

## The curious case of a Ru-Fe sensitizer-catalyst dyad for CO<sub>2</sub> reduction

Philipp Gotico,<sup>1</sup> A. Trapali,<sup>2,4</sup> C. Herrero,<sup>2</sup> M-H Ha-Thi,<sup>3</sup> T. Pino,<sup>3</sup> W. Leibl,<sup>1</sup> G. Charalambidis,<sup>4</sup>

A. Coutselos,<sup>4</sup> Z. Halime,<sup>2</sup> A. Aukauloo<sup>1,2</sup>

<sup>1</sup> Institut de Biologie Intégrative de la Cellule, CEA, Université Paris Saclay, France

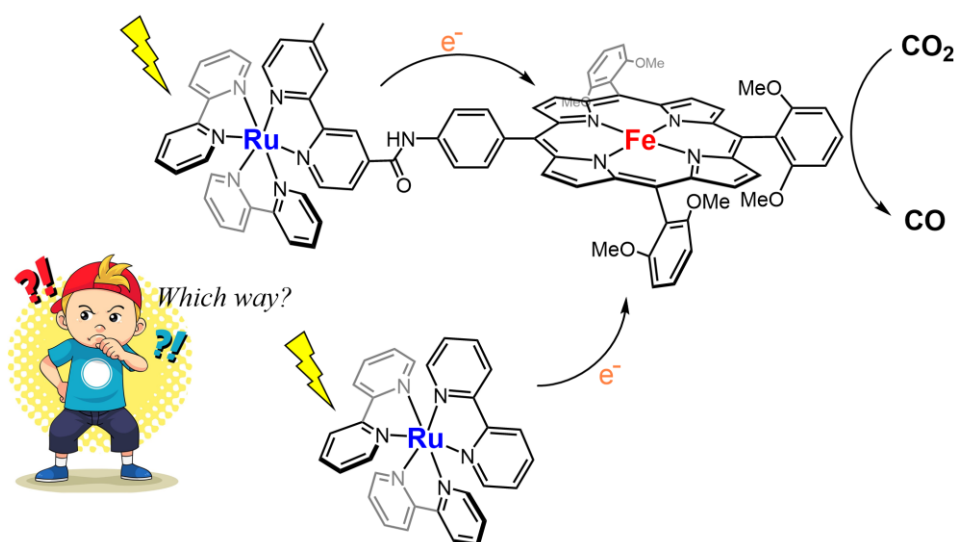
<sup>2</sup> Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Saclay, France

<sup>3</sup> Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, France

<sup>4</sup> Laboratory of Bioinorganic Chemistry, Chemistry Department, University of Crete, Greece

Email: philipp.gotico@cea.fr

Light-activation of catalysts *via* sensitizer units provides a practical route for valorizing electrocatalyst design developments within the framework of solar-driven chemistry. We were curious to know if covalently attaching the well-known iron porphyrin electrocatalyst (Fe) with the typical ruthenium trisbipyridine sensitizer (Ru) would activate the system towards photocatalytic CO<sub>2</sub> reduction [1]. Photophysical studies of the Ru-Fe dyad, however, point to the complete extinction of the sensitizer unit that undergoes non-productive quenching process with the Fe catalyst - the unavoidable dilemma in this type of molecular assemblies. Nevertheless, in presence of exogenous Ru sensitizer, the Ru-Fe dyad presents a significant catalytic enhancement of the turnover number and CO<sub>2</sub>-to-CO selectivity compared to the Fe catalyst analogue under the same conditions. Comprehensive analyses of the photophysical and electrochemical results suggest that the catalytic enhancement displayed by the dyad can be attributed to an interesting electron reservoir role played by the appended Ru moiety.



**Figure 1.** Molecular structure of Ru-Fe sensitizer-catalyst dyad.

[1] A. Trapali, P. Gotico, C. Herrero, M.-H. Ha-Thi, T. Pino, W. Leibl, G. Charalambidis, A. Coutsolelos, Z. Halime, A. Aukauloo, *Comptes Rendus. Chimie* **2021**, *24*, 1–14.