

PhD offer at the CEISAM laboratory from September or October 2025 for 3 years

Supervisors	Dr. Clémence Queffélec (50%), Dr. Yann Pellegrin (50%)
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Keywords	Photocatalysis, CO ₂ , copper and nickel complexes

Topic presentation:

The reckless consumption of fossil fuels has propelled pollution to alarming levels. Notably, industrial activities have resulted in the substantial accumulation of carbon dioxide in the atmosphere, contributing significantly to the ongoing global warming crisis. Given the improbable prospect of a near-term reduction in global CO₂ production, it becomes imperative to design systems capable of valorizing CO₂.¹ This is particularly crucial in the context of ensuring the sustained viability of life on Earth. In this context, a very promising method is to perform the reduction of CO₂ into added value carbon-based compounds, such as CO or methanol.

However, the reduction of CO₂ is a very energy demanding chemical process because it is a remarkably stable molecule. In other words, the energy cost to reduce CO₂ is so high that it cannot be achieved in a sustainable way.

How then is it possible to perform CO₂ reduction, all through a sustainable green process?

By solving two main problems: (1) decreasing the energy cost, and (2) finding a renewable source of energy to drive the reactions.

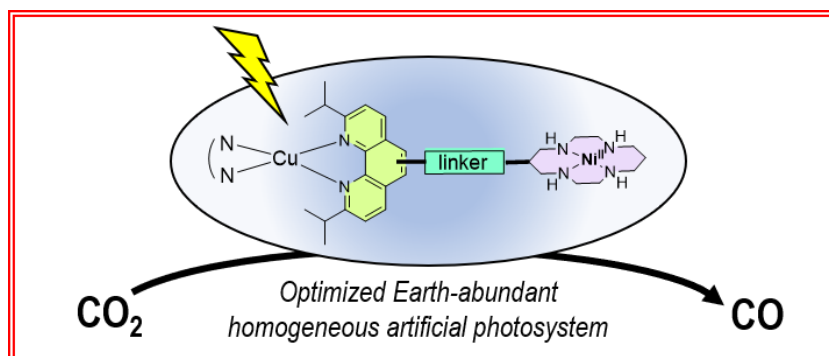
Problem (1) can be partially solved through the principles of chemical catalysis, using well-defined molecular CO₂ reduction catalysts (MC_{CO2}) which can decrease high activation barriers.² As regards problem (2), light is a natural, free, democratic source of energy. To domesticate the energy of photons, the use of molecular photosensitizers (PS) is often necessary,³ as exemplified in many photochemical processes (the most famous example being of course chlorophylls as PS in natural photosynthesis).

Unfortunately, MC_{CO2} and PS are often complexes of rare earth metals like ruthenium, palladium, rhodium, and rhenium. The scarcity of these elements generates geopolitical problems, incompatible with the envisioned sustainable approach.

The joint Franco-American project **BICEPS** aims at addressing both problems by covalently linking MC_{CO2} with PS, all exclusively based on Earth abundant metal species. More precisely, Nickel-cyclam based MC_{CO2} are chosen because of their efficiency and selectivity.⁴ As regards

PS, copper(I)-phenanthroline complexes are selected because of their spectacular excited state reactivity, particularly adapted to reduction processes.⁵

The PhD will consist in synthesizing a set of PS-Linker-MC_{CO2} molecular dyads based only on earth-abundant systems where the length, the nature and the position of the linker between PS and MC_{CO2} will be varied consistently in order to provide a clear, definitive rationale on the long-sought after structure-reactivity relationships in photosensitive dyads. The US partner will be in charge of studying the structures and photocatalytic properties of the obtained PS-Linker-MC_{CO2} systems.



Profil: The candidate should have prior experience in organic and/or organometallic chemistry and a strong interest in catalysis and photocatalysis. They should demonstrate curiosity, strong motivation, enthusiasm, and autonomy. Good communication skills (both written and oral) are also expected.

Application deadline: May 15, 2025.

Please submit a detailed CV, a cover letter, the names and email addresses of two references (for recommendations), as well as your academic transcripts.

Context: This project is part of a collaboration with Dr. Gonghu Li from the University of New Hampshire. As part of the PhD program, one-month research stays will be planned each year in Prof. Gonghu Li's laboratory in the United States.

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