

Supplementary Information

Coming full circle: constructing a [Gd₆] wheel dimer by dimer and the importance of spin topology

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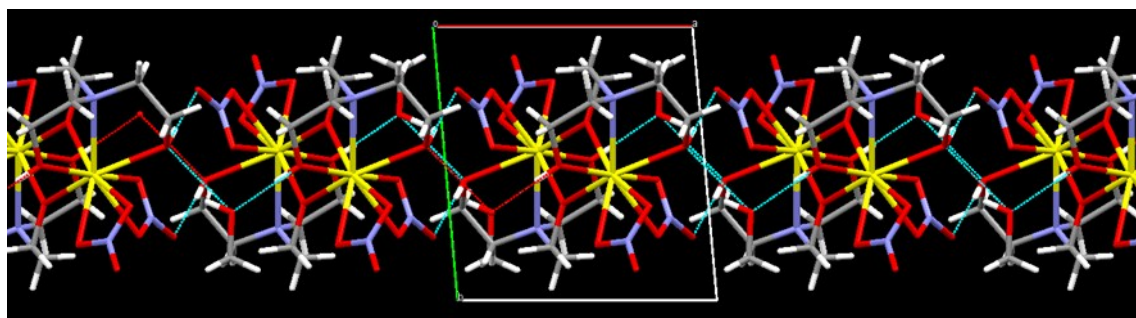


Figure S1. Packing of complex **1** (Gd₂) in the extended structure, viewed in the *bc* plane and highlighting the H-bonding interactions (dashed lines) that direct the formation of chains. Colour code: Gd, yellow; O, red; N, blue; C, grey; H, white.

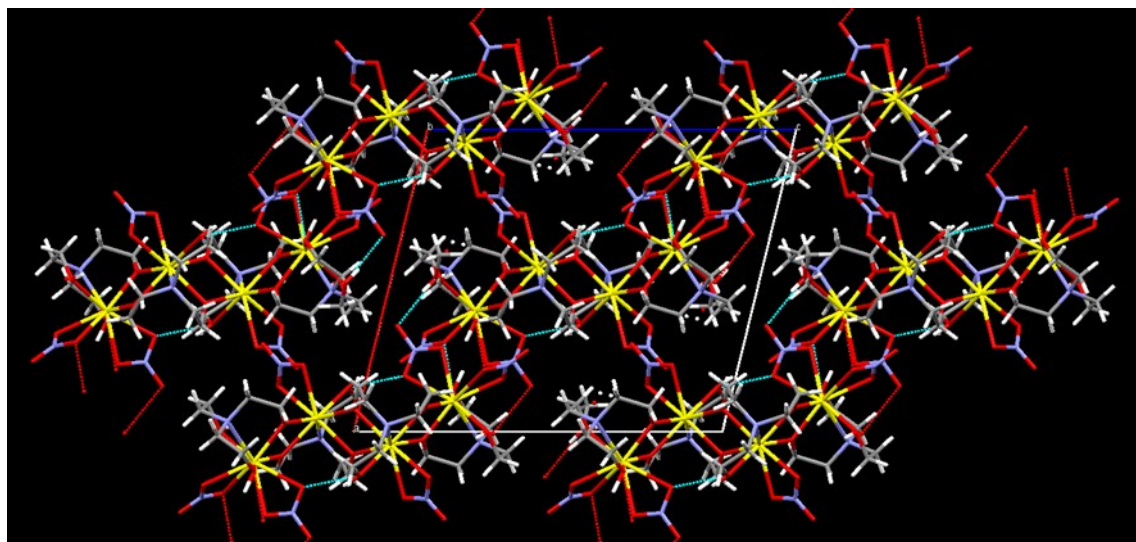


Figure S2. Packing of complex **2** (Gd₄) in the extended structure, viewed down the *b*-axis, highlighting the H-bonding interactions (dashed lines). Colour code: Gd, yellow; O, red; N, blue; C, grey; H, white.

