université PARIS-SACLAY

M2
Proposition de stage 2026-2027

Nom et label de l'unité de recherche : ILV (Institut Lavoisier de Versailles) UMR 8180
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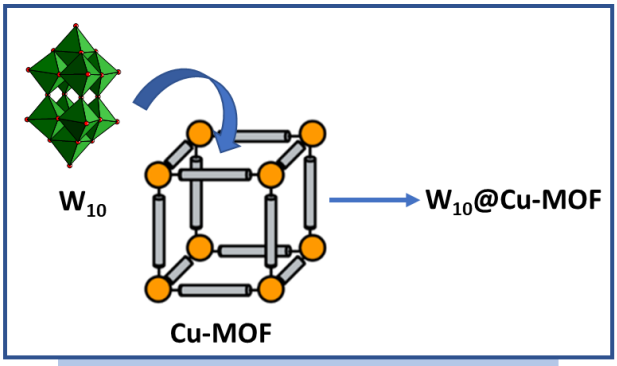
New W_{10}@MOF composites as photoredox-HAT catalysts

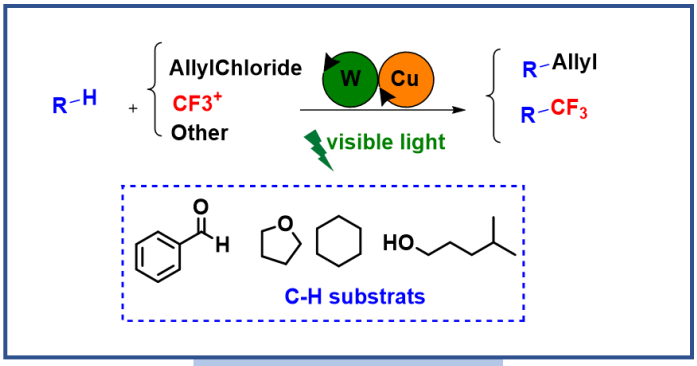
Over the past decades, the activation of inert C–H bonds has attracted considerable attention, as it represents a valuable strategy for the functionalization of organic molecules. In particular, photoredox approaches have enabled the development of new hydrogen atom transfer (HAT) processes and **the decatungstate anion, $[W_{10}O_{32}]^{4-}$ (W_{10}) that belongs to the polyoxometalate (POM) family, has emerged as one of the most prominent examples of a combined photoredox–HAT catalyst** [1]. However, despite its high efficiency, W_{10} requires UV irradiation, which involves the use of energy-intensive light sources. Moreover, most of the reported catalytic studies with the decatungstate POM are performed in homogeneous conditions, which prevents catalyst recycling and product separation. In ILV, we have started a project with **heterogeneous catalysts based on W_{10} immobilized in the cavities of Metal-Organic Frameworks (MOFs)**. MOFs are crystalline porous materials build from the connection of metal clusters with organic linkers. The first MOFs investigated served only as catalyst supports and required UV-light irradiation.

Building on these studies, the proposed M2 internship project will explore the synthesis of composites consisting of decatungstate POMs immobilized within MOFs, with the aim of inducing photocatalytic activity under visible-light irradiation. Furthermore, the resulting composites will provide an opportunity to explore dual catalytic reactions that have so far been scarcely reported and investigated only under homogeneous conditions [2]. The most relevant example has been described by the Nobel price Pr MacMillan on C(sp^3)-H trifluoromethylation [3].

[1] P. P. Singh *et al*. *Org. Biomol. Chem*. **2024**, *22*, 3799; [2] Fañanás-Mastral *et al.* Org. Lett. **2022**, *24*, 6874.
[3] MacMillan *et al.* Nature Chem., 12, 2020, 459.



Schematic representation of the catalyst synthesis



Example of targeted reactions

This multidisciplinary project will involve collaboration between the MIM and SORG teams of ILV. The recruited M2 student will have to carry out the synthesis of the composite materials W_{10}@MOF and their characterization (UV-Vis and IR spectroscopies, thermogravimetry analysis, powder X-ray diffraction) as well as investigate deeply their catalytic activity. The photocatalytic reaction will be followed by NMR. Recycling experiments will be performed on the best catalysts.

Keywords: **Polyoxometalates • Metal-Organic Frameworks • Photocatalysis • HAT reactions**