ELECTRONIC SUPPLEMENTARY INFORMATION

Beyond anisotropy barrier: slow relaxation of the magnetization in both easy-axis and easy-plane Ln(trensal) complexes

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1 Synthesis

Powder microcrystalline samples of Er(trensal) and Dy(trensal) were obtained by the synthetic procedure reported in ref. (*1*). Yttrium diluted samples were obtained by adding the desired molar ratio of Y(trensal) and Er(trensal) or Dy(trensal) in MeOH, refluxing for 30 min and cooling at room temperature. After filtration under vacuum the solid was washed with MeOH and dried under nitrogen flux. The obtainment of the correct $P\bar{3}c1$ phase was checked by powder X-ray diffractograms (figure S1). All the patterns are superimposable to the one obtained from the crystallographic information file (.cif) of the solved molecular structure (Er derivative) (*2*).
Extremely diluted samples (0.5 %) were obtained for Dy derivative, but this did not result in any detectable change of the magnetic properties, except an increased signal-to-noise ratio due to the lower amount of material probed, so we chose the few percent dilution.

2 Experimental setup

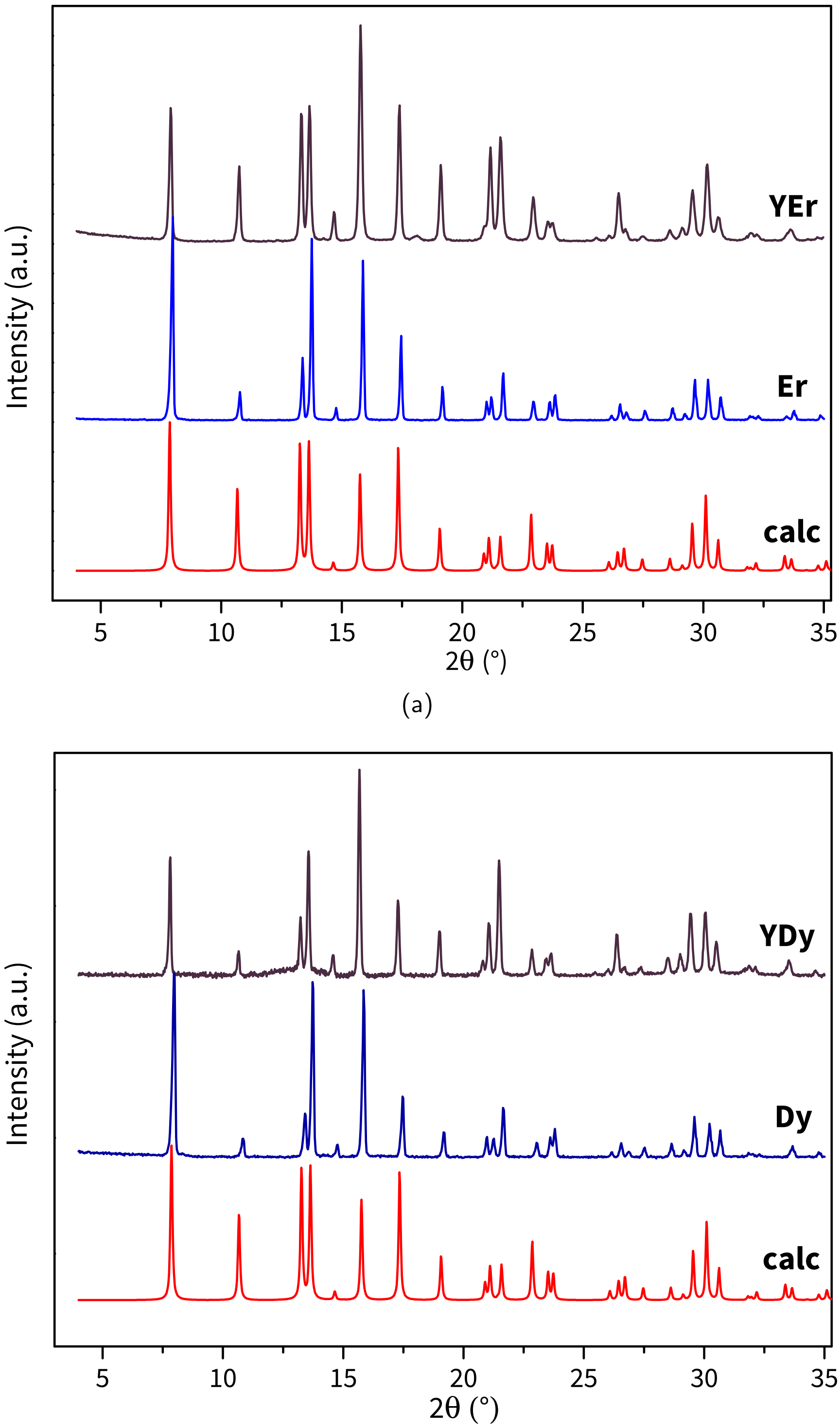
X-ray powder diffraction patterns of both pure and Y-diluted samples were measured with a Bruker D8 Advance powder diffractometer equipped with a Cu source (K_α, $\lambda = 1.54$ Å).
Dc magnetic measurements were performed by using a Quantum Design MPMS SQUID magnetometer on powders pressed in a pellet to avoid field induced orientation of the crystallites. The concentration of Dy and Er in Y diluted samples was estimated by treating the corresponding magnetic data as if the samples contained only Y and then comparing the residual room temperature χT with that of the pure sample from Curie law (14.17 emu K mol^{-1} for Dy and 11.48 emu K mol^{-1} for Er).
Ac susceptibility was measured using Quantum Design PPMS in *ac* mode for the frequency range $1\div10^4$ Hz. The Quantum Design MPMS SQUID magnetometer was used for low frequencies ($0.1\div10^3$ Hz).
EPR spectra were recorded at 5 K and 10 K with a E500 Bruker spectrometer for the X band ($\nu \sim 9.4$ GHz) and a E600 Bruker spectrometer for the W band ($\nu \sim 94$ GHz).

