The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2269-16

**Workshop on New Materials for Renewable Energy**

*17 - 21 October 2011*

# Molecular catalysts that oxidize water to dioxygen

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# Molecular Catalysts that Oxidize Water to Dioxygen


ICTP, Miramare, Trieste, October 17th 2011

*Xavier Sala, UAB, Barcelona, Spain*

## *OUTLINE*

1. INTRODUCTION

2. Ru-based WOCs: from the Blue Dimer to mononuclear species

3. Iridium WOCs

4. All-inorganic POM complexes

5. First-row transition-metal based WOCs

6. Heterogeneous WOCs

7. WOCs in Photoelectrochemical cells (PECs)

8. FINAL REMARDKS AND CONCLUSIONS

## *INTRODUCTION - Today's Energy Situation*

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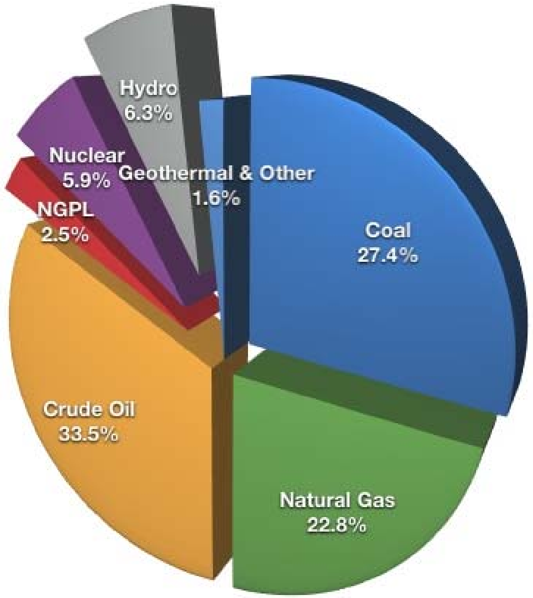
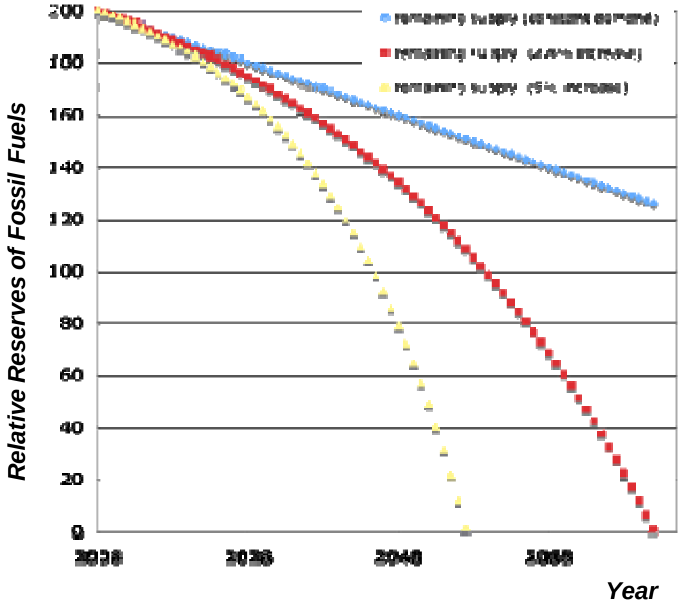
Global Energy Demand

*2004*: 14.5 TW

*2050*: 30-60 TW

x 2.5




*Exhausting profiles of oil products* **(2004)**, Exxon-Mobile.

*Solar Energy Utilization Workshop* **(2005)** US-DOE, Washington DC.

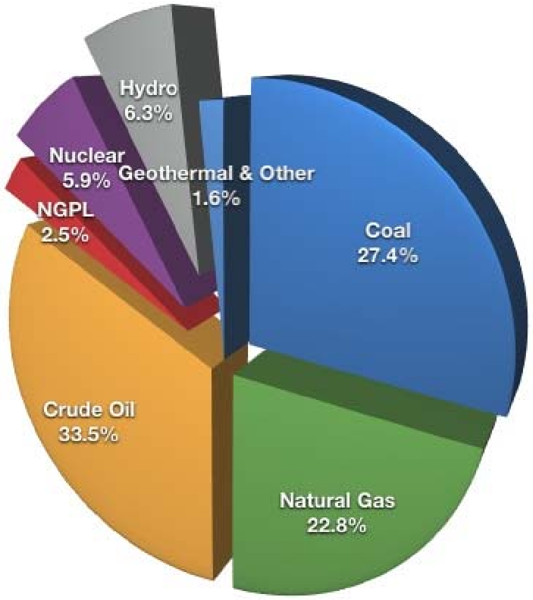
Menzel, A. et al. *Global Change Biology*, **2006**, *12*, 1-8.

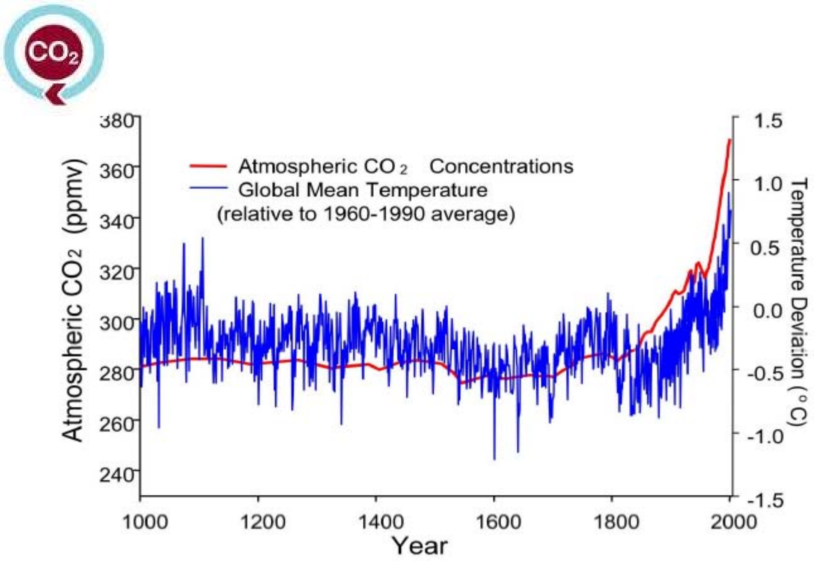
Global Energy Demand

*2004*: 14.5 TW

*2050*: 30-60 TW

x 2.5

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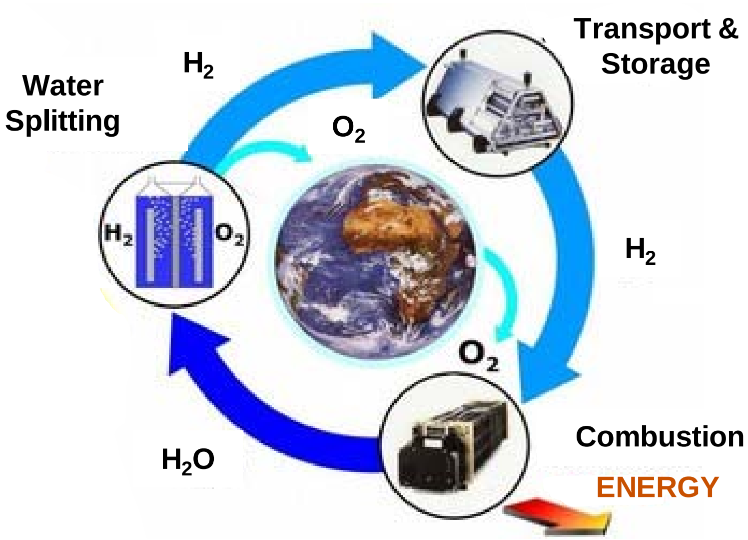
*Exhausting profiles of oil products* **(2004)**, Exxon-Mobile.

*Solar Energy Utilization Workshop* **(2005)** US-DOE, Washington DC.

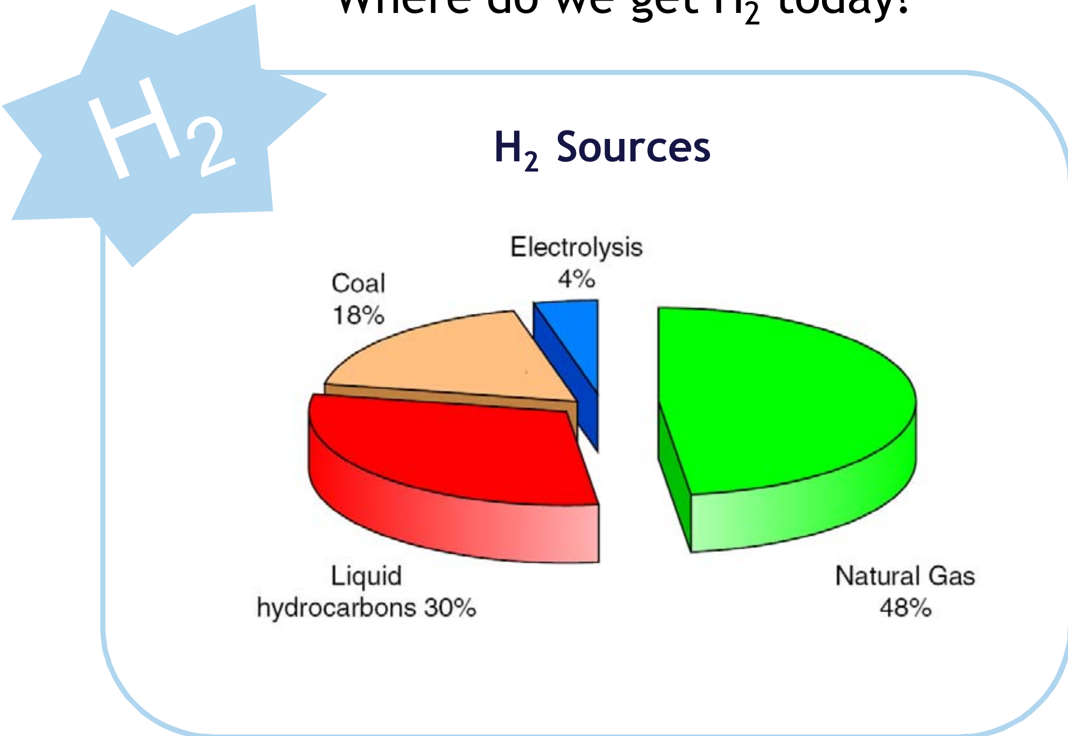
Menzel, A. et al. *Global Change Biology*, **2006**, *12*, 1-8.

- ✓ **High energy content/kg (**3 x gasoline)
- ✓ **Highest heating value per mass** of all chemical fuels




- ✓ **Combustion only releases energy and** pure **water** (Clean & Carbon Free)

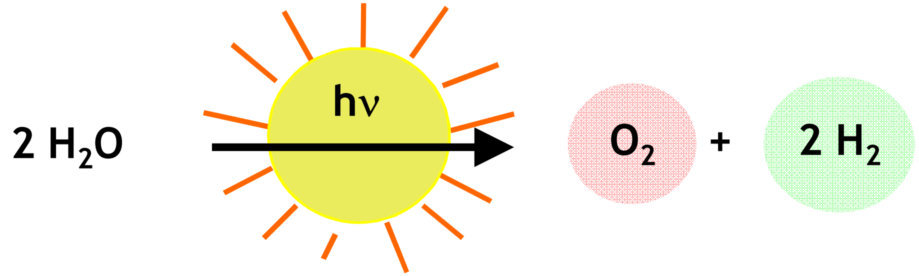
Where do we get $H_2$ today?

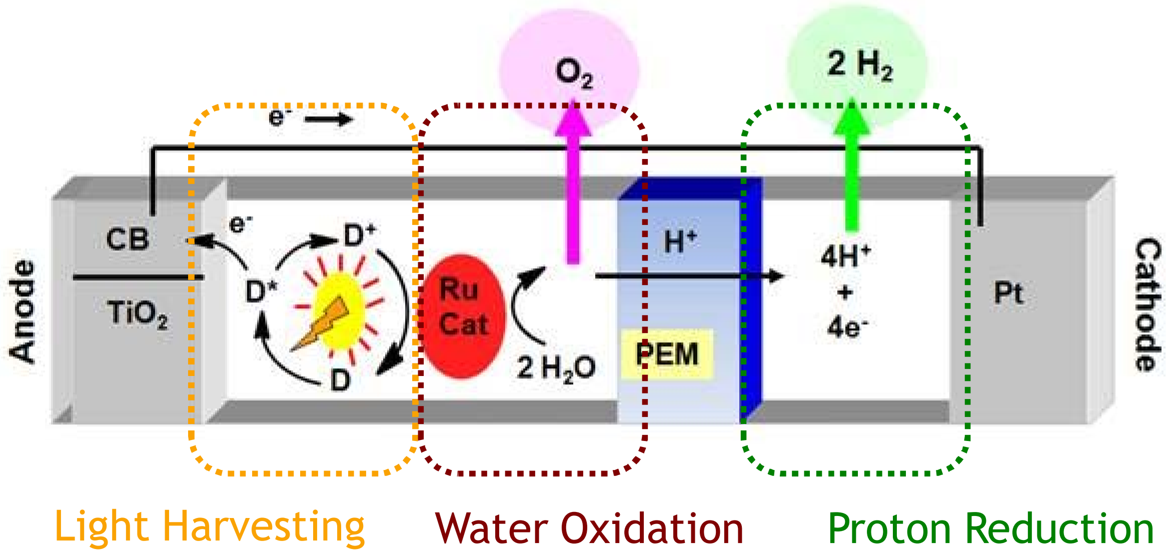



**96%** comes from **fossil fuels**

Eggert, A. et al. *Chem. Eng. News*, **2004**, *82(41)*, 48-49

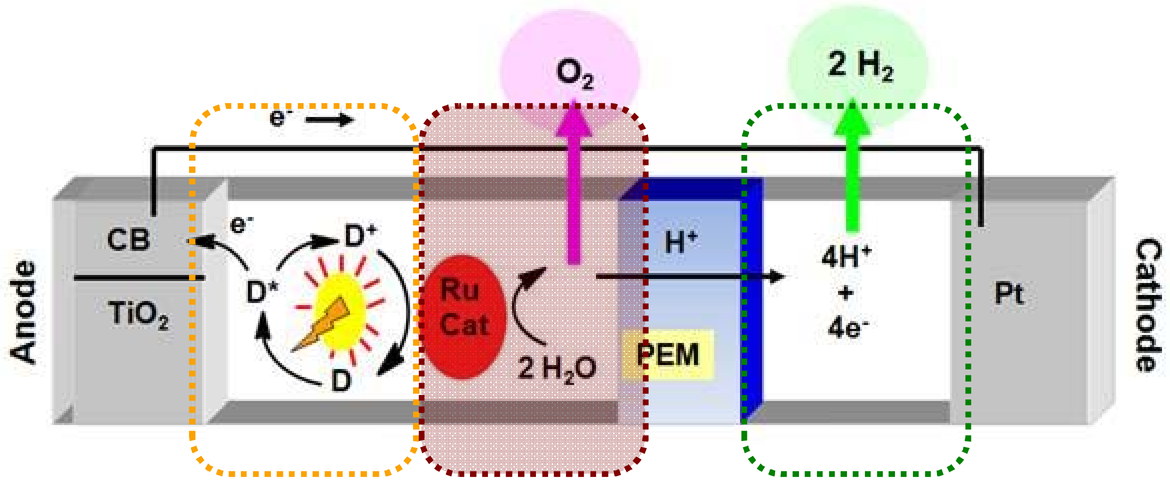
Freemantle, M. *Chem. Eng. News*, **2003**, *81(3)*, 32-36




Sala, X.; Escriche, Ll.; Llobet, A. *Angew. Chem. Int. Ed.*, **2009,** 48, 2-13

# *INTRODUCTION* – Water Oxidation: bottleneck process




Light Harvesting — Water Oxidation — Proton Reduction

↳ **BOTTLENECK PROCESS**

$$2\,H_2O \xrightarrow{h\nu} O_2 + 4\,H^+ + 4e^-$$

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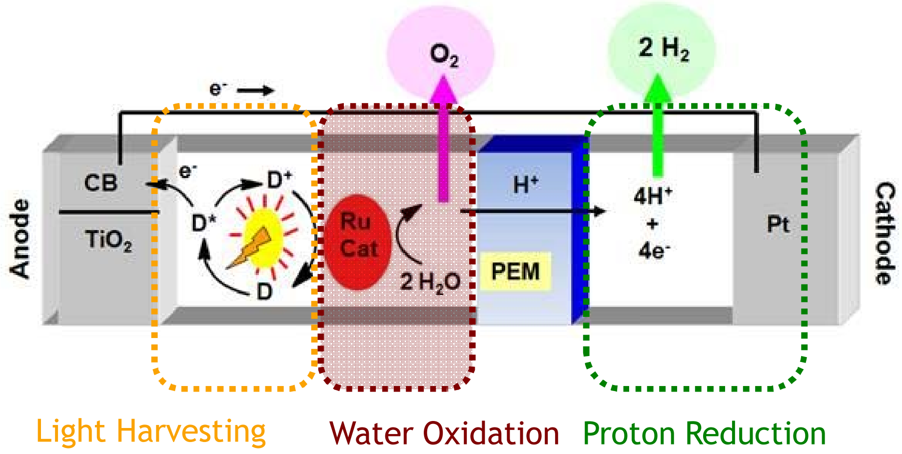
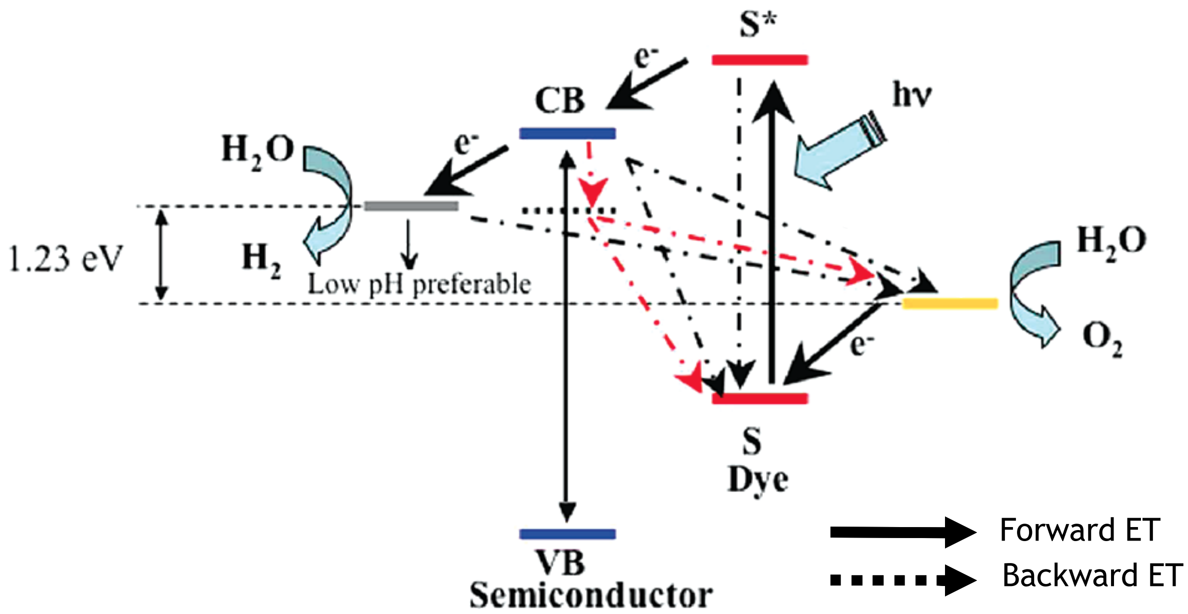
Sala, X.; Escriche, Ll.; Llobet, A. *Angew. Chem. Int. Ed.*, **2009**, 48, 2-13

