

ELECTRONIC SUPPORTING INFORMATION

New structural topologies in 4f-metal cluster chemistry from vertex-sharing butterfly units: $\{\text{Ln}^{\text{III}}_7\}$ complexes exhibiting slow magnetization relaxation and ligand-centred emissions

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Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials as received. The organic ligand saphH₂ (orange crystalline solid) was synthesized by following a well-known synthetic protocol for the synthesis of Schiff base ligands. This includes the condensation in refluxing absolute methanol of equimolar amounts of 2-aminophenol and salicylaldehyde, in accordance with literature methods for the same ligand.¹

(NH₄Et₃)[Gd₇(OH)₂(saph)₁₀(Me₂CO)₂] (1): To a stirred, orange solution of saphH₂ (0.043 g, 0.2 mmol) and NEt₃ (84 μ L, 0.6 mmol) in Me₂CO (20 mL) was added solid Gd(NO₃)₃·6H₂O (0.045 g, 0.1 mmol). The resulting yellow solution was stirred for 30 min, during which time all the solids dissolved and the color of the solution became more intense yellow. The solution was filtered, and the filtrate was left to evaporate slowly at room temperature. After 2 days, very thin needle-like crystals of **1** had appeared, and these were found to be suitable enough for X-ray diffraction studies. The crystals were collected by filtration, washed with cold Me₂CO (2 x 2 mL) and dried in air. The yield was 45 %. The air-dried solid was found to be slightly hygroscopic and analyzed as **1**·2H₂O: C, 48.71; H, 3.57; N, 4.40 %. Found: C, 48.62; H, 3.42; N, 4.49 %.

(NH₄Et₃)[Tb₇(OH)₂(saph)₁₀(Me₂CO)₂] (2): This complex was prepared in the same manner as complex **1** but using Tb(NO₃)₃·6H₂O (0.045 g, 0.1 mmol) as the Ln salt. Again, after 2 days, very thin needle-like crystals of **2** had appeared, albeit this time the crystals were not of sufficient quality (very small in size) to allow for a complete X-ray diffraction analysis. The crystals were collected by filtration, washed with cold Me₂CO (2 x 2 mL) and dried in air. The yield was 52 %. The air-dried solid was analyzed as **2**·2H₂O: C, 48.55; H, 3.56; N, 4.39 %. Found: C, 48.36; H, 3.44; N, 4.55 %.

(NH₄Et₃)[Dy₇(OH)₂(saph)₁₀(Me₂CO)₂] (3): This complex was prepared in the same manner as complex **1** but using Dy(NO₃)₃·6H₂O (0.046 g, 0.1 mmol) as the Ln salt. Again, after 2 days, very thin needle-like crystals of **3** had appeared and these were not suitable for a complete X-ray

¹ A. Kagkelari, G. S. Papaefstathiou, C. P. Raptopoulou and T. F. Zafirooulos, *Polyhedron*, 2009, **28**, 3279.

diffraction analysis. The crystals were collected by filtration, washed with cold Me₂CO (2 x 2 mL) and dried in air. The yield was 55 %. The air-dried solid was analyzed as 3·2H₂O: C, 48.21; H, 3.53; N, 4.35 %. Found: C, 48.16; H, 3.29; N, 4.48 %.

Single-crystal X-ray diffraction studies. Crystalline material of the compounds (NH₄Et₃)[Ln₇(OH)₂(saph)₁₀(Me₂CO)₂] [Ln³⁺ = Gd³⁺ (**1**), Tb³⁺ (**2**) and Dy³⁺ (**3**)] were manually harvested and mounted on cryoloops using an appropriated inert oil.² Complete diffraction data have been collected only for compound **1** at 150.0(2) K on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer controlled by the APEX2 software package (Mo K_α graphite-monochromated radiation, λ = 0.71073 Å),³ and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely with the software interface Cryopad.⁴ As mentioned previously, the small size and apparently the weak diffraction of several crystals of compounds **2** and **3** tested in the X-ray diffractometer prevented the acquisition of full data sets; however, it was possible to obtain unequivocal indexations of the respective unit cells.

