*ESI*

# Pentanuclear [2.2] Spirocyclic Lanthanide(III) Complexes: Slow Magnetic Relaxation of the $Dy^{III}$ Analogue

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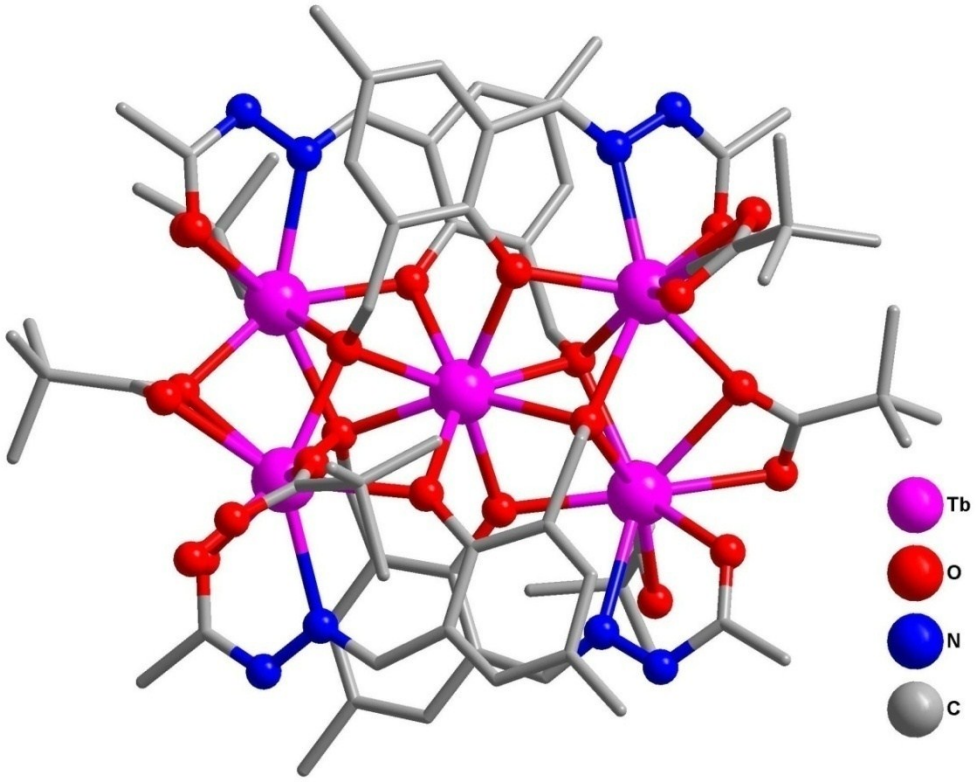


**Figure S1.** Molecular Structure of **2**(selected hydrogen atoms, chloride and the solvent molecules have been omitted for clarity).

