CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Angular-Resolved Magnetometry Beyond Triclinic Crystals: Out-of-Equilibrium Studies of Cp*ErCOT Single-Molecule Magnet**

Marie-Emmanuelle Boulon,[a] Giuseppe Cucinotta,[a] Shan-Shan Liu,[b] Shang-Da Jiang,[b] Liviu Ungur,[c] Liviu F. Chibotaru,[c] Song Gao,[b] and Roberta Sessoli*[a]

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I/ Synthesis and crystallization method

The samples were prepared as described in [REF1]. NaCp* (Cp* = pentamethylcyclopentadiene anion) and COTErCl(thf)$_x$ (COT = cyclooctatetraene dianion) were mixed together in THF and left to stir for one day. The crude product was extracted by toluene and the resulting pink solution was stored into a freezer. Single crystals of size and quality sufficient for magnetometry were obtained after several days.

II/ Angular dependence of the magnetic susceptibility

All the rotations were performed on single crystal with an applied magnetic field H=1000Oe.
The two rotations were performed along the following directions (ω is the rotation axis**,** ***a***, ***b*** and ***c*** are the unit cell vectors):

- Temperature-dependence experiments

Rot1: along $\omega_1 = 0.614004\boldsymbol{a} - 0.340304\boldsymbol{b} + 0.712175\boldsymbol{c}$

Rot2: along $\omega_2 = 0.317728\boldsymbol{a} + 0.931653\boldsymbol{b} + 0.176271\boldsymbol{c}$

- Slow/fast experiments:

Rot2: along $\omega = 0.001728\boldsymbol{a} + 0.999571\boldsymbol{b} - 0.029253\boldsymbol{c}$

The curves of the rotation at 10 K were fitted according to the relation :

$$\chi = A\,[\cos^2(\delta + \theta) + \cos^2(\delta + \varphi + \theta)] \qquad \text{EQUATION S1}$$

The fitting procedure (Fig S1) provided a value of $A = 1.69 \pm 0.01$ emu mol^{-1} for the amplitude and a reciprocal angular displacement of $\varphi = 94.65° \pm 0.05°$.

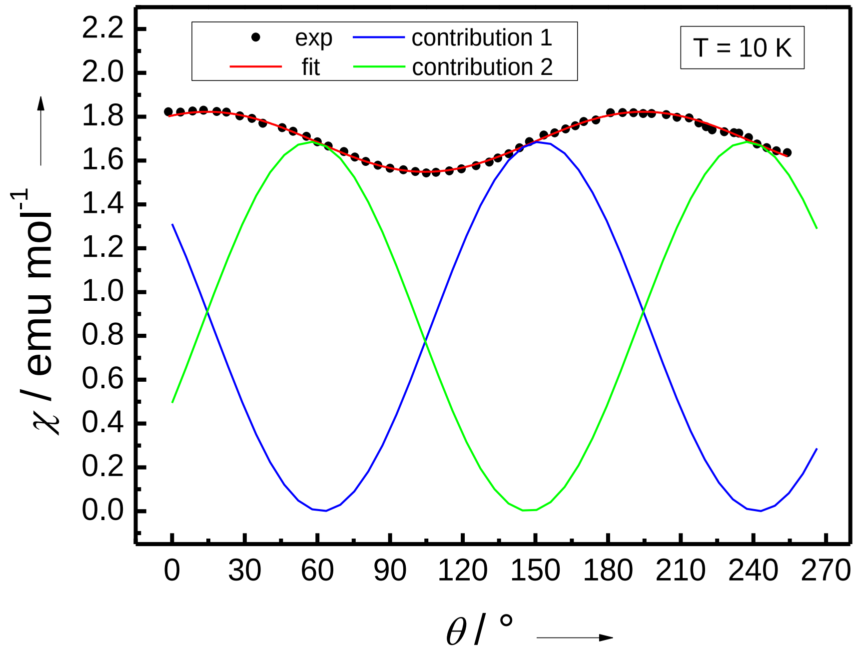

FIGURE S1: Angular dependence of magnetic susceptibility at T = 10 K and H = 1 kOe for the rotation **Rot2.** Red line is the result of the fit obtained considering the magnetic susceptibility measured as the sum of two contributions, represented by the blue and the green lines, according to EQUATION S1.

