

Investigation of Ln³⁺ complexation by a DOTA derivative substituted by an imidazothiadiazole: synthesis, solution structure, luminescence and relaxation properties

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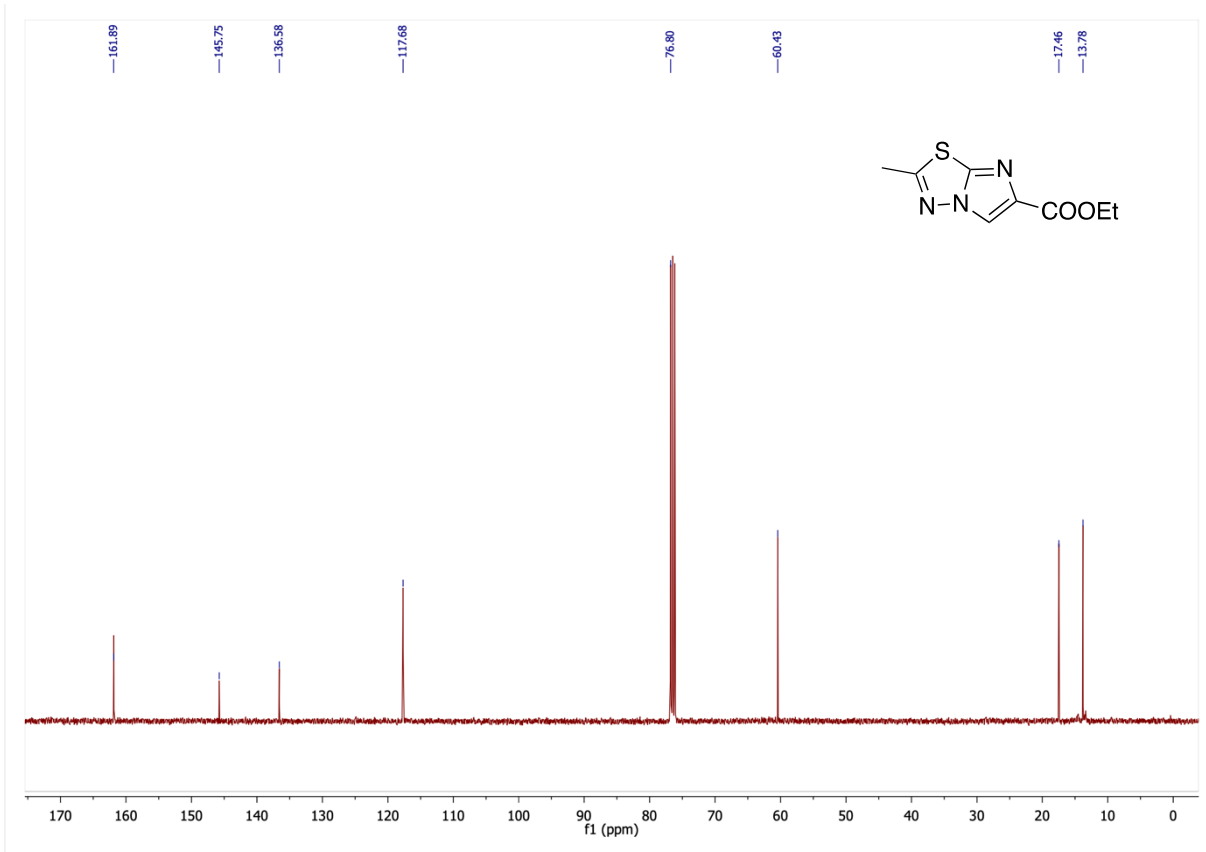
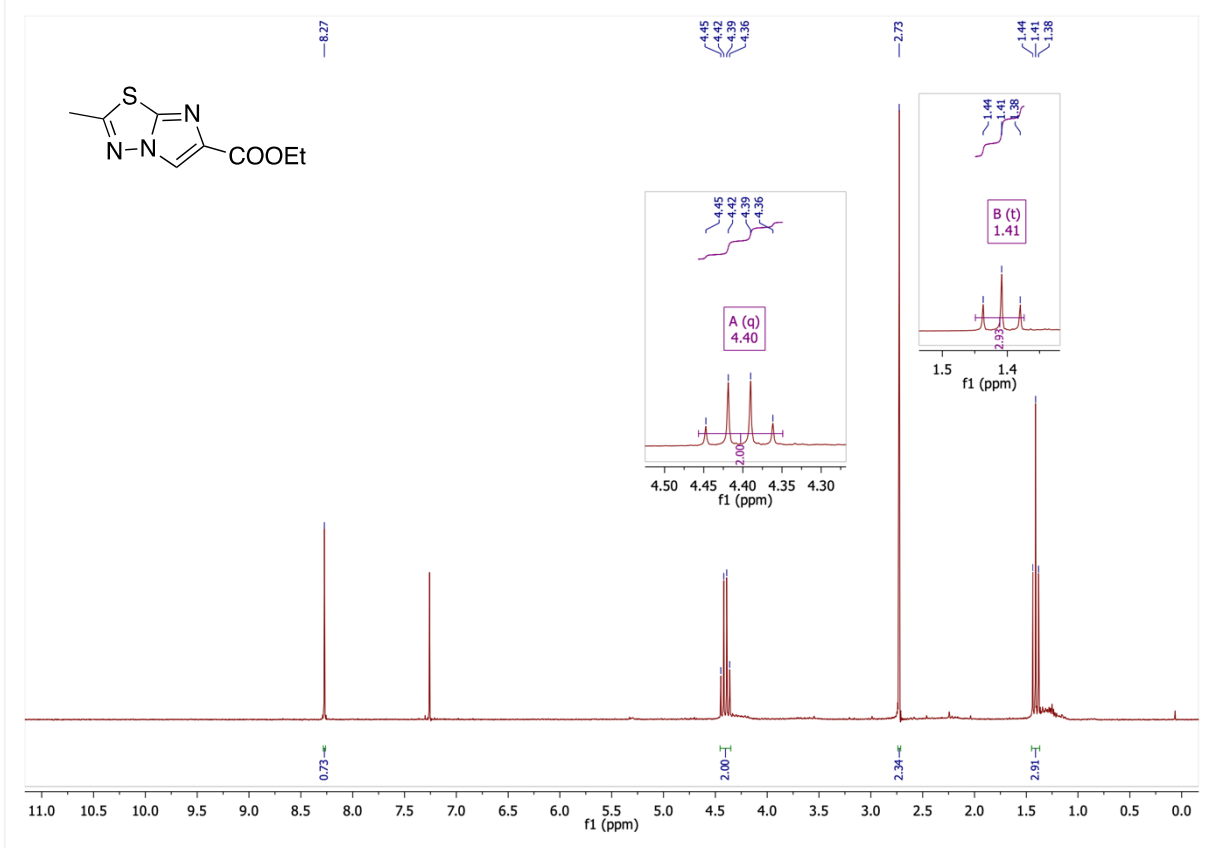
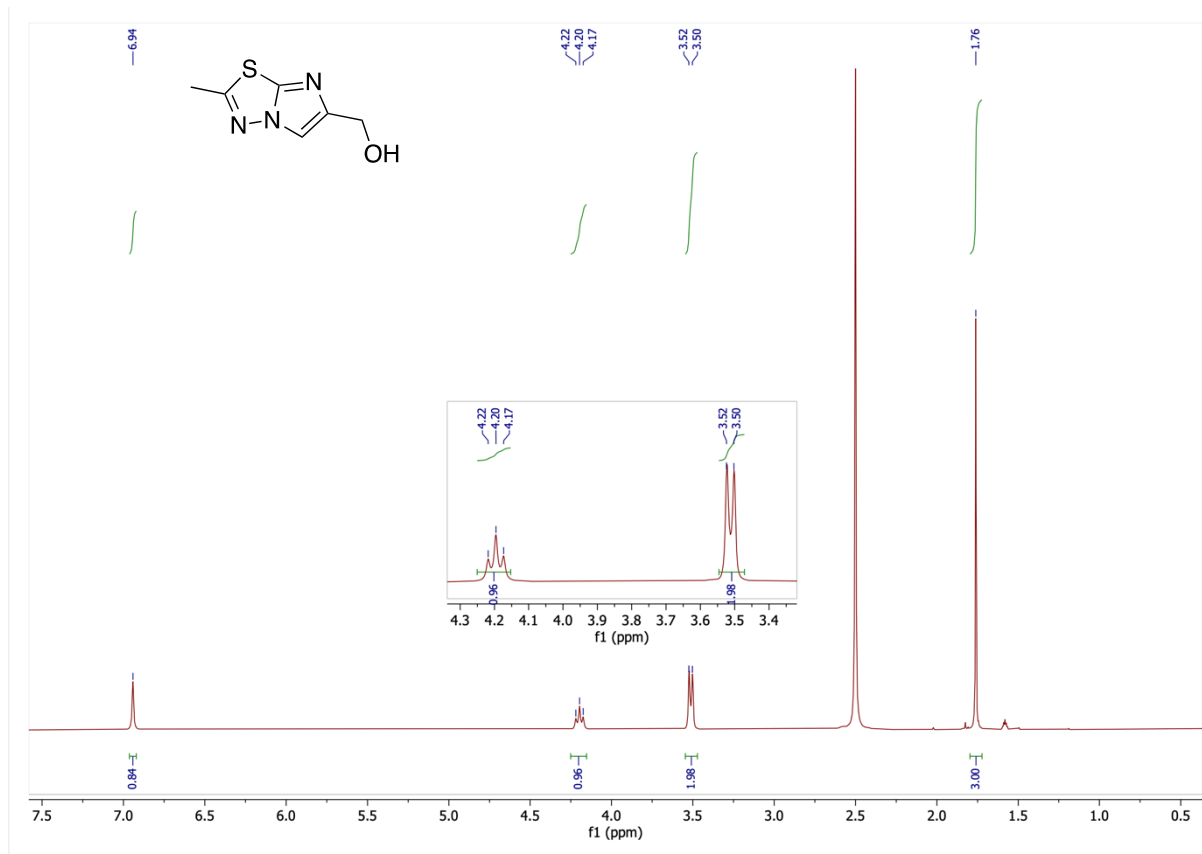


