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 sensors[2]. Thanks to the collaborative functionalities of permanent porosity and luminescent property, MOFs can serve the two required functions as receptors (recognition of molecules) and tranducers (production of a signal). The luminescence in MOFs can arise from the organic linkers, the framework metal cations, the antenna effect, some adsorbed lumophore 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 verstaility 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 using carboxylate and azolate ligands known to easily coordinate the metal cations, using solvothermal, microwave and mechanochemistry routes. MOFs and guest@MOFs (MOFs loaded with guest molecules) crystal structures will be investigated from single-crystal and powder X-ray diffraction. Reactivity and thermal stability of the MOFs will be checked from thermal analyses to control the conditions of application of the sensors. 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 (Hg^{2+}, Cd^{2+}, Pb^{2+}), anions (halogen, CN^-, $NO3^-$, ClO_4^-), small molecules (xylenes) or vapors (CO_2, H_2, O_2,VOC, NH_3, H_2O) 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. Olivier Guillou (INSA Rennes), Prof. Nathalie Audebrand (INSA Rennes/UR1)

Contact persons: Olivier Guillou : olivier.guillou@insa-rennes.fr ; 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 ; *Chem. Soc. Rev*. 2017, 46, 3242-3285.