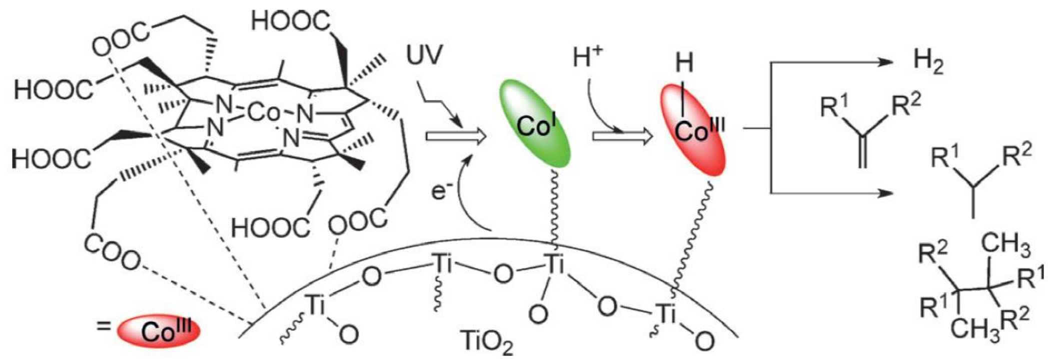


Introduction: Solar fine chemicals

Reduction of olefins

TiO_2 modified with the B_{12} complex

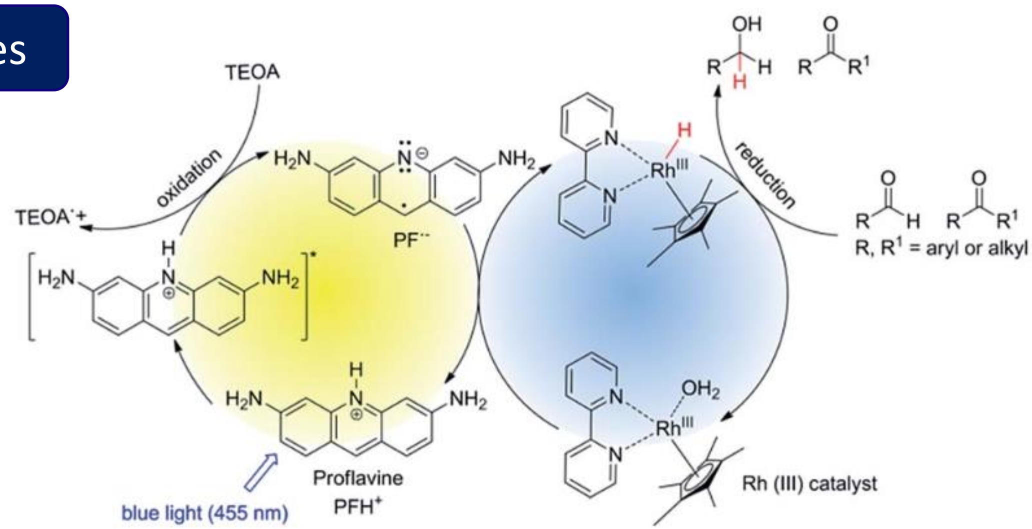
Under UV irradiation (λ = 365 nm)



Hisaeda, Y. *et al. ChemPlusChem.* **2014**, *79*, 1250

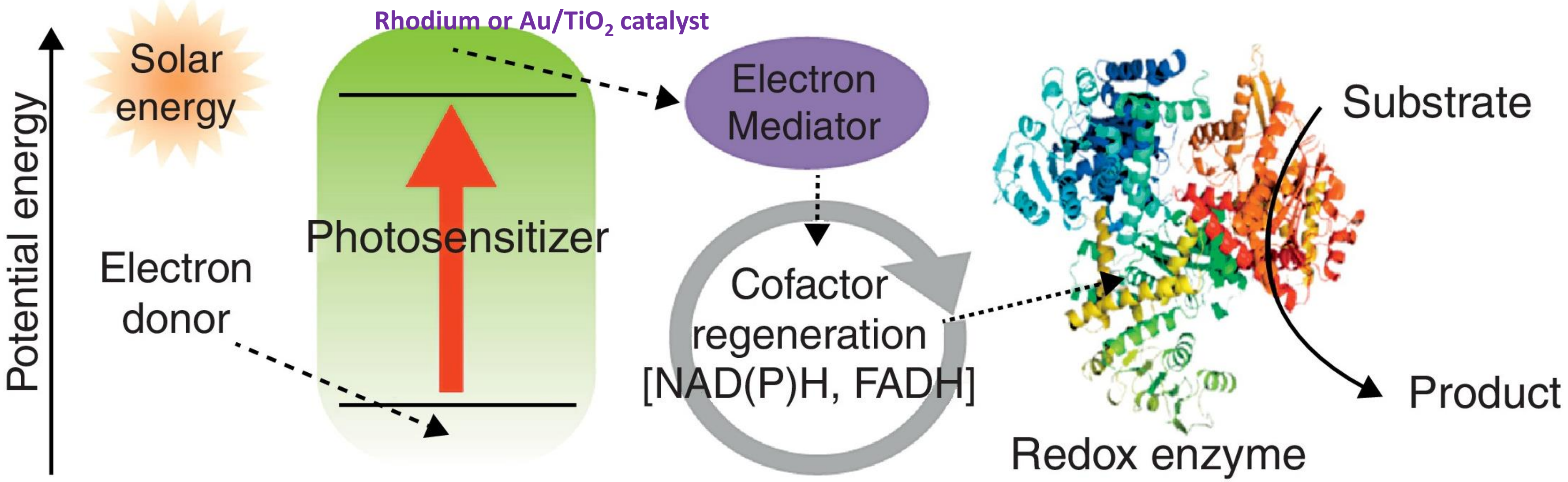
Reduction of ketones and aldehydes

Under visible light irradiation (λ = 455 nm)



