Supramolecular Architectures for Artificial Photosynthesis: the Quantasome Vision

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1222·2022 800 ANNI

UNIVERSITÀ DEGLI STUDI DI PADOVA

ITM Istituto per la Tecnologia delle Membrane
Consiglio Nazionale delle Ricerche

FOUNDED IN
1222

1545
BOTANICAL GARDEN CREATED

1595
FIRST PERMANENT ANATOMICAL THEATRE COMPLETED

1610
GALILEO PUBLISHES THE SIDEREUS NUNCIUS

1678
FIRST WOMAN GRADUATE

Elena Lucrezia Cornaro Piscopia

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NMC LAB

www.chimica.unipd.it/NanoMolCat

MARIE CURIE ACTIONS

N_2LIGHT-2019

MARIE CURIE ACTIONS

Photo2BIO-2019

DECADE

Horizon 2020
European Union Funding
for Research & Innovation

FIRB MIUR
NANOSOLAR

Fondazione
Cassa di Risparmio
di Padova e Rovigo

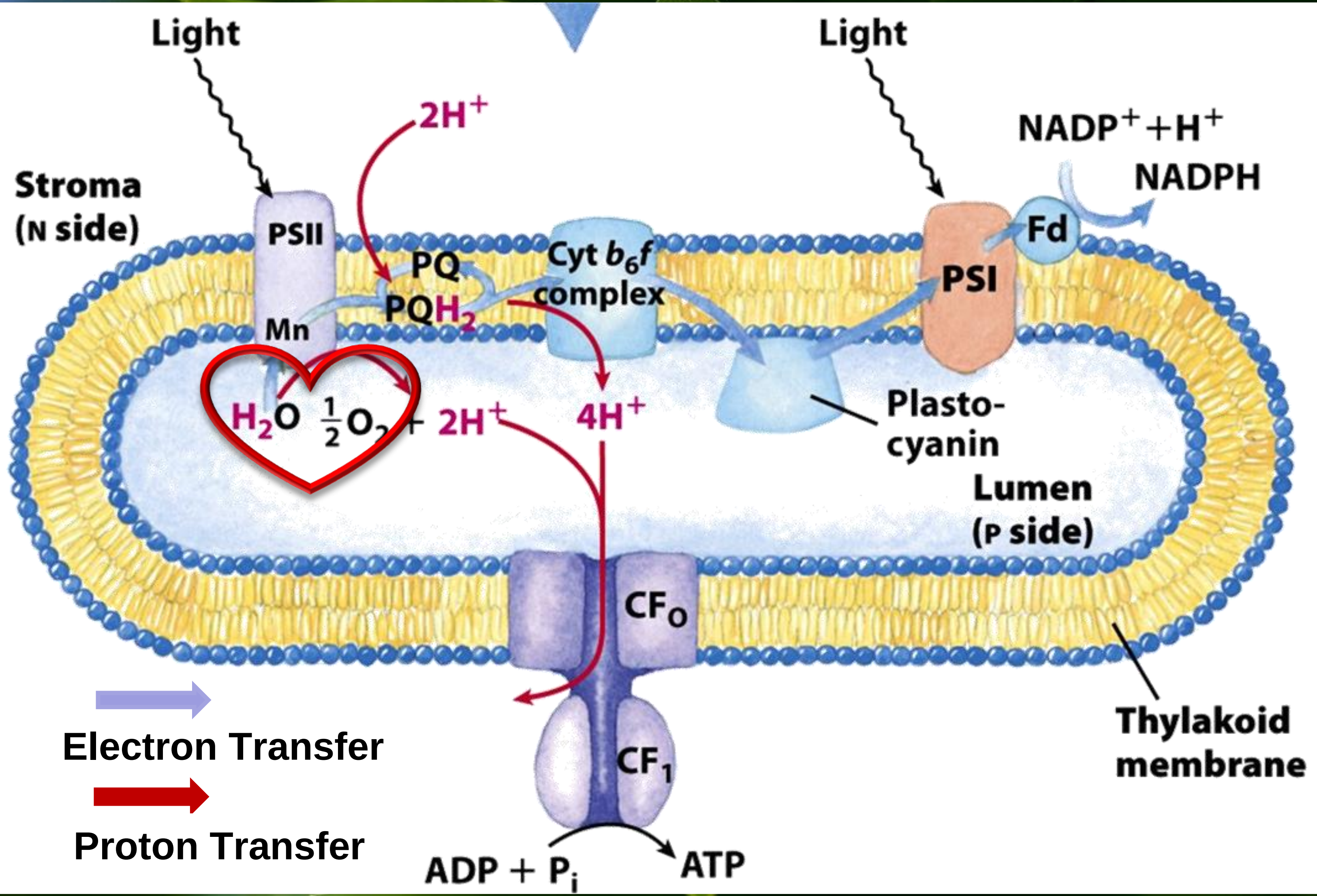
COST
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

BioNexGen
Clean Water.
Clear Solutions.

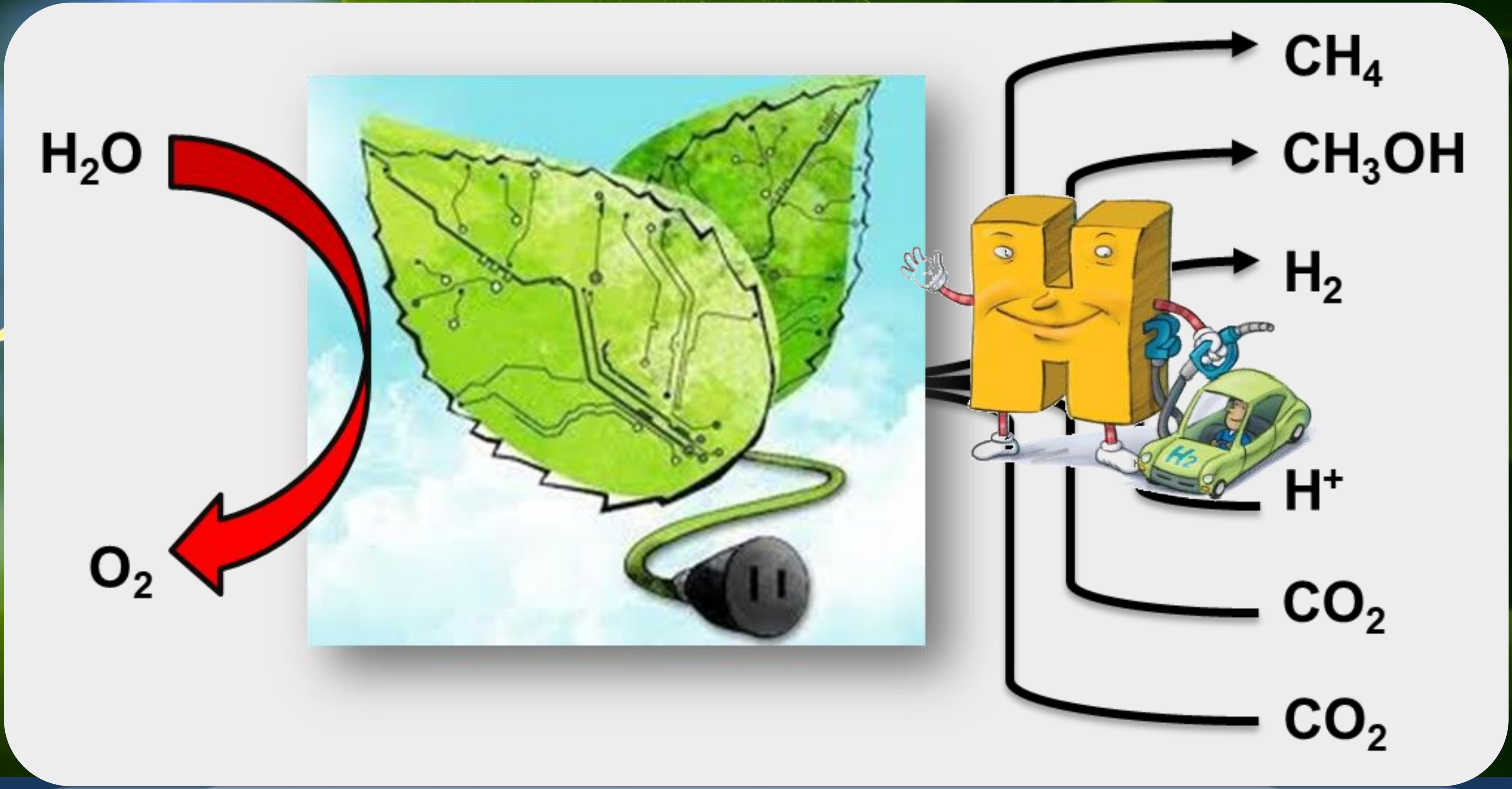
VicInAqua H2020
WATER-2015-RIA

NATURAL PHOTOSYNTHESIS

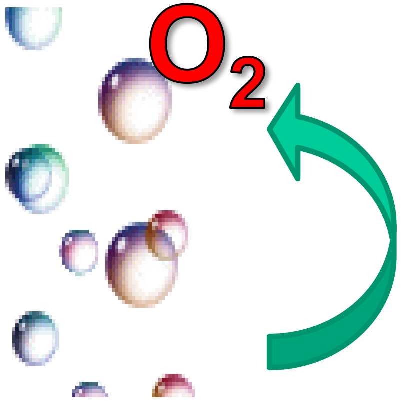
Solar Energy Capture/Conversion/Storage



THE ARTIFICIAL LEAF:
two tandem photosystems
PHOTO-ELECTROCATALYTIC CELL (PEC)



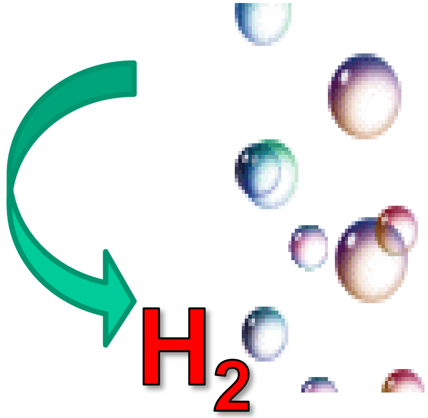
<u>Splitting</u> of water into **Hydrogen** and **Oxygen**



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

$$4H^+ + 4e^- \rightleftharpoons 2H_2$$

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

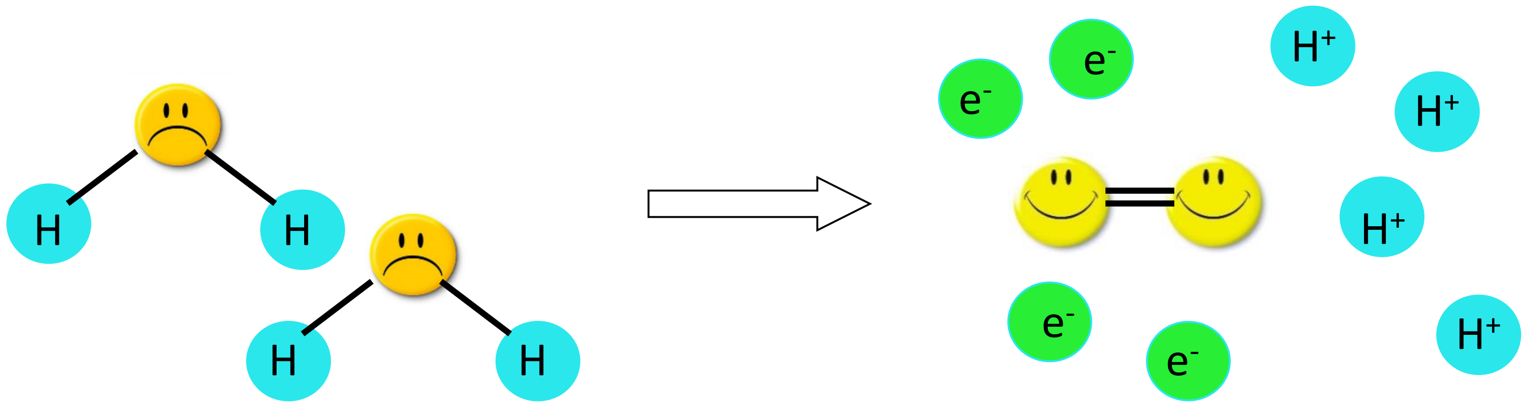


- Thermal splitting of water requires temperatures above 2500°C

-Electrochemical splitting of water (ΔE^0= 1.23 V/e^-)

the $2H_2O/O_2$ half reaction is the bottleneck of the overall process

Water Oxidation: The key step
Thermodinamic and Kinetic challenges

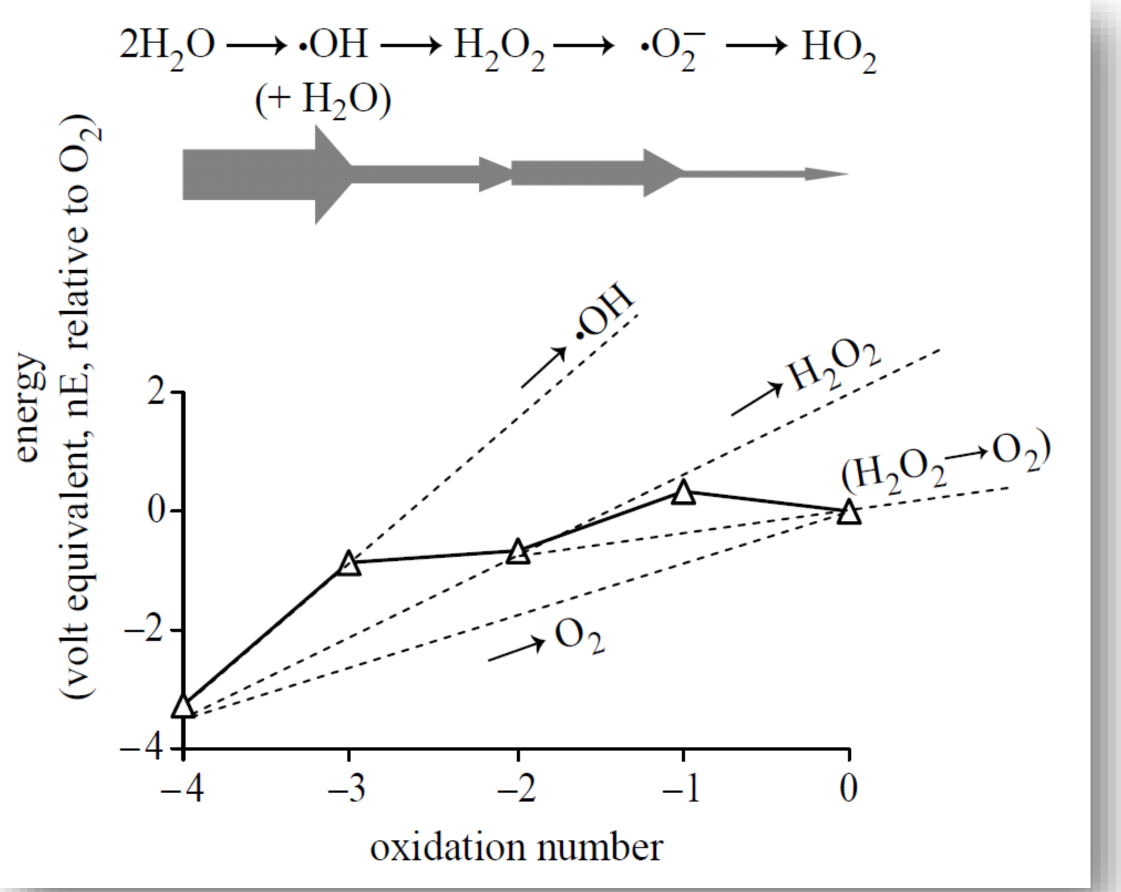


<u>the $2H_2O/O_2$ half reaction is considerably more complex</u>

- ✓**the removal of 4-electrons from 2 H_2O molecules**
- ✓**the removal of 4 protons**
- ✓**the formation of a new oxygen-oxygen bond**

Water Oxidation :
Energy landscape for plausible intermediates

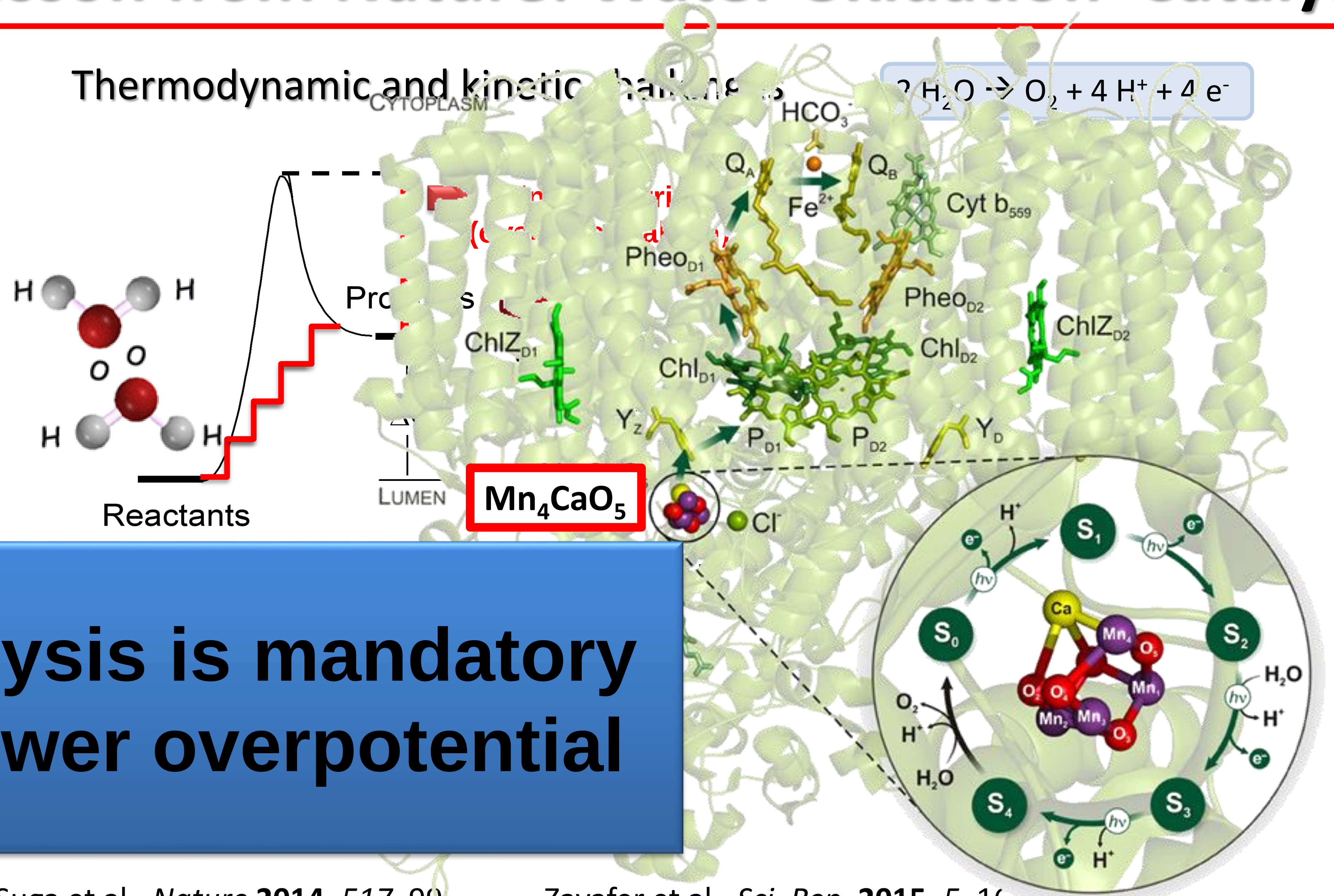
F.A. Armstrong, *Phil Trans. R. Soc B*, **2008**



Energy Profile of oxygen generation via multi-electron oxidation of two water molecules, considering the reduction potentials of selected intermediates (pH=7). Block arrows are drawn to indicate the relative thermodynamic hurdles for the different oxidation stages

Lesson from Nature: Water Oxidation Catalysis

Thermodynamic and kinetic challenges



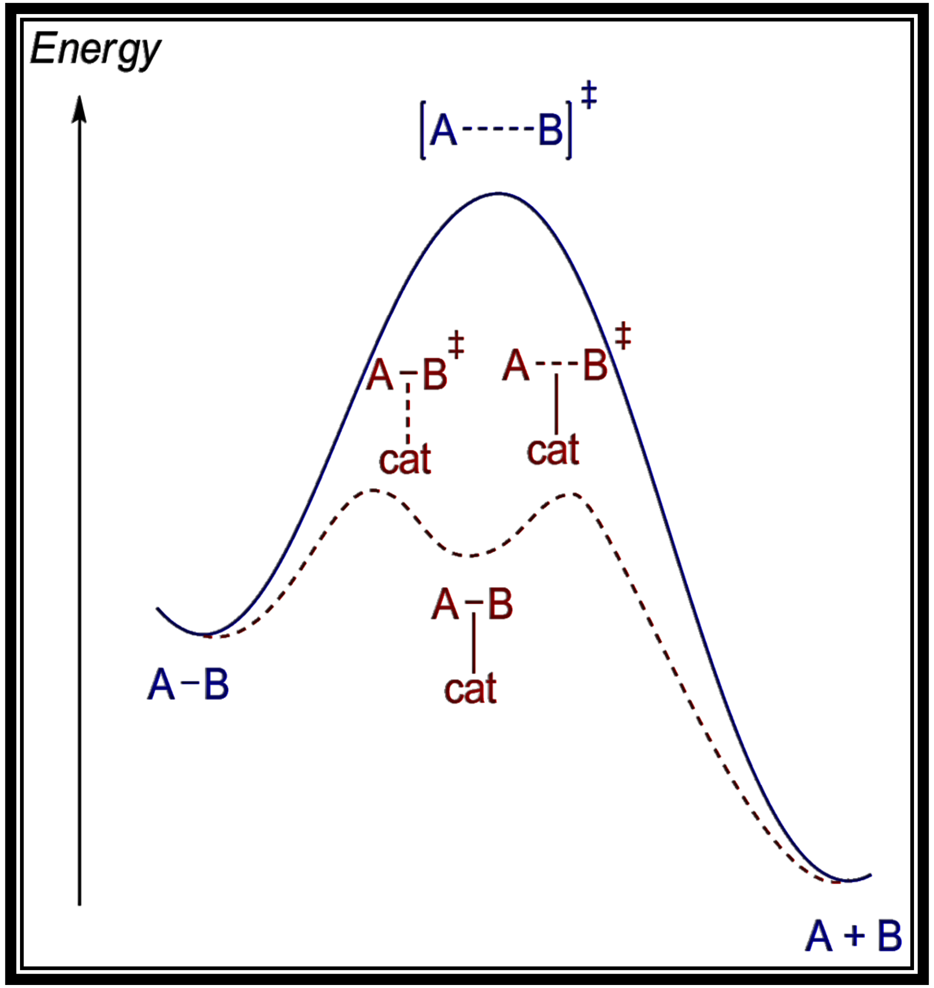
catalysis is mandatory to lower overpotential

Suga et al., *Nature* **2014**, *517*, 99   Zavafer et al., *Sci. Rep.* **2015**, *5*, 16363

TRANSITION METAL-BASED CATALYSIS

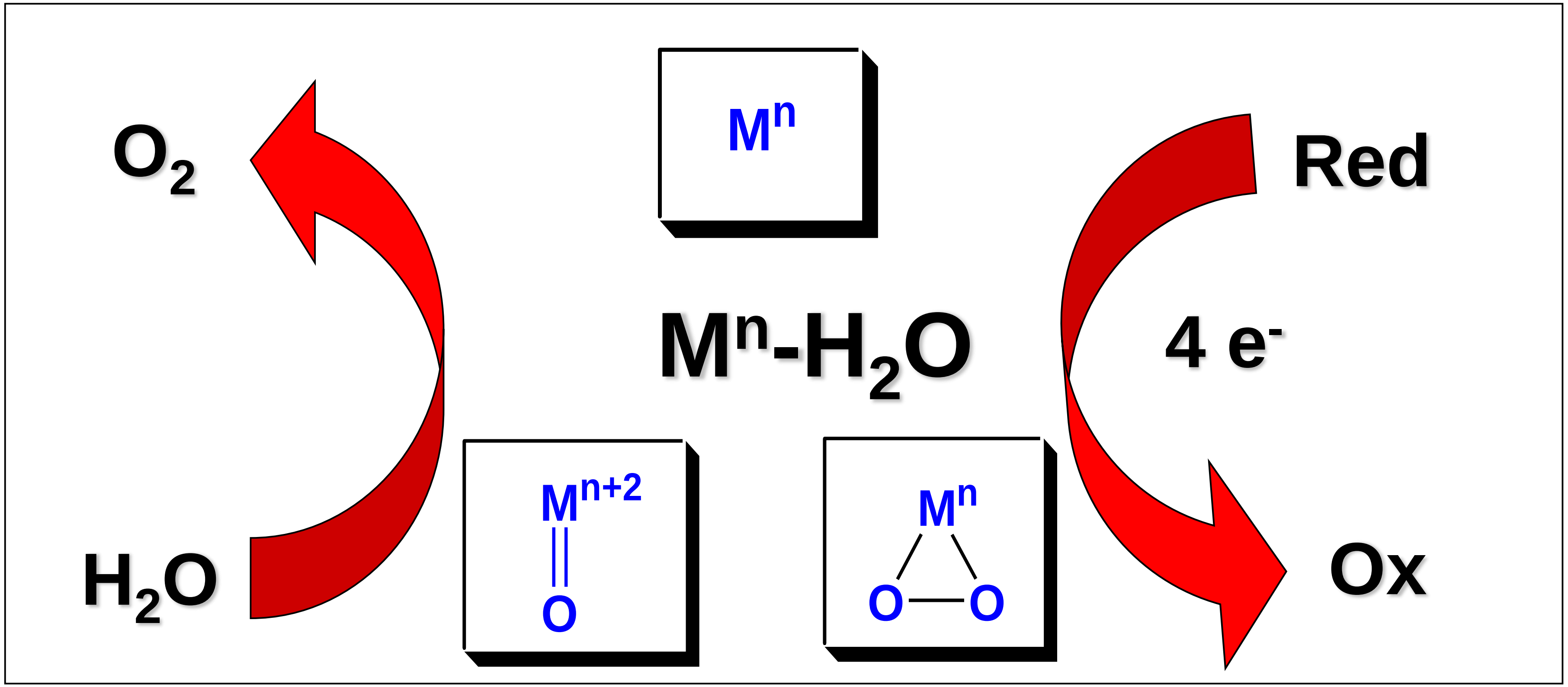
The Catalyst:

- increases the reaction rate without itself being changed by the reaction.
- works by changing the mechanism of a chemical reaction.
- Sets the selectivity (stereo-regio-chemical) constrains of the reaction



Modern Physical Organic Chemistry; Anslyn E. V., Dougherty, D., A.; University Science Books: Sausalito, 2006

Oxygenic Catalysis by Transition Metal Complexes



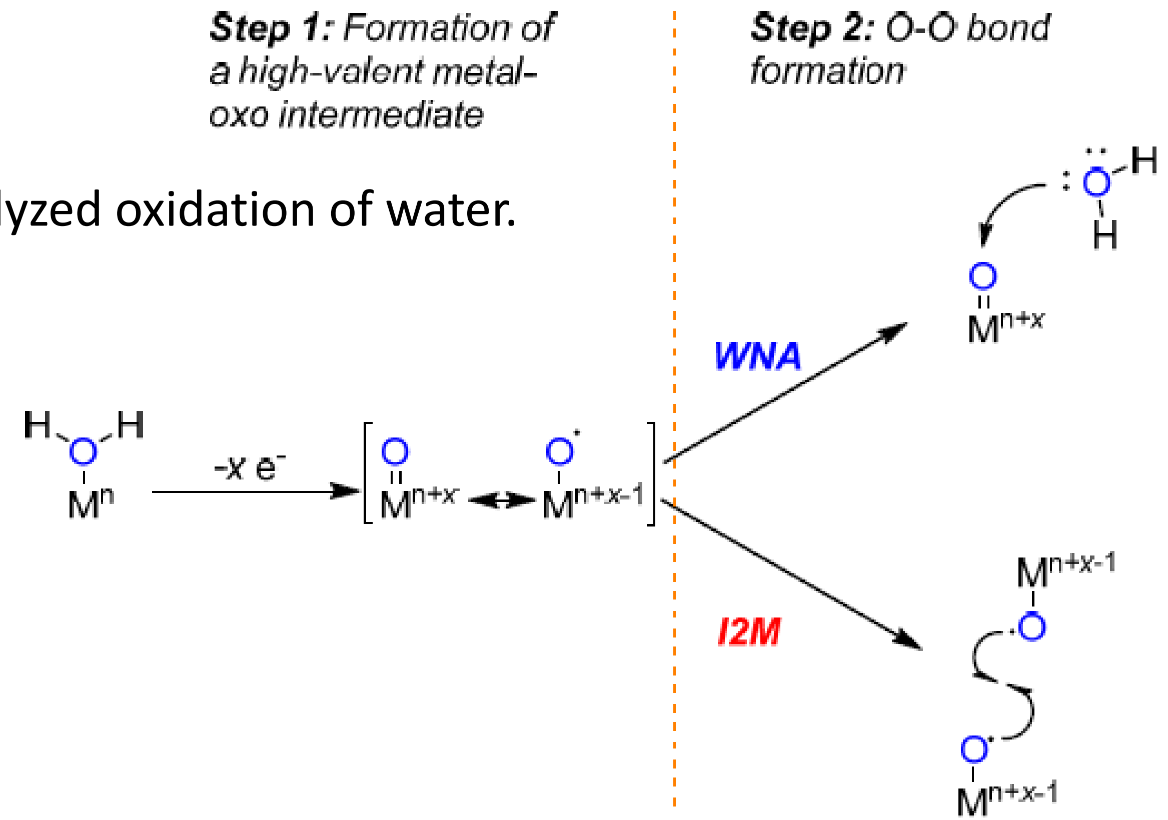
I. G. Denisov, T. M. Makris, S. G. Sligar, I. Schlichting, *Chem. Rev.* 105, 2253 (2005); E. I. Solomon et al., Chem. Rev. 100, 235 (2000); M. Costas, M. P. Mehn, M. P. Jensen, L. Que Jr., *Chem. Rev.* 104, 939 (2004); L. Que et al. *Science* 315, 835 (2007). P. J Deuss, R. den Heeten, W. Laan, P. C. J. Kamer, *Chem. Eur. J.* 17, 4680 (2011).

