Electronic Supplementary Information

Soft-donor dipicolinamide derivatives for selective actinide(III) / lanthanide(III) separation: The role of S- vs. O- donor sites†

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Section 1: Experimental Details

Materials and Methods:

All chemicals and solvents were purchased from Aldrich Chemical Company or ACROS Organics, were standard reagent grade and were used without further purification unless otherwise noted. 2,6-pyridinedicarbonyl dichloride was purchased from ACROS Organics (CAS: 3739-94-4). (N^2,N^6-diphenyl)pyridine-2,6-dicarboxamide (**1**)[1] was prepared from 2,6-pyridinedicarbonyl dichloride and aniline in DMF by a modification of previously published procedures.[1] (N^2,N^6-diphenyl)pyridine-2,6-bis(carbothioamide) (**2**)[2] was prepared by an improved method from (**1**) by reaction with Lawesson's reagent in toluene, and was found to be spectroscopically identical to the reported compound.[2] ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer and referenced to the residual solvent resonances. All chemical shifts, δ, are reported in ppm. Fluorescence spectra recorded on a Cary Eclipse fluorescence spectrophotometer and UV-Vis spectra were recorded on a Cary 100 UV-Visible spectrophotometer.

(N^2,N^6-diphenyl)pyridine-2,6-dicarboxamide (1):[1] Pyridine-2,6-dicarbonyl chloride (503 mg, 2.46 mmol) was dissolved in 10 mL of DMF. Aniline (2.00 mL, 21.9 mmol) was added dropwise to the stirring solution and was allowed to react for 3h, at room temperature under N_2. Deionized water (150 mL) was added, and a white precipitate formed. The formed solid was filtered, and dried (350.1 mg, 1.10 mmol, 45% yield). The same method was also used for a gram scale preparation at slightly lower yields, after recrystallization from DMSO. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.05 (s, 2H), 8.41 (d, J = 7.7 Hz, 2H), 8.31 (t, J = 8.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 4H), 7.45 (t, J = 7.7 Hz, 4H), 7.20 (t, J = 7.5 Hz, 2H). FT-IR (ATR) cm^{-1}: 1655 (m, C=O), 3271 (bd m, N-H). UV/Vis(CH_3CN): λ_{max} 282 nm.

(N^2,N^6-diphenyl)pyridine-2,6-bis(carbothioamide) (2):[2] (N^2,N^6-diphenyl)pyridine-2,6-dicarboxamide **1** (200.8 mg, 0.633 mmol) was dissolved in dry and distilled toluene under a flow of N_2. A solution of Lawesson's reagent (503 mg, 1.24 mmol) in dry-distilled toluene was added dropwise under N_2 to the stirring solution. After 2 h the volatiles were evaporated and the residue was purified by silica gel column chromatography in EtOAc/Hexane (1:4). A yellow crystalline compound was obtained that was recrystallized from dichloromethane/hexane to give the pure product (64 mg, 0.182 mmol, 30% yield): ^{1}H NMR (400 MHz, CH_2Cl_2-d_2) δ 11.17 (s, 2H), 8.95 (d, J = 7.9 Hz, 2H), 8.09 (t, J = 7.9 Hz, 1H), 7.97 (d, J = 7.6 Hz, 4H), 7.52 (t, J = 7.9 Hz, 4H), 7.32 (t, J = 7.4 Hz, 2H).^{13}C-NMR (400 MHz, CH_2Cl_2-d_2) δ 189.21 (s), 150.7 (s), 139.4 (s), 139.2 (s), 129.7 (s), 128.2 (s), 127.7 (s), 124.1 (s). FT-IR (ATR) cm^{-1}: 1078 (m, C=S), 3210 (bd m, N-H). UV/Vis(CH_3CN): λ_{max} 311 nm.

N^2,N^6-bis(4-(tert-butyl)phenyl)pyridine-2,6-dicarboxamide (3)[3]**:** 2,6-Pyridinedicarboxylic acid dichloride, 97% (500 mg; 2.9 mmol) and 4-tert-Butylaniline 98% (CAS: 769-92-6; Oakwood Chemical) (0.94 mL; 5.8 mmoL) were mixed together in 3 mL of DMF. The 5 mL

conical flask remained uncapped and under stirring for 48 h at room temperature. The reaction mixture was poured into 500 mL of water causing formation of a white powder. The solid was filtered out, dried under vacuum and recrystallized from hot ethanol (Yield: 1.08 g; 82%). ^{1}H NMR (400 MHz, CH_2Cl_2-d_2) δ 9.53 (2H, s), 8.51 (d, J = 7.8 Hz, 2H), 8.19 (t, J = 7.8 Hz, 1H), 7.74 (d, J = 8.7 Hz, 4H), 7.49 (d, J = 8.7 Hz, 4H), 1.39 (s, 18H). ^{13}C-NMR (400 MHz, CH_2Cl_2-d_2) δ 161.4 (s), 149.5 (s), 148.4 (s), 140.3 (s), 135.1 (s), 126.3 (s), 125.7 (s), 120.3 (s), 34.8 (s), 31.5 (s). FT-IR(ATR) cm^{-1}: 1673 (m, C=O), 3358 (bd m, N-H). UV/Vis(CH_3CN): λ_{max} 287 nm. Elemental analysis: Anal. Calcd. for $C_{27}H_{31}N_3O_2$: C, 75.49; H, 7.27; N, 9.78. Found: C, 75.15; H, 7.25; N, 9.72.

Synthetic procedure for $[Nd(3)_3]I_3$:

NdI_3 : 0.2 mL of concentrated HI (without stabilizer) was added to 3.0 mg (8.92 μmol) of Nd_2O_3 in a 6 mL glass vial. The suspension was then heated at 150 ˚C until the excess HI evaporated off, leaving 9.4 mg of putative $NdI_3 \cdot nH_2O$.

$[Nd(3)_3]I_3 \cdot 3CH_3CN$

In a 6 mL glass vial, 9.4 mg (17.8 μmol) of NdI_3 was added to 23.0 mg (53.5 μmol) of **3**. This mixture was then dissolved in 2 mL of acetonitrile and was allowed to evaporate slowly over a 24 h period resulting in yellow, acicular crystals (30% yield). ^{1}H NMR (400 MHz, CH_3CN-d_3) δ 10.00 (s, 4H), 9.31 (d, J = 6.0 Hz, 2H), 9.08 (d, J = 4.7 Hz, 4H), 8.85 (t, J = 7.5 Hz, 1H), 8.80 (s, 2H), 8.42 (d, J = 7.8 Hz, 4H), 8.22 (t, J = 7.4 Hz, 2H), 7.79 (d, J = 8.3Hz, 8H), 7.66 (d, J = 5.7 Hz 4H), 7.48 (d, J = 8.6Hz, 8H), 1.39 (s, 18H), 1.34 (s, 36H). FT-IR (ATR) cm^{-1}: 1620 (m, C=O), 3186 (bd m, N-H). Elemental analysis: Anal. Calcd. For $C_{81}H_{93}I_3N_9NdO_6 \cdot HI \cdot 3H_2O$: C, 48.75; H, 5.05; N, 6.32. Found: C, 48.38; H, 5.00; N, 6.41.

UV-Visible Titrations:

Solutions of ligands **1**, **2**, or **3** in CH_3CN were titrated with solutions of lanthanide salts, including $La(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and $Lu(NO_3)_3 \cdot 6H_2O$ at constant ligand concentration. In a typical experiment, a solution of **1** (2 x 10^{-5} M) in CH_3CN (solution A) was titrated with a solution of $Ln(NO_3)_3 \cdot 6H_2O$ (1.0 x 10^{-3} M) and **1** (2.0 x 10^{-5} M) (solution B) prepared by accurately weighing approximately 180 mg of $Ln(NO_3)_3 \cdot 6H_2O$ in a 5.00 mL volumetric flask and diluting with solution A. For spectra collection, 2.30 mL of solution A were added to the UV-Visible cuvette and solution B was added in 2-150 μL increments until a total of 1000 μL had been added.

UV-Visible Job plots:

Solutions of the ligand **1** (4.7 x 10^{-5} M) and $La(NO_3)_3 \cdot 6H_2O$ (4.5 x 10^{-5} M) in CH_3CN were prepared. Eleven vials were filled with 1000 μL of solutions that contain ligand and metal in the following volume ratios (in μL). 1000:0, 900:100, 800:200, 700:300, 600:400, 500:500, 400:600, 300:700, 200:800, 100:900 and 0:1000. Each of them was transferred to the cuvette and spectra

were recorded. Job plots were obtained by plotting mol. fraction against Abs x [L]/([M]+[L]) (where L is (**1**) ligand and M is La^{3+}).

Fluorescence titrations:

Solutions of ligands in CH_3CN were titrated with solutions of lanthanide salts, including $La(NO_3)_3{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$ and $Lu(NO_3)_3{\cdot}6H_2O$ at constant ligand concentration. Fluorescence emission was measured at increments of 0.5 nm, and integration time of 0.1 s, excitation slit width of 10 nm, emission slit width of 5 nm. For ligand **1** excitation at 282 nm produces an emission at 338 nm. In a typical experiment, a solution of **1** (2×10^{-5} M) in CH_3CN (solution A) was titrated with a solution of $Ln(NO_3)_3{\cdot}6H_2O$ (1×10^{-3} M) and **1** (2×10^{-5} M) (solution B) prepared by accurately weighing approximately 180 mg of $Ln(NO_3)_3{\cdot}6H_2O$ in a 5.00 mL volumetric flask and diluting with solution A. For spectra collection, 2.3 mL of solution A were added to the cuvette and solution B was added in 2-150 μL increments until a total of 1000 μL had been added. The Stern-Volmer fluorescence quenching method[4] was used to determine the Stern-Volmer quenching constant of the fluorescence titrations. A more sensitive system will have a steeper slope and, as a result, a higher K_{sv} value.

^{1}H-NMR Titrations:

Ligand solutions (2.4×10^{-3} M) were titrated in acetone-d_6 with $La(NO_3)_3{\cdot}6\ H_2O$ solutions (2×10^{-1} M) in a constant ligand concentration. In a typical experiment, a solution of **1**, (2.4×10^{-3} M) in acetone d_6 was prepared in a 2.00 mL volumetric flask (solution A). A $La(NO_3)_3{\cdot}6H_2O$ solution (Solution B) was prepared by a dilution of an accurately weighed amount of $La(NO_3)_3{\cdot}6H_2O$ with solution A in a 1.00 mL volumetric flask (Solution B). Solution A (0.700 mL) was placed in an NMR tube. Solution B was added in increments with a μL syringe until a total of 950 μL was added.

