

# Vers la photosynthèse artificielle: des catalyseurs bioinspirés

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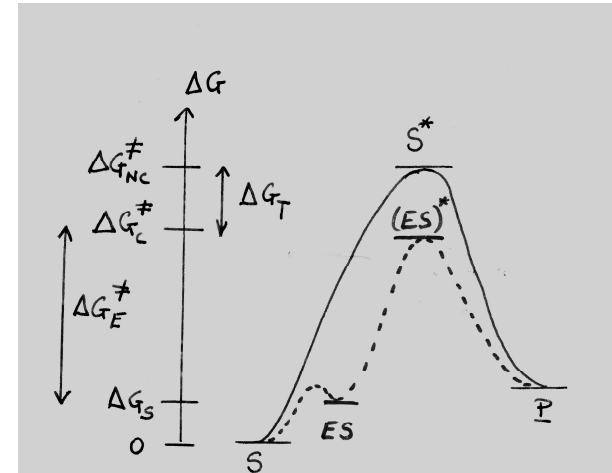
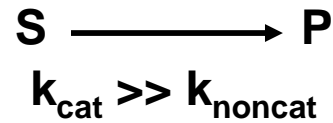


COLLÈGE  
DE FRANCE  
— 1530 —

cea



# Chimie verte: Catalyse



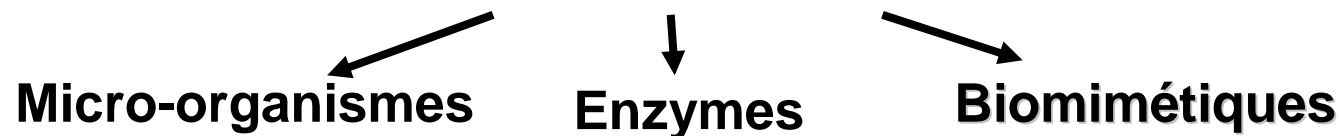
- Economique
- Limitation des déchets
- Limitation de la dépense énergétique



80 % des produits chimiques  
(de l'industrie chimique et pharmaceutique)  
sont obtenus par des processus catalytiques



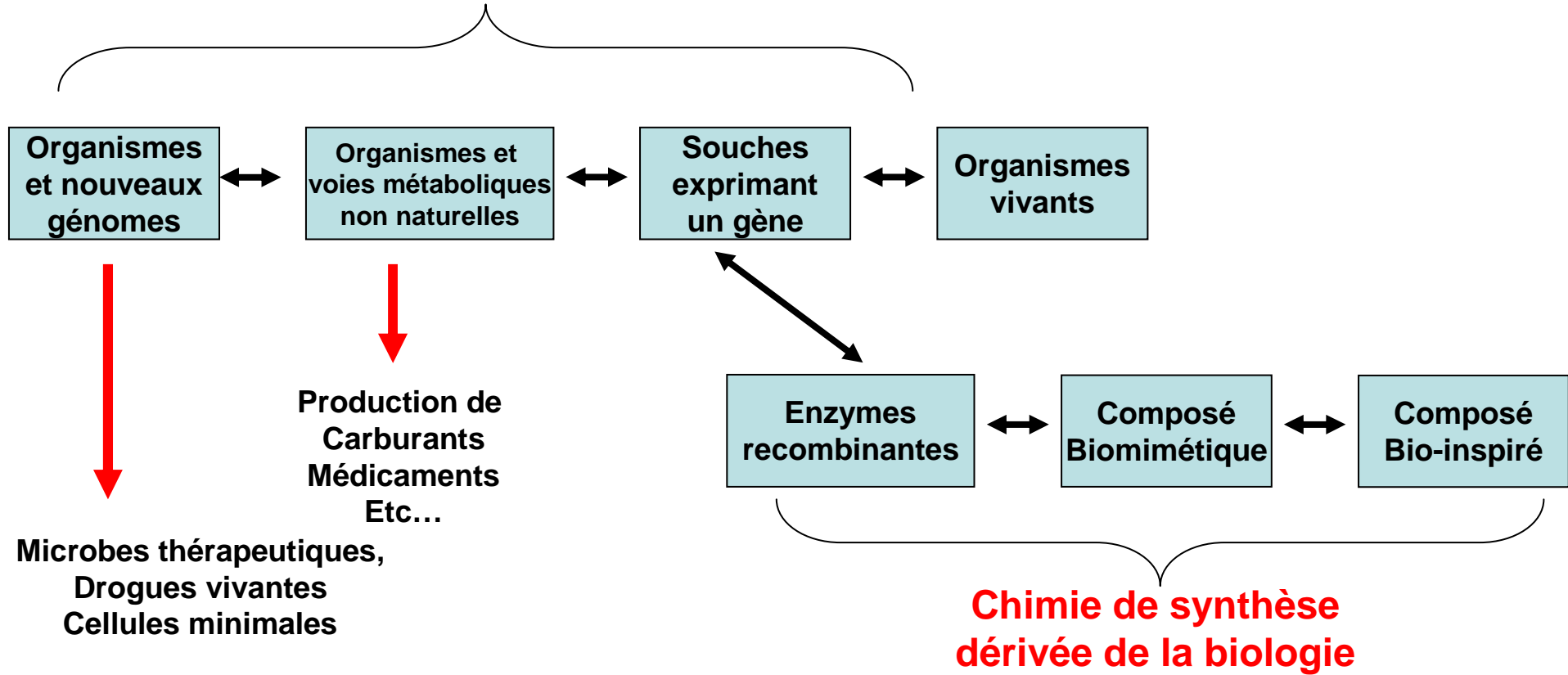
**BIOTECHNOLOGIES**  
(5% en 2003 à 30% en 2030)



# De la Biologie à la Synthèse

Comprendre/exploiter le vivant et la nature en la reconstruisant

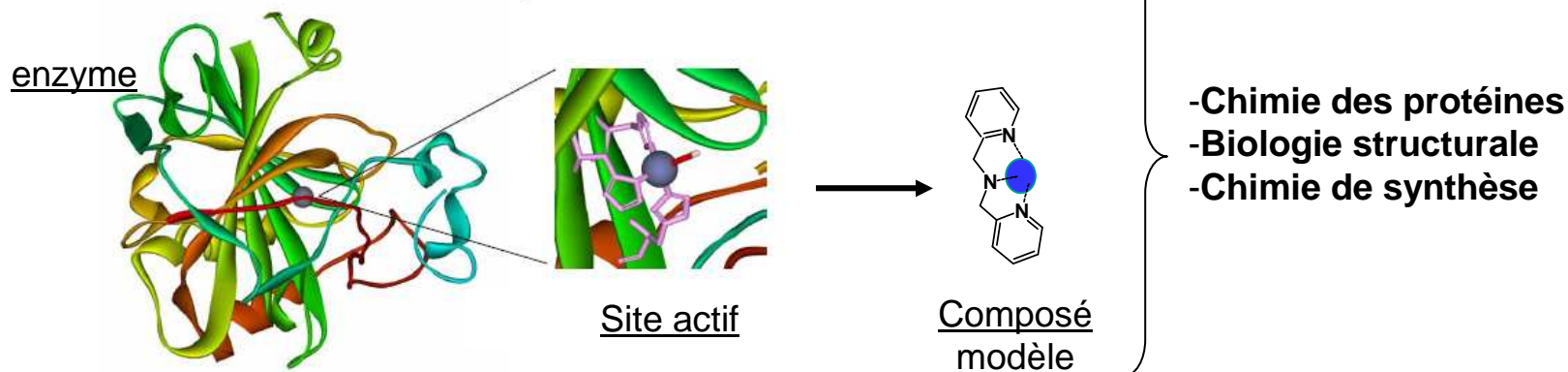
## Biologie synthétique



**BIOSECURITE ?**

# Chimie Biomimétique et Bioinspirée

## → La stratégie (optimale ?)



- ## → Les objectifs
- Découvrir de nouveaux catalyseurs peu coûteux, respectueux de l'environnement (métaux non toxiques) par « plagiat » et « minimalisme »
  - Mettre au point de nouveaux outils chimiques pour l'étude de mécanismes enzymatiques

## → Mimétisme et inspiration ?

« les poètes immatures copient, les poètes accomplis dérobent » T.S. Eliot

## → Avantages et inconvénients

- + Plus petits, faciles à synthétiser et à caractériser, moins coûteux, plus robustes dans des conditions extrêmes, moins substrat-spécifiques, plus facilement modulables (sélectivités et spécificités)
- Vitesses de réaction plus faibles à T et P ambiantes, moins de cycles catalytiques, moins solubles dans l'eau, moins sélectifs

**Contexte:**  
**Société et science au XXI<sup>e</sup> siècle:**  
**L'ENERGIE!!!**

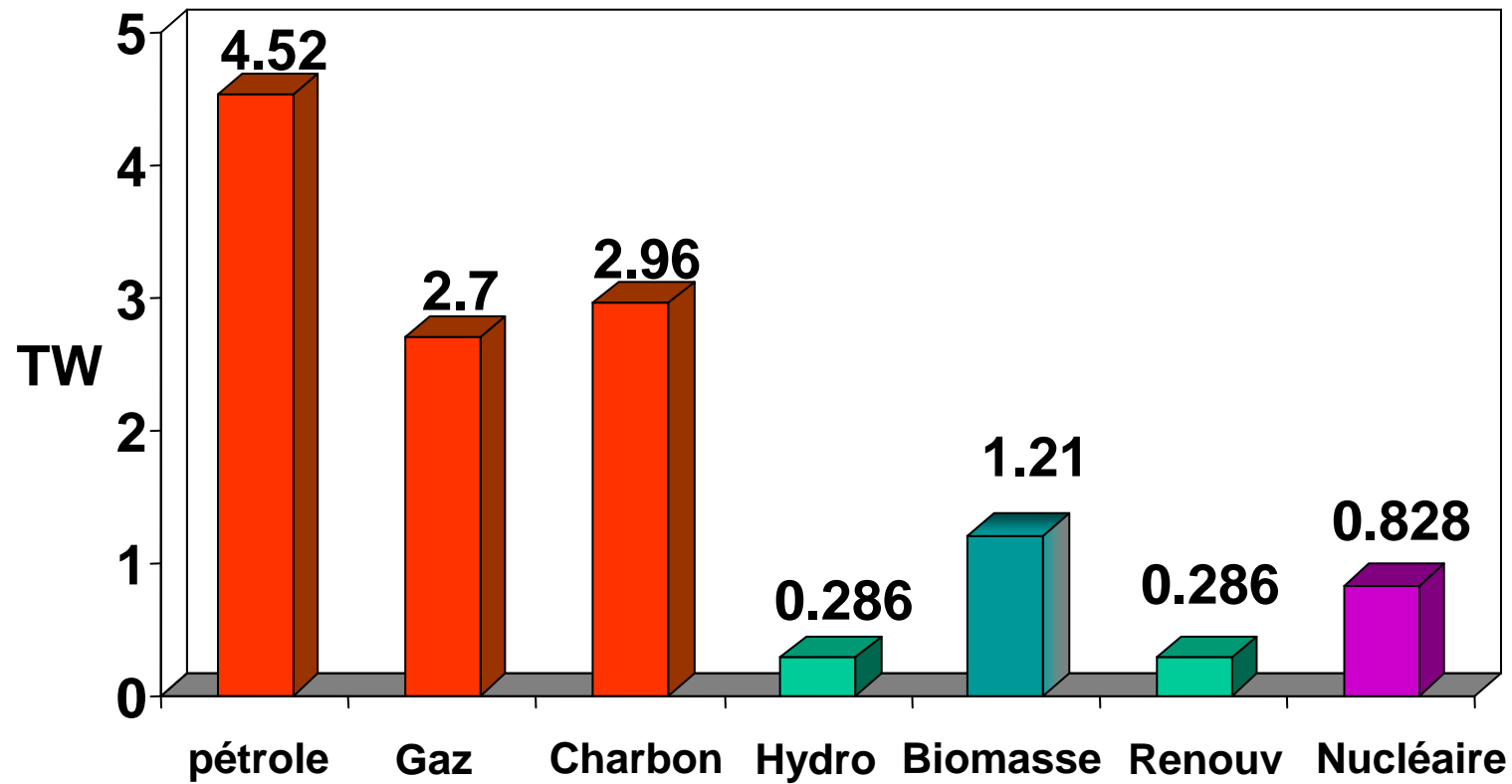
**Doublement de la demande énergétique en 40-50 ans  
(de 13 à 27 TW)**

- accroissement de la population mondiale  
(d'ici 2050 de 6 à 9/10 milliards d'habitants)
- croissance des pays émergents (Chine et Inde)

