Iron-sulfur clusters: synthetic challenges and applications to catalysis

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The synthesis of Fe_4S_4 complexes has been an important tool contributing to the better understanding of their biological counterparts in enzymatic systems. It has enabled our modern-day understanding of electron-transfer in nature as well as of the fundamental properties of multinuclear metal complexes. Nevertheless, among hundreds of reported synthetic cuboidal Fe_4S_4 clusters supported by thiolate ligands, a cluster in its all-ferrous oxidation state, $[Fe_4S_4]^0$, has never been synthetically isolated, and the preparation of a complete redox series of Fe_4S_4 complexes bearing the same ligand set had still never been achieved. In addition, despite their ubiquitous distribution in enzymatic systems, only very few catalytic systems involving synthetic Fe_4S_4 systems have been reported.

In this talk, we demonstrate that the use of a bulky arylthiolate ligand promoting the encapsulation of potassium cations in the vicinity of the cubane enables the synthesis of a complete redox series of Fe_4S_4 clusters, from the all ferric to the all ferrous oxidation states, and introduce the detailed spectroscopic characterization of this series via EPR, variable-field variable-temperature ^{57}Fe Mössbauer spectroscopy, SQUID magnetometry, UV-Vis electronic absorption and X-ray diffraction analysis.[1]

In addition, we 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. 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.[2]

[1] L. Grunwald, M. Clémancey, D. Klose, L. Dubois, S. Gambarelli, G. Jeschke, M. Wörle, G. Blondin, V. Mougel, *ChemRXiv*, **2021**, doi:10.26434/chemrxiv-2021-4qzlh.
[2] S. Dey, F. Masero, E. Brack, M. Fontecave, V. Mougel, *Nature*, **2022**, *under press.*