

## Optical control of (photo)electrochemical devices

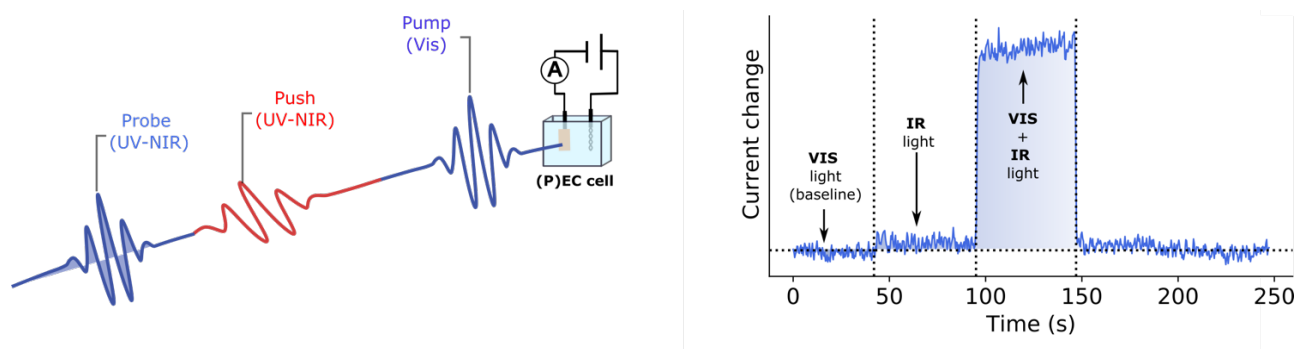
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Traditionally, structural defects have been considered detrimental for the performance of (photo)electrochemical devices. For example, point defects can introduce trap states that act as recombination centres lowering quantum yields. However, recent advances in spectroscopy, microscopy and modelling, have opened the door to ground-breaking studies which are challenging our views of disorder. New evidence suggests that defects could play a much more active role than anticipated. In this talk I will discuss the many different shapes and forms in which disorder can emerge in (photo)electrocatalysis. I will present examples of how disorder-associated phenomena can be monitored in situ and how it can be correlated with catalytic function. Moreover, I will discuss an experimental approach in which infrared photons are used to selectively modulate structural disorder in oxides and enhance device activity. Finally, I will discuss the implications and opportunities that optical control of defects offers to control the efficiency and selectivity of (photo)electrochemical reactions.



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## Combiner l'électrochimie et la fluorescence pour contrôler et détecter les propriétés magnétiques de monocouches.

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Les composés électrofluorochromes, dont les propriétés d'émission sont modulées par leur état redox, sont généralement utilisés pour des applications d'affichage à l'instar de leurs parents électrochromes (1). Cependant, d'autres champs d'applications peuvent également être envisagés notamment dans le stockage de l'information. En effet, la possibilité d'associer au sein d'une même entité moléculaire une composante redox et un fluorophore peut également être mise à profit pour une combinaison de type 'écriture-lecture', l'application d'un signal électrochimique déclenchant un phénomène qui sera détecté optiquement par l'entité luminescente. En utilisant des complexes métalliques comme entité redox, notamment à base de fer ou de cobalt, on peut induire une modification du spin entre un état réduit haut spin et un état oxydé bas spin par exemple. L'état magnétique résultant de ce changement peut alors être lu optiquement par l'état d'émission du fluorophore. Pour réaliser ce défi, deux étapes sont nécessaires : la première est le design d'une dyade moléculaire associant le complexe métallique à un fluorophore avec une bonne communication électronique entre les deux entités ; la seconde est l'immobilisation de la dyade sur une électrode transparente.

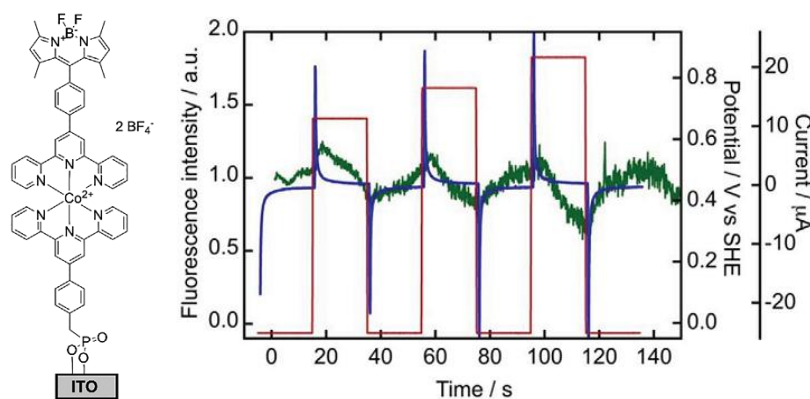


Figure 1 : Design moléculaire de la dyade immobilisée sur surface et modulation de la fluorescence de la monocouche induite électrochimiquement.

