

# Appel à projets doc *iSiM* 2023

L'Initiative de Sciences et Ingénierie Moléculaires lance son troisième appel à projets Doc. Il a pour objectif de soutenir des collaborations entre **équipes de l'Alliance Sorbonne Université aux savoir-faire complémentaires** dans le but de développer une recherche d'excellence à l'échelle moléculaire. Ces projets devront **impérativement** être présentés par un minimum de **deux équipes différentes de l'Alliance SU**. Les demandes de **Post-doc, Doc et Equipement iSiM** sont exclusives l'une de l'autre. **Une même personne ne peut porter qu'un seul projet.**

L'échelle moléculaire est revendiquée par beaucoup de disciplines : la chimie évidemment, mais aussi la physique, la biologie, la médecine, les géosciences etc... Notre but est de renforcer l'impact de la recherche de l'Alliance SU en concentrant les moyens sur quelques projets fédérateurs impliquant des compétences multiples autour des sciences et de l'ingénierie moléculaires.

La molécule correspond à l'échelle élémentaire et structurante de la matière, de l'atome au nano-objet, et se trouve de ce fait à la croisée de nombreuses préoccupations scientifiques et d'enjeux sociétaux primordiaux que sont la santé, l'énergie, l'environnement, l'information et ce dans un contexte d'économie circulaire. En effet, toutes les disciplines scientifiques expérimentales majeures s'appuient fortement sur les propriétés moléculaires pour analyser, comprendre, reproduire et manipuler la complexité de la matière. Une approche multidisciplinaire à l'échelle de la molécule précisément identifiée est donc essentielle pour relever des défis scientifiques majeurs autour de questions fondamentales ou appliquées telles que le biomimétisme, la photosynthèse artificielle, l'origine cosmique des briques moléculaires du vivant, la vie artificielle, le stockage et la transmission moléculaire et supramoléculaire de l'information, la catalyse, la modélisation théorique d'assemblages moléculaires complexes, les machines moléculaires...

# **Modèle de description du projet de recherche à rédiger en anglais**

## **Grandes lignes de la demande**

**Titre du projet/ Title of the project :**

***MOlecular MOdification of COpper surfaces for CO electroreduction catalysis***

**Acronyme MOMOCOCO**

***CV des porteurs de chaque équipe (1 page max/personne)/CV of the Pls of each partner***

**Partner 1 : M. Fontecave, Collège de France, Paris**

After a PhD at Ecole Normale Supérieure in Paris (1984), a post-doctoral internship at Karolinska Institute, Stockholm (1985-1986), 20 years as Professor of Chemistry at University Joseph Fourier, Grenoble (1988-2008), Marc Fontecave is, since 2009, Professeur at Collège de France, Paris, holder of the Chair of Chemistry of Biological Processes. He is a member of the French Academy of Sciences since 2005 and of the Royal Swedish Academy of Sciences since 2019. He is the Director of the Laboratory of Chemistry of Biological Processes (UMR CNRS/Collège de France/Sorbonne Université). His research focusses on the study of catalysts (homogeneous, heterogeneous, bioinspired) and biocatalysts (metalloenzymes and artificial enzymes) as well as of electrochemical devices for water splitting and carbon dioxide reduction as strategies for chemical storage of renewable energies (artificial photosynthesis). He is the author of 450 publications. In addition, he is the President of the Fondation du Collège de France and member of a number of scientific councils of chemical companies (EDF, Veolia Water Technologies, Forvia).

