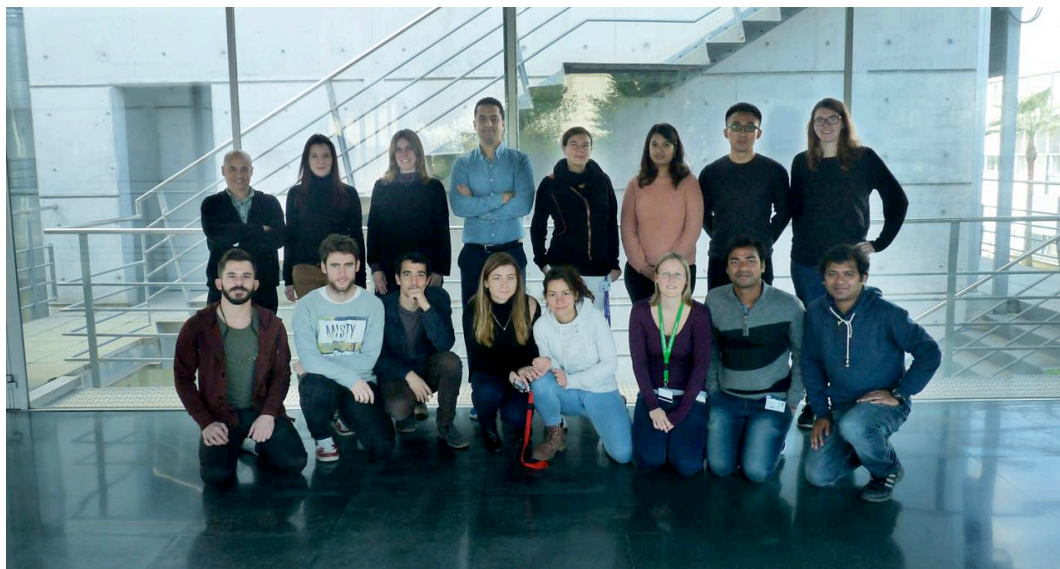


## Llobet Research Group



**Group Leader:** Antoni Llobet

**Postdoctoral researchers:** Carolina Gimbert / Chuanjun Wang / Sayantan Paria / Laura Dura / Serena Berardi (until Jan.)

**PhD students:** Roc Matheu / Pablo Garrido / Sergi Grau / Md Asmaul Hoque / Abolfazl Ghaderian / Primavera Pelosin (until Oct.) / Nataliia Vereshchuk

**Visiting Professor:** Prof. R. Tom Baker (April-July)

**Visiting postdocs:** Antonio Picón (Mar.) / Dooshaye Moonshiram (Mar.)

**Visiting students:** Jordi Creus (July) / Jonathan de Tovar (Apr.-May) / Marcos Gil (Apr.-May) / Cgristina Felbek (Oct.-Dec.) / Marine Ribals (Apr.-Aug.) / Xiaoxue Song (Oct.-Apr.) / Jana Lücken (Sept.-Dec.) / Albert Serra (Nov.)

**Summer fellows:** Anastasiya Ushenkina

**Administrative support:** M<sup>a</sup> José Gutiérrez

### Abstract

The group carries out research in the field of redox catalysis using transition metal complexes. We are interested in the oxidation and reduction of both organic and inorganic substrates, and mainly those that are of technological interest. Our overall objective is to understand the various factors that affect catalyst's efficiency and selectivity with special

focus on the transition metal electronic structure and space disposition.

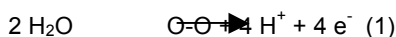
Particular attention is being paid to the catalytic oxidation of water to molecular dioxygen, given the implications of this reaction for new energy conversion schemes based on *artificial photosynthesis*. The final objective of this route consists on the photo-production of hydrogen from water and sunlight.

Mother Nature uses a whole range of metalloproteins to carry out a wide variety of oxidation processes in a highly selective and efficient manner. Our general philosophical approach is inspired by nature's extraordinary performance. Thus we develop our transition metal redox catalysts based on nature's wisdom, mimicking her structural motives and reactivity strategies.

Our catalyst development involves the interplay of a variety of disciplines including, synthetic organic and inorganic chemistry, spectroscopy, electrochemistry, kinetics and catalysis.