## *INTRODUCTION – harmonic assembly and* **recombination**



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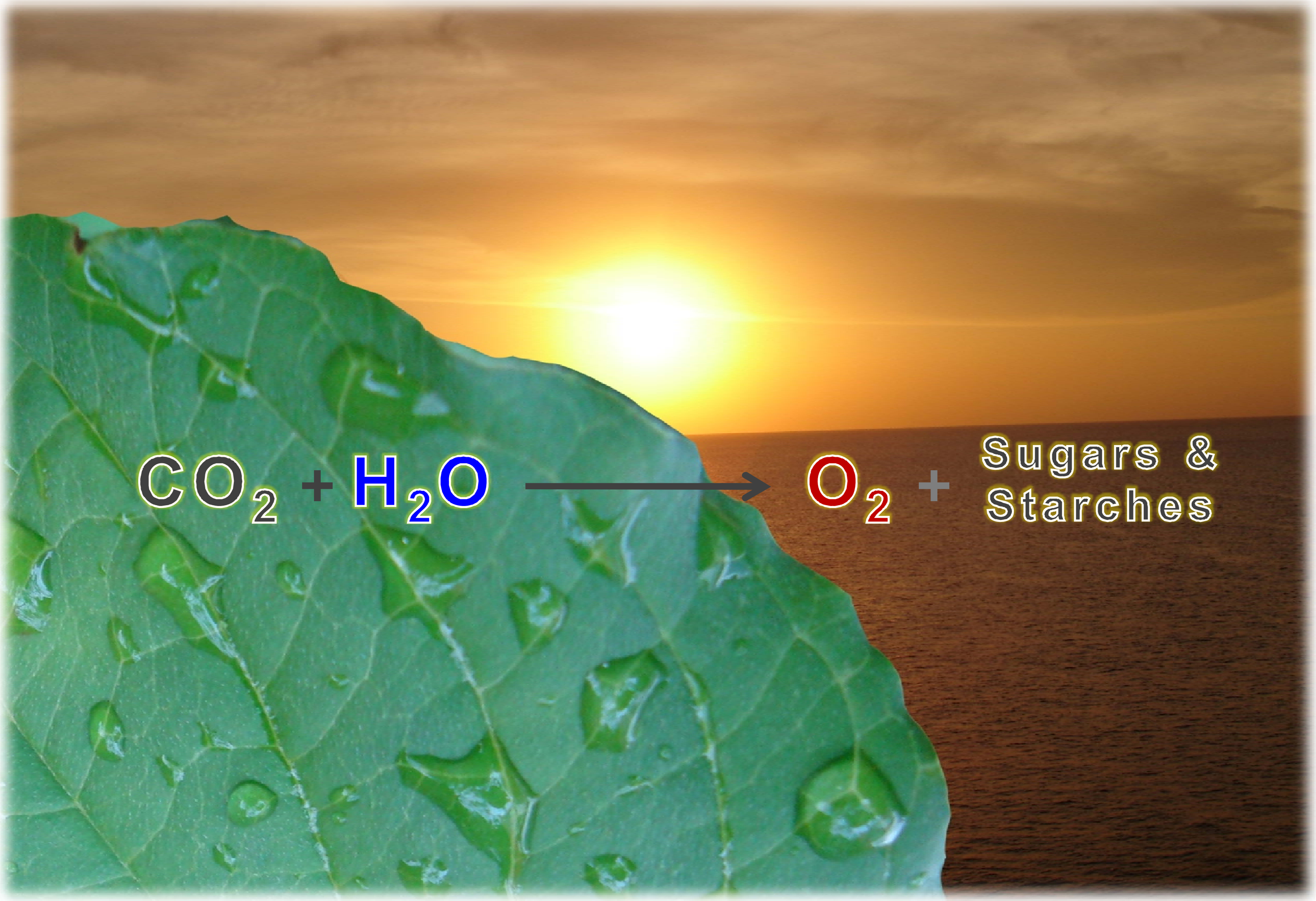
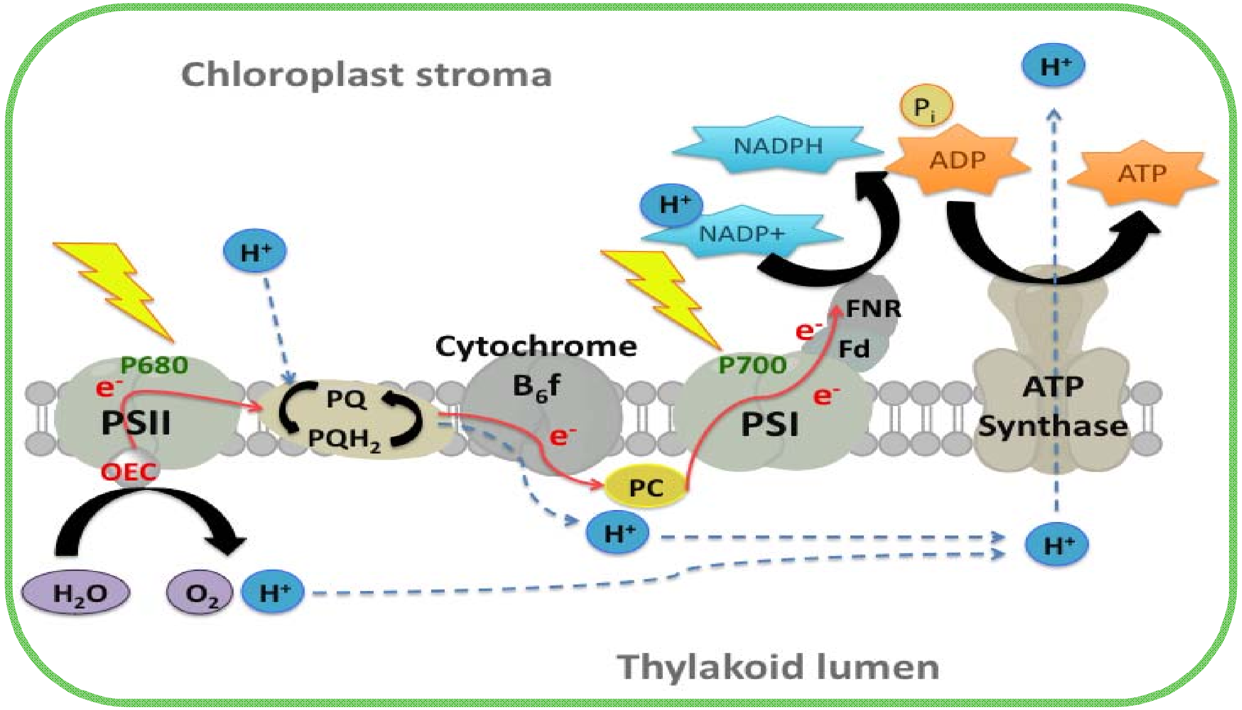
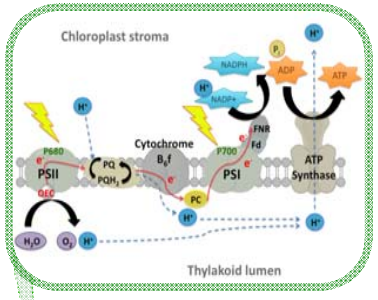
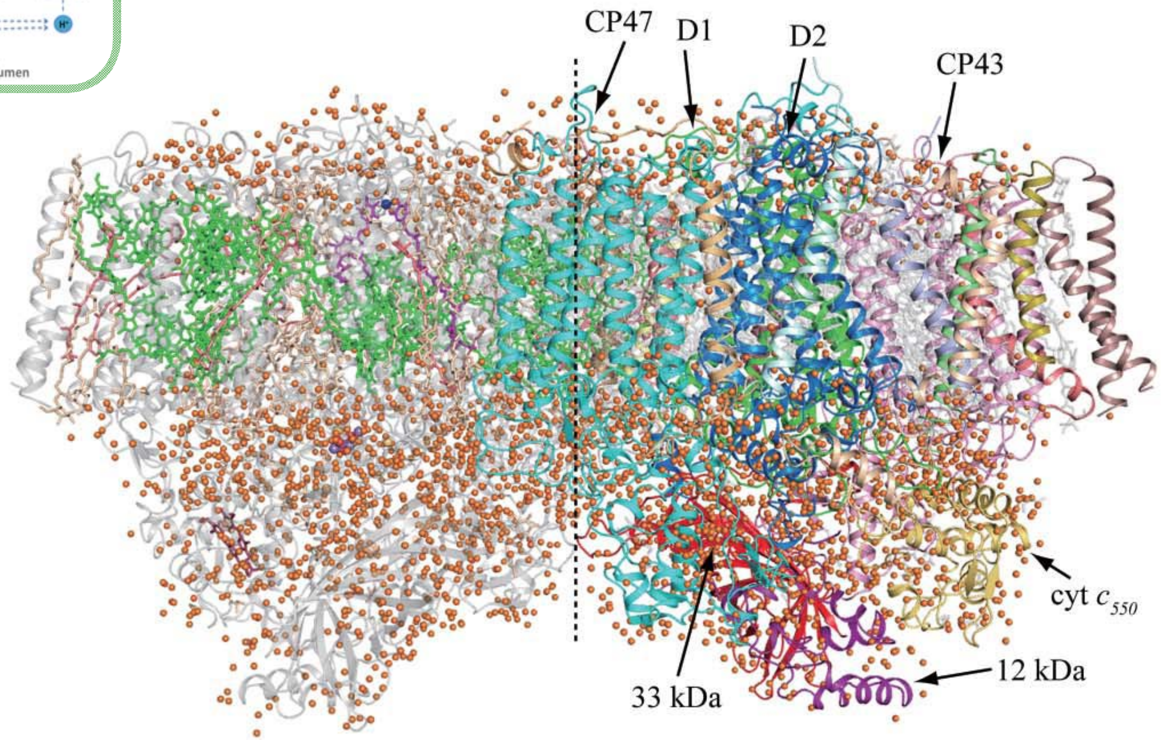


$$3\ CO_2 + 3\ H_2O \xrightarrow{h\nu} C_3H_6O_3 + 3\ O_2$$






$$3\,CO_2 + 3\,H_2O \xrightarrow{h\nu} C_3H_6O_3 + 3\,O_2$$




**PSII structure from *T. Vulcanus* at 1.9 Å resolution**

Umena, Y.; Kawakami, K. et al. *Science*, **2011**, *473*, 55

## *INTRODUCTION – Oxygen evolving complex PSII*

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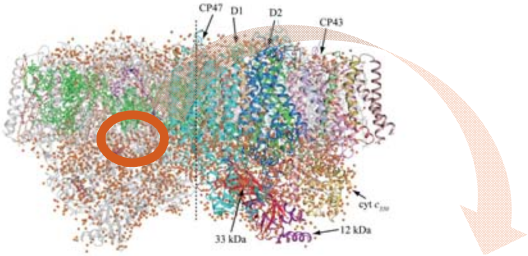
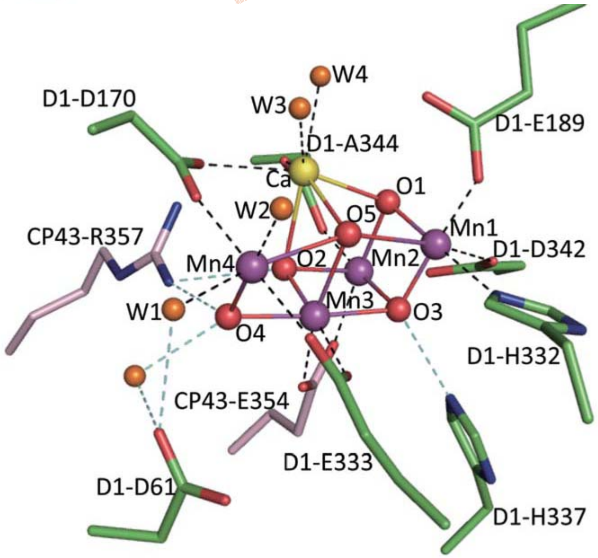
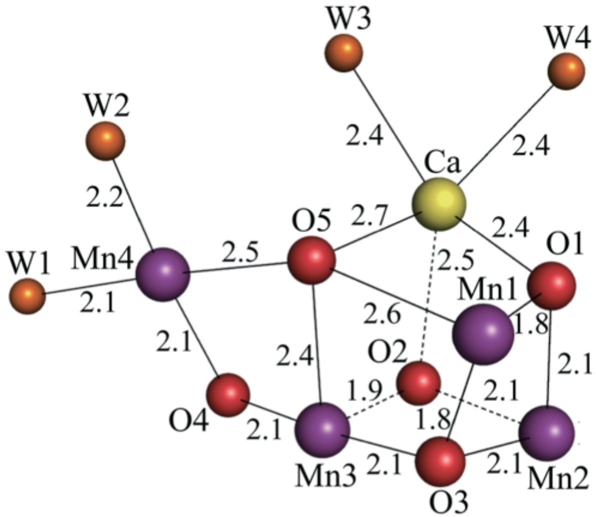



$$2\ H_2O \longrightarrow O\text{-}O + 4\ H^+ + 4\ e^-$$




**Low MW Structural/Functional Models**

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Umena, Y.; Kawakami, K. et al. *Science*, **2011**, *473*, 55

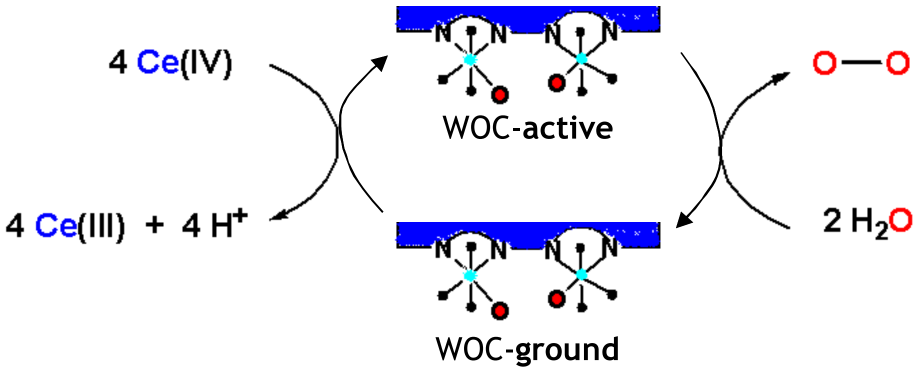
Loll, B.; Kern, J.; Saenger, W.; Zouni, A.; Biesiadka, J. *Nature*, **2005**, *438*, 1040

Messinger, J.; Zouni, A.; Yachandra, V. K. et al. *Science*, **2006**, *314*, 821

## *INTRODUCTION – Oxidizing equivalents and $O_2$ measuring*

$$H_2O \xrightarrow{WOC_{active}} O_2 + 4H^+ + 4e^-$$

- **Chemical** equivalents (preferently OSET)




Ce(IV)

- **Electrochemical** equivalents (controlled potential electrolysis)

$$H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

$(M(II)\text{-}OH_2)_2 \longrightarrow (M(IV)\text{-}O)_2$     $(M(II)\text{-}OH_2)_2$

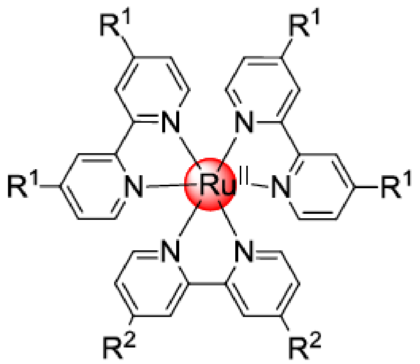
CPE

# *INTRODUCTION – Oxidizing equivalents and $O_2$ measuring*



- **Photochemical** equivalents (photosensitizers)


$Ru_p$ =




Co = $[Co(NH_3)_5Cl]^{n+}$

$Ru_c$ = WOC (reduced form)
$Ru_{AC}$ = WOC (active form)

---

Sala, X.; Escriche, Ll.; Llobet, A. in *Molecular Sola Fuels* (Chapter 4), RSC Publishing **2011**, in press.

# *INTRODUCTION – Oxidizing equivalents and $O_2$ measuring*

$$H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

$$(M(II)\text{-}OH_2)_2 \longrightarrow (M(IV)\text{-}O)_2 \curvearrowright (M(II)\text{-}OH_2)_2$$

| *Differential pressure manometry* | *On-line Mass spectrometry* | *Gas Chromatography* |
|---|---|---|
|   |   |  |
| Total gas evolved | Gas composition | $O_2$ quatification |

# *INTRODUCTION – Oxidizing equivalents and $O_2$ measuring*

$$H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

$$(M(II)\text{-}OH_2)_2 \longrightarrow (M(IV)\text{-}O)_2 \qquad (M(II)\text{-}OH_2)_2$$

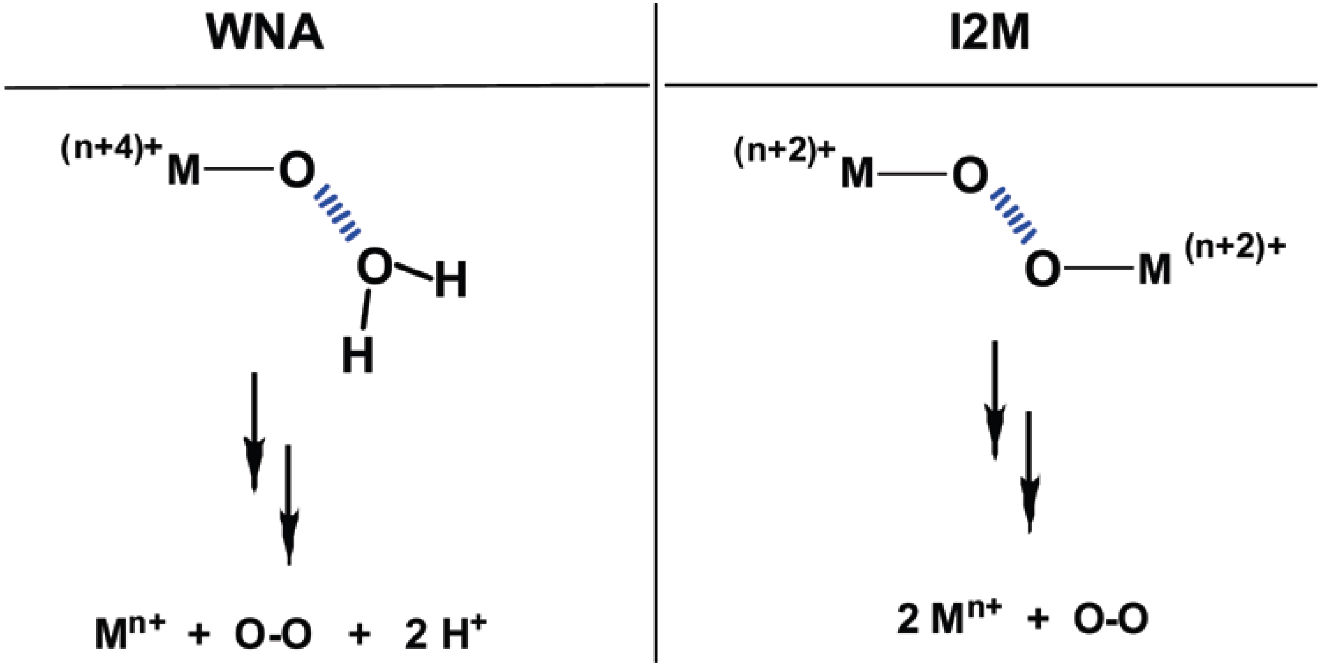
*Clark electrodes*

Liquid phase

gas phase

*Fluorescence Probes*

$O_2$ selective




Romain, S.; Vigara, L.; Llobet, A. *Acc. Chem. Res.* **2009**, 42 1944-1953.

