## PhD on Photobiocatalytic water oxidation

We are seeking for a highly motivated candidate for a PhD thesis on photo-induced water oxidation based on the integration of the laccase enzyme in photochemical devices.

The thesis relies on a collaboration between the Laboratory of Surface Reactivity (Mixed University CNRS unit 7197) of the Pierre and Marie Curie University, Paris and the Institute for Integrative Cell Biology (Mixed University CNRS unit 9198) of the French Atomic Energy Commission in Saclay. Supervisors will be Dr Alberto Mezzetti (Université Pierre et Marie Curie) and Dr Winfried Leibl (CEA-Saclay).

The candidate must have a M.Sc. degree in chemistry or physics (or similar), ideally with a background on interfaces between biomolecules and inorganic surfaces. Skills in molecular spectroscopy and electrochemistry are considered as a plus. Good marks in diplomas are an asset.

Students who will obtain their M. Sc. before the summer can also apply.

Previous research experience (e.g. internship in laboratories, scientific publication etc) is an asset; motivation, curiosity, and willingness to learn are the necessary qualities.

The candidate should have a strong commitment to research and to a scientific career.

Good knowledge of English in required; knowledge of French may be useful but is not required.

The Pierre and Marie Curie University is located in downtown Paris, close to the Seine river. The Laboratory of Surface Reactivity has a long-standing tradition in biointerfaces and catalysis; the Institute for Integrative Cell Biology has a long-standing tradition in natural and artificial photosynthesis, as well as in photobiology.

Salary per month is around 1350 € net, + ~150 € roughly acting as a teaching assistant.

Help in finding a suitable lodging is also provided.

The duration of the PhD is 3 years.

Deadline for application is May 8<sup>th</sup>. Preliminary interviews will be conducted by skype.

A selection procedure will take place at the beginning of June in Paris.

Interested candidates must contact Dr. Alberto Mezzetti at <u>alberto.mezzetti@libero.it</u> as soon as possible, joining their CV, a motivation letter, and the name of two reference persons.

The research towards new renewable energy sources has led to the development of biofuel cells that use molecules coming from biomass (glucose, methanol) as electron source and  $O_2$  as the final electron acceptor. These reactions are catalysed by enzymes, with laccases often used for oxygen reduction.

Recently, it has been shown that laccase can also catalyse the opposite reaction, i.e. water oxidation to  $O_2$  [1]. This opens new perspectives in the field of hydrogen production, as the critical point is the kinetic limitations in the oxidation of water [2]. In plants, photosystem II is the light-driven enzyme which oxidizes water; however, it is a very complicated system whose stability is poor, especially in isolated form outside of the plant cells. In contrast, laccase, which is a very stable, industrially used enzyme could represent an interesting alternative.

Recently, it has been shown that the Cu(II) ions forming the active site of laccase can be reduced through electron transfer not from the natural substrates, but from the excited state of a chromophore (porphyrines or Ruthenium-polypyridine complexes).

These two proofs on concept, i.e. the achievement of a redox reaction between laccase copper ions and a photoactivated organometallic complex, and water oxidation catalysed by laccase can be associated in order to develop a photobiocatalytic device for water oxidation at an anode.

The working mechanism of the device can be described as follows: 1) photo-activation of the organometallic complex P to a strongly reducing P\* species, giving its electron to the anode (this electron will then be used at the cathode for  $H_2$  production starting from  $H^+$ . 2) the formed P<sup>+</sup>, strongly oxidising (+1.2 V), oxidises Cu (I) of the T1 site of laccase, which has been reduced after water oxidation. When the 4 copper ions of the enzyme have all been oxidised to Cu(II), laccase is back to the initial state and ready for a new catalytic cycle.

The choice of the organometallic complex will take into account several criteria: quantum yield, lifetime of intermediates (compatible with intermolecular electron transfer), redox potential of the  $P^+/P^*$  and  $P^+/P$  couples, in order to make them suitable for the electron transfer reactions. Ru bypiridine complexes are good candidates [4]. The CEA lab, which has a long-standing experience in the synthesis of these complexes, made a Ru complex whose bypiridine ligands are functionalised by phenol groups [5]. Normally, molecules bearing phenol moieties are good substrates for laccase, and should therefore have a good affinity for the T1 site, thereby making the intermolecular electron transfer of step 2) easier.

One of the key parameters of the two different electron transfer steps (from the organometallic complex to the electrode and from the enzyme to the organometallic complex) is the spatial organisation. The goal will be to immobilize covalently the photoactive complex to the electrode, and/or to the enzyme. This would make it possible to optimise their relative orientation. In this framework, the LRS expertise in the oriented immobilisation of laccase on surfaces, and of its characterisation (PM-IRRAS, XPS) will be extremely useful. On the other hand, the spectroscopic techniques available in the lab (laser flash photolysis, EPR, High field EPR, Resonance Raman) will make it possible to study the electron transfer reaction kinetics and to characterize some reaction intermediates.

From a fundamental research point of view, as the water oxidation mechanism by laccase is presently completely unknown, time-resolved FTIR difference spectroscopy [8] (with electrochemical or photochemical triggering) will represent a new approach to investigate not only electron transfer reactions, but also proton transfer pathways, redox-induced structural changes of the enzyme, and formation of reaction intermediates.

From an applicative research point of view, the goal will be to optimize the light-driven electron transfer chain in order to get the highest (and most stable) current possible.

## References

[1] Pita M, Mate DM, Gonzalez-Perez D, Shleev S, Fernandez VM, Alcalde M, et al JACS. 2014;136:5892-5.

[2] Najafpour MM, Fekete M, Sedigh DJ, Aro E-M, Carpentier R, Eaton-Rye JJ, et al. ACS Catalysis. 2015;5:1499-512.

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[4]Sartorel A., Bonchio M, Campagna S, Scandola F, Chem Rev Soc 2013, 42, 2262-2280.

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