Solvent Extraction:

Extraction experiments with Am-243 and Eu-154 were carried out as follows: Initially saturated dichloromethane solutions of each ligand (10 mL for each) were prepared. To assist in ensuring that each ligand was saturated, the solutions were sonicated for 5 min, and then filtered to remove any undissolved ligand. An aliquot of an Am-243 or Eu-154 solution was added to 1.5 mL of 1.0 M or 6.5 M nitric acid. 1.5 mL of the ligand in organic solvent was then added to the aqueous solution containing the radionuclide and was mixed on a vortex stirrer for 5 min. After the layers were allowed to separate, 1.00 mL of each phase was pipetted out into scintillation vials and counted for 10 min. using an ORTEC GEM50P4 coaxial HPGe detector and DSPEC gamma spectrometer. The average dead time for each sample was 8.5 %. Distribution values for the extraction were obtained by the ratio of the number of counts of the desired radionuclide in the organic phase relative to the amount in the aqueous phase. The separation factor (SF) is the ratio of the distribution values for Am-243 relative to Eu-154. In 6.5 M nitric acid, **1** had a distribution ratio of 0.02 (123 counts in the organic phase, and 5739 in the aqueous phase), while

2 had an Am-243 distribution ratio of 0.42 (3724 counts organic phase, 1546 counts aqueous phase). In 6.5 M nitric acid, **1** did not extract any Eu-154 (28 counts in the organic phase, 6150 counts in the aqueous phase). Under similar conditions (6.5 M nitric acid), **2** also did not extract Eu-154 (133 counts in the organic phase, 5482 counts in the aqueous phase – D value of 0.02). In 1.0 M nitric acid, the Am-243 extraction with both ligands was lower than in 6.5 M nitric acid; **2** had a measured distribution ratio of 0.26 (756 organic counts, 2941 aqueous counts), and **1** showed no extraction (D value of 0.01).

DFT calculations:

DFT calculations were performed on the following molecules: **1**, **2**, **3**, $Nd(NO_3)_3(H_2O)_4$, $Nd(NO_3)_3(\mathbf{3})(H_2O)$, $M(NO_3)_3(L)(H_2O)$ (M=Nd, Eu, Am; L= **1** or **2**), $M(H_2O)_9^{3+}$ and $M(NO_3)(H_2O)_8^{2+}$ (M=Eu, Am). Geometry optimizations were performed by employing the hybrid functional PBE0[5] as implemented in the Amsterdam Density Functional (ADF 2016.104).[6–8] The Slater basis sets with the quality of triple-ζ plus two polarization functions (TZ2P) were used.[9] The frozen core approximation was applied to the $[1s^2\text{-}4f^{14}]$ cores of Am, and$[1s^2\text{-}4d^{10}]$ cores of Nd and Eu, and $[1s^2]$ cores of C, N and O, and $[1s^2\text{-}2p^6]$ core of S, with the rest of the electrons explicitly treated variationally. All the geometric structures were fully optimized by DFT/PBE0 at the scalar-relativistic (SR) zero-order-regular approximation (ZORA)[10] with the gradient convergence of 10^{-4} in gas phase. In the vibrational frequency calculations, all frequencies were real, indicating that the structures were true minima on the energy surface. To account for the sovlation effects, a subsequent single-point calculation for the above molecules was performed at PBE0 level using the implicit COSMO[11,12] solvation model with the default Delley surface[13] and a radius of 2.045 for Am and of 1.870 for Nd and of 1.820 for Eu and the default van der Waals radius from the MM3 method divided by 1.2 for other atoms.[14] The UV-Vis spectra of ligand and $Nd(NO_3)_3(ligand)(H_2O)$ (ligand=**1**, **2, 3**) were simulated as the Kohn-Sham orbital energy differences from SR-DFT/PBE0 calculations, i.e., the energy difference between an occupied orbital and a virtual orbital of the ground state. All the calculated transition intensities were evenly broadened with a Gaussian function of full-width at half-maximum of 35 nm (i.e., peak width) to emulate the experimental spectra. For a specific electronic excitation, the oscillator strength was calculated using the transition-dipole approximation between this occupied MO and the virtual MOs.

Gas phase experiments (CID-ESI-MS):

$[Eu^{III}(\mathbf{1})_2(\mathbf{2}\text{-H})]^{2+}$ and $[Am^{III}(\mathbf{1})_2(\mathbf{2}\text{-H})]^{2+}$ dication complexes were produced by electrospray ionization (ESI) of ethanol solutions containing 100 μM of either $AmCl_3$ or $EuCl_3$, and 100 μM of both **1** and **2** ligands. The employed ^{243}Am isotope has an alpha-decay half-life of 7370 y. The gas phase experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer (QIT/MS) with the ESI source located inside a radiological containment glovebox.[15] The gas-phase cation complex of interest was isolated and subjected to collision induced dissociation (CID) whereby ions are excited and undergo multiple energetic collisions

with helium to ultimately induce dissociation. As discussed elsewhere, the background H_2O and O_2 pressures in the ion trap are estimated to be on the order of 10^{-6} Torr, while the helium buffer gas pressure in the trap is constant at $\sim 10^{-4}$ Torr.[16] Cation mass spectra were acquired using the following instrumental parameters: solution flow rate, 60 μL min^{-1}; nebulizer gas pressure,18 psi; capillary voltage, -3500 V; end plate voltage offset, −500 V; dry gas flow rate, 4 L/min; dry gas temperature, 325 °C; capillary exit, 94.0 V; skimmer, 40.0 V; octopole 1 and 2 dc, 12.0 and 1.7 V; octopole RF amplitude, 171.0 Vpp; lens 1 and 2, −5.0 and −60.0 V; trap drive, 52.0. The high-purity nitrogen gas for nebulization and drying in the ion transfer capillary was the boil off from a liquid nitrogen Dewar.

Section 2: UV-Visible and Fluorescence Titrations

Spectroscopic UV-Vis titrations in acetonitrile were performed in order to understand the binding properties of **1** vs. **2** in solution. The Figure S1 (left) shows no significant changes upon the titration of ligand **2** with $Nd(NO_3)_3 \cdot 6H_2O$.

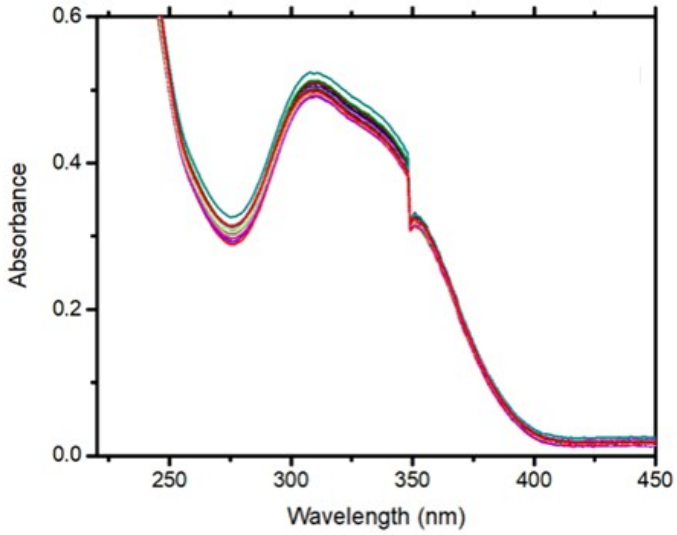


Figure S1: UV-Vis titration in CH_3CN of ligand **2** (3.4×10^{-5} M) with $Nd(NO_3)_3 \cdot 6H_2O$ (1.1×10^{-3} M)

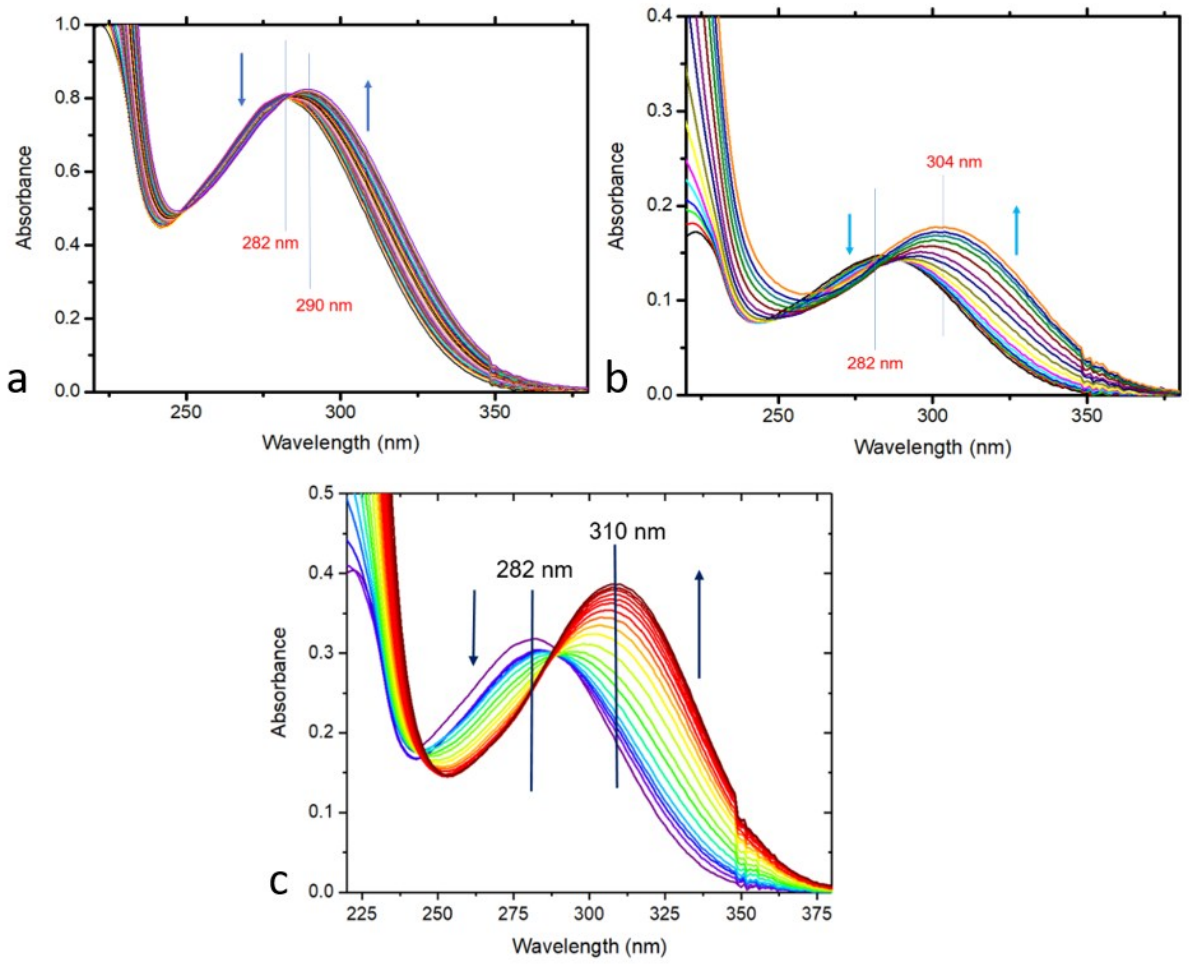


Figure S2: a) UV-Vis titration in CH_3CN of ligand **1** (2.6 x 10^{-5} M) with $La(NO_3)_3 \cdot 6H_2O$ (1.2 x 10^{-3} M). b) UV-Vis titration in CH_3CN of ligand **1** (1.3 x 10^{-5} M) with $Eu(NO_3)_3 \cdot 6H_2O$ (1.0 x 10^{-3}M) c) UV-Vis titration in CH_3CN of ligand **1** (2.8 x 10^{-5} M) with $Lu(NO_3)_3 \cdot 6H_2O$ (1.9 x 10^{-3} M).

