PhD proposal: ***Efficient and Selective Oxidation of Methane via Caged Macrocyclic Complexes.***

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- Team : Chirosciences
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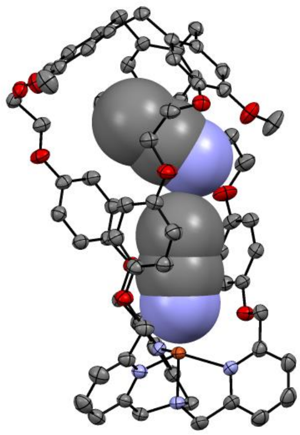
Description of the proposal :

Méthane (CH_4) is a particularly powerful greenhouse gas with a global warming potential of 33 times the baseline of CO_2. CH_4 is however widely present nature under a natural gas form. The direct conversion of methane to valuable industrial compounds, like methanol, is one of the major challenges posed to the scientific community because of its crucial **industrial** and **ecological benefits**. The selective transformation of CH_4 is particularly difficult due to the extreme inertness of its C-H bonds (the most stable in organic chemistry with ΔH_{C-H} = 440 kJ mol^{-1}).

In nature, however, metalloenzymes called methane monooxygenases are able to perform the selective oxidation of methane to methanol under physiological conditions. These natural catalysts display an active metal center (Fe or Cu) confined in the enzymatic cavity. This **hydrophobic structure** maximized efficiency and selectivity, owing to **1)** substrate (CH_4) recognition and **2)** product (CH_3OH) release.

Aiming at reproducing the remarkable chemistry found in nature, our team develop bioinspired catalysts displaying a cage structure (**hydrophobic cavity**) that act as a filter to select the targeted substrate (see adjacent figure).[1-3] We have recently demonstrated that some caged catalysts – based on non-macrocyclic ligands – results in a more selective oxidation of methane compared to the corresponding model catalysts devoid of cavity.[4] However, their efficiency remain too low, and the development of new catalysts displaying enhanced activity is highly needed. This project will focus on the development of new caged catalysts based on Fe- or Cu-complexes build from **macrocyclic ligands**. These structures will strongly enhanced the catalytic efficiency while keeping an excellent selectivity. This project aims at **1)** preparing the caged ligands (organic chemistry), **2)** characterizing the corresponding complexes (spectroscopy), and **3)** evaluating their catalytic properties in the oxidation of light alkanes (including CH_4), under mild conditions (homogeneous catalysis). By tackling this fundamental issue, a new method for the selective conversion of the CH_4 greenhouse gas, will be developed.



Key words: Bioinspired catalysts, Supramolecular catalysis, methane conversion.

References

1. C. Colomban and co., *Chem. Commun.* **2021**, 57, 2281
2. A. Martinez and co., *Chem. Sci.* **2017**, 8, 789
3. A. Martinez and co., *Acs catal.* **2017**, 7, 7340
4. C. Colomban et al., *Inorg. chem.* **2019**, 58, 7220

Details of the application :

The candidate: The candidate should be highly motivated, hardworking, able to work as part of a team, and should demonstrate a background in organic synthesis and/or synthetic coordination chemistry. She/he **must** own a master academic degree in organic chemistry, coordination chemistry or supramolecular chemistry (**passing grade** for **Msc.**: **12/20** in the French system or equivalent).

The procedure: Candidates must send:

- a curriculum vitae;
- a cover letter;
- a recommendation letter from previous supervisors;
- copies of Master transcripts (exams marks and ranking).

Applications must be sent at:

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