SPectroscopy AT the single molecule level - Insights for electrocatALysis (SPATIAL)

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Facing the complexity of reactive paths for systems of interest in molecular electronics, energy harvesting, and environmental remediation also requires the development of innovative investigation tools, ideally at the single molecule level in order to analyse the influence of the often complex environment. In organometallic catalysis, a fine tuning of electronic properties is possible through specific ligation on the metal. **In this project, we wish to forecast the possibility to analyse at the single molecule level the behavior of a well-known class of molecular catalysts that trigger the activation of O_2 reduction.**
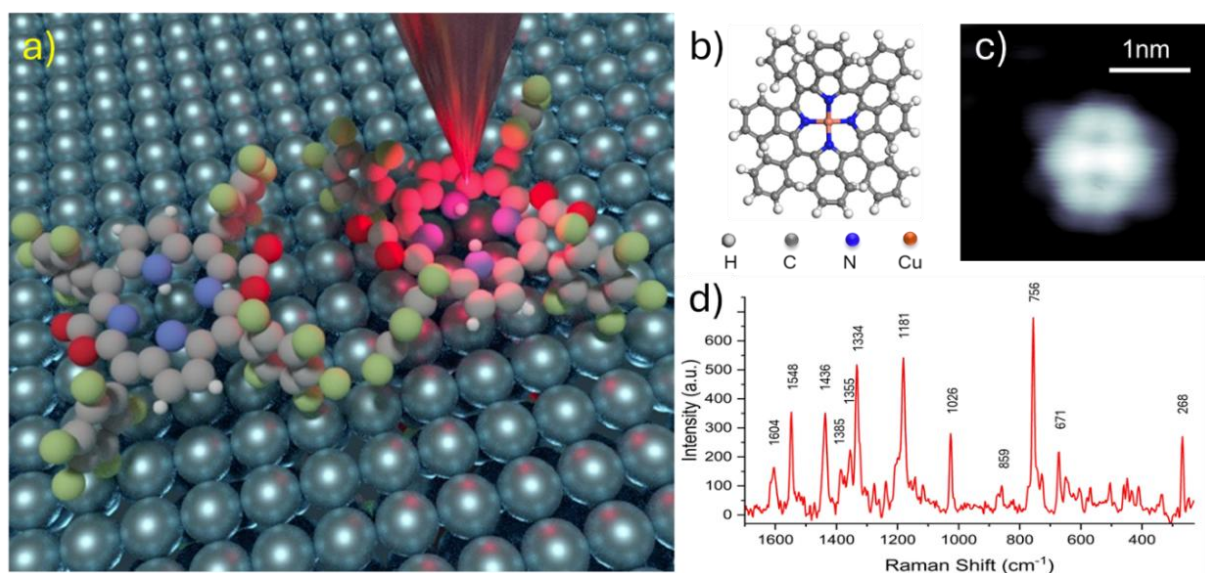

Fig. 1. a) Sketch of preliminary TERS experiments featuring those that will be implemented either in electrochemical conditions or in vacuum. b) Cu(II) 5,10,15,20-(tetraphenyl) tetrabenzoporphyrin and: c) STM image with submolecular resolution. d) TERS spectrum of the single molecule obtained at University of Illinois Chicago (similar spectra for several molecules were obtained in Paris).

1) Context

a) Tip-Enhanced Raman Spectroscopy: chemical identification at the molecular level

Nowadays, many characterization techniques are proposing *operando* adaptations. However, they are often not well suited to investigate the interaction between the metal substrate and adsorbed species of low molecular weight, and are difficult to implement in liquids. Conversely, vibrational spectroscopies provide the possibility to perform chemical identification and are sensitive to the configuration of adsorbed molecules. Detecting adsorbed intermediates by classical infrared measurements may be carried out in a liquid environment but signal absorption by the solvent allows for the use of only thin layers of electrolyte. Moreover, probing metal-adsorbate interactions which require energies below 1000 cm^{-1} can be challenging due to significant absorption by water, which hinders direct observation in this range.

