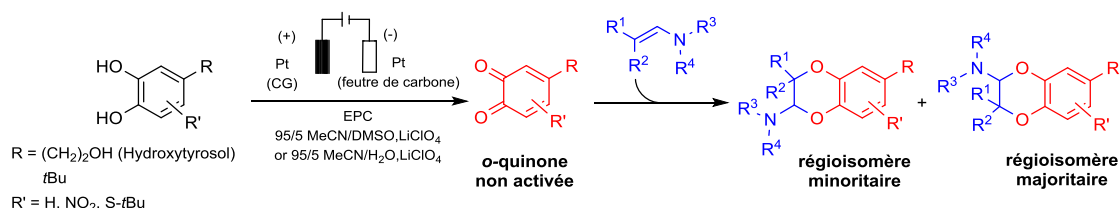


Synthèse électrochimique de 2-amino-2,3-dihydro-1,4-benzodioxanes dérivés de l'hydroxytyrosol

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L'hydroxytyrosol, catéchol abondant dans l'huile d'olive et doté de fortes propriétés antioxydantes, participe aux effets bénéfiques du régime méditerranéen dans la diminution du risque d'athérosclérose. Cherchant à diversifier ses analogues structuraux possédant un noyau catéchol protégé, nous avons voulu accéder à des composés 1,4-benzodioxanes plurisubstitués¹ via une [4+2] cycloaddition entre une énamine (diénophile) et l'*o*-quinone issue de son oxydation (diène), espèces toutes deux instables. A la différence d'autres catéchols, l'oxydation enzymatique de l'hydroxytyrosol conduit à divers produits de suroxydation (ou de dimérisation) de l'*o*-quinone.^{2,3}



Dans ce travail, nous avons montré que l'*o*-quinone de l'hydroxytyrosol peut être électrogénérée de manière stable par électrolyse à potentiel contrôlé dans des mélanges acétonitrile/diméthylsulfoxyde 95/5 ou acétonitrile/eau 95/5. Après addition d'une énamine (aromatique ou aliphatique), deux 2-amino-1,4-benzodioxanes régioisomères sont obtenus par réaction de Diels-Alder à demande électronique inverse (rendements globaux compris entre 65 et 95%). La substitution du catéchol par des groupements attracteurs ou donneurs d'électrons permet de rendre la réaction régiospécifique.⁴

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Correlating substrates reactivities at electrified interfaces with electrolyte structuring in organic solvent/water mixtures

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Inspired by recent developments in electrocatalysis and battery science, mastering the electrolyte structure has emerged as a means to introduce an additional level of control in electrosynthetic routes.¹ In pursuit of using greener reactants, mixtures of organic solvent and water are currently investigated to harness water either as the oxygen-atom source in anodic reactions²⁻⁴ or as the proton/deuterium source in electrochemical protonation/deuteration of alkyl halides.⁵

In this work, we investigate how the solvation properties of organic solvent/water mixtures can affect the electrochemical reactivity of water and the outcome of electrosynthetic reactions. For that, we study mixtures of acetonitrile (ACN), acetone, N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) with 5.0 M water and 0.1 M supporting salt by NMR and IR spectroscopy, small-angle X-ray scattering, bulk molecular dynamics simulations and electrochemistry. Heterogeneity exists at the microscale in ACN/water mixtures, with the formation of aqueous and organic domains.^{3,6} We demonstrate that microheterogeneity also exists in acetone and THF/water mixtures whereas no sign of such microheterogeneity is found for DMF/water mixtures, as previously predicted by MD simulations.⁷ Interestingly, we show that water's structuring in the different mixtures modulates its reactivity at electrified interfaces as probed by performing hydrogen evolution and oxygen evolution reactions at polycrystalline platinum and gold electrodes, respectively. By comparing these results with those collected for two model electrosynthetic reactions, namely the electrochemical oxidation of thioanisole into its sulfoxide and the electrochemical deuteration of benzyl bromide, we demonstrate that the effect of aqueous heterogeneities in organic electrolytes depends on the mechanism. The impact of the nature of the supporting salt for the different electrochemical reactions at stake is also investigated.

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Efficient, selective and scalable electrocatalytic reduction of CO₂ to methane by copper cluster immobilized on carbon nanotubes

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CO₂ reduction reaction (CO₂RR) is extensively studied as a means to use man-emitted CO₂ to store renewable energy into value-added fine chemicals and fuels.^[1,2] Methane is one of the most interesting products from the CO₂RR as it is the main component of natural gas, accounting for a quarter of global electricity production, a market worth USD 4.3 billion a year.^[3,4] CO₂RR using low-cost copper catalysts has shown great promise as a viable and scalable process for the industrial production of methane from renewable energies.

In this context, we reproduce previous results from the literature using a copper phthalocyanine (CuPc) deposited on multi-wall carbon nanotubes.^[5] The molecular catalyst plays the role of a precursor for the generation of copper clusters that are highly active for the reduction of CO₂ into methane. A faradaic efficiency up to 55% was obtained at -1.15 V vs RHE, with a current density of -13 mA cm⁻². Our journey in this research has highlighted key points to consider in order to implement this type of system on gas diffusion electrodes within membrane-electrode assemblies,^[6] paving the way for scalable electrolysis on a larger scale.

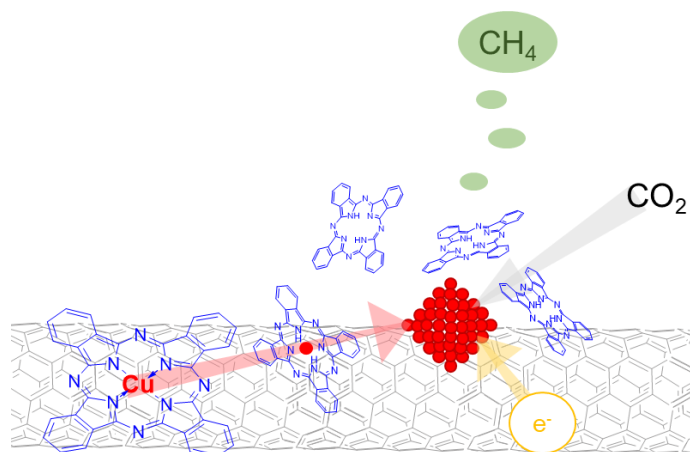


Figure 1: Scheme of the atomic agglomeration from CuPc for selective reduction of CO₂ to methane.

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Diazonium Electrografting Modulation: Towards a better Understanding of the Structure

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Diazonium electrografting is a simple and well-known method for surface functionalization allowing the immobilization of a wide range of molecular structures for many applications. It involves the electrochemical reduction of aryl diazonium salts on conductive substrates, resulting in the formation of robust organic layers. However, despite its well-spread use, the precise structuring of these organic nanofilms remains an ongoing debate. In the vast majority of the reported work, the diazonium approach remains used as a molecular glue, but in the context of the development of fine applications (molecular electronic, selective catalysis, sensing) a perfect understanding of the structure-property relationships of the nanofilm and the existing interaction between substrate and organic layers is required.

In this study, we address this gap by investigating the impact of grafting parameters on the composition of the generated film. By playing on experimental parameters and exploiting redox inhibitors, we provide crucial insights into the structuration dynamics and demonstrate that the film growth can follow two routes. Through a comprehensive approach involving electrochemical measurements, X-ray photoelectron spectroscopy (XPS) analyses, and thickness profiling, we aim to elucidate the mechanism of diazonium electrografting and show the possibility to modulate the film structure. Our findings contribute to the advancement of knowledge in surface chemistry and provide valuable insights for the optimization of diazonium-based surface modification techniques.