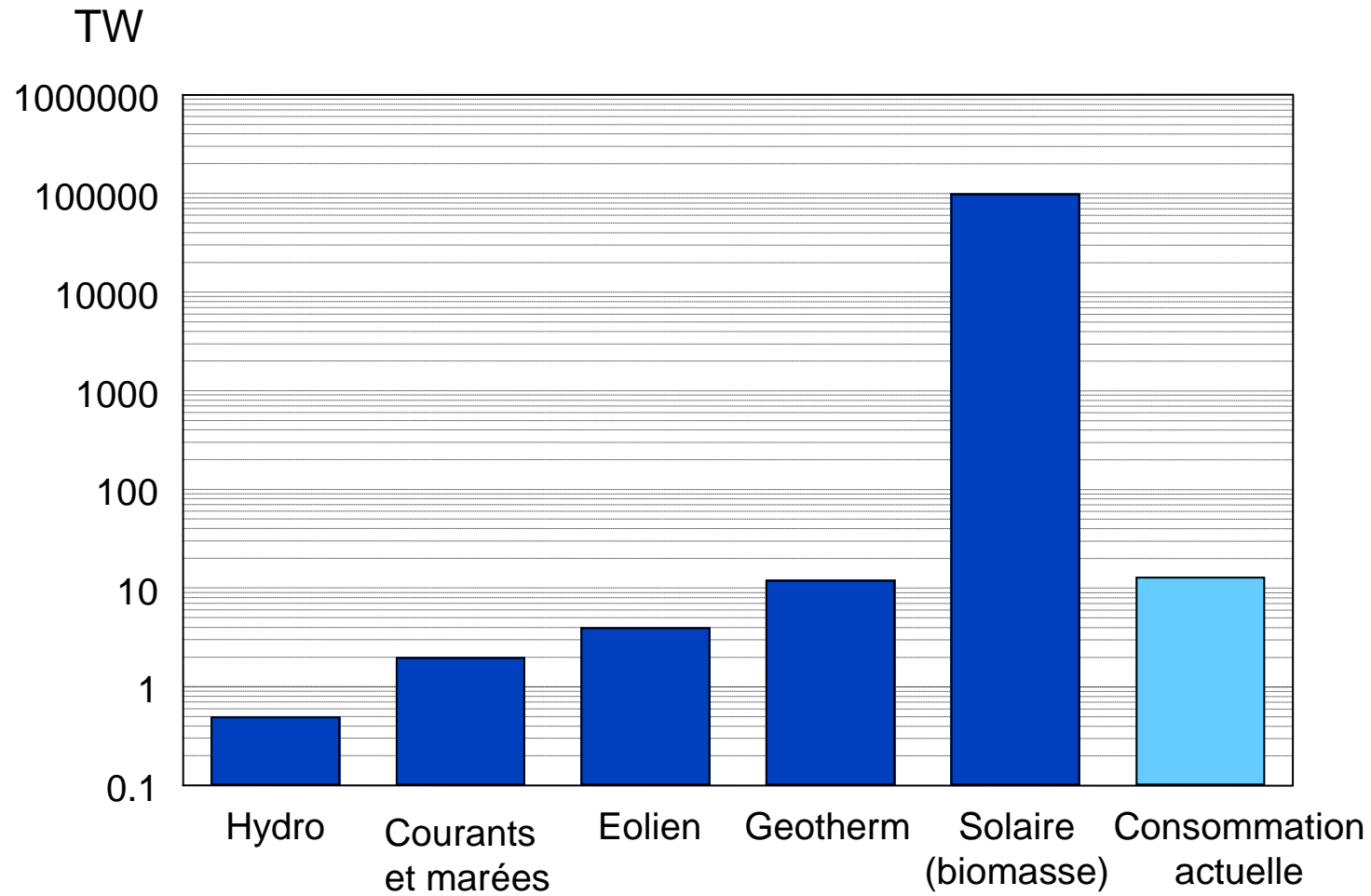
**Limitation des émissions des gaz à effet de serre (CO<sub>2</sub>).  
(tendance: 380 en 2008 ; 550 ppm en 2035)**

**Epuisement des réserves carbonées fossiles** (pétrole, gaz, charbon)  
( à l'échelle mondiale 80% des sources primaires d'énergie)  
charbon: > 200 ans; gaz: >100 ans; pétrole: 50-100 ans.  
Uranium: 150 ans, (surgénérateurs 500 ans).

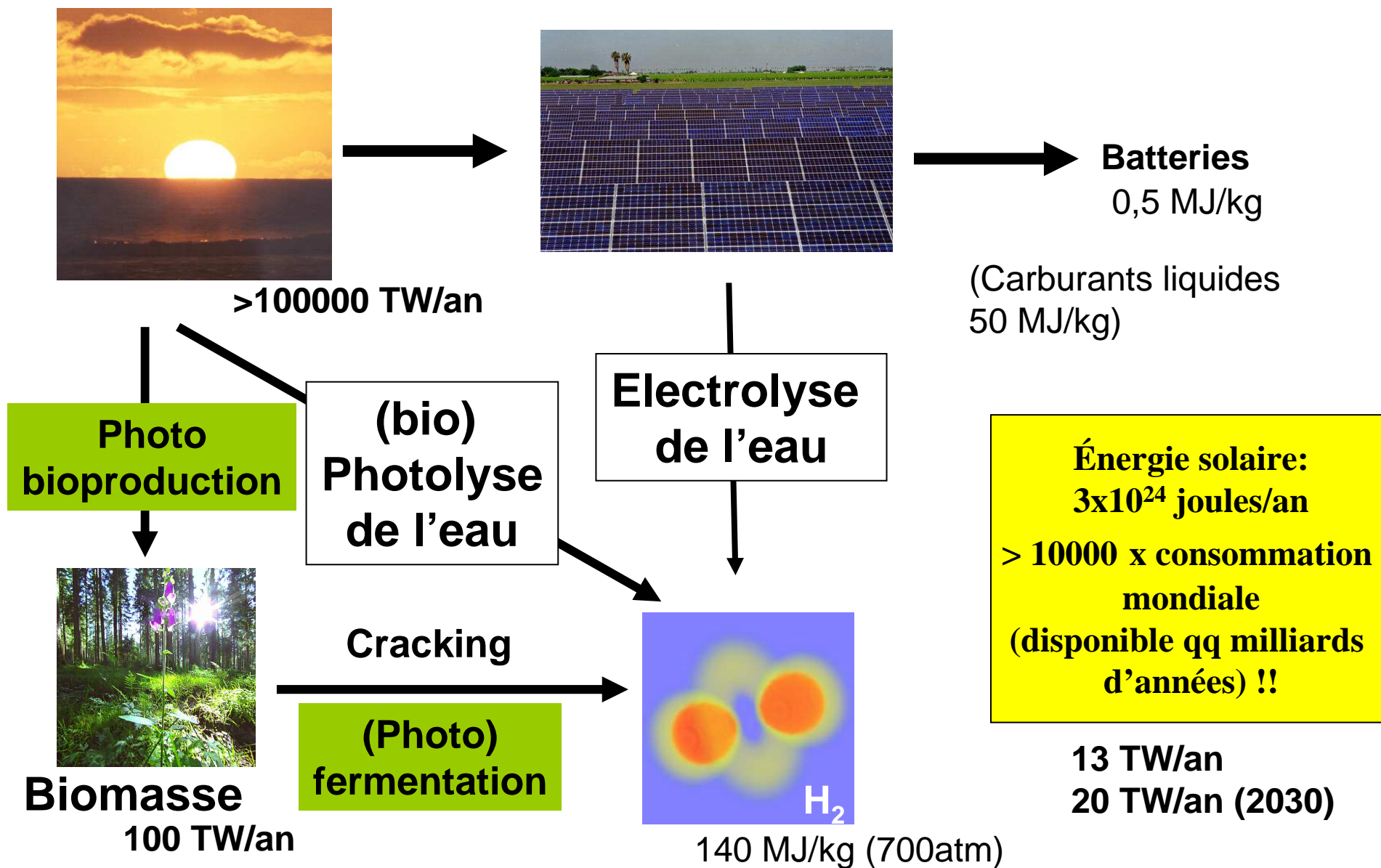
# Consommation globale d'énergie (Total 13.5 TW)



# Potentiel des sources d'énergie renouvelables



# Soleil: la source d'énergie ! la stocker sous forme d'hydrogène







La lumière n'agit pas directement sur l'eau !!

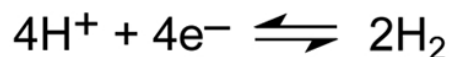
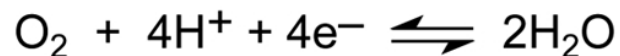
→ **-Un collecteur de photons**

1  $h\nu$  → 1 trou/1 électron

→ **-Des catalyseurs pour accumuler/utiliser**

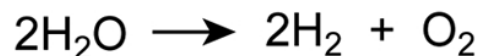
4 « trous » (formation  $\text{O}_2$ ): *photosystème*

2x2 électrons (formation  $2 \text{H}_2$ ) : *hydrogénases*



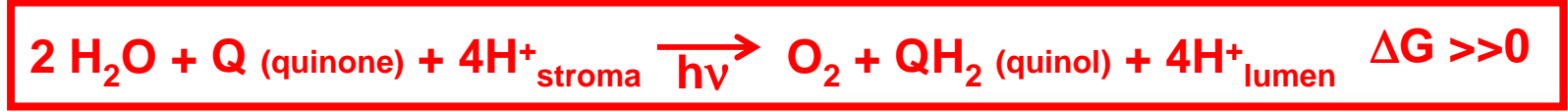
$$E_{\text{anode}} = 1.23 \text{ V} - 0.059 (\text{pH}) \text{ V vs NHE}$$

$$E_{\text{cathode}} = 0 \text{ V} - 0.059 (\text{pH}) \text{ V vs NHE}$$

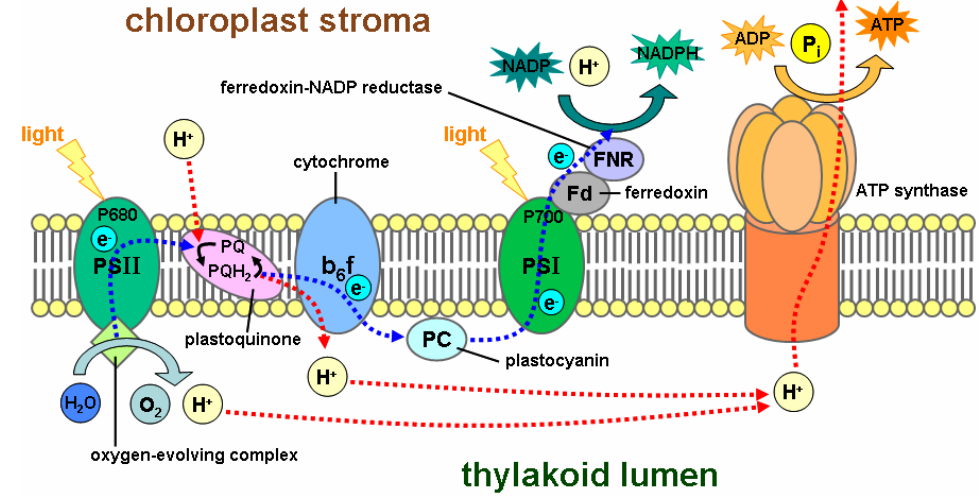
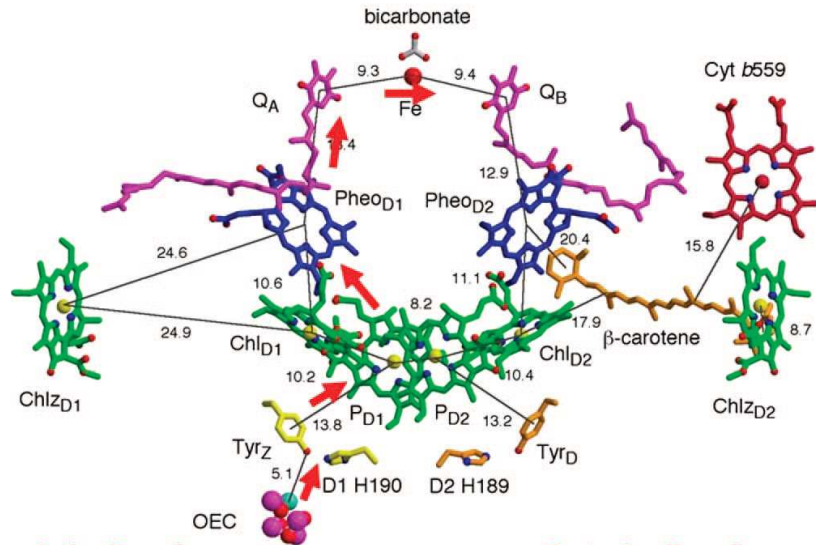


$$E_{\text{rxn}} = -1.23 \text{ V}$$

# Photosynthèse (plantes): production d'oxygène

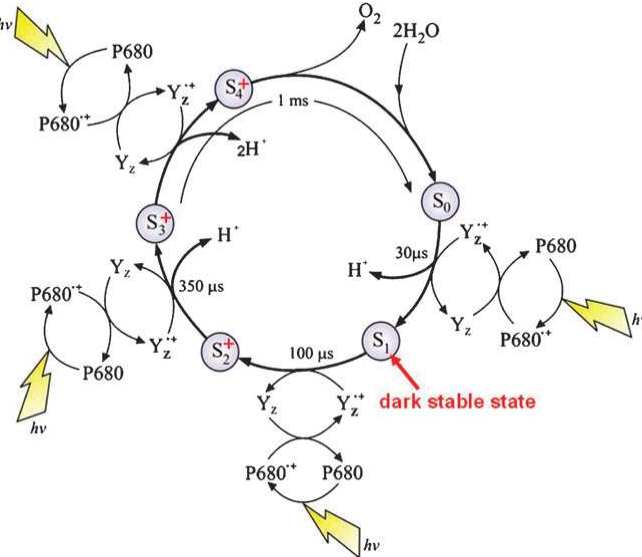
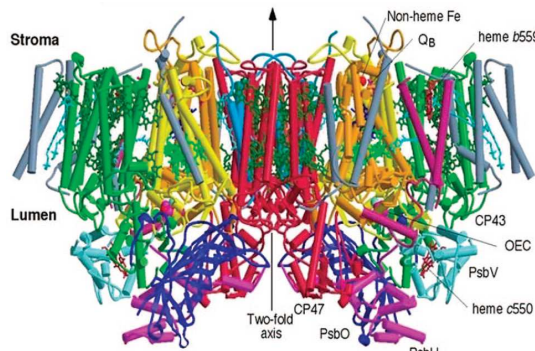