**Table S1**. Selected bond distances(Å) and bond angles (deg) parameters for **2**

| **Selected bond length around Tb1** | |
|---|---|
| Tb(1)-O(8) | 2.316(8) |
| Tb(1)-O(16) | 2.320(9) |
| Tb(1)-O(18) | 2.332(9) |
| Tb(1)-O(12) | 2.352(7) |
| Tb(1)-O(9) | 2.406(8) |
| Tb(1)-O(3) | 2.447(7) |
| Tb(1)-O(17) | 2.465(8) |
| Tb(1)-N(3) | 2.488(10) |
| **Selected bond length around Tb2** | |
| Tb(2)-O(5) | 2.356(8) |
| Tb(2)-O(13) | 2.399(8) |
| Tb(2)-O(3) | 2.401(7) |
| Tb(2)-O(6) | 2.402(8) |
| Tb(2)-O(14) | 2.477(8) |
| Tb(2)-O(12) | 2.478(8) |
| Tb(2)-O(15) | 2.486(8) |
| Tb(2)-O(16) | 2.544(9) |
| Tb(2)-N(5) | 2.554(10) |
| **Selected bond length around Tb3** | |
| Tb(3)-O(4)2.323(8) | |
| Tb(3)-O(2) | 2.335(8) |
| Tb(3)-O(3) | 2.349(7) |
| Tb(3)-O(5) | 2.367(8) |
| Tb(3)-O(12) | 2.387(7) |
| Tb(3)-O(7) | 2.388(8) |
| Tb(3)-O(11) | 2.393(8) |
| Tb(3)-O(8) | 2.426(8) |
| **Selected bond length around Tb4** | |
| Tb(4)-O(21) | 2.330(9) |
| Tb(4)-O(2) | 2.383(8) |
| Tb(4)-O(1) | 2.399(9) |
| Tb(4)-O(22) | 2.407(10) |
| Tb(4)-O(7) | 2.417(9) |
| Tb(4)-O(4) | 2.504(8) |
| Tb(4)-O(23) | 2.507(11) |
| Tb(4)-N(7) | 2.510(10) |
| Tb(4)-O(20) | 2.656(12) |
| **Selected bond length around Tb5** | |
| Tb(5)-O(20) | 2.290(11) |
| Tb(5)-O(11) | 2.309(8) |
| Tb(5)-O(24) | 2.370(9) |
| Tb(5)-O(19) | 2.372(9) |
| Tb(5)-O(4) | 2.416(8) |
| Tb(5)-O(7) | 2.421(8) |
| Tb(5)-O(30) | 2.463(11) |
| Tb(5)-N(2) | 2.521(12) |
| **Selected Bond angles around Tb** | |
| Tb(3)-O(3)-Tb(2) 96.5(3)Tb(3)-O(3)-Tb(1) 94.5(3) Tb(2)-O(3)-Tb(1) 97.1(3)Tb(2)-O(5)-Tb(3) 97.3(3) Tb(1)-O(12)-Tb(2) 97.6(3)Tb(3)-O(12)-Tb(2) 93.6(3)Tb(3)-O(4)-Tb(5) 96.0(3)Tb(3)-O(4)-Tb(4) 95.3(3)Tb(5)-O(4)-Tb(4) 96.4(3) Tb(1)-O(12)-Tb(3) 96.0(3)Tb(3)-O(7)-Tb(4) 95.9(3)Tb(3)-O(7)-Tb(5) 94.2(3)Tb(4)-O(7)-Tb(5) 98.6(3) Tb(5)-O(11)-Tb(3) 97.0(3)Tb(3)-O(2)-Tb(4) 98.3(3) Tb(1)-O(16)-Tb(2) 96.6(3) Tb(5)-O(20)-Tb(4) 95.5(4)Tb(1)-O(8)-Tb(3) 95.9(3) | |

