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Organometallics : Materials and Catalysis
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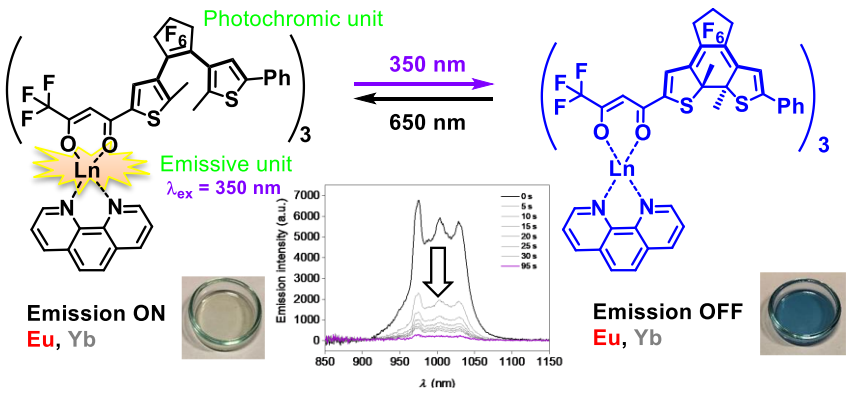
Luminescent lanthanide complexes with tunable dynamic optical responses

Counterfeiting is a worldwide problem that challenges companies, governments, and customers. Therefore, anti-counterfeiting systems that make genuine items harder to copy and easy to authenticate are important for the protection of brands, valuable documents, or medicine as counterfeit substances can severely endanger human health. The number of forgeries is now so important that the demand in highly-secured, advanced and complex authentication systems has grown exponentially. Our group has recently operated a major breakthrough in this field by designing a photochromic (light switchable) lanthanide complex to switch reversibly the luminescence of lanthanide ions, either in the visible or in the near infrared (NIR) ranges, in order to achieve a multi-level anti-counterfeiting system (see scheme).[1,2] Knowing that lanthanide based luminescent systems are already used for securing banknotes, our patented invention shows great promises.



Our objective is now to design new improved switchable complexes featuring significant brightness and ON/OFF ratio to reach application standards. Our systems are simply composed of the lanthanide center (the light emitter), a photochromic dithienylethene unit which state can be controlled remotely by irradiation at a given wavelength, and also an additional antenna. The role of the PhD student will be (i) to extend the control of the luminescence to other emission colors, by changing the lanthanide ions, and (ii) to optimize of the optical properties that will require the synthesis of new families of photochromic and/or antennae ligands in order to also understand the photophysics of these objects and establish structure-property relationships. Finally, to meet the current requirements of security labels and tags, we envisage encapsulating our molecules into systems compatible with current printing or labelling technologies, such as in polymer matrices, in beads etc...

This work will this consist in 1/ the **synthesis** of new lanthanide complexes, involving multi-step organic synthesis and coordination chemistry along with the use of the corresponding characterization tools (NMR, IR, X-Ray crystallography), and 2/ the photophysical studies (absorption, emission, photochromism) in Rennes and with our partner in Lyon during internship(s) for the PhD student.

The PhD student will be integrated in a *highly complementary and experienced team* (molecular synthesis and spectroscopic measurements, as well as theoreticians). Our group benefits of a high-quality laboratory environment and equipment (https://iscr.univ-rennes1.fr/omc-team-responsive-organometallic-and-boron-scafolds-robos). The team gathers two senior scientists, four young chemists, one technical staff member, several postdocs and students from various countries and cultures (France, Lebanon, India, Vietnam…).

The candidate should have a good training in organic synthesis and/or coordination chemistry. Skills in optical spectroscopy will also be appreciated but are not mandatory. This work requires a strong motivation, a transdisciplinary open mind, and will allow the candidate (i) to get involved in different aspects of the topic and (ii) to acquire complementary skills in synthesis and chemical physics.

Keywords: Organic synthesis - Coordination chemistry - lanthanide Ions - Photochromism - Luminescence

[1] Al Sabea, H.; Norel, L.; Galangau, O.; Roisnel, T.; Maury, O.; Riobé, F.; Rigaut, S., *Adv. Funct. Mater.* **2020**, 2002943.
[2] Al Sabea, H.; Norel, L.; Galangau, O.; Hijazi, H.; Métivier, R.; Roisnel, T.; Maury, O.; Bucher, C.; Riobé, F.; Rigaut, S., *J. Am. Chem. Soc.* **2019**, *141*, 20026-30.