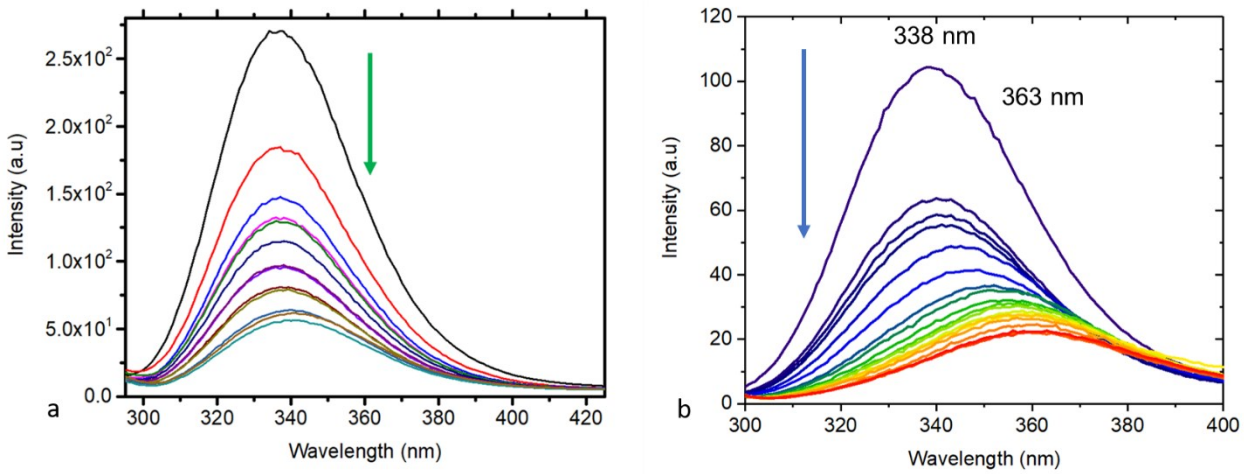


Figure S3: a. Fluorescence titration in CH_3CN of **1** (1.3 x 10^{-5} M) with $La(NO_3)_3 \cdot 6H_2O$ (8.8 x 10^{-3} M). b. Fluorescence titration in CH_3CN of **1** (2.8 x 10^{-5} M) with $Lu(NO_3)_3 \cdot 6H_2O$ (1.9 x 10^{-3} M).

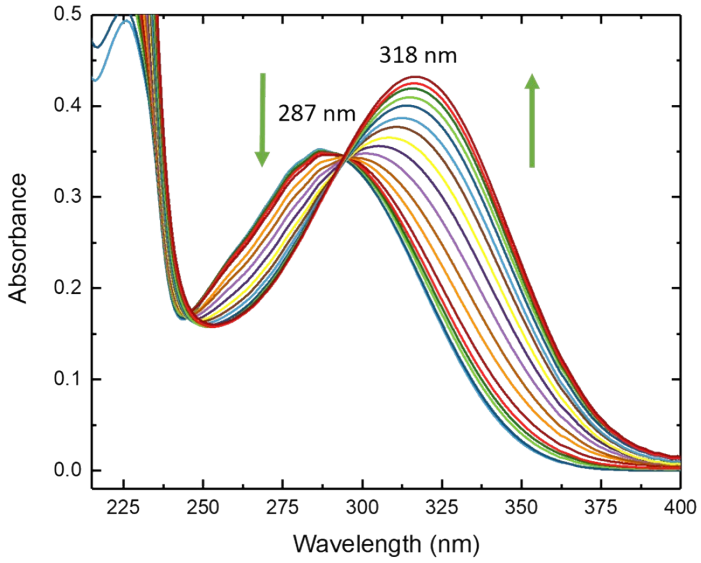


Figure S4. UV-visible titration in CH_3CN of ligand **3** (2.6 x 10^{-5} M) with $Nd(NO_3)_3 \cdot 6H_2O$ (1.0 x10^{-3} M).

Section 3: ^{1}H-NMR titrations

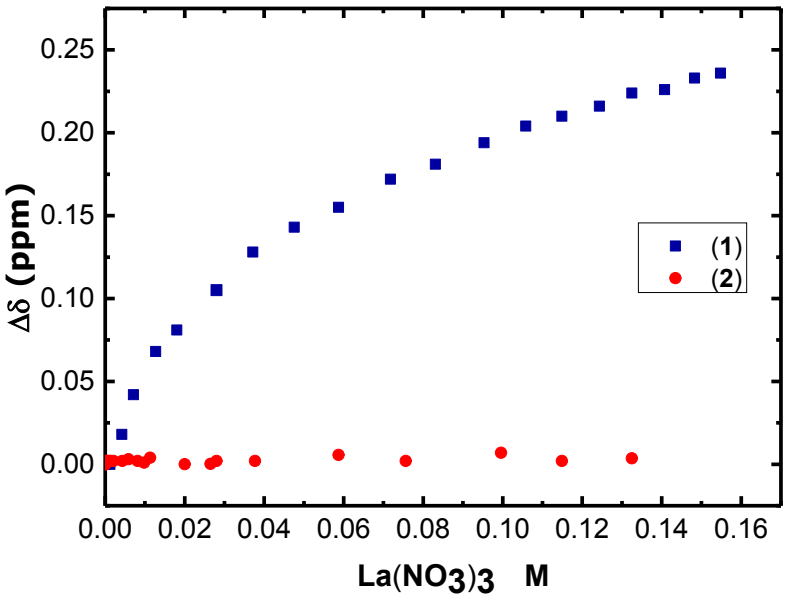


Figure S5. ^{1}H-NMR titration (acetone-d_6): (2.4 mM of **1** and 1.4 mM of **2**) titrated with $La(NO_3)_3 \cdot 6H_2O$.

Section 4: Continuous Variation Method (Job Plots)

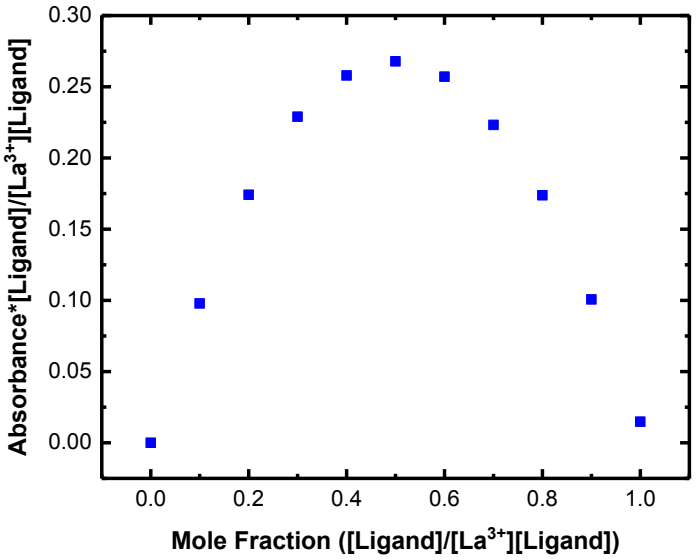


Figure S6. Job Plot for **1** and $La(NO_3)_3$ in CH_3CN showing 1:1 binding stoichiometry

Section 5: Solvent Extraction

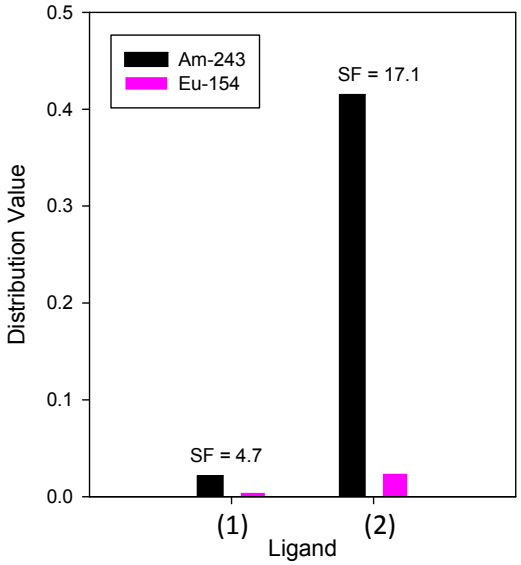


Figure S7. Distribution values of ligands **1** and **2** after extraction experiments with Am-243 and Eu-154 in CH_2Cl_2/HNO_3(6.5M)