Figure S1: ^1H and ^{13}C NMR spectra of compound **2**



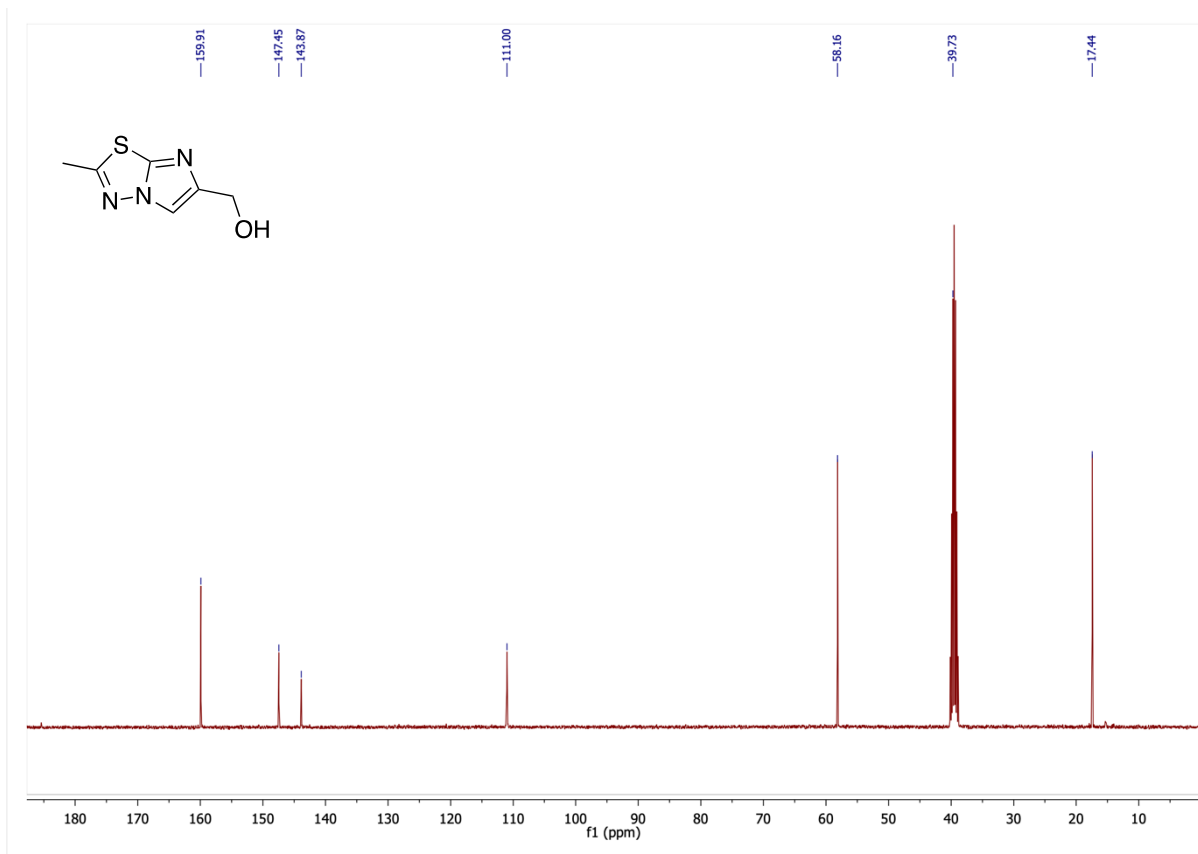


Figure S2: ^1H and ^{13}C NMR spectra of compound 3

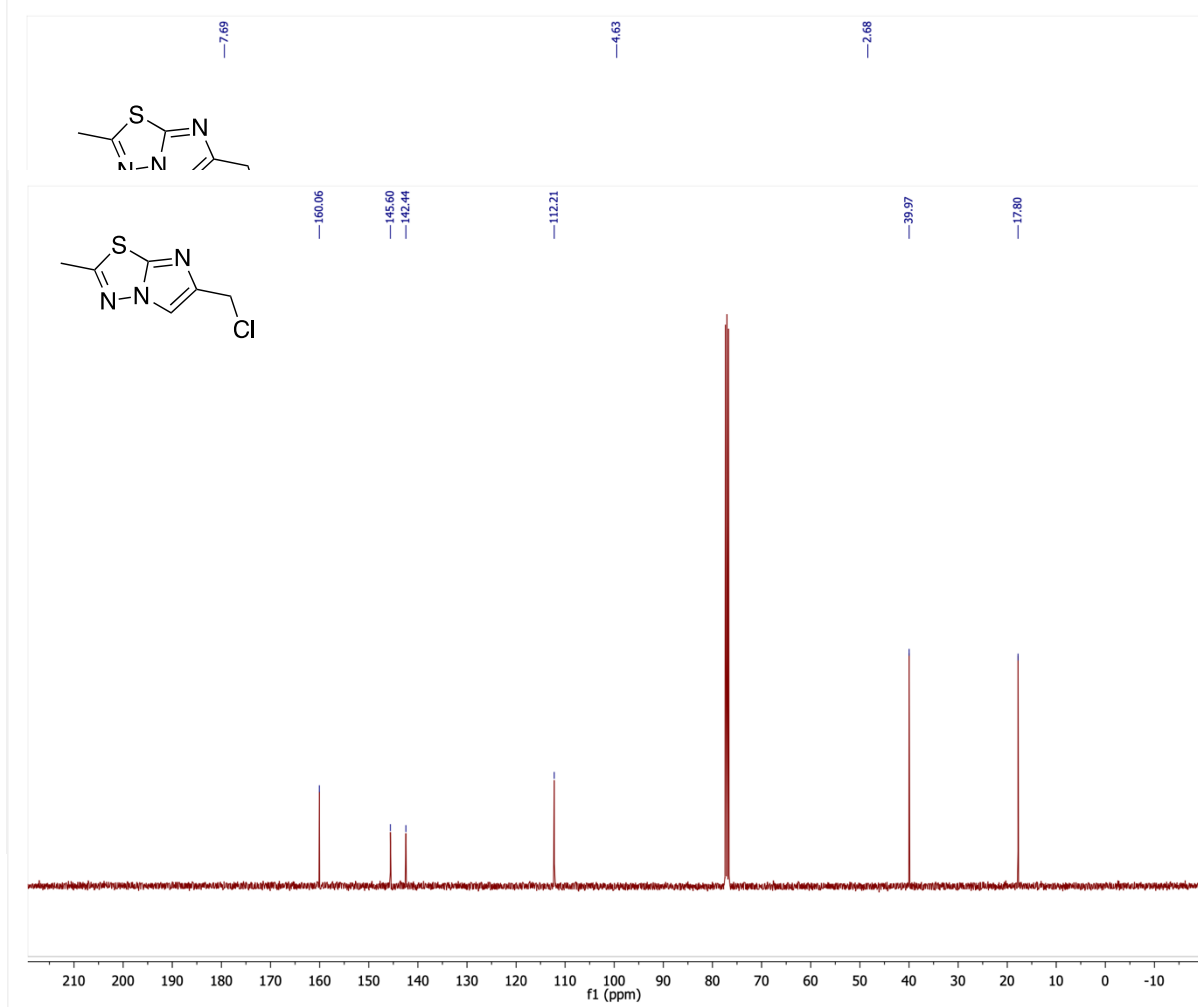


Figure S3: ^1H and ^{13}C NMR spectra of compound 4

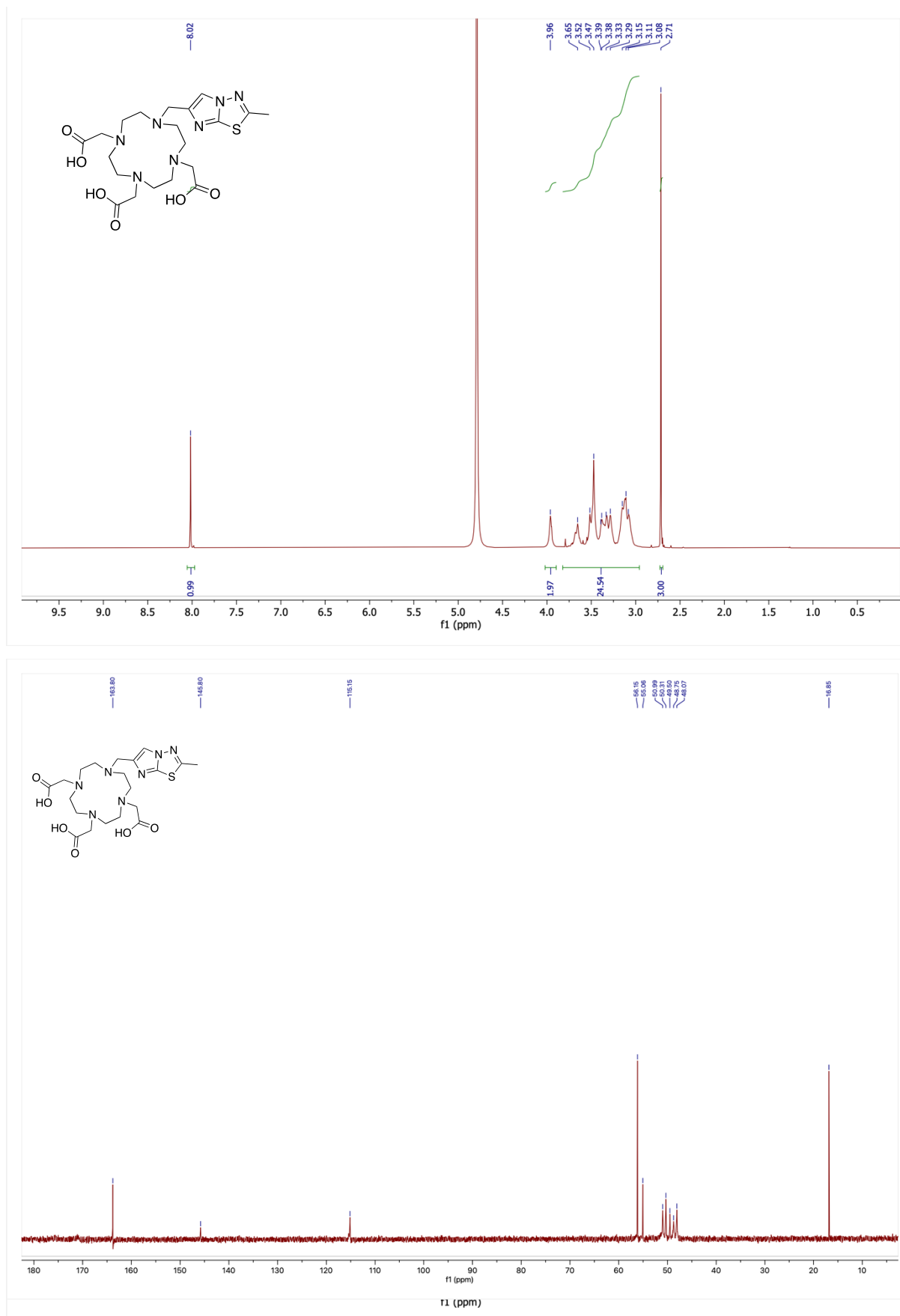


Figure S4: ^1H and ^{13}C NMR spectra of compound **L3**

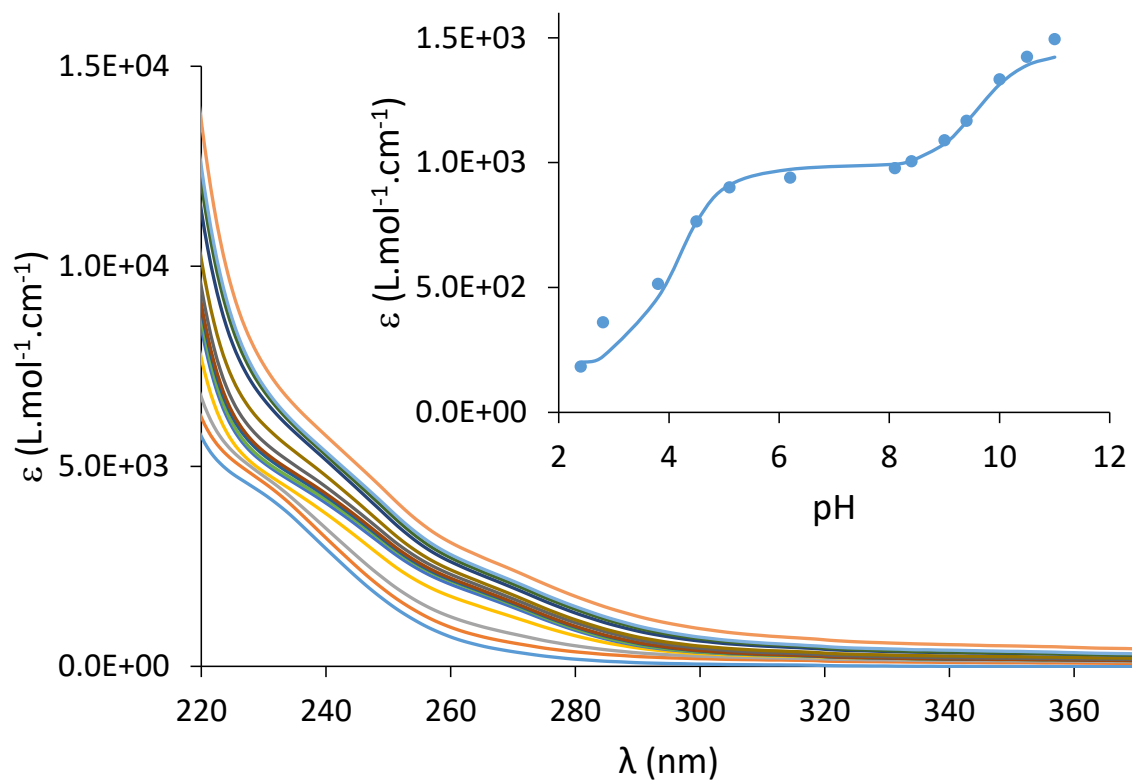


Figure S5. Absorption spectra of L3 (150 μM) in NaCl 0.15 M at 25°C ; inset : molar absorption coefficients at 280 nm as a function of pH (the line represents the best fit with the values presented in Table 2).

