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Electronic Supporting Information for

# Coexistence of long-range antiferromagnetic order and slow relaxation of the magnetization in the first lanthanide complex of a 1,2,4-benzotriazinyl radical

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# Section S1 Synthetic Details

**General Methods and Procedures.** The solvent used (dichloromethane) was of at least reagent grade and dried via an MBraun SPS. All reactions were performed under argon unless otherwise stated. Infrared spectra (solid state) were recorded on a Bruker Alpha Platinum-ATR FTIR spectrometer at 2 cm<sup>-1</sup> resolution. Dy(tbacac)<sub>3</sub> was purchased from Strem Chemicals and used as received. Elemental analyses were performed by Elina Hautakangas at the University of Jyväskylä.

Preparation of 1-phenyl-3(pyridin-2-yl)-benzo[e][1,2,4]triazolyl (1). As previously reported.<sup>1</sup>

**Preparation of Dy(tbacac)<sub>3</sub>(1), (2).** A solution of **1** (28.8 mg, 0.1 mmol) in dry dichloromethane (10 mL) was slowly added to a solution of Dy(tbacac)<sub>3</sub> (72 mg, 0.1 mmol) in dry dichloromethane (20 mL) under argon during which the solution changed from colourless to dark red. The solution was stirred for 1 hour after which the solvent was evaporated under reduced pressure. The resulting red powder was crystallized slowly from a concentrated pentanes solution at  $-20^{\circ}$ C to give thin red plates of **2**. Yield: 63 mg (63 %). Anal. calcd. for C<sub>51</sub>H<sub>70</sub>N<sub>4</sub>O<sub>6</sub>Dy: C, 61.40; H, 7.07; N, 5.62, found: C, 61.25; H, 6.96; N, 5.34. IR(cm<sup>-1</sup>): 2947 (s), 2901 (m), 2864 (m), 1608, (s), 1585 (s), 1574 (m), 1533 (m), 1502 (m), 1485 (m), 1451 (w), 1408 (s), 1387 (m), 1355 (w), 1286 (w), 1244 (w), 1225 (w), 1178 (w), 1138 (w), 867 (w), 790 (w), 768 (w), 747 (w), 626 (w), 612 (w), 584 (w), 523 (w), 472 (w).

## Section S2 X-ray Crystallography

**Methods:** The single crystal X-ray data for **2** were collected with Agilent SuperNova diffractometer equipped with multilayer optics monochromated dual source (Cu and Mo) and Atlas detector, using CuKa (1.54184 Å) radiation at a temperature of 123 K. Data acquisitions, reductions and analytical face-index based absorption corrections were made using program CrysAlis<sup>PRO.1</sup> The structure was solved using ShelXS<sup>2</sup> and Superflip<sup>3</sup> programs and refined on  $F^2$  by full matrix least squares techniques with the ShelXL<sup>2</sup> program in the Olex<sup>2</sup> (v.1.2) program package.<sup>4</sup> All hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 larger than the respective host atoms. Lists of selected bond parameters and intermolecular distances are given in Tables S1 and S2, whereas Figure S1 illustrates the packing of metal–radical complexes in the crystal structure of **2**. Crystallographic data for complex **2** are summarized in Table S3.

Continuous shape measures (CShM) were used to analyze the coordination geometry of 2 by relation to reference polyhedra with eight vertices. The coordination environment shape, obtained by assigning the dysprosium as the central atom and the two nitrogen and six oxygen atoms as ligands, was compared to all 12 reference polyhedra available within the Shape 2.1 program package.<sup>5</sup> The two polyhedra that best describe this shape are triangular dodecahedron (DD) and square antiprism (SAPR) with shape measures of 0.850 and 1.258, respectively; increasingly larger values were obtained for the other reference polyhedra as given in Table S4.