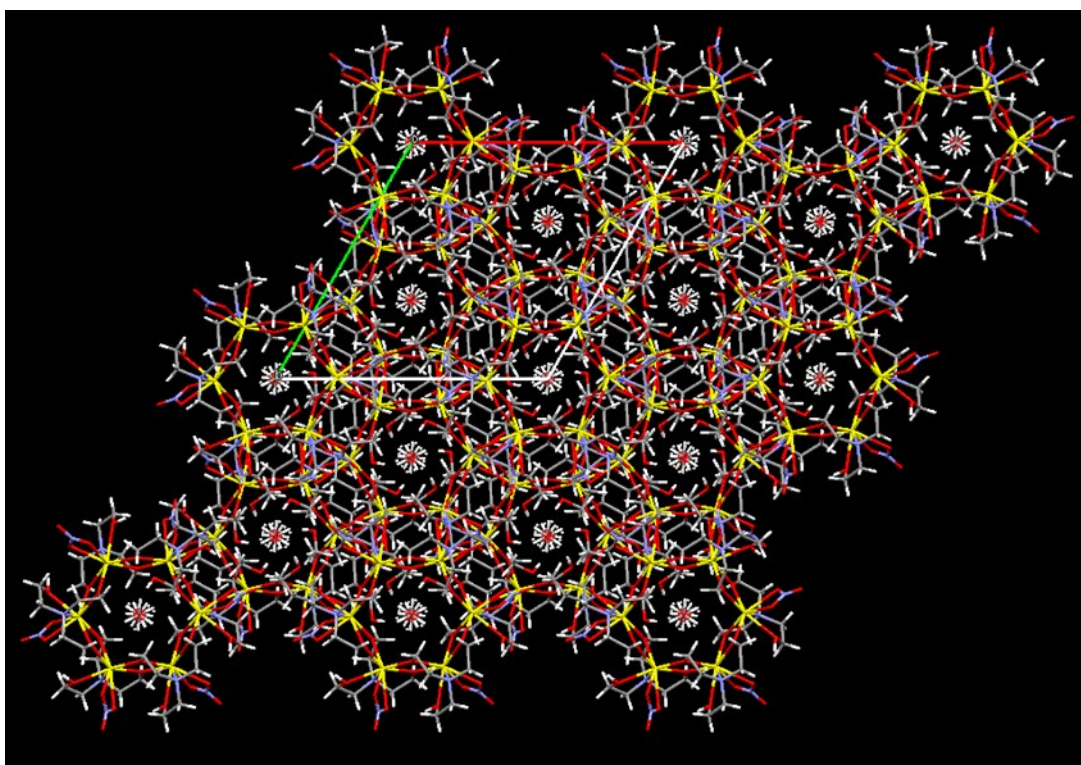


Figure S3. Packing of complex **3** (Gd_6) in the extended structure, viewed down the c -axis. Colour code: Gd, yellow; O, red; N, blue; C, grey; H, white.