3 Computation

The CF hamiltonian for a C_3 point symmetry is:

$$\begin{aligned} V_c(C_3) = {} & B^2_0\mathbf{C}^2_0 + B^4_0\mathbf{C}^4_0 + B^4_3(\mathbf{C}^4_{-3} - \mathbf{C}^4_3) + \mathrm{i}B'^4_3(\mathbf{C}^4_{-3} + \mathbf{C}^4_3) + B^6_0\mathbf{C}^6_0 \\ & + B^6_3(\mathbf{C}^6_{-3} - \mathbf{C}^6_3) + \mathrm{i}B'^6_3(\mathbf{C}^6_{-3} + \mathbf{C}^6_3) + B^6_6(\mathbf{C}^6_{-6} + \mathbf{C}^6_6) + \mathrm{i}B'^6_6(\mathbf{C}^6_{-6} - \mathbf{C}^6_6) \end{aligned} \tag{1}$$

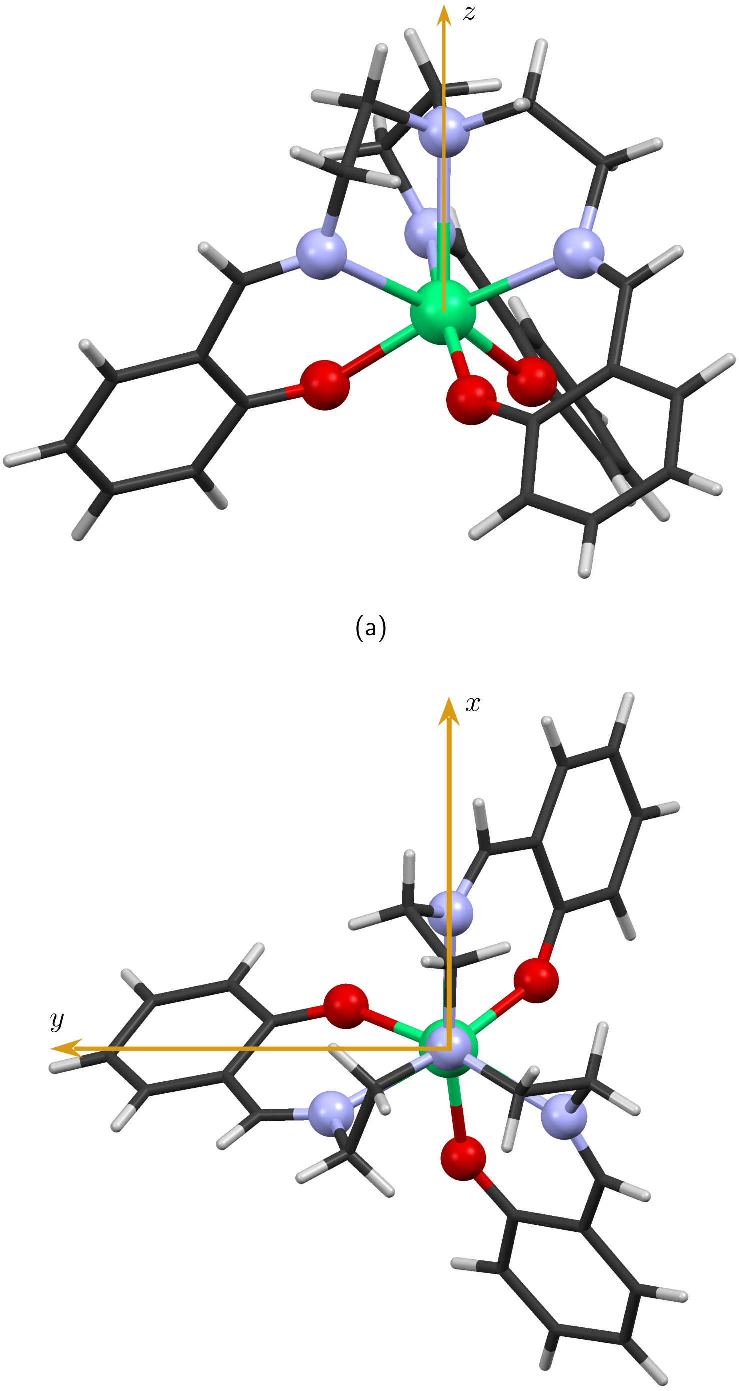
In this symmetry one can always choose an orientation of xy axes such that $B'^4_3 = 0$ so to minimize the number of CF parameters (see table S1). The energy levels, the wavefunction composition and the corresponding g_eff expected on the basis of the reported CF parameters (table S1) were calculated using a home-developed software which allowed to include the effect of mixing of the higher lying multiplets arising form the same spectroscopic term of the ground one. The composition of the ground multiplet of Dy(trensal) was calculated including $J = \frac{13}{2}$ and $J = \frac{11}{2}$ but no major effects were noticed on considering the two excited multiplets. On the contrary for Er(trensal) inclusion of excited multiplets ($J = \frac{13}{2}, \frac{11}{2}, \frac{9}{2}$) results in an increased admixing of $|JM_J\rangle$ components contributing to the ground state wavefunction.



