Electronic Supplementary Information

Table S1. Selected structural data of crystals under study

Name	AQ_{Gd9}	AQ_{Gd8}	AQ_{Lu8}	$EDTA_{Gd9}$	$EDTA_{Lu8}$
Chemical formula	$C_3H_{18}F_9GdO_{18}S_3$	$C_{10}H_{36}Cl_3GdO_{13}$	$C_{12}H_{48}Cl_3LuO_{18}$	$C_{11}H_{24}GdN_5O_{11}$	$C_{12}H_{40}ClLuN_8O_{20}$
M_r	766.60	627.99	761.82	559.60	826.94
Crystal system, space group	Hexagonal, $P6_3/m$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, P
Temperature (K)	100	100	100	100	100
a, b, c (Å)	13.811 (3), 7.338 (2)	9.161 (2), 17.174 (3), 15.221 (3)	10.308 (4), 18.561 (9), 15.946 (6)	11.236 (2), 8.604 (1), 18.677 (3)	11.064 (3), 11.133 (3), 13.009 (4)
α, β, γ (°)		92.74 (2)	102.07 (4)	90.10 (2)	90.70 (2), 91.64 (2), 110.49 (3)
V (Å^3)	1212.2 (6)	2392.0 (8)	2983 (2)	1805.6 (5)	1500.0 (8)
μ (mm^{-1})	3.13	3.16	3.65	3.74	3.47
Crystal size (mm)	0.31 × 0.25 × 0.06	0.22 × 0.16 × 0.12	0.31 × 0.27 × 0.21	0.29 × 0.28 × 0.21	0.52 × 0.37 × 0.22
T_{min}, T_{max}	0.622, 0.842	0.625, 0.728	0.455, 0.574	0.495, 0.626	0.437, 0.673
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3325, 1343, 1255	13705, 5582, 4912	16846, 7168, 5078	10400, 5151, 4461	12699, 6777, 6293
R_{int}	0.028	0.053	0.059	0.028	0.052
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.736	0.679	0.679	0.738	0.844
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.047, 1.04	0.056, 0.158, 1.07	0.058, 0.177, 1.08	0.027, 0.061, 1.03	0.049, 0.133, 0.98
No. of refelctions	1343	5582	7168	5151	6777
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.89, −0.66	3.65, −2.26	3.33, −3.16	0.64, −1.03	1.98, −3.15

Name	$CDTA_{Lu}$	$EGTA_{Gd9}$	$DTPA_{Gd9}$	$DOTA_{Gd9}$	$DOTA_{Lu8}$
Chemical formula	$C_{30}H_{67}Lu_2N_{10}O_{24}$	$C_{15}H_{32}GdN_5O_{13}$	$C_{15}H_{32}GdN_7O_{13}$	$C_{16}H_{34}GdN_4NaO_{13}$	$C_{16}H_{33.20}ClK_2LuN_4O_{12.85}$
M_r	1301.87	647.70	675.72	670.71	775.88
Crystal system, space group	Triclinic, P	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, P	Monoclinic, $C2/c$
Temperature (K)	100	100	100	100	100
a, b, c (Å)	8.392 (2), 16.491 (4), 16.752 (4)	16.842 (2), 9.267 (1), 16.890 (2)	15.505 (3), 17.707 (3), 17.389 (3)	8.632 (2), 9.152 (2), 15.614 (3)	37.315 (2), 8.885 (2), 16.592 (2)
α, β, γ (°)	88.53 (2), 83.24 (2), 83.52 (2)	119.87 (2)	91.97 (2)	83.01 (2), 85.17 (2), 81.32 (2)	111.12 (2)
V (Å^3)	2287.3 (10)	2285.9 (6)	4771.3 (15)	1207.6 (5)	5131.5 (15)
μ (mm^{-1})	4.39	2.98	2.86	2.84	4.35
Crystal size (mm)	0.38 × 0.19 × 0.08	0.41 × 0.22 × 0.18	0.34 × 0.23 × 0.16	0.25 × 0.17 × 0.10	0.20 × 0.14 × 0.04
T_{min}, T_{max}	0.335, 0.709	0.443, 0.680	0.487, 0.688	0.636, 0.798	0.644, 0.884
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16242, 9993, 8915	35036, 10000, 9384	25675, 9944, 8419	19544, 10253, 9658	16620, 5965, 5014
R_{int}	0.046	0.045	0.042	0.051	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.840	0.844	0.649	0.847	0.677
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.129, 1.03	0.036, 0.109, 1.21	0.048, 0.140, 1.10	0.044, 0.124, 1.12	0.031, 0.064, 1.08
No. of refelctions	9993	10000	9944	10253	5965
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.28, −2.06	1.76, −3.24	3.20, −1.99	1.93, −3.32	1.34, −1.69