The images collected for compound **1** were processed with the software SAINT+,⁵ and the absorption effects were corrected by the multi-scan method implemented in SADABS.⁶ The structure was solved using the algorithm implemented in SHELXT-2014,^{7,8} allowing the immediate location of all the Gd³⁺ centers. Remaining non-hydrogen elements were located from difference Fourier maps and calculated by successive full-matrix least-squares refinement cycles on *F*² using SHELXL-v.2014.^{7,9} All non-hydrogen atoms of the anionic Gd₇ cluster compound were successfully refined with anisotropic displacement parameters, except from the carbon atoms of the coordinated acetone (Me₂CO) molecules and the NH₄Et₃⁺ counter-cation which were only refined with isotropic parameters. Hydrogen atoms were placed at their geometrical

² T. Kottke and D. Stalke, *J. App. Cryst.*, 1993, **26**, 615-619.

³ APEX2, *Data Collection Software Version 2012.4*, Bruker AXS, Delft, The Netherlands, 2012.

⁴ Cryopad, *Remote monitoring and control, Version 1.451*, Oxford Cryosystems, Oxford, United Kingdom, 2006.

⁵ SAINT+, *Data Integration Engine v. 8.27b*®, 1997-2012, Bruker AXS, Madison, Wisconsin, USA.

⁶ G. M. Sheldrick, *SADABS 2012/1*, Bruker AXS Area Detector Scaling and Absorption Correction Program, 2012, Bruker AXS, Madison, Wisconsin, USA.

⁷ G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.

⁸ G. M. Sheldrick, *SHELXT v. 2014/3*, Program for Crystal Structure Solution, University of Göttingen, 2014.

⁹ G. M. Sheldrick, *SHELXL v. 2014*, Program for Crystal Structure Refinement, University of Göttingen, 2014.

positions and included in subsequent refinement cycles. A substantial dispersed electron density was found, most probably due to disordered lattice solvate molecules. The effort to locate and model these solvent molecules revealed to be unsuccessful, and the investigation of the total potential solvent area using the software package PLATON¹⁰ revealed the presence of voids with potential solvent accessible void volume. Consequently, the contribution of these highly disordered molecules was removed using the program SQUEEZE.¹¹

Unit cell parameters, structure solution and refinement details for all complexes are listed in Table S1. Further crystallographic details of the structure of compound **1** can be found in the corresponding CIF file provided in the Supporting Information. Crystallographic data (excluding structure factors) for the structure of **1** have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number: CCDC-1429027. Copies of the data can be obtained online using <https://summary.ccdc.cam.ac.uk/structure-summary-form>.

Table S1. Crystal and structure refinement details for complex **1-3**

	1	2	3
Formula ^a	C ₁₄₂ H ₁₂₀ Gd ₇ N ₁₁ O ₂₄	C ₁₄₂ H ₁₂₀ Tb ₇ N ₁₁ O ₂₄	C ₁₄₂ H ₁₂₀ Dy ₇ N ₁₁ O ₂₄
Fw ^a / g mol ⁻¹	3465.23	3477.06	3502.08
Crystal type	Yellow needle	Yellow needle	Yellow needle
Crystal size / mm	0.16×0.08×0.06	0.12×0.04×0.03	0.10×0.05×0.03
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	Bravais Lattice <i>P</i>	Bravais Lattice <i>P</i>
<i>a</i> / Å	15.5132(16)	15.793(2)	15.642(2)
<i>b</i> / Å	20.762(2)	20.459(3)	20.753(2)
<i>c</i> / Å	24.831(3)	25.003(3)	25.149(3)
<i>α</i> / °	106.288(4)	106.025(5)	105.978(5)
<i>β</i> / °	103.085(5)	102.852(6)	102.976(2)
<i>γ</i> / °	105.827(4)	105.789(5)	106.012(4)
Volume / Å ³	6977.1(1)	7074.6(2)	7134.0(2)
<i>Z</i>	2	-	-

¹⁰ A. L. Spek; *J. Appl. Crystallogr.* 2003, **36**, 7.

¹¹ P. Van der Sluis and A. L. Spek, *Acta Cryst. A*, 1990, **46**, 194.

