



UNIVERSITÉ DE NANTES



Master 2 Internship at CEISAM Nantes University

Laboratoire: CEISAM, UMR CNRS 6230, équipe IMF

Encadrant(s): Fabrice ODOBEL et Stéphane DIRING

Title of the project: Synthesis of porphyrinoid based catalysts for CO₂ reduction

Description of the project:

The catalytic reduction of CO₂ into fuels or useful chemicals has attracted much attention because this technology can potentially solve both energy and environmental problems. In the past few decades, extensive efforts have been made to develop efficient molecular catalysts for the reduction of CO₂. Among these compounds, porphyrinoids such as iron porphyrins¹ or cobalt phthalocyanines² are among of the most active catalytic systems, because of their (i) high turnover frequency (TOF), (ii) high selectivity, and (iii) robustness. However, their catalytic activities can be still improved by introducing some substituents in the second coordination sphere, such as acid/base groups, electron-donating/withdrawing moieties, and pendant imidazolium moieties, which accelerate the CO₂ binding step and also stabilize intermediates and transition states to decrease overpotential and enhance product selectivity. This strategy is indeed exemplified by the auxiliary functional groups found in enzymes such as in the CO dehydrogenase enzyme.³ Moreover, the success of this approach is illustrated with synthetic catalysts such as iron porphyrins bearing trimethylammonium or phenol groups that achieve unprecedented electrocatalytic efficiency for CO₂ reduction catalysis.¹ This is attributed to the Coulombic interaction between the negatively charged Fe–CO₂ adduct and the positively charged trimethylammonium groups. Inspired by this successes, we propose to tune the second coordination sphere of metal phthalocyanines to enhance their catalytic performances towards CO₂ with the goal to improve their selectivities, e.g. orient the product towards a single compound, and to decrease their overpotentials. Indeed, although being highly stable, the phthalocyanine based catalysts display quite high overpotential and the selectivity to CO₂ reduction is hampered by H₂ evolution particularly at low applied potential.⁴ The introduction of these stabilization substituents in close proximity of the catalytic center will be achieved by preparing tetrabenzotriazaporphyrin (TBTP) or tetrabenzodiazaporphyrin (TBDP) according to a strategy initially developed by Cheprakov⁵ and Cammidge⁶ respectively (Figure). Recently we have successfully applied the method of Cheprakov for the preparation of dyes for solar cells.⁷

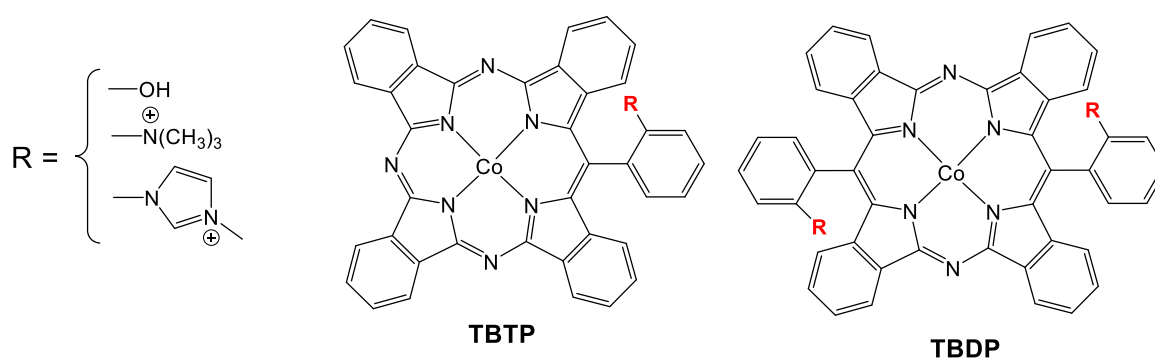


Figure. Structure of the tetrabenzotriazaporphyrin TBTP and tetrabenzodiazaporphyrin TBDP CO₂ reduction catalysts proposed in this project.

This research project deals with organic synthesis and coordination chemistry and the catalytic properties of the cobalt tetrabenzodiazaporphyrin with be investigated by electrochemistry during this internship.

References:

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3. Jeoung, J.-H., et al., *Science*, **2007**, *318* (5855), 1461, <https://www.science.org/doi/abs/10.1126/science.1148481>.
4. Morlanés, N., et al., *ACS Catal.*, **2016**, *6* (5), 3092, <https://doi.org/10.1021/acscatal.6b00543>.
5. Andrianov, D. S., et al., *Chem. Commun.*, **2014**, *50* (59), 7953, <http://dx.doi.org/10.1039/C4CC02405B>.
6. Alkorbi, F., et al., *Angew. Chem. Int. Ed.*, **2021**, *60* (14), 7632, <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.202016596>.
7. Andrianov, D. S., et al., *J. Photochem. Photobiol., A*, **2016**, *330*, 186, <https://www.sciencedirect.com/science/article/pii/S1010603016303215>.

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WEB page: <https://ceisam.univ-nantes.fr/equipe-imf/materiaux-energie-information/>

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