

Supporting Information

Field-Dependent ^1H Relaxometry as a General Probe of Hydration Dynamics in Paramagnetic Ln^{3+} Complexes

Marco Ricci,^a Lorenzo Risolo,^a Fabio Carniato^{a,b}, Daniela Lalli,^{a,b}, Carlos Platas-Iglesias,^c Mauro Botta^{a,b}

^a *Dipartimento di Scienze e Innovazione Tecnologica Università del Piemonte Orientale, Viale T. Michel 11,
Alessandria 15121, Italy.*

^b *Magnetic Resonance Platform (PRISMA-UPO), Università del Piemonte Orientale, Alessandria, Italy*

^c *Centro Interdisciplinar de Química e Bioloxía (CICA) and Departamento de Química, Facultade de
Ciencias Universidade da Coruña, 15071 A Coruña, Galicia, Spain*

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Data treatment

The presence of a paramagnetic complex in solution causes an increase in the longitudinal (R_1) and transverse (R_2) magnetic relaxation rates of the proton nuclei of the water molecules. The observed relaxation rate (R_i^{obs}) is usually expressed as a sum of the diamagnetic (R_i^d) and paramagnetic (R_i^p) contributions:

$$R_i^{obs} = R_i^d + R_i^p \quad \text{with } i = 1,2 \quad (S1)$$

In the absence of solute-solute interactions, the solvent relaxation rates are linearly dependent on the concentration of the paramagnetic species ($[M]$).¹

$$R_i^{obs} = R_i^d + r_i[M] \quad (S2)$$

The angular coefficient of the linear equation (S2) is known as relaxivity (r_i). It is defined as the increase in the relaxation rate of water protons in the presence of a 1 mM concentration of the paramagnetic ion. The chemical interactions that bring the water protons into the immediate proximity of the metal ion play an important role in transmitting the paramagnetic effect to the bulk.² Relaxivity is described by three contributions, depending on the type of interaction:

$$r_i = r_i^{IS} + r_i^{SS} + r_i^{OS} \quad (S3)$$

The inner-sphere (IS) contribution to relaxivity originates from water molecules directly coordinated to the metal centre. The outer-sphere (OS) contribution is associated with bulk water molecules diffusing near the paramagnetic complex. The second-sphere (SS) contribution arises from water molecules interacting with the complex, generally via hydrogen bonds, and characterized by a residence time long enough to enable effective paramagnetic relaxation.³ For hydrated complexes, the relaxation enhancement is usually principally given by the inner sphere contribution, described by:

$$\left(\frac{1}{T_1}\right)_{IS} = \frac{1}{1000} \cdot \frac{C \times q}{55.56} \cdot \frac{1}{T_{1M} + \tau_M} = \frac{p_m}{T_{1M} + \tau_M} \quad (S4)$$

$$\left(\frac{1}{T_2}\right)_{IS} = \frac{p_m}{\tau_M} \cdot \frac{T_{2M}^{-1}(T_{2M}^{-1} + \tau_M^{-1}) + \Delta\omega_M^2}{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2} \quad (S5)$$

Where p_m is the mole fraction of the bound water molecules; q is the number of inner-sphere water molecules (hydration number); τ_M is the residence time of an inner-sphere water molecule; T_{1M} and T_{2M} are the longitudinal and transverse proton relaxation times of bound water, respectively; and $\Delta\omega_M$ is the ¹H chemical shift difference between the bound water and bulk-water resonances (in the absence of chemical exchange).

In accordance with the Solomon-Bloembergen-Morgan (SBM) theory, T_{1M} and T_{2M} can be further described as the sum of three mechanisms: dipole-dipole (DD), scalar (SC) and Curie (Cu).^{4,5}

$$\frac{1}{T_{kM}} = \frac{1}{T_k^{DD}} + \frac{1}{T_k^{SC}} + \frac{1}{T_k^{Cu}} \quad (S6)$$

For Ln(III) hydrated complexes, the scalar coupling constant A/\hbar is usually small, so the $1/T_k^{SC}$ can be neglected.^{6,7} The dipole-dipole and Curie contributions for both the longitudinal and transverse relaxation process are defined as:

$$\left(\frac{1}{T_1^{DD}}\right)_{IS} = \frac{2}{15} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 g_J^2 \mu_B^2}{r^6} J(J+1) \left[\frac{7\tau_{c2}}{1 + \omega_S^2 \tau_{c2}^2} + \frac{3\tau_{c1}}{1 + \omega_I^2 \tau_{c1}^2} \right] \quad (S7)$$

$$\left(\frac{1}{T_2^{DD}}\right)_{IS} = \frac{1}{15} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 g_J^2 \mu_B^2}{r^6} J(J+1) \left[\frac{13\tau_{c2}}{1 + \omega_S^2 \tau_{c2}^2} + \frac{3\tau_{c1}}{1 + \omega_I^2 \tau_{c1}^2} + 4\tau_{c1} \right] \quad (S8)$$

$$\left(\frac{1}{T_1^{Cu}}\right)_{IS} = \frac{2}{5} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\omega_I^2 \mu_B^4 g_J^4}{(3k_B T)^2 r^6} J^2 (J+1)^2 \left(\frac{3\tau_{Cu}}{1 + \omega_S^2 \tau_{Cu}^2} \right) \quad (S9)$$

$$\left(\frac{1}{T_2^{Cu}}\right)_{IS} = \frac{1}{5} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\omega_I^2 \mu_B^4 g_J^4}{(3k_B T)^2 r^6} J^2 (J+1)^2 \left(4\tau_{Cu} + \frac{3\tau_{Cu}}{1 + \omega_I^2 \tau_{Cu}^2} \right) \quad (S10)$$

Where J is the total spin quantum number; γ_I is the nuclear gyromagnetic ratio; g_J is the Landé g-factor; μ_B is the Bohr magneton; r is the nuclear spin – electron distance; ω_I and ω_S are the nuclear and electron Larmor frequencies and k_B is the Boltzmann constant.^{8,9} For each lanthanide ion, the Landé g-factor and the effective magnetic moment (μ_{eff}) (reported in Table S1) were obtained using the following equations:

$$g_J \approx 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (S11)$$

$$\mu_{eff} = g_J \sqrt{J(J+1)} \quad (S12)$$

The correlation times, that appear in eqn. (S7)-(S10), are defined as follows:

$$\frac{1}{\tau_{ci}} = \frac{1}{\tau_R} + \frac{1}{\tau_M} + \frac{1}{T_{ie}} \quad (S13)$$

$$\frac{1}{\tau_{Cu}} = \frac{1}{\tau_R} + \frac{1}{\tau_M} \quad (S14)$$

Where τ_R is the rotational correlation time, τ_M is the average water residence lifetime, and T_{1e} and T_{2e} are the longitudinal and transverse electronic relaxation times. For all paramagnetic Ln³⁺ (except Gd³⁺), the value of T_{2e} is small and very close to T_{1e} , so a single parameter (τ_s) can be used.^{10,11}

The outer-sphere is also given by the sum of the dipolar and Curie relaxations which are commonly described by the Freed^{12,13} and Ayant¹⁴ models:

$$\left(\frac{1}{T_1^{DD}}\right)_{OS} = \frac{32\pi(\mu_0)^2 N_A[M]}{405(4\pi)^2 aD} \gamma_I^2 \mu_B^2 g^2 J(J+1) [7J_2(\omega_S) + 3J_1(\omega_I)] \quad (S15)$$

$$\left(\frac{1}{T_2^{DD}}\right)_{OS} = \frac{16\pi(\mu_0)^2 N_A[M]}{405(4\pi)^2 aD} \gamma_I^2 \mu_B^2 g^2 J(J+1) [13J_2(\omega_S) + 3J_1(\omega_I) + 4J_1(0)] \quad (S16)$$

$$J_k(\omega) = \text{Re} \left[\frac{1 + \frac{1}{4} \left(i\omega\tau_D + \frac{\tau_D}{T_{ke}} \right)^{\frac{1}{2}}}{1 + \left(i\omega\tau_D + \frac{\tau_D}{T_{ke}} \right)^{\frac{1}{2}} + \frac{4}{9} \left(i\omega\tau_D + \frac{\tau_D}{T_{ke}} \right) + \frac{1}{9} \left(i\omega\tau_D + \frac{\tau_D}{T_{ke}} \right)^{\frac{3}{2}}} \right] \quad (S17)$$

$$\left(\frac{1}{T_1^{Cu}}\right)_{OS} = \frac{96\pi(\mu_0)^2 N_A[M] \omega_I^2 \mu_B^4 g^4}{405(4\pi)^2 aD (3k_B T)^2} J^2(J+1)^2 [J(\omega_I)] \quad (S18)$$

$$\left(\frac{1}{T_2^{Cu}}\right)_{OS} = \frac{48\pi(\mu_0)^2 \omega_I^2 \mu_B^4 g^4}{405(4\pi)^2 (3k_B T)^2} J^2(J+1)^2 [4J(0) + 3J(\omega_I)] \quad (S19)$$

$$J(\omega) = \text{Re} \left[\frac{1 + \frac{1}{4} (i\omega\tau_D)^{\frac{1}{2}}}{1 + (i\omega\tau_D)^{\frac{1}{2}} + \frac{4}{9} (i\omega\tau_D) + \frac{1}{9} (i\omega\tau_D)^{\frac{3}{2}}} \right] \quad (S20)$$

Where N_A is Avogadro constant, a is the nuclear spin – electron distance for the OS, D is the diffusion coefficient, τ_D is the correlation time for the translational diffusion such that $\tau_D = a^2/D$, while $J(\omega)$ is the spectral density function. The temperature dependence of the water exchange rate constant (k_{ex}) is described by eqn (S21) where ΔH_M is the activation enthalpy.¹⁵

$$k_{ex} = \frac{1}{\tau_M} = \frac{k_{ex}^{298}}{298.15} \exp \left[\frac{\Delta H_M}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] = \frac{k_B T}{h} \exp \left(\frac{\Delta S}{R} - \frac{\Delta H_M}{RT} \right) \quad (21)$$

The temperature dependence of correlation times and diffusion constant is assumed to follow Arrhenius-type equations.

$$\tau_R = \tau_R^{298} \exp \left[\frac{E_R}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (S22)$$

$$\tau_s = \tau_s^{298} \exp \left[\frac{E_s}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (S23)$$

$$D = D^{298} \exp \left[\frac{E_D}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \quad (S24)$$

Table S1. Electronic Configurations and Magnetic Properties of the Trivalent Lanthanide Ions.^a

Lanthanide ion	4f configuration	Spectroscopic ground state symbol	S	L	J	g_J	μ_{eff}
La ³⁺	4f ⁰	¹ S ₀	–	–	–	–	–
Ce ³⁺	4f ¹	² F _{5/2}	1/2	3	5/2	6/7	2.54
Pr ³⁺	4f ²	³ H ₄	1	5	4	4/5	3.58
Nd ³⁺	4f ³	⁴ I _{9/2}	3/2	6	9/2	8/11	3.62
Pm ³⁺	4f ⁴	⁵ I ₄	2	6	4	3/5	2.68
Sm ³⁺	4f ⁵	⁶ H _{5/2}	5/2	5	5/2	2/7	0.85
Eu ³⁺	4f ⁶	⁷ F ₀	3	3	0	–	–
Gd ³⁺	4f ⁷	⁸ S _{7/2}	7/2	0	7/2	2	7.94
Tb ³⁺	4f ⁸	⁷ F ₆	3	3	6	3/2	9.72
Dy ³⁺	4f ⁹	⁶ H _{15/2}	5/2	5	15/2	4/3	10.65
Ho ³⁺	4f ¹⁰	⁵ I ₈	2	6	8	5/4	10.60
Er ³⁺	4f ¹¹	⁴ I _{15/2}	3/2	6	15/2	6/5	9.58
Tm ³⁺	4f ¹²	³ H ₆	1	5	6	7/6	7.56
Yb ³⁺	4f ¹³	² F _{7/2}	1/2	3	7/2	8/7	4.54
Lu ³⁺	4f ¹⁴	¹ S ₀	–	–	–	–	–

^a From ref.16

To have an independent estimation of the $\Delta\omega_M$, we measured the paramagnetic shift $\Delta\omega_p$ of the water proton signal, that is the difference in chemical shift between the water signal in the presence and in absence of the complex (see **Experimental and computational section**). Indeed, the magnetic anisotropy of Ln(III)-ions, deriving from the anisotropic distribution of electrons in the 4f orbitals being prolate for Pm(III), Sm(III), Er(III), Tm(III), and Yb(III) or oblate for Ce(III), Pr(III), Nd(III), Tb(III), Dy(III), and Ho(III), shifts the proton NMR signal of water from its diamagnetic value.^{17,18} The $\Delta\omega_p$ value is given by:

$$\Delta\omega_p = fq \frac{\Delta\omega_M}{\left(1 + \frac{\tau_M}{T_{2M}}\right)^2 + \tau_M^2 \Delta\omega_M^2} \quad (\text{S25})$$

This equation can be simplified to $\Delta\omega_p = \frac{cq}{55.56} \Delta\omega_M$ if $\tau_M^2 \Delta\omega_M^2 \ll 1$ and $\frac{\tau_M}{T_{2M}} \ll 1$.

In general, the extraction of multiple interdependent parameters (e.g., τ_R , τ_M , τ_S) from NMR relaxometry data can theoretically lead to ambiguous results or local minima during the minimization procedure if the parameter space is not adequately constrained. In this work, this potential limitation is effectively overcome by the simultaneous analysis of the longitudinal and transverse relaxation rates over a remarkably broad range of magnetic fields (corresponding to proton Larmor frequencies from 30 to 600 MHz).

The uniqueness and stability of this multifield approach stem from the fact that r_1 and r_2 exhibit distinctly different mathematical dependencies on the underlying correlation times and operational frequencies. Specifically:

- **Longitudinal relaxivity** is predominantly sensitive to faster modulations, such as the rotational correlation time and the electronic relaxation parameters.
- **Transverse relaxivity**, conversely, includes a significant contribution at higher magnetic fields that is inherently and acutely sensitive to the water exchange kinetics.

Consequently, fitting both the r_1 and r_2 datasets simultaneously across a wide field range imposes stringent and orthogonal boundary conditions on the theoretical SBM model. These intrinsic constraints effectively disentangle the physical variables during the regression. As a result, the different molecular parameters are robustly determined and demonstrate a high degree of uniqueness, without being overly sensitive to the initial estimates provided for the electronic relaxation parameters. This methodological stability ensures that the extracted hydration dynamics correctly capture the physical behavior of the investigated Ln(III) complexes rather than representing mere mathematical artifacts.

Experimental and computational section

Chemicals and Reagents. All chemicals were purchased from Merck/Sigma-Aldrich (St Louis, MO, USA), Thermo Fisher Scientific (Waltham, MA, USA) or BLD Pharm (Karlsruhe, Germany) and used without further purification.

Synthesis of the complexes. The ligands were dissolved in milliQ water and pH was adjusted to 4.5 with an aqueous solution of NaOH (1 M). Then the ligand solution was divided into 6 different aliquots. For each solution, 0.95 eq. of Ln(NO₃)₃·5H₂O (where Ln³⁺ = Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Sigma-Aldrich) were added and the pH adjusted to 5.0 with NaOH. The solutions were stirred at room temperature for 24 h and neutralized with dilute HNO₃. The same procedure was then repeated for the light lanthanide ions, using

$\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln}^{3+} = \text{Pr}^{3+}, \text{Nd}^{3+}$). The concentration of Ln^{3+} complexes was evaluated by ^1H NMR measurements at 11.75 T and 300 K, using the Bulk Magnetic Susceptibility (BMS) method.^{19,20}

Table S2. The concentration of the Ln^{3+} complex solutions under investigation.

Conc. (mM)	Pr^{3+}	Nd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
$[\text{Ln}(\text{DTPA})]^{2-}$	33.8	19.8	26.6	25.7	26.2	25.5	26.6	25.7
$[\text{Ln}(\text{AAZTA})]^-$	7.0	9.4	20.3	22.4	21.7	20.5	18.2	18.8

NMR Experiments. ^1H spectra of the Ln^{3+} complexes were recorded at 300 K using a Bruker 500 UltraShieldTM spectrometer equipped with a 5 mm double resonance TXI probe and a wide bore 11.75 T magnet. An independent estimation of the $\Delta\omega_{\text{M}}$ was carried out by measuring the paramagnetic shift $\Delta\omega_{\text{p}}$ of the water proton signal in the presence and in the absence of the Ln^{3+} complexes at 11.75 T. The bulk magnetic susceptibility contribution to the observed ^1H chemical shift was removed by adding *tert*-Butyl alcohol as an internal reference (10% v/v) to the samples.