$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.649	-	-
μ / mm^{-1}	3.348	-	-
θ range / °	3.68 – 25.03	-	-
Index ranges	$-18 \leq h \leq 18$	-	-
	$-24 \leq k \leq 24$		
	$-28 \leq l \leq 28$		
Collected reflections	121671	-	-
Independent reflections	23766	-	-
	[R(int) = 0.0507]		
Final $R^{a,b}$ indices	$R1 = 0.0652$	-	-
[$I > 2\sigma(I)$]	$wR2 = 0.1398$		
Final $R^{a,b}$ indices	$R1 = 0.0864$	-	-
(all data)	$wR2 = 0.1489$		
$(\Delta\rho)_{\text{max,min}} / \text{e \AA}^{-3}$	1.881 and -1.151	-	-

^a $R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. ^b $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

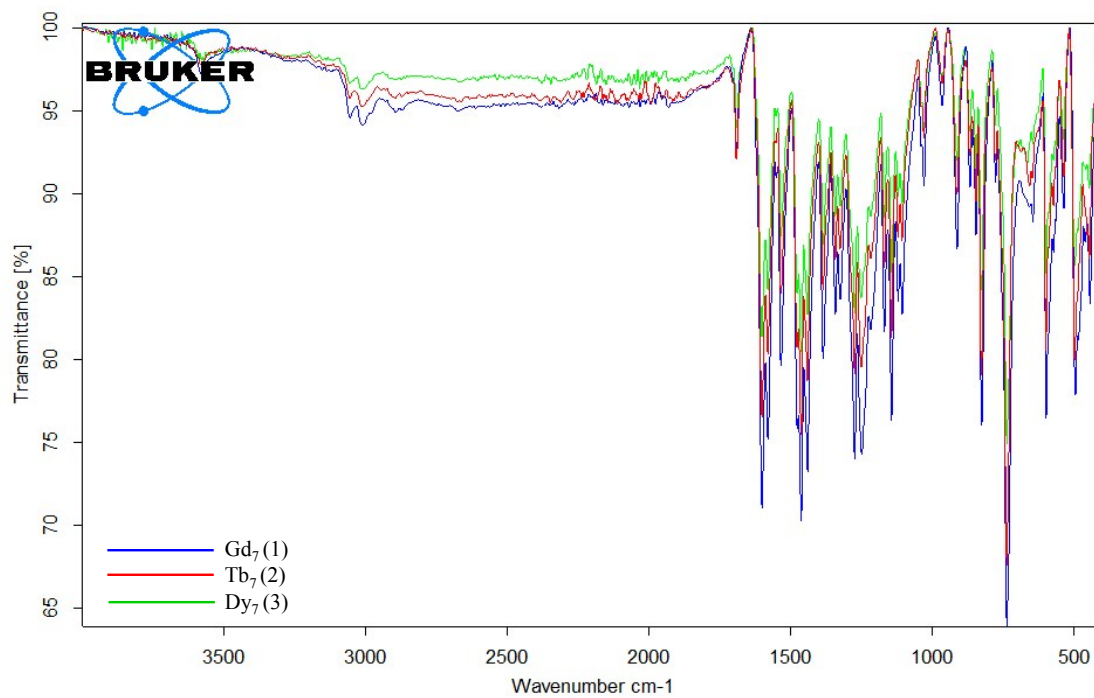


Fig. S1. ATR spectra of complexes 1-3.