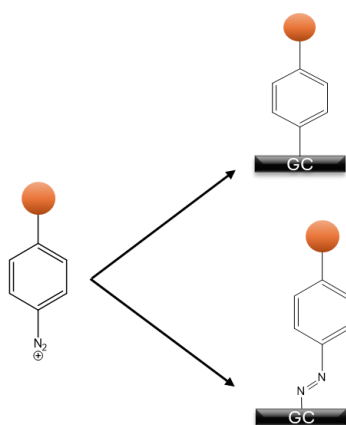


Figure 1: Modulation of the organic nanofilm structure.

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A new electrochemical sensor for lithium hexafluorophosphate detection

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ABSTRACT:

Lithium-ion batteries (LIBs) represent the largest share of the electrical battery storage of our modern society and are considered to be a valid technology during the next twenty years for plug-in hybrid applications and electric vehicles. One issue in conversion of chemical into electrical energy is that damages such as overcharging lead to fatal composition changes and leaks outside the battery. To respond to the massive societal increasing needs battery safety issues have to evolve to overcome these limitations.

This study presents the development of a new sensor based on gold nanoparticles for detecting lithium during battery leakages. An experimental plan involving two factors, pH and gold concentration, was developed to achieve a dendritic shape of nanosensors; at this level, temperature and the time of electroplating were also optimized. The dendritic shape was further confirmed through SEM characterization. Finally, the sensor's ability to detect lithium hexafluorophosphate was investigated using both cyclic voltammetry and impedance spectroscopy techniques using various electrolytes commonly used in the batteries industry.

Results showed that the sensor has successfully detected lithium in acetonitrile across a range of concentrations using cyclovoltammetry analysis, while impedance spectroscopy results indicated detection capabilities in methyl acetate up to a very low concentration.

However, further research is needed to explore the sensor's potential for detecting lithium in gaseous states.

Keywords: sensor, dendritic shape, cyclovoltammetry, impedance spectroscopy, Lithium

Hybrid Electroanalytical Techniques to Understand the Behavior of the Phenylurazole-Tyrosine Click Electrochemical Reaction

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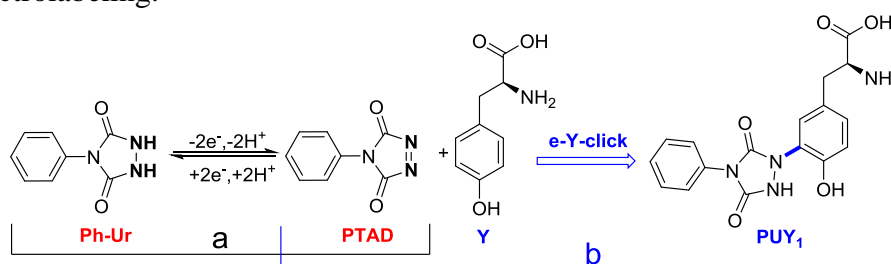
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Abstract

The electrochemical behavior of 4-phenylurazole (Ph-Ur) was studied and the latter was used as a molecular anchor for the electrochemical bioconjugation of tyrosine (Y). Cyclic voltammetry (CV) and controlled potential coulometry (CPC) allowed to generate *in situ* from phenylurazole the PTAD (4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione) species on demand for tyrosine electrolabeling.



Electrochemical oxidation/activation of 4-phenylurazole and (b) e-Y-click reaction between PTAD and tyrosine (Y).

To evaluate the performance of tyrosine electrolabeling, coulometric analyses at controlled potentials were performed on solutions of phenylurazole and the phenylurazole-tyrosine mixture in different proportions (2:1, 1:1, and 1:2). The electrolysis of the phenylurazole-tyrosine mixture in the ratio (1:2) produced a charge of 2.07 C, very close to the theoretical value (1.93 C) with high reaction kinetics, a result obtained here for the first time. The products obtained were identified and characterized by liquid chromatography coupled to high-resolution electrospray ionization mass spectrometry (LC-HRMS and LC-HRMMS). Two products were formed from the click reactions, one of which was the majority. Another part of this work was to study the electrochemical degradation of the molecular anchor 4-phenylurazole (Ph-Ur). Four stable degradation products of phenylurazole were identified (C₇H₉N₂O, C₆H₈N, C₆H₈NO, C₁₄H₁₃N₄O₂) based on chromatographic profiles and mass spectrometry results. The charge generated during the electrolysis of phenylurazole (two-electron process) (2.85 C) is inconsistent with the theoretical or calculated charge (1.93 C), indicating that secondary/parasitic reactions occurred during the electrolysis of the latter. In conclusion, the electrochemically promoted click phenylurazole-tyrosine reactions give rise to click products with high reaction kinetics and yields in the (1:2) phenylurazole-tyrosine ratios, and the presence of side reactions is likely to affect the yield of the click phenylurazole-tyrosine reaction.

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Electrochemical investigation of copper-based nanoparticles synthesized by radiolysis for CO₂ reduction

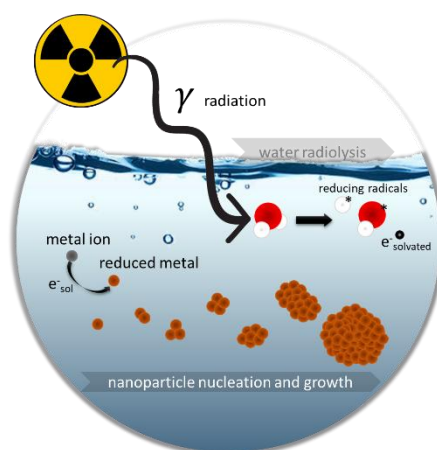
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The electrochemical reduction of CO₂ (CO₂RR) using copper-based electrocatalysts offers an alternative for the valorization of CO₂ into added-value products. Copper-based materials exhibit good performance during the electrochemical conversion of CO₂ into different by-products such as carbon monoxide, methanol, methane, formaldehyde, and formic acid. However, the selectivity remains a challenge. Nanomaterials, particularly bimetallic nanoparticles, enhance the selectivity, activity, and stability of the electrocatalysts due to geometric and electronic effects. The combination and cooperation of metals have shown interesting properties. In this work nanoparticles (NPs) synthesized via radiolysis route were evaluated as electrocatalysts for the CO₂RR. The physicochemical characterization of the nanomaterials was performed by UV-Vis spectroscopy, XRD and SEM/EDS, while the electrochemical properties were characterized using cyclic voltammetry and EIS techniques. The products of the CO₂RR were identified using micro-GC and UV-Vis spectroscopy for the gas and liquid phases, respectively. Among the synthesized nanoparticles, CuPd NPs showed superior performance in converting CO₂ into formic acid (HCOOH) in the liquid phase. Bimetallic NPs improved the selectivity and activity, with Pd increasing HCOOH production and Cu reducing H₂ production. These results highlight the synergetic effects of bimetallic catalysts for CO₂ valorization.