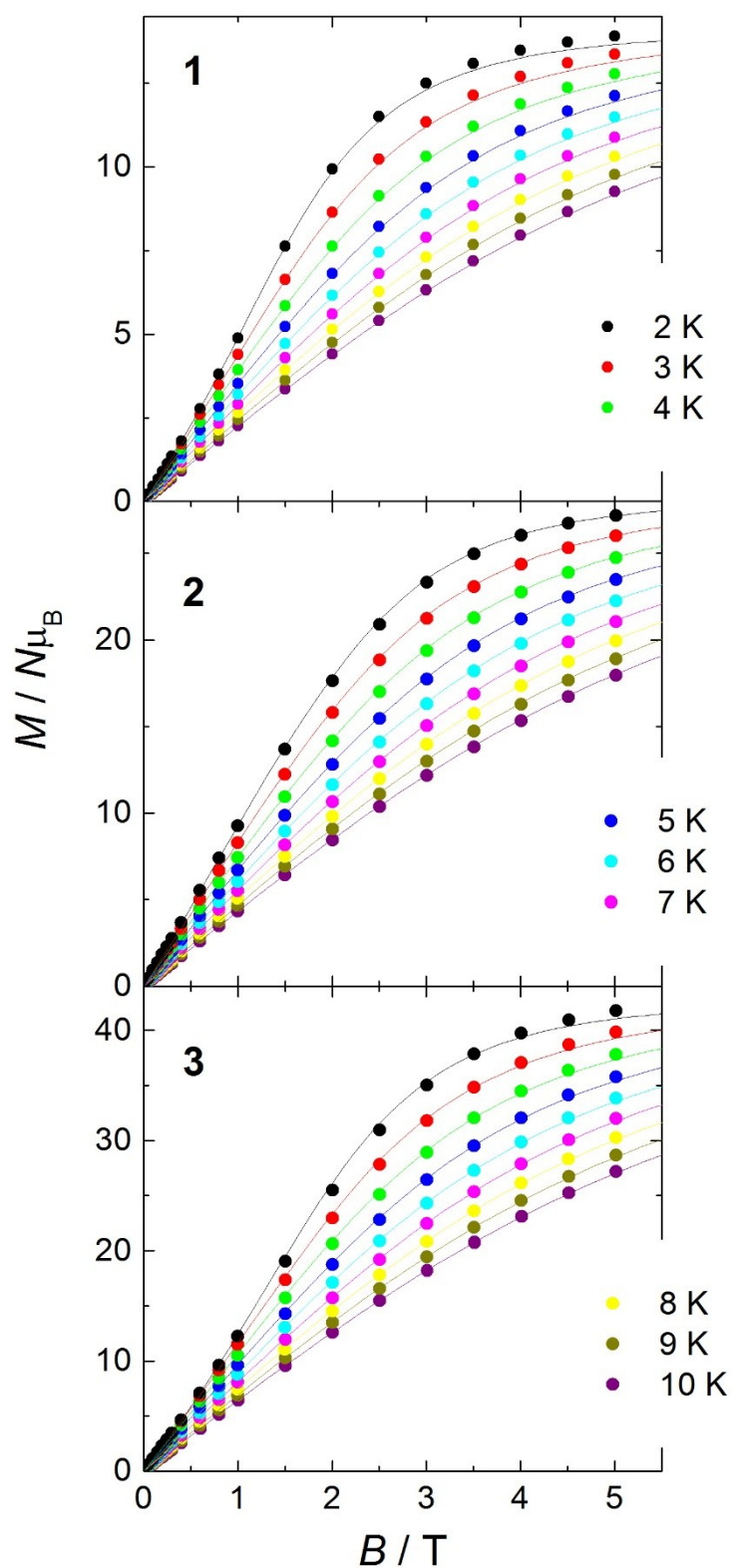


Figure S4. For complexes **1** (top), **2** (middle) and **3** (bottom), field-dependence of the experimental molar magnetization M for temperatures ranging from 2 to 10 K, with a 1 K step between adjacent isothermal curves. The solid lines are a fit of the experimental data employing the Hamiltonians of equations (1) - (3). See main text for details.