Metal-assisted Oxygen-Oxygen bond formation

Douglas B. Grotjahn
Molecules **2019**, 24, 494;doi:10.3390/molecules24030494

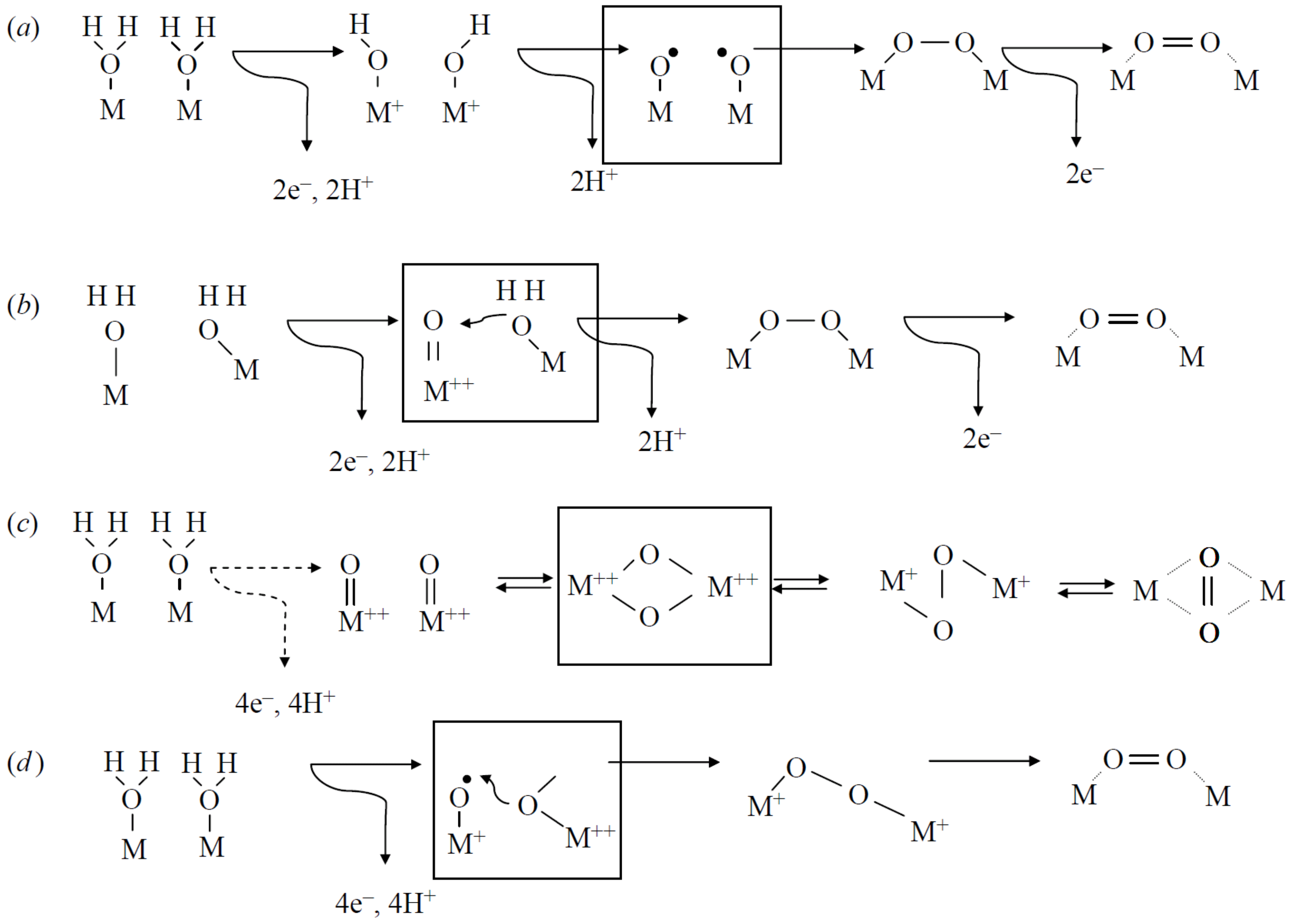
Prevalent mechanistic scenarios for metal catalyzed oxidation of water.

- **water nucleophilic attack (WNA)**
- **bimolecular radical oxo-coupling (I2M)**



Requisite to both scenarios is the generation of a high-valent metal oxo intermediate formed from an aquo ligand through successive proton-coupled electron transfers.

Metal-assisted Oxygen-Oxygen bond formation



F. A. Armstrong, *Phil Trans. R. Soc B*, **2008**

Bio-inspired Oxidations

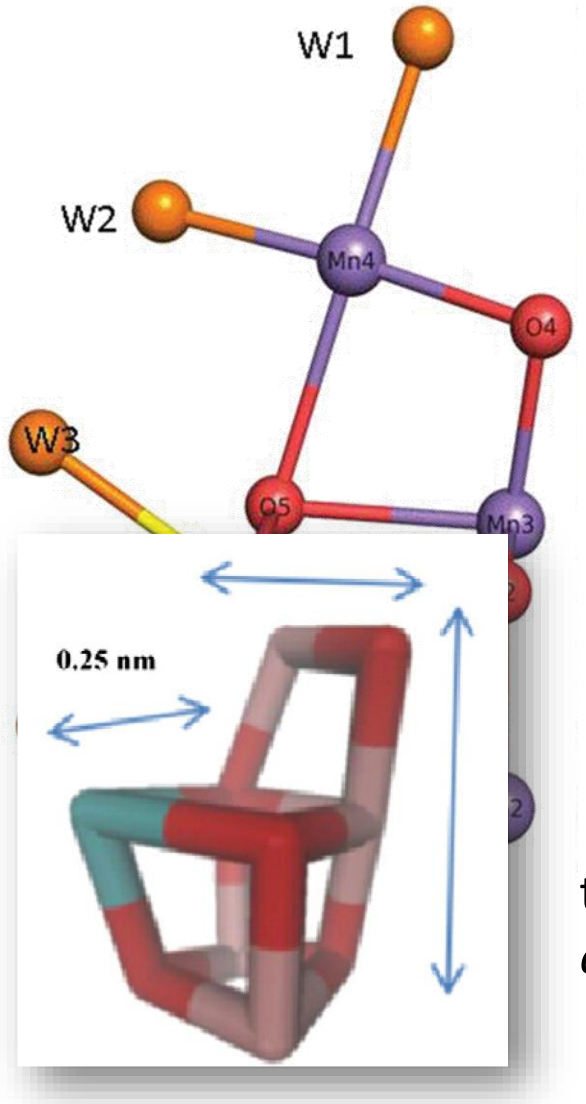
Use of Bio-relevant Metals (Fe, Mn, Cu, Co, V) and/or Bio-inspired Guidelines (Ru, Ir)

Metal	Crustal average (ppm)	Seawater (mg/l)	Examples of specific functions
Sodium	2.8×10^4	1.1×10^4	Osmotic control, electrolytic equilibria, currents
Magnesium	2.1×10^4	1.4×10^3	Phosphate metabolism, chlorophyll
Aluminium	8.1×10^4	1×10^{-3}	Neurotoxic, solubilized by acid rain
Silicon	2.8×10^5	3	Prevents aluminium toxicity
Potassium	2.6×10^4	3.9×10^{-2}	Osmotic control, electrolytic equilibria, currents
Calcium	3.6×10^4	4.1×10^{-2}	Second messenger, muscle activation, biominerals
Vanadium	135	2×10^{-3}	Nitrogenase, peroxidases
Chromium	100	5×10^{-4}	Glucose metabolism?
Manganese	950	2×10^{-3}	Oxygen production and metabolism, structure
Cobalt	25	4×10^{-4}	B_{12} coezymes, alkyl transfer
Nickel	75	7×10^{-3}	Hydrogenases, urease
Copper	55	3×10^{-3}	Electron transfer, oxidases, oxygen transport
Zinc	70	1×10^{-2}	Lewis acid catalysis, regulation (DNA binding)
Selenium	5×10^{-2}	9×10^{-9}	Glutathione peroxidase
Molybdenum	1.5	1×10^{-2}	Nitrogenase, oxidases, oxo-transfer
Tungsten	1.5	1×10^{-4}	Dehydrogenases
Iron	5×10^4	3×10^{-3}	Oxygen transport, storage, activation and detoxification, electron transfer, nitrogen fixation, ribose reduction, etc.

Mason, B. and Moore, C.B. (1982). *Principles of Geochemistry, Fourth Edition, Wiley, New* York.

Natural Born Catalysts: PSII- Oxygen Evolving Center

M. M. Najafpour et al. *Dalton Trans.* ***2011***



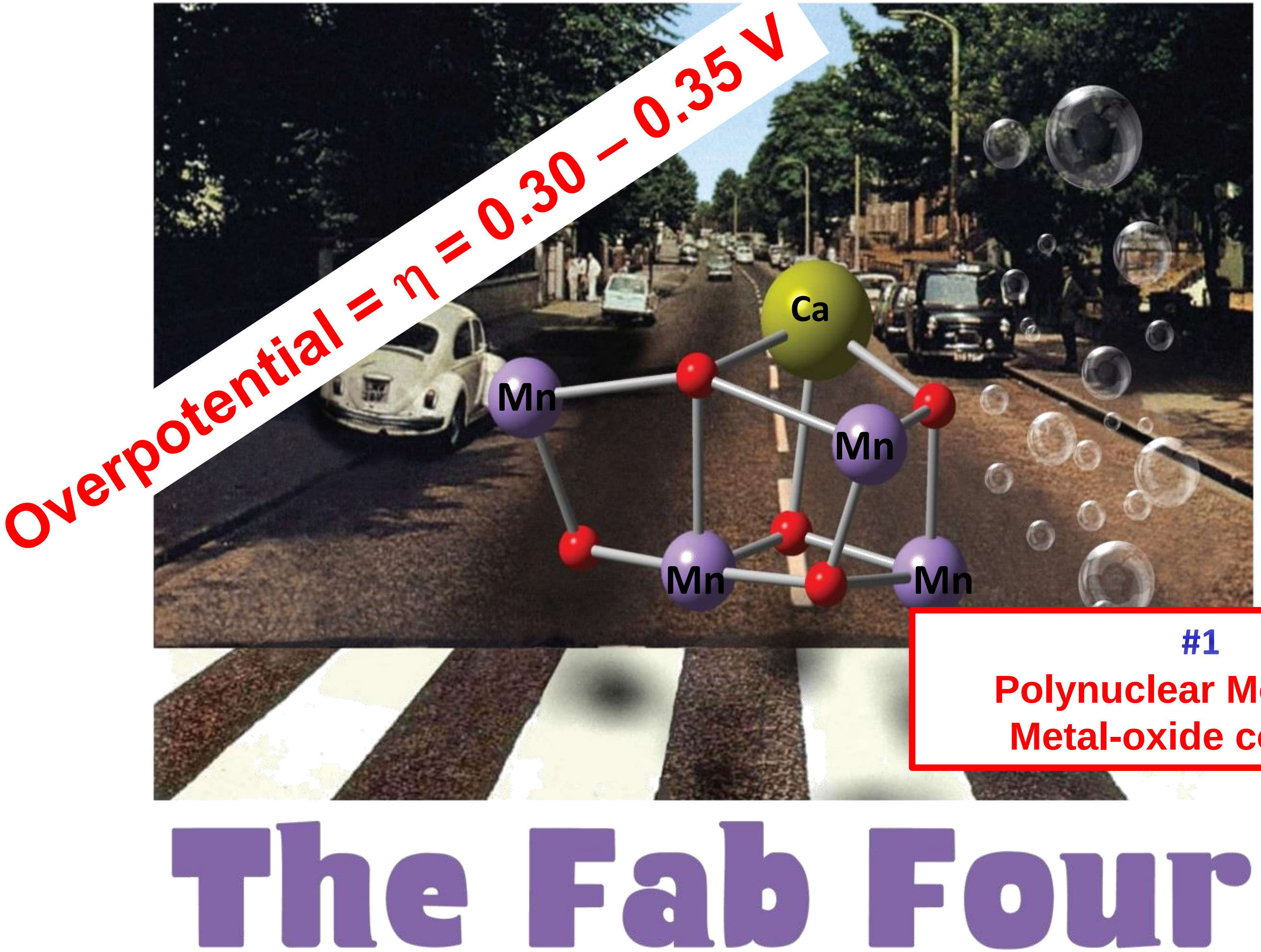
A unique **Mn_4CaO_5** cluster shaped as a a *distorted chair, with the asymmetric cubane serving as the seat base and* the isolated Mn(4) and O(4) atoms serving as the back

Four water molecules (W) are present in the **Mn_4CaO_5** : W1 and W2 bound to M(4) ; W3 and W4 bound to Ca
Five bridging Oxygens: *this is a Polyoxometalate cluster*

Five oxidation states available for **Mn_4CaO_5** : the Kok-Joliot cycle includes the evolution of the cluster along S0-S1-S2-S3-S4 states by a sep-wise 4 electron removal, and Mn(II)/Mn(III)/Mn(IV)/Mn(V) manifolds

the **Mn_4CaO_5** *is a Nano-dimensional cluster of ca =0.5nm embedded within the protein matrix*

Natural Born Catalysts: Oxygen Evolving Center



#1
Polynuclear Molecular Metal-oxide complex

Umena Y. et al, *Nature* **2011**, *473*, 55–60; *Chem. Soc. Rev* . **2013**, *42*, 2262;

HYBRID CATALYSIS @ FUNCTIONAL INTERFACES

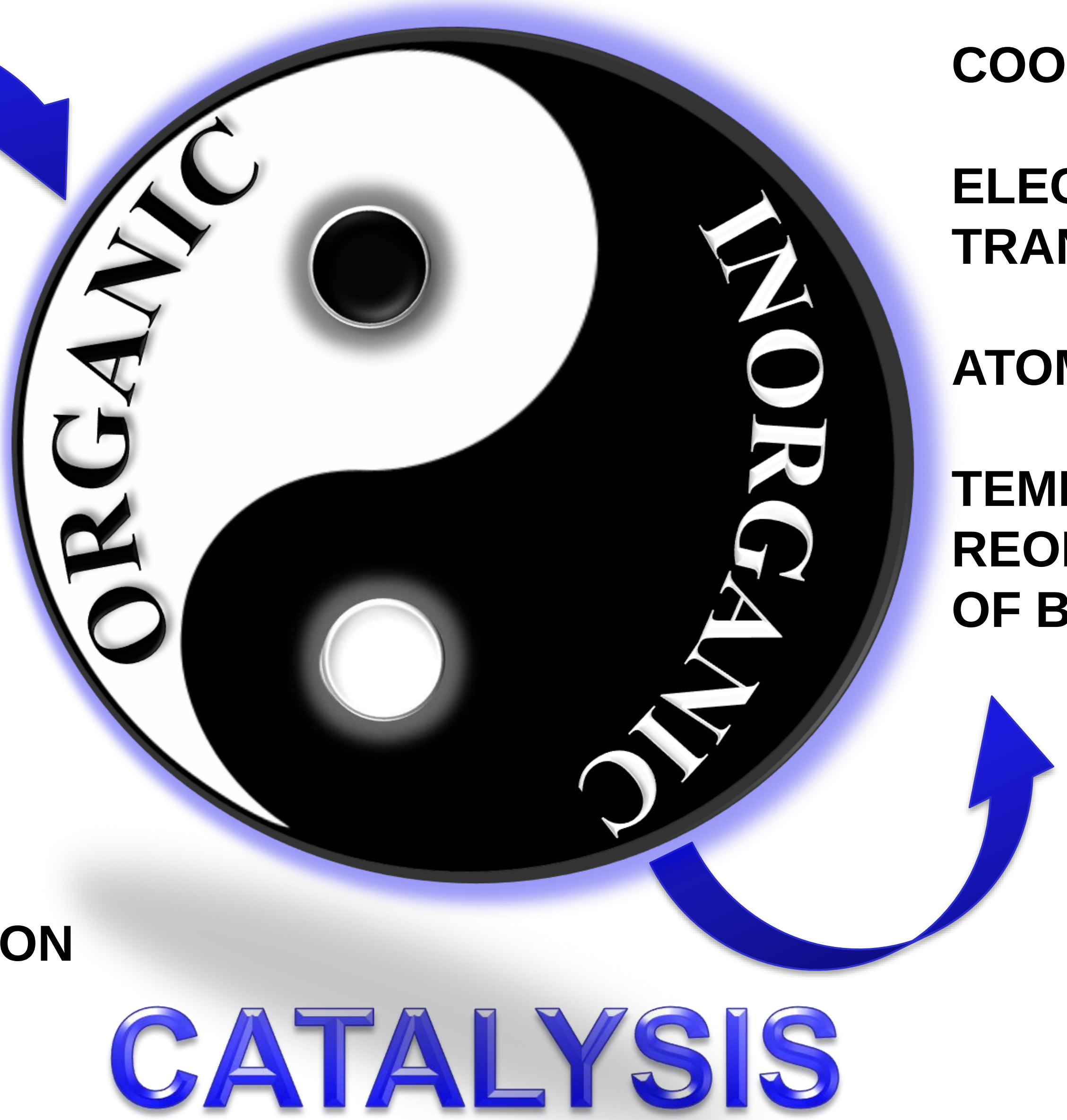
RECOGNITION

STABILIZATION

STEREO-ELECTRONIC CONTROL

PHOTO/THERMAL TRIGGERS

PROTON TRANSLOCATION



COORDINATION

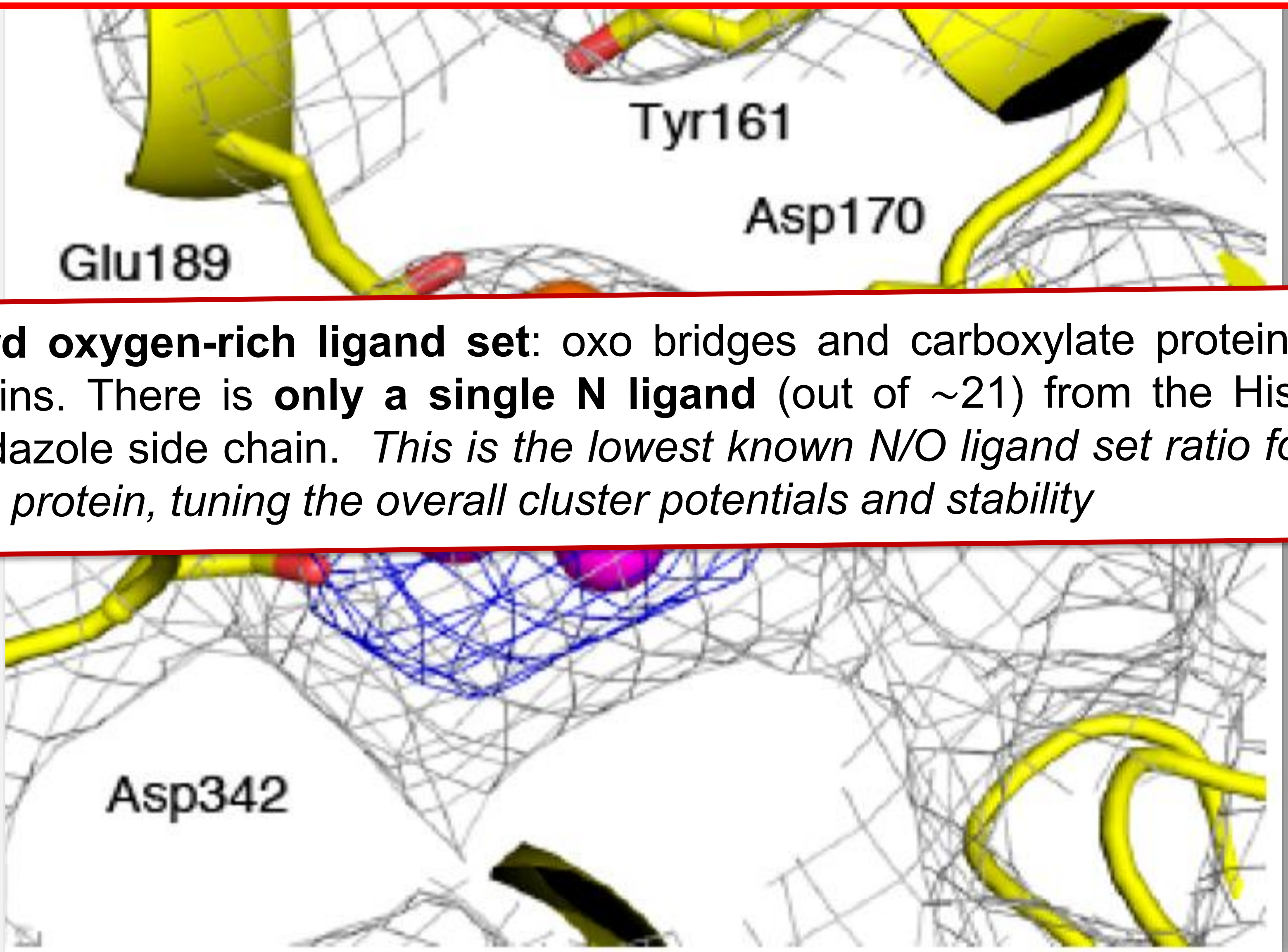
ELECTRON-TRANSLOCATION

ATOM TRANSFER

TEMPLATING THE REORGANIZATION OF BONDS

Energy & Environmental Science 2021, 5816-5833

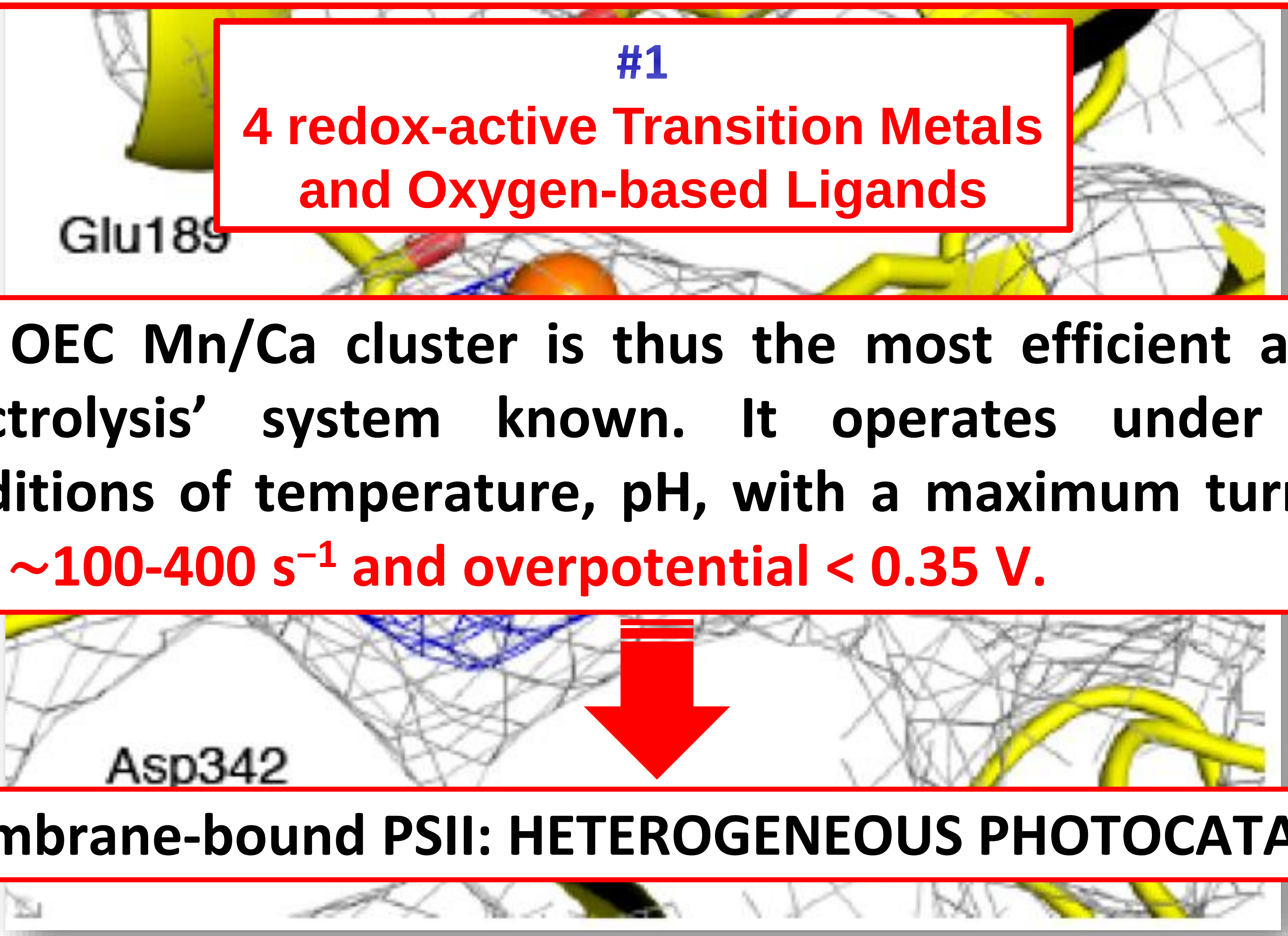
Lesson from Nature: the PSII-Oxygen Evolving Center



Hard oxygen-rich ligand set: oxo bridges and carboxylate protein side chains. There is **only a single N ligand** (out of ~21) from the His 332 imidazole side chain. *This is the lowest known N/O ligand set ratio for Mn in a protein, tuning the overall cluster potentials and stability*

J. Yano and V. Yachandra *Chem. Rev.* **2014**, 114, 4175−4205

Lesson from Nature: the PSII-Oxygen Evolving Center



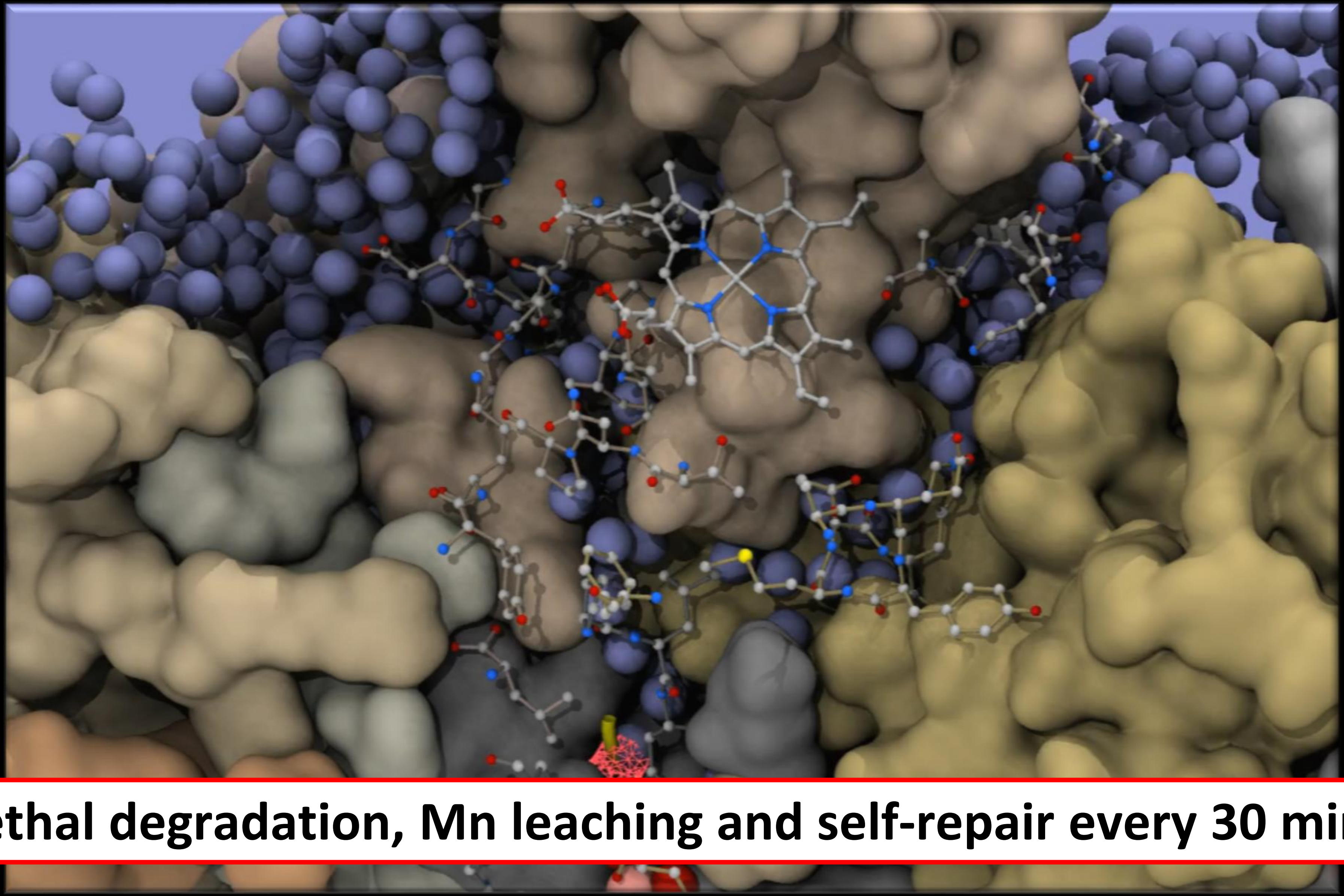
#1

4 redox-active Transition Metals and Oxygen-based Ligands

The OEC Mn/Ca cluster is thus the most efficient anodic ‘electrolysis’ system known. It operates under mild conditions of temperature, pH, with a maximum turnover rate ~100-400 s^{-1} and overpotential < 0.35 V.

Membrane-bound PSII: HETEROGENEOUS PHOTOCATALYSIS

J. Yano and V. Yachandra *Chem. Rev.* **2014**, 114, 4175−4205 wave front of O2 propagation in PSII showing the fastest pathways of oxygen migration.