Table S2. Oscillator strengths ($P \cdot 10^8$) of the A and B bands determined for the Gd(III) systems in single crystals (marked in black) and in aqueous solution (marked in red)

	A	B
Gd^{3+}_{aq}	170.4	80.2
$[Gd(H_2O)_9]^{3+}$	130.2	47.2
$[Gd(H_2O)_8]^{3+}$	147.8	65.5
$[Gd(H_2O)_8]^{3+}$	163.5	78.0
$[Gd(EDTA)]^-_{aq}$	291.5	136.1
$[Gd(EDTA)(H_2O)_3]^-$	294.0	122.3
$[Gd(EDTA)(H_2O)_2]^-$	318.8	142.0
$[Gd(CDTA)]^-_{aq}$	261.4	129.7
$[Gd(EGTA)]^-_{aq}$	304.6	141.2
$[Gd(EGTA)(H_2O)]^-$	294.0	122.3
$[Gd(DTPA)]^{2-}_{aq}$	304.4	136.7
$[Gd(DTPA)(H_2O)]^{2-}$	284.9	132.7
$[Gd(DOTA)]^-_{aq}$	285.6	133.1
$[Gd(DOTA)(H_2O)]^-$	210.0	77.8

Table S3. Crystal field splitting of the $^6P_{7/2}$, $^6P_{5/2}$ and $^6I_{7/2}$ multiplets

	$^6P_{7/2}$	$^6P_{5/2}$	$^6I_{7/2}$
$[Gd(H_2O)_9]^{3+}$ in AQ_{Gd9}	32150	32746	35896
	32171	32774	35920
	32179		
Gravicenter	**32167**	**32760**	**35908**
Δ_{CFS}	29	28	23
$[Gd(H_2O)_8]^{3+}$ in AQ_{Gd8}	32107	32714	35850
	32130	32733	35878
	32150	32765	35912
	32179		
Gravicenter	**32142**	**32737**	**35880**
Δ_{CFS}	72	52	62
$[Gd(H_2O)_8]^{3+}$ in AQ_{Lu8}	32095	32688	35832
	32113	32723	35858
	32144	32753	35876
	32161		35914
Gravicenter	**32128**	**32721**	**35870**
Δ_{CFS}	66	64	82
$[Gd(EDTA)(H_2O)_3]^-$ in $EDTA_{Gd9}$	32035	32639	35795
	32073	32673	35820
	32094	32705	35829
	32123		35847
Gravicenter	**32081**	**32672**	**35823**
Δ_{CFS}	88	66	53
$[Gd(EDTA)(H_2O)_2]^-$ in $EDTA_{Lu8}$	31974*	32547*	35694
	31990*	32573*	35727
	32000*	32595*	35763
			35799
Gravicenter	**31988**	**32572**	**35746**
Δ_{CFS}	26	48	105
$[Gd(CDTA)(H_2O)_2]^-$ in $CDTA_{Lu8}$	32053*	32638*	35693*
	32029*	32625*	35724*
	31988*	32584*	35759*
			35786*
Gravicenter	**32023**	**32616**	**35741**
Δ_{CFS}	65	54	93
$[Gd(EGTA)(H_2O)]^-$ in $EGTA_{Gd9}$	31996	32597	35742
	32035	32633	35773
	32057	32675	35788
	32082		35809
Gravicenter	**32043**	**32635**	**35778**
Δ_{CFS}	86	79	67

Table S3. Crystal field splitting of the $^6P_{7/2}$, $^6P_{5/2}$ and $^6I_{7/2}$ multiplets