*OUTLINE*

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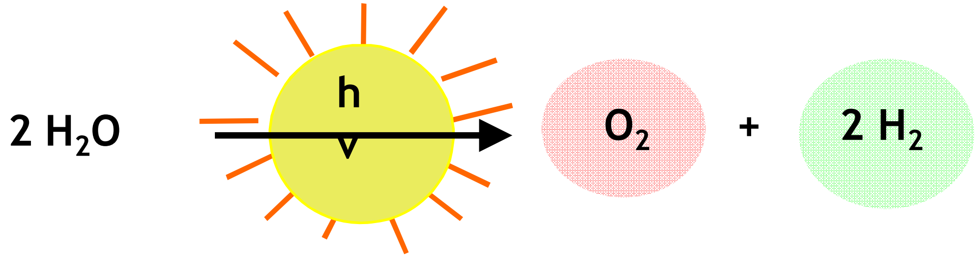



$$2\,H_2O \longrightarrow O\text{-}O + 4\,H^+ + 4\,e^-$$

$$4\,H^+ + 4\,e^- \longrightarrow 2\,H\text{-}H$$

$$LRu^{II}\text{-}OH_2 \underset{}{\overset{-e^-\ -H^+}{\rightleftharpoons}} LRu^{III}\text{-}OH \underset{}{\overset{-e^-\ -H^+}{\rightleftharpoons}} LRu^{IV}{=}O \quad \boxed{X\ 2}$$

---

Meyer,T.J. et al. *Inorg. Chem.* **1984**, 23, 1845

$H_2O$-$^{II}$Ru — BL — $Ru^{II}$-$OH_2$

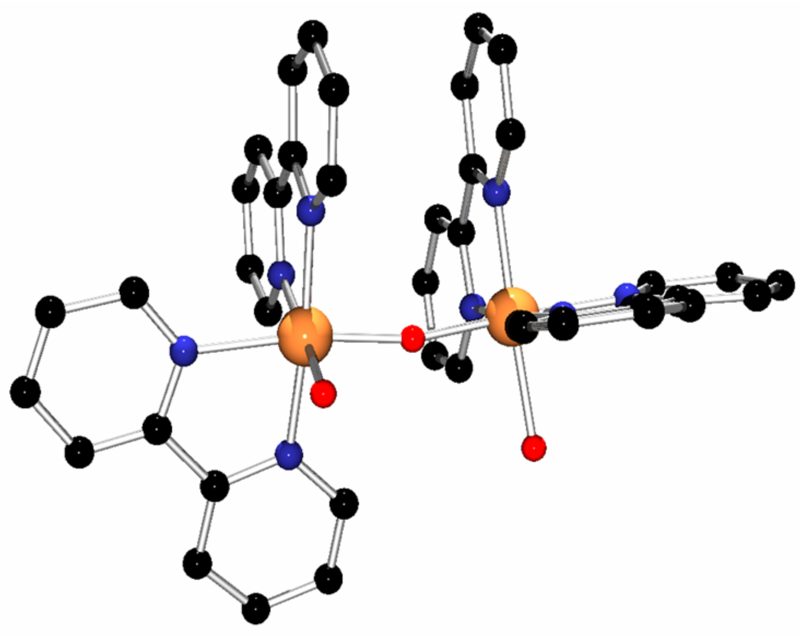
**BL: Bridging Ligand**

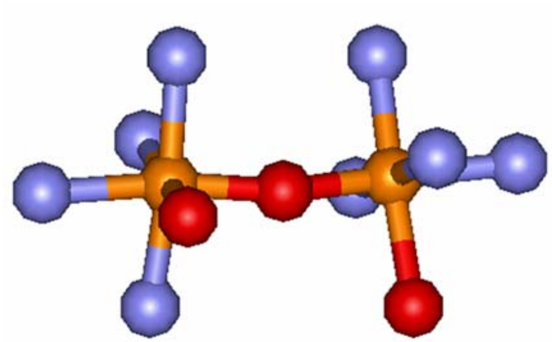
**Electronic Coupling between Ru**

**Interactions Through Space**

# *Ru-BASED WOCs: the Blue Dimer*

$[(bpy)_2Ru^{III}(H_2O)\text{-}O\text{-}Ru^{III}(OH_2)(bpy)_2]^{4+}$ $\xrightarrow{-\,4H^+,\ -\,4e^-}$ $[(bpy)_2Ru^{V}(=O)\text{-}O\text{-}Ru^{V}(=O)(bpy)_2]^{4+}$ → O-O





**O-O**

**4-5 MC**

*Ce(IV):WOC 100:1*
*pH = 1 buffer*

**Ce(IV)**

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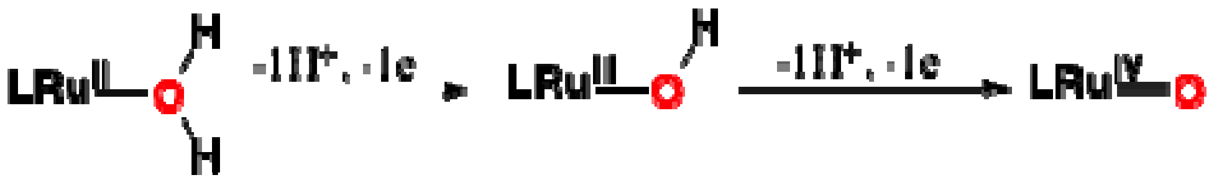
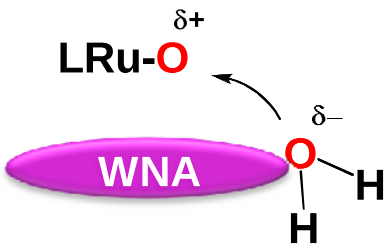
Gestern, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.*, **1982,** *104*, 4029

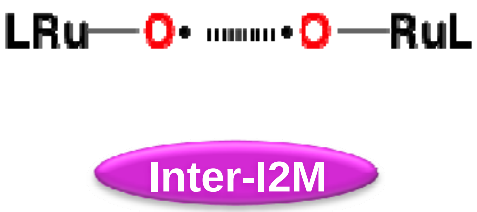
Gilbert, J. A.; Eggleston, D. S.; Meyer, T. J. et al. *J. Am. Chem. Soc.*, **1985,** *107*, 3855

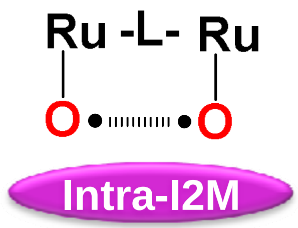



## O-O Coupling Pathways

| Water Nucleophilic Attack | Intermolecular O-O Coupling | Intramolecular O-O Coupling |
|---|---|---|



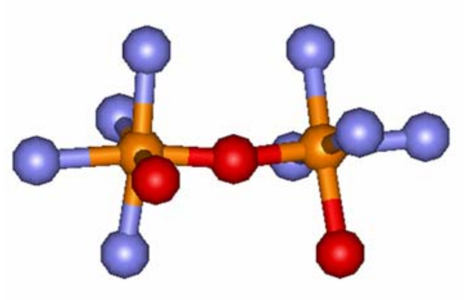



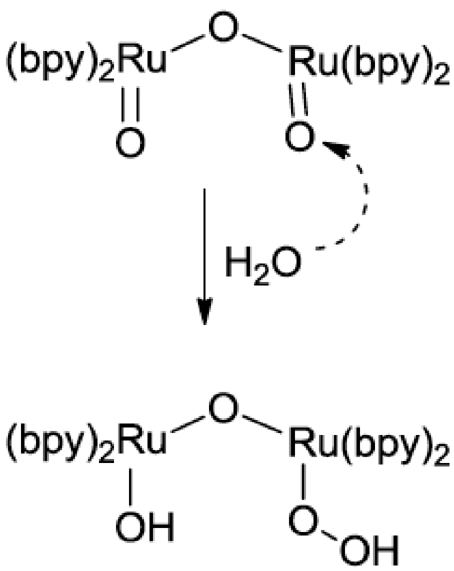

T. J. Meyer et al., *Inorg. Chem.* **2003**, *42*, 8140.

A. Llobet et al., *Acc. Chem. Res.* **2009**, *42*, 1944.

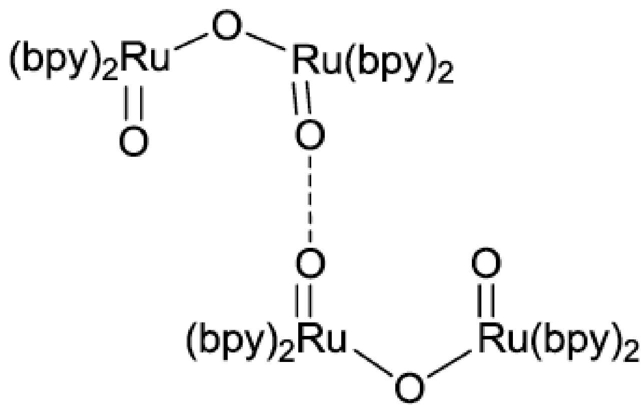
## Ru-BASED WOCs: O-O bond formation in the Blue Dimer



WNA

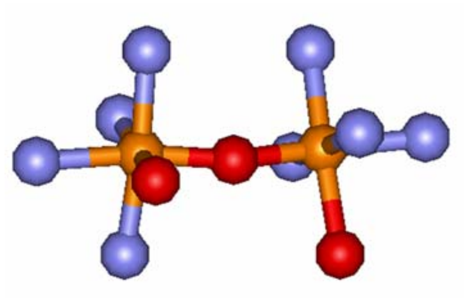


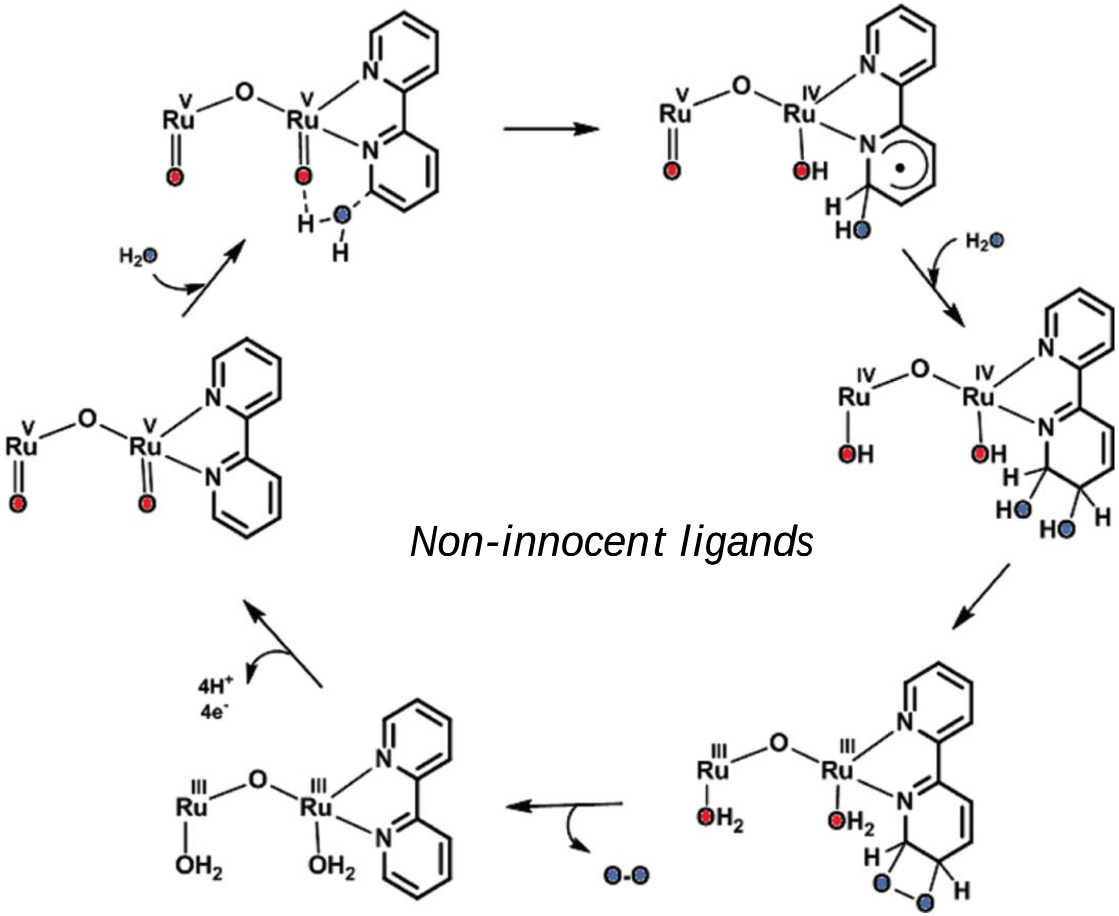

Inter-I2M



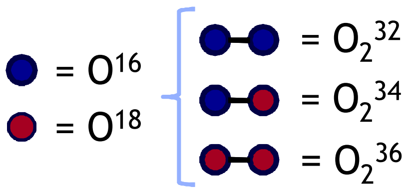

Binstead, R. A.; Chronister, C. W.; Meyer, T. J., et al. *J. Am. Chem. Soc.*, **2000,** *122,* 8464

Yamada, H.; Siems, W. F.; Koike, T.; Hurst, J. K. *J. Am. Chem. Soc.*, **2004,** *126,* 9786






*Non-innocent ligands*




Cape, J. L.; Hurst, J. K. *J. Am. Chem. Soc.*, **2008,** *130,* 827-829

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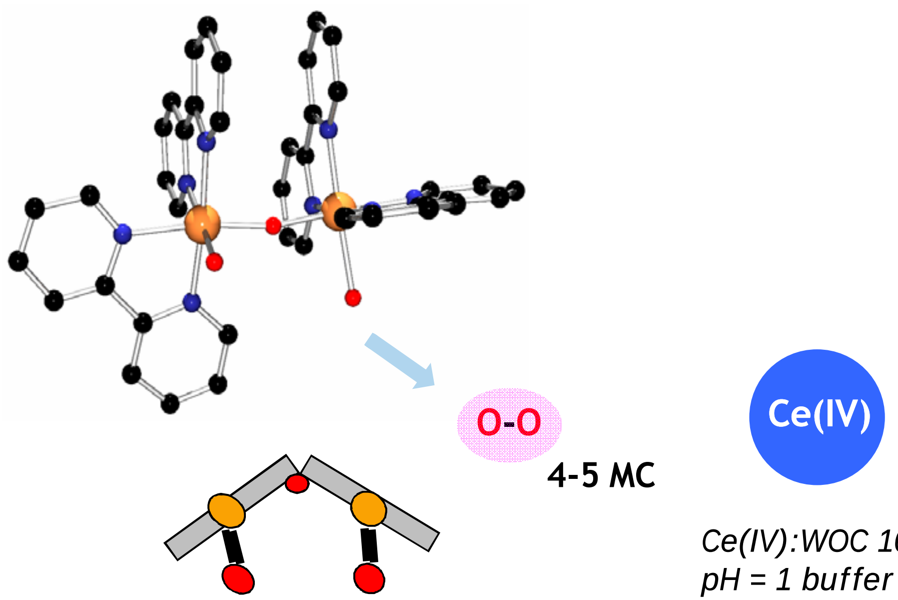
$$LRu^{II}\text{-}OH_2 \overset{-e^-\ -H^+}{\rightleftharpoons} LRu^{III}\text{-}OH \overset{-e^-\ -H^+}{\rightleftharpoons} LRu^{IV}=O$$

X 2

$$[(bpy)_2Ru^{III}(H_2O)\text{-}O\text{-}Ru^{III}(OH_2)(bpy)_2]^{4+} \xrightarrow{-\ 4H^+,\ -\ 4e^-} [(bpy)_2Ru^{V}(=O)\text{-}O\text{-}Ru^{V}(=O)(bpy)_2]^{4+}$$

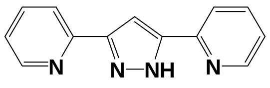



*Ce(IV):WOC 100:1*
*pH = 1 buffer*

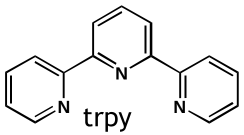
Gestern, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.*, **1982**, *104*, 4029

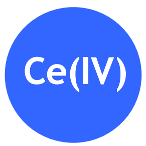
# *Ru-BASED WOCs: the Blue Dimer vs. Hbpp complexes*

$$2\ X \quad LRu^{II}\text{-}OH_2 \underset{}{\overset{-e^-\ -H^+}{\rightleftharpoons}} LRu^{III}\text{-}OH \underset{}{\overset{-e^-\ -H^+}{\rightleftharpoons}} LRu^{IV}{=}O$$




