Development of redox-active Metal Organic Framework (MOF) and MOF thin films

In our group we are developing porous coordination polymers also called Metal Organic Frameworks (MOFs) based on redox active ligands and/or metals. MOFs represent a class of sophisticated nanostructured crystalline solids; they consist of infinite networks of metal clusters or ions coordinated by organic linkers in a 2 or 3D structure. These functional solids display great potential for applications in catalysis and especially for the study of structure-properties relationship[1-4]. In this research project we are first aiming to synthesize stable porous MOFs based on redox active ligands such as porphyrins. Stability towards hydrolysis[5] as well as thermal and chemical properties of MOFs will be assessed. Then, these solids will be electrochemically characterized to explore their activity in electrocatalysis for small molecules activation (such as O_2 and CO_2).
Moreover, a part of the project will focus on the development of MOF thin film growth using molecular layer deposition (MLD) technique. True implementation of MOFs in energy-related technologies offers a tremendous potential but requires the growth of thin films to allow construction of device-like architectures. So far MOF thin films have been produced by solution-based methods[6] and have several limitations for large-scale industrial deposition processes. An attractive alternative to the solution based methods is the vapor phase fabrication of MOF thin films. The use of molecular layer deposition (MLD) technique is strongly innovative in the field of MOF chemistry[7-9].This self-limiting growth process at the vapour/surface interface provides potential to create novel ordered molecular stacking sequences achieving MOFs with unexplored features. Regarding all the studies on MLD of MOFs reported so far MOF crystallinity appears to be generally poor. The nature and impact of the substrate was never considered as a parameter influencing MOF thin film quality. In this project, the substrate/film interface will be explored for epitaxial growth of thin films[10].

<u>Techniques:</u>
The project will include classical synthesis of coordination polymers, materials characterizations (XRD, TGA, IR, UV-vis, BET, SEM, TEM), electrochemical studies, technical optimisation of the ALD system for MOF growth to understand the underlying parameters and optimize the crystallinity of the thin films.
National and international collaborations are possible in the frame of this project.

<u>Skills:</u>
Candidates with a strong background in synthesis, coordination chemistry, electrochemistry and/or diffraction studies, and electronic microscopy are encouraged to apply.
<u>Starting date:</u>
October 2019 - This position is funded for 12 months with a 6 months extension possibility.

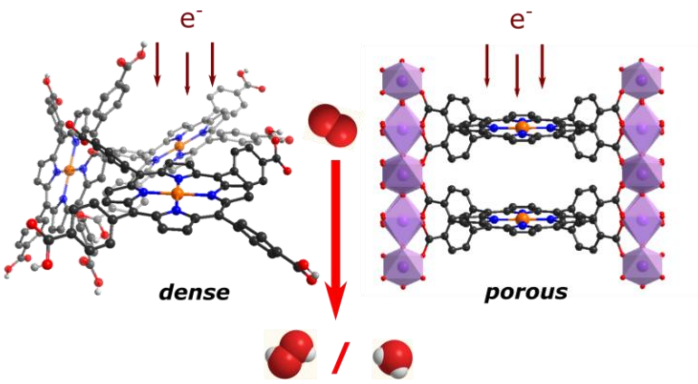

Figure: Oxygen reduction reaction (ORR) catalysis study using a molecular porphyrin and porphyrin-based MOF[2]

Contact/additional information: Alexandra Fateeva alexandra.fateeva@univ-lyon1.fr

Catherine Marichy catherine.marichy@univ-lyon1.fr

Laboratoire des Matériaux et Interfaces, Université Lyon 1

References

1. A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angewandte Chemie International Edition*, 2012, **51**, 7440-7444.
2. M. Lions, J. B. Tommasino, R. Chattot, B. Abeykoon, N. Guillou, T. Devic, A. Demessence, L. Cardenas, F. Maillard and A. Fateeva, *Chemical Communications*, 2017, **53**, 6496-6499.
3. G. Mouchaham, B. Abeykoon, M. Giménez-Marqués, S. Navalon, A. Santiago-Portillo, M. Affram, N. Guillou, C. Martineau, H. Garcia, A. Fateeva and T. Devic, *Chemical Communications*, 2017, **53**, 7661-7664.
4. B. Abeykoon, T. Devic, J.-M. Grenèche, A. Fateeva and A. B. Sorokin, *Chemical Communications*, 2018, **54**, 10308-10311.
5. J. Canivet, A. Fateeva, Y. Guo, B. Coasne and D. Farrusseng, *Chemical Society Reviews*, 2014, **43**, 5594-5617.
6. J.-L. Zhuang, A. Terfort and C. Wöll, *Coordination Chemistry Reviews*, 2016, **307, Part 2**, 391-424.
7. E. Ahvenniemi and M. Karppinen, *Chemical Communications*, 2016, **52**, 1139-1142.
8. I. Stassen, D. De Vos and R. Ameloot, *Chemistry – A European Journal*, 2016, **22**, 14452-14460.
9. J. Penttinen, M. Nisula and M. Karppinen, *Chemistry – A European Journal*, 2017, **23**, 18225-18231.
10. J. K. Bristow, K. T. Butler, K. L. Svane, J. D. Gale and A. Walsh, *Journal of Materials Chemistry A*, 2017, DOI: 10.1039/C7TA00356K.