

## 3D Architectures for the photocatalytic valorization of CO<sub>2</sub>

Gaël ZUCCHI (CNRS Researcher)  
Ecole Polytechnique - IP Paris  
Laboratoire de Chimie Moléculaire (UMR CNRS 9168)  
Route de Saclay  
91128 Palaiseau

Laurence BODELOT (Prof. École Polytechnique)  
Ecole Polytechnique - IP Paris  
Laboratoire de Mécanique des Solides (UMR CNRS 7649)  
Route de Saclay  
91128 Palaiseau

### **The context :**

Emissions of carbon dioxide and methane, primarily caused by the use of fossil fuels (gas, oil), are partly responsible for the greenhouse effect leading to global warming. To limit, or even slow, these harmful effects, mitigation strategies range from carbon storage to the transformation of these gases into chemical compounds with added value. CO<sub>2</sub> thus appears as an inexhaustible source of carbon. However, the chemical transformation of CO<sub>2</sub> involves kinetically limited reactions, necessitating the development of catalysts. The search for new catalysts that can replace rare and expensive noble metals represents a challenge to which we wish to contribute with this proposal. We envision the development of three-dimensional objects at the micrometer scale that can effectively act as photocatalysts in CO<sub>2</sub> reduction.

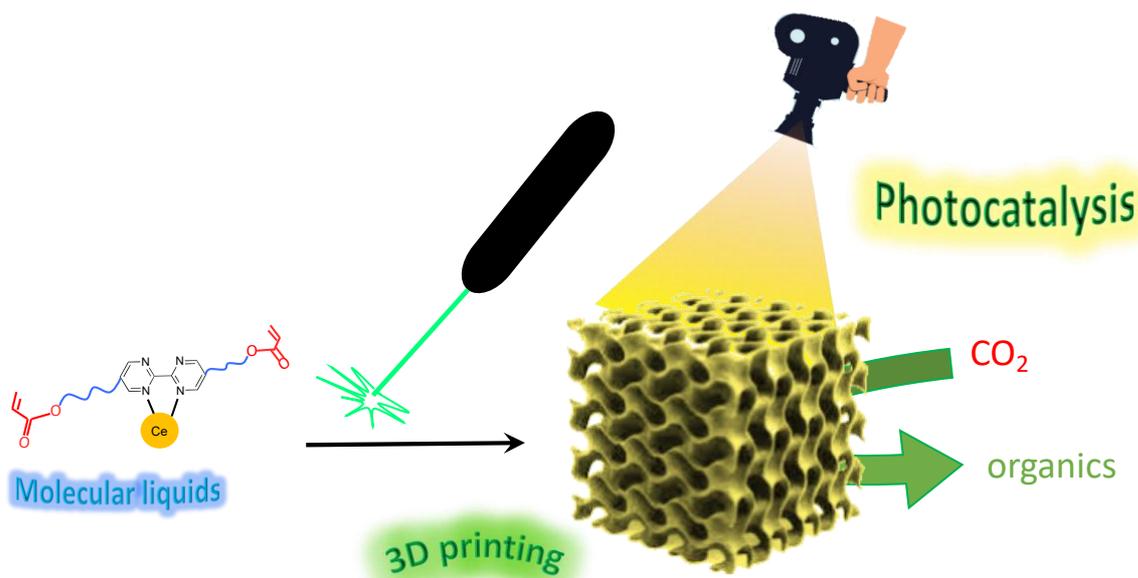
### **The Project:**

Hybrid 3D architectures consisting of a polymer network to which cerium ions will be coordinated are the target objects of this project. Cerium is very attractive for photocatalysis applications for several reasons. It is relatively abundant, and therefore inexpensive. It has two accessible oxidation states, allowing charge transfers between the ligands and the metal ion, which can particularly be initiated by light absorption. The excited Ce(III) ion is strongly reducing and can then be obtained in two ways: by photoreduction of Ce(IV) after electron transfer from the ligands, or by direct light absorption via an allowed 5d-4f transition. Also, due to its size, cerium has high coordination numbers. The ionic radii range from 1.01 to 1.34 Å for Ce(III) and from 0.87 to 1.14 Å for Ce(IV), with respective coordination numbers ranging from 6 to 12. It is therefore possible to obtain stable compounds with vacant coordination sites to which CO<sub>2</sub> can bind, promoting the interaction between the catalytic metal center and the substrate. These ions will be inserted by coordination into the porous three-dimensional structures obtained through additive manufacturing. The synthesis of innovative precursors enabling access to these structures will be carried out. These precursors will be molecular liquids, the study of which we have recently begun.<sup>1</sup> They will allow the formulation of solvent-free photosensitive resins. Avoiding solvents will increase the stability of formulations and the reproducibility of prints, in addition to eliminating toxicity issues. Their structure will be based on 2,2'-bipyrimidine, for which we have

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<sup>1</sup> C. Noè, S. Laroui, G. Zucchi, L. Bodelot, *ACS Appl. Eng. Mater.* **2026**, ASAP Article, <https://doi.org/10.1021/acsaenm.5c01101>.

developed synthetic functionalization methods,<sup>2</sup> in addition to demonstrating its high structural potential in the synthesis of luminescent compounds with lanthanide ions.<sup>3</sup> In the second part of the work, these architectures will be studied as heterogeneous photocatalysts in CO<sub>2</sub> reduction. Thanks to the very large specific surface area associated with the significant number of catalytic sites that will bind CO<sub>2</sub> through cerium coordination, we expect high activity of such objects as catalysts. Figure 1 provides a schematic representation of the project.



**Figure 1.** Schematic representation of the project key steps.

#### Organization:

This project will be carried out as a collaboration between the Laboratory of Molecular Chemistry (LCM, represented by Gaël ZUCCHI) and the Solid Mechanics Laboratory (LMS, represented by Laurence BODELOT). The synthesis of precursors and photocatalysis tests will be performed at the LCM, while the printing of 3D microstructures will take place at the LMS, which has acquired the necessary equipment and characterization tools. A recent joint project between the two laboratories has demonstrated the feasibility of formulating resins leading to functional 3D microstructures from liquid molecular.<sup>1</sup>

#### Candidate Profile:

The successful candidate will have solid experience in molecular synthesis and will be able to work independently. He/she will demonstrate strong motivation to work on a multidisciplinary project as well as good communication and writing skills. Knowledge of coordination chemistry and catalysis would be an asset.

<sup>2</sup> S. Wang, C.J. Murga Cotrina, J.-P. Roblin, A. Barros, N. Casaretto, A.H. Denawi, H. Vach, G. Chadeyron, G. Zucchi, *ACS Appl. Opt. Mater.* **2025**, *3*, 2026–2038; <https://doi.org/10.1021/acsaom.5c00228>.

<sup>3</sup> G. Zucchi, O. Maury, P. Thuéry, F. Gumy, J.-C. G. Bünzli, M. Ephritikhine, *Chem. Eur. J.* **2009**, *15*, 9686–9696; <https://doi.org/10.1002/chem.200901517>; G. Zucchi, *Int. J. Inorg. Chem.* **2011**, 1–13; <https://doi.org/10.1155/2011/918435>