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Insertion material for catalytic hydrogen production

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Among all the ways of storing energy, hydrogen production is one of the most promising.^[1] The **hydrogen evolution reaction (HER)** lies at the heart of converting electricity into H₂. Electrolysers use catalysts on both electrodes to promote HER and OER, these catalysts are based on noble metals and are difficult to replace. On the contrary, in **aqueous batteries**, HER is a recurring problem and occurs even under unfavorable conditions (basic pH)^[2]. Here, electrodes are often oxide-based insertion materials^[3]. The objective of this project is to determine whether **inserting materials** usually used in **battery** could be **used for HER catalysis** under different pH conditions.

This fundamental work focuses on nanosized anatase TiO₂ electrode, originally studied as a negative electrode candidate in aqueous batteries^[3,4]. The goal of this study is to understand what is the potential role played by the inserted cation(s) (Li⁺, Na⁺, H⁺, Mg²⁺) in TiO₂ on the HER thermodynamics and/or kinetics.^[5] Ultimately, we intend to use **Operando Electrochemical Spectroscopic Ellipsometry** (OESE) to precisely study the evolution of the optical properties of titanium and thereby monitoring the insertion reactions; while the quantity of each specific inserted cations will be provided by **Operando Electrochemical Quartz Microbalance** (EQCM).

However, prior to designing these two challenging and in-depth operando experiments, we needed to reproducibly tailor robust electrodes, which would fulfill many requirements: (i) an active material accessible to the electrolyte, (ii) a film processing which would not impact the piezoelectric properties of the quartz substrate (for EQCM). (iii) a film of optical quality (for ellipsometry), and finally (iv) an electrochemically inert substrate upon reduction and towards HER-catalysis. Mesoporous grid-like anatase TiO₂ films obtained by combining the sol-gel chemistry and the evaporation induced self-assembly^[6], followed by a 400°C-thermal treatment, on titanium on glass (or quartz) substrate, were found to be a trusting match.

The next step of the study, our current work, consists in studying how the HER characteristics evolves depending on the type of electrolyte used using classical three-electrode cell cyclic voltammetry experiments.^[7] Buffered aqueous electrolyte solutions (pH 5, 7, and 9) are investigated to study the interplay between the H⁺ insertion reaction and the HER. The impact of adding lithium and sodium salts into these buffered electrolytes are also studied. We will eventually explore more complex cations mixture, such as seawater.

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Detection of CO₂ Reduction Reaction (CO₂RR) products catalyzed by AuNPs using Rotating Ring Disk Electrode vs. Gas Chromatography

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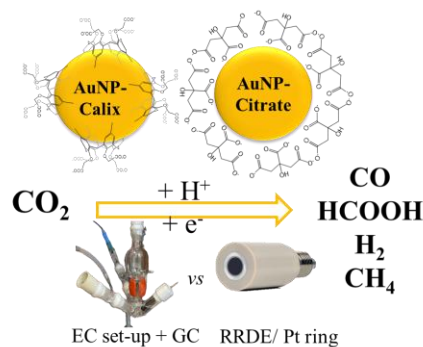
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The electrochemical reduction of carbon dioxide (CO₂RR) is an efficient and selective way to obtain carbonaceous products. However, this reaction is considered to be difficult to activate due to the very stable nature of CO₂. Also, CO₂RR is a multi-step reaction involving from 2 to 12 electrons, with poor selectivity and faradic efficiency due to the competing hydrogen evolution reaction (HER). Therefore, most of the works in the field focus on developing an effective catalyst for CO₂RR while suppressing HER.¹

Herein, we compare two ways of detecting the produced carbonaceous products after CO₂RR: i) an electrochemical one, using a Rotating Ring Disk Electrode (RRDE) where the formed products were detected at the ring, and ii) by gas chromatography. The last one was used for the detection of gaseous products, namely H₂, CO, and CH₄ after a long-time electrolysis, required to accumulate the formed products. In contrast, RRDE was used as an alternative method for instantaneous detection of the formed products by oxidizing them on the ring thanks to the forced convection imposed by rotation.²

In this work, the CO₂RR selectivity, at different potentials (-1.35 V < E < -0.35 V vs RHE) and in a CO₂ saturated 0.1 M NaHCO₃ aqueous solution, will be compared between gold nanoparticles (AuNPs) stabilized with calix[4]arene-tetradiazonium salt and citrate surfactant.³ According to the results obtained on RRDE with a Pt ring, when using calix[4]arene stabilized AuNPs, CO, and HCOO⁻ are detected for applied potential E ≤ -0,95 V vs RHE whereas only CO is detected when E ≥ -0,95 V vs RHE. Using citrate-stabilized AuNPs as a catalyst, CO₂ is mainly reduced to CO for E ≤ -0,95 V vs RHE, with traces of H₂ and HCOO⁻. At E > -1,15 V vs RHE, under the same conditions, CO and H₂ are detected as the main products. To compare this detection method with gas chromatography, three representative potentials were picked: -0.84 V, -0.9 V, and -1.15 V vs RHE. The results show that 2h-electrolysis leads to the production of a high amount of H₂ and CO, regardless of the applied potentials, and a very small fraction of CH₄, showing strong discrepancies with the qualitative measurements made with RRDE. All results will be discussed to rationalize these different behaviors.



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A Chiral, Conductive and Redox-Active Supramolecular Gel Exhibiting Reversible Electrically-Induced Phase Transitions

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Gels are “soft” material in which a large amount of solvent is trapped in a given network. In supramolecular gels, the network is built from non-covalent bonding (π - π stacking, H-bonding...) established between discrete molecules, commonly called low molecular weight gelling agents (LMWG) [1]. One distinctive feature of supramolecular gels, which is inherent to the non-covalent nature of the bonds involved in their structures, is their ability to undergo self-healing processes or to respond reversibly to external stimulation. Such responsiveness to stimulation (pH, T, P, light) has for instance proved useful in numerous fields ranging from catalysis to electronics [1]. Responsiveness to electrical stimuli remains to date however almost unexplored, despite being essential to ensure implementation of such materials in devices [1].

Our group has been focusing over the past few years on the development of responsive metal-organic supramolecular gels involving electrogenerated π -radicals as key responsive and/or assembling elements [2-5]. We now wish to report on the synthesis and on the properties of electro- and photo-responsive supramolecular organogels built from spontaneous self-association of a dicationic viologen-based gelator in alcohols. This presentation will focus on the electrical, structural, spectroscopic and rheological properties of a series of transparent and conductive gels. We will show that their properties are strongly dependent on the ionic composition of the mixtures used for gelation and that a reduction of the viologen units triggers a gel/sol transition coming along with a collapse of the gel microstructure. Such a reversible phase transition could be triggered either by photochemical or electrochemical stimulation, which opens exciting prospects for the development of new electrosensitive devices.

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Electron-Triggered Spin State Switching in a Viologen-Substituted Nickel Porphyrin

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In recent years, controlling molecular motions has emerged as a promising approach for the development of molecules exhibiting switchable magnetic states, the underlying idea being that modifying the structure of a molecular system could induce drastic modifications of its magnetic properties. From a practical standpoint, these ambitious objectives have so far mainly been addressed with coordination complexes using light as an input signal [1, 2] In contrast, far less progress has been made in these directions with electron-responsive systems even though electrochemistry stands as a particularly attractive trigger in the perspective of applications in solid-state devices or to avoid risks of bleaching associated to high energy light irradiations. In this context, our recent efforts have focused on the development of molecular systems for which large amplitude movements actuated by electron transfer can be used to control the magnetic state of magnetically active metalloporphyrin centers.