(a)

(b)

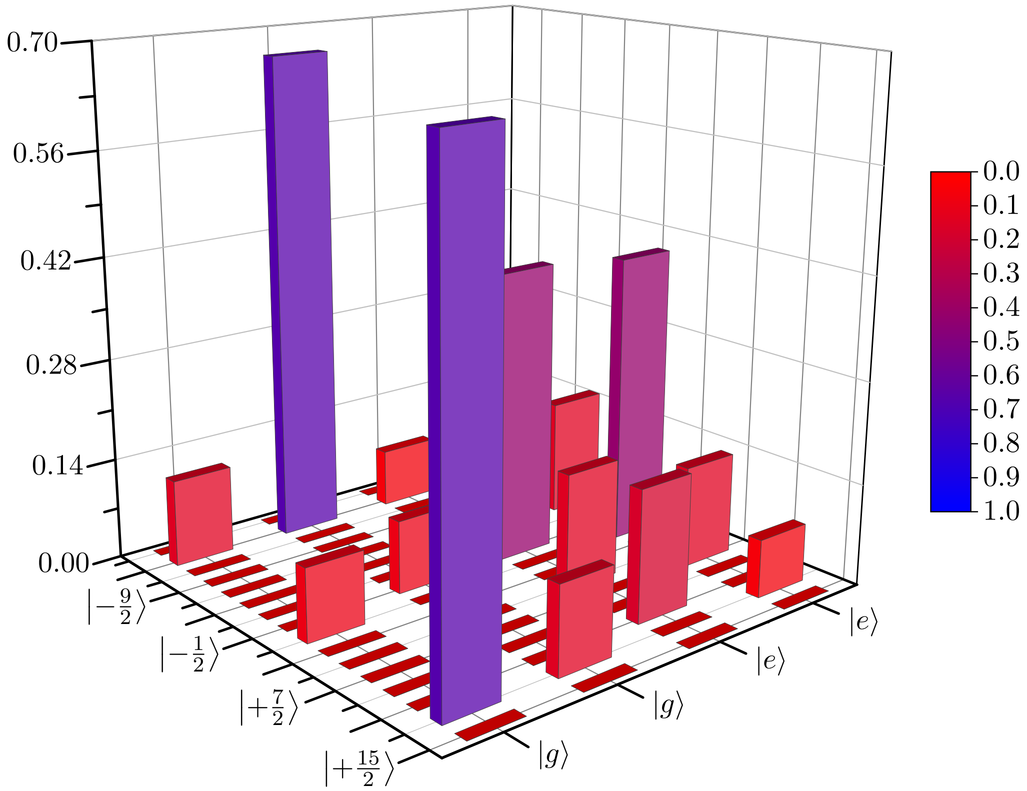
Figure S1: X-ray diffraction spectra of Er(trensal) and Dy(trensal) and of their Y-diluted samples. The red lines represent the calculated diffraction pattern for reported molecular structure (*2*).



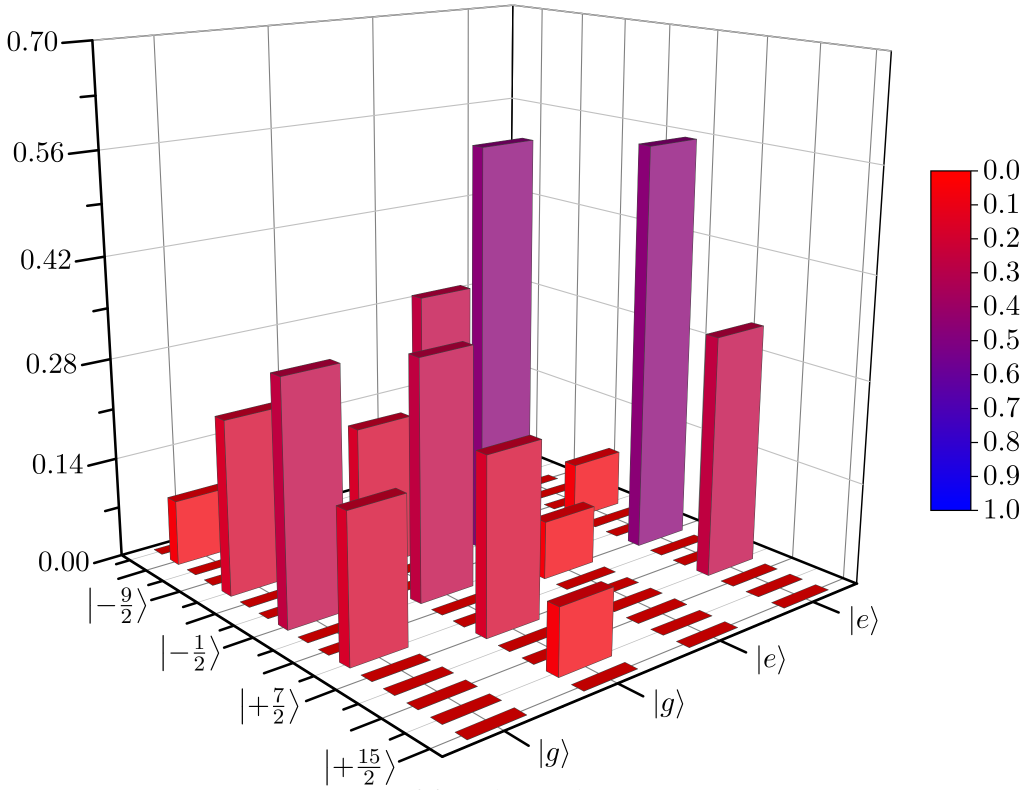
(a)

(b)

Figure S2: Molecular structure of Ln(trensal). The orientation of x and y axes is not defined *a priori* but it has been chosen in order to have a minimal set of CF parameters (*2*). The green colour identifies Ln, the red the oxygen, the light blue the nitrogen, the grey the carbon and the white the hydrogen.



