

Tailor-made Macroligands for Heterogenized Photocatalytic Carbon

Dioxide conversion.

Marcelo Alves Favaro¹, Florian Wisser¹, Elsje Alessandra Quadrelli², Regina Palkovits³, Jérôme Canivet¹

marcelo.alves-favaro@ircelyon.univ-lyon1.fr

¹IRCELYON, Université de Lyon, Université Claude Bernard Lyon 1, CNRS, 2 Avenue Albert Einstein, 69626, Villeurbanne, France.

²Université de Lyon, Université Claude Bernard Lyon 1, CPE Lyon, 43 Bvd du 11 Novembre 1918, 69616, Villeurbanne, France.

³ITMC, RWTH-University, Worringerweg 2, 52074, Aachen, Germany.

Using sunlight as a renewable source of energy to promote carbon dioxide (CO₂) conversion is an interesting approach to address sustainable chemicals and fuels production as well as mitigation of climate change. However, in most photocatalytic systems, the utilization of a homogeneous photosensitizer represent a key limitation for long-term reactions due to its low stability. Therefore, novel, more efficient and stable photocatalyst materials and photocatalytic processes are required.

Here, we present a strategy of structuration at the molecular-level photocatalytic systems, seeking for enhanced long-term stability. The integration of photo-active centers into a molecularly defined support improve their stability. Moreover, the incorporation of chelating moieties, such as bipyridine, offer a unique possibility for heterogenization of organometallic complex, profiting at the same time from enhanced selectivity of the molecular catalyst and easy handling and separation from its heterogeneous nature. Macroligands, a solid acting like the ligand in the corresponding molecular complex, is a key strategy to bridge the gap between homogeneous and heterogeneous catalysis. Porous organic polymers (POPs), e.g. conjugated microporous polymers are attracting a growing interest for this task ^[1]. The key of their success is the tunability of the polymer's properties. By judiciously chosen the proper tailored precursor, it is possible to carefully control light absorption and porosity. In this context, POPs can be precisely designed in order to contain both, a photoactive moiety and chelating site for the heterogenization of molecular catalysts within the structure.

In our all-in-one concept, a (Cp*)-Rhodium complex was heterogenized within different dye containing macroligands.^[2] Those materials catalyze the carbon dioxide photoreduction driven by visible light to produce up to three grams of formate per gram of catalyst during four days, without any changes in catalytic activity. In this contribution, we will demonstrate the benefit of covalent tethering of the two active sites into a single framework to play a key role in the visible light activation of the catalyst. The photoinduced electron transfer from the light harvesting moiety to the catalytic site will be discussed based on quantum mechanical calculations and *in-situ* ultrafast time-resolved spectroscopy.^[2]

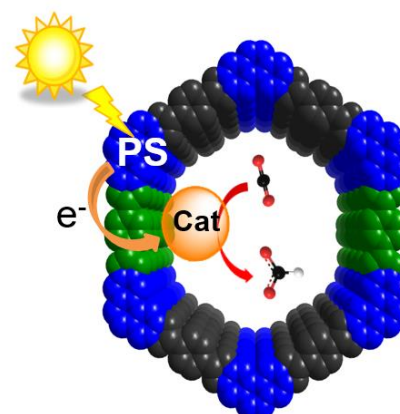


Figure 1 : Tailor-made macroligand for stable visible light-drive carbon dioxide conversion.

[1] Bonillo, B., Sprick, R. S. and Cooper, A. I. (2016), Tuning Photophysical Properties in Conjugated Microporous Polymers by Comonomer Doping Strategies. *Chemistry of Materials*, 28 (10), 3469-3480.

[2] Wisser, F. M., Duguet, M., Perrinet, Q., Ghosh, A. C., Alves-Favaro, M., Mohr, Y., Lorentz, C., Quadrelli, E. A., Palkovits, R., Farrusseng, D., Mellot-Draznieks, C., De Waele, V. and Canivet, J. (2020), Molecular Porous Photosystems Tailored for Long-Term Photocatalytic CO₂ Reduction. *Angew. Chem. Int. Ed.* doi:10.1002/anie.201912883