The following are some of the topics we are currently involved in:

**Catalysts for Artificial Photosynthesis.** The prediction for energy demand by the year 2050 is in the range of 30-50 TW which is more than a 100% increase with regard to what we have consumed by the year 2004. Furthermore, given the rate of CO<sub>2</sub> increase and the catastrophic consequences this is producing to our planet, it is obvious that our society has an urgent need for a carbon-neutral renewable energy source. An attractive and clean energy vector to solve this problem could be H<sub>2</sub>, but while the storage and separation of hydrogen has already been achieved with certain degree of success, the question of where do we get a sustainable hydrogen source still remains to be answered. Nature has been using water and sunlight as a source of energy in its photosynthetic processes for a long time. Oxidation of water to O<sub>2</sub>,



is the terminal reaction of photosystem II (PSII) in green plants which takes place at a polynuclear Ca-Mn<sub>4</sub> complex. This reaction is a thermodynamically demanding reaction since E° = 1.23 V (vs. SHE) at pH = 0.0. On the other hand it is of tremendous molecular complexity from a mechanistic perspective, since it involves the oxidation of water by 4 H<sup>+</sup> and 4 e<sup>-</sup> with the formation of an oxygen-oxygen bond. It is thus an important reaction to be modeled since efficient low molecular weight models can lead to a first step towards creating a clean renewable energy source. The mastering of the performance of this reaction is nowadays the bottleneck for the development of artificial photosynthetic devices, capable of producing H<sub>2</sub> from water and sunlight. Thus it constitutes the key to access a clean renewable fuel such as H<sub>2</sub>, the energy vector of the future.

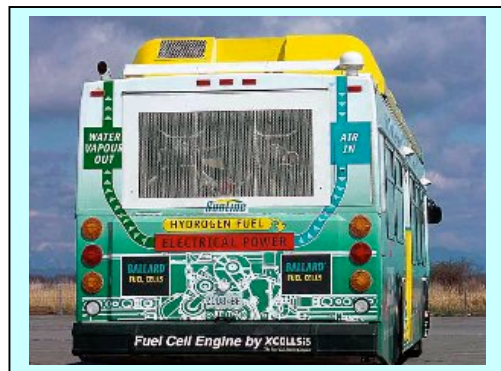


Fig. 1 - Zero-Emission Fuel-Cell Bus.

We have recently prepared a family of dinuclear Ru-aqua complexes containing dinucleating polypyridylic ligands. These ligands are chosen because they enforce a particular metal preorganization and because they impose a delicate balance between the Ru-aqua entities. That is: they are sufficiently close so that they can interact to one another but at the same time they are sufficiently apart so that an oxo bridging reaction can not take place. The latter would be highly detrimental since it would basically kill the catalytic activity with regard to water oxidation.

The higher oxidation states of this Ru dinuclear complexes have been shown to be active with regard to the oxidation of water to molecular dioxygen. We are currently studying the effects of electronic perturbations over the performance of the catalysts as well as the reaction mechanisms through which those reactions proceed. Furthermore, we are designing specific ligands and complexes that will allow us to discriminate between potential intramolecular versus intermolecular mechanisms involving water nucleophilic attack to a Ruthenium-oxo electrophilic entity.

The high thermodynamic potential required for a catalyst capable of oxidizing water to molecular dioxygen implicates that its active species will also be capable of oxidizing a wide range of organic compounds. Therefore intermolecular catalyst-catalyst deactivation is one of the main deactivation pathways. For this purpose we are designing new dinucleating ligands that maintain the intrinsic electronic and coordination abilities of the original ligands but that contain a functionalized group that is able to be attached into an oxidatively rugged solid support. This will bring about a restricted translational mobility that would avoid those undesirable intermolecular interactions.

The combination of spectroscopic, electrochemical and mechanistic information allows us to design and develop new and more efficient water oxidation catalysts based on Ru

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complexes. Those complexes are to be integrated in complex solar cells in a serious first step towards a viable commercial application.

We are also at the moment developing the parallel chemistry, substituting the Ru metal center by Mn, and modifying the ligands taking into account the specific chemistry of such a first row transition metal. The aim here is to increase the velocity of the water oxidation process and to understand the reaction pathways through which they proceed.

**Photochemical oxidation of organic substrates.** We are in the process of developing the adequate transition metal complexes that can be attached into TiO<sub>2</sub> semiconductors, or alternatively into quantum dots, so that they can perform the oxidation of organic substrates with just sunlight. This reaction concept benefits from the absence of a generally polluting and expensive chemical oxidant and also from the formation of H<sub>2</sub> as a byproduct.

