

**Experiment title:**

Hard X-ray magnetochiral dichroism in lanthanide based molecular helices with six fold symmetry

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HC-1810

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Three different helicoidal compounds of formula $[\text{Ln}(\text{Hnic})(\text{nic})_2(\text{NO}_3)]_n$, where Hnic is nicotinic acid and Ln = Tb, Dy, Er have been produced as single enantiopure chiral crystals (see Fig1 left). The single site anisotropy determined through capacitive torque magnetometry. All the systems reveal a pronounced spin non-collinearity with enhanced magnetic anisotropy of the Dy derivative (Fig. 1 right).

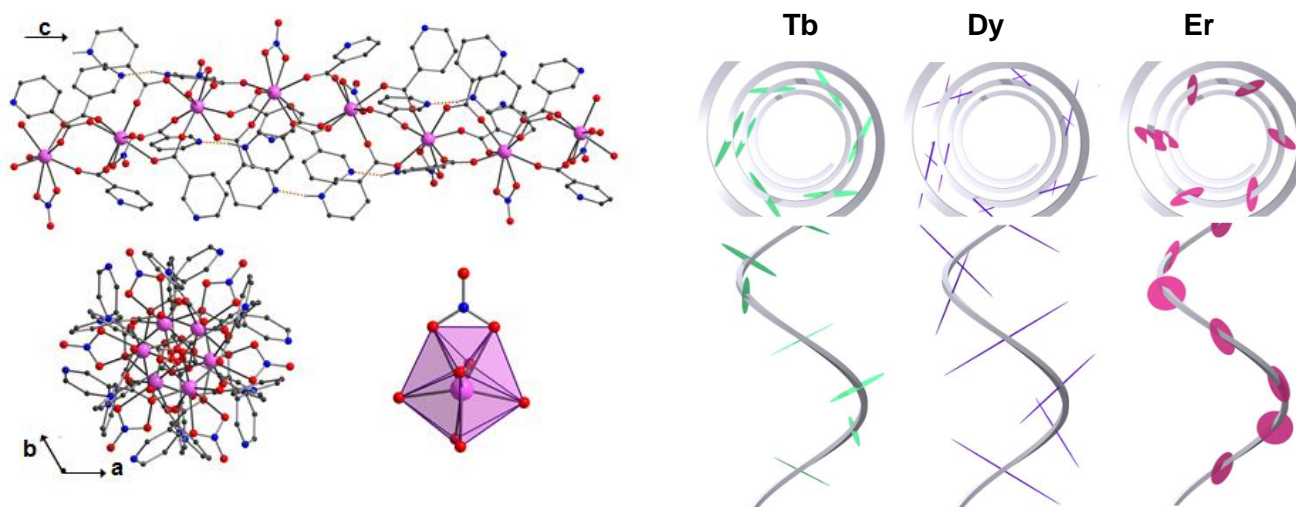


Figure 1. Left: Crystal structure of the investigated helicoidal compounds crystallizing in the chiral $P6_1/P6_5$ space groups. The Ln ions are shown in pink. Right: Schematic representation of the spin helicity obtained by plotting the susceptibility tensors (top: view along c , bottom: view along the ab plane). The susceptibility of the hard directions (x and y) of Dy has been multiplied by a factor of 5 to give a more solid aspect to the ellipsoids.

The compounds therefore exhibit the typical features of chirality, orbital contribution and spin non-collinearity that have characterized the Co-radical helices that have provided evidences of strong magneto-chiral dichroism.¹

We have concentrated the attention on the Dy derivatives, which appears to have the largest magnetic response and the largest magnetic anisotropy.

