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Supporting Information

Hard X-ray Magnetochiral Dichroism in a Paramagnetic Molecular 4f Complex

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Experimental

1 was synthesized from Ho_2O_3, oxydiacetic acid (H_2ODA), $NaHCO_3$ and $NaBF_4$ according to a previously reported protocol.[1]

After several recrystallizations, single crystals of **1Λ** and **1Δ** were obtained by slow evaporation of the aqueous solutions since upon crystallisation **1** undergoes spontaneous resolution. Small samples for the crystallographic analyses were cleaved from larger crystals that were used in X-ray absorption experiments. In the X-ray crystallographic studies single crystals of **1Λ** and **1Δ** were coated with mineral oil, placed on nylon loops, and mounted in the nitrogen cold stream of the diffractometer. The diffraction studies were performed at 120(2) K on a Bruker D8 VENTURE diffractometer equipped with a Mo *K*α high-brilliance I*μ*S radiation source (λ = 0.71073 Å), a multilayer X-ray mirror and a PHOTON 100 CMOS detector, and an Oxford Cryosystems low temperature device. The instrument was controlled with the APEX2 software package using SAINT.[2] Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the program SADABS.[3] The structures were solved in Olex2 using the olex2.solve program (Charge Flipping)[4] and refined using SHELXL.[5]

X-ray dichroism experiments at the Ho L_3-edge were carried out at the ID12 beamline of the European Synchrotron Radiation Facility (Grenoble, France), dedicated to polarization dependent X-ray spectroscopy in the 2–15 keV energy range.[6] For the experiments at the Ho L_3-edge, circularly polarized photons were generated by an HELIOS-II undulator. X-rays were monochromatized by a Si‹111› double crystal monochromator. The circular polarization rate of the monochromatic X-rays was about 0.92. The spectra were obtained using the total fluorescence yield detection mode in backscattering geometry, with the crystal trigonal c axis set parallel to incident X-ray beam. The experimental spectra were collected as a series of cyclically alternating polarisation of X-rays and magnetic field direction (**L+**/**L-**/**R-**/**R+**/**R-**/**R+**/**L+**/**L-**) where L and R stands for right and left circular polarization and +/- for parallel and antiparallel orientation of the magnetic field with respect to the X-ray wave vector. This sequence allows the effects of eventual drift of the X-ray beam and of radiation damage of the samples to be minimized in the final dichroic spectra. The spectra were then averaged and scaled using normalization of the absorption spectrum to unity at 8.12 keV, i.e. well above the absorption edge. Finally, the spectra were corrected for re-absorption effect using a standard procedure previously described.[7] For these experiments, the samples were mounted on the cold finger of a constant-flow helium cryostat inserted in the bore of a superconducting solenoid producing a magnetic field up to 17 T. The temperature of the samples was 2.7 K.

Table S1. Crystallographic data for **1Δ** and **1Λ**.

Compound	**1Δ**	**1Λ**
Empirical formula	$C_{12}H_{24}B_2F_8HoNa_5O_{21}$	
Moiety formula	$C_{12}H_{12}HoNa_3O_{15}$, 2 BF_4Na, 6 H_2O	
Formula weight	957.81	
Temperature / K	120(2)	
Crystal system	trigonal	
Space group	*R*32	
a / Å	9.5798(3)	9.5788(10)
b / Å	9.5798(3)	9.5788(10)
c / Å	27.9126(11)	27.884(3)
α / °	90	
β / °	90	
γ / °	120	
Volume / $Å^3$	2218.42(16)	2215.7(5)
Z	3	
ρ_{calc} / $g.cm^{-3}$	2.151	2.151
μ / mm^{-1}	2.89	2.89
F(000)	1404	1404
Crystal size / mm^3	0.52 × 0.46 × 0.17	0.36 × 0.21 × 0.16
Radiation	MoKα (λ = 0.71073 Å)	
2Θ range for data collection / °	2.561 to 30.502	2.561 to 30.495
Index ranges	-13 ≤ h ≤ 13 -13 ≤ k ≤ 13 -39 ≤ l ≤ 39	-13 ≤ h ≤ 13 -13 ≤ k ≤ 12 -39 ≤ l ≤ 39
Reflections collected	17645	23006
Independent reflections	1517 [R_{int} = 0.037, R_{sigma} = 0.021]	1522 [R_{int} = 0.039, R_{sigma} = 0.0208]
Data/restraints/parameters	1517/0/84	1522/0/84
[a] Goodness-of-fit on F^2	1.130	1.09
[a] Final R indexes [I>=2σ (I)]	R_1 = 0.0116, wR_2 = 0.0292	R_1 = 0.0125, wR_2 = 0.0280
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.67	0.35/-0.37
Flack parameter	0.015(4)	0.008(4)

[a] $I > 2\sigma(I)$, $R_1 = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. GoF (goodness of fit on F^2) = $\{\Sigma[w(F_o^2 - F_c^2)^2]/ (n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of refined parameters.

