Funded Ph.D. position
Marseille, France
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Efficient and Selective Oxidation of Methane via Caged Bioinspired Catalysts

- **Laboratory** : Institut des Sciences Moléculaires de Marseille, iSm2.
- **Team :** Chirosciences.
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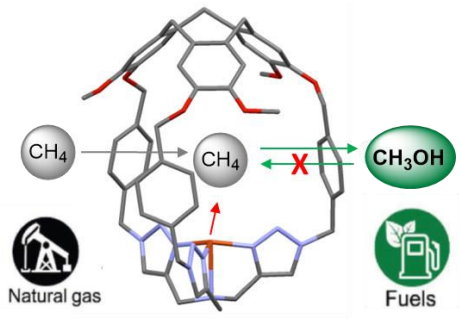
Context of the study.

This Ph.D. thesis is **funded by the ANR** (JCJC).
Approximatively 70-90% of natural gas is constituted of methane CH_4, a particularly powerful greenhouse gas with a global warming potential of 30 times the baseline of CO_2. In its last report, the GIEC has defined methane as **the priority target for emission reduction**, along with CO_2. Its direct transformation to energy vectors (such as methanol) is an environmental and energetical challenge ("**waste-to-wealth**" approach to fight the global warming and produce cheap energy).
But 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 $\Delta H_{C-H} = 440$ kJ.mol^{-1}).
In nature, however, some metalloenzymes 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**.

Description of the project.

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.[3] 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 macrocyclic Fe- or Cu- complexes. These structures will **strongly enhance the catalytic efficiency** while keeping **an excellent selectivity**. This project aims at :



1) preparing the caged ligands and corresponding complexes, and
2) evaluating their catalytic properties in the oxidation of CH_4, under mild conditions.

By tackling this fundamental issue, a new method for the selective conversion of the CH_4 greenhouse gas, will be developed.

Références.

1. C. Colomban and co., *Chem. Commun.* **2021**, 57, 2281
2. A. Martinez and co., *Angew. Chem. Int. Ed.* **2018**, 57,14212
3. C. Colomban et al., *Inorg. chem.* **2019**, 58, 7220

Profile. The candidate should demonstrate a background in organic and/or synthetic coordination chemistry. She/he must own a master academic degree in chemistry (organic, coordination or supramolecular chemistry, catalysis or related, in the French system or equivalent).

Procédure. Curriculum vitae, cover letter and exams marks/ranking, should be sent to cedric.colomban@univ-amu.fr. Deadline: April 10th, 2023.