	$^6P_{7/2}$	$^6P_{5/2}$	$^6I_{7/2}$
$[Gd(DTPA)(H_2O)]^{2-}$ in $DTPA_{Gd9}$	31988	32597	35749
	32037	32638	35781
	32070	32680	35788
	32092		35817
Gravicenter	**32047**	**32638**	**35784**
Δ_{CFS}	105	83	68
$[Gd(DOTA)(H_2O)]^{-}$ in $DOTA_{Gd9}$	31982	32590	35745
	32004	32609	35791
	32047	32676	35799
	32105		
Gravicenter	**32035**	**32625**	**35778**
Δ_{CFS}	123	85	54
$[Gd(DOTA)]^{-}$ in $DOTA_{Lu8}$	31949*	32579*	
	31985*		
	32000*		
	32051*		
Gravicenter	**31996**	**32579**	
Δ_{CFS}	102		
**$[Gd(ODA)_3]^{3-}$ in $Na_3[Gd(ODA)_3]\cdot 2NaClO_4\cdot 6H_20$[1]	32040	32616	35745
	32054	32635	35788
	32058	32638	35790
	32065		35809
Gravicenter	**32054**	**32630**	**35783**
Δ_{CFS}	15	22	64

(*) data taken from the excitation luminescence spectra

(**) The spectroscopic data of the $[Gd(ODA)_3]^{3-}$ complex were taken from Ref. [1] for comparison purposes with the $[Gd(EGTA)(H_2O)]^{-}$ complex (oxygen donor atom from ether groups).

Table S4. The fitted values of ν_0 and nephelauxetic parameters for the Gd(III) systems under study

Experimental parameter	
$\nu_0(^6P_{7/2})$ / cm^{-1}	34542
$\nu_0(^6P_{5/2})$ / cm^{-1}	35131
$\nu_0(^6I_{7/2})$ / cm^{-1}	38280
δ_{H_2O} / Å·cm^{-1}	5782
$\delta_{CO\bar{}_2}$ / Å·cm^{-1}	6011
$\delta_{O-ether}$ / Å·cm^{-1}	6706
$\delta_{N-amino}$ / Å·cm^{-1}	6162

The Authors of the previously published data on Gd(III) compounds pointed out that there are no correlation between crystal field strength and chemical bonding parameters. [2] Therefore attempts of finding the simple experimental dependence between the energy of gravicenter of the selected $^{2S+1}L_J$ multiplets (collected in **Table S3**) and the C.N. of the Gd(III) ion have been undertaken. The following equations (1,2) were used for such calculations:

$$\nu_{exp} = \nu_0 - \frac{\sum \frac{\delta_i n_i}{r_i}}{n_i} \equiv \nu_{calc} \qquad (1)$$

$$C.N. = \frac{\sum \frac{\delta_i n_i}{r_i}}{\nu_0 - \nu_{exp}} \qquad (2)$$

where: ν_{exp} and ν_{calc} are the experimental and calculated values of the energy of the $^{2S+1}L_J$ multiplet, ν_0 is the fitted parameter which may reflect the energy of the $^{2S+1}L_J$ multiplet of the gaseous Gd(III) ion (Gd(III) with no coordinating donor atoms);[3] δ_i is the empirical parameter; n_i is the number of the coordinating donor atoms of the type "i"; r_i is the Ln-L bond length calculated using the data collected in Table 2 in the main text.

Minimizing the sum $\Sigma(\nu_{exp} - \nu_{calc})^2$ it was possible to find the values of ν_0 and nephelauxetic parameters. The obtained parameters are collected in **Table S4**. The plot of the calculated energy (ν_{calc}) versus ν_{exp} for a given

$^{2S+1}L_J$ multiplet is presented in **Figure S1** in ESI. The determined values of the δ_i parameters (**Table S4)** correspond to the position of the N_{amino}, O_{ether}, CO_2^-, H_2O ligands in the nephelauxetic series.[4]

Table S5. Emission lifetimes of the excited $^6P_{7/2}$ state of the Gd(III) systems under study

