Molecular Bio-Inspired Strategies for Small Molecule Activation

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Enzymatic systems have evolved complex strategies to maximize the efficiency and product selectivity in small molecule activation, among which CO_2 reduction. Beside unique active sites containing by definition earth-abundant elements, enzyme further control catalytic activity through second sphere interactions and a fine control of electron transfer chains.

In this talk, we will introduce a series of bio-inspired strategies for the design of electrocatalytic systems for small molecule activations. We will highlight a series of earth-abundant metal based molecular catalysts inspired by the active sites of enzymatic systems [1-2] and will introduce a new strategy for the electrocatalytic metal hydride generation using synthetic Fe_4S_4 clusters acting as concerted proton electron transfer (CPET) mediators.[3] We will demonstrate that the combination of synthetic Fe_4S_4 clusters with the CO_2 electroreduction catalyst $[Mn^{I}(bpy)(CO)_3Br]$ (bpy = 2,2'-bipyridine) allows the preparation of a benchmark catalytic system for HCOOH generation. Further exploring bio-inspired strategies for electron transfers and storage, we will finally introduce the preparation of the first complete redox series of Fe_4S_4 complexes [4] and their use to generate potent strong reducing agents via entatic activation strategies.

[1] S. Dey, T. Todorova, M. Fontecave, V. Mougel, *Angew. Chem. Int. Ed.*, **2020**, *59*(36), 15726-15733
[2] A. Mouchfiq, T. Todorova, S. Dey , M. Fontecave, V. Mougel, *Chem. Sci.*, **2020**, *11*, 5503-5510.
[3] S. Dey, F. Masero, E. Brack, M. Fontecave, V. Mougel, *Nature*, **2022**, *607* (7919), 499-506
[4] L. Grunwald, M. Clémancey, D. Klose, L. Dubois, S. Gambarelli, G. Jeschke, M. Wörle, G. Blondin, V. Mougel, *PNAS*, **2022**, *119* (31), e2122677119