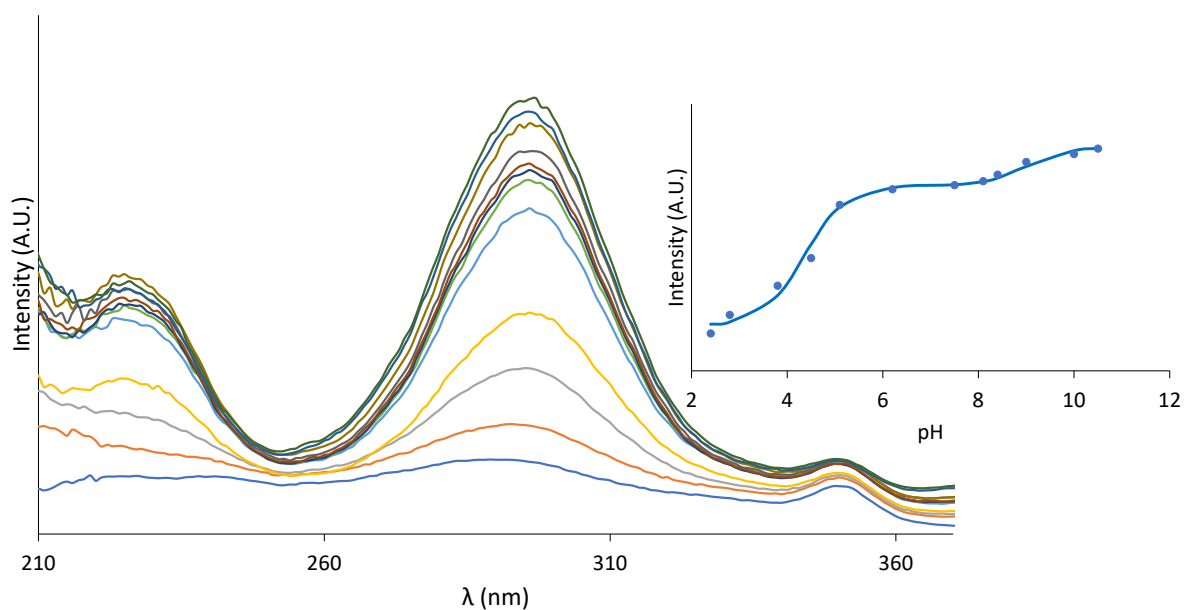


Figure S6. Normalized excitation spectra ($\lambda_{em} = 400$ nm) of L3 (150 μ M) in NaCl 0.15 M at 25°C ; inset : Excitation intensities at 295 nm as a function of pH (the line represents the best fit with the values presented in Table 2).

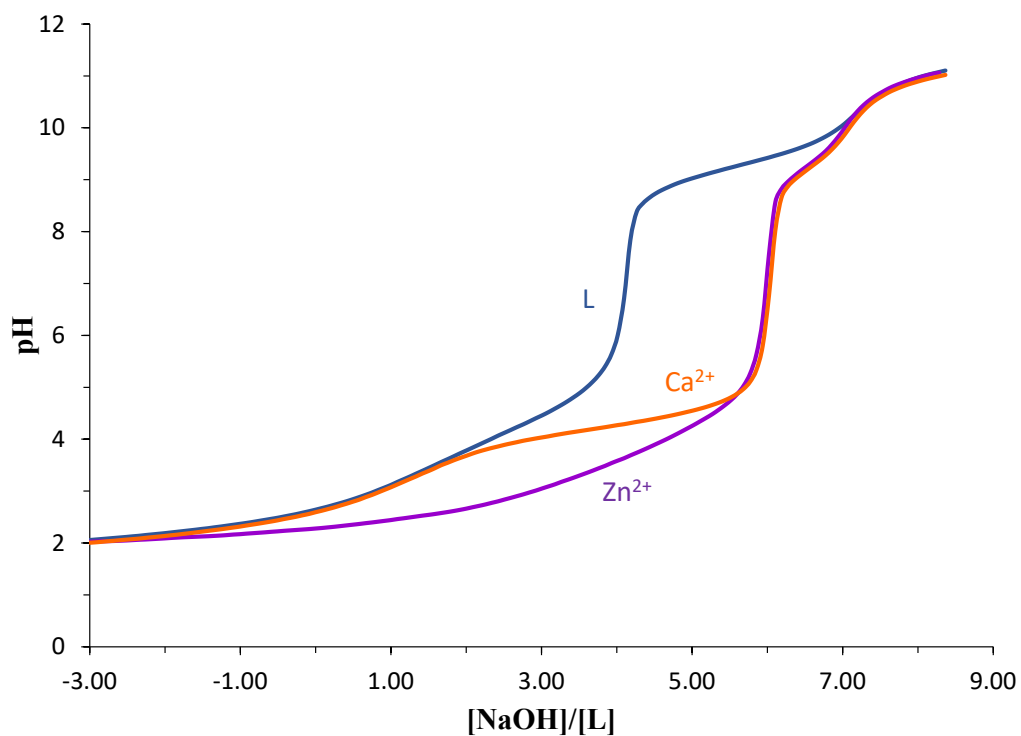


Figure S7. Potentiometric titrations of L3 (1.3 mM) in the absence and in the presence of 1 eq. of Zn²⁺ and Ca²⁺ in NaCl 0.15 M at 25°C

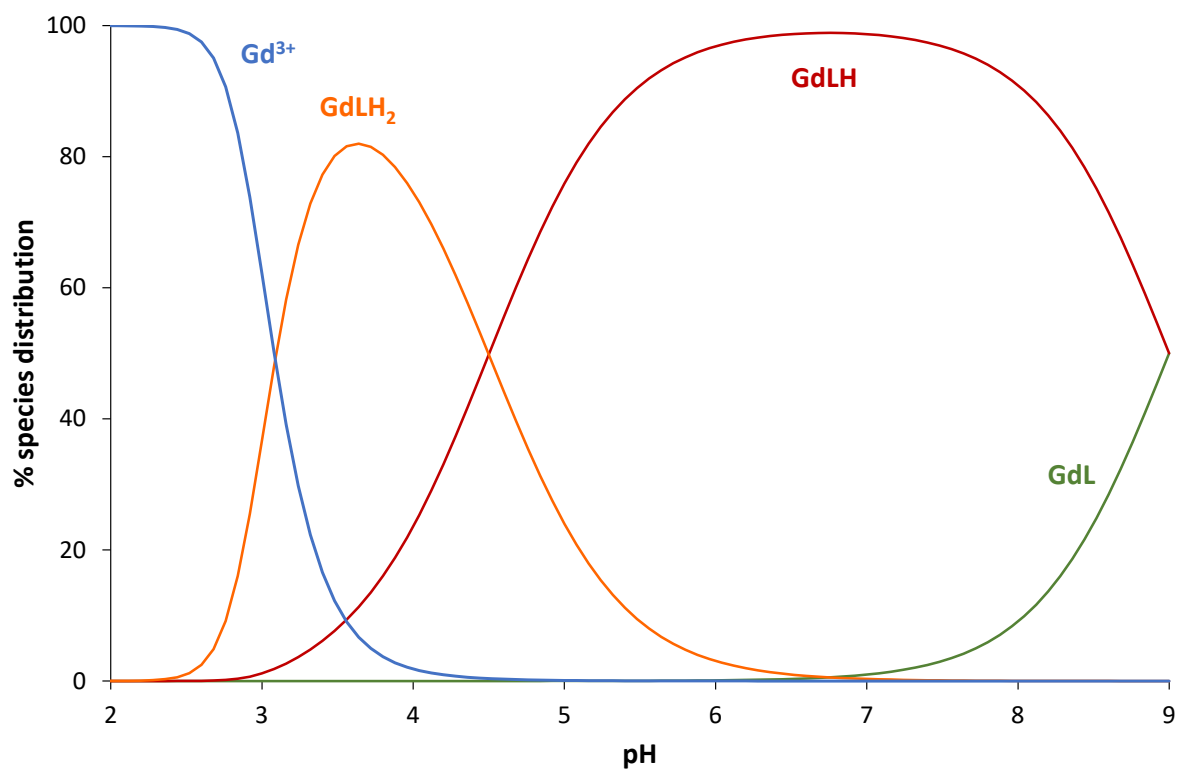


Figure S8. Speciation diagram of a Gd/L system in a 1/1 ratio with the Stability constants from Table 3.

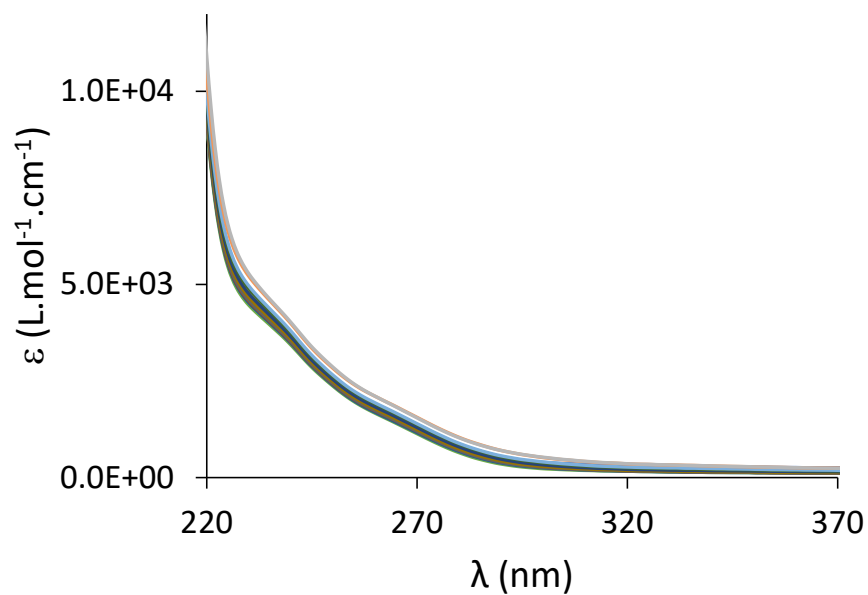


Figure S9. Absorption spectra of GdL3 (150 μM) in NaCl 0.15 M at 25°C at various pH ranging from 3 to 11.

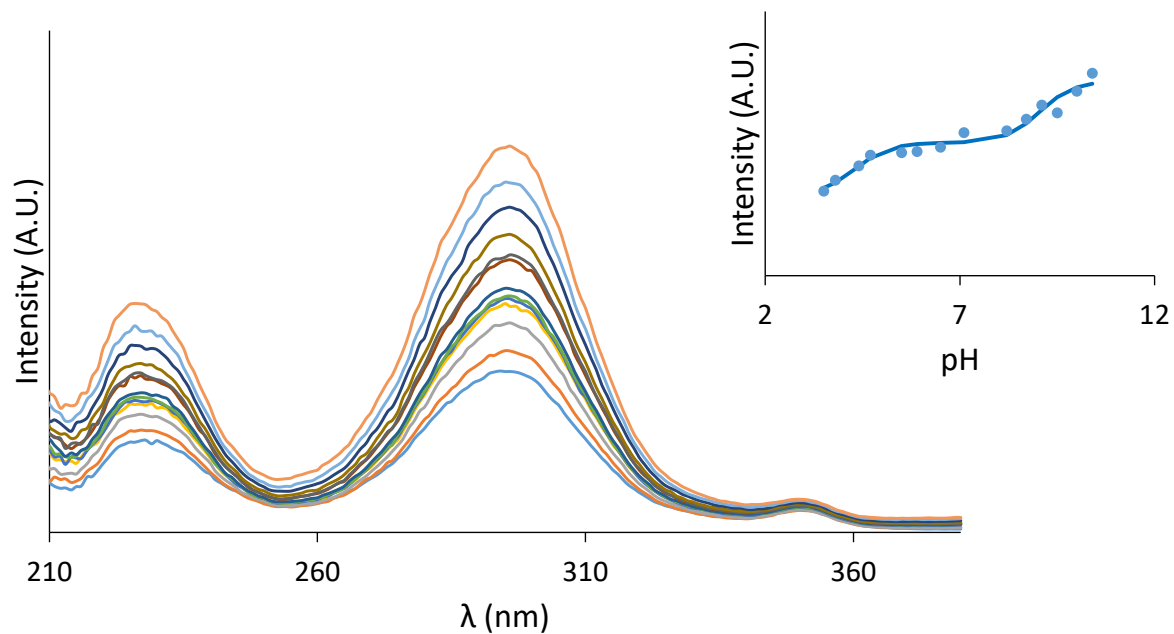


Figure S10. Normalized excitation spectra of GdL3 (150 μM) in NaCl 0.15 M at 25°C ($\lambda_{\text{em}} = 400 \text{ nm}$) ; inset : Excitation intensities at 295 nm as a function of pH (the line represents the best fit with the values presented in Table 2).