## Electron transport cofactors



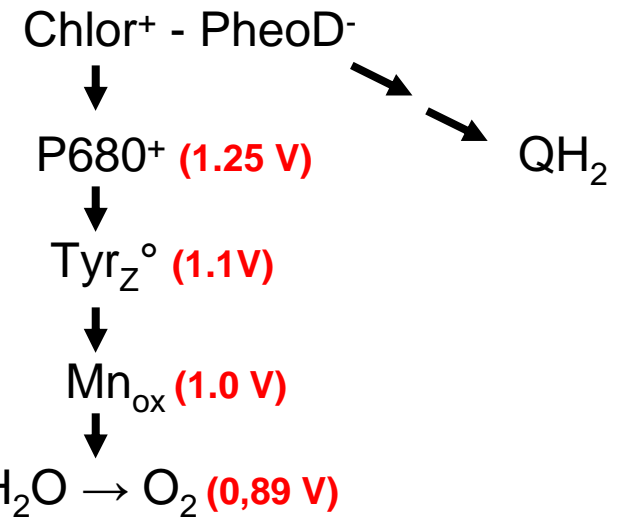
## Active Branch

## Protective Branch



## Chlorophyll-PheophytinD1

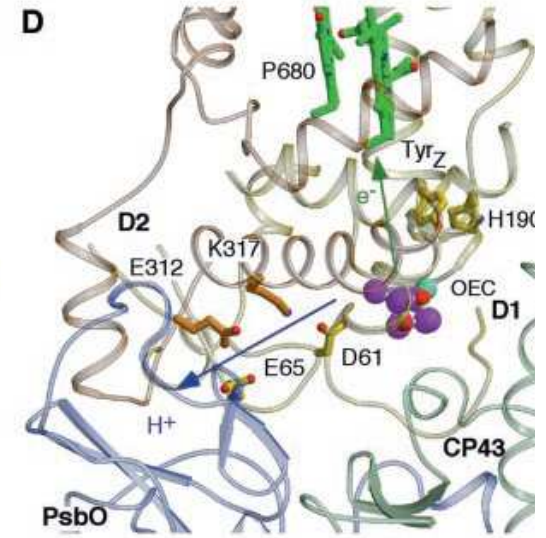
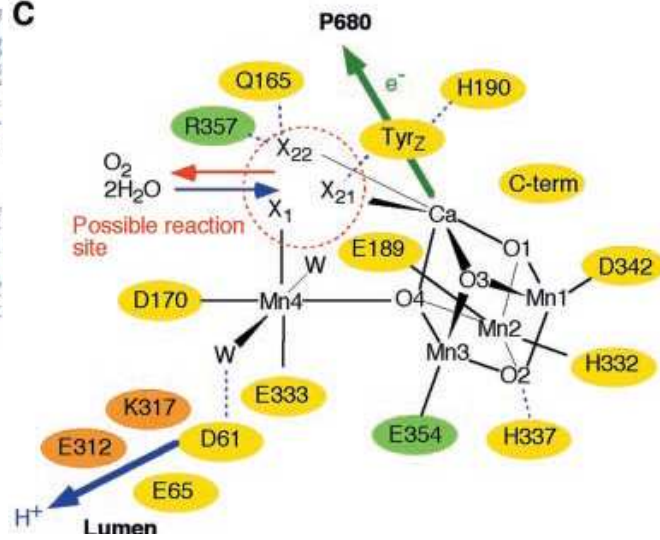
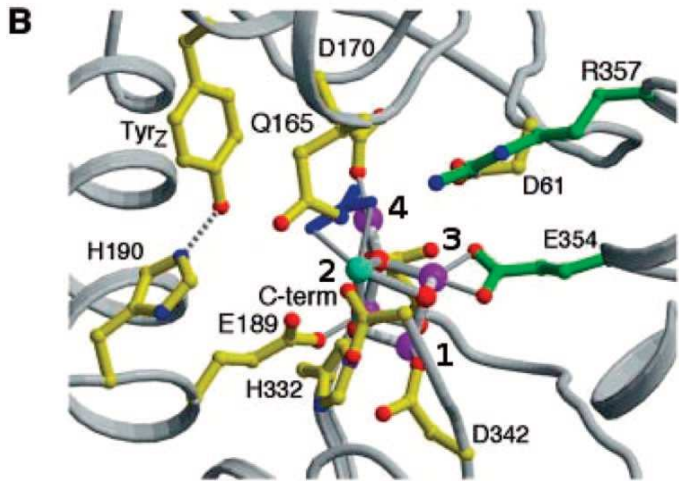
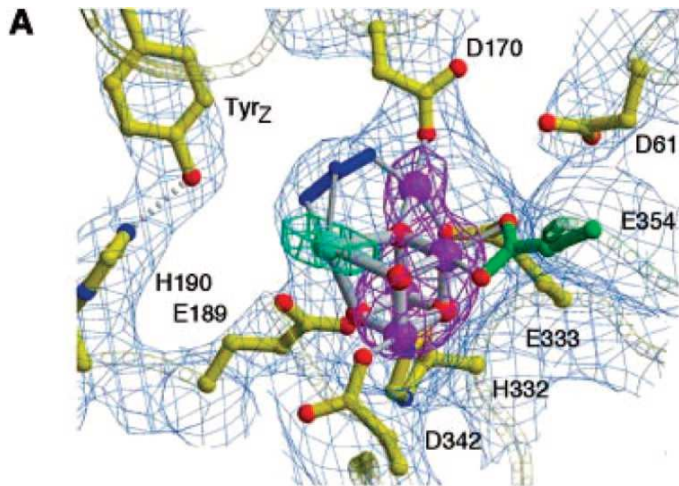
$\downarrow h\nu (680 \text{ nm} = 1,8 \text{ eV})$



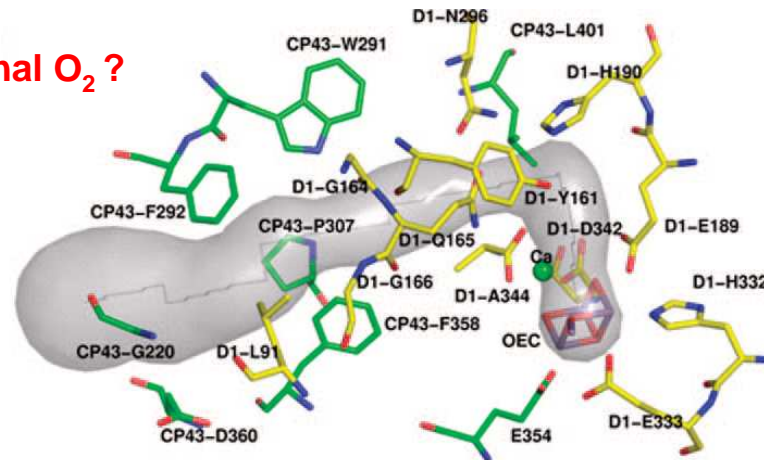
# Informations structurales I: modèle A

Science 2004 303 1831

3,5 Å résolution

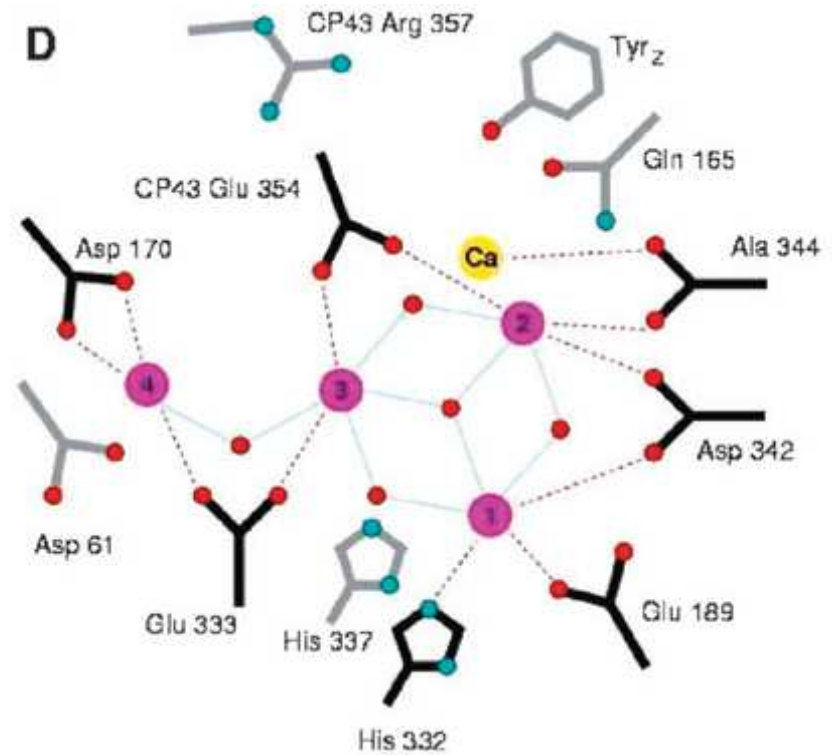
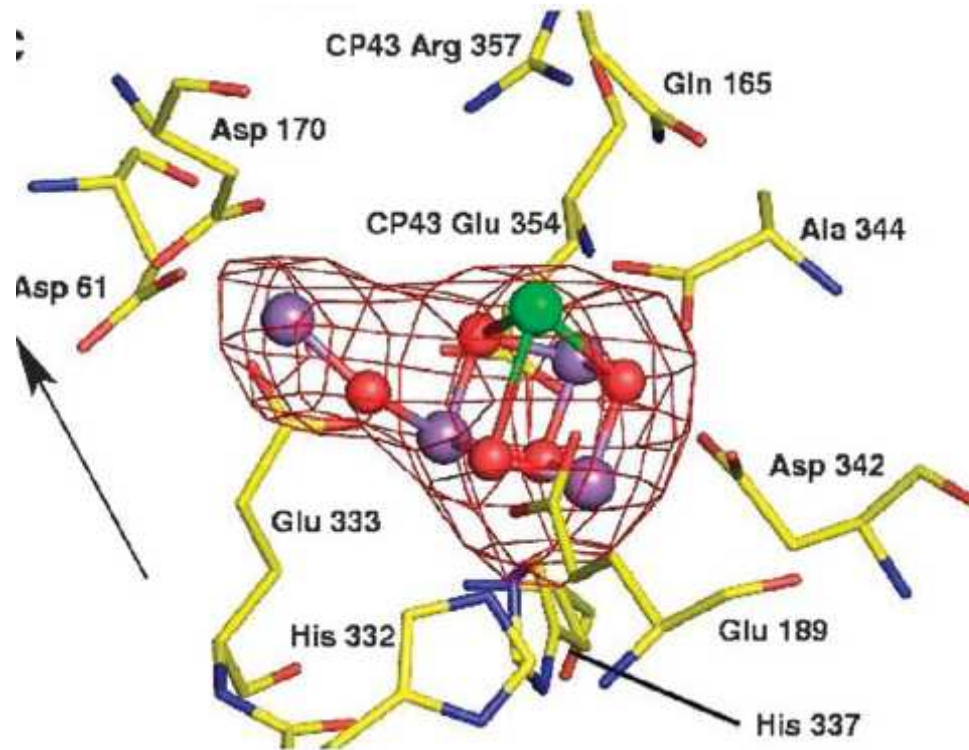


Canal O<sub>2</sub> ?

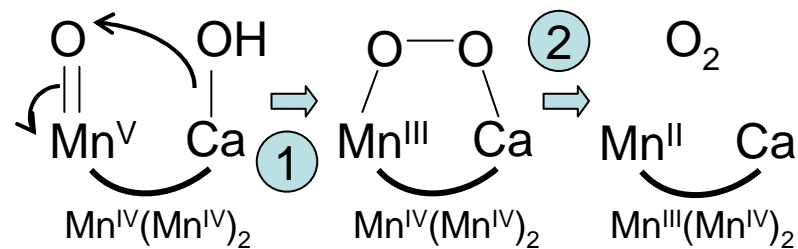
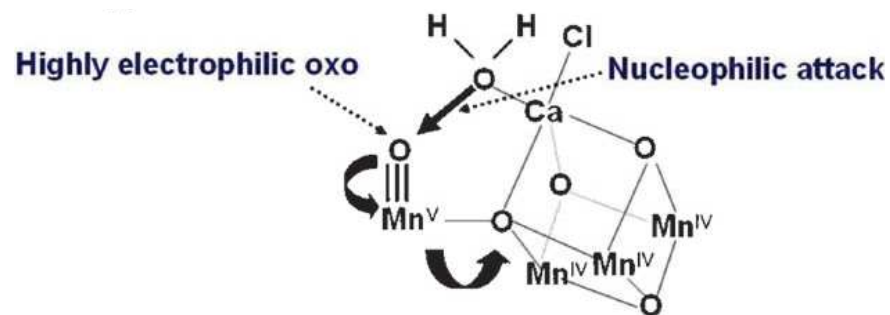
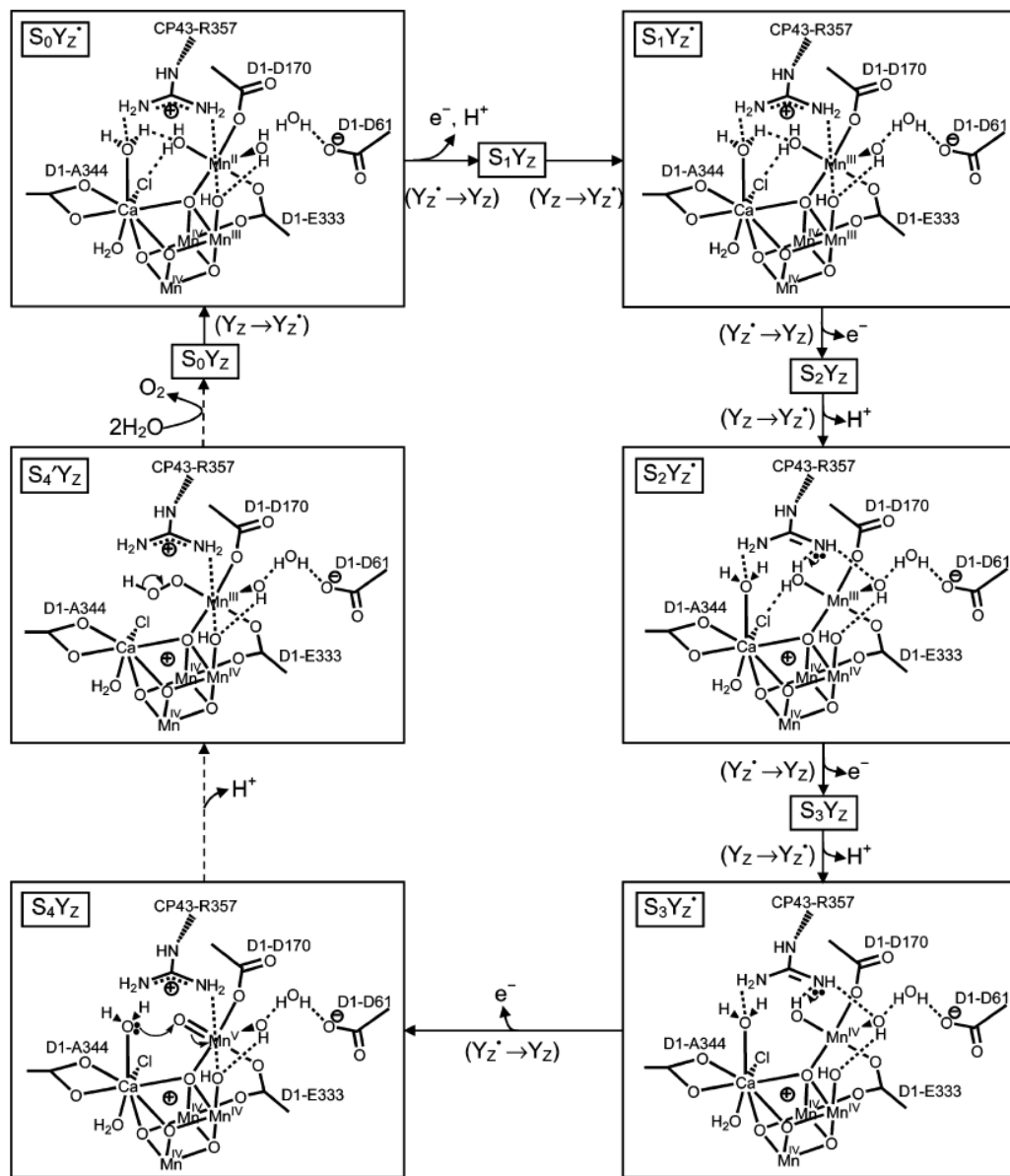


