Supporting Information for:

Trends in the Stability and Dissociation Kinetics of Lanthanide(III) Complexes with Cyclen-Based Ligands Across the Lanthanide Series

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Supporting Information Summary

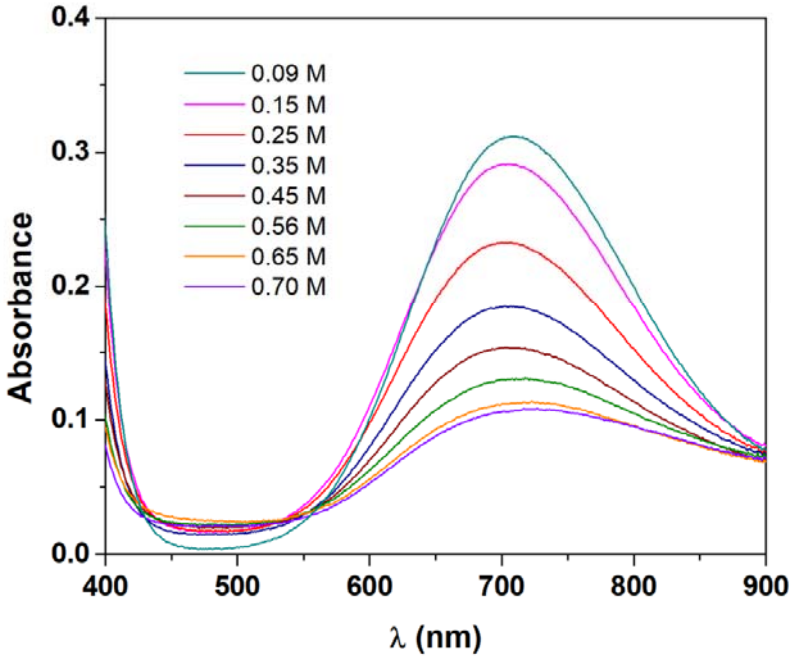

Figure S1. VIS spectra of the solutions containing nearly equimolar amounts of Cu^{2+} and 1,7-DO2APA^{3-} (c_{Cu2+}=2.50 mM, c_{Lig}=2.51 mM) as a function of acid concentration (93.2, 149.1, 251.7, 354.2, 447.4, 559.3, 652.5 and 699.1 mM in 1.0 M NaCl).