Dy1	N4	2.550(3)
Dy1	O1A	2.292(3)
Dy1	N22	2.595(4)
Dy1	O2B	2.326(3)
Dy1	O1B	2.293(3)
Dy1	O2C	2.319(3)
Dy1	01C	2.321(3)
Dy1	O2A	2.330(3)
N4	C3	1.329(6)
N4	C5	1.388(5)
O1A	C5A	1.271(5)
N22	C21	1.346(5)
N22	C17	1.338(6)
C7A	O2A	1.245(5)
O2B	C7B	1.263(5)
O1B	C5B	1.283(5)
O2C	C7C	1.269(5)
C5C	01C	1.259(5)
O1A	C5A	1.271(5)

**Table S1.** Selected bond distances (Å) of **2** taken from single crystal X-ray data measured at 123 K.

C12	C12'	3.313(6)
N1	C13'	3.420(6)
N1	C14	3.773(7)
N2	C13'	3.299(6)
C11	C13'	3.457(7)
C12	C11'	3.418(6)
C12	C16'	3.771(7)
C20	С9'	3.522(7)
C7	O1B'	3.896(5)
C8	O1B'	3.386(5)
C8	O2B'	3.973(6)
C8	O2C'	3.886(5)
C8	C10C'	3.768(8)
C20	С9'	3.522(7)
C3B	C3CC'	3.08(2)

**Table S2.** Selected intermolecular distances (Å) between complexes of **2** taken from single crystal X-ray data measured at 123 K.



**Figure S1**. Packing of metal–radical complexes in the crystal structure of **2**. The complexes form weakly interacting pairs (illustrated by coloured rectangles) that have multiple close contacts between neighbouring pairs.

Empirical formula	$C_{51}H_{70}DyN_4O_6$
Formula weight	997.61
Temperature / K	123.00(10)
Crystal system	monoclinic
Space group	$P2_{1}/n$
<i>a</i> / Å	10.3358(2)
<i>b</i> / Å	23.0105(7)
c / Å	21.1555(6)
α / °	90
eta / °	90.640(2)
γ/°	90
Volume / Å <sup>3</sup>	5031.1(2)
Ζ	4
$ ho_{ m calc}$ / $ m gcm^{-3}$	1.317
$\mu / \mathrm{mm}^{-1}$	8.336
<i>F</i> (000)	2072.0
Crystal size / mm <sup>3</sup>	$0.0761 \times 0.0502 \times 0.0175$
Radiation	$CuK\alpha (\lambda = 1.54184 \text{ Å})$
$2\Theta$ range for data collection / °	8.36 to 134
Index ranges	$-8 \le h \le 12,  -25 \le k \le 27,  -23 \le l \le 25$
Reflections collected	16383
Independent reflections	8927 [ $R_{int} = 0.0439, R_{sigma} = 0.0765$ ]
Data/restraints/parameters	8927/92/660
Goodness-of-fit on $F^2$	0.998
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0434, wR_2 = 0.0845$
Final <i>R</i> indexes [all data]	$R_1 = 0.0671, wR_2 = 0.0932$
Largest diff. peak/hole / eÅ <sup>-3</sup>	0.59/-0.69

 Table S3. Crystallographic data for 2

Table S4. CShM values for 2 with respect to input polyhedra in program SHAPE 2.1.

Octagon	29.298
Heptagonal pyramid	22.965
Hexagonal bipyramid	14.717
Cube	8.117
Square antiprism	1.258
Triangular dodecahedron	0.850
Johnson gyrobifastigium J26	15.396
Johnson elongated triangular bipyramid J14	27.439
Biaugmented trigonal prism J50	2.145
Biaugmented trigonal prism	1.956
Snub diphenoid J84	3.624
Triakis tetrahedron	8.916

