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# ELECTRONIC SUPPORTING INFORMATION

## Tetranuclear lanthanide-based silsesquioxanes: towards a combination of a slow relaxation of the magnetization and a luminescent thermometry

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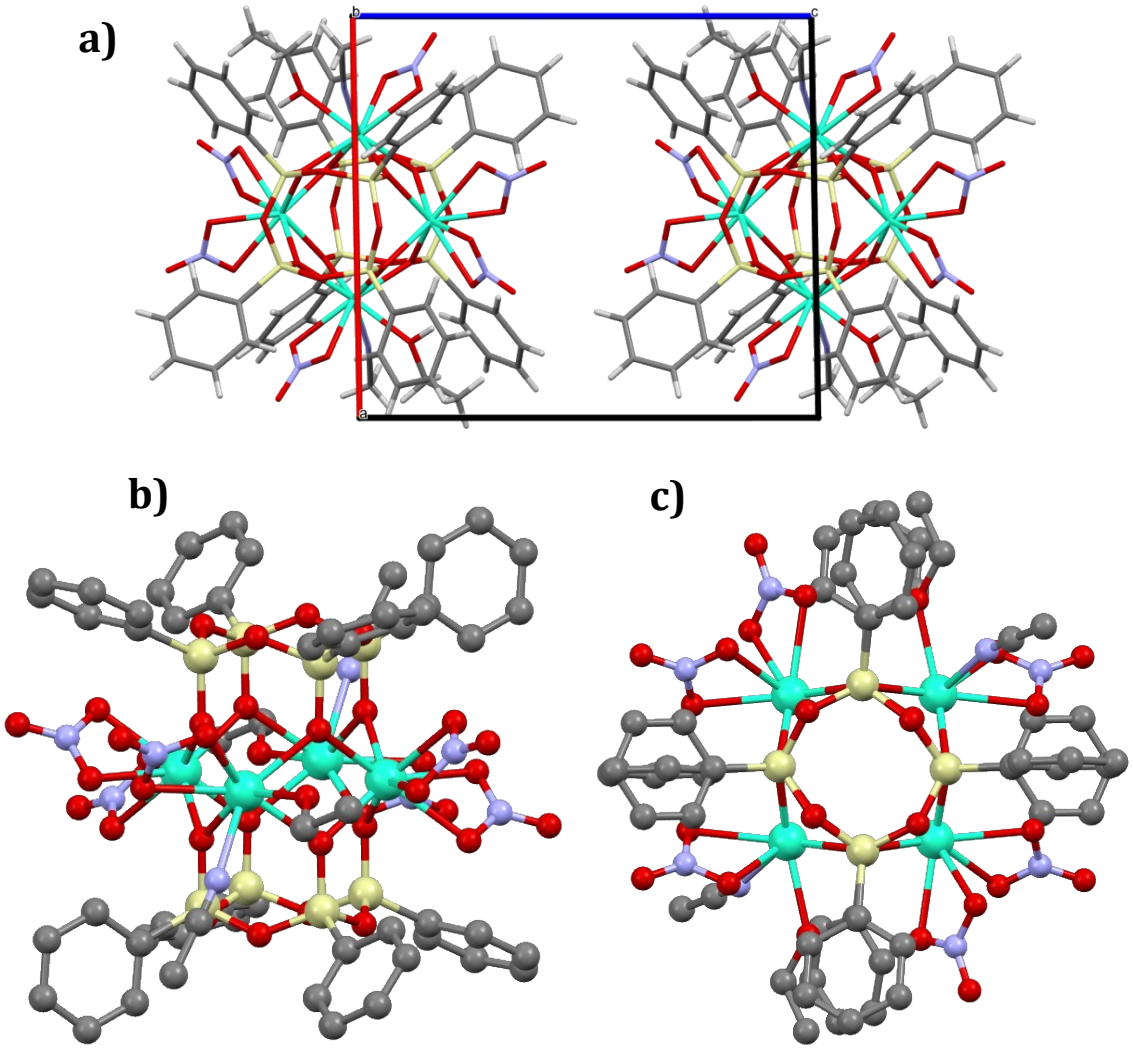


**Figure S1.** a) Perspective view of the crystal packing for **2** along the crystallographic axis *b*; b) and c) Molecular structure of **2** showing the prism-like polyhedron in the form of a new year paper lantern. Colour code: light green Dy/Tb; light yellow Si; red O; blue N; grey C. Hydrogen atoms and crystallized acetonitrile molecules have been omitted for clarity.