5 publications significatives :

*Pyranopterin Related Dithiolene Molybdenum Complexes as Homogeneous Catalysts for CO<sub>2</sub> Photoreduction*, T. Fogeron, P. Retailleau, L.-M. Chamoreau, Y. Li, M. Fontecave, *Angew. Chem. Int. Ed. Engl.* **2018**, 57, 17033-17037

*Electroreduction of CO<sub>2</sub> on Single-Site Copper-Nitrogen-Doped Carbon Material: Selective Formation of Ethanol and Reversible Restructuration of the Metal Sites*, D. Karapinar, Ngoc Tran Huan, N. Ranjbar Sahraie, D. W. Wakerley, N. Touati, S. Zanna, D. Taverna, L.H. Galvão Tizei, A. Zitolo, F. Jaouen, V. Mougél, M. Fontecave, *Angew. Chem. Int. Ed. Engl.* **2019**, 58, 15098-15103

*Low-cost high efficiency system for solar-driven conversion of CO<sub>2</sub> to hydrocarbons*, Huan Ngoc Tran, D. Alves Dalla Corte, S. Lamaison, L. Lutz, N. Menguy, M. Foldyna, S.-H. Turren-Cruz, A. Hagfeldt, F. Bella, M. Fontecave, V. Mougél., *Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740.

*Bio-inspired hydrophobicity promotes CO<sub>2</sub> reduction on a Cu surface*, D. Wakerley, S. Lamaison, F. Ozanam, N. Menguy, D. Mercier, P. Marcus, M. Fontecave, V. Mougél *Nature Materials* **2019**, 18, 1222-1227

*Highly selective copper-based catalysts for electrochemical conversion of carbon monoxide to ethylene using a gas-fed flow electrolyzer*. H. Phong Duong, Ngoc-Huan Tran, G. Rousse, S. Zanna, M. W. Schreiber, M. Fontecave. *ACS Catalysis* **2022**, 12, 10285-10293

## **Partner 2 : Louis Fensterbank, Sorbonne Université, Paris**

Louis Fensterbank obtained his PhD on silanols chemistry in 1993 at SUNY Stony Brook. After a lecturer position in 1994 at the Université Pierre & Marie Curie (UPMC), he was appointed in 1995 as a CNRS Chargé de Recherche at the same place. In 2004, he became Professor at UPMC, now Sorbonne Université. His research interests concern the discovery of new molecular transformations relying on radical or organometallic processes, and their combination, as well as their applications to the synthesis of substrates with relevant properties (natural products, ligands). He is also interested in organosilicon derivatives as Lewis acids and biological probes. Recently, he has been involved in the design and development of new surface ligands (carbenes) for metallic nanoparticles. Co-author of more than 240 publications, he has received several awards, notably the Silver Medal of CNRS in 2017. He is also Fellow of the Royal Society of Chemistry and Senior Member of Institut Universitaire de France since 2021.

5 publications significatives :

*Carbonylation of Alkyl Radicals Derived from Organosilicates through Visible-Light Photoredox Catalysis*, Cartier, A.; Levernier, E.; Corcé, V.; Fukuyama, T.; Dhimane, A.-L.; Ollivier, C.; Ryu, I.; Fensterbank, L. *Angew. Chem. Int. Ed.* **2019**, 58, 1789-1793.

*Photosensitized oxidative addition to gold(I) enables alkylnative cyclization of o-alkynylphenols with iodoalkynes*, Xia, Z.; Corcé, V.; Zhao, F.; Przybylski, C.; Espagne, A.; Jullien, L.; Le Saux, T.; Gimbert, Y.; Dossmann, H.; Mouriès-Mansuy, V.; Ollivier, C.; Fensterbank, L. *Nat. Chem.* **2019**, 11, 797-805.

*Indolizy Carbene Ligands. Evaluation of Electronic Properties and Applications in Asymmetric Gold(I) Catalysis*, Martinez, T.; Vanitcha, A.; Troufflard, C.; Vanthuyne, N.; Forté, J.; Gontard, G.; Lemièrre, G.; Mouriès-Mansuy, V.; Fensterbank, L. *Angew. Chem. Int. Ed.* **2021**, 60, 19879-19888.

*Synthesis and Optical Resolution of Configurationally Stable Zwitterionic Pentacoordinate Silicon Derivatives*, Deis, T.; Maury, J.; Medici, F.; Marion, J.; Forte, J.; Vanthuyne, N.; Fensterbank, L.; Lemièrre, G. *Angew. Chem. Int. Ed.* **2022**, e202113836.

