Design and Studies of Novel Iron-based Complexes for Hydrogen Photo-evolution

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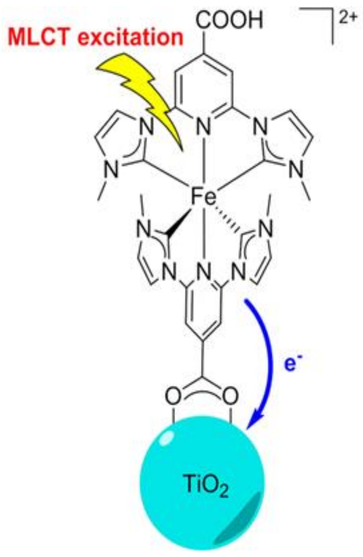
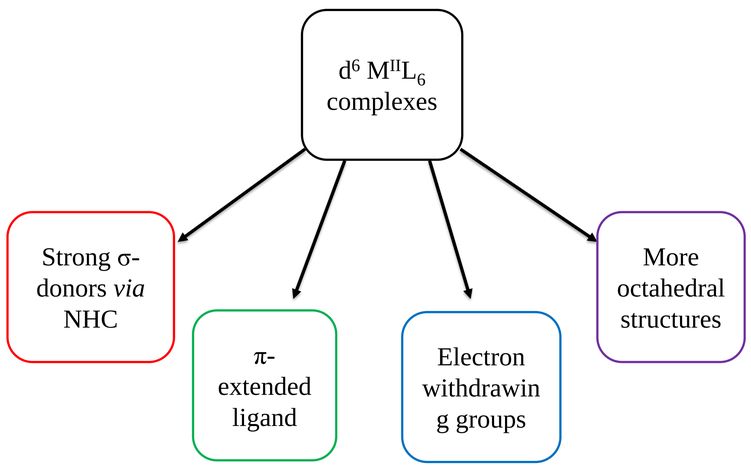
General Introduction : Development of novel iron-based sensitizers[1] and Supramolecular cobaloxime-based photocatalysts[2]

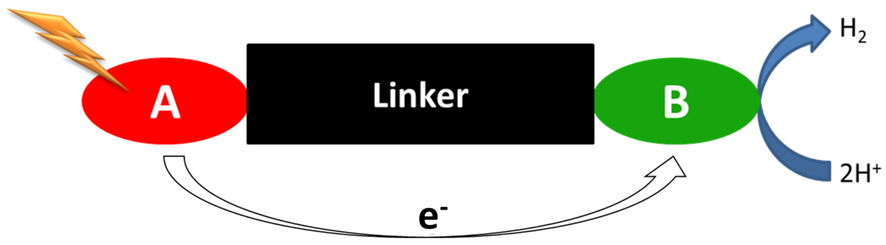
Recently, the design of a novel kind of ligand **to improve of the stability** of iron-based complexes excited state allowed the development of a complex linked to the semi-conductor TiO_2. Thanks to an efficient **electron transfer potential photosensitizer** for hydrogen production.[1a,1b]



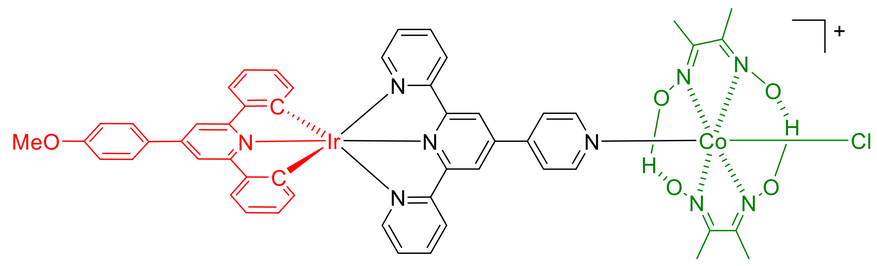


Moreover, **several strategies** have been developed for **extending the ^{3}MLCT lifetime of d^6 $M^{II}L_6$ complexes**: use of strong σ-donor ligands (*e.g.* NHC), π-extended network, electron withdrawing groups (EWG) and a more octahedral structure.[1c]