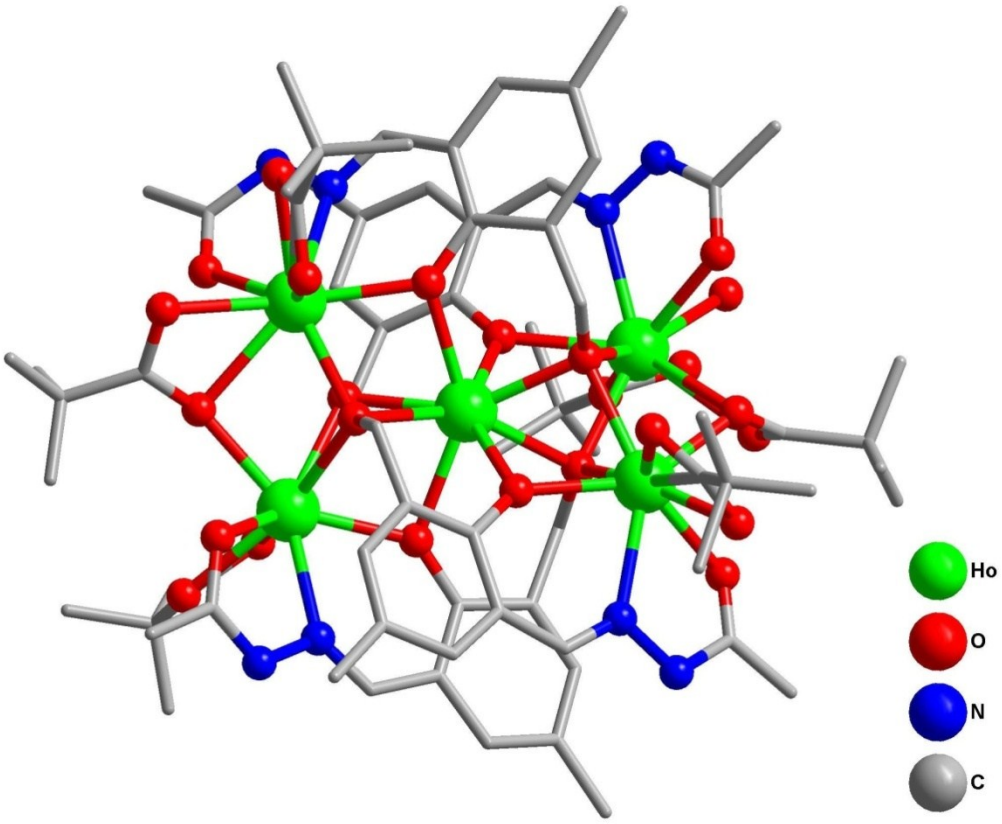


**Figure S2.** Molecular Structure of **3**,(selected hydrogen atoms, chloride and the solvent molecules have been omitted for clarity).

**Table S2**. Selected bond distances (Å) and bond angles (deg) parameters for **3.**

| **Selected bond length around Ho1** | |
|---|---|
| Ho(1)-O(20) | 2.312(10) |
| Ho(1)-O(8) | 2.332(10) |
| Ho(1)-O(7) | 2.339(11) |
| Ho(1)-O(19) | 2.361(10) |
| Ho(1)-O(4) | 2.360(10) |
| Ho(1)-O(9) | 2.356(10) |
| Ho(1)-O(2) | 2.376(11) |
| Ho(1)-O(3) | 2.417(11) |
| **Selected bond length around Ho2** | |
| Ho(2)-O(17) | 2.317(11) |
| Ho(2)-O(20) | 2.379(11) |
| Ho(2)-O(21) | 2.390(12) |
| Ho(2)-O(4) | 2.386(10) |
| Ho(2)-O(5) | 2.399(13) |
| Ho(2)-O(8) | 2.461(10) |
| Ho(2)-N(2) | 2.482(13) |
| Ho(2)-O(23) | 2.484(14) |
| Ho(2)-O(18) | 2.630(14) |
| **Selected bond length around Ho3** | |
| Ho(3)-O(12) | 2.287(12) |
| Ho(3)-O(16) | 2.289(10) |
| Ho(3)-O(3) | 2.313(10) |
| Ho(3)-O(19) | 2.326(9) |
| Ho(3)-O(24) | 2.363(11) |
| Ho(3)-O(15) | 2.394(11) |
| Ho(3)-O(7) | 2.390(10) |
| Ho(3)-N(8) | 2.457(14) |
| **Selected bond length around Ho4** | |
| Ho(4)-O(9) | 2.317(11) |
| Ho(4)-O(10) | 2.400(11) |
| Ho(4)-O(14) | 2.411(13) |
| Ho(4)-O(7) | 2.423(10) |
| Ho(4)-O(19) | 2.434(10) |
| Ho(4)-O(11) | 2.431(11) |
| Ho(4)-O(13) | 2.438(11) |
| Ho(4)-O(12) | 2.501(11) |
| Ho(4)-N(3) | 2.506(13) |
| **Selected bond length around Ho5** | |
| Ho(5)-O(18) | 2.243(11) |
| Ho(5)-O(2) | 2.269(11) |
| Ho(5)-O(22) | 2.332(11) |
| Ho(5)-O(4) | 2.376(10) |
| Ho(5)-O(1) | 2.383(11) |
| Ho(5)-O(8) | 2.397(11) |
| Ho(5)-O(31) | 2.401(13) |
| Ho(5)-N(6) | 2.450(15) |
| **Selected Bond angles around Ho** | |
| Ho(3)-O(19)-Ho(1) | 96.2(4) |
| Ho(3)-O(19)-Ho(4) | 98.4(3) |
| Ho(1)-O(19)-Ho(4) | 94.2(4) |
| Ho(4)-O(9)-Ho(1) | 97.5(4) |
| Ho(1)-O(4)-Ho(5) | 94.7(3) |
| Ho(1)-O(4)-Ho(2) | 96.7(3) |
| Ho(5)-O(4)-Ho(2) | 99.3(4) |
| Ho(1)-O(7)-Ho(3) | |
| 95.1(4)Ho(1)-O(7)-Ho(4) | |
| 95.0(4) Ho(3)-O(7)-Ho(4) | |
| 96.9(4) Ho(1)-O(8)-Ho(5) | |
| 94.9(4) Ho(1)-O(8)-Ho(2) | |
| 95.4(4) Ho(5)-O(8)-Ho(2) | |
| 96.7(4) Ho(3)-O(3)-Ho(1) | |
| 95.1(4) Ho(1)-O(20)-Ho(2) | |
| 98.2(4) Ho(5)-O(2)-Ho(1) | |
| 97.2(4) Ho(5)-O(18)-Ho(2) | |
| 96.0(5) Ho(3)-O(12)-Ho(4) | |
| 97.5(4) | |