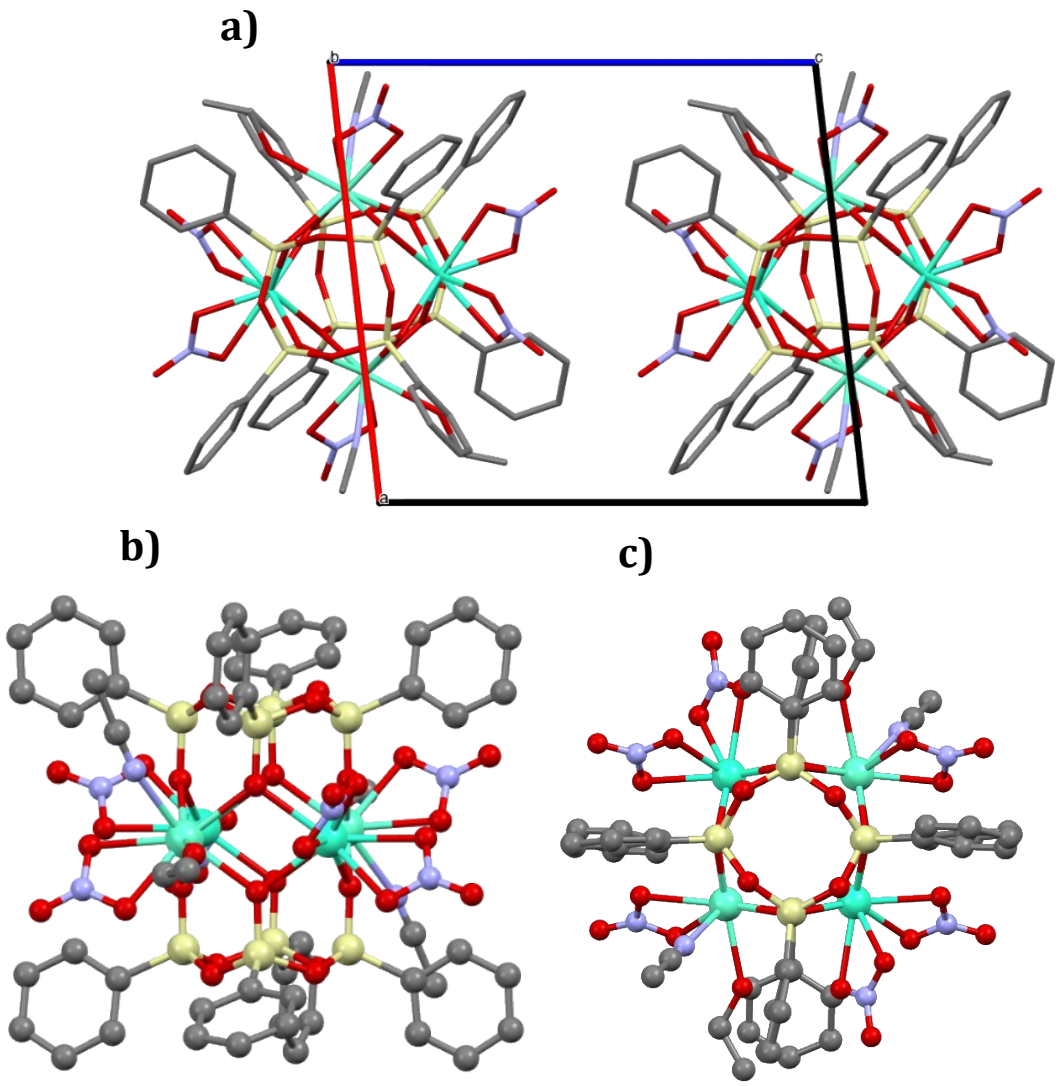


**Figure S2.** a) Perspective view of the crystal packing for **3** along the crystallographic axis *b*; b) and c) Molecular structure of **3** showing the prism-like polyhedron in the form of a new year paper lantern. colour code: light green Eu/Tb/Y; light yellow Si; red O; blue N; grey C. Hydrogen atoms and crystallized acetonitrile molecules have been omitted for clarity.

