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SUPPORTING INFORMATION

A new family of Ln_7 clusters with an ideal D_{3h} metal-centered trigonal prismatic geometry, and SMM and photoluminescence behaviors

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Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials as received. The organic ligand sachH_2 (yellow 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-aminocyclohexanol (*cis-* and *trans*-mixture) and salicylaldehyde, in accordance with literature methods for the similar ligand saphH_2.[1] ***Caution!*** *Although no such behavior was observed during the present work, perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.*

$[Gd_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot 11MeOH$ (1·11MeOH): To a stirred, yellow solution of sachH_2 (0.13 g, 0.6 mmol) and $Me_4NOH\cdot 5H_2O$ (0.11 g, 0.6 mmol) in MeOH (20 mL) was added $Gd(ClO_4)_3\cdot 6H_2O$ (0.11 g, 0.2 mmol). The resulting yellow solution was stirred for 10 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 12 days, X-ray quality pale yellow plate-like crystals of **1**·11MeOH had appeared and were collected by filtration, washed with cold MeOH (2 x 2 mL) and dried in air. The yield was 32 %. The air-dried solid was analyzed as **1**: C, 36.26; H, 4.30; N, 2.92 %. Found: C, 36.02; H, 4.12; N, 2.99 %. Selected IR data (ATR): *v*= 2928 (m), 2910 (m), 1627 (s), 1594 (m), 1543 (m), 1471 (m), 1442 (m), 1357 (m), 1304 (mb), 1194 (m), 1151 (m), 1129 (w), 1060 (m), 984 (m), 901 (m), 840 (m), 820 (w), 756 (s), 603 (m), 579 (w), 507 (w).

The carbonate-related IR absorption bands are located at ~1440 and 845 cm^{-1}, as seen for other carbonato 4f-metal complexes.[2]

$[Tb_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot 3MeOH$ (2·3MeOH): This complex was prepared in the same manner as complex **1** but using $Tb(ClO_4)_3\cdot 6H_2O$ (0.11 g, 0.2 mmol) as the Ln salt. After 6 days, pale yellow plate-like crystals of **2**·3MeOH had appeared and were collected by filtration, washed with cold MeOH (2 x 2 mL) and dried in air. The yield was 25 %. The air-

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

[2] X. Liang, J. A. Parkinson, S. Parsons, M. Weishaupl and P. J. Sadler, *Inorg. Chem.*, 2002, **41**, 4539.

dried solid was analyzed as **2**: C, 36.12; H, 4.28; N, 2.90 %. Found: C, 36.16; H, 4.44; N, 2.80 %. Selected IR data (ATR): *ν*= 2930 (m), 2914 (m), 1628 (s), 1591 (m), 1541 (m), 1467 (m), 1440 (m), 1360 (m), 1301 (mb), 1198 (m), 1148 (m), 1134 (w), 1062 (m), 990 (m), 900 (m), 843 (m), 822 (w), 751 (s), 600 (m), 583 (w), 505 (w).

$[Dy_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot 6MeOH$ (3·6MeOH): This complex was prepared in the same manner as complex **1** but using $Dy(ClO_4)_3\cdot 6H_2O$ (0.11 g, 0.2 mmol) as the Ln salt. After ~10 days, pale yellow plate-like crystals of **3**·6MeOH had appeared and were collected by filtration, washed with cold MeOH (2 x 2 mL) and dried in air. The yield was 35 %. The air-dried solid was analyzed as **3**: C, 35.81; H, 4.25; N, 2.88 %. Found: C, 36.12; H, 4.56; N, 2.72 %. Selected IR data (ATR): *ν*= 2928 (m), 2911 (m), 1631 (s), 1590 (m), 1544 (m), 1472 (m), 1444 (m), 1361 (m), 1299 (mb), 1203 (m), 1152 (m), 1130 (w), 1060 (m), 998 (m), 905 (m), 840 (m), 825 (w), 750 (s), 601 (m), 589 (w), 504 (w).