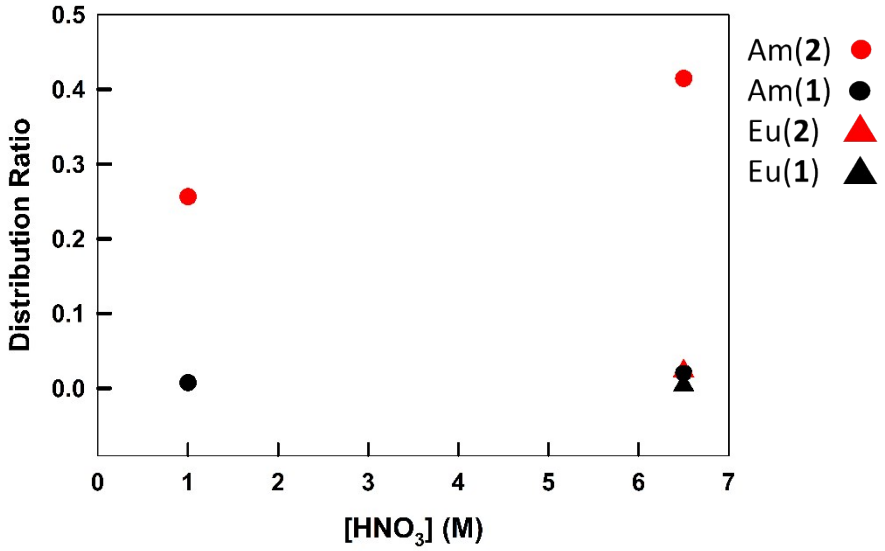
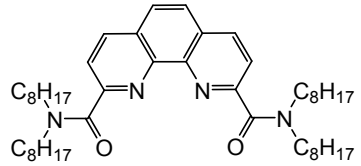
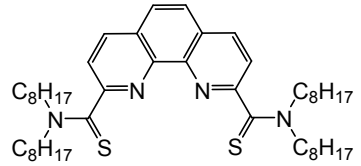
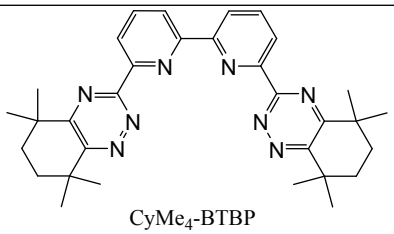
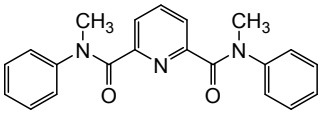
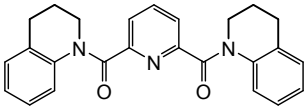
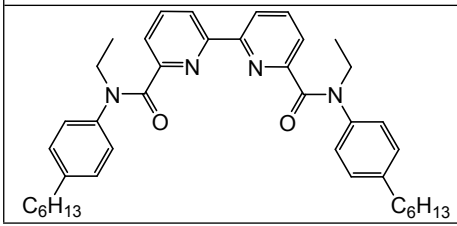


Figure S8. Distribution ratios for extraction of Am and Eu by ligands **1** and **2** at 1 M HNO_3 and 6.5 M HNO_3.

Table S1. Separation factors ($SF_{Am/Eu}$) for extraction from highly-acidic media found in literature.

Extractant	Solvent	$[HNO_3]_t$ (M)	$SF_{Am/Eu}$	Reference
	o-nitrophenyl hexyl ether (NPHE) +Br Cosan*	1.00	3.96	Galletta *et al.*[17]
		3.82	8.71	
	NPHE +Br Cosan*	1.00	2.31	Galletta *et al.*[17]
		3.82	4.87	
 CyMe$_4$-BTBP	*n*-octanol + DMDOHEMA (catalyst)	1.00	120	Geist *et al.* [18]
	CH_2Cl_2	6.00	3.13	Babain *et al.*[19]
	CH_2Cl_2 + Metanitrobenzotrifluoride	6.00	3.00	Babain *et al.*[19]
	1,2-dichloroethane	3.00	7.6	Alyapyshev *et al.*[20]
		6.00	12	

*Brominated cobalt bis(dicarbollide) anion as a synergistic lipophilic anion

Section 6: X-ray Crystallography

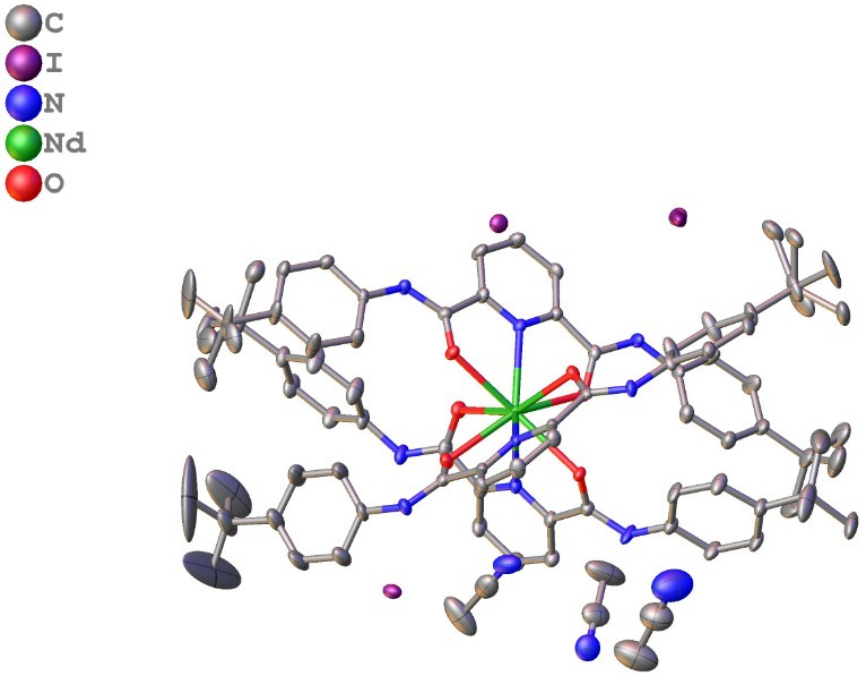


Figure S9: Structure of $[Nd(\mathbf{3})_3]I_3 \cdot 3CH_3CN$ drawn at 50 percent probability. Hydrogens are omitted for clarity.

The bulky nature of the ligand creates challenges in packing three such ligands around a single metal center. One of the (**3**) ligands is relatively co-planar (labeled as the 100 series in the CIF); whereas the other two ligands both have substantial distortions. For the (**3**) ligand labeled with the 200 series, there is substantial twisting of one of the peripheral phenyl rings by 55.08(5)˚ with respect the rest of the ligand, which is roughly co-planar. The second distorted (**3**) ligand (labeled as the 1 series in the CIF) accommodates the bulky ligand packing by twisting at one of the amide-pyridine linkages 23.69(5)˚ with respect the plane of the pyridine ring. These distortions allow for improved packing of the t-butyl groups one adjacent (**3**) ligands. Remarkably, even though there are substantial distortions of two of the three ligands, the Nd-N and Nd-O bond distances do not reflect these features, and even in the most pronounced example, the Nd-O bond distances are not statistically different at the 3σ limit.

Files can be retrieved from the CCDC (1854275).

$[Nd(3)_3]I_3 \cdot 3CH_3CN$

Table S2 Crystal data and structure refinement for Nd(3).

Identification code	Nd(3)
Empirical formula	$C_{87}H_{102}I_3N_{12}NdO_6$
Formula weight	1936.74
Temperature/K	120.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.754(3)
b/Å	18.809(3)
c/Å	25.655(4)
α/°	90
β/°	108.127(3)
γ/°	90
Volume/Å^3	8600(2)
Z	4
ρ_{calc}g/cm^3	1.496
μ/mm^{-1}	1.739
F(000)	3900.0
Crystal size/mm^3	0.09 × 0.08 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.332 to 55.29
Index ranges	$-24 \leq h \leq 24$, $-24 \leq k \leq 24$, $-33 \leq l \leq 33$
Reflections collected	132580
Independent reflections	19967 [R_{int} = 0.0472, R_{sigma} = 0.0298]
Data/restraints/parameters	19967/0/1044
Goodness-of-fit on F^2	1.158
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.1125
Largest diff. peak/hole / e Å^{-3}	2.12/-0.98

Section 7: Theory

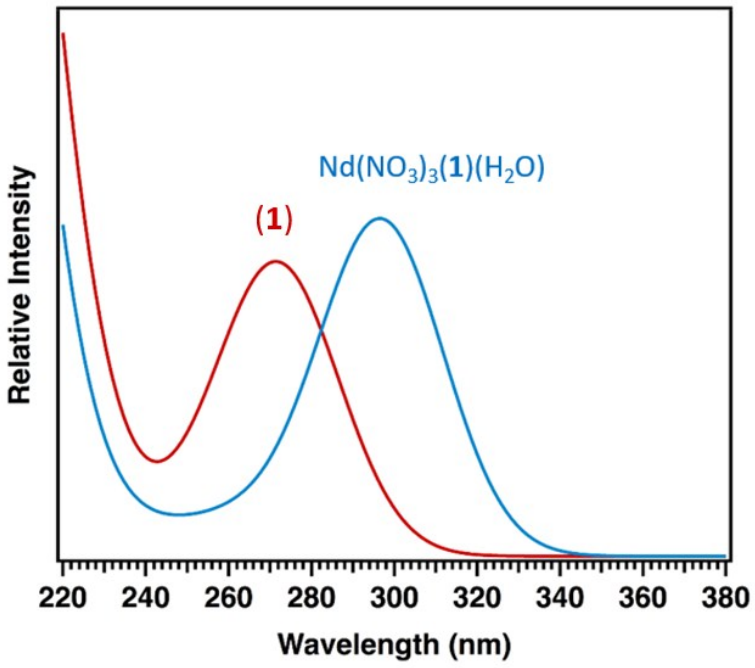


Figure S10. DFT/PBE0 simulated UV-Vis spectra of **1** and $Nd(NO_3)_3$(**1**)(H_2O) complex.

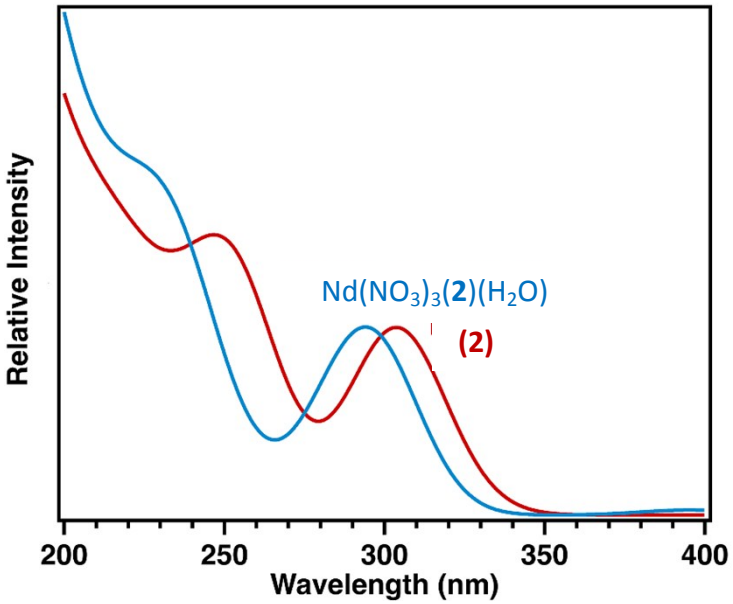


Figure S11. DFT/PBE0 simulated UV-Vis spectra of **2** and $Nd(NO_3)_3$(**2**)(H_2O) complex.