Relaxometric characterization. $1/T_1$ and $1/T_2$ ^1H Nuclear Magnetic Relaxation Dispersion (NMRD) profiles in the 30-120 MHz frequency range were recorded with a High Field Relaxometer (Stelar, Mede (PV), Italy) equipped with the HTS-110 3T Metrology Cryogen-free Superconducting Magnet. The relaxometer operates under computer control with an absolute uncertainty of $\pm 1\%$ s^{-1} . The temperature was controlled during the measurements with a Stelar VTC-91 airflow heater equipped with a copper-constantan thermocouple (uncertainty of $\pm 0.1\%$ $^\circ\text{C}$). The temperature inside the probe head was furthermore monitored with a Fluke 52k/j digital thermometer (Fluke, Zürich, Switzerland). The $1/T_1$ data were collected using the standard inversion recovery sequence (16 experiments, 3 scans) with a conventional 90° pulse width of 3.5 μs , and the reproducibility of the data was within $\pm 0.5\%$. The $1/T_2$ data were collected using a standard CPMG sequence with a conventional 90° pulse calibrated for each sample, with a reproducibility of the data within $\pm 1.0\%$. The high-field $1/T_1$ and $1/T_2$ proton relaxation rates were recorded by means of three different NMR spectrometers: Bruker Avance Neo 400 (9.4 T), Bruker 500 UltraShieldTM (11.7 T) and Bruker Avance 600 (14.1 T). The diamagnetic contribution for both $1/T_1$ and $1/T_2$ was measured by collecting ^1H NMRD profiles of pure water. The longitudinal and transverse relaxivities (r_1 and r_2 , $\text{mM}^{-1} \text{s}^{-1}$) at different magnetic fields were obtained by measuring the longitudinal and transverse relaxation rates of the paramagnetic samples, subtracting the diamagnetic contribution, and dividing by the mM concentration of the paramagnetic ion.

Computational section: Geometry optimizations of the Ln^{3+} complexes were performed with the Gaussian 16 program package (Rev C.01)²¹ using restricted calculations with the wB97X-D functional and the Def2-TZVPP basis set²² for C, H, N and O atoms. The Stuttgart–Bonn large-core quasi-relativistic effective core potentials were used for Ln^{3+} ions²³. Solvent effects were incorporated with a polarized continuum model using the default settings [scrf = (pcm, solvent = water)] implemented in Gaussian 16²⁴. The integration grid was increased using the integral = ultrafine keyword. Frequency calculations were used to confirm that the

optimized structures corresponded to stationary points. Wave function analysis was carried out with the computer program Multiwfn 3.2.²⁵ which allows computing the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at the bond critical points (BCPs).

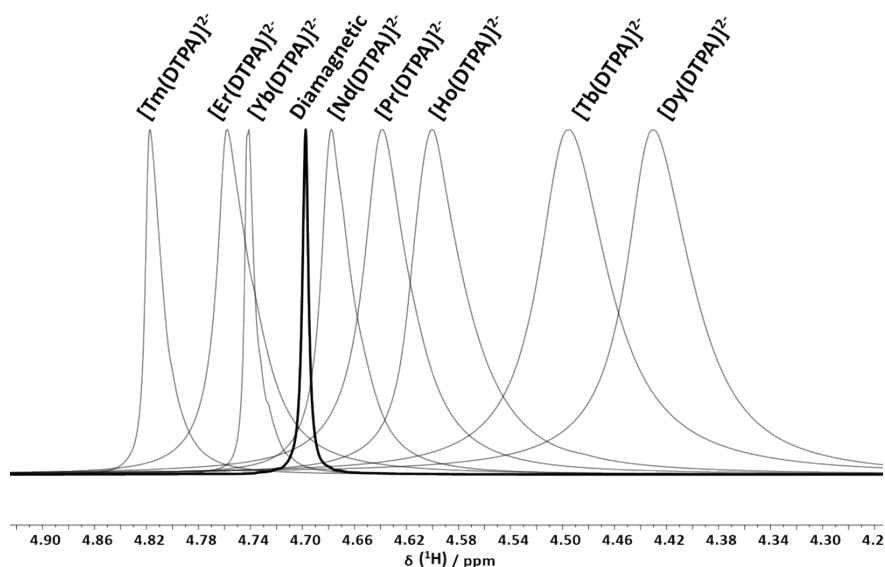


Figure S1. ^1H chemical shift of the water signals for aqueous solutions of the investigated paramagnetic $[\text{Ln}(\text{DTPA})]^{2-}$ complexes and for the diamagnetic reference. The concentrations of the Ln^{3+} complexes are reported in *Table S2*.

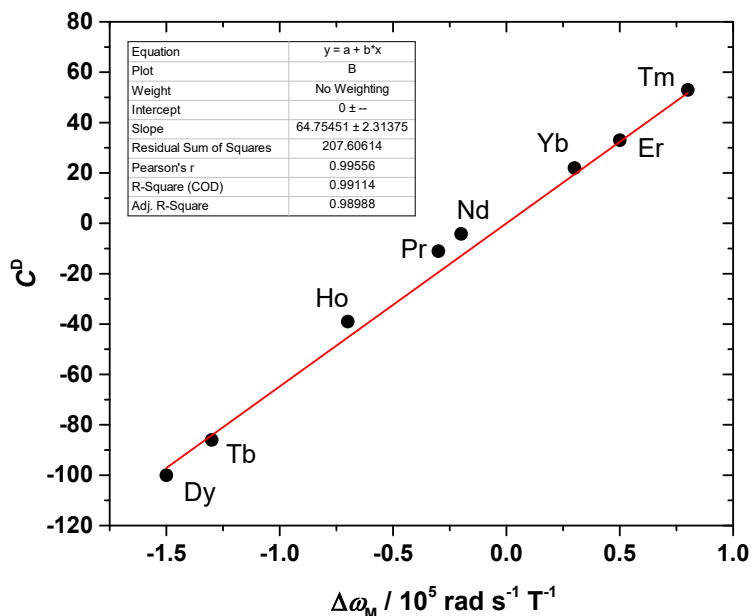


Figure S2. Plot of $\Delta\omega_m$ versus the Bleaney C^D constant for $[\text{Ln}(\text{DTPA})]^{2-}$ along the lanthanide series. The linear dependence is consistent with a dominant pseudocontact contribution and an essentially conserved structural geometry along the lanthanide series.

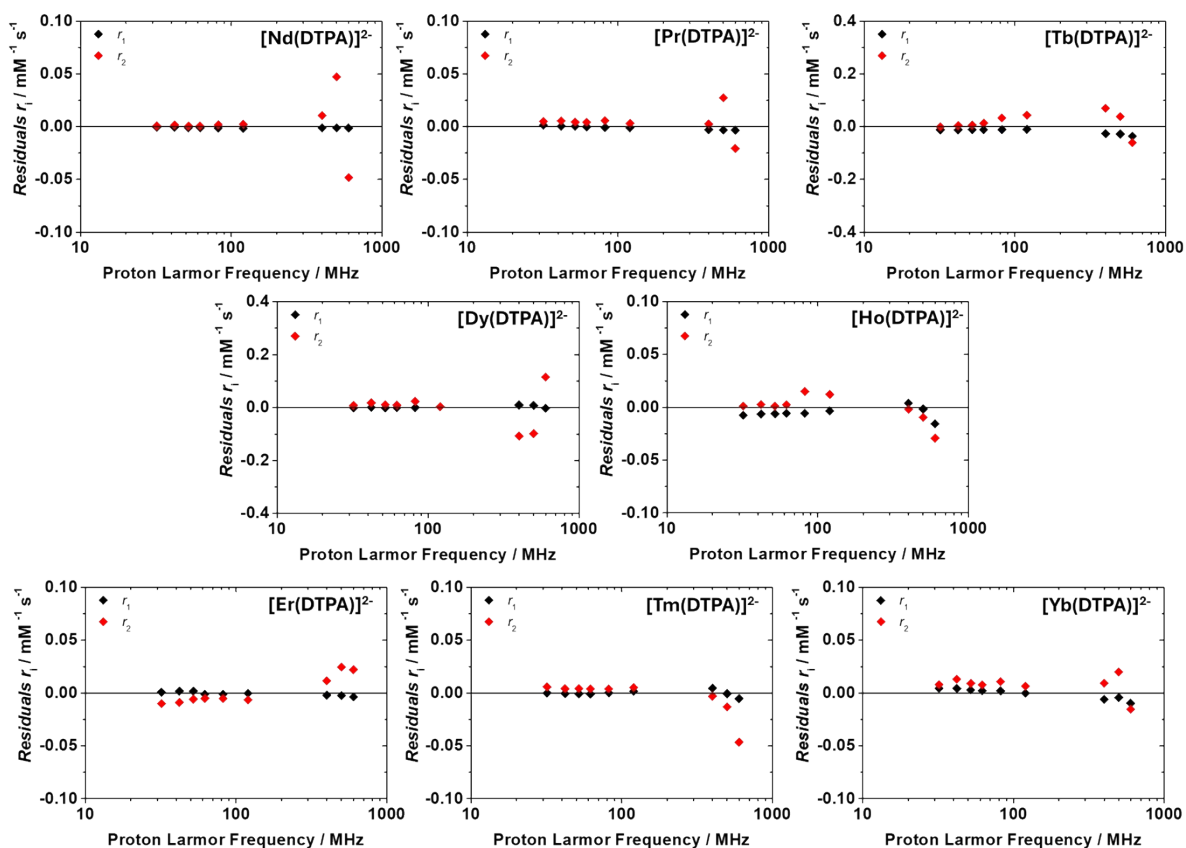


Figure S3. Residual plots for the simultaneous fitting of the longitudinal (r_1 , black) and transverse (r_2 , red) relaxivity data across the $[\text{Ln}(\text{DTPA})]^{2-}$ series as a function of proton larmor frequency.

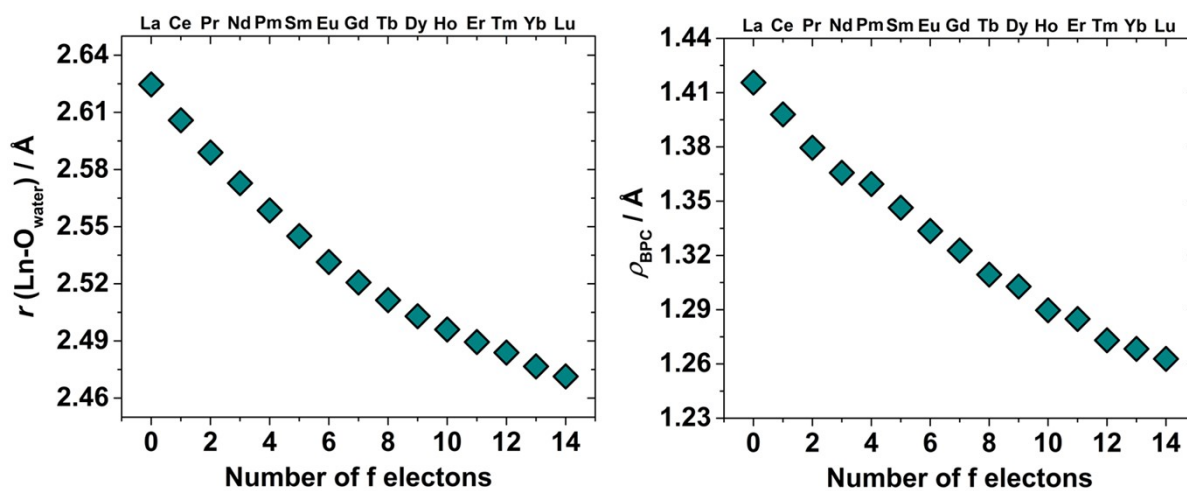


Figure S4. Distances between the metal ion and the oxygen atom of the inner sphere water molecule (left) and bond critical points values (right) for the $[\text{Ln}(\text{DTPA})]^{2-}$ complexes obtained with DFT calculations.

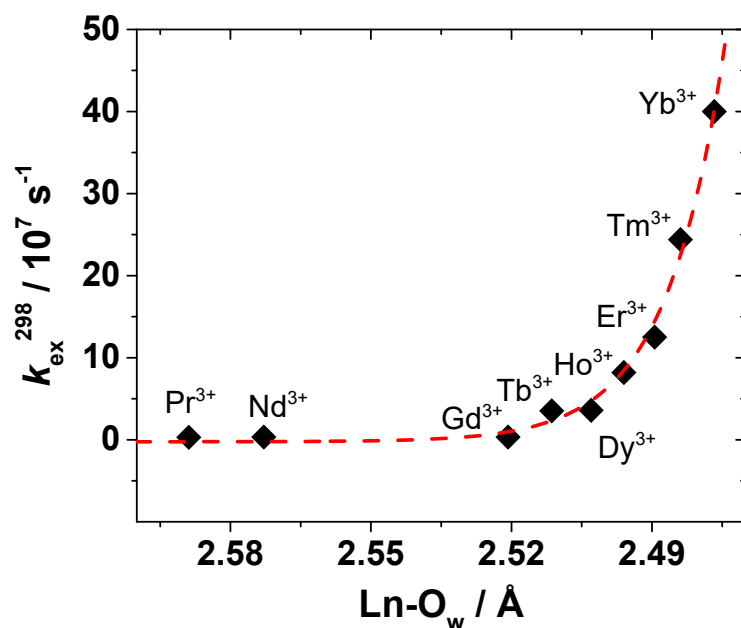


Figure S5. Plot of the k_{ex}^{298} values calculated for the $[\text{Ln}(\text{DTPA})]^{2-}$ complexes as a function of Ln-O_w distance obtained from DFT geometry optimizations. For $[\text{Gd}(\text{DTPA})]^{2-}$, the average of the values reported in the literature (303 ns)^{26,27,28} was considered.

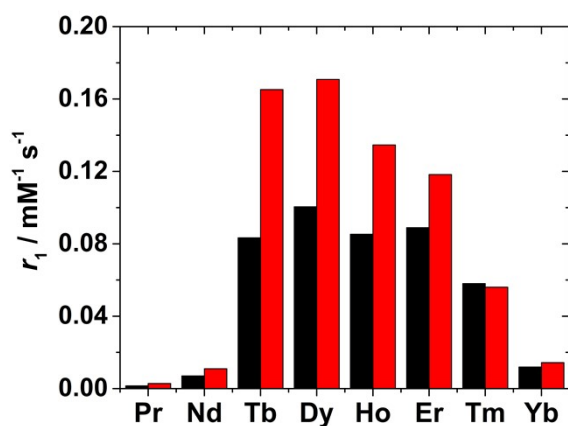


Figure S6. Comparison of the r_1 values at 32 MHz and 298 K for $[\text{Ln}(\text{DTPA})]^{2-}$ (**black**) and $[\text{Ln}(\text{AAZTA})]^{-}$ (**red**).

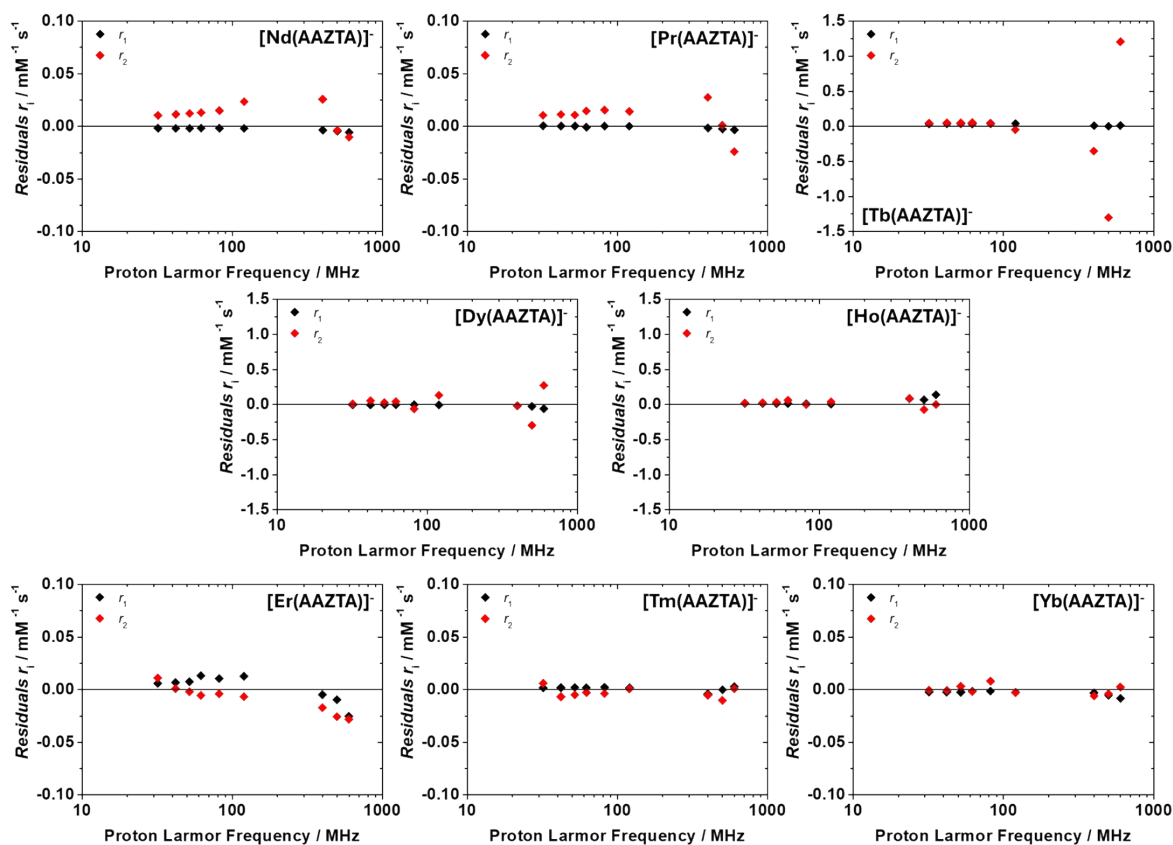


Figure S7. Residual plots for the simultaneous fitting of the longitudinal (r_1 , black) and transverse (r_2 , red) relaxivity data across the $[\text{Ln}(\text{AAZTA})]^-$ series as a function of proton larmor frequency.