Cette communication présentera les différentes étapes de la réalisation de la synthèse du composé moléculaire jusqu'à la monocouche, puis la validation finale du concept comme illustré sur la figure 1. Le mécanisme impliqué dans la commutation de fluorescence induite électrochimiquement sera également analysé (2).

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## Determination of the shape and dimensions of a meniscus under stress for pipette based electrochemical microscopies

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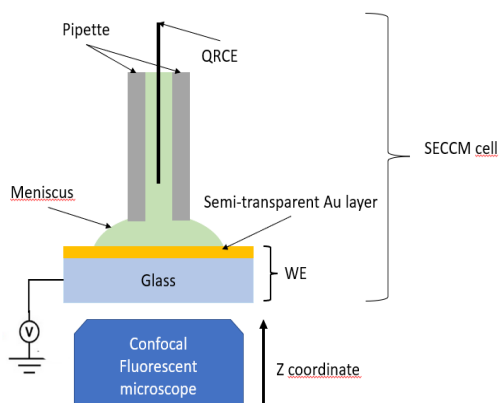
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Scanning electrochemical cell microscopy (SECCM) and other local electrochemical probe microscopies based on (nano)pipettes enable the simultaneous acquisition of topography and local electrochemical reactivity. As such, they have been successfully employed to study many electrochemical reactions at the nanoscale<sup>1</sup>. This is possible due to the confinement of the reaction cell in the meniscus formed between the nanopipette and the substrate. To drive the electrochemical reactions, a potential is applied between a quasi-reference counter electrode (QRCE) and the substrate which acts as the working electrode (WE). A schematic is shown in Figure 1.

The electrochemical response is directly dependent on the exact shape and dimensions of the meniscus, i.e. on the pipette inner and outer diameter, pipette-substrate distance, meniscus footprint on the substrate, etc. Most often, to interpret the experimental data, experimenters must rely on assumptions and numerical simulations to assess the approximate shape of the meniscus.

In the present work, we have implemented confocal fluorescence microscopy as an efficient methodology to determine the dimensions of a meniscus. The method consists in using a fluorescent dye dissolved in solution and to reconstruct in 3D the shape of the meniscus from a series of 2D fluorescence images recorded at different heights of the meniscus (a so called “z-stack”)<sup>2</sup>.

In this work, we use a custom-made semitransparent gold substrate as working electrode. In the aim of modifying the wettability of the surface, we used self-assembled monolayers (SAMs). A large choice of thiolated molecules allows us making the surfaces more hydrophilic or hydrophobic.



We compress or stretch the meniscus in the z-coordinate and evaluate how the shape of the meniscus is affected by the movement and resist to the stress. Different pipette diameters below 100  $\mu\text{m}$  have been investigated and compared to the SECCM (electrochemical response) and SEM (footprint view) results. This work allowed a direct determination of the exact meniscus shape for electroanalytical methods, in the micro scale. As such, it provides a better understanding of the voltammetric responses measured in SECCM.

Figure 1 Representation of the experimental setup, SECCM and confocal microscopy

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## Spectro-Electrochemical Study of Water Structure in the Electrical Double Layer at the Electrode-Electrolyte Interface

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### Abstract

The interfacial structure of water molecules at the electrode/electrolyte interface has provoked a great interest in the applications of physical, chemical, and biological processes. Therefore, the understanding of the interactions and orientations of water at the metal/aqueous solution interface in the charged aqueous solution is of pivotal importance. Since the electrical double layer (EDL) acts as a core for the fundamental studies in electrochemical processes, its structure was commonly deciphered by the theories based on various models of Helmholtz, Gouy, Chapman, Stern, and Grahame [1-3]. Although most advanced techniques (atomic force microscopy, electrical impedance spectroscopy, electrokinetics, and electrophoresis) were endeavored to rationalize the network and organization of water molecules in the defined Stern and diffuse layers, the interpretation of the results is still ambiguous and debatable [2, 4]. To overcome the shortcomings of previous strategies, a newly versatile spectro-electrochemical cell in this study was fabricated and operated to either maneuver the dynamics of water molecules in contact with a working metal electrode (Pt electrode) via electrochemical control or non-invasive nonlinear optical spectroscopies. To examine these optical modifications, we used the state-of-the-art IR-Vis two-color sum-frequency generation (2C-SFG, picosecond reaction kinetics) to analyse electrochemically charged interfaces whilst second harmonic generation (SHG) is combined with the excitation of ultrashort femtosecond and intense THz pulses to study in a dynamic mode. We investigated some key parameters in solution such as solution pH and electrolyte composition that influence the behavior of water at the Pt/charged water interface. Hence, to quantitatively analyse the molecular organization of water under the action of a continuous electrical field and the polarization of THz field, we made more effort to separately distinguish the specific interfacial information of constituent layers of the EDL (Stern and diffuse). In particular, the SFG vibrational spectrum of the Stern layer would reveal its microscopic structure and ionic or intermolecular interactions while the spectrum of the diffuse layer would disclose the surface direct current field strength. The newly designed spectro-electrochemical cell will differentiate the spectral fingerprint of water molecules of hydrogen bond ( $3200\text{-}3400\text{ cm}^{-1}$ ) and free-OH surface ( $\approx 3670\text{ cm}^{-1}$ ) as a function of the THz pulses and the electrical field on the Pt electrode.