(a) Er(trensal)



(b) Dy(trensal)

Figure S3: Composition of the ground doublet and of the first excited doublet for Er(trensal)(figure a) and Dy(trensal) (figure b). For clarity reasons contribution of M_J states less than 8 % are not included. More details can be found in tables S2 and S3.

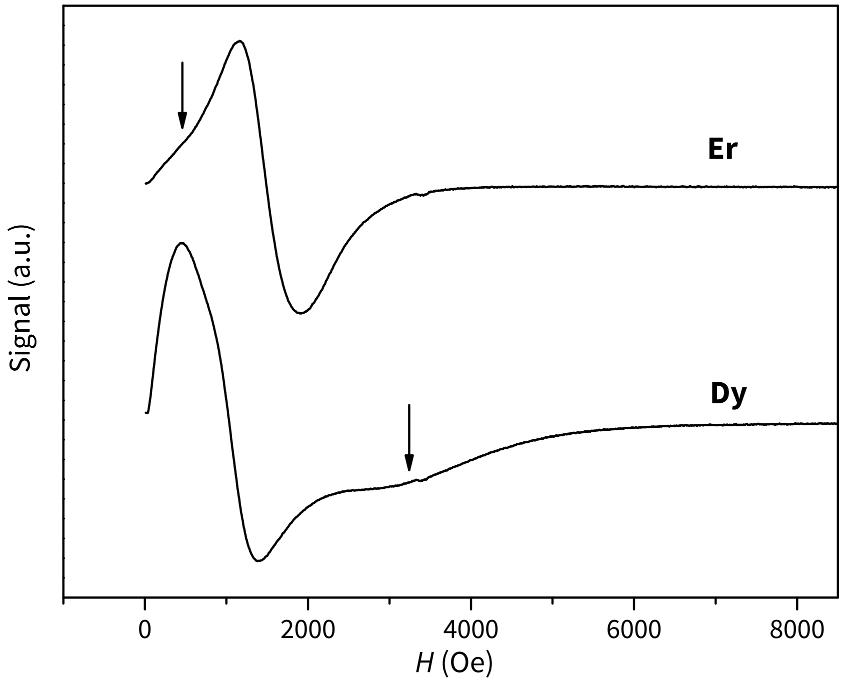


Figure S4: X band spectrum (9.4 GHz) of microcrystalline powder of Er(trensal) and Dy(trensal). The arrows evidence the parallel component of g_{eff} for the two compounds.