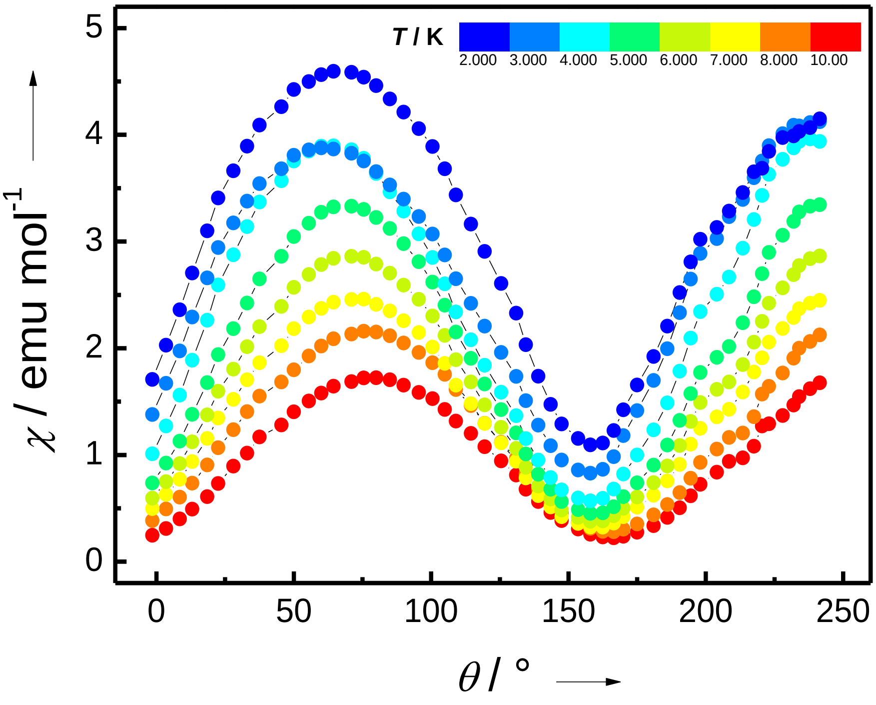

FIGURE S2: Angular dependence of magnetic susceptibility at H = 1 kOe for the rotations **Rot1** at different temperatures (color scale in the inset).

III/ Temperature dependence of the hysteretic behavior

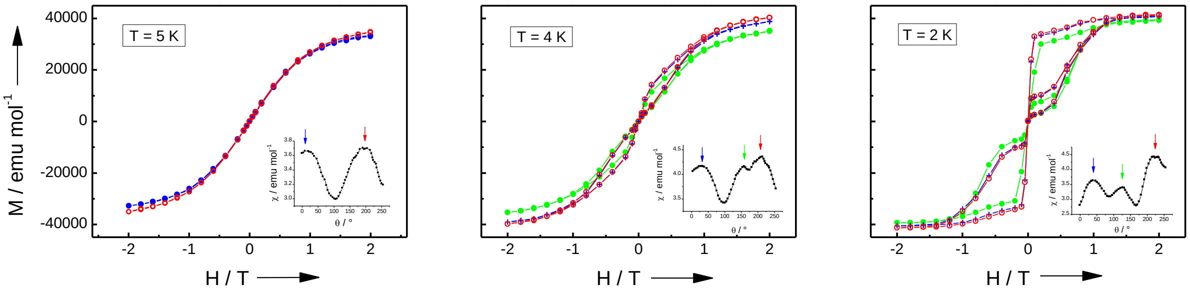

FIGURE S3: Hysteresis loops recorded at the three maxima of the rotation on a single crystal at 5, 4 and 2 K.