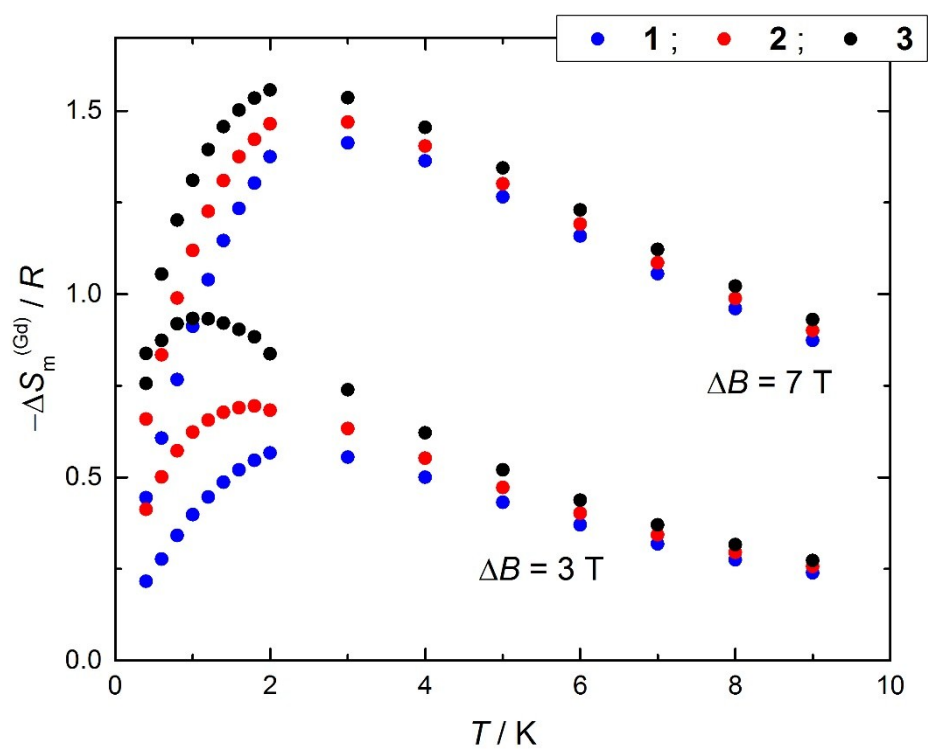


Figure S5. Temperature-dependence of the magnetic entropy change, ΔS_m , normalized per molar Gd, as obtained from magnetization data (see Figure S1) for the indicated applied-field changes ΔB .