Crystallographic data (including structure factors) for **1Δ** and **1Λ** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1899691 for **1Δ** and 1899692 for **1Λ**). Copies of the data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

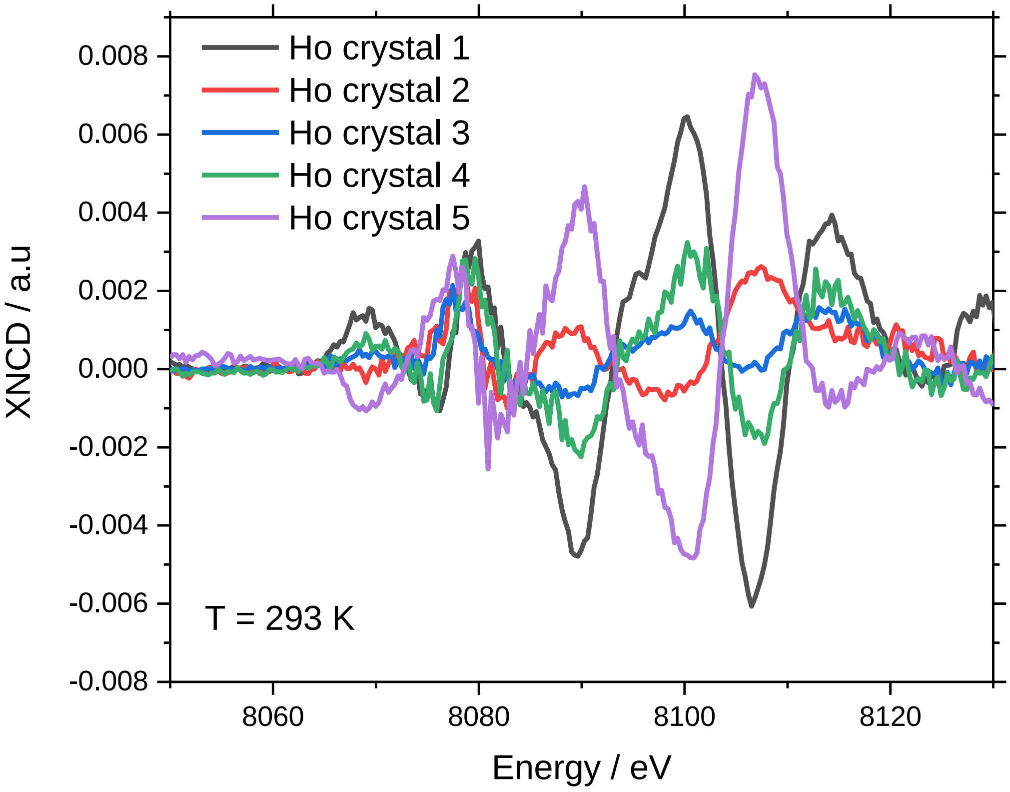

Figure S1. Room temperature, zero magnetic field, non-normalized XNCD spectra of several crystals of **1** recorded to identify a pair of enantiopure crystals with optimal XNCD response.

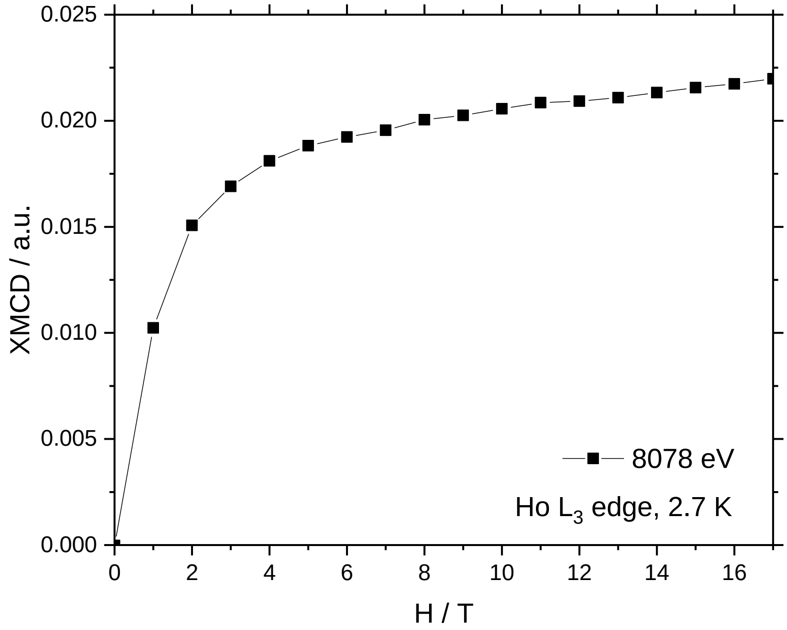

Figure S2. Field dependence of the XMCD maximum at the Ho L_3 edge for a single crystal of **1** oriented with the *c* axis parallel to the X-ray propagation vector, measured at 8078 eV and at T = 2.7 K.

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