Modeling chiroptical phenomena in lanthanide complexes: from Circularly Polarized Luminescence to Magneto-Chiral Dichroism

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Lanthanide complexes display remarkable optical and magnetic properties arising from the inner-shell character of their 4f orbitals. When chirality is introduced, these features give rise to a range of chiroptical effects with potential applications in sensing [1], anti-counterfeiting [2], and photonic devices [3]. Among them, Circularly Polarized Luminescence (CPL) and Magneto-Chiral Dichroism (MChD) emerge as complementary spectroscopic techniques to probe electronic structure, chirality, and magnetism.

CPL corresponds to the differential emission of left- and right-circularly polarized light by a chiral luminescent system (see Fig. 1a), whereas MChD manifests as a differential absorption of unpolarized light by a chiral system under magnetization (see Fig. 1b [4]). Although quantum chemistry has played a crucial role in understanding the ground-state electronic structure of lanthanide complexes, modeling their luminescence properties remains a major challenge: quantitative agreement with experiment is still lacking for CPL, and theoretical treatments of MChD are still at a preliminary stage.

In this work, we employ advanced wavefunction-based quantum chemistry methods (CASSCF/PT2, SISO) to compute the electronic properties underlying CPL and MChD in chiral lanthanide complexes, and simulate the corresponding spectra using an in-house post-processing code [5]. Comparison with experimental data enables us to evaluate the accuracy of current approaches and to establish a computational protocol tailored to the description of chiroptical properties in lanthanide systems.

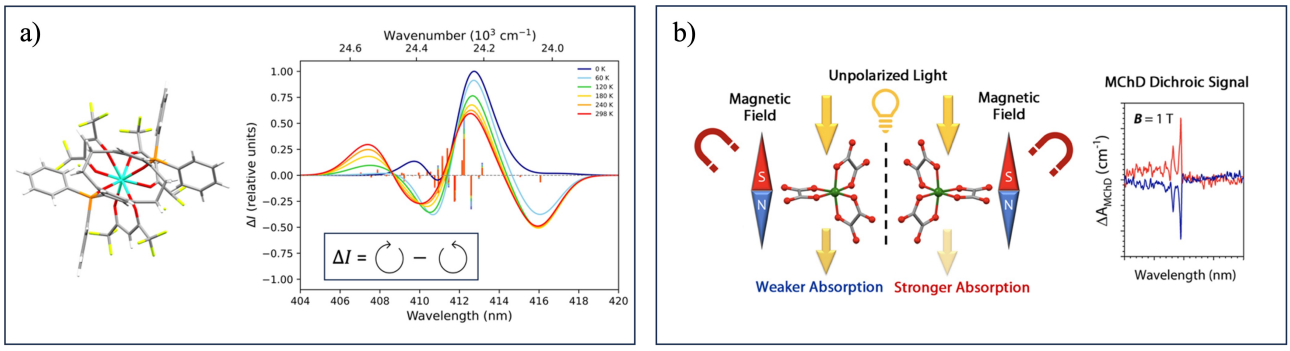

Figure 1: Chiral lanthanide complex (left) and associated simulated CPL spectrum (right). b) Schematic representation of the conditions needed to observe a MChD signal on a chiral molecule (left) and generic MChD dichroic signal (right) [4]

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