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Bioinspired iron complexes for dioxygen activation.

In the present economic, environmental and climatic contexts, there is a need to develop ***new chemical processes*** that are ***environmentally and economically viable***. At the industrial scale, the conversion of organic molecules into more valuable oxidized products is generally carried out following stoichiometric reactions and severe conditions (high temperature and pressure, strong oxidants such as $S_2O_8^{2-}$, and/or harmful metal oxides such as permanganate, solid Molybdenum oxide, high-valent Ruthenium oxides).[1] Thus, there is an obvious interest in using dioxygen (***O_2***) as an oxidant since it is ***inexpensive, abundant, and environmentally benign***. However, due to its fundamental triplet spin state (S = 1), its activation is necessary to overcome the kinetic barrier of its reaction with diamagnetic species.

Some ***metalloenzymes***, such as cytochromes P450[2] or Rieske Dioxygenases,[3] perform very specific and ***selective oxidation of small organic molecules*** using molecular oxygen following its so-called "***reductive activation***" at their active site which an Fe atom (cf. Fig. 1). Hence, modeling such natural catalysts with simpler synthetic systems is relevant from fondamental (deciphering of mechanisms) as well as from practical (valorization of abundant feedstock) point of views.

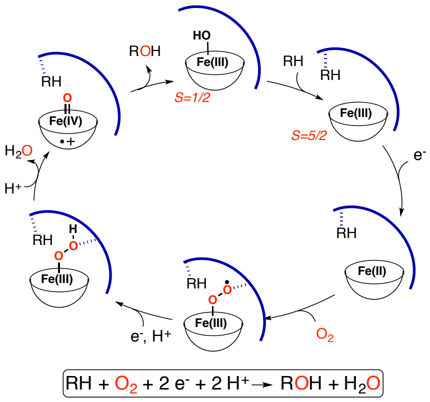

Figure 1. *Catalytic cycle and net reaction for P450s enzymes. The blue line depicts the second sphere aminoacid residues.*

The reasons why these enzymes efficiently activate O_2 are that (a) the coordination sphere of the metal contains electron rich ligands favoring Fe^{II}-to-O_2 electron transfer (hence coordination of O_2); (b) the successive Fe-O_2 species are stabilized via H-bonds provided by protein residues in the active site. In this project, we want to investigate the first aspect (a).

Numerous synthetic complexes prepared with simple amine/pyridine ligands allow generating similar reaction intermediates (***Fe^{III}(OOH), Fe^{IV}O***) using chemical oxidants (H_2O_2, PhIO, peracids).[4] ***All of these intermediates are known to oxidize small organic molecules*** *(alkenes, aromatic hydrocarbons, thioethers…)*. In contrast, these synthetic complexes barely react with O_2. Hence, efforts are required for the *development of* ***catalytic systems using O_2 as oxidant and a sacrificial source of electrons***. An obvious strategy to optimize the reactivity with O_2 is illustrated in Fig. 2. Donating electron density at the Fe^{II} center will destabilize the ferrous form in favor of the ferric one. It is expected that modifying the ligands with electron donating groups (EDG) will i) modulate the Fe^{II}/O_2 association constant and ii) favor the $Fe^{III}(OO^{\circ})$ *vs* Fe^{II}-O_2 character of the resulting adduct, iii) tune the potential of its first reduction to $Fe^{III}OO^{-}$.

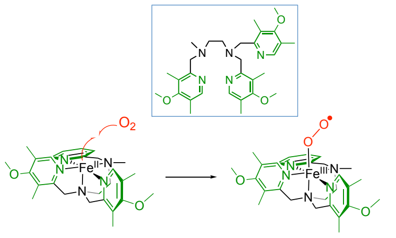

Figure 2. *A synthetically accessible amine/pyridine ligand with EDG designed to promote the Fe^{II}-to-O_2 electron transfer.*

The work program is detailed below.

1/ Synthesis of the ligand.

The ligand depicted on Fig. 2 will be synthesized following conventional methods from commercially available reactants. It will be characterized using useful techniques (^{1}H and ^{13}C NMR, ESI-MS).

2/ Synthesis of the Fe^{II} complexes.

A series of Fe^{II} complexes will be prepared using different Fe^{II} salts. They will be characterized in detail in the solid state (X-ray crystallography, magnetic measurements) and in solution (ESI-MS, UV-visible spectrophotometry, Cyclic Voltammetry).

3/ Generation of reaction intermediates with chemical oxidants.

The Fe^{II} precursors will be reacted with chemical oxidants (peroxides, single oxygen atom donors) to generate and identify reaction intermediates as those described in Fig. 1. Mechanistic informations on the formation and degradation of these species will be obtained by monitoring the reactions at variable T by UV-visible and EPR spectroscopy. These studies will serve as benchmark for the reactivity studies of the Fe^{II} complexes with O_2.

4/ Mechanistic investigations of the reaction of the Fe^{II} complexes with O_2.

The reactivity of the Fe^{II} precursors with dioxygen will be studied by Cyclic Voltammetry. Mechanistic informations will be obtained by thorough analysis of the intensity-potential curves recorded.

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other recent selected publications from the host group : *Chem. Sci.*, 2015, **6**, 2323; *Chem. Eur. J.*, 2017, **23**, 2894; *Angew. Chem. Int. Ed.* **2019**, *58*, 854; *Chem. Eur. J.* **2019**, *25*, 12405.