*Reactant-Induced Photoactivation of In Situ Generated Organogold Intermediates Leading to Alkynylated Indoles via Csp<sup>2</sup>-Csp Cross-Coupling*, Zhao, F.; Abdellaoui, M.; Hagui, W.; Ballarin Marion, M.; Berthet, J. Corcé, V.; Delbaere, S.; Dossmann, H.; Espagne, A.; Forté, J.; Jullien, L.; Le Saux, T.; Mouriès-Mansuy, V.; Ollivier, C.; Fensterbank, L. *Nature Comm.* **2022**, 13, 2295.

***Résumé du projet/Summary of the project***

Problems associated with CO<sub>2</sub> electroconversion to C<sub>2</sub> products (ethylene and ethanol) has led to consider tandem systems in which CO<sub>2</sub> is first converted to CO and then CO electroreduced. Here we address an unexplored strategy aiming at modifying the surface of copper catalysts with molecules in order to tune the efficiency and the selectivity of CO electroreduction to C<sub>2</sub> products. We propose to use molecular radical precursors, specifically iodonium and sulfonium compounds as well as hypercoordinate bis-catecholato silicon compounds (silicates), for electrodeposition of the molecular layer on the catalyst.

## Description scientifique / Scientific description (5 pages max.)

### **Objectifs et description du projet/Objectives and description of the project (2 pages environ<sup>1</sup>)**

On the way to massive defossilization, renewable carbon sources, such as biomass or CO<sub>2</sub>, have to be exploited in order to replace petrochemicals. In particular, CO<sub>2</sub> electroconversion into organic molecules, an energy-requiring process, is an attractive strategy as it combines: (i) capture of CO<sub>2</sub> from the atmosphere; (ii) storage of intermittent renewable energies (wind, sun) in a stable chemical form; (iii) exploitation of CO<sub>2</sub> as a carbon feedstock, alternative to fossil sources [1]. To achieve the complex electroreduction of CO<sub>2</sub> into multi-carbon compounds, such as ethylene, ethanol and propanol for example, the only possibility is to use copper (Cu) catalysts [2]. Therefore, *only Cu will be considered in this project*. Metals such as Ag, Au, Zn, catalyze CO formation while other ones (Sn, In, Bi) catalyze formic acid formation. However, CO<sub>2</sub> electroreduction raises a number of problems which have yet to be addressed, related to the chemical stability of CO<sub>2</sub>, its low solubility in water, its propensity to react with hydroxides to form carbonates, and the lack of selectivity towards C2 and C3 products.

As a consequence, it is now considered that a more viable (both technologically and economically) approach might reside in a tandem system [3]. It consists in a two-step process, with first CO<sub>2</sub> electroreduction to CO using for example a solid oxide electrolysis cell (SOEC) and Ag or Au catalysts, followed by CO electroreduction to ethylene, since no CO<sub>2</sub> is lost as carbonate in either step [4]. While CO<sub>2</sub> aqueous electroreduction to CO is already quite well technologically advanced and close to industrial implementation,[5], electroreduction of CO to C2 products has been much less studied. These investigations were first carried out in standard H-cells, however suffering from low current densities because of the low solubility of CO, [6], but recently other cell configurations have been explored such as gas phase flow cells and membrane electrode assemblies (MEAs), both using gas diffusion electrodes (GDEs) [7]. Such electrodes can efficiently increase the CO diffusion at the gas/liquid/solid interface. In 2022, M. Fontecave and collaborators have reported flow cells and MEA systems for CO reduction which, thanks to an original porous dendritic copper oxide catalytic material, achieved CO conversion to ethylene at high current density and at a record faradic efficiency of 80 % [8].