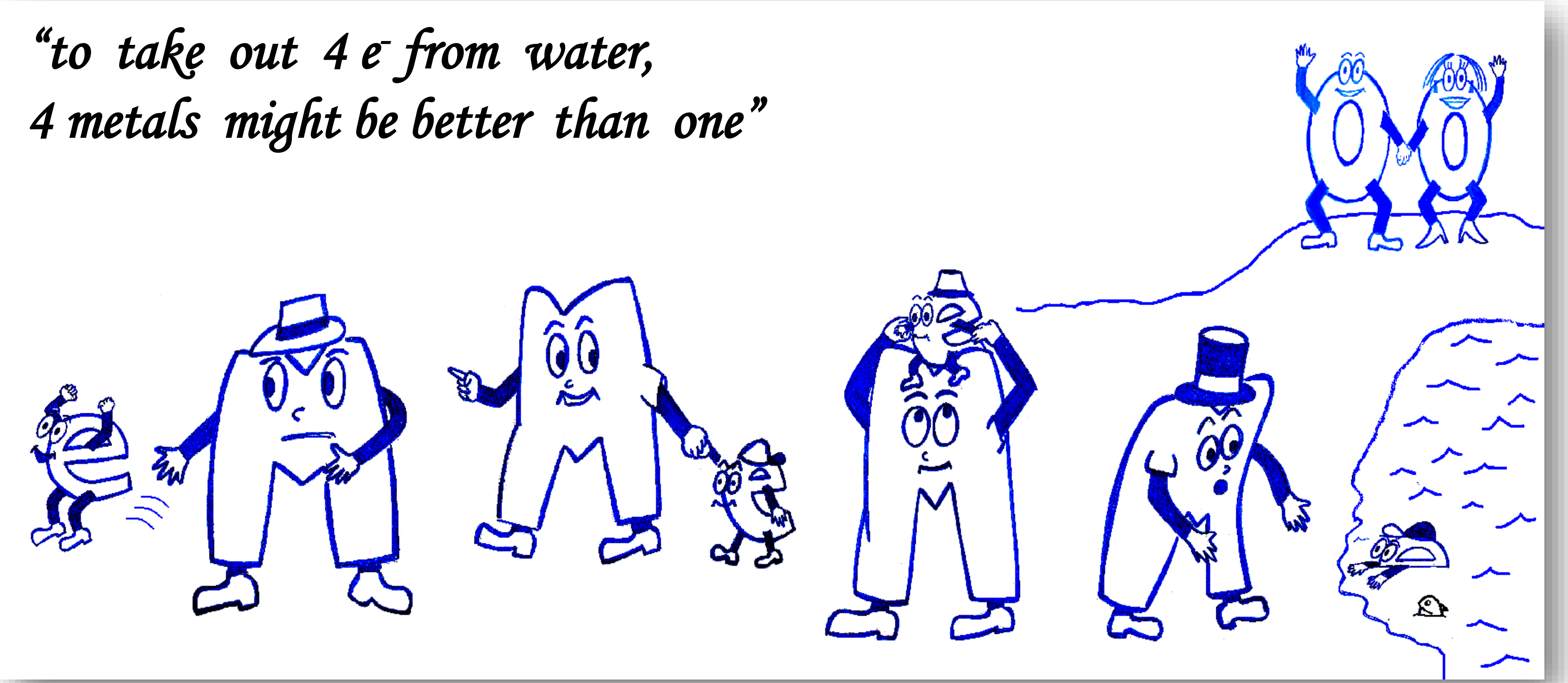


Lethal degradation, Mn leaching and self-repair every 30 min

Serguei Vassiliev ∗ et al. ***Biochimica et Biophysica Acta 1827 (2013) 1148–1155***

The ***DESIGN*** of a **totally synthetic and robust**

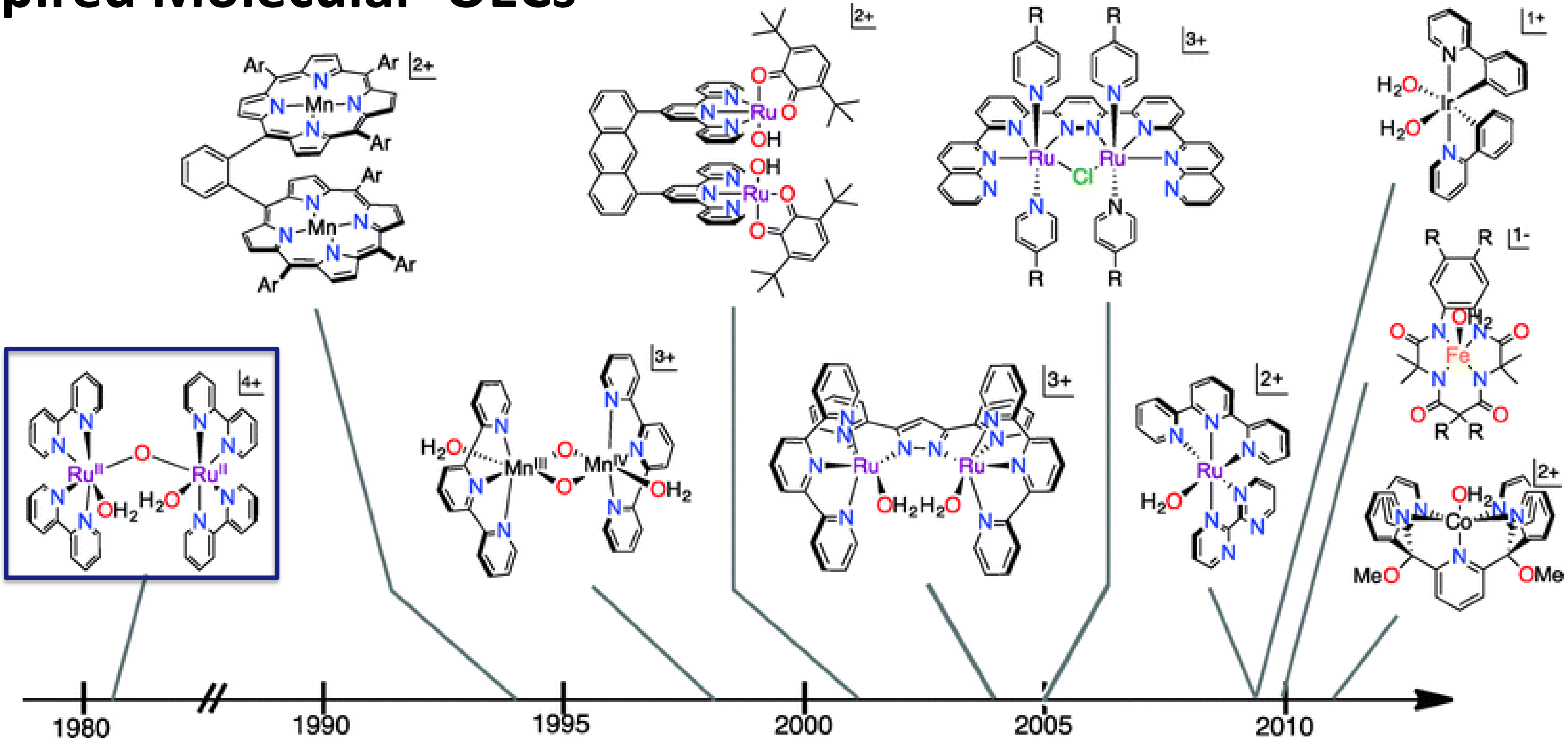
Oxygen Evolving Catalyst



artwork by Andrea Sartorel

Energy Environ. Sci. **2012**, *5*, 5592-5603

Bio-inspired Molecular OECs



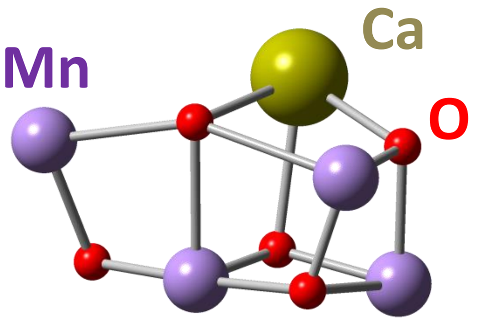
The Ruthenium Blue Dimer

the first molecular catalyst for water oxidation.

Meyer, *JACS* **1982**, *104*, 4029

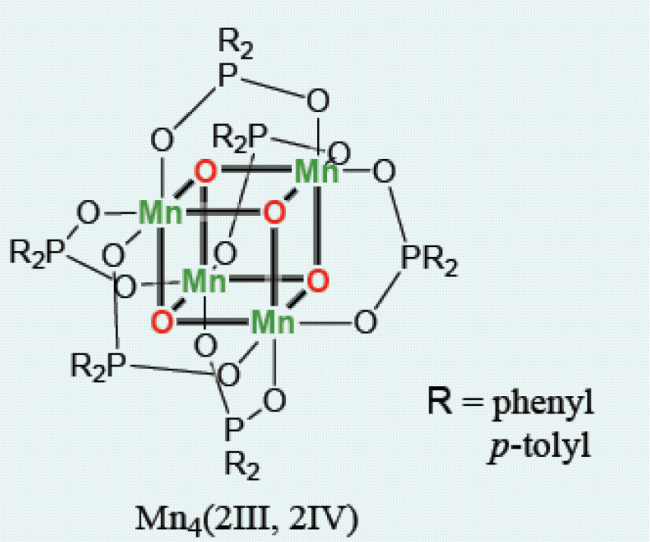
C. Berlinguette et al. Chem. Commun., **2013**, 49, 218--227

Bio-inspired Tetra-nuclear OECs



$CaMn_4Ox$

Umena, Nature 2011
Suga, Nature 2014



$Mn_4O_4(O_2PPh_2)_6$

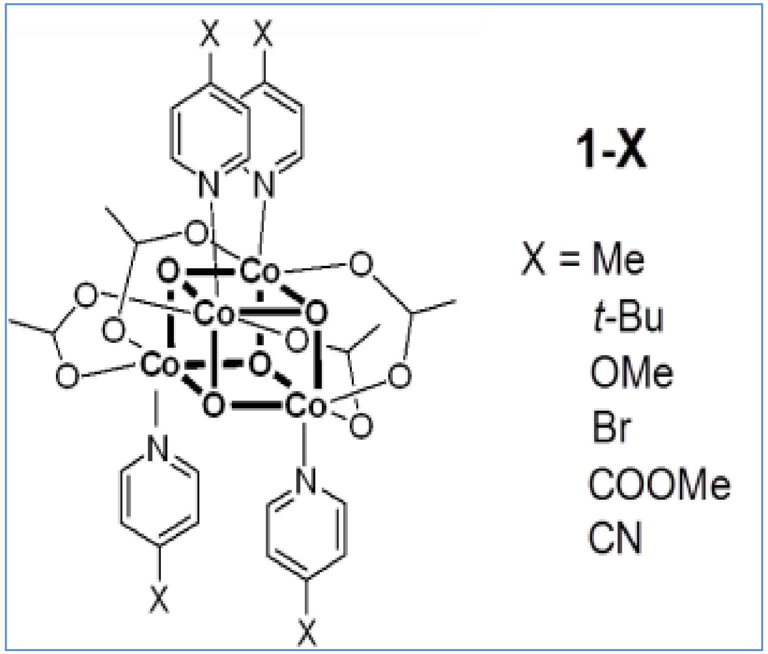
tetra-**Manganese** cubane

Dismukes et al,
Angew Chem Int Ed **2008**, 47, 7335

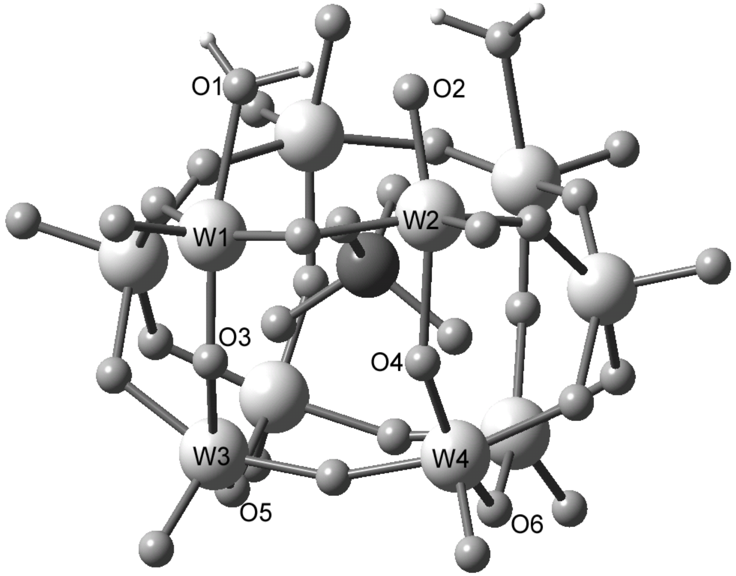
$[Co_4O_4(O_2CMe)_4(py)_4]$

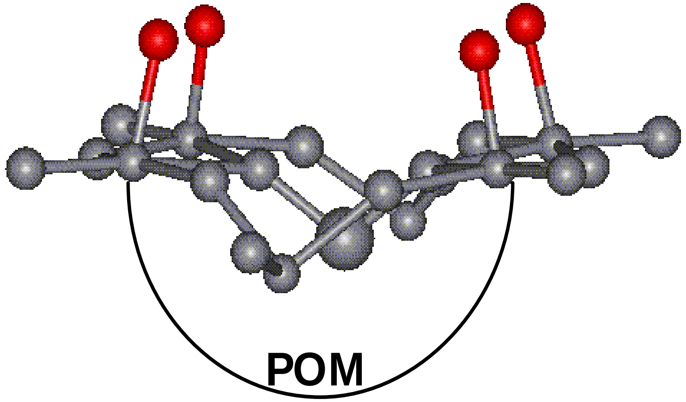
tetra-**Cobalt** cubane

Faraday Disc. **2015**, doi: 10.1039/C5FD00076A.
Faraday Disc. **2012**, *155*, 177
JACS **2012**, *134*, 11104
Dismukes et al. JACS **2011**, *133*, 11446

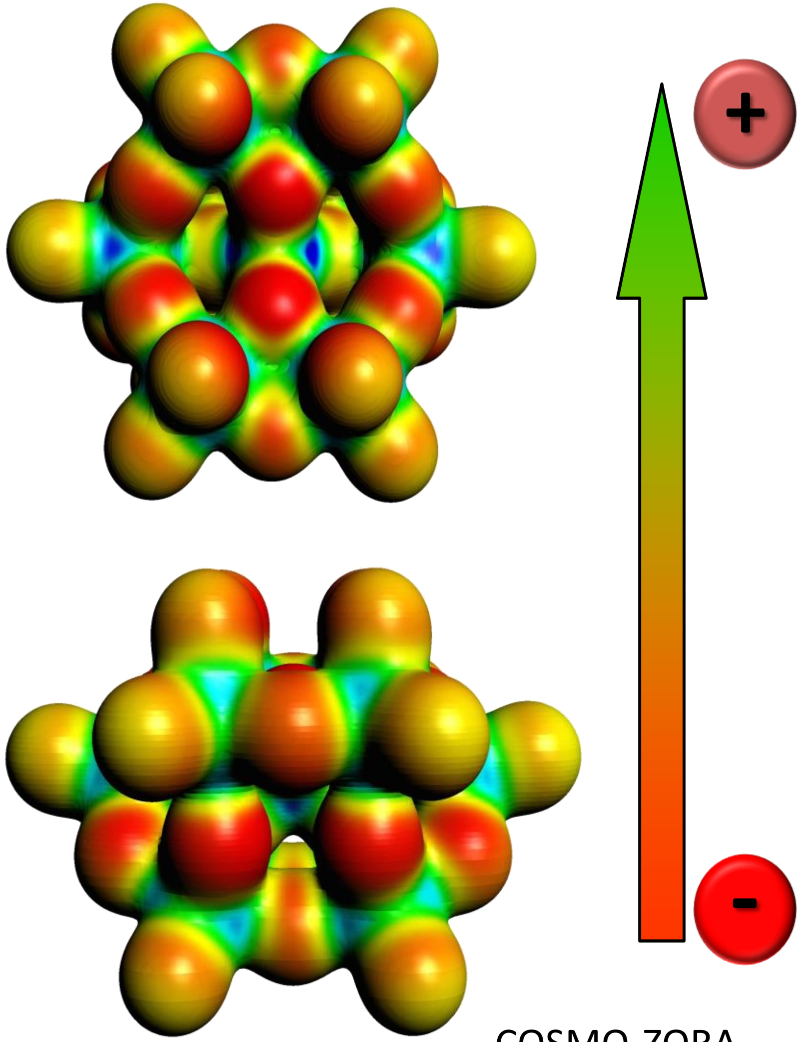


Totally Inorganic oxo-ligands: The Great Beauty of POLYOXOMETALATES





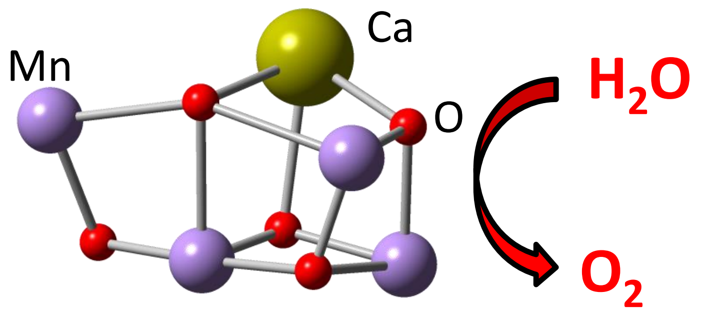
γ-$[(SiO_4)W_{10}O_{32}]^{8-}$



COSMO-ZORA
scalar BP/S-I level

Angew. Chem. Int. Engl. Ed, **2005**, *44*, 2023; *Angew. Chem. Int. Ed*, **2007**, 46, 3255

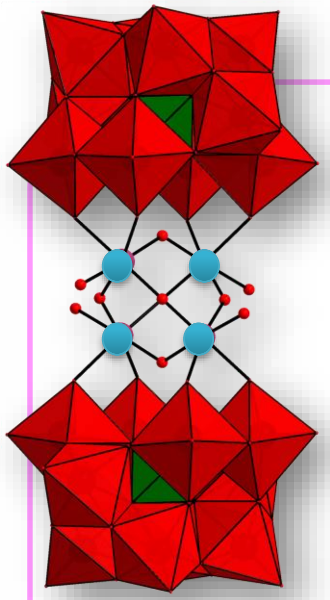
Bio-inspired POLYOXOMETALATE OECs



η <0.30 V
pH gradient (5-7)
TOF = 100-400 s^{-1}

Oxygen Evolving Centre = $CaMn_4Ox$

Suga et al., *Nature* **2015**, *517*, 99



η = 0.20 - 0.35 V
pH 1 - 7
TOF_{max} = 280 s^{-1}

The tetraruthenium polyoxometalate as the first example of a series of all-inorganic **POM**- based OECs

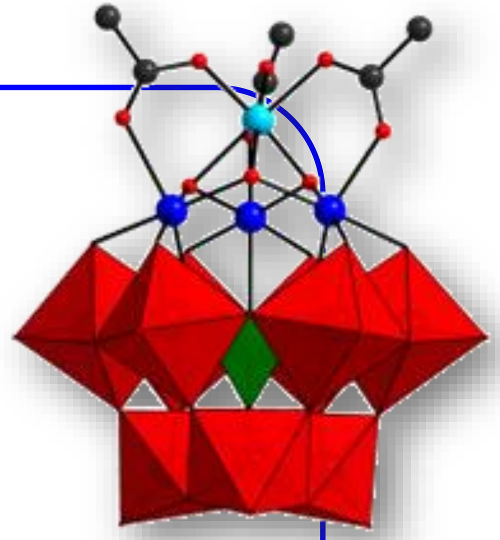
Ru_4POM

Energy Environ. Sci. **2012**, *5*, 5592

η = 0.53 V
pH 5.2
TOF_{max} = 2.84 x 10^{-3} s^{-1}

Mn_4POM has structural features and the behaviour in a photoactivated cycle reminescent of the natural OEC.

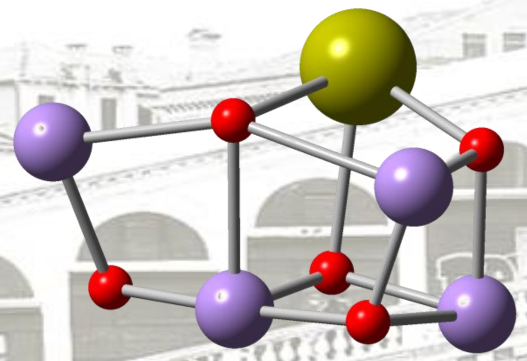
Mn_4POM



Angew. Chem. **2014** , 126, 11364

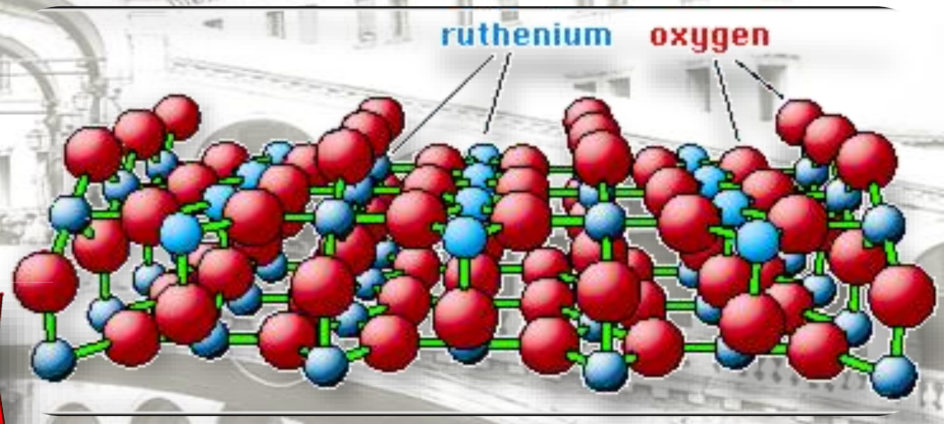
From Natural to Artificial OEC

PSII-OEC

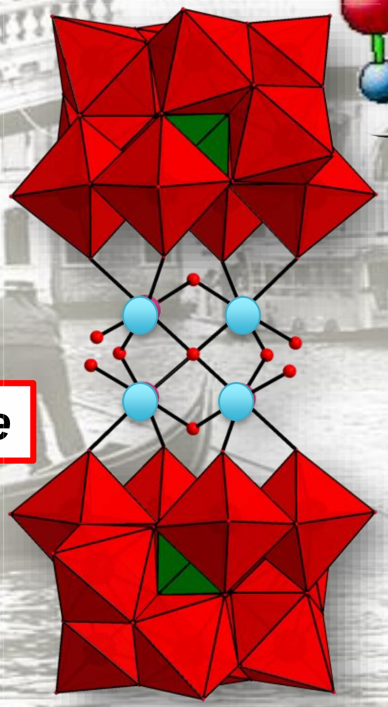


Umena, *Nature* **2011**, 473, 55

RuO_2 rutile structure



J.K. Nørskov *Nature Chem.*,**2009**



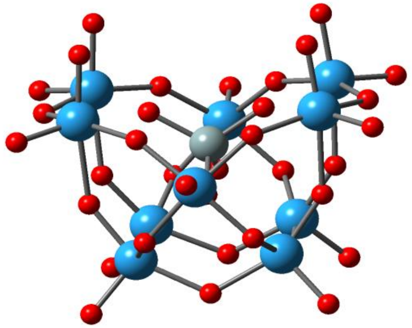
Ru_4O_6 core

PNAS **2013**, *110*, 4917

$[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\gamma\text{-}(SiW_{10}O_{36}]^{10-}$

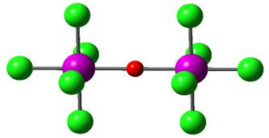
Ru_4POM: $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\gamma\text{-}(SiW_{10}O_{36})_2]^{10-}$

Andrea Sartorel



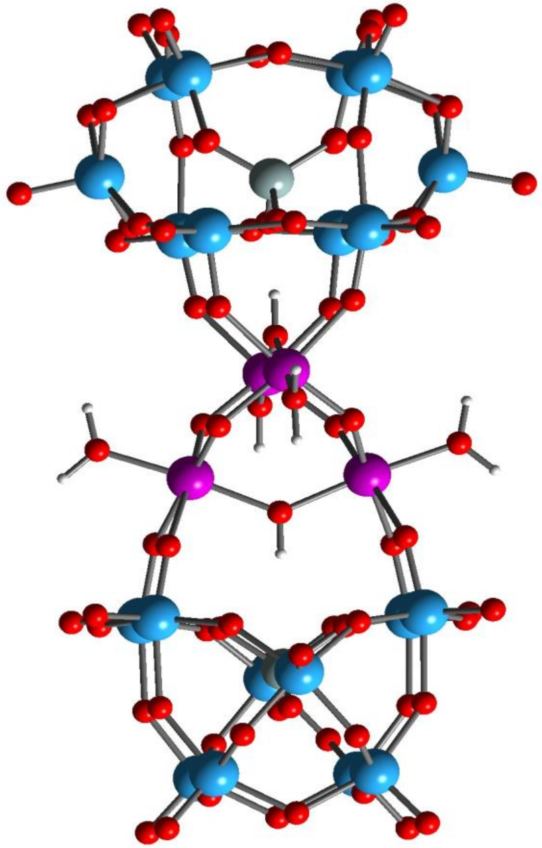
$K_8\gamma$-[$(SiO_4)W_{10}O_{36}$]

+



$K_4(\mu\text{-}O)Ru_2Cl_{10}$

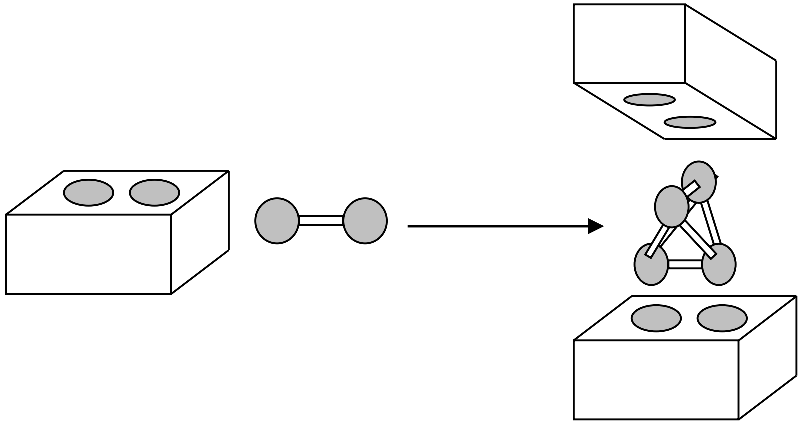
1. H_2O, 70°C, 1 h
2. CsCl



Ru_4POM

80% isolated yield

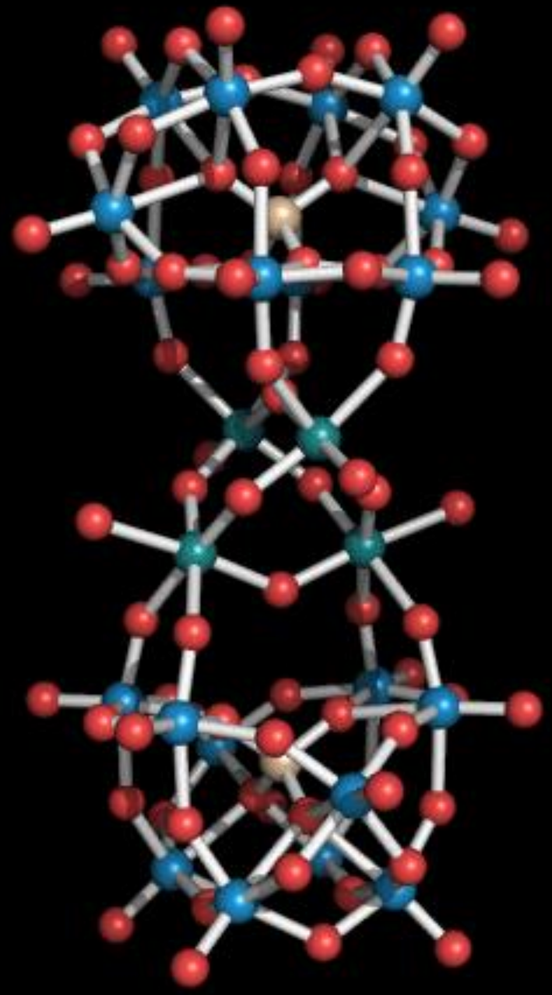
gram-scale



J. Am. Chem. Soc. **2008**, *130*, 5006; *J. Am. Chem. Soc.* **2009**, *131*, 16051.

Highlight by Georg Suess-Fink *Angew. Chem. Int. Ed.* **2008**, 47, 5888 – 5890

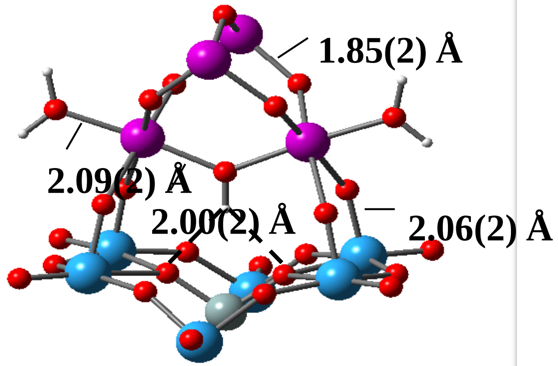
➢ POM embedded tetra-Ruthenium(IV)-OEC

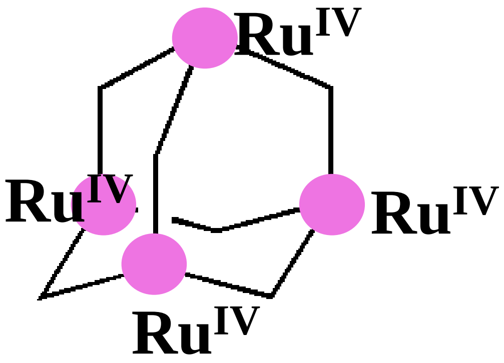


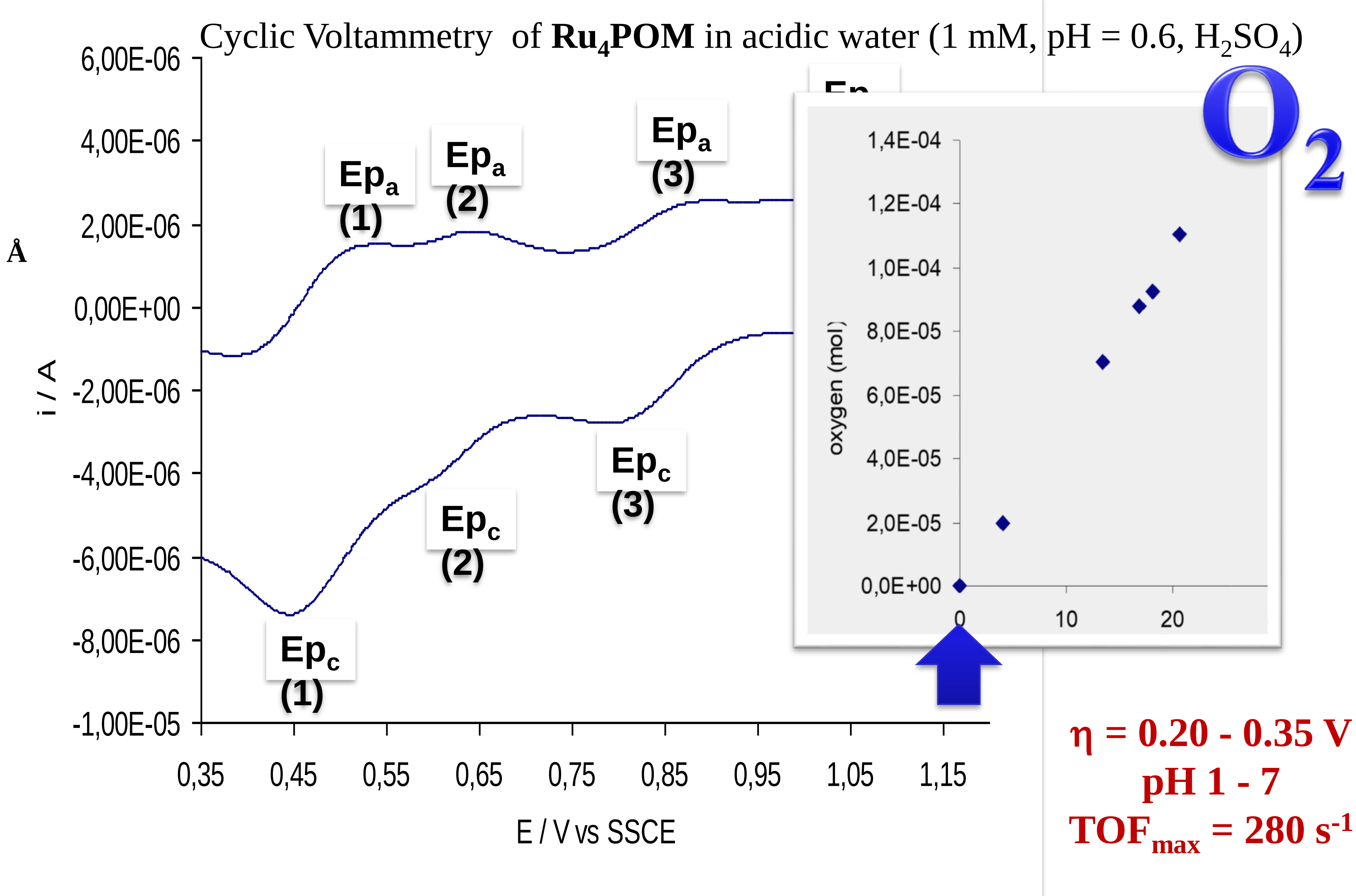
Crystal Structure solved @UniTS by Rita De Zorzi & Silvano Geremia

J. Am. Chem. Soc. **2008**, *130*, 5006; *J. Am. Chem. Soc.* **2009**, *131*, 16051.
Highlight by Georg Suess-Fink *Angew. Chem. Int. Ed.* **2008**, 47, 5888 – 5890

tetra-ruthenium(IV)-OEC-core / Artificial Kok-Joliot cycle ($4e^-$ /$4H^+$)