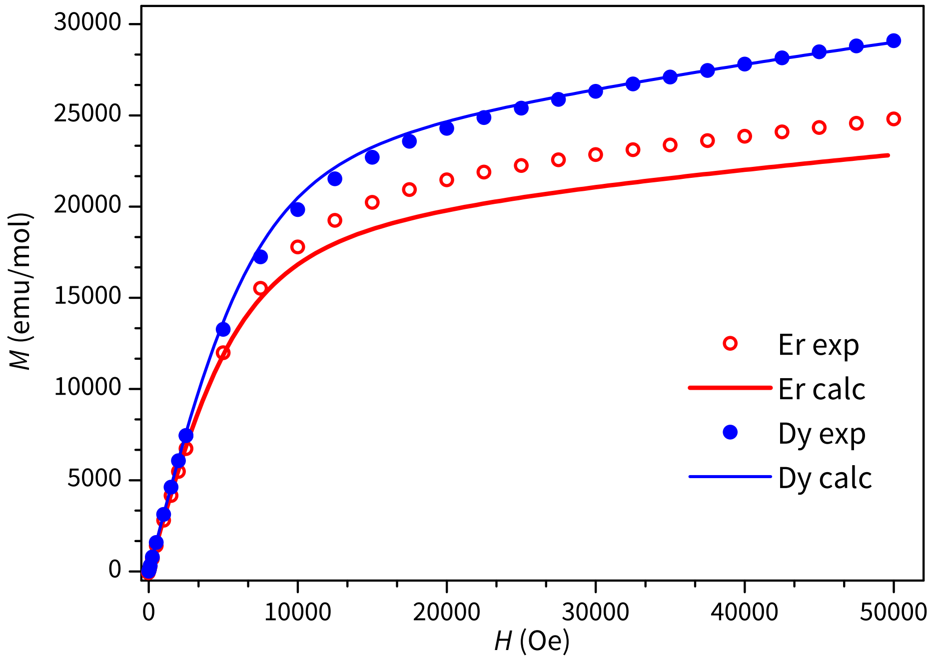
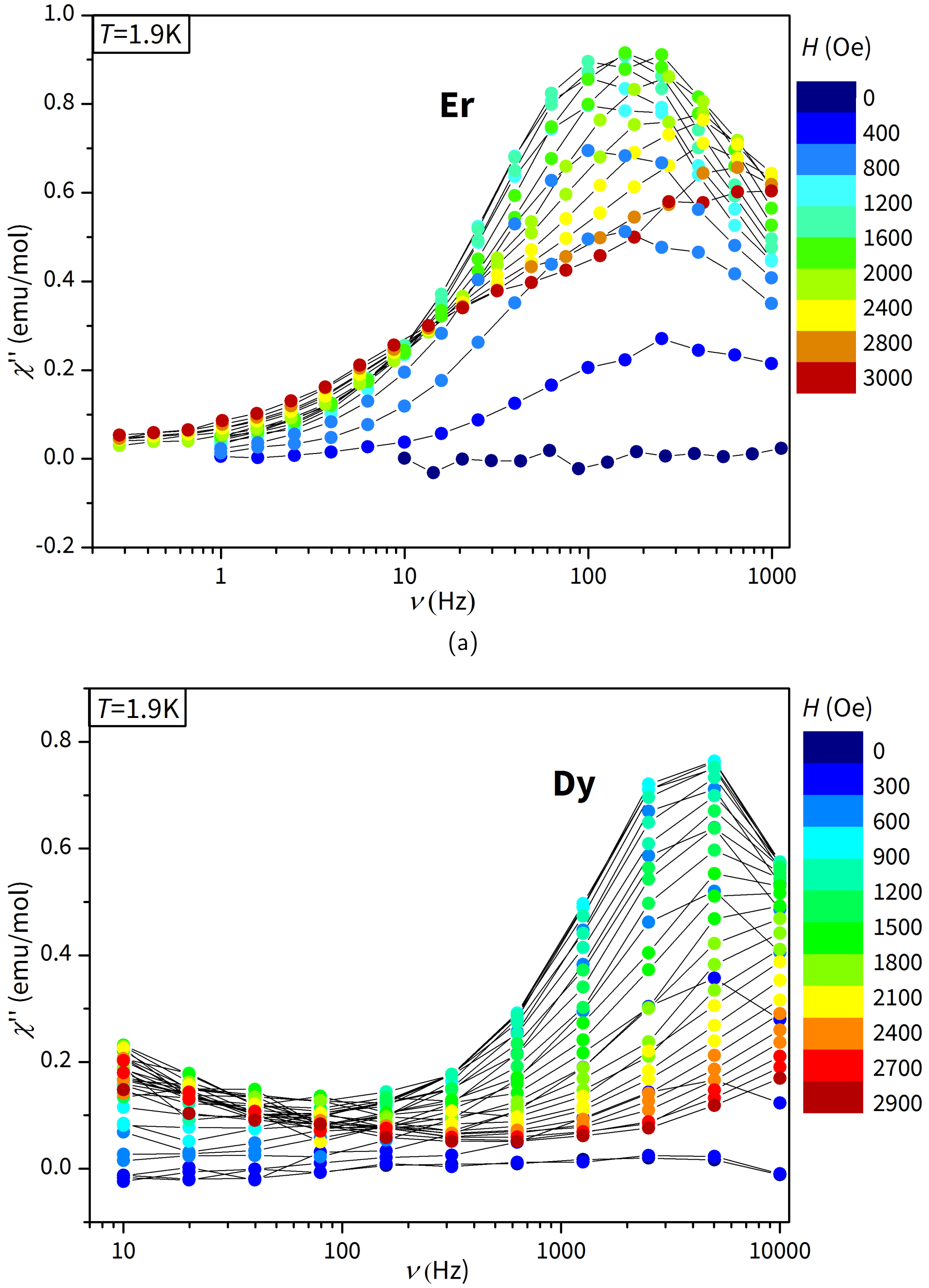


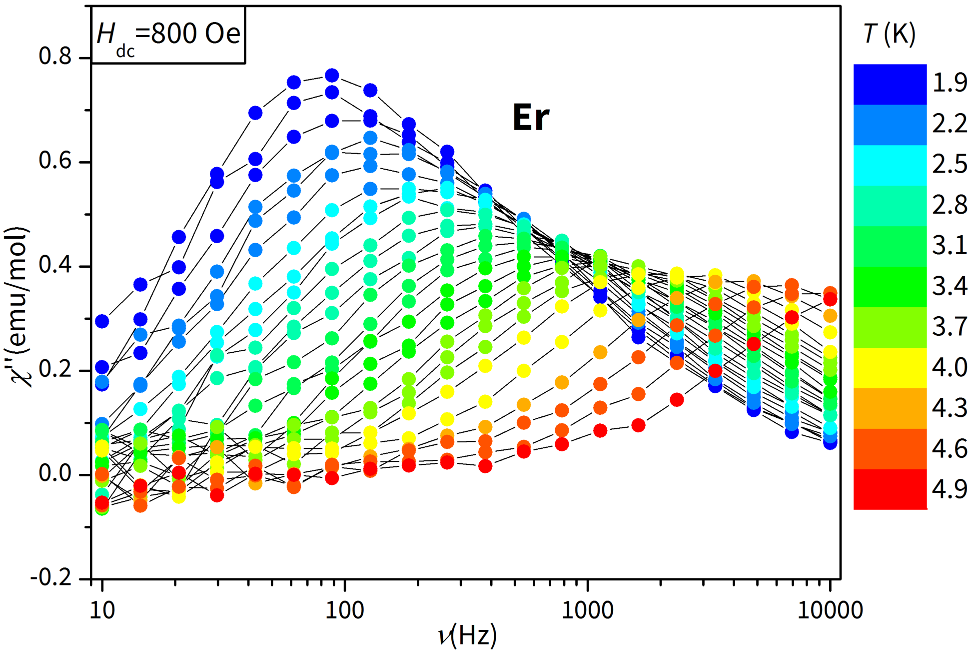
Figure S5: M vs H curves ($T = 1.9\,\mathrm{K}$): the circles represent the experimental data for Er(trensal) (empty) and for Dy(trensal) (full). The solid lines are the powder average magnetizations calculated using the CF parameters of reference (*2*) and a 55 points grid.