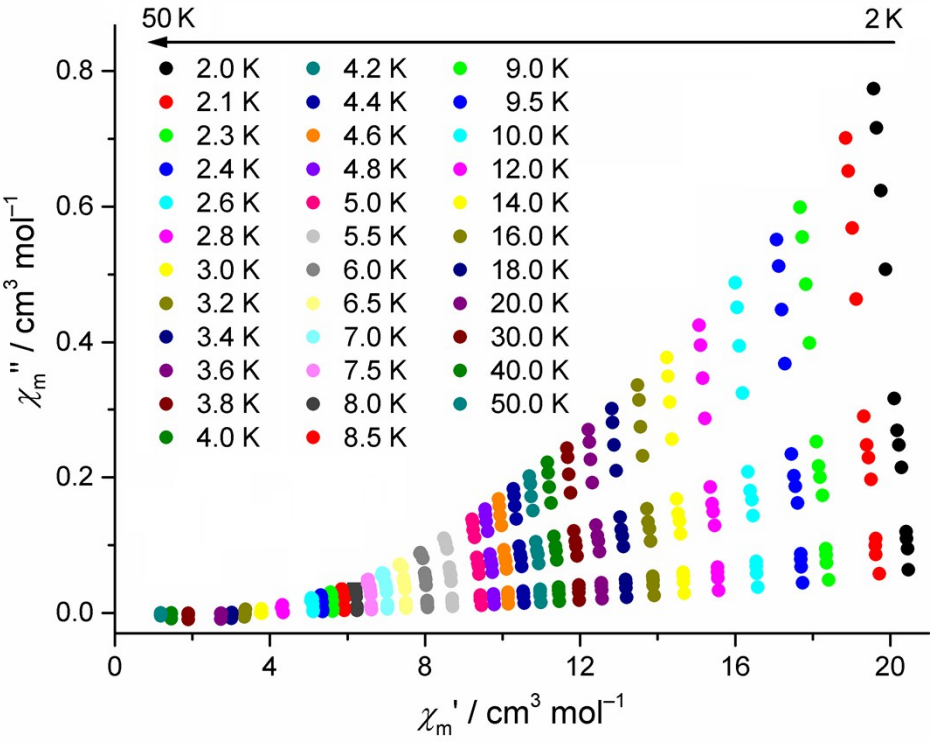


**Figure S3.** Cole-Cole plot of **1** at different temperatures and zero dc field; frequencies range from 3–1000 Hz**.**