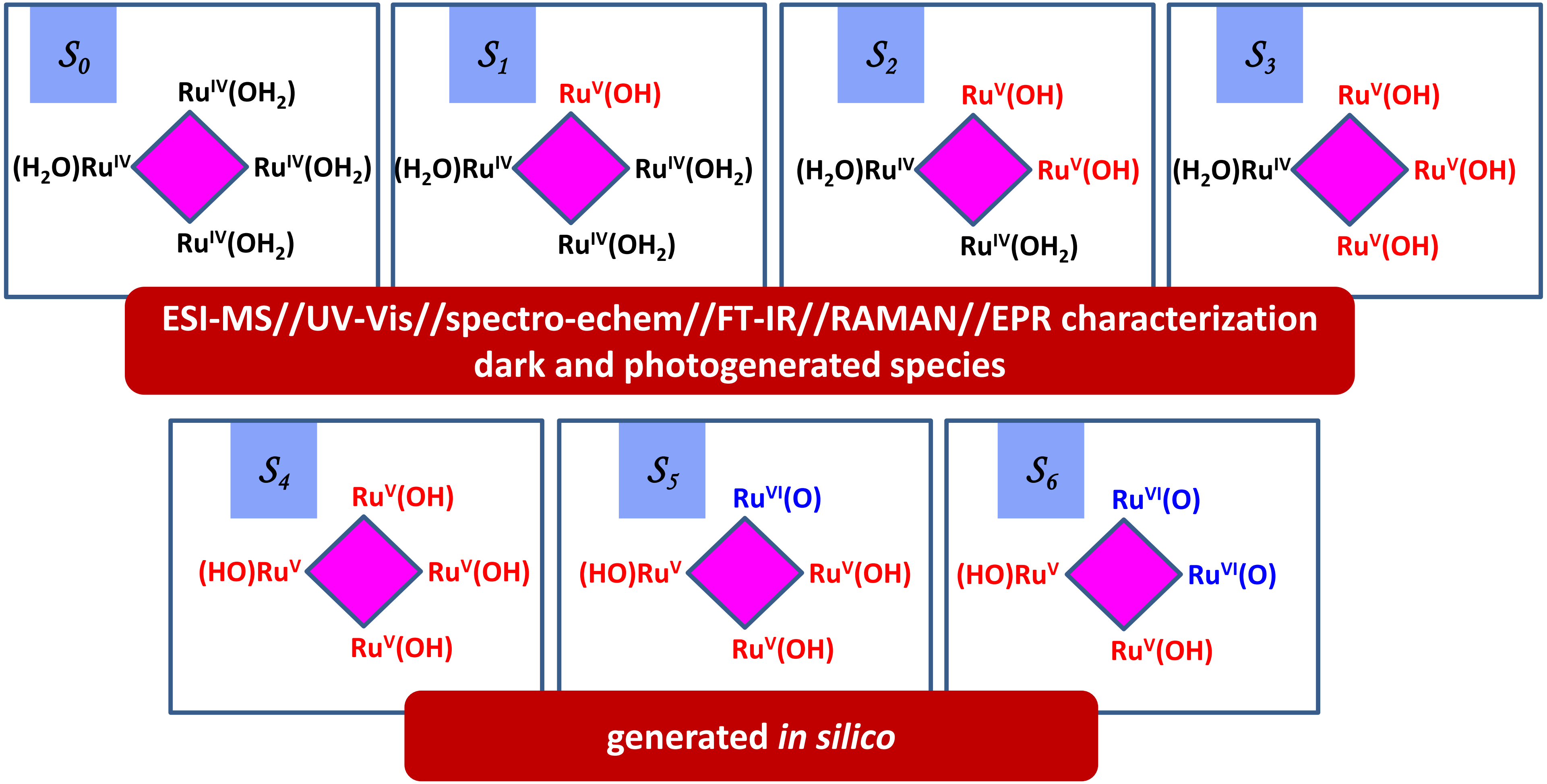


η = 0.20 - 0.35 V
pH 1 - 7
TOF_{max} = 280 s^{-1}

J. Am. Chem. Soc. **2009**, *131*, 16051.
PNAS **2013**, *110*, 4917

Oxygen evolution (followed by GC) during the electrolysis of 15.9 10^{-6} mol of **Ru_4POM** at 1.15 V, using a carbon grid as working electrode

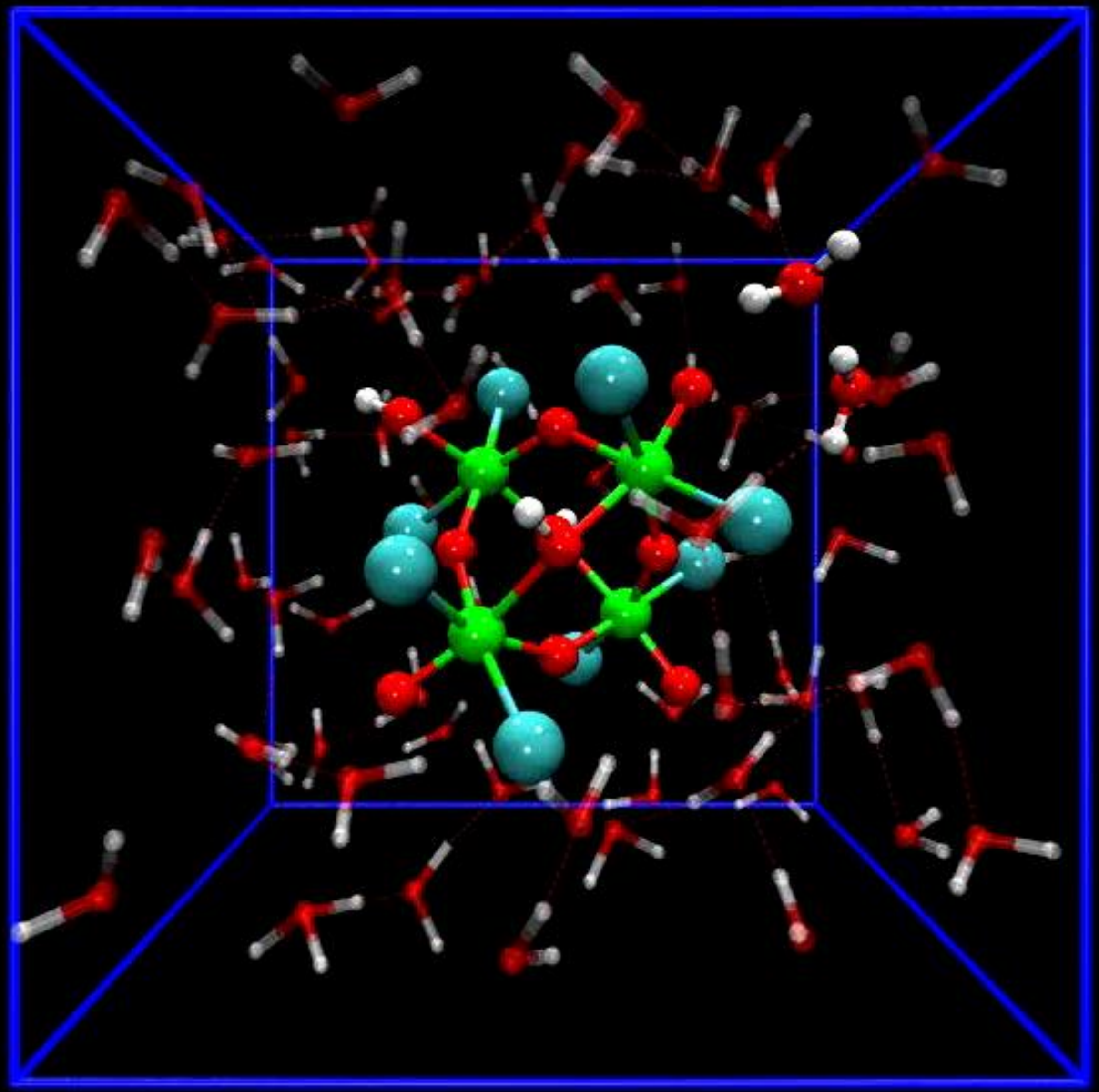
Ru_4POM OEC – Artificial Kok-Joliot cycle ($4e^-$ /$4H^+$)



Ru^{VI} states are needed to reach the thermodynamic for water oxidation
The rate determining step is a **Water Nucheophilic Attack** forming the oxygen-oxygen bond

PNAS **2013**, *110*, 4917 *with S. Piccinin, S. Fabris (SISSA, Trieste, Italy)*

➢ Water Nucleophilic Attack at Ru(VI)-oxo sites: Ru-PEROXIDE



PNAS **2013**

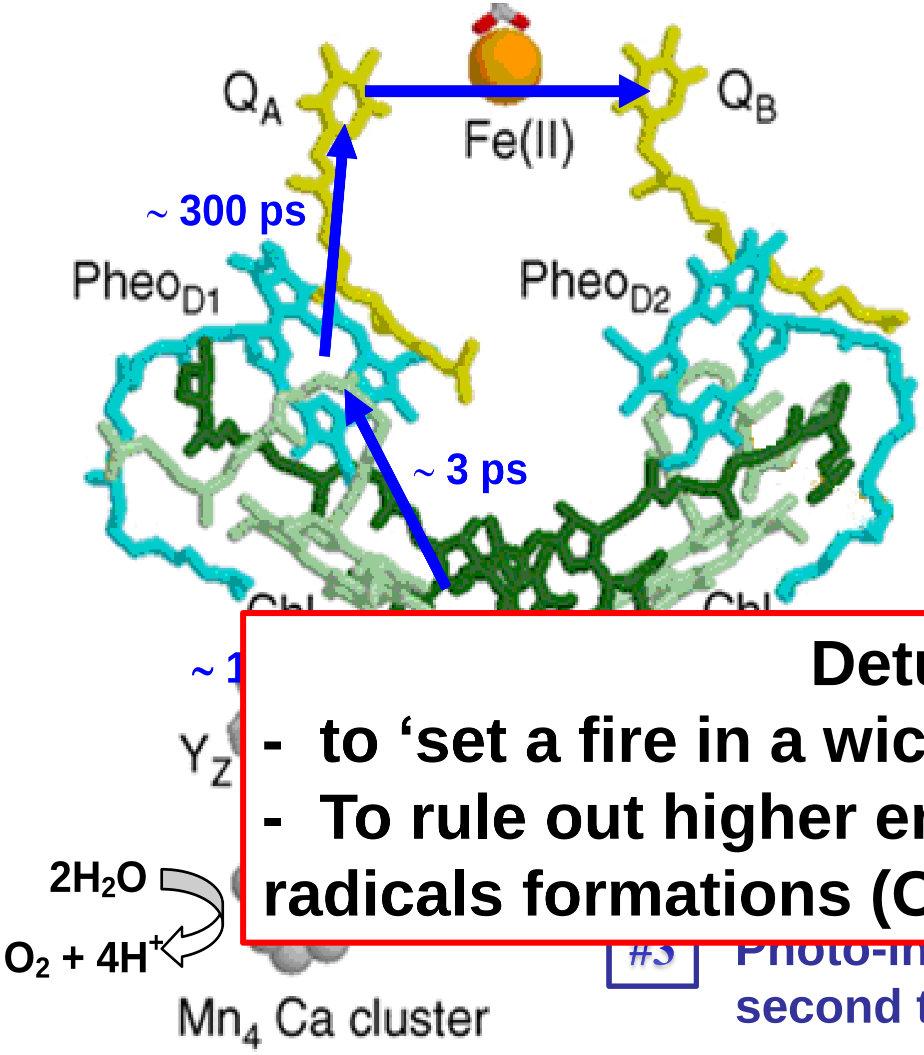
with S. Piccinin, S. Fabris (SISSA, Trieste, Italy)

Tuning
Artificial Photosynthesis @

Nano-hybrid Interfaces

OEC @ FUNCTIONAL INTERFACES

#2 **An electron road: electron transfer cascade**



(1) the photo-oxidised reaction centre, **P680/P680+·**, has a redox potential of ~1.3–1.4 V

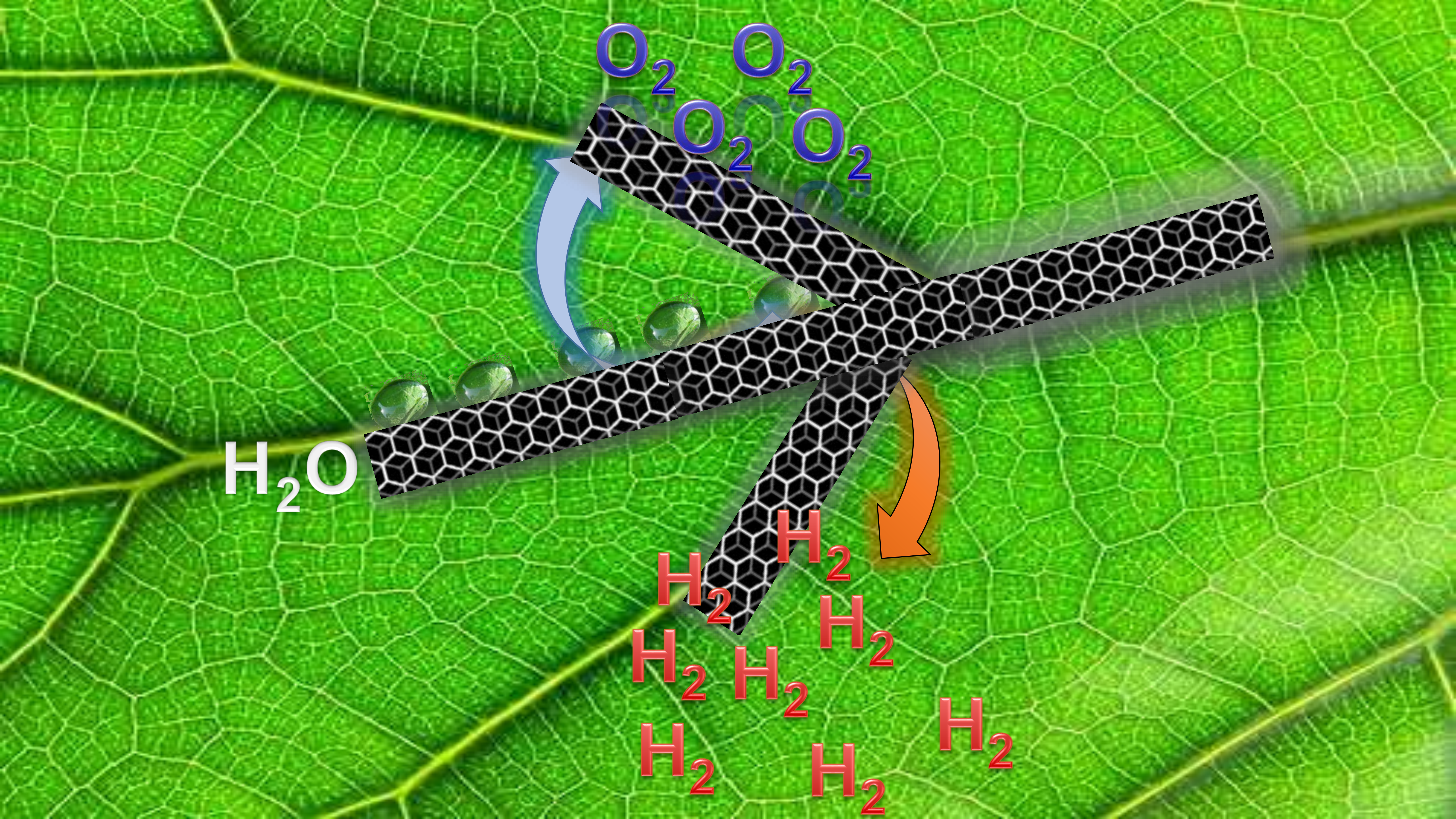
(2) this is ‘detuned’ to 1.0–1.1 V on passage through the tyrosine (Yz), before communicating directly with the Mn cluster in the OEC, which must operate at a level close to 0.9 V

(3) pH=5-7 implies a minimal overpotential

Detuning the OEC allows

- **to ‘set a fire in a wicker basket, without burning the basket’**
- **To rule out higher energy pathways resulting in free radicals formations (OH·/HOOH)**

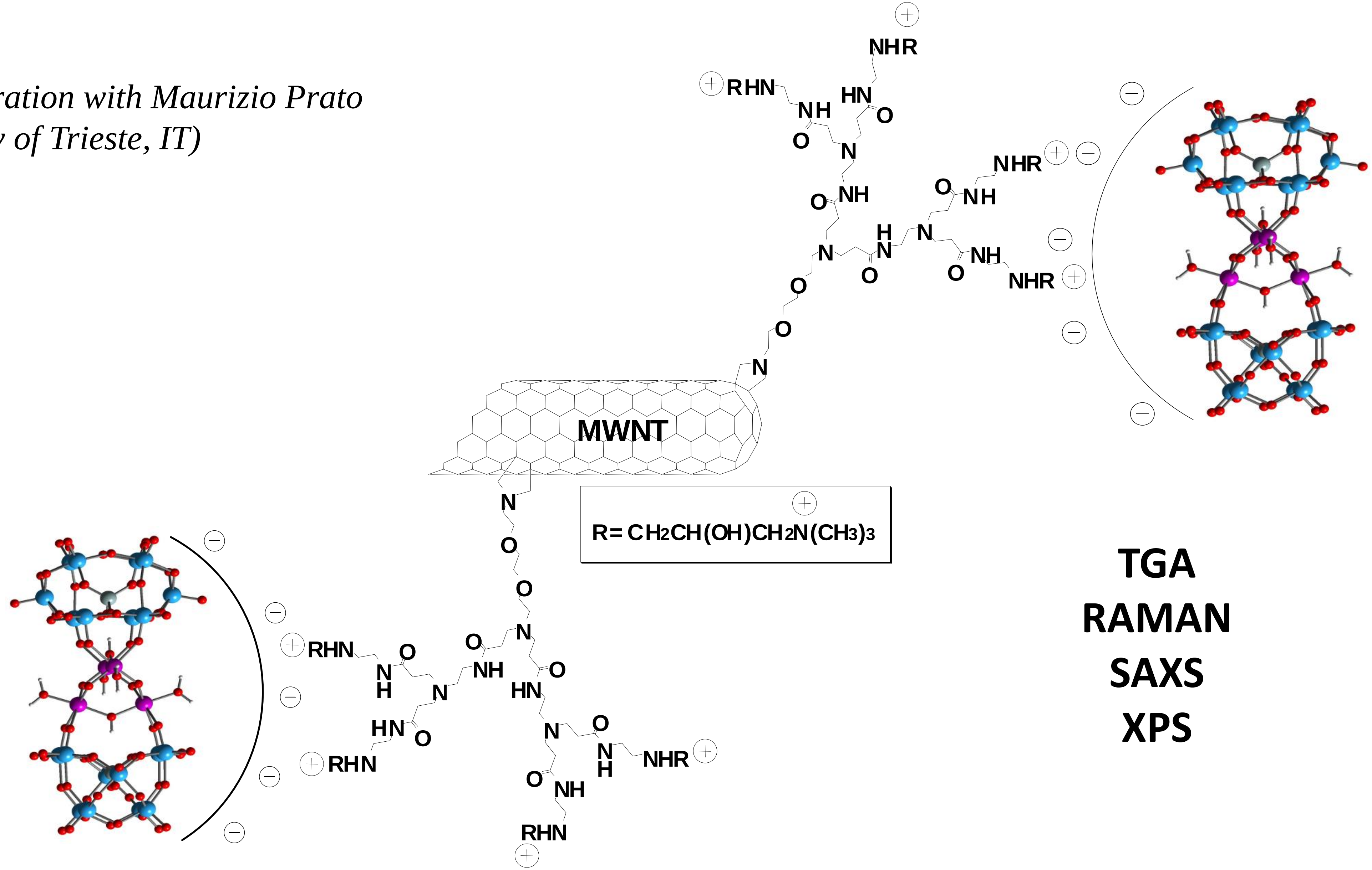
#3 **Photo-induced ET within nano- to micro-second time domain**



O2 O2
O2 O2
H2O
H2
H2
H2
H2
H2
H2
H2
H2

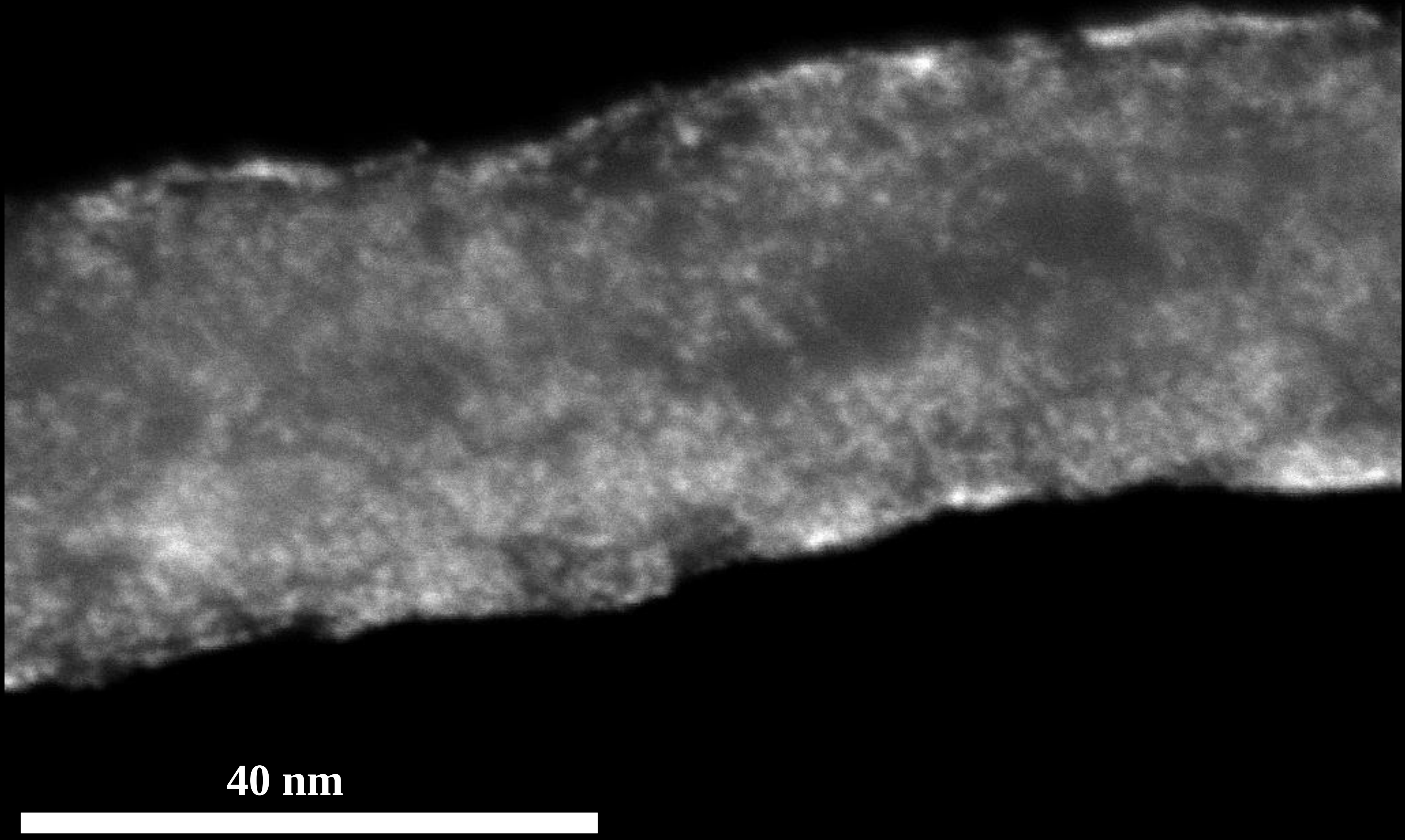
OEC @ FUNCTIONAL INTERFACES: CNTs decorated with Ru_4POM

In collaboration with Maurizio Prato (University of Trieste, IT)

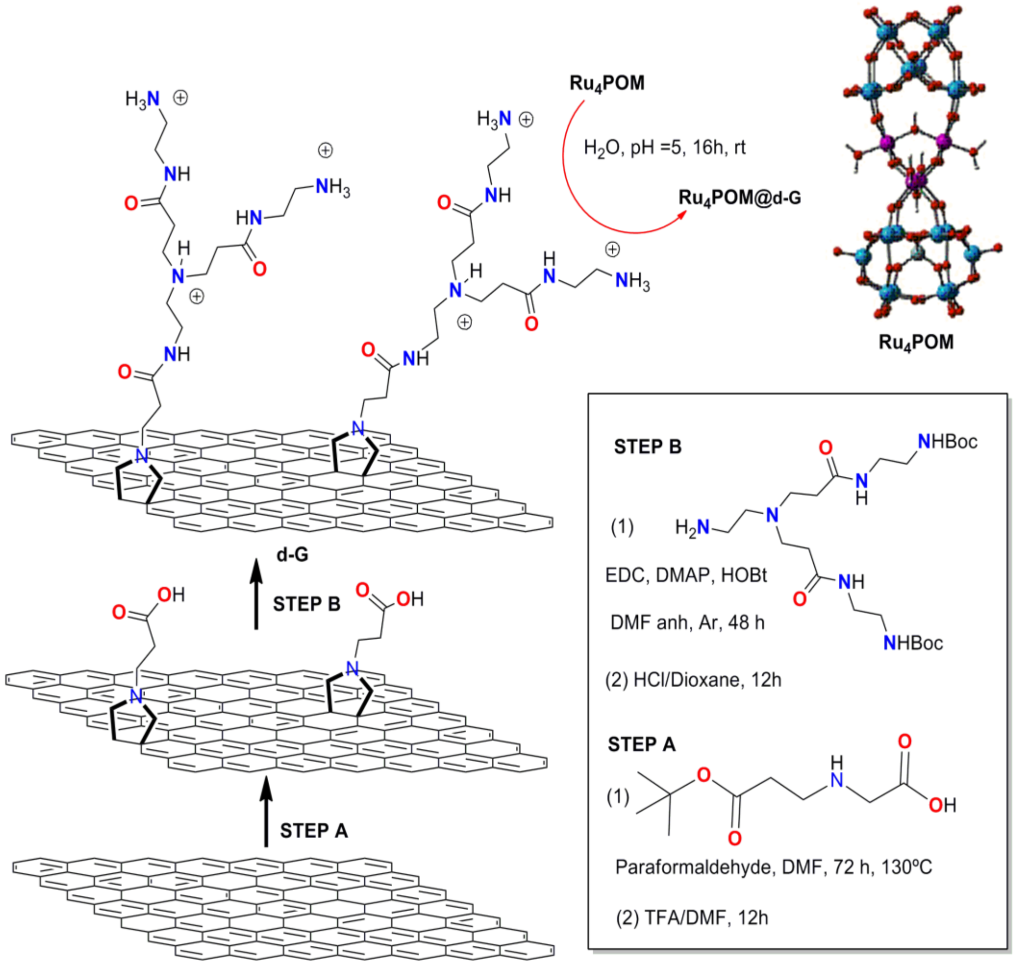


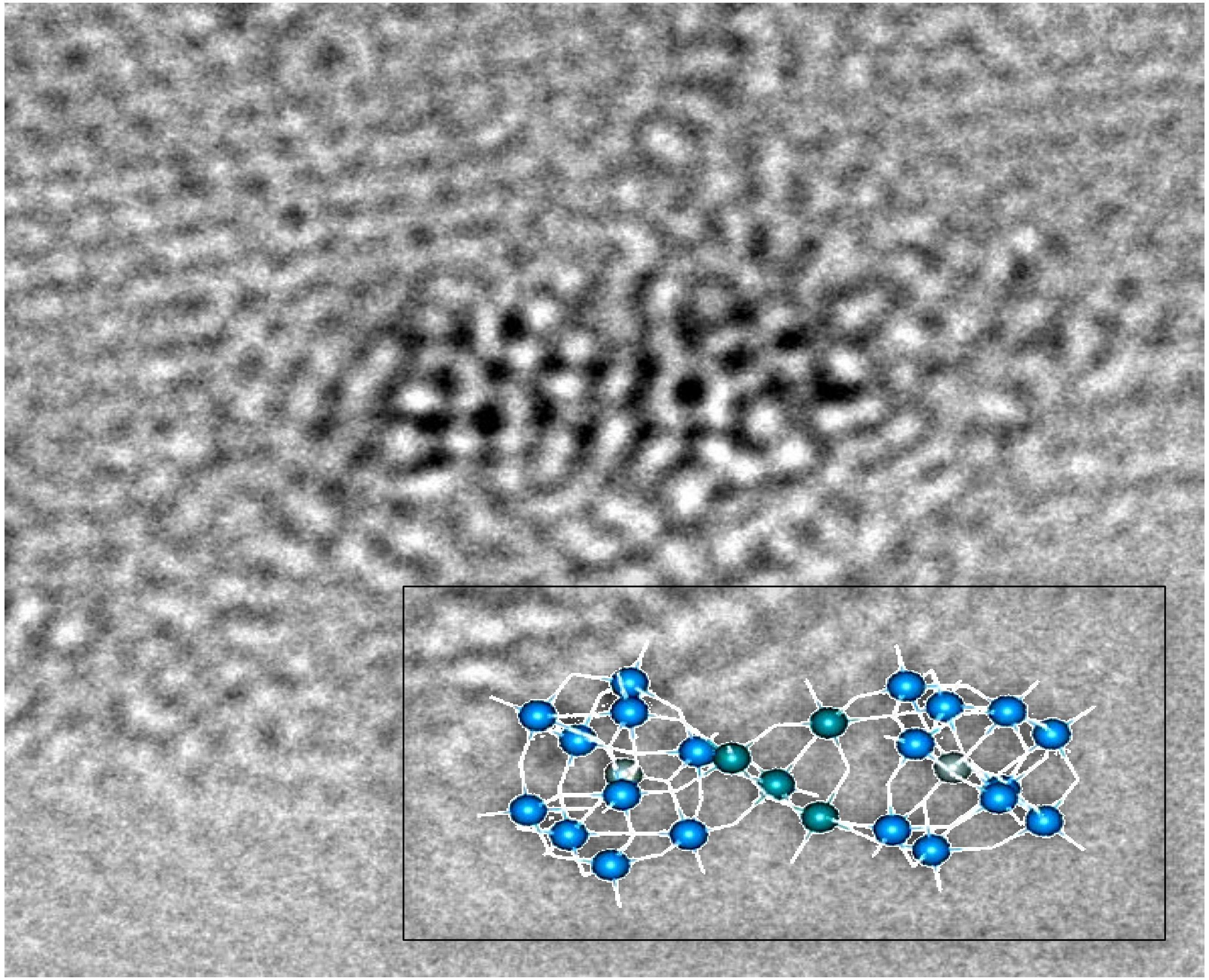
TGA
RAMAN
SAXS
XPS

Nature Chem. **2010**, *2*, 826-831


40 nm

Ru_4POM@d-G: positive 2D-graphene nano-platform





with Maurizio Prato (University of Trieste, Italy)