Compound	τ_{exp} / ms
$[Gd(H_2O)_9]^{3+}$ in AQ_{Gd9}	14.96
$[Gd(H_2O)_8]^{3+}$ in AQ_{Gd8}	8.25
$[Gd(H_2O)_8]^{3+}$ in AQ_{Lu8}	7.62
$[Gd(EDTA)(H_2O)_3]^{-}$ in $EDTA_{Gd9}$	8.63
$[Gd(EDTA)(H_2O)_2]^{-}$ in $EDTA_{Lu8}$	5.88
$[Gd(CDTA)(H_2O)_2]^{-}$ in $CDTA_{Lu8}$	6.18
$[Gd(EGTA)(H_2O)]^{-}$ in $EGTA_{Gd9}$	7.20
$[Gd(DTPA)(H_2O)]^{2-}$ in $DTPA_{Gd9}$	3.38
$[Gd(DOTA)(H_2O)]^{-}$ in $DOTA_{Gd9}$	8.85
$[Gd(DOTA)]^{-}$ in $DOTA_{Lu8}$	5.70

Table S6 The average Ln-L bond lengths in anionic complexes of $[Sm(EDTA)(H_2O)_3]^-$ [5]; $[Sm(CDTA)(H_2O)_3]^-$ [6]; $[Yb(EDTA)(H_2O)_2]^-$ [7]; $[Yb(CDTA)(H_2O)_2]^-$ [7]

	Ln–O(carb)	Ln–OH_2	Ln–N
$[Sm(EDTA)(H_2O)_3]^-$	2.420(21)	2.494(66)	2.667(23)
$[Sm(CDTA)(H_2O)_3]^-$	2.453(40)	2.512(66)	2.733(36)
$[Yb(EDTA)(H_2O)_2]^-$	2.254(25)	2.322(2)	2.577(7)
$[Yb(CDTA)(H_2O)_2]^-$	2.271(11)	2.317(22)	2.549(10)

The Ln(III)-EDTA complexes may crystallize as eight- or nine-coordinate species, and it strongly depends on the ionic radius of Ln(III) and types of counter cation used for crystallization.[8] Out of the 28 crystal structures determined for Ln(III)-CDTA compounds [9] the only one $[Sm(CDTA)(H_2O)_3]^-$ complex [6] was found as the nine-coordinate species, while in the remaining compounds the Ln(III) ions are eight-coordinate. The conformations of EDTA and CDTA ligands are very similar in $[Yb(EDTA)(H_2O)_2]^-$ and $[Yb(CDTA)(H_2O)_2]^-$ complexes, thus the Yb-L bond lengths are practically the same.[7] Comparing the structures of the $[Sm(EDTA)(H_2O)_3]^-$ [5] and $[Sm(CDTA)(H_2O)_3]^-$ [6] systems the substantial changes of the ligand conformations as well as Sm–L bond lengths may be observed (**Figure S6** and **Table S6**). One of three coordinated water molecules in the $[Sm(CDTA)(H_2O)_3]^-$ complex, cannot enter the space between neighboring carboxylic groups, connected with the same nitrogen atom due to presence of the transcyclohexane group. This would result in too small room between carboxylic groups and trans cyclohexane unit in the $[Sm(CDTA)(H_2O)_3]^-$ complex. Consequently Sm(III) cation is pulled out from the cage formed by 6 donor atoms of CDTA ligand, and the Sm–O(CO_2^-) and Sm–N bond lengths are longer in the $[Sm(CDTA)(H_2O)_3]^-$ in comparison with those in $[Sm(EDTA)(H_2O)_3]^-$ complex. Simultanously the Sm-OH_2 bond lengths are very similar. This is probably a reason of lower stability of nine-coordinate $[Ln(CDTA)(H_2O)_3]^-$ complex than the eight-coordinate $[Ln(CDTA)(H_2O)_2]^-$ one.