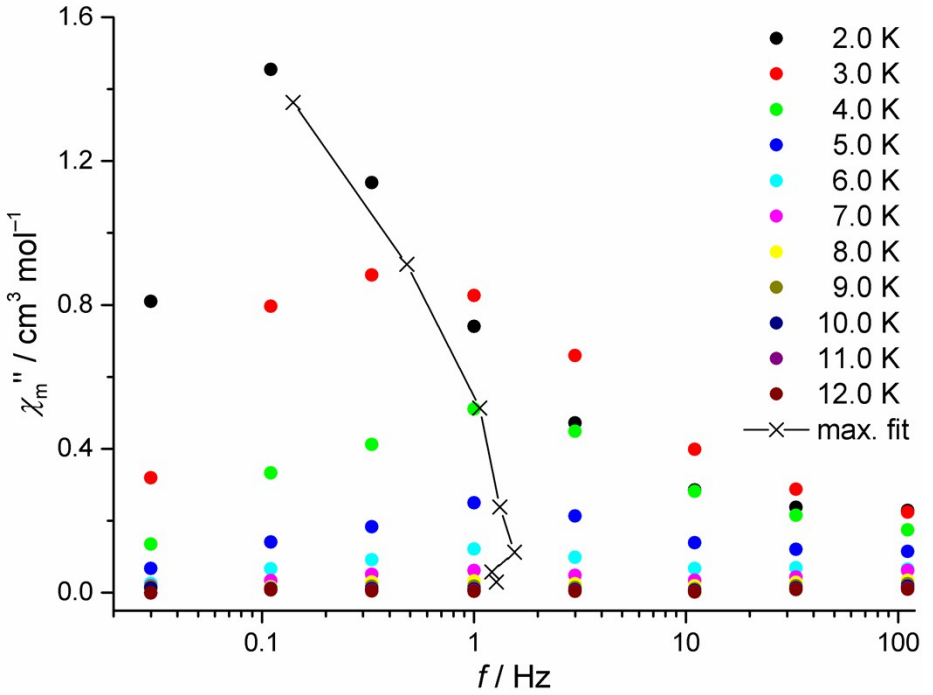


**Figure S4.** $\chi_m''$ vs. $f$ of **1** at different temperatures $T$ at 3000 G dc field; X indicate the maxima according to the fit to the Cole-Cole expression.

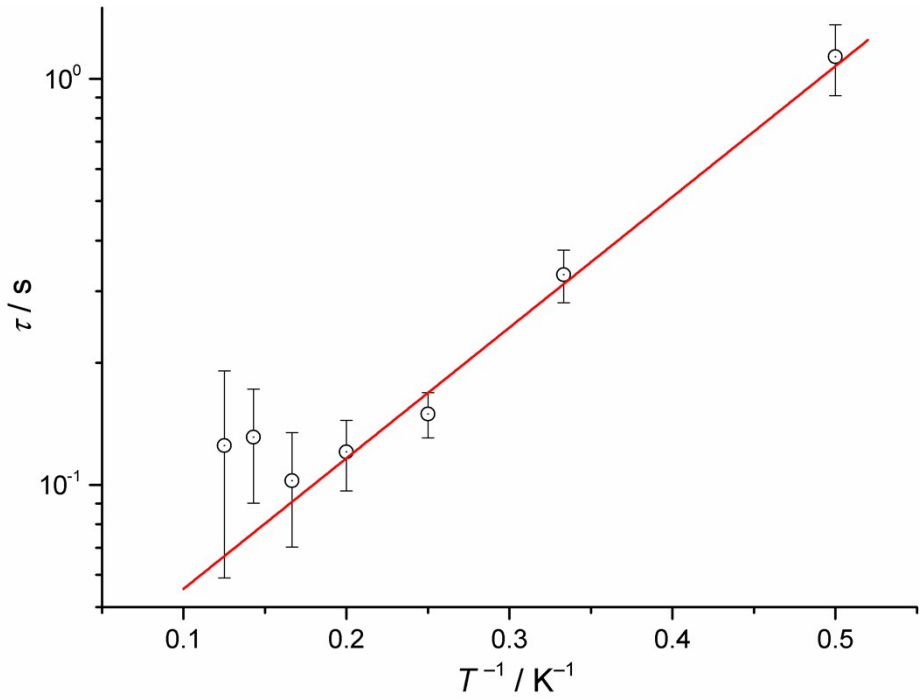


**Figure S5.** $\tau$ vs. $T^{-1}$ of **1** at 3000 G dc field: Cole-Cole equation parameters determined from Cole-Cole plot (open circles), fit to Arrhenius expression $\tau = \tau_0' \cdot \exp(\Delta U/k_B T)$ (solid line).