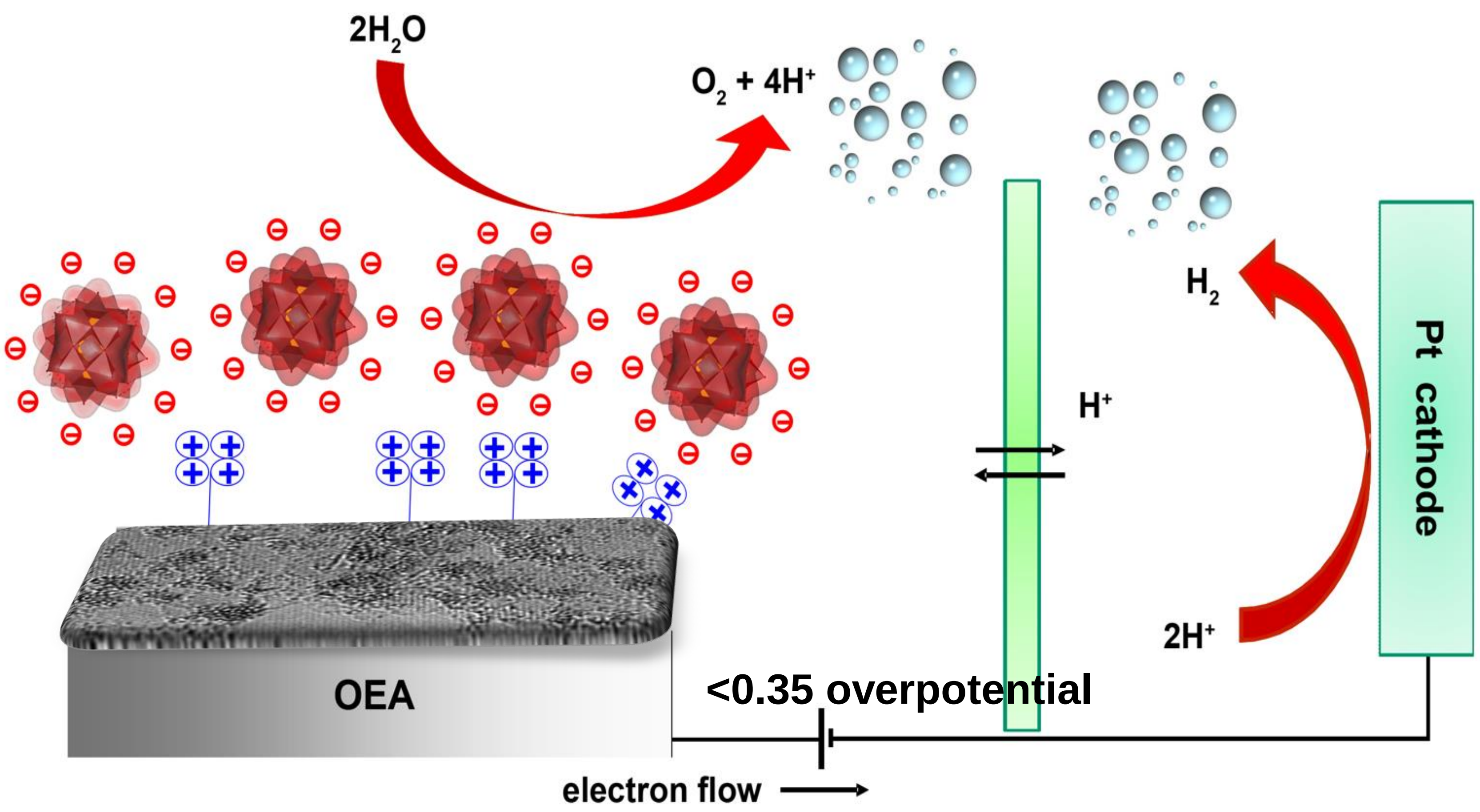
Nature Chem. **2010**, *2*, 82, 831; *Chem Sus Chem* **2011**, *4*, 1447, *ACS Nano* **2013** , *7*, 811

Dynamics of Ru_4POM on the Graphene nano-platform

POM changes its orientation continuously along the time (HRTEM electron beam 80 kV)

With X. Ke C. Bittencourt, G. Van Tendeloo SMALL ***2013***

Ru_4POM@CNS: electrocatalytic nano-interfaces



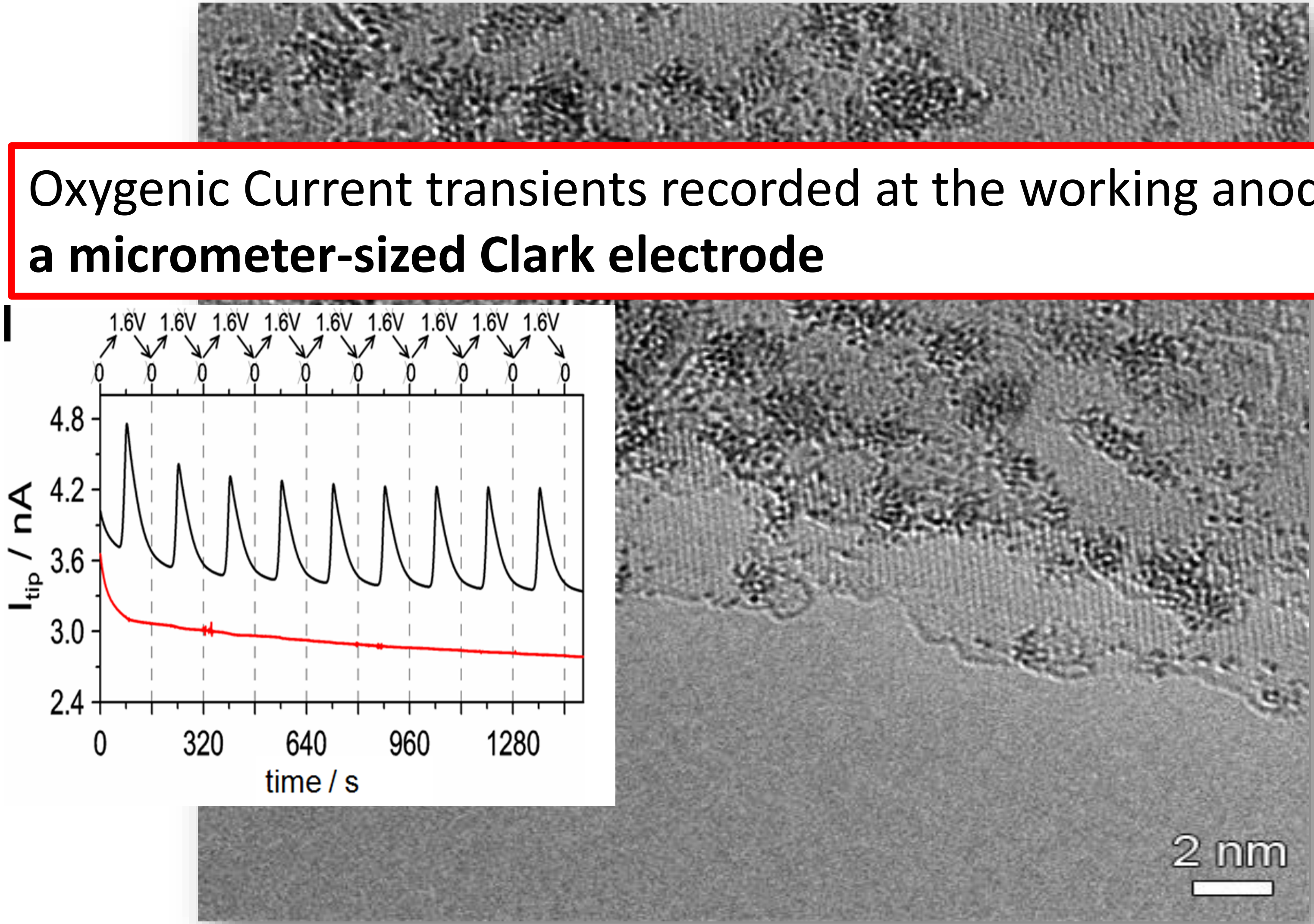
Boosting effect in O_2 evolution with functionalized CNSs at overpotential 0.30-0.35V

Nature Chem. **2010**, *2*, 82, 831; *Chem Sus Chem* **2011**, *4*, 1447, *ACS Nano* **2013** , *7*, 811

ELECTROCATALYTIC SURFACES:

Graphene nano-sheets decorated with Ru_4POM

Oxygenic Current transients recorded at the working anode **by a micrometer-sized Clark electrode**

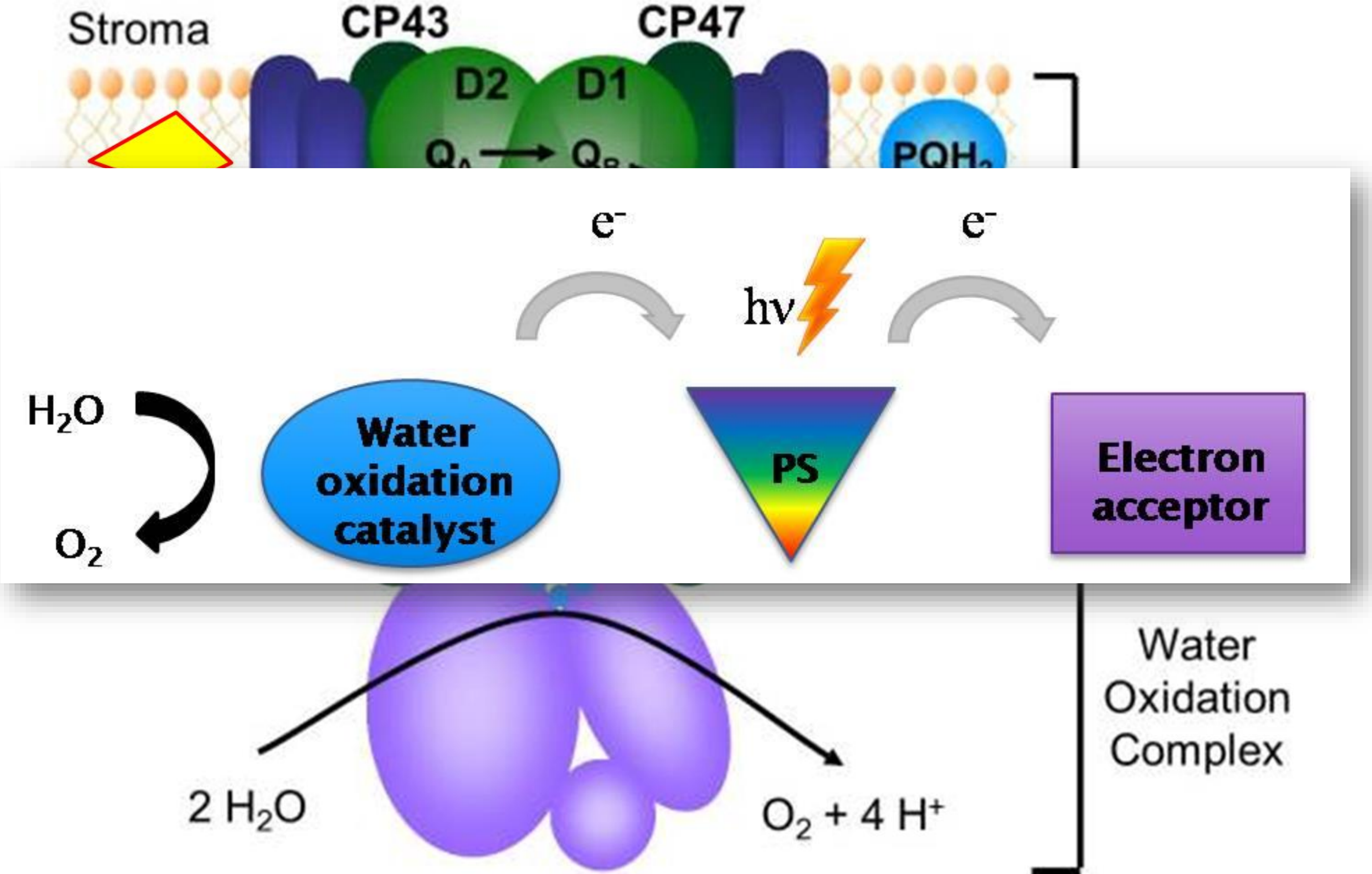


with Francesco Paolucci (University of Bologna, Italy)

Nature Chem. **2010**, *2*, 82, 831; *Chem Sus Chem* **2011**, *4*, 1447, *ACS Nano* **2013** , *7*, 811

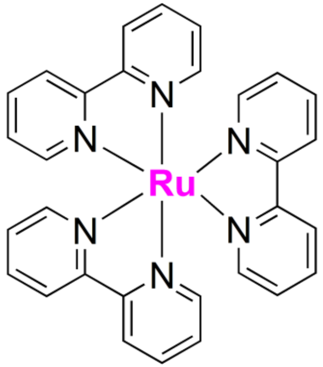

s.harris

PSII: photo-induced water oxidation

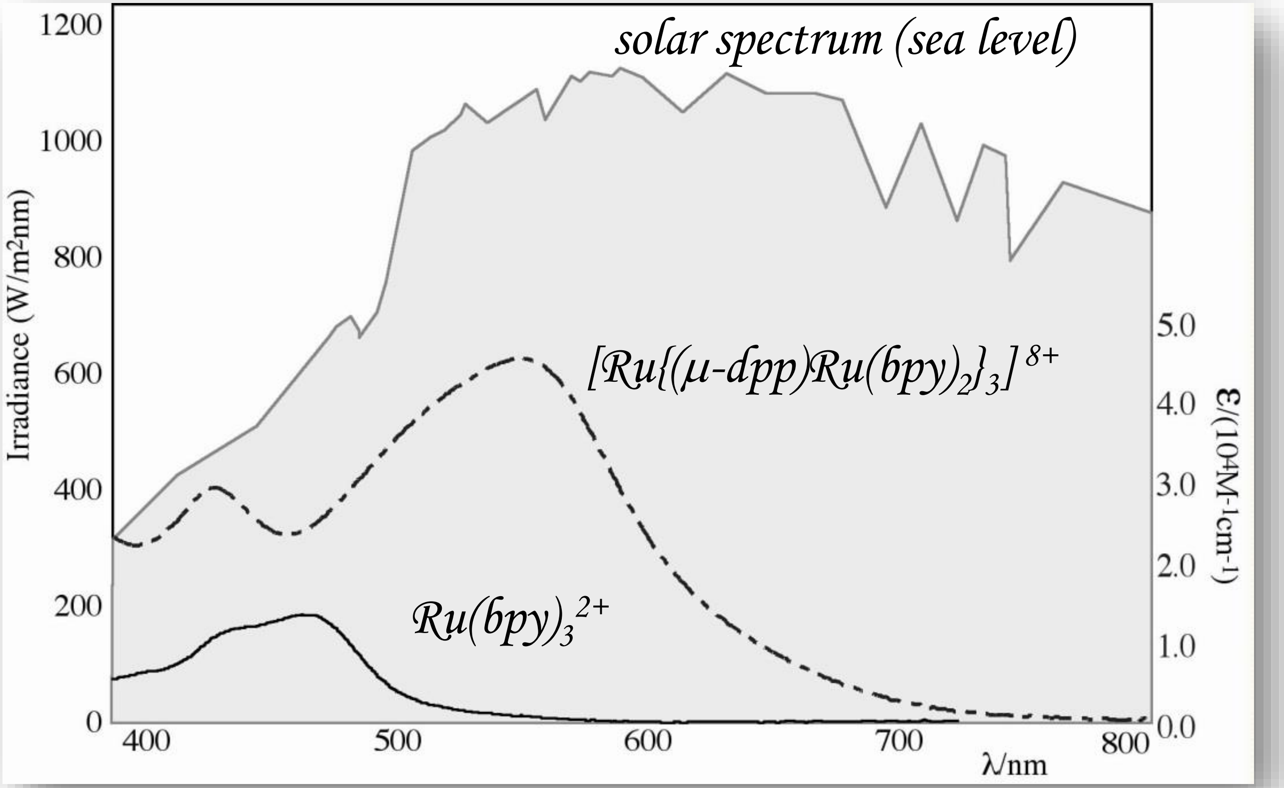


➢ Antenna-type Dendrimeric Ru(II) Sensitizers

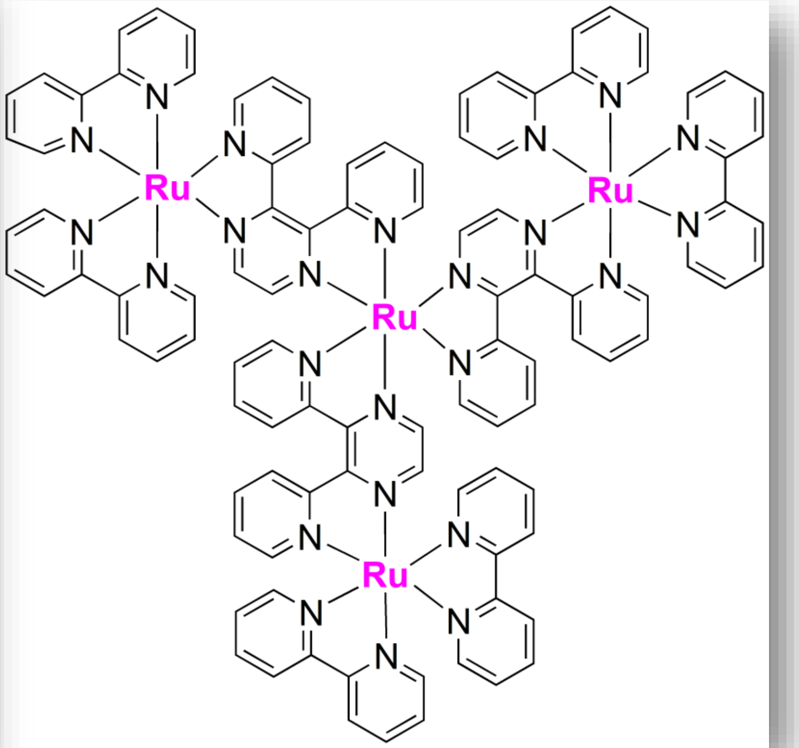
In collaboration with S. Campagna, F. Puntoriero, G. La Ganga (Univ. of Messina)



Ru(bpy)$_3^{2+}$



Extended absorption in the Visible (better match with solar emission)



Ru{(μ-dpp)Ru(bpy)$_2$}$_3^{8+}$

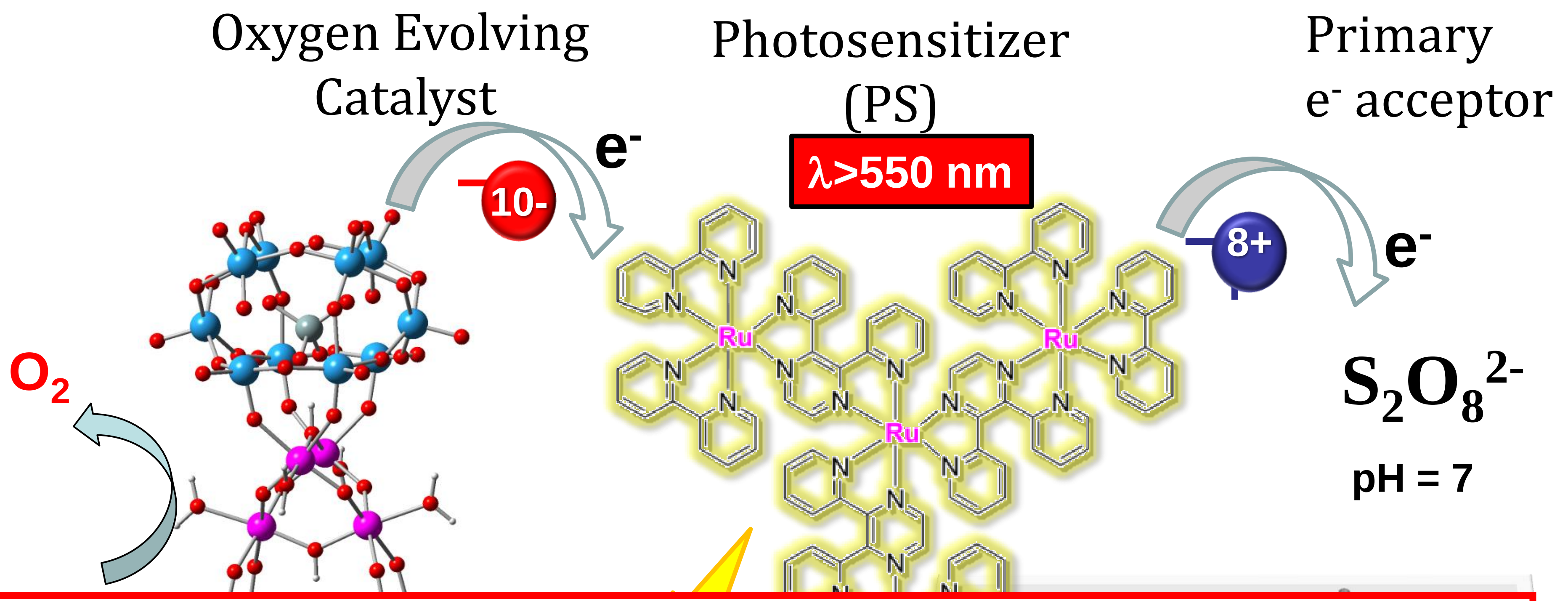
E Ru(bpy)$^{3+/2+}$ **= +1.26 V vs NHE**

E Ru$_4$PS$^{*8+/7+}$ **= +1.38 V vs NHE**

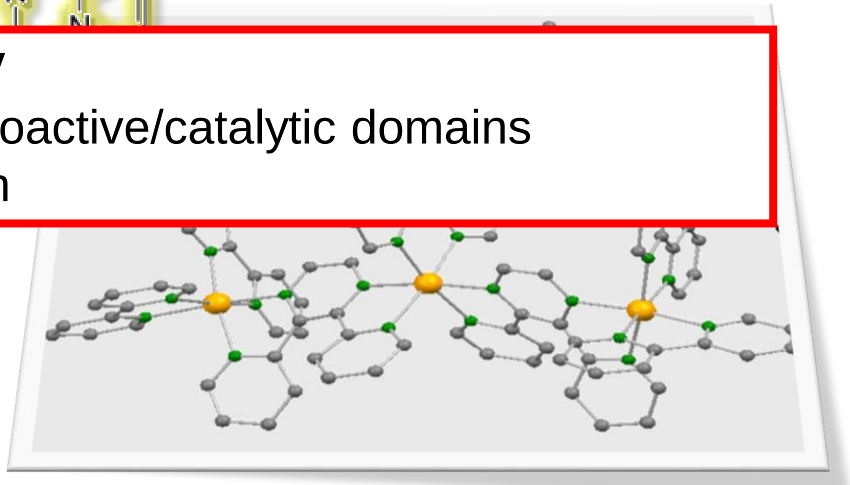
Coord. Chem. Rev. **2011**, *255*, 2594; *Topics in Current Chemistry* **2011**, *303*, 121

Antenna-type $Ru(II)_4$ photosensitizers

S. Campagna (University Messina) F. Scandola and M. Natali (University of Ferrara)



- Higher Thermodinamic driving force > 200 mV
- **electrostatic assembly**/organization of the photoactive/catalytic domains
- **High chemical yield** >90% persulfate conversion



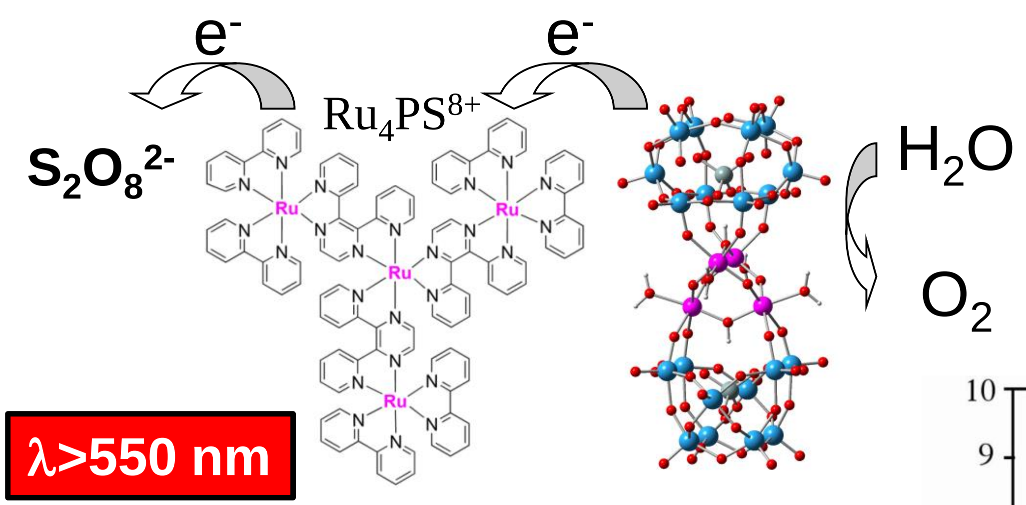
Ru_4POM

$[Ru_4dend]^{8+}$

Chem. Commun. **2010**, *46*, 4725
J. Phys. Chem. C **2015**, *119*, 2371

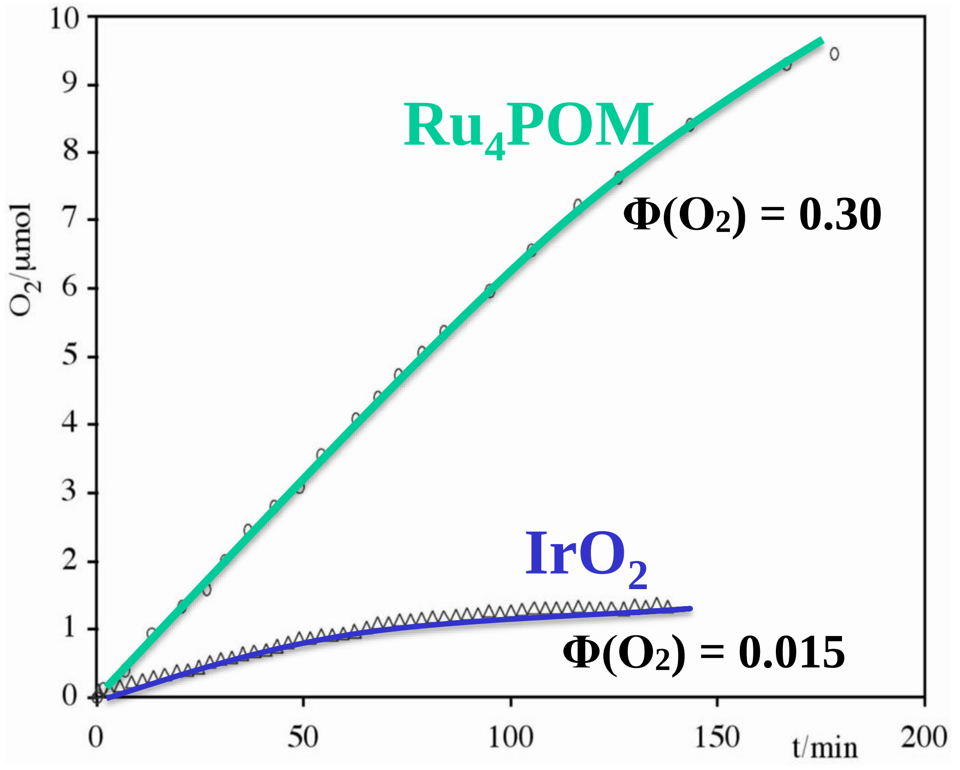
$Ru(II)_4$ dendrimer / Ru_4POM – Oxygen Evolution

with S. Campagna, F. Puntoriero, G. La Ganga (University Messina)



Oxidant species	E (V) vs NHE	Φ (O_2)
$Ru(bpy)^{3+/2+}$	+1.26	0.045
$Ru_4PS^{*8+/7+}$	+1.38	0.30

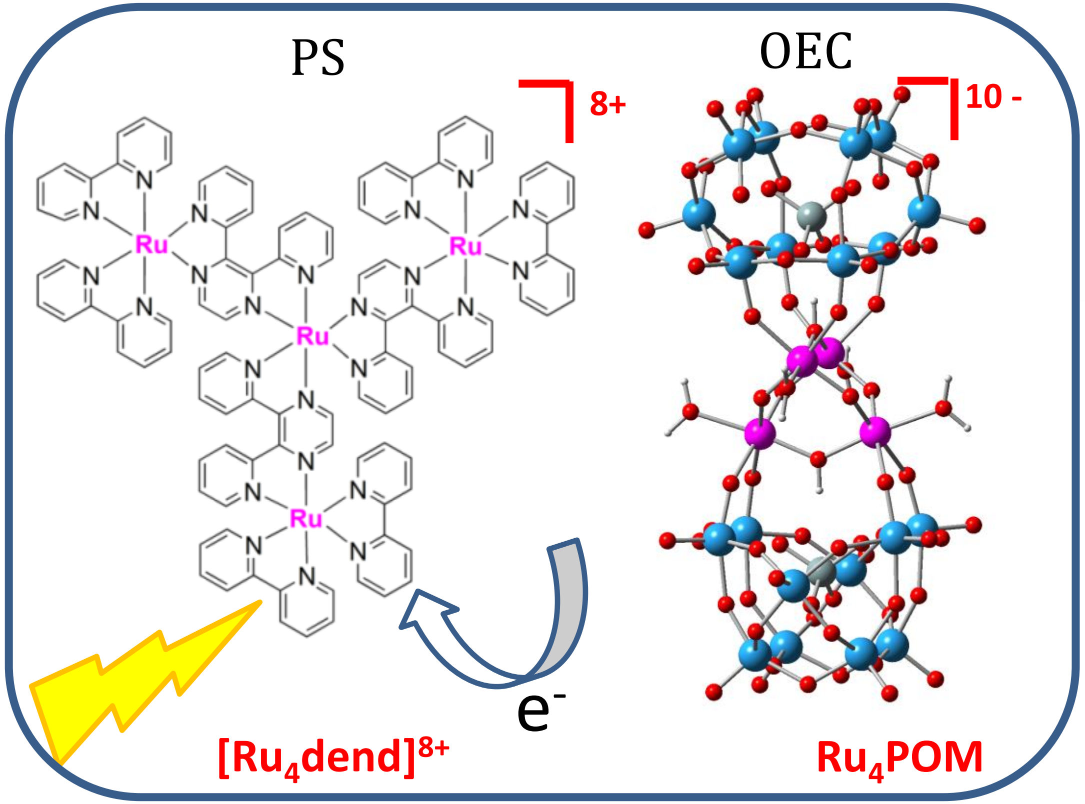
[Ru_4PS] = 100 µM
[Ru_4POM] = 60 µM
[S_2O_8]$^{2-}$ = 10 mM
pH 7



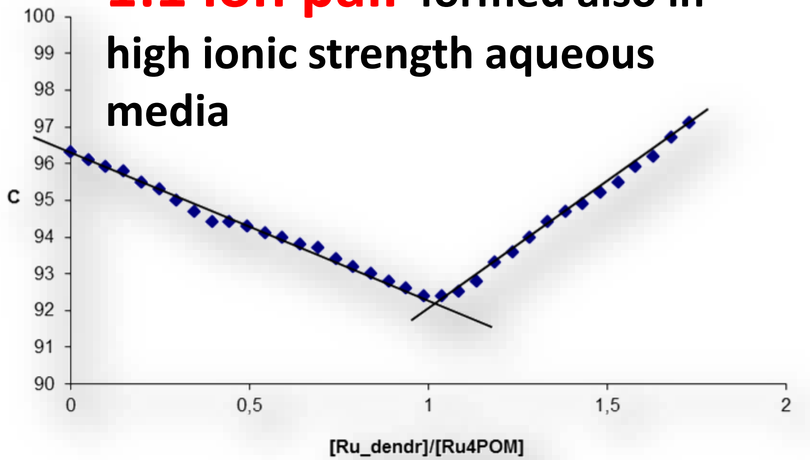
Chem. Commun. **2010**, *46*, 4725
J. Phys. Chem. C **2015**, *119*, 2371