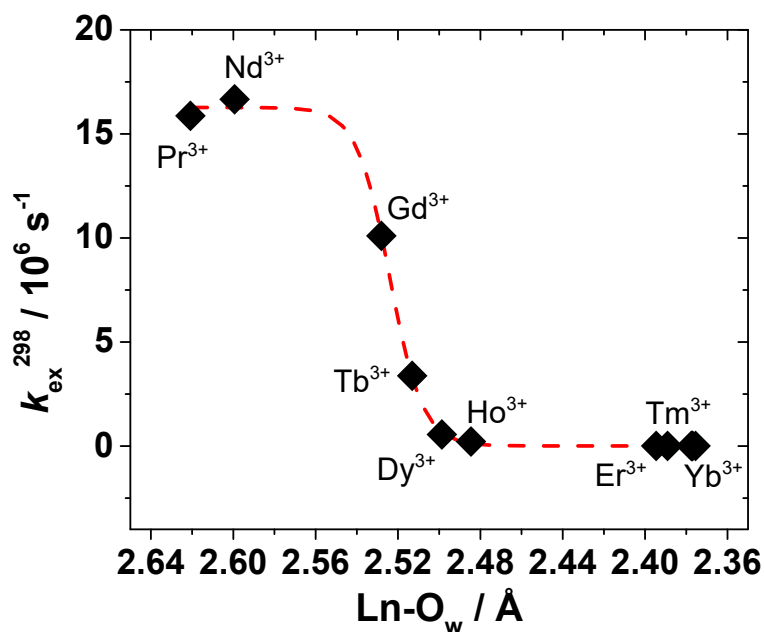


Figure S8. Plot of the k_{ex}^{298} measured for the $[\text{Ln}(\text{AAZTA})]^-$ complexes as a function of $\text{Ln}-\text{O}_w$ distance obtained from DFT geometry optimizations. For $[\text{Gd}(\text{AAZTA})]^-$, the average water residence lifetime of the two inner sphere water molecules (99 ns)²⁹ was considered.

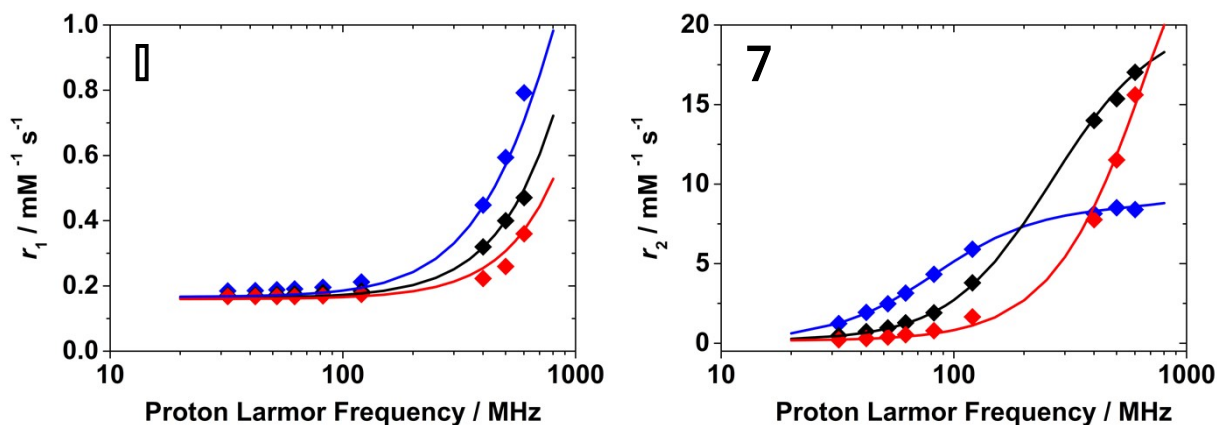


Figure S9. (A) $1/T_1$ and (B) $1/T_2$ ^1H NMRD profiles of $[\text{Dy}(\text{AAZTA})]^-$ at 283 K (\blacklozenge), 298 K (\blacklozenge) and 310 K (\blacklozenge).

Optimized Cartesian coordinates (\AA) obtained with DFT calculations

Table S3. Optimized Cartesian coordinates (\AA) of the $[\text{La}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	La	-0.07972	0.397453	0.117346
2	O	-2.33044	1.069037	1.21937
3	O	-4.03932	0.567043	2.55883
4	O	-1.68768	0.25416	-1.82185
5	O	-3.86329	0.628499	-2.09984
6	O	1.412562	0.411052	-1.89294
7	O	2.469877	-0.54155	-3.60473
8	O	0.185531	-1.01979	2.17293
9	O	1.288027	-2.10913	3.769999
10	O	1.751925	1.88574	1.063486
11	O	3.68028	2.769871	0.417005
12	O	-0.40009	2.864993	-0.71771
13	N	-2.22675	-1.49312	0.283713
14	N	0.469377	-2.10598	-1.02917
15	N	2.551773	-0.66249	0.724269
16	C	-1.60562	-2.81722	0.208098
17	H	-1.01534	-2.95013	1.113683
18	C	-0.72778	-2.96985	-1.02195
19	C	1.536532	-2.74221	-0.23751
20	H	1.847563	-3.67617	-0.72477
21	H	1.122483	-3.01332	0.731782
22	C	2.778969	-1.88637	-0.04879
23	H	3.544172	-2.51243	0.427048
24	H	3.177481	-1.61091	-1.02307
25	C	-2.81604	-1.23575	1.594078
26	H	-3.73376	-1.81068	1.75502

27	H	-2.09007	-1.51945	2.356382
28	C	-3.11258	0.25204	1.814975
29	C	-3.21414	-1.24275	-0.7749
30	H	-4.21058	-1.12648	-0.34793
31	H	-3.27382	-2.09525	-1.45513
32	C	-2.90846	-0.01286	-1.63523
33	C	0.908979	-1.86792	-2.40966
34	H	0.02007	-1.7732	-3.03364
35	H	1.49304	-2.71002	-2.79441
36	C	1.683072	-0.56515	-2.65429
37	C	2.566739	-0.91596	2.163459
38	H	3.36935	-1.60771	2.43977
39	H	2.76127	0.028029	2.67469
40	C	1.244427	-1.41342	2.753754
41	C	3.493922	0.398034	0.374777
42	H	3.68387	0.364974	-0.69633
43	H	4.459133	0.28693	0.882351
44	C	2.941249	1.79917	0.653437
45	O	-3.1586	3.000335	-0.56729
46	H	-1.31499	3.190692	-0.74579
47	H	0.230297	3.577843	-0.5088
48	H	-3.42463	2.376564	-1.26003
49	H	-2.99202	2.412329	0.192575
50	H	-2.36215	-3.61278	0.188588
51	H	-0.43927	-4.02299	-1.12154
52	H	-1.3147	-2.72374	-1.9042
53	O	1.681583	4.642458	-0.23287
54	H	2.011503	5.0544	-1.03134
55	H	2.384837	4.022872	0.050964

Table S4. Optimized Cartesian coordinates (Å) of the $[\text{Ce}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Ce	-0.07014	0.375469	0.084944
2	O	-2.26316	1.079479	1.210732
3	O	-3.96829	0.616059	2.568457
4	O	-1.67689	0.249068	-1.82813
5	O	-3.85256	0.626581	-2.10175
6	O	1.412485	0.392737	-1.90576
7	O	2.438814	-0.55633	-3.63828
8	O	0.172111	-0.98251	2.153027
9	O	1.244987	-2.07624	3.766996
10	O	1.705013	1.865611	1.074167
11	O	3.634993	2.783699	0.479437
12	O	-0.38194	2.82849	-0.73711
13	N	-2.21293	-1.48795	0.284471
14	N	0.469331	-2.11616	-1.03442
15	N	2.543207	-0.6626	0.716421

16	C	-1.59982	-2.81669	0.21804
17	H	-1.0081	-2.94629	1.123166
18	C	-0.7258	-2.98349	-1.01287
19	C	1.545301	-2.74502	-0.24784
20	H	1.859804	-3.67704	-0.73618
21	H	1.138293	-3.01913	0.723967
22	C	2.781598	-1.87903	-0.06432
23	H	3.555545	-2.49951	0.404467
24	H	3.172154	-1.59424	-1.03908
25	C	-2.79719	-1.21482	1.594116
26	H	-3.72892	-1.76673	1.754286
27	H	-2.08009	-1.51454	2.358067
28	C	-3.05702	0.279435	1.815377
29	C	-3.20294	-1.24143	-0.77273
30	H	-4.19851	-1.12344	-0.3442
31	H	-3.26383	-2.09595	-1.45018
32	C	-2.89791	-0.01508	-1.63761
33	C	0.898234	-1.88451	-2.41974
34	H	0.004932	-1.79452	-3.03808
35	H	1.481099	-2.72732	-2.80453
36	C	1.668586	-0.58178	-2.67481
37	C	2.55401	-0.92673	2.153948
38	H	3.337597	-1.64208	2.423716
39	H	2.776009	0.006367	2.673764
40	C	1.220106	-1.39104	2.74303
41	C	3.47321	0.411658	0.378828
42	H	3.659096	0.396438	-0.69357
43	H	4.441204	0.305115	0.881707
44	C	2.902234	1.800767	0.681488
45	O	-3.14169	2.998286	-0.57527
46	H	-1.29745	3.152575	-0.76869
47	H	0.23821	3.543155	-0.50359
48	H	-3.4167	2.369836	-1.26032
49	H	-2.96073	2.416643	0.185766
50	H	-2.36072	-3.60812	0.206455
51	H	-0.43499	-4.03694	-1.09989
52	H	-1.31599	-2.75073	-1.8966
53	O	1.649902	4.645902	-0.18937
54	H	1.987054	5.068463	-0.97924
55	H	2.357239	4.033866	0.101987

Table S5. Optimized Cartesian coordinates (Å) of the $[\text{Pr}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Pr	-0.06036	0.35724	0.05783
2	O	-2.21009	1.09196	1.195732
3	O	-3.90543	0.662185	2.576263
4	O	-1.66368	0.238868	-1.83557

5	O	-3.83842	0.620502	-2.11081
6	O	1.415606	0.379686	-1.91293
7	O	2.411891	-0.56385	-3.66587
8	O	0.163013	-0.94311	2.136208
9	O	1.20485	-2.04777	3.762732
10	O	1.664764	1.841822	1.089056
11	O	3.592775	2.792582	0.538681
12	O	-0.36899	2.790837	-0.76968
13	N	-2.19942	-1.4802	0.28796
14	N	0.470039	-2.12174	-1.03908
15	N	2.538334	-0.66559	0.709878
16	C	-1.59207	-2.812	0.229031
17	H	-0.99647	-2.93714	1.132314
18	C	-0.72445	-2.99001	-1.00484
19	C	1.55307	-2.74659	-0.25851
20	H	1.86823	-3.67737	-0.74835
21	H	1.152376	-3.02225	0.71583
22	C	2.785227	-1.87383	-0.07962
23	H	3.566367	-2.49099	0.381434
24	H	3.168225	-1.57971	-1.05449
25	C	-2.77712	-1.19237	1.597408
26	H	-3.71842	-1.72668	1.76055
27	H	-2.06481	-1.50101	2.361806
28	C	-3.00915	0.306873	1.814117
29	C	-3.19297	-1.23782	-0.76683
30	H	-4.186	-1.11123	-0.33501
31	H	-3.26108	-2.09738	-1.43714
32	C	-2.88533	-0.02018	-1.64228
33	C	0.888487	-1.89409	-2.42847
34	H	-0.00924	-1.8055	-3.04043
35	H	1.46859	-2.73772	-2.81538
36	C	1.657077	-0.592	-2.69077
37	C	2.544476	-0.94151	2.145239
38	H	3.30687	-1.68178	2.407446
39	H	2.79562	-0.02105	2.674037
40	C	1.199199	-1.37054	2.733233
41	C	3.456445	0.421532	0.384414
42	H	3.638387	0.423744	-0.68885
43	H	4.427012	0.319576	0.88297
44	C	2.867954	1.798248	0.710131
45	O	-3.12593	2.991987	-0.58977
46	H	-1.28717	3.108799	-0.79699
47	H	0.238236	3.507209	-0.50826
48	H	-3.4087	2.359102	-1.26764
49	H	-2.935	2.41627	0.173321
50	H	-2.35568	-3.60078	0.226791
51	H	-0.43344	-4.04384	-1.08434
52	H	-1.319	-2.76508	-1.88765
53	O	1.612164	4.640159	-0.14622

54	H	1.95848	5.076041	-0.9248
55	H	2.322726	4.035177	0.152823

Table S6. Optimized Cartesian coordinates (Å) of the [Nd(DTPA)(H₂O)]²⁻·2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Nd	-0.05561	0.346395	0.048418
2	O	-2.18209	1.095082	1.182826
3	O	-3.86194	0.686959	2.588386
4	O	-1.64696	0.232361	-1.83282
5	O	-3.81927	0.611827	-2.12845
6	O	1.414283	0.37944	-1.90456
7	O	2.395833	-0.55366	-3.67121
8	O	0.157719	-0.92433	2.12119
9	O	1.179559	-2.02774	3.760831
10	O	1.643018	1.827493	1.088888
11	O	3.569686	2.795193	0.563247
12	O	-0.36419	2.763335	-0.77789
13	N	-2.19156	-1.47669	0.291714
14	N	0.469074	-2.12075	-1.0386
15	N	2.536128	-0.66816	0.706359
16	C	-1.58871	-2.81028	0.234468
17	H	-0.99149	-2.93558	1.136652
18	C	-0.72418	-2.99076	-1.00098
19	C	1.555808	-2.74682	-0.26403
20	H	1.869658	-3.67612	-0.75728
21	H	1.159072	-3.02491	0.711395
22	C	2.78671	-1.87234	-0.0871
23	H	3.5707	-2.48862	0.370264
24	H	3.166316	-1.57398	-1.062
25	C	-2.76613	-1.1821	1.600782
26	H	-3.71391	-1.70478	1.764071
27	H	-2.05825	-1.49814	2.365888
28	C	-2.97974	0.319801	1.815537
29	C	-3.1855	-1.2332	-0.76217
30	H	-4.17618	-1.09424	-0.32894
31	H	-3.26378	-2.09687	-1.42617
32	C	-2.87006	-0.02463	-1.64652
33	C	0.881568	-1.89033	-2.42945
34	H	-0.01885	-1.79988	-3.03709
35	H	1.460063	-2.73298	-2.82076
36	C	1.648721	-0.58752	-2.69049
37	C	2.538305	-0.94945	2.140517
38	H	3.288208	-1.70321	2.399984
39	H	2.805065	-0.03602	2.673809
40	C	1.18632	-1.35845	2.726203
41	C	3.448658	0.424685	0.386967
42	H	3.631547	0.433425	-0.6861

43	H	4.419204	0.326668	0.886238
44	C	2.84962	1.794908	0.719489
45	O	-3.12006	2.983868	-0.60075
46	H	-1.28276	3.080052	-0.80839
47	H	0.237422	3.48089	-0.50672
48	H	-3.40313	2.349607	-1.27711
49	H	-2.92266	2.409972	0.162127
50	H	-2.3543	-3.59712	0.234774
51	H	-0.43198	-4.04424	-1.07929
52	H	-1.32091	-2.76816	-1.88288
53	O	1.591145	4.633537	-0.13091
54	H	1.938871	5.071432	-0.90773
55	H	2.303969	4.032853	0.172052

Table S7. Optimized Cartesian coordinates (Å) of the [Pm(DTPA)(H₂O)]²⁻ · 2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Pm	-0.05104	0.335366	0.03959
2	O	-2.15089	1.097498	1.17603
3	O	-3.81782	0.709467	2.602139
4	O	-1.63252	0.228499	-1.82878
5	O	-3.80241	0.605125	-2.14397
6	O	1.412354	0.378201	-1.89841
7	O	2.382505	-0.54562	-3.67611
8	O	0.152033	-0.91179	2.107243
9	O	1.158123	-2.01323	3.757609
10	O	1.620743	1.816541	1.084299
11	O	3.548023	2.79821	0.587341
12	O	-0.35805	2.73657	-0.78844
13	N	-2.18487	-1.47329	0.294455
14	N	0.468156	-2.12038	-1.03886
15	N	2.532478	-0.6693	0.703401
16	C	-1.5866	-2.80873	0.237995
17	H	-0.98838	-2.93512	1.139318
18	C	-0.72438	-2.99142	-0.99859
19	C	1.557601	-2.74696	-0.26834
20	H	1.871047	-3.675	-0.76401
21	H	1.163732	-3.02704	0.70777
22	C	2.787022	-1.87037	-0.09272
23	H	3.573415	-2.48533	0.362245
24	H	3.164042	-1.56865	-1.06758
25	C	-2.75593	-1.17288	1.603501
26	H	-3.71072	-1.68282	1.766102
27	H	-2.0531	-1.4984	2.368917
28	C	-2.94921	0.331356	1.819288
29	C	-3.1793	-1.22807	-0.75816
30	H	-4.16771	-1.07814	-0.32348
31	H	-3.26699	-2.0949	-1.41698