Single-crystal X-ray diffraction studies. Single-crystals of the complexes $[Ln_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot n(MeOH)$ ($Ln^{3+} = Gd^{3+}$ and $n = 11$ for complex **1**; $Ln^{3+} = Tb^{3+}$ and $n = 3$ for **2**; $Ln^{3+} = Dy^{3+}$ and $n = 6$ for **3**) were manually harvested and mounted on cryoloops using inert oil.[3] Diffraction data were collected 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[4] (Mo K_α graphite-monochromated radiation, $\lambda = 0.71073$ Å), and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely with the software interface Cryopad.[5] Images were processed with the software SAINT+,[6] and absorption effects corrected with the multi-scan method implemented in SADABS.[7] The structures were solved by direct methods employed in SHELXS-97,[8,9] allowing the immediate location of the Ln atoms. The remaining non-H-atoms of the complexes were located from difference Fourier maps calculated by successive full-matrix least-squares refinement cycles on F^2 using SHELXL-97,[9,10]

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

[4] APEX2, *Data Collection Software Version 2.1-RC13, Bruker AXS, Delft, The Netherlands*, 2006.

[5] Cryopad, *Remote monitoring and control, Version 1.451, Oxford Cryosystems, Oxford, United Kingdom*, 2006.

[6] SAINT+, *Data Integration Engine v. 7.23a* ©, 1997-2005, Bruker AXS, Madison, Wisconsin, USA.

[7] G. M. Sheldrick, *SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program*, 1998, Bruker AXS, Madison, Wisconsin, USA.

[8] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution, University of Göttingen*, 1997.

[9] G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.

and have been successfully refined with anisotropic displacement parameters, while the MeOH solvent molecules were refined with isotropic parameters.

The H-atoms attached to C-atoms of the ligands were placed at their geometrical positions using appropriate *HFIX* instructions in SHELXL and incorporated in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at 1.2 or 1.5 × U_{eq} of the parent C-atom. Furthermore, the H-atoms of the coordinated OH- and MeOH-groups were clearly visible in the difference Fourier maps, and included in subsequent refinement stages with the O–H distances restrained to 0.92(2) Å, using a riding-motion approximation with an isotropic thermal displacement parameter fixed at 1.5 × U_{eq} of the respective O-atom. Besides the identification and successful refinement of several crystallization MeOH solvate molecules in all structures, the spaces originated by the close packing of complexes also contained some electron density, mainly due to disordered solvent molecules, which was not possible to modulate and refine properly (particularly in the structures of complexes **1** and **3**). Searches for the total potential solvent area using the software package *PLATON*[11,12] revealed the existence of cavities with a potential solvent accessible voids in both the structures of **1** and **3**. The original data sets were then treated with the *SQUEEZE*[13] to remove the contribution of these disordered molecules in the solvent-accessible volume, and the calculated solvent-free reflection lists were consequently utilized for the final structures refinements.

Crystal data for $[Gd_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot 11(MeOH)$ (**1**·11MeOH): $C_{98}H_{164}Gd_7N_6O_{44}$, $M = 3231.10$, hexagonal, $P6_3/m$, $a = b = 17.237(2)$ Å, $c = 25.135(4)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 6467.6(16)$ Å^3, $T = 150.0(2)$ K, $Z = 2$, $\mu = 3.614$ mm^{-1}, $\rho_c = 1.659$ g cm^{-3}, pale yellow rod-like crystal with $0.44 \times 0.12 \times 0.12$ mm^3; 83384 reflections measured with 5046 being independent ($R_{int} = 0.0418$); the final R_1 and $wR(F^2)$ values were 0.0334 [$I > 2\sigma(I)$] and 0.0780 (all data), respectively; data completeness to $\theta = 27.48^\circ$, 99.3%; CCDC-991355.

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[10] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen*, 1997.

[11] A. L. Spek, *Acta Cryst. A*, 1990, **46**, C34.

[12] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

[13] P. van der Sluis and A. L. Spek, *Acta Cryst. A*, 1990, **46**, 194-201.

