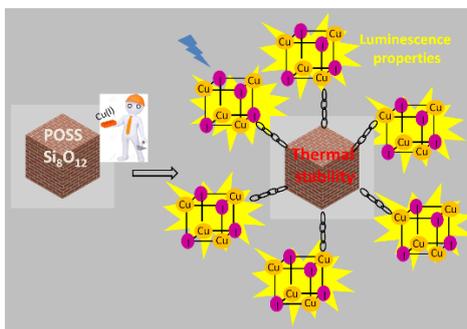


Construction of Organic-Inorganic Porous and Luminescent Hybrid Materials and MOFs by Self-Assembly of Polysilsesquioxanes and Metal Salts

Context and objectives:

Cu(I)-based coordination polymers (CPs) have attracted much interest due to the facile synthetic approach and the aptitude of CuX (X = halide) salts to aggregate into polynuclear clusters featuring very rich structural diversity. These CPs found also numerous applications in different domains such as for optoelectronics, catalysis or gas adsorption. We and several other research groups have studied the assembly of diverse CPs and MOFs by reacting copper (I) halides with different thioethers R-S-R.¹ This project deals with the construction of organic-inorganic hybrid MOF-type materials (Metal Organic Frameworks) presenting in particular luminescence properties, thermal stability, electronic conductivity and porosity. The originality of this project relies on the use of polysilsesquioxanes (POSS) as molecular bricks, cube-like compounds of composition Si_8O_{12} . These nano-sized POSS units having a diameter of 1-3 nm can be considered as the smallest silica particles. Preliminary investigations recently realised in our group have revealed that these POSS bearing thioether functions can be easily coordinated on Cu(I) salts generating 3D networks. The molecular materials thus obtained present very interesting luminescence properties associated with high thermal stability.²

The topic and objective of the proposed thesis concerns the synthesis of novel POSS bricks functionalised by thioether groups by varying the flexibility and steric hindrance of the POSS-SR spacer, but also by introducing functional groups capable of built up donor or acceptor interactions or hydrogen bonding. After complexation by Cu(I) salts, photophysical studies will be primordial. Furthermore, we wish to study the electric conductivity of these polymeric materials as well as their capacity for gas absorption and vapochromism for the most porous networks. These investigations could also be extended towards other salts such as silver (I), bismuth (III) or paramagnetic Cu(II) ions.



Practical details:

This PhD project will be realised within the research group « *Matériaux et Surfaces Fonctionnels* » of the Institut UTINAM in Besançon: <https://www.utinam.cnrs.fr>. This project will be performed in close collaboration with national and international research groups from the Universities of Montpellier, Dortmund (Germany) and Sherbrooke (Canada).



Profile:

This PhD offer is open to candidates with a **Master degree in Organic Chemistry** or synthetic **Material Sciences**. The candidate should have a high interest not only for organic synthesis and coordination chemistry, but also for luminescence studies required to characterize and valorise the materials. The candidate should demonstrate a high motivation for the project and prove his (her) capacity to work in an autonomous and rigorous manner. (S)he will also have to show that (s)he will be able to integrate a multidisciplinary research team and have excellent communication skills (both oral and written), notably in English.

Note that only applications of candidates having at least a Master diploma with a B grade will be considered.

Application procedure:

To apply, please send your CV, a motivation letter and recommendation letter, your Masters grades & ranking to lydie.viau@univ-fcomte.fr and Michael.knorr@univ-fcomte.fr

References:

¹ A. Raghuvanshi, N. J. Hamad, M. Knorr, L. Viau, C. Strohmann, L. Knauer, “1,3-Dithiolane and 1,3-Ferrocenyl-dithiolane as Assembling Ligands for the Construction of Cu(I) Clusters and Coordination Polymers” *J. Inorg. Organomet. Polym. Mat.* **2017**, 27, 1501–1513.

² A. Raghuvanshi, C. Strohmann, J.-B. Tissot, S. Clément, A. Mehdi, S. Richeter, L. Viau, M. Knorr “Assembly of Coordination Polymers using Thioether-Functionalized Octasilsesquioxanes. Occurrence of (CuX)_n Clusters (X = Br and I) within 3D-POSS Networks” *Chem. Eur. J.* **2017**, 23, 16479–16483.

³ A. Schlachter, L. Viau, D. Fortin, L. Knauer, C. Strohmann, M. Knorr, P. D. Harvey “Control of Structures and Emission Properties of (CuI)_n 2-methyldihtiane Coordination Polymers” *Inorg. Chem.* **2018**, 57, 13654-13576.