Ru(II)$_4$ dendrimer / Ru$_4$POM electrostatic assembly

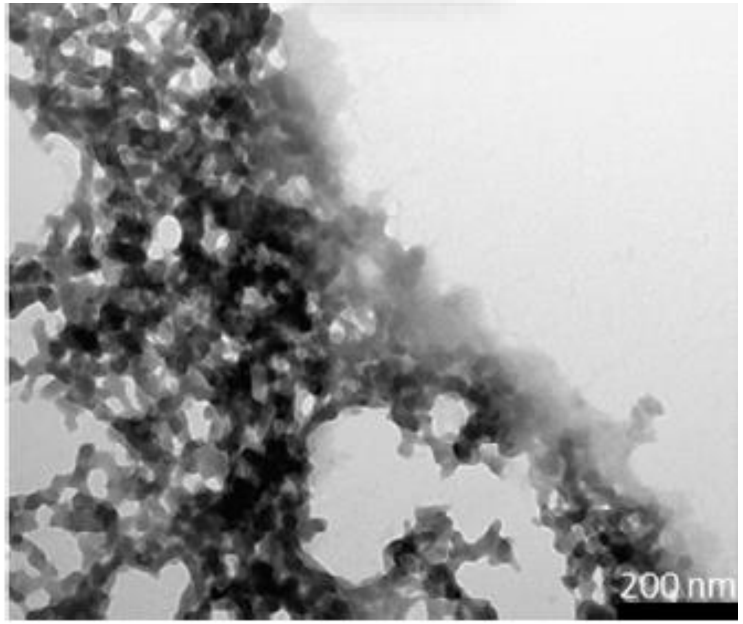
S. Campagna (University Messina) F. Scandola and M. Natali (University of Ferrara)



1:1 ion pair formed also in high ionic strength aqueous media



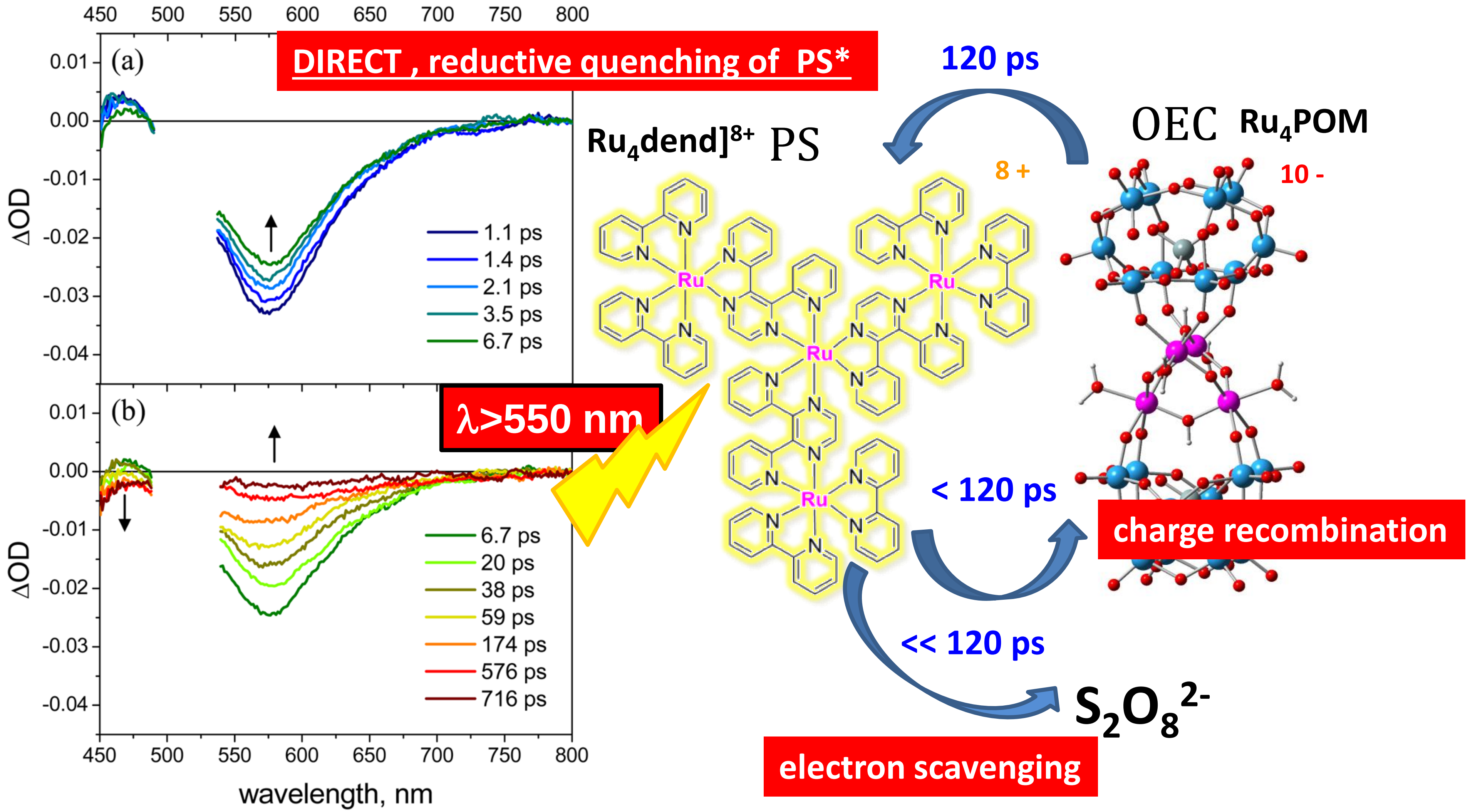
TEM evidence of 3D-porous amorphous aggregates



Chem. Commun. **2010**, *46*, 4725
J. Phys. Chem. C **2015**, *119*, 2371

Ru(II)$_4$ dendrimer / Ru$_4$POM electrostatic assembly

S. Campagna (University Messina) F. Scandola and M. Natali (University of Ferrara)



ultrafast spectroscopy: (i) bleach recovery of the MLCT band
(ii) POM (h+) observed as the permanent bleach at 475 nm

Chem. Commun. **2010**, *46*, 4725;
J. Phys. Chem. C **2015**, *119*, 2371

But WHY are light-harvesting antennas needed at all?

Rienk van Grondelle NATURE|Vol 463|4 February 2010

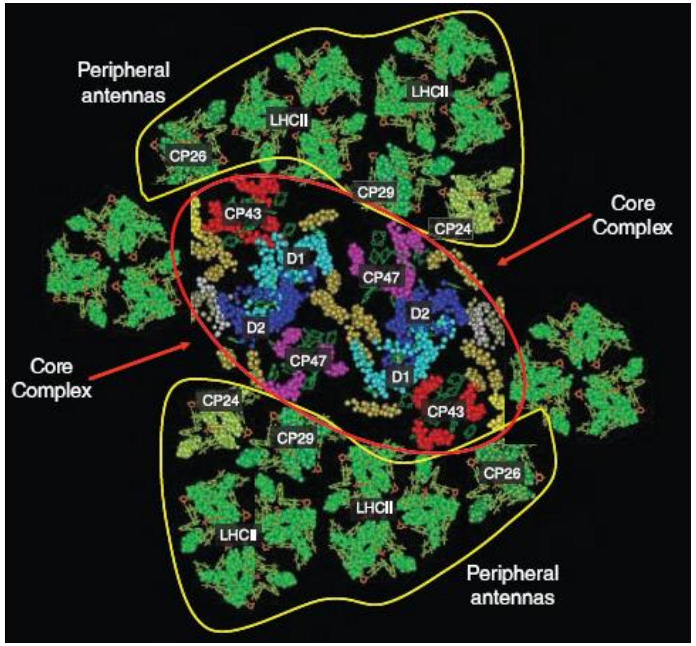
1) **Antennas act to concentrate the electronic excitations** from hundreds of light-absorbing pigments into a single reaction centre: Photosynthetic reactions require more then ONE-photon/ ONE electron mechanism. For example, water oxidation requires the cumulative effect of four electronic excitations, within a certain time, to feed the RC/ catalytic OEC.
2) **Antennas allow photosynthesis to occur using few reaction centres/OEC** catalysts, that are 'expensive' and need to be self repaired.
3) **Antennas contain different pigments** and allow a broad range of the solar spectrum to be exploited for photosynthesis at reaction centers/OEC.
4) **Antennas can modulate the flow of excitation energy**, adapting self-quenching to light conditions. This provides a way of protecting plants from harmful excess sunlight.

And … HOW

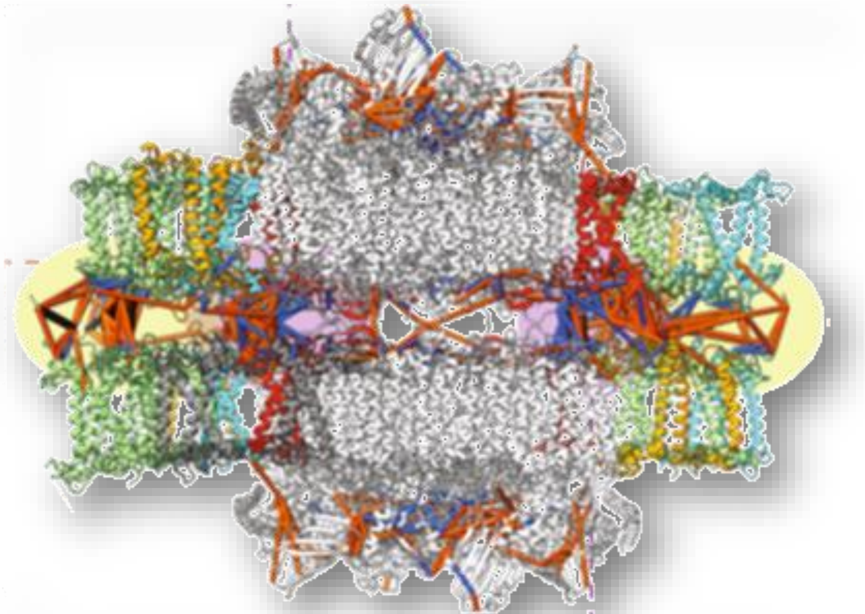
1) **Geometry and Spacing**: the pigments in light-harvesting antennas are optimally spaced - just close enough to enable fast energy transfer, but far enough apart to prevent deactivation and quenching
2) **Linkers and Bonding**: the supramolecular organization of the photosynthetic apparatus, allows dynamics to access a multitude of energy-delivery, and self-healing/adapting strategies

PSII: SETTING THE PARADIGM TO RETHINK ARTIFICIAL PHOTO-ELECTROLYSERS

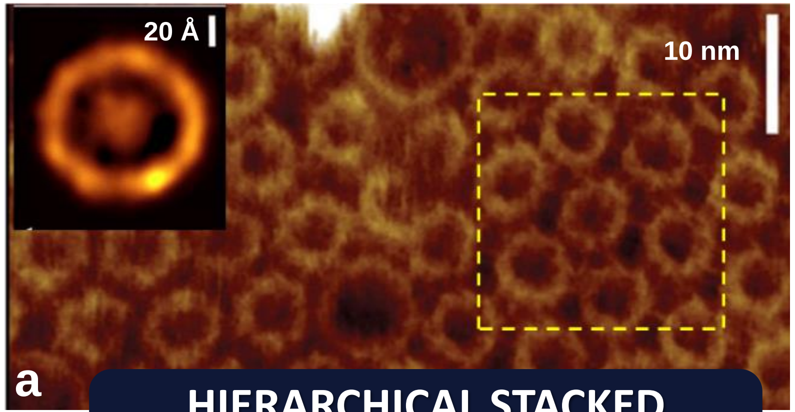
✓ **PSII IS A *SUPERCOMPLEX* WITH INTEGRATED ~ 30 CHROMOPHORES (CHLOROPHYLLS) PER REACTION WHERE 4-LIGHT QUANTA ARE USED TO OXIDIZE WATER AND EVOLVE OXYGEN**



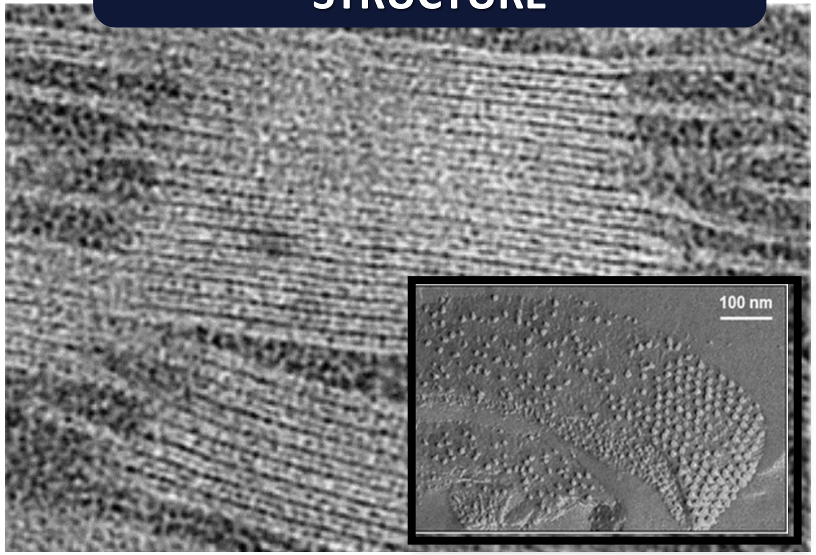
PSII – LHCII SUPERCOMPLEX



CO-AXIAL ORGANIZATION



HIERARCHICAL STACKED STRUCTURE



PSII native assembly architecture (a) AFM of hexagonally packed LH complexes (dashed box), Inset: PSII core-complex showing the RC completely surrounded by an elliptical LH1 assembly, scale 20 Å
(b) TEM and SEM imaging of the thylakoid membrane showing the appressed membranes and a fluid-to-paracrystalline organization of PSII domains left (b)

R. Bassi, G. R. Fleming et al. *Science* **2008**, *320*, pp. 794-797; J. Barber et al. *Inorganic Chemistry*, **2008**, 47, 1700-1710
S. Scheuring and J. N. Sturgis, *Science*, **2005**, *309*, 484-487

The quantasome concept

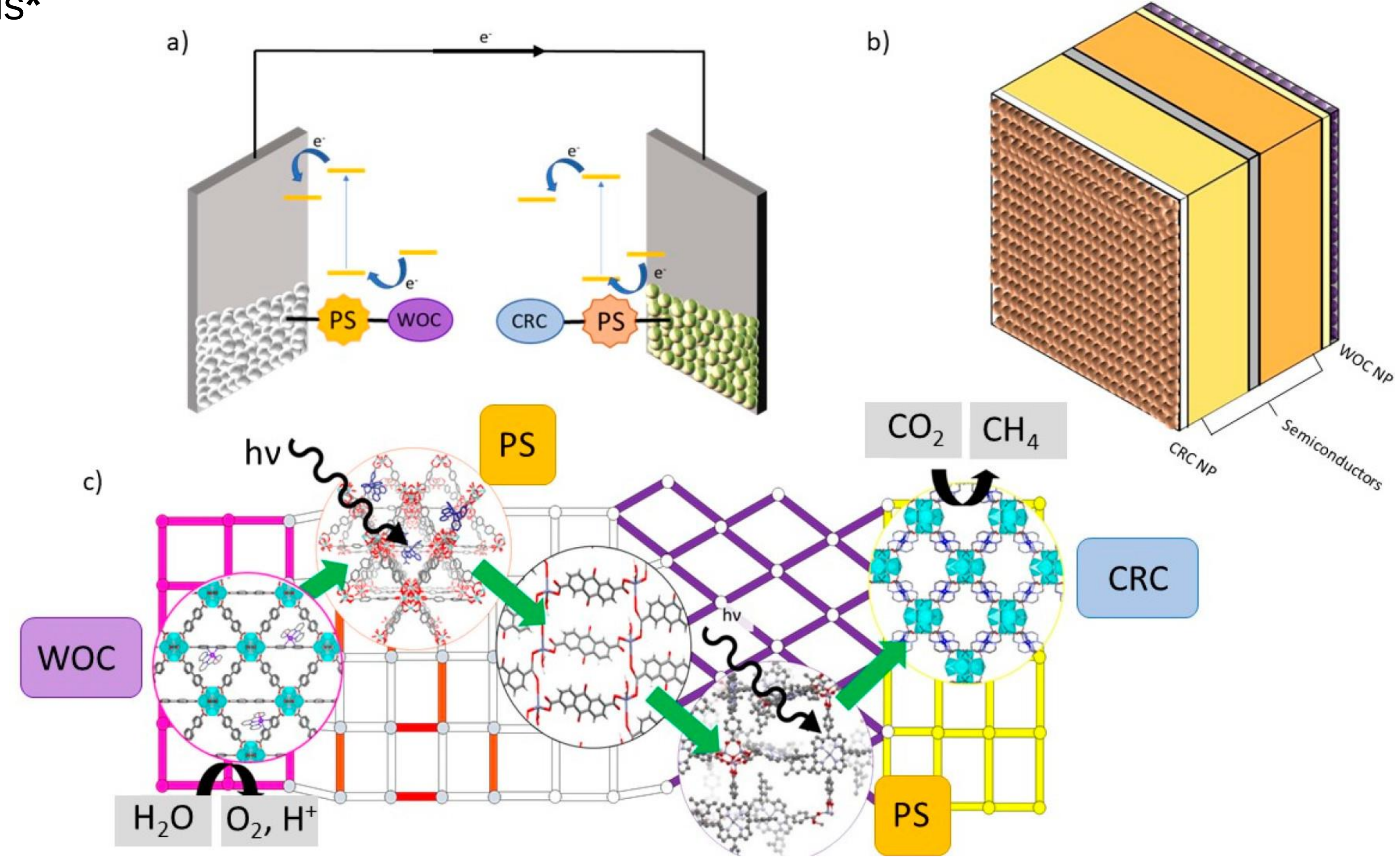
R. B. Park, J. Biggins, Quantasome: Size and Composition (1964) *Science* **144**, 1009

- ✓ **identifies the minimal photosynthetic unit responsible for the "quantum" solar energy conversion**, taking place within the chloroplast membrane. In its essentials: the integration of a light-harvesting (LH) antenna in combination with catalytic co-factors.

- ✓ **goes beyond a simple photocatalytic dyad** based on a 1:1 conjugation of a light absorber with the catalyst. The quantasome model calls for a significantly different approach: **the LH components, of selected type and number, together with their spatial organization need to be specifically optimized according to the CATALYST requirements, with the final aim to leverage its multi-ET mechanism**.

Roadmap to Integrated Artificial Photosynthetic Arrays

Perspective by Amanda J. Morris*



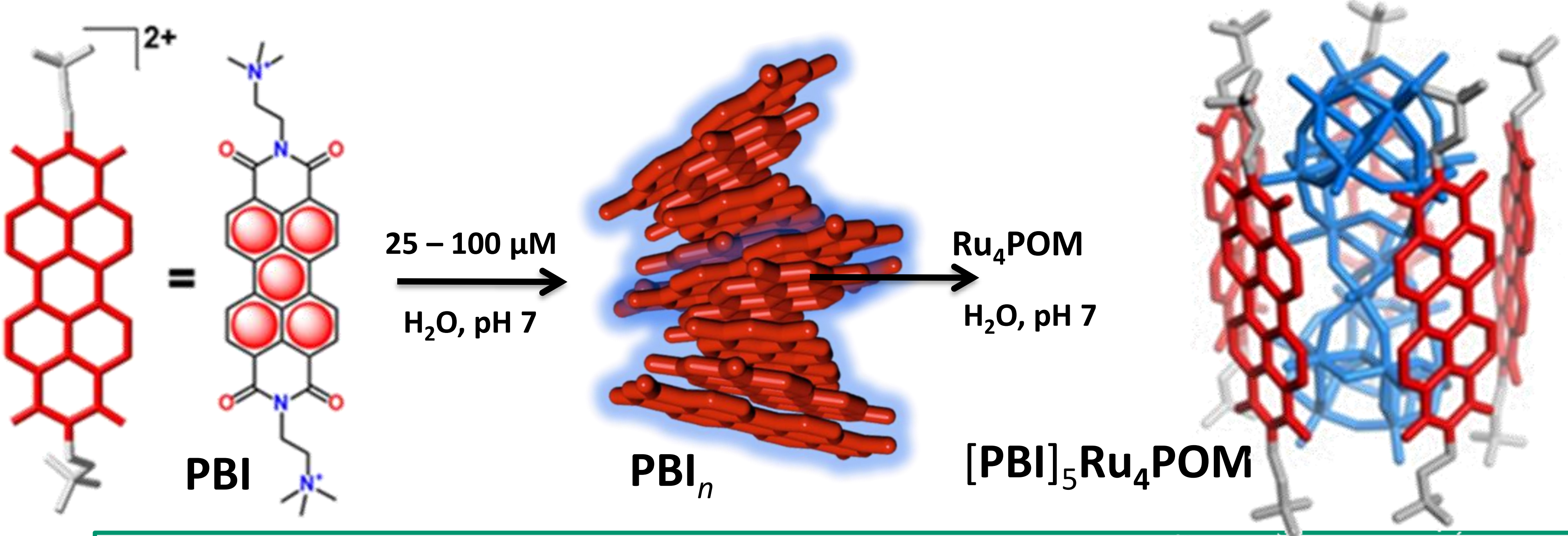
Schematics for artificial photosynthetic assemblies showing DSPECs featuring a photosensitizer (PS), water oxidation catalyst (WOC), and CO_2 reduction catalyst (CRC) (a), multijunction semiconductors with catalytic nanoparticles (NP) (b), and a proposed all-MOF artificial photosynthetic assembly (c).

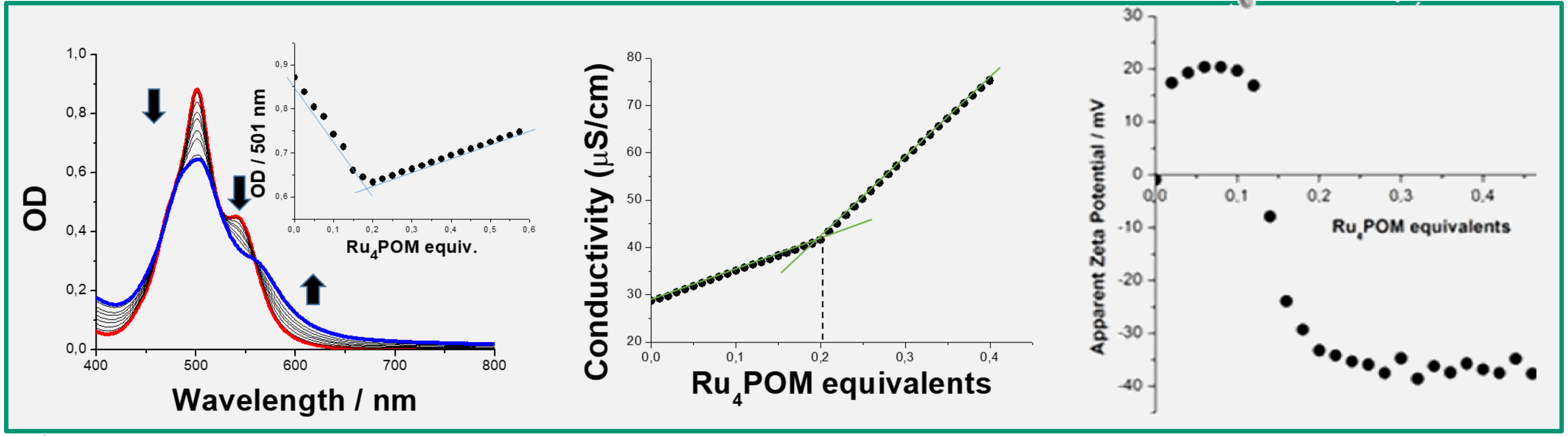
J. Am. Chem. Soc. 2022 Sep 20. doi: 10.1021/jacs.2c04144. Online ahead of print.

Artificial Quantasomes: integrated LH-OEC by Perylene exfoliation with Ru_4POM

Erica Pizzolato

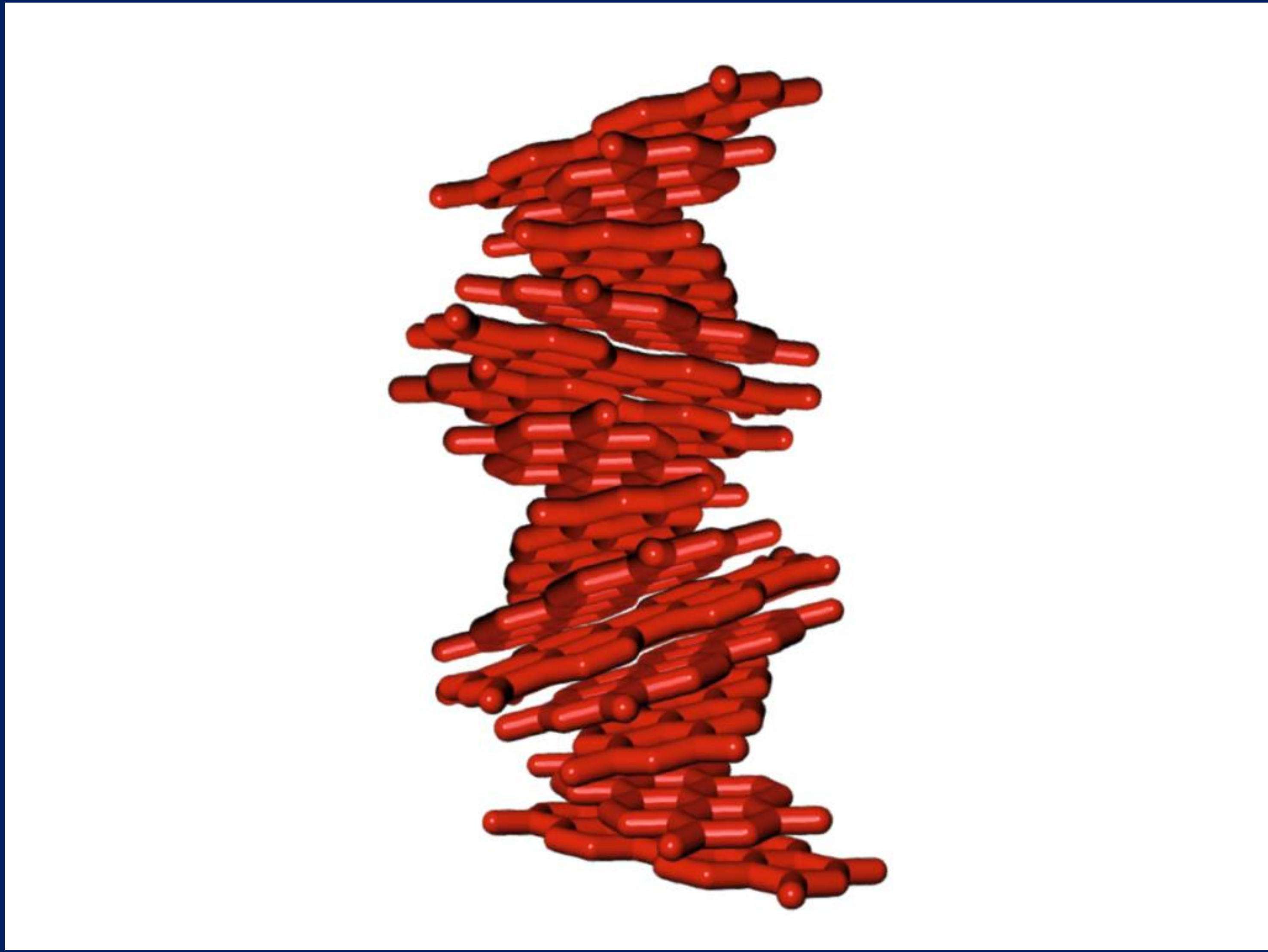
Francesco Rigodanza





Nature Chemistry **2019**, 11, 146

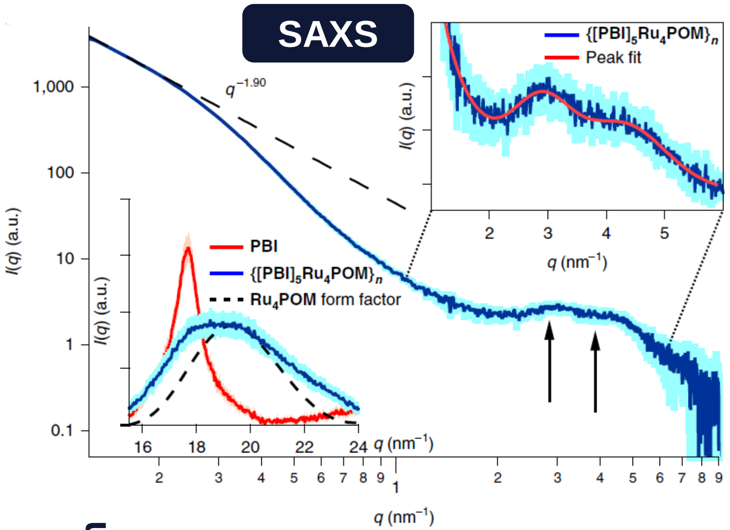
Self Assembly of Perylene Quantasomes in water

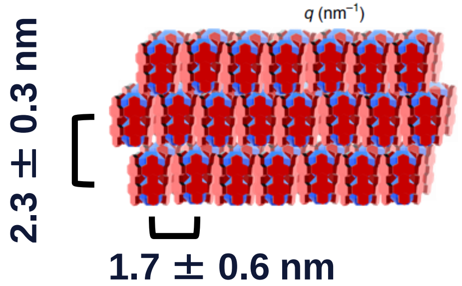


with Maurizio Prato (University of Trieste, Italy)

STRUCTURAL CHARACTERIZATION AND IMAGING OF THE PBI-QUANTASOME

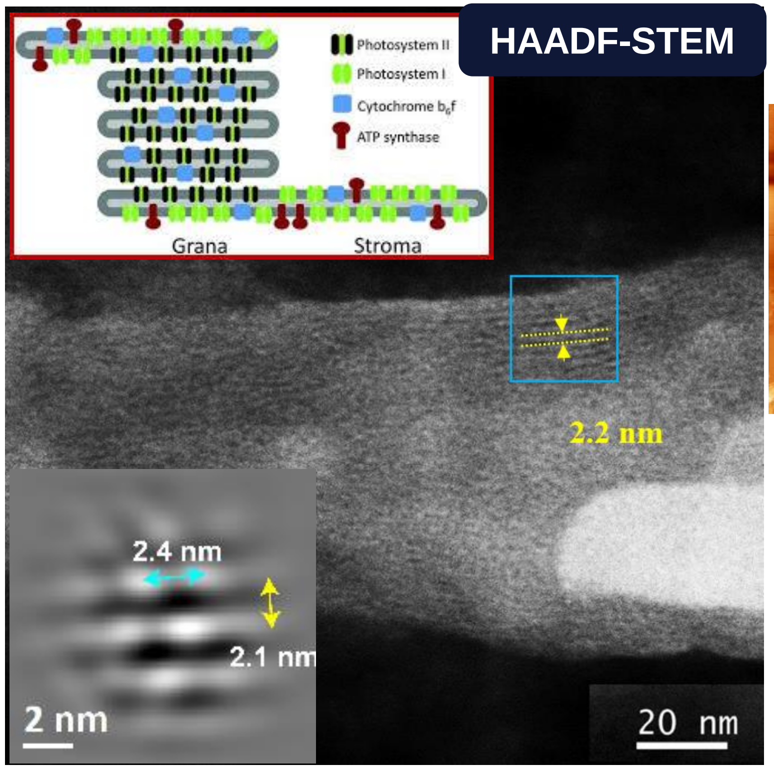
SAXS





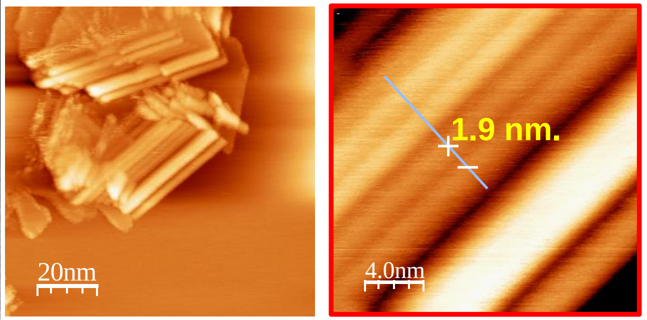
Nature Chemistry **2019**, 11, 146

HAADF-STEM

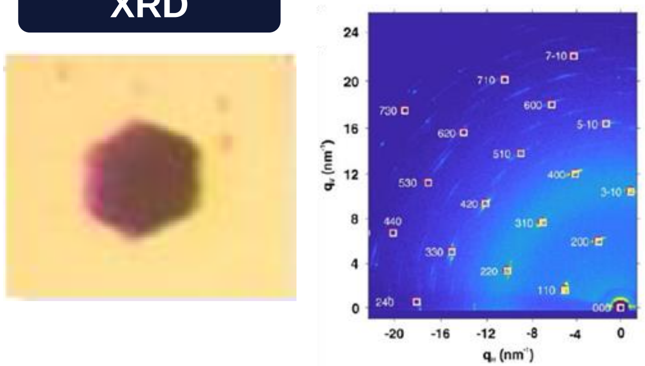


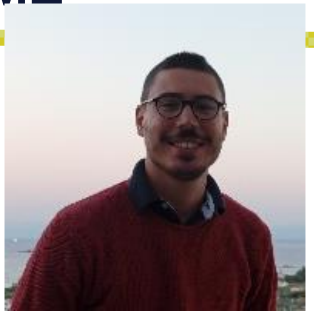
In collaboration with Sara Bals (University of Antwerp)