Hbpp

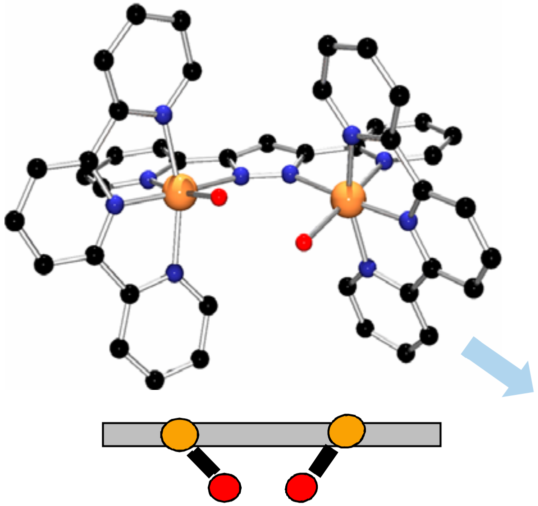



*Ce(IV):WOC 100:1*
*pH = 1 buffer*

$[(trpy)Ru^{II}\text{-}(bpp)\text{-}Ru^{II}(trpy)]^{3+}$

$H_2O$ | $OH_2$

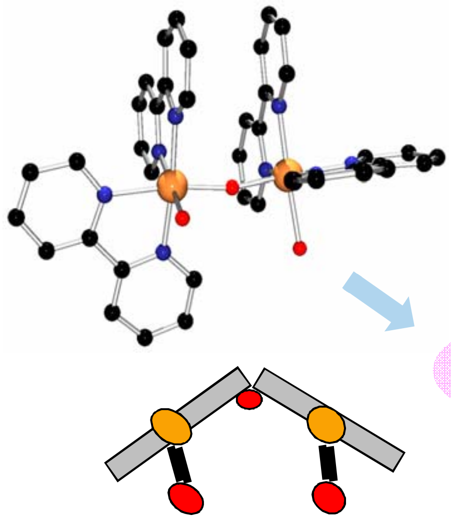


O-O

18 MC

$[(bpy)_2Ru^{V}\text{-}O\text{-}Ru^{V}(bpy)_2]^{4+}$

O || O



O-O

4-5 MC

Sens, C., Llobet, A. et al., *J. Am. Chem. Soc.*, **2004**, 126, 7798

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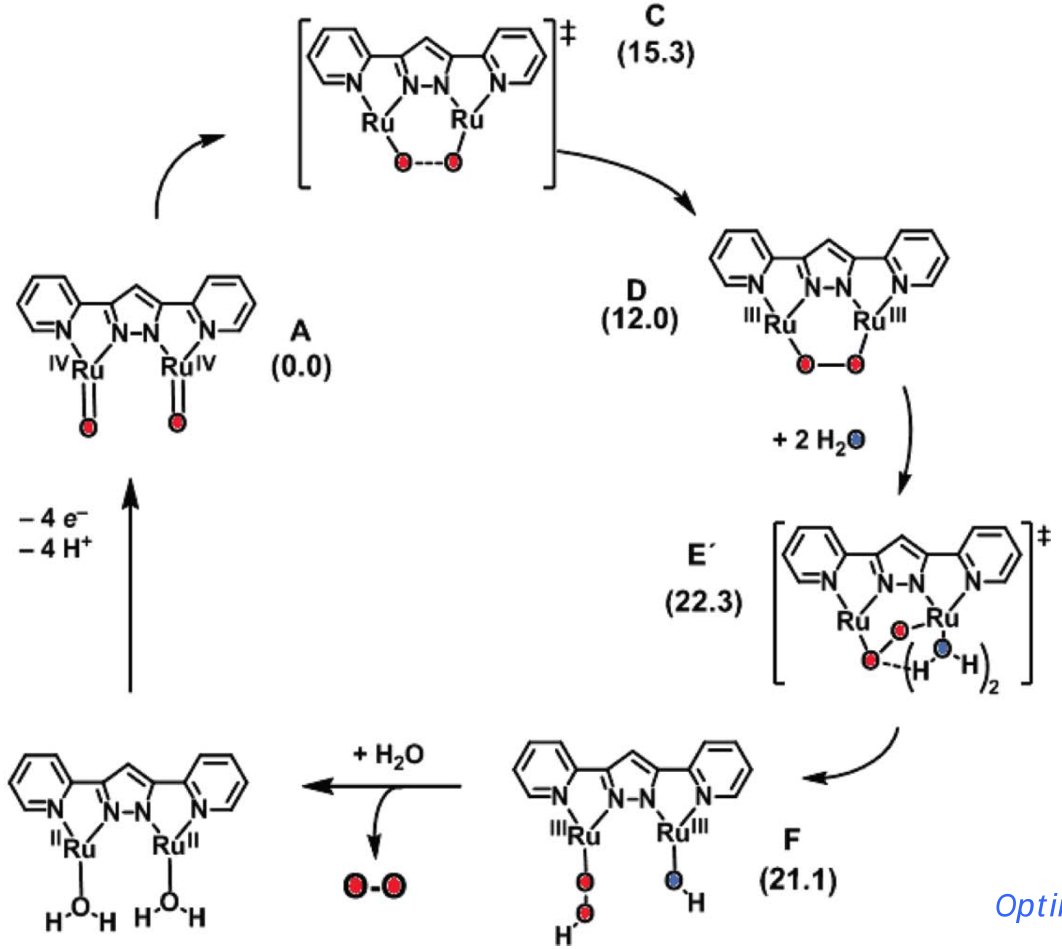
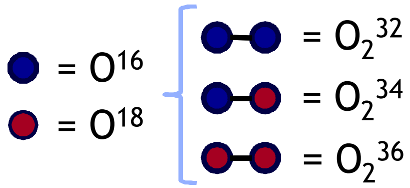
Intra-I2M




Ce(IV)

*Optimized conditions*

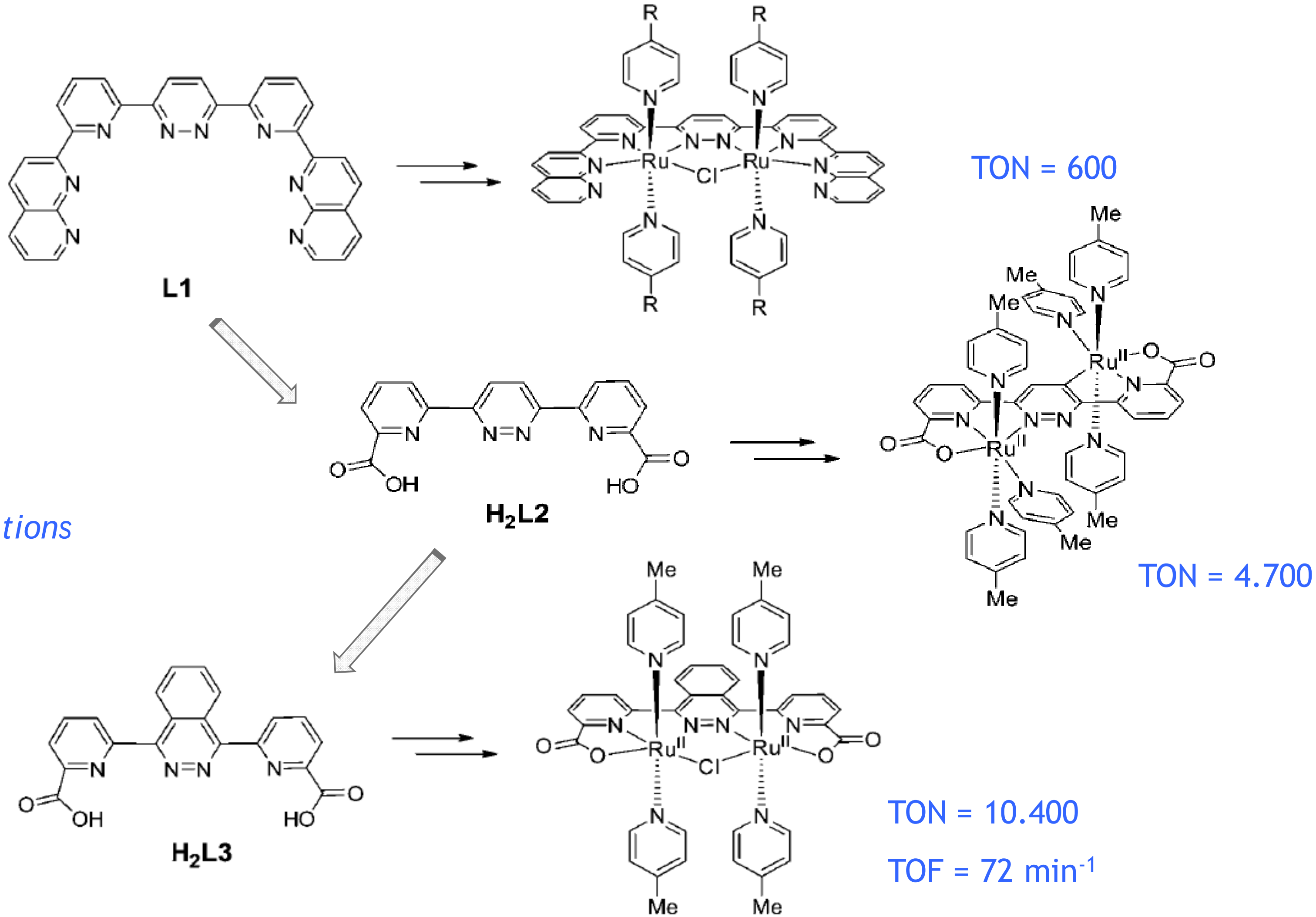
TON = 570

Romain, S.; Sala, X.; Llobet, A. et al. *J. Am. Chem. Soc.* **2009**, 131, 2768-2769
Bozoglian, F.; Romain, S.; Cramer, C.; Gagliardi, L.; Llobet, A. et al. *J. Am. Chem. Soc.* **2009**,131, 15176

## *Ru-BASED WOCs: other key dinuclear systems*

Ce(IV)

*Optimized conditions*

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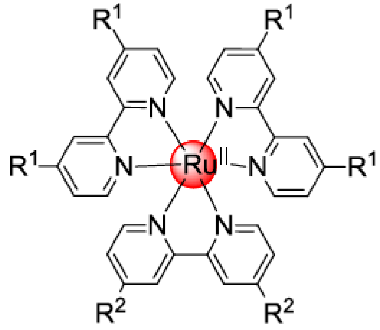
*Deng, G.; Thummel, R. et al. Inorg. Chem.* **2008**, 47, 1835
Xu, Y.; Akermark, B.; Sun, L. et al. *Inorg. Chem.* **2009**, 48, 2717

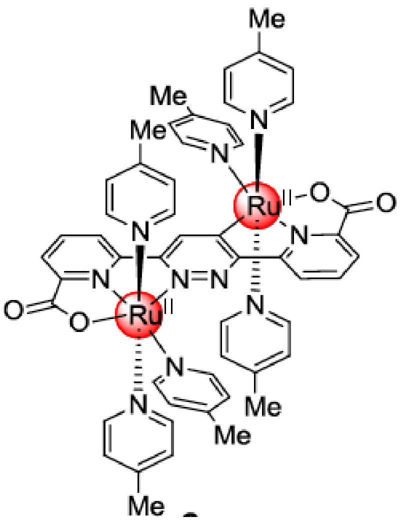
Universitat Autònoma de Barcelona

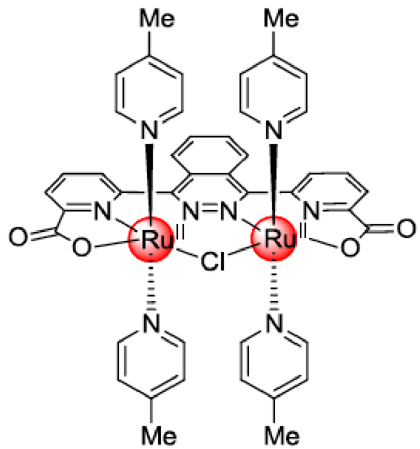
P*

$Ru_p$ =




Co = $[Co(NH_3)_5Cl]^{n+}$




TON = 60

TOF = 6 $min^{-1}$

$[Ru(bpy)_3]$ as $Ru_p$

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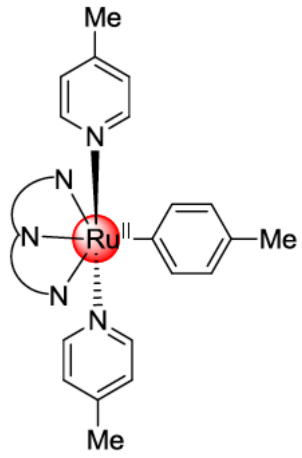
*Xu, Y.; Akermark, B.; Sun, L. et al Angew. Chem. Int. Ed.* **2010**, 49, 8934
Xu, Y.; Akermark, B.; Sun, L. et al. *Chem Commun* **2010**, 46, 6506

# *Ru-BASED WOCs: mononuclear systems*

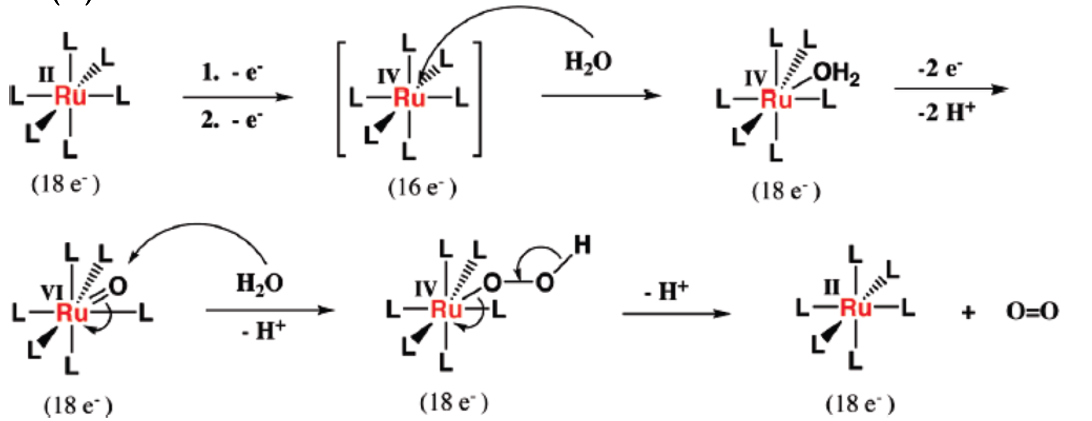
Ce(IV)




TON = 89 (22h)

Ru(II)-N6

*Metal coord. expansion*

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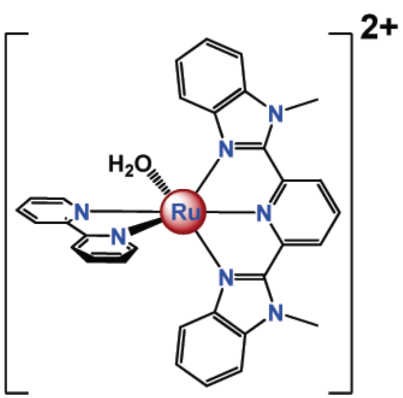
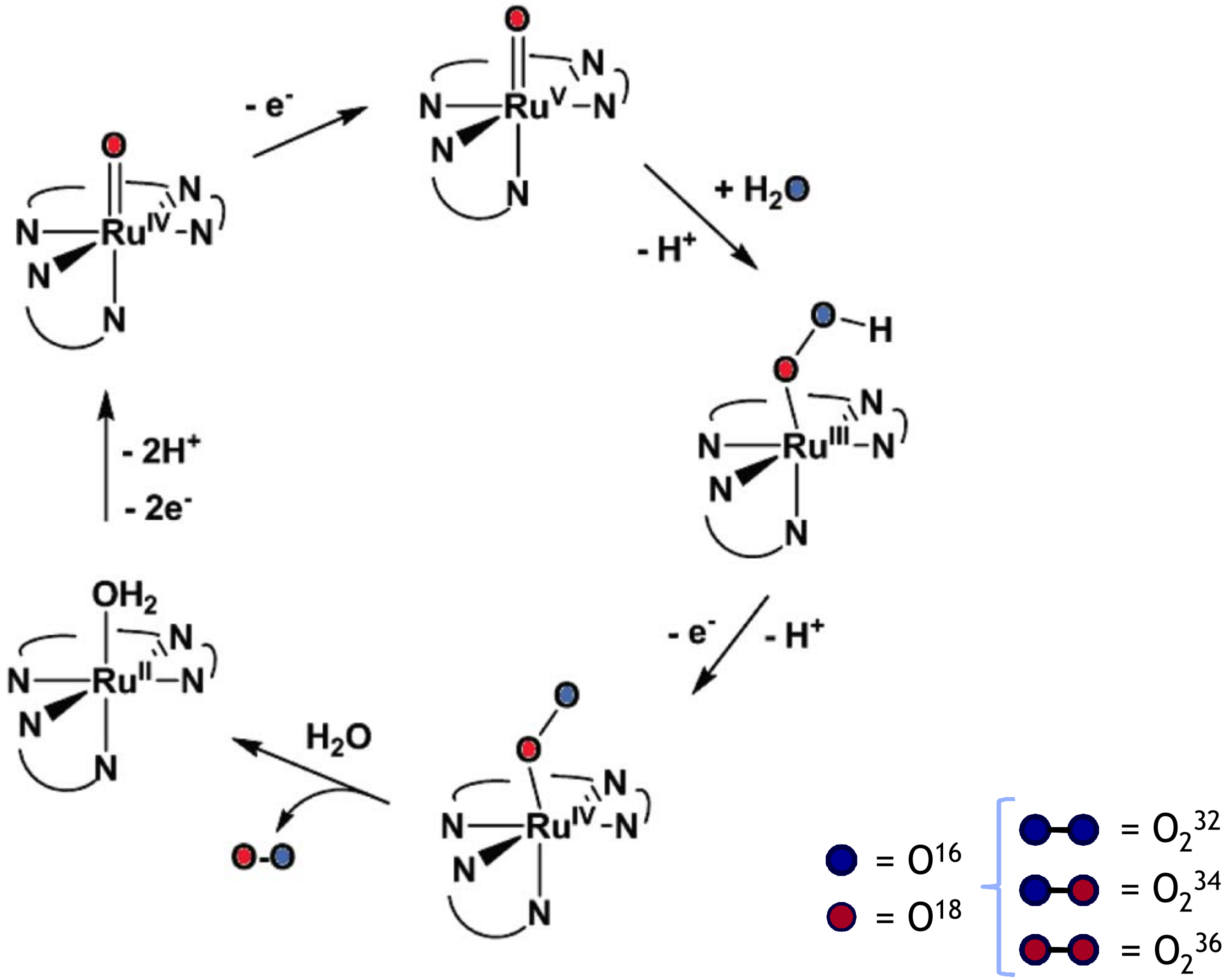
*Deng, G.; Thummel, R. et al. Inorg. Chem.* **2008**, 47, 1835

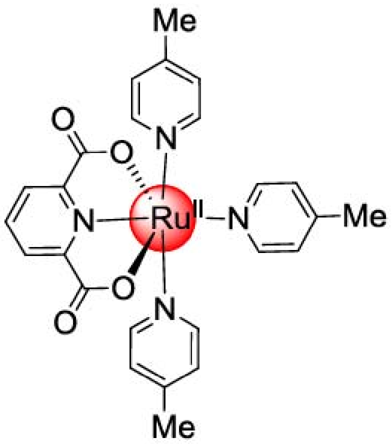
## *Ru-BASED WOCs: mononuclear systems*

Ce(IV)