IV/ Time dependence study at 3.5 K

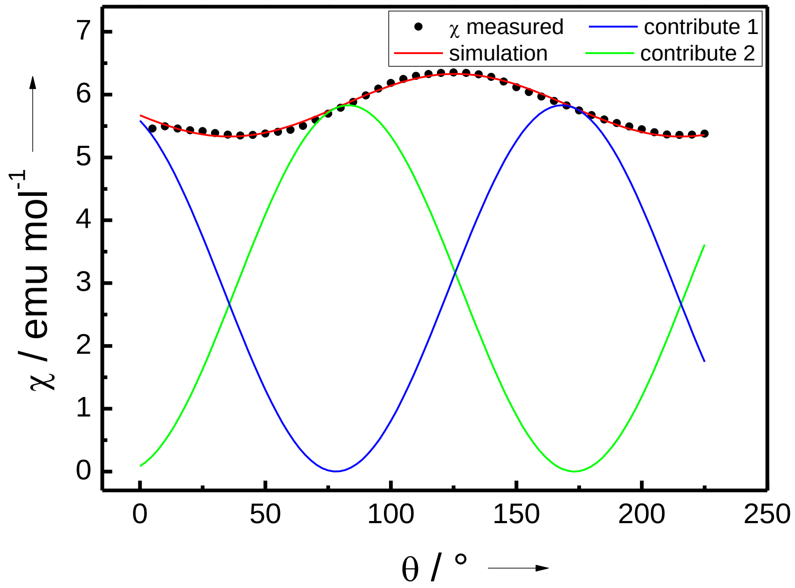

FIGURE S4: Angular dependence of the magnetic susceptibility at 3.5 K during a slow rotation **Rot2** (2300 s between each point, measured each 5°). Data were fitted by two square cosine functions with an amplitude of 5.831(6) emu·mol^{-1} and separated by an angle of 94.90(6)°.

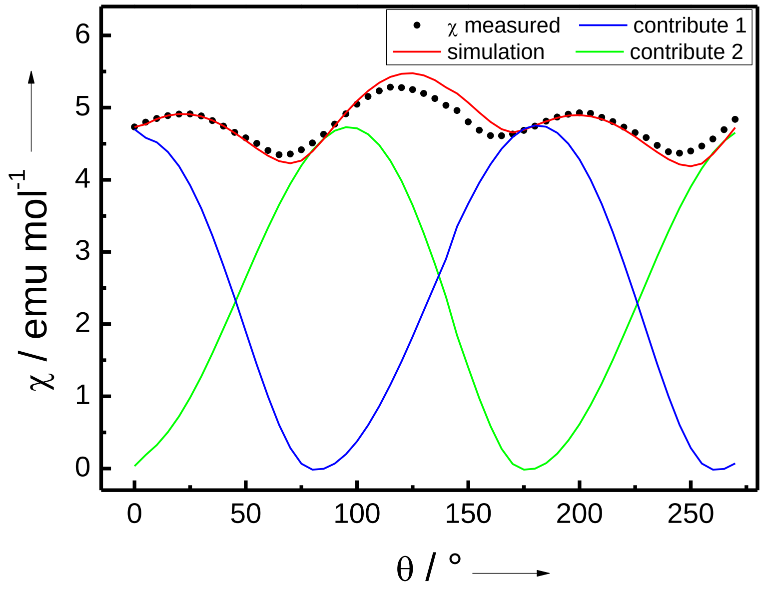

FIGURE S5: Angular dependence of the magnetic susceptibility at 3.5 K during a fast **Rot2** (50 s between each points, measured each 5°). Data were fitted following the procedure described in the article. The values obtained for the parameters are: τ_0 = 55(1) s; A_{incr} = 0.37 Oe^{-1} and A_{dec} = 0.35 s Oe^{-1}.

V/ Ab-initio calculations

1. Computational details

All calculations have been performed with MOLCAS 7.8 program package and were of CASSCF / RASSI / SINGLE_ANISO type.

The following contractions of the basis set were employed: Er [8s7p5d4f2g1h]; C [4s3p2d1f]; H [2s1p].

Active space of the CASSCF method included 11 electrons spanning 7 orbitals of Er^{3+} ion.

The number of roots mixed by spin-orbit coupling within RASSI program was the maximum available for the chosen active space (35 quartet spin states and 112 doublet spin states), giving rise to 364 spin-orbital states.

Optimization of the structure of the molecule was started from the experimental structure of the conformer 1 or of the conformer 2 leading to almost identical optimized structures. Optimization was done employing Split-Valence Basis Sets at B3LYP level of DFT theory using ORCA [2] software.