## Informations structurales II: modèle B

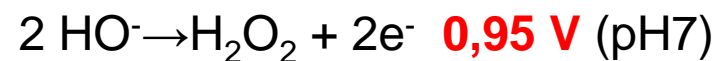
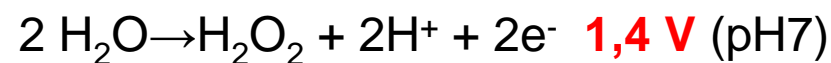
Science 2006 314 821 (EXAFS);  
Barber J: Chem Soc Rev 2009, 38, 185; Inorg Chem 2008, 47, 1700



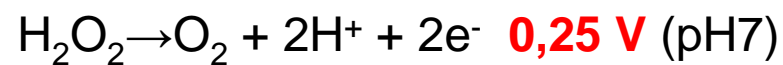
# Mécanisme



① Formation de peroxyde

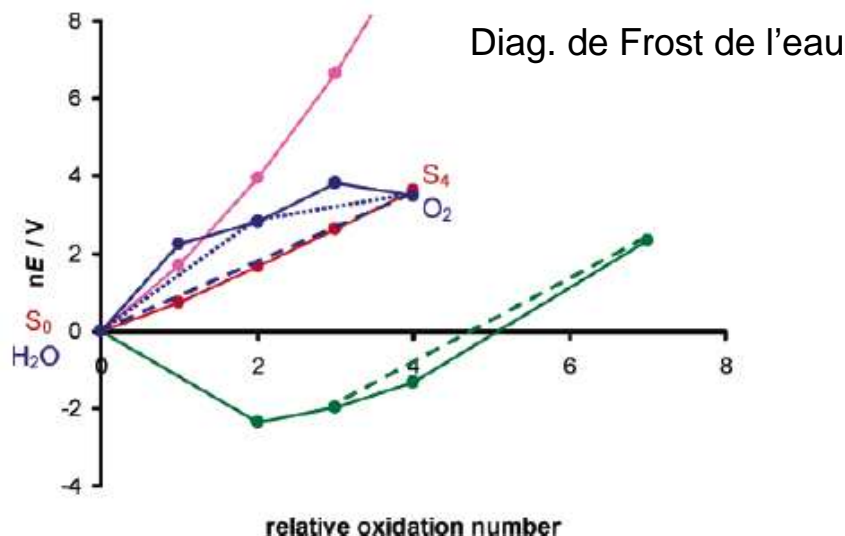
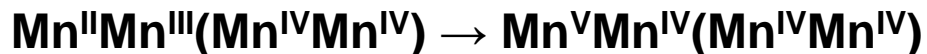


② Oxydation du peroxyde en O<sub>2</sub>

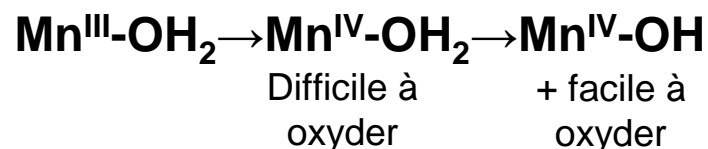


# Les propriétés remarquables du centre à Mn

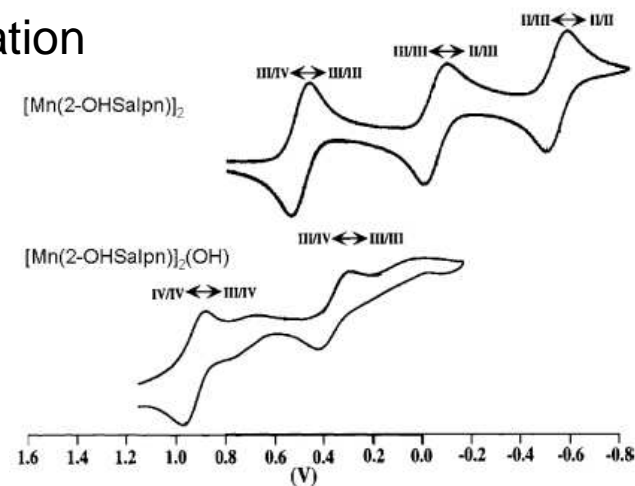
⇒ Accumulation de 4 équivalents oxydants



- Une oxydation de l'eau à 4 électrons est plus favorable
- le potentiel de S4 est juste celui qui est nécessaire pour oxyder H<sub>2</sub>O
- le couplage transfert d'électrons/ transfert de protons est essentiel



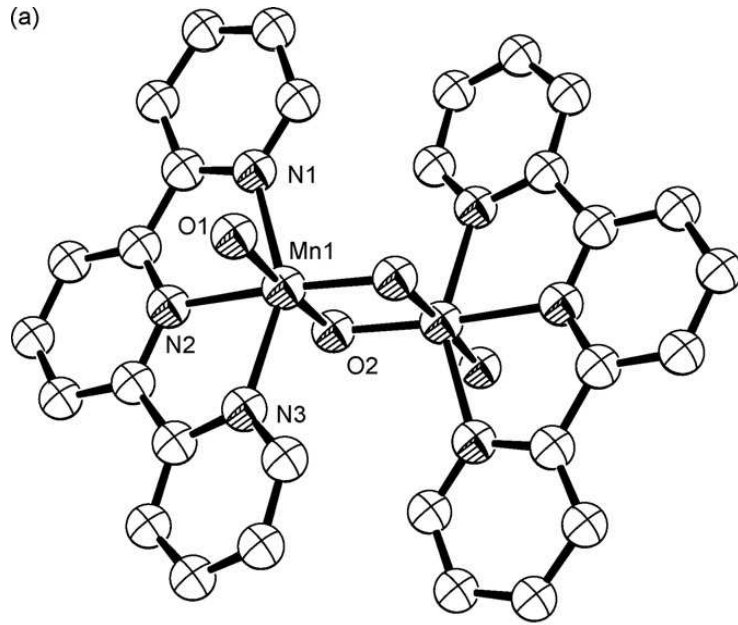
⇒ Le potentiel reste constant à ~1 V à chaque oxydation (nécessite un perte de charge +)



# Composés modèles Manganèse

Activité du système naturel

~ 1000 O<sub>2</sub> s<sup>-1</sup>



**Catalyseur de Brudvig**  
(Brudvig, Crabtree, Science 1999)

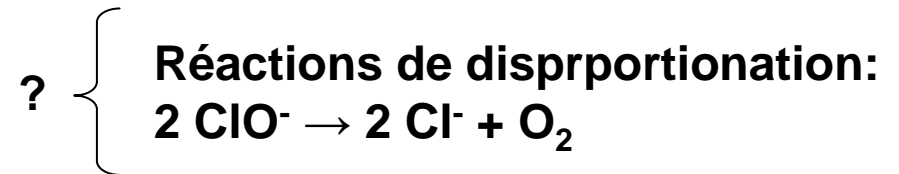
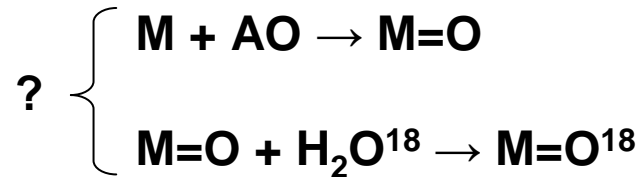
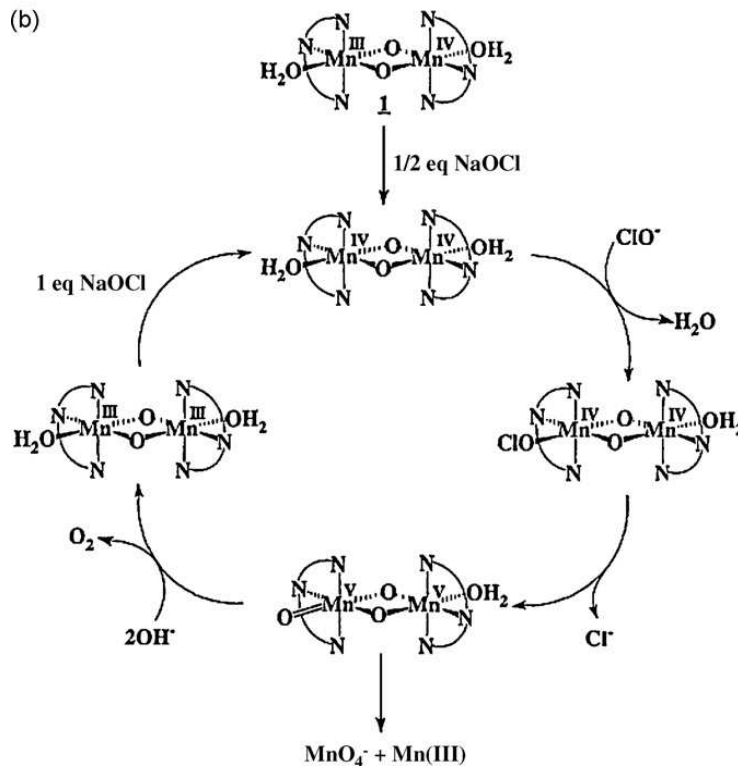
$\text{ClO}^-$  : 5 mol  $\text{O}_2$ /mol cata

$\text{HSO}_5^-$  : 50 mol/mol

$\text{Ce}^{4+}$  : 0

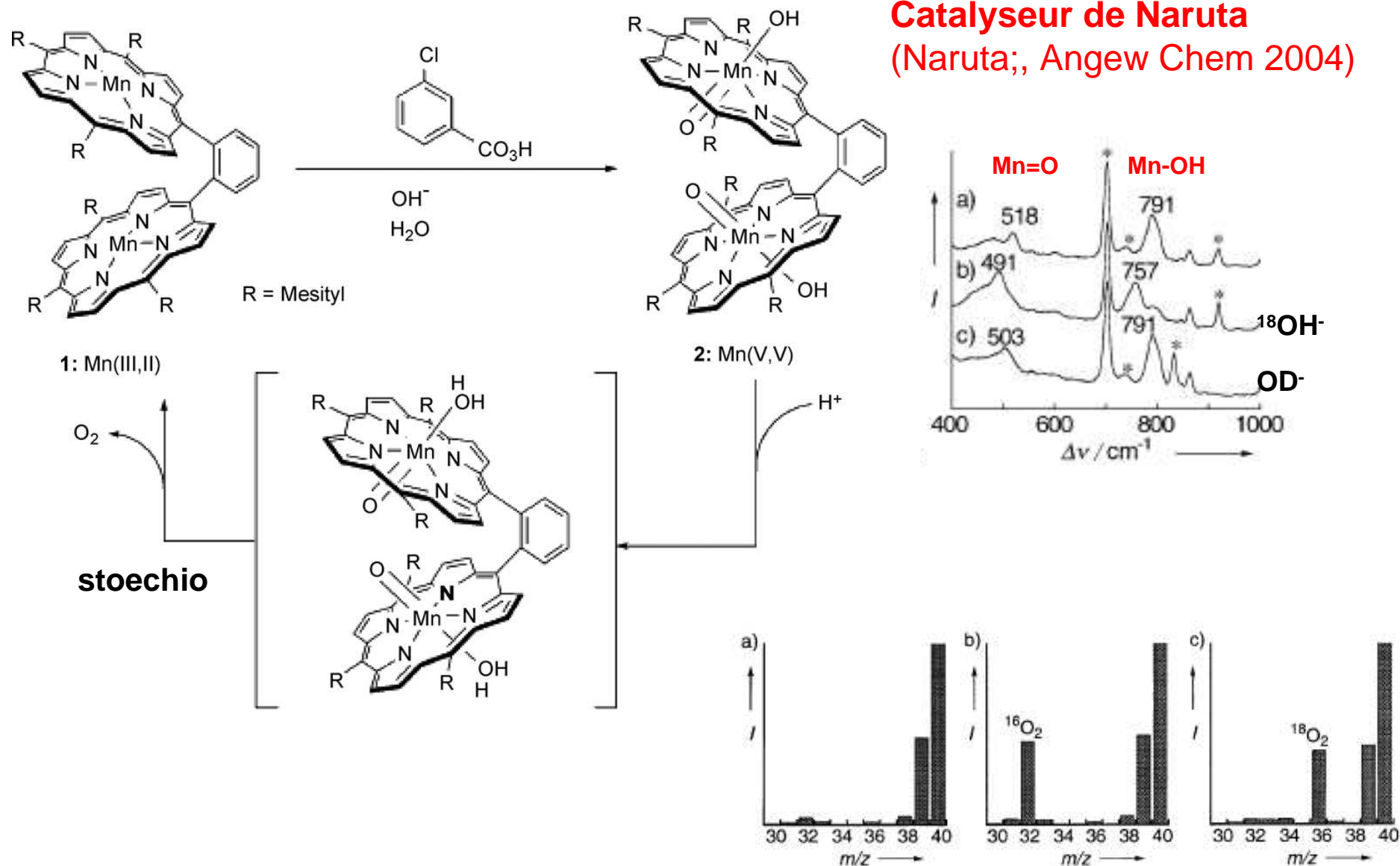
Marquage isotopique  $\text{H}_2\text{O}^{18}$ :