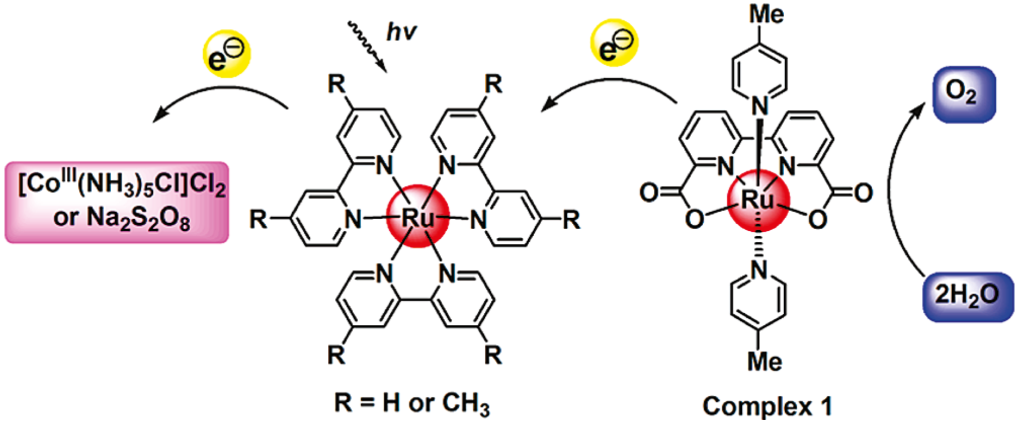

*Concepcion, J. J.; Meyer, T. J. et al. J. Am. Chem. Soc.* **2008**, 130, 16462
*Concepcion, J. J.; Meyer, T. J. et al. J. Am. Chem. Soc.* **2010**, 132, 1545




Ce(IV)

TON = 2000

TOF 2500 $min^{-1}$




P*

TON = 100

TOF 3.7 $min^{-1}$

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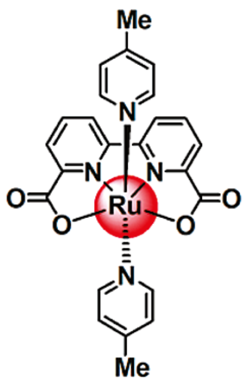
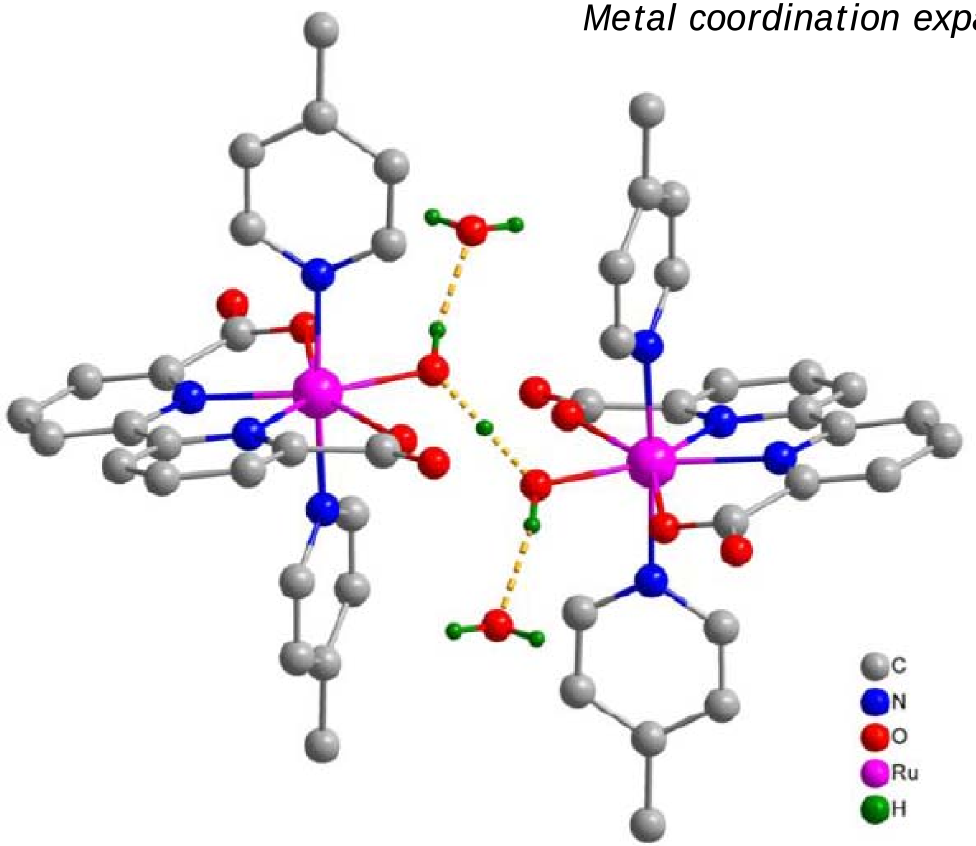
*Duan, L.; Sun, L. et al. Chem. Eur. J.* **2010**, 16, 4659
Duan, L.; Sun, L. et al. Inorg. Chem. **2010**, 49, 209



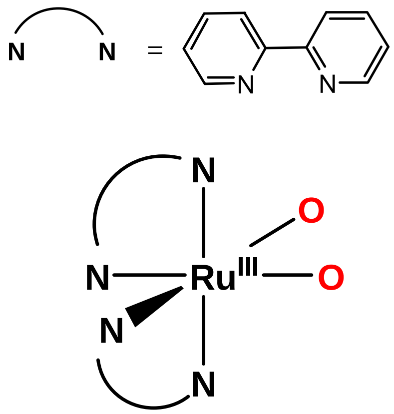

*Metal coordination expansion to 7*




Duan, L.; Sun, L. et al. *J. Am. Chem. Soc.* **2009**, 131, 10397.
Nyhlén, J.; Akermark, B.; Sun, L. Privalov, T. *et al. Angew. Chem. Int. Ed.* **2010**, 49, 1773

# *Ru-BASED WOCs: mononuclear systems- $(Ru{=}O)_2$*

**Ce(IV)**

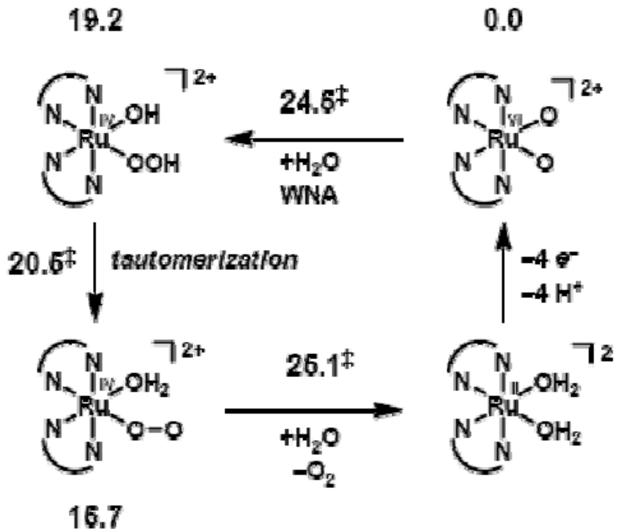



*cis*

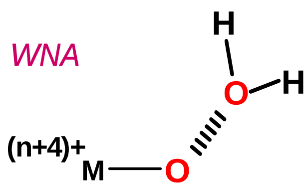
TON = 6

TOF = 1.2 min$^{-1}$

$O_2$ labelling +

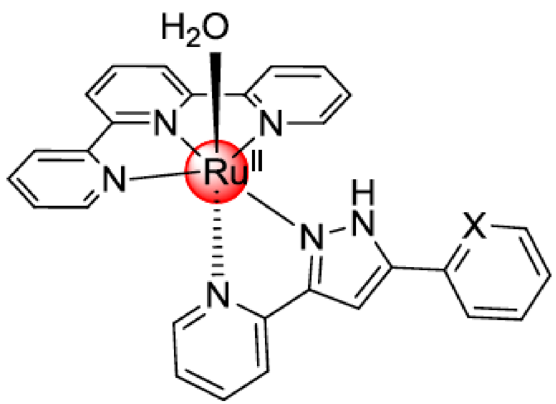



*WNA*

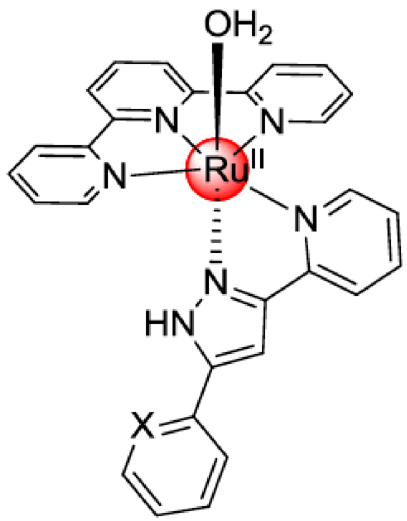



Sala, X.; Gagliardi, L.; Cramer, C.; Llobet, A. et al. *Angew. Chem. Int. Ed.* **2010**, 49, 7745.

Ce(IV)  CPE  P*




*In*-Hppp, X = CH
*In*-Hbpp, X = N




*Out*-Hppp, X = CH
*Out*-Hbpp, X = N

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*Röser, S.; Farràs, P.; Llobet, A. et al. ChemSusChem* **2011**, 49, 1773

## *OUTLINE*

UAB
Universitat Autònoma de Barcelona

1. INTRODUCTION
2. Ru-based WOCs: from the Blue Dimer to mononuclear species
3. Iridium WOCs
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6. Heterogeneous WOCs
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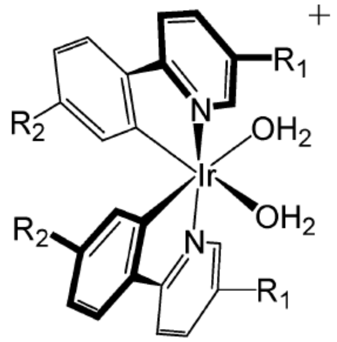
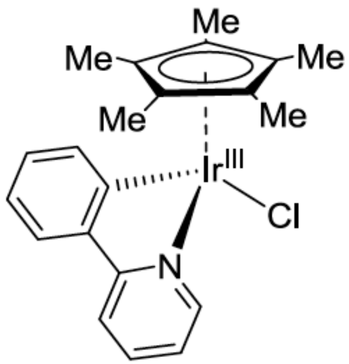
8. FINAL REMARDKS AND CONCLUSIONS




TON = 2760 (≈ one week)

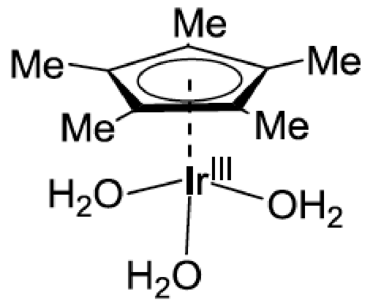
TOF = 0.27 $min^{-1}$

Bernhard, S. et al. *ACIE* **2008**, 130, 210.




TON = > 1500 (5.5h)

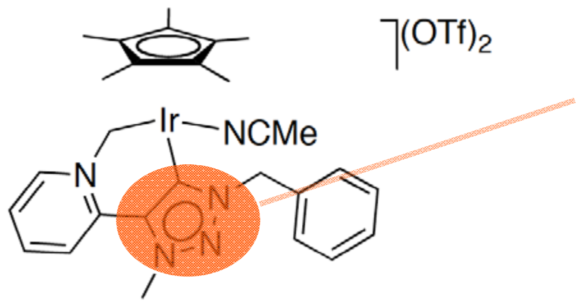
TOF = 54 (init.) to 0.1 $min^{-1}$




TON = > 1500 (5.5h)

TOF = 0.1 $min^{-1}$

Crabtree, J.; Brudvig, G. W. et al. *JACS* **2009**, 131, 8730 and JACS **2010**, 132, 16017.




*"Abnormal" Carbene*

Ce(IV)

TON = 10.000 (5 days)

TOF = 1.39 $min^{-1}$

Albrecht, M. et al. *ACIE* **2011**, 4, 238.

# OUTLINE

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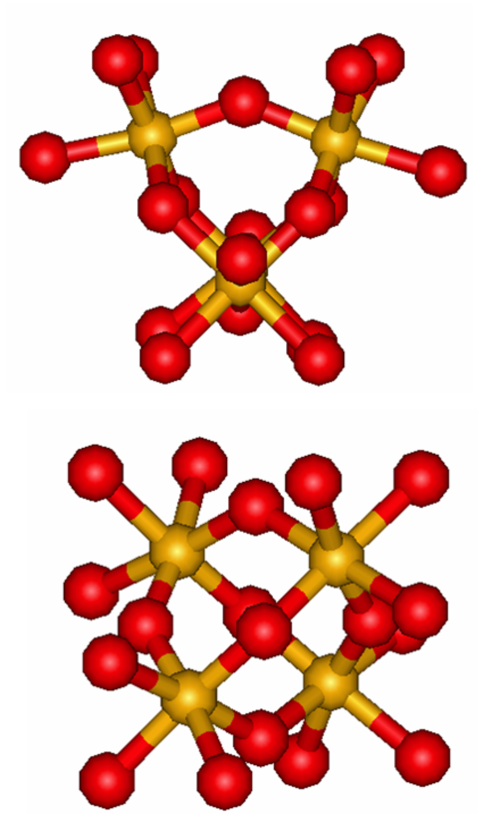

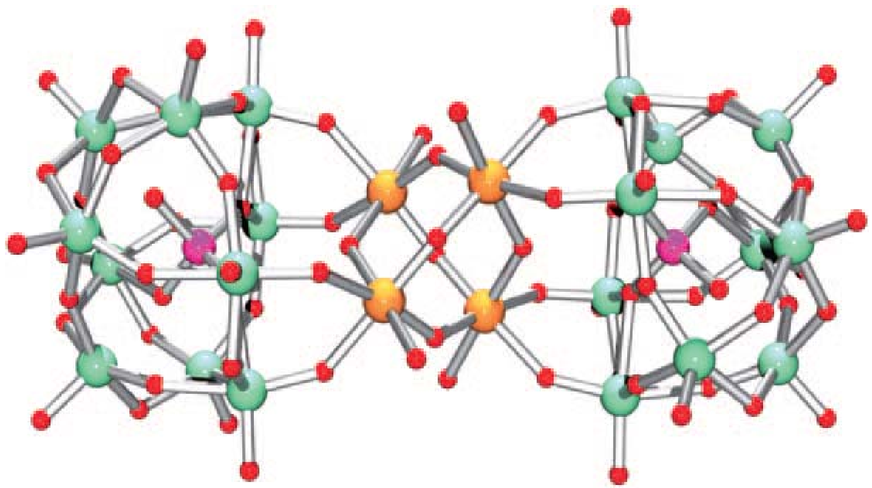

Cuban like $[Ru_4O_4(OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$

TON = highly stable, no deactivation

TOF = 7.5 $min^{-1}$

**Ce(IV)**

Sartorel, A.; Bonchio, M. et al. *J. Am. Chem. Soc*. **2008**, *130, 5006.*
Geletii, Y. V.; Hill, C. Angew. Chem. Int. Ed. **2008**, 47, 3896

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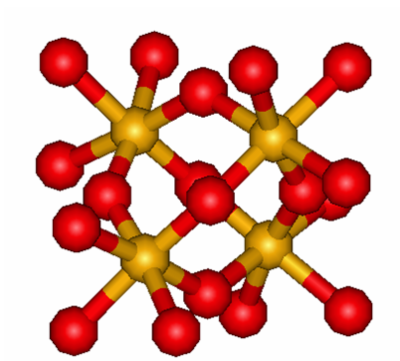
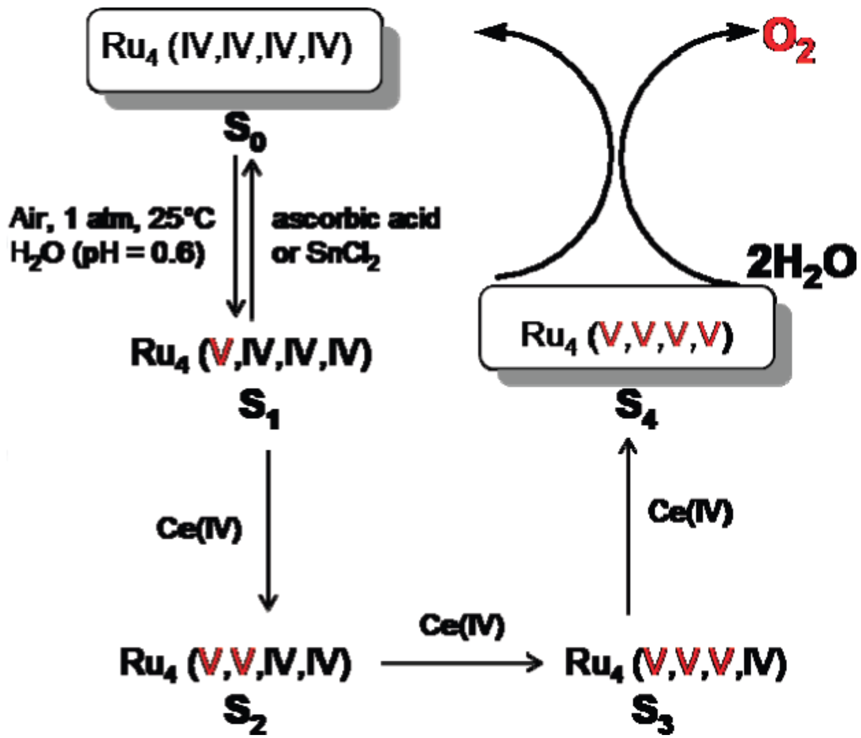
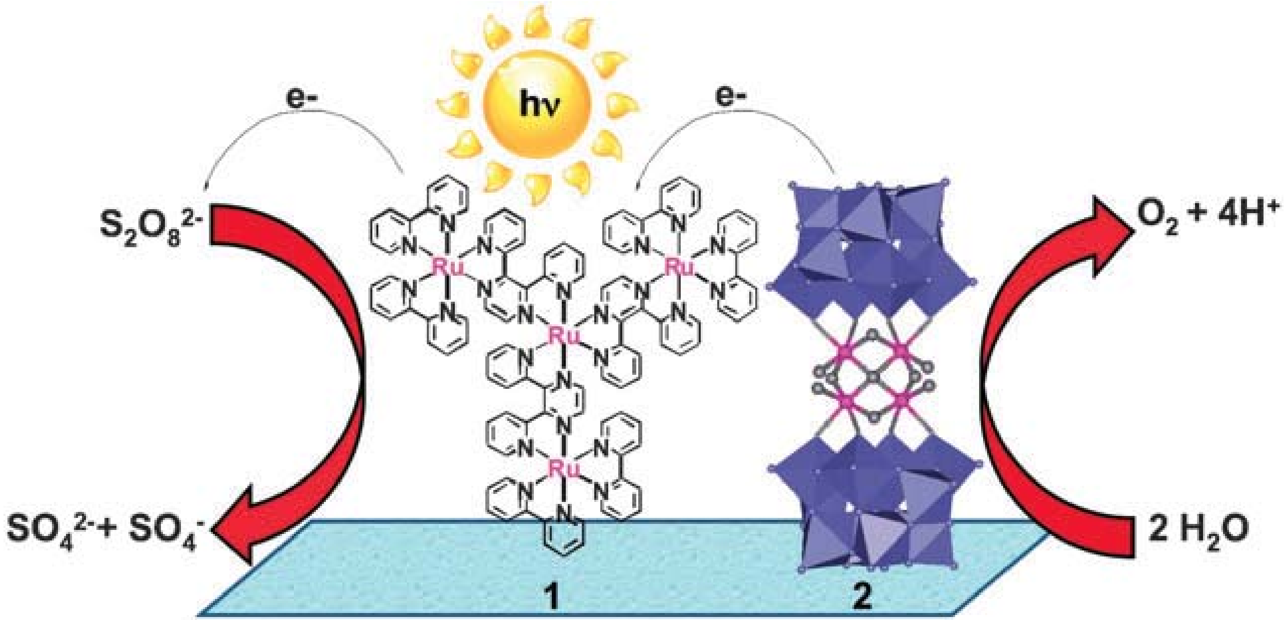





Ce(IV)

Sartorel, A.; Llobet, A.; Bo, C.; Bonchio, M. et al. *J. Am. Chem. Soc.* **2009**, 131, 16051

**P***




P* collects a broad range of the EM spectra

Fast Hole Scavenging of the Ru-POM

$\phi = 0.3$

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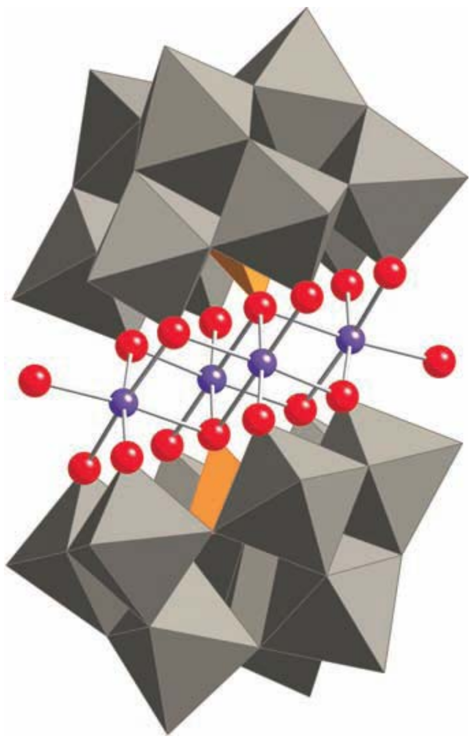
*Puntoriero, F.; ; Bonchio, M.; Campagnia, S. et al. Chem. Commun.* **2010**, 46, 4725.
Orlandi, M.; Bonchio, M.; Scandola, S. *Chem. Commun*. **2010**, 46, 3152.



