

# Circularly Polarized Luminescence of Enantiopure Lanthanide Complexes at Variable Temperature

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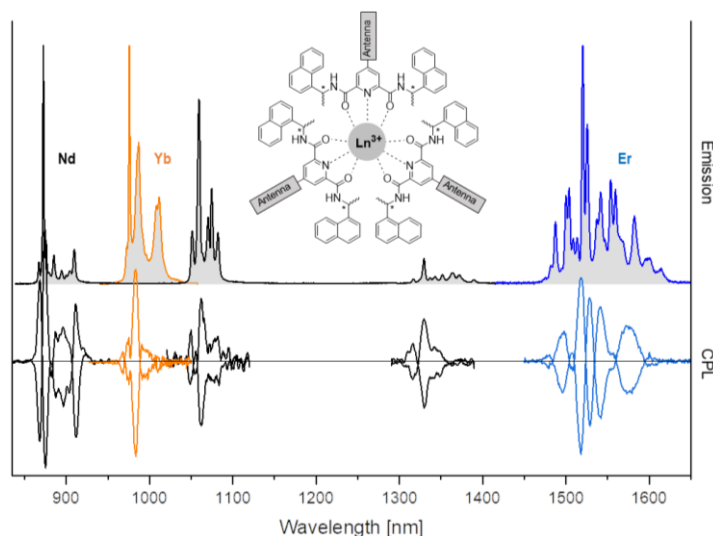
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Rooted on the fundamental principle of chirality, circularly polarized luminescence (CPL) has become a well-researched phenomenon, observable as emission of light with one preferential sense of circular polarization.<sup>1</sup> As the corresponding luminescence dissymmetry is favored by allowed magnetic and suppressed electric dipole transitions, promising materials for CPL applications are found in lanthanide-based coordination complexes which meet these criteria.<sup>2,3</sup> The molecular and hence the electronic structure of such metalorganic systems are strongly interrelated with the respective optical and magnetic properties. As a consequence, 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 energetic contribution in the obtained spectra.

Generally, the 4f transitions in isolated Ln(III) ions are forbidden by symmetry rules and therefore weak in intensity. Thus, the presence of a coordinating sphere of suitable ligands is required to both induce chirality and to ensure efficient sensitization of the lanthanide.<sup>4</sup> In view of this, enantiopure tridentate ligands with



**Figure:** Structure of the investigated complexes (Ln = Nd, Yb, Er) and their emission and circularly polarized luminescence.

different conjugated antenna attached to the chelidamic acid structure motif were synthesized. Governed by their stereochemistry, these wrap around the Ln(III) ions in a preferred sense during complexation and thereby induce either  $\Lambda$ - or  $\Delta$ -type helical chirality. The resulting enantiomeric pairs of 9-coordinated Ln(III) complexes (Ln = e.g. Nd, Yb, Er) emit CPL in the near infrared (NIR) wavelength region. Their optical and chiroptical properties are thoroughly investigated by absorption- and luminescence-based spectroscopic techniques, including CD and CPL studies. In addition to the characterization of solutions or solid samples, a procedure was elaborated to immobilize complexes in polymer matrices in a random, but fixed orientation, comparable to organic glasses. By means of a self-constructed setup, NIR-CPL at low temperature (4 K) can be monitored for these specimen. This allows the identification of individual energetic transitions and overcomes the limitations of previous NIR-CPL data acquired at ambient temperature, restricted by the superposition of various contributions in the spectra.<sup>5,6</sup> By combination of temperature-variable CPL measurements, linear optics and ab initio calculations, a detailed elucidation of the electronic structure and the crystal field splitting in chiral lanthanide complexes can be realized.

## REFERENCES:

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