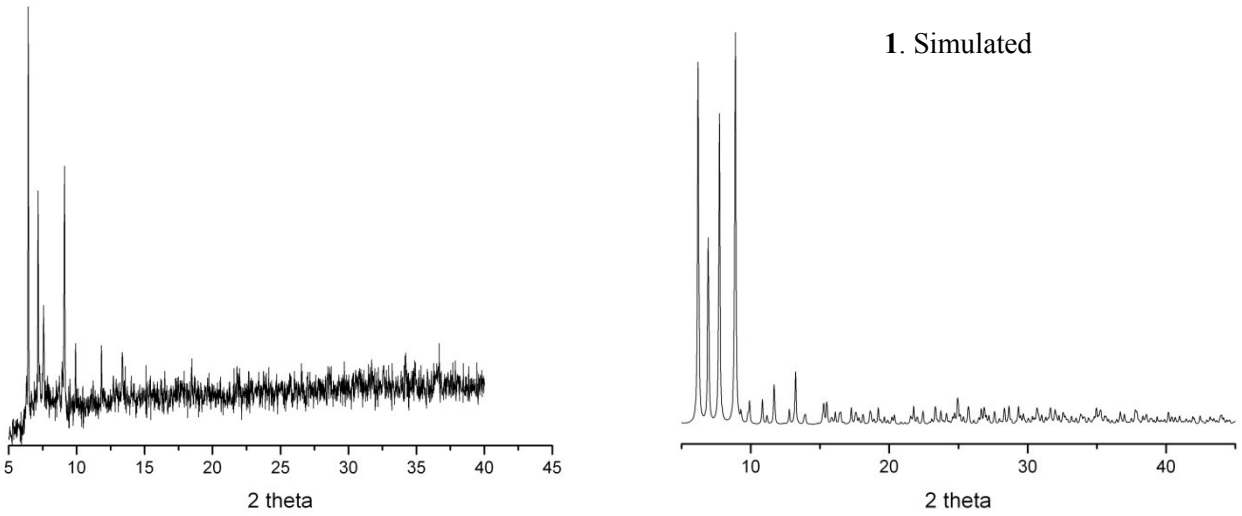


**Figure S6.** PXRD pattern for **1**.

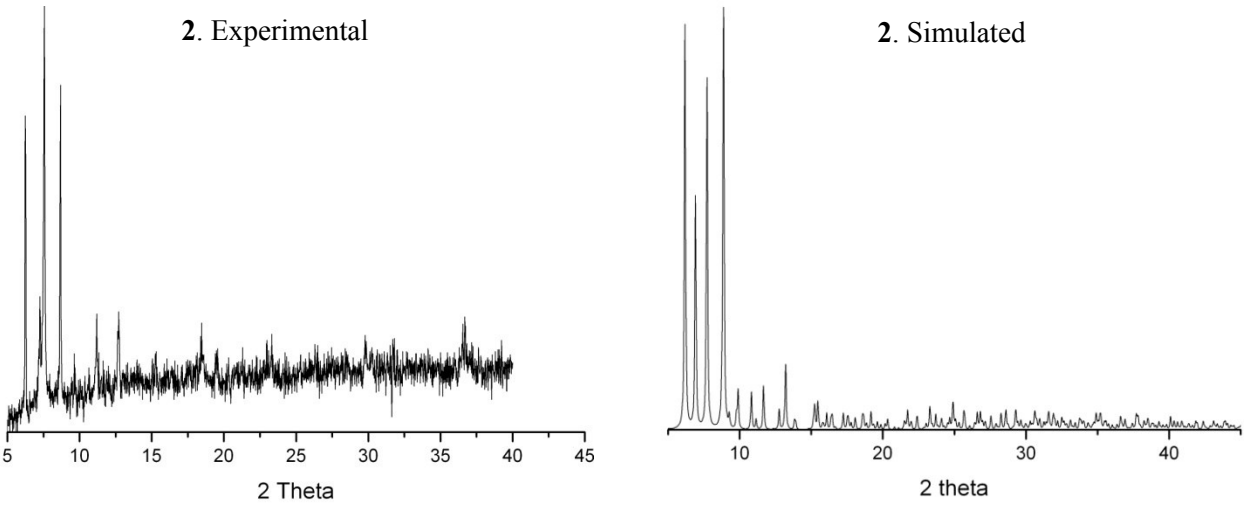


**Figure S7.** PXRD pattern for **2**.

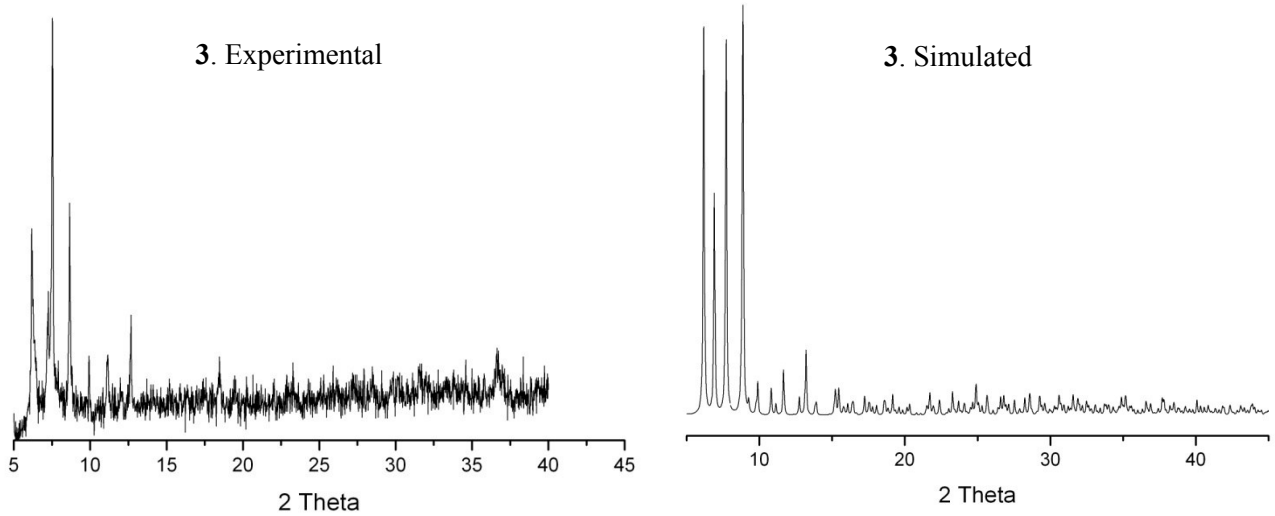