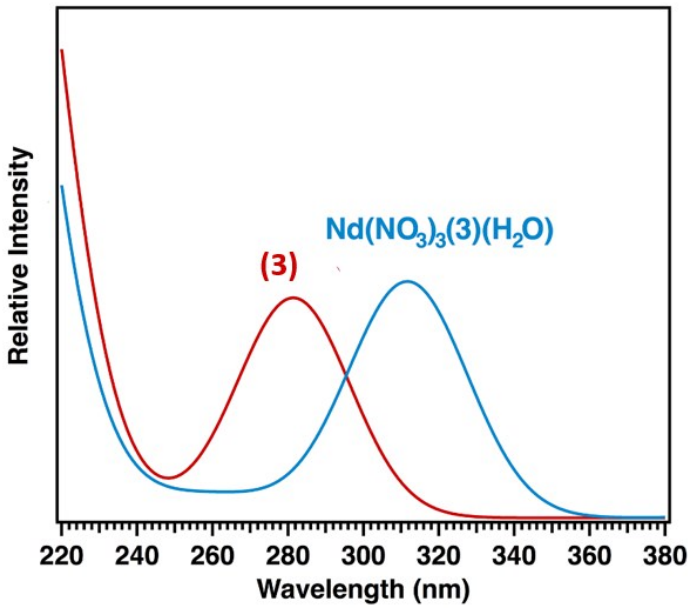


Figure S12. DFT/PBE0 simulated UV-Vis spectra of **3** and $Nd(NO_3)_3$(**3**)(H_2O) complex.

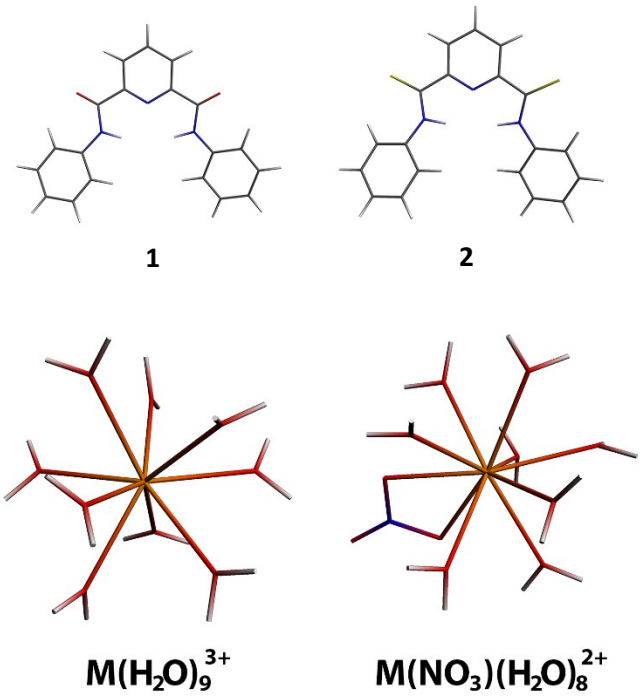


Figure S13. Optimized geometrical structures of **1**, **2** and M(III) hydrate and nitrate hydrate complexes with M=Eu and Am.

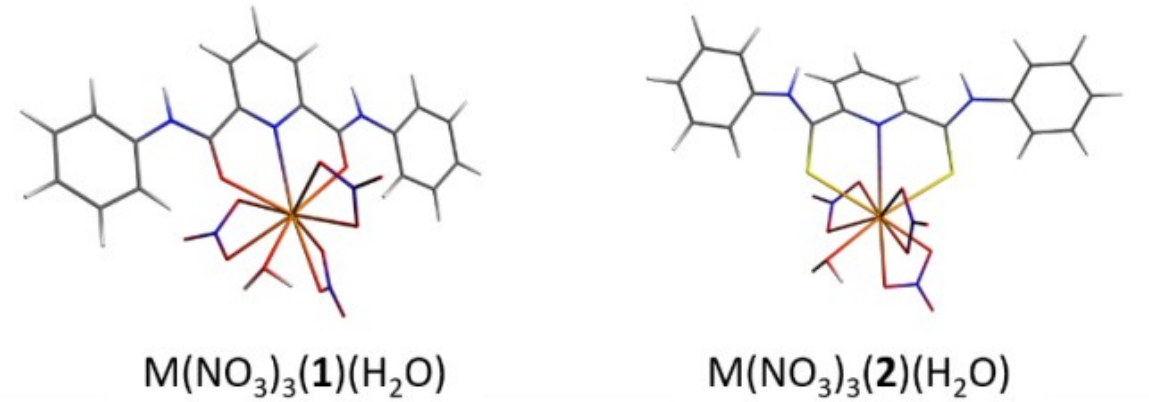


Figure S14. Optimized geometries $M(NO_3)_3$(**1**)$(H_2O)$and $M(NO_3)_3$(**2**)(H_2O) (M=Nd, Eu, Am).

Table S3. Calculated Gibbs free energies (ΔG in kcal/mol) of the complexation reaction of ligand with $Nd(NO_3)_3(H_2O)_4$ in CH_3CN.

Reaction	L=**1**	L=**2**
$Nd(NO_3)_3(H_2O)_4 + L \rightarrow Nd(NO_3)_3(L)(H_2O) + 3H_2O$	–15.49	–3.77

Table S4. Calculated Gibbs free energies (ΔG in kcal/mol) of the ligand exchange reaction $M(NO_3)_3$(**2**)(H_2O) + **1** → $M(NO_3)_3$(**1**)(H_2O) + **2**, where M=Nd, Eu and Am, in CH_3CN and CH_2Cl_2, respectively.

Solvents	Nd	Eu	Am
CH_3CN	–11.72	–15.11	–14.63
CH_2Cl_2	–11.93	–15.10	–14.53

Table S5. Calculated and Experimental Gibbs free energies (ΔG in kcal/mol) of the reactions of the M(III) hydrates and nitrate hydrates (M=Am and Eu) with ligands **1** and **2** in CH_2Cl_2/HNO_3

Reaction	ΔG(Eu)	ΔG(Am)	ΔΔG(Am-Eu)	
	Theory	Theory	Theory	Expt
$M(H_2O)_9^{3+}{}_{(aq)} + 3NO_3^-{}_{(aq)} + \mathbf{1}_{(org)} \rightarrow M(NO_3)_3(\mathbf{1})(H_2O)_{(org)} + 8H_2O_{(aq)}$	–50.36	–51.83	–1.47	–0.92
$M(H_2O)_9^{3+}{}_{(aq)} + 3NO_3^-{}_{(aq)} + \mathbf{2}_{(org)} \rightarrow M(NO_3)_3(\mathbf{2})(H_2O)_{(org)} + 8H_2O_{(aq)}$	–35.26	–37.30	–2.04	–1.68
$M(NO_3)(H_2O)_8^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + \mathbf{1}_{(org)} \rightarrow M(NO_3)_3(\mathbf{1})(H_2O)_{(org)} + 7H_2O_{(aq)}$	–37.92	–38.95	–1.03	–0.92
$M(NO_3)(H_2O)_8^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + \mathbf{2}_{(org)} \rightarrow M(NO_3)_3(\mathbf{2})(H_2O)_{(org)} + 7H_2O_{(aq)}$	–22.82	–24.42	–1.60	–1.68

Table S6. Gibbs free energy (ΔΔΔG in kcal/mol) of the competition reaction: $Eu(NO_3)_3(\mathbf{2})(H_2O) + Am(NO_3)_3(\mathbf{1})(H_2O) \rightarrow Eu(NO_3)_3(\mathbf{1})(H_2O) + Am(NO_3)_3(\mathbf{2})(H_2O)$ in CH_2Cl_2

Reaction	ΔΔΔG	
	Theory	Expt
$Eu(NO_3)_3(\mathbf{2})(H_2O) + Am(NO_3)_3(\mathbf{1})(H_2O) \rightarrow Eu(NO_3)_3(\mathbf{1})(H_2O) + Am(NO_3)_3(\mathbf{2})(H_2O)$	–0.57	–0.77

Table S7. Cartesian coordinates of PBE0 optimized geometries of ligands and metal complexes

(1)			
1.C	1.147414	-1.963562	-0.017753
2.C	1.197775	-3.357892	-0.026719
3.C	0.000054	-4.064000	-0.000340
4.C	-1.197688	-3.357934	0.026132
5.C	-1.147368	-1.963602	0.017354
6.N	0.000011	-1.282604	-0.000152
7.H	0.000072	-5.151049	-0.000413
8.H	2.168348	-3.843040	-0.050026
9.H	-2.168248	-3.843114	0.049367
10.C	2.456664	-1.197069	-0.019383
11.C	-2.456647	-1.197157	0.019059
12.N	2.283087	0.142921	0.126029
13.C	3.237825	1.164955	0.199601
14.C	4.611386	0.942653	0.035940
15.C	2.773334	2.465023	0.447818
16.C	5.491895	2.018689	0.121700
17.H	4.969348	-0.061905	-0.151885
18.C	3.664208	3.527610	0.530628
19.H	1.706967	2.639193	0.582440
20.C	5.032215	3.310632	0.367507
21.H	6.556094	1.837534	-0.007046
22.H	3.287033	4.528143	0.726091
23.H	5.730838	4.140284	0.432631
24.N	-2.283120	0.142860	-0.126156
25.C	-3.237901	1.164860	-0.199647
26.C	-2.773448	2.464997	-0.447570
27.C	-4.611471	0.942458	-0.036192
28.C	-3.664368	3.527552	-0.530300
29.H	-1.707074	2.639248	-0.582027
30.C	-5.492026	2.018463	-0.121869
31.H	-4.969403	-0.062153	0.151412
32.C	-5.032384	3.310474	-0.367387
33.H	-3.287222	4.528141	-0.725535
34.H	-6.556232	1.837227	0.006711
35.H	-5.731043	4.140099	-0.432452
36.H	1.312164	0.413084	0.212947
37.H	-1.312205	0.413078	-0.212995
38.O	3.522654	-1.778326	-0.131500
39.O	-3.522618	-1.778473	0.131055