A well-known strategy to tune the selectivity of CO<sub>2</sub> electroreduction consists in modifying the surface of the catalysts with molecules. It can be small molecules or polymers, via covalent or non-covalent grafting [9]. This strategy has been widely used and resulted in some success recently, including from M. Fontecave laboratory [9,10]. However, intriguingly, there is no report so far of a molecularly modified Cu catalyst used specifically for CO electroreduction. This project aims at studying, *for the first time*, how an organic moiety, adsorbed or grafted on the surface of a Cu material, can tune the reactivity and the selectivity of the metal active sites for CO reduction. We anticipate original outcomes from this study since CO activation requirements are different from CO<sub>2</sub> activation and hope finding highly selective Cu catalysts for C2 products, thanks to an appropriate molecular modification.

While molecules/polymers are generally deposited on the surface of solid catalysts via physical methods (adsorption, dropcast, etc..), we herein propose to explore a chemical electrodeposition method. It is based on the electrochemical one-electron reduction (or oxidation) of a radical precursor at the surface of the Cu electrode and formation of an organic layer resulting from subsequent reactions of the formed radicals. This strategy has been widely used with carbon electrodes (including carbon nanotubes) and diazonium compounds for example, but much more rarely in the case of Cu materials. Furthermore we here propose to investigate a wide variety of radical precursors, including sulfonium and iodonium salts as well as hypercoordinate bis-catecholato silicon compounds (silicates),

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<sup>1</sup> Police Arial ; Taille de police 11 ; interligne simple, **Taille max. du fichier 5Mo**

allowing a fine tuning of the electronic and steric properties of the active aryl or alkyl radicals. Apart from the very recent works (2023) of Agapie [11], which compare the grafting of aryl-iodoniums with diazoniums, these compounds have not been explored yet for Cu surface modification. This part of the work will benefit from the expertise of L. Fensterbank group in the synthesis of radical precursors and their reactivity. Indeed, partner 2 has already studied these different radical precursors in the context of photoactivation processes and is thus familiar with their synthesis and reactivity [12]. Partner 1, on his side, has the full expertise in electrochemistry and electrocatalysis to achieve the controlled electrodeposition of radical-derived products and to characterize the modified Cu materials for their catalytic properties during CO electroreduction.

The project is thus expected to provide original insights into the following issues:

- Developping new methods of modification of the surface of electrocatalysts.
- Evaluating the impact of Cu surface molecular modification for CO electroreduction,
- Identifying new Cu-based catalysts selective for CO reduction to C2/C3 products, specifically ethylene, ethanol and propanol, among the most interesting products.

### ***Faisabilité. Evaluation et gestion des risques / Feasibility. Risk assessment and management (1/2 page environ1)***

The project is likely to reach its goal as it is based on the collaboration of two complementary groups with appropriate expertise for addressing such questions. M. Fontecave one has recently set up all the technical tools for studying carbon monoxide electroreduction with the first papers published in 2022 (*ACS Appl. Mat. Int.* 2022, 14, 31933; *ACS Catalysis* 2022, 12, 10285) and has some experience in copper surface modification (*Nature Materials* 2019, 18, 1222, *Angew.Chem.* 2022, 61, e202206279). L. Fensterbank one is well known for his achievements in radical precursors synthesis and light-induced free radical generation for subsequent organic transformations (*Adv. Synth. Catal.* 2013, 355, 1477 ; *Chem. Eur.J.* 2013, 19, 10809 ; *Angew. Chem.* 2015, 54, 11414). As there is very little precedent for such an approach, implying an original electrogeneration of aryl [11] and alkyl [13] radicals on Cu surfaces (Cu nanoparticles, Cu dendrites), we indeed anticipate preliminary difficulties in finding the good radical precursor/ Cu electrode combination. However the risk is limited as a great variety of radical precursors is synthetically available and preliminary experiments with imidazolium compounds also proved successfull (unpublished). Finally, in case the original approach is unsuccessfull, Cu surfaces can be modified with molecules *via* other standard deposition methods and the resulting electrodes studied for CO electrodeposition.