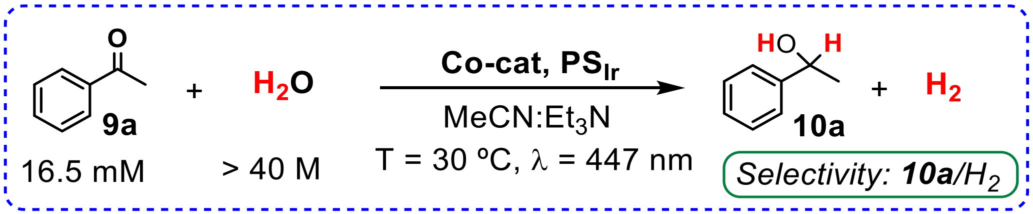
König, B. *and co. Chem. Sci.* **2015**, *6*, 2027

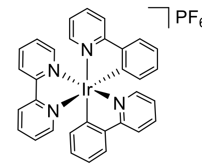
Bio-catalyzed Light-driven Reductions



$CO_2 \rightarrow HCO_2H$	*J. Am. Chem. Soc.*, **2012**, *134*, 11455	Jin-Ook Beak, C.B. Park
L-Glutamate dehydrogenase	*ACS Appl. Mater. Interf.*, 2014, *6*, 8434	A. Corma, F. Hollmann
Ketone reductions	*Angew. Chem.*, 2012, *124*, 11792	Fraser A. Armstrong….
Hydrogenation	*Nature Commun.*, 2014, *5*, 3145	

Ketones Reduction





PS_{Ir}

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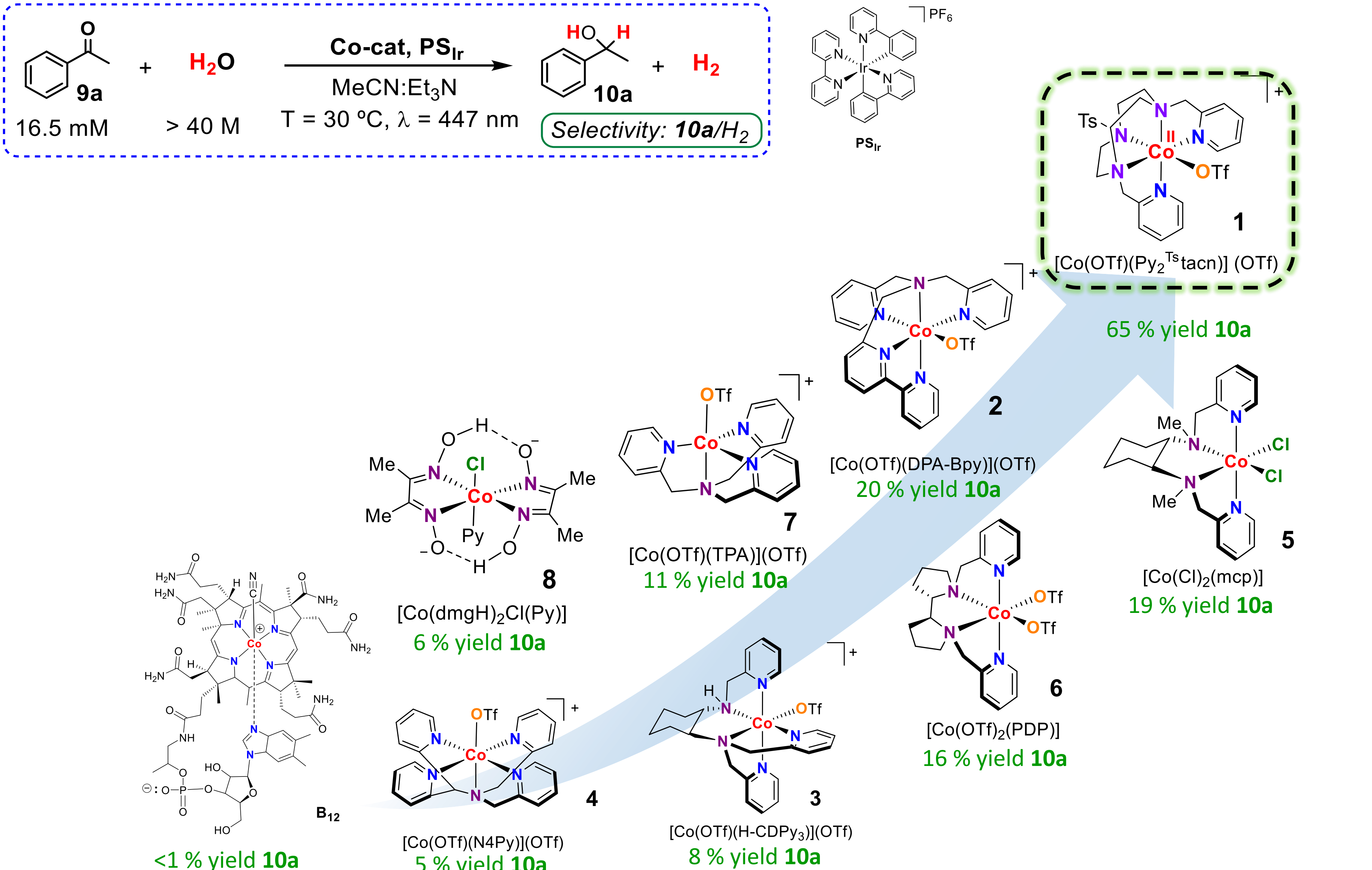
Photocatalytic reduction of acetophenone