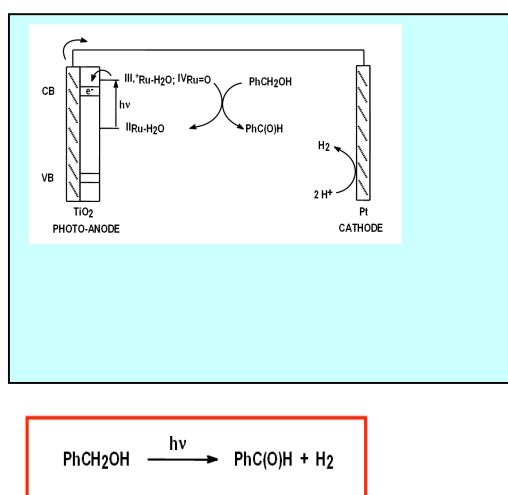


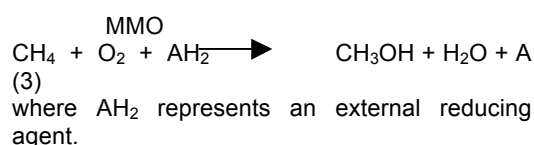
Fig. 2 - Proposed photo-oxidation scheme for organic substrates based on Ru complexes.

**Selective chemical oxidation of organic substrates under mild conditions.** There is an important number of dinuclear copper-containing proteins that use molecular dioxygen to carry out a variety of oxidations, including the industrially relevant oxidation of cyclohexane to cyclohexanol. In this topic we are centering our efforts in the synthesis, characterization and reactivity of transition metal complexes using mononucleating and dinucleating ligands. The appropriate design of dinucleating ligands permits to situate two transition metals in relatively close proximity so that cooperation phenomena can take place as well as its fine tuning. These spatial effects combined with electronic effects, permit the generation of synergic phenomena and in some cases the

viability of a given reaction that is not observable with a mononuclear complex. In nature a large number of metalloproteins exists, whose function consists on the breaking of O-O bonds under very smooth conditions,



for its subsequent incorporation in a specific substrate with high efficiencies and selectivity. As an example the oxidation of methane to methanol can be cited catalyzed by MMO (methane monooxygenase),



At present the chemical industry carries out a number of oxidation processes in a stoichiometric as well as in a catalytic manner but with low efficiencies and selectivity. Besides in general, expensive, highly toxic and environmentally harmful substances are used as oxidants. Here we deal with the field of the activation of oxygen utilizing models inspired in the molecular engineering of non-heme processes developed by nature, that is conceptually the inverse reaction of water oxidation.

Our objective is to elucidate the mechanisms through which these reactions occur in order to extract the key information to be able to design and build low molecular weight analogues. We are particularly interested in understanding the parameters that govern the intermolecular interaction between active species and external substrate. The key substrates we are dealing with at the moment are unsaturated hydrocarbons, alcohols, olefins and sulfides. With the last two ones we are also engaged in building up their corresponding chiral analogues to perform the catalytic oxidation in an enantioselective manner.

**Supramolecular catalysis.** In this project we are combining molecular recognition with oxidative catalysis in order to achieve a selective functionalization of a given substrate, a process that nature also performs. The challenge here is to prepare non-symmetric bifunctional molecules that are geometrically designed so that they are capable to perform both tasks in a harmonized manner: the recognition process through a non covalent bond (coulombic interaction, hydrogen bonding,  $\pi$ -stacking) and the oxidative process.

**Activation of C-H and C-F bonds.** This project aims at the understanding of the fundamental chemistry involved in the activation of C-H and C-F bonds by transition metal complexes.

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Selective activation of C-H bonds by metals under mild conditions is a major subject of research, targeting the final functionalization of organic substrates. The characterization of the usually unstable intermediates of the C-H bond activation prior to functionalization is crucial for the mechanistic comprehension of the reaction. It is thus of great importance in organometallic chemistry and catalyst development because it

can contribute to deepen our knowledge related to the reactivity of stable bonds and the selective replacement of F atoms..

### Articles

"Light Driven Styrene Epoxidation and Hydrogen Generation Using H<sub>2</sub>O as an Oxygen Source in a Photoelectrosynthesis Cell"

*Green Chem.*, **2016**, 18 (1), 255-260.

Farras, P.; Di Giovanni, C.; Clifford, J. N.; Garrido-Barros, P.; Palomares, E.; Llobet, A.

"Dinuclear Cobalt Complexes of a Decadentate Ligand Scaffold: Hydrogen Evolution and Oxygen Reduction Catalysis"

*Chem. Eur. J.* **2016**, 22(1), 361-369.

Di Giovanni, C.; Gimbert-Suriñach, C.; Nippe, M.; Benet-Buchholz, J.; Long, J. R.; Sala, X.; Llobet, A.

"Preface for Small-Molecule Activation: From Biological Principles to Energy Applications. Part 3: Small Molecules Related to (Artificial) Photosynthesis"

*Inorg. Chem.* **2016**, 55 (2), 371-377.

Darensbourg, M. Y.; Llobet, A.