Following our previous works on porphyrin-based redox-responsive mechanoreactive (supra)molecular architectures [3-5], we will detail in this presentation our strategies to control the local environment and the electronic configuration (High Spin versus Low Spin states) of a nickel porphyrin with an electric trigger. In more specific terms, we will for instance show, on the ground of electrochemical, spectro-electrochemical and magnetic measurements supported by DFT data, that a coordination induced spin state switching process can be actuated in solution by the mechanical folding and unfolding of isolated molecules triggered by application of suitable potential values [6].

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Modulation de l'interaction ferrocène-ferrocène dans des peptides hélicoïdaux fonctionnels induite par différentes conceptions de séquences peptidiques L-Dap/Aib.

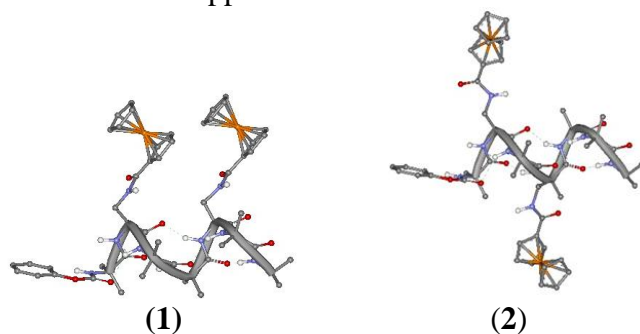
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La conjugaison de composés organométalliques avec des biomolécules telles que acides aminés, peptides et ADN a fourni de nouveaux systèmes qui reflètent les propriétés des fragments organométalliques et biologiques [1]. Les peptides avec des ferrocényles (Fc) pendants ont été exploités comme squelettes organométalliques pour la construction de foldamères via liaisons H intramoléculaire et comme sondes redox dans l'étude du transfert de charge et/ou d'électrons dans les chaînes polypeptidiques.

Nous avons développé deux nouveaux systèmes hybrides polyfonctionnels dans lesquels la présence d'antennes redox Fc insérées *ad hoc* le long de chaînes peptidiques, à travers de stratégies synthétiques ciblées, permet de moduler leurs propriétés électroniques [2]. Plus précisément, nous avons synthétisé deux hexapeptides hélicoïdaux contenant quatre résidus Aib (acide α -amionisobutyrique) et deux résidus L-Dap (acide 2,3-diamino propionique). Les chaînes latérales L-Dap ont ensuite été fonctionnalisées avec des fragments Fc. Les structures des deux peptides 3_{10} hélicoïdaux, à savoir Z-Aib-L-Dap(Fc)-Aib-Aib-L-Dap(Fc)-Aib-NH-iPr (**1**) et Z-Aib-L-Dap(Fc)-Aib-L-Dap(Fc)-Aib-Aib-NH-iPr (**2**), ont été étudiés par diffraction des rayons X, 2D-RMN, Dichroïsme Circulaire (CD), IR spectroscopies et par des études électrochimiques. En raison de la conformation hélicoïdale, dans (**1**) les groupes Fc sont situés sur la même face de l'hélice, tandis qu'en (**2**) ils sont situés sur des faces opposées.



Étonnamment, deux bandes ont été trouvées via Voltamétrie Impulsionnelle Différentielle (DPV) pour (**2**), indiquant une interaction électrostatique entre les groupes Fc malgré leur distance réciproque plus longue par rapport à celui de (**1**). Des expériences de CD à différentes concentrations ont mis en évidence une agrégation évidente pour (**2**), même à des dilutions élevées, suggérant ainsi la nature intermoléculaire de l'interaction électrostatique Fc-Fc.

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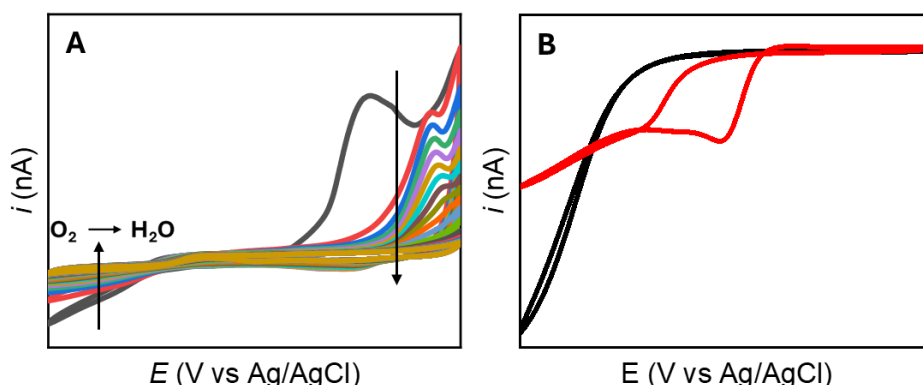
Détection sélective de la réduction du peroxyde d'hydrogène sur microélectrode d'or modifiée

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Les espèces réactives de l'oxygène (ROS) sont des espèces qui jouent un rôle protecteur et régulateur dans des conditions normales et des conditions pathophysiologiques ¹. Un déséquilibre entre pro- et anti-oxydants peut entraîner des dommages et pathologiques (détérioration de l'ADN, inflammations, etc.). Afin d'étendre la compréhension de leur production et leur fonctionnement dans des milieux physiologiques, il est donc important de disposer de méthodes de suivi local et en temps réel de ces espèces. L'électrochimie couplée à l'utilisation de microélectrodes peut permettre de répondre à ces besoins, et conduire à la mise au point de capteurs électrochimiques. La sélectivité et la sensibilité de mesures doit cependant être contrôlée, notamment par la modification de surface d'électrodes ².

Dans ce travail, nous avons évalué la détection de peroxyde d'hydrogène sur microélectrode d'or modifiée par électrodépôt de polymère obtenu par oxydation d'un dérivé de l'aniline. Après la mise au point des conditions de dépôt du polymère, l'étude de la réduction de H₂O₂ sur cette électrode modifiée a notamment mis en évidence une surtension plus faible que celle de l'électrode non modifiée. Notre approche permet aussi de s'affranchir de l'interférence des principaux interférents présents en milieu biologique, d'obtenir une sensibilité améliorée comparativement à une électrode non modifiée ainsi qu'une limite de détection (LOD) similaire à celles de la littérature (~100 nM). Cette étude est complétée par la caractérisation morphologique des films et de leur stabilité.



(A) Voltammogramme d'une microélectrode d'or (25 μm) dans une solution de dérivé d'aniline en milieu tampon phosphate pH 7,4. (B) Voltammogrammes d'une microélectrode d'or modifiée (rouge) ou non (noire) par le polymère dans une solution de 1 mM H₂O₂ en milieu tampon phosphate pH 7,4.

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Electrochemical monitoring of grafting and electropolymerization of an hybrid polyoxometalates (TBA)₃PW₁₁(SiC₆H₅NH₂)₂O on ITO surface

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Abstract

The use of PolyOxoMetalates (POMs) has attracted growing interest over the past decade in the field of molecular electronics, with regard to their interesting electrical and magnetic properties.¹ One crucial steps for this application is to ensure a stable and proper attachment of POM on electrode surfaces. For this purpose, widely useful techniques involve using organically modified POM as a monomer, with the organic part acting as a binder with electrode surface and the other monomers.² This is the background to the present work, in which an ITO electrode is used as a support for grafting and electropolymerization of a hybrid POM ((TBA)₃PW₁₁(SiC₆H₅NH₂)₂O).

