

## Development of new catalysts for oxidation and reduction chemistry in the context of Artificial Photosynthesis

 *Timeline* | 06/2020 to 05/2023    
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 *Budget* | 169,400 €    
  *Call* | [Proyectos I+D - Retos Investigación 2019](#)

### SUMMARY

The **AP2Chem** project entails the long-term aim of using visible light or redox potential as driving force for the synthesis of fuels and high value chemicals. To this end, there is still a need for more robust, energetically efficient (low overpotentials), selective and faster (TOF) water oxidation catalysts (or oxygen-evolving reaction catalysts),  $H_2O$  and  $CO_2$  reduction catalysts, and catalysts for more elaborated transformations, as well as, the understanding in detail of the fundament processes involve. Towards this direction, the project aims to develop catalysts based on earth abundant elements and to understand how the mechanism operates at fundamental level. The ground-breaking features of this project are:

A) Mechanistic investigations, characterization of key intermediates in the water reduction, and  $CO_2$  reduction. Mechanistic aspects deserve special consideration. Despite the collection of mechanisms proposed, there is a lack of characterization of reaction intermediates. Likewise, understanding the thermodynamic and kinetic factors that control reaction rates is crucial to reduce overpotentials and increase rates and selectivity. Likewise, we will explore and study advanced strategies for the reduction of  $CO_2$  to CO with molecular complexes. During the last years we have developed well-defined coordination complexes with aminopyridine ligands, which have been proven to be very active catalysts for the photo- and electro-catalytic reduction of protons to  $H_2$  and  $CO_2$  reduction. Since these complexes are excellent modular and tuneable platforms we will study and evaluate their effect by introducing pendant hydrogen bonding units and Lewis acids. B) Fully implementation of functional Artificial Photosynthetic (AP) schemes requires that both oxidation and reductive catalytic sites operate together without crossover reactivity. To this end we aim to compartmentalize the reactivity by catalyst immobilization over (photo)electrodes, maintaining the spatial separation between them. To this end, we plan to develop mix metal oxides, and reticular materials such as covalent organic frameworks (COFs) will be chosen for implementation in devices. Mix metal oxides are among the most promising materials for applications; however, there is a lack of understanding. Nevertheless, interesting per se, COFs can serve as a matrix to embed catalysts, photosensitizers, and electron carriers, all working in a synchronized manner. C) We also aim to develop new light- or electro-driven regio- and/or enantioselective catalytic reductions using the same family of well-defined coordination complexes with aminopyridine ligands. Electronic and supramolecular interactions ( $\pi$ -stacking, and chiral pockets) will be studied for proper control of the selectivity in i) the reduction of C=E and C=C bonds and ii) in the C-C inter- and intramolecular reductive homo- or heterocouplings. As a proof of concept, our previous developed cobalt catalysts based on aminopyridine ligands, have shown to be highly active as catalysts i) for the reduction of water to hydrogen,  $CO_2$  to CO, ii) for the light-driven reduction of ketones, aldehydes, olefins and iii) intramolecular reductive cyclization using water as the source of hydrogen atoms. Moreover, preliminary data shows the high catalytic activity and stability of COFs and MMOx developed in the group.