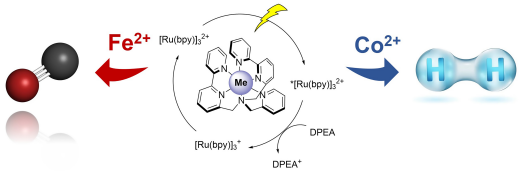
A tale of two metals: switching selectivity towards CO_2 reduction in heptacoordinate complexes

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Solar fuels, i.e. fuels generated by using sunlight as a source of energy, are the most promising alternatives to fossil fuels, both because of their availability and of their reduced environmental impact. CO_2 reduction, in particular, is one of the most popular strategies to obtain solar fuels[1]. However, protons and efficient catalysts are necessary to respectively decrease the thermodynamic and kinetic barrier. These conditions often also trigger the reduction of protons to hydrogen, which represents a competitive process[2]. We have recently found that a heptacoordinate Co complex (known to efficiently produce hydrogen)[3] can also catalyze CO_2 reduction in acetonitrile/water solutions, although with low selectivity, the hydrogen generation being the predominant process. Remarkably, replacement of the Co(II) center with Fe(II) induces a switch in selectivity towards CO_2 reduction. The resulting heptacoordinate Fe(II) catalyst is extremely active and it reaches selectivities > 90% in carbon-based products (CO + formate) in the presence of 1-10% H_2O as proton source. In this talk we will present our results concerning the electrochemical, photochemical and computational investigations of these two catalysts.



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