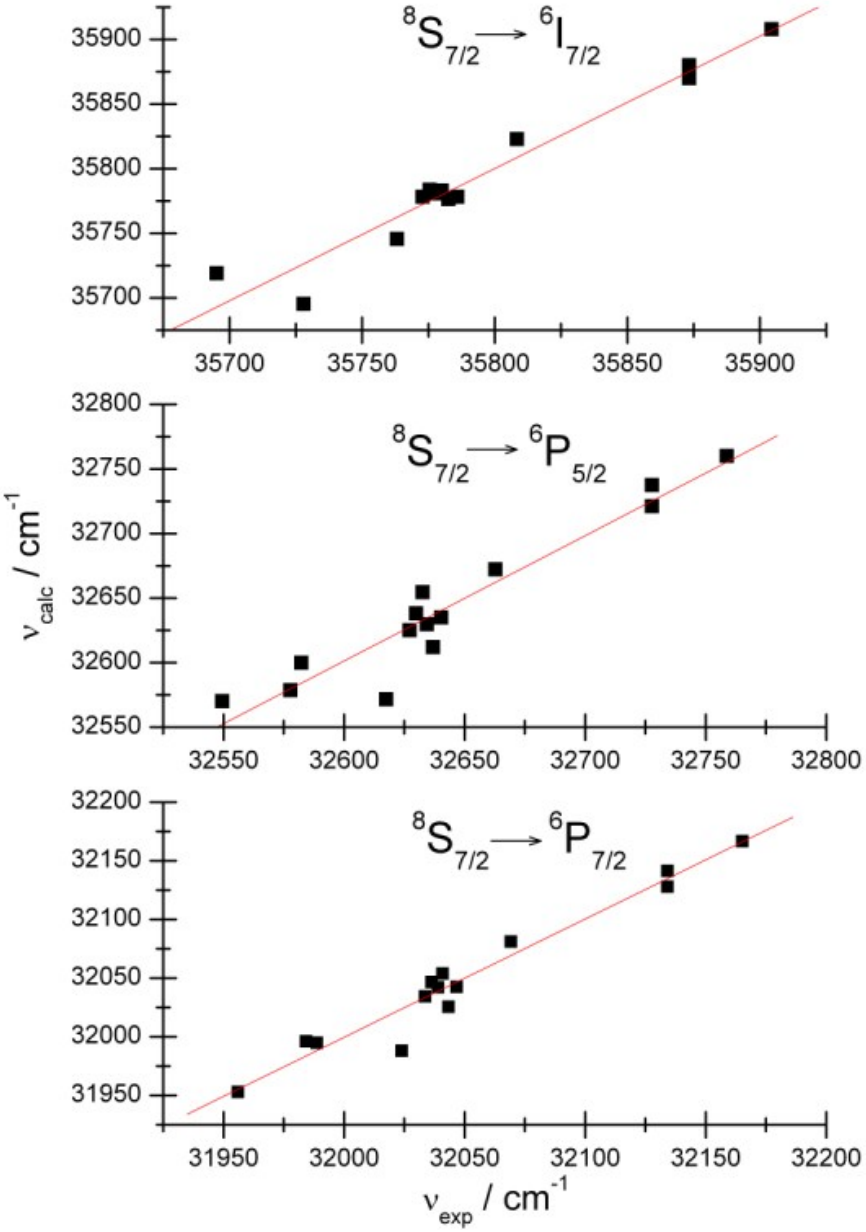


Figure S1. Plot of the predicted (ν_{calc}) vs experimental (ν_{exp}) gravicenter values for the selected $^{2S+1}L_J$ multiplets for the Gd(III) complexes. The solid line represents a linear fit to the data with a correlation coefficient of 0.98 for $^6I_{7/2}$, 0.95 for $^6P_{5/2}$ and 0.97 for $^6P_{7/2}$.

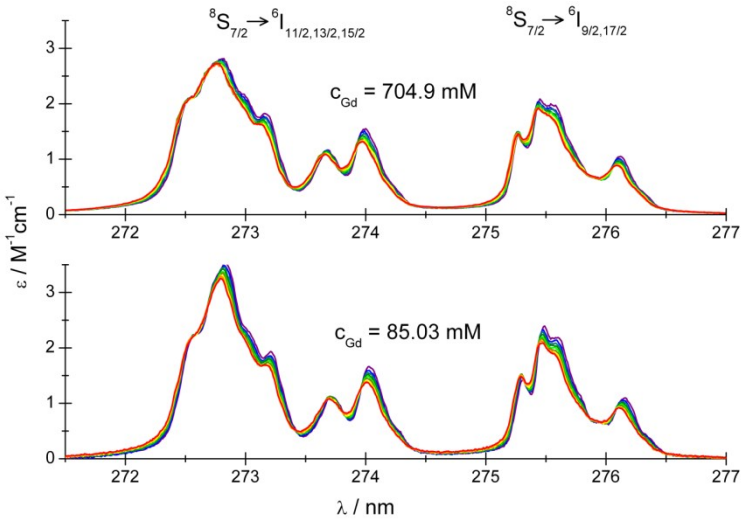


Figure S2. UV spectra of the Gd(III) aqua ion at different concentrations (85.03 mM and 704.9 mM) and temperatures between 283K (blue) and 363K (red).

