LIGH INDUCED REDOX CATALYSIS AND DEVICES

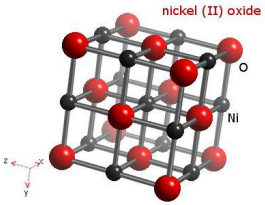
Nuevas formas de almacenamiento de energía renovable: fotosíntesis artificial

Buenos Aires, 22-26 de Octubre, 2018

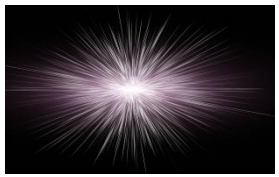
Antoni Llobet Research Group, ICIQ-UAB

hν CATALYSIS AND DEVICES

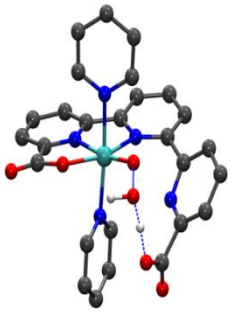
1. INTRODUCTION



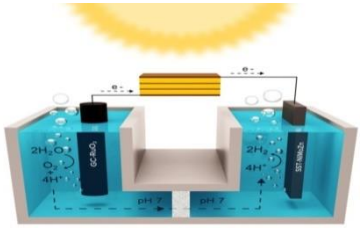
2. hν WOC-PR HOMOGENEOUS PHASE



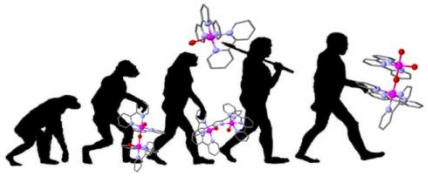
3. MOLEC ELECTROANODES



4. MOLEC PHOTOANODES

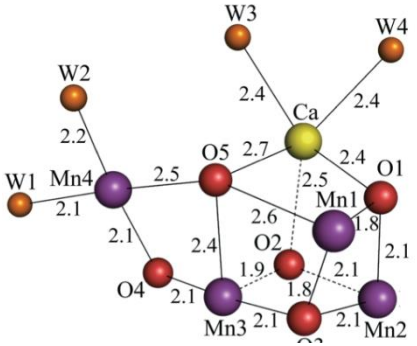


5. COMPLETE DEVICES



6. CONCS & ACKS

ARTIFICIAL PHOTOSYNTHESIS



hν

PHOTO-SYNTHESIS

$$6\,CO_2 + 6\,H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2$$

WATER SPLITTING

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

hν

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

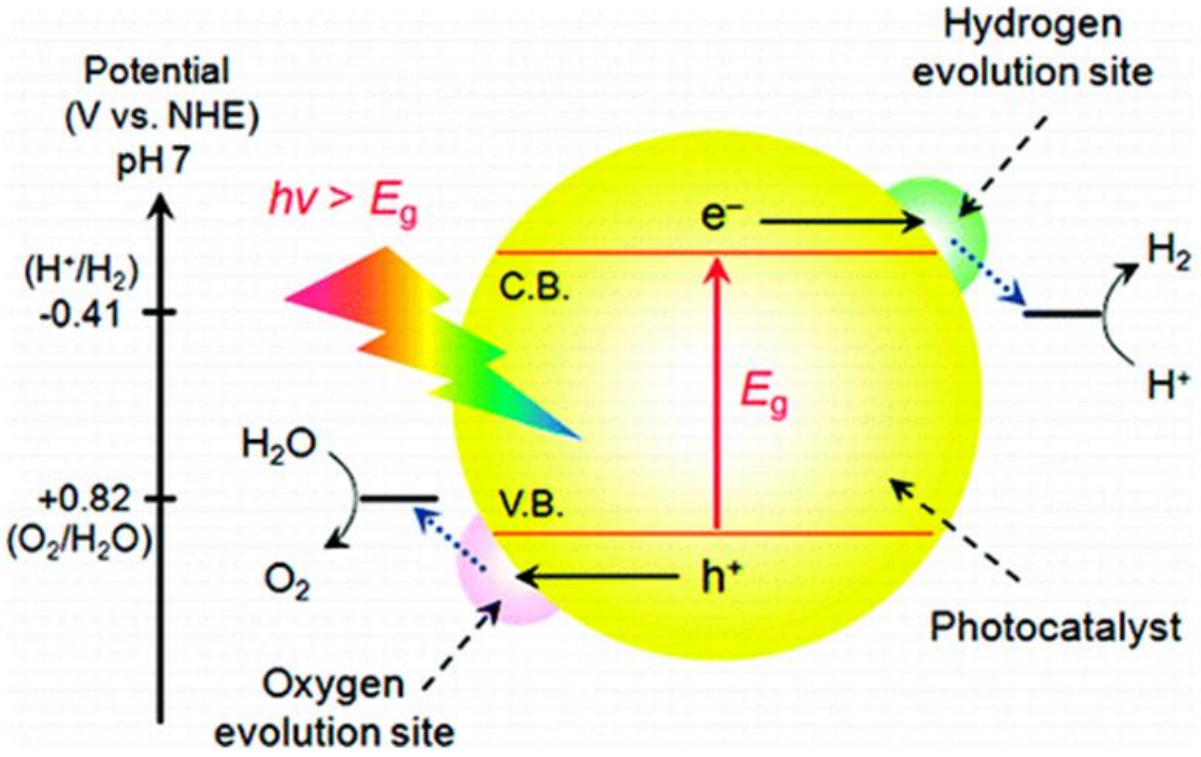
$$4\,H^+ + 4\,e^- \xrightarrow{PRC} 2\,H_2$$

REPLACING FOSSIL FUELS BY SOLAR FUELS

Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S. *Science,* **2004,** *303*, 1831-1838

Berardi, S.; Francàs, L.; Gimbert-Suriñach, C.; Llobet, A. et al. *Chem. Soc. Rev.* **2014**, *43,* 7501

NEW ENERGY CONVERSION SCHEMES



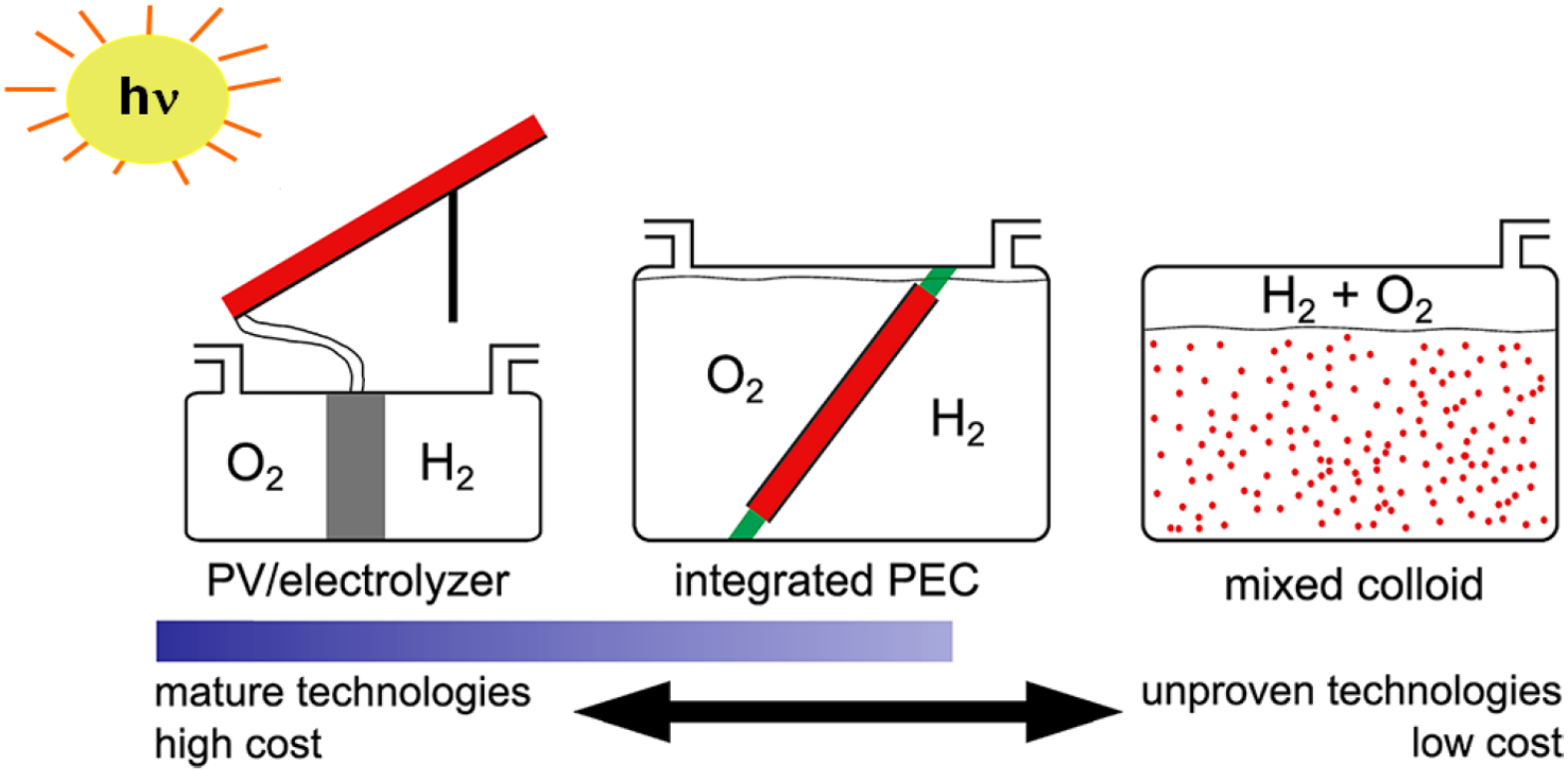
3-C

REPLACING FOSSIL FUELS BY SOLAR FUELS F-H eff./PS-II

Maeda, K.; Domen, K. *J. Phys. Chem. Lett.*, **2010**, *1*, 2655-2661

Fujishima, A.; Honda, K., *Nature,* **1972**, *238*, 37 - 38

SOLAR DRIVEN WATER SPLITTING DEVICES

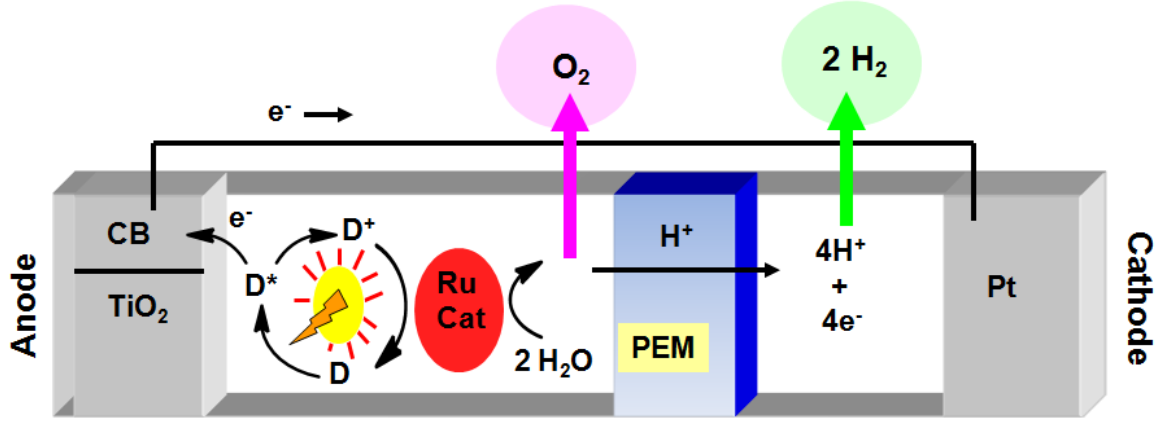


ultimately

McKone, J. R.; Lewis, N. S.; Gray, H. B., *Chem. Mater.,* **2014**, *26*, 403-414

PEC FOR WATER SPLITTING / MAT-SCI MOL CHEM

$$2\,H_2O \xrightarrow{h\nu} O_2 + 2\,H_2 \qquad \Delta G^o > 0$$



1. Anode (Photo)
2. Water Oxidation Cat (WOC)

3. Proton Reduction Cat (PRC)
4. Cathode (Photo)

5. PEM + Cell

Berardi, S.; Drouet, S.; Francàs, L.; Gimbert, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. *Chem. Soc. Rev.*, **2014**, web

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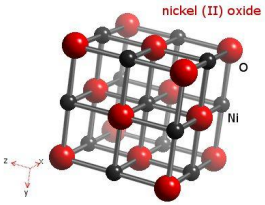

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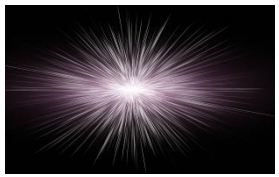

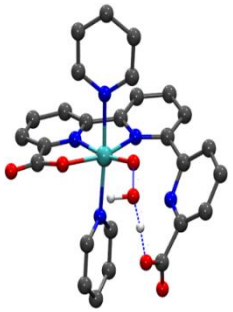

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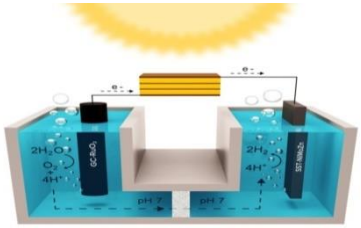

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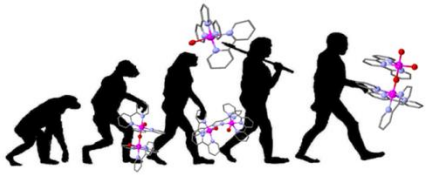
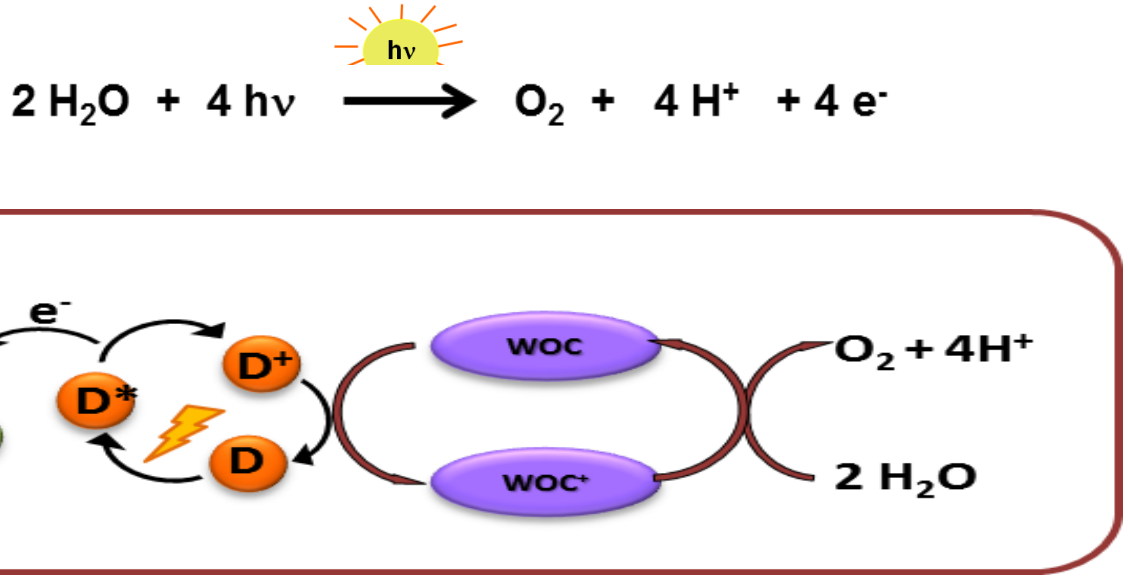
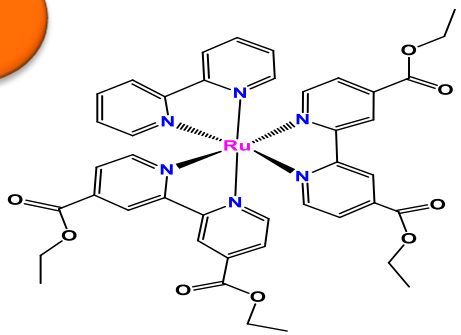


6. CONCS & ACKS

LIGHT INDUCED WOC



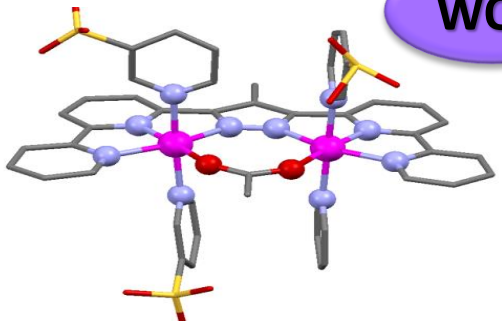
D



SEA

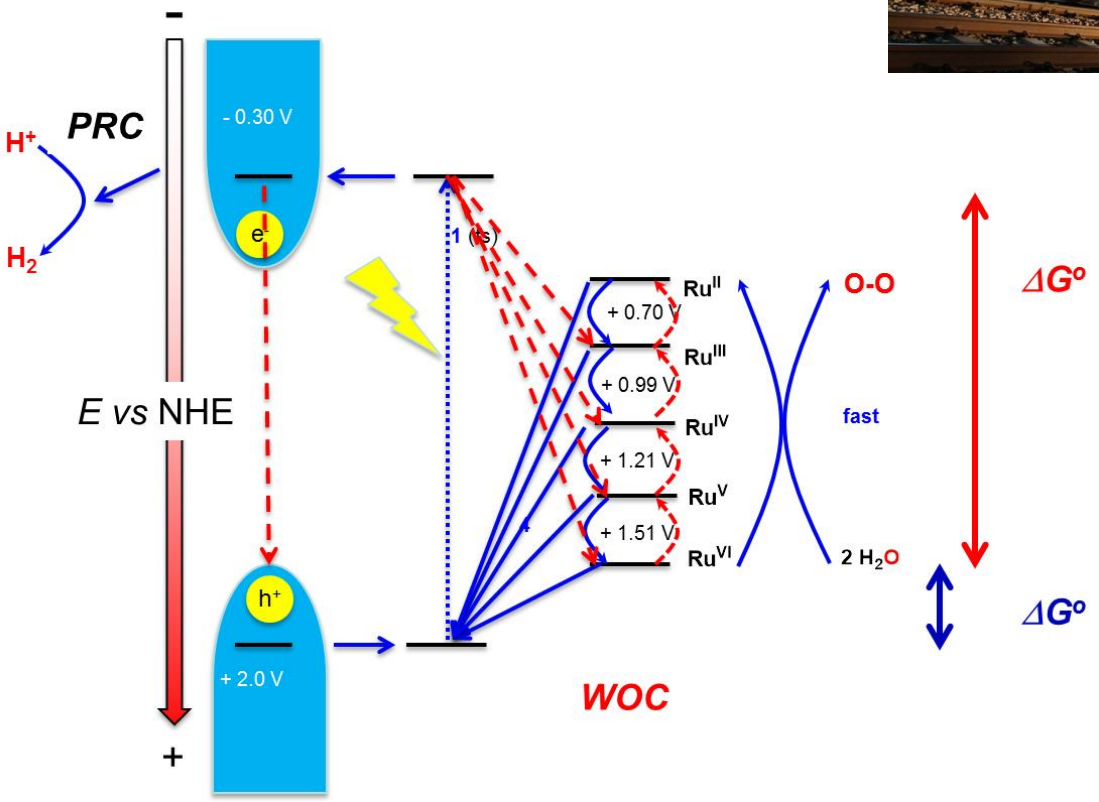
$Na_2S_2O_8$

WOC



Neudeck, S.; Meyer, F., Llobet, A., et al., *J. Am. Chem. Soc.*, **2014**, *136*, 24-27.

