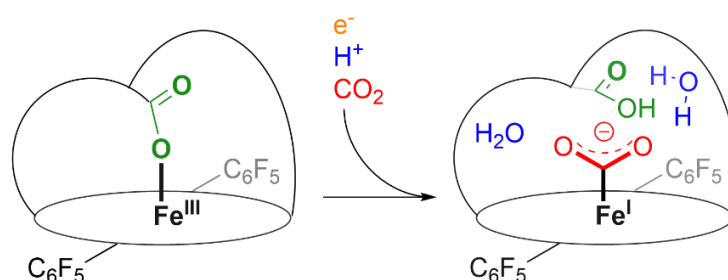


## Dynamics of Strapped Iron Porphyrin with a Carboxylate Function on the Electrochemical Performance of CO<sub>2</sub> reduction

Adrien Smith,<sup>a</sup> Bernard Boitrel,<sup>b</sup> Philipp Gotico,<sup>c</sup> Zakaria Halime,<sup>a</sup> Ally Aukauloo<sup>a,c</sup>

<sup>a</sup> Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO, UMR 8182, CNRS), Université Paris-Saclay, 91400, Orsay, France; <sup>b</sup> Institut des Sciences Chimiques de Rennes (ISCR, UMR 6226, CNRS), Université de Rennes, 35042, Rennes, France; <sup>c</sup> Institut des Sciences du vivant Frédéric Joliot, Institut de Biologie Intégrative de la Cellule (UMR 9198, CEA, CNRS) Université Paris-Saclay, 91191, Gif-Sur-Yvette, France

Transforming CO<sub>2</sub> into valuable reduced forms of carbon is a strategy that is currently attracting the interest of both the scientific community and the industry. Converting and not only capturing CO<sub>2</sub> can be a way to recycle this greenhouse gas by introducing non-fossil fuel based C1 building blocks back into the carbon cycle. The design of new molecular catalysts for the reduction of CO<sub>2</sub> is therefore essential to better understand how to activate and reduce efficiently this stable molecule. Tetraphenyl iron porphyrins and derivatives have been shown to be efficient and selective catalysts for CO<sub>2</sub> reduction to CO.<sup>[1]</sup> Introducing electron-withdrawing groups can lower the catalytic overpotential but at the expense of a lower turnover frequency.<sup>[2]</sup> Cationic functions in the second coordination sphere of porphyrins showed greater improvement of both the overpotential and the catalytic rates,<sup>[3]</sup> while negatively charged sulfonate groups resulted to a decrease in activity.<sup>[4]</sup> Herein, the effects of electrostatic activator is revisited by synthesizing a strapped iron porphyrin holding a carboxylate function.<sup>[5]</sup> It is found that the carboxylate moiety, which lies in the second coordination sphere of the reduced iron center, plays a beneficial role on CO<sub>2</sub> reduction, even though it is negatively charged. In presence of water, we found that the carboxylate-strapped porphyrin shifts the electrocatalytic performance to a high turnover frequency as the nonfunctionalized iron tetraphenylporphyrin, while keeping a lower overpotential as for the perfluorinated analogues. Electrochemical studies were undertaken to optimize the performance of the catalyst and determine its binding aptitude with CO<sub>2</sub> and the proton transfer process.



**Figure:** Sketches of the COO-strapped porphyrin and the assumed Fe-CO<sub>2</sub> adduct formed in catalytic conditions.

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