(2)			
1.C	1.154357	-2.132409	-0.089722
2.C	1.197072	-3.528031	-0.099977
3.C	0.000045	-4.226840	-0.000297
4.C	-1.196992	-3.528064	0.099492
5.C	-1.154288	-2.132442	0.089427
6.N	0.000027	-1.466101	-0.000107
7.H	0.000055	-5.313890	-0.000378
8.H	2.158638	-4.023615	-0.182924
9.H	-2.158552	-4.023671	0.182374
10.C	2.420387	-1.310444	-0.162617
11.C	-2.420339	-1.310516	0.162415
12.N	2.174748	-0.024029	0.145169
13.C	2.965057	1.129577	0.221364
14.C	4.320969	1.195240	-0.123563
15.C	2.313932	2.290113	0.674745
16.C	4.996549	2.409222	-0.012835
17.H	4.829434	0.304124	-0.469102
18.C	3.000115	3.491236	0.780189
19.H	1.262163	2.241531	0.953564
20.C	4.350812	3.558286	0.435219
21.H	6.048627	2.449078	-0.283719
22.H	2.479249	4.376286	1.135869
23.H	4.892057	4.496850	0.517774
24.N	-2.174752	-0.024072	-0.145288
25.C	-2.965119	1.129499	-0.221427
26.C	-2.314061	2.290085	-0.674774
27.C	-4.321032	1.195078	0.123517
28.C	-3.000311	3.491173	-0.780173
29.H	-1.262293	2.241569	-0.953605
30.C	-4.996679	2.409026	0.012833
31.H	-4.829445	0.303924	0.469032
32.C	-4.351009	3.558139	-0.435191
33.H	-2.479496	4.376264	-1.135830
34.H	-6.048757	2.448815	0.283727
35.H	-4.892307	4.496676	-0.517714
36.H	1.190945	0.123863	0.356015
37.H	-1.190959	0.123876	-0.356139
38.S	-3.872972	-2.014434	0.579646
39.S	3.873053	-2.014287	-0.579861

(3)			
1.C	1.145962	-1.996875	0.056611
2.C	1.196081	-3.391340	0.055034
3.C	-0.000323	-4.097527	-0.003148
4.C	-1.196706	-3.391191	-0.059956
5.C	-1.146604	-1.996727	-0.057765
6.N	-0.000340	-1.315632	0.000689
7.H	-0.000326	-5.184621	-0.004470
8.H	2.166176	-3.875827	0.100292
9.H	-2.166763	-3.875561	-0.107229
10.C	2.455148	-1.233419	0.127106
11.C	-2.455682	-1.233123	-0.128845
12.N	2.281655	0.112731	0.163219
13.C	3.238098	1.133638	0.237009
14.C	4.615663	0.902565	0.260136
15.C	2.776678	2.456767	0.289855
16.C	5.496179	1.982206	0.334173
17.H	4.987175	-0.113905	0.221159
18.C	3.669729	3.514115	0.363558
19.H	1.706169	2.656306	0.274797
20.C	5.057569	3.307519	0.388047
21.H	6.559115	1.762511	0.349798
22.H	3.269875	4.524389	0.403659
23.N	-2.282337	0.113232	-0.157241
24.C	-3.238577	1.134251	-0.232079
25.C	-2.777523	2.458123	-0.266423
26.C	-4.615566	0.902536	-0.274936

$Nd(NO_3)_3$(**3**)(H_2O)			
1.Nd	1.446295	1.728293	2.630807
2.H	-1.280616	6.346857	1.754506
3.C	-0.297335	4.598173	1.812752
4.N	1.778491	4.464621	2.944595
5.C	0.901064	5.305018	2.408019
6.C	1.117829	6.684788	2.393187
7.H	0.424929	7.373529	1.918662
8.C	2.280424	7.177814	2.974619
9.H	2.486970	8.244372	2.969965
10.C	3.179864	6.291089	3.554615
11.H	4.089498	6.677496	4.004724
12.C	2.885421	4.926055	3.516923
13.C	3.741567	3.815648	4.084418
14.H	5.060588	5.156069	4.788431
15.N	2.783163	-0.886643	2.468223
16.O	3.404106	0.201941	2.690193
17.O	1.527420	-0.766062	2.322299
18.O	3.343874	-1.948140	2.403107
19.N	0.115566	1.688249	5.248560
20.O	0.720555	0.676958	4.778522
21.O	-0.421511	1.681999	6.325751
22.O	0.116567	2.719906	4.498406
23.O	2.750519	2.884992	0.803623
24.O	1.382911	1.356962	0.164852
25.N	2.208287	2.268771	-0.164597
26.O	2.450026	2.531277	-1.314659

27.C	-3.670346	3.515534	-0.342075
28.H	-1.707464	2.658220	-0.235237
29.C	-5.495848	1.982235	-0.350864
30.H	-4.986793	-0.114470	-0.249634
31.C	-5.057572	3.308260	-0.387122
32.H	-3.270787	4.526408	-0.367383
33.H	-6.558311	1.761991	-0.382604
34.H	1.309982	0.392189	0.137680
35.H	-1.310840	0.392734	-0.126019
36.O	3.522956	-1.823109	0.149899
37.O	-3.523256	-1.822910	-0.158961
38.C	-6.010058	4.505045	-0.473708
39.C	-5.711674	5.303603	-1.756236
40.H	-6.380419	6.168922	-1.828653
41.H	-4.681673	5.673339	-1.772539
42.H	-5.859289	4.681498	-2.645458
43.C	-5.803531	5.414657	0.751515
44.H	-6.472132	6.281403	0.697149
45.H	-6.019275	4.873622	1.679045
46.H	-4.776085	5.786972	0.811220
47.C	-7.480473	4.072820	-0.508281
48.H	-7.699503	3.446156	-1.379372
49.H	-7.763134	3.521137	0.394625
50.H	-8.120382	4.959303	-0.568866
51.C	6.010307	4.504252	0.472588
52.C	5.731116	5.288681	1.768083
53.H	6.399808	6.154147	1.839290
54.H	4.700989	5.656627	1.804475
55.H	5.893492	4.657291	2.648140
56.C	7.481440	4.073156	0.479653
57.H	7.714777	3.438154	1.340935
58.H	7.750214	3.530683	-0.433014
59.H	8.121489	4.959629	0.538922
60.C	5.784047	5.426679	-0.739515
61.H	6.453022	6.293219	-0.686498
62.H	5.985383	4.895675	-1.676029
63.H	4.755656	5.799062	-0.779113

27.O	-0.776924	0.588788	1.882389
28.H	-0.600724	-0.340311	2.083394
29.H	-0.663149	0.658311	0.924690
30.O	3.363833	2.652268	3.956885
31.O	-0.246937	3.385089	1.626080
32.N	-1.365643	5.367356	1.533464
33.N	4.878520	4.168716	4.705230
34.C	5.862741	3.344587	5.298625
35.C	6.839825	3.981506	6.066343
36.C	5.914762	1.956011	5.134332
37.C	7.855188	3.247083	6.668663
38.H	6.808654	5.062169	6.200747
39.C	6.939012	1.244112	5.746633
40.H	5.173164	1.438945	4.537612
41.C	7.929863	1.857595	6.526218
42.H	8.594427	3.778919	7.258563
43.H	6.955779	0.167202	5.601183
44.C	-2.623379	5.000475	1.004942
45.C	-3.475689	6.036179	0.617274
46.C	-3.056620	3.676448	0.881713
47.C	-4.740013	5.759569	0.108739
48.H	-3.150756	7.071704	0.709498
49.C	-4.322892	3.423923	0.368257
50.H	-2.417462	2.860391	1.193572
51.C	-5.196172	4.445014	-0.032279
52.H	-5.371231	6.593227	-0.180899
53.H	-4.635195	2.386096	0.285824
54.C	9.028202	1.013060	7.178014
55.C	10.016862	1.869605	7.976978
56.H	10.781781	1.224320	8.421550
57.H	10.529911	2.599256	7.340947
58.H	9.523116	2.406666	8.794211
59.C	8.382283	-0.005080	8.135793
60.H	7.825994	0.504035	8.930107
61.H	7.688380	-0.669711	7.612677
62.H	9.154989	-0.625755	8.602989
63.C	9.810295	0.262344	6.084518
64.H	10.286150	0.964999	5.392075
65.H	10.594113	-0.354121	6.538524
66.H	9.161062	-0.397107	5.500984
67.C	-6.578437	4.100109	-0.594137
68.C	-7.387368	5.353720	-0.945575
69.H	-8.365718	5.057797	-1.338350
70.H	-7.561453	5.985079	-0.067487
71.H	-6.892324	5.956235	-1.714859
72.C	-7.368455	3.292153	0.451656
73.H	-8.357168	3.031834	0.057760
74.H	-6.858391	2.361351	0.716921
75.H	-7.508384	3.872456	1.369861
76.C	-6.409067	3.257397	-1.871711
77.H	-5.857065	3.813989	-2.636565
78.H	-5.865905	2.328197	-1.674809
79.H	-7.390025	2.993203	-2.282226

$Nd(NO_3)_3$(**1**)(H_2O)			
1.Nd	1.361230	1.699476	2.819075
2.H	-1.359440	6.314323	1.786692
3.C	-0.362802	4.574044	1.936570
4.N	1.709436	4.449743	3.072533
5.C	0.798172	5.289996	2.594142
6.C	0.947930	6.674785	2.699856
7.H	0.219806	7.370506	2.293627
8.C	2.078564	7.172257	3.337409
9.H	2.223531	8.243955	3.440687
10.C	3.020306	6.283790	3.843111
11.H	3.894717	6.670952	4.357834
12.C	2.795139	4.915072	3.681781
13.C	3.695426	3.804234	4.175592
14.H	5.129820	5.134510	4.628364
15.N	2.587805	-0.970937	2.891286
16.O	3.218615	0.092953	3.189793

$Nd(NO_3)_3$(**2**)(H_2O)			
1.Nd	1.461736	1.130969	2.343124
2.H	-0.636534	6.493738	1.876385
3.C	-0.345821	4.537350	1.682953
4.N	1.854764	4.139372	2.648428
5.C	1.110914	4.880712	1.825656
6.C	1.636764	5.943733	1.079856
7.H	1.017554	6.472693	0.361283
8.C	2.983066	6.250535	1.216807
9.H	3.439843	7.025371	0.607225
10.C	3.736179	5.541721	2.142024
11.H	4.794864	5.748695	2.268442
12.C	3.123201	4.499375	2.851153
13.C	3.918983	3.732684	3.870117
14.H	4.586115	5.516843	4.446257
15.N	2.922058	-1.342115	1.831255
16.O	3.500544	-0.221215	2.020316