Cuban like, B-type $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$

**$[Ru(bpy)_3]^{3+}$**

TON = very stable

TOF = ≥ 300 $min^{-1}$ (init.)

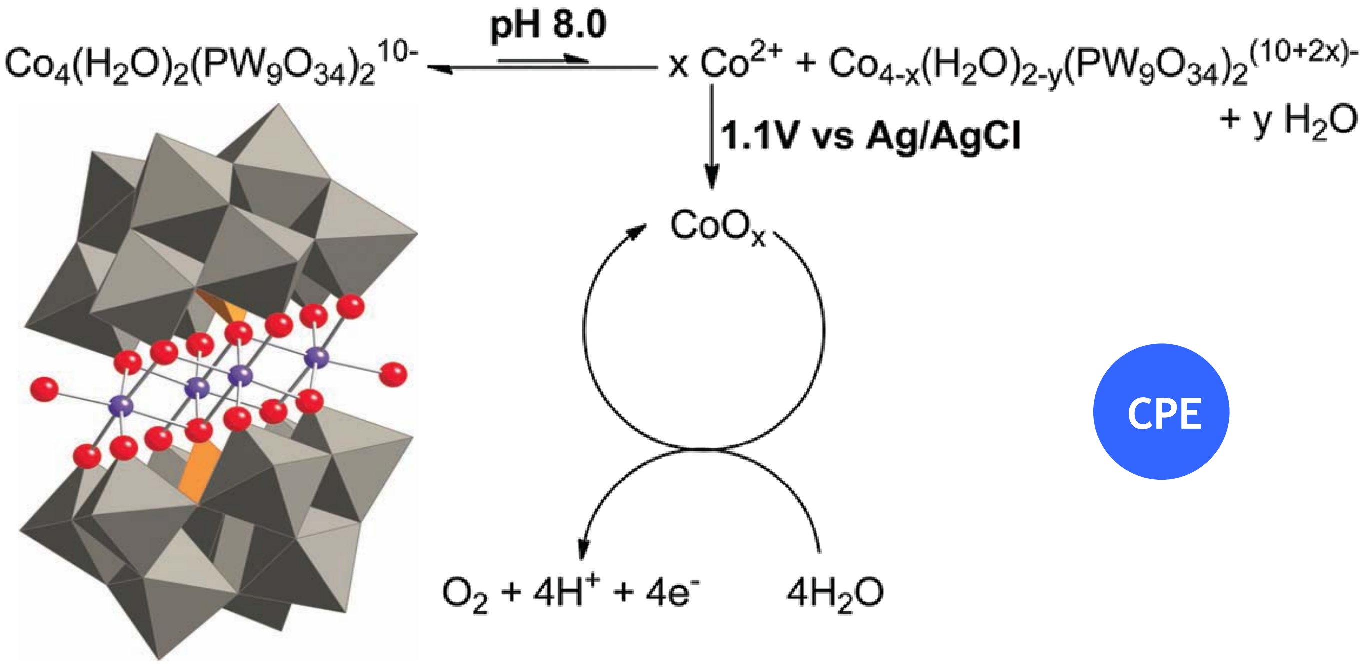
*TON and TOF highly pH dependant*

**P***

TON = ≥ 220

$\phi$ = 0.15

Yin, Q.; Hill, C. et al. *Science* **2010**, 328, 342
Huang, Z.; Hill, C.; Lian, T. et al. *J. Am. Chem. Soc.* **2011**, 133, 2068




CPE

Stracke, J. J.; Finke, R. G. et al. *J. Am. Chem. Soc.* **2011**, 133, 14872

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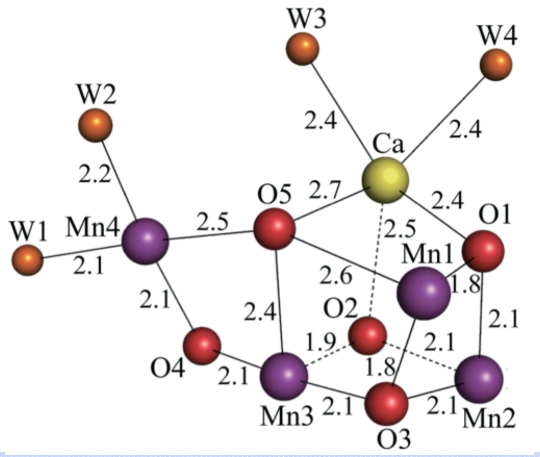



**HClO**

Crabtre and Brudvig et al.

TON = 4 (6h)

TOF = 0.01 $min^{-1}$

**Ce(IV)**

Yagi, et al.

TON = 17 (6h)

TOF = 0.05 $min^{-1}$

**P***

Yagi, et al.

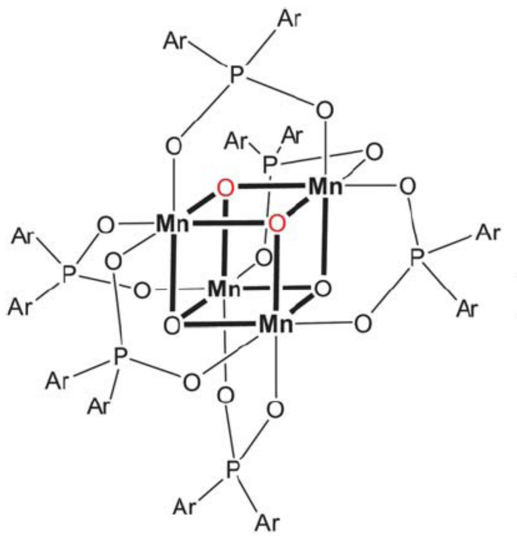
TON = 4 (17h)

TOF = 0.003 $min^{-1}$

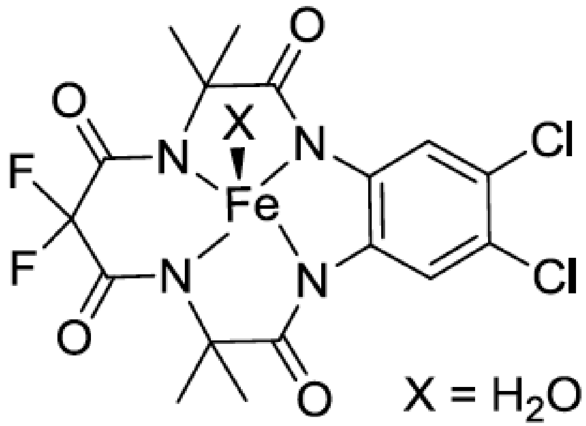
Limburg, J.; Crabtree, R. H.; Brudvig, G. W. et al. *Science* **1999**, 283, 1524
Yagi, M. *et al. J. Am. Chem. Soc.* **2004**, 126, 8084 and *Chem. Commun.* **2010**, 46, 8594

## *First row transition-metal based WOCs: manganese*






Dismukes, G. C.; Spiccia, L. et al. *Acc. Chem. Res.* **2009**, 42, 1935.
Brimblecombe, R.; Dismukes, G. C.; Spiccia, L. et al. *J. Am. Chem. Soc.* **2010**, 132, 2802.




TON = 11

TOF = 78 $min^{-1}$

*Fast and Cheap*

Ce(IV)

Bernhard, S.; Collins, T. et al. *J. Am. Chem. Soc.* **2010**, 132, 10990.

# *First row transition-metal based WOCs: iron*

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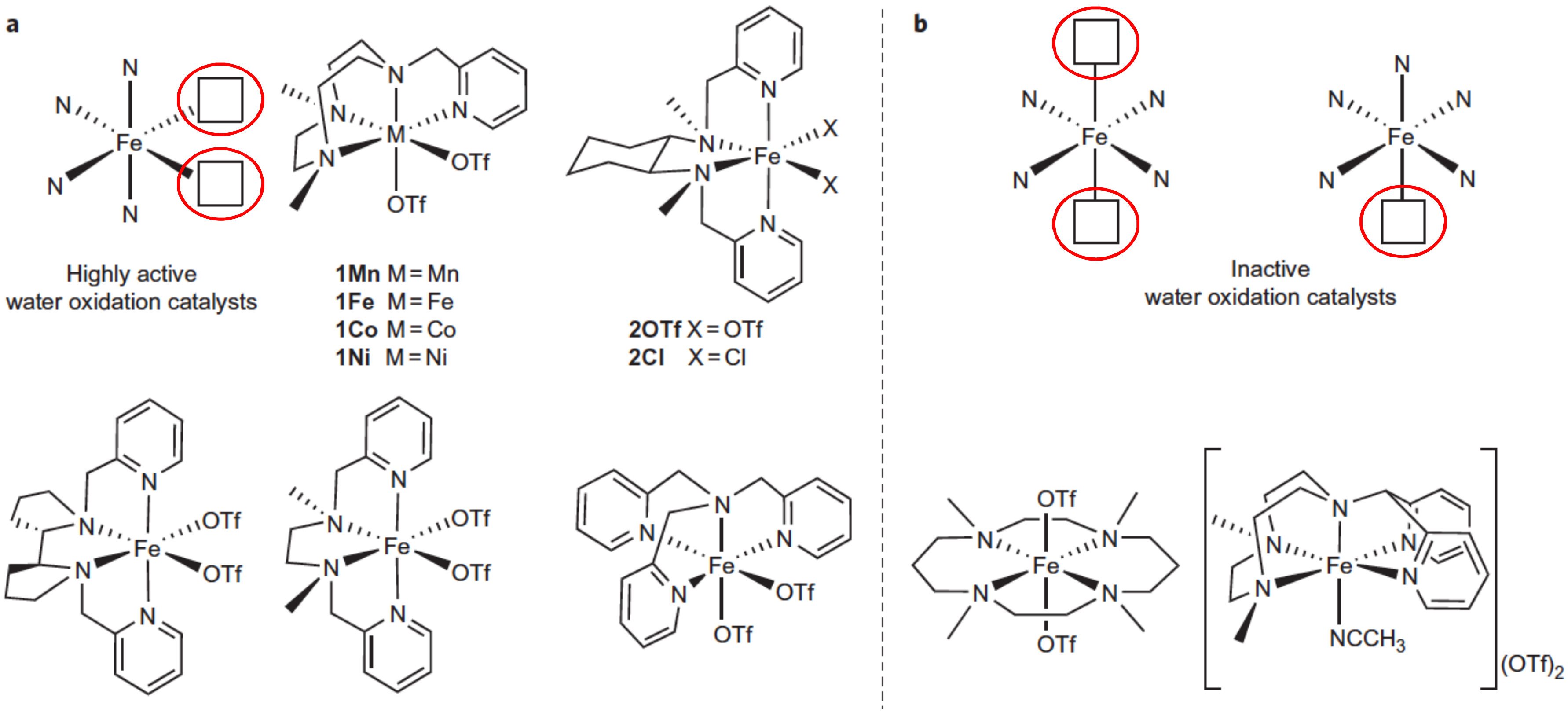


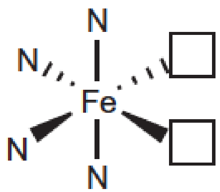

Ce(IV)

$TON_{max}$ = ≥ 1.050

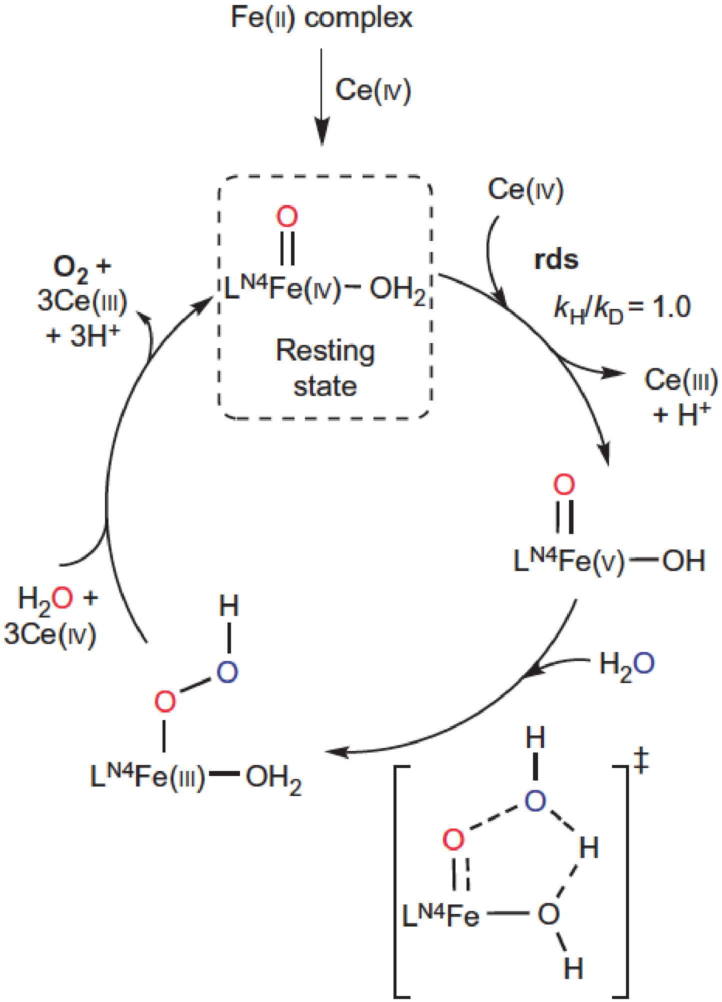
$TOF_{max}$ = 3,7 $min^{-1}$

*Lloret, J.; Costas, M. et al. Nat. Chem.* **2011**, 3, 807.

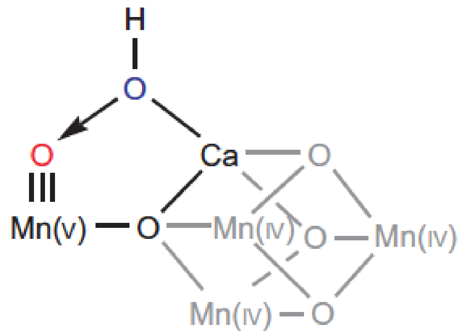
# *First row transition-metal based WOCs: iron*




Highly active WOC




| | 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 |




*Lloret, J.; Costas, M. et al. Nat. Chem.* **2011**, 3, 807.