49%  $^{16}\text{O}_2$ , 12%  $^{18}\text{O}_2$ , 39%  $^{16}^{18}\text{O}_2$



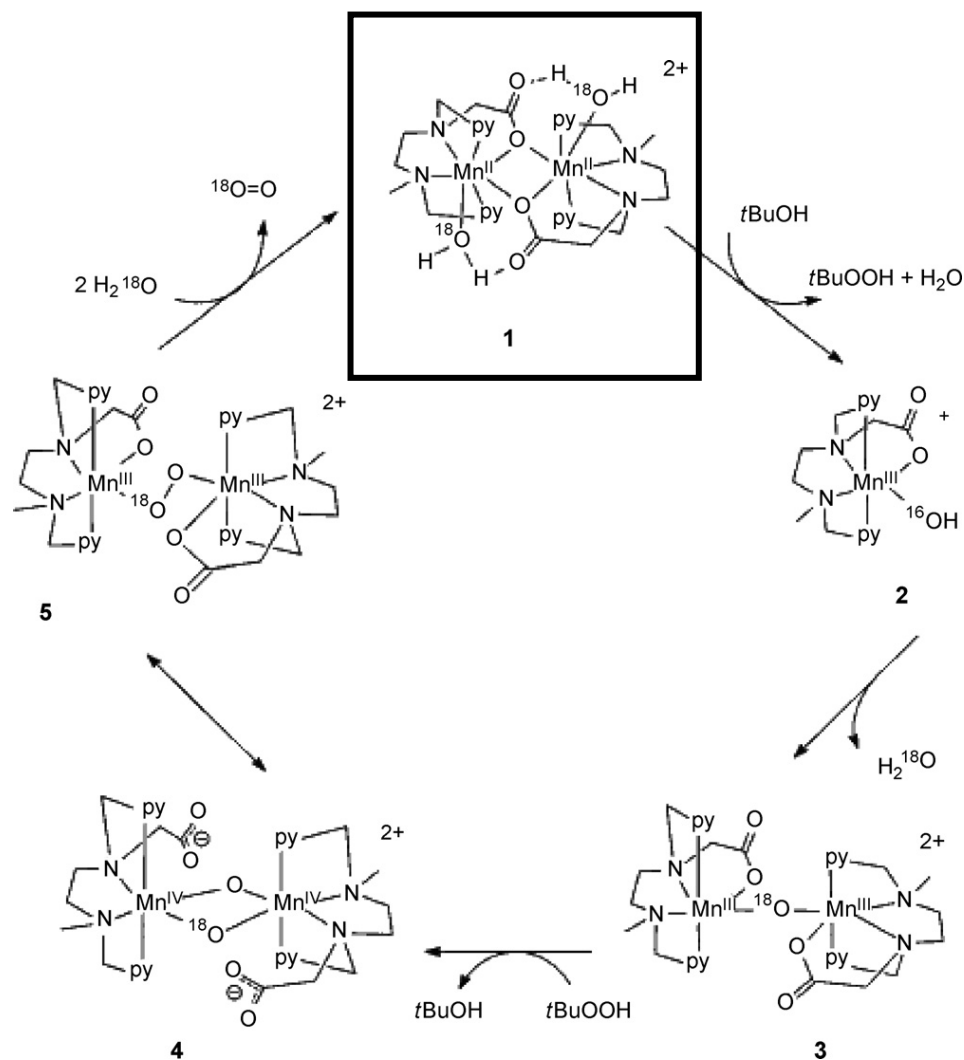


## Catalyseur de Naruta (Naruta; Angew Chem 2004)



**Figure 2.** Mass spectrometric gas analysis upon the addition of  $\text{CF}_3\text{SO}_3\text{H}$  to **2** under an Ar atmosphere. a) Before addition of  $\text{CF}_3\text{SO}_3\text{H}$  to **2**, b) addition of 40 equiv  $\text{CF}_3\text{SO}_3\text{H}$  to **2** in  $\text{H}_2^{16}\text{O}/^{16}\text{OH}^-$ , c) addition of 40 equiv  $\text{CF}_3\text{SO}_3\text{H}$  to **2** in  $\text{H}_2^{18}\text{O}/^{18}\text{OH}^-$ .

## Catalyseur de Mc Kenzie (Mc Kenzie;, Angew Chem 2005)

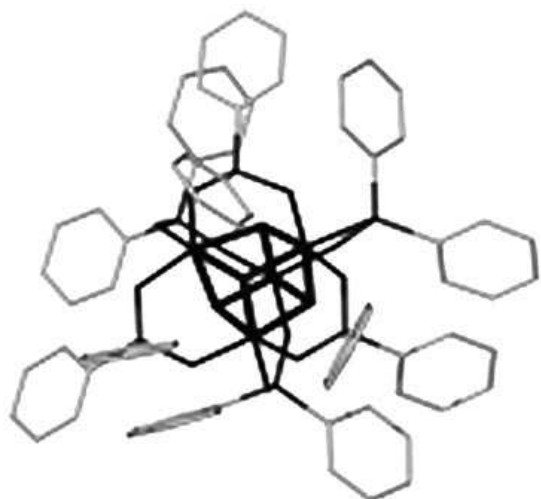


$t\text{BuOOH}$  : 6 mol/mol/3h

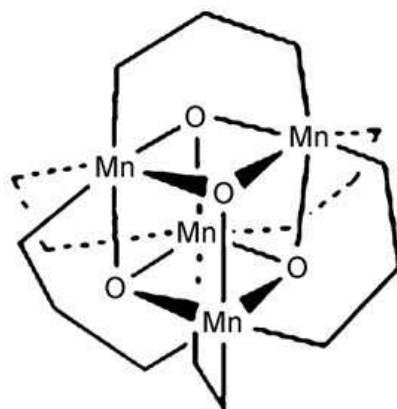
Marquage isotopique  $\text{H}_2\text{O}^{18}$  :  
100%  $^{16}\text{O}_2$   
Idem avec  $\text{Ce}(\text{NO}_3)_6^{2-}$



## Catalyseur de Dismukes (Dismukes; Angew Chem 2008)

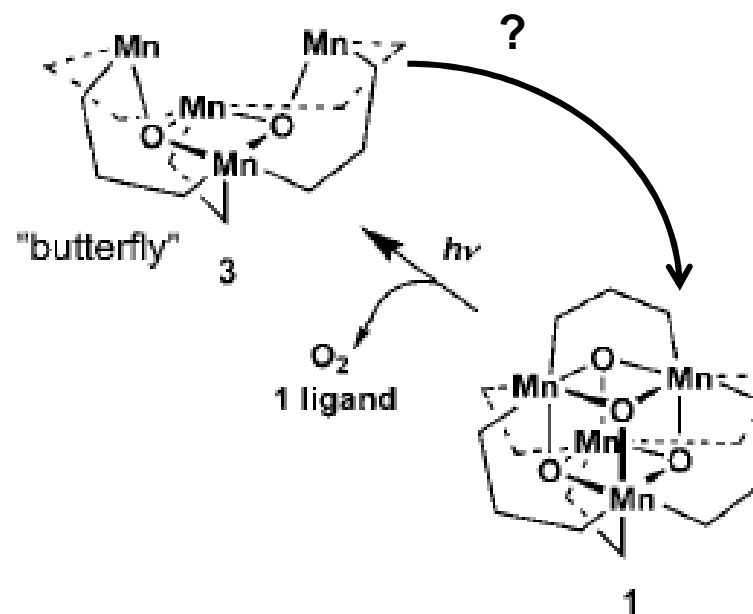


Ligand:  $(Ar)_2PO_2^-$   
diarylphosphinate

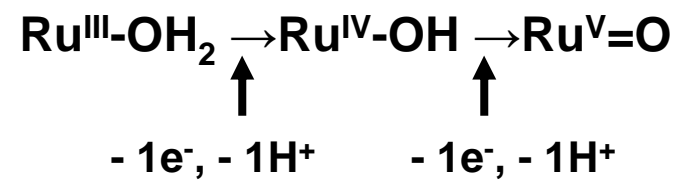


Incorporé dans une membrane de Nafion  
Sur électrode potentiel **1 Volt**  
Irradiation lumière blanche (Xe)

**O<sub>2</sub>: 1000 mol/mol (65 h)**



## Composés modèles Ruthénium

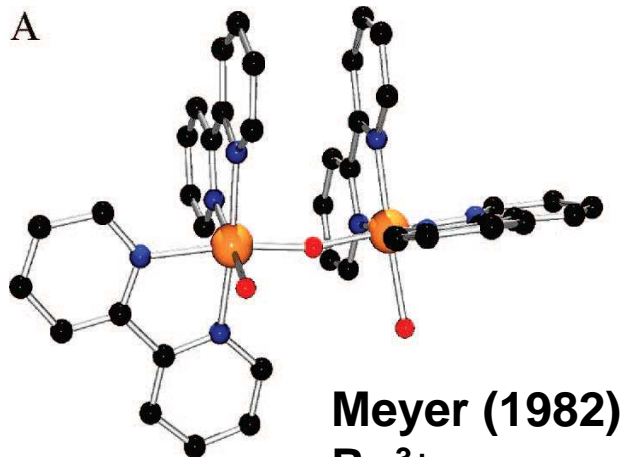


Activités

**~ 1 O<sub>2</sub> s<sup>-1</sup>**

# Complexes binucléaires Ru-X-Ru

Ce<sup>4+</sup>: 1,53V (NHE) pH1

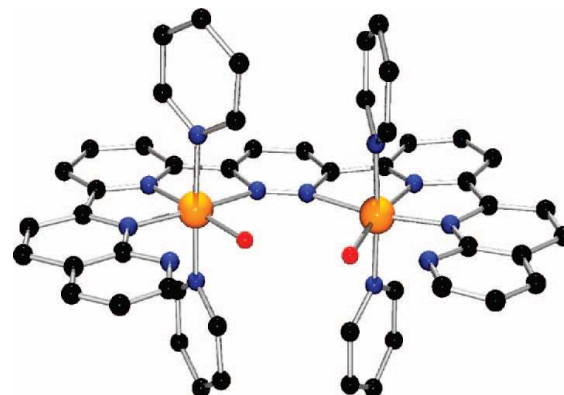


Meyer (1982)

Ru<sup>3+</sup>

X = O

Ce<sup>4+</sup> : 13-70

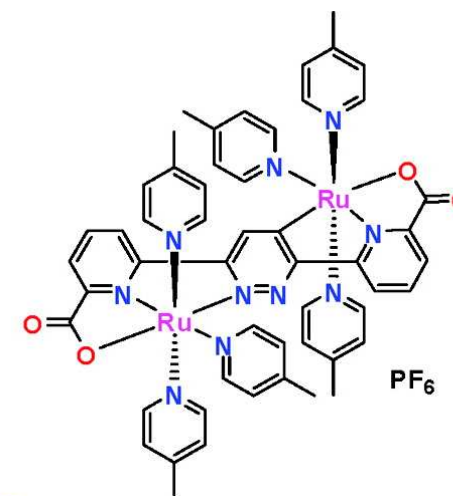


Thummel (2005)

Ru<sup>2+</sup>

X = pyrazole

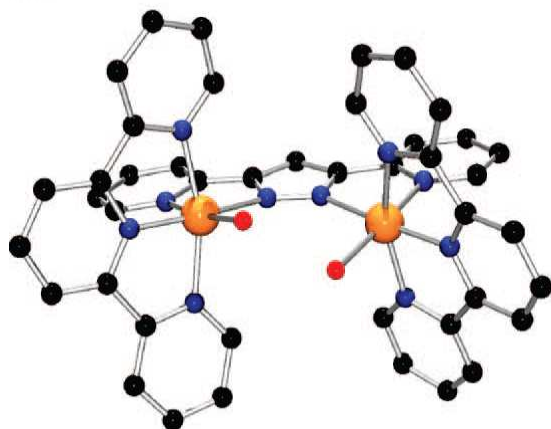
Ce<sup>4+</sup> : 100-500



Sun (2009)

Ru<sup>2+</sup>

Ce<sup>4+</sup> : 1700



Llobet (2004)