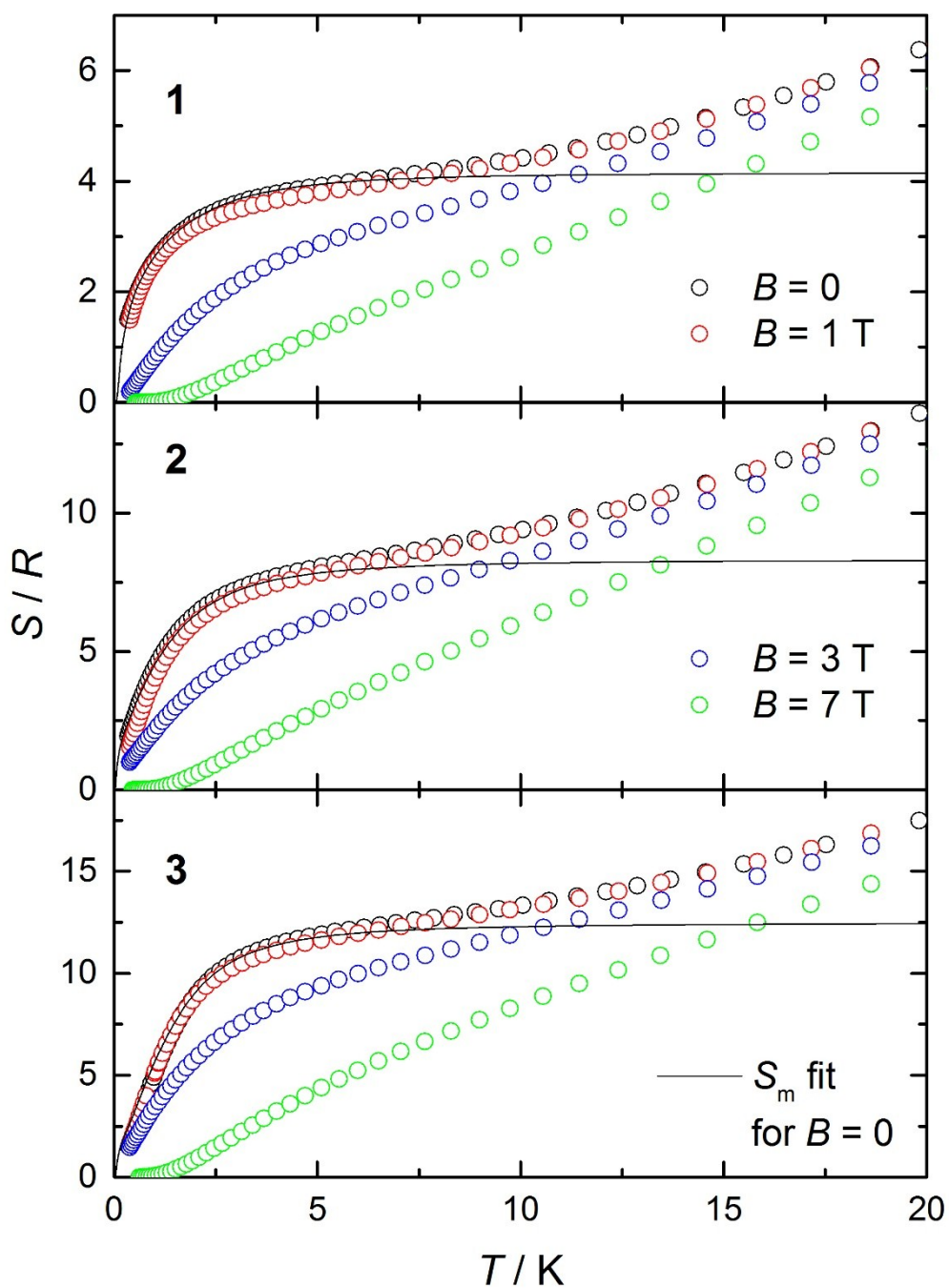


Figure S6. For complexes **1** (top), **2** (middle) and **3** (bottom), temperature-dependence of the experimental molar entropy S for applied field values of 0, 1, 3, and 7 T, as labelled. The solid lines are a fit of the experimental magnetic contribution (S_m) for $B = 0$, employing the Hamiltonians of equations (1) - (3). See main text for details.

Computational Details

DFT calculations were performed using the experimental geometries obtained by X-ray diffraction and two different computational approaches. The first is the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code,¹⁻² with the generalized-gradient approximation (GGA) functional proposed by Perdew, Burke, and Ernzerhof.³ Only valence electrons are included in the calculations, with the core being replaced by norm-conserving scalar relativistic pseudopotentials factorized in the Kleinman-Bylander form.⁴ The pseudopotentials are generated according to the procedure of Troullier and Martins.⁵ For the Gd pseudopotential we have used the one proposed by Pollet et al.⁶ This methodology has been previously tested and correctly reproduced exchange interactions in Gd-containing polynuclear compounds.⁷

The second approach consists of the use of the all-electron FHI-Aims code and numerical local orbital basis set.⁸ Its main improvement is the implementation of the hybrid B3LYP functional⁹ and the resolution of identity (RI) technique to facilitate the treatment of the two-electron Coulomb repulsion integrals.¹⁰ Hybrid functionals provide more accurate exchange coupling constants than the GGA functional. Previous reported studies performed by some of us showed that “light” basis sets were able to reproduce the magnetic exchange couplings in a Fe₄₂ complex. For a smaller Fe₄ model the effect of the basis set was also tested, the increase of the basis set from “light” to “tight” to “really tight” changed the coupling constant *J* by less than 1%.¹¹ Due to the presence of the Gd(III) ion and to avoid an error in the accuracy of onsite integrals, the “tight” basis set was employed for the Gd ions while the other atoms were described by the “light” basis set. For the dinuclear complex **1**, the use of the “tight” basis set for all of the atoms was checked and the calculated *J* value is the same as the one obtained from applying this basis set only to the Gd ions. The relativistic effects were included using the atomic ZORA approximation.⁸ The SCF parameters to reach a good convergence in the calculations were a Gaussian occupation type with a parameter of 0.01, a Pulay mixer with 15 cycles and a mixing parameter of 0.1.

References

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