"CuO functionalized silicon photoanodes for photoelectrochemical water splitting devices"

*ACS Appl. Mater. Interfaces*, **2016**, 8(1), 696-702.

Shi, Y.; Gimbert-Suriñach, C.; Han, T.; Berardi, S.; Lanza, M.; Llobet, A.

"Ru-bpp-based Water Oxidation Catalysts Anchored on TiO<sub>2</sub>: The Importance of the Nature and Position of the Anchoring Group"

*Chem. Eur. J.* **2016**, 22, 5261-5268.

Francas, L.; Richmond, C. J.; Garrido-Barros, P.; Planas, N.; Roeser, S.; Benet-Buchholz, J.; Escriche, L.; Sala, X.; Llobet, A.

"Synthesis, Structure, Spectroscopy and Reactivity of New Heterotrinnuclear Water Oxidation Catalysts"

*Chem. Sci.*, **2016**, 7, 3304-3312.

Mognon, L.; Mandal, S.; Castillo, C. E.; Fortage, J.; Molton, F.; Aromi, G.; Benet-Buchholz, J.; Collomb, M.-N.; Llobet, A.

"Establishing the Family of Diruthenium Water Oxidation Catalysts Based on the Bis(bipyridyl)pyrazolate Ligand System".

*Inorg. Chem.* **2016**, 55(5), 2508-2521.

Neudeck, S.; Maji, S.; López, I.; Dechert, S.; Benet-Buchholz, J.; Llobet, A.; Meyer, F.

"Water Oxidation Catalysis with Ligand Substituted Ru-bpp-type Complexes"

*Cat. Sci. Technol.*, **2016**, 6, 5088-5101.

Roeser, S.; Bozoglian, F.; Richmond, C. J.; League, A. B.; Ertem, M. Z.; Francas, L.; Miro, P.; Benet-Buchholz, J.; Cramer, C. J.; Llobet, A.

"Neutral Water Splitting Catalysis with a High FF Triple Junction Polymer Cell"

*ACS Catalysis*, **2016**, 6, 3310-3316

Elias, X.; Liu, Q.; Gimbert-Suriñach, C.; Matheu, R.; Mantilla-Perez, P.; Martinez-Otero, A.; Sala, X.; Martorell, J.; Llobet, A.

"Incorporation of the ruthenium-bis(pyridine)pyrazolate (Ru-bpp) water oxidation catalyst in a hexametallic macrocycle"

*Cat. Sci. Technol.*, **2016**, 6, 6697-6704

Richmond, C. J.; Llobet, A.

"Tracking the Structural and Electronic Configurations of a Cobalt Proton Reduction Catalyst in Water"

*J. Am. Chem. Soc.* **2016**, 138 (33), 10586-10596

Moonshiram, D.; Gimbert-Suriñach, C.; Guda, A.; Picon, A.; Lehmann, C. S.; Zhang, X.; Doumy, G.; March, A. M.; Benet-Buchholz, J.; Soldatov, A.; Llobet, A.; Southworth, S. H.

"Synthesis and Isomeric Analysis of RuII-Complexes Bearing the Pentadentate bpy2PYMe Scaffold."

*Inorg. Chem.* **2016**, 55(21), 11216-11229.

Gil-Sepulcre, M.; Axelson, J. C.; Long, J. R.; Aguiló, J.; Solà, L.; Francàs, L.; Poater, A.; Blancafort, L.; Benet-Buchholz, J.; Guirado, G.; Escriche, L.; Llobet, A.; Bofill, R.; Sala, X.

"Foot of the Wave Analysis for Mechanistic Elucidation and Benchmarking Applications in Molecular Water Oxidation Catalysis"

*ChemSusChem*. **2016**, 9,(23) 3361-3369.

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Matheu, R.; Neudeck, S.; Meyer, F.; Sala, X.; Llobet, A.

“A million Turnover Molecular Anode for Catalytic Water Oxidation”

Angew. Chem. Int. Ed. **2016**, *55*, 15382-15386  
Creus, J.; Matheu, R.; Peñafiel, I.; Moonshiram, D.; Blondeau, P.; Benet-Buchholz, J.; García-Antón, J.; Sala, X.; Godard, C.; Llobet, A.

“Structural and Spectroscopic Characterization of Reaction Intermediates Involved in a Dinuclear Co-Hbpp Water Oxidation Catalyst.”

*J. Am. Chem. Soc.* **2016**, *138*, 47, 15291-15294  
Gimbert-Suriñach, C.; Moonshiram, D.; Francas, L.; Planas, N.; Bernal, V.; Bozoglian, F.; Guda, A.; Mognon, L.; López, I.; Hoque, Md A.; Gagliardi, L.; Cramer, C. J.; Llobet, A.