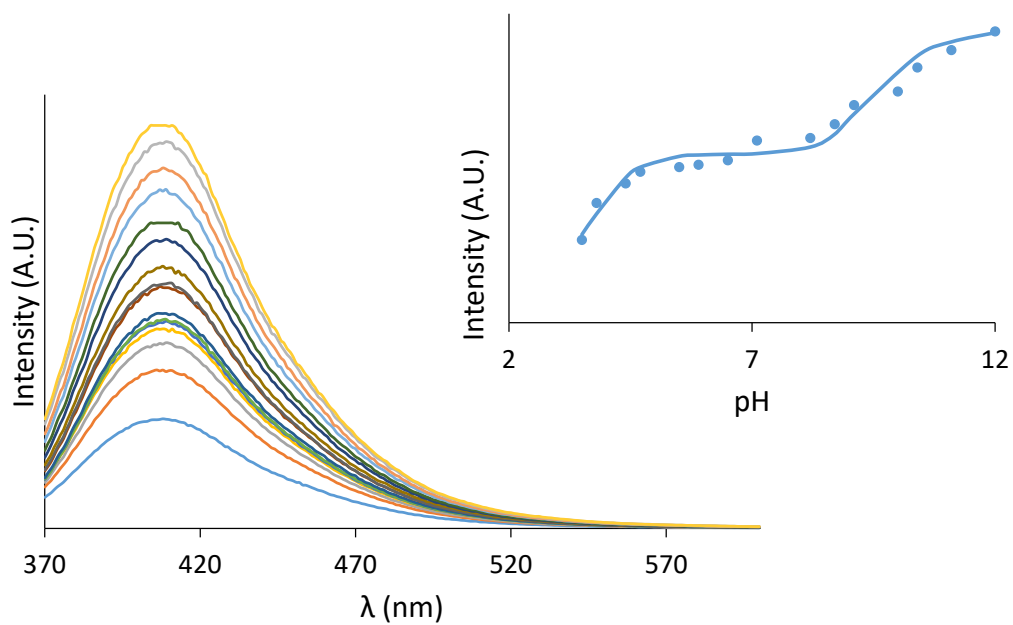


Figure S11. Normalized emission spectra of GdL3 (150 μM) in NaCl 0.15 M at 25°C ($\lambda_{\text{exc}} = 300 \text{ nm}$); inset : Emission intensities at 400 nm as a function of pH (the line represents the best fit with the values presented in Table 2).

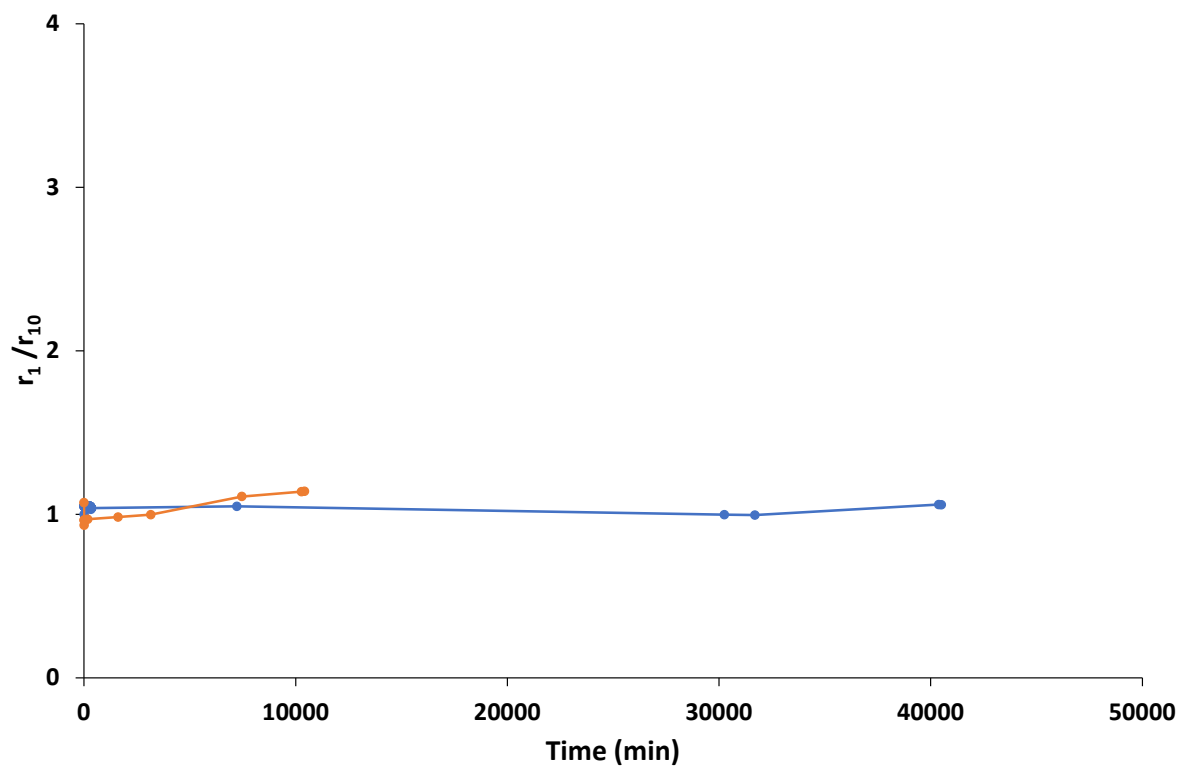


Figure S12. Normalized relaxivity at 60 MHz of a solution of GdL3H (0.4 mM) in NaCl 0.15 M at 25°C in the presence of 20 eq. of Zn^{2+} at pH 5 (●), or 10 eq. of Zn^{2+} at pH 2 (●).

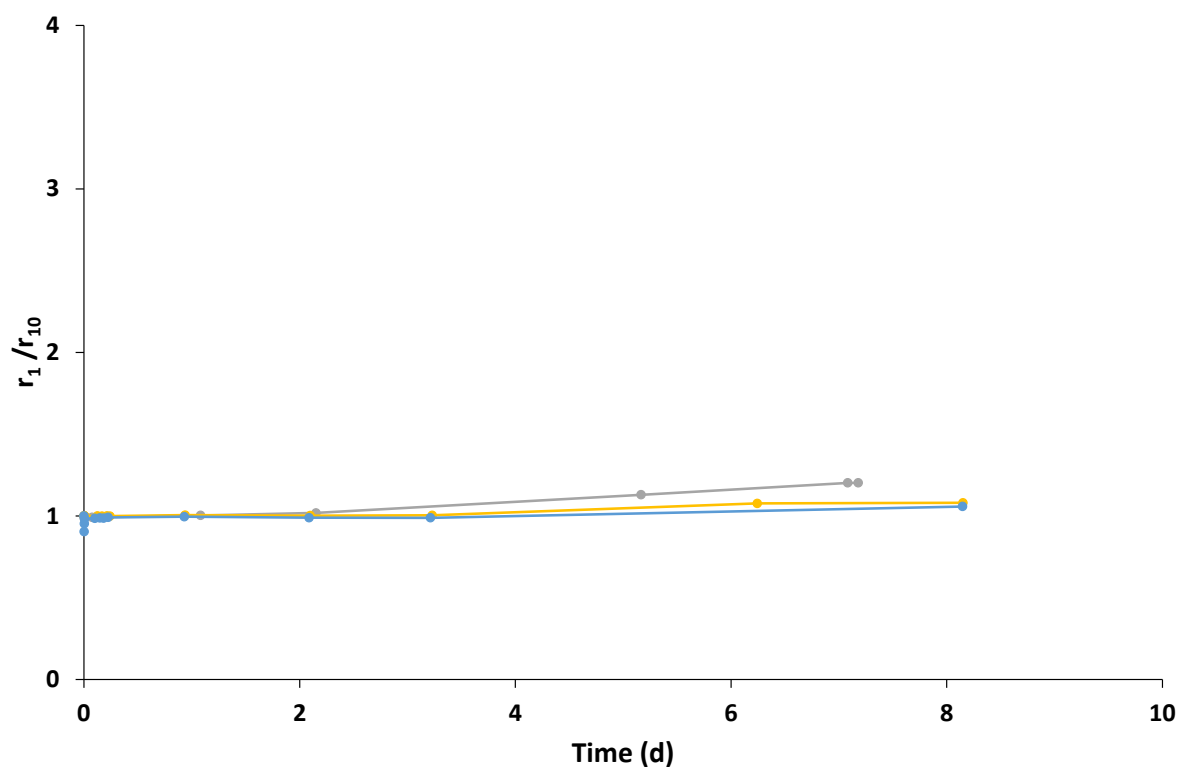


Figure S13. Normalized relaxivity at 60 MHz of a solution of GdL3H (0.4 mM) in NaCl 0.15 M at 25°C in the presence of 10 eq. of Eu^{3+} at pH 2 (●), pH 3 (●), or pH 5.5 (●).

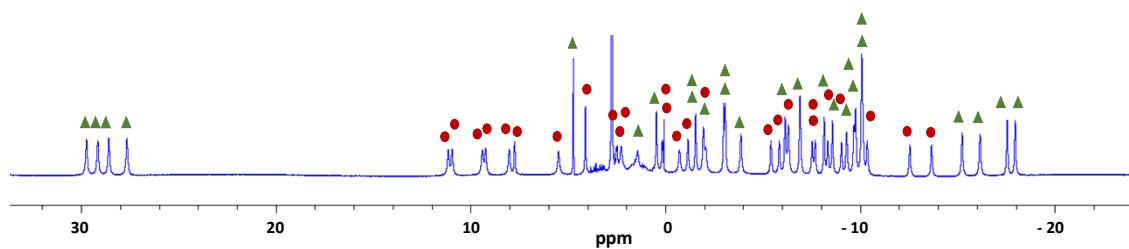


Figure S14. ^1H NMR spectra (700 MHz) of EuL3H in D2O at pD 6.97, 298K.