(TBA)₃PW₁₁(SiC₆H₅NH₂)₂O was obtained according to a previously described synthesis protocol and the synthesis was confirmed by ¹H-NMR spectroscopy.² The electrografting (EG) process of this POM onto the ITO surface has been made possible by in-situ synthesis of diazonium salt from a mixture of POM and NOBF₄ in a solution of TBAClO₄ in acetonitrile (Fig.1a). The CVs recorded after 10 min of reaction showed a broad irreversible peak in reduction around -0,17V vs Ag/AgCl, of which the intensity decrease during cycles confirming the EG process (Fig.1b). This modified surface (ITO@PW₁₁-SiPhNH₂) was then used as a support to initiate the POM electropolymerization (EP) in a mixed HClO₄/ACN solution (Fig.1c). The analyses carried out by CV showed a growth in terms of peak current intensities of the first redox system (EP control system) of W centres of the POM, highlighting a progressive accumulation of the latter at the electrode surface and the effectiveness of the EP (Fig.1d). A much greater stability of the film after EP was observed with ITO@PW₁₁-SiPhNH₂ compared with the one formed during direct EP without EG step.

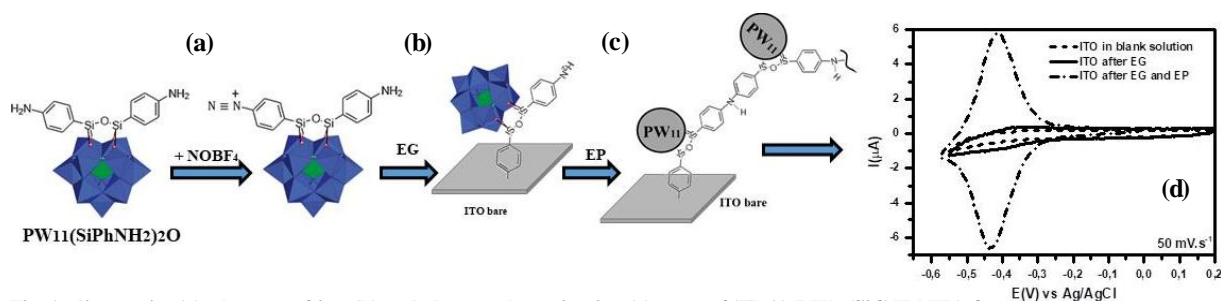


Fig.1: diazotation(a), electrografting (b) and electropolymerization (c) steps of (TBA)₃PW₁₁(SiC₆H₅NH₂)₂O

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Synthesis of Multinuclear Transition Metal complexes Via Electropolymerization

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One of the most investigated areas of organic electronics in recent years is that of electrochromic devices [1]. Electrochromism is defined as the capability of a material to changes of its optical properties in response to an external electric stimulus. The ultimate goal of this work is to synthesize and characterize multinuclear metal complexes deposited on an electrode surface using terpyridine-based ligands with different metals (Fe^{2+} , Ru^{2+} , Zn^{2+} , Co^{2+} ...). Such molecular wires are of great interest in electrochromic devices due to their stability, chromophore character, and their rapid electronic communication [2].

The synthesis of the Bis (aminophenyl terpyridine) metal complexes is done by following a procedure previously described in the literature. Then these complexes undergo polymerization on ITO electrodes using electrochemistry. Then the modified surfaces obtained are characterized using CV, UV-Vis, and XPS.

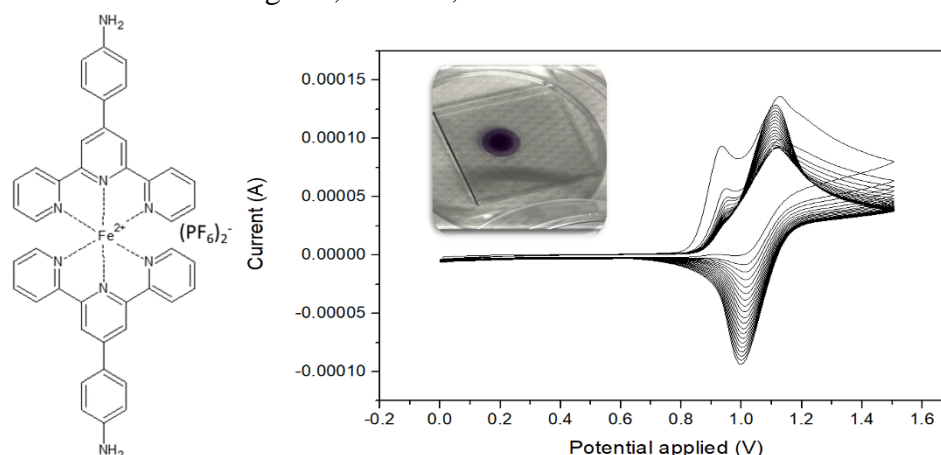


Figure 1: Cyclic voltammetry for electropolymerization of Iron (II) Bis (aminophenyl terpyridine) complex using 20 scans.

In order to obtain a covalent link between the electrode surface and the coordination complex, their corresponding monodiazonium cations are generated in situ and electrochemically reduced [3]. Then, we use cyclic voltammetry polymerization which is a good technique to obtain uniform molecular wires which is deduced by observing an increase in the peak current for the oxidative and reductive peak for the corresponding metal in the complex. Furthermore, using UV-Vis we emphasize the successful polymerization based on an increase in the absorbance across the MLCT band.

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Nanoparticles Synthesis within Reverse Micelles driven by Atmospheric Pressure Plasma Jet and Ultrafast Pulsed Laser for Applications in Electrocatalysis

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With the aim of producing efficient nanocatalysts, we propose in this work an original bottom-up synthesis route of Au and AuPd nanoparticles (NPs), in which the metallic precursors are encapsulated inside reverse micelles. They consist of aqueous microemulsions dispersed in an organic phase and stabilized by molecular (SDS) or polymeric (PS-P2VP) surfactants. Spatial confinement induced by this method allows to better control NPs formation and configuration, and thus, to tailor specific properties.¹ Reduction of the metallic salts inside the reverse micelles has already been achieved thanks to chemical agents, or by electrochemistry.^{1,2} Here, we propose to take advantage of the highly reactive species produced by an atmospheric plasma source (Fig. 1a) or an ultrafast pulsed laser (Fig. 1b) to treat reverse micelles directly in solution. The obtained Au and AuPd NPs are further deposited onto glassy carbon for analysis by scanning electron microscopy (SEM, Fig. 1c) and electrochemistry (Fig. 1d). Hence, we can probe the goodness of the synthesis and the cleaning procedure as well as the electrocatalytic activity of the NPs towards hydrogen evolution reaction (HER). While the laser route allows the irradiation of small volumes of solution, the plasma one offers the advantage of treating the reverse micelles in presence of C black as supporting material for the NPs.