With the aim of producing H_2 photocatalytically, **cobaloxime** was designed and used with Ru^{II}- or Ir^{III}-based photocatalyst.[2a] This kind of system was first tested with the separated components and then combined, resulting in a novel class : supramolecular photocatalysts, initiated in 2008.[2a,2b,2c] The concept is based on the combination of the **photosensitizer A** with the **catalytic site B** connected thanks to a **linker**.

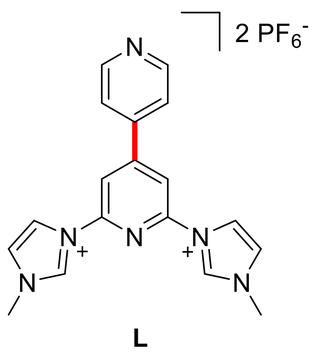


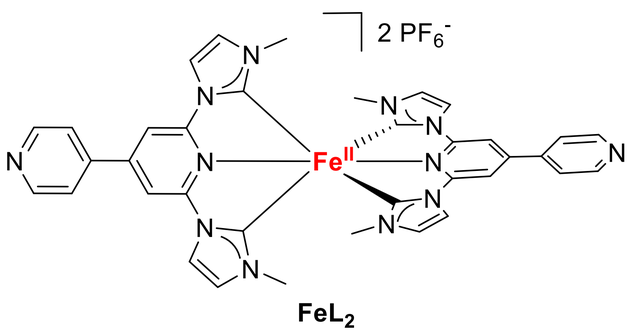
Indeed, as showed by the exemple below, a **cyclometalated Ir^{III}-based complex** was combined to a **cobaloxime site**. The photoexcitation of the photosensitizer provides an **electron transfer** from the Ir^{III} site to the cobalt site which will be able to **convert a proton source into H_2**. [2d]



Goals of this project

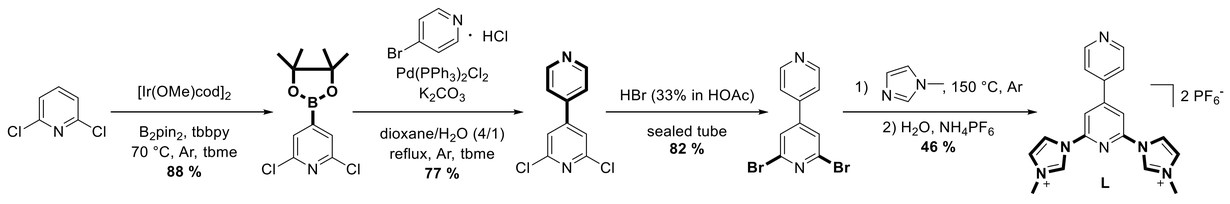
The primary aim of this project is **the development of the ditopic ligands** containing **CNC pincer type** and **pyridine group**. The developped ligand will play the role of a linker between the **Fe^{II}-core** (linked with C^N^C) and the cobaloxime-based **catalyst** (linked with pyridine function). Those two compartiments can be connected thanks to a **C-C coupling**. The resulting complex was then used as photocatalysts for **hydrogen photo-evolution**.