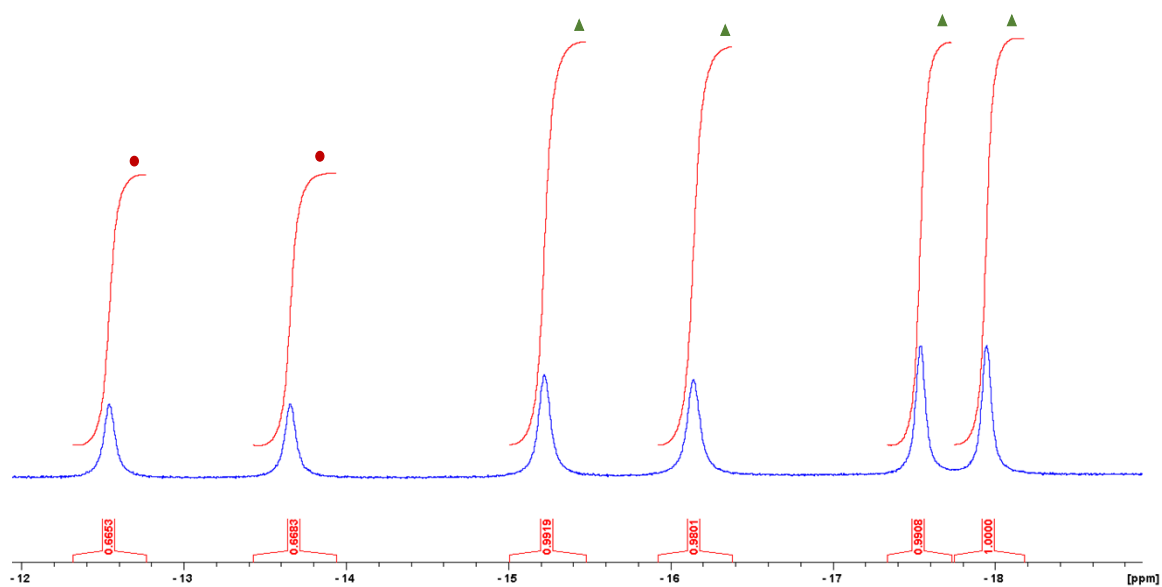


Figure S15. Partial ^1H NMR spectra (700 MHz) of EuL3H 1.98 mM in D2O at pD 6.97, 298K.

DFT calculations

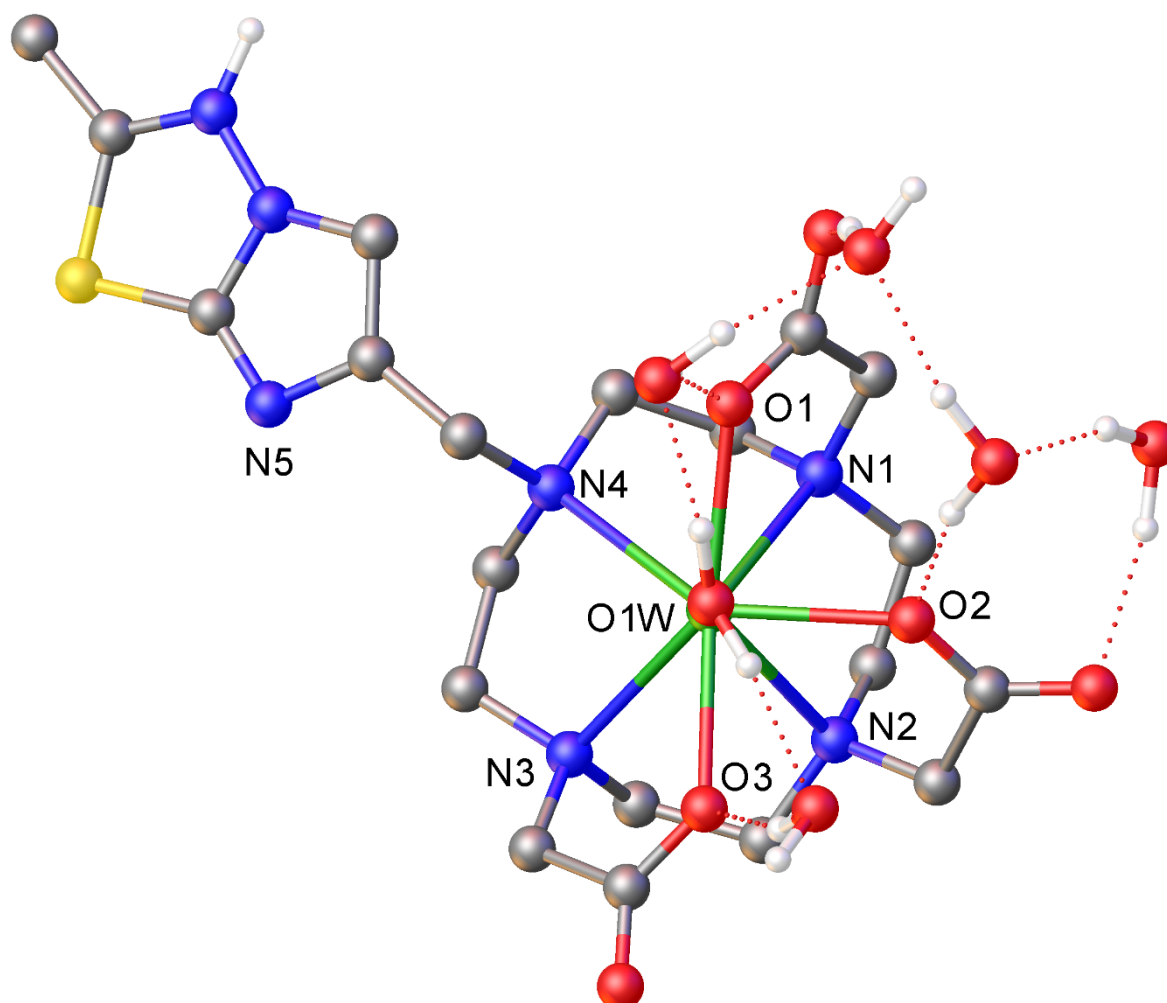


Figure S16: Geometry of the GdL3H-6H2O system (N_4O_4 donor set) optimized using DFT calculations (wB97XD functional). Hydrogen atoms bonded to C atoms are omitted for simplicity. Bond distances of the Gd(III) coordination environment (\AA): Gd-N1, 2.704; Gd-N2, 2.689; Gd-N3, 2.692; Gd-N4, 2.740; Gd-O1, 2.406; Gd-O2, 2.336; Gd-O3, 2.386; Gd-O1w, 2.449.

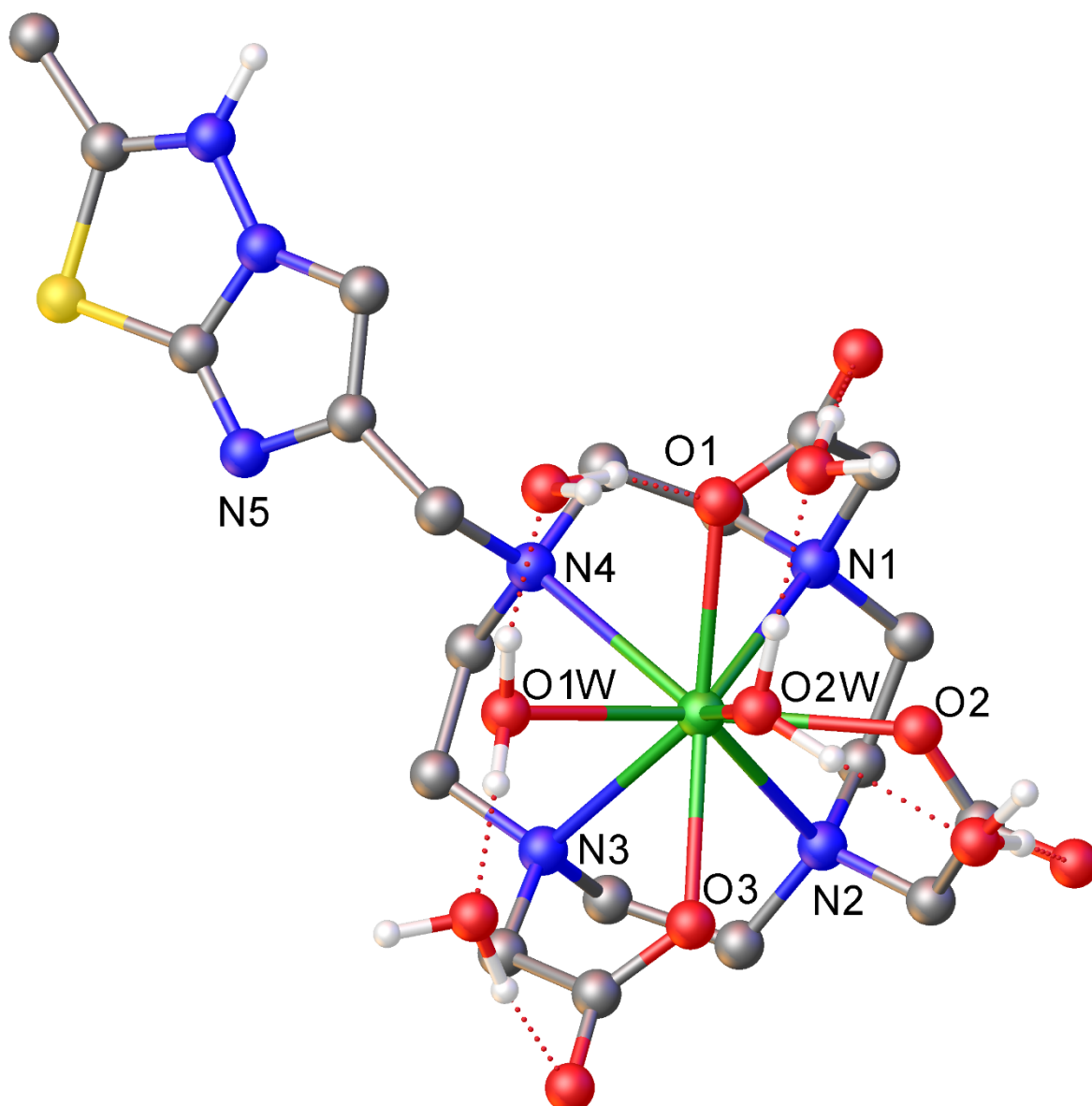


Figure S17: Geometry of the GdL3H·6H₂O system (N₄O₅ donor set) optimized using DFT calculations (wb97XD functional). Hydrogen atoms bonded to C atoms are omitted for simplicity. Bond distances of the Gd(III) coordination environment (Å): Gd-N1, 2.709; Gd-N2, 2.704; Gd-N3, 2.683; Gd-N4, 2.823; Gd-O1, 2.374; Gd-O2, 2.350; Gd-O3, 2.362; Gd-O1w, 2.514; Gd-O2w, 2.566.

Table S1. Cartesian coordinates (Å) obtained for the GdL3H-6H₂O system (N₅O₄ donor set) using DFT calculations (wB97XD functional, 0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	0.487750	-2.172154	-2.617153
2	6	1.589118	-2.870594	-1.922644
3	6	1.346694	-3.062288	-0.438619
4	7	1.219974	-1.808239	0.327340
5	6	0.614134	-2.085212	1.644297
6	6	-0.884195	-2.313487	1.573649
7	7	-1.648291	-1.184514	1.008579
8	6	-2.963514	-1.657760	0.538623
9	6	-2.880611	-2.381438	-0.791530
10	7	-2.393797	-1.545975	-1.909916
11	6	-1.985436	-2.411961	-3.033440
12	6	-0.648113	-3.094367	-2.812764
13	6	2.526207	-1.160875	0.499289
14	6	2.944346	-0.232791	-0.632189
15	8	4.134892	0.082173	-0.707773
16	8	2.023331	0.214002	-1.390691
17	6	-1.805909	-0.113197	2.000032
18	6	-0.558626	0.755548	2.145861
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21	6	-3.446245	-0.618287	-2.345953
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24	8	-2.433335	1.055620	-0.989528
25	1	3.320568	-1.890910	0.675529
26	1	2.483304	-0.512913	1.378525
27	1	-2.097168	-0.506559	2.976748
28	1	-2.592781	0.559339	1.655658
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37	1	-1.246678	-2.542671	2.581459
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58	1	5.133958	3.143823	-0.619978
59	1	4.398477	1.794614	-0.883708
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66	6	0.985620	-1.653058	-3.901814
67	1	1.061790	-2.443065	-4.654595
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72	7	-0.329020	0.399083	-3.523339
73	6	-0.876621	1.333505	-4.249834
74	16	-1.696238	2.835022	-4.019479
75	6	-1.867607	2.976547	-5.716497
76	7	-0.763101	1.048489	-5.562133
77	7	-1.323219	1.976663	-6.364553
78	1	-1.291744	1.866355	-7.370744
79	6	-2.554127	4.095540	-6.392425
80	1	-2.290000	4.127698	-7.445934
81	1	-3.631716	3.957901	-6.296929
82	1	-2.286040	5.037654	-5.920018

E(RwB97XD) = -2507.4064232 Hartree

Zero-point correction = 0.676929

Thermal correction to Energy = 0.723829

Thermal correction to Enthalpy = 0.724773

Thermal correction to Gibbs Free Energy = 0.598762

Sum of electronic and zero-point Energies = -2506.729494

Sum of electronic and thermal Energies = -2506.682594

Sum of electronic and thermal Enthalpies = -2506.681650

Sum of electronic and thermal Free Energies = -2506.807661

Table S2. Cartesian coordinates (Å) obtained for the GdL3H·6H₂O system (N₄O₅ donor set) using DFT calculations (wB97XD functional, 0 imaginary frequencies).