## *OUTLINE*

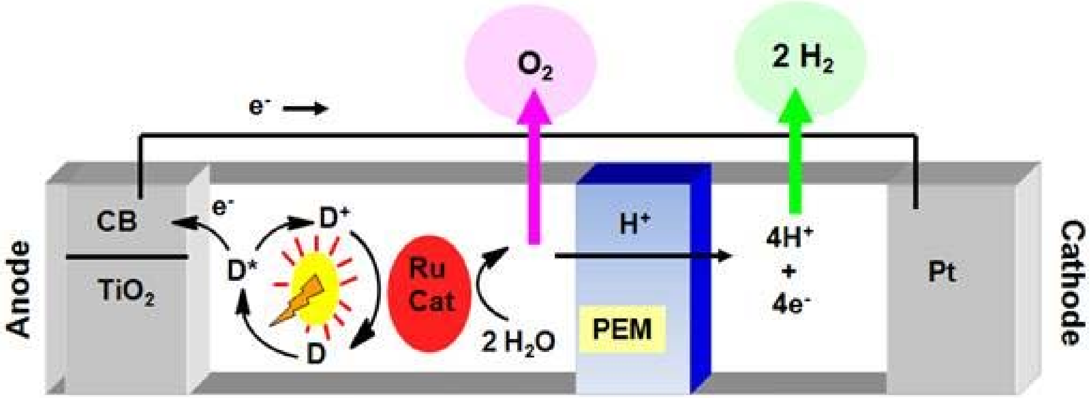
1. INTRODUCTION

2. R

ır species

3. I

4. A




5. First-row transition-metal based WOCs

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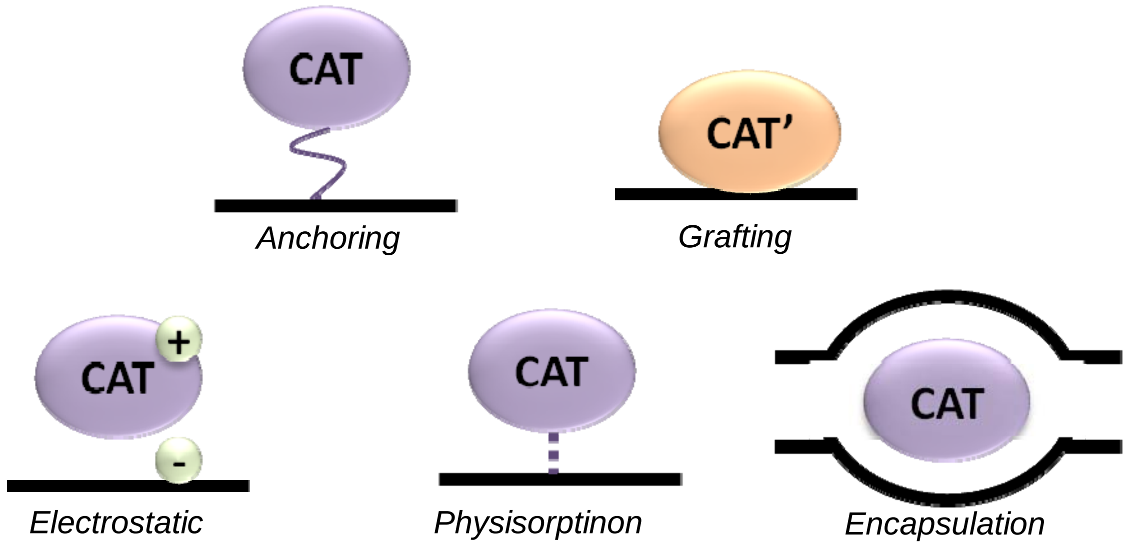
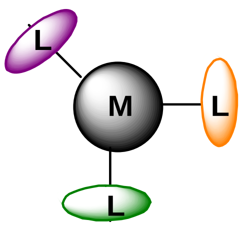
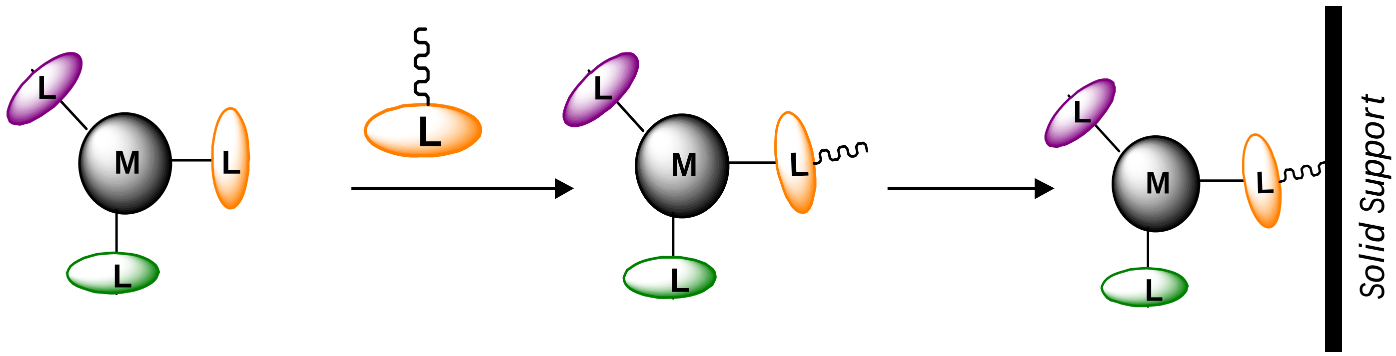
## Heterogeneous WOCs: covalent attachment

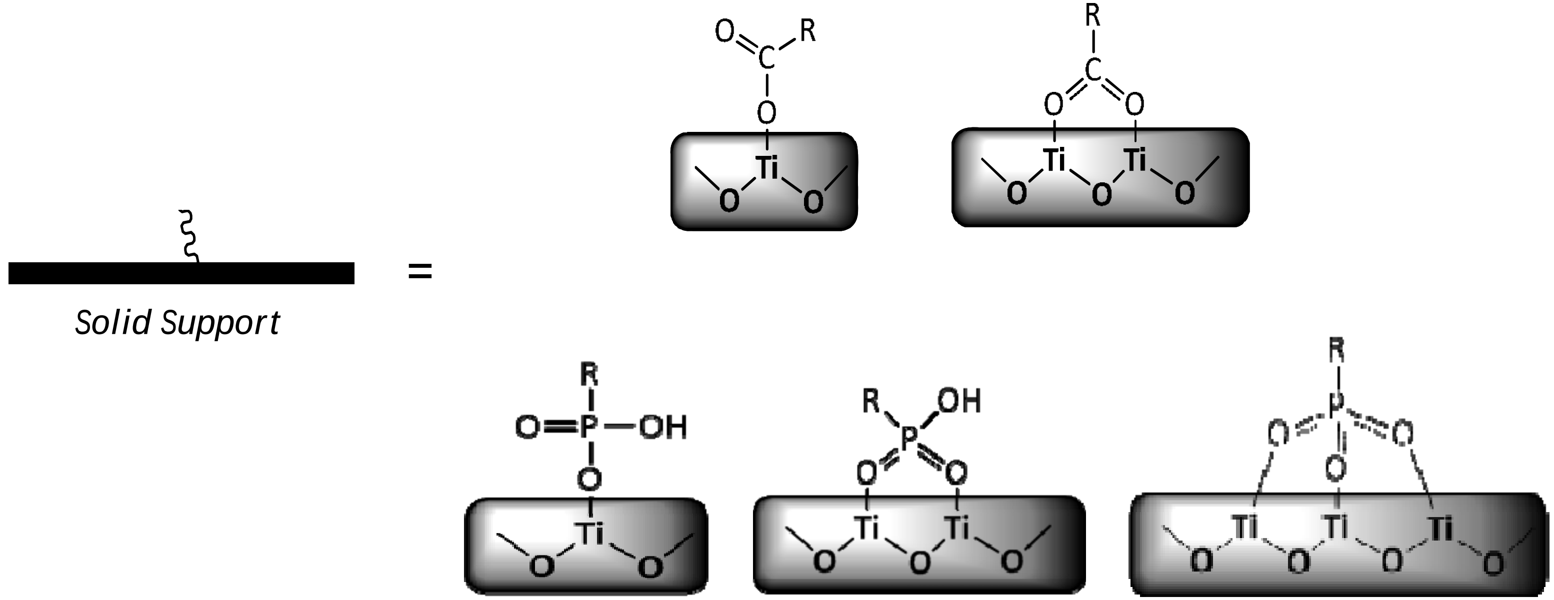




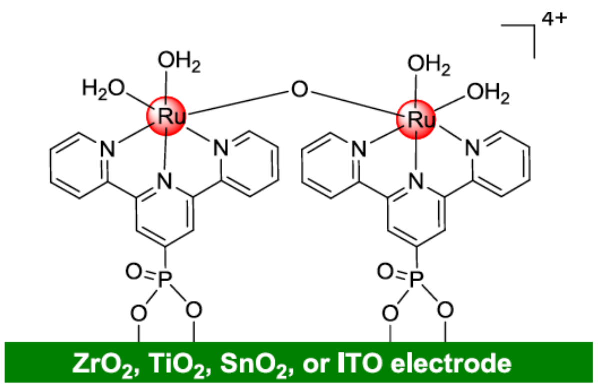



# *Heterogeneous WOCs: covalent attachment*

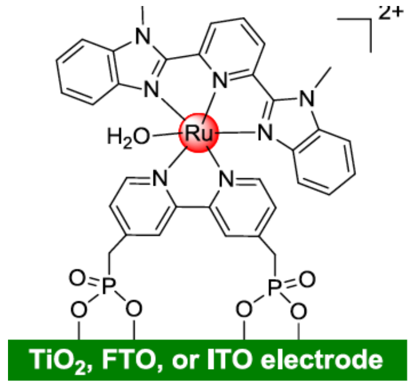


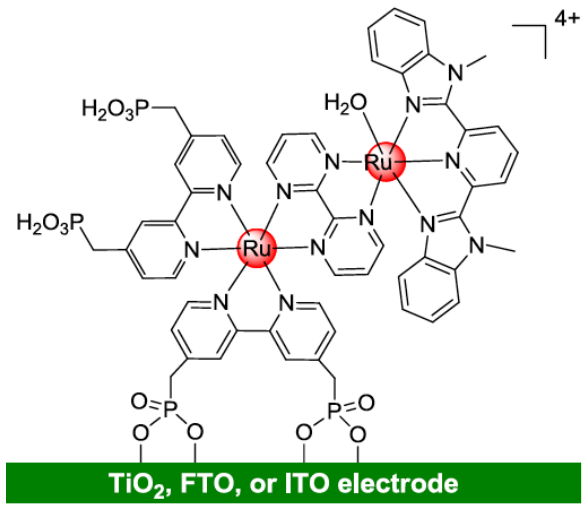
# *Heterogeneous WOCs: covalent attachment*



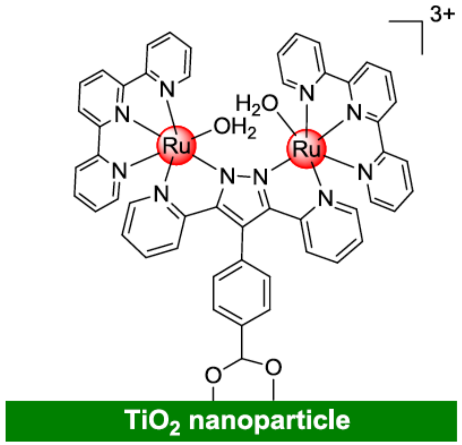

Meyer, T. J. et al. *JACS* **2007**, 129, 2446.




Meyer, T. J. et al. *JACS* **2009**, 131, 15580.




Meyer, T. J. et al. *ACIE* **2009**, 48, 9473.




Sala and Llobet et al. *ChemSusChem* **2009**, 2, 321.

## *Heterogeneous WOCs: electropolymerization*

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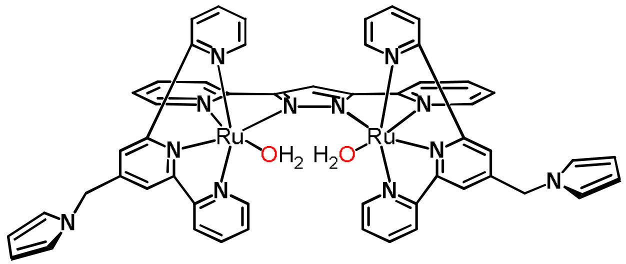


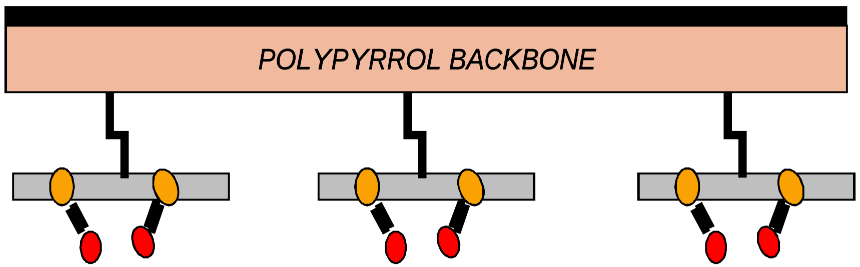


**CPE**

**Ce(IV)**

TON = 250 (18 in homog. Phase)

TOF = 0.1 $min^{-1}$ (1 homog. Phase)

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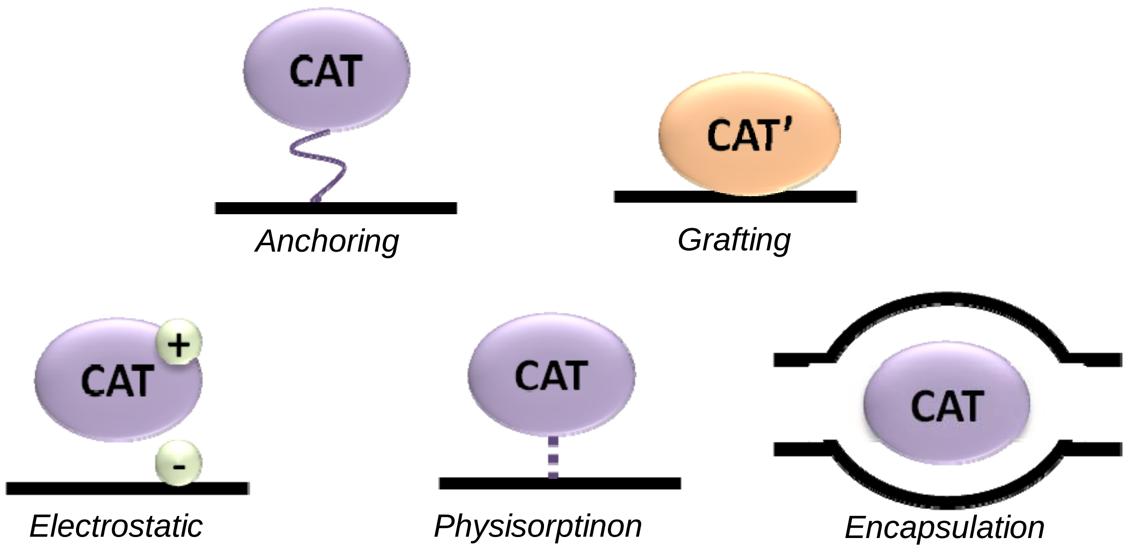
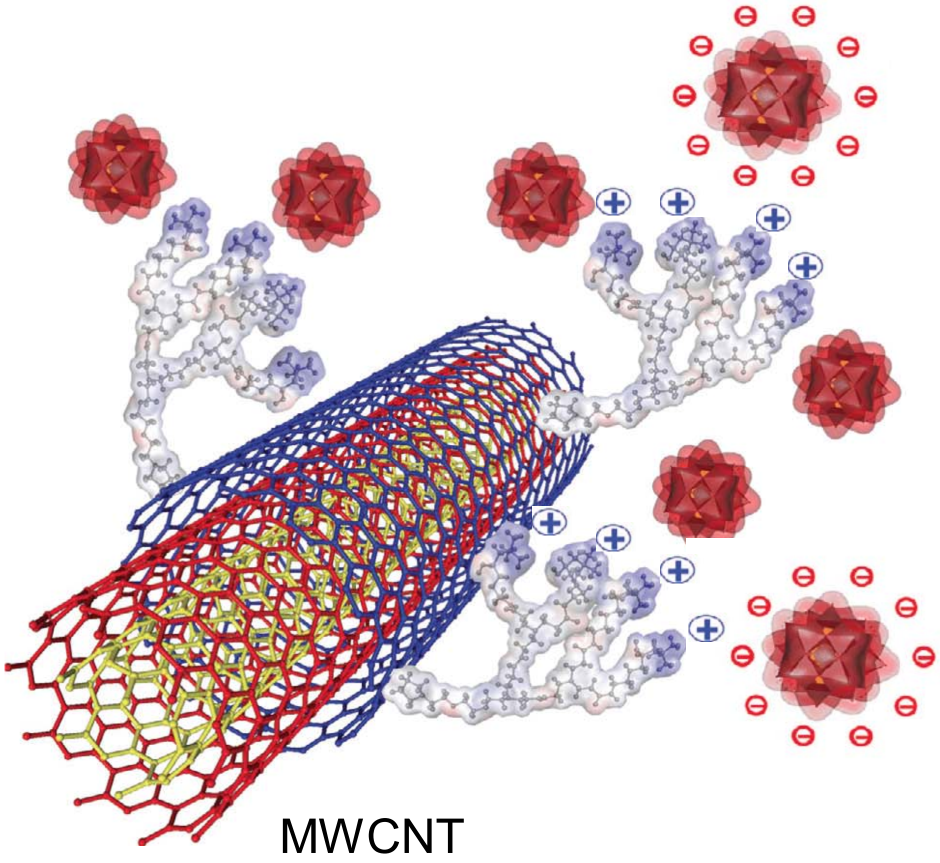
Mola, J.; Sala, X.; Llobet, A. et al. *Angew. Chem. Int. Ed.* **2008**, 47, 5830

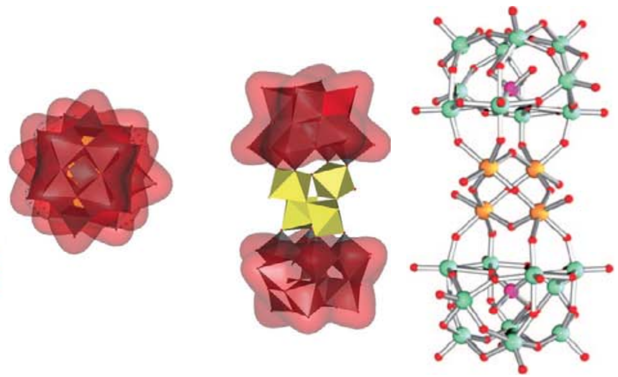
*Heterogeneous WOCs: electrostatic interaction*



## *Heterogeneous WOCs: electrostatic interaction*




$[Ru_4O_4(OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$



TOF = 0.6 $min^{-1}$ (1.17 V vs. NHE)

5.1 $min^{-1}$ (1.42 V vs. NHE)

CPE

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Toma, F. M.; Prato, M.; Bonchio M. et al. *Nat. Chem.* **2010**, 2, 826

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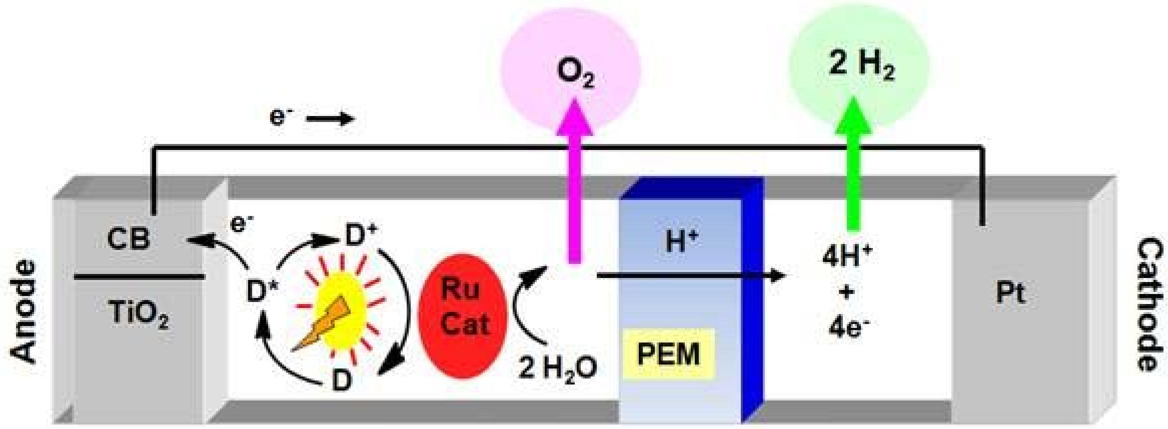
## *WOCs in Photoelectrochemical cells (PECs)*