32	C	-2.85685	-0.02731	-1.64978
33	C	0.876933	-1.88867	-2.43069
34	H	-0.02485	-1.79883	-3.03623
35	H	1.455753	-2.73014	-2.82395
36	C	1.641694	-0.58463	-2.69086
37	C	2.531406	-0.95439	2.136667
38	H	3.272531	-1.71724	2.394532
39	H	2.808479	-0.04604	2.673399
40	C	1.174564	-1.34985	2.719285
41	C	3.439879	0.428661	0.389108
42	H	3.623662	0.442888	-0.68376
43	H	4.4103	0.334446	0.889211
44	C	2.831322	1.793095	0.727027
45	O	-3.1136	2.975703	-0.60777
46	H	-1.27683	3.052184	-0.82154
47	H	0.237882	3.454711	-0.50669
48	H	-3.39815	2.340102	-1.28215
49	H	-2.90863	2.40408	0.154711
50	H	-2.35432	-3.59348	0.23972
51	H	-0.43158	-4.04472	-1.07585
52	H	-1.32265	-2.77048	-1.87988
53	O	1.571837	4.628587	-0.1177
54	H	1.921706	5.067727	-0.89285
55	H	2.286206	4.031904	0.189903

Table S8. Optimized Cartesian coordinates (Å) of the $[\text{Sm}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Sm	-0.04839	0.326671	0.033109
2	O	-2.12462	1.098136	1.172775
3	O	-3.77784	0.725475	2.618479
4	O	-1.62004	0.225859	-1.8234
5	O	-3.78724	0.598107	-2.1599
6	O	1.409558	0.379882	-1.88958
7	O	2.375262	-0.534	-3.6747
8	O	0.147041	-0.90175	2.093145
9	O	1.138275	-2.00159	3.753234
10	O	1.603653	1.808064	1.074621
11	O	3.531782	2.799481	0.601466
12	O	-0.35423	2.712902	-0.79729
13	N	-2.18001	-1.47056	0.296885
14	N	0.467386	-2.11831	-1.03858
15	N	2.53006	-0.67068	0.701416
16	C	-1.58556	-2.80737	0.239027
17	H	-0.9867	-2.93624	1.139517
18	C	-0.72503	-2.98958	-0.99866
19	C	1.557666	-2.74691	-0.27073
20	H	1.869911	-3.6742	-0.76842

21	H	1.165125	-3.02836	0.705558
22	C	2.78694	-1.87029	-0.09533
23	H	3.573848	-2.485	0.35909
24	H	3.16344	-1.56732	-1.07002
25	C	-2.74734	-1.16673	1.60652
26	H	-3.70822	-1.66533	1.768223
27	H	-2.04891	-1.50181	2.371506
28	C	-2.92225	0.339035	1.82543
29	C	-3.17511	-1.22262	-0.75404
30	H	-4.16085	-1.0611	-0.31754
31	H	-3.27321	-2.09233	-1.40773
32	C	-2.84547	-0.02971	-1.65276
33	C	0.875343	-1.88462	-2.43043
34	H	-0.02645	-1.79586	-3.03599
35	H	1.455923	-2.72439	-2.82459
36	C	1.637466	-0.57872	-2.68747
37	C	2.525029	-0.95703	2.134154
38	H	3.259668	-1.72583	2.392782
39	H	2.808192	-0.0517	2.672839
40	C	1.163895	-1.34258	2.712351
41	C	3.434036	0.430385	0.390367
42	H	3.620217	0.446867	-0.68206
43	H	4.403554	0.339992	0.892837
44	C	2.8177	1.790873	0.728841
45	O	-3.10946	2.96647	-0.61174
46	H	-1.27308	3.027949	-0.8315
47	H	0.237549	3.431406	-0.50797
48	H	-3.39466	2.330394	-1.28527
49	H	-2.89796	2.396327	0.149965
50	H	-2.35501	-3.59039	0.240393
51	H	-0.43226	-4.04272	-1.07744
52	H	-1.32418	-2.76747	-1.87906
53	O	1.555627	4.623087	-0.11077
54	H	1.906403	5.063679	-0.88467
55	H	2.271613	4.029761	0.199798

Table S9. Optimized Cartesian coordinates (Å) of the [Eu(DTPA)(H₂O)]²⁻·2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Eu	-0.04555	0.317999	0.025906
2	O	-2.098	1.099382	1.171249
3	O	-3.73668	0.741271	2.636686
4	O	-1.60543	0.220455	-1.81918
5	O	-3.76893	0.587138	-2.18258
6	O	1.407423	0.381668	-1.8804
7	O	2.371011	-0.52308	-3.67118
8	O	0.142745	-0.89305	2.077773
9	O	1.119351	-1.99026	3.747929

10	O	1.58787	1.799075	1.063221
11	O	3.515991	2.800234	0.611873
12	O	-0.35123	2.690378	-0.80274
13	N	-2.17565	-1.46693	0.299859
14	N	0.466543	-2.11566	-1.03806
15	N	2.528392	-0.67238	0.698966
16	C	-1.58501	-2.80507	0.239967
17	H	-0.98543	-2.93683	1.139482
18	C	-0.72633	-2.98643	-0.99901
19	C	1.557166	-2.74702	-0.27278
20	H	1.86765	-3.67373	-0.77248
21	H	1.165708	-3.02956	0.703639
22	C	2.786934	-1.87121	-0.09753
23	H	3.573565	-2.48612	0.35712
24	H	3.163699	-1.56795	-1.07204
25	C	-2.73897	-1.16008	1.610254
26	H	-3.70605	-1.64685	1.770831
27	H	-2.04527	-1.50554	2.374545
28	C	-2.89476	0.346998	1.832957
29	C	-3.1715	-1.21581	-0.74917
30	H	-4.15329	-1.03785	-0.3103
31	H	-3.28415	-2.08983	-1.39494
32	C	-2.83228	-0.03434	-1.65855
33	C	0.874109	-1.88014	-2.42986
34	H	-0.02762	-1.79127	-3.0354
35	H	1.455687	-2.71869	-2.82499
36	C	1.63474	-0.57301	-2.68315
37	C	2.519175	-0.9588	2.131357
38	H	3.248154	-1.73234	2.391724
39	H	2.806875	-0.05566	2.671351
40	C	1.153987	-1.3356	2.704586
41	C	3.429185	0.431364	0.390402
42	H	3.617985	0.449214	-0.68153
43	H	4.397609	0.345069	0.895603
44	C	2.805037	1.788112	0.728292
45	O	-3.10732	2.95357	-0.6176
46	H	-1.26996	3.004929	-0.8402
47	H	0.236238	3.409443	-0.50619
48	H	-3.39172	2.317452	-1.29122
49	H	-2.88929	2.384772	0.14316
50	H	-2.35625	-3.58631	0.240723
51	H	-0.43423	-4.03951	-1.08019
52	H	-1.32629	-2.76192	-1.87827
53	O	1.537962	4.618038	-0.10067
54	H	1.888051	5.062254	-0.8728
55	H	2.256377	4.02771	0.210253

Table S10. Optimized Cartesian coordinates (Å) of the [Gd(DTPA)(H₂O)]²⁻ · 2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Gd	-0.04519	0.31545	0.027828
2	O	-2.08936	1.09638	1.167939
3	O	-3.71485	0.745956	2.649753
4	O	-1.59016	0.214838	-1.81209
5	O	-3.74907	0.57436	-2.20672
6	O	1.404234	0.38938	-1.8645
7	O	2.370342	-0.50492	-3.65895
8	O	0.141408	-0.88336	2.069528
9	O	1.10775	-1.98304	3.743712
10	O	1.584372	1.793737	1.049091
11	O	3.512069	2.797797	0.604231
12	O	-0.35249	2.675462	-0.80284
13	N	-2.17365	-1.46583	0.303602
14	N	0.464681	-2.11005	-1.03508
15	N	2.529184	-0.67486	0.697423
16	C	-1.58564	-2.80431	0.23955
17	H	-0.98568	-2.94015	1.138213
18	C	-0.72809	-2.98098	-1.00054
19	C	1.554354	-2.74662	-0.2729
20	H	1.861467	-3.67302	-0.77524
21	H	1.163431	-3.03027	0.703439
22	C	2.786252	-1.87436	-0.09759
23	H	3.571178	-2.49097	0.357836
24	H	3.164215	-1.57274	-1.0722
25	C	-2.73482	-1.15978	1.614591
26	H	-3.70465	-1.64134	1.774658
27	H	-2.04327	-1.51042	2.378291
28	C	-2.88203	0.347634	1.838496
29	C	-3.16896	-1.20972	-0.74424
30	H	-4.14658	-1.01395	-0.3037
31	H	-3.29733	-2.08744	-1.38227
32	C	-2.81838	-0.03987	-1.66377
33	C	0.872791	-1.86915	-2.42584
34	H	-0.02877	-1.77744	-3.03115
35	H	1.454756	-2.70591	-2.82412
36	C	1.632888	-0.56073	-2.67194
37	C	2.516889	-0.95958	2.129725
38	H	3.241764	-1.73618	2.392568
39	H	2.807475	-0.05719	2.669509
40	C	1.148813	-1.32967	2.699825
41	C	3.430263	0.427941	0.388347
42	H	3.623682	0.442412	-0.68276
43	H	4.396678	0.344655	0.897958
44	C	2.8027	1.784272	0.719263
45	O	-3.11045	2.941116	-0.62423

46	H	-1.27114	2.989484	-0.8427
47	H	0.233083	3.394954	-0.50388
48	H	-3.39036	2.305094	-1.2996
49	H	-2.8898	2.372741	0.136108
50	H	-2.35786	-3.58465	0.237855
51	H	-0.43599	-4.03362	-1.08692
52	H	-1.32846	-2.75213	-1.8784
53	O	1.528891	4.613301	-0.09802
54	H	1.876025	5.061819	-0.86898
55	H	2.249452	4.023169	0.208521

Table S11. Optimized Cartesian coordinates (Å) of the $[\text{Tb}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Tb	-0.03854	0.298532	0.008302
2	O	-2.0306	1.108872	1.164815
3	O	-3.65849	0.789526	2.65042
4	O	-1.57912	0.208377	-1.81731
5	O	-3.73611	0.56587	-2.22371
6	O	1.403128	0.375097	-1.87188
7	O	2.351057	-0.51706	-3.67714
8	O	0.137841	-0.88349	2.047064
9	O	1.091676	-1.96647	3.739092
10	O	1.550572	1.778065	1.045711
11	O	3.477494	2.803634	0.6488
12	O	-0.33882	2.649983	-0.82093
13	N	-2.16626	-1.45771	0.303544
14	N	0.46435	-2.11744	-1.03701
15	N	2.525672	-0.67531	0.690477
16	C	-1.58364	-2.79939	0.248776
17	H	-0.98258	-2.93051	1.14725
18	C	-0.72824	-2.98861	-0.99122
19	C	1.560054	-2.74933	-0.27904
20	H	1.86894	-3.67447	-0.78236
21	H	1.174014	-3.03431	0.698902
22	C	2.788693	-1.87093	-0.10771
23	H	3.578213	-2.48413	0.344334
24	H	3.161982	-1.56506	-1.08274
25	C	-2.7222	-1.13606	1.61324
26	H	-3.70261	-1.59541	1.7729
27	H	-2.0404	-1.50023	2.378915
28	C	-2.83641	0.374423	1.836977
29	C	-3.16244	-1.20597	-0.74416
30	H	-4.13869	-1.00315	-0.3038
31	H	-3.29498	-2.0877	-1.37573
32	C	-2.8081	-0.0446	-1.67227
33	C	0.864491	-1.88163	-2.43101
34	H	-0.04017	-1.7918	-3.03186

35	H	1.44468	-2.71943	-2.82959
36	C	1.623082	-0.57379	-2.68337
37	C	2.51162	-0.96428	2.121708
38	H	3.229159	-1.74836	2.382096
39	H	2.811046	-0.06718	2.665476
40	C	1.140107	-1.32424	2.688446
41	C	3.415802	0.437194	0.387281
42	H	3.603716	0.463302	-0.6847
43	H	4.384864	0.359476	0.892474
44	C	2.774224	1.783205	0.734122
45	O	-3.09804	2.931148	-0.63409
46	H	-1.25863	2.959475	-0.86461
47	H	0.233411	3.368795	-0.49584
48	H	-3.38334	2.29111	-1.30326
49	H	-2.86409	2.369529	0.126841
50	H	-2.35885	-3.57663	0.253594
51	H	-0.43608	-4.04193	-1.06718
52	H	-1.33021	-2.76924	-1.87044
53	O	1.493685	4.613932	-0.04969
54	H	1.845319	5.076432	-0.81029
55	H	2.21683	4.027554	0.258049

Table S12. Optimized Cartesian coordinates (Å) of the $[\text{Dy}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Dy	-0.03515	0.290446	0.000285
2	O	-2.0006	1.112578	1.157916
3	O	-3.6198	0.812718	2.656766
4	O	-1.56649	0.203632	-1.8152
5	O	-3.72019	0.554454	-2.24307
6	O	1.4004	0.371439	-1.86834
7	O	2.337881	-0.51421	-3.68217
8	O	0.13615	-0.87784	2.032546
9	O	1.079	-1.95372	3.735039
10	O	1.532804	1.767262	1.036678
11	O	3.458913	2.804801	0.668955
12	O	-0.33151	2.632433	-0.83173
13	N	-2.16173	-1.45379	0.305775
14	N	0.462981	-2.11831	-1.03603
15	N	2.524885	-0.67679	0.686038
16	C	-1.58289	-2.79701	0.253916
17	H	-0.98107	-2.92756	1.151896
18	C	-0.72913	-2.99012	-0.98652
19	C	1.561421	-2.75025	-0.28186
20	H	1.86917	-3.67486	-0.78672
21	H	1.178416	-3.03599	0.697102
22	C	2.789656	-1.87067	-0.11329

23	H	3.580888	-2.48306	0.33691
24	H	3.160593	-1.56346	-1.08877
25	C	-2.71426	-1.12451	1.614804
26	H	-3.70079	-1.57059	1.77416
27	H	-2.03851	-1.49693	2.38159
28	C	-2.80887	0.387345	1.837576
29	C	-3.15757	-1.20176	-0.74167
30	H	-4.13126	-0.9874	-0.30114
31	H	-3.29921	-2.08688	-1.36659
32	C	-2.79625	-0.04978	-1.67823
33	C	0.859185	-1.88303	-2.43131
34	H	-0.0469	-1.79429	-3.03006
35	H	1.43945	-2.72024	-2.83094
36	C	1.615678	-0.57449	-2.68439
37	C	2.508632	-0.96743	2.116604
38	H	3.219685	-1.75755	2.376398
39	H	2.81513	-0.07399	2.6625
40	C	1.134018	-1.31797	2.680703
41	C	3.40973	0.44001	0.385592
42	H	3.596872	0.470469	-0.68644
43	H	4.379242	0.366313	0.890445
44	C	2.759659	1.780479	0.737415
45	O	-3.0934	2.921071	-0.64472
46	H	-1.25189	2.938993	-0.87944
47	H	0.231976	3.350749	-0.49097
48	H	-3.3794	2.279409	-1.31184
49	H	-2.85238	2.362489	0.116022
50	H	-2.35986	-3.57247	0.260884
51	H	-0.43656	-4.04346	-1.05966
52	H	-1.33227	-2.7738	-1.86569
53	O	1.471768	4.612156	-0.02113
54	H	1.824597	5.084988	-0.77479
55	H	2.197232	4.027704	0.284856

Table S13. Optimized Cartesian coordinates (Å) of the [Ho(DTPA)(H₂O)]²⁻ · 2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Ho	-0.0326	0.284228	-0.0071
2	O	-1.97451	1.115044	1.151016
3	O	-3.581	0.832214	2.666462
4	O	-1.5543	0.198298	-1.81325
5	O	-3.70452	0.54271	-2.26219
6	O	1.397454	0.369516	-1.86288
7	O	2.327922	-0.5087	-3.68379
8	O	0.134847	-0.86914	2.017958
9	O	1.064585	-1.93867	3.731395
10	O	1.517847	1.756656	1.026494
11	O	3.442794	2.804746	0.684926