Ru<sup>2+</sup>

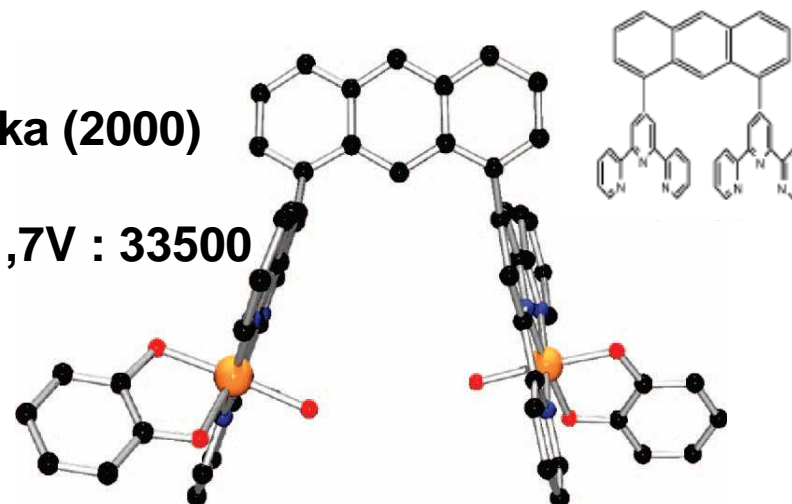
X = pyrazole

Ce<sup>4+</sup> : 18-200

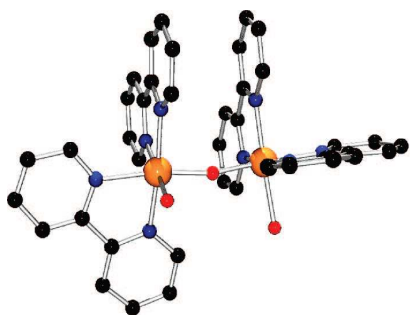
Tanaka (2000)

Ru<sup>2+</sup>

ITO/1,7V : 33500



# Complexe de Meyer

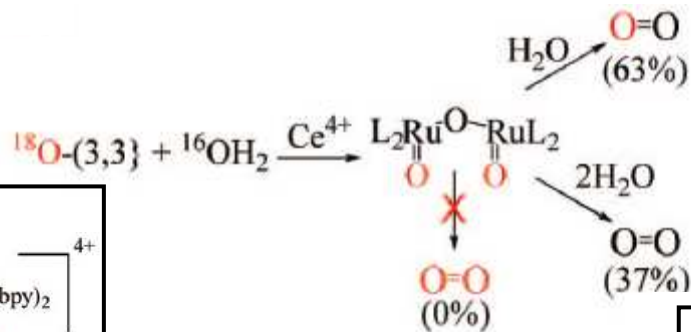


# Mécanismes (Hurst, Inorg Chem 2008 47 1753)

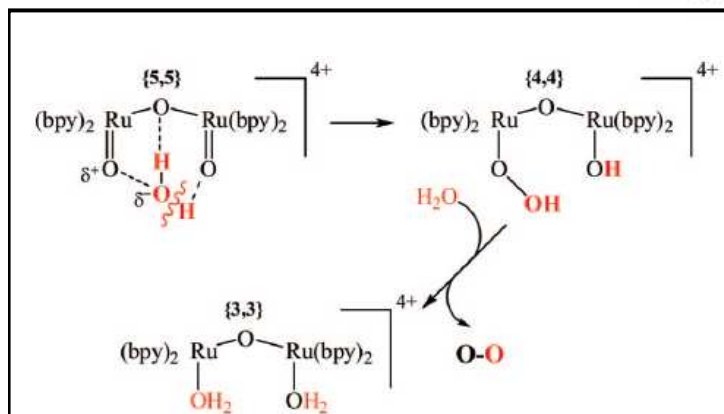


Echange avec  $^{18}OH_2$

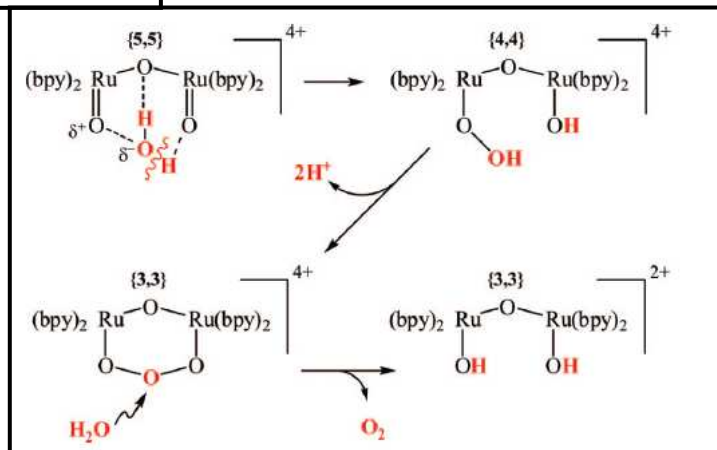
Pas d'échange avec  $^{18}OH_2$



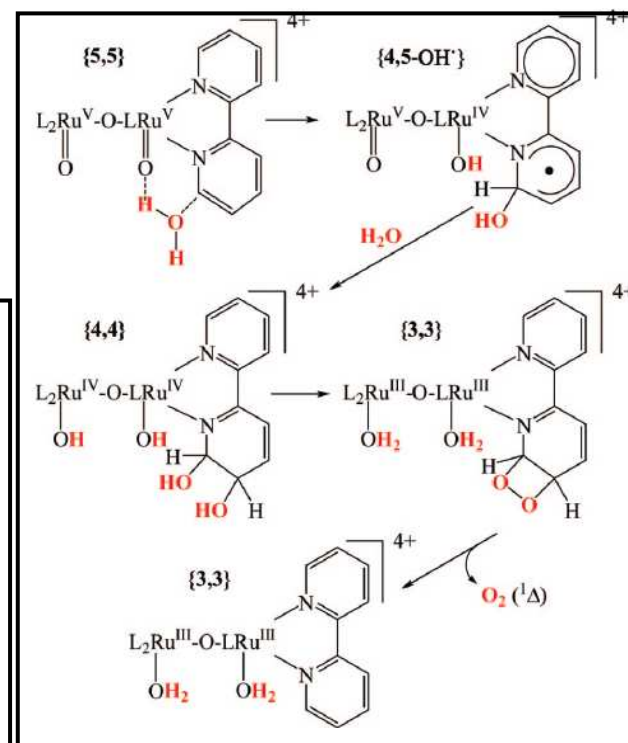
## Méca A



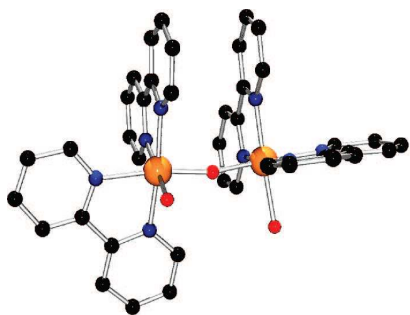
## Méca B



## Méca C

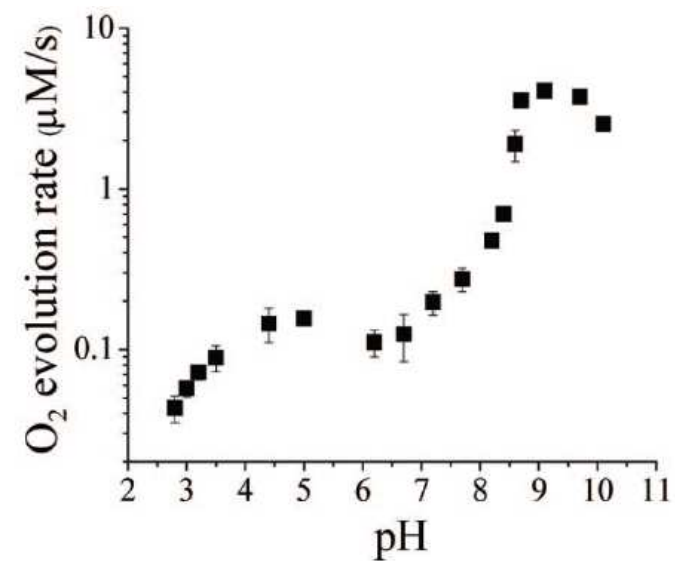
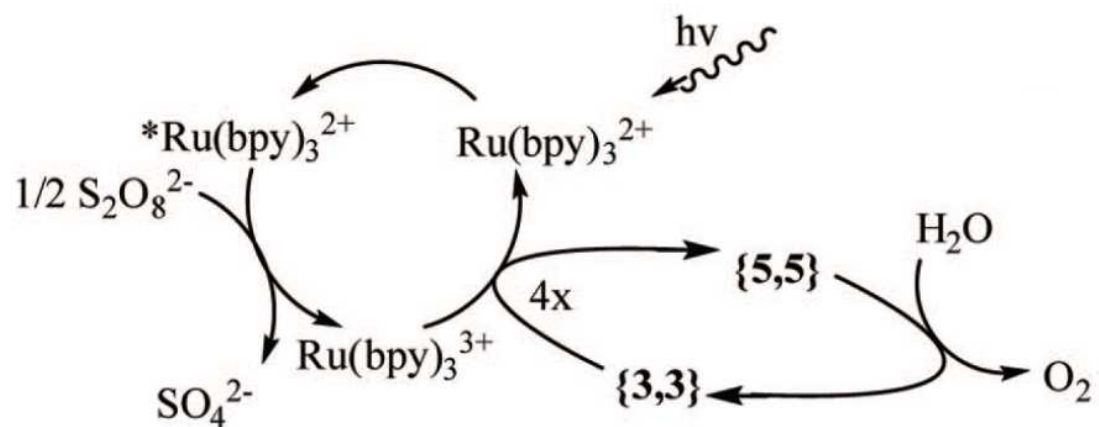


Complexe  
de Meyer

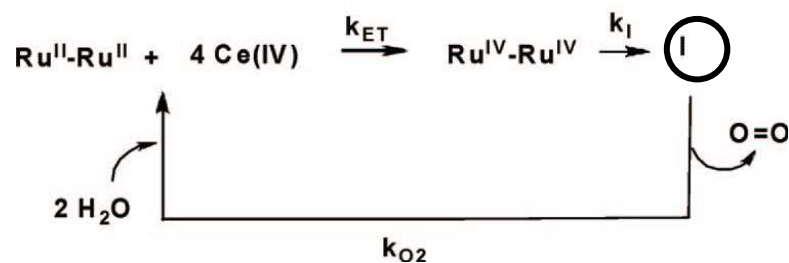
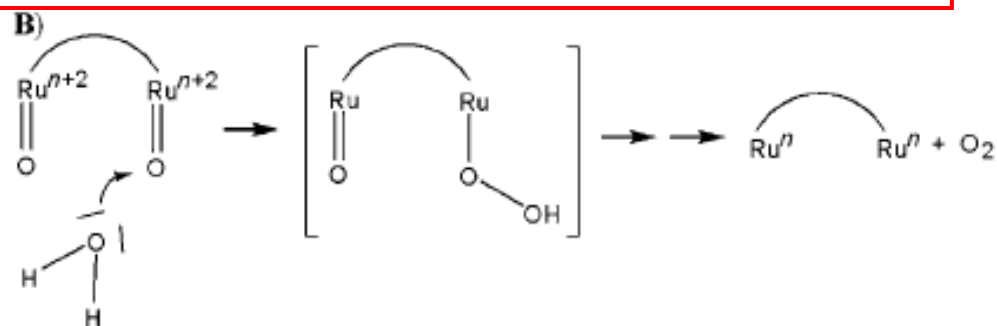
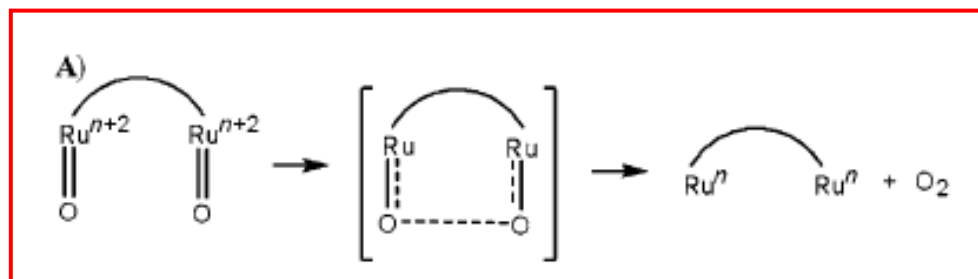
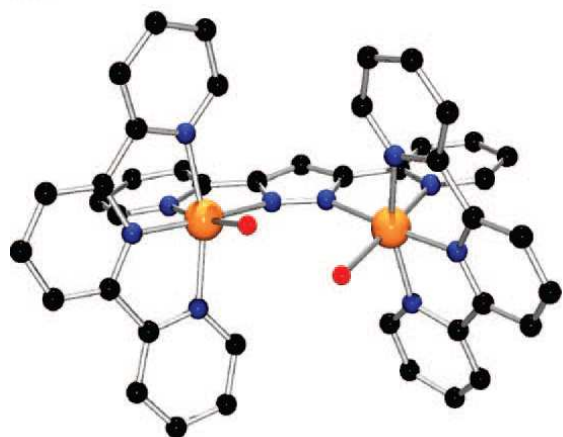


## Photooxydation de l'eau

(Hurst, Inorg Chem 2008 47 1753)



## Mécanismes (Llobet, JACS 2009 131 2769)



① Ru-O-O-Ru ??