2. Electronic and magnetic properties of the [Cp*ErCOT] complex (experimental structure at 120K) – CASSCF / RASSI

TABLE S1: Energies of the lowest spin-orbit states (cm^{-1}).

experimental structure at 120 K		DFT optimized structure	
conformer 1	conformer 2	starting from 1	starting from 2
0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0
84.8	115.9	134.9	135.2
84.8	115.9	134.9	135.2
104.7	130.0	143.9	143.7
104.7	130.0	143.9	143.7
120.4	149.3	151.4	151.3
120.4	149.3	151.4	151.3
135.0	161.2	161.0	160.7
135.0	161.2	161.0	160.7
164.9	195.9	179.5	179.6
164.9	195.9	179.5	179.6
190.2	212.4	213.9	214.4
190.2	212.4	213.9	214.4
276.0	308.0	235.2	234.6
276.0	308.0	235.2	234.6
6605.0	6602.5	6610.7	6610.7
6605.0	6602.5	6610.7	6610.7
6664.8	6682.4	6698.9	6698.8
6664.8	6682.4	6698.9	6698.8
6673.2	6695.5	6702.1	6702.1
6673.2	6695.5	6702.1	6702.1
6680.6	6704.2	6707.7	6707.6
6680.6	6704.2	6707.7	6707.6
6692.3	6725.6	6723.9	6723.8
6692.3	6725.6	6723.9	6723.8
6708.6	6731.4	6733.3	6733.7
6708.6	6731.4	6733.3	6733.7
6767.7	6798.2	6751.6	6751.3
6767.7	6798.2	6751.6	6751.3
10648.6	10650.1	10661.6	10661.7
10648.6	10650.1	10661.6	10661.7
…	…	…	…

TABLE S2: Energies (cm^{-1}) and g tensors of the lowest Kramers doublets (KD).

KD		experimental structure at 120 K				DFT optimized structure			
		conformer 1		conformer 2		starting from conformer 1		starting from conformer 2	
		E	g	E	g	E	g	E	g
1	g_X	0.0	0.00062	0.0	0.00057	0.0	0.00000	0.000	0.00002
	g_Y		0.00086		0.00085		0.00005		0.00002
	g_Z		17.94713		17.93937		17.94526		17.94461
2	g_X	84.8	2.1888	115.9	0.4202	134.9	0.1587	135.2	0.2346
	g_Y		6.0126		2.8501		4.0137		3.0216
	g_Z		10.8041		10.7079		11.6236		11.9501
3	g_X	104.7	8.1455	130.0	5.4599	143.9	6.4365	143.7	4.2379
	g_Y		5.3451		4.8482		6.3418		5.5728
	g_Z		0.6657		3.0324		4.4060		7.1355
4	g_X	120.4	0.7729	149.3	2.2535	151.4	3.7652	151.3	1.8247
	g_Y		3.4796		3.4207		2.9409		2.3503
	g_Z		7.0917		10.4973		1.4190		4.0264
5	g_X	135.0	0.2360	161.2	3.3915	161.0	9.6056	160.7	9.0719
	g_Y		2.9907		3.5066		8.4962		8.9326
	g_Z		7.4113		7.9879		0.3891		0.3695
6	g_X	164.9	0.7861	195.9	0.5828	179.5	0.1122	179.6	0.0125
	g_Y		1.9624		1.1950		0.3106		0.4459
	g_Z		14.5523		12.2438		9.9586		9.9112
7	g_X	190.2	0.4164	212.4	0.0794	213.9	0.1424	214.4	0.1385
	g_Y		0.4621		0.1356		0.1481		0.1476
	g_Z		13.0058		10.9427		15.3565		15.3719
8	g_X	276.0	0.0180	308.0	0.0023	235.2	0.1008	234.6	0.1084
	g_Y		0.0321		0.0091		0.1252		0.1380
	g_Z		16.6221		16.7342		15.4457		15.3491

TABLES S3: Directional cosines of the main anisotropy axis in the ground doublet state of the Er^{3+} ion with respect to the crystallographic axes. The ± sign refers to the two symmetry-related families of molecules.

	a	b	c
Conformer 1	±0.663443	0.000000	0.748225
Conformer 2	±0.660586	-0.000000	0.750749
*Optimized structure 1**	±0.679138	-0.000000	0.734010
*Optimized structure 2***	±0.682031	-0.000024	0.731322