**Figure S8.** PXRD pattern for **3.**

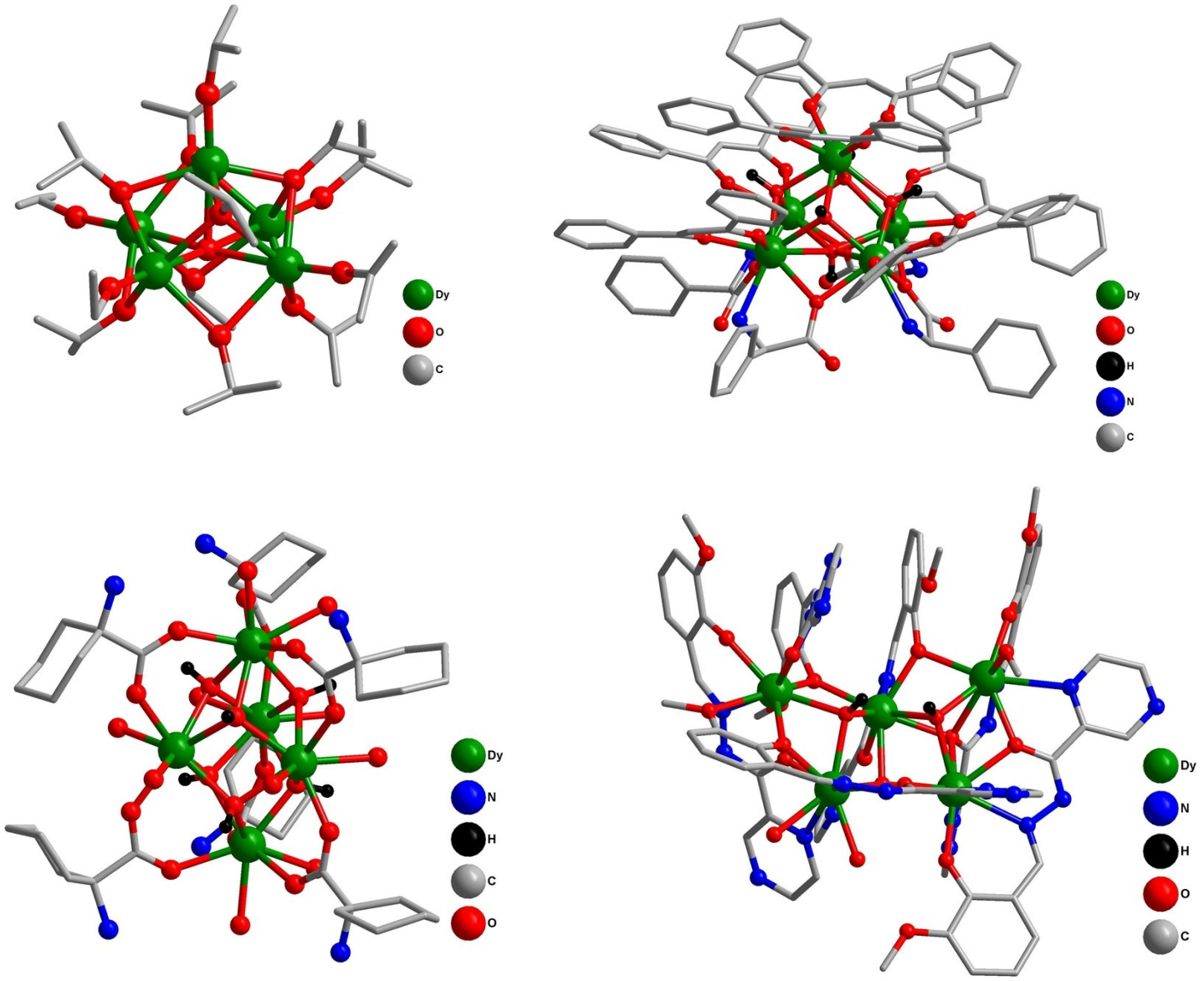


**Figure S9**. Examples of reported discrete pentanuclear lanthanide complexes.

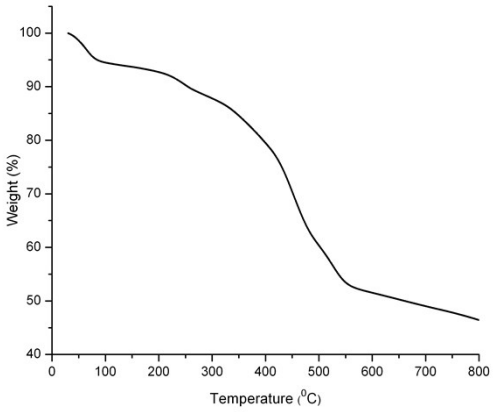