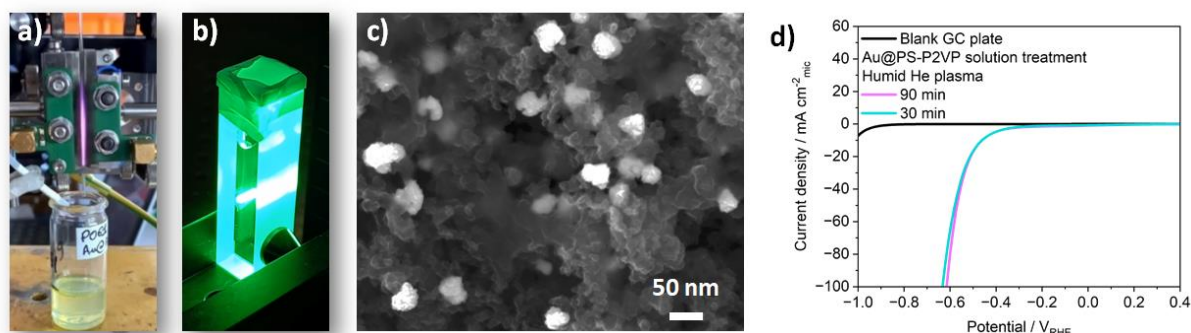


Fig 1. Picture of the treatment of Au@PS-P2VP reverse micelle solution of with a) atmospheric pressure plasma jet; b) ultrafast pulsed laser; c) SEM image of AuNPs supported on C black after plasma; d) corresponding linear sweep voltammograms in H_2SO_4 0.1 M on GC to probe HER activity (0.01 Vs^{-1})

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Complementarity Electrochemical Impedance Spectroscopy / Ultrafast Cyclic Voltammetry for understanding Kinetic Distributions in Adsorbed Supramolecular Structures

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Understanding kinetic distributions within self-assembled monolayers (SAMs) is crucial to control electron transfers between the redox centres in the SAM and the surface on which it is anchored. The complexity of supramolecular structures, exhibiting high number of degrees of freedom, makes these systems good candidates to reveal such distributions. The supramolecular adsorbates chosen for this study are pillar[5]arene rotaxanes, immobilised as SAMs onto a gold surface, and incorporating ferrocene redox centres (Fig. 1a). Their high electron transfer kinetics is probed by ultrafast cyclic voltammetry (UFCV) and electrochemical impedance spectroscopy (EIS), thanks to the use of ultramicroelectrodes.¹ Two models are investigated: a gaussian distribution of the logarithm of the rate constant based on the variation of distance of the redox centre to the electrode, and the constant phase element (CPE) for the adsorption pseudocapacitance. Simulation of voltammograms (Fig. 1b) and complex capacitance diagrams (Fig. 1c), chosen as the most adapted transfer function to represent the EIS data, show the efficiency of the gaussian distribution of distances to model the electrochemical behaviour of the system, while a complementarity between CV and EIS is also observed for the CPE model.

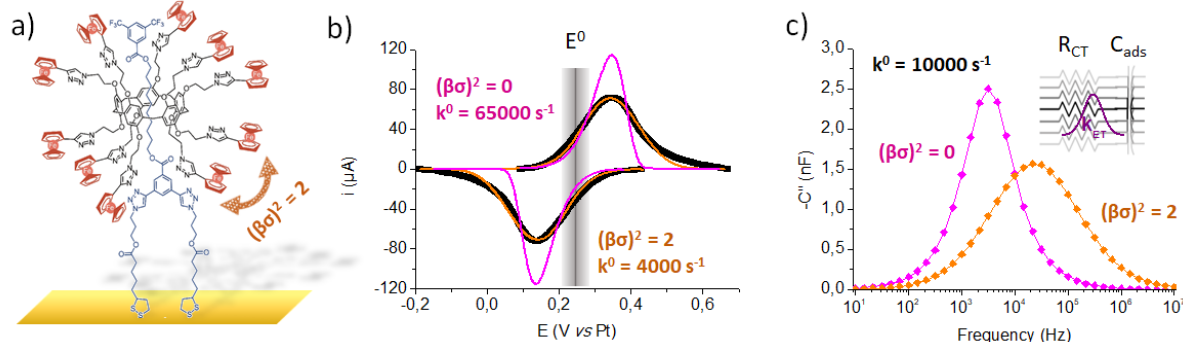


Fig. 1 a) giant rotaxane bearing 10 ferrocene redox centres; b) experimental (black) and simulated CV data at 19600 Vs⁻¹ using two values of average rate constant k^0 and standard deviation $(\beta\sigma)^2$ of the gaussian distribution of distances; c) imaginary part of the complex capacitance simulation for a faradic impedance composed of a $R_{CT}C_{ads}$ series circuit for a single value of k^0 and two values of $(\beta\sigma)^2$.

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Growth of organic layer on Ni/graphene electrode for Spin filtering effects

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We present a bias-controlled spin-filtering mechanism in spin-valves including a hybrid organic chain/graphene interface^[1]. Wet growth conditions of oligomeric molecular chains would usually lead, during standard CMOS-compatible fabrication processes, to the quenching of spintronics properties of metallic spin source due to oxidation. We demonstrate by X-ray photoelectron spectroscopy that the use of a protective graphene layer fully preserves the metallic character of the ferromagnetic surface and thus its capability to deliver spin polarized currents. We focus here on a small aromatic chain of controllable lengths, formed by nitrobenzene monomers and derived from the commercial 4-nitrobenzene diazonium tetrafluoroborate, covalently attached to the graphene passivated spin sources thanks to electroreduction. An unique bias dependent switch of the spin signal is then observed in devices, from minority to majority spin carriers filtering. First-principles calculations are used to highlight the key role played by the spin-dependent hybridization of electronic states present at the different interfaces^[2]

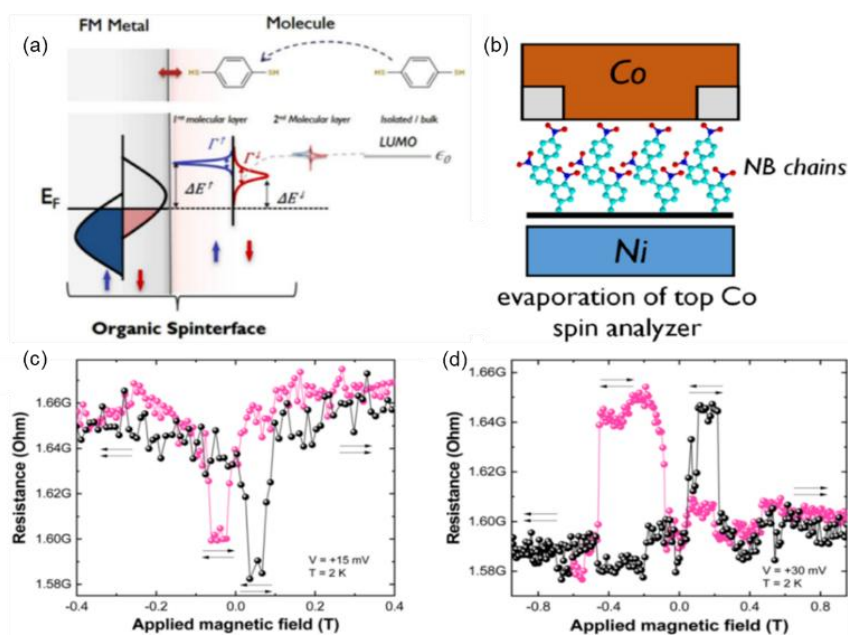


Figure: a). Schematic explaining the hybridization between a ferromagnetic surface and a molecular orbital. Extracted from Delprat *et al.*, *J. Phys. D: App. Phys.* **51** 473001 (2018) b). Schematics of the molecular magnetic junction. c) and d). Magnetoresistive signals measured in Ni/graphene/molecule/Co magnetic junctions.