12	O	-0.32718	2.617475	-0.84327
13	N	-2.15773	-1.45021	0.308114
14	N	0.461901	-2.11805	-1.03493
15	N	2.525484	-0.6791	0.682392
16	C	-1.58228	-2.79468	0.257735
17	H	-0.97981	-2.92567	1.155153
18	C	-0.73008	-2.99002	-0.98333
19	C	1.562116	-2.75098	-0.284
20	H	1.867942	-3.67545	-0.79015
21	H	1.181521	-3.03692	0.695877
22	C	2.790809	-1.87151	-0.1179
23	H	3.582986	-2.48401	0.330569
24	H	3.159901	-1.56342	-1.09381
25	C	-2.70662	-1.1148	1.616869
26	H	-3.69874	-1.5484	1.775874
27	H	-2.03659	-1.49547	2.38435
28	C	-2.78271	0.397954	1.83969
29	C	-3.15345	-1.19728	-0.73873
30	H	-4.12404	-0.97045	-0.29768
31	H	-3.30529	-2.08569	-1.35665
32	C	-2.7848	-0.05523	-1.68402
33	C	0.855575	-1.88271	-2.43098
34	H	-0.05126	-1.79508	-3.02862
35	H	1.436566	-2.71903	-2.83134
36	C	1.609903	-0.5732	-2.68328
37	C	2.505904	-0.97102	2.112255
38	H	3.208904	-1.7683	2.371986
39	H	2.820745	-0.08173	2.660245
40	C	1.127503	-1.30982	2.673334
41	C	3.405687	0.441292	0.384448
42	H	3.593421	0.474805	-0.68741
43	H	4.375066	0.371839	0.890121
44	C	2.747554	1.776973	0.738874
45	O	-3.09184	2.910339	-0.65357
46	H	-1.24813	2.921383	-0.89271
47	H	0.228841	3.334829	-0.48886
48	H	-3.37765	2.267688	-1.31962
49	H	-2.84374	2.35389	0.10627
50	H	-2.36078	-3.56859	0.265956
51	H	-0.43753	-4.04337	-1.05549
52	H	-1.33425	-2.77479	-1.86207
53	O	1.451439	4.609277	0.002971
54	H	1.805358	5.091602	-0.74414
55	H	2.178934	4.026417	0.307099

Table S14. Optimized Cartesian coordinates (Å) of the [Er(DTPA)(H₂O)]²⁻ · 2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Er	-0.0303	0.278706	-0.01441
2	O	-1.94976	1.117573	1.144278
3	O	-3.5442	0.851072	2.675051
4	O	-1.54201	0.192199	-1.81201
5	O	-3.68864	0.531378	-2.28091
6	O	1.394338	0.367941	-1.85687
7	O	2.318818	-0.50254	-3.68445
8	O	0.134353	-0.85983	2.00307
9	O	1.049935	-1.92229	3.72829
10	O	1.502857	1.745574	1.01831
11	O	3.425775	2.804603	0.700799
12	O	-0.32398	2.603717	-0.85429
13	N	-2.154	-1.4465	0.310386
14	N	0.461111	-2.1177	-1.03387
15	N	2.527019	-0.68188	0.679195
16	C	-1.5816	-2.79204	0.261546
17	H	-0.9786	-2.92336	1.158502
18	C	-0.73075	-2.98977	-0.97998
19	C	1.563261	-2.75161	-0.28646
20	H	1.867194	-3.67589	-0.79406
21	H	1.185242	-3.03799	0.694339
22	C	2.792527	-1.87236	-0.12273
23	H	3.585711	-2.48537	0.323428
24	H	3.159557	-1.56295	-1.09901
25	C	-2.69943	-1.10515	1.618799
26	H	-3.69674	-1.52683	1.777464
27	H	-2.03501	-1.49354	2.387056
28	C	-2.75788	0.408311	1.841379
29	C	-3.14942	-1.19273	-0.73596
30	H	-4.11687	-0.95347	-0.29461
31	H	-3.31135	-2.08429	-1.3469
32	C	-2.7733	-0.06077	-1.68997
33	C	0.851943	-1.88188	-2.43061
34	H	-0.05579	-1.79484	-3.02688
35	H	1.433423	-2.71723	-2.83224
36	C	1.604294	-0.57138	-2.68173
37	C	2.503807	-0.9758	2.108085
38	H	3.197461	-1.78139	2.367257
39	H	2.828319	-0.09162	2.65879
40	C	1.121279	-1.30131	2.666007
41	C	3.401785	0.442662	0.384078
42	H	3.590287	0.479538	-0.68755
43	H	4.371024	0.378073	0.890671
44	C	2.734971	1.773229	0.741338
45	O	-3.09127	2.899783	-0.66154

46	H	-1.24564	2.904891	-0.90381
47	H	0.225422	3.319956	-0.48771
48	H	-3.37605	2.255308	-1.32611
49	H	-2.83644	2.346281	0.098064
50	H	-2.3615	-3.56455	0.270978
51	H	-0.43824	-4.0432	-1.05071
52	H	-1.33584	-2.77614	-1.8585
53	O	1.432267	4.605134	0.023871
54	H	1.787116	5.096351	-0.71697
55	H	2.161564	4.023593	0.326511

Table S15. Optimized Cartesian coordinates (Å) of the $[\text{Tm}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Tm	-0.02911	0.273068	-0.02158
2	O	-1.92594	1.120371	1.137711
3	O	-3.51029	0.870075	2.681293
4	O	-1.53124	0.186559	-1.81137
5	O	-3.67459	0.520106	-2.29822
6	O	1.392393	0.366828	-1.85199
7	O	2.311425	-0.49784	-3.68498
8	O	0.134855	-0.85352	1.989372
9	O	1.037498	-1.90706	3.726565
10	O	1.487288	1.733913	1.010623
11	O	3.407466	2.804314	0.716876
12	O	-0.32086	2.590576	-0.86647
13	N	-2.15028	-1.44242	0.312689
14	N	0.460404	-2.11673	-1.03274
15	N	2.529709	-0.68532	0.676975
16	C	-1.5808	-2.78904	0.265502
17	H	-0.97729	-2.92045	1.162026
18	C	-0.73127	-2.98908	-0.97651
19	C	1.564642	-2.75193	-0.28925
20	H	1.866423	-3.6758	-0.79877
21	H	1.189248	-3.03909	0.692361
22	C	2.794739	-1.87323	-0.12759
23	H	3.588843	-2.4874	0.315525
24	H	3.159483	-1.56184	-1.1041
25	C	-2.69225	-1.09517	1.620826
26	H	-3.69406	-1.50595	1.779531
27	H	-2.03273	-1.4901	2.389773
28	C	-2.73461	0.418893	1.842285
29	C	-3.14578	-1.18824	-0.73305
30	H	-4.11004	-0.93729	-0.29127
31	H	-3.31726	-2.08284	-1.33699
32	C	-2.76314	-0.0661	-1.6956
33	C	0.84799	-1.88047	-2.43038
34	H	-0.06096	-1.79264	-3.02458

35	H	1.428656	-2.71549	-2.83375
36	C	1.599715	-0.56977	-2.68047
37	C	2.502871	-0.98195	2.104649
38	H	3.187088	-1.79596	2.362667
39	H	2.837254	-0.10339	2.658514
40	C	1.116481	-1.2946	2.659767
41	C	3.398062	0.444037	0.38483
42	H	3.587518	0.484304	-0.68652
43	H	4.367079	0.385227	0.892561
44	C	2.721674	1.769219	0.744248
45	O	-3.09057	2.889963	-0.6694
46	H	-1.24301	2.889512	-0.91637
47	H	0.222181	3.305477	-0.48825
48	H	-3.37481	2.244301	-1.33284
49	H	-2.82855	2.338769	0.089279
50	H	-2.36208	-3.56014	0.276169
51	H	-0.43863	-4.0425	-1.04583
52	H	-1.33735	-2.77714	-1.85476
53	O	1.412523	4.601148	0.043532
54	H	1.76871	5.100696	-0.69105
55	H	2.143339	4.020868	0.345177

Table S16. Optimized Cartesian coordinates (Å) of the $[\text{Yb}(\text{DTPA})(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Yb	-0.0293	0.270942	-0.02674
2	O	-1.90969	1.121426	1.130964
3	O	-3.48169	0.883239	2.688787
4	O	-1.52124	0.182135	-1.80842
5	O	-3.66093	0.508311	-2.3151
6	O	1.388954	0.368037	-1.84291
7	O	2.306485	-0.48826	-3.68043
8	O	0.13558	-0.8446	1.973816
9	O	1.022921	-1.88755	3.724863
10	O	1.477509	1.723937	0.998712
11	O	3.395382	2.802619	0.722867
12	O	-0.32108	2.580624	-0.87185
13	N	-2.14794	-1.43989	0.314963
14	N	0.459712	-2.1147	-1.03101
15	N	2.534775	-0.68958	0.675286
16	C	-1.58031	-2.78695	0.268145
17	H	-0.97629	-2.91893	1.164205
18	C	-0.73173	-2.98735	-0.97437
19	C	1.564959	-2.75219	-0.29088
20	H	1.863727	-3.67612	-0.80204
21	H	1.191501	-3.03962	0.691412
22	C	2.797088	-1.87584	-0.13105
23	H	3.590907	-2.49248	0.309452

24	H	3.160302	-1.56365	-1.10792
25	C	-2.68664	-1.08855	1.62302
26	H	-3.69189	-1.49072	1.782132
27	H	-2.03094	-1.48882	2.392316
28	C	-2.71644	0.425795	1.843651
29	C	-3.14306	-1.18455	-0.73026
30	H	-4.10419	-0.92212	-0.28833
31	H	-3.32402	-2.08159	-1.32791
32	C	-2.75365	-0.07144	-1.7002
33	C	0.845643	-1.8767	-2.42875
34	H	-0.06372	-1.78844	-3.02218
35	H	1.426865	-2.71048	-2.83383
36	C	1.595924	-0.56499	-2.67548
37	C	2.502262	-0.98728	2.101801
38	H	3.175523	-1.81026	2.360456
39	H	2.846863	-0.11426	2.658261
40	C	1.111148	-1.28499	2.653114
41	C	3.398114	0.442894	0.384621
42	H	3.590149	0.483701	-0.68628
43	H	4.366234	0.390091	0.894834
44	C	2.713815	1.764563	0.741742
45	O	-3.09311	2.880426	-0.67646
46	H	-1.2434	2.878232	-0.9232
47	H	0.21761	3.293987	-0.48482
48	H	-3.37523	2.234424	-1.34025
49	H	-2.82565	2.330322	0.081016
50	H	-2.36229	-3.55736	0.279207
51	H	-0.43892	-4.04069	-1.04382
52	H	-1.33849	-2.77569	-1.85223
53	O	1.397464	4.597667	0.058909
54	H	1.752446	5.103424	-0.672
55	H	2.130031	4.017547	0.356868

Table S17. Optimized Cartesian coordinates (Å) of the [Lu(DTPA)(H₂O)]²⁻ @2H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Lu	-0.02857	0.266553	-0.03077
2	O	-1.89421	1.122585	1.125014
3	O	-3.45632	0.89579	2.694339
4	O	-1.511	0.17878	-1.80561
5	O	-3.64702	0.497774	-2.33124
6	O	1.386651	0.368984	-1.83632
7	O	2.301842	-0.48106	-3.67786
8	O	0.135942	-0.84064	1.962841
9	O	1.013817	-1.87378	3.724204
10	O	1.467712	1.714527	0.990579
11	O	3.382537	2.801385	0.72699
12	O	-0.3201	2.57021	-0.87694

13	N	-2.14478	-1.43661	0.317108
14	N	0.458991	-2.11273	-1.02943
15	N	2.537273	-0.69296	0.673566
16	C	-1.57999	-2.78459	0.27036
17	H	-0.97565	-2.9178	1.165981
18	C	-0.73254	-2.98535	-0.9727
19	C	1.564861	-2.75265	-0.29214
20	H	1.861073	-3.67644	-0.80498
21	H	1.19301	-3.04053	0.690633
22	C	2.798325	-1.87794	-0.13393
23	H	3.592273	-2.49593	0.30464
24	H	3.160177	-1.56514	-1.11113
25	C	-2.68098	-1.08196	1.625105
26	H	-3.6892	-1.47664	1.784119
27	H	-2.02879	-1.48691	2.394777
28	C	-2.69971	0.432571	1.8446
29	C	-3.13976	-1.17971	-0.72746
30	H	-4.0974	-0.90564	-0.28508
31	H	-3.33064	-2.07894	-1.31879
32	C	-2.7438	-0.07567	-1.70468
33	C	0.843975	-1.87389	-2.42737
34	H	-0.06547	-1.7862	-3.02065
35	H	1.426071	-2.70674	-2.83301
36	C	1.592836	-0.56128	-2.67204
37	C	2.501611	-0.99136	2.099303
38	H	3.167656	-1.82021	2.35802
39	H	2.853198	-0.12216	2.657416
40	C	1.107676	-1.27911	2.648427
41	C	3.396396	0.442219	0.383949
42	H	3.590445	0.483586	-0.68655
43	H	4.363732	0.394322	0.896189
44	C	2.705092	1.760515	0.739673
45	O	-3.09467	2.871516	-0.68352
46	H	-1.24261	2.866157	-0.93065
47	H	0.213484	3.282444	-0.48113
48	H	-3.37501	2.224828	-1.3472
49	H	-2.82239	2.323018	0.073295
50	H	-2.36331	-3.55364	0.281483
51	H	-0.43989	-4.03865	-1.04269
52	H	-1.33993	-2.77344	-1.85007
53	O	1.382582	4.595099	0.074156
54	H	1.735592	5.106312	-0.65391
55	H	2.116963	4.014839	0.367748

Table S18. Optimized Cartesian coordinates (Å) of the [La(AAZTA)(H₂O)₂]⁻•4H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	La	-0.46291	0.080846	0.309722
2	O	0.741133	2.035147	1.455788
3	N	2.036944	-0.9392	-0.12223
4	C	2.001572	-2.41708	-0.15448
5	H	2.794059	-2.82764	0.470924
6	H	2.202381	-2.79168	-1.15537
7	O	1.733383	4.027343	1.537109
8	N	0.160096	-0.47821	-2.34963
9	C	0.679967	-3.08172	0.260292
10	N	1.134565	1.832909	-1.25334
11	C	2.507174	-0.31472	-1.40405
12	C	2.471677	1.216283	-1.29865
13	H	3.024059	1.535831	-0.42035
14	H	3.025176	1.6154	-2.15529
15	C	0.581068	1.963386	-2.61135
16	H	1.391363	2.142873	-3.32414
17	H	-0.06699	2.835067	-2.64413
18	O	0.738279	-4.26092	0.608454
19	O	-0.37704	-2.38894	0.149904
20	C	-0.24876	0.754557	-3.03148
21	H	-0.18741	0.631448	-4.11912
22	H	-1.2942	0.931005	-2.7841
23	O	0.801101	-0.81979	2.331838
24	C	1.589738	-0.76631	-2.55816
25	H	1.946557	-0.28768	-3.47462
26	H	1.709399	-1.8327	-2.72643
27	O	2.741951	-1.1752	3.365649
28	C	2.799568	-0.53987	1.071729
29	H	2.911265	0.540508	1.112193
30	H	3.796245	-0.98406	1.089476
31	O	-1.86141	2.303192	-0.21863
32	C	2.074673	-0.89466	2.37554
33	C	1.223868	3.140721	-0.60158
34	H	0.316513	3.699243	-0.82987
35	H	2.074896	3.723044	-0.96626
36	O	-2.36656	-0.67937	-1.30917
37	C	1.266418	3.069628	0.925172
38	O	-2.97212	-2.23518	-2.78111
39	C	3.946841	-0.71436	-1.74308
40	H	4.647094	-0.29582	-1.02081
41	H	4.069206	-1.79638	-1.74757
42	C	-0.69665	-1.58021	-2.7871
43	H	-0.29787	-2.5139	-2.39511
44	H	-0.72688	-1.66128	-3.87862
45	C	-2.13619	-1.50289	-2.27164

46	O	-2.40093	0.089858	2.424145
47	H	4.223886	-0.3429	-2.72885
48	H	-2.03727	-0.48316	3.129661
49	H	-3.12051	-0.40332	1.98812
50	H	-2.02254	2.730876	0.639569
51	H	-2.71878	2.17829	-0.66825
52	O	-1.78226	2.937235	2.520487
53	H	-2.16549	2.069378	2.711548
54	H	-0.83518	2.750432	2.429913
55	O	-4.0566	1.458725	-1.58695
56	H	-4.15631	1.750086	-2.49356
57	H	-3.59896	0.59959	-1.6293
58	O	-4.13632	-1.27094	0.742085
59	O	-0.98751	-1.37435	4.226547
60	H	-4.19469	-2.21197	0.90904
61	H	-3.60842	-1.1822	-0.07348
62	H	-1.16289	-2.31508	4.249077
63	H	-0.21405	-1.25883	3.629227