### ***Situation du projet sur le plan national et international/Position of the project within national and international context (1/2 page environ1)***

CO electroreduction is a completely new field. It has started, after 20 years of research aiming at developping direct CO<sub>2</sub> electroreduction to multi-carbon compounds. However, intrinsic limitations related to the low solubility of CO<sub>2</sub> in water, its great stability and its propensity to convert into carbonates, has led a couple of years ago considering tandem reactions, CO<sub>2</sub> electroreduction to CO followed by CO electroreduction to multi-carbon compounds. The first paper came out in 2014 [14] but the field has really started to develop only since 2020 [15]. Fontecave group is one of the few groups in the world investigating this reaction.

As for catalyst surface modification (with small molecules and polymers), it has been developed extensively all over the world during the last 10 years and as such it is not new but it has been studied *exclusively* for solid electrocatalysts of CO<sub>2</sub> reduction. To our knowledge, there is no study of the impact of copper catalyst surface modification with molecules on CO electroreduction efficiency and selectivity.

***Positionnement du projet par rapport aux objectifs de l'iSiM/Position of the project in regard to the iSiM objectives (1/2 page environ1)***

The project fits in iSiM objectives even though it deals with solid materials as catalysts for CO electroreduction. Indeed, its main goal is not to develop novel Cu solid materials (here standard Cu electrodes will be used in a first approach) but to evaluate the effects of molecules, with various steric and electronic properties, when deposited on the surface of the material, with respect to its catalytic activity during CO electroreduction. The chemistry under investigation is thus molecular as the project aims to study the electroreduction of molecular radical precursors on Cu electrodes and the behaviour of the generated radicals on the Cu surface. The project is clearly multidisciplinary (combining molecules and solids) and covers the field of catalysis, a keyword of iSiM objectives.

It is only feasible through the association of organic chemists, materials chemists and electrochemists. It is indeed such an association which is mobilized for that project with organic chemistry provided by L. Fensterbank group, at Sorbonne Université, and solid electrochemistry by M. Fontecave, at Collège de France.

***Faire apparaître la complémentarité des compétences/ Highlight partners complementarity***

The two partners have the complementary competences requested for the project. M. Fontecave is an expert in molecular and material chemistry, specifically in electrocatalysis (water splitting and CO<sub>2</sub>/CO reduction). L. Fensterbank is an organic chemist, with achievements in developing original activation processes for organic synthesis.

## Références / Bibliography

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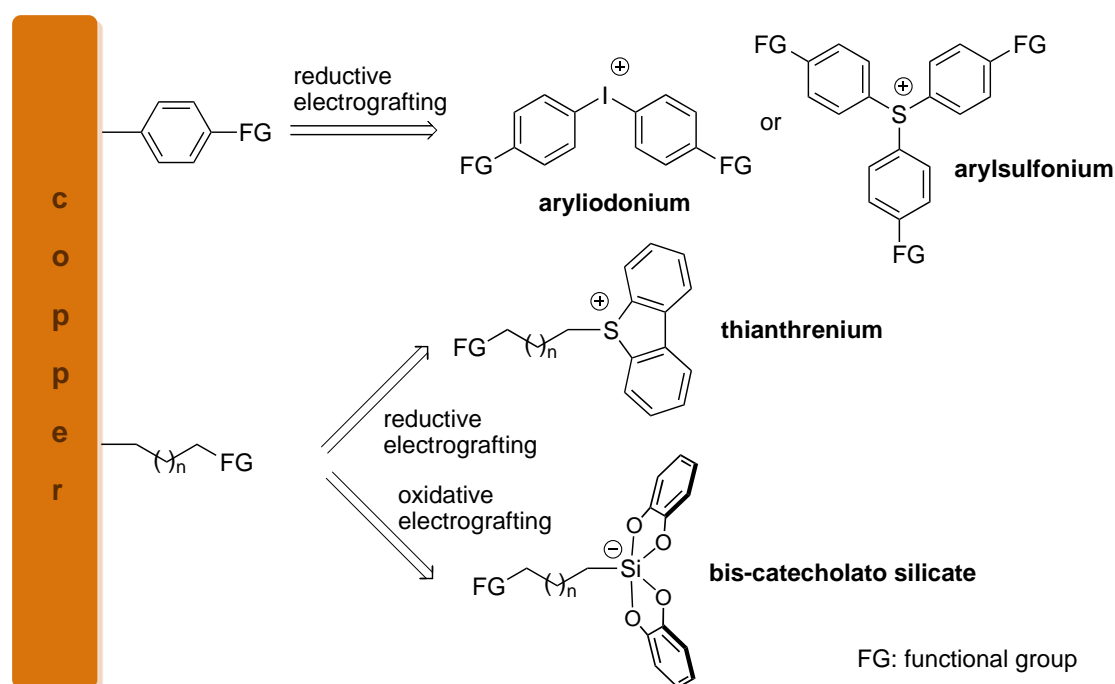
## Programme de travail /