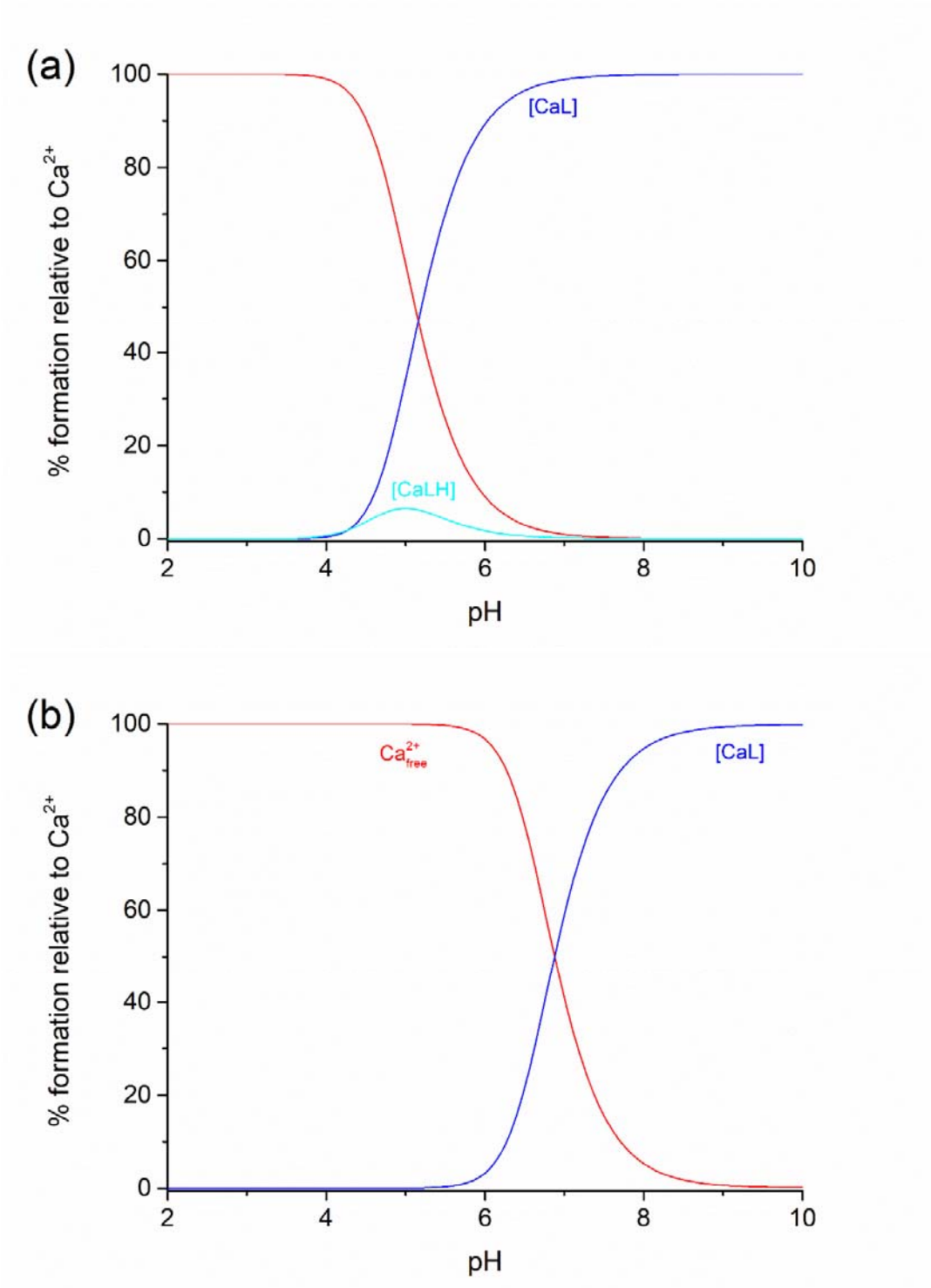

Figure S2. Speciation diagrams calculated for the Ca^{2+}:1,4-DO2APA^{3-} (a) and Ca^{2+}:1,7-DO2APA^{3-} (b) systems ($c_{Ca^{2+}}$=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl, 25 ºC, 0.15 M NaCl).