#### Section S3 Magnetic Measurements

The magnetization and magnetic susceptibility measurements were carried out with the use of MPMS-XL Quantum Design SQUID magnetometer and PPMS-9 susceptometer. These instruments work between 1.8 and 400 K with applied dc fields ranging from -7 to 7 T (MPMS) and from -9 to 9 T (PPMS). Measurements were performed on a finely ground crystalline sample of **2** (13.31 mg) sealed in a polyethylene bag ( $30 \times 6 \times 0.2$  mm). Ac susceptibility measurements were made with an oscillating field of 1 Oe with frequency from 10 to 10000 Hz (PPMS). Prior to the experiments, the field-dependent magnetization was measured at 100 K in order to detect the presence of any bulk ferromagnetic impurities. In fact, paramagnetic or diamagnetic materials should exhibit a perfectly linear dependence of the magnetization that extrapolates to zero at zero dc field. The sample appeared to be free of any significant ferromagnetic impurities. The magnetic data were corrected for the sample holder, paratone oil and the intrinsic diamagnetic contributions.



**Figure S2**. Temperature dependence of the dc susceptibility (at 0.1 T) and of the real ( $\chi$ ') and imaginary ( $\chi$ '') parts of the ac susceptibility in zero dc field for a polycrystalline sample of **2**. Solid lines are guides for the eye.



**Figure S3.** Frequency dependence of the real  $(\chi', \text{ left})$  and imaginary  $(\chi'', \text{ right})$  parts of the ac susceptibility for a polycrystalline sample of **2** at 1.9 K at different dc field between 0 and 8500 Oe. Solid lines are guides for the eye.



**Figure S4**. Frequency dependence of the real  $(\chi', \text{ left})$  and imaginary  $(\chi'', \text{ right})$  parts of the ac susceptibility for a polycrystalline sample of **2** at 1.9 K at different dc field between 8500 and 30000 Oe. Solid lines are guides for the eye.



**Figure S5.** Generalized Debye fits (solid lines) of the frequency dependence of the real ( $\chi$ ', left) and imaginary ( $\chi$ '', right) parts of the ac susceptibility for a polycrystalline sample of **2** at 1.9 K at different dc field.



Figure S6. Generalized Debye fits (solid lines) of the Cole-Cole experimental plots for a polycrystalline sample of 2 at 1.9 K at different dc field.



**Figure S7**. Field dependence of the parameters ( $\alpha$ ,  $\chi_0$ ,  $\chi_\infty$ ,  $\chi_0$ - $\chi_\infty$ , and the characteristic frequency,  $\nu$ ) deduced from the Debye generalized fits of the experimental data of **2** at 1.9 K.



**Figure S8.** Frequency dependence of the real  $(\chi', \text{ left})$  and imaginary  $(\chi'', \text{ right})$  parts of the ac susceptibility for a polycrystalline sample of **2** at 0.85 T at different temperatures between 3.8 and 6 K. Solid lines are guides for the eye.



**Figure S9**. Generalized Debye fits (solid lines) of the frequency dependence of the real ( $\chi$ ', left) and imaginary ( $\chi$ '', right) parts of the ac susceptibility for a polycrystalline sample of **2** at 8500 Oe at different temperatures.



**Figure S10**. Generalized Debye fits (solid lines) of the Cole-Cole experimental plots for a polycrystalline sample of **2** at 8500 Oe at different temperatures.



**Figure S11**. Temperature dependence of the parameters ( $\alpha$ ,  $\chi_0$ ,  $\chi_\infty$ ,  $\chi_0$ - $\chi_\infty$ , and the characteristic frequency,  $\nu$ ) deduced from the Debye generalized fits of the experimental data in **2** at 8500 Oe.

#### Section S4 Computational Details

All calculations were performed with the Orca suite of programs version  $3.0.3^6$  using density functional theory (DFT) within the broken symmetry (BS) formalism of Noodleman and co-workers<sup>7</sup>. In order to extract all important magnetic interactions within the complex **2** and its neighboring complexes, two geometries were extracted from the crystal structure. These correspond to a complex and its different neighbors along the crystal *a* and *b* axes respectively and are labeled **a** and **b** respectively. Both structures include two metal ions and two radical ligands and are illustrated in Figure S12. The *tert*-butyl groups in the auxiliary ligands were replaced with hydrogens to reduce computational costs. These groups do not carry any spin density and thus any error introduced by this approximation is assumed to cancel out when relative energetics of different spin states are calculated. The Dy<sup>III</sup> ions were replaced with Gd<sup>III</sup> ions. The completely quenched angular momentum of the Gd<sup>III</sup> ion allows the estimations of exchange couplings in an identical crystal field environment as in **2** without the need to explicitly consider effects arising from orbital momentum.