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Heterogenization of molecular catalysts in layered hydroxide host materials towards CO₂ electrochemical reduction application

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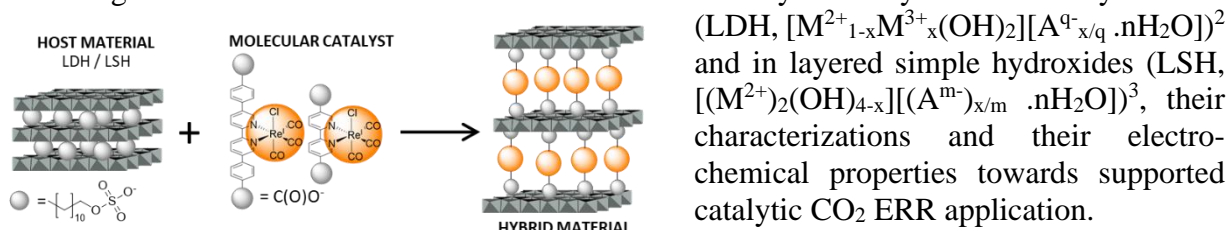
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The reduction of CO₂ is a domain of intense activity with the aim to use CO₂ as a source of carbon for fuels or, more broadly, for commodity molecules. Efforts are thus made to develop selective catalysts for CO₂ electroreduction reaction (CO₂ERR). In that endeavour, molecular catalysts have an advantage which is the fine control of their structure and properties. Molecular catalysts are usually first studied as homogeneous catalysts to evaluate their activity however, to move toward applications, it is often better to design devices in which the molecular catalyst is heterogenized on electrode surface. Among the various strategies to immobilize molecular catalysts, chemical bonding to electrode conductive materials presents some advantages because of the robustness of the linkage. When the catalyst is a transition metal complex, the anchoring group has to be connected to the complex through the ligands, and an important question is thus raised on the influence of this function on the redox and on the catalytic properties of the complex.

We illustrate this issue through an investigation of the effect of the chemical anchoring groups used to immobilize molecular catalysts on host materials for supported CO₂ electroreduction.¹ For rhenium bipyridyl carbonyl complexes, we shown that if the bipyridine ligand is directly linked with an anchoring function, such as carboxylate, there is a drastic effect on the catalytic activity of the corresponding Re complex toward CO₂ERR in solution. In that case, the reducing equivalents are mainly accumulated on the ligand and prevent the formation of Re(0) to interact with CO₂. Alternatively, phenyl-carboxylate substituents on the bpy ligand preserves the catalytic activity of the Re complex. We present preliminary results with hybrid materials resulting from immobilization of such Re-molecular catalysts in layered double hydroxides



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Electrodeposition of Ni-Co Catalytic Films in DES for the Activation of Oxygen Evolution Reaction

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Efficient and affordable activation of small fuel molecules is a promising milestone in decarbonizing energy production. To address this challenge, electrodeposition is a straightforward and up scalable procedure to obtain efficient catalysts. Despite the simplicity of this deposition process, electrodeposition in water suffers from several drawbacks such as limited electrochemical and thermal windows, hydrogen embrittlement, and potentially hazardous and toxic electrolytes. To overcome these issues, numerous studies have explored the alternative of using ionic liquids as electrodeposition media. Among their numerous advantages over the aqueous solvents, ionic liquids exhibit a good thermal stability, negligible vapor pressure, high ionic conductivity, large electrochemical window and the ability to process water sensitive species.¹ Among the plentiful classes of ionic liquids, deep eutectic solvents (DES) have emerged as a greener alternative.^{2,3} In this context, deep eutectic solvents (DES) as electrodeposition media have drawn a peculiar interest in the last decade as they induce the formation of metallic films exhibiting atypical morphologies.^{4,5} This behavior can be explained by both the changes of the metallic ion's chemical environment but also to the hydrogen bond interactions between the precursors of the DES, inducing a templating phenomenon during electrodeposition. While the nucleation and growth of these unusual objects has been extensively studied on bare surfaces, little attention has been paid to their impact over their catalytic activity.

In this study, we investigate the impact of the electrodeposition medium of nickel-cobalt catalytic films over their activity towards oxygen evolution reaction in alkaline conditions. Morphological and chemical properties of the metallic films were investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) while thermodynamic and kinetic behavior were probed by electrochemistry. For the first time, we show that the use of dry ethaline, a deep eutectic solvent, as an electrodeposition medium leads to a clear improvement of the catalytic activity when compared to metallic films deposited in the presence of a gradual amount of water (from $\eta = 330$ mV and 450 mV @ 10mA.cm⁻², in pure ethaline and water, respectively). While providing insights about the improvement of performances of Ni-Co films deposited in ethaline, this work postulates a praiseful and easily scalable strategy to promote efficient catalysts for aqueous batteries.

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Mécanismes moléculaires impliqués dans le fonctionnement de memristors.

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Les molécules organiques sont d'excellentes candidates pour la miniaturisation et l'optimisation de dispositifs électroniques tels que les mémoires non volatiles.¹ La synthèse organique permet de façonner des molécules portant des fonctions d'ancrage (thiols, diazonium), des fonctions électro-commutables (ponts azo) ou encore des fonctions chélatantes (terpyridine, phénantroline). Celles-ci sont choisies afin d'élaborer des jonctions métal/molécule/métal pourvues de propriétés de mémoires non volatiles. La compréhension des mécanismes de transfert électronique à travers ces films moléculaires est essentielle au développement de ces dispositifs mémoires.

Un complexe organométallique de fer présentant des ligands terpyridines et une fonction diazonium terminales a été étudié. Le dépôt de celui-ci en couche mince par électroréduction a été optimisé de telle sorte que la couche résultante présente ou non des fonctions azoïques en son sein.² En effet, l'entité azoïque est soupçonnée d'être responsable d'une commutation de la couche organique entre un état conducteur et un état résistif.³

Des jonctions Au/complexe/Ag ont été fabriquées par impression jet d'encre et présentaient un switch électrique (Cf. figure 1).

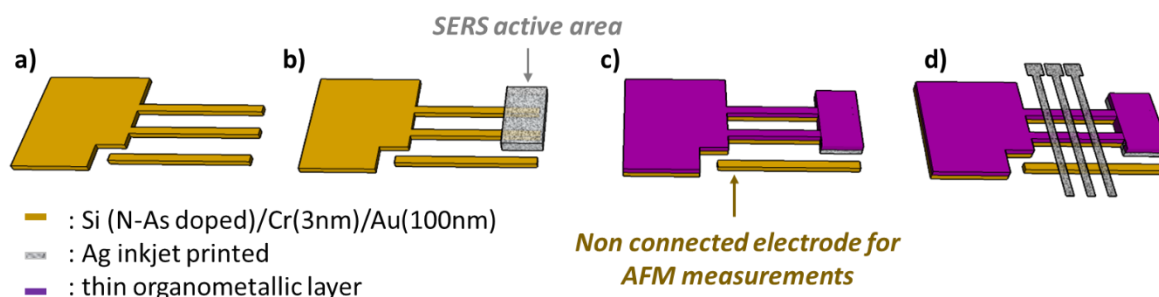


Figure 1 : Schéma des jonctions moléculaires Au/complexe/Ag étudiées.

