

Name of supervisors: Dr Petra Ágota Szilágyi, Prof Unni Olsbye, MSc Rafael Cortez Sgroi Pupo

Preferred background of candidates: Chemistry/Materials Science

Number of available projects: 2

Preferred project period: within the mid-June to mid-August period

Project rationale

Arguably, our society is manufactured by the activation of C-H bonds, suffice it to consider that current technology uses carbohydrates fossil sources, mostly crude oil, for the producing a huge range of items from polymers to pharmaceuticals. Although it is highly desirable to replace carbohydrates entirely by, say, biomass, it would also require a complete industrial paradigm shift and as such a significant amount of time to be implemented. On the other hand, we may look at replacing the carbohydrate source with renewable ones, *e.g.*, biogas. Such approach is desirable as it requires well-defined technological advances rather than the reshaping of the whole value chain, and particularly so if the products may be used as carbon-neutral fuels themselves, *i.e.* methanol. It is not however without challenges, C-H activation in CH₄ is fiendishly difficult if its complete oxidation to CO₂ is to be avoided.¹

To address this, Prof Olsbye has been recently awarded an ERC Synergy grant (CuBE) as PI, in which UiO is specifically looking at how to translate and integrate enzymatic active centres into metal-organic frameworks (MOFs).^{2,3} The proposed internship is aimed at probing a specific research question we have recently encountered therein. Evaluating the high-performance *p*MMO enzyme for partial methane oxidation to methanol, it has been recently found that highly hydrophobic regions, or 'pockets', around the active site increase its performance, probably by densifying the CH₄ (Fig. 1), otherwise in relatively low concentration.⁴

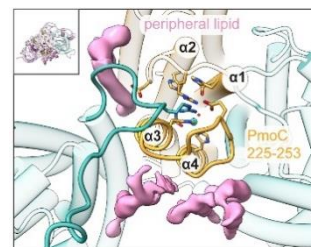


Figure 1 Local *p*MMO structure showing hydrophobic 'pockets' (pink) surrounding the active site (yellow). Reproduced from [4]

Previously the Catalysis section has been able to develop MOFs containing moieties successfully mimicking the enzyme active sites. However, we have not been evaluated the **effect of MOF hydrophobicity on the catalyst performance**. This is the specific research question, this UiO:Energy Summer Internship will answer.

Methodology

It should be noted that MOFs, built up of inorganic nodes interconnected by organic linkers in a regular and periodic fashion, thereby intrinsically yielding a crystalline and highly porous class of materials, naturally contain such 'pockets', in the form of pores surrounding the ones bearing the enzyme mimicking moieties. We therefore propose to use the hydrophobic 'pockets' of the enzymes as inspiration and make the MOF pores more hydrophobic to probe and mimic this hypothesis is therefore the specific undertaking of this research.

In particular, we propose to use perfluorinated linkers, *i.e.* octafluorobiphenyldicarboxylic acid (FBPDC) as the main linker of the UiO-67 structure, which is the main MOF topology used – conventionally with the biphenyl-4,4'-dicarboxylic acid (BPDC) linker. Since the proposed linker is not commercially available, we have designed two proposed synthesis routes (Fig. 2) to afford them. Although two synthesis routes are given, the second serves as a safety net in case one of them is found to be not accessible. Successful synthesis and linker purity will be checked using NMR, MS and FTIR.

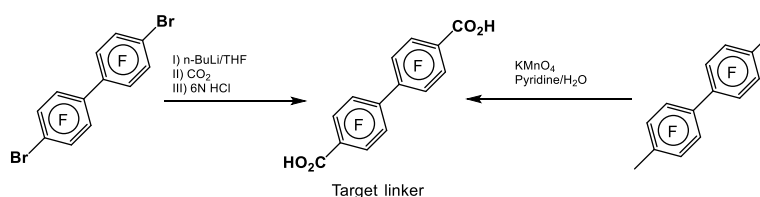


Figure 2 Proposed synthetic routes for the octafluorobiphenyldicarboxylic acid (FBPDC) linker.

The perfluorinated linkers will be incorporated into the UiO-67 MOF structure by using standard solvothermal synthesis already developed in the group, we will explore different synthetic conditions and/or modulator acids (*e.g.* benzoic acid, acetic acid) in case of the perfluorinated UiO-67 (F-UiO-67) does not form in the conventional approach. The resultant MOFs will be characterised using BET surface area measurements, PXRD, TGA, and FTIR. For comparison, conventional UiO-67 MOF will also be synthesised and characterised. In addition, isotherms of methane, water vapour, and CO₂ adsorption will be measured to compare the hydrophobicity and gas uptake of the new F-UiO-67 with that of UiO-67. In addition, we will assess, the F-UiO-67 stability in air, and in case it is unstable, a partially fluorinated version shall be synthesised.

Lastly, the incorporation of the enzyme mimetic linker will be done by post-synthetic linker exchange, and this new MOF shall be thoroughly characterised using to the above techniques.

Expected outcomes and deliverables

The expected project outcomes are as follows:

- The perfluorinated linker synthesis procedure will be optimised.
- New perfluorinated MOFs with potential implication in applications such gas storage and separation, water repellent nanoparticles, sensors, *etc.*
- As the perfluorinated linkers are more hydrophobic, their MOF derivatives are expected to densify methane in the pores
- A model system for directly probing the effect of hydrophobic 'pockets' onto enzymatic CH₄ valorisation. *N.B.* this approach can be generalised to systems wherein densification of a poorly interacting reactant is beneficial
- Ultimately, we anticipate better performing catalyst for CH₄ to methanol conversion. This aspect has important energy and environmental implications.
- The students will receive cutting-edge training and valuable work experience.

The expected project deliverables are as follows:

- New perfluorinated metal-organic frameworks with enhanced interactions with methane
- Project report
- Manuscript in Energy & Environmental Science / Advanced Materials, *etc.*

Project schedule

Week 1: H&S training, lab introduction/training; first linker synthesis (small batch), UiO-67 synthesis

Week 2: Linker characterisation, linker synthesis upscaling, UiO-67 characterisation

Week 3: Integration of perfluorinated linker into MOF structure (small batch), MOF characterisation

Week 4: MOF characterisation cont'd (stability testing, adsorption; F-MOF synthesis upscaling

Week 5: Post-synthetic linker-exchange (small batch); characterisation

Week 6: Additional characterisation and report writing

References

1 N. F. Dummer, *et al.*, *Chem. Rev.*, DOI:10.1021/acs.chemrev.2c00439.

2 I. Gerz, *et al.*, *Eur. J. Inorg. Chem.*, 2021, **2021**, 4762–4775.

3 B. Centrella, *et al.*, *Dalton Trans.*, 2022, **51**, 14439–14451.

4 C. W. Koo, *et al.*, *Science*, 2022, **375**, 1287–1291.