17.O	1.384836	-0.791483	2.523881	17.O	1.654170	-1.306745	1.910650
18.O	3.091988	-2.060298	2.950326	18.O	3.529506	-2.350237	1.598369
19.N	-0.051102	1.721031	5.389872	19.N	0.430073	0.894951	5.077701
20.O	0.515885	0.679713	4.941476	20.O	0.966022	-0.085564	4.459817
21.O	-0.623249	1.747926	6.447840	21.O	0.025346	0.799661	6.205555
22.O	0.027436	2.750010	4.636896	22.O	0.356762	1.975200	4.413102
23.O	2.798203	2.712618	1.027453	23.O	2.430625	2.433967	0.439358
24.O	1.310050	1.320496	0.347507	24.O	1.120999	0.815615	-0.091350
25.N	2.221591	2.153699	0.042068	25.N	1.851087	1.778920	-0.485211
26.O	2.512771	2.399713	-1.099602	26.O	1.976933	2.060112	-1.647969
27.O	-0.877338	0.615372	2.040783	27.O	-0.781810	-0.125374	2.074586
28.H	-0.744032	-0.311243	2.282242	28.H	-0.675489	-0.840283	2.717066
29.H	-0.739582	0.644845	1.084280	29.H	-0.729014	-0.555691	1.211400
30.O	3.286131	2.646812	4.125228	30.N	-1.127248	5.634888	1.665493
31.O	-0.288294	3.363655	1.750900	31.N	4.736428	4.526961	4.587822
32.N	-1.425483	5.327728	1.594542	32.C	5.687536	4.257952	5.595369
33.N	4.905781	4.152260	4.643580	33.C	6.037323	5.340396	6.415911
34.C	5.942601	3.327236	5.139859	34.C	6.309630	3.019072	5.779974
35.C	7.042917	3.984579	5.705120	35.C	6.988088	5.186638	7.415345
36.C	5.917525	1.930186	5.068826	36.H	5.552473	6.304997	6.272954
37.C	8.114190	3.254094	6.202636	37.C	7.262981	2.879507	6.786370
38.H	7.058049	5.072483	5.757682	38.H	6.054093	2.176405	5.151320
39.C	7.000796	1.213509	5.573127	39.C	7.604946	3.950355	7.607520
40.H	5.077108	1.410521	4.625636	40.H	7.244387	6.032954	8.046681
41.C	8.096109	1.861165	6.139402	41.H	7.741448	1.913562	6.923810
42.H	8.961918	3.774675	6.639848	42.H	8.346858	3.824759	8.391250
43.H	6.978849	0.128730	5.513264	43.C	-2.514675	5.832185	1.512605
44.H	8.931988	1.285730	6.527574	44.C	-2.984093	7.118870	1.820286
45.C	-2.639095	4.931776	0.987489	45.C	-3.413435	4.859080	1.062918
46.C	-3.441631	5.950540	0.459664	46.C	-4.329796	7.429042	1.687828
47.C	-3.065446	3.601351	0.926030	47.H	-2.286866	7.878124	2.172128
48.C	-4.659586	5.644910	-0.134580	48.C	-4.762239	5.185515	0.934089
49.H	-3.107225	6.985710	0.508922	49.H	-3.066586	3.863245	0.822473
50.C	-4.287875	3.311015	0.324672	50.C	-5.229326	6.459148	1.244265
51.H	-2.456734	2.811926	1.347944	51.H	-4.676450	8.428856	1.934230
52.C	-5.086790	4.319896	-0.208252	52.H	-5.453500	4.423074	0.584956
53.H	-5.272702	6.443731	-0.542758	53.H	-6.284531	6.696642	1.141854
54.H	-4.617513	2.276445	0.280403	54.S	-0.845308	2.956711	1.533613
55.H	-6.037465	4.077090	-0.674740	55.S	3.785752	2.078392	4.008740
$Eu(NO_3)_3$(**1**)(H_2O)				$Eu(NO_3)_3$(**2**)(H_2O)			
1.Eu	1.318246	1.755740	2.917911	1.Eu	1.458467	1.123250	2.367072
2.H	-1.195083	6.317884	1.467034	2.H	-0.677051	6.521701	1.849899
3.C	-0.410265	4.550240	2.013781	3.C	-0.358264	4.564865	1.722019
4.N	1.673556	4.431234	3.135195	4.N	1.837073	4.194574	2.693021
5.C	0.750203	5.267432	2.672712	5.C	1.093146	4.927489	1.865562
6.C	0.871961	6.650058	2.831323	6.C	1.616790	5.988426	1.115022
7.H	0.115415	7.344599	2.478923	7.H	0.999735	6.512297	0.390713
8.C	1.992983	7.148254	3.485084	8.C	2.962105	6.300244	1.255070
9.H	2.111263	8.218051	3.632659	9.H	3.416929	7.076362	0.645585
10.C	2.954186	6.263165	3.959105	10.C	3.718376	5.591717	2.178244
11.H	3.820453	6.648361	4.488797	11.H	4.777493	5.799096	2.301085
12.C	2.749929	4.896675	3.760176	12.C	3.106560	4.548383	2.887205
13.C	3.657890	3.785086	4.238102	13.C	3.905018	3.762284	3.888395
14.H	5.100915	5.112391	4.681696	14.H	4.594780	5.530928	4.483939
15.N	2.838605	-0.669987	2.526333	15.N	2.893194	-1.335570	1.907477
16.O	3.361816	0.489186	2.475899	16.O	3.458785	-0.218784	2.162056
17.O	1.593767	-0.683033	2.773173	17.O	1.627153	-1.286685	1.861074
18.O	3.477811	-1.674623	2.356860	18.O	3.515593	-2.345274	1.726114
19.N	0.280934	1.788981	5.641333	19.N	0.528205	0.815236	5.069428
20.O	0.812188	0.758813	5.118086	20.O	1.061984	-0.141792	4.415704
21.O	-0.110601	1.807939	6.780079	21.O	0.153883	0.692513	6.204004
22.O	0.192601	2.798883	4.874755	22.O	0.423519	1.907138	4.426196
23.O	2.214067	2.803363	0.872614	23.O	2.429758	2.425971	0.537392
24.O	0.877851	1.148215	0.580330	24.O	1.087228	0.854202	-0.041270
25.N	1.592079	2.057480	0.052373	25.N	1.828449	1.818363	-0.407493
26.O	1.666375	2.208613	-1.139628	26.O	1.948088	2.143903	-1.558515
27.O	-0.892116	0.512430	2.763415	27.O	-0.759497	-0.055112	2.075964
28.H	-0.778317	-0.205909	3.399454	28.H	-0.625812	-0.856819	2.600080
29.H	-0.832338	0.094733	1.894361	29.H	-0.763518	-0.354609	1.157385
30.O	3.243938	2.628841	4.197281	30.N	-1.154560	5.649981	1.662877

31.O	-0.441752	3.324063	2.026929
32.N	-1.357213	5.323975	1.448366
33.N	4.880214	4.129277	4.675951
34.C	5.921497	3.286399	5.136881
35.C	6.944036	3.894250	5.874341
36.C	5.973728	1.918420	4.851768
37.C	8.015180	3.138579	6.335243
38.H	6.896461	4.959834	6.094016
39.C	7.053565	1.175230	5.322883
40.H	5.193728	1.443180	4.268904
41.C	8.071670	1.772372	6.063068
42.H	8.803094	3.618392	6.909384
43.H	7.093309	0.112885	5.097953
44.H	8.906548	1.177829	6.423633
45.C	-2.547656	4.948024	0.788413
46.C	-3.302161	5.983661	0.221757
47.C	-2.992458	3.625442	0.691224
48.C	-4.491176	5.704157	-0.438933
49.H	-2.954300	7.013021	0.296971
50.C	-4.186825	3.362045	0.024401
51.H	-2.413879	2.823107	1.129358
52.C	-4.939497	4.387853	-0.541555
53.H	-5.066050	6.516528	-0.875070
54.H	-4.528340	2.333136	-0.050333
55.H	-5.868200	4.165056	-1.059374

31.N	4.736692	4.537749	4.610427
32.C	5.701277	4.246872	5.598485
33.C	6.092589	5.321811	6.410467
34.C	6.297710	2.993990	5.773627
35.C	7.059782	5.147648	7.390506
36.H	5.627739	6.297407	6.275555
37.C	7.268341	2.834274	6.760438
38.H	6.008893	2.156156	5.152929
39.C	7.652279	3.897915	7.572192
40.H	7.348241	5.988808	8.014862
41.H	7.726608	1.857497	6.890022
42.H	8.407296	3.756398	8.340518
43.C	-2.541775	5.825002	1.484453
44.C	-3.027403	7.120553	1.722368
45.C	-3.425943	4.821875	1.073361
46.C	-4.374205	7.410211	1.558218
47.H	-2.341900	7.903558	2.043912
48.C	-4.775953	5.128103	0.911539
49.H	-3.066601	3.818651	0.888244
50.C	-5.258933	6.410899	1.151652
51.H	-4.733286	8.417555	1.750220
52.H	-5.455456	4.342268	0.592440
53.H	-6.314842	6.632636	1.024159
54.S	-0.835140	2.972944	1.626732
55.S	3.757705	2.107262	3.995526

$Am(NO_3)_3$(**1**)(H_2O)			
1.Am	1.340332	1.720465	2.888464
2.H	-1.227524	6.341607	1.561242
3.C	-0.387460	4.561016	1.979221
4.N	1.687642	4.421709	3.132435
5.C	0.776086	5.263579	2.652421
6.C	0.912646	6.646457	2.796771
7.H	0.175366	7.346445	2.415984
8.C	2.027693	7.141086	3.462354
9.H	2.155448	8.211287	3.598613
10.C	2.971454	6.251255	3.960557
11.H	3.831294	6.632791	4.503066
12.C	2.760424	4.884735	3.768419
13.C	3.665045	3.779293	4.270751
14.H	5.118526	5.114418	4.660387
15.N	2.909505	-0.723919	2.539984
16.O	3.437813	0.431263	2.487531
17.O	1.658863	-0.733322	2.770965
18.O	3.544895	-1.733570	2.387013
19.N	0.035881	1.736406	5.542667
20.O	0.577188	0.702112	5.033546
21.O	-0.477357	1.723802	6.632143
22.O	0.075750	2.779704	4.820342
23.O	2.317046	2.785514	0.857655
24.O	1.021453	1.115618	0.469474
25.N	1.750104	2.040013	-0.005089
26.O	1.891100	2.209689	-1.188760
27.O	-0.906870	0.434680	2.509367
28.H	-0.854754	-0.308066	3.123948
29.H	-0.770319	0.055016	1.631842
30.O	3.248381	2.623569	4.266021
31.O	-0.400578	3.336595	1.923012
32.N	-1.362277	5.346973	1.480196
33.N	4.891877	4.133155	4.690900
34.C	5.929871	3.300795	5.177934
35.C	6.944496	3.923426	5.913971
36.C	5.986552	1.927832	4.919137
37.C	8.011349	3.177514	6.400276
38.H	6.893736	4.992885	6.112986
39.C	7.061591	1.194359	5.415911
40.H	5.214077	1.441298	4.335589
41.C	8.071300	1.806299	6.155518
42.H	8.793066	3.668912	6.973129
43.H	7.104891	0.128065	5.211184
44.H	8.902634	1.219442	6.536223