* -- optimization started from the experimental structure of the conformer 1

** -- optimization started from the experimental structure of the conformer 2

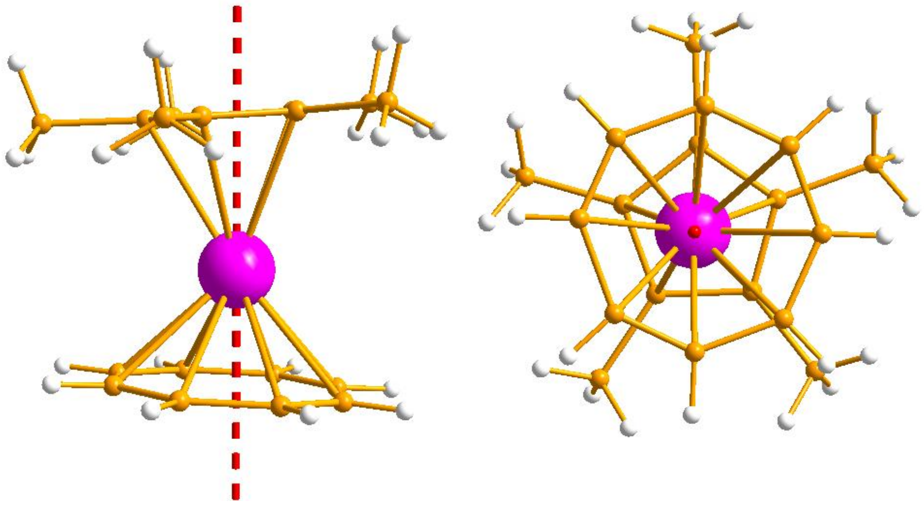

FIGURE S6: Orientation of the main anisotropy axis in the ground Kramers doublet of [Cp*ErCOT]. Color Scheme: Er, purple; C, yellow; H, white.

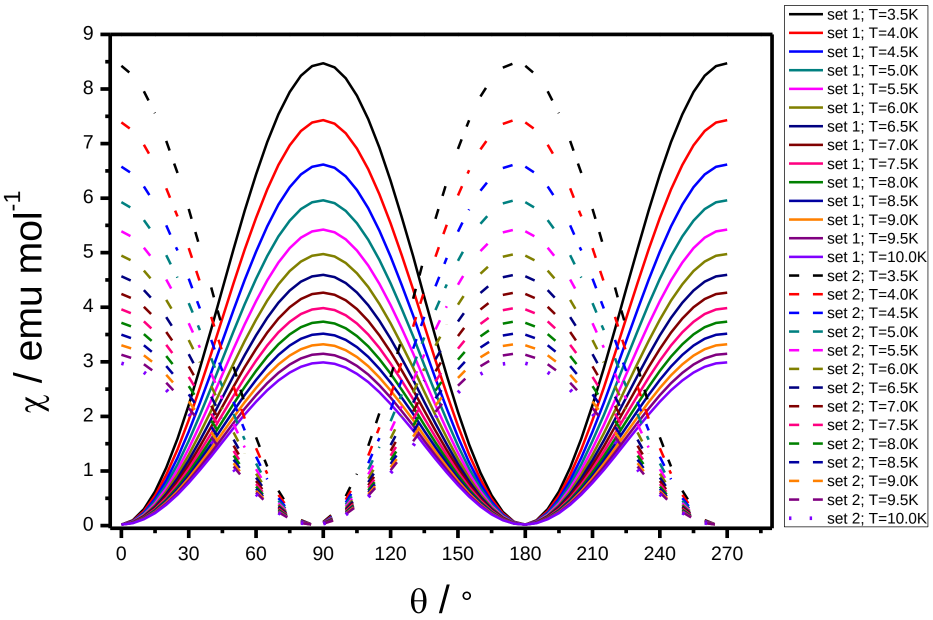

FIGURE S7: Calculated angular dependence of the magnetic susceptibility for the two symmetry-related families of molecules. The susceptibility of each set was averaged over the two conformers with rotated COT ligand. The angle between the easy axis of the ground doublet of the two conformers is only 0.22°.