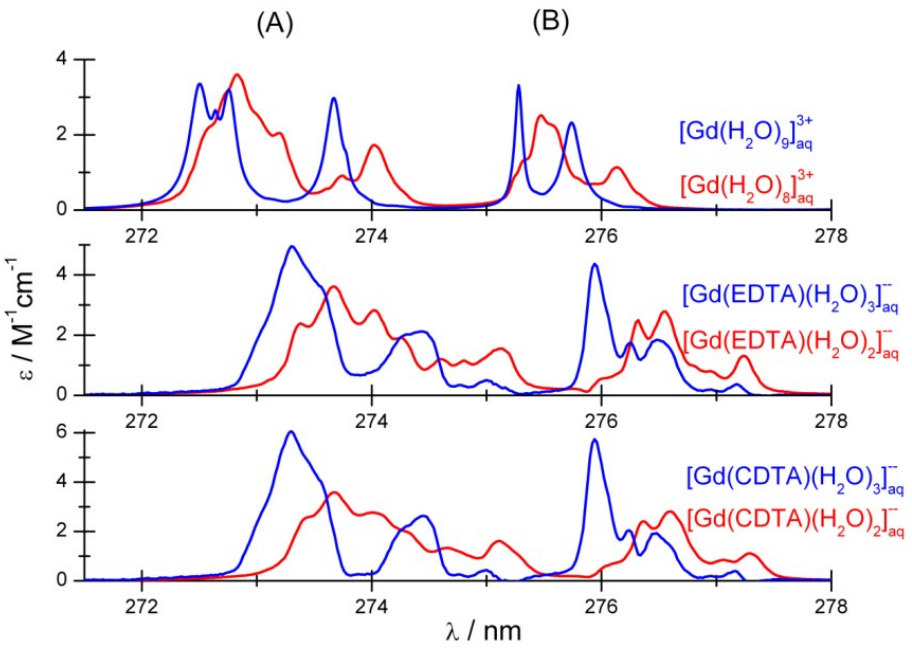


Figure S3. The simulated UV spectra of the variously hydrated $[Gd(H_2O)_m]^{3+}$; $[Gd(EDTA)(H_2O)_n]^-$ and $[Gd(CDTA)(H_2O)_p]^-$ species in solutions. (A) and (B) bands are ascribed to the $^8S_{7/2} \nleftrightarrow {}^6I_{11/2}$, $^6I_{13/2}$, $^6I_{15/2}$ and $^8S_{7/2} \nleftrightarrow {}^6I_{9/2}$, $^6I_{17/2}$ transitions, respectively.