Two relatively large (ca. $2.5 \times 0.2 \times 0.2$ mm) enantiopure single crystals of opposite chirality (P61, Flack $\chi = -0,016(8)$; P65, Flack $\chi = -0.017(6)$) were selected for X-ray absorption experiments. The Dy L3-edge XANES and XNCD spectra were measured at room temperature and shown in Fig. 2. The isotropic contribution to the X-ray Absorption (XANES) is dominated by the characteristic intense peak due to transitions into 5d empty orbitals, the so-called “white line” with maximum at 7795 eV. Quadrupolar transitions into unoccupied 4f orbitals occur at about 5-10 eV lower in energies due to a strong interaction of the $2p_{3/2}$ hole and 4f electrons, which however can be hardly seen in isotropic XANES spectra dominated by the white line. A rather weak XNCD signal is observed at the Dy L3-edge, with opposite sign for the P6₁ and P6₅ enantiomeric crystals. The magnitude of the normalized XNCD signal is in the low 10^{-3} range. The relatively weak dichroism can reasonably be ascribed to the fact that *f* orbitals are strongly localized on the lanthanide ion, thus are scarcely influenced by a supramolecular chiral arrangement such as that of the nicotinate helix studied in this work. This is also confirmed by the very weak XNCD intensities at photon energies where electronic transitions to states with a strong 4f character is expected (ca. 7787 eV). On the other hand, quadrupolar transitions at the L3 edge to extended 6p states of rare-earth are also allowed by the selection rules, thus giving rise to a finite XNCD signal in a wide energy range up to 30 eV above the edge. These extended states are indeed strongly affected by the chiral arrangement of ligands. In this respect X-ray optical activity at the L3-edge of rare-earth in Dy helices strongly differs from previously investigated Co^{II} and Mn^{II} ones which revealed a large natural circular dichroism signal due to interference of $1s \rightarrow 3d$ quadrupolar and $1s \rightarrow 4p$ dipolar transitions.¹

Any attempts to detect the magnetochiral response resulted in a XM χ D signal below the detection limit. These findings suggest that, despite the fact that strong spin noncollinearity of lanthanide-based helices makes them strong candidates for the observation of magnetochiral effects, use of hard X-rays does not appear to be straightforward for such investigations, in contrast with what observed for transition metal molecular helices.

A publication has been produced reporting the outcome of this investigation.²

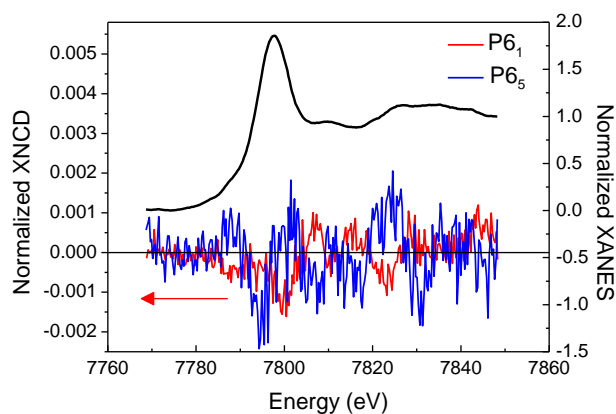


Figure 2. Near edge X-ray absorption spectrum (XANES) at the L3 edge of Dy measured at room temperature in zero field (black line) obtained as $1/2(\sigma + \sigma')$ and X-ray natural circular dichroism spectra given by $(\sigma - \sigma')$ for two enantiomeric crystals. σ and σ' denotes x-ray absorption cross section for right- and left- circularly polarized X-rays, respectively.

References

- 1 Sessoli, R., Boulon, M.-E., Caneschi, A., Mannini, M., Poggini, L., Wilhelm, F. & Rogalev, A. Strong magneto-chiral dichroism in a paramagnetic molecular helix observed by hard X-rays. *Nat Phys* 11, 69-74, (2015).
- 2 Mihalcea, I., Perfetti, M., Pineider, F., Tesi, L., Mereacre, V., Wilhelm, F., Rogalev, A., Anson, C. E., Powell, A. K. & Sessoli, R. Spin Helicity in Chiral Lanthanide Chains. *Inorg. Chem.* 55, 10068-10074, (2016).