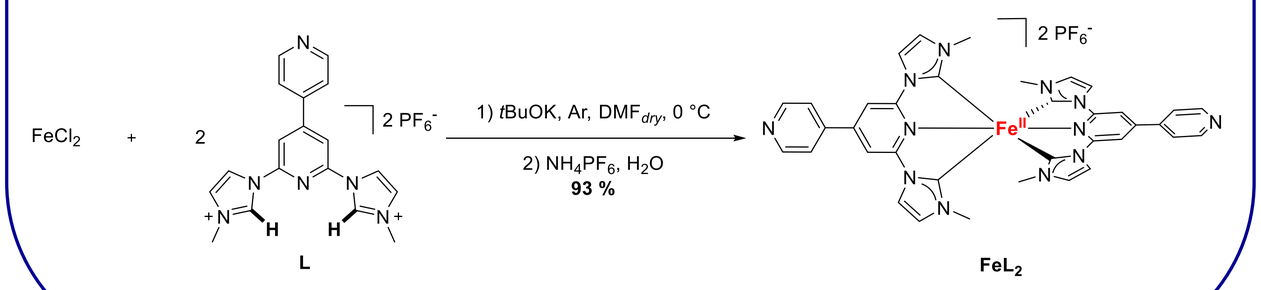


Synthetic pathway of the ligand and the iron-based complex [3]

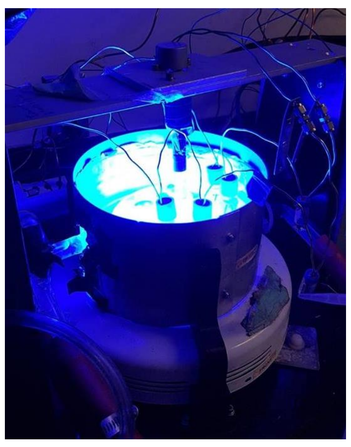
The **proposed ligand L** is synthesized through a **synthetic pathway** starting from the 2,6-dichloropyridine which was functionalized in **4**-position with a **boronic ester** which allows the coupling with another **pyridine fragment**.[3a,b] The **chloride** were substituted by **bromide functions** and then followed by the **imidazolium salt formation**. [2d,3c]



The **Fe^{II} complex FeL_2** was obtained by the **deprotonation** of the NHC precursor **L** in presence of an iron source, followed by the anion exchange. The resulting product was characterized by **^{1}H NMR, high resolution mass-spectrometry, cyclic voltammetry and absorption technique** (steady-state and time-resolved).



Hydrogen photo-evolution with iron-based complex and colloidal K_2PtCl_4

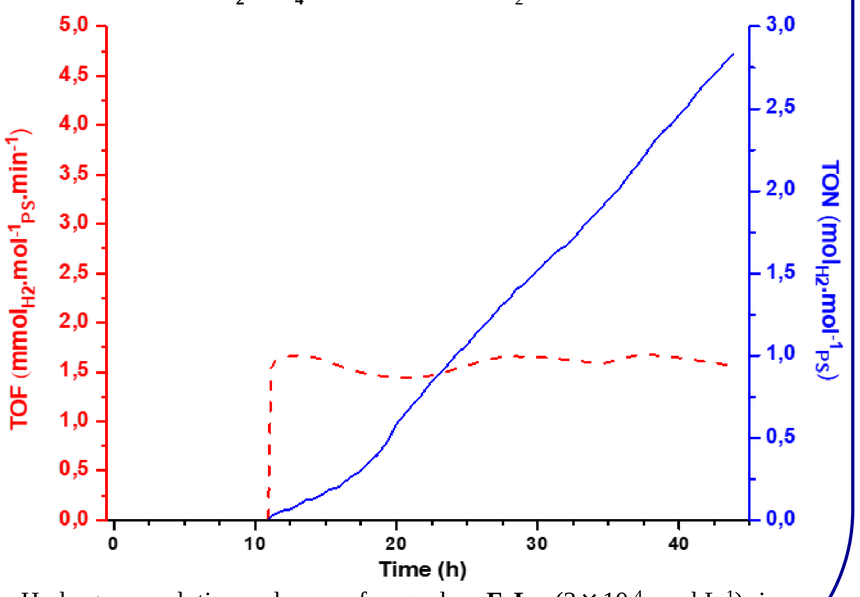


The **hydrogen-evolution experiments** were carried out in collaboration with the group of Prof. G. S. Hanan from the Université de Montréal. Different conditions have been tested **varying some parameters** such as solvent, concentration, sacrificial electron donor, catalyst and irradiation wavelength.