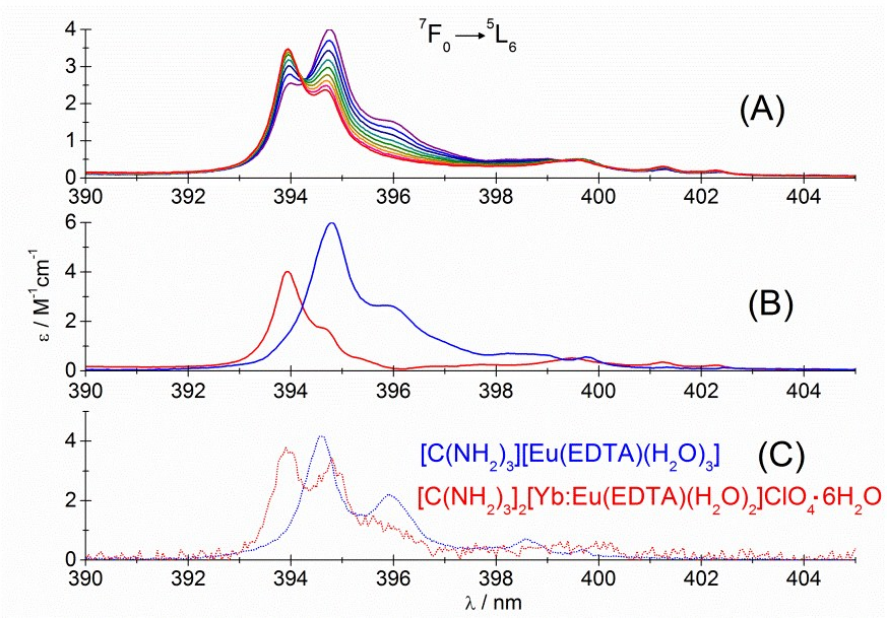


Figure S4. UV absorption spectra of the Eu(III)-EDTA system: (A) in solution at different temperatures between 283 and 363K, (B) simulated spectra of the pure $[Eu(EDTA)(H_2O)_2]^-$ (marked in red) and $[Eu(EDTA)(H_2O)_3]^-$ (marked in blue) complexes in solution, (C) the spectra of monocrystals.

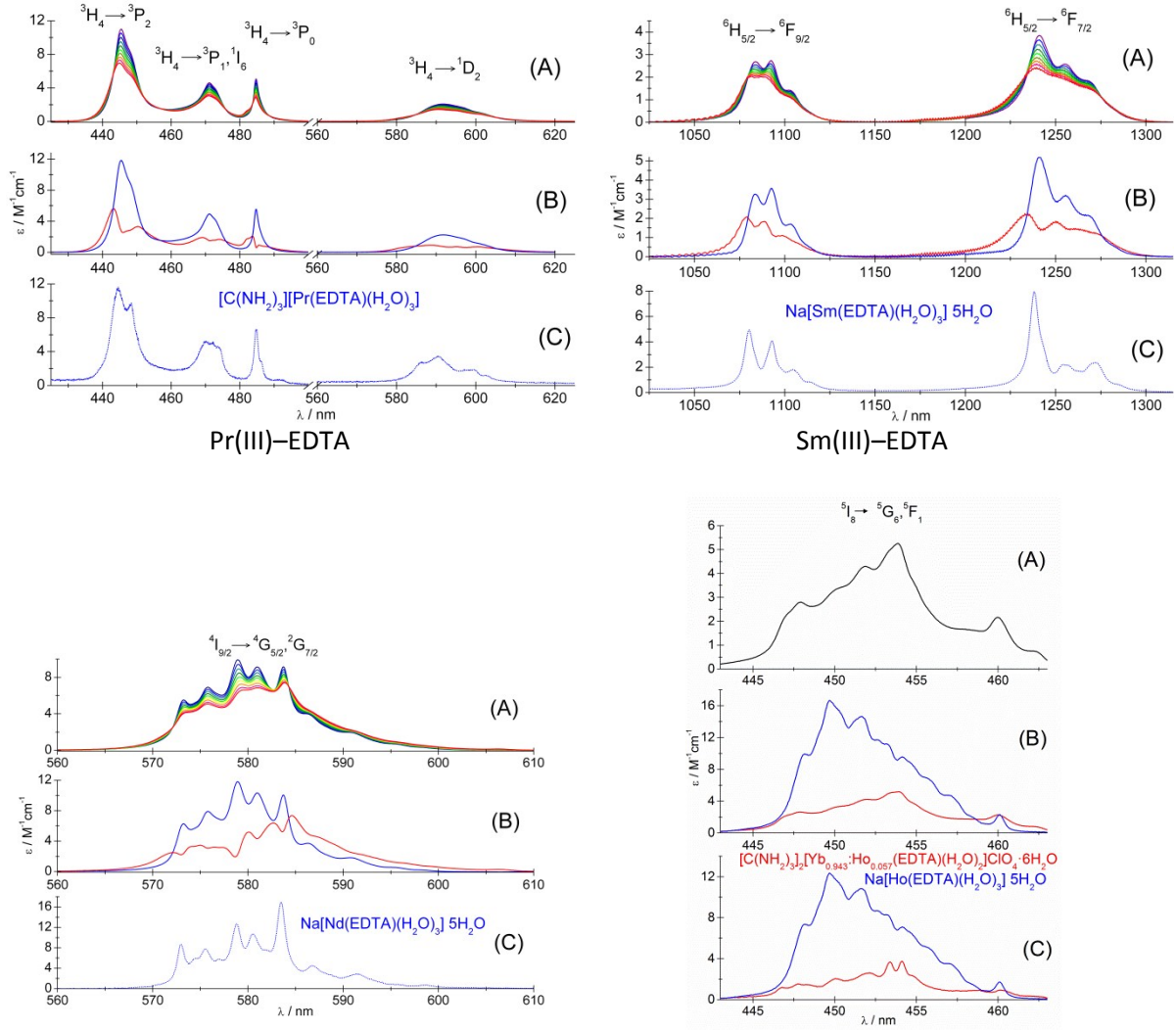
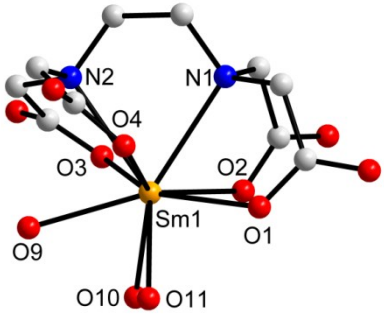
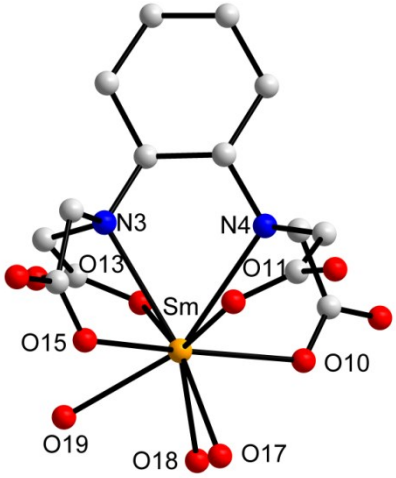