**Figure S10.** TGA curve of complex **1**.

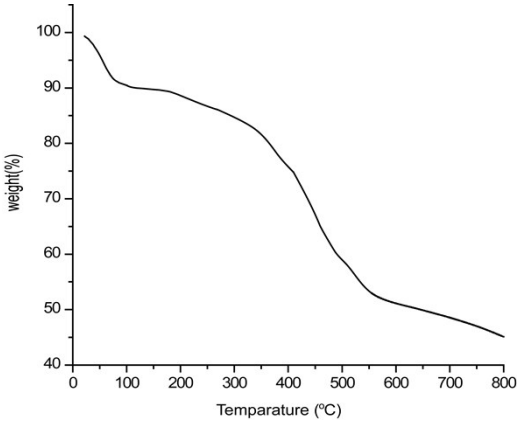


**Figure S11.** TGA curve of complex **2**.

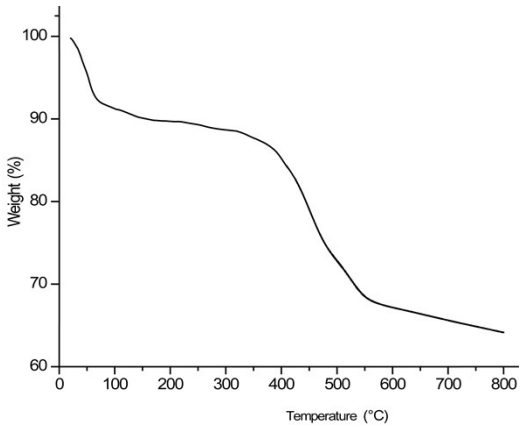


**Figure S12.** TGA curve of complex **3**.