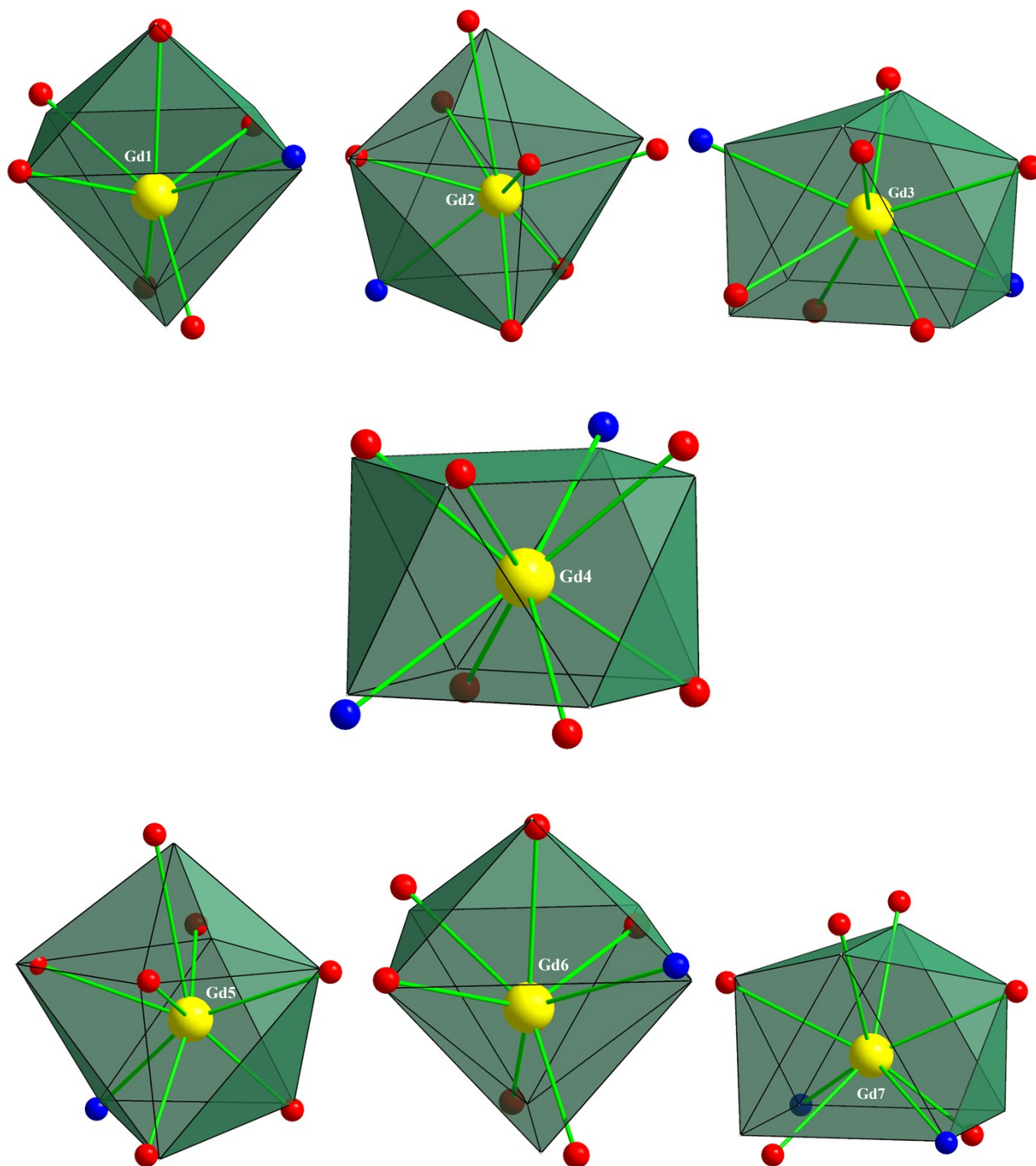


Fig. S2. Capped octahedron (Gd1 and Gd6), triangular dodecahedral (Gd2 and Gd5), biaugmented trigonal prismatic (Gd3 and Gd7) and square antiprismatic (Gd4) geometries of the gadolinium atoms in the structure of **1**. The points connected by the black lines define the vertices of the ideal polyhedron. The so-called Continuous Shape Measures (CShM) approach essentially allows one to numerically evaluate by how much a particular structure deviates from

an ideal shape. The obtained CShM values were 1.69 (Gd1), 1.54 (Gd2), 2.84 (Gd3), 1.42 (Gd4), 1.37 (Gd5), 2.36 (Gd6) and 2.69 (Gd7). Values of CShM between 0.1 and 3 usually correspond to a not negligible but still small distortion from ideal geometry, while values larger than 3 refer to very distorted coordination environments.

