M2

Proposition de stage 2025-2026

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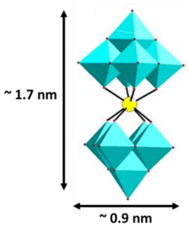
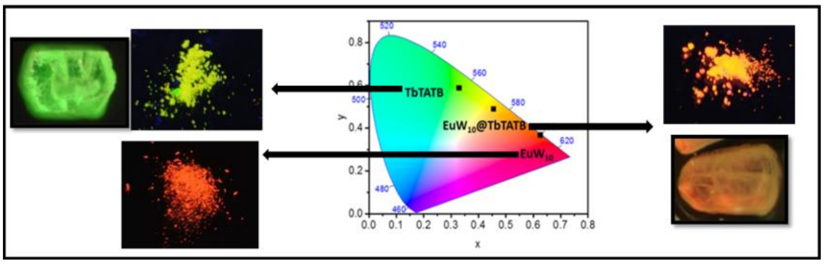
New sensors based on multiluminescent (POM,complex)@MOF composites

MOFs (Metal–Organic Frameworks) are crystalline, porous organic–inorganic hybrid compounds obtained by coordinating metal centers (or metal clusters) with polydentate ligands such as di- or tricarboxylic acids. In particular, luminescent MOFs represent a well-developed class of materials, with key applications in white-light emission and optical sensing.[1] Polyoxometalates (POMs),[2] on the other hand, are a family of inorganic compounds known for their wide range of applications, including in optics. In recent years, our team has developed POM@MOF systems exhibiting dual luminescence by incorporating red-emissive Eu-POM into a green-emissive terbium-based MOF, yielding the EuW$_{10}$@Tb-TATB composite (see Figure).[3] Another example involves the integration of the same Eu-POM, along with green-emissive carbon dots (GCDs), into a zinc-based MOF, resulting in the (EuW$_{10}$,GCDs)@ZIF-8[2] compound.[4] These materials have demonstrated good sensitivity to temperature variations and can therefore be considered as ratiometric luminescent thermometers. Notably, (EuW$_{10}$,GCDs)@ZIF-8[2] also represents a cheap material, incorporating only 0.23 wt% of rare earth elements, compared to 23.1 wt% in the terbium-based composite. However, the structure of carbon dots remains poorly defined, limiting in-depth structure–property investigations, and their purification process remains particularly challenging. Moreover, the use of MOF-based dual-probe systems exhibiting opposite luminescence responses to temperature or analyte variations remains to be developed.





EuW$_{10}$ **Luminescent properties of EuW$_{10}$@Tb-TATB**

The internship offered here aims to elaborate a new generation of (POM,complex)@MOF sensors incorporating commercially available or easily synthesized coordination complexes selected for their excellent optical complementarity with EuW$_{10}$ POM. In addition to the development of luminescent thermometers, the use of these materials as sensors for the detection of pollutants will be explored. The targeted materials will be synthesized and characterized in Versailles using complementary techniques, including IR, XRD, TGA, ICP-MS, BET and SEM-EDS. Optical measurements (UV-Vis and emission spectra) of the solid materials will be carried out in collaboration with Dr Hélène Serier-Brault from IMN, Nantes University.

This M2 internship will be funded by ILV.

Keywords: **Metal-Organic Frameworks • Polyoxometalates • Coordination complexes • Luminescent materials • Sensing applications**

1) Y. Shu *et al.*, *ACS Sens.* **2021**, *6*, 641-658; 2) A. Dolbecq *et al.*, *Chem. Rev.* **2010**, *110*, 10, 6009; 3) C. Viravaux *et al.*, *J. Mater. Chem. C* **2021**, *9*, 8323; 4) C. Viravaux *et al.*, *J. Mater. Chem. C* **2024**, *12*, 15535.