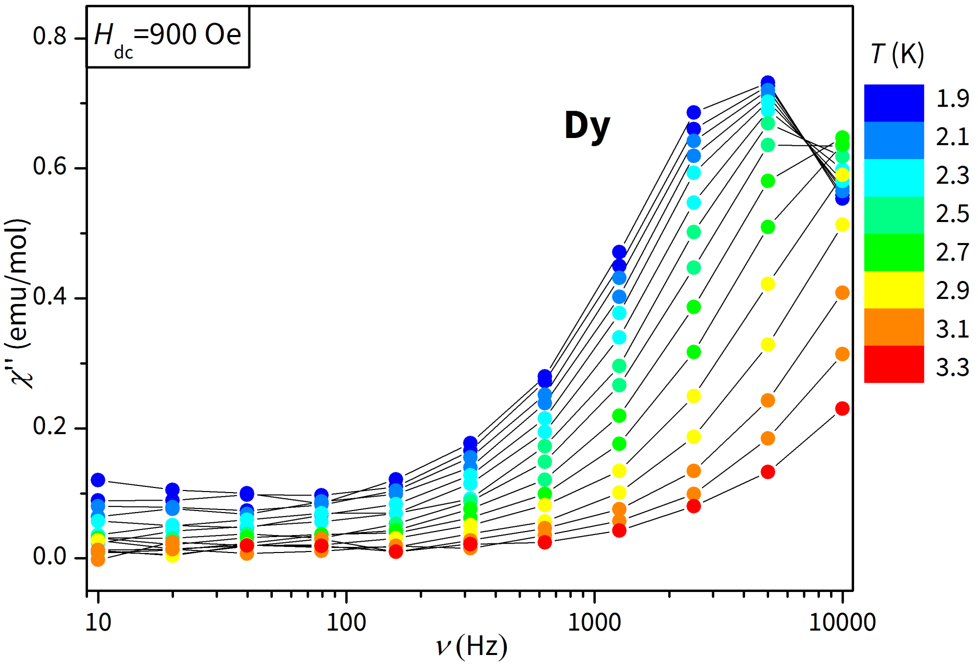
(a)

(b)

Figure S6: Imaginary susceptibility χ'' for different values of static *dc* field ($T = 1.9\,\mathrm{K}$).



(a)



(b)

Figure S7: Imaginary susceptibility χ'' for different values of temperature T at the indicated static field.

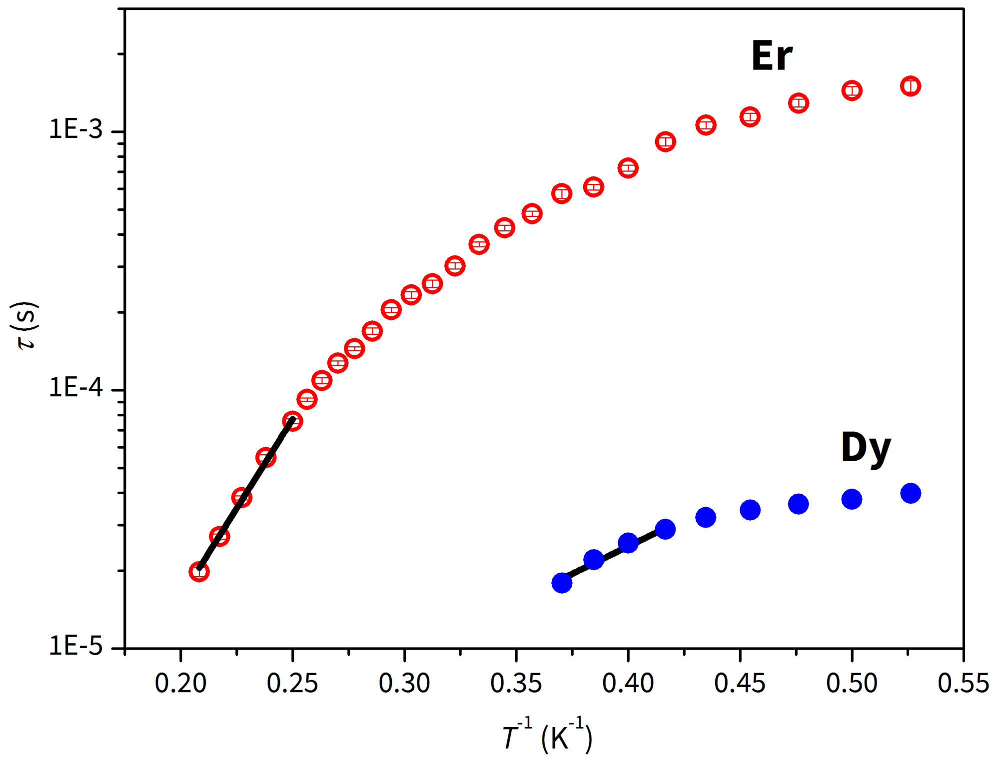
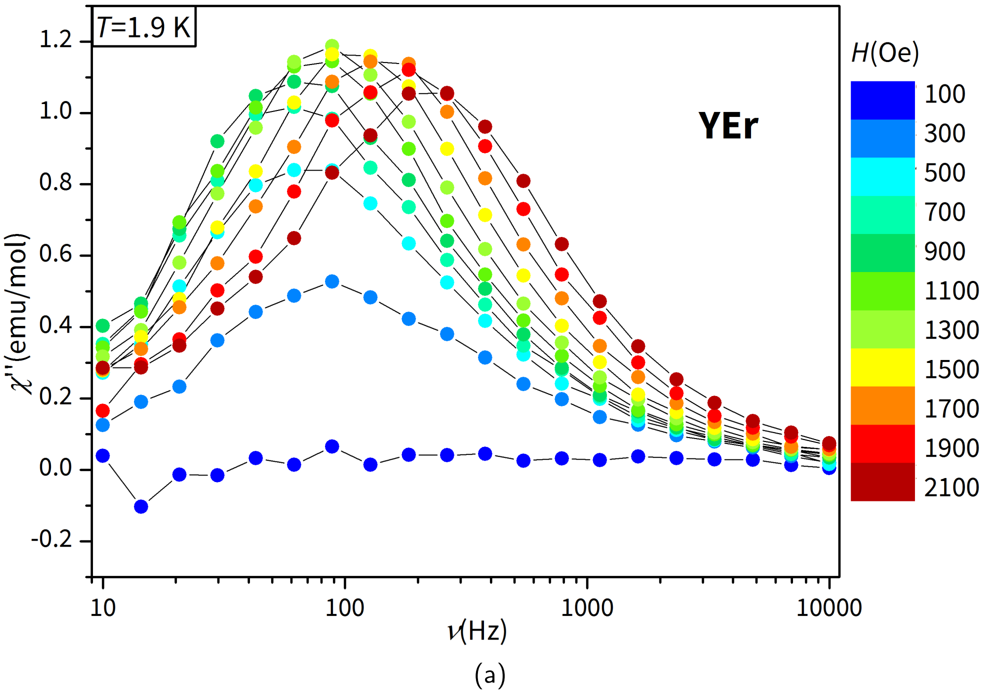