Crystal data for $[Tb_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot 3(MeOH)$ (**2**·3MeOH): $C_{90}H_{132}Tb_7N_6O_{36}$, $M = 2986.46$, hexagonal, $P6_3/m$, $a = b = 15.7469(9)$ Å, $c = 27.7469(3)$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$, $V = 5977.5(8)$ Å^3, $T = 150.0(2)$ K, $Z = 2$, $\mu = 4.156$ mm^{-1}, $\rho_c = 1.659$ g cm^{-3}, pale yellow block-like crystal with $0.10 \times 0.08 \times 0.06$ mm^3; 64198 reflections measured with 3555 being independent ($R_{int} = 0.0517$); the final R_1 and $wR(F^2)$ values were 0.0893 [$I > 2\sigma(I)$] and 0.2228 (all data), respectively; data completeness to $\theta = 25.03°$, 99.4%; CCDC-991356.

Crystal data for $[Dy_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]\cdot 6(MeOH)$ (**3**·6MeOH): $C_{93}H_{144}Dy_7N_6O_{39}$, $M = 3107.64$, hexagonal, $P6_3/m$, $a = b = 15.5912(7)$ Å, $c = 28.0106(13)$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$, $V = 5896.7(5)$ Å^3, $T = 150.0(2)$ K, $Z = 2$, $\mu = 4.455$ mm^{-1}, $\rho_c = 1.750$ g cm^{-3}, pale yellow plate-like crystal with $0.10 \times 0.05 \times 0.03$ mm^3; 61297 reflections measured with 3537 being independent ($R_{int} = 0.0388$); the final R_1 and $wR(F^2)$ values were 0.0726 [$I > 2\sigma(I)$] and 0.01554 (all data), respectively; data completeness to $\theta = 25.02°$, 99.4%; CCDC-991357.

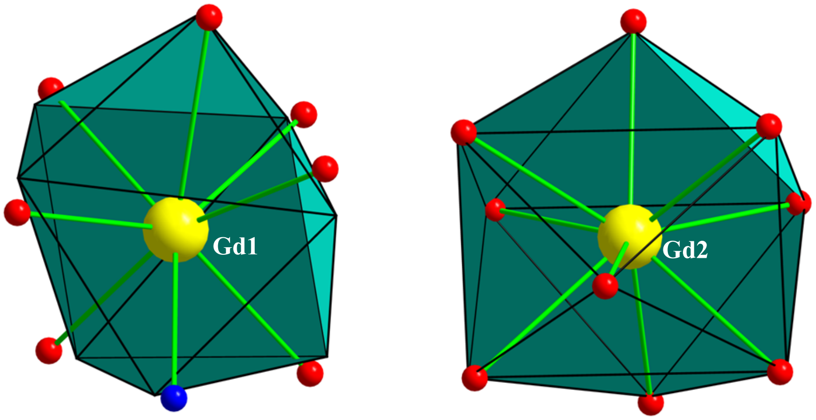

Fig. S1. Triangular dodecahedral (Gd1) and spherical tricapped trigonal prismatic (Gd2) geometries of the gadolinium atoms in the structure of **1**. The points connected by the black lines define the vertices of the ideal polyhedron. Note that in order to estimate the closer coordination polyhedra defined by the donor atoms around all Gd atoms in **1**, a comparison of the experimental structural data with the theoretical data for the most common polyhedral structures with 8 and 9 vertices was performed by means of the program SHAPE.[14]