Center	Atomic	Coordinates (Angstroms)			
Number	Number	X	Y	Z	

1	7	0.254479	-2.240887	-2.606049	
2	6	1.388733	-2.950367	-1.984824	
3	6	1.240518	-3.138365	-0.487287	
4	7	1.164908	-1.884127	0.285235	
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6	6	-0.894811	-2.349232	1.613280	
7	7	-1.646811	-1.191589	1.093054	
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13	6	2.489516	-1.265367	0.411497	
14	6	2.895601	-0.373139	-0.750433	
15	8	4.090922	-0.091968	-0.873225	
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17	6	-1.703662	-0.116205	2.089412	
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20	8	0.159382	0.897236	1.016942	
21	6	-3.570830	-0.536640	-2.158732	
22	6	-3.578305	0.745105	-1.324217	
23	8	-4.604016	1.408552	-1.266727	
24	8	-2.461764	1.061589	-0.779432	
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36	1	0.877811	-1.331357	2.277300	
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48	8	2.369433	2.693064	0.971219	


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H     -2.78987183 -2.30040735 -0.61950776
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C	0.51290242	-1.86601497	-10.54648101
H	-0.05702938	-2.75822902	-10.79925993
H	0.23195060	-1.07280555	-11.23845533
H	1.57420812	-2.07385379	-10.64992627

E(RwB97XD) = -2507.3869216 Hartree

Zero-point correction = 0.676859

Thermal correction to Energy = 0.723975

Thermal correction to Enthalpy = 0.724919

Thermal correction to Gibbs Free Energy = 0.598028

Sum of electronic and zero-point Energies = -2506.710062

Sum of electronic and thermal Energies = -2506.662946

Sum of electronic and thermal Enthalpies = -2506.662002

Sum of electronic and thermal Free Energies = -2506.788894

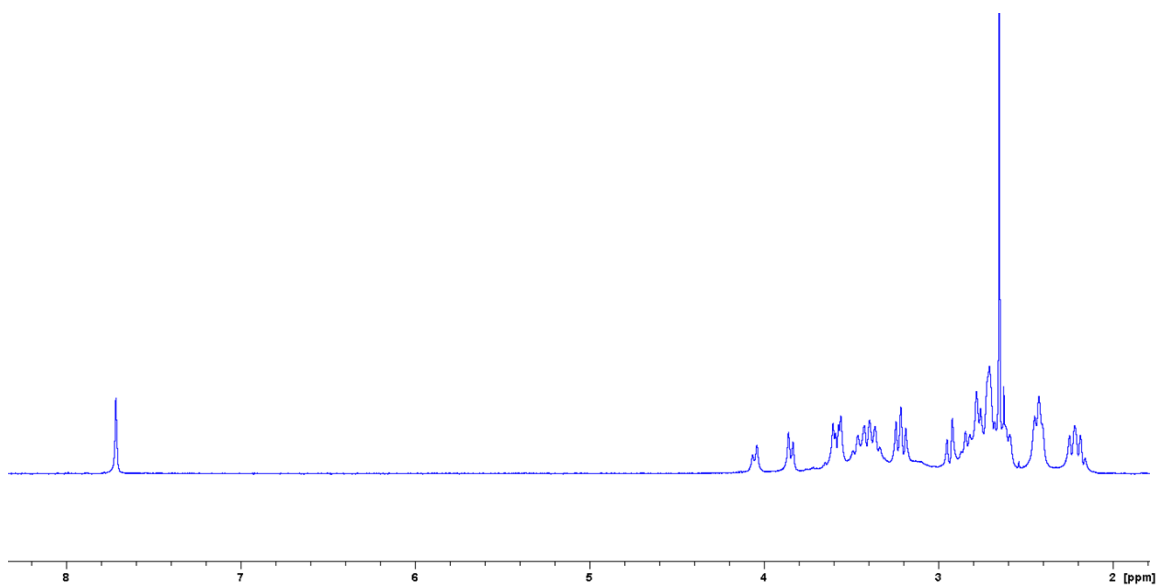


Figure S18. ^1H NMR spectrum (600 MHz) of YL3H 4.6 mM in D_2O at pD 7.36, 298 K.

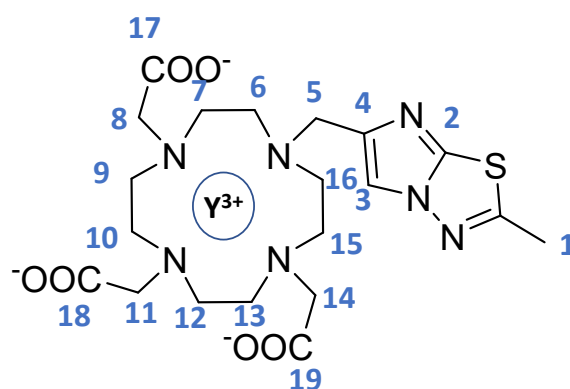


Figure S19: Numbering of the C and corresponding H in YL3 used in Table S2 and S3

Table S4 : ^1H NMR (600 MHz) chemical shifts (δ ppm) of YL3H in D_2O .

	YL3
H1	2.57
H3	7.64
H5a	3.77
H5b	3.98
H6a	3.32
H6b	2.16
H7a/b	2.54
H8a	3.49
H8b	3.15
H9a	2.71
H9b	2.77
H10a/b	3.33
H11a	2.86

H11b	2.62
H12a/b	2.64
H13a	3.38
H13b	2.35
H14a	3.52
H14b	3.12
H15a	2.35
H15b	2.11
H16a	2.68
H16b	2.61

Table S5 : ^{13}C NMR (150 MHz) for YL3H chemical shifts (δ ppm) in D_2O .

	L3
C1	164.23
C2	146.57
C3	109.06
C4	143.43
C5	59.25
C6	55.47
C7	55.58
C8	65.74
C9	56.21
C10	55.38
C11	66.10
C12	55.94
C13	55.36
C14	65.82
C15	57.06
C16	56.16
C17	180.72
C18	180.5
C19	180.6

Table S6. Cartesian coordinates (\AA) obtained for the YL3H-6 H_2O system (N_5O_4 donor set) using DFT calculations (TPSSH functional, 0 imaginary frequencies).

	Center	Atomic	Coordinates (Angstroms)		
	Number	Number	X	Y	Z

1	7	0.410376	-2.253873	-2.676440	
2	6	1.534724	-2.983968	-2.030675	
3	6	1.327324	-3.194105	-0.543237	
4	7	1.220906	-1.929283	0.227831	
5	6	0.650777	-2.222964	1.568500	
6	6	-0.850914	-2.434509	1.516238	
7	7	-1.589935	-1.266457	0.970938	
8	6	-2.946117	-1.702566	0.549927	
9	6	-2.919647	-2.416757	-0.788833	

10	7	-2.405509	-1.571096	-1.901207
11	6	-2.064711	-2.448986	-3.051071
12	6	-0.744633	-3.172115	-2.849610
13	6	2.550939	-1.302681	0.373483
14	6	2.915068	-0.323303	-0.735166
15	8	4.095847	0.058121	-0.802192
16	8	1.963384	0.089572	-1.489105
17	6	-1.692547	-0.207286	1.996969
18	6	-0.450356	0.677361	2.079989
19	8	-0.194966	1.226647	3.158991
20	8	0.216121	0.819703	0.987734
21	6	-3.451170	-0.603000	-2.299792
22	6	-3.457031	0.673378	-1.459140
23	8	-4.478670	1.356285	-1.402412
24	8	-2.330308	0.969468	-0.897724
25	1	3.343565	-2.051292	0.472552
26	1	2.552770	-0.707368	1.288487
27	1	-1.914366	-0.625101	2.983681
28	1	-2.514443	0.455675	1.719232
29	1	-3.261324	-0.292198	-3.329539
30	1	-4.446543	-1.057773	-2.280796
31	1	2.442789	-2.407804	-2.201835
32	1	1.681662	-3.962267	-2.504729
33	1	2.161525	-3.794389	-0.158986
34	1	0.421514	-3.773235	-0.367919
35	1	1.118010	-3.115270	2.002894
36	1	0.892079	-1.387631	2.223372
37	1	-1.212176	-2.665664	2.525799
38	1	-1.084841	-3.299238	0.896497
39	1	-3.387475	-2.372472	1.297755
40	1	-3.581916	-0.820514	0.500461
41	1	-2.291987	-3.304386	-0.723028
42	1	-3.931892	-2.764463	-1.028170
43	1	-2.023117	-1.829102	-3.945110
44	1	-2.852551	-3.194212	-3.215819
45	1	-0.800704	-3.807309	-1.966860
46	1	-0.571139	-3.838976	-3.702904
47	39	-0.307612	-0.160083	-1.037752
48	8	2.111167	3.114378	1.092575
49	8	-0.021952	2.228518	-1.554091
50	1	1.529547	2.339963	0.971729
51	1	2.880901	2.974629	0.507178
52	1	0.859708	2.567350	-1.846846
53	1	-0.452907	2.866679	-0.942654
54	8	2.225944	2.490846	3.831046
55	1	2.402099	2.827370	2.930801
56	1	1.376020	2.027615	3.688545
57	8	4.299414	2.740693	-0.682539
58	1	5.186066	3.081760	-0.520815
59	1	4.378003	1.757227	-0.757884
60	8	-1.823443	3.483842	0.058940
61	1	-2.340854	4.178248	-0.365356

62	1	-2.248075	2.636954	-0.213921
63	8	2.390361	2.562484	-2.702020
64	1	2.401429	1.606446	-2.480978
65	1	3.110679	2.913218	-2.144151
66	6	0.878164	-1.756215	-3.992525
67	1	0.864960	-2.549073	-4.748109
68	1	1.915054	-1.438155	-3.868272
69	6	0.108504	-0.567542	-4.461498
70	6	-0.122628	-0.128594	-5.742525
71	1	0.081466	-0.536477	-6.715708
72	7	-0.346918	0.338611	-3.521455
73	6	-0.829615	1.342911	-4.218540
74	16	-1.535615	2.896036	-3.941024
75	6	-1.700319	3.114359	-5.636830
76	7	-0.724858	1.098353	-5.552660
77	7	-1.217817	2.096277	-6.323551
78	1	-1.182411	2.022088	-7.336067
79	6	-2.308652	4.303370	-6.277781
80	1	-2.044844	4.344500	-7.332975
81	1	-3.395428	4.245357	-6.181684
82	1	-1.969225	5.210662	-5.779694

E(RTPSSh) = -2510.3196644 Hartree

Zero-point correction = 0.664392

Thermal correction to Energy = 0.711818

Thermal correction to Enthalpy = 0.712762

Thermal correction to Gibbs Free Energy = 0.586315

Sum of electronic and zero-point Energies = -2509.655272

Sum of electronic and thermal Energies = -2509.607847

Sum of electronic and thermal Enthalpies = -2509.606903

Sum of electronic and thermal Free Energies = -2509.733350

Table S7. Cartesian coordinates (Å) obtained for the YL3H-6H₂O system (N₄O₄ donor set) using DFT calculations (TPSSh functional, 0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	7	0.675860	-2.258612	-2.449153
2	6	1.776979	-2.950160	-1.731551
3	6	1.470033	-3.187433	-0.262684
4	7	1.265531	-1.940536	0.518178
5	6	0.590671	-2.268135	1.801557
6	6	-0.893995	-2.514472	1.615242
7	7	-1.601513	-1.349405	1.026004
8	6	-2.922218	-1.793602	0.506137
9	6	-2.796889	-2.489249	-0.837624
10	7	-2.199876	-1.628758	-1.892782
11	6	-1.744382	-2.481671	-3.025424
12	6	-0.439915	-3.201811	-2.728839

