Activity report for the research proposal "Magnetic circular dichroism measurements for complexes based on lanthanide ions and helicenes"

A research visit to the Miyasaka Laboratory within the ICC-IMR Fellowship for Young Scientists gave the opportunity to perform magnetic circular dichroism (MCD) measurements for complexes based on lanthanide ions and helicenes prepared in the Pinkowicz Group. MCD spectra were measured in the UV-Vis region in a series of magnetic fields and temperatures. Particularly interesting results were obtained for the erbium complex with azahelicene.

During a one-month research visit (2023.10.27-2023.12.02) to the Laboratory of Prof. Hitoshi Miyasaka, a series of lanthanide-based compounds were screened to find the best candidates for more detailed magnetic circular dichroism (MCD) measurements. The compounds for the study included a series of optically pure complexes with the smallest helicene - {Δ-[Ln(phendo)$_4$]}{Δ-[As(cat)$_3$]}$_2$(NO$_3$)·5MeCN Δ-Ln (Ln = Gd, Tb, Dy, Ho, Er, Yb; phendo = 1,10-phenanthroline-N,N'-dioxide; cat = catecholate dianion) as well as the (Λ, Λ) forms (**LnAsphendo**) and optically pure complexes with a larger helicene ligand - [Er(BHT)$_3$]$_2$((*M*/*P*)-azahelicene) (BHT = butylated hydroxytoluene anion; azahelicene = benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-k][1,10]phenanthroline) (**Er$_2$azahel**).

Each sample was ground to fine powder and mixed with Apiezon® grease. The thin layer of such a mixture was placed between two BaF_2 windows. All operations for **Er$_2$azahel** were carried out under an inert atmosphere, since erbium ions in this complex have an unsaturated coordination sphere and are prone to coordination of additional water or other solvent molecules. NCD (natural circular dichroism) and MCD spectra of BaF_2 windows with pure Apiezon® grease were also measured to exclude any signals from these components.

For one enantiomer of each complex (7 compounds in total), NCD (without magnetic field) and MCD (at +/- 1.5 T) were measured at 5 K. Complete MCD study was performed only for the most promising compounds (both enantiomers). The full MCD study included measurements of the field dependence of the spectrum at 5 K (from -1.5 T to +1.5 T), a more precise study of the field dependence of the MCD signals at certain wavelengths (in maxima) and the temperature dependence of the MCD spectra (5-300 K).

Among the **LnAsphendo** complexes, Er- and Dy-based compounds show MCD signals (at 519.5 nm and 314 nm, respectively). Unfortunately, the signals for both compounds are quite weak and visible only at very low temperature. On the other hand, the MCD spectrum for **Er$_2$azahel** shows really strong signals (maxima at: 376, 380, 517, 522 and 525 nm) that are visible up to room temperature. Fig. 1 shows the MCD spectra of the *M* enantiomer of **Er$_2$azahel**, extracted from the measured combination of NCD and MCD. The temperature dependence of the MCD signal is compared with the absorption spectra of unpolarized light for **Er$_2$azahel** and $ErCl_3$. Based on this comparison, one can say which erbium transitions are active in MCD ($^4I_{15/2} \rightarrow {}^4G_{11/2}$ and $^4I_{15/2} \rightarrow {}^2H_{11/2}$).

The results of these measurements will complete the full magneto-chiral characteristic of the obtained compounds: NCD, MCD and magneto-chiral dichroism (MChD). We already have preliminary results of MChD measurements from the collaboration with Dr. Matteo Atzori (LNCMI, CNRS, Grenoble, France).

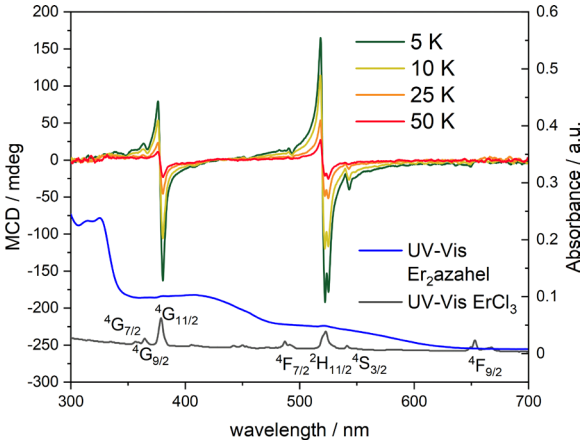

Fig. 1 Magnetic circular dichroism spectra of [Er(BHT)$_3$]$_2$((M)-(-)-azahelicene) compared with UV-Vis spectra of **Er$_2$azahel** and $ErCl_3$ salt.

Keywords: optical properties, magnetic properties, lanthanide
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