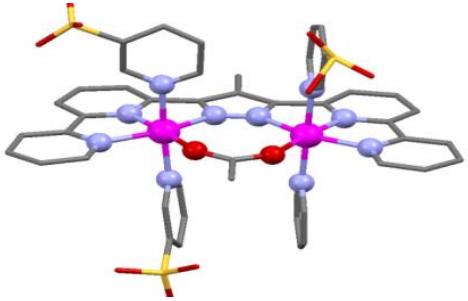
LIGHT INDUCED WO - FAST CATS



FAST WO CATs

- ***Enhance stability of VB^+***
- ***Reduce Back ET at VB^+***
- ***Enhance Stability of Intermediate Cat species***

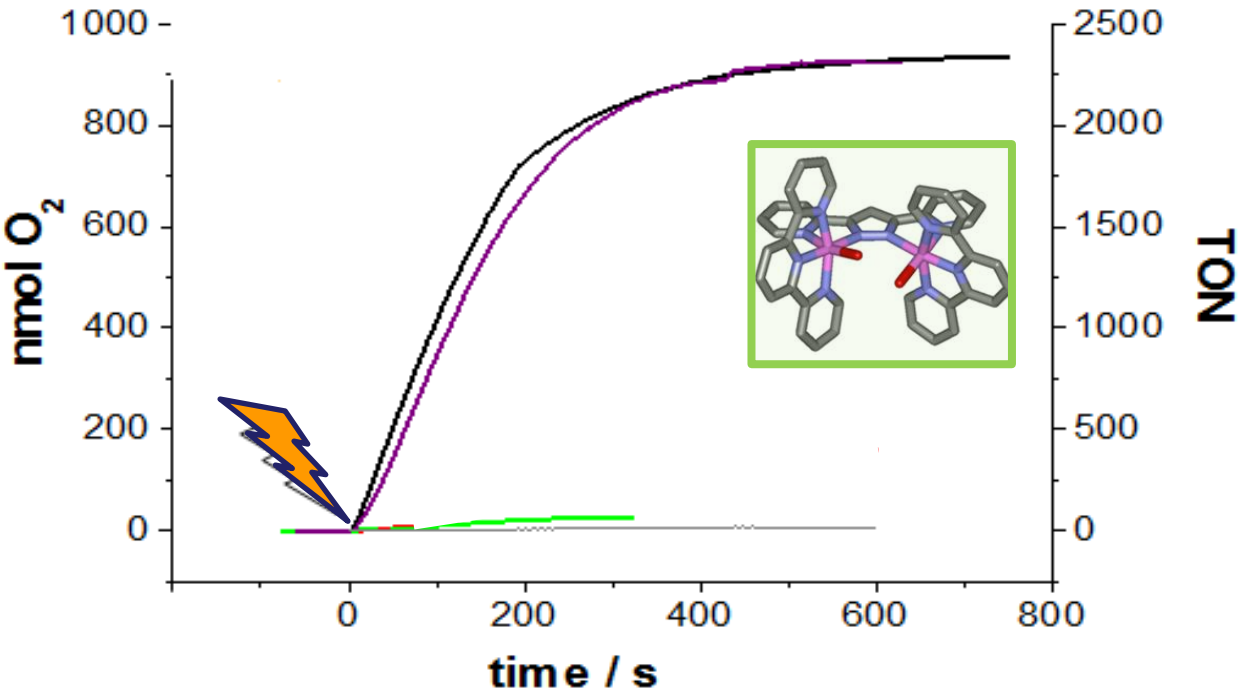
stablishing kinetics and thermodynamics and understanding how to manipulate them



LIGHT INDUCED WOC: MEC EFFECT

pH = 7.0

1 sun



WOC

0.2 μM Ru-Cat

D

0.2 mM Ru-bpy

SEA

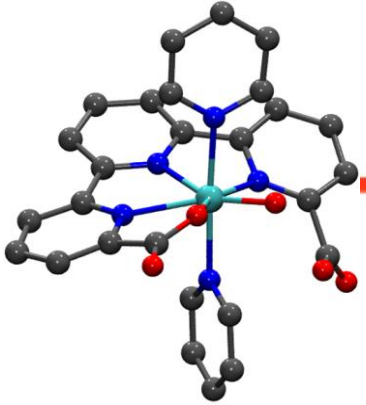
10 mM $Na_2S_2O_8$

V = 2 mL; T = 25 °C.

hν 1 Sun; λ > 400 nm

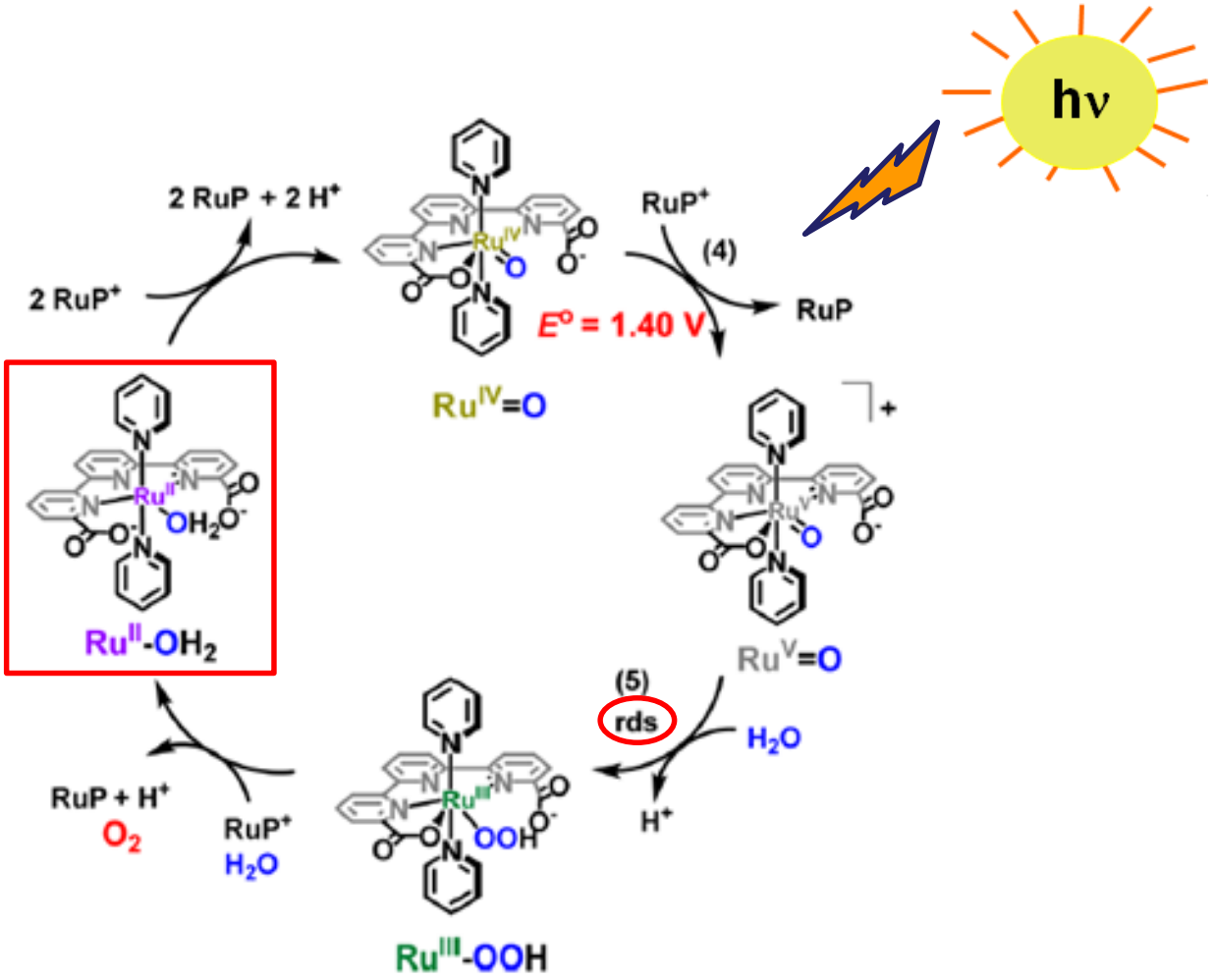
Berardi, S.; Llobet, A. et al., *ChemSusChem,* **2015**, *8,* 3688–3696.

Neudeck, S.; Meyer, F., Llobet, A., et al., *J. Am. Chem. Soc*., **2014**, *136*, 24-27.



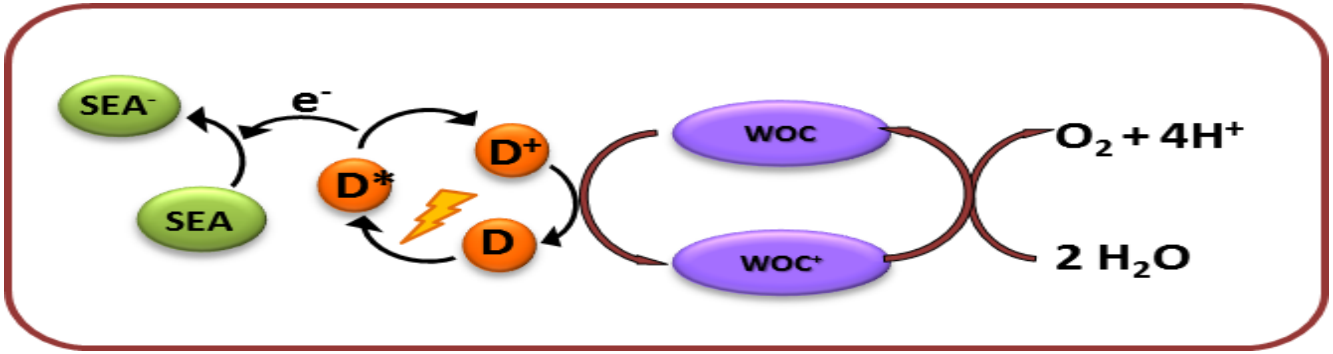
LIGHT INDUCED WOCs KINETICS

TRANSIENT ABSORBANCE SPECTROSCOSPY - TAS



Francas, L., Matheu, R.; Durrant, J, Llobet, A., et al., *ACS Catal*. **2017**, *7*, 5142−5150

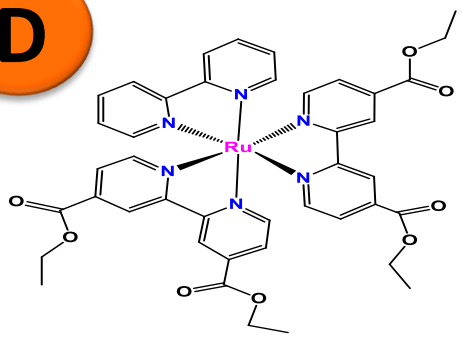
LIGHT INDUCED WOCs KINETICS



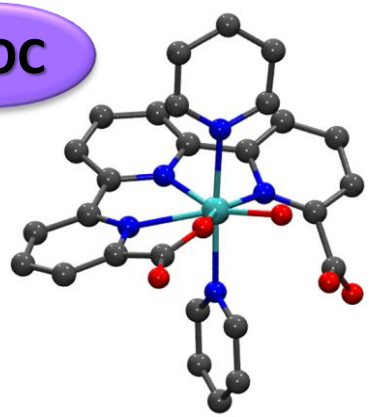
SEA

$Na_2S_2O_8$

D



WOC



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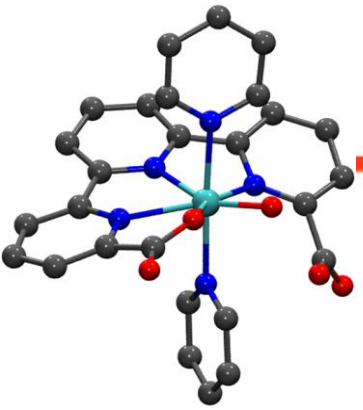
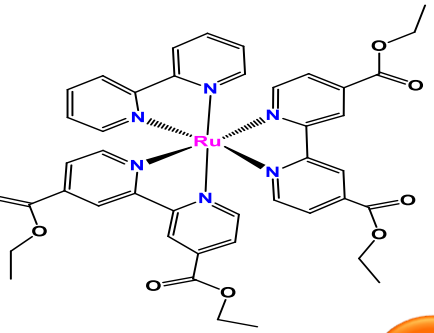


WOC

1-16 μM Ru-Cat



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D

SEA

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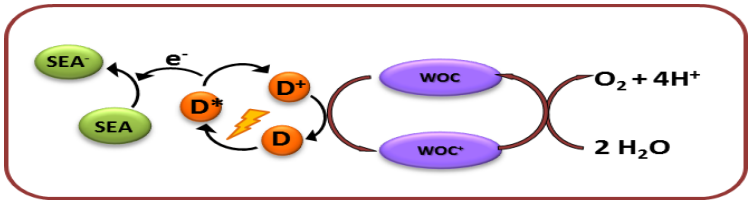
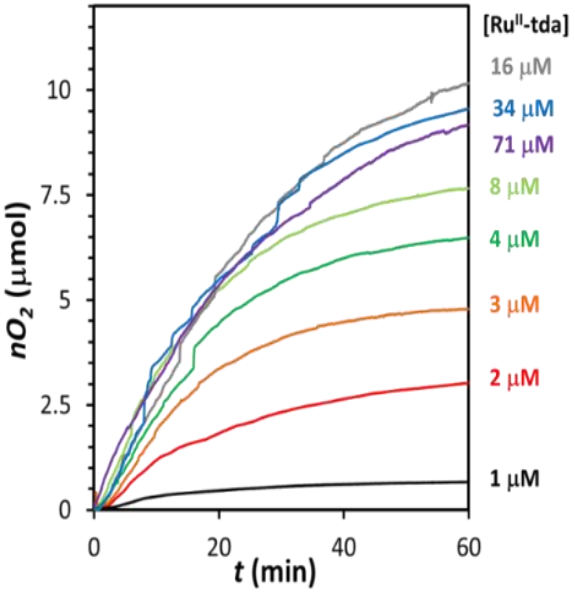
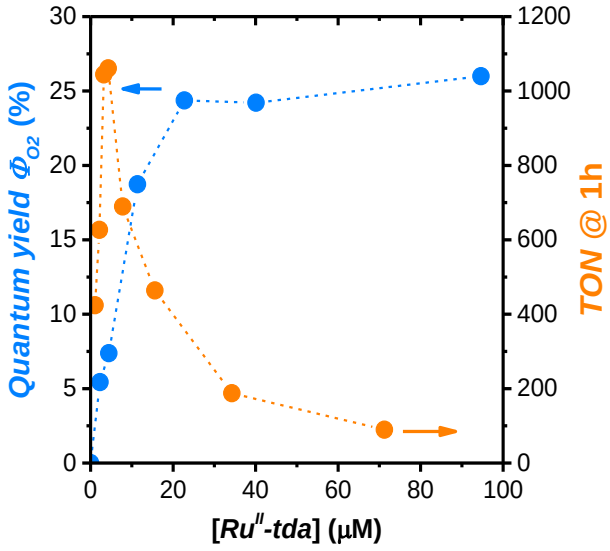
1 sun





O_2 evolution vs. *t*



Quantum yield, ϕ_{O2}
TONs (Ru)

Francas, L., Matheu, R.; Durrant, J, Llobet, A., et al., *ACS Catal*. **2017**, *7*, 5142−5150

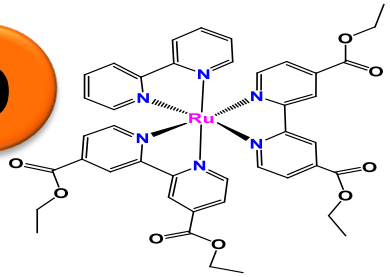
LIGHT INDUCED WOCs KINETICS

Light absorption:	$RuP + h\upsilon \rightarrow RuP^*$ (1)
Direct generation of RuP^+:	$RuP^* + S_2O_8^{2-} \rightarrow RuP^+ + SO_4^{2-} + SO_4^{\cdot-}$ (2)
Dark generation of RuP^+:	$RuP + SO_4^{\cdot-} \rightarrow RuP^+ + SO_4^{2-}$ (3)
Overall rxs (1)-(3)	$2\,RuP + h\upsilon + S_2O_8^{2-} \rightarrow 2\,RuP^+ + 2\,SO_4^{2-}$ (4)
Bimolecular electron transfer	$RuP^+ + Ru^{IV}{=}O \rightarrow RuP + Ru^{V}{=}O$ (5)
Oxygen formation	$2\,H_2O + h\nu \rightarrow O_2 + 4H_+ + 4e^-$ (6)

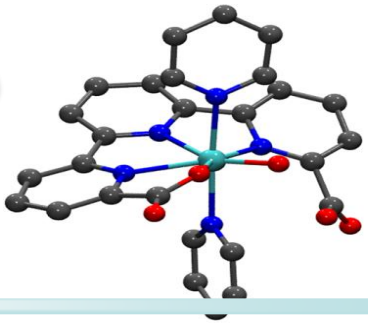
SEA

$Na_2S_2O_8$

D



WOC



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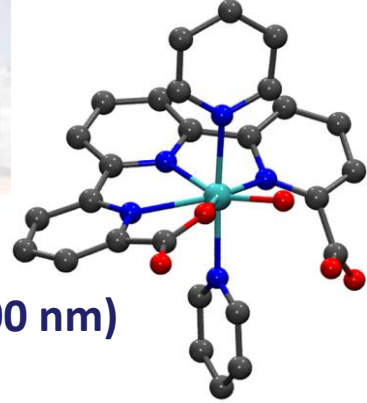

