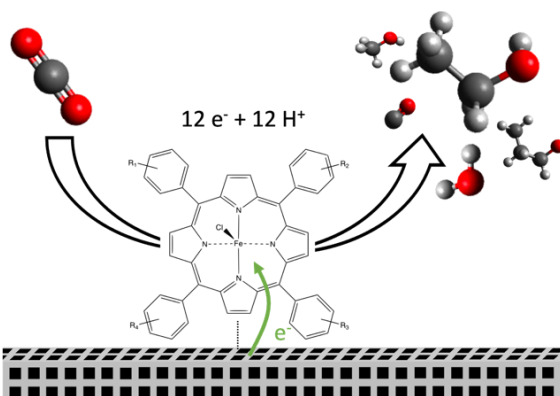


## Unleashing C-C bond formation in CO<sub>2</sub> electrochemical reduction with molecular catalysts

**Summary of the project.** The pursuit of solar fuels through the utilization of CO<sub>2</sub> as a reactant remains a significant challenge for chemists. This endeavor holds the potential to establish the groundwork for a circular economy, wherein CO<sub>2</sub> serves as a renewable feedstock. Moreover, it promises to aid in recycling greenhouse gases and reducing the carbon footprint, particularly in industrial settings. Within this expansive framework, our project aims to investigate the electrocatalytic reduction of CO<sub>2</sub>, employing organometallic complexes to facilitate the efficient generation of multi-carbon liquid products, with a focus on ethanol. **The project will be jointly developed (co-directed) at Sorbonne Université and at University of Copenhagen with theoretical simulations of the reaction processes in the group of Prof. Jan Rossmeisl, a world leader in electrocatalysis.** Building upon promising preliminary results, our project distinguishes itself through its innovative approach to electrocatalytic CO<sub>2</sub> reduction. Specifically, we aim to surmount the limitations associated with traditional redox-mediated mechanisms of organometallic catalysts. The crux of our innovation lies in the development of a molecular electrocatalyst system that challenges conventional reaction pathways, thereby enabling the electrochemical conversion of CO<sub>2</sub> into ethanol with high yields and minimal by-products. This endeavor is bolstered by a synergistic blend of experimental and theoretical methodologies.

**State-of-the art and positioning of the project.** Organometallic catalysts show potential in CO<sub>2</sub> reduction owing to their capability to form adducts in reduced states. Nonetheless, their redox-mediated mechanisms necessitate the regeneration of the oxidation state to maintain activity. Traditionally limited to producing 2-electron products, modifications and tandem catalysis provide pathways for generating higher-electron products.<sup>1</sup> Immobilization on inert carbon-based electrodes enhances turnover numbers, albeit challenges persist. Changes in the metal oxidation state during CO<sub>2</sub> reduction present limitations, impeding the formation of higher-electron products. A potential solution lies in embedding the molecular catalyst within the electric double layer, as demonstrated by recent examples conjugated to graphene, creating 'metal-like molecules' that overcome redox-mediated constraints. In line with this, we have recently contributed to a molecular electrocatalyst system that deviates from the traditional redox-mediated reaction mechanisms of organometallic compounds, facilitating electrochemical conversion of CO<sub>2</sub> to ethanol with good selectivity (a publication is currently under revision in Nat. Catal.).

Upon coupling an iron tetraphenylporphyrin (Fe-TPP) with a nickel electrode, we stabilized the iron oxidation state during electrocatalytic CO<sub>2</sub> reduction to enable further reductions and coupling of \*CO intermediates (Figure 1). This represents a significant shift from the behavior observed with the same metalloporphyrin deposited onto carbon-based electrodes. Despite obtaining some spectroscopic results (XAS, XPS, ...) and conducting preliminary calculations, the exact mechanism by which the C-C bond coupling occurs at the Fe metal center and the factors governing the reactivity remain unknown. One possibility is that a \*CHO intermediate bound to the Fe may couple with a CO molecule confined within the electrocatalytic material. The potential role of the Ni surface in the catalysis, beyond electronic interaction with the Fe complex, remains essentially unexplored. Further exploration of the extensive parameter space encompassing molecular catalysts and metal electrodes holds promise for discovering novel chemistries and attainable metrics.



**Figure 1.** Schematic representation of the reduction of CO<sub>2</sub> to CH<sub>3</sub>CH<sub>2</sub>OH using iron tetraphenylporphyrin as an organometallic molecular catalyst adsorbed onto a nickel electrode. With the molecular catalyst positioned within the electrical double layer, electron transfers occur from the electrode during the reaction, thereby preventing substantial oxidation of the hybrid organometallic catalyst or of its metal center.

