

PhD Thesis at INSA Rennes - Institute of Chemical Sciences, Rennes, France

“Luminescent MOFs as chemical sensors”

Metal-Organic-Frameworks (MOFs) are coordination polymers containing organic ligands and metal cations or polynuclear centers with potential voids. These materials have been extensively studied over the last twenty years due to the variety of their crystalline structure, their porosity and therefore their applications for the storage of molecules, like greenhouse gases or H₂, for purification, separation, catalysis and even the controlled release of active ingredients (5000 articles/year)¹. MOFs are highly crystalline materials, which facilitates their crystal structure characterizations, and they possess a high tunability of their architectures. Indeed, from a judicious choice of the building units, organic linker and metal polyhedra, it can be possible to modulate the size and shape of the pores and to functionalize the framework of the porous material. Luminescent MOFs have been studied for their potential applications as chemical sensors². Thanks to the collaborative functionalities of permanent porosity and luminescent property, MOFs can serve the two required functions as receptors (recognition of molecules) and transducers (production of a signal). The luminescence in MOFs can arise from the organic linkers, the framework metal cations, the antenna effect, some adsorbed luminophore or by excimer and exciplex formation. Usually the mechanisms of luminescence sensing in MOFs arise from luminescence quenching/enhancement. Due to the intrinsic hybrid nature of the MOFs it is possible to modulate the luminescence of the material by playing on the organic and inorganic building units. The structural versatility of the MOFs permit them to store and select guest molecules and make them good candidates as chemical sensors of a large variety of target gas and vapor phase analytes for applications in industrial process management, chemical threat detection, environmental monitoring etc.

The PhD project will consist in the synthesis of MOFs built from carboxylate ligands known to easily coordinate the metal cations, using solvothermal, microwave and mechanochemistry routes, the last one being known as green route. From previous results, commercial ligands like pyrazine/pyridine/benzene carboxylates ligands will be used preferentially and transition metals (3d, 4d) will be used for the inorganic building units. MOFs and guest@MOFs (MOFs loaded with guest molecules) crystal structures will be investigated from powder X-ray diffraction. To control the conditions of application of the sensors, the reactivity and thermal stability of the MOFs as well as their chemical stability in various solvents and pH will be checked. A preponderant part of the PhD work will consist in the study of the luminescent properties of the MOFs by spectroscopy studies (measurements of excitation/emission spectra, quantum yield, luminance) for the host MOFs and guest@MOFs. Influence of the nature of the cations and linkers on the detection will be studied. The investigated analytes will be either cations of heavy metals (Hg²⁺, Cd²⁺, Pb²⁺), anions (halogen, CN⁻, NO₃⁻, ClO₄⁻), small molecules (xylenes) or vapors (CO₂, H₂, O₂, VOC, NH₃, H₂O) possibly down to target quantities of the order of ppm with a particular focus on the molecules selectivity within a mixture of analytes.

PhD supervisors: Prof. Nathalie Audebrand (INSA Rennes/URennes)

Contact persons: Nathalie Audebrand : nathalie.audebrand@insa-rennes.fr

¹ *Chem. Soc. Rev.* 2014, Special issue, vol. 16.

² *Chem. Soc. Rev.* 2012, 112, 1105-1125; *Chem. Soc. Rev.* 2017, 46, 3242-3285 ; *Coord. Chem. Rev.*, 2018, 354, 28-45.