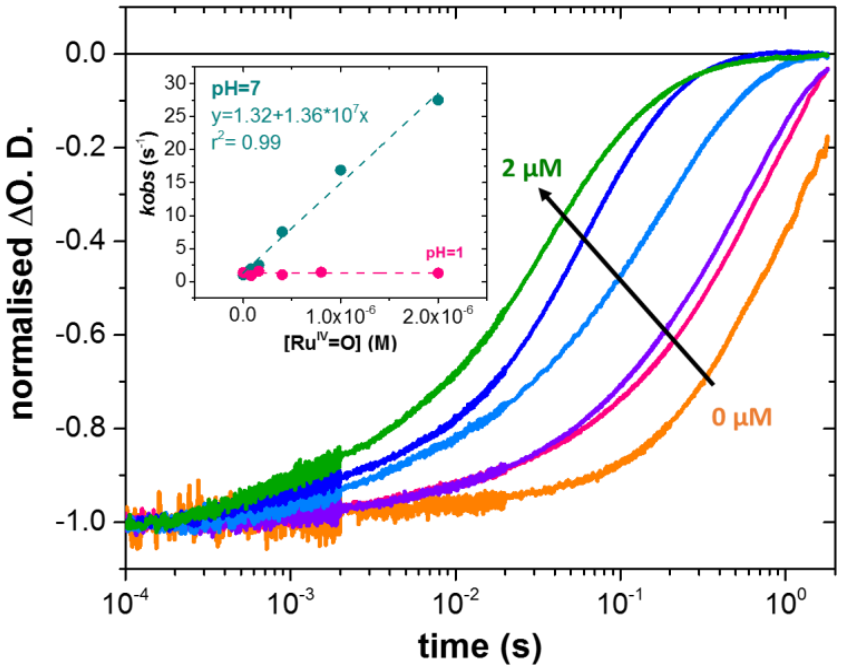

TA decays at 460 nm (λ_{ex} = 500 nm)

20 μM **RuP**, 10 mM $S_2O_8^{2-}$

[Ru^{IV}=O] 2 μM
1 μM
0.4 μM
160 nM
80 nM
0 nM

pH = 7.0

$$v = k_{ET}[Ru^{IV}{=}O][RuP^{+}] \quad (5a)$$

$$[Ru^{IV}{=}O] >> [RuP^{+}] \quad k_{obs} = k_{ET}[Ru^{IV}{=}O] \quad (5b)$$

$$v = k_{obs}[RuP^{+}] \quad (5c)$$

k_{ET} = 1.4·10^7 M^{-1} s^{-1}

RuP^+ + Ru^{IV}=O -> RuP + Ru^{V}=O (5)

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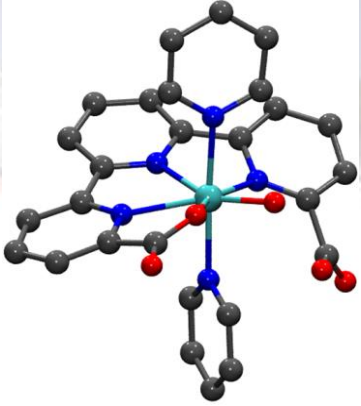

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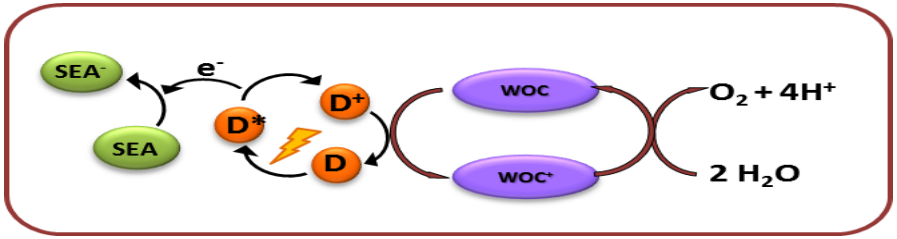

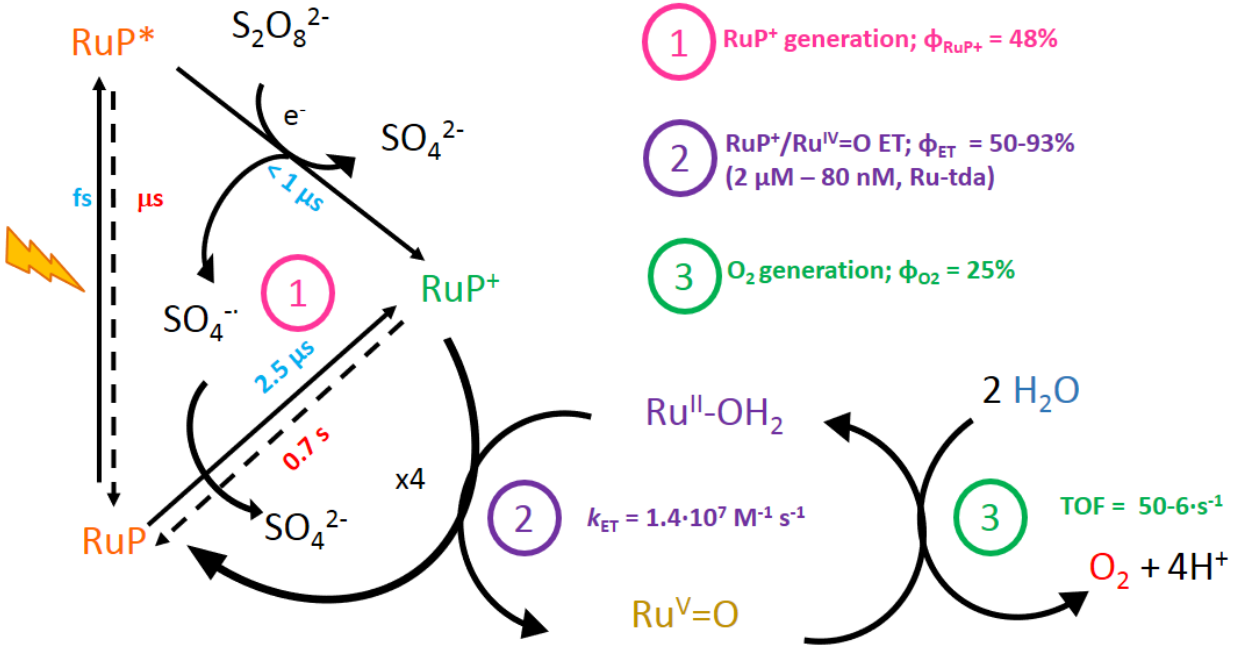

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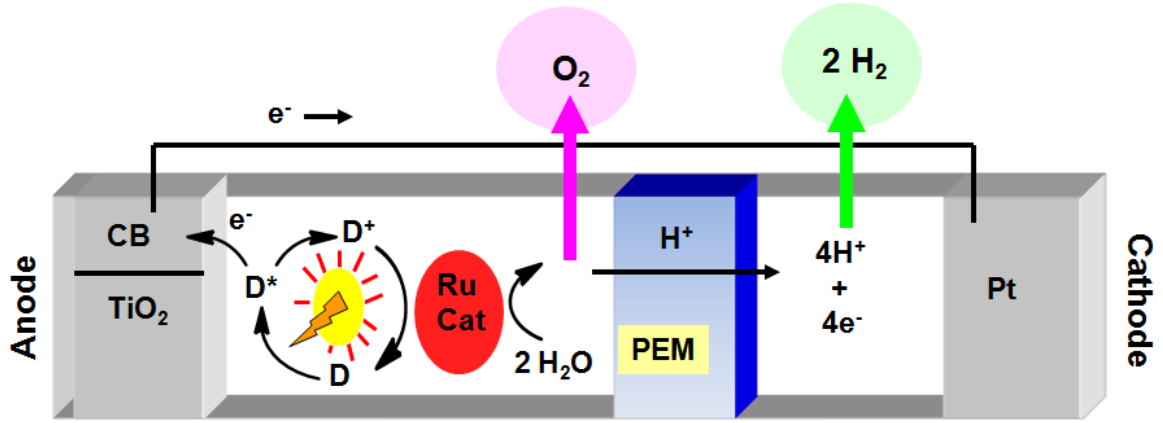

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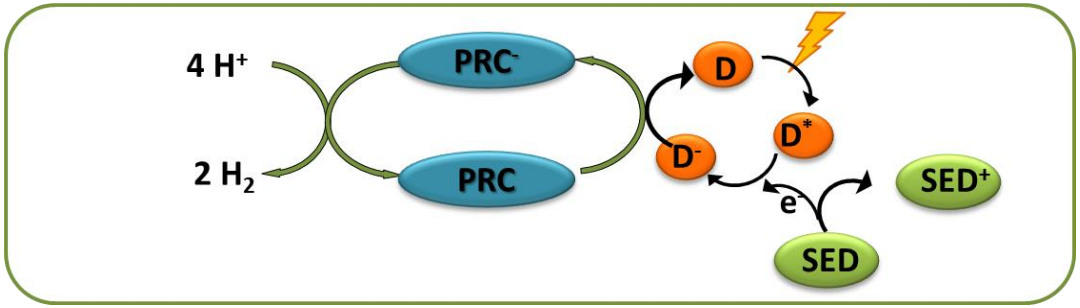
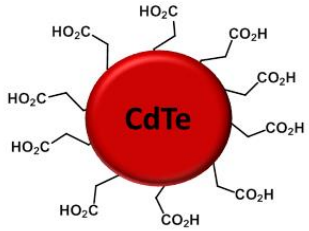
Co COMP. & LIGHT INDUCED PRC



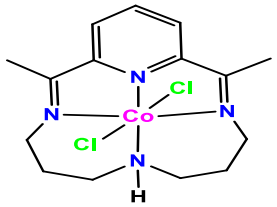
D

5.9 × 10^{-5} M

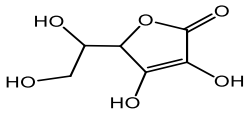


PRC

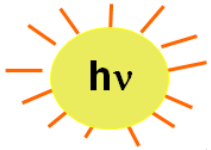
7.5 × 10^{-5} M



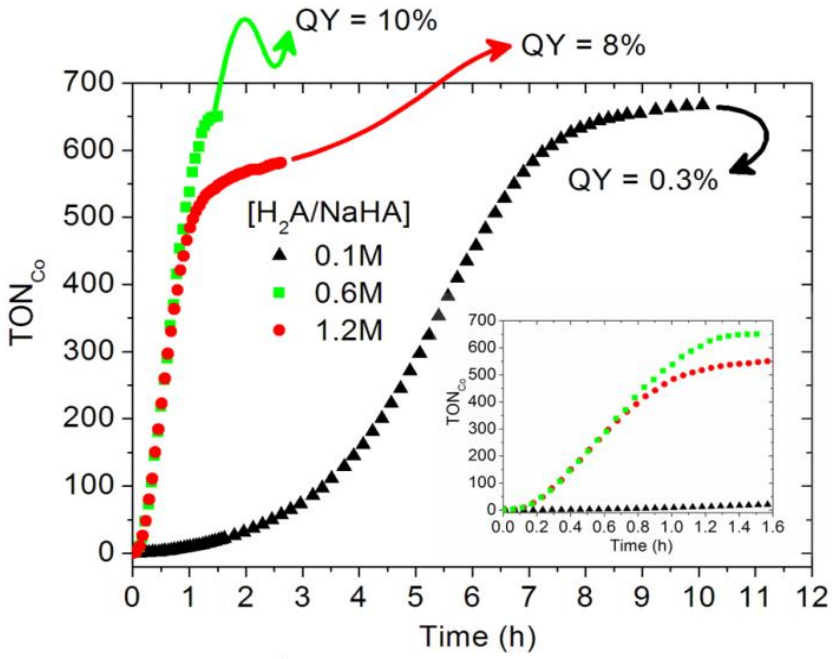
SED



pH = 4.1



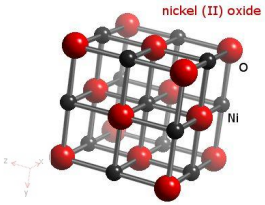
hν 1 Sun
λ > 400 nm



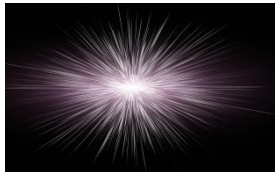
Gimbert, C.; Stoll, T.; Palomares, E.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2014**, *136*, 7655-7661

hν CATALYSIS AND DEVICES

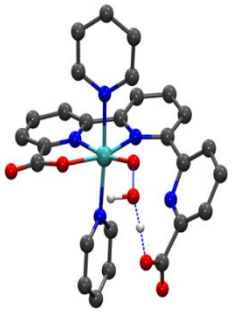
1. INTRODUCTION



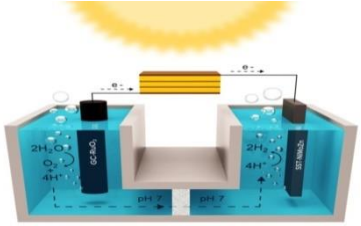
2. hν WOC-PR HOMOGENEOUS PHASE



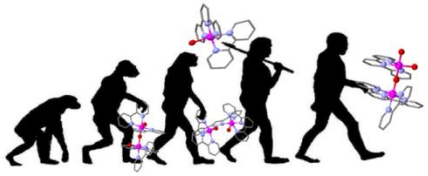
3. MOLEC ELECTROANODES



4. MOLEC PHOTOANODES

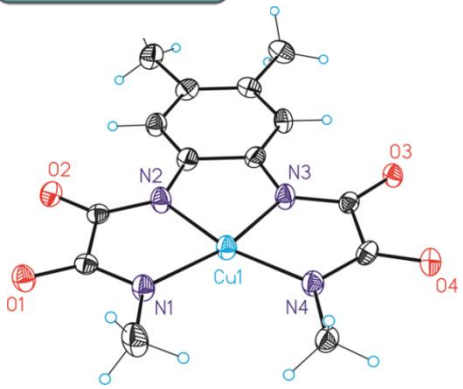


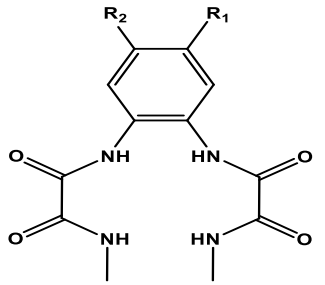
5. COMPLETE DEVICES



6. CONCS & ACKS

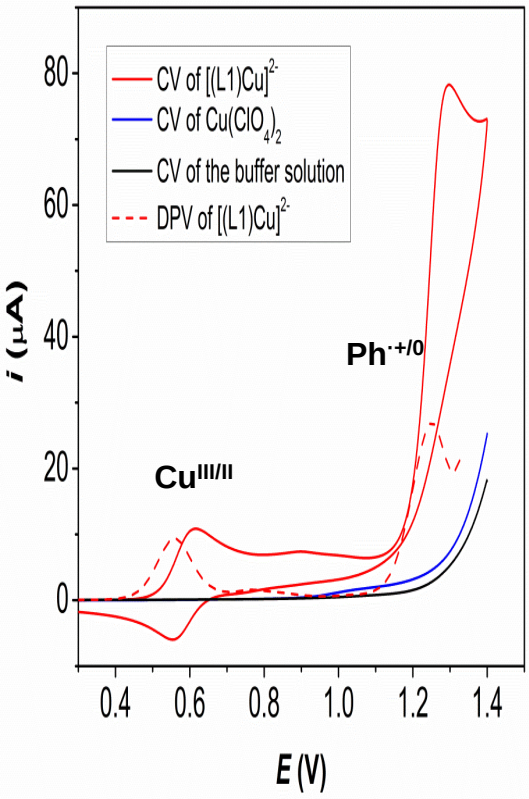
Cu-BASED WOCs w. REDOX ACTIVE LIGANDS

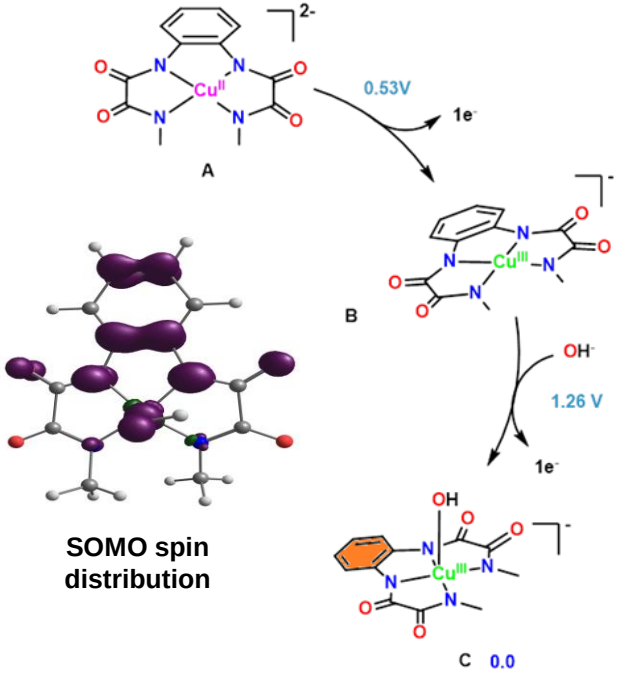




$R_1 = R_2 = H$; H_4L1 | $R_1 = H$, $R_2 = OMe$; H_4L3

$R_1 = R_2 = Me$; H_4L2 | $R_1 = R_2 = OMe$; H_4L4





SOMO spin distribution

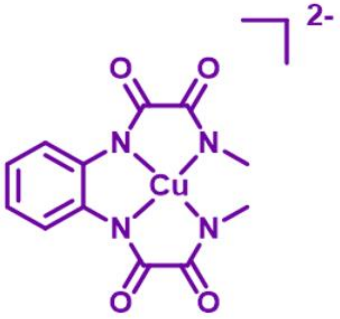
$TOF_i = 4\ s^{-1}$ (pH = 11.5)

$TOF_i = 50\ s^{-1}$ (pH = 12.5)

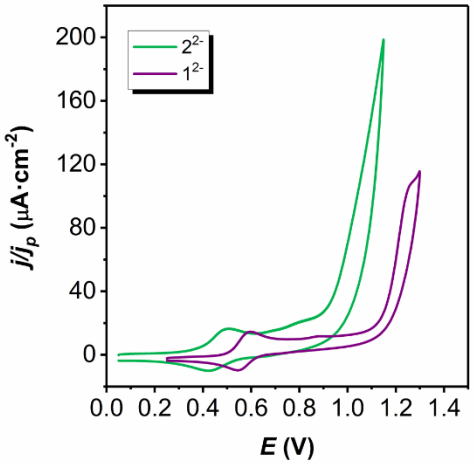
- tetra-anionic ligand strong bonds / small reorganizational energy/