<sup>1</sup> M.R. et al. *Nat. Commun.* 2023, 14, 3401 <https://www.nature.com/articles/s41467-023-39153-6>

**Methodology – Synergistic collaboration with U Copenhagen.** The project aims to explore this innovative electrocatalytic chemistry by integrating experimental and theoretical approaches. Our research will investigate the reactivity of various molecular catalysts that we have developed over the years, each exhibiting notable catalytic efficiency. For instance, we have shown that cobalt phthalocyanine can not only convert CO<sub>2</sub> to CO but can also produce formaldehyde with 4 electrons and methanol with 6 electrons.<sup>1,2</sup> Our study will compare the performance of porphyrins and phthalocyanines containing iron and cobalt as metal centers on porous 3D nickel electrodes, using different loadings and ink compositions. Studies at plain Ni electrode obtained from ALD (atomic layer deposition) deposition will also be performed for comparison. Spectroscopic characterization of the electrodes (pre- and post-electrocatalysis) will involve high-resolution SEM, XPS, EDX, and XAS operando studies (collaboration with Dr. B. Lassalle at Soleil Synchrotron). Electrocatalytic studies will be performed in H-cell at various pH and further in flow-cell with gas diffusion electrodes, while analytical methods to probe for both the liquid and the gas phase will mainly include <sup>1</sup>H NMR, GC, GC/MS, ionic chromatography as well as DEMS (Differential Electrochemical Mass Spectroscopy). Experimental work will be supplemented by comprehensive CV studies and in situ spectro-electrochemistry (IR, Raman) to explore intermediates involved in the catalysis.

In parallel to studying the experimental facets of these electrocatalytic systems, we will perform theoretical investigation of these complexes adsorbed on electrode surfaces. International collaboration with Prof. Jan Rossmeisl (U Copenhagen, world leader in theoretical electrocatalysis) will focus on atomic scale simulations of the catalytic reactions.<sup>3</sup> The Danish partner has previously investigated CO<sub>2</sub> reduction on similar catalysts and been able to classify the product selectivity based on binding energies of intermediates. While activity can often be associated with a single descriptor, selectivity can obviously not. The different reaction paths show different dependence on metal center and potential DFT simulations of the energetics of the competing reaction pathways will be investigated. This approach is essential for understanding the carbon dioxide reduction mechanism.

Finally, the interaction between metal complexes and surface will be explored by state-of-the-art ab initio density functional theory DFT calculations in collaboration with Prof. M. Calatayud (LCT, Sorbonne Université). Such computing will lead to an accurate characterization of the geometry, energetics, and electronic structure of the systems.<sup>4</sup> Emphasis will be placed on the role of the solid support, as adsorption strength appears to influence catalytic properties. Various supports will be explored (nickel, carbon), for which structural models for flat and irregular surfaces will be developed.

***While individual groups will coordinate the efforts per each work package, we seek to have one or two visits (3 months each) of the PhD student to the University of Copenhagen and to set a long-term collaboration with the Danish partner. On-site (Sorbonne U) proximity will favor synergistic efforts between the PI and Prof. M. Calatayud group (Lab. Chimie Théorique). The international collaborative efforts of the three research groups are expected to yield unprecedented results and breakthroughs in CO<sub>2</sub> reduction to multi-carbon products with precise atomic control.***

**Practical implementation of the project.** The PhD student will be supervised by Prof. Marc Robert and will benefit from scientific support within the host team, in particular with Dr. Elodie Anxolabéhère-Mallart (coordination chemistry, spectroelectrochemistry), and Prof. Julien Bonin (time-resolved spectroscopies). The PhD student will have full access to a range of instruments (electrochemistry, chromatography, NMR, spectroscopy) perfectly suited to mechanistic studies. The thesis will be financially supported by the supervisor's IUF (Institut Universitaire de France) funds (15 keuros/year until October 2027) and by the Power-CO<sub>2</sub> project (PEPR SPLEEN, 25 keuros for functioning expenses, until July 2026). These two financial envelopes will cover operating expenses of the thesis and mobility expenses of the candidate (participation to congress, stays at U Copenhagen).

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<sup>2</sup> a. M. R. et al. *Angew. Chem. Int. Ed.* 2019, 58, 16172-16176. <https://doi.org/10.1002/anie.201909257> b. M.R. et al. *Nat. Catal.* 2023, 6, 818-828 <https://www.nature.com/articles/s41929-023-01005-3>

<sup>3</sup> J. R. et al. *Nat. Nanotech.* 2019, 14, 1063-1070. <https://www.nature.com/articles/s41565-019-0551-6>

<sup>4</sup> M.C. et al. *Materials Today* 2023, 67, 344 <https://doi.org/10.1016/j.mattod.2023.05.029>