Table S19. Optimized Cartesian coordinates (Å) of the $[\text{Ce}(\text{AAZTA})(\text{H}_2\text{O})_2]^- \cdot 4\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Ce	-0.41675	0.119229	0.310712
2	O	0.746344	2.066661	1.447876
3	N	2.045455	-0.92092	-0.11199
4	C	1.990591	-2.39846	-0.12541
5	H	2.790357	-2.81256	0.488278
6	H	2.16413	-2.78728	-1.12595
7	O	1.748368	4.054273	1.518876
8	N	0.154393	-0.47036	-2.3244
9	C	0.666919	-3.03628	0.325338
10	N	1.153048	1.842979	-1.26172
11	C	2.510878	-0.31454	-1.40441
12	C	2.48694	1.218459	-1.31451
13	H	3.050417	1.544046	-0.44548
14	H	3.033713	1.60492	-2.18106
15	C	0.58774	1.964737	-2.61629
16	H	1.392508	2.130894	-3.33828
17	H	-0.0542	2.840776	-2.65254
18	O	0.714166	-4.20562	0.705134
19	O	-0.38309	-2.33274	0.207946
20	C	-0.25409	0.757079	-3.01635
21	H	-0.2034	0.621324	-4.10292
22	H	-1.29631	0.942555	-2.76197
23	O	0.817841	-0.74255	2.341896
24	C	1.579695	-0.7706	-2.54605
25	H	1.930173	-0.30206	-3.47002
26	H	1.690759	-1.83906	-2.70673

27	O	2.754678	-1.11354	3.377585
28	C	2.818621	-0.51634	1.073408
29	H	2.95198	0.562121	1.096347
30	H	3.806992	-0.97853	1.095428
31	O	-1.8465	2.283138	-0.18557
32	C	2.090301	-0.83757	2.384531
33	C	1.249047	3.154001	-0.61629
34	H	0.34769	3.718696	-0.85342
35	H	2.106314	3.728062	-0.97902
36	O	-2.34774	-0.63912	-1.22544
37	C	1.28022	3.094828	0.91189
38	O	-2.99502	-2.21735	-2.6533
39	C	3.943335	-0.73152	-1.75117
40	H	4.65377	-0.31509	-1.03773
41	H	4.052948	-1.81502	-1.74778
42	C	-0.7185	-1.57071	-2.73271
43	H	-0.31576	-2.50477	-2.34579
44	H	-0.77825	-1.65878	-3.82236
45	C	-2.14275	-1.48014	-2.18006
46	O	-2.32432	-0.04916	2.18496
47	H	4.216501	-0.37133	-2.74221
48	H	-2.01302	-0.58195	2.948453
49	H	-3.10442	-0.50009	1.800971
50	H	-2.01337	2.700248	0.676574
51	H	-2.70045	2.17655	-0.64641
52	O	-1.78236	2.796214	2.556038
53	H	-2.1306	1.903973	2.687029
54	H	-0.82526	2.667515	2.465006
55	O	-4.05486	1.491618	-1.55967
56	H	-4.14846	1.771255	-2.47066
57	H	-3.60418	0.629333	-1.58774
58	O	-4.22524	-1.27089	0.683915
59	O	-1.02667	-1.35874	4.157934
60	H	-4.32268	-2.21215	0.830634
61	H	-3.65898	-1.18231	-0.10672
62	H	-1.15159	-2.30663	4.206189
63	H	-0.21957	-1.22033	3.612569

Table S20. Optimized Cartesian coordinates (Å) of the [Pr(AAZTA)(H₂O)₂]⁻•4H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Pr	-0.39548	0.11873	0.299356
2	O	0.738138	2.050862	1.439879
3	N	2.047861	-0.91629	-0.11151
4	C	1.990042	-2.39384	-0.11965
5	H	2.788132	-2.80723	0.496653
6	H	2.16422	-2.78661	-1.11851
7	O	1.714417	4.050382	1.52662

8	N	0.156427	-0.47032	-2.31884
9	C	0.664277	-3.02669	0.332399
10	N	1.154583	1.841671	-1.26496
11	C	2.513763	-0.31434	-1.40557
12	C	2.489333	1.219027	-1.31953
13	H	3.054356	1.547014	-0.45243
14	H	3.033795	1.603848	-2.18817
15	C	0.587222	1.963216	-2.61858
16	H	1.390468	2.129978	-3.34204
17	H	-0.05582	2.838443	-2.65402
18	O	0.707638	-4.19653	0.710936
19	O	-0.38329	-2.31906	0.217575
20	C	-0.25347	0.753865	-3.01571
21	H	-0.20241	0.613733	-4.10159
22	H	-1.29578	0.939112	-2.76192
23	O	0.812123	-0.73107	2.331928
24	C	1.58059	-0.77331	-2.54455
25	H	1.928972	-0.3072	-3.47042
26	H	1.690187	-1.84229	-2.70265
27	O	2.743938	-1.08545	3.382774
28	C	2.819485	-0.50864	1.0738
29	H	2.957719	0.569226	1.091697
30	H	3.805786	-0.9749	1.101183
31	O	-1.83478	2.252366	-0.17017
32	C	2.084601	-0.82053	2.383383
33	C	1.246421	3.15103	-0.61594
34	H	0.347447	3.717133	-0.8585
35	H	2.106651	3.725956	-0.96994
36	O	-2.3263	-0.62397	-1.18645
37	C	1.26422	3.087523	0.911943
38	O	-3.00061	-2.20941	-2.59314
39	C	3.945788	-0.73261	-1.75129
40	H	4.656122	-0.31537	-1.03819
41	H	4.054777	-1.81616	-1.74606
42	C	-0.72328	-1.56986	-2.71388
43	H	-0.31727	-2.50477	-2.33283
44	H	-0.80031	-1.65836	-3.80234
45	C	-2.13798	-1.47266	-2.13878
46	O	-2.28644	-0.05714	2.112118
47	H	4.219428	-0.37409	-2.74282
48	H	-1.99398	-0.58452	2.887931
49	H	-3.08747	-0.48653	1.74475
50	H	-1.99988	2.675731	0.689004
51	H	-2.68766	2.156834	-0.63501
52	O	-1.76894	2.76294	2.572166
53	H	-2.1132	1.8651	2.671341
54	H	-0.81202	2.63877	2.472542
55	O	-4.04817	1.493657	-1.55366
56	H	-4.13448	1.769487	-2.46654

57	H	-3.59716	0.63182	-1.57419
58	O	-4.24973	-1.24429	0.677851
59	O	-1.0478	-1.35332	4.124475
60	H	-4.35792	-2.18274	0.834863
61	H	-3.67407	-1.17015	-0.10726
62	H	-1.17385	-2.30111	4.172374
63	H	-0.23093	-1.21574	3.593454

Table S21. Optimized Cartesian coordinates (Å) of the [Nd(AAZTA)(H₂O)₂]⁻•4H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Nd	-0.38835	0.10004	0.281175
2	O	0.688314	2.012757	1.446984
3	N	2.044951	-0.92124	-0.12051
4	C	1.987663	-2.39892	-0.13367
5	H	2.782947	-2.81414	0.484968
6	H	2.166645	-2.78832	-1.13299
7	O	1.675942	4.004053	1.57473
8	N	0.159093	-0.47074	-2.32526
9	C	0.659985	-3.03267	0.310709
10	N	1.149475	1.833247	-1.25259
11	C	2.514544	-0.31522	-1.41093
12	C	2.486811	1.217029	-1.31801
13	H	3.055603	1.542841	-0.45256
14	H	3.02492	1.608018	-2.18773
15	C	0.577785	1.968135	-2.60333
16	H	1.37785	2.152974	-3.32585
17	H	-0.074	2.837187	-2.62405
18	O	0.699823	-4.20602	0.678133
19	O	-0.38549	-2.32099	0.201883
20	C	-0.25241	0.756126	-3.01644
21	H	-0.19187	0.623897	-4.10274
22	H	-1.29764	0.933155	-2.76961
23	O	0.799345	-0.74619	2.312755
24	C	1.583746	-0.77018	-2.55304
25	H	1.931344	-0.29805	-3.47614
26	H	1.695441	-1.8381	-2.71681
27	O	2.725406	-1.09106	3.377207
28	C	2.813037	-0.51701	1.068157
29	H	2.953675	0.56047	1.088593
30	H	3.798454	-0.98487	1.098384
31	O	-1.82824	2.214275	-0.18449
32	C	2.071521	-0.8301	2.373055
33	C	1.236969	3.134637	-0.58675
34	H	0.344303	3.707985	-0.83496
35	H	2.10436	3.710182	-0.92104
36	O	-2.31571	-0.63404	-1.18496
37	C	1.230806	3.052231	0.940066

38	O	-2.99416	-2.21748	-2.59215
39	C	3.947616	-0.7306	-1.75472
40	H	4.655646	-0.3172	-1.03712
41	H	4.057168	-1.8141	-1.7557
42	C	-0.71961	-1.56956	-2.72491
43	H	-0.3088	-2.50673	-2.35492
44	H	-0.80275	-1.64873	-3.8136
45	C	-2.13094	-1.48006	-2.14037
46	O	-2.22699	-0.01923	2.113724
47	H	4.223817	-0.36602	-2.74333
48	H	-1.94254	-0.53727	2.899479
49	H	-3.0377	-0.44225	1.759101
50	H	-1.99423	2.649594	0.668811
51	H	-2.67905	2.124722	-0.65366
52	O	-1.80085	2.787867	2.548702
53	H	-2.14442	1.889299	2.646114
54	H	-0.845	2.652858	2.454395
55	O	-4.04555	1.474959	-1.57622
56	H	-4.1252	1.746306	-2.49106
57	H	-3.59551	0.612691	-1.58918
58	O	-4.2159	-1.20368	0.714257
59	O	-1.02972	-1.31203	4.148603
60	H	-4.33295	-2.13754	0.89107
61	H	-3.65048	-1.15141	-0.08017
62	H	-1.18117	-2.25567	4.204674
63	H	-0.21934	-1.19975	3.60122

Table S22. Optimized Cartesian coordinates (Å) of the $[\text{Pm}(\text{AAZTA})(\text{H}_2\text{O})_2]^- \cdot 4\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Pm	-0.37474	0.09984	0.27288
2	O	0.678591	1.999226	1.443963
3	N	2.044222	-0.91408	-0.12255
4	C	1.985128	-2.39191	-0.13211
5	H	2.779425	-2.80656	0.488083
6	H	2.164306	-2.78395	-1.13034
7	O	1.65082	3.996922	1.585591
8	N	0.158046	-0.46854	-2.32165
9	C	0.656315	-3.02226	0.313396
10	N	1.146789	1.833487	-1.25229
11	C	2.514251	-0.31155	-1.41411
12	C	2.485373	1.220566	-1.32337
13	H	3.057472	1.548252	-0.46083
14	H	3.018843	1.611358	-2.19595
15	C	0.570727	1.970801	-2.60092
16	H	1.367824	2.161065	-3.32524
17	H	-0.08454	2.837274	-2.61659
18	O	0.693042	-4.1968	0.677185

19	O	-0.38706	-2.30683	0.209319
20	C	-0.25587	0.756496	-3.01481
21	H	-0.19366	0.622936	-4.10076
22	H	-1.30168	0.930995	-2.76912
23	O	0.796645	-0.73661	2.303183
24	C	1.581981	-0.76817	-2.55399
25	H	1.926791	-0.29645	-3.47828
26	H	1.693563	-1.83619	-2.71716
27	O	2.719825	-1.0686	3.377012
28	C	2.813167	-0.50805	1.064964
29	H	2.957209	0.568959	1.082032
30	H	3.797125	-0.97876	1.0972
31	O	-1.814	2.197835	-0.17774
32	C	2.068636	-0.81531	2.369016
33	C	1.232321	3.132658	-0.58189
34	H	0.342238	3.708561	-0.83301
35	H	2.102339	3.708169	-0.90908
36	O	-2.30512	-0.62606	-1.16581
37	C	1.216863	3.044489	0.94424
38	O	-2.99722	-2.21292	-2.56221
39	C	3.946905	-0.72765	-1.75777
40	H	4.655295	-0.31386	-1.04075
41	H	4.056093	-1.81121	-1.75791
42	C	-0.72273	-1.56785	-2.71515
43	H	-0.3096	-2.50512	-2.34813
44	H	-0.81393	-1.64718	-3.80313
45	C	-2.12894	-1.47576	-2.11974
46	O	-2.19727	-0.03504	2.085161
47	H	4.222801	-0.36394	-2.74679
48	H	-1.91963	-0.55444	2.872494
49	H	-3.017	-0.44658	1.737241
50	H	-1.98193	2.633112	0.675203
51	H	-2.66378	2.113241	-0.64949
52	O	-1.80175	2.771584	2.558254
53	H	-2.14113	1.870425	2.645055
54	H	-0.84569	2.639271	2.461961
55	O	-4.03772	1.478238	-1.57141
56	H	-4.11673	1.747385	-2.48696
57	H	-3.59053	0.614657	-1.58183
58	O	-4.2194	-1.19435	0.716532
59	O	-1.027	-1.33723	4.130367
60	H	-4.34186	-2.12753	0.893338
61	H	-3.65194	-1.14523	-0.07653
62	H	-1.17487	-2.28232	4.169417
63	H	-0.21522	-1.21255	3.587692

Table S23. Optimized Cartesian coordinates (Å) of the [Sm(AAZTA)(H₂O)₂]⁻ · 4H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Sm	-0.36478	0.101501	0.265331
2	O	0.672446	1.989631	1.438223
3	N	2.040926	-0.908	-0.12046
4	C	1.977755	-2.38592	-0.12404
5	H	2.768798	-2.80017	0.500499
6	H	2.159214	-2.78268	-1.11995
7	O	1.635865	3.990649	1.58929
8	N	0.158765	-0.46957	-2.3181
9	C	0.645943	-3.0102	0.320556
10	N	1.146679	1.831442	-1.2544
11	C	2.514228	-0.31207	-1.41361
12	C	2.485852	1.220019	-1.32817
13	H	3.060511	1.550622	-0.46848
14	H	3.016237	1.608289	-2.2037
15	C	0.568336	1.969555	-2.60189
16	H	1.363622	2.163719	-3.32714
17	H	-0.08982	2.83384	-2.61459
18	O	0.676787	-4.18565	0.681745
19	O	-0.39391	-2.2893	0.218957
20	C	-0.25487	0.75292	-3.01611
21	H	-0.18878	0.616086	-4.10135
22	H	-1.3016	0.926313	-2.77412
23	O	0.789385	-0.72338	2.295914
24	C	1.582007	-0.7714	-2.55194
25	H	1.926184	-0.30217	-3.47768
26	H	1.692578	-1.83994	-2.71238
27	O	2.708025	-1.04254	3.381827
28	C	2.81021	-0.49938	1.066032
29	H	2.959014	0.576949	1.078265
30	H	3.792012	-0.97424	1.101826
31	O	-1.79916	2.18479	-0.17606
32	C	2.061039	-0.79796	2.3689
33	C	1.231562	3.129643	-0.58217
34	H	0.344011	3.707989	-0.83622
35	H	2.10413	3.704024	-0.90434
36	O	-2.29536	-0.61735	-1.15341
37	C	1.208875	3.038191	0.943321
38	O	-3.00016	-2.20682	-2.54016
39	C	3.946536	-0.73132	-1.75393
40	H	4.654708	-0.3162	-1.03747
41	H	4.05409	-1.81505	-1.75043
42	C	-0.72413	-1.569	-2.70636
43	H	-0.31101	-2.50625	-2.33934
44	H	-0.81983	-1.6503	-3.79377
45	C	-2.12681	-1.47131	-2.10478

46	O	-2.17519	-0.04306	2.059693
47	H	4.224027	-0.37125	-2.74385
48	H	-1.90358	-0.56373	2.848276
49	H	-3.0016	-0.44524	1.716414
50	H	-1.96757	2.619006	0.677461
51	H	-2.64858	2.104414	-0.64887
52	O	-1.80043	2.761615	2.559804
53	H	-2.13755	1.859028	2.639809
54	H	-0.84416	2.630533	2.463158
55	O	-4.03068	1.482787	-1.57004
56	H	-4.10496	1.750403	-2.48645
57	H	-3.58506	0.618486	-1.57688
58	O	-4.22259	-1.18299	0.71428
59	O	-1.02943	-1.35165	4.115567
60	H	-4.34814	-2.11547	0.892604
61	H	-3.65266	-1.13694	-0.07718
62	H	-1.17282	-2.29793	4.140619
63	H	-0.21671	-1.21566	3.576842