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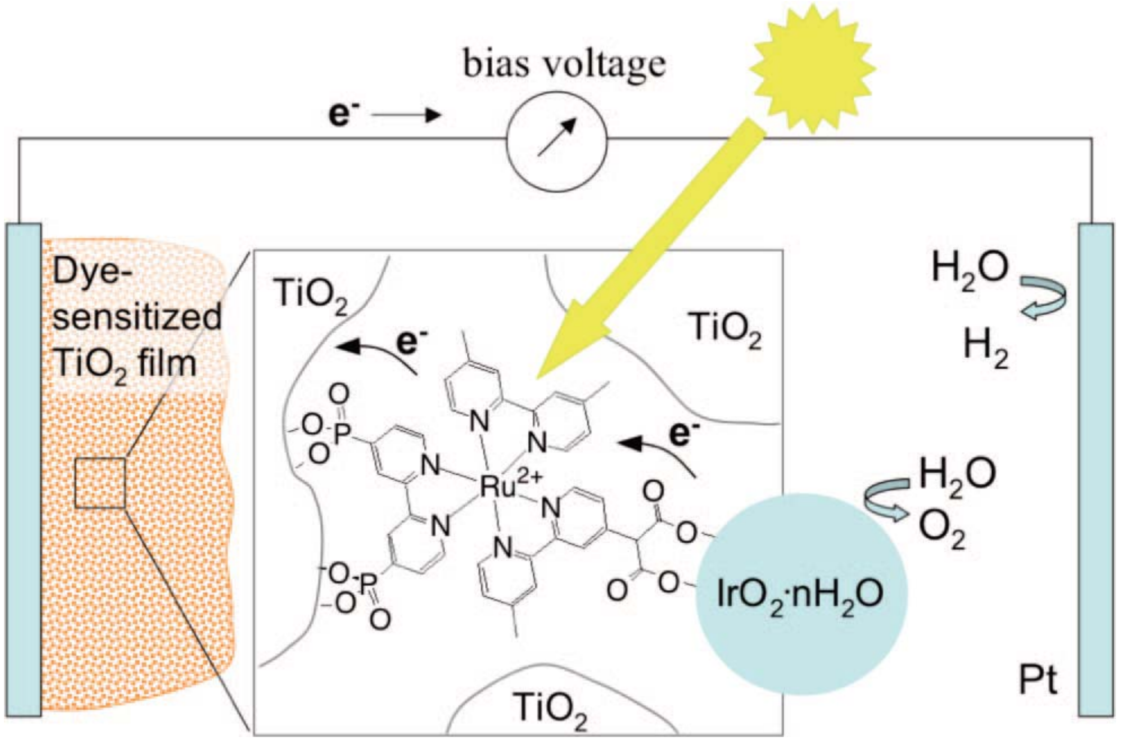
Sala, X.; Escriche E.; Llobet A. et al. *Angew. Chem. Int. Ed.* **2009**, 48, 2842

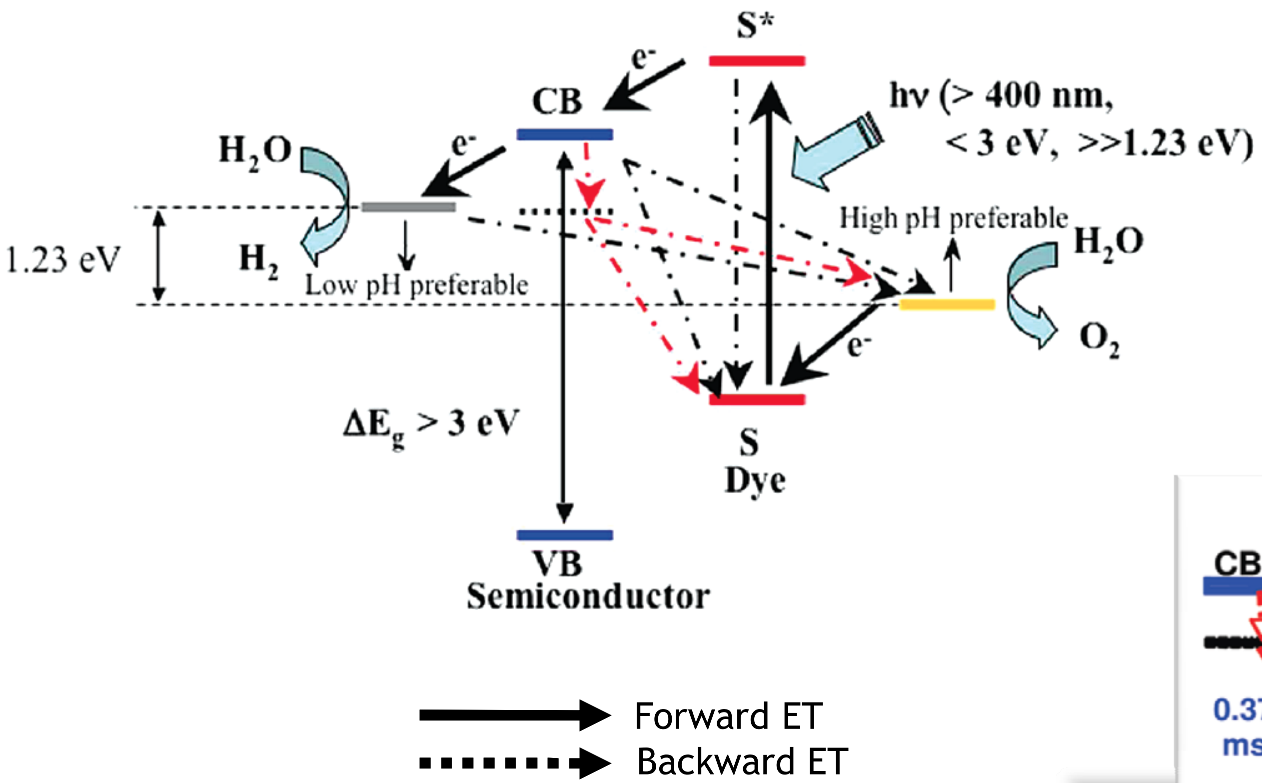


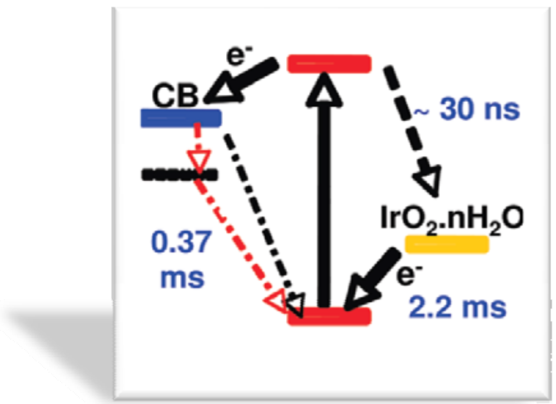

TON = 16 (per dye molecule)

Small bias needed

$\phi$ = 0.09

Youngblood, W. J.; Mallouk, T. E. et al. *J. Am. Chem. Soc.* **2009**, 131, 923 and *Acc. Chem. Res.* **2009**, 42, 1966.



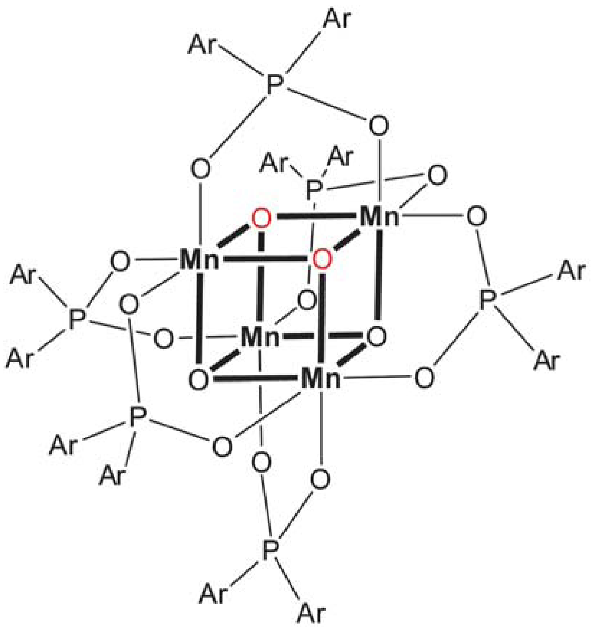



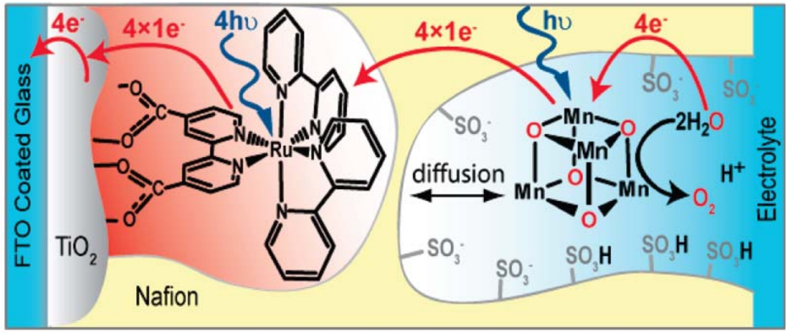

Backward ET one order faster

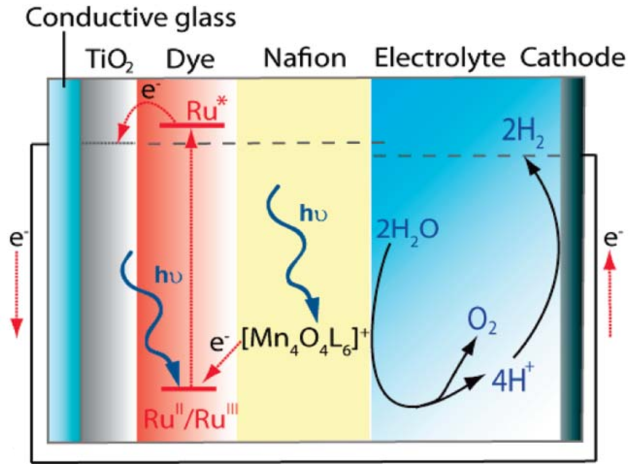
Youngblood, W. J.; Mallouk, T. E. et al. *J. Am. Chem. Soc.* **2009**, 131, 923 and *Acc. Chem. Res.* **2009**, 42, 1966.

# *First row transition-metal based WOCs: manganese*








TON = 13 (per cluster molecule)

TOF = 0.83 $min^{-1}$

No bias needed

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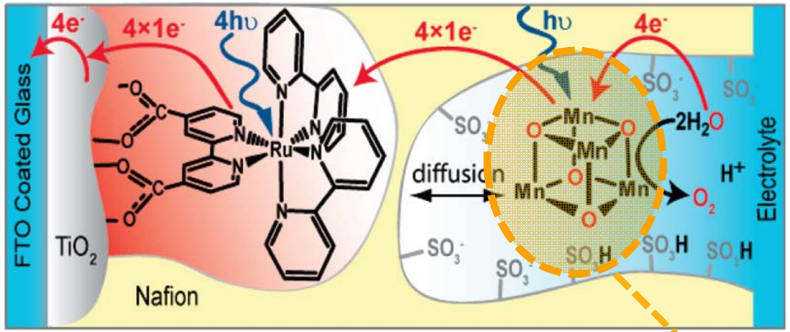
Dismukes, G. C.; Spiccia, L. et al. *Acc. Chem. Res.* **2009**, 42, 1935.
Brimblecombe, R.; Dismukes, G. C.; Spiccia, L. et al. *J. Am. Chem. Soc.* **2010**, 132, 2802.

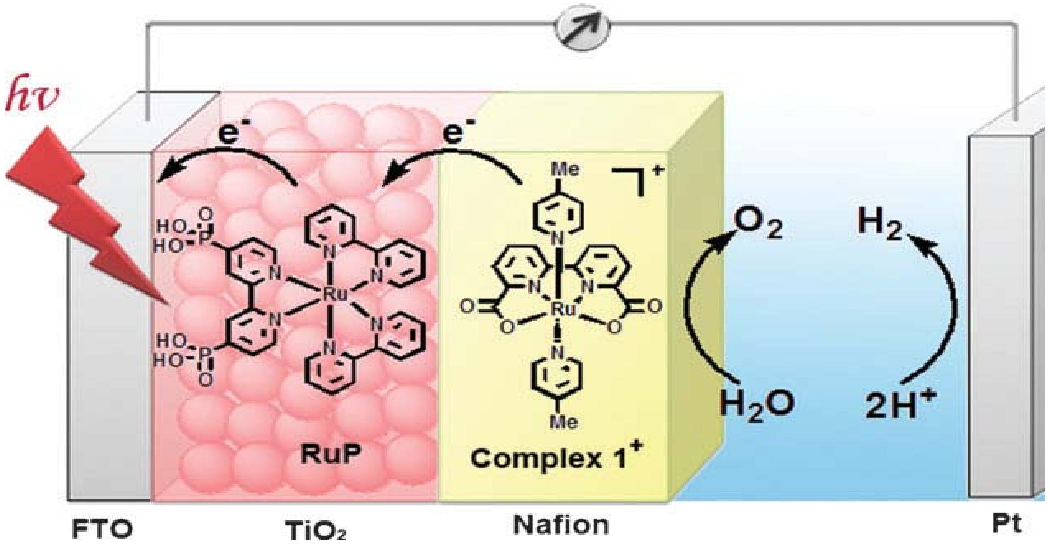



*photoreduction*

$Mn^{2+}$ ⟷ Mn(III/IV) – oxide phase

$O_2$ $2H_2O$

Hocking R. K..; Spiccia, L. et al. Nat. Chem. 2011, 3, 461.




TON = 16

TOF = 0.45 min$^{-1}$

Li, L.; Sun, L. et al. *Chem. Commun.* **2010**, 46, 7307

1. INTRODUCTION

2. Ru-based WOCs: from the Blue Dimer to mononuclear species

3. Iridium WOCs

4. All-inorganic POM complexes

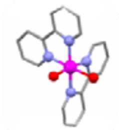
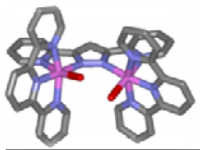
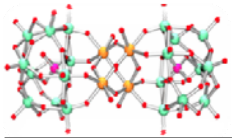
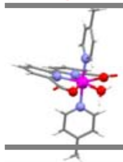
5. First-row transition-metal based WOCs

6. Heterogeneous WOCs

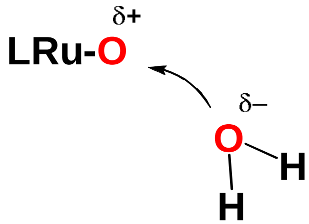
7. WOCs in Photoelectrochemical cells (PECs)

8. FINAL REMARDKS AND CONCLUSIONS

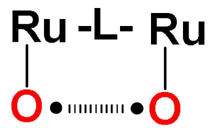
# WOCs MECHANISTIC SUMMARY

| | | Active Ox. State | Mechanism |
|---|---|---|---|
|  | *cis*-$[Ru(bpy)_2(OH_2)_2]^{2+}$ | VI | WNA |
|  | *in,in*-$[\{Ru(Trpy)(OH_2)\}_2(\mu\text{-bpp})]^{3+}$ | IV | Intra-I2M |
|  | $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10+}$ | V | WNA |
|  | $[Ru(dcb)(pic)_2(OH)]^{+}$ | IV | Inter-I2M |

WNA




Intra-I2M

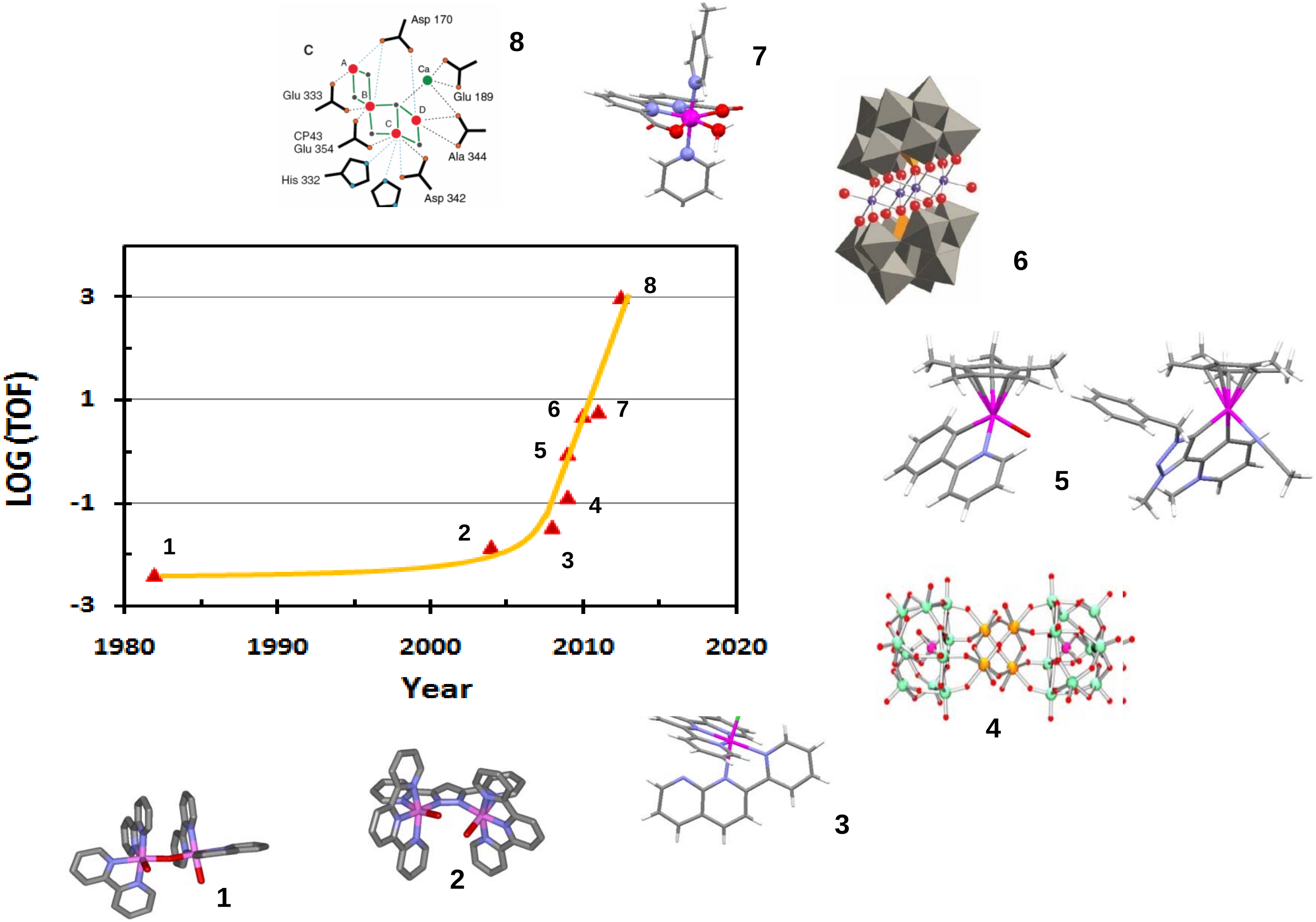



Inter-I2M


- The Nature of the Ru=O moieties in the corresponding active oxidation state

- The role of Bridging Ligand (e-coupling/through-space interactions)

## WOCs KINETICS SUMMARY

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1. Meyer, JACS-1982; 2. Llobet, JACS-2004; 3. Thummel, IC-2008; 4. Hill&Bonchio JACS-ACIE-2008; 5. Albrecht-Crabtree-Brudvig, ACIE-2010-JACS-2009; 6. Hill, Science-2010

# Molecular Catalysts that Oxidize Water to Dioxygen


ICTP, Miramare, Trieste, October 17th 2011

*Xavier Sala, UAB, Barcelona, Spain*