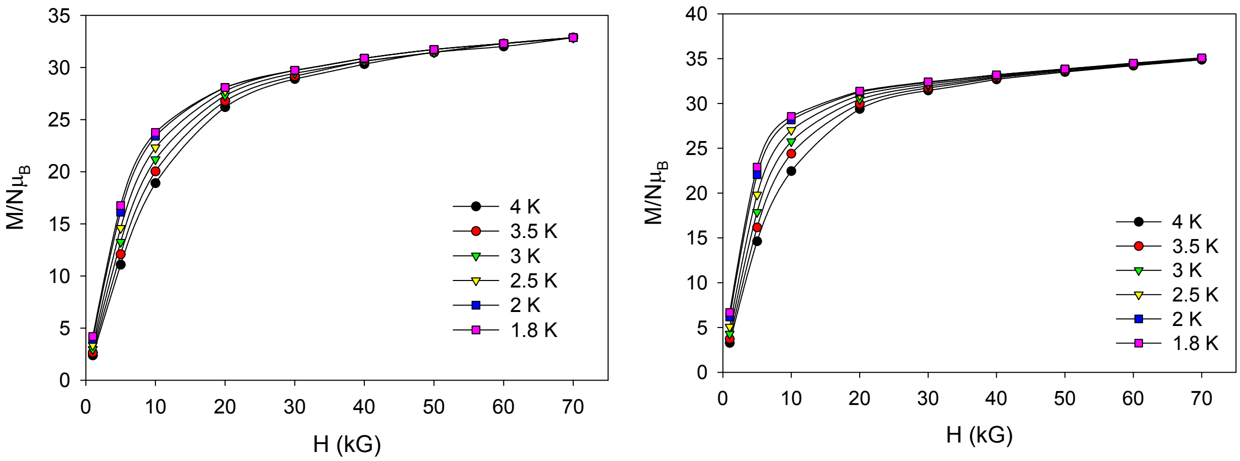

Fig. S2. Plots of magnetization (*M*) *vs* field (*H*) for complexes **2** (left) and **3** (right) at different low temperatures.

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[14] S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, *Coord. Chem. Rev.*, 2005, **249**, 1693.

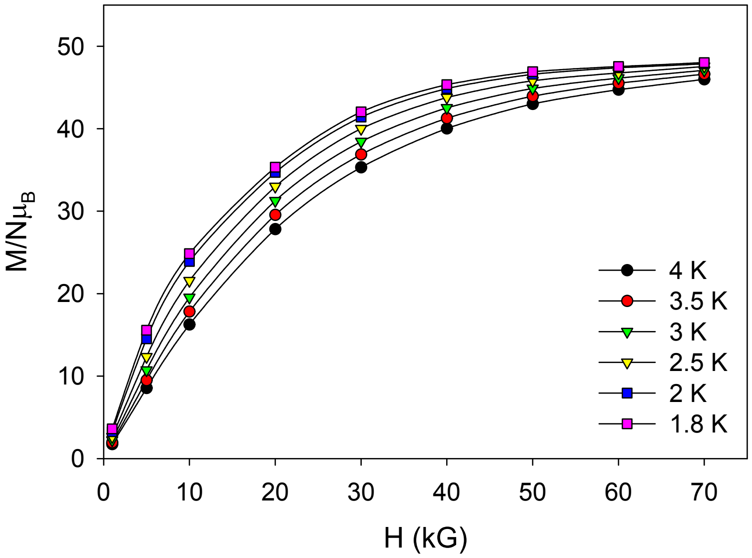

Fig. S3. Plot of magnetization (*M*) *vs* field (*H*) for complex **1** at different low temperatures.