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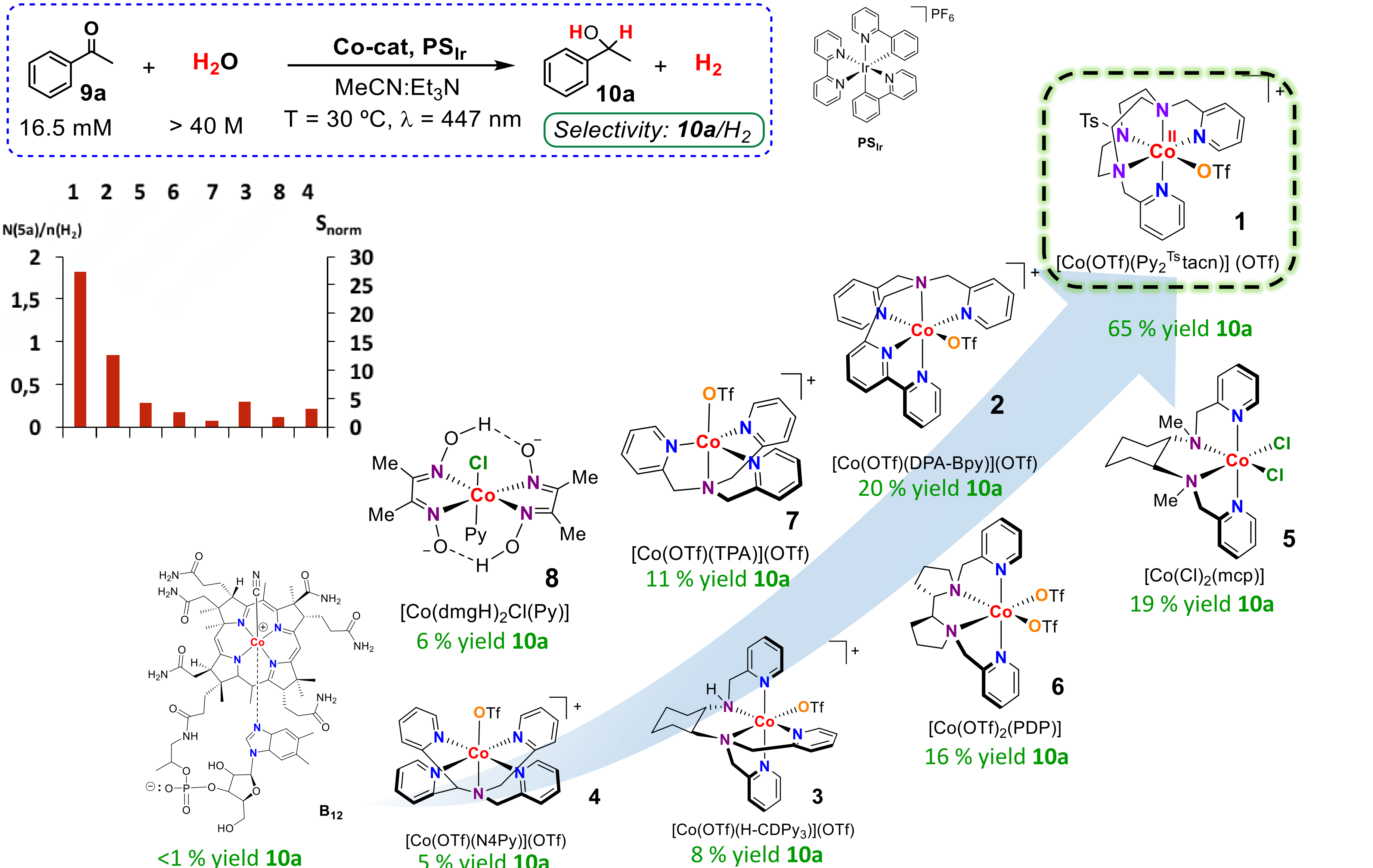
Photocatalytic reduction of acetophenone