Table S24. Optimized Cartesian coordinates (Å) of the $[\text{Eu}(\text{AAZTA})(\text{H}_2\text{O})_2]^- \cdot 4\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Eu	-0.35725	0.098623	0.259042
2	O	0.663819	1.974071	1.433752
3	N	2.038276	-0.90373	-0.11942
4	C	1.97324	-2.38176	-0.11918
5	H	2.759774	-2.79515	0.51153
6	H	2.160688	-2.78181	-1.11264
7	O	1.618152	3.978063	1.599011
8	N	0.159494	-0.47088	-2.3153
9	C	0.63833	-3.00279	0.31974
10	N	1.145803	1.828408	-1.25441
11	C	2.514332	-0.31242	-1.41351
12	C	2.485765	1.219414	-1.33156
13	H	3.062851	1.552201	-0.47435
14	H	3.012909	1.606474	-2.20954
15	C	0.565121	1.968655	-2.60048
16	H	1.358486	2.167821	-3.32645
17	H	-0.09627	2.830465	-2.60931
18	O	0.66362	-4.1803	0.674268
19	O	-0.39828	-2.27674	0.221749
20	C	-0.25416	0.749862	-3.01654
21	H	-0.18394	0.611217	-4.10124
22	H	-1.30188	0.921461	-2.77818
23	O	0.782362	-0.71778	2.288183
24	C	1.582251	-0.77392	-2.55058
25	H	1.925689	-0.30647	-3.47749
26	H	1.692341	-1.84284	-2.70886

27	O	2.697304	-1.01883	3.385822
28	C	2.807204	-0.49309	1.066581
29	H	2.959921	0.582604	1.075116
30	H	3.787244	-0.97125	1.105819
31	O	-1.78432	2.168569	-0.17785
32	C	2.053749	-0.78491	2.36806
33	C	1.229097	3.124568	-0.57833
34	H	0.343826	3.705245	-0.83462
35	H	2.103975	3.69889	-0.89414
36	O	-2.2862	-0.6121	-1.14391
37	C	1.198686	3.026851	0.946273
38	O	-3.00027	-2.20664	-2.51978
39	C	3.946549	-0.73346	-1.7511
40	H	4.654165	-0.31777	-1.03443
41	H	4.053336	-1.81726	-1.74593
42	C	-0.72459	-1.5703	-2.70079
43	H	-0.31022	-2.50808	-2.33674
44	H	-0.82523	-1.65066	-3.78781
45	C	-2.1236	-1.47039	-2.09219
46	O	-2.15574	-0.045	2.038248
47	H	4.225468	-0.37508	-2.74125
48	H	-1.88965	-0.56375	2.829972
49	H	-2.98731	-0.44026	1.699273
50	H	-1.95204	2.607169	0.673441
51	H	-2.63336	2.092837	-0.65211
52	O	-1.79999	2.756764	2.558299
53	H	-2.13833	1.85414	2.631569
54	H	-0.844	2.622692	2.463633
55	O	-4.02087	1.485843	-1.57204
56	H	-4.09438	1.75092	-2.48925
57	H	-3.57865	0.619904	-1.57599
58	O	-4.2232	-1.17017	0.713216
59	O	-1.03169	-1.34893	4.108775
60	H	-4.35476	-2.10142	0.893628
61	H	-3.65216	-1.12931	-0.07772
62	H	-1.17484	-2.29524	4.13435
63	H	-0.21821	-1.2129	3.57105

Table S25. Optimized Cartesian coordinates (Å) of the $[\text{Gd}(\text{AAZTA})(\text{H}_2\text{O})_2]^- \cdot 4\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Gd	-0.35027	0.095537	0.254862
2	O	0.658124	1.959774	1.431066
3	N	2.03605	-0.90057	-0.11926
4	C	1.969676	-2.3787	-0.11677
5	H	2.7522	-2.79163	0.519136
6	H	2.162549	-2.78085	-1.10832
7	O	1.604227	3.966414	1.608286

8	N	0.159898	-0.47149	-2.31323
9	C	0.632107	-2.99733	0.316316
10	N	1.1447	1.825733	-1.25343
11	C	2.514195	-0.31262	-1.4137
12	C	2.485365	1.21899	-1.33407
13	H	3.064671	1.553314	-0.47898
14	H	3.009487	1.605388	-2.21412
15	C	0.561746	1.968478	-2.59813
16	H	1.353354	2.172442	-3.32468
17	H	-0.10248	2.828104	-2.60303
18	O	0.652299	-4.17749	0.662121
19	O	-0.40137	-2.26629	0.223618
20	C	-0.25404	0.748054	-3.01639
21	H	-0.18043	0.608615	-4.10073
22	H	-1.3026	0.917862	-2.78092
23	O	0.776789	-0.71591	2.280972
24	C	1.582137	-0.77536	-2.54997
25	H	1.924985	-0.30878	-3.47752
26	H	1.691904	-1.8445	-2.70717
27	O	2.688795	-0.99962	3.388371
28	C	2.804829	-0.4888	1.06639
29	H	2.96109	0.586296	1.072259
30	H	3.783321	-0.96986	1.108296
31	O	-1.77111	2.153145	-0.17727
32	C	2.047929	-0.77544	2.366592
33	C	1.226932	3.119927	-0.57388
34	H	0.343238	3.702521	-0.83106
35	H	2.103348	3.694451	-0.88486
36	O	-2.27785	-0.60719	-1.13486
37	C	1.19098	3.016375	0.949816
38	O	-3.00135	-2.20347	-2.50355
39	C	3.946376	-0.7347	-1.74948
40	H	4.653601	-0.31849	-1.0327
41	H	4.052925	-1.81852	-1.74318
42	C	-0.72533	-1.57061	-2.6962
43	H	-0.31026	-2.50896	-2.33455
44	H	-0.8304	-1.65026	-3.78284
45	C	-2.12107	-1.46816	-2.08155
46	O	-2.13976	-0.04483	2.021517
47	H	4.226171	-0.37743	-2.73979
48	H	-1.8785	-0.56261	2.815392
49	H	-2.9748	-0.43541	1.685299
50	H	-1.9395	2.59654	0.671306
51	H	-2.6191	2.081512	-0.65407
52	O	-1.79917	2.753029	2.558831
53	H	-2.13814	1.850165	2.62559
54	H	-0.8435	2.616839	2.46443
55	O	-4.01148	1.488836	-1.57402
56	H	-4.08578	1.754062	-2.49112

57	H	-3.57331	0.620991	-1.57827
58	O	-4.22315	-1.15916	0.713664
59	O	-1.03362	-1.34833	4.102768
60	H	-4.35991	-2.08934	0.895783
61	H	-3.6514	-1.12287	-0.07699
62	H	-1.17831	-2.29442	4.12767
63	H	-0.2196	-1.21301	3.565698

Table S26. Optimized Cartesian coordinates (Å) of the [Tb(AAZTA)(H₂O)₂]⁻•4H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Tb	-0.34306	0.092193	0.250033
2	O	0.649826	1.9457	1.429137
3	N	2.034553	-0.8967	-0.11979
4	C	1.967132	-2.37486	-0.11474
5	H	2.74594	-2.78712	0.526074
6	H	2.16501	-2.7793	-1.10436
7	O	1.591119	3.95308	1.619892
8	N	0.159348	-0.47117	-2.30976
9	C	0.627181	-2.991	0.313324
10	N	1.143729	1.823716	-1.25157
11	C	2.513974	-0.3119	-1.41482
12	C	2.484967	1.21936	-1.33715
13	H	3.067382	1.554998	-0.48469
14	H	3.005251	1.60527	-2.21965
15	C	0.557044	1.969364	-2.59415
16	H	1.345985	2.178162	-3.32221
17	H	-0.11003	2.826738	-2.59396
18	O	0.642585	-4.17329	0.651898
19	O	-0.40337	-2.25547	0.224761
20	C	-0.25602	0.747552	-3.0137
21	H	-0.18111	0.607777	-4.09783
22	H	-1.30494	0.915609	-2.77899
23	O	0.772446	-0.71369	2.272811
24	C	1.580992	-0.7755	-2.54958
25	H	1.922104	-0.30937	-3.47796
26	H	1.690353	-1.84478	-2.70613
27	O	2.681212	-0.98194	3.389672
28	C	2.803227	-0.4834	1.065351
29	H	2.961811	0.591291	1.068825
30	H	3.780714	-0.96628	1.109444
31	O	-1.75672	2.13816	-0.18225
32	C	2.043256	-0.76617	2.364156
33	C	1.225362	3.1155	-0.56775
34	H	0.34403	3.700929	-0.82622
35	H	2.10404	3.689605	-0.87288
36	O	-2.26916	-0.60425	-1.12261
37	C	1.182888	3.005313	0.954949

38	O	-3.0033	-2.19935	-2.48673
39	C	3.945812	-0.73513	-1.74997
40	H	4.653178	-0.31901	-1.03328
41	H	4.051833	-1.81899	-1.74333
42	C	-0.7268	-1.57019	-2.69069
43	H	-0.3104	-2.50916	-2.33232
44	H	-0.8366	-1.64835	-3.77695
45	C	-2.11897	-1.46612	-2.06947
46	O	-2.12182	-0.04309	2.004487
47	H	4.225876	-0.37836	-2.7404
48	H	-1.8637	-0.55926	2.800356
49	H	-2.96	-0.4305	1.672334
50	H	-1.92571	2.585227	0.664291
51	H	-2.60451	2.067912	-0.65946
52	O	-1.80448	2.754521	2.551891
53	H	-2.14206	1.850989	2.615982
54	H	-0.84841	2.617868	2.463563
55	O	-4.00572	1.486415	-1.57323
56	H	-4.08009	1.747903	-2.49141
57	H	-3.5702	0.617354	-1.57411
58	O	-4.21941	-1.15625	0.718181
59	O	-1.03374	-1.35035	4.09501
60	H	-4.35293	-2.086	0.904876
61	H	-3.64723	-1.122	-0.07222
62	H	-1.18174	-2.29612	4.111932
63	H	-0.21951	-1.21373	3.55844

Table S27. Optimized Cartesian coordinates (Å) of the $[\text{Dy}(\text{AAZTA})(\text{H}_2\text{O})_2]^- \cdot 4\text{H}_2\text{O}$ system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Dy	-0.33627	0.089171	0.246744
2	O	0.644514	1.930621	1.426898
3	N	2.032556	-0.89162	-0.12122
4	C	1.964336	-2.36994	-0.1139
5	H	2.738886	-2.78131	0.532544
6	H	2.168422	-2.77656	-1.10133
7	O	1.578901	3.939684	1.630789
8	N	0.158274	-0.47006	-2.30763
9	C	0.622053	-2.9844	0.308037
10	N	1.141256	1.822685	-1.25053
11	C	2.512969	-0.30983	-1.41707
12	C	2.483204	1.221086	-1.34146
13	H	3.068892	1.558316	-0.49189
14	H	2.999156	1.606677	-2.22662
15	C	0.550533	1.971552	-2.59073
16	H	1.336437	2.187115	-3.32011
17	H	-0.12053	2.825739	-2.58454
18	O	0.633202	-4.16902	0.638469

19	O	-0.40596	-2.24489	0.224186
20	C	-0.25801	0.747525	-3.01303
21	H	-0.17948	0.60737	-4.09682
22	H	-1.30793	0.912871	-2.78139
23	O	0.769361	-0.71192	2.26444
24	C	1.579316	-0.77493	-2.55014
25	H	1.918808	-0.30974	-3.47957
26	H	1.688415	-1.84443	-2.70543
27	O	2.6756	-0.96241	3.389759
28	C	2.802129	-0.47718	1.062968
29	H	2.963551	0.596995	1.064108
30	H	3.778391	-0.96236	1.108519
31	O	-1.74484	2.12314	-0.17895
32	C	2.039919	-0.75603	2.360816
33	C	1.222041	3.111835	-0.5621
34	H	0.342014	3.699274	-0.82017
35	H	2.101853	3.686649	-0.8625
36	O	-2.26177	-0.59994	-1.11286
37	C	1.175651	2.994247	0.959536
38	O	-3.00503	-2.19612	-2.4706
39	C	3.944662	-0.73363	-1.75144
40	H	4.65199	-0.31711	-1.03496
41	H	4.05067	-1.81748	-1.74424
42	C	-0.72882	-1.56891	-2.68663
43	H	-0.31105	-2.50856	-2.33185
44	H	-0.84336	-1.64536	-3.77251
45	C	-2.11744	-1.46357	-2.05875
46	O	-2.10416	-0.04648	1.990673
47	H	4.224803	-0.37746	-2.74208
48	H	-1.84827	-0.56368	2.786502
49	H	-2.9458	-0.42922	1.661879
50	H	-1.91383	2.571799	0.666711
51	H	-2.5921	2.05678	-0.65739
52	O	-1.80366	2.747865	2.555158
53	H	-2.1401	1.843563	2.613788
54	H	-0.84755	2.61113	2.468703
55	O	-3.99959	1.488262	-1.57154
56	H	-4.0719	1.748618	-2.4902
57	H	-3.56735	0.617691	-1.57059
58	O	-4.21687	-1.15039	0.721458
59	O	-1.03089	-1.35998	4.086803
60	H	-4.35181	-2.0796	0.909789
61	H	-3.64432	-1.11849	-0.06875
62	H	-1.17888	-2.30586	4.096524
63	H	-0.21679	-1.21943	3.551076

Table S28. Optimized Cartesian coordinates (Å) of the [Ho(AAZTA)(H₂O)₂]⁻•4H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Ho	-0.31617	-0.00477	0.250928
2	O	0.670974	1.741207	1.441656
3	N	2.04442	-0.95018	-0.15324
4	C	1.981413	-2.42811	-0.20002
5	H	2.764313	-2.86032	0.422339
6	H	2.17579	-2.798	-1.20366
7	O	0.771531	3.940932	1.699899
8	N	0.160891	-0.47055	-2.31315
9	C	0.646047	-3.06277	0.214304
10	N	1.142781	1.809435	-1.2102
11	C	2.518155	-0.31794	-1.4283
12	C	2.48411	1.211905	-1.29776
13	H	3.052481	1.516806	-0.42532
14	H	3.016516	1.626686	-2.16042
15	C	0.55926	1.972314	-2.55097
16	H	1.350929	2.173928	-3.27847
17	H	-0.09863	2.836353	-2.54993
18	O	0.664887	-4.25872	0.500606
19	O	-0.38582	-2.32504	0.168176
20	C	-0.26855	0.764127	-2.97918
21	H	-0.21669	0.649728	-4.06782
22	H	-1.31145	0.929283	-2.71809
23	O	0.794633	-0.88305	2.239936
24	C	1.583819	-0.75133	-2.57412
25	H	1.913586	-0.24929	-3.48753
26	H	1.703904	-1.81298	-2.76977
27	O	2.708494	-1.12638	3.354224
28	C	2.819101	-0.57811	1.041441
29	H	2.975206	0.495728	1.081013
30	H	3.796545	-1.06276	1.063548
31	O	-1.71143	2.032122	-0.19713
32	C	2.064964	-0.90573	2.331972
33	C	1.178355	3.075655	-0.47202
34	H	0.407649	3.737967	-0.85705
35	H	2.132485	3.597616	-0.5889
36	O	-2.24668	-0.6652	-1.09471
37	C	0.869598	2.917242	1.014935
38	O	-2.98511	-2.22989	-2.49274
39	C	3.950903	-0.72324	-1.78089
40	H	4.659182	-0.32129	-1.05701
41	H	4.063976	-1.80621	-1.80305
42	C	-0.71983	-1.56658	-2.71504
43	H	-0.28662	-2.51243	-2.39724
44	H	-0.84893	-1.60919	-3.80117
45	C	-2.10268	-1.49959	-2.06627

46	O	-2.00681	0.039799	2.037097
47	H	4.223672	-0.33882	-2.76303
48	H	-1.76665	-0.44799	2.85574
49	H	-2.87636	-0.30497	1.743067
50	H	-1.91374	2.517865	0.624077
51	H	-2.53384	1.97592	-0.7155
52	O	-1.93339	2.99227	2.383642
53	H	-1.89206	2.046788	2.575604
54	H	-1.01603	3.302156	2.427012
55	O	-3.95141	1.436174	-1.65513
56	H	-3.99695	1.657592	-2.58569
57	H	-3.54542	0.554993	-1.60815
58	O	-4.16827	-1.03286	0.808585
59	O	-0.9661	-1.2376	4.171264
60	H	-4.33853	-1.94351	1.050917
61	H	-3.60023	-1.06868	0.014421
62	H	-1.2052	-2.16025	4.260861
63	H	-0.17256	-1.21789	3.586804

Table S29. Optimized Cartesian coordinates (Å) of the [Er(AAZTA)(H₂O)]⁻ · 5H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Er	0.129578	-0.00303	0.343766
2	O	1.344839	-1.90378	0.848414
3	N	-2.43246	-0.11114	-0.071
4	C	-2.97615	1.245044	0.150758
5	H	-3.36193	1.291572	1.169866
6	H	-3.8212	1.463129	-0.49952
7	O	1.572419	-4.11729	0.941018
8	N	-0.37498	0.420427	-2.19986
9	C	-1.96664	2.392823	0.070358
10	N	-0.54312	-2.04925	-1.07874
11	C	-2.5621	-0.59405	-1.48388
12	C	-1.9172	-1.98758	-1.60529
13	H	-2.53217	-2.72631	-1.09868
14	H	-1.9341	-2.276	-2.65881
15	C	0.439865	-1.95026	-2.16755
16	H	0.351523	-2.81187	-2.83745
17	H	1.436696	-1.9847	-1.72978
18	O	-2.38322	3.513939	-0.20056
19	O	-0.75711	2.095592	0.344493
20	C	0.278056	-0.65827	-2.9691
21	H	-0.28757	-0.83699	-3.88653
22	H	1.26819	-0.32751	-3.27191
23	O	-1.07745	-0.54253	2.239098
24	C	-1.83336	0.402827	-2.39755