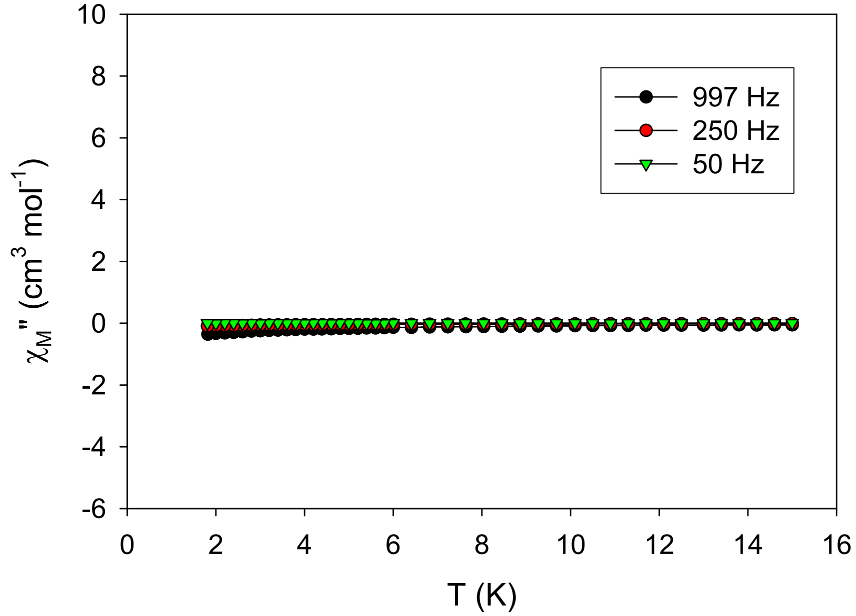

Fig. S4. The out-of-phase (χ''_M) *vs* *T* ac susceptibility signals for **2** in a 3.5 G field oscillating at the indicated frequencies.

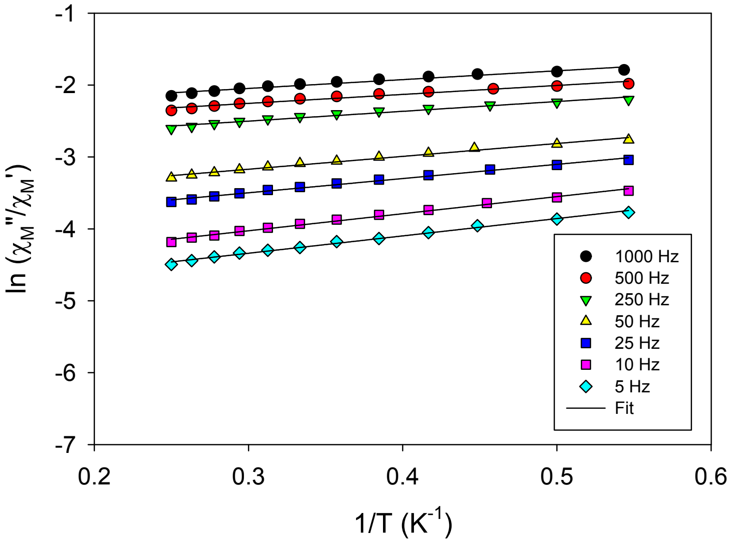

Fig. S5. Plots of $\ln(\chi''/\chi')$ *vs* $1/T$ for **3** at different frequencies of the 3.5 G oscillating ac field. The solid lines are the best-fit curves; see the text for the fit parameters.