STM



XRD



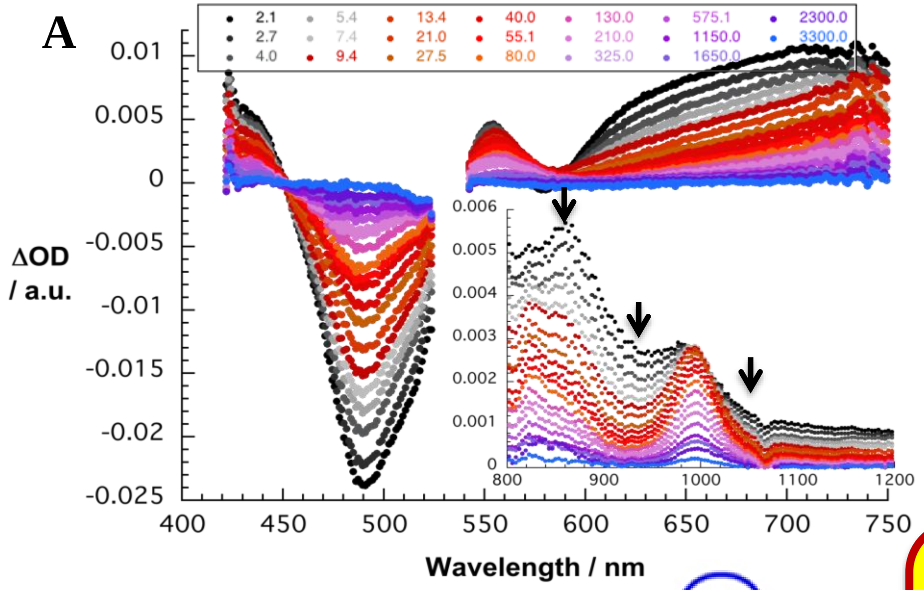


Thomas Gobbato

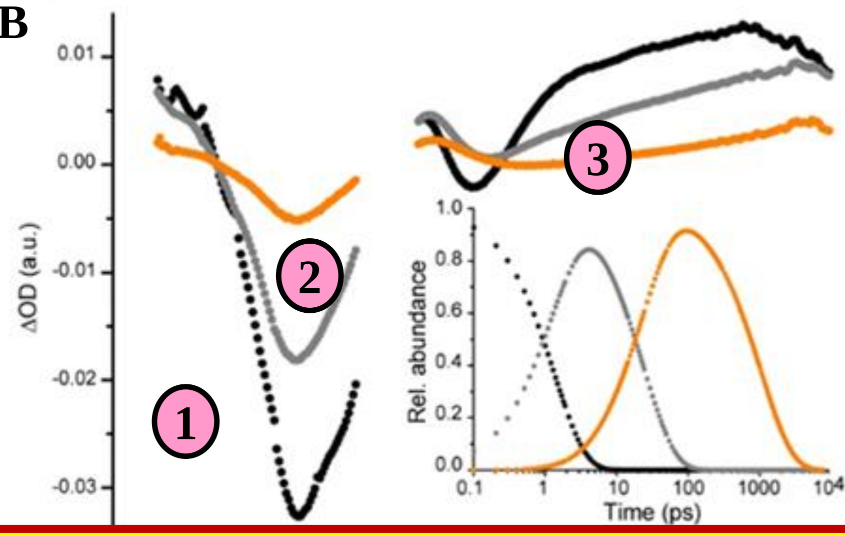
- **HAADF-STEM SHOWS LAMELLAR ARRENGEMENT OF QS, RESEMBLING PSII HIERARCHICAL STACKING**
- **STM EXPERIMENTS OF QS DEPOSITED ON HOPG REPORTED A HIERARCHICAL STACKED MEMBRANE STRUCTURE WITH AN INTER-LAMELLAR DISTANCE OF 2 nm IN AGREEMENT WITH SAXS DATA AND HAADF-STEM**
- **FFT ANALYSIS LEADS TO HEXAGONAL PACKING OBSERVATION ASSOCIATED TO METAL ATOMS CENTERS CONFIRMING THE XRD PATTERNS AND DISTANCES REGISTERED ON THE MICRO-SIZED HEXAGONAL-SHAPED LAMINAR CRYSTALLINE AGGREGATES OF QS.**

Perylene Quantasomes: the minimal photocatalytic unit

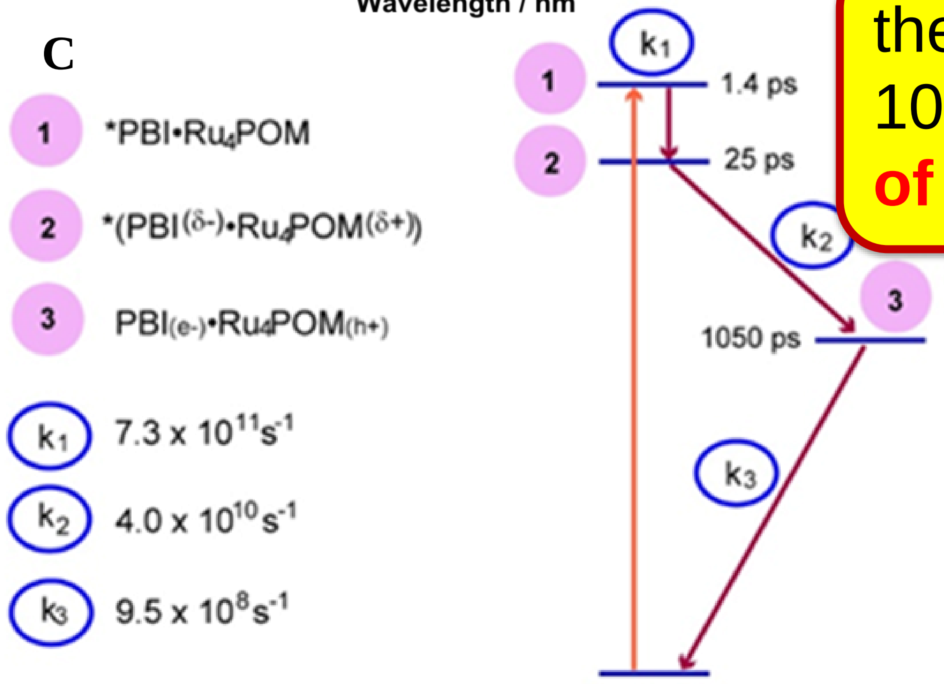
A



B



C



the charge-separated state ($k_3 = k_{cr} = 9.5 \times 10^8\ s^{-1}$) decays to the ground state **2 orders of magnitude slower** than its formation

ps (red) and 3300 ps (blue) obtained upon femtosecond flash photolysis (530 nm) in the range 400-750 nm. The inset displays the peak shaped absorption at 990 nm ascribed to the PBI radical anion transient. **B,** Deconvoluted transient absorption spectra, associated via GloTarAn analysis to states 1 (black), 2 (grey), and 3 (orange) according to the kinetic model **C** inset shows the time evolution of state population

with Dirk Guldi (University of Erlangen)

Nature Chemistry **2019**, 11, 146

Photocatalytic Oxygen Evolution by the Artificial Quantasomes $\{[PBI]_5Ru_4POM\}_n$

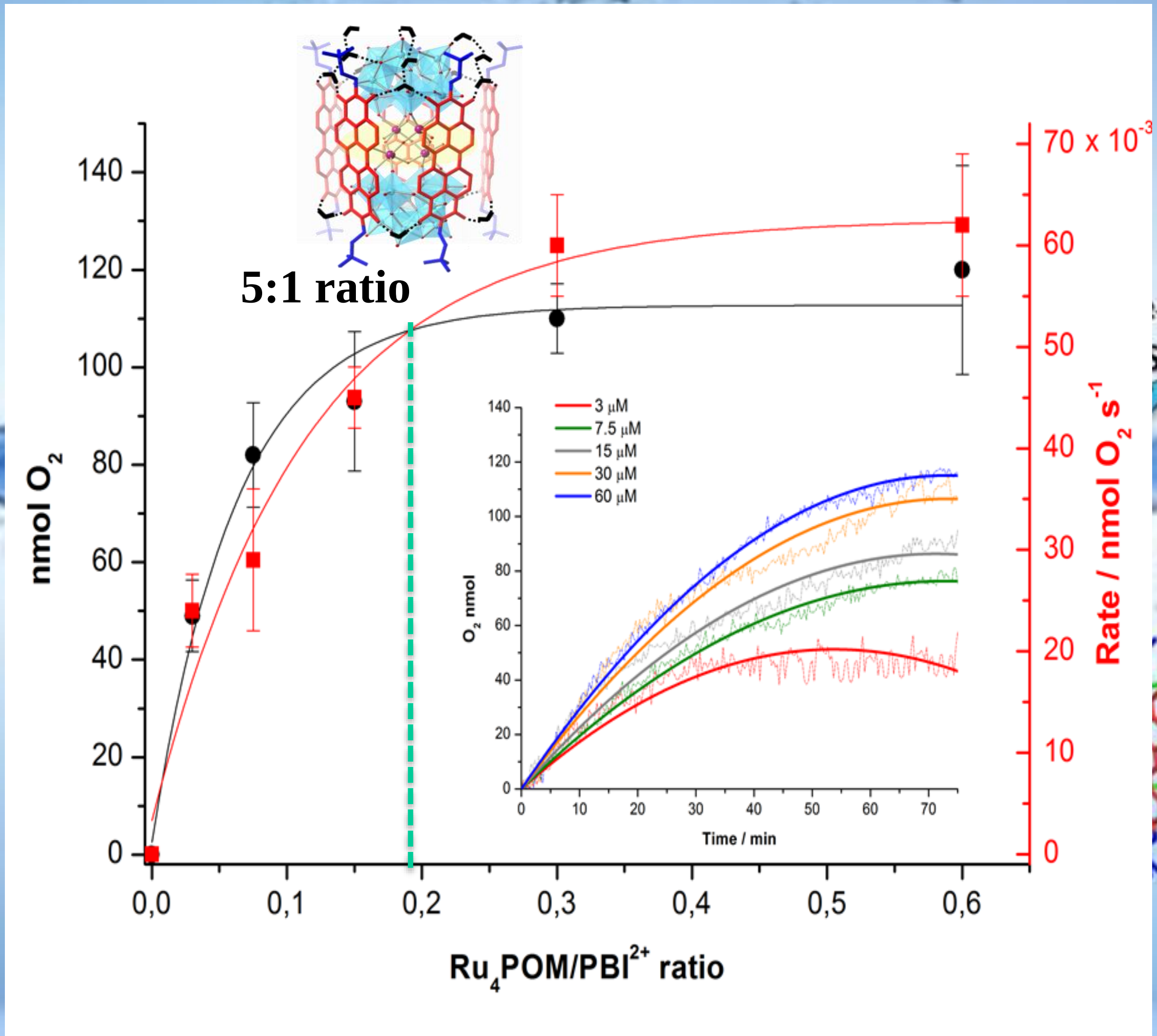
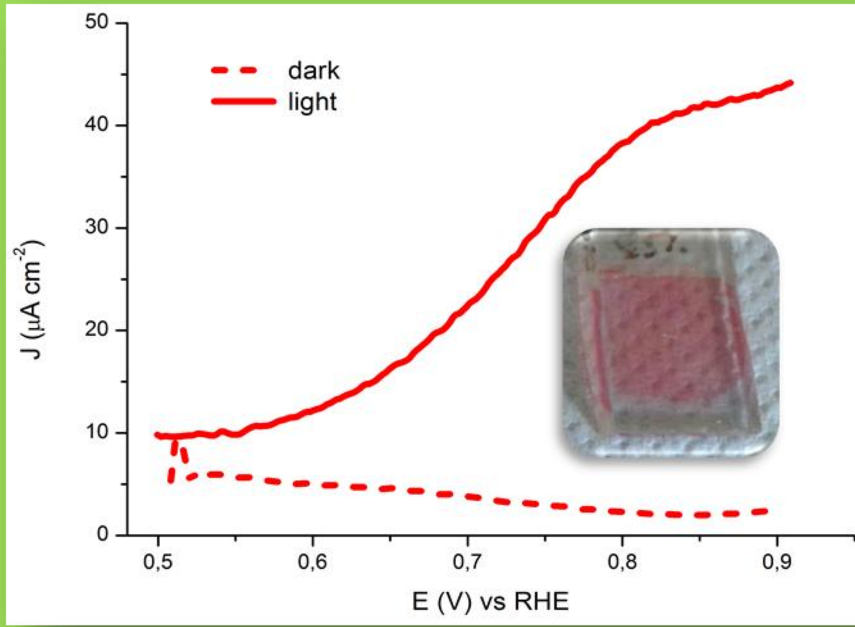


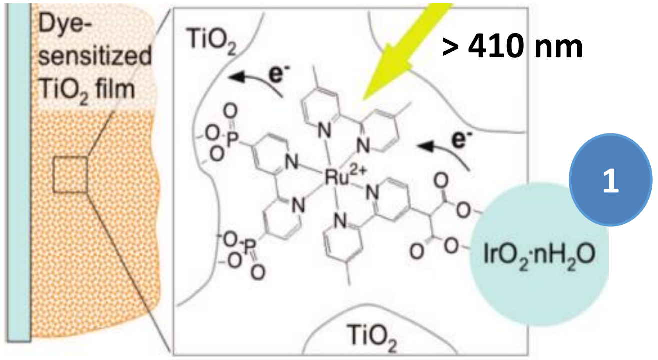
Photo-Oxidant	E (V) vs NHE	LHE
$PBI^*/PBI^{\cdot-}$	+2.20	**40%**

***nano*WO_3|$\{[PBI]_5Ru_4POM\}_n$ photoanodes**
faradaic yield > 97 % , **LHE = 40%**,
APCE% = 1.3 (λ> 450 nm, 0.91 V vs RHE)

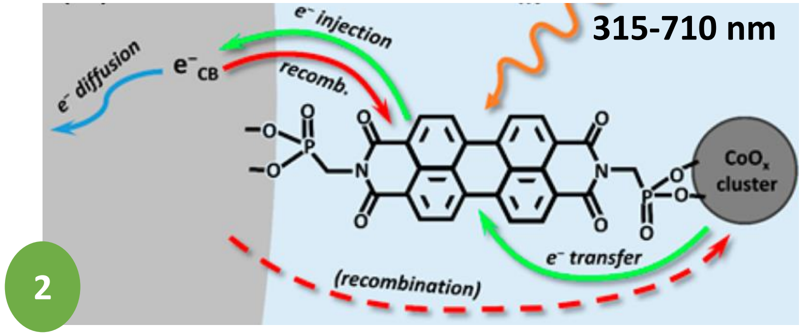


Nature Chemistry **2019**, 11, 146

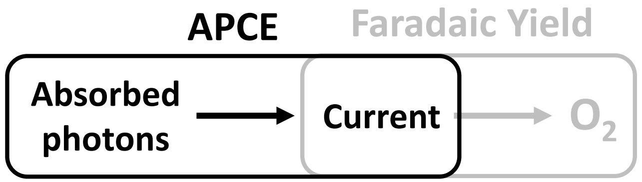
Quantasome Bio-inspired photoanodes:

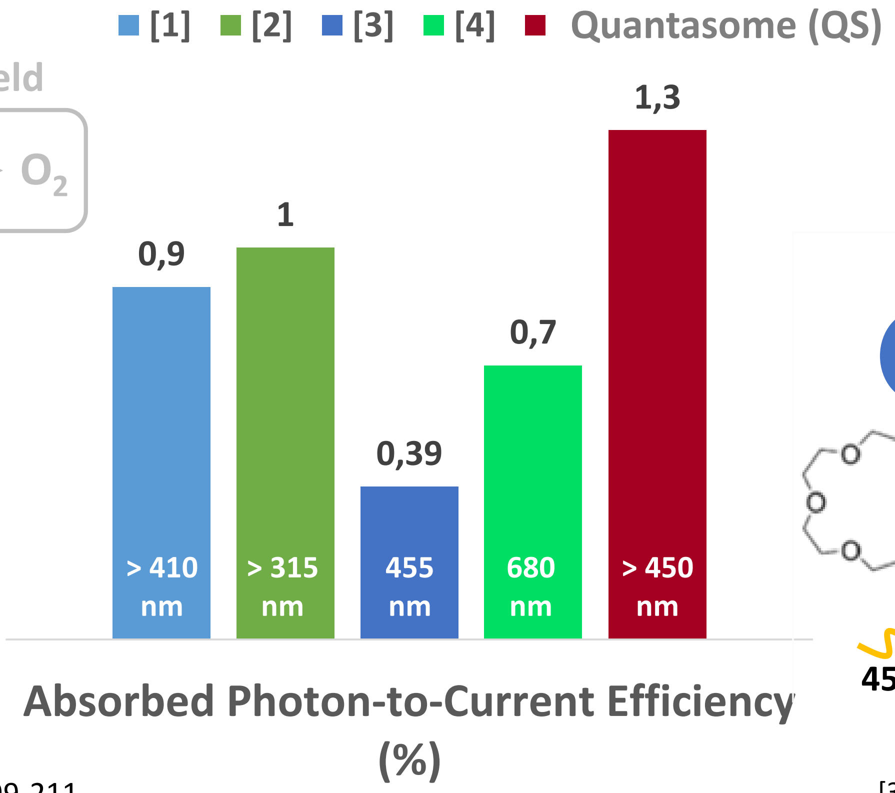


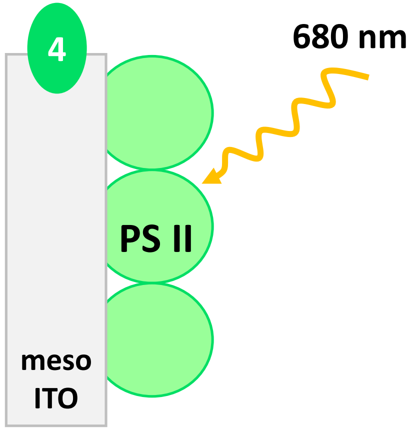
[1] Mallouk, *J. Am. Chem. Soc.* 2009, **131**, 926



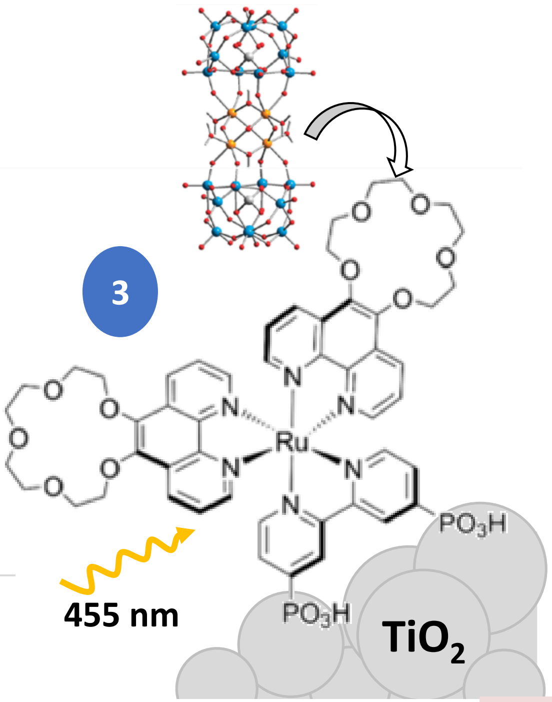
[2] Finke, *ACS Appl. Mater. Interfaces* 2014, **6**, 13367







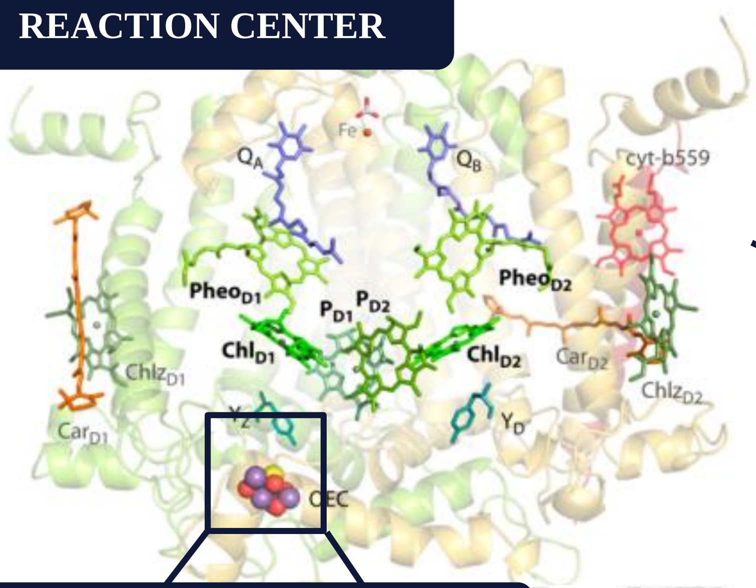
[4] Reisner, *Faraday Discuss.* 2014, **176**, 199-211



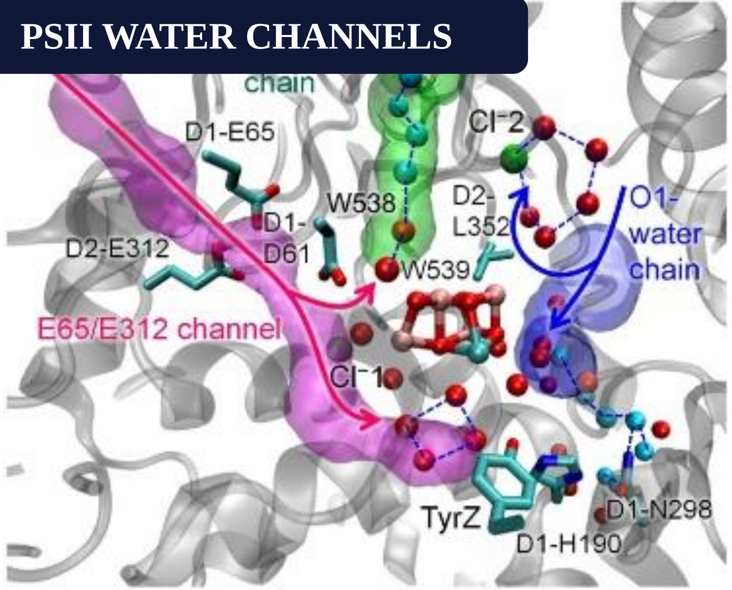
[3] Hill, *Chem. Sci.* 2015, **6**, 5531

PSII: SETTING THE PARADIGM TO RETHINK ARTIFICIAL PHOTO-ELECTROLYSERS

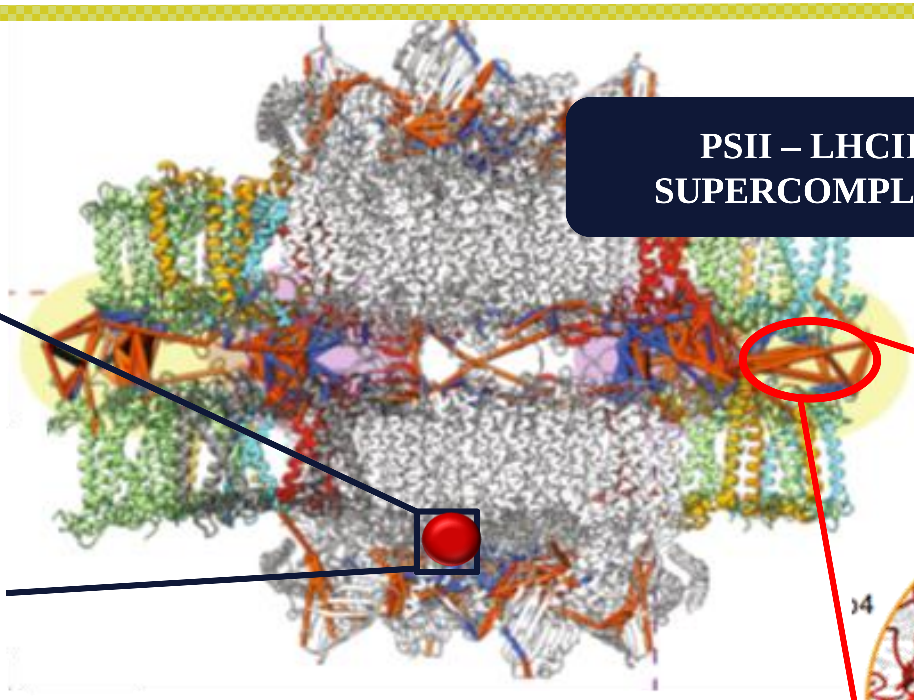
REACTION CENTER



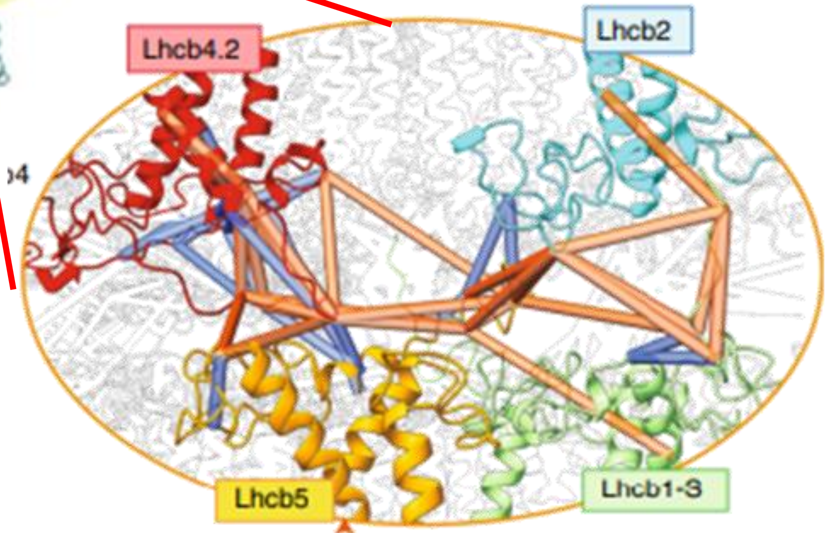
PSII WATER CHANNELS



PSII – LHCII SUPERCOMPLEX



LOCKING INTERACTIONS



- SPATIALLY CONTROLLED TRANSPORT OF WATER AT THE REACTION CENTER IS ESSENTIAL FOR EFFICIENT WATER OXIDATION REACTION AND IT IS ACHIEVED BY THE PRESENCE OF WATER CHANNELS

- IN NATIVE CHLOROPLASTS, PSII PAIRED FUNCTION IS REGULATED BY PROTEIN-PROTEIN INTERACTIONS, HOLDING TOGETHER THE MEMBRANE STACKS, WHILE FAVORING THE PSII CONTACT

Nat Commun **12,** 6531 (2021), *Nat Commun* **11,** 1361 (2020), *Biochemistry* **56**, 24, 3049–3057 (2017), *J. Am. Chem. Soc.* **142**, 42, 18174–18190 (2020)

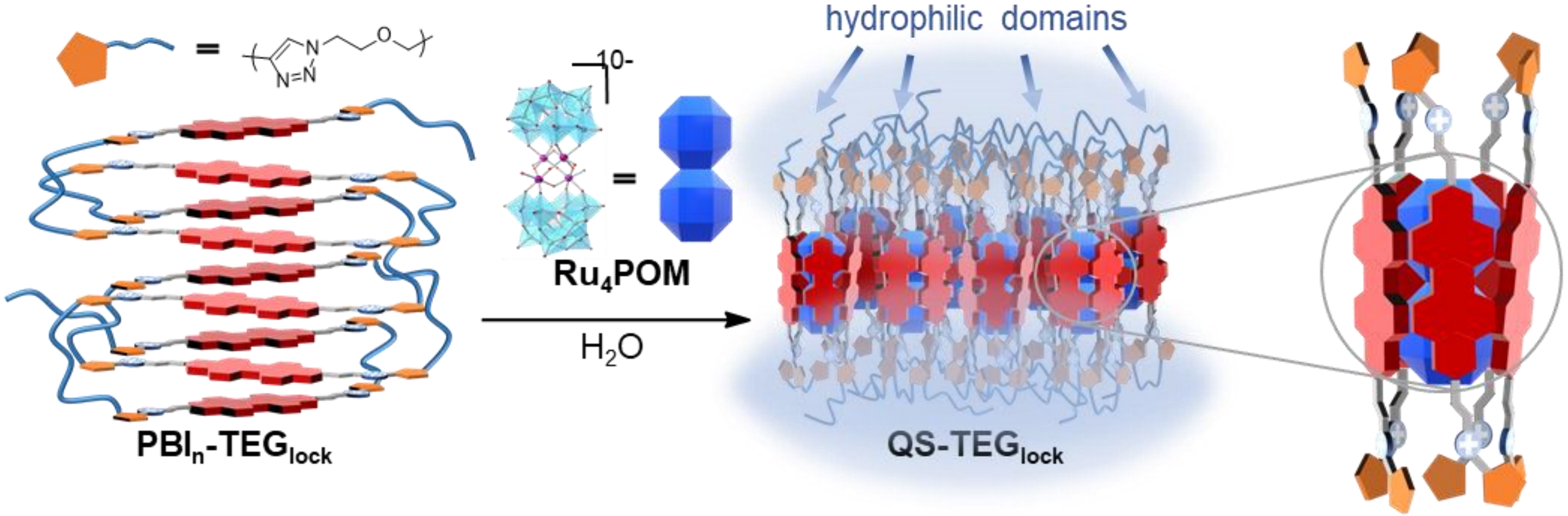
From Natural to Artificial: The Next-Generation Quantasomes