25	H	-2.0766	0.159355	-3.43589
26	H	-2.22426	1.401822	-2.22057
27	O	-2.94347	-1.09942	3.31672
28	C	-3.01324	-1.00982	0.936346
29	H	-2.88076	-2.05029	0.651895
30	H	-4.08499	-0.85266	1.062123
31	O	3.713474	-1.16468	-1.8046
32	C	-2.31956	-0.86614	2.293306
33	C	-0.27198	-3.24859	-0.28419
34	H	-0.19092	-4.14456	-0.90487
35	H	-1.0923	-3.40754	0.417179
36	O	1.868926	0.982868	-0.91193
37	C	0.997863	-3.10741	0.564823
38	O	2.04627	3.048779	-1.71067
39	C	-4.01365	-0.71684	-1.95171
40	H	-4.59523	-1.3299	-1.26449
41	H	-4.49844	0.253469	-2.04255
42	C	0.233761	1.719344	-2.49885
43	H	-0.45674	2.518683	-2.24063
44	H	0.480478	1.833033	-3.55824
45	C	1.490825	1.955276	-1.66309
46	O	1.5327	1.006145	1.993136
47	H	-4.04811	-1.18973	-2.93254
48	H	1.215712	0.999029	2.917923
49	H	1.861266	1.897427	1.768561
50	H	3.935066	-1.40968	-0.89138
51	H	3.131086	-0.40672	-1.6898
52	O	4.094342	-1.47375	1.005515
53	H	4.199303	-0.5088	1.014639
54	H	3.140541	-1.6329	1.107261
55	O	4.365646	1.254354	0.401027
56	H	4.216986	2.00036	0.987758
57	H	3.537359	1.209959	-0.10591
58	O	2.568171	3.391173	1.047392
59	O	0.2982	0.486968	4.344878
60	H	2.236724	4.229246	1.369374
61	H	2.418924	3.386585	0.083639
62	H	-0.19362	1.185247	4.777422
63	H	-0.33862	0.041882	3.750906

Table S30. Optimized Cartesian coordinates (Å) of the [Tm(AAZTA)(H₂O)]⁻ · 5H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Tm	0.119196	0.001631	0.334542
2	O	1.351731	-1.87393	0.836353
3	N	-2.43596	-0.10485	-0.07474
4	C	-2.9753	1.253362	0.14382
5	H	-3.36324	1.302858	1.161959

6 H	-3.8178	1.474213	-0.50887
7 O	1.574427	-4.08616	0.964013
8 N	-0.37771	0.418489	-2.20281
9 C	-1.96038	2.396127	0.064684
10 N	-0.54509	-2.04128	-1.07384
11 C	-2.56546	-0.59138	-1.48605
12 C	-1.91908	-1.98471	-1.60177
13 H	-2.53302	-2.72284	-1.09305
14 H	-1.93436	-2.27722	-2.65411
15 C	0.437438	-1.95063	-2.16368
16 H	0.346723	-2.81551	-2.82892
17 H	1.434289	-1.98377	-1.72622
18 O	-2.37055	3.519718	-0.20486
19 O	-0.75223	2.091959	0.338398
20 C	0.275414	-0.66178	-2.96991
21 H	-0.29074	-0.84331	-3.88641
22 H	1.2652	-0.33148	-3.27431
23 O	-1.06851	-0.55382	2.221916
24 C	-1.83574	0.402579	-2.40218
25 H	-2.07848	0.156647	-3.44
26 H	-2.22551	1.402536	-2.22809
27 O	-2.92861	-1.10205	3.313821
28 C	-3.01877	-1	0.934512
29 H	-2.9005	-2.04109	0.646236
30 H	-4.08772	-0.8317	1.068781
31 O	3.715581	-1.16579	-1.79608
32 C	-2.31263	-0.86817	2.285837
33 C	-0.27275	-3.23248	-0.26784
34 H	-0.19454	-4.13528	-0.87884
35 H	-1.09052	-3.38249	0.438482
36 O	1.860941	0.97041	-0.90865
37 C	1.000539	-3.08112	0.574038
38 O	2.054431	3.03401	-1.71022
39 C	-4.01674	-0.71552	-1.95366
40 H	-4.59815	-1.32746	-1.26527
41 H	-4.50168	0.254629	-2.04584
42 C	0.234897	1.715524	-2.50059
43 H	-0.45302	2.517209	-2.24266
44 H	0.483789	1.829164	-3.55944
45 C	1.491305	1.944509	-1.66226
46 O	1.520999	0.995439	1.974719
47 H	-4.05124	-1.19001	-2.93373
48 H	1.218453	0.974305	2.903884
49 H	1.847545	1.889373	1.758196
50 H	3.940508	-1.40792	-0.88302
51 H	3.126207	-0.41326	-1.6807
52 O	4.099659	-1.46135	1.017143
53 H	4.208159	-0.49683	1.01969
54 H	3.143884	-1.61411	1.111302

55	O	4.362125	1.26388	0.398649
56	H	4.20833	2.009937	0.984023
57	H	3.53191	1.208945	-0.10404
58	O	2.555229	3.38844	1.048854
59	O	0.324626	0.433471	4.33688
60	H	2.214565	4.223762	1.368356
61	H	2.411116	3.381603	0.084381
62	H	-0.16384	1.120697	4.790398
63	H	-0.31777	0.000269	3.740259

Table S31. Optimized Cartesian coordinates (Å) of the [Yb(AAZTA)(H₂O)]⁻ · 5H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Yb	0.100412	0.135232	0.361013
2	O	1.412898	-1.62731	0.910136
3	N	-2.42664	-0.07753	-0.05225
4	C	-3.0196	1.263754	0.133809
5	H	-3.42198	1.318105	1.146
6	H	-3.86188	1.439909	-0.53246
7	O	2.010992	-3.75878	0.755092
8	N	-0.379	0.471066	-2.19037
9	C	-2.048	2.442945	0.043437
10	N	-0.44645	-1.95607	-1.01434
11	C	-2.52824	-0.60044	-1.45297
12	C	-1.8258	-1.97137	-1.53055
13	H	-2.4049	-2.71682	-0.99258
14	H	-1.83721	-2.29722	-2.57309
15	C	0.519782	-1.85749	-2.11738
16	H	0.456904	-2.74326	-2.7576
17	H	1.521959	-1.83864	-1.69296
18	O	-2.50058	3.547435	-0.23622
19	O	-0.82864	2.18763	0.317765
20	C	0.301424	-0.59743	-2.94845
21	H	-0.27219	-0.81795	-3.85141
22	H	1.275277	-0.24184	-3.27496
23	O	-1.06278	-0.40164	2.260377
24	C	-1.83504	0.407028	-2.38636
25	H	-2.07306	0.138866	-3.4196
26	H	-2.25748	1.395894	-2.22467
27	O	-2.90879	-0.98406	3.358556
28	C	-2.97992	-0.97071	0.97564
29	H	-2.80896	-2.01306	0.720023
30	H	-4.05686	-0.84822	1.094115
31	O	3.737102	-0.85759	-2.07572
32	C	-2.29367	-0.76377	2.327036
33	C	-0.09675	-3.10851	-0.17971
34	H	-0.01518	-4.02999	-0.76074
35	H	-0.86599	-3.2524	0.580587

36	O	1.833721	1.063936	-0.87938
37	C	1.223597	-2.83518	0.554317
38	O	2.086238	3.071018	-1.79884
39	C	-3.97079	-0.79456	-1.92354
40	H	-4.52989	-1.41677	-1.2259
41	H	-4.49514	0.152661	-2.03666
42	C	0.211283	1.77521	-2.49448
43	H	-0.47692	2.56843	-2.2109
44	H	0.433622	1.899969	-3.55778
45	C	1.488653	2.005462	-1.68297
46	O	1.44552	1.249779	1.998902
47	H	-3.98075	-1.28885	-2.89431
48	H	1.094785	1.269279	2.913488
49	H	1.702964	2.158026	1.724852
50	H	3.987806	-1.40955	-1.31586
51	H	3.129507	-0.20656	-1.7078
52	O	4.414199	-2.20044	0.327606
53	H	4.238993	-1.32246	0.707102
54	H	3.646802	-2.73855	0.576811
55	O	3.994323	0.500709	1.022525
56	H	3.283086	0.545905	1.673776
57	H	3.546032	0.832602	0.233854
58	O	2.31691	3.613935	0.982109
59	O	0.194877	0.801403	4.341847
60	H	1.697602	4.335786	1.095673
61	H	2.350353	3.458587	0.021256
62	H	-0.34455	1.494324	4.723378
63	H	-0.40244	0.286509	3.763179

Table S32. Optimized Cartesian coordinates (Å) of the Lu(AAZTA)(H₂O)]⁻ · 5H₂O system obtained with DFT calculations (0 Imaginary Frequencies).

Tag	Symbol	X	Y	Z
1	Lu	0.095422	0.137509	0.351431
2	O	1.415162	-1.60737	0.901535
3	N	-2.42641	-0.07598	-0.0533
4	C	-3.01773	1.265975	0.132261
5	H	-3.42171	1.321005	1.14374
6	H	-3.85848	1.44399	-0.53543
7	O	2.010637	-3.74126	0.771707
8	N	-0.38302	0.470389	-2.1913
9	C	-2.04311	2.442429	0.04361
10	N	-0.44727	-1.95131	-1.01196
11	C	-2.53074	-0.60079	-1.4527
12	C	-1.82681	-1.97086	-1.52789
13	H	-2.40436	-2.71623	-0.98821
14	H	-1.83775	-2.29906	-2.56965
15	C	0.517456	-1.85699	-2.11667
16	H	0.451823	-2.74395	-2.75485

17	H	1.520213	-1.8386	-1.69396
18	O	-2.49227	3.549137	-0.23222
19	O	-0.82406	2.182281	0.315323
20	C	0.298564	-0.59786	-2.94897
21	H	-0.27469	-0.81922	-3.85189
22	H	1.272068	-0.24141	-3.27554
23	O	-1.05142	-0.40523	2.248353
24	C	-1.8389	0.405556	-2.388
25	H	-2.07654	0.135822	-3.42087
26	H	-2.26176	1.394485	-2.22776
27	O	-2.89029	-0.98617	3.358994
28	C	-2.97828	-0.96754	0.97665
29	H	-2.8142	-2.0105	0.719238
30	H	-4.05386	-0.83988	1.101413
31	O	3.732853	-0.85689	-2.06996
32	C	-2.28247	-0.76496	2.323326
33	C	-0.09543	-3.09908	-0.17197
34	H	-0.01252	-4.02334	-0.74834
35	H	-0.86391	-3.24049	0.589529
36	O	1.825103	1.061252	-0.87841
37	C	1.224638	-2.8189	0.559629
38	O	2.086098	3.065415	-1.8019
39	C	-3.97381	-0.7965	-1.92047
40	H	-4.53094	-1.41896	-1.22147
41	H	-4.49929	0.150205	-2.03285
42	C	0.207097	1.774365	-2.49601
43	H	-0.4806	2.567993	-2.2123
44	H	0.429226	1.898878	-3.55934
45	C	1.484342	2.00239	-1.68422
46	O	1.437094	1.244095	1.984126
47	H	-3.98512	-1.29117	-2.89104
48	H	1.093207	1.258605	2.901185
49	H	1.693406	2.153509	1.713405
50	H	3.986064	-1.40756	-1.31
51	H	3.121627	-0.20917	-1.70213
52	O	4.417512	-2.19499	0.334003
53	H	4.246053	-1.31511	0.710926
54	H	3.648444	-2.72926	0.58651
55	O	3.993415	0.50681	1.021955
56	H	3.274886	0.546035	1.665716
57	H	3.549349	0.834502	0.229336
58	O	2.311492	3.612376	0.978048
59	O	0.211795	0.777113	4.337082
60	H	1.692606	4.334843	1.089861
61	H	2.346845	3.456479	0.017352
62	H	-0.32813	1.462707	4.730911
63	H	-0.38706	0.266823	3.755902

References:

- [1] R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901–927.
- [2] E. Tóth, L. Helm and A. Merbach, in *The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging*, ed. A. Merbach, L. Helm and E. Tóth, John Wiley & Sons, Chichester, 2nd edn, 2013, pp. 25–81.
- [3] P. Caravan, C. T. Farrar, L. Frullano and R. Uppal, *Contrast Media Mol. Imaging*, 2009, **4**, 89–100.
- [4] S. Aime, M. Botta, D. Esteban-Gómez and C. Platas-Iglesias, *Mol. Phys.*, 2019, **117**, 898–909.
- [5] L. Helm, in *Contrast Agents for MRI: Experimental Methods*, ed. V. C. Pierre and M. J. Allen, Royal Society of Chemistry, Cambridge, 2017, pp. 122–127.
- [6] J. A. Peters, J. Huskens and D. J. Raber, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1996, **28**, 283–350.
- [7] L. Vander Elst, A. Roch, P. Gillis, S. Laurent, F. Botteman, J. W. M. Bulte and R. N. Muller, *Magn. Reson. Med.*, 2002, **47**, 1121–1130.
- [8] S. Karimi and L. Helm, *Inorg. Chem.*, 2016, **55**, 4555–4563.
- [9] D. Cicolari, F. Santanni, L. Grassi, F. Brero, M. Filibian, T. Recca, P. Arosio, M. Perfetti, M. Mariani, R. Sessoli and A. Lascialfari, *J. Chem. Phys.*, 2021, **155**, 214201.
- [10] I. Bertini, F. Capozzi, C. Luchinat, G. Nicastro and Z. Xia, *J. Phys. Chem.*, 1993, **97**, 6351–6354.
- [11] P. H. Fries and E. Belorizky, *J. Chem. Phys.*, 2012, **136**, 074513.
- [12] L. P. Hwang and J. H. Freed, *J. Chem. Phys.*, 1975, **63**, 118–130.
- [13] J. H. Freed, *J. Chem. Phys.*, 1978, **68**, 4034–4037.
- [14] Y. Ayant, E. Belorizky, P. Fries and J. Rosset, *J. Phys.*, 1977, **38**, 325–337.
- [15] H. J. Eyring, *J. Chem. Phys.*, 1935, **3**, 107–115.
- [16] D. R. Lide, *CRC Handbook of Chemistry and Physics: A Ready-reference Book of Chemical and Physical Data*, CRC Press, 1995.
- [17] B. Bleaney, *J. Magn. Reson.*, 1972, **8**, 91–100.
- [18] A. M. Funk, K.-L. N. A. Finney, P. Harvey, A. M. Kenwright, E. R. Neil, N. J. Rogers, P. K. Senanayake and D. Parker, *Chem. Sci.*, 2015, **6**, 1655–1662.
- [19] D. F. Evans, *J. Chem. Soc.*, 1959, 2003–2005.
- [20] D. M. Corsi, C. Platas-Iglesias, H. van Bekkum and J. A. Peters, *Magn. Reson. Chem.*, 2001, **39**, 723–726.
- [21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Rev. C.01*, Gaussian, Inc., Wallingford, CT, 2016.
- [22] J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
- [23] M. Dolg, H. Stoll, A. Savin and H. Preuss, *Theor. Chim. Acta*, 1989, **75**, 173–194.
- [24] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.
- [25] T. Lu, *J. Chem. Phys.*, 2024, **161**, 082503. 25 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.
- [26] K. Micskei, L. Helm, E. Brucher and A. E. Merbach, Oxygen-17 NMR study of water exchange on gadolinium polyaminopolyacetates $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$ and $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ related to NMR imaging, *Inorg. Chem.*, 1993, **32**, 3844–3850.

- [27] D. H. Powell, O. M. N. Dhubhghaill, D. Pubanz, L. Helm, Y. S. Lebedev, W. Schlaepfer and A. E. Merbach, Structural and Dynamic Parameters Obtained from ^{17}O NMR, EPR, and NMRD Studies of Monomeric and Dimeric Gd^{3+} Complexes of Interest in Magnetic Resonance Imaging: An Integrated and Theoretically Self-Consistent Approach, *J. Am. Chem. Soc.*, 1996, **118**, 9333–9346.
- [28] K. I. Hardcastle, M. Botta, M. Fasano and G. Digilio, Experimental Evidence for a Second Coordination Sphere Water Molecule in the Hydration Structure of YbDTPA – Insights for a Re-Assessment of the Relaxivity Data of GdDTPA, *Eur. J. Inorg. Chem.*, 2000, **2000**, 971–977.
- [29] D. Lalli, F. Carniato, L. Tei, C. Platas-Iglesias and M. Botta, Surprising Complexity of the $[\text{Gd}(\text{AAZTA})(\text{H}_2\text{O})_2]^-$ Chelate Revealed by NMR in the Frequency and Time Domains, *Inorg. Chem.*, 2022, **61**, 496–506.