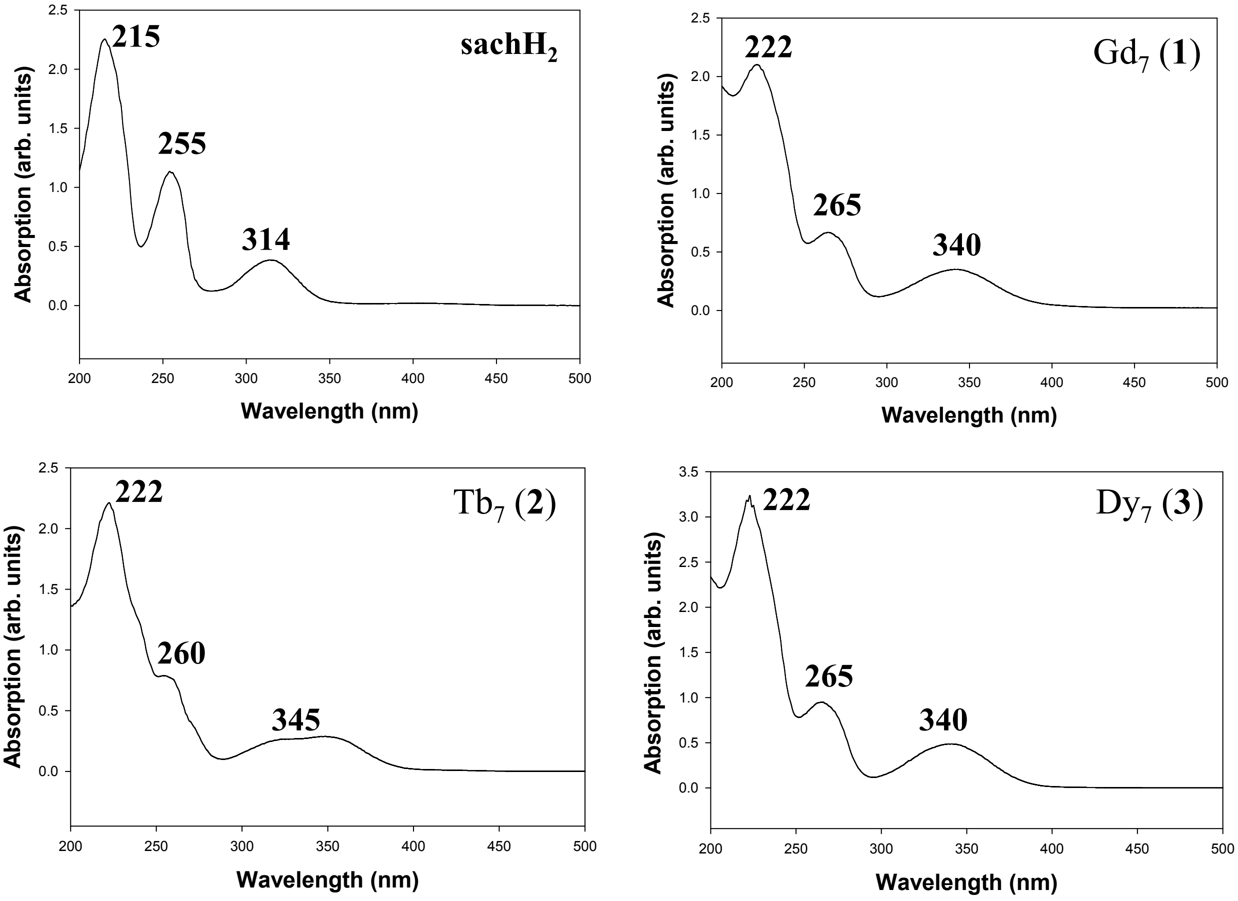

Fig. S6. Absorption spectra of the free ligand sachH$_2$ and complexes **1-3** in MeCN ($\sim10^{-5}$ M).