13	6	2.559851	-1.279702	0.788172
14	6	2.981297	-0.275071	-0.274422
15	8	4.132224	0.187372	-0.214964
16	8	2.093732	0.067478	-1.134818
17	6	-1.781205	-0.290276	2.043844
18	6	-0.597616	0.669128	2.159368
19	8	-0.445881	1.279914	3.222711
20	8	0.132595	0.808211	1.104841
21	6	-3.200439	-0.648240	-2.371462
22	6	-3.274208	0.621401	-1.524669
23	8	-4.267043	1.343867	-1.611507
24	8	-2.232329	0.876467	-0.802882
25	1	3.362995	-2.008145	0.939890
26	1	2.468939	-0.703827	1.710614
27	1	-2.006361	-0.713822	3.026931
28	1	-2.628282	0.328418	1.742474
29	1	-2.908739	-0.321277	-3.372338
30	1	-4.195240	-1.097207	-2.452454
31	1	2.671988	-2.337767	-1.834836
32	1	1.994825	-3.918245	-2.196919
33	1	2.291398	-3.768316	0.174639
34	1	0.571780	-3.796035	-0.164763
35	1	1.044267	-3.151642	2.266456
36	1	0.749404	-1.433194	2.482704
37	1	-1.337758	-2.770305	2.585029
38	1	-1.054551	-3.371626	0.962354
39	1	-3.405311	-2.477400	1.214006
40	1	-3.560570	-0.916675	0.422261
41	1	-2.177605	-3.379966	-0.740330
42	1	-3.789559	-2.829971	-1.156336
43	1	-1.623324	-1.833972	-3.893882
44	1	-2.510126	-3.222448	-3.284114
45	1	-0.553375	-3.848564	-1.859528
46	1	-0.194508	-3.852106	-3.573505
47	39	-0.206117	-0.260428	-0.875398
48	8	1.782403	3.286943	1.078553
49	8	0.083301	1.851780	-1.918361
50	1	1.282513	2.452440	1.009376
51	1	2.607776	3.150178	0.571901
52	1	0.965974	2.200515	-2.195104
53	1	-0.491890	2.603407	-1.641075
54	8	1.735031	2.941066	3.872596
55	1	1.936461	3.207094	2.954199
56	1	0.969953	2.347982	3.731760
57	8	4.133218	2.880980	-0.448767
58	1	4.966483	3.298203	-0.202827
59	1	4.274117	1.903135	-0.382181
60	8	-1.738519	3.558204	-0.838818
61	1	-2.337530	4.034903	-1.425427
62	1	-2.167433	2.684857	-0.686080
63	8	2.626271	2.266084	-2.729493
64	1	2.656169	1.385907	-2.295740

65	1	3.183860	2.799701	-2.133255
66	6	1.202401	-1.646246	-3.707903
67	1	1.894408	-0.860889	-3.408271
68	1	0.369184	-1.174692	-4.228853
69	6	1.909283	-2.570156	-4.654865
70	6	3.275599	-2.681497	-4.814313
71	1	4.116275	-2.196666	-4.351077
72	7	1.218901	-3.412637	-5.515256
73	6	2.155346	-4.032147	-6.179911
74	16	2.285329	-5.223732	-7.437879
75	6	3.994607	-5.110155	-7.379823
76	7	3.408362	-3.629853	-5.799045
77	7	4.408056	-4.237261	-6.480643
78	1	5.377027	-4.008104	-6.278189
79	6	4.918906	-5.904597	-8.223190
80	1	5.942913	-5.559460	-8.095557
81	1	4.855808	-6.956920	-7.939154
82	1	4.632657	-5.816076	-9.271343

E(RTPSSh) = -2510.3196813 Hartree

Zero-point correction = 0.663653

Thermal correction to Energy = 0.711310

Thermal correction to Enthalpy = 0.712254

Thermal correction to Gibbs Free Energy = 0.583399

Sum of electronic and zero-point Energies = -2509.656029

Sum of electronic and thermal Energies = -2509.608371

Sum of electronic and thermal Enthalpies = -2509.607427

Sum of electronic and thermal Free Energies = -2509.736282

Table S8. Cartesian coordinates (Å) obtained for the YL3H-6H₂O system (N₅O₅ donor set) using DFT calculations (TPSSh functional, 0 imaginary frequencies).

Center	Atomic	Coordinates (Angstroms)			
Number	Number	X	Y	Z	

1	7	-0.323384	-0.843948	-2.676827	
2	6	0.665826	-1.937794	-2.804515	
3	6	0.725420	-2.849229	-1.593861	
4	7	1.122079	-2.173717	-0.335065	
5	6	0.769480	-3.053828	0.811084	
6	6	-0.714686	-3.009607	1.134959	
7	7	-1.196156	-1.656202	1.504665	
8	6	-2.672900	-1.589641	1.368610	
9	6	-3.106958	-1.454256	-0.077992	
10	7	-2.578032	-0.234460	-0.740694	
11	6	-2.723435	-0.384029	-2.214975	
12	6	-1.711195	-1.343961	-2.818026	
13	6	2.573700	-1.882036	-0.325783	
14	6	2.945714	-0.493475	-0.839813	

15	8	4.145208	-0.183210	-0.897917
16	8	1.977676	0.296198	-1.138733
17	6	-0.804168	-1.323991	2.891353
18	6	0.539267	-0.610781	2.983506
19	8	0.993695	-0.347676	4.112686
20	8	1.089001	-0.279169	1.881857
21	6	-3.329465	0.957441	-0.285314
22	6	-2.708350	1.685710	0.907531
23	8	-3.339135	2.649953	1.378877
24	8	-1.552196	1.304743	1.289344
25	1	3.140123	-2.632878	-0.888228
26	1	2.927767	-1.918856	0.704646
27	1	-0.795608	-2.211325	3.534102
28	1	-1.539382	-0.633123	3.305275
29	1	-3.349725	1.686010	-1.097807
30	1	-4.371893	0.711164	-0.056769
31	1	1.639379	-1.475658	-2.969081
32	1	0.453358	-2.559954	-3.682998
33	1	1.428550	-3.663410	-1.813672
34	1	-0.244901	-3.317190	-1.432839
35	1	1.051477	-4.093190	0.600600
36	1	1.349718	-2.728458	1.671352
37	1	-0.917735	-3.716659	1.949375
38	1	-1.293897	-3.350600	0.277298
39	1	-3.147820	-2.480506	1.798524
40	1	-3.017780	-0.731693	1.943181
41	1	-2.774337	-2.320536	-0.647658
42	1	-4.203493	-1.453144	-0.121263
43	1	-2.596501	0.605381	-2.653724
44	1	-3.735263	-0.725831	-2.466387
45	1	-1.773013	-2.318196	-2.335226
46	1	-1.965793	-1.504619	-3.870546
47	39	-0.056123	0.192450	-0.036501
48	8	1.220106	2.227760	0.816632
49	8	-0.538888	2.132758	-1.432005
50	1	1.359217	2.187924	1.790448
51	1	2.128686	2.300687	0.453082
52	1	0.300027	2.480198	-1.823316
53	1	-0.946465	2.910182	-0.977440
54	8	1.751611	2.245471	3.591392
55	1	2.692841	2.413747	3.714528
56	1	1.621048	1.299138	3.842487
57	8	3.884711	2.484261	-0.185399
58	1	4.534380	2.725963	0.484451
59	1	4.114606	1.566301	-0.465024
60	8	-1.734408	4.317233	-0.219817
61	1	-2.275613	4.819511	-0.840527
62	1	-2.366612	3.942413	0.428473
63	8	1.951382	2.706452	-2.439872
64	1	2.198518	1.849881	-2.023484
65	1	2.480361	3.349562	-1.949520
66	6	-0.027439	0.197918	-3.702784

67	1	0.951697	0.606356	-3.464052
68	1	-0.757069	0.996965	-3.594596
69	6	-0.015349	-0.257797	-5.134425
70	6	1.096944	-0.587793	-5.882356
71	1	2.150351	-0.618552	-5.669179
72	7	-1.183196	-0.356461	-5.880724
73	6	-0.782926	-0.748747	-7.058975
74	16	-1.473419	-1.126639	-8.608986
75	6	0.088077	-1.460943	-9.232202
76	7	0.577018	-0.902541	-7.114668
77	7	1.033317	-1.295710	-8.327006
78	1	2.028252	-1.438094	-8.476679
79	6	0.372761	-1.880422	-10.624407
80	1	-0.230489	-2.751839	-10.880176
81	1	0.114243	-1.071780	-11.310487
82	1	1.427584	-2.123691	-10.735842

E(RTPSSh) = -2510.3156777 Hartree

Zero-point correction = 0.663423

Thermal correction to Energy = 0.711209

Thermal correction to Enthalpy = 0.712153

Thermal correction to Gibbs Free Energy = 0.584550

Sum of electronic and zero-point Energies = -2509.652254

Sum of electronic and thermal Energies = -2509.604468

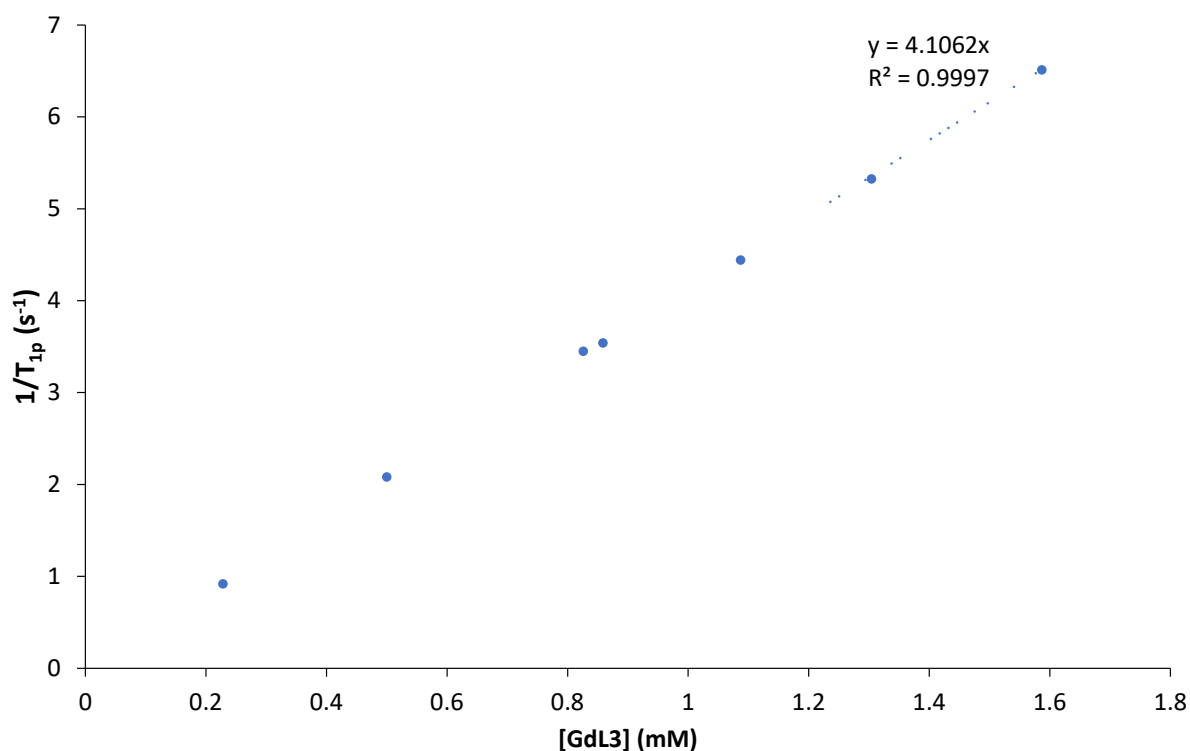
Sum of electronic and thermal Enthalpies = -2509.603524

Sum of electronic and thermal Free Energies = -2509.731128

Table S9. Tb^{III}-centered luminescence lifetimes of 0.5 mM solutions of TbL3H.^a

Solvent	τ_{obs} (ms)
HEPES, pH 7.4	1.5(1): 94(2)% 0.44(1): 6(2)% $\tau_{\text{av}} = 1.5(1)$
D ₂ O	2.6(1): 92(2)% 0.83(2): 8(2)% $\tau_{\text{av}} = 2.4(1)$

^a 2σ values are given between parentheses. Experimental error: $\pm 5\%$. Under excitation at 266 nm.