Afin de comprendre le mécanisme mis en jeu dans cette commutation, ces films ont été étudiés par différentes techniques en conditions électrochimiques. (i) la spectroscopie UV-vis couplée à l'électrochimie (A-SEC). Cette étude a mis en évidence la formation d'une espèce pendant la réduction des ponts azo, disparaissant lors de la réoxydation du film. (ii) la spectroscopie Raman exaltée en conditions électrochimiques a également permis de suivre la composition chimique du film déposé sur un substrat d'or. (iii) des mesures complémentaires de microbalance à quartz (E-QCM) ont été réalisées. La compréhension des mécanismes de commutation de ce complexe nous a permis mettre en évidence les caractéristiques nécessaires pour l'élaboration de mémoires non volatiles.

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Electrochemical Properties of Pyta-based and BPTA-based Luminescent Rhenium Complexes

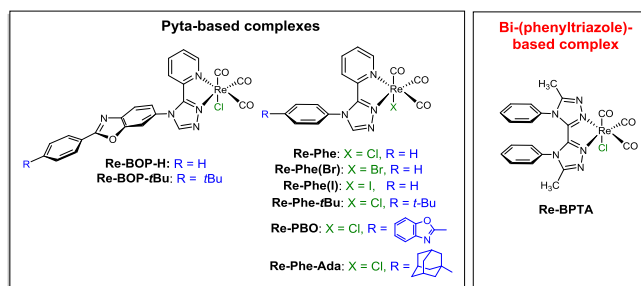
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Interested by complexes that exhibit strong solid-state luminescence enhancement for their numerous applications¹, we have prepared new tricarbonylrhenium(I) complexes with a versatile molecular structure. Their bidentate chelating ligand, i.e. a 3-(2-pyridyl)-1,2,4-triazole or a 4-(2-pyridyl)-1,2,3-triazole (**pyta**) moiety with appended phenyl ring, differs by its isomerism. It was evidenced that grafting a non-coordinated π -conjugated fragment on the N(4) atom of a 1,2,4-triazole group can be of high value for the design of efficient light-emitting materials based on rhenium complexes² (Fig.1). Some of them even present highly sought mechanoresponsive luminescence properties, and unsurpassed for Re complexes.^{3a-c} To access rational design of such complexes, a new symmetrical bi-(1,2,4-triazole) unit grafted with two phenyl rings (**BPTA**) and its **Re-BPTA** complex were prepared. The intramolecular π - π stacking of the phenyl rings in the complex improves its rigidity, providing a high PLQY. This complex can be seen as a new starting block for the preparation of valuable families of SLE-active photoluminescent materials.^{3d}



We will present the electrochemical characteristics of these compounds, and show how electrochemistry is a method of choice to clearly visualize and better understand some key factors of this study. Moreover, the provided data are in perfect agreement with theoretical calculations and optical properties.

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Bubble Dynamics at Single-Phase Nickel Nitride and Sulfide for Hydrogen Evolution Reaction

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Hydrogen (H₂) is considered as a clean and sustainable alternative energy carrier to fossil fuels for meeting future energy demands.¹ Electrocatalytic water splitting is a promising approach to produce eco-friendly H₂ involving a hydrogen evolution reaction (HER) at the cathode and an oxygen evolution reaction (OER) at the anode.² However, during these electrochemical gas evolution reactions, gas bubbles evolving at the surface of the electrocatalyst may result in undesired blockage of active sites and can influence the performance of the electrocatalytic process.³

In this study, we optimized the direct growth of single-phase nickel sulfide and nitride (Ni₃S₂@NF and Ni₃N@NF) on metallic nickel foil (NF) and investigated the influence of surface hydrophilicity or hydrophobicity on electrochemical HER through *in situ* hydrogen bubble dynamics. Contact angle measurements revealed that metallic NF, Ni₃S₂@NF, and Ni₃N@NF electrodes followed a trend of decreasing contact angle in an alkaline solution, indicating that Ni₃N@NF exhibited the highest hydrophilicity/aerophobicity.⁴

In situ bubble visualization demonstrated that hydrophilic/aerophobic Ni₃N@NF led to smaller and faster bubble departure, offering more active sites and lower overpotential. Conversely, decreasing hydrophilicity or aerophobicity resulted in larger bubbles and longer retention times, leading to the unwanted blockage of the active sites and requiring high overpotential for HER. This highlights the significant impact of surface-wetting properties/hydrophilicity on electron and mass transfer during hydrogen generation, particularly at higher current densities.

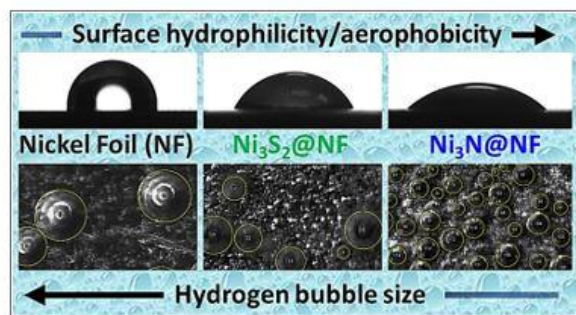


Figure. Scheme showing the effect of the surface hydrophilicity/aerophobicity of electrocatalyst on hydrogen gas bubbles during electrochemical HER.

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Étude électrochimique et spectrale des solutions de l'euporium(III) dans des solvants eutectiques profonds

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Les solvants eutectiques profonds (DES) constituent une nouvelle classe de solvants-électrolytes prometteurs pour le traitement et le stockage des déchets radioactifs. Ces solvants peuvent être facilement préparés à partir de composés peu toxiques, peu volatils et biodégradables (1, 2). En particulier, les DES représentent une alternative intéressante pour la séparation sélective des éléments *f* par des méthodes électrochimiques. L'objectif de notre travail est donc d'explorer la spéciation et les propriétés redox des lanthanides et des actinides en milieu DES et de développer de nouvelles méthodes de retraitement du combustible nucléaire usé.

La présente étude porte sur les propriétés redox des composés d'euporium(III) (en tant qu'analogie chimique des actinides mineurs trivalents) dans une série des DES. Nous avons étudié le comportement électrochimique du bis(trifluorométhylsulfonyl)imide d'euporium(III) et du nitrate d'euporium(III) dans les DES contenant du chlorure de choline et du 1,2-propanediol ou du 1,3-propanediol en fonction de la concentration en sel métallique, de la température et de la teneur en eau. Les mécanismes redox, les coefficients de diffusion des espèces Eu(III) et les énergies d'activation de diffusion ont été déterminés.

Les caractérisations photophysiques des solutions de l'euporium(III) en fonction de la teneur en eau dans le système ont été réalisées par différentes techniques de spectroscopie stationnaire et résolue dans le temps. L'émission des échantillons a d'abord été étudiée par luminescence stationnaire, puis des mesures résolues dans le temps ont été effectuées par excitation à différentes longueurs d'onde d'absorption des échantillons. Les spectres transitoires des états excités de l'euporium ainsi que leur durée de vie ont été déterminés afin d'évaluer l'interaction entre les ions Eu(III) et l'environnement. Pour mieux comprendre le processus de complexation de l'euporium(III) en milieu DES, des simulations numériques par méthode DFT ont été effectuées.

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