Unfortunately, in combination with the **cobaloxime catalyst**, the complex **FeL_2** was not able to produce hydrogen in any conditions tested. However, the use of colloidal **K_2PtCl_4** contributes to the H_2-evolution.[4a,b]

After a induction time, the complex **FeL_2** was able to reach a **TON** of approximately **3** under **blue light**.

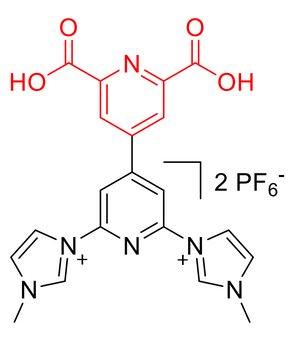
It is worth noting that the ligand itself was also able to photo-produce hydrogen under the same conditions. Further investigations are ongoing.

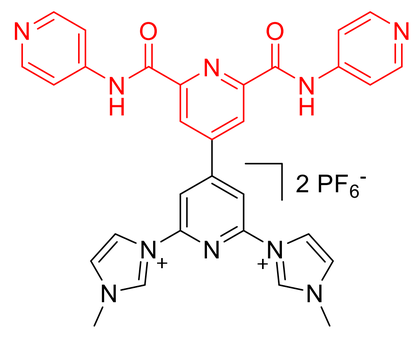


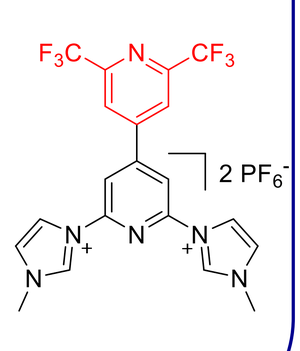
Hydrogen evolution scheme of complex **FeL_2** (2×10^{-4} mol.L^{-1}) in presence of K_2PtCl_4 (1×10^{-4} mol.L^{-1})in DMF/H_2O (95/5) and triethylamine (0.36 mol.L^{-1}) under blue light.

Conclusions and futur works

Although we aim to photo-produce hydrogen using free-noble metal complexes, we designed and studied **a new Fe^{II}-based complex for hydrogen-photoevolution** using colloidal K_2PtCl_4 as catalyst. New ligands with **other functions in 4-position** have been designed and their synthesis are in progress.







References

[1] (a) K. Wärnmark *et al.*, *Nat. Chem.*, **2015**, 7, 883 – 889 ; (b) P. C. Gros *et al.*, *Eur. J. Inorg. Chem.*, **2015**, 2469 – 2477 ; (c) K. Wärnmark *et al.*, *Acc. Chem. Res.*, **2016**, *49*, 1477 – 1485. [2] (a) M. Fontecave *et al.*, *Angew. Chem. Int. Ed.*, **2011**, *50*, 7238 – 7266 ; (b) M. Fontecave *et al.*, *Angew. Chem. Int. Ed.*, **2008**, *47*, 564 – 567 ; (c) M. Fontecave *et al.*, *Dalton Trans.*, **2008**, 5567 – 5569 ; (d) B. Elias *et al.*, *Eur. J. Inorg. Chem.*, **2016**, 1779 – 1783. [3] (a) P. G. Steel *et al.*, *Org. Lett.*, **2009**, *11*, 3586 – 3589 ; (b) T. Ohmura *et al.*, *J. Am. Chem. Soc.*, **2015**, *137* (8), 2852–2855 ; (c) J. Su *et al.*, *J. Med. Chem.*, **2017**, *60*, 3851 – 3865. [4] (a) M. Bauer *et al.*, *Eur. J. Inorg. Chem.* **2017**, 1504–1509 ; (b) M. Bauer *et al.*, *Eur. J. Inorg. Chem.* **2018**, in press.

Acknowledgements

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