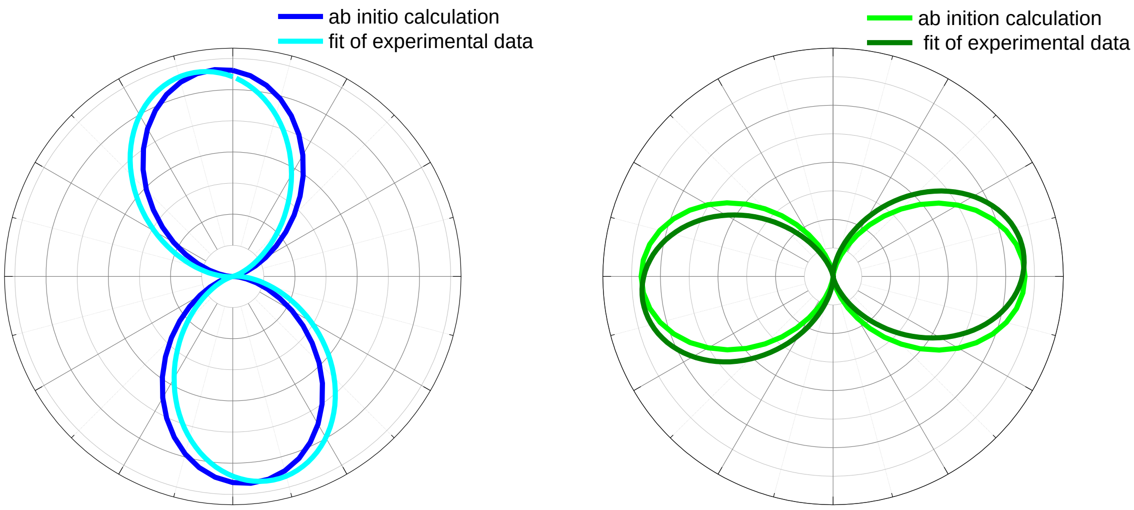

FIGURE S8: Polar plot of the angular dependence of the magnetic susceptibility, comparison between the result of the *ab-initio* calculation for each molecule and the contributions extracted from the fit of the experimental data (color code in the insets).

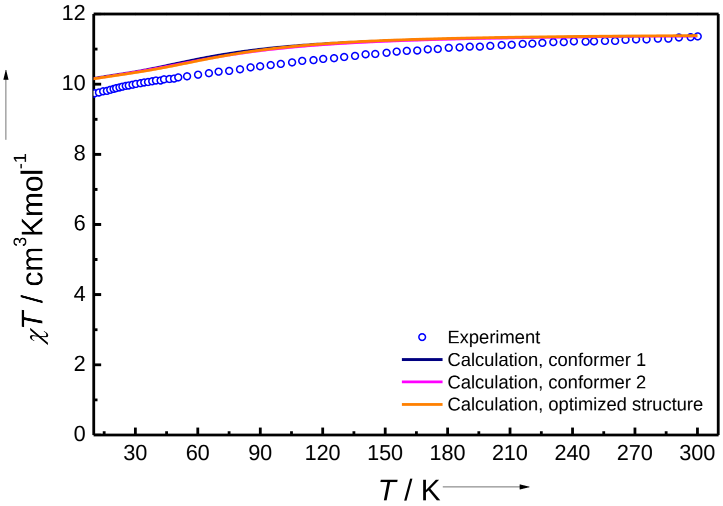

FIGURE S9: Comparison between measured and calculated temperature dependence of the magnetic susceptibility of a powder sample of [Cp*ErCOT].

References:

[1] (a) H. Schumann, R. D. Kohn, F. W. Reier, A.Dietrich, J. Pickardt, *Organometallics* **1989**, *8*, 1388; (b) A. L. Wayda, *Organometallics* **1983**, *2*, 565; (c) S.-D. Jiang, B.-W. Wang, H.-L. Sun, Z.-M. Wang, S. Gao, J. Am. Chem. Soc. **2011**, *133*, 4730-4733.

[2] F. Neese," ORCA. An Ab Initio, Density Functional and Semiempirical Program Package", Version 2.9.0; Universität Bonn: Bonn, Germany, **2010**.