Figure S8: Arrhenius plot of temperature dependence of the relaxation rates of pure samples of Er(trensal) and Dy(trensal). Solid lines represent the best fit of the high temperature region using the Arrhenius formula $\tau = \tau_0 \mathrm{e}^{\Delta E/k_\mathrm{B}T}$ (see text for details).



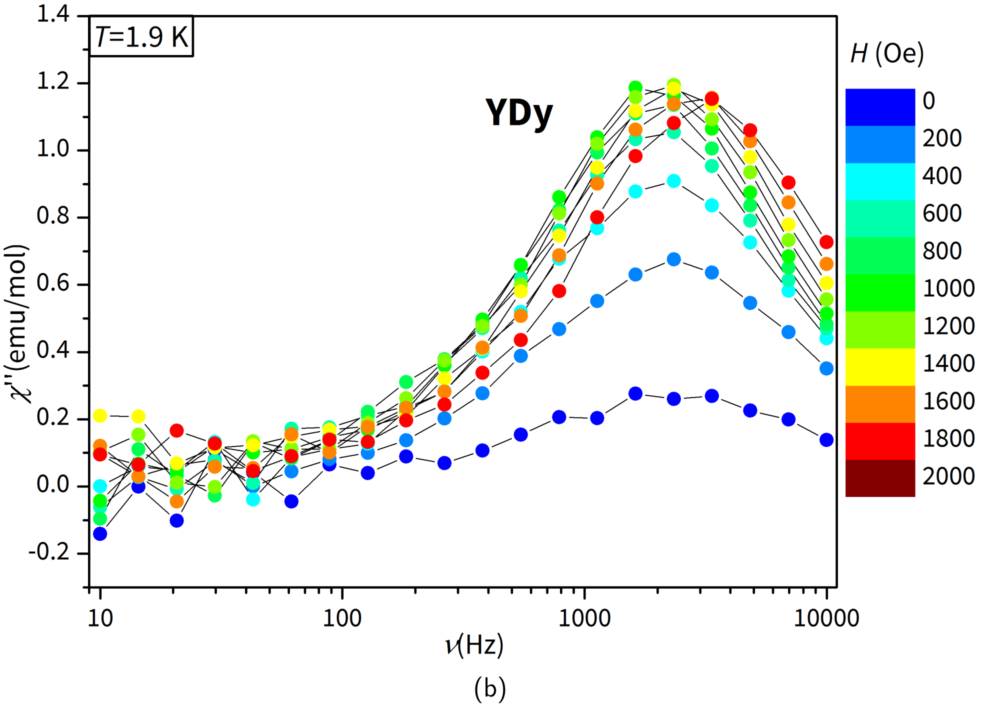


Figure S9: Imaginary susceptibility χ'' for Y-diluted samples at different values of static *dc* field. The dilutions are 5.8 % for Y:Er(trensal) and 3.1 % forY:Dy(trensal).