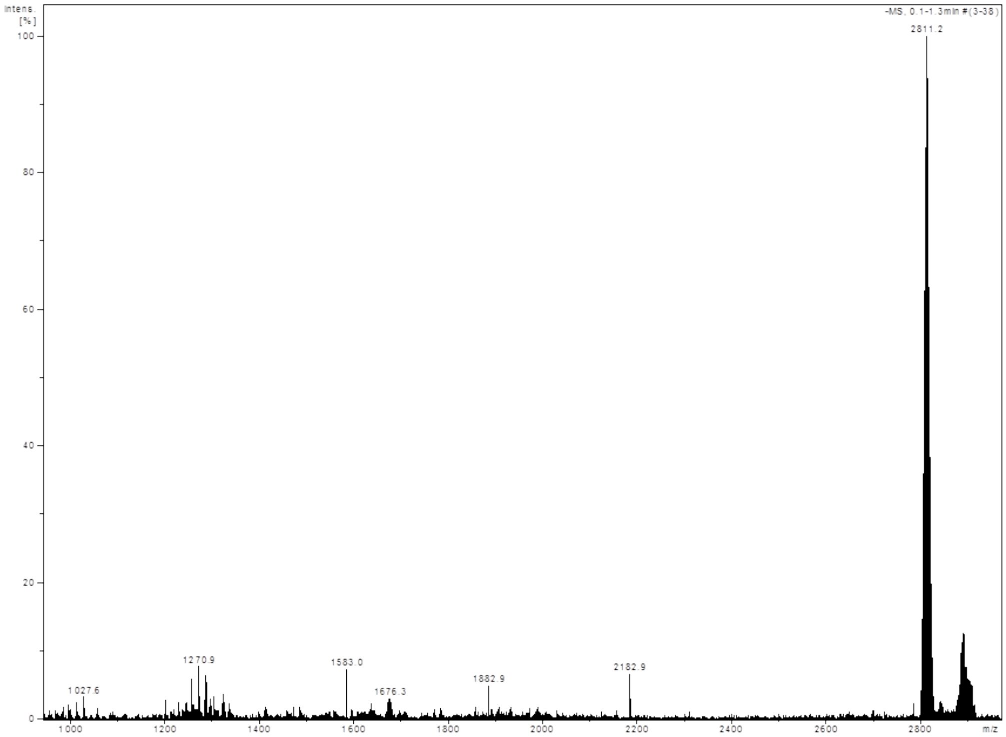

Fig. S7. Negative ion mass spectrum of **1** shown in the 1000 to 3000 m/z range.

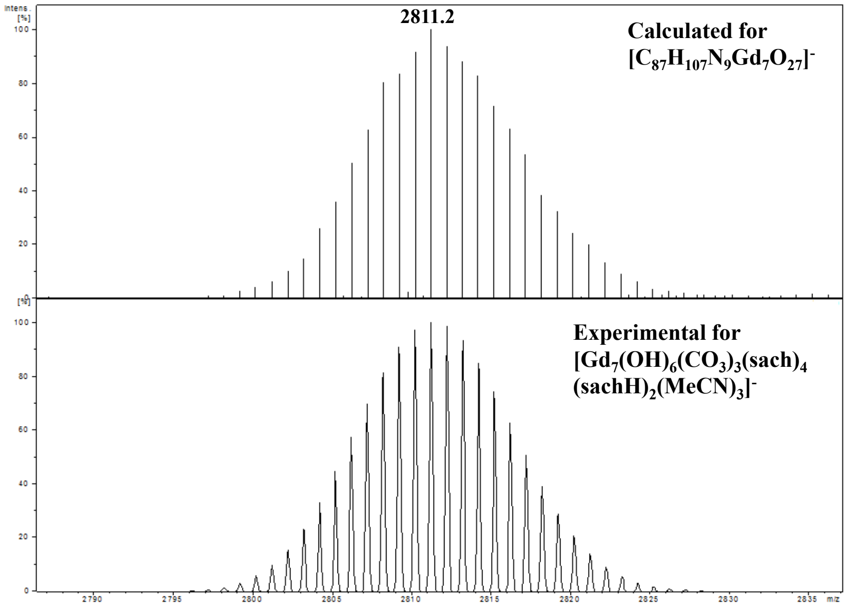

Fig. S8. Comparison of the theoretical (top) and experimental (bottom) isotopic patterns of complex **1** under negative ion ES-MS.

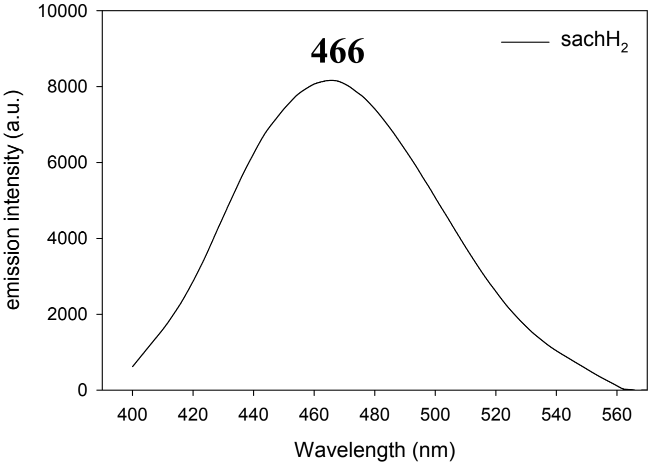

Fig. S9. Emission spectrum of sachH_2 (excitation at 310 nm; MeCN solution 10^{-5} M).