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Organometallics : Materials and Catalysis
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Temporal resolution of lanthanide photo-controlled emission

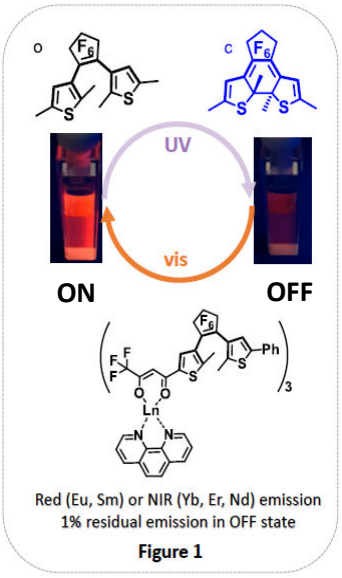

Figure 1

Among all luminophores, lanthanide ions are playing an important role. They display unique photophysical properties giving them "fingerprints" easily distinguishable in imaging. Surprisingly, despite its interest and its highly relevant potentials in material science, for applications such as anticounterfeiting tags or in super-resolution imaging, the photo-controlled quenching of lanthanide emissions remains underdeveloped. Indeed, this phenomenum is restricted to Eu^{III} and Yb^{III} ions, and is limited to P-type photochromism, ie. with photochromic units thermally stable in both states and that require two different wavelengths (UV and vis) for switching operation (Figure 1).

Depending on the targeted application, if the emission quenching induced by UV irradiation is needed only for a limited time, a spontaneous thermal recovering of the initial state (back reaction) is highly desirable (Figure 2). High temporal and spatial resolution can be obtained with a T-type photochromism.

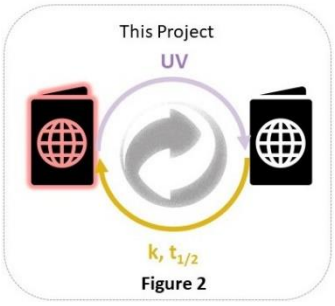

Figure 2

In this project, we target innovative lanthanide complexes displaying photo-controllable emission quenching in the visible or the NIR range with a tailored timescale of the back reaction of the order of seconds. We will adapt field proven T-type diarylethene systems by achieving structural variations to taylor the kinetic of the thermal back-reaction. **Overall, we will achieve a feature in which the luminescence response is dynamic (i.e. controlled by the photochromic reaction) and self-reversible (i.e. controlled by the thermal back reaction).** The design of unique complexes issued from several lanthanides (Tb^{III}, Eu^{III} ,Sm^{III},Dy^{III},Nd^{III}, Yb^{III}, Er^{III}) with controllable emissions with one irradiation wavelength is a strong motivation (i) to improve the basic knowledge in the field, and (ii) to open the door to new applications to be discovered. In particular, we can expect major breakthroughs in anticounterfeiting/coding devices and in bio-imaging.

Therefore, this work will consist in (i) the **synthesis** of new lanthanide complexes and photochromic systems involving multi-step organic synthesis and coordination chemistry, along with the use of the corresponding characterization tools (NMR, IR, X-Ray crystallography), and (ii) the **photophysical studies** (absorption, emission, photochromism) of the obtained systems. **The emission properties of all dyes will be studied during internship of recruited PhD** students in ENS Lyon, in collaboration with Dr. O. Maury.

The student will be integrated in a *highly complementary and experienced team* (synthesis and spectroscopic measurements). Our group is multicultural and benefits from a high-quality laboratory environment (https://iscr.univ-rennes.fr/omc-team-responsive-organometallic-and-boron-scafolds-robos).

This multidisciplinary research requires a strong motivation, good skills in organic synthesis and curiosity concerning photophysical properties (organic and lanthanide systems). Thanks to his/her transdisciplinary open mind, the candidate will exploit state-of-the-art synthetic methodologies and perform advanced photophysical studies together with more applied device-oriented research, with encapsulation into polymeric films compatible with current labelling technologies, and will thus develop a broad range of skills.

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.