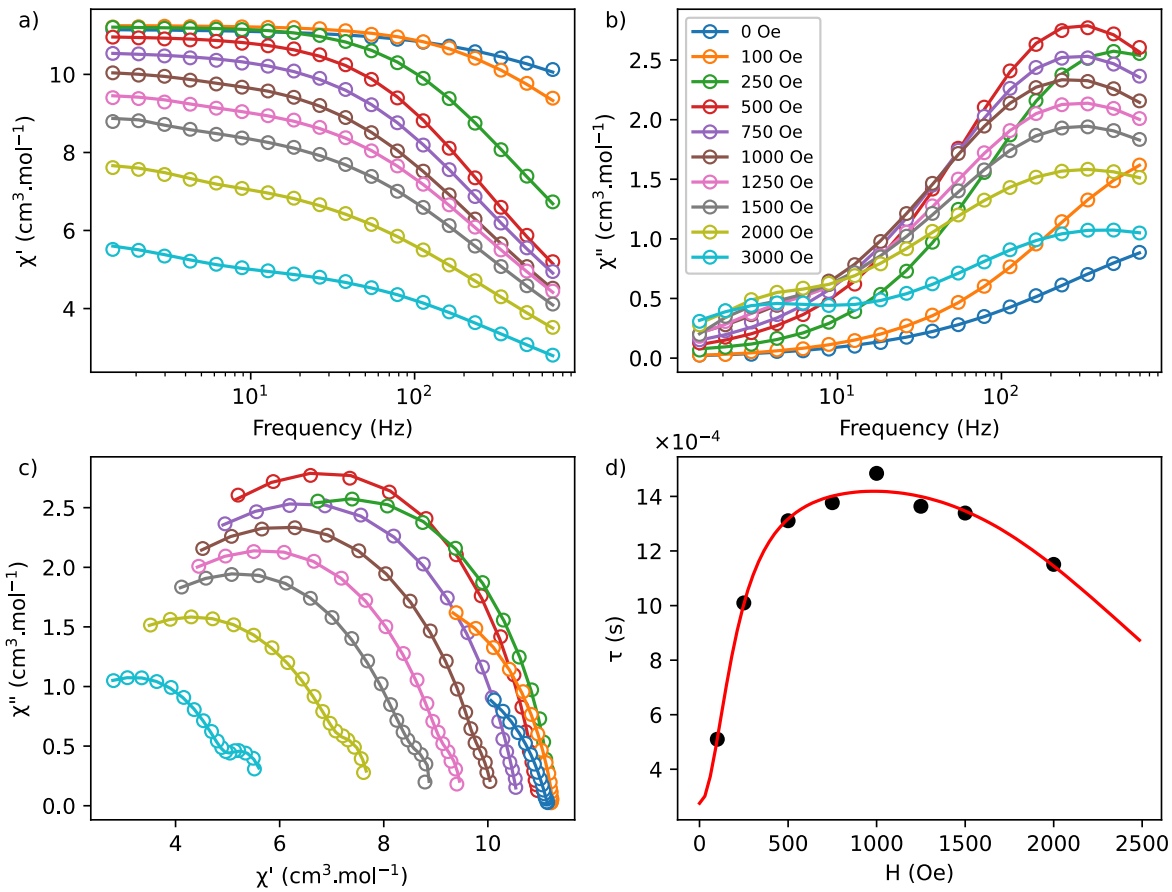


**Figure S3.** In-phase, $\chi'$, (a) and out-of-phase, $\chi''$, (b) components of the ac magnetic susceptibility as a function of frequency at different magnetic fields measured for **1**; c) Cole-Cole (Argand) plots obtained using the field dependence of the ac susceptibility data for **1.** The solid lines correspond to the best fit obtained with a generalized Debye model; d) Field dependence of the relaxation time for **1** at 1.8 K. The red solid line represents the fits done by using the equation (2).