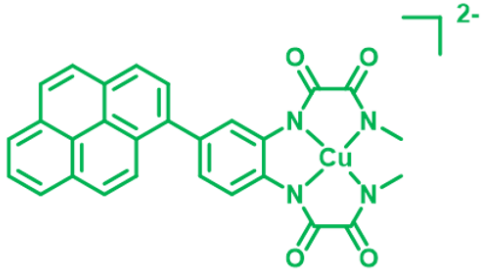
Garrido-Barros, P.; Drouet, S.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2015**, *137*, 6758

Cu-BASED MOLECULAR ELETROANODES

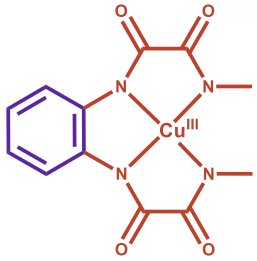


$[(L)Cu]^{2-}$ (1^{2-})

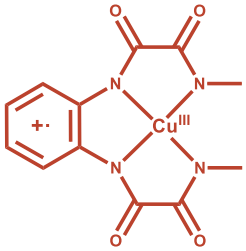




$[(L_{py})Cu]^{2-}$ (2^{2-})



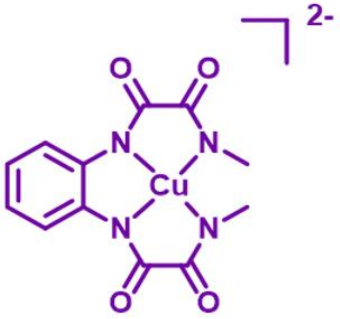
1st OX



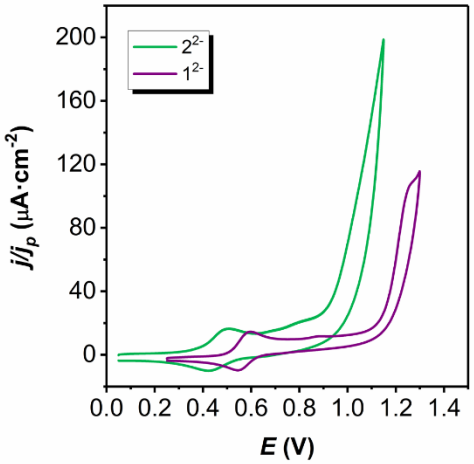
2nd OX

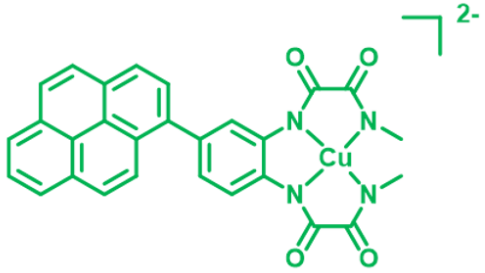
Garrido-Barros, P.; Batista, V. S.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 12907–12910

Cu-BASED MOLECULAR ELETROANODES

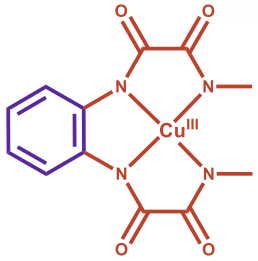


[(L)Cu]$^{2-}$ (1^{2-})

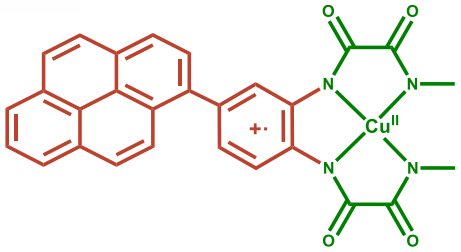


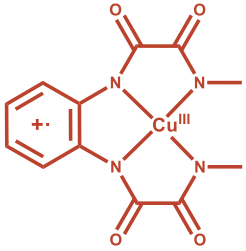


[(L_{py})Cu]$^{2-}$ (2^{2-})

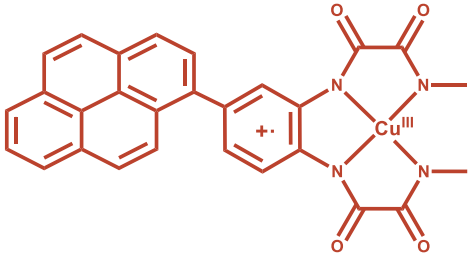


1st OX



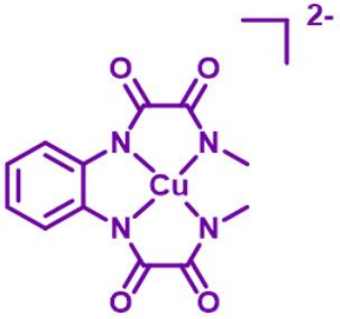


2nd OX

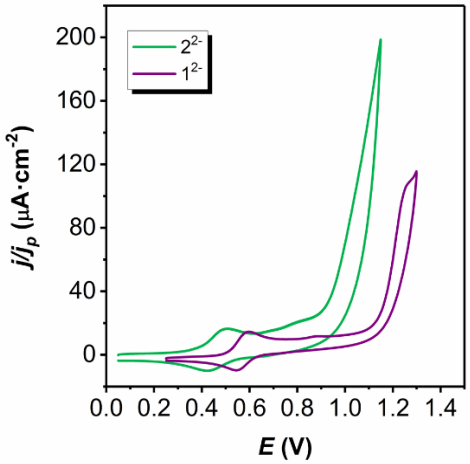


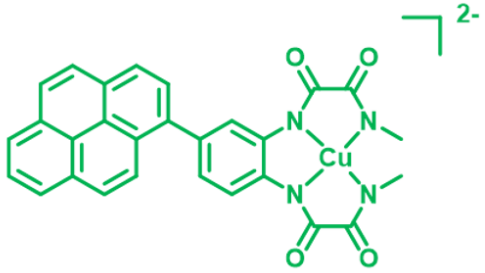
Garrido-Barros, P.; Batista, V. S.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 12907–12910

Cu-BASED MOLECULAR ELETROANODES ON GRAPHENE

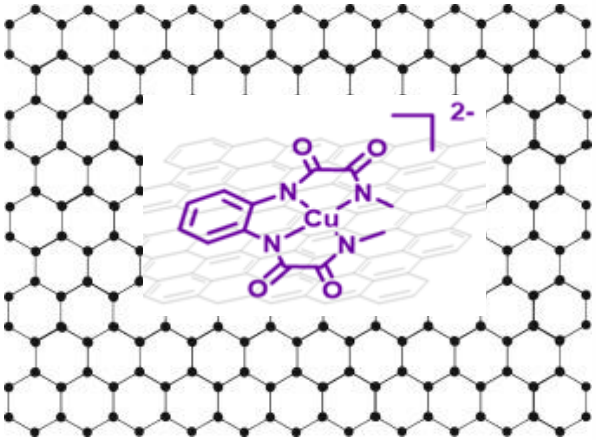


$[(L)Cu]^{2-}$ (1^{2-})

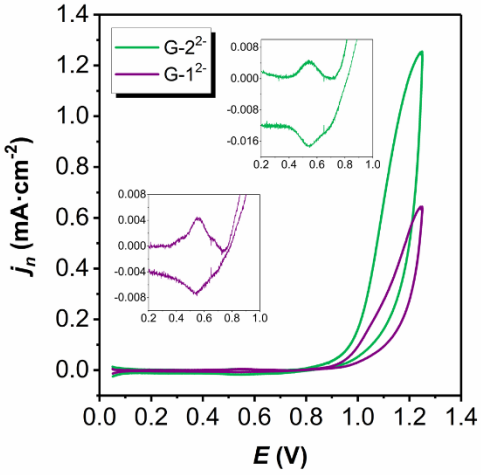


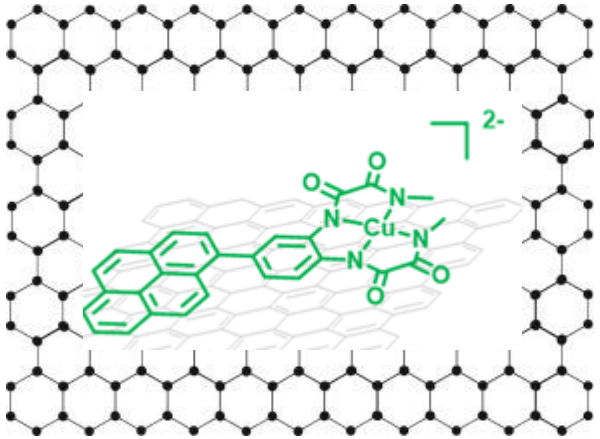


$[(L_{py})Cu]^{2-}$ (2^{2-})



GC@G@$[(L)Cu]^{2-}$ (G-1^{2-})

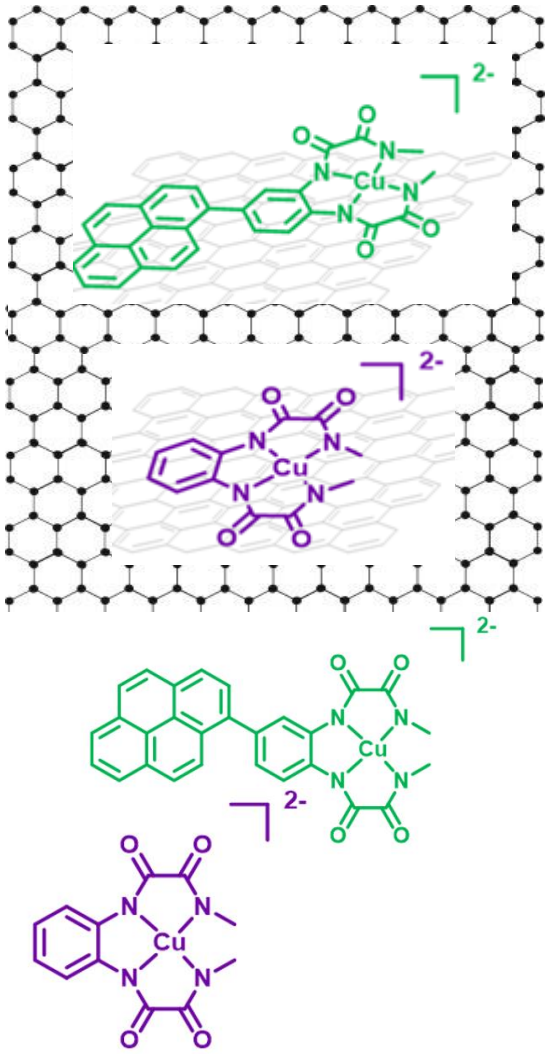




GC@G@$[(L_{py})Cu]^{2-}$ (G-2^{2-})

Garrido-Barros, P.; Batista, V. S.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 12907–12910

Cu-BASED MOLECULAR ELETROANODES ON GRAPHENE



GC@G@[$(L_{py})Cu]^{2-}$ ($G\text{-}2^{2-}$)

GC@G@[$(L)Cu]^{2-}$ ($G\text{-}1^{2-}$)

$[(L_{py})Cu]^{2-}$ (2^{2-})

$[(L)Cu]^{2-}$ (1^{2-})

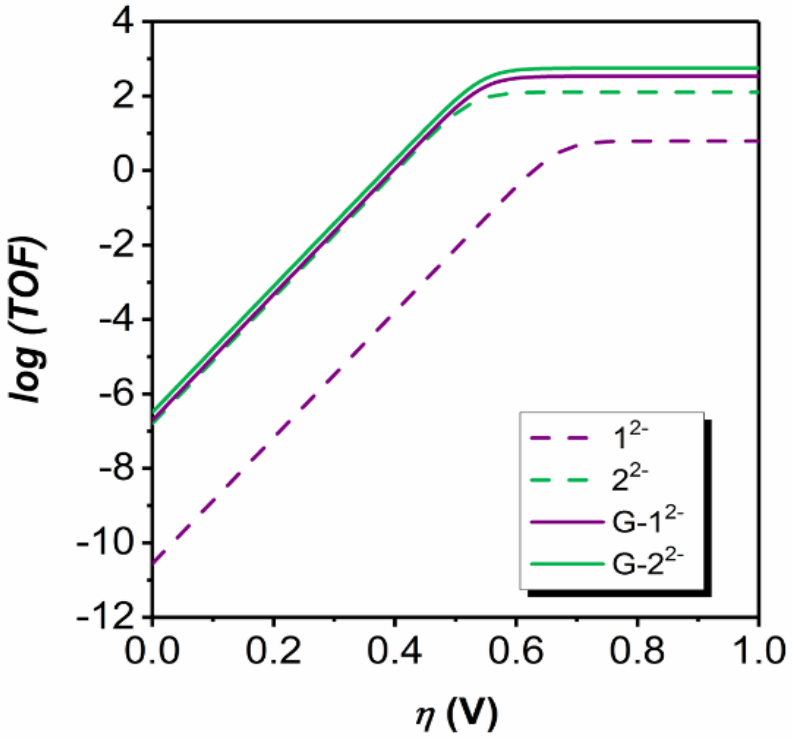
TOF_{max}

540 s^{-1}

320 s^{-1}

128 s^{-1}

6.2 s^{-1}



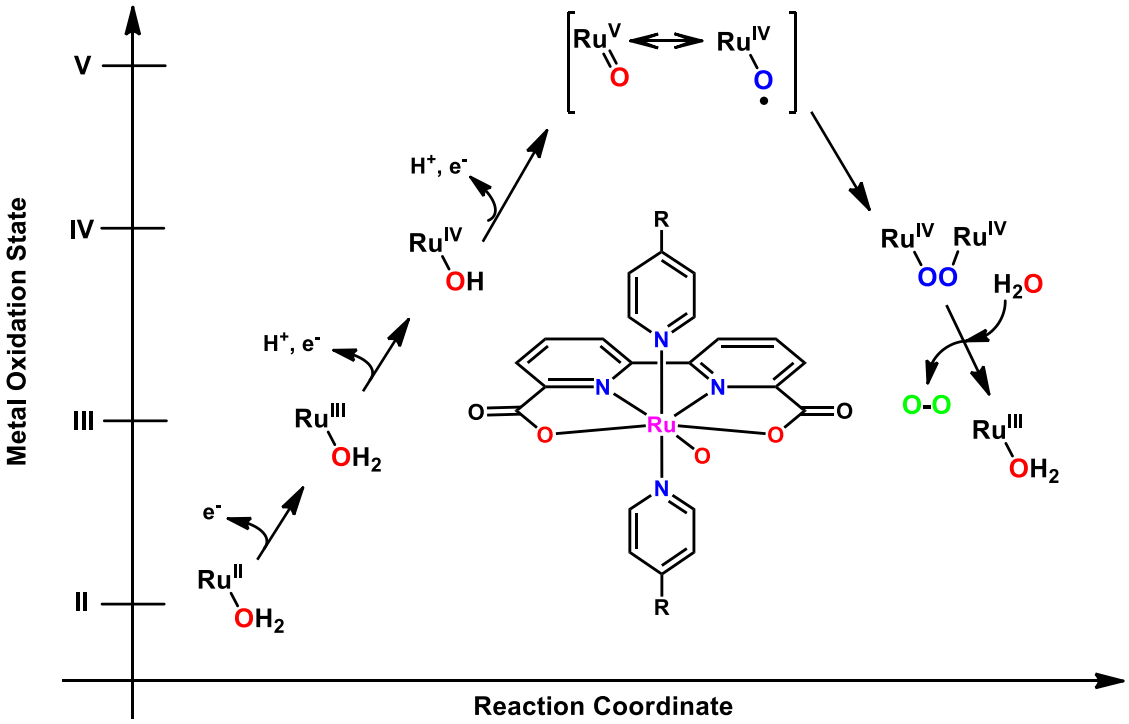
Increasing π-deloc.

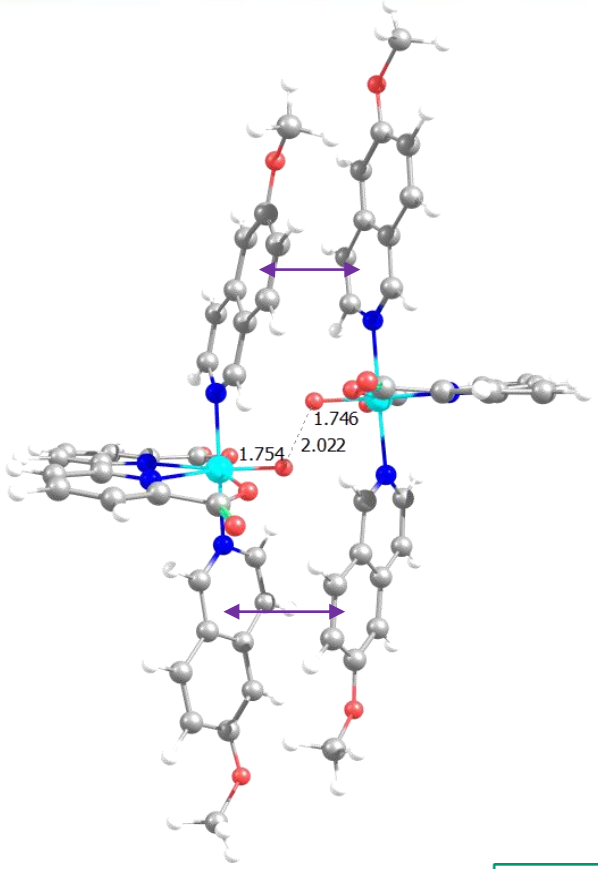
Increases TOF_{max}

Garrido-Barros, P.; Batista, V. S.; Llobet, A. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 12907–12910

I2M

Ru-bda CATALYSIS





TOF = 6 s^{-1}

TOF > 1000 s^{-1}

I2M to WNA

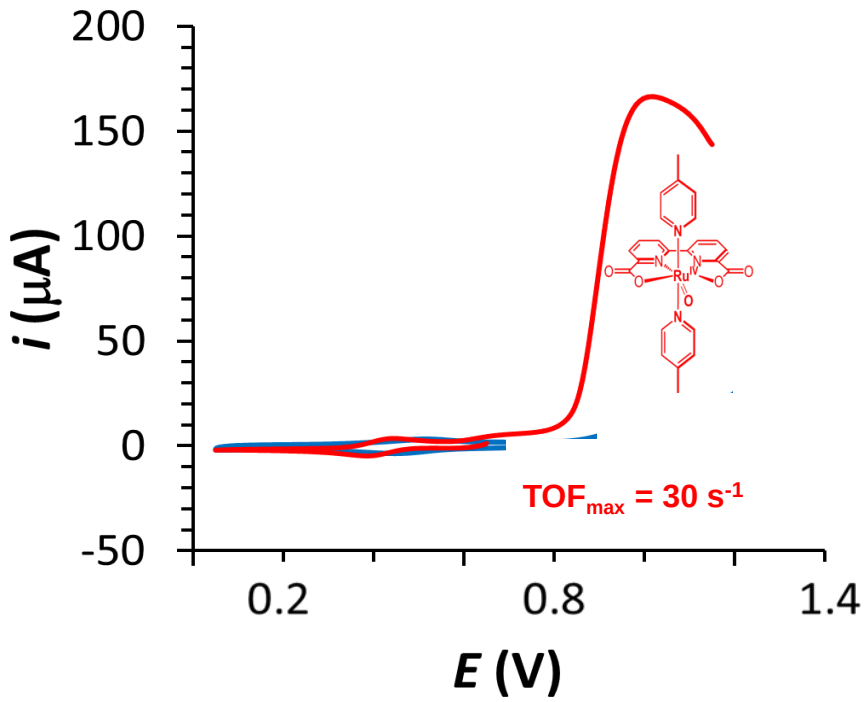
Duan, L.; Mandal, S.; Bozoglian, F.; Privalov, T.; Llobet, A.; Sun, L. *Nat. Chem*. **2012**, *4*, 418-423