The crystal structure coordinates were used without further geometry optimizations. In all calculations, scalar relativistic effects were introduced using the zeroth order regular approximation (ZORA) following the formulation of van Wüllen.<sup>8</sup> Relativistic SARC2-ZORA-QZVP basis set<sup>9</sup> was used for the Gd<sup>III</sup> ions and ZORA-def2-TZVP basis sets<sup>10</sup> optimized for ZORA calculations were used for other atoms.

All possible exchange couplings between the four spin sites in both structures were extracted. Values of the coupling constant were calculated from the results by mapping the energies of the BS states to the spectrum of the Ising Hamiltonian:

$$\widehat{H}_{\text{Ising}} = -2\sum_{i\neq j} J_{ij}\widehat{S}_z^{i} \cdot \widehat{S}_z^{j},$$

where the effective spin operators act only on the *z*-component of the spin vector. The Ising coupling constants are equivalent to the respective Heisenberg coupling constants when the BS energies are interpreted as expectation values of the Heisenberg Hamiltonian acting on the said state.<sup>11</sup>

The possible coupling constants are labeled as  $J_{MR}^a$ ,  $J_{RRI}^a$ ,  $J_{MRI}^a$ ,  $J_{MRI}^a$ ,  $J_{MRI}^b$ , and  $J_{MRI}^b$ , and  $J_{MRI}^b$ ,  $J_{MRI}^b$ , and  $J_{MRI}^b$ ,  $J_{MRI}^b$ 

$$2J_{MR}^{a} = -\frac{1}{_{14}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} - \frac{1}{_{14}}E_{\uparrow\uparrow\downarrow\downarrow} + \frac{1}{_{14}}E_{\uparrow\downarrow\downarrow\uparrow} + \frac{1}{_{14}}E_{\uparrow\downarrow\downarrow\uparrow} = -9.38 \text{ cm}^{-1}$$

$$2J_{RR'}^{a} = -\frac{1}{_{2}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} - E_{\uparrow\uparrow\uparrow\downarrow\downarrow} + E_{\uparrow\uparrow\downarrow\downarrow\uparrow} + \frac{1}{_{2}}E_{\uparrow\downarrow\downarrow\downarrow} + \frac{1}{_{2}}E_{\uparrow\downarrow\downarrow\uparrow\downarrow} - \frac{1}{_{2}}E_{\uparrow\downarrow\downarrow\uparrow} = -15.75 \text{ cm}^{-1}$$

$$2J_{MR'}^{a} = -\frac{1}{_{14}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} + \frac{1}{_{14}}E_{\uparrow\uparrow\downarrow\downarrow\downarrow} - \frac{1}{_{14}}E_{\uparrow\downarrow\uparrow\downarrow\downarrow} + \frac{1}{_{14}}E_{\uparrow\downarrow\downarrow\uparrow} = 0.00 \text{ cm}^{-1}$$

$$2J_{MM'}^{a} = -\frac{1}{_{98}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} + \frac{1}{_{49}}E_{\uparrow\uparrow\uparrow\downarrow\downarrow} + \frac{1}{_{49}}E_{\uparrow\uparrow\downarrow\downarrow\uparrow} + \frac{1}{_{98}}E_{\uparrow\uparrow\downarrow\downarrow\downarrow} - \frac{1}{_{98}}E_{\uparrow\downarrow\downarrow\downarrow} - \frac{1}{_{98}}E_{\uparrow\downarrow\downarrow\downarrow} = 0.00 \text{ cm}^{-1}$$

and for structure b:

$$2J_{MR}^{b} = -\frac{1}{_{14}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} - \frac{1}{_{14}}E_{\uparrow\uparrow\uparrow\downarrow\downarrow} + \frac{1}{_{14}}E_{\uparrow\downarrow\uparrow\downarrow} + \frac{1}{_{14}}E_{\uparrow\downarrow\downarrow\uparrow}} = -9.47 \text{ cm}^{-1}$$

$$2J_{RR'}^{b} = -\frac{1}{_{2}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} - E_{\uparrow\uparrow\uparrow\downarrow\downarrow} + E_{\uparrow\uparrow\downarrow\downarrow\uparrow} + \frac{1}{_{2}}E_{\uparrow\uparrow\downarrow\downarrow\downarrow} + \frac{1}{_{2}}E_{\uparrow\downarrow\uparrow\downarrow\downarrow} - \frac{1}{_{2}}E_{\uparrow\downarrow\downarrow\downarrow\uparrow}} = 0.41 \text{ cm}^{-1}$$

$$2J_{MR'}^{b} = -\frac{1}{_{14}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} + \frac{1}{_{14}}E_{\uparrow\uparrow\downarrow\downarrow\downarrow} - \frac{1}{_{14}}E_{\uparrow\downarrow\downarrow\uparrow\downarrow} + \frac{1}{_{14}}E_{\uparrow\downarrow\downarrow\uparrow\uparrow}} = -0.02 \text{ cm}^{-1}$$

$$2J_{MM'}^{b} = -\frac{1}{_{98}}E_{\uparrow\uparrow\uparrow\uparrow\uparrow} + \frac{1}{_{49}}E_{\uparrow\uparrow\uparrow\downarrow\downarrow} + \frac{1}{_{49}}E_{\uparrow\uparrow\downarrow\downarrow\uparrow} + \frac{1}{_{98}}E_{\uparrow\downarrow\downarrow\downarrow} - \frac{1}{_{98}}E_{\uparrow\downarrow\downarrow\downarrow} - \frac{1}{_{98}}E_{\uparrow\downarrow\downarrow\downarrow} = 0.00 \text{ cm}^{-1}$$

The Gd-radical coupling constant can be determined as an average of the corresponding coupling constants  $(J_{MR}^{a} \text{ and } J_{MR}^{b})$  in structures **a** and **b**:  $2J_{Gd-R} = -9.42 \text{ cm}^{-1}$ . The magnitude of the coupling between a Dy<sup>III</sup> ion and the radical in the same coordination environment can be estimated by scaling  $2J_{Gd-R}$  with a factor of 5/7:  $2J_{Dy-R} = -6.73 \text{ cm}^{-1}$ . The radical-radical coupling constant,  $J_{R-R}$ , referred in the main text is equal to  $J_{RR'}^{a}$ . The coupling constants  $J_{RR'}^{b}$  and  $J_{MR'}^{b}$  should be interpreted as "small but non-zero" as accurate prediction of the sign and value of energy differences less than a wave number is impossible within the error margins of DFT calculations. Coupling constants  $J_{MM'}^{a}$  and  $J_{MM'}^{b}$  deviate from zero at the third decimal but for a value this small it is impossible to say whether it is an actual energy difference or just numerical noise.  $J_{MM'}^{a}$  is zero up to numerical accuracy.

The coupling constants  $J_{RR'}^b$  and  $J_{MR'}^b$  can, in principle, propagate the magnetic ordering along the *b* crystal axis. However, this is still not enough to explain the ordering in three dimensions and, furthermore, the calculated values are clearly too small in magnitude to alone support magnetic ordering at 8.6 K. Based on these results the magnetic ordering must be explained by dipolar interaction between the Dy<sup>III</sup> ions assisted by the weak radical-radical couplings.



Figure S12. The structures  $\mathbf{a}$  (above) and  $\mathbf{b}$  (below) used in the DFT calculations. Structure  $\mathbf{a}$  consists of complex pairs circled in Figure S1 and structure  $\mathbf{b}$  consist of two neighboring complexes along the crystal axis *c* in Figure S1.

### Section S5 References

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