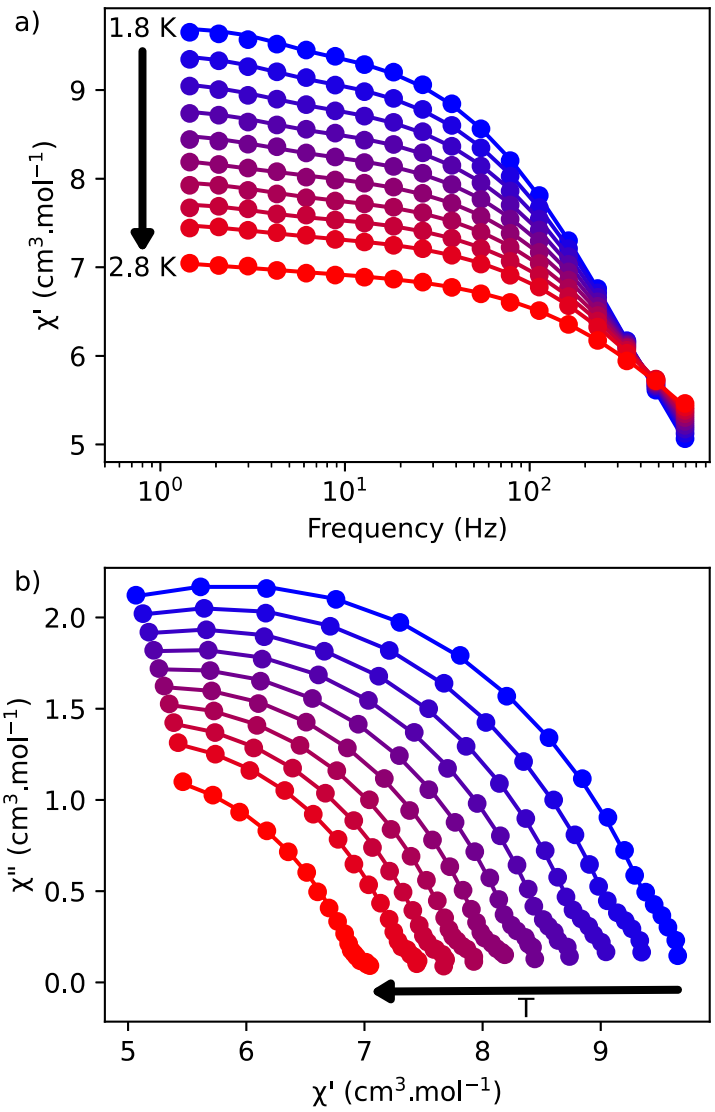


**Figure S4.** a) In phase, $\chi'$, component of the ac magnetic susceptibility as a function of frequency at different temperatures measured under an optimal dc field of 1000 Oe for **1**; b) Cole-Cole (Argand) plots obtained using the ac susceptibility data for **1** under an optimal magnetic field of 1000 Oe. The solid lines correspond to the best fit obtained with a generalized Debye model.

**Table S1:** Crystal data, data collection and structure refinement details for **1**-**3**.

| Identification code | **1** • 4MeCN | **2** • 4MeCN | **3** • *4MeCN$_{sq}$* |
|---|---|---|---|
| Empirical formula | $C_{80}H_{110}DyEu_3N_{14}O_{36}Si_8$ | $C_{80}H_{110}Dy_3N_{14}O_{36}Si_8Tb$ | $C_{80}H_{110}EuN_{14}O_{36}Si_8TbY_2$ |
| Formula weight | 2686.95 | 2714.97 | 2557.23 |
| Crystal size, mm | 0.15×0.13×0.12 | 0.18×0.15×0.15 | 0.09×0.09×0.06 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | *P*-1 | *P*-1 | *P*-1 |
| *a*, Å | 13.27830(13) | 13.2584(2) | 12.8840(2) |
| *b*, Å | 13.34642(15) | 13.3275(2) | 13.9471(2) |
| *c*, Å | 16.09392(18) | 16.0668(2) | 15.3005(2) |
| $\alpha$, deg. | 68.0627(10) | 68.1098(15) | 67.2399(15) |
| $\beta$, deg. | 85.3464(9) | 85.3999(14) | 82.6403(13) |
| $\gamma$, deg. | 80.1123(9) | 80.1109(15) | 86.2713(13) |
| *V*, Å$^3$ | 2605.87(5) | 2594.78(7) | 2514.08(7) |
| *Z* | 1 | 1 | 1 |
| Density (calc.), g/cm$^3$ | 1.712 | 1.737 | 1.689 |
| Absorption coefficient, mm$^{-1}$ | 2.668 | 2.987 | 2.638 |
| *F*(000) | 1343 | 1351 | 1294 |
| Theta range, deg. | 2.051-35.300 | 2.055-35.427 | 2.190-35.386 |
| Index ranges | -21 ≤ h ≤ 20,<br>-21 ≤ k ≤ 21,<br>-26 ≤ l ≤ 25 | -19 ≤ h ≤ 21,<br>-21 ≤ k ≤ 21,<br>-25 ≤ l ≤ 26 | -19 ≤ h ≤ 20,<br>-22 ≤ k ≤ 21,<br>-24 ≤ l ≤ 23 |
| Reflections collected | 99913 | 97988 | 66219 |
| Independent reflections, $R_{int}$ | 21545, 0.0477 | 21453, 0.0611 | 20143, 0.1160 |
| Reflections with $I > 2\sigma(I)$ | 17201 | 17586 | 12723 |
| Parameters refined | 713 | 758 | 544 |
| Goodness-of-fit on $F^2$ | 1.040 | 1.031 | 1.030 |
| $R_1$ / w$R_2$ for $I > 2\sigma(I)$ | 0.0282 / 0.0615 | 0.0354 / 0.0821 | 0.0883 / 0.1886 |
| $R_1$ / w$R_2$ for all data | 0.0439 / 0.0656 | 0.0491 / 0.0891 | 0.1274 / 0.2038 |
| $T_{max}$, $T_{min}$ | 0.696, 0.633 | 0.632, 0.523 | 0.844, 0.752 |
| $\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å$^{-3}$ | 1.580 / -1.583 | 2.749 / -2.495 | 2.758 / -2.895 |