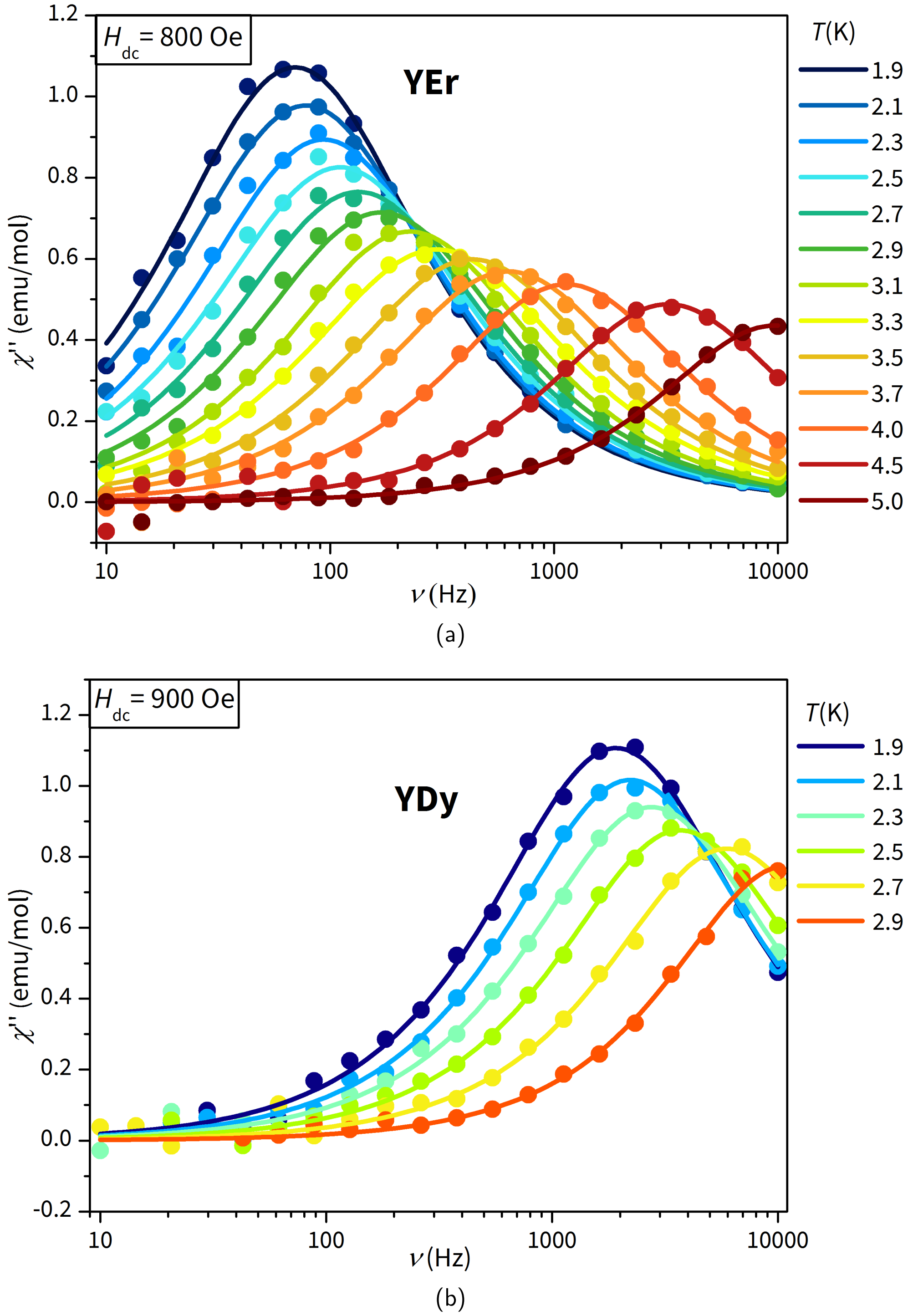


Figure S10: Imaginary susceptibility χ'' for Y-diluted samples at different values of temperature T. The solid lines are fits of the curves using the Debye formula (*3*).

Table S1: Crystal field parameters B^k_q for Dy(trensal) and Er(trensal). The values are expressed in cm^{-1} and the uncertainties are in brackets (*2*).

	Dy	Er
B^2_0	$-671(39)$	$-720(59)$
B^4_0	$-186(77)$	$-44(106)$
B^4_3	$-2153(34)$	$-2121(83)$
B'^4_3	0	0
B^6_0	1241(57)	988(36)
B^6_3	439(41)	353(49)
B'^6_3	$-284(83)$	92(53)
B^6_6	660(49)	545(34)
B'^6_6	145(137)	311(36)

Table S2: Composition of the ground doublet and of the first excited doublet for Er(trensal).

state	composition
ground state	$68.4\,\%\ \lvert\pm\frac{13}{2}\rangle$, $11.6\,\%\ \lvert\mp\frac{13}{2}\rangle$, $10.4\,\%\ \lvert\pm\frac{1}{2}\rangle$, $5\,\%\ \lvert\pm\frac{7}{2}\rangle$
1° excited state	$40\,\%\ \lvert\mp\frac{1}{2}\rangle$, $18\,\%\ \lvert\pm\frac{11}{2}\rangle$, $16\,\%\ \lvert\pm\frac{5}{2}\rangle$, $14\,\%\ \lvert\mp\frac{7}{2}\rangle$, $8\,\%\ \lvert\mp\frac{13}{2}\rangle$

Table S3: Composition of the ground doublet and of the first excited doublet for Dy(trensal).

state	composition
ground state	$33.1\,\%\ \lvert\mp\frac{1}{2}\rangle$, $24.3\,\%\ \lvert\mp\frac{7}{2}\rangle$, $20.2\,\%\ \lvert\pm\frac{5}{2}\rangle$, $8.7\,\%\ \lvert\mp\frac{13}{2}\rangle$, $5.3\,\%\ \lvert\mp\frac{11}{2}\rangle$
1° excited state	$56\,\%\ \lvert\mp\frac{3}{2}\rangle$, $33\,\%\ \lvert\mp\frac{9}{2}\rangle$, $8\,\%\ \lvert\pm\frac{3}{2}\rangle$

References

1. P. V Bernhardt *et al.*, *Australian Journal of Chemistry* **53**, 229–231 (2000).

2. B. M. Flanagan *et al.*, *Inorganic Chemistry* **41**, 5024–5033 (2002).

3. D. Gatteschi *et al.*, *Molecular Nanomagnets* (Oxford University Press, 2006).