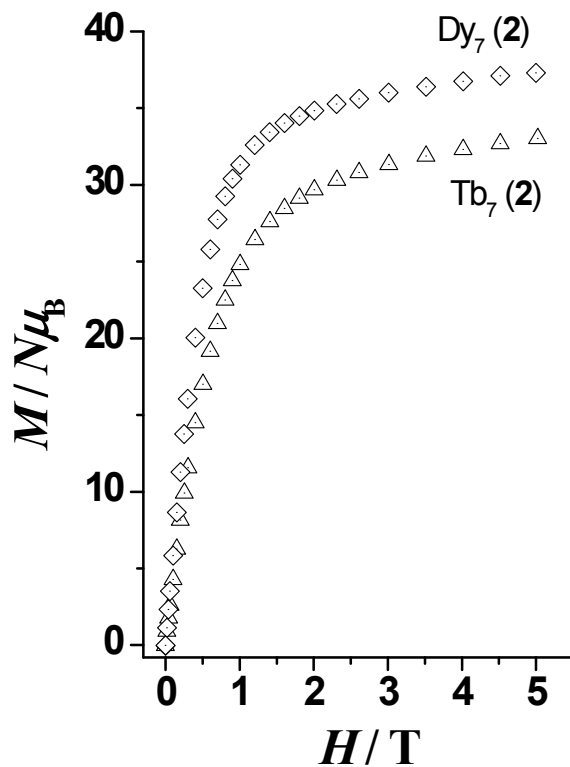


Fig. S3. Plots of magnetization (M) vs field (H) for complexes 2 and 3 at 2 K.

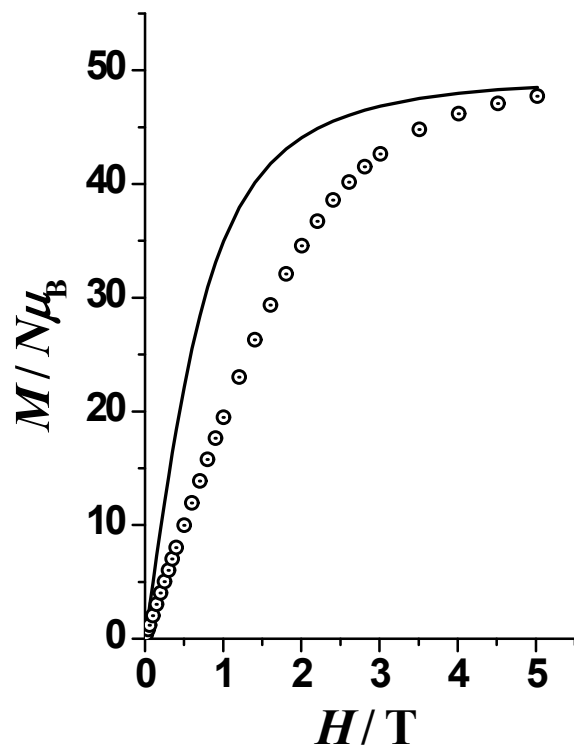


Fig. S4. Plot of magnetization (M) vs field (H) for complex **1** at 2 K; the solid line corresponds to the Brillouin function for 7 non-coupled Gd^{III} ions.

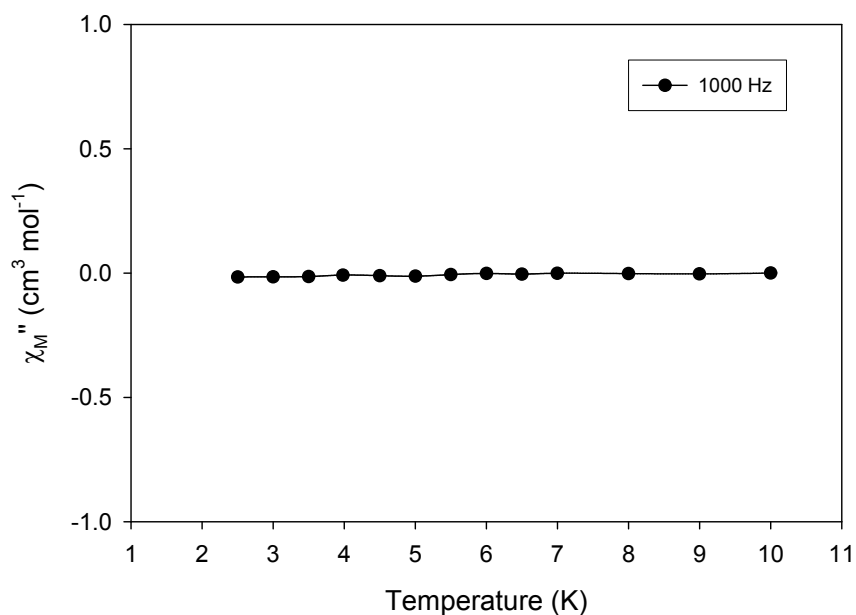


Fig. S5. The out-of-phase (χ''_M) vs T ac susceptibility signals for **2** in a 4.0 G field oscillating at 1000 Hz.