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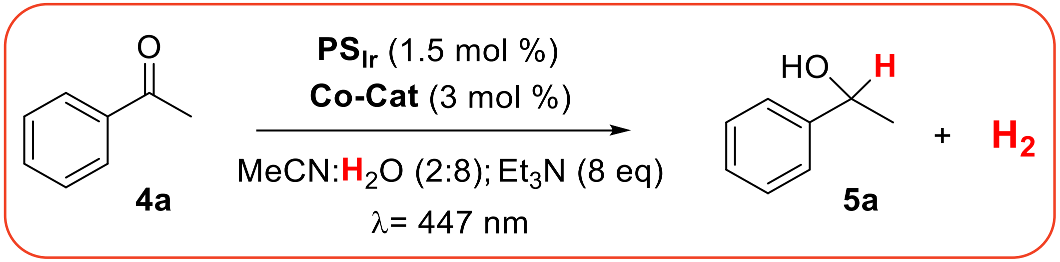
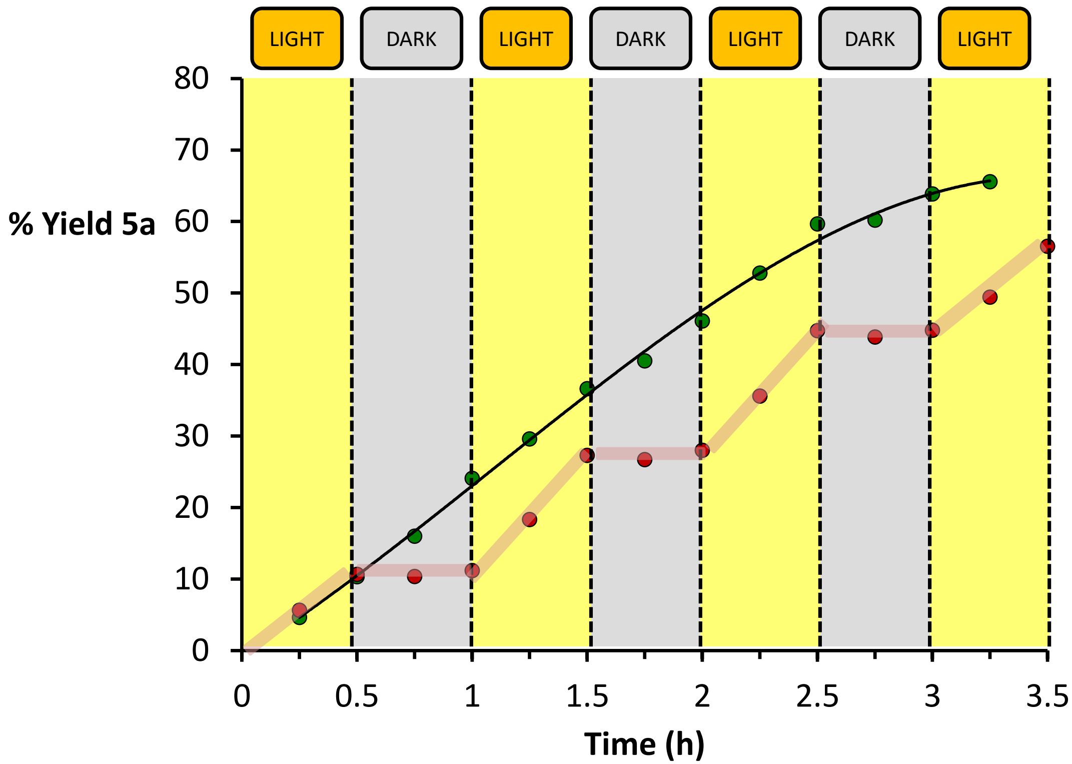
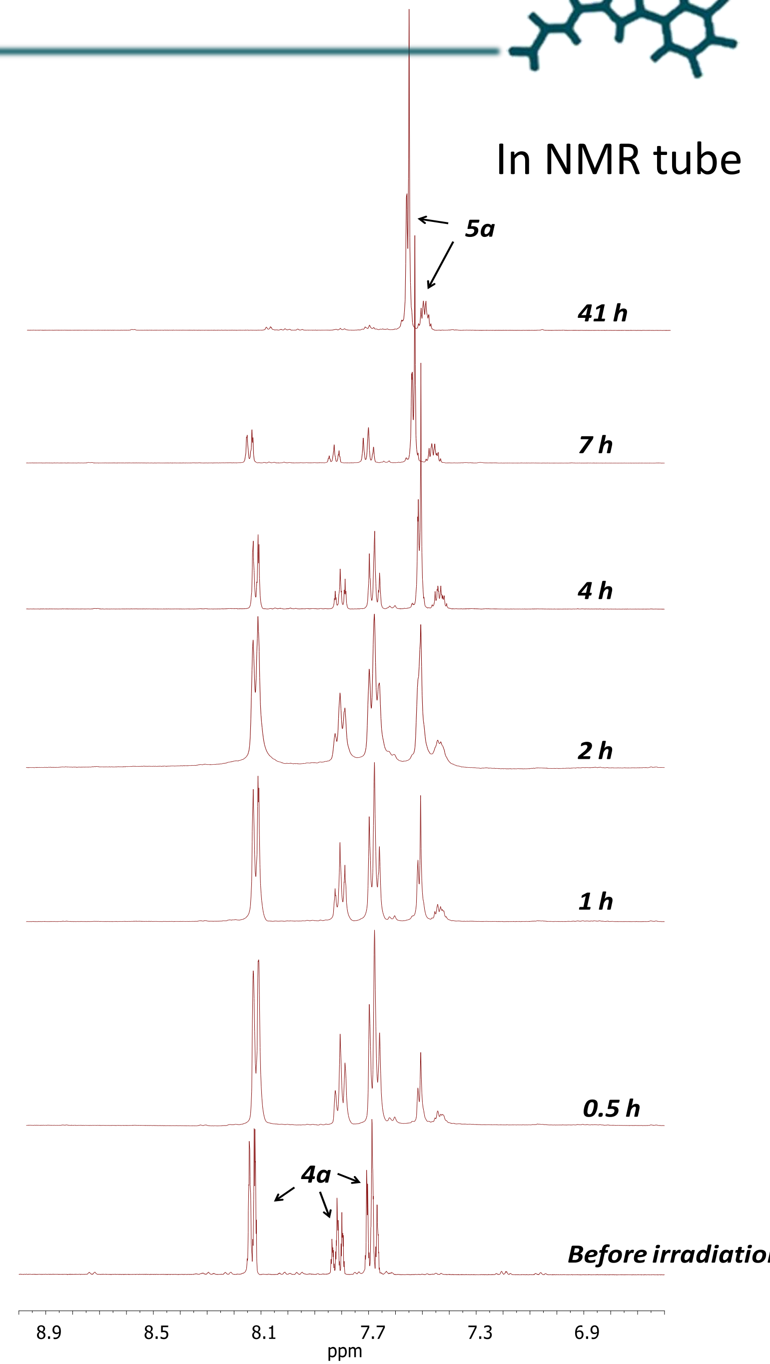
Photocatalytic reduction of acetophenone