Figure S5. UV-vis-NIR absorption spectra of the: (A) Ln(III)-EDTA systems at different temperatures, the spectra at low temperature (283K) are marked in blue; the highest temperature spectra (333K) are marked in red; (B) pure solution species $[Ln(EDTA)(H_2O)_2]^-$ (marked in red), $[Ln(EDTA(H_2O)_3]^-$ (marked in blue) derived from the factor analysis used for the quantitative analysis of solutions; (C) spectra of monocrystals .

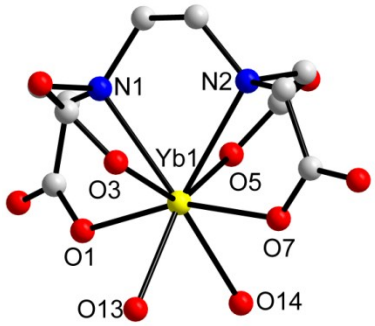
For the Ho(III)-EDTA system the predominate species is the eight coordinate $[Ln(EDTA)(H_2O)_2]^-$ complex (~90%). Thus it is difficult to obtain reliable ΔH and ΔS values for this system based on the temperature dependent UV-vis spectra of the hypersensitive transition.



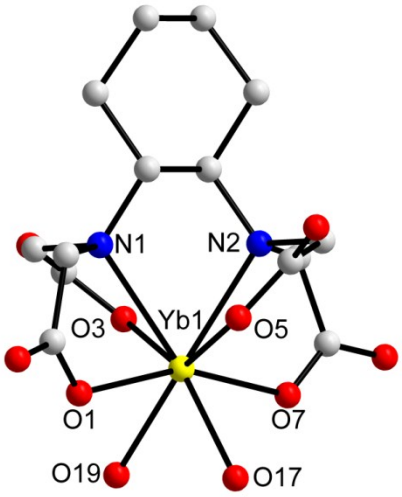
$[Sm(EDTA)(H_2O)_3]^-$



$[Sm(CDTA)(H_2O)_2]^-$



$[Yb(EDTA)(H_2O)_2]^-$



$[Yb(CDTA)(H_2O)_2]^-$

Figure S6. Molecular structures of the $[Sm(EDTA)(H_2O)_3]^-$, 5$[Sm(CDTA)(H_2O)_3]^-$,6 $[Yb(EDTA)(H_2O)_2]^-$,7 $[Yb(CDTA)(H_2O)_2]^-$ 7complex anions.

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