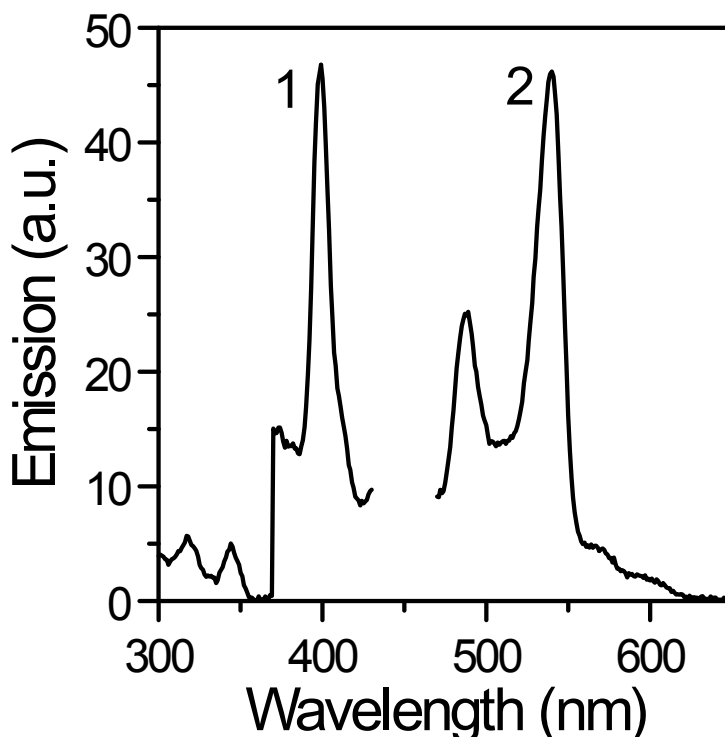
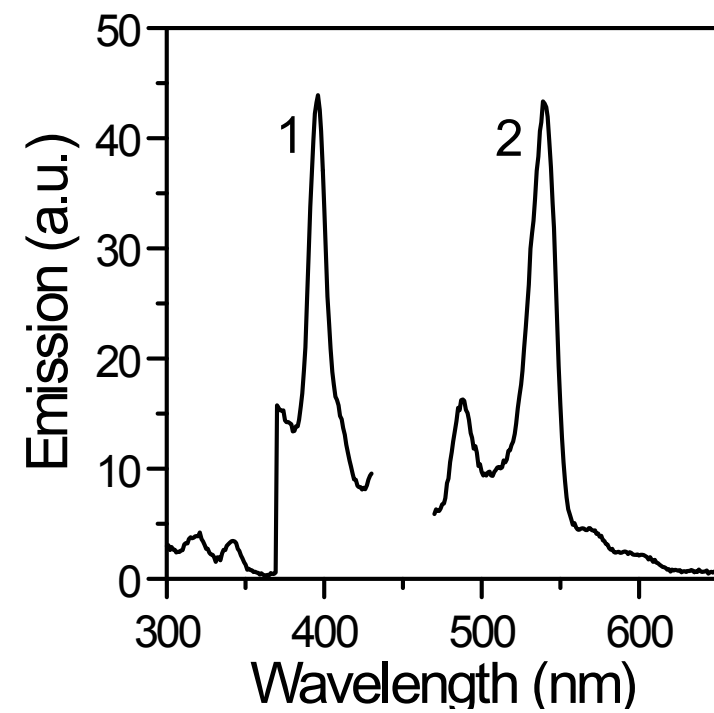


Fig. S6. Excitation (1) and emission (2) spectra of complexes **1** (top) and **2** (bottom) at room temperature.