### Programme de recherche / Research program (1 page max.)

In practice, the project implies: (i) developing an efficient deposition method yielding a stable organic layer on the surface; (ii) characterizing the novel material and specifically the structure of the organic layer; (iii) evaluating the catalytic properties of the material for electroreduction of CO in a flow-cell electrolyzer.

#### 1. Electrodeposition: radical chemistry

For that purpose, we will select the following Cu materials : (i) commercially available Cu nanoparticles, (ii) more elaborated Cu-based materials developed in partner 1 laboratory such as porous dendritic copper and bimetallic (CuAg for example) materials. As for the radical precursors, we will assess the grafting of aryl and alkyl radicals. A recent study by Agapie suggests that aryl-diazonium and -iodonium while acting as smooth aryl radicals precursors under reductive mode do not lead to identical grafting on Cu, the layer obtained from iodoniums being more stable and stable [11]. Although harder to reduce ( $E_{red} < 1.0$  V), arylsulfoniums never used in this context and for which we have expertise [12c] will be engaged. In parallel, different types of layers will be accessible using alkyl radicals. Alkylhalides are possible precursors but generally necessitate highly negative potentials, especially when dealing with primary radicals,[13] or special tricks to be grafted [16]. This is why, we are interested in the recently developed and more easily reduced S-thianthrenium salts [17]. Alternatively, under oxidative electrografting [18], the alkyl bis-catecholato silicates of partner 2 featuring the lowest oxidative potentials of the known radical precursors ( $< 1.0$  V, even for primary unstabilized radicals) [12c] are obvious candidates. Obtained from commercially available or easily synthesized (for instance *via* hydrosilylation) trialkoxysilanes, they allow a wide array of functions, from apolar to polar ones.



## 2. Characterization of the surface organic layer

The Cu materials will be analyzed after electrodeposition by standard methods, including microscopy (SEM and TEM), spectroscopy (IR spectroscopy, XPS, ...) as well as with NMR spectroscopy after detachment/solubilization of the organic layer.

## 3. Evaluation of the electrocatalytic performances

The obtained materials will serve as cathode materials in flow electrolysis cells, available in partner 1 laboratory, and evaluated by standard electrochemical methods for their catalytic properties during CO reduction: cyclic voltammetry, linear sweep voltammetry, controlled-potential and -current electrolysis. Gaseous products (methane, ethylene, ethane, hydrogen, ..) will be monitored by on-line gas chromatography and liquid products (ethanol, propanol, ..) by NMR spectroscopy, allowing determination of Faradic yields as a probe of the selectivity of the reaction. All the equipments and expertise are available in partner 1 laboratory.

Thanks to this experimental approach, the best class of radical precursors (as defined by their ability to impact the selectivity of the modified catalysts) will be further studied in order to evaluate more detailed activity-structure relationships, via the synthetic introduction of a variety of chemical functions within the selected class of radical precursors.