In contrast, Raman spectroscopy relies on laser irradiation usually in the visible range so that it can be easily adapted to liquids, and more specifically, water. Nevertheless, Raman requires an amplification strategy because the scattering process is intrinsically inefficient. It is very common to rely on Surface Enhanced Raman Spectroscopy (SERS) or Tip Enhanced Raman Spectroscopy (TERS) in order to enhance the Raman signal. Here, a gold or silver nanostructure amplifies the electric field so that a very good sensitivity can be retrieved, allowing even single molecules to be detected. Invented in 2000, TERS uses a **Scanning Tunneling Microscope** (STM) or Atomic Force Microscope (AFM) tip to retrieve the topography and electrical or mechanical information with a **vibrational spectrum** at the same position. The spatial resolution accessible in TERS may be exceptional when performed in vacuum and at low temperatures, and is mastered in the group of Nan Jiang who will cosupervise the PhD project. Recently, a single oxygen adatoms on a boron monolayer (*i.e.*, borophene) was analysed by Jiang group via TERS with **0.48 nm** spatial resolution and single bond (B-O) sensitivity.[1] On the other side, Electrochemical TERS (EC-TERS) is available in Paris, and allows to work in *operando* conditions but the methodology (well-handled at IPCM) is still in its infancy.[2] The presently published best resolution is 4 nm.[3] Both groups therefore propose very complementary expertises.

b) Porphyrins and phthalocyanines as active catalysts

In the electrochemical community, porphyrins (Pos) and phtalocyanins (Pcs) are a class of molecules very well known for their catalytic activity. For example Co-Pos are identified to trigger oxygen electroreduction.[4] Nevertheless, minute

physical and/or chemical changes in the cobalt atom environment (solvent, additional apical ligand) may change the catalytic properties. Therefore, when shifting from studies in solution towards systems immobilized on surfaces relevant for potential applications, the properties may change, opening the field for additional fundamental studies. A common way for immobilizing systems relies on the use of self-assembled monolayers. When using an additional ligand that can coordinate the porphyrin apically as presented in Fig. 2, one more parameter is offered.[5] In Raman spectroscopy, this class of molecules is also very well suited because they present important (often resonant) signal amplification in TERS, and are thus ideal candidates for detection at the single molecule level.

2) Objectives

a) Surface modification (Sorbonne Université)

We wish to produce **surfaces modified with porphyrins and phtalocyanins** as sketched in Fig. 2. Here, a gold substrate will be first immersed in a solution modified with a pyridine ligand and potentially another thiol that will act as diluent. Then, a Po or Pc molecule will be coordinated on top of the pyridine. Pyridines with donating of attracting substituents will be used so as to adjust the redox potential and electron density of the metal center. This strategy will allow the production of various surface concentrations of catalysts on the surface. Coverages will be evaluated by fast electrochemistry as commonly performed in ERMMES. Then, electrocatalytic properties will be macroscopically evaluated.

Fig. 2. Molecular assemblies considered in SPATIAL

b) TERS investigations in ambient conditions (Sorbonne Université)

The systems considered here appear ideal to probe and improve the spatial resolution of TERS imaging in solution. Therefore, we will first perform STM imaging in air to image single molecules that should be easily identified for dilute systems. Then, TERS acquisitions will be performed, with the aim of getting high-resolution spectroscopic images. We have already demonstrated that imaging with only 1 nm per pixel and 5 ms temporal resolution is possible, and we can target even lower acquisition times thanks to a new camera that may be acquired with funds from another project. We believe that we could reach submolecular resolution with further optimization. We will then dive into electrochemical conditions. Here, we will rely on our specific configuration and instrumentation, that should offer similar resolution in electrochemistry compared to air. By progressively diminishing the electrode potential, we will be able to follow how the spectral signature of the catalyst is affected, but also potentially detect apparition of **new bands characteristic of reactive intermediates** such as peroxo or oxo ones. We will therefore be able to determine if and how the mechanism is affected by immobilization of the catalyst.

c) TERS investigations at the submolecular level (University of Illinois Chicago)

Our colleague Nan Jiang has built an original low-temperature STM-TERS setup and has extensive experience in surfaces modified by catalyst and/or molecules. The first step of the catalytic cycle is oxygen ligation. Thanks to the exquisite resolution of TERS in those conditions, we will aim to identify the nature but also configuration of the adsorbate. Previous TERS investigations by the Van Duyne group evidenced that during the introduction of O2 on a Co-Po layer, both non-dissociated (Co-O_2) or dissociated (C-O) bonds may be formed with the metal.[6] We will study how this behavior may be influenced by the underlying ligand within Ångstrom spatial resolution. To this end, the use of deuterated O_2 will be considered.

This project is clearly high risk/high gain, but we believe that we can achieve it within the project duration because of the fine control of self-organization and spectroscopic properties of the system, and thanks to our skills in physical chemistry instrumentation.

We plan to recruit a PhD student with good experience in physical chemistry and more specifically, in scanning probe microscopy. Experience in surface modification and electrochemistry will be appreciated. She/he will spend two years in Paris and one year in Chicago.
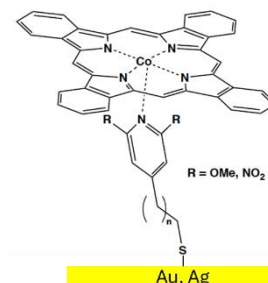
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