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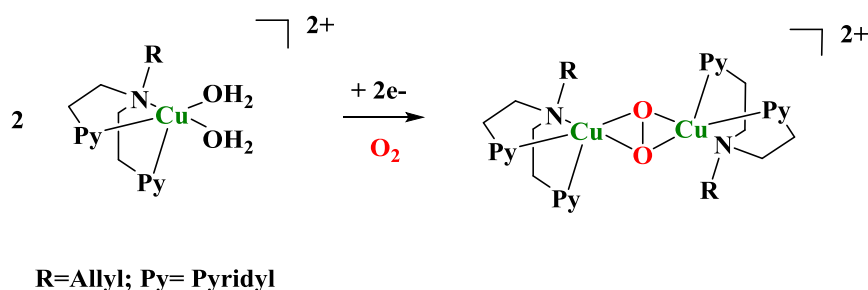
# Cryo-spectroelectrochemistry for reactive species detection: application to peroxo dicopper complexes derivated from a RPY2-type ligand

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Copper centers play a key role in chemical oxidation reactions involving molecular oxygen. In biological processes, copper enzymes are capable of selectively oxidizing substrates through the formation of transient  $\text{Cu}_n\text{:O}_2$  species generated by the reaction of copper(I) and  $\text{O}_2$ . Over decades, several types of these copper-dioxygen adducts such as superoxide, peroxide and oxide have been identified in metalloproteins<sup>1</sup> and in their bioinorganic model Cu complexes.<sup>2</sup> While a significant number of X-ray structures, spectroscopic UV and Raman data of copper-dioxygen complexes have been reported, few data are available concerning redox potential and electron-transfer properties.<sup>3-5</sup> Here, we report our investigations about the formation of a peroxo dicopper complex derivated from RPY2-type ligand<sup>6</sup> by using cryo-electrochemistry and cryo-spectroelectrochemistry.



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## Spectroelectrochemical and reactivity studies of mono- and di-salphen metal complexes (M = Ni(II), Cu(II), Pd(II))

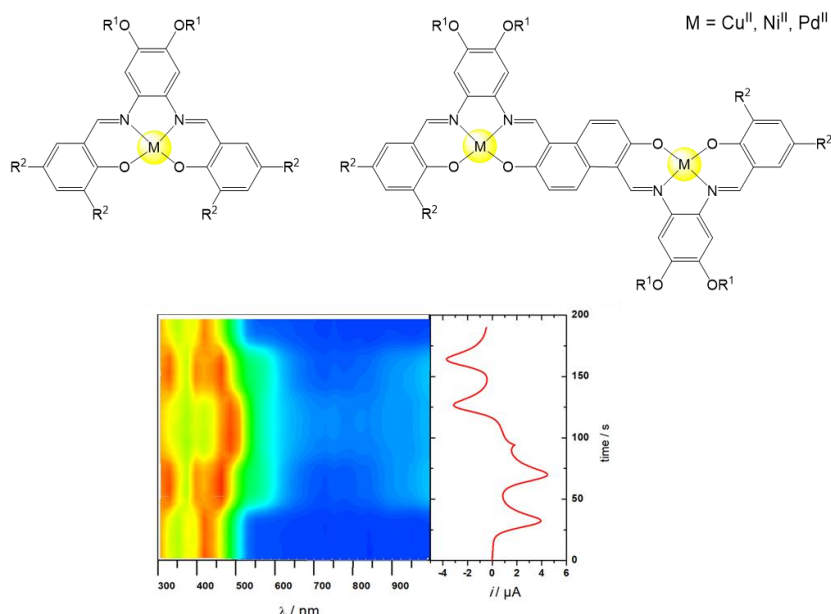
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Galactose Oxidase, a monocopper enzyme derived from the fungus *Fusarium graminearum*, is able to perform catalytic oxidation of galactose under air through the generation of reactive tyrosyl radical species.<sup>1</sup> Aiming at reproducing such property for C-H bond activation, we have developed new synthetic models of this enzyme using new salphen-type ligands that may generate phenoxyl radical moieties. We present here the results obtained with three different metal complexes (Cu<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>) for mono- and di-salphen ligands. Through thorough electrochemical and *in-situ* UV-Vis-NIR spectroelectrochemical studies based on a specific setup,<sup>2</sup> we have investigated the significant role of metal and ligand topology on redox and spectroscopic properties. Furthermore, time-course spectroscopic measurements have been used to examine the reactivities of oxidized species towards benzyl alcohol for benzaldehyde production in terms of kinetics.



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