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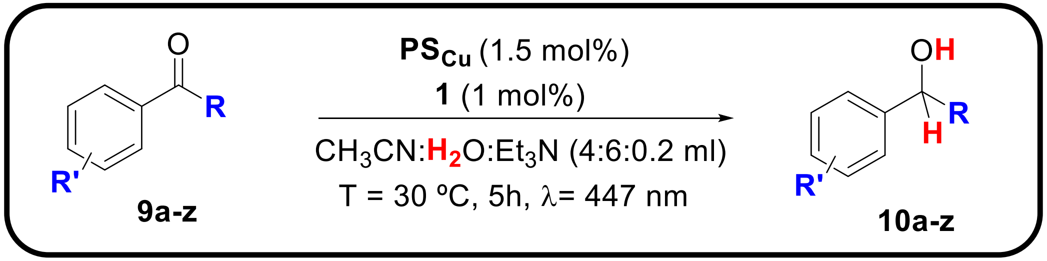
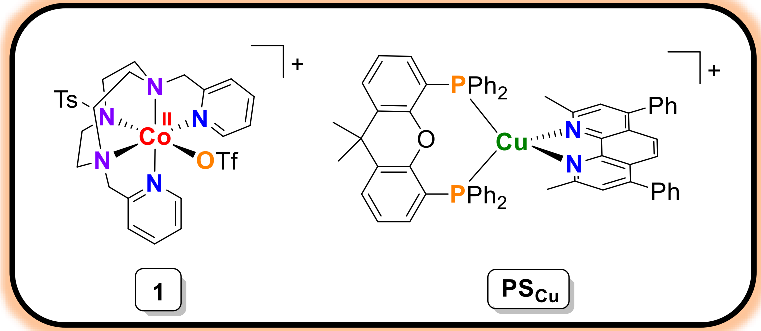
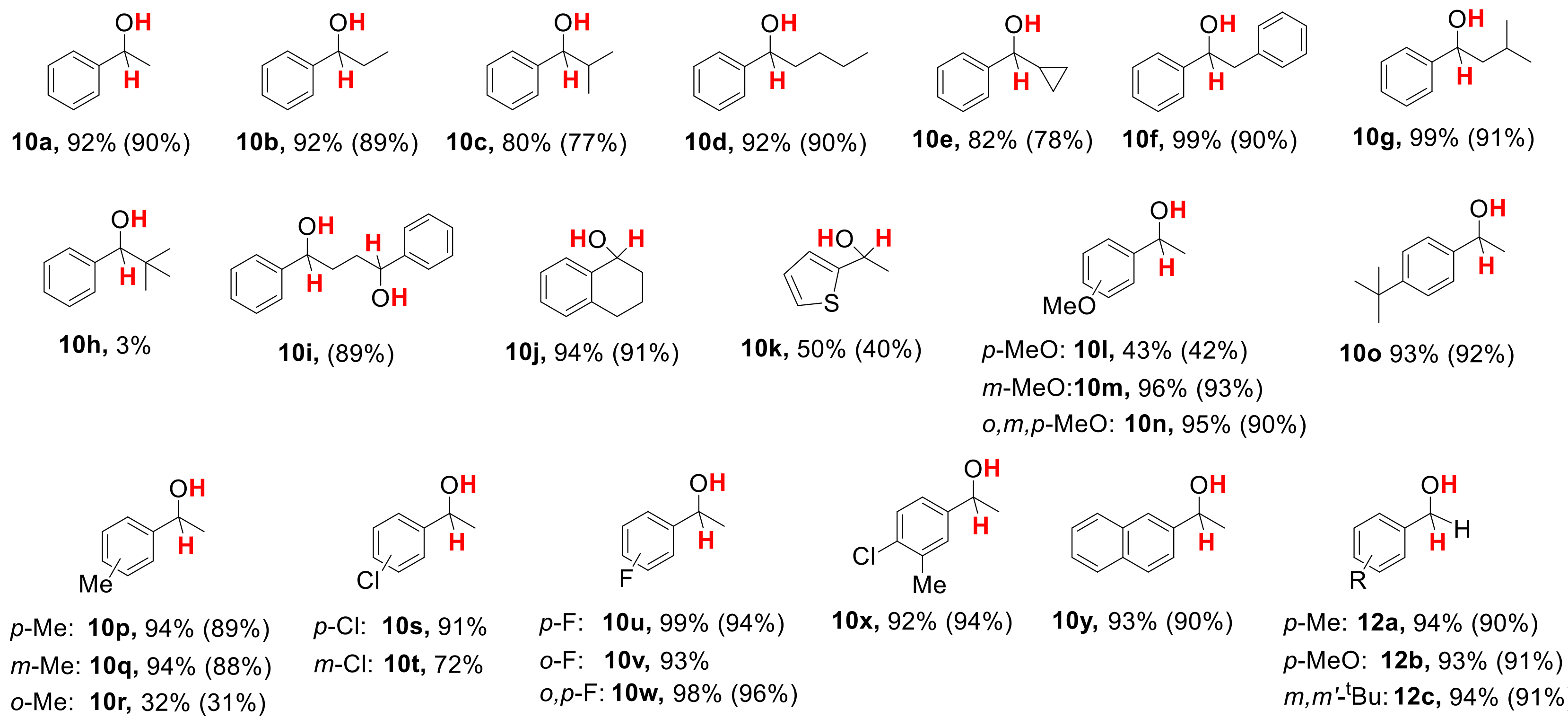
Photocatalytic reduction of aromatic ketones and aldehydes