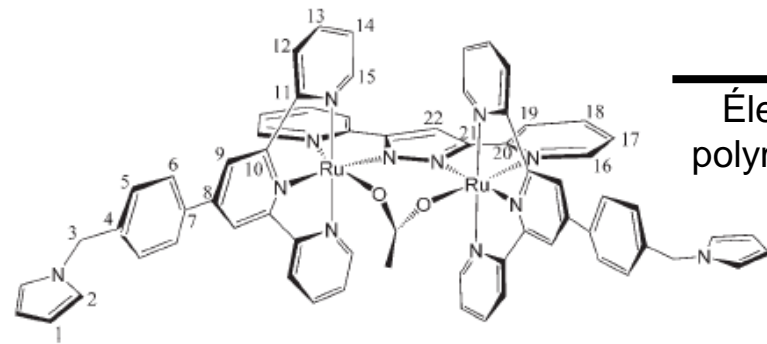
entry	<sup>18</sup> O labeling (%) <sup>b</sup>		isotopic ratios				
	catalyst	solvent	O <sub>2</sub>	exch <sup>c</sup>	nuc <sup>d</sup>	intra <sup>e</sup>	exptl
1	0	12.00	<sup>16</sup> O <sub>2</sub>	77.44	88.00	99.52	99.50
2			<sup>16</sup> O <sup>18</sup> O	21.12	12.00	0.48	0.47
3			<sup>18</sup> O <sub>2</sub>	1.44	2 × 10 <sup>-4</sup>	4 × 10 <sup>-4</sup>	0.03
4	16.13	11.90	<sup>16</sup> O <sub>2</sub>	77.60	74.60	70.34	69.97
5			<sup>16</sup> O <sup>18</sup> O	21.00	14.50	27.05	27.48
6			<sup>18</sup> O <sub>2</sub>	1.40	1.90	2.61	2.55
7	22.73	18.52	<sup>16</sup> O <sub>2</sub>	66.39	62.96	59.70	60.20
8			<sup>16</sup> O <sup>18</sup> O	30.18	32.83	35.13	35.10
9			<sup>18</sup> O <sub>2</sub>	3.43	4.21	5.17	4.70

<sup>b</sup> Calculated ratios of isotopic O<sub>2</sub> obtained in the case of a fast exchange (“exch”) process with the solvent. <sup>d</sup> Calculated ratios in the case of nucleophilic (“nuc”) attack by the solvent on the Ru=O groups. <sup>e</sup> Calculated ratios in the case of intramolecular (“intra”) oxygen-oxygen coupling from the Ru=O groups.



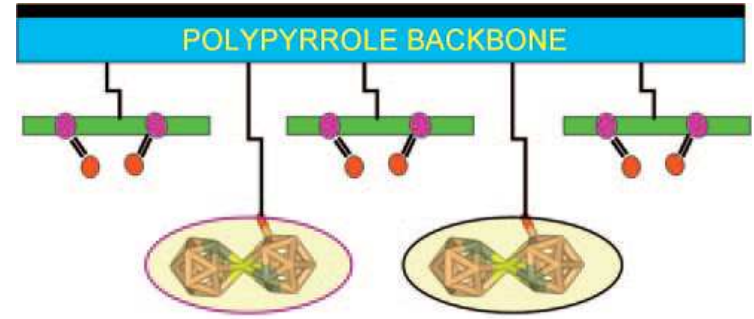
# Catalyseurs hétérogénéisés

Llobet Angew Chem 2008 47 5830

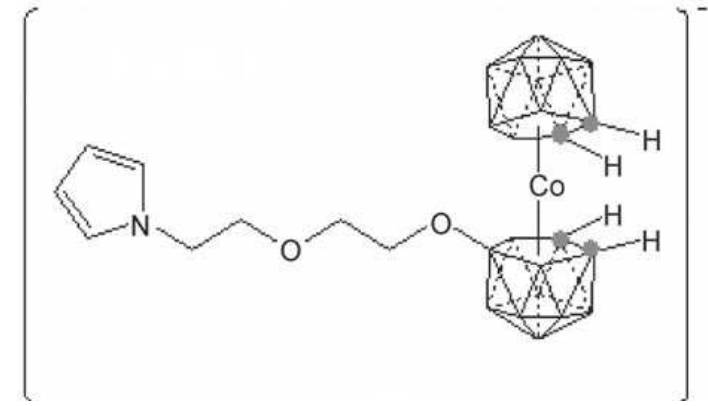


Électro-co-polymérisation

FTO ou VCS



**Ce<sup>4+</sup>: 250 cycles catalytiques !!**  
**1,17 V (ECS): 120 cycles !!**



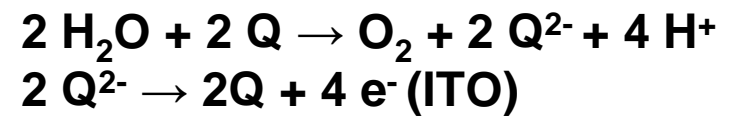
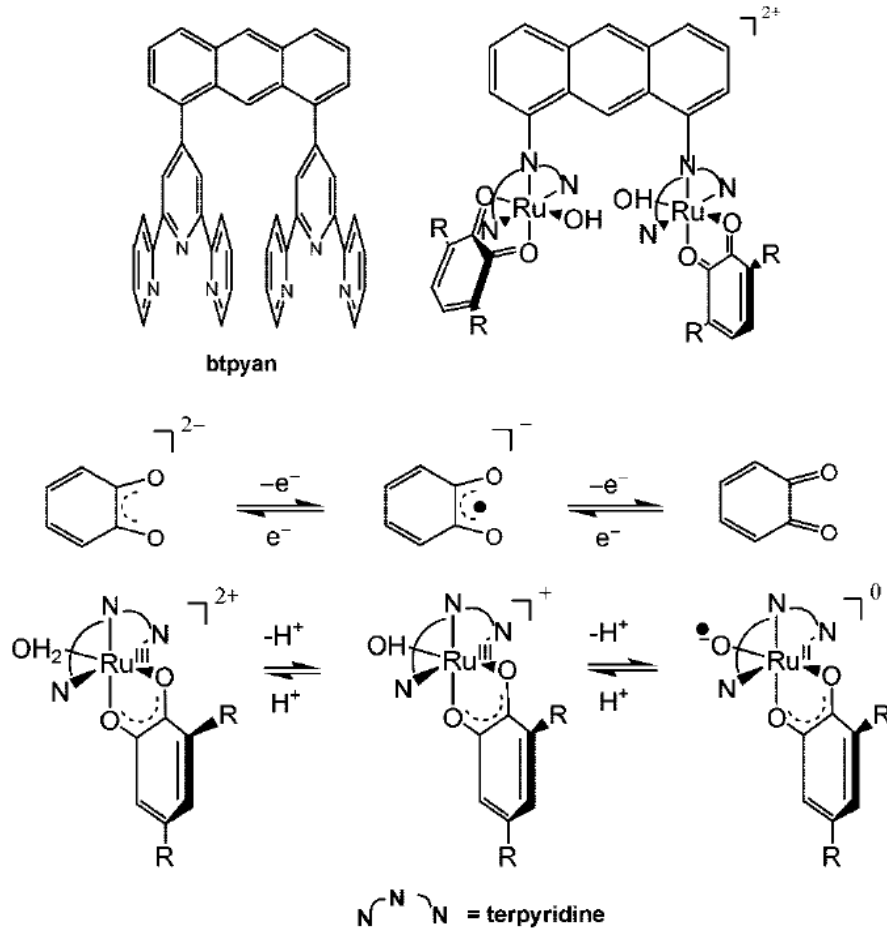
## Mécanismes (Tanaka, Inorg Chem 2008 47 1787)

-Ru reste à l'état 2+

-La quinone joue le rôle d'accepteur des électrons de l'eau

-ceci est possible grâce à la déprotonation de l'eau (pouvoir réducteur augmente)

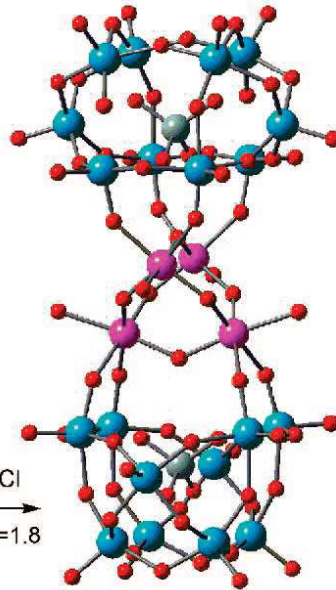
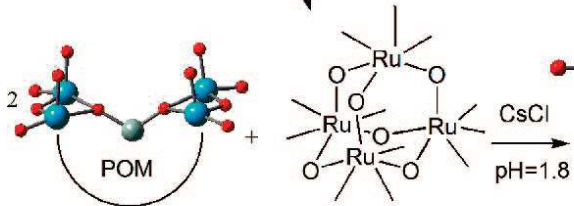
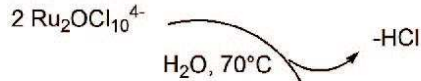
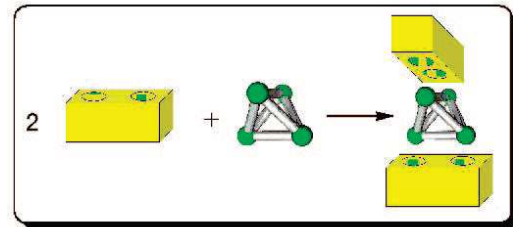
-La proximité des Ru et le déplacement des charges – permet la formation de O-O



# Divers

## Ru: polyoxométallate

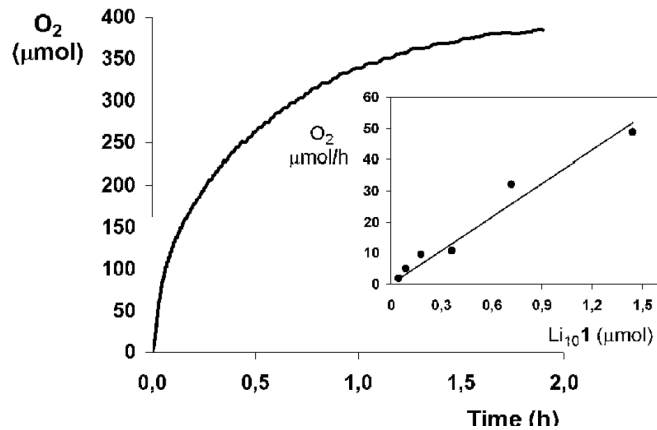
Bonchio, Hill (2008)  
 Ce<sup>4+</sup> : 385/90% (2h)



$\gamma\text{-SiW}_{10}$

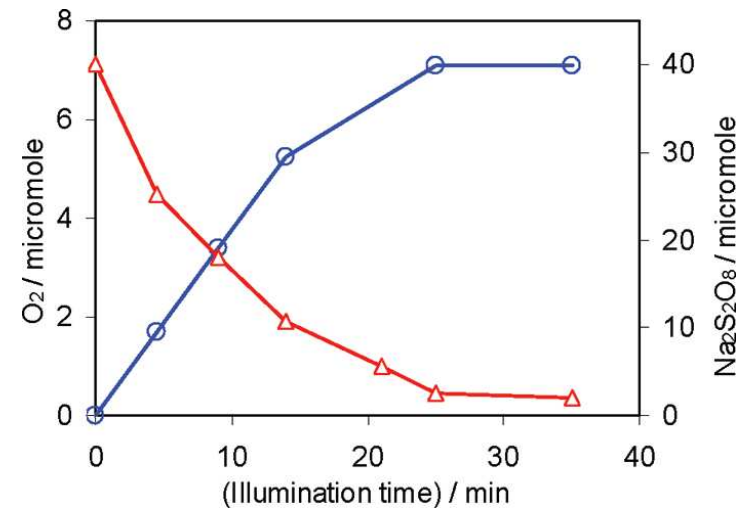
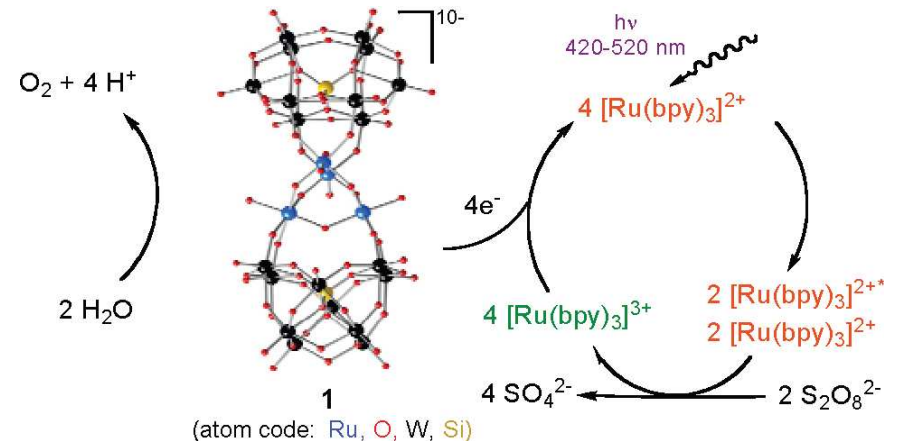
$\text{Ru}_4\text{O}_6^{4+}$

$\text{Cs}_{10}\mathbf{1}$



## Photooxydation de l'eau

(CL Hill J Am Chem Soc 2009)