$Am(NO_3)_3$(**2**)(H_2O)			
1.Am	1.488379	1.060960	2.353300
2.H	-0.673557	6.526402	1.903895
3.C	-0.343325	4.575158	1.732278
4.N	1.869021	4.221037	2.671626
5.C	1.107537	4.947705	1.855053
6.C	1.610799	6.012093	1.095101
7.H	0.977196	6.531282	0.381671
8.C	2.955420	6.336012	1.214956
9.H	3.393635	7.117609	0.600291
10.C	3.732119	5.632029	2.124589
11.H	4.791051	5.847998	2.234059
12.C	3.139857	4.581678	2.839713
13.C	3.968003	3.795593	3.816378
14.H	4.584900	5.571832	4.462305
15.N	2.830466	-1.548969	2.233897
16.O	3.385715	-0.476634	2.657119
17.O	1.642339	-1.403995	1.819753
18.O	3.401367	-2.604980	2.229995
19.N	0.269223	0.755987	4.985888
20.O	0.551288	-0.241493	4.240960
21.O	-0.236411	0.629731	6.067361
22.O	0.565001	1.890344	4.493630
23.O	2.535645	2.389330	0.543021
24.O	1.240074	0.820416	-0.141215
25.N	1.981005	1.802221	-0.446029
26.O	2.149235	2.165623	-1.579804
27.O	-0.766095	-0.058172	1.727323
28.H	-0.761688	-0.839513	2.295957
29.H	-0.645551	-0.384954	0.826813
30.N	-1.148420	5.654622	1.709762
31.N	4.763681	4.581800	4.566255
32.C	5.734333	4.306628	5.552328
33.C	6.108574	5.389924	6.361878
34.C	6.347210	3.062594	5.734768
35.C	7.074809	5.233115	7.345445
36.H	5.630984	6.358702	6.222025
37.C	7.316721	2.920359	6.725616
38.H	6.070063	2.218196	5.117747
39.C	7.683942	3.992272	7.533984
40.H	7.349617	6.080681	7.967280
41.H	7.787083	1.950145	6.861173
42.H	8.438446	3.864215	8.305209
43.C	-2.539679	5.823077	1.557030
44.C	-3.030719	7.109205	1.831684

45.C	-2.561640	4.980128	0.830917
46.C	-3.332534	6.024951	0.304586
47.C	-3.002139	3.657789	0.710588
48.C	-4.532662	5.755134	-0.339967
49.H	-2.988390	7.054067	0.398082
50.C	-4.207853	3.404356	0.060482
51.H	-2.413158	2.847299	1.119068
52.C	-4.976167	4.439316	-0.466402
53.H	-5.119994	6.574791	-0.744735
54.H	-4.546252	2.375756	-0.031095
55.H	-5.913613	4.224020	-0.971433

$Eu(H_2O)_9^{3+}$			
1.Eu	0.009192	0.000949	-0.007994
2.O	-0.934937	0.008207	-2.322430
3.H	-0.636310	0.547137	-3.068964
4.H	-1.677080	-0.516076	-2.656063
5.O	-1.498062	-0.000718	2.014041
6.H	-1.392833	-0.525162	2.820712
7.H	-2.301674	0.522293	2.146080
8.O	2.494077	-0.005192	0.249538
9.H	3.128617	-0.543271	-0.245311
10.H	3.020525	0.519800	0.869501
11.O	-1.727242	1.775693	-0.206850
12.H	-2.406949	1.833335	-0.893956
13.H	-1.837299	2.569877	0.335542
14.O	0.687141	1.771530	1.590373
15.H	0.435058	1.821246	2.523862
16.H	1.191603	2.578094	1.411480
17.O	1.019477	1.819842	-1.353540
18.H	1.950159	1.891603	-1.610580
19.H	0.591951	2.624477	-1.680452
20.O	-1.721310	-1.763245	-0.211708
21.H	-2.544834	-1.811723	0.295178
22.H	-1.695390	-2.568911	-0.747648
23.O	0.687111	-1.780027	1.597302
24.H	0.196240	-2.574507	1.852098
25.H	1.537072	-1.840420	2.057081
26.O	1.015394	-1.816879	-1.356372
27.H	1.449328	-2.621624	-1.038347
28.H	0.999631	-1.888501	-2.321824

$Am(H_2O)_9^{3+}$			
1.Am	0.014412	0.000712	-0.015791
2.O	-0.902220	0.011538	-2.384519
3.H	-0.597465	0.563705	-3.118914
4.H	-1.633661	-0.515496	-2.737206
5.O	-1.525487	0.006046	2.055783
6.H	-1.413700	-0.505631	2.869582
7.H	-2.334643	0.521236	2.183856
8.O	2.545598	-0.016322	0.185881
9.H	3.161804	-0.572081	-0.312719
10.H	3.092966	0.511756	0.784890
11.O	-1.788318	1.802035	-0.229690
12.H	-2.460347	1.856957	-0.924576
13.H	-1.923727	2.586451	0.321111
14.O	0.702385	1.807741	1.619634
15.H	0.452922	1.854724	2.553962
16.H	1.202183	2.617471	1.442146
17.O	1.024706	1.895497	-1.352379
18.H	1.950231	1.981104	-1.623546
19.H	0.583832	2.701772	-1.656749
20.O	-1.757398	-1.798381	-0.201046
21.H	-2.579628	-1.839871	0.308575
22.H	-1.736155	-2.609822	-0.728364
23.O	0.728076	-1.798177	1.656537
24.H	0.236108	-2.580602	1.944350
25.H	1.585392	-1.855212	2.102980
26.O	1.000253	-1.901329	-1.359031
27.H	1.416238	-2.707410	-1.020894
28.H	0.994301	-1.990583	-2.323118

45.C	-3.422654	4.822550	1.137130
46.C	-4.381961	7.392264	1.694747
47.H	-2.345938	7.889877	2.160362
48.C	-4.777148	5.122087	1.002800
49.H	-3.058506	3.826449	0.924394
50.C	-5.265487	6.395544	1.279290
51.H	-4.745408	8.392223	1.915078
52.H	-5.455853	4.338492	0.676584
53.H	-6.324857	6.612102	1.173020
54.S	-0.808197	2.980727	1.603212
55.S	3.894039	2.132143	3.855474

$Eu(NO_3)(H_2O)_8^{2+}$			
1.Eu	-0.030765	-0.005049	-0.423222
2.O	0.461655	-0.387682	-2.819676
3.H	1.302010	-0.113893	-3.211039
4.H	-0.061592	-0.781475	-3.527931
5.O	0.045623	0.276843	3.588707
6.H	1.009162	0.211607	3.651984
7.H	-0.281851	0.366254	4.493599
8.O	-2.244523	1.120766	-0.899179
9.H	-2.849933	1.236719	-1.641613
10.H	-2.602020	1.639223	-0.165802
11.O	-0.643395	1.643708	1.314843
12.H	-0.450459	1.354127	2.234365
13.H	-0.317637	2.549051	1.239812
14.O	0.466484	2.294422	-1.269524
15.H	1.395460	2.492125	-1.451671
16.H	-0.060273	2.960696	-1.726991
17.O	-1.677132	-1.689644	-1.305162
18.H	-2.635731	-1.692319	-1.412515
19.H	-1.376730	-2.602324	-1.405868
20.O	-0.861138	-1.215825	1.525887
21.H	-1.607367	-1.812714	1.646052
22.H	-0.588838	-0.887568	2.413040
23.O	0.909787	-2.352092	-0.563798
24.H	1.104181	-2.811863	0.263804
25.H	1.621096	-2.590491	-1.172811
26.O	3.802553	0.232250	0.715565
27.N	2.669060	0.173292	0.387312
28.O	2.271278	0.338944	-0.827662
29.O	1.703104	-0.064377	1.200292

$Am(NO_3)(H_2O)_8^{2+}$			
1.Am	-0.048914	0.015129	-0.439949
2.O	0.507128	-0.418169	-2.882821
3.H	1.364762	-0.163144	-3.248193
4.H	-0.018667	-0.755246	-3.618101
5.O	0.131018	0.233648	3.612432
6.H	1.091384	0.123901	3.657728
7.H	-0.174667	0.327135	4.524466
8.O	-2.317514	1.227469	-0.775708
9.H	-2.991349	1.343983	-1.456463
10.H	-2.607354	1.743463	-0.011541
11.O	-0.550743	1.684129	1.386790
12.H	-0.343239	1.365194	2.293005
13.H	-0.217179	2.587780	1.329435
14.O	0.461420	2.354719	-1.312102
15.H	1.384861	2.564216	-1.507103
16.H	-0.077451	3.030021	-1.741132
17.O	-1.773567	-1.659388	-1.362135
18.H	-2.732262	-1.656932	-1.468360
19.H	-1.481330	-2.573392	-1.473552
20.O	-0.889652	-1.219735	1.562063
21.H	-1.616650	-1.836526	1.698525
22.H	-0.588412	-0.905524	2.443650
23.O	0.847728	-2.423919	-0.619024
24.H	1.063764	-2.900328	0.193351
25.H	1.506565	-2.699858	-1.269308
26.O	3.832477	0.156635	0.663971
27.N	2.693707	0.125008	0.351728
28.O	2.278757	0.354843	-0.847446

				29.O	1.737448 -0.142404 1.166588
$Nd(NO_3)_3(H_2O)_4$					
1.O	1.518091	4.492986	5.545259		
2.O	0.827800	5.484392	7.346988		
3.N	1.725745	5.117393	6.545009		
4.Nd	2.293396	6.744762	8.926540		
5.O	2.921647	5.473501	6.883200		
6.O	5.350442	6.361634	6.423003		
7.O	2.445699	4.170665	12.133890		
8.O	2.257965	6.169256	11.310272		
9.N	2.387464	4.902332	11.188595		
10.O	2.460511	4.485292	9.986221		
11.O	1.166257	8.621636	7.816016		
12.O	0.126633	7.724004	9.468226		
13.N	0.128500	8.622514	8.567800		
14.O	-0.759905	9.411544	8.431910		
15.O	4.767284	5.985811	9.147122		
16.O	3.865616	8.314368	7.644325		
17.O	3.134245	8.622923	10.417816		
18.H	4.557491	5.836781	6.192713		
19.H	5.241785	6.009849	8.296675		
20.H	3.312845	8.924638	7.140781		
21.H	3.195703	8.373516	11.347531		
22.H	4.725597	5.056401	9.404482		
23.H	6.019028	6.198426	5.752131		
24.H	4.474950	7.872228	7.022824		
25.H	3.931628	9.109248	10.185755		

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