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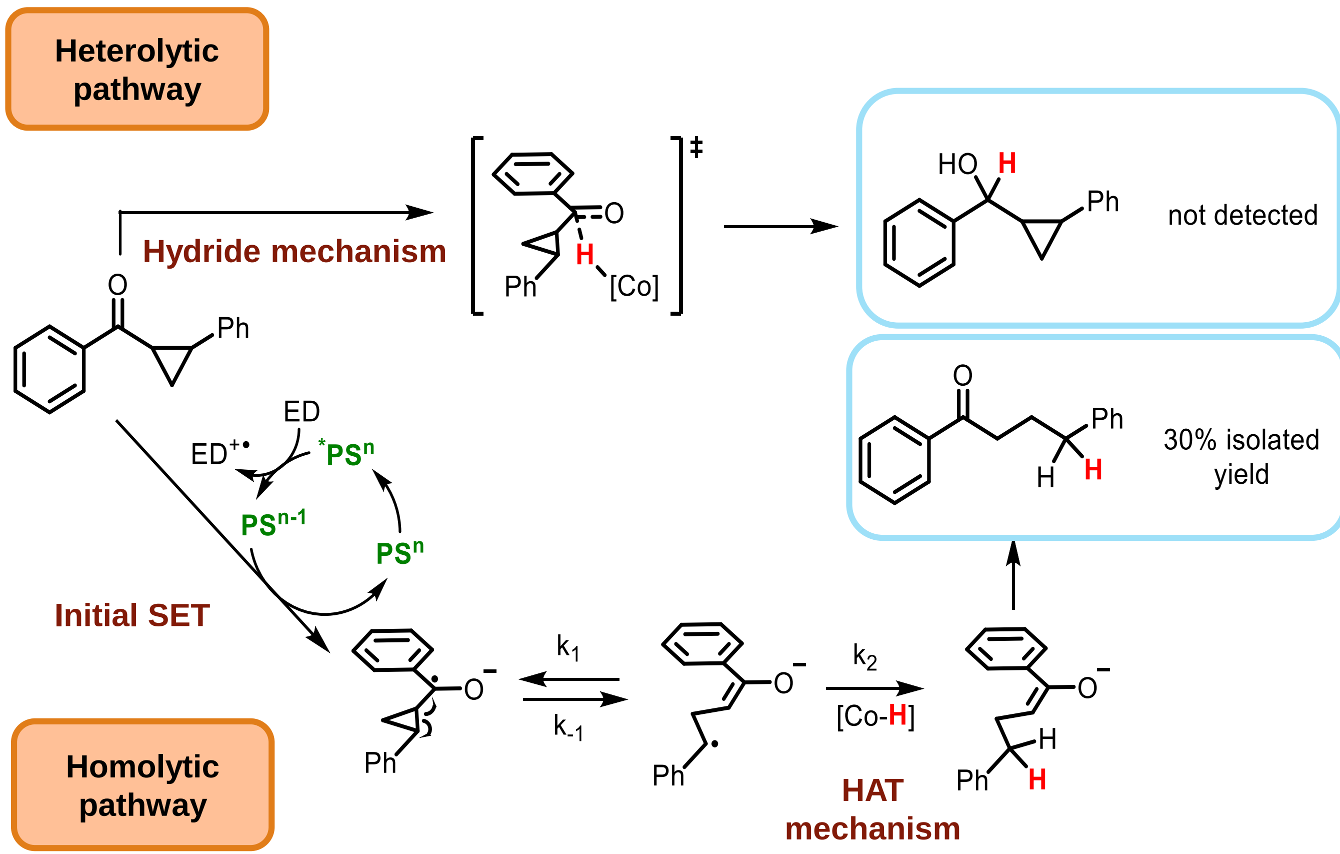
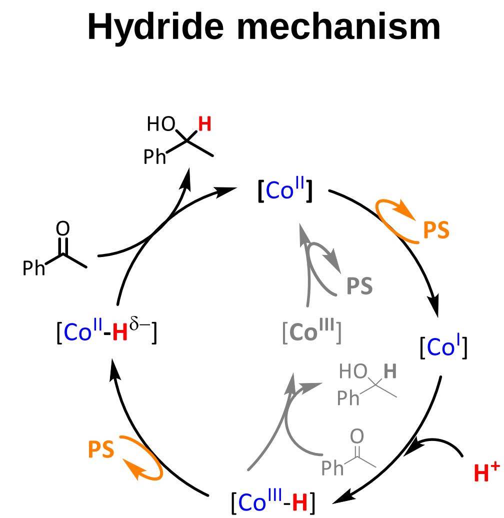
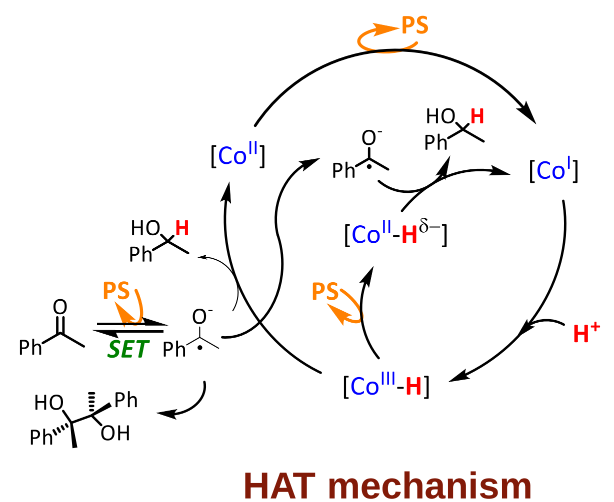
Photocatalytic reduction of aromatic ketones and aldehydes