Richmond, C. J.; Matheu, R.; Llobet, A. et al. *Chem. Eur. J.,* **2014,** *20,* 17282-17286

Ru-BDA ON SOLID SUPPORTS

CONSEQUENCES OF Ru-BDA UNDER RESTRICTED MOBILITY

pH = 7.0

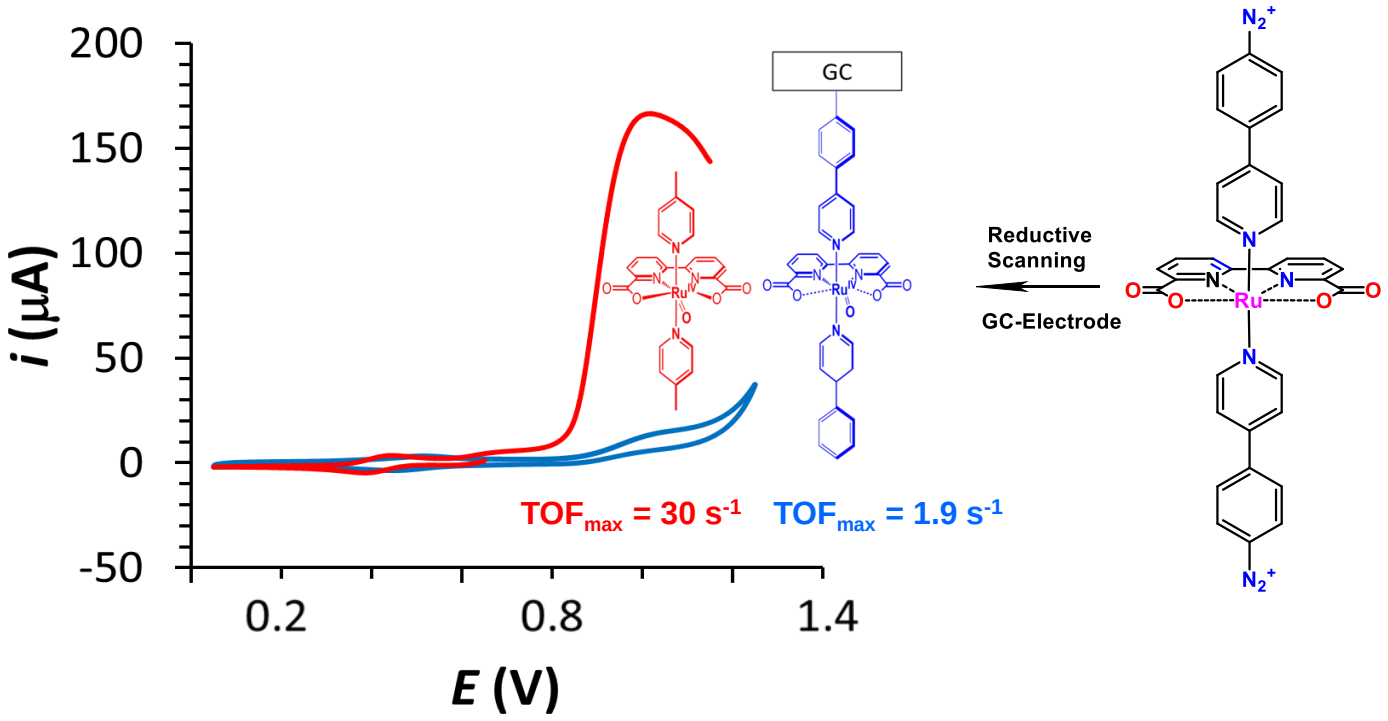


Matheu, R.; Llobet, A. et al., *ACS Catal*. **2015**, *5*, 3422-3429

Duan, L.; Llobet, A.; Sun, L. et al. *Nat. Chem*. **2012**, *4*, 418-423

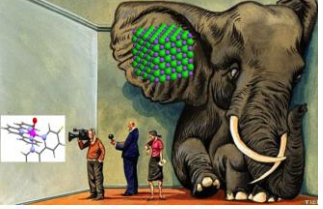
CONSEQUENCES OF Ru-BDA UNDER RESTRICTED MOBILITY

pH = 7.0



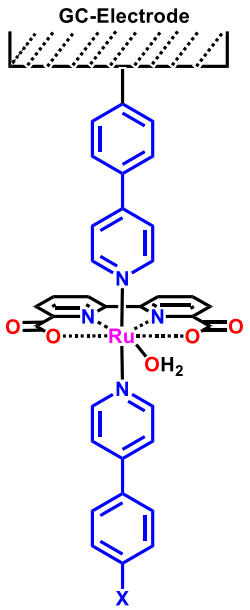
Matheu, R.; Llobet, A. et al., *ACS Catal*. **2015**, *5*, 3422-3429

Duan, L.; Llobet, A.; Sun, L. et al. *Nat. Chem*. **2012**, *4*, 418-423



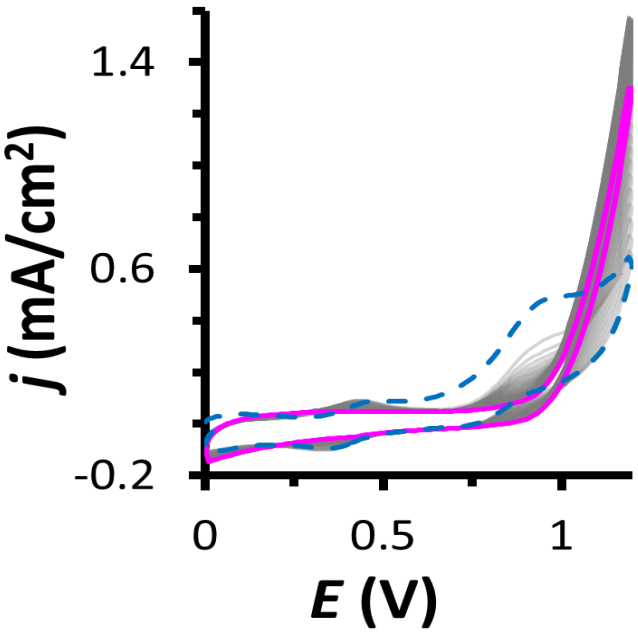
SOLID STATE ANODES FOR CAT WO

CONSEQUENCES OF Ru-BDA UNDER RESTRICTED MOBILITY



I2M

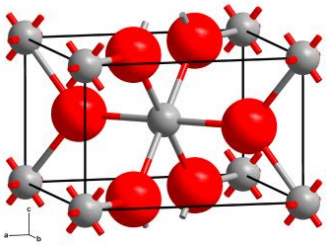
loose: pi-pi int/bimol int



***E vs*. NHE at pH = 7.0**

RuO_2

XAS



I2M to WNA

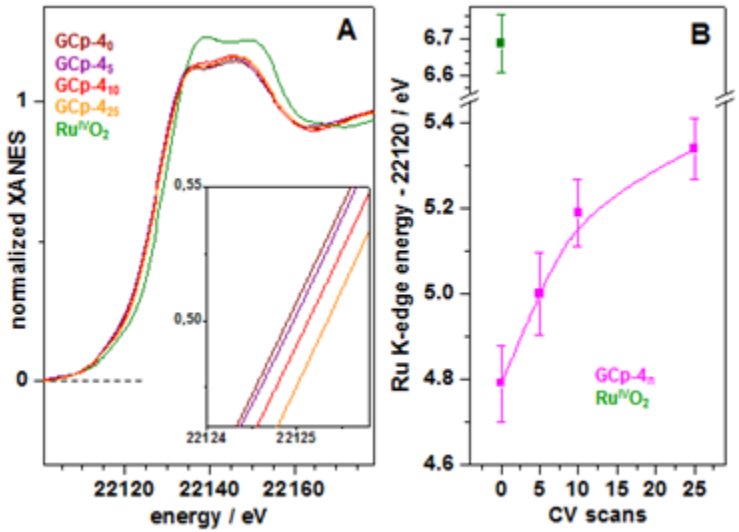
Engineering perspective
Building devices

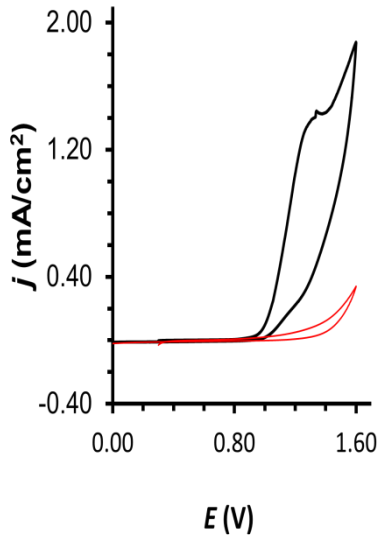
Matheu, R.; Llobet, A. et al., *ACS Catal*. **2015**, *5*, 3422-3429

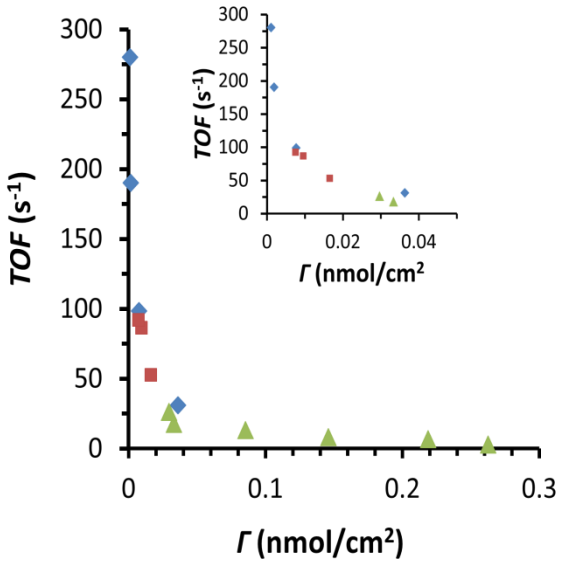
Coehn, A.; Gläser, M. *Zeits. Anorg. Chem*., **1902,** *33*, 9-24

Ru-BDA UNDER RESTRICTED MOBILITY

XAS, XANES, EXAFS







GC-RuO_2

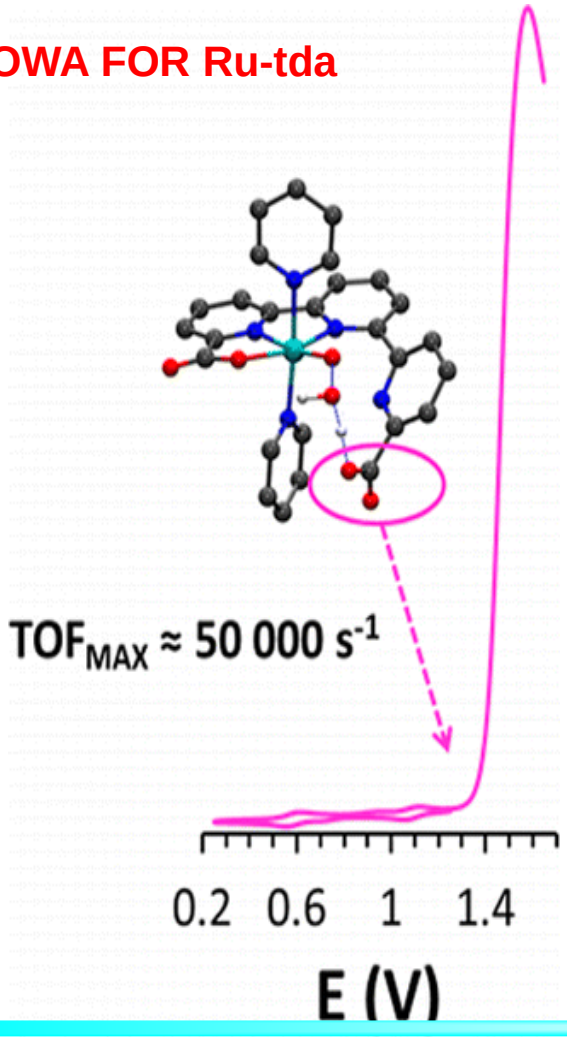
TOF_i = 300 s^{-1} (1.0 pmol/cm^2)

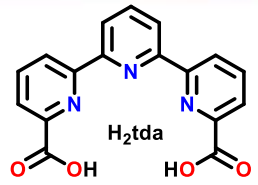
TONs > 45.000

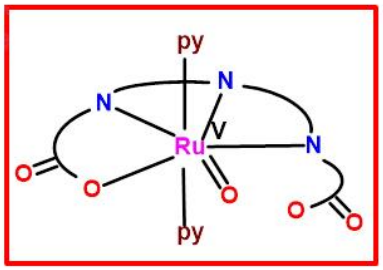
Matheu, R.; Llobet, A. et al., *ACS Catal*. **2015**, *5*, 3422-3429

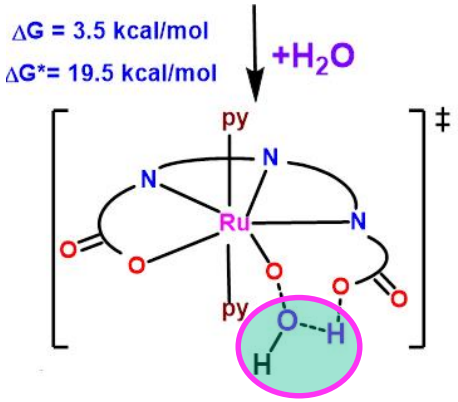
GIANT ECAT WAVE - INTRAMOLEC H^+ TRANSFER

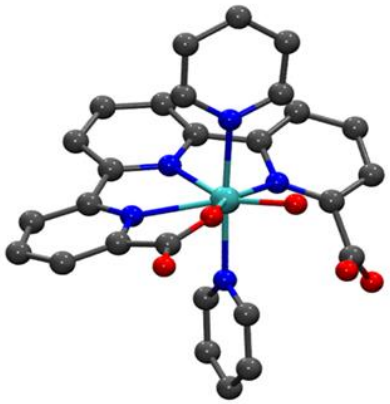
FOWA FOR Ru-tda

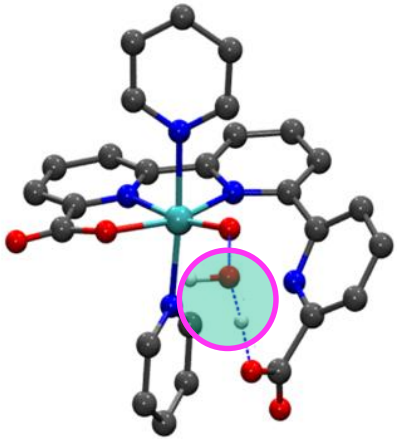


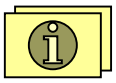








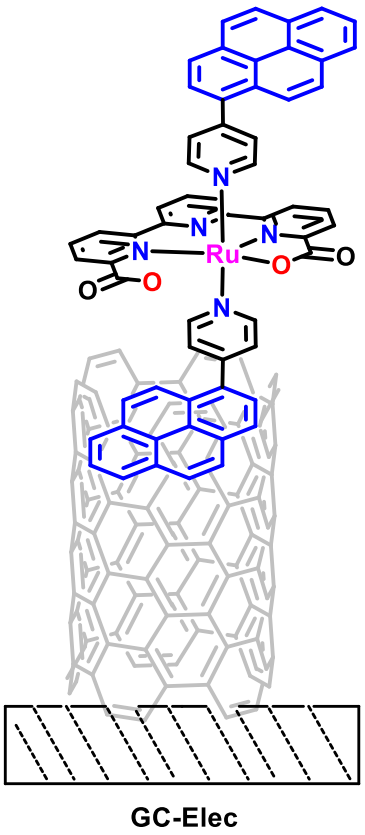




Matheu, R., Ertem, Z.; Batista, V. S.; Llobet , A. et al. *J. Am. Chem. Soc.*, **2015,** *137,* 10786-10795.