**Figure S20.** Paramagnetic Relaxation Enhancement measurements in the presence of GdL3H at 60 MHz, 25°C.**Table S10.** Parameters obtained from the simultaneous fitting of the transverse ¹⁷O NMR relaxation rates and chemical shifts as a function of temperature at 9.4 T, and of the NMRD profiles at 298 K, 310 K, and 323 K, using the Solomon Bloembergen and Morgan theory presented below.

	GdL3
k_{ex}^{298} ($10^6 s^{-1}$)	4.8 (6)
ΔH^\ddagger (kJ.mol ⁻¹)	27 (4)
τ_R^{298} (ps) ^{[a],[b]}	75 (2)
E_R (kJ.mol ⁻¹)	19 (3)

τ_v^{298} (ps)	14 (2)
Δ^2 (10^{20}s^{-1})	0.83 (6)
D_{GdH}^{298} ($10^{-9}\text{m}^2\text{s}^{-1}$) ^a	26
E_{DGdH} ($\text{kJ}\cdot\text{mol}^{-1}$)	22 (3)

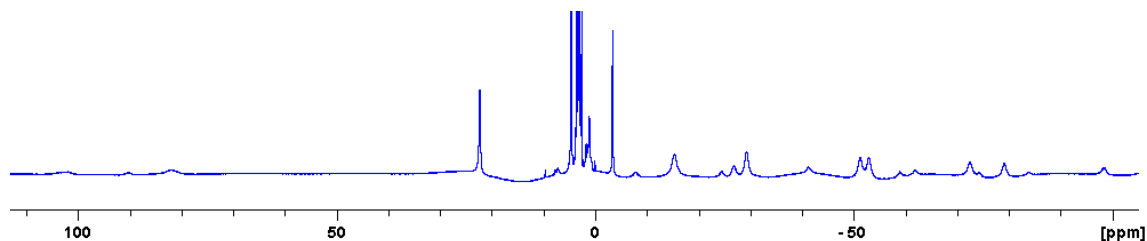


Figure S21. ^1H NMR spectra (700 MHz) of TbL3H 1.5 mM in D₂O at pH 7.0, 298K.

Equations used for the analysis of the ^{17}O NMR and NMRD data

^{17}O NMR spectroscopy

From the measured ^{17}O NMR relaxation rates and angular frequencies of the paramagnetic solutions, $1/T_2$, $1/T_1$ and ω , and from the acidified water reference, $1/T_{2A}$, $1/T_{1A}$ and ω_A , it is possible to calculate the reduced relaxation rates and chemical shifts, $1/T_{2r}$, $1/T_{1r}$ and $\Delta\omega_r$ (Eq. 1-3), where $1/T_{1m}$ and $1/T_{2m}$ are the relaxation rate of the bound water and $\Delta\omega_m$ is the chemical shift difference between bound and bulk water, τ_m is the mean residence time or the inverse of the water exchange rate k_{ex} and P_m is the mole fraction of the bound water.^[1]

$$\frac{1}{T_{1r}} = \frac{1}{P_m} \left[\frac{1}{T_1} - \frac{1}{T_{1A}} \right] = \frac{1}{T_{1m} + \tau_m} + \frac{1}{T_{1os}} \quad [1]$$

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left[\frac{1}{T_2} - \frac{1}{T_{2A}} \right] = \frac{1}{\tau_m} \frac{T_{2m}^{-2} + \tau_m^{-1} T_{2m}^{-1} + \Delta\omega_m^2}{(\tau_m^{-1} + T_{2m}^{-1})^2 + \Delta\omega_m^2} + \frac{1}{T_{2os}} \quad [2]$$

$$\Delta\omega_r = \frac{1}{P_m} (\omega - \omega_A) = \frac{\Delta\omega_m}{(1 + \tau_m T_{2m}^{-1})^2 + \tau_m^2 \Delta\omega_m^2} + \Delta\omega_{os} \quad [3]$$

The outer sphere contributions to the ^{17}O relaxation rates $1/T_{1os}$ and $1/T_{2os}$ can be neglected according to previous studies.^[2] Eqs. 1-2 can be further simplified into Eqs. 4-5:

$$\frac{1}{T_{1r}} = \frac{1}{T_{1m} + \tau_m} \quad [4]$$

$$\frac{1}{T_{2r}} = \frac{1}{T_{2m} + \tau_m} \quad [5]$$

The exchange rate is assumed to be described by the Eyring equation (Eq 6), where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation for the water exchange process, and k_{ex}^{298} is the exchange rate at 298.15 K. R is the usual gas constant whereas h and k_B are the Planck and Boltzmann constants, respectively:

$$\frac{1}{\tau_m} = k_{ex} = \frac{k_B T}{h} \exp\left\{\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right\} = \frac{k_{ex}^{298} T}{298.15} \exp\left\{\frac{\Delta H^\ddagger}{R} \left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad [6]$$

In the transverse relaxation the scalar contribution, $1/T_{2sc}$, is the most important. In Eq. 7 $1/\tau_{s1}$ is the sum of the exchange rate and the electron spin relaxation rate constants.

$$\frac{1}{T_{2m}} \cong \frac{1}{T_{2sc}} = \frac{S(S+1)}{3} \left(\frac{A}{h}\right)^2 \left(\tau_{s1} + \frac{\tau_{s2}}{1 + \omega_S^2 \tau_{s2}^2}\right) \quad [7]$$

$$\frac{1}{\tau_{s1}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}} \quad [8]$$

The ^{17}O longitudinal relaxation rates in Gd^{3+} solutions are the sum of the contributions of the dipole-dipole (dd) and quadrupolar (q) mechanisms as expressed by Equations (11-13) for non-extreme narrowing conditions, where γ_S is the electron and γ_I is the nuclear gyromagnetic ratio ($\gamma_S = 1.76 \times 10^{11} \text{ rad s}^{-1} \text{ T}^{-1}$, $\gamma_I = -3.626 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$), r_{GdO} is the effective distance between the electron charge and the ^{17}O nucleus, I is the nuclear spin (5/2 for ^{17}O), χ is the quadrupolar coupling constant and η is an asymmetry parameter :

$$\frac{1}{T_{1m}} = \frac{1}{T_{1dd}} + \frac{1}{T_{1q}} \quad [9]$$

with:

$$\frac{1}{T_{1dd}} = \frac{2}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_I^2 \gamma_S^2}{r_{\text{GdO}}^6} S(S+1) \times [3J(\omega_I; \tau_{d1}) + 7J(\omega_S; \tau_{d2})] \quad [10]$$

$$\frac{1}{T_{1q}} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \chi^2 (1 + \eta^2/3) \times [0.2J_1(\omega_I) + 0.8J_2(\omega_I)] \quad [11]$$

In Eq. 3, the chemical shift of the bound water molecule, $\Delta\omega_m$, depends on the hyperfine interaction between the Gd^{3+} electron spin and the ^{17}O nucleus and is directly proportional to the scalar coupling constant, $A\hbar$, as expressed in Eq. 7.^[3]

$$\Delta\omega_m = \frac{g_L \mu_B S(S+1) B A}{3k_B T \hbar} \quad [12]$$

The isotopic Landé g factor is equal to 2.0 for the Gd³⁺, B represents the magnetic field, and k_B is the Boltzmann constant.

¹H NMRD

The measured longitudinal proton relaxation rate, R_1^{obs} is the sum of the paramagnetic and diamagnetic contributions as expressed in Eq. 13, where r_1 is the proton relaxivity:

$$R_1^{obs} = R_1^d + R_1^p = R_1^d + r_1 \times c_{Gd} \quad [13]$$

The relaxivity can be divided into terms of inner and outer sphere, as follows:

$$r_1 = r_{1is} + r_{1os} \quad [14]$$

The inner sphere term is obtained in Eq. 15, where q is the number of inner sphere water molecules.^[4]

$$r_{1is} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m}^H + \tau_m} \quad [15]$$

The longitudinal relaxation rate of inner sphere protons, $1/T_{1m}^H$ is expressed by Eq. 16, where r_{GdH} is the effective distance between the electron charge and the ¹H nucleus, ω_I is the proton resonance frequency and ω_S is the Larmor frequency of the Gd^{III} electron spin.

$$\frac{1}{T_{1m}^H} = \frac{2}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_I^2 \gamma_S^2}{r_{GdH}^6} S(S+1) \times [3J(\omega_I; \tau_{d1}) + 7J(\omega_S; \tau_{d2})] \quad [16]$$

$$\frac{1}{\tau_{di}} = \frac{1}{\tau_m} + \frac{1}{\tau} + \frac{1}{T_{ie}} \quad [17]$$

The longitudinal and transverse electronic relaxation rates, $1/T_{1e}$ and $1/T_{2e}$ are expressed by Eq. 18-19, where τ_v is the electronic correlation time for the modulation of the zero-field-splitting interaction, E_v the corresponding activation energy and Δ^2 is the mean square zero-field-splitting energy. We assumed a simple exponential dependence of τ_v versus $1/T$.

$$\left(\frac{1}{T_{1e}}\right)^{ZFS} = \frac{1}{25} \Delta^2 \tau_v \{4S(S+1) - 3\} \left\{ \frac{1}{1 + \omega_S^2 \tau_v^2} + \frac{4}{1 + 4\omega_S^2 \tau_v^2} \right\} \quad [18]$$

$$\left(\frac{1}{T_{2e}}\right)^{ZFS} = \Delta^2 \tau_v \left(\frac{5.26}{1 + 0.372\omega_S^2 \tau_v^2} + \frac{7.18}{1 + 1.24\omega_S \tau_v} \right) \quad [19]$$

$$\tau_v = \tau_v^{298} \exp\left\{ \frac{E_v}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right\} \quad [20]$$

The outer-sphere contribution can be described by Eq. 17 where N_A is the Avogadro constant, and J_{os} is its associated spectral density function.^{[5],[6]}

$$r_{1os} = \frac{32N_A \pi}{405} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_S^2 \gamma_I^2}{a_{GdH} D_{GdH}} S(S+1) [3J_{os}(\omega_I, T_{1e}) + 7J_{os}(\omega_S, T_{2e})] \quad [21]$$

$$J_{os}(\omega, T_{je}) = \text{Re} \left[\frac{1 + \frac{1}{4} \left(i\omega\tau_{GdH} + \frac{\tau_{GdH}}{T_{je}} \right)^{1/2}}{1 + \left(i\omega\tau_{GdH} + \frac{\tau_{GdH}}{T_{je}} \right)^{1/2} + \frac{4}{9} \left(i\omega\tau_{GdH} + \frac{\tau_{GdH}}{T_{je}} \right) + \frac{1}{9} \left(i\omega\tau_{GdH} + \frac{\tau_{GdH}}{T_{je}} \right)^{3/2}} \right] \quad j = 1, 2 \quad [22]$$

The diffusion coefficient for the diffusion of a water proton away from a Gd^{III} complex, D_{GdH} , is assumed to obey an exponential law versus the inverse of the temperature, with an activation energy E_{GdH} , as given in Eq. 23 D_{GdH}^{298} is the diffusion coefficient at 298.15 K.

$$D_{GdH} = D_{GdH}^{298} \exp\left\{\frac{E_{GdH}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad [23]$$

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