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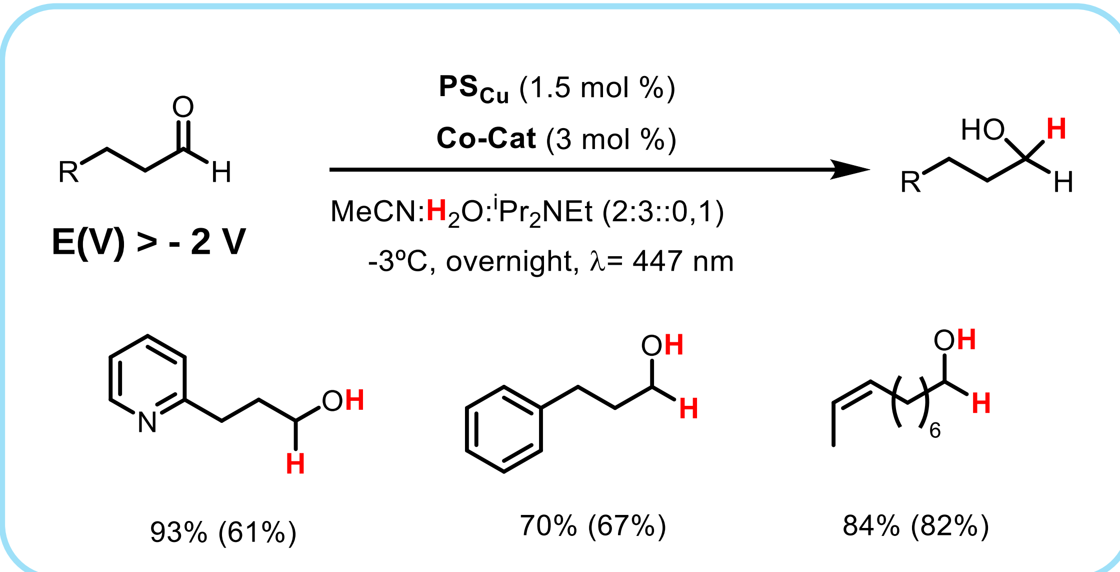
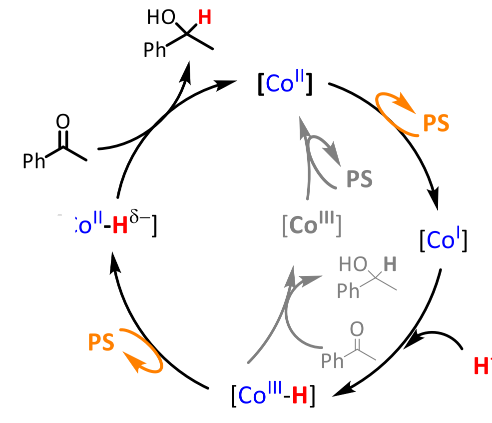
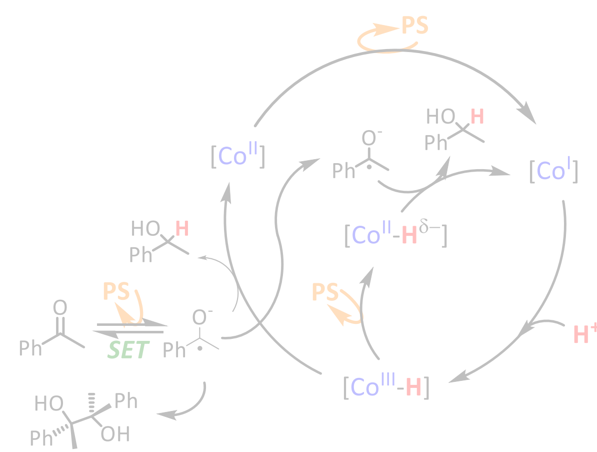
Photocatalytic reduction of aliphatic aldehydes



Hydride mechanism





HAT mechanism

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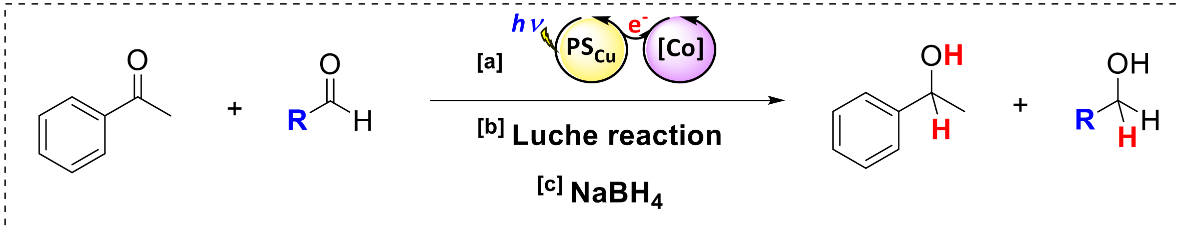
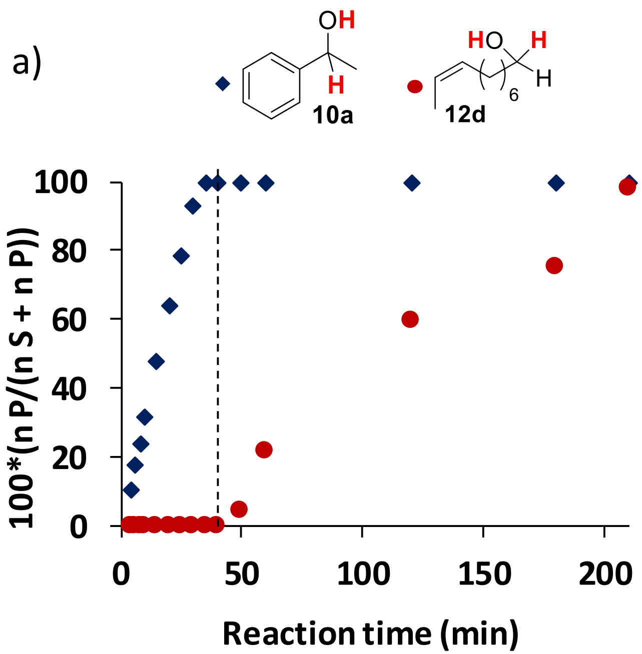
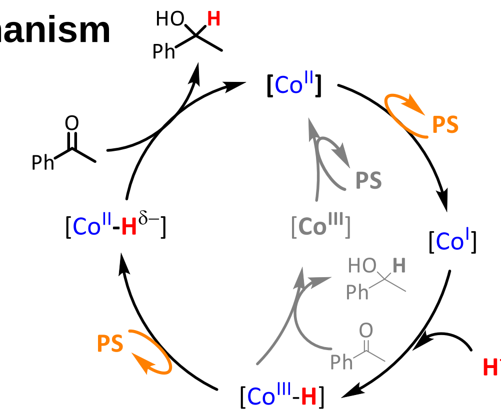
High chemoselectivity towards aromatic ketones