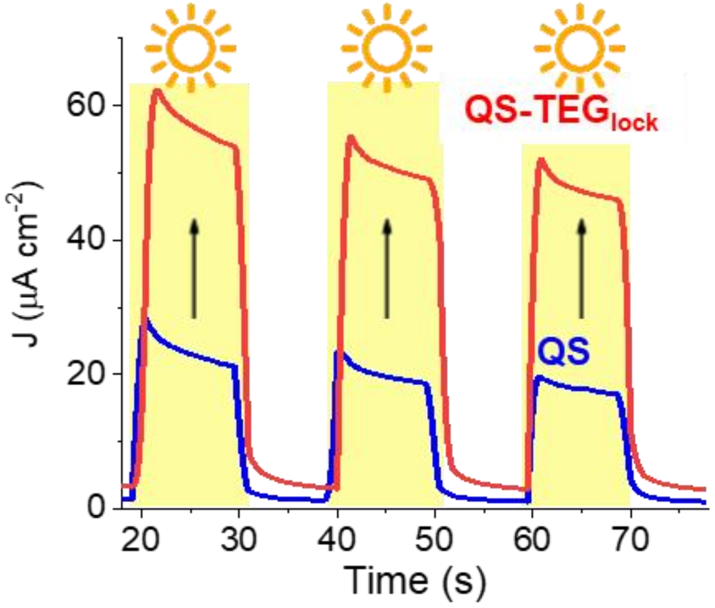
Francesco Rigodanza

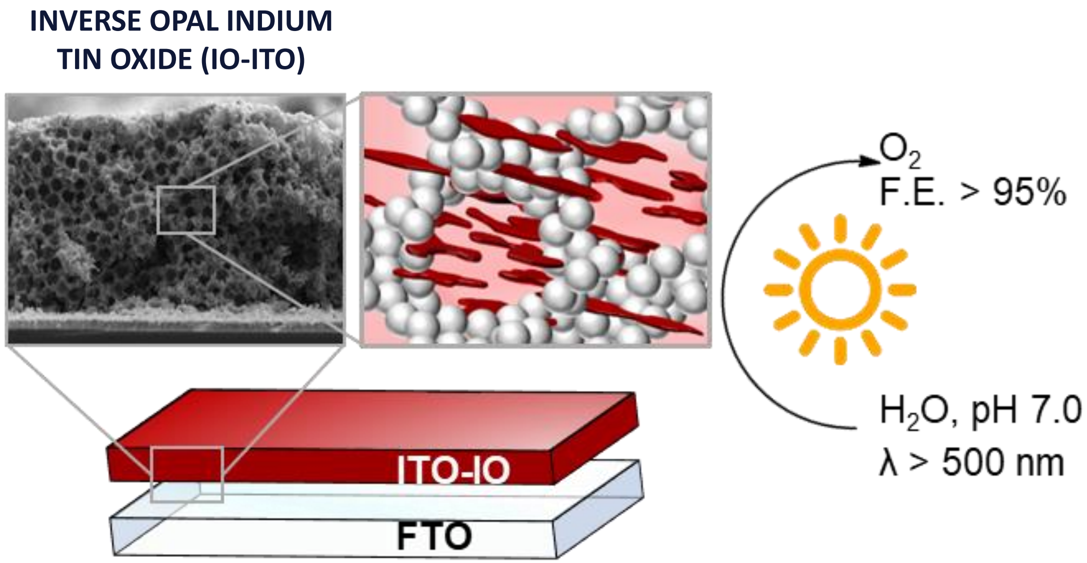
Thomas Gobbato

Elisabetta Benazzi

Ilaria Crea

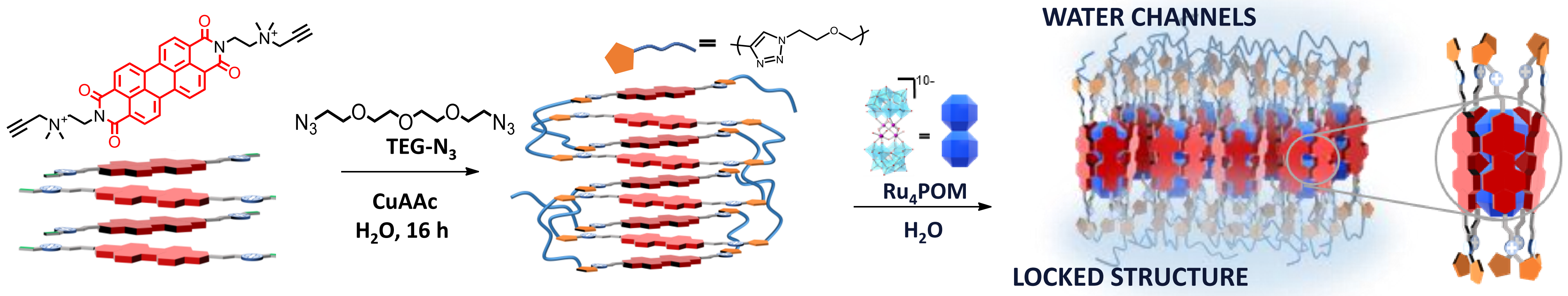






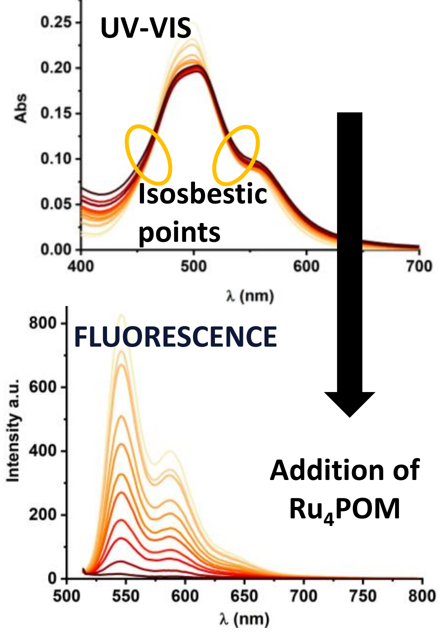
J. Am. Chem. Soc. 2022, 144, 31, 14021–14025

INTERLOCKING QUANTASOMES via SUPRAMOLECULAR AND CLICK-CHEMISTRY STRATEGIES with TETRAETHYLENE GLYCOL (TEG) CROSS-LINKERS

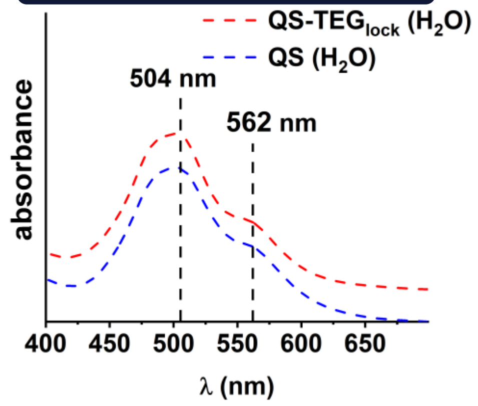


PBI-YNYL | PBI_n-TEG_{lock} | QS-TEG_{lock} | 5:1 RATIO

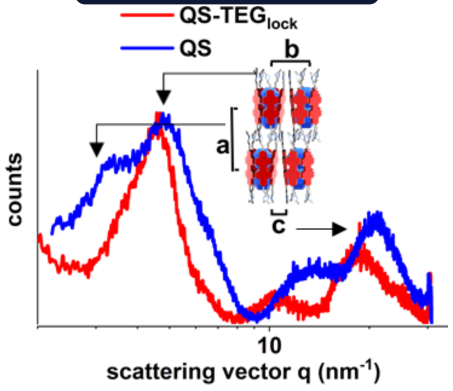
PBI_n-TEG_{lock} TITRATION



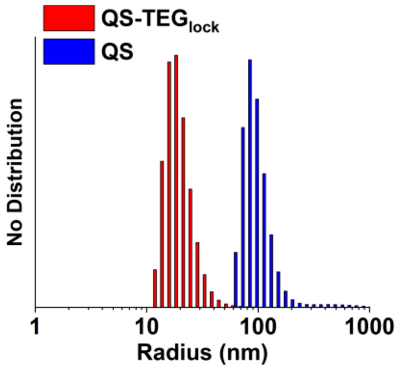
SPECTRAL FINGERPRINT



PXRD PATTERN



DLS

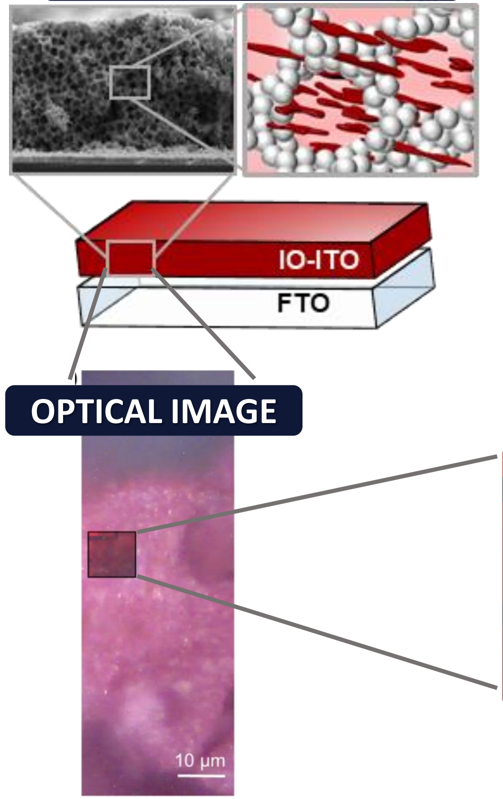


- UV – VIS SPECTRAL FINGERPRINT IS TYPICAL OF THE QUANTASOME ASSEMBLY
- PXRD PATTERN CONSISTENT WITH A LAMELLAR-TYPE STRUCTURE
- DLS INDICATES SMALLER DIMENSIONS FOR QS-TEG_{lock} COMPARED TO QS, WITH R (QS-TEG_{lock})=20 nm AND R(QS)=95 nm

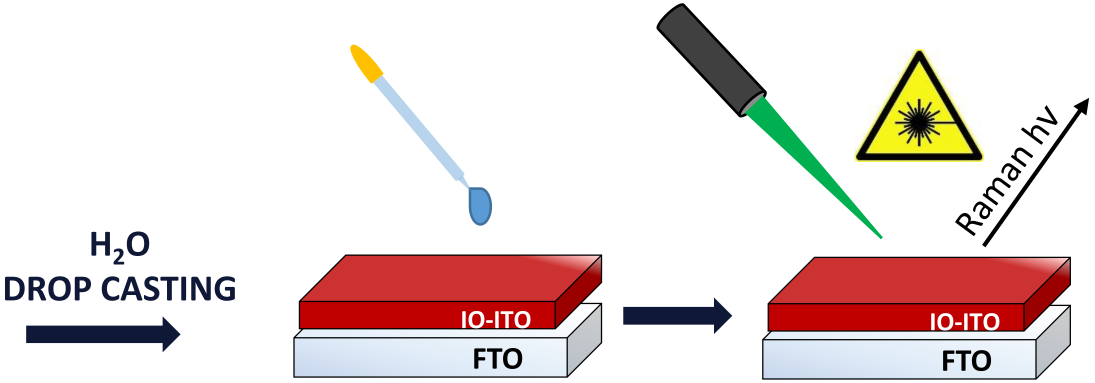
J. Am. Chem. Soc. 2022, 144, 31, 14021–14025

QS-TEG$_{lock}$ vs QS PERFORMANCE COMPARISON:
RAMAN IMAGING OF WATER SOLVATION SHELLS TEMPLATED BY HYDROPHILIC TEG-CROSS LINKERS

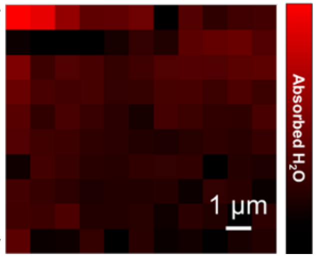
IO-ITO|QS or QS-TEG$_{lock}$



OPTICAL IMAGE

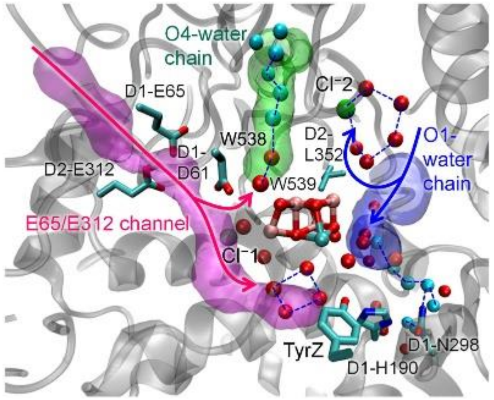


RAMAN MAPPING

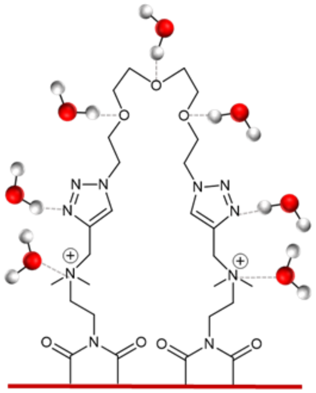


DISTRIBUTION OF SURFACE WATER BY MAPPING WATER RAMAN SIGNALS (3000 – 3600 cm^{-1})

Biochemistry **56**, 24, 3049–3057 (2017), *Nat. Chem.* **14**, 40–45 (2022)

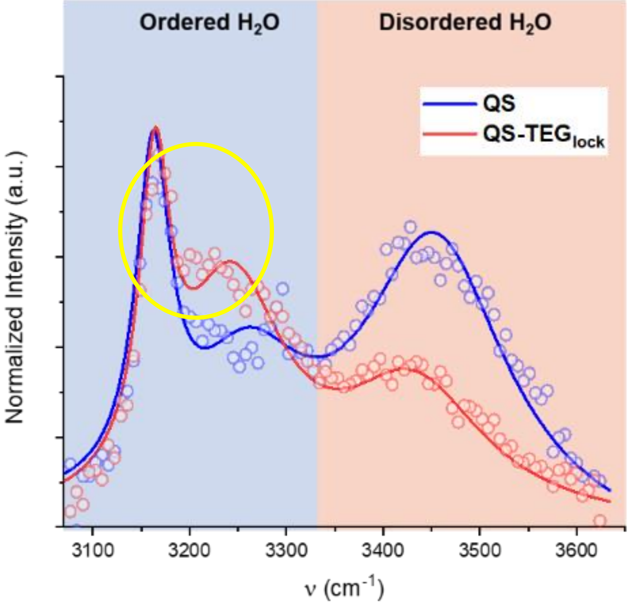


PSII



QS – TEG$_{lock}$

RAMAN SPECTRA



- **TEG-TEMPLATED HYDRATION SHELLS (3000 -3300 cm^{-1}) MIMICKING PSII WATER CHANNELS**

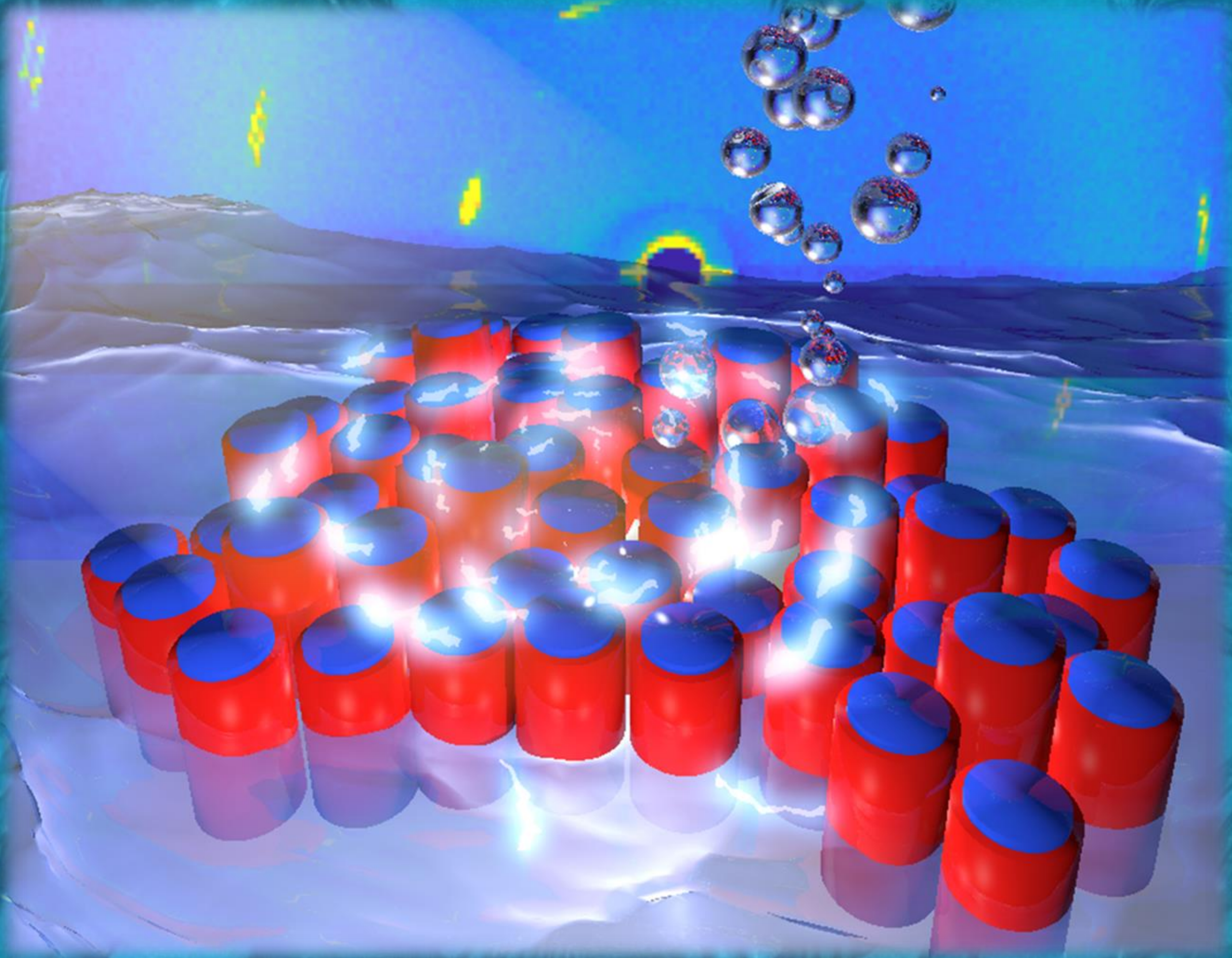
J. Am. Chem. Soc. 2022, 144, 31, 14021–14025

CONCLUSIONS

- **THE QUANTASOME PROJECT WILL EXPLORE A MODULAR, BIOMORPHIC DESIGN OF INTEGRATED PHOTOSYNTHETIC ARCHITECTURES TO FACE THE ARTIFICIAL PHOTOSYNTHESIS CHALLENGE.**

THE SHAPE OF WATER

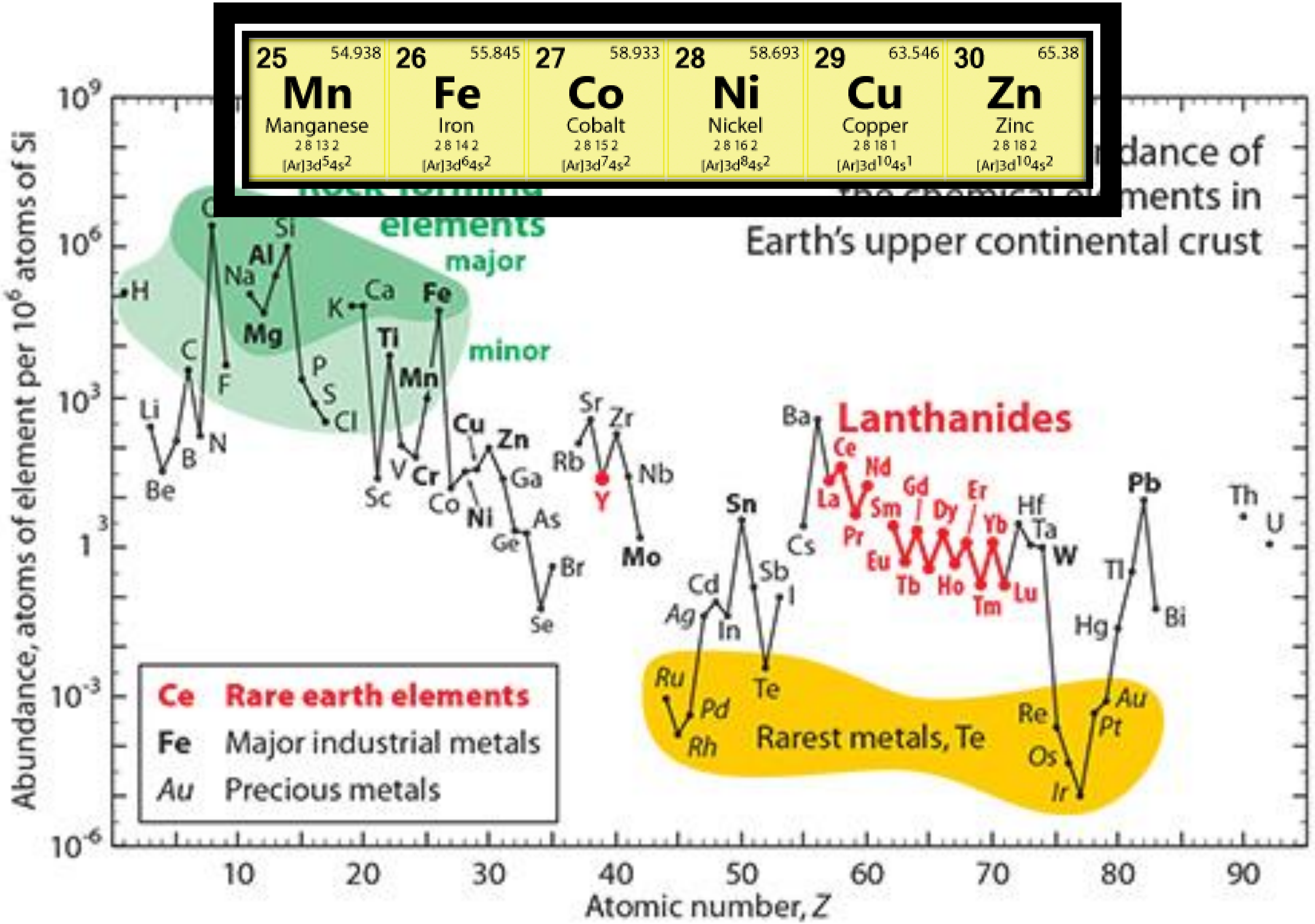
Unable to perceive the shape of you, I find you all around me. Your presence fills my eyes, It humbles my heart, for you are everywhere."



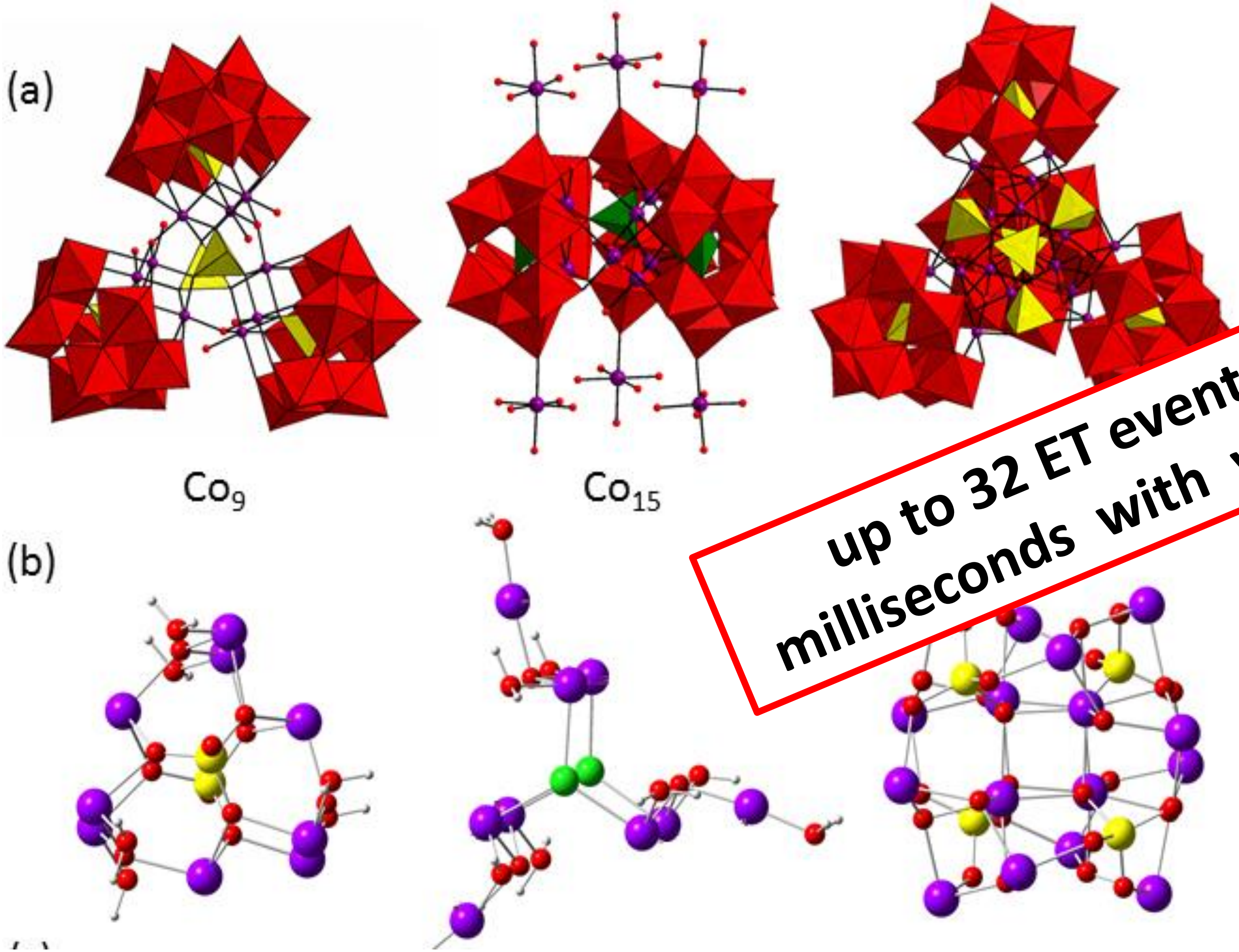
Nature Chemistry **2019**, 11, 146

J. Am. Chem. Soc. **2022**, 144, 31, 14021–14025

The Challenge



high-nuclearity Cobalt-oxo cores as OECs



up to 32 ET events in 60 milliseconds with visible light

Catal Today, **2017**, 290, 39-50

Green Chem, **2017**,*19*, 2416-2426

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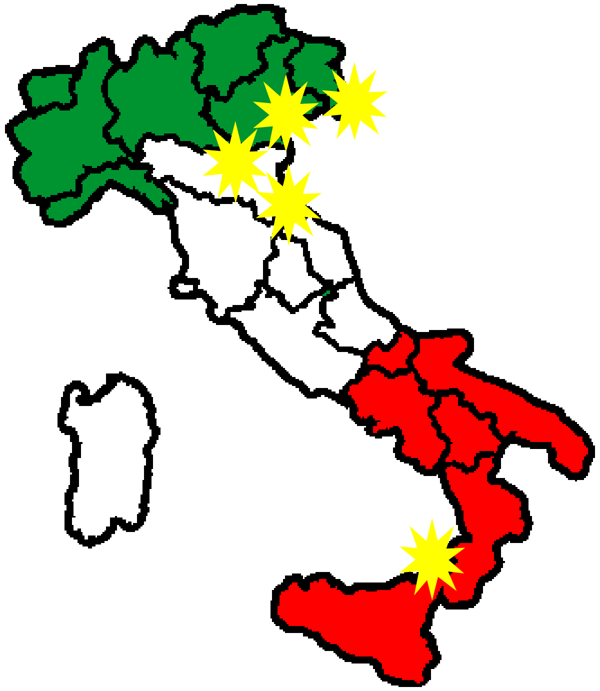
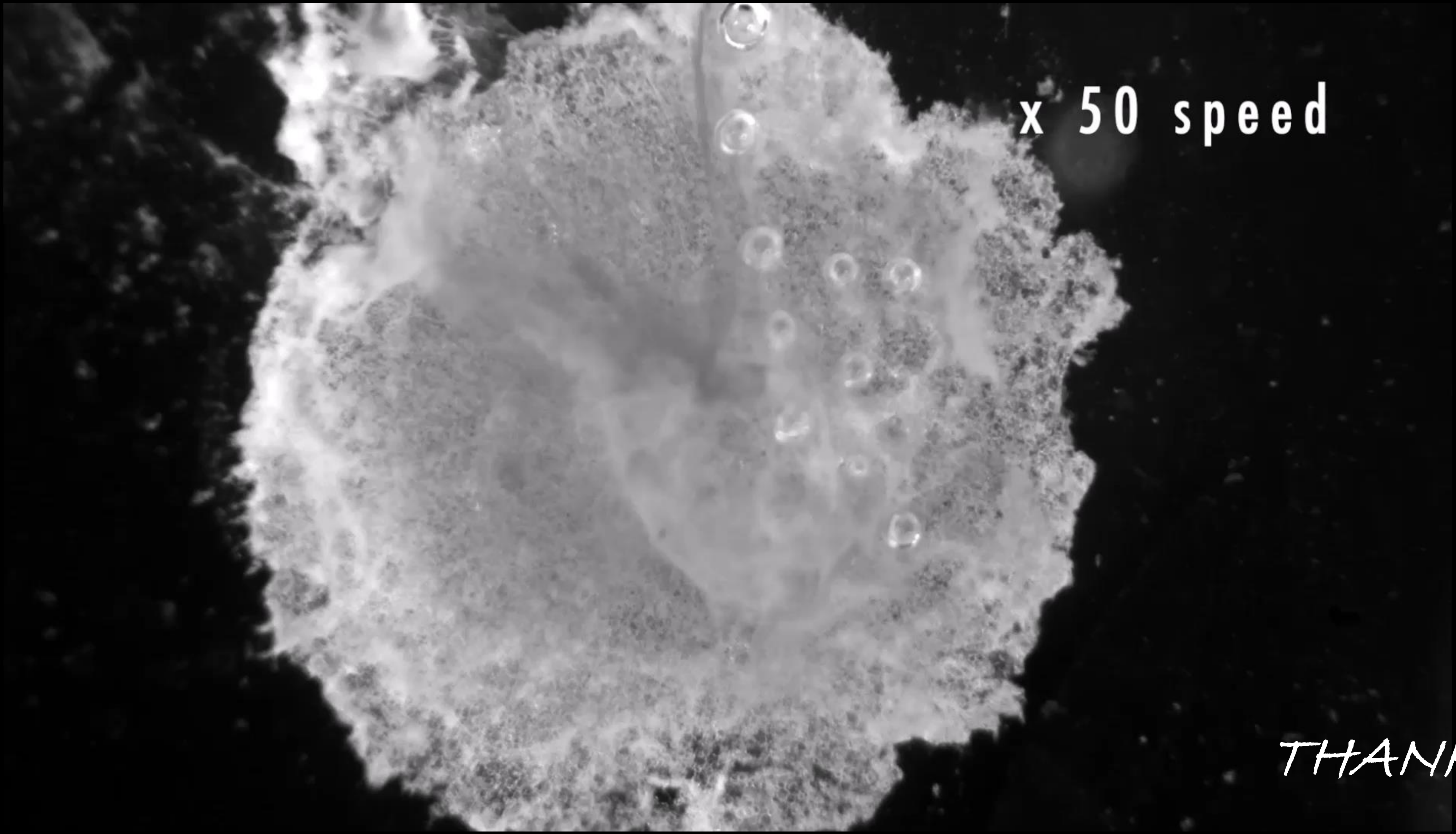
European Union Funding
for Research & Innovation



NANOSOLAR



THANK YOU

with Aina Rebasa Vallverdu, Pierangelo Gobbo, Steven Mann *Nature Commun* **2020**