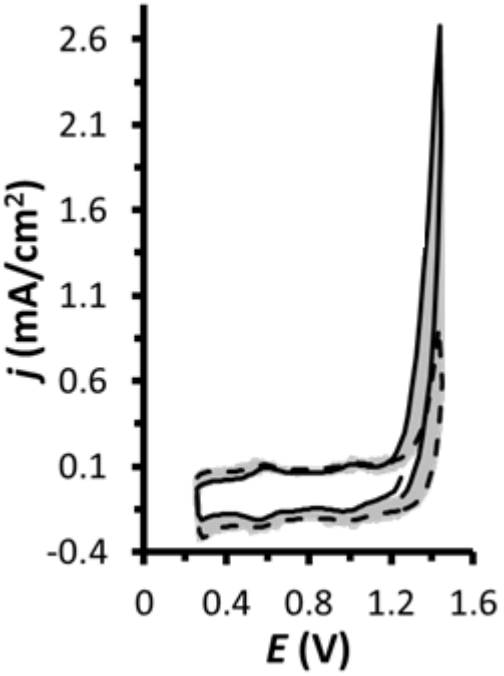
WNA

SOLID STATE ANODES: GC-MWCNT WITH WOCs

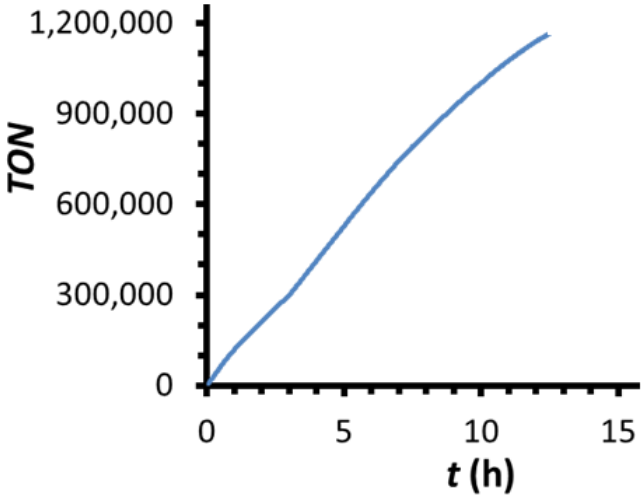


GC-Elec

Ru-TDA UNDER TRANSLATIONAL RESTRICTED MOBILITY



***E vs.* NHE at pH = 7.0**



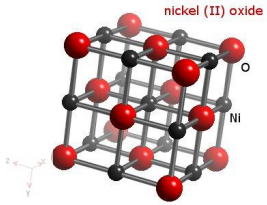
1,18 million TONs

NO DEACTIVATION

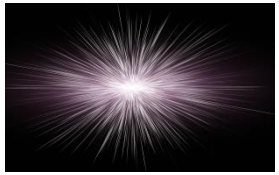
Creus, L.; Matheu, R.; Llobet, A. *et al. Angew. Chem. Int. Ed.* **2016**, *55*, 15382-15386.

hν CATALYSIS AND DEVICES

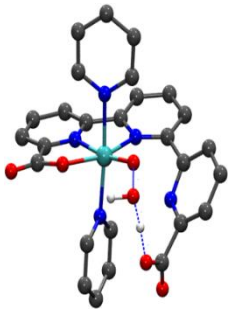
1. INTRODUCTION



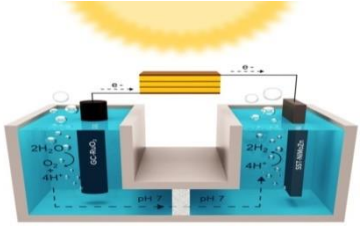
2. hν WOC-PR HOMOGENEOUS PHASE



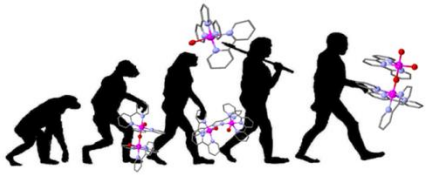
3. MOLEC ELECTROANODES



4. MOLEC PHOTOANODES

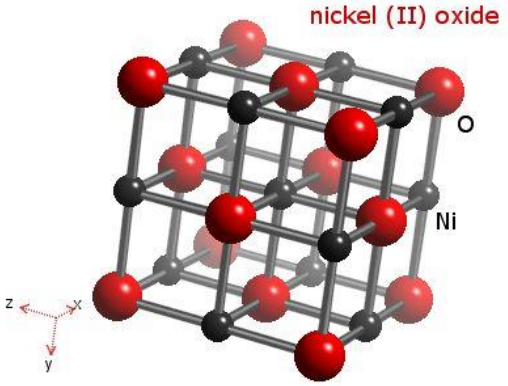


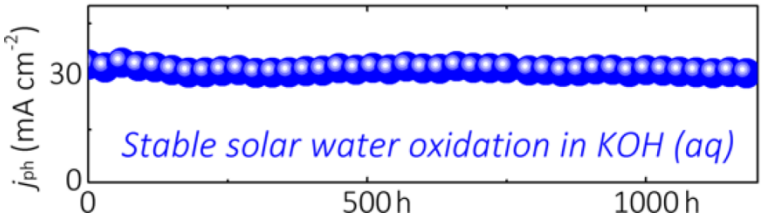
5. COMPLETE DEVICES



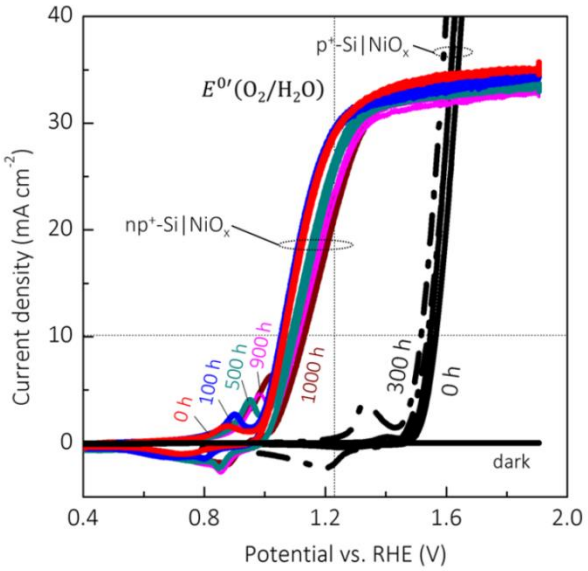
6. CONCS & ACKS

Si-BASED PHOTOANODES





photocurrent-onset potentials of
−180 ± 20 mV Ref. to E^{o}_{eq} for O2(g),



30 mA/cm^2 x 1000 h = 108.000 C/cm^2

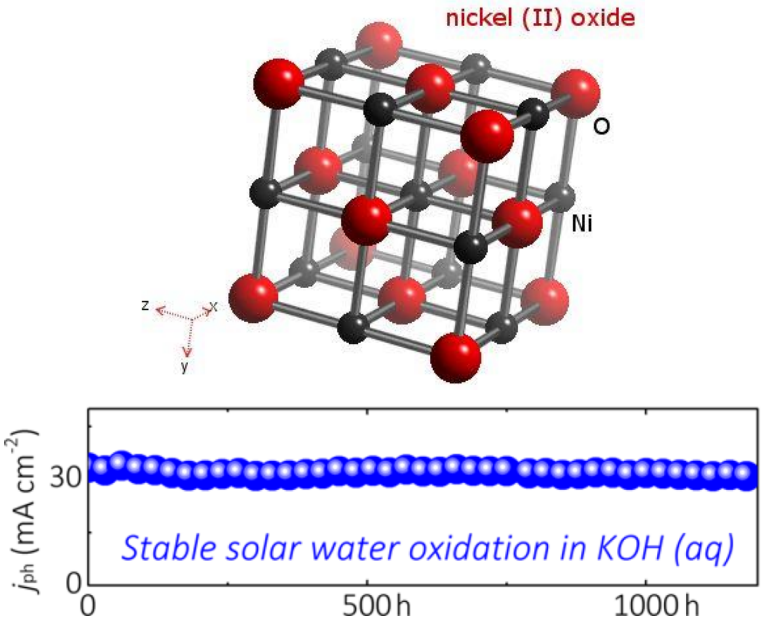
pH = 14.0; Cat, 10 mC/cm^2

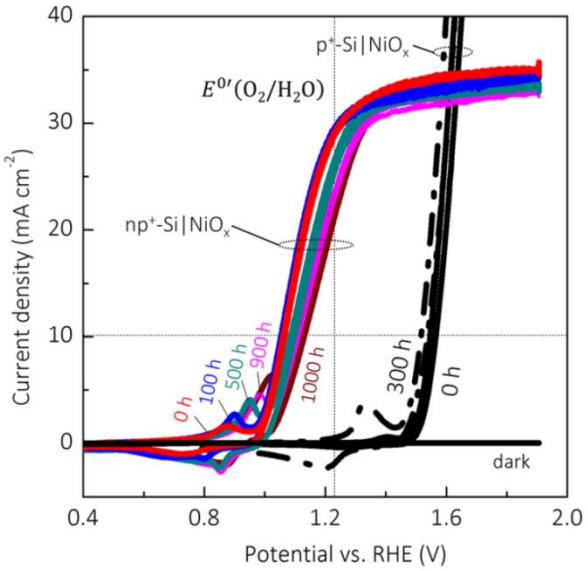
TON = 2.7 x 10^6
in 41.6 days

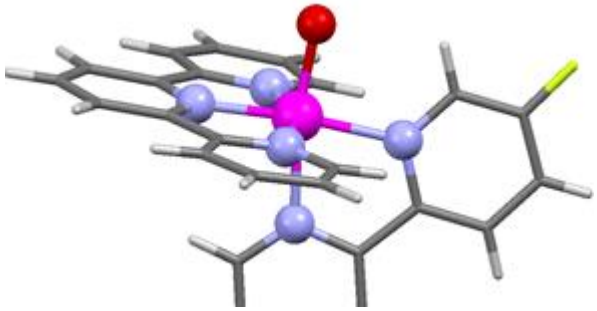
Sun, K.; Lewis, N. S. et al., *Phys. Chem. Let.,* **2015**, *6*, 592-598

Hu, S.; Lewis, N. S. et al., *Science*, **2014**, *344*, 1005-1009

WOCs: MOLECULAR *vs*. OXIDES







30 mA/cm^2 x 1000 h = 108.000 C/cm^2

pH = 14.0; Cat, 10 mC/cm^2

→ **TON = 2.7 x 10^6 in 41.6 days**

Ru-abc, TOF = 5.0 x 10^4 s^{-1}

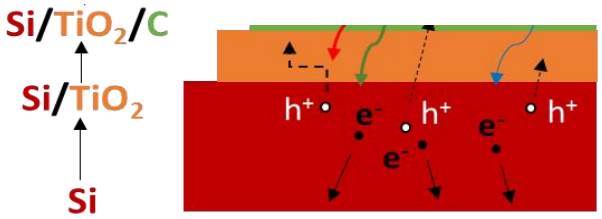
pH = 12.0

→ **54 sec**

Sun, K.; Lewis, N. S. et al., *Phys. Chem. Let.,* **2015**, *6*, 592-598

Hu, S.; Lewis, N. S. et al., *Science*, **2014**, *344*, 1005-1009

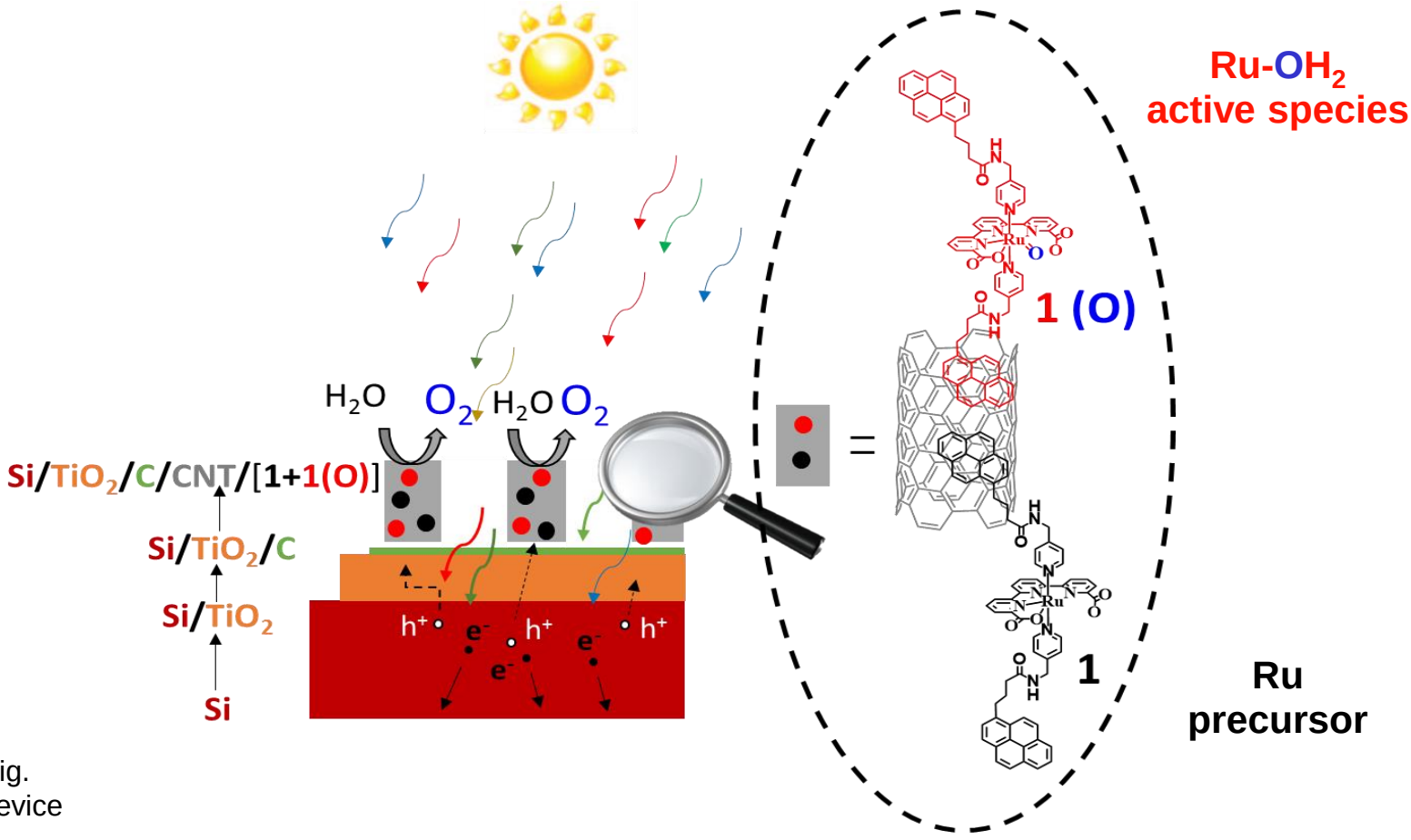
MOLECULAR Si PHOTOANODES



Si/TiO_2/C config.
buried junction device

Matheu, R.; Llobet, A.; Lewis, N. S. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 11345-11348

MOLECULAR Si PHOTOANODES



Si/TiO_2/C config.
buried junction device

Matheu, R.; Llobet, A.; Lewis, N. S. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 11345-11348

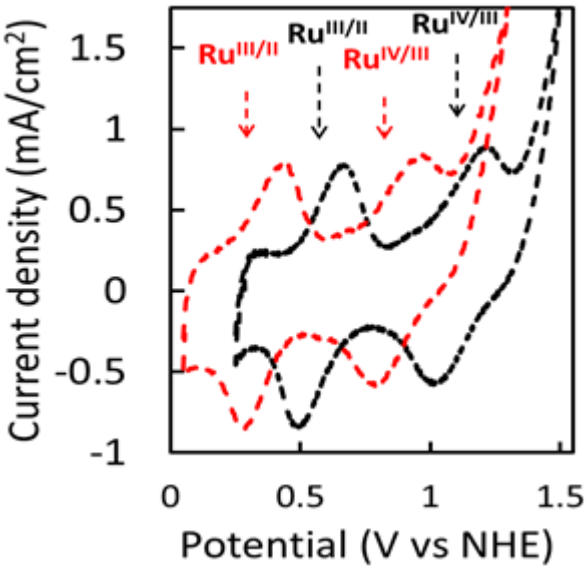
MOLECULAR Si PHOTOANODES

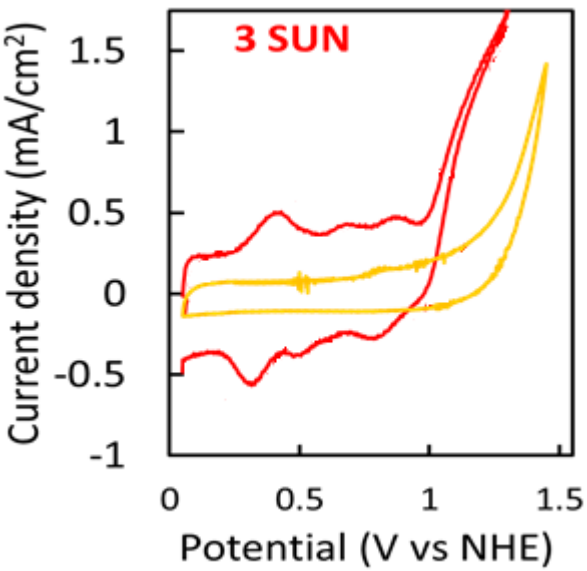
hν - 240 mV
cathodic shift

Ru precursor

pH = 7.0

Ru-OH_2 active species





BORON-DOPEP
p+-Si electrodes

– – n-Si/TiO_2/C/CNT/**1**, 3 sun

– – p^+-Si/TiO_2/C/CNT/**1**, dark

— n-Si/TiO_2/C/CNT/[**1**+**1(O)**], 3 sun

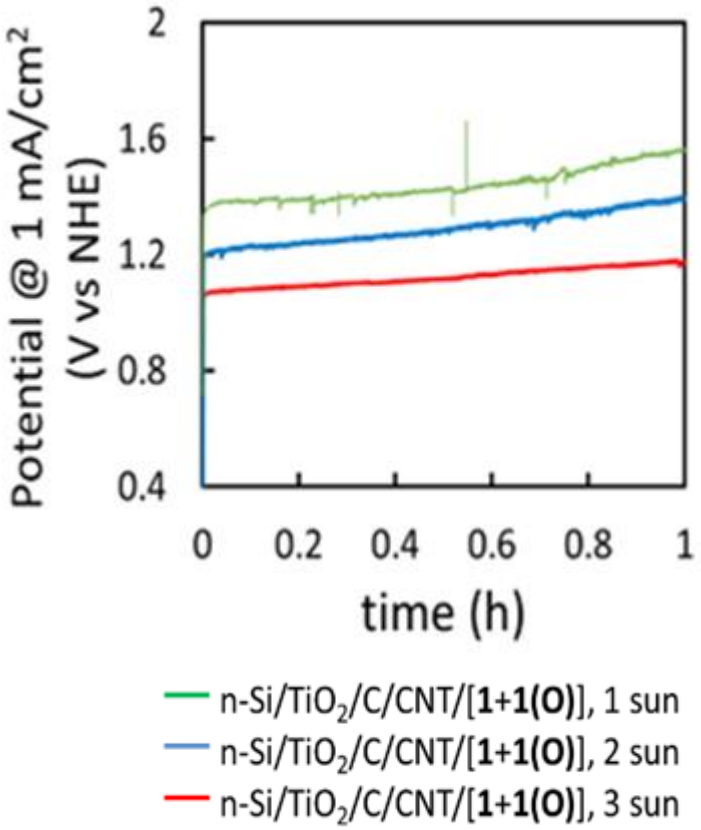
— n-Si/TiO_2/C/CNT, 3 sun

Matheu, R.; Llobet, A.; Lewis, N. S. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 11345-11348