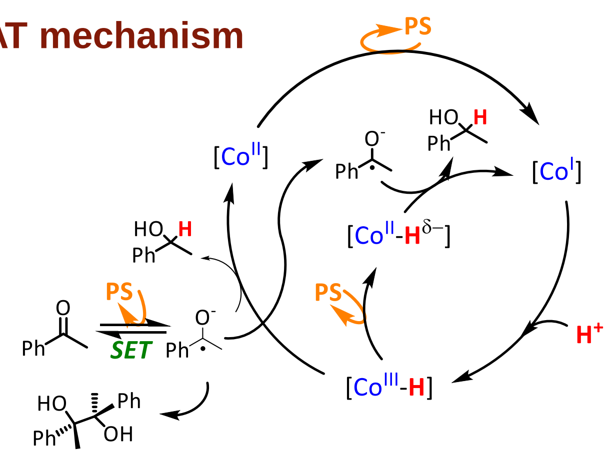




Hydride mechanism



SET-HAT mechanism



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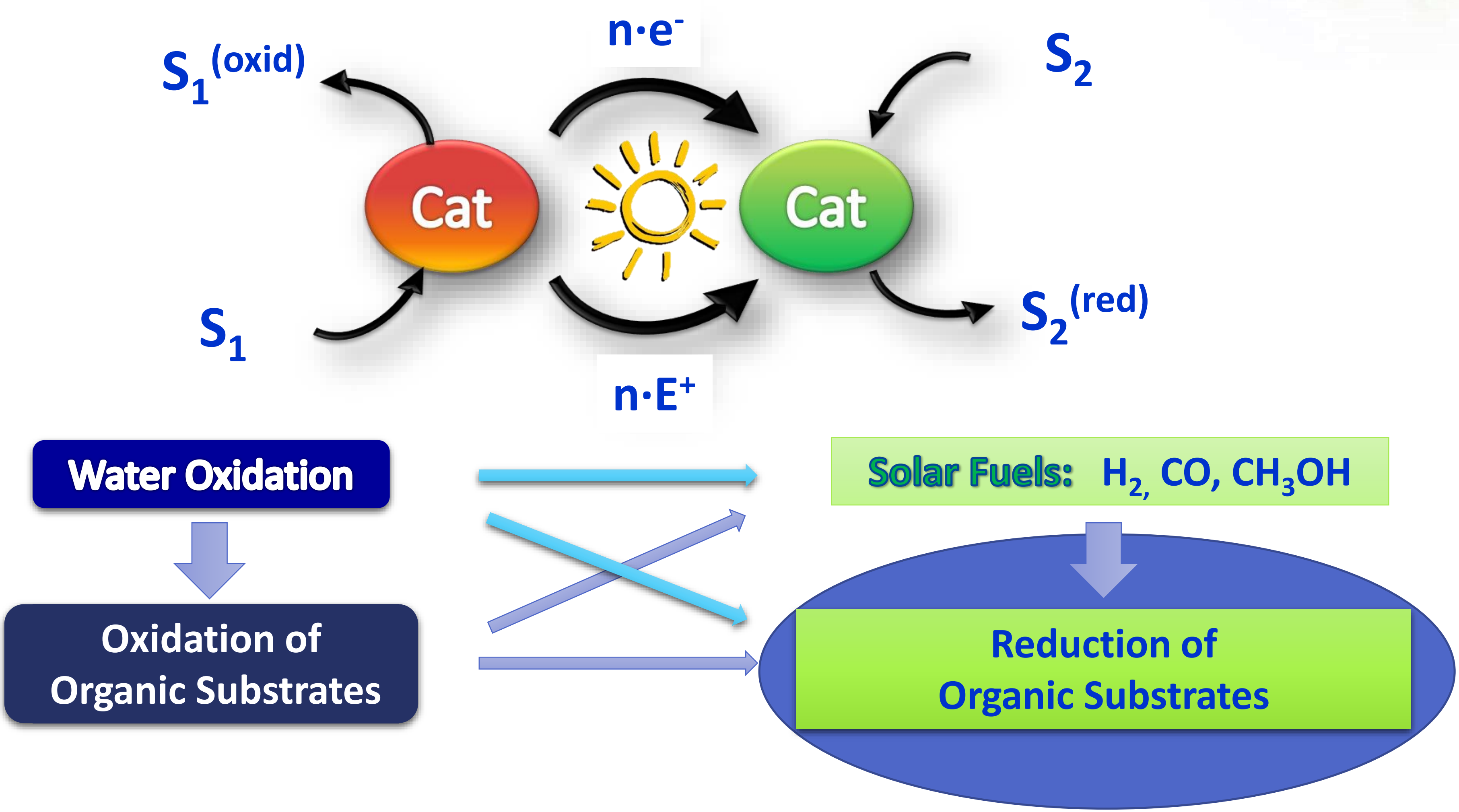

S1(oxid)
n·e-
S2
Cat
Cat
S1
S2(red)
n·E+
Water Oxidation
Oxidation of Organic Substrates
Solar Fuels: H2, CO, CH3OH
Reduction of Organic Substrates

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