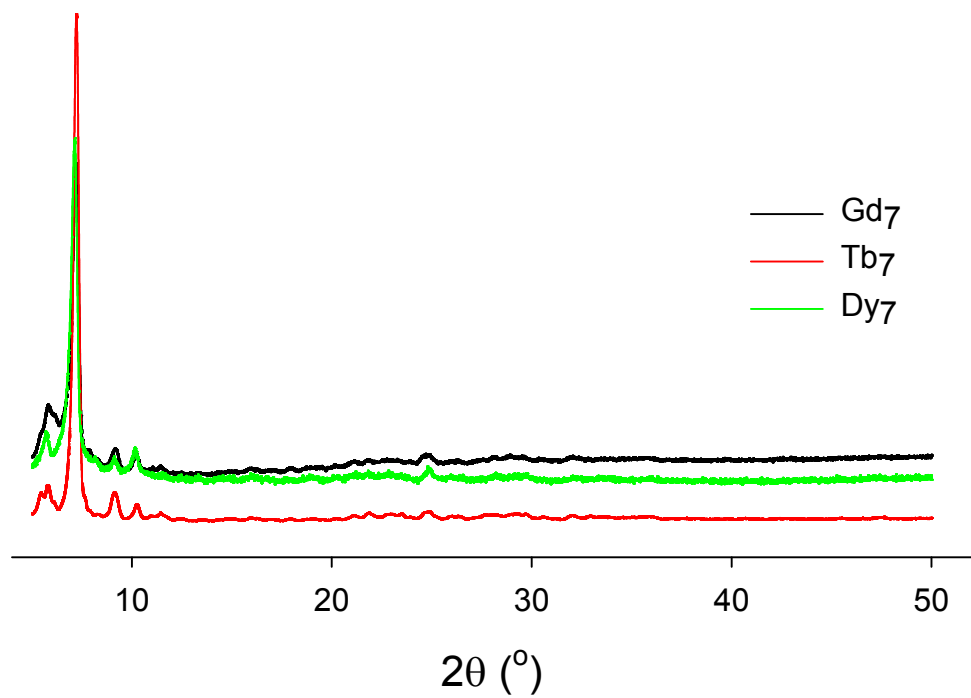


Fig. S7. Powder-XRD spectra of complexes 1-3.

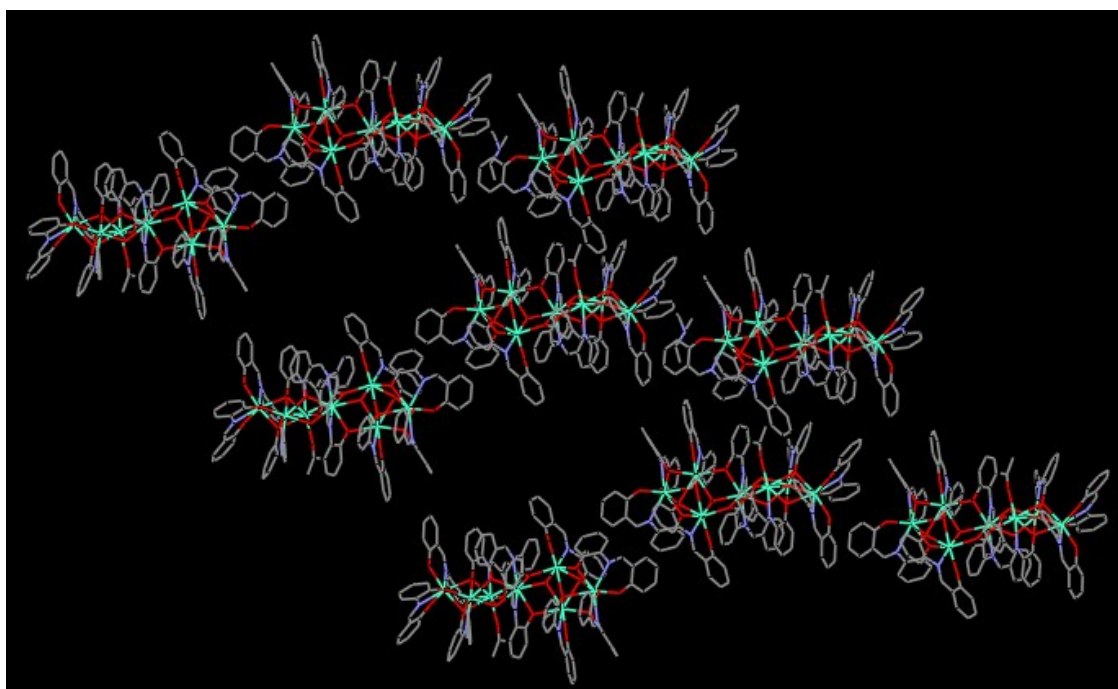


Fig. S8. The packing of the Gd₇ clusters in the crystal of **1**.