MOLECULAR Si PHOTOANODES

Chronoamp. @ 1 mA/cm²

pH = 7.0



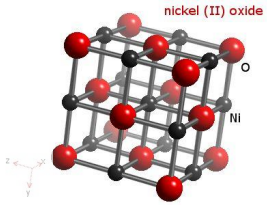
Faradaic Eff > 90%

TON > 60.000

Matheu, R.; Llobet, A.; Lewis, N. S. et al., *J. Am. Chem. Soc.*, **2017**, *139*, 11345-11348

hν CATALYSIS AND DEVICES

1. INTRODUCTION



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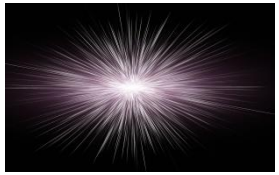
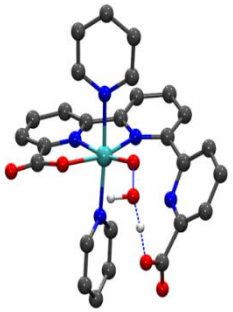
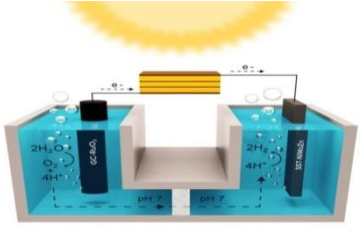


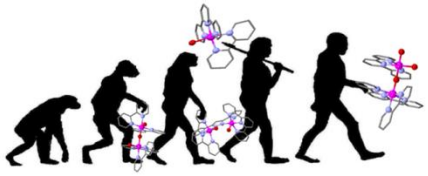
3. MOLEC ELECTROANODES



4. MOLEC PHOTOANODES

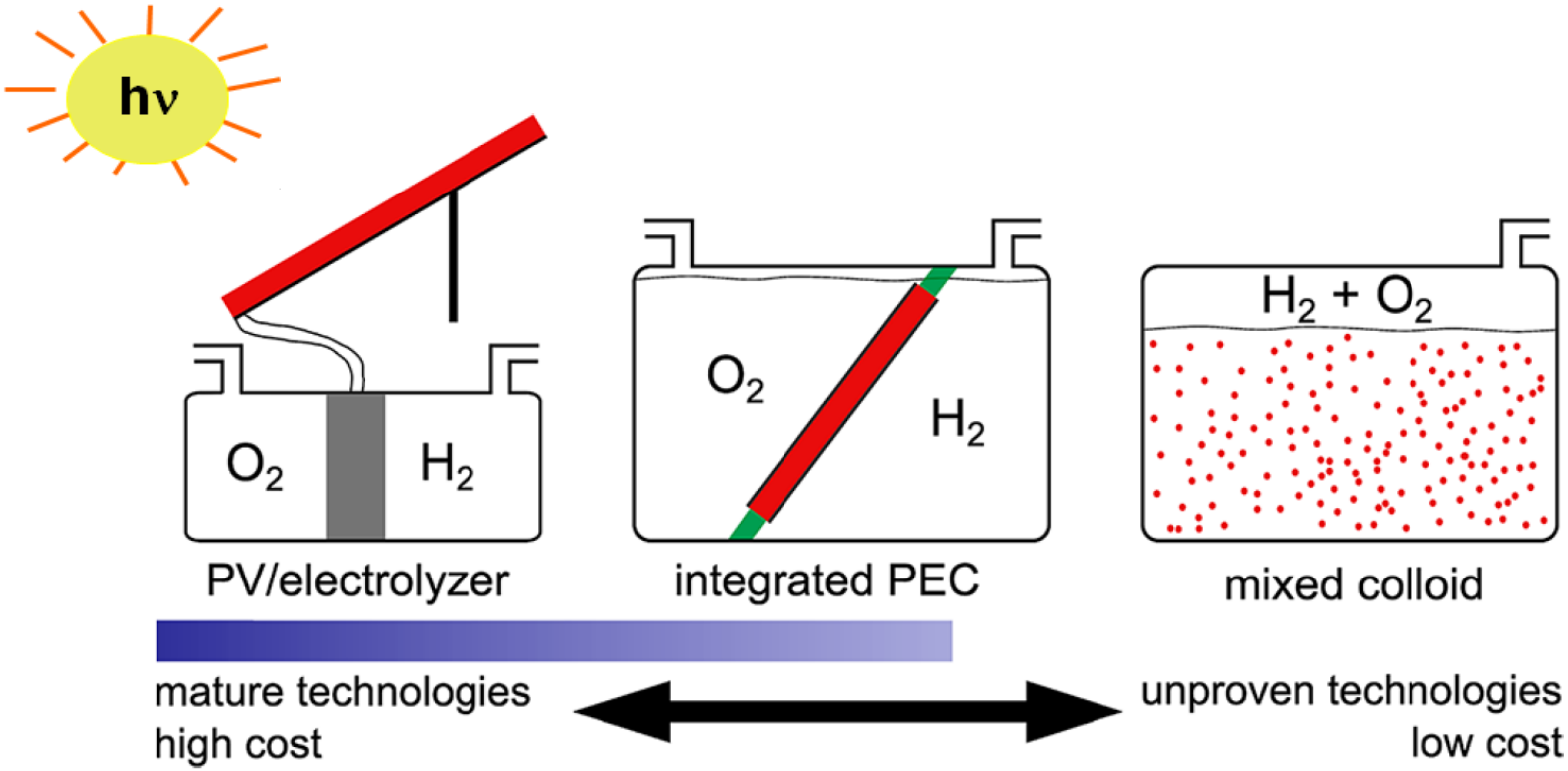


5. COMPLETE DEVICES



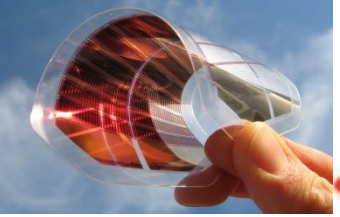
6. CONCS & ACKS

SOLAR DRIVEN WATER SPLITTING DEVICES

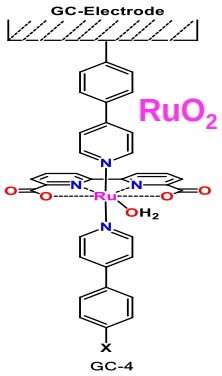


ultimately

McKone, J. R.; Lewis, N. S.; Gray, H. B., *Chem. Mater.,* **2014**, *26*, 403-414



TRIPLE JUNCTION ORGANIC SOLAR CELL



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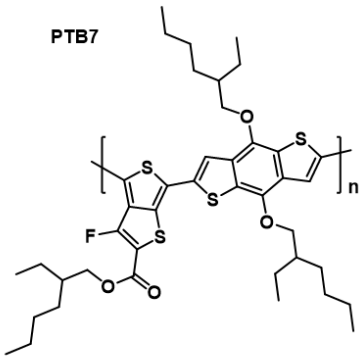
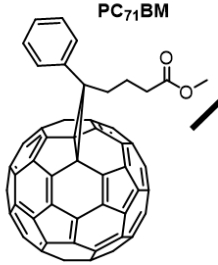
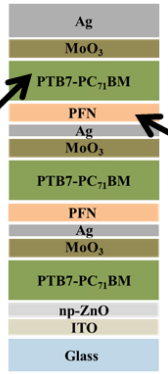
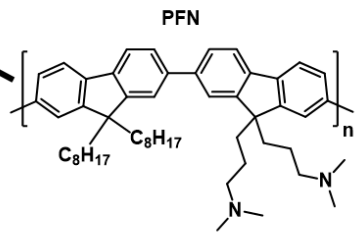
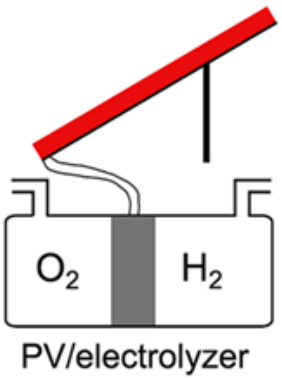


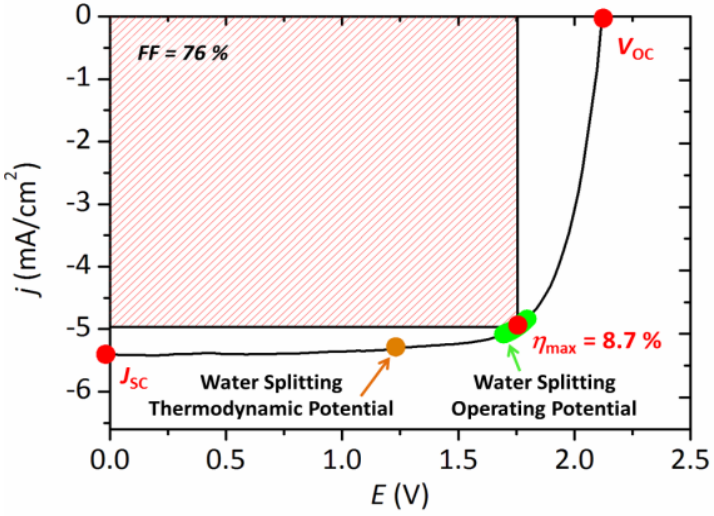






ICFO
The Institute of Photonic Sciences



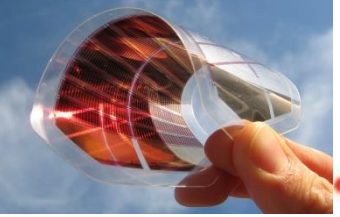


Max. Eff. η = 8.7 %

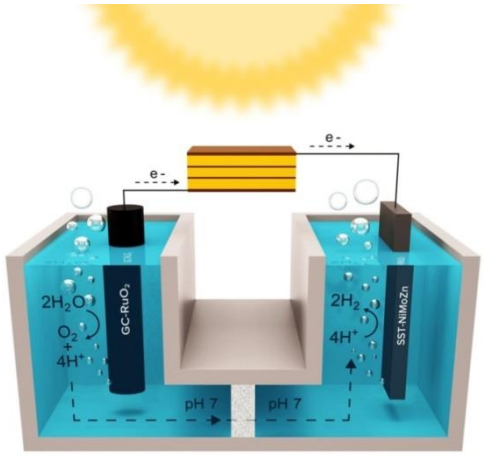
Conversion Efficiency

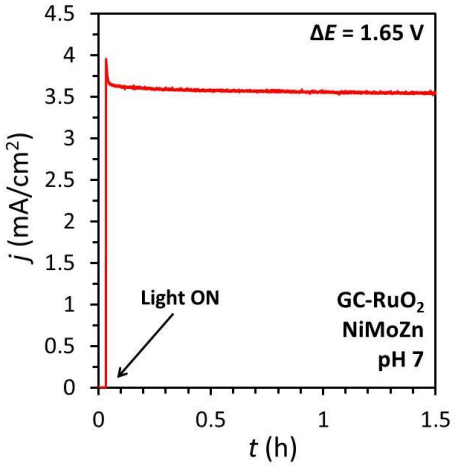
@ 1.70-1.75 V

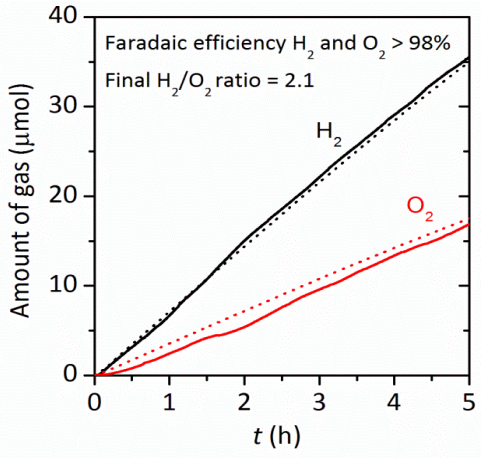
Gimbert, C.; Martorell, J.; Llobet, A. et al., *ACS Catal*. **2016**, *6*, 3310-3316



TRIPLE JUNCTION ORGANIC SOLAR CELL





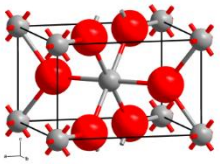


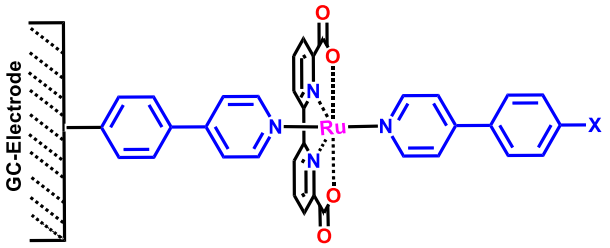
pH = 7.0

NiMoZn/RuO_2 (nmol/cm²)

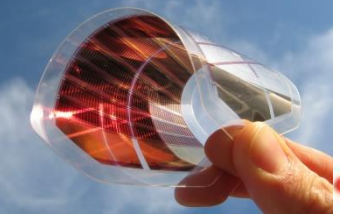
STH eff 5.5-6.0 % with filtered UV light

RECORD HIGH FOR OPV

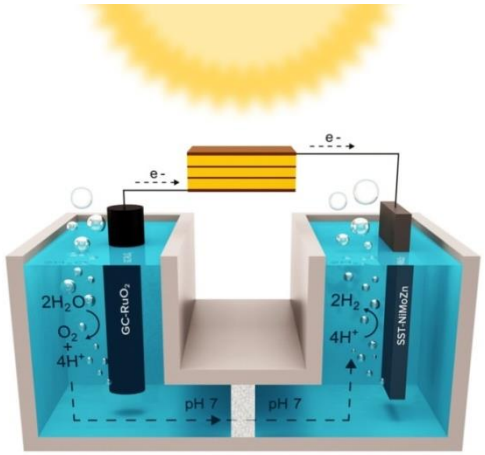


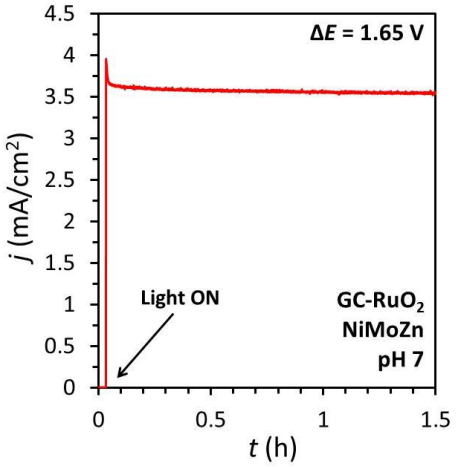


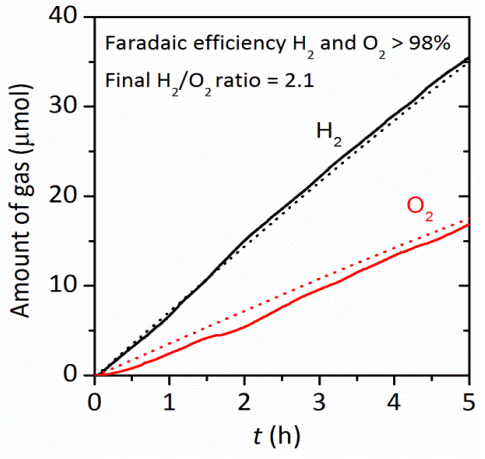
Gimbert, C.; Llobet, A. et al., *ACS Catal*. **2016**, *6*, 3310-3316



TRIPLE JUNCTION ORGANIC SOLAR CELL





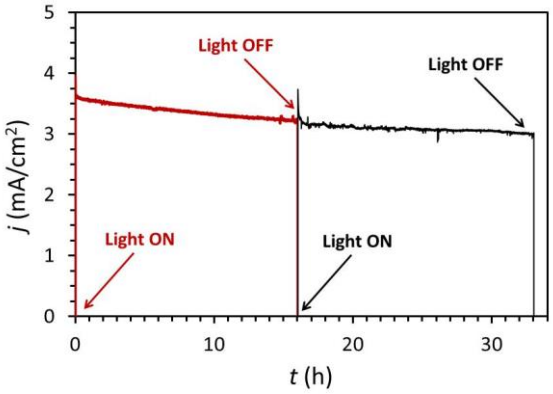


pH = 7.0

NiMoZn/RuO_2 (nmol/cm^2)

STH eff 5.5-6.0 % with filtered UV light

RECORD HIGH FOR OPV

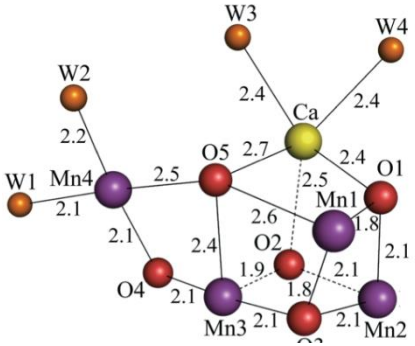


TOF_i = 3.7 s^{-1}

TONs > 20.000

Gimbert, C.; Llobet, A. et al., *ACS Catal*. **2016**, *6*, 3310-3316

SOLAR TO HIGH VALUE ADDED PRODUCTS



hν

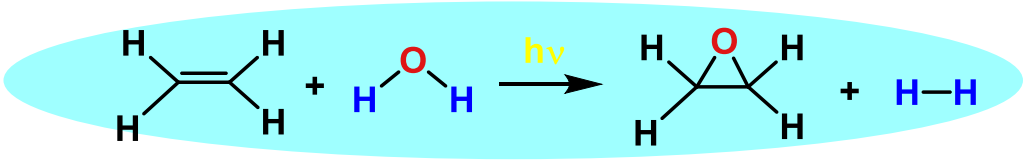
PHOTO-SYNTHESIS

$$6\,CO_2 + 6\,H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2$$

WATER SPLITTING

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

OSA WATER SPLITTING

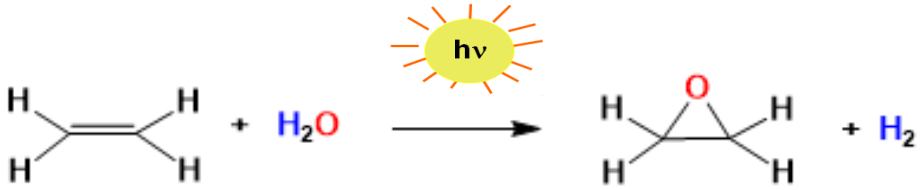


INSPIRED but not CONSTRAINED

Berardi, S.; Francàs, L.; Gimbert-Suriñach, C.; Llobet, A. et al. *Chem. Soc. Rev.* **2014**, *43,* 7501

Farras, P., Garrido P.; Llobet, A. et al., *Green Chem*., **2016,** *18*, 255-260.