## Divers

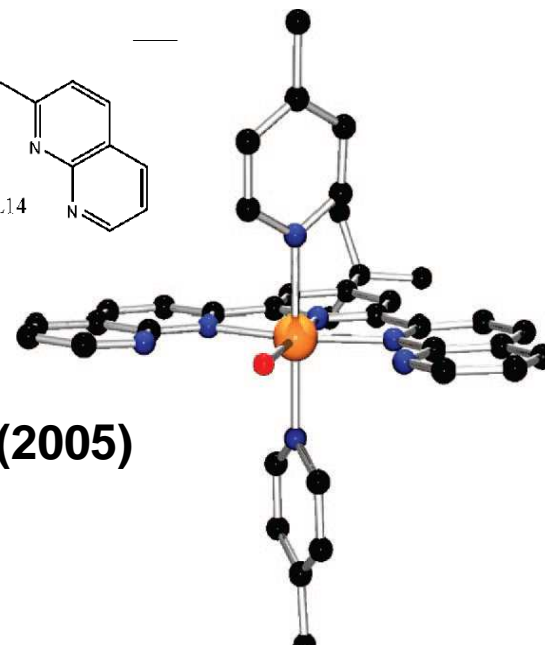
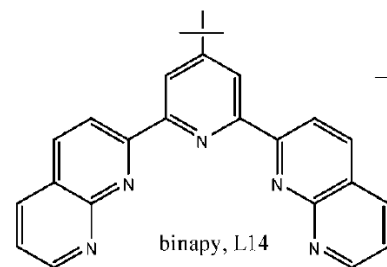
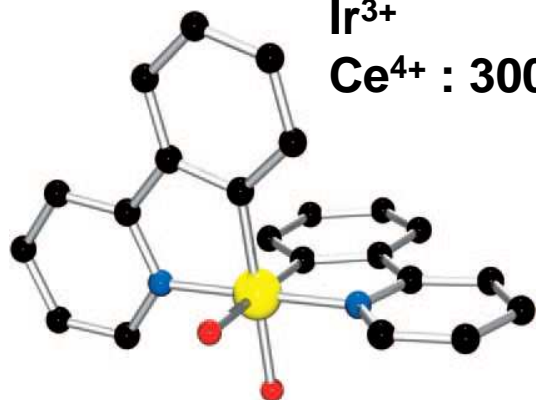
**Ru**: mononucléaire

**Ir**: mononucléaire

**Bernhard (2007)**

**Ir<sup>3+</sup>**

**Ce<sup>4+</sup> : 3000 (jours)**



**Thummel (2005)**

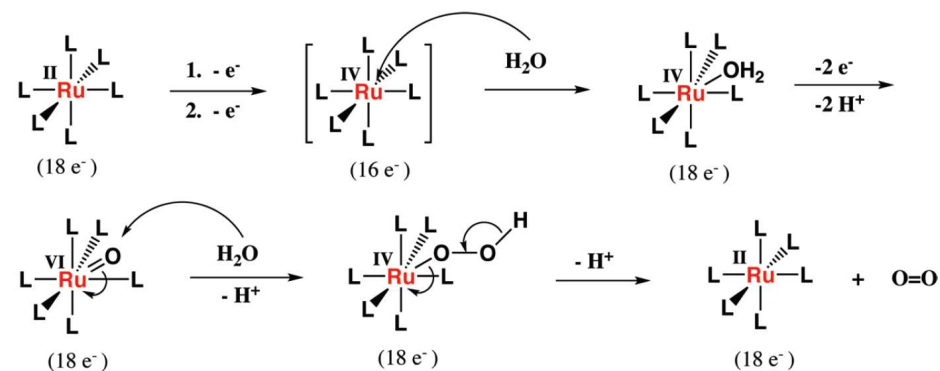
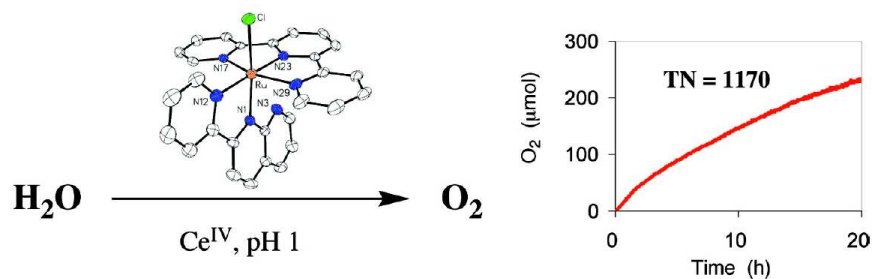
**Ru<sup>2+</sup>**

**Ce<sup>4+</sup> : 260**

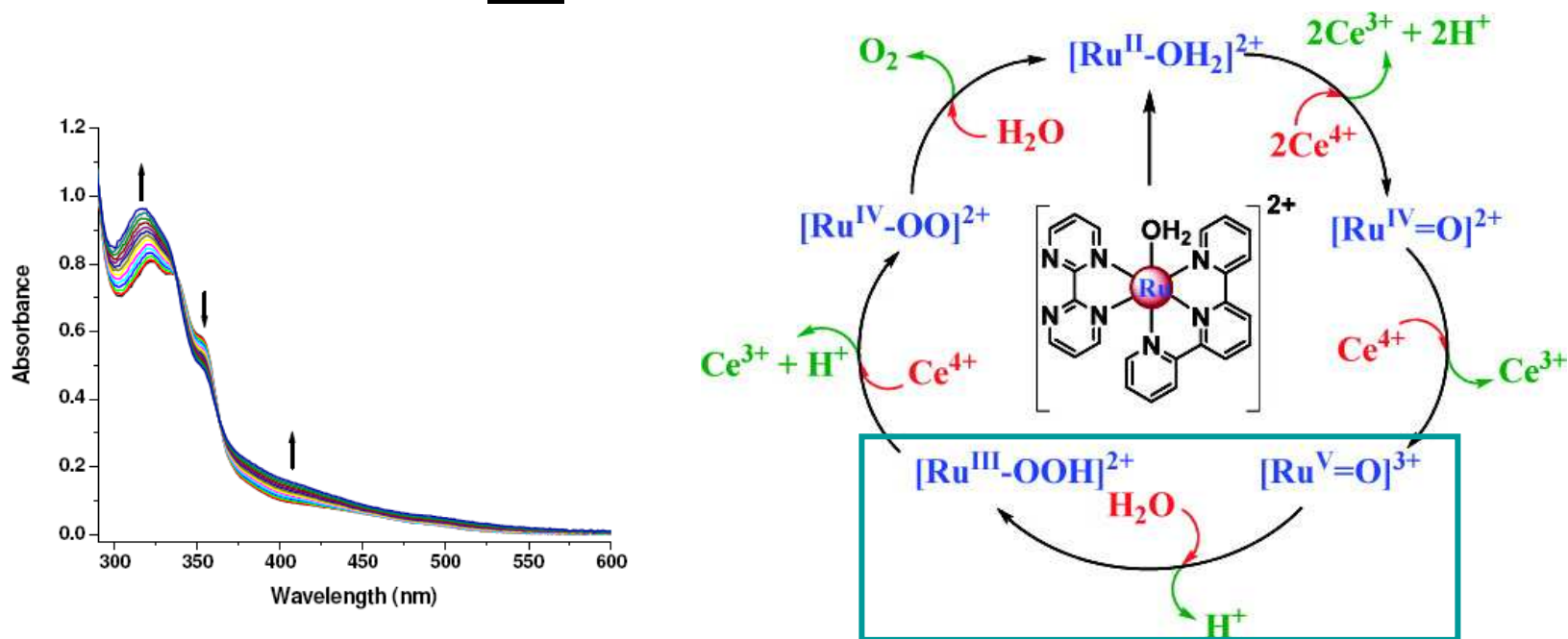
# Divers

## Ru: mononucléaire

Thummel Inorg. Chem 2008 47 11763



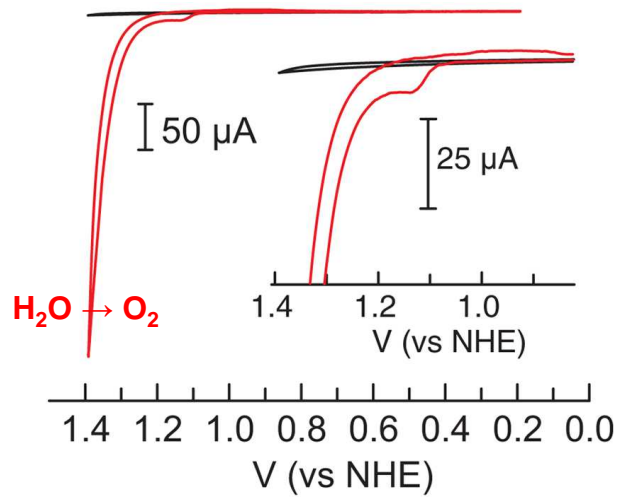
Meyer J. Am. Chem. Soc. 2008 130 16462



**Nouveaux développements  
2008-2009**

# Un catalyseur à base de Co !

D. Nocera, Science 2008 321 1072



Voltammétrie cyclique sels de  $\text{Co}^{2+}$   
Tampon phosphate, pH 7



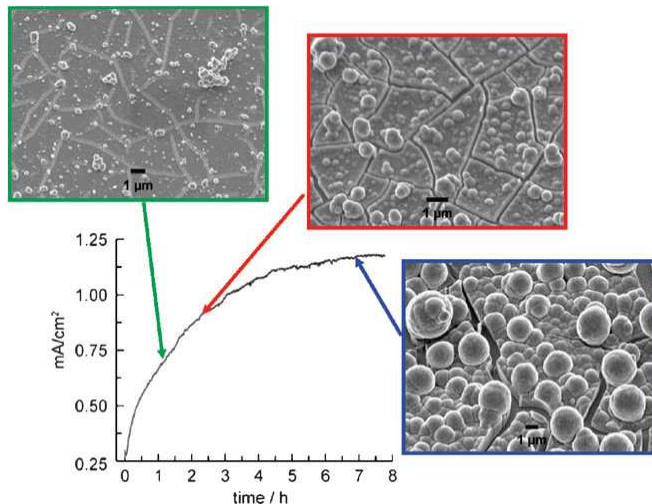
**Oxydation de  $\text{Co}^{2+}$  à 1,13V**  
**Vague catalytique à 1,23 V**

Électrolyse (ITO) de sels de  $\text{Co}^{2+}$   
Tampon phosphate, pH 7, 1,3V



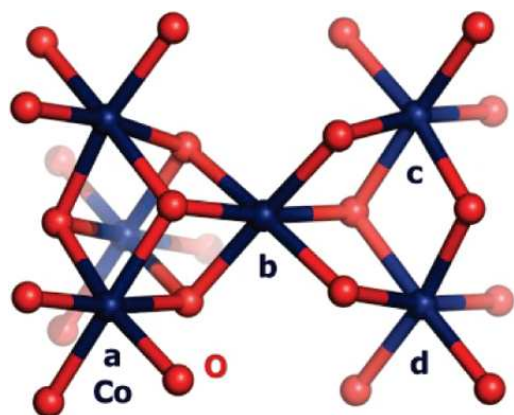
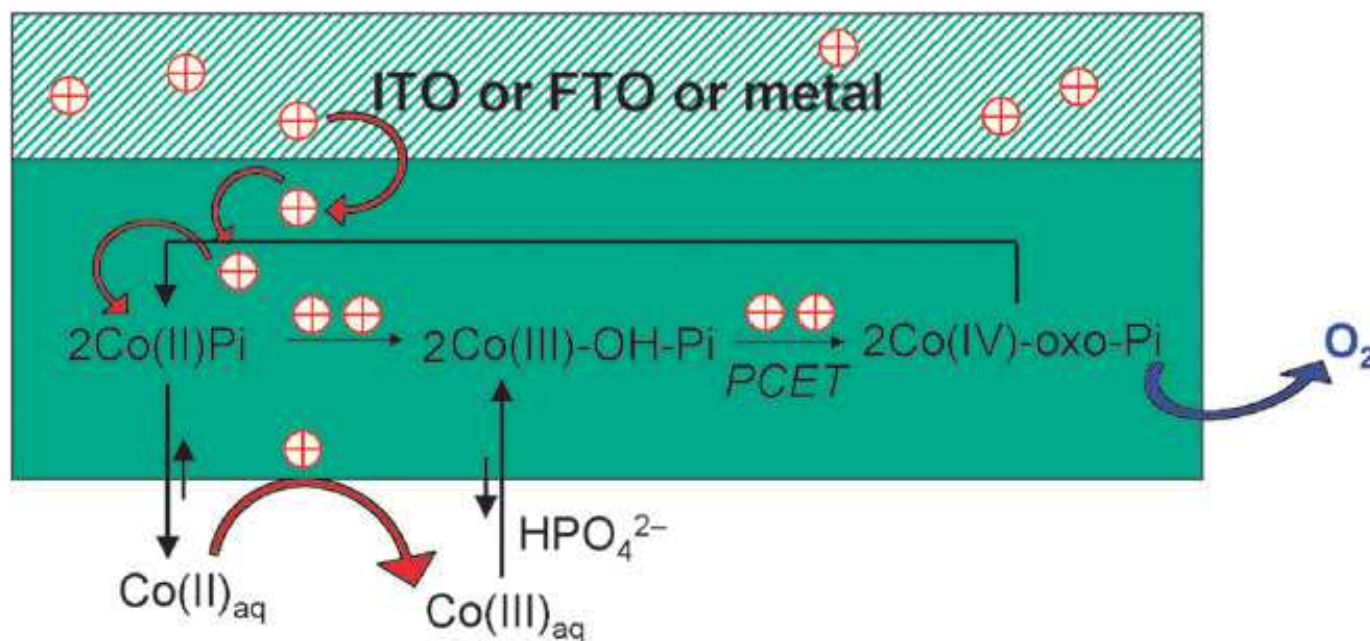
**Dépôt de nanoparticules**  
 **$\text{Co}^{3+}(\text{O})(\text{OH})(\text{Pi})$**   
**sur électrode**

**Dégagement  $\text{O}_2$  (marquage isotopique)**  
**Rendt: 100%**  
**Surtensions: 400 mV**



## Phosphate:

- Échange de protons
- Précipitation de  $\text{Co}^{3+}$



D. Nocera Chem soc Rev 2009 38 109

D. Nocera J. Am. Chem. Soc 2009 131 3838

Dau, H J. Am. Chem. Soc 2009



## Vers une photoanode (J. Am. Chem. Soc. 2009 131 6086)

### $\text{Fe}_2\text{O}_3$ matériau « idéal » pour une photoanode

- + peu coûteux, robuste, absorbe dans le visible, potentiel de la bande de valence adéquate..
- Cinétique inefficace et surtensions, potentiel de la bande de conduction inadéquate



### Catalyseur (Co-Pi)

