

Circularly Polarized Luminescence of Enantiopure Lanthanide Complexes at Variable Temperature

Annika Sickinger,^a François Riobé,^a Laure Guy,^a Bruno Baguenard,^b Amina Bensalah-Ledoux,^b Stephan Guy,^b and Olivier Maury.^a

a) Laboratoire de Chimie, ENS de Lyon, 46 allée d'Italie 69364 Lyon Cedex 07, France.

b) Institut Lumière Matière, 10 rue Ada Byron, 69622 Villeurbanne Cedex, France.

annika.sickinger@ens-lyon.fr, www.ens-lyon.fr/CHIMIE

Rooted on the fundamental principle of chirality, circularly polarized luminescence (CPL) has become a well-researched phenomenon, observable as emission of light with one preferential sense of circular polarization.¹ As the corresponding luminescence dissymmetry is favored by allowed magnetic and suppressed electric dipole transitions, promising materials for CPL applications were found in lanthanide-based coordination complexes which meet these criteria.^{2,3} The molecular and hence the electronic structure of such metalorganic systems are strongly interrelated with the respective optical and magnetic features. Consequently, luminescence and absorption measurements allow profound insight into electronic structure and crystal field splitting of the complex. The appearance of CPL or circular dichroism (CD) introduces additional selection rules for the transitions between energetic ground and excited states, thereby improving the discrimination of each contribution in the obtained spectra.

In view of this, we present the preparation of enantiopure Ln(III) complexes (Ln = e.g. Nd, Yb, Er) with tridentate ligands, which emit CPL in the near infra-red (NIR) wavelength region. However, the 4f transitions in isolated Ln(III) ions are symmetry-forbidden and therefore weak in intensity. Thus, the

design of the chelidamic acid based ligands not only considers the chirality aspect, but also needs to ensure efficient sensitization of the lanthanide.⁴ The ligands wrap around the Ln(III) ions upon complexation in a preferred sense, governed by their stereochemistry, and induce either Λ - or Δ -type helical chirality. The optical properties of both complex enantiomers are

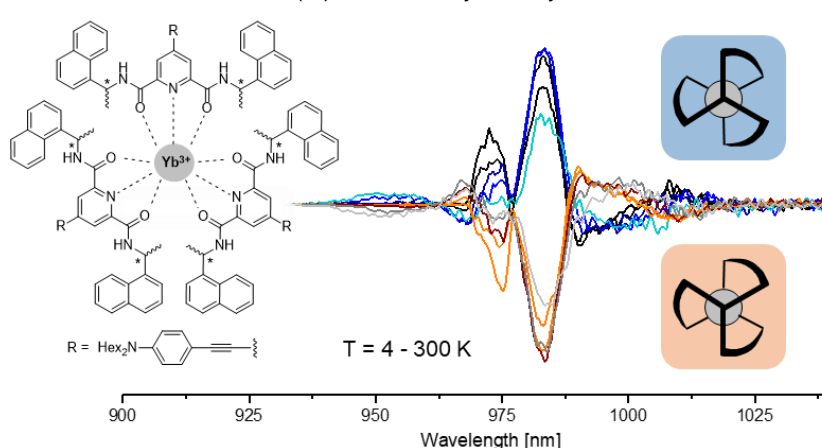


Figure: Structure of Yb(III) complexes studied with their NIR-CPL spectra.

thoroughly investigated by absorption and luminescence studies, including CD and CPL measurements. By means of a self-constructed setup, NIR-CPL at variable temperature can be monitored. Thereby, the limitations of previous studies on comparable Yb(III) complexes are overcome: these revealed significant NIR-CPL at ambient temperature, but the superposition of various energetic contributions impeded the identification of individual transitions.^{5,6} By combination of the required low-temperatures measurements with magnetic studies and ab initio calculations, a detailed characterization of the electronic structure and the crystal field splitting in chiral lanthanide complexes is envisaged.

REFERENCES: 1) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986**, *86*, 1. 2) Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048. 3) Zinna, F.; Di Bari, L. *Chirality* **2015**, *27*, 1. 4) Bünzli, J.-C. G. *Coord. Chem. Rev.* **2015**, *293*, 19. 5) Gunnlaugsson, T. et al. *J. Am. Chem. Soc.* **2007**, *129*, 10986. 6) Gendron, F.; Di Pietro, S. et al. *Inorg. Chem. Front.* **2021**, *8*, 914.

KEYWORDS: Circularly Polarized Luminescence, Lanthanide Complexes, Helicoidal Chirality