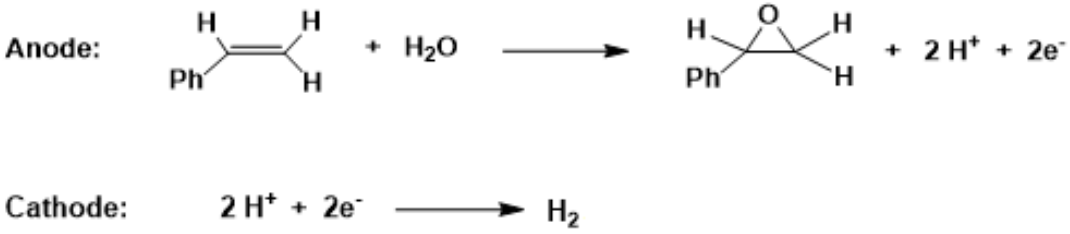
OSA PHOTO ECHEM SYNTHESIS CELL

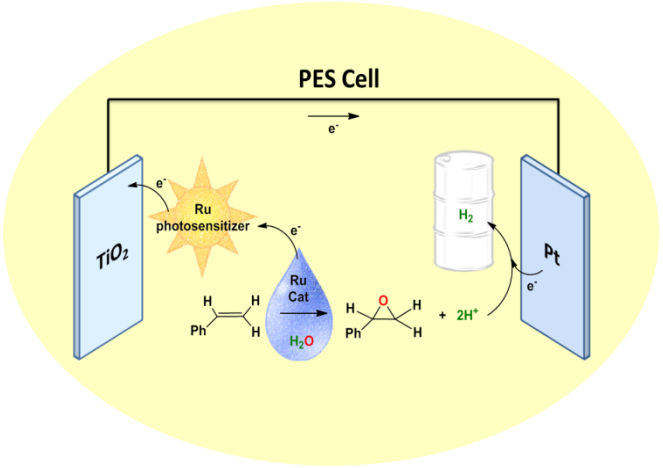


$\Delta G^{o} = -37.35\ \text{Kcal}\cdot\text{mol}^{-1}$

1. Clean and with no inorganic oxidants or peroxides

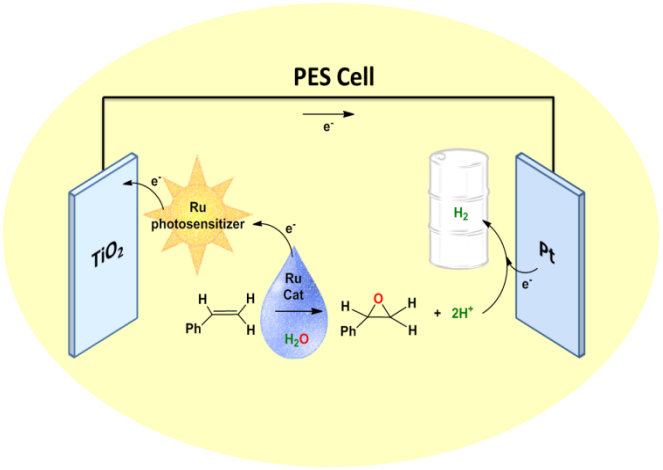
2. H_2 to Energy. World prod. ethylene oxide: 20 million tons/y // 2500 tons of hydrogen/day -> 2700 MWh/day.

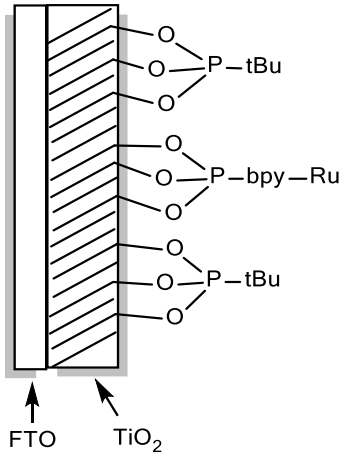


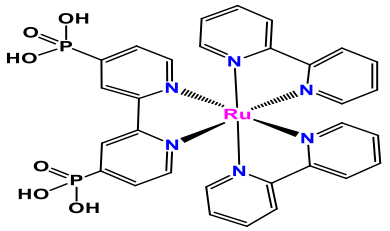


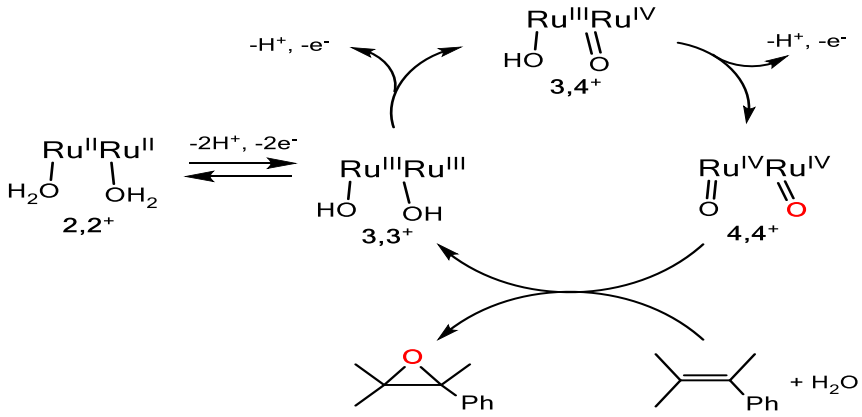
Farras, P., Llobet, A. et al., *Green Chem.*, **2016,** *18*, 255-260.

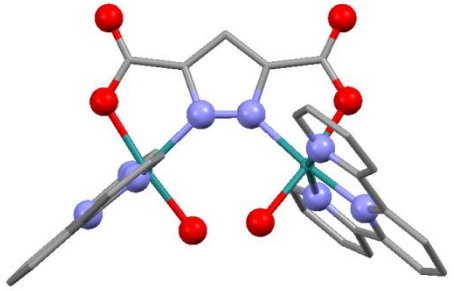
PHOTOANONDES AND CATS FOR PES CELL

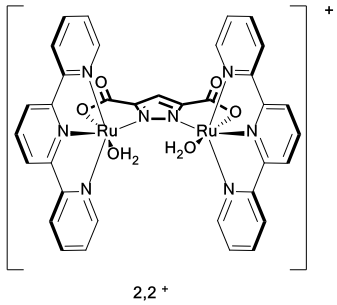








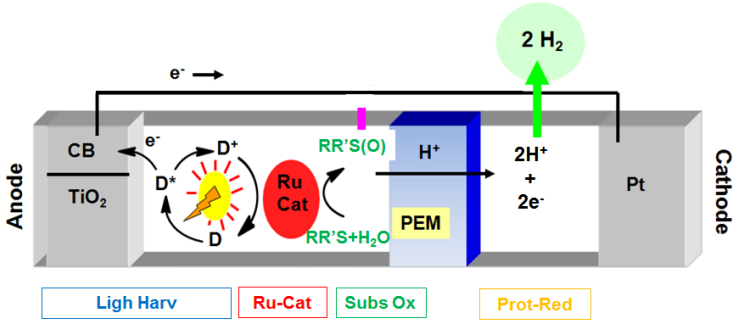


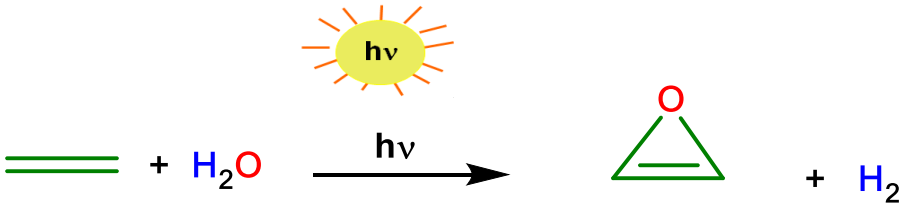


Farras, P., Llobet, A. et al., *Green Chem*., **2016,** *18*, 255-260

Di Giovanni, C.; Llobet, A. ,*Chem. Eur. J.,* **2014**, *20,* 3898-3902

OSA PEC WATER SPLITTING



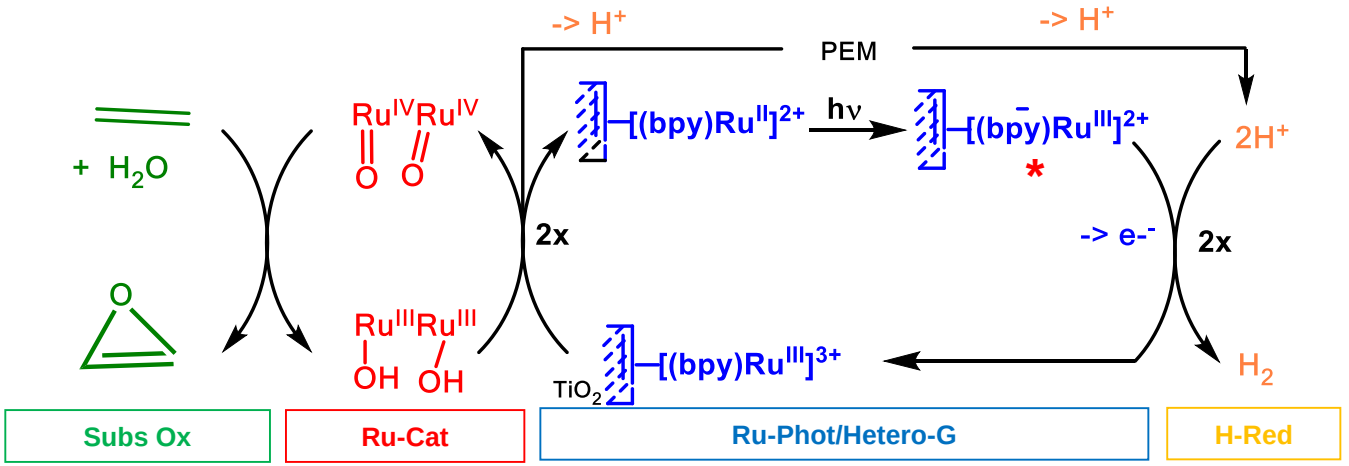


hν vis

400 nm filter

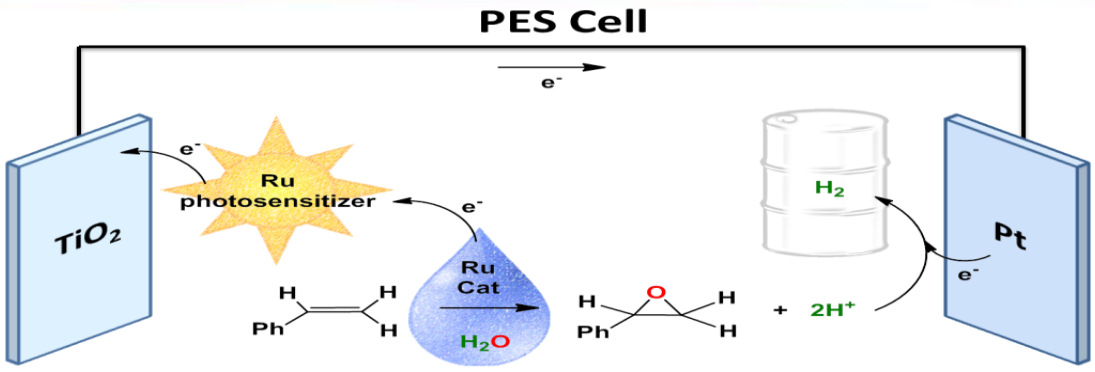
E_{app} = 0.3 V

Vs. NHE

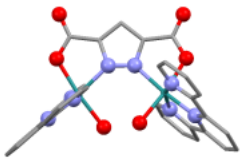


Farras, P., Llobet, A. et al., *Green Chem.*, **2016,** *18*, 255-260

OSA PEC WATER SPLITTING



ANODE
FTO/TiO_2-P-bpy-Ru (Γ = 8.8 x 10^{-8} mol cm^{-2})
CAT, 0.01 mM
Styrene, 20 mM



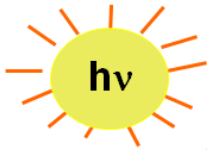
CATHODE
Pt mesh

pH 1.0, 0.1 M $LiClO_4$/$HClO_4$ (V = 9 mL)

6.1 µmol of **H_2** (92 % faradaic eff)

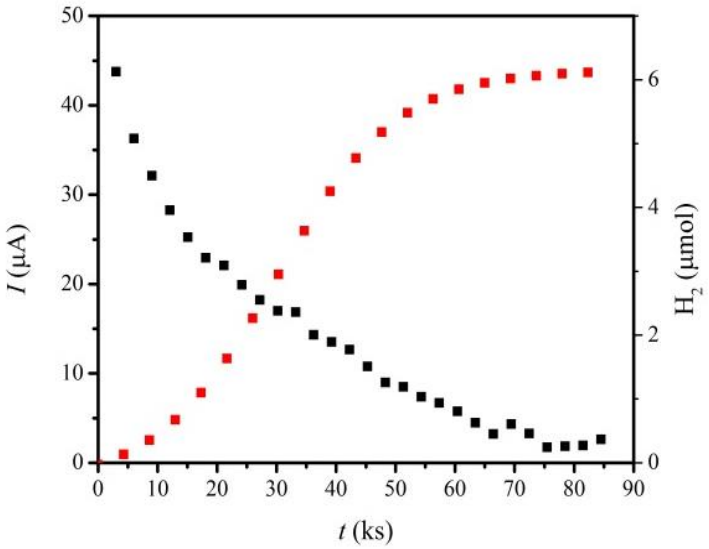
7% subs. conv. to **styrene epoxide**
(70 TN/0.8 ks^{-1} TOF)

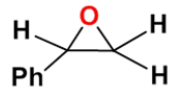
pH = 1.0



hν 1 Sun
λ > 400 nm

***E_{app}* = 0.3 V**
***vs.* NHE**



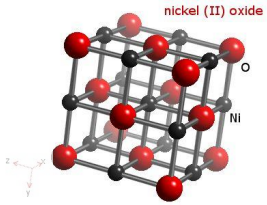


36 ks = 10h

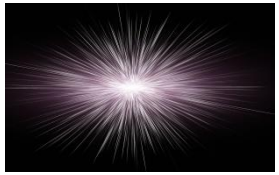
Farras, P., Garrido, P.; Llobet, A. et al., *Green Chem.*, **2016,** *18*, 255-260.

hν CATALYSIS AND DEVICES

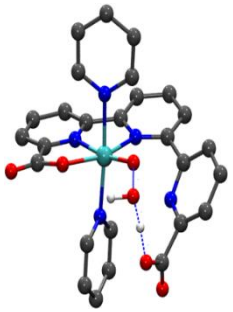
1. INTRODUCTION



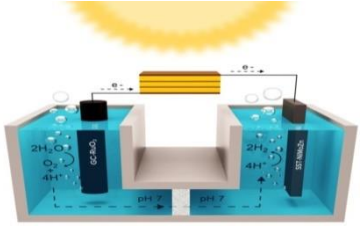
2. hν WOC-PR HOMOGENEOUS PHASE



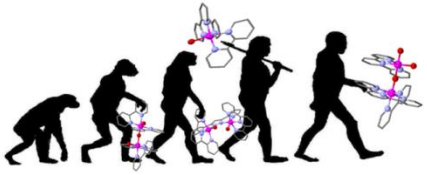
3. MOLEC ELECTROANODES



4. MOLEC PHOTOANODES



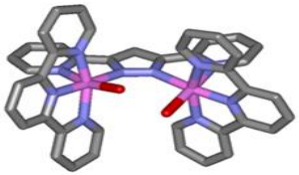
5. COMPLETE DEVICES



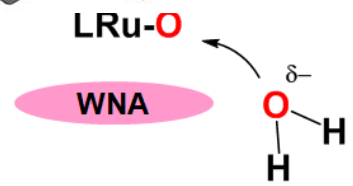
6. CONCS & ACKS

hν CATALYSIS AND DEVICES

1. Design of efficient WOCs homogeneous phase

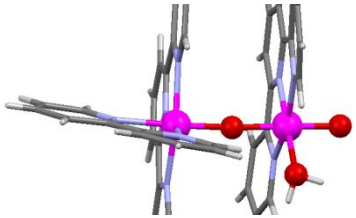


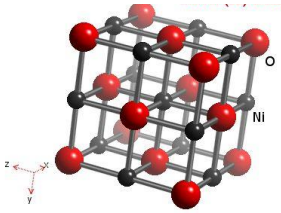
2. Mechanistic understanding of rxn pathways



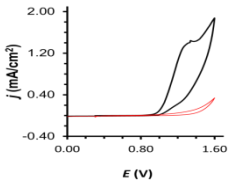
I2M

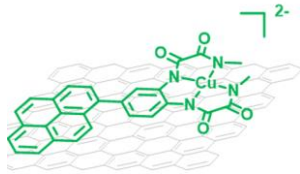
3. Deactivation pathways





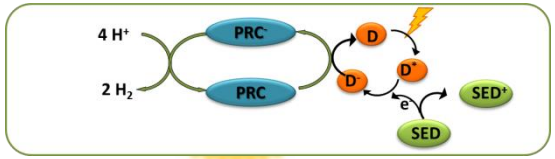
4. Anchor cats in solid surfaces (mechs&deact)



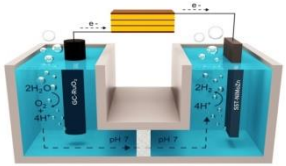


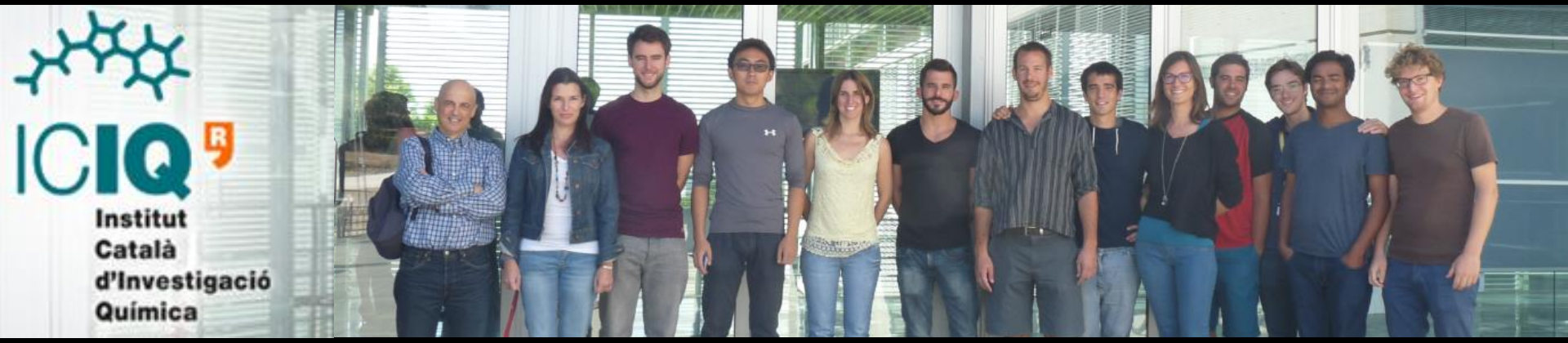
GC@G@[(L$_{py}$)Cu]$^{2-}$ (G-2^{2-})

5. Light induced catalysis and Photoanodes



6. Devices for light induced WS and OSA-WS

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Severo Ochoa, Pgr.

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SOLAR-H2, Energy Prg. UE

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