**Table S2:** Main structural parameters for **1**-**3**.

| Sample | Ln-O distance, Å | Ln-N distance, Å | Ln-Ln distance, Å | ∠ O-Ln-O, ° |
|---|---|---|---|---|
| **1** | Ln-O(Ln): 2.310(9)-2.356(9);<br>Ln-$NO_3$: 2.436(4)-2.563(3);<br>Ln-EtOH: 2.460(3), 2.468(8) | 2.551(4), 2.554(10) | 3.726(3)-3.777(3) | (Ln)O-Ln-O(Ln):<br>70.99(9)-81.46(12);<br>$NO_3$: 50.66(15)-51.52(8) |
| **2** | Ln-O(Ln): 2.243(8)-2.376(8);<br>Ln-$NO_3$: 2.380(10)-2.567(8);<br>Ln-EtOH: 2.394(8), 2.456(3) | 2.524(4), 2.527(12) | 3.648(2)-3.742(2) | (Ln)O-Ln-O(Ln):<br>70.98(10)-83.4(2)<br>$NO_3$: 50.26(15)-52.13(8) |
| **3** | Ln-O(Ln): 2.289(4)-2.356(4);<br>Ln-$NO_3$: 2.453(5)-2.534(6);<br>Ln-EtOH: 2.442(5), 2.477(6) | 2.486(6), 2.520(7) | 3.646(5)-3.718(4) | (Ln)O-Ln-O(Ln):<br>72.04(14)-83.11(16)<br>$NO_3$: 51.0(2)-52.70(18) |

**Table S3:** Main parameters for **1-3** regarding their magnetic properties.

| Sample | Experimental $\chi T$ values, $cm^3.K.mol^{-1}$ | Calculated $\chi T$ values, $cm^3.K.mol^{-1}$ | Calculated $\chi T$ values for $Ln^{3+}$ | Magnetization values at 7 kOe, *Nb* |
|---|---|---|---|---|
| **1** | 14.2 $cm^3.K.mol^{-1}$ | $Eu_{3.08}Dy_{0.92}$ 13.03 $cm^3.K.mol^{-1}$ | $Dy^{3+}$ ($J$=15/2, $g$ = 4/3): 14.17 $cm^3.K.mol^{-1}$ $Eu^{3+}$ is diamagnetic | 8.8 |
| **2** | 53.9 $cm^3.K.mol^{-1}$ | $Dy_{3.18}Tb_{0.82}$ 54.74 $cm^3.K.mol^{-1}$ | $Dy^{3+}$ ($J$=15/2, $g$ = 4/3): 14.17 $cm^3.K.mol^{-1}$ $Tb^{3+}$ ($^7F_6$, S = 3, L = 3, g = 3/2): $\chi T$ = 11.82 $cm^3.K.mol^{-1}$ | 29.1 |
| **3** | 11.9 $cm^3.K.mol^{-1}$ | $Y_{2.11}Eu_{0.87}Tb_{1.01}$ 11.93 $cm^3.K.mol^{-1}$ | $Tb^{3+}$ ($^7F_6$, S = 3, L = 3, g = 3/2): $\chi T$ = 11.82 $cm^3.K.mol^{-1}$ $Eu^{3+}$ is diamagnetic | 6.8 |