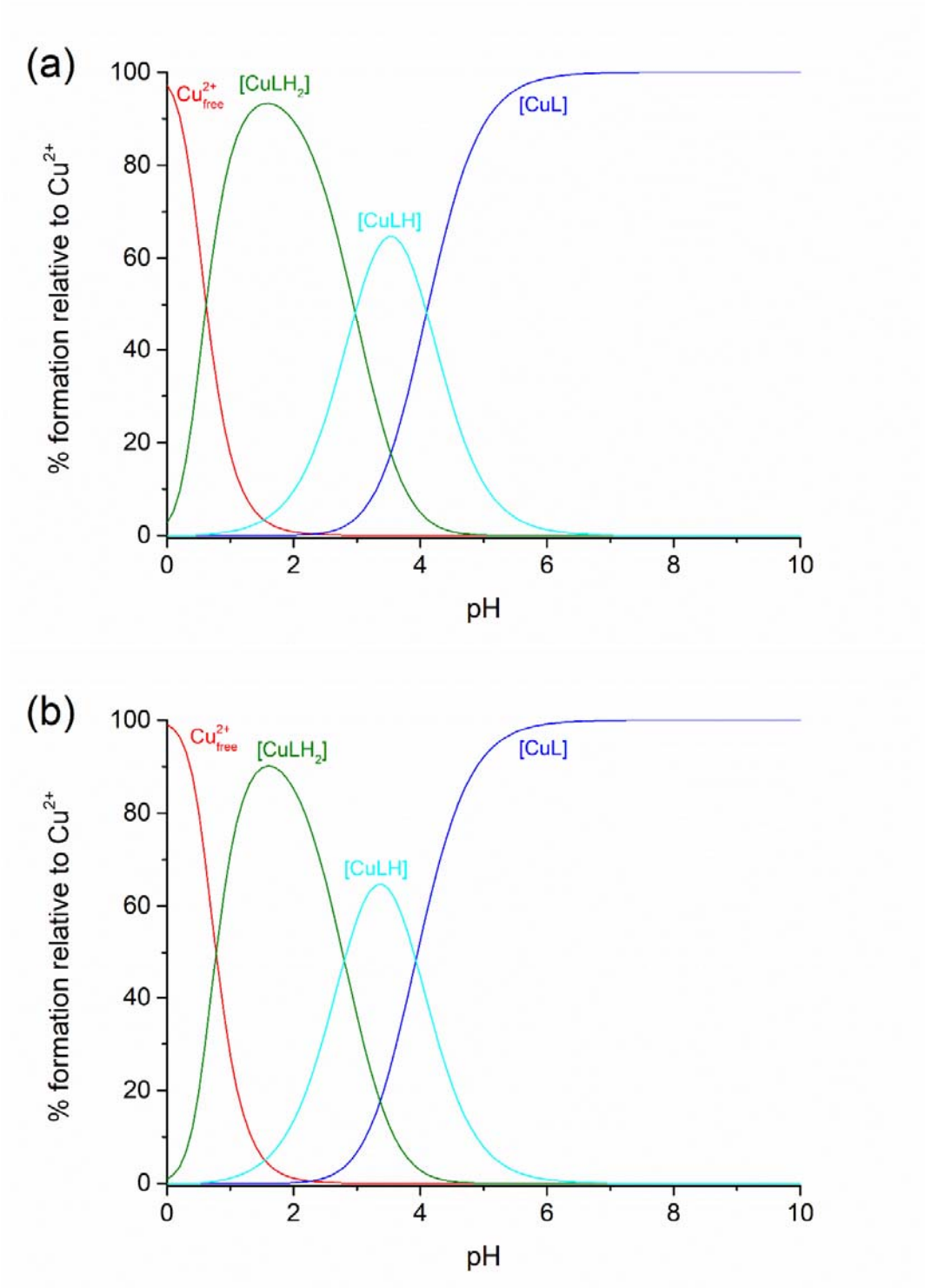

Figure S3. Speciation diagrams calculated for the Cu^{2+}:1,4-DO2APA^{3-} (a) and Cu^{2+}:1,7-DO2APA^{3-} (b) systems (c_{Cu2+}=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl).

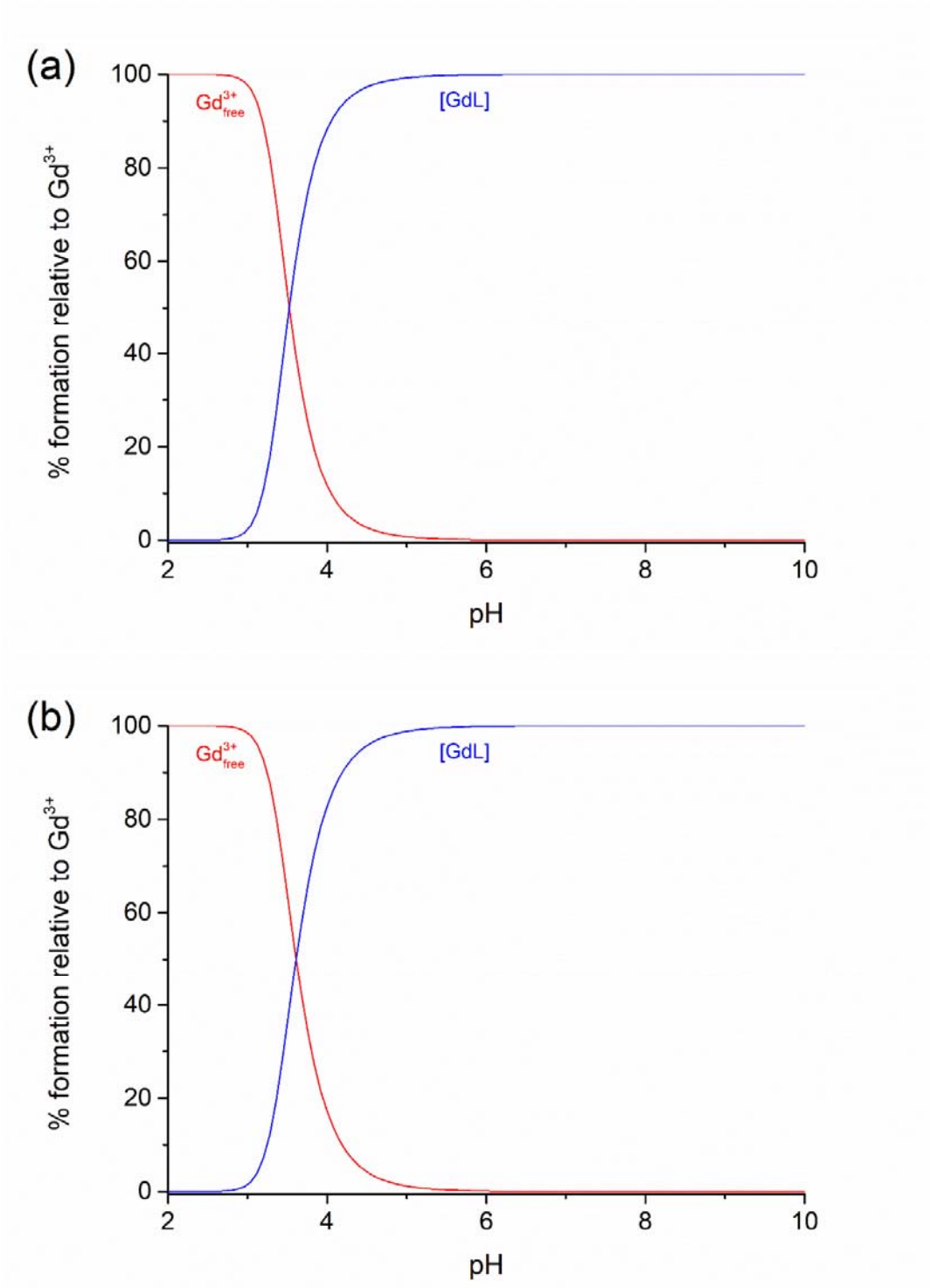

Figure S4. Speciation diagrams calculated for the Gd^{3+}:1,4-DO2APA^{3-} (a) and Gd^{3+}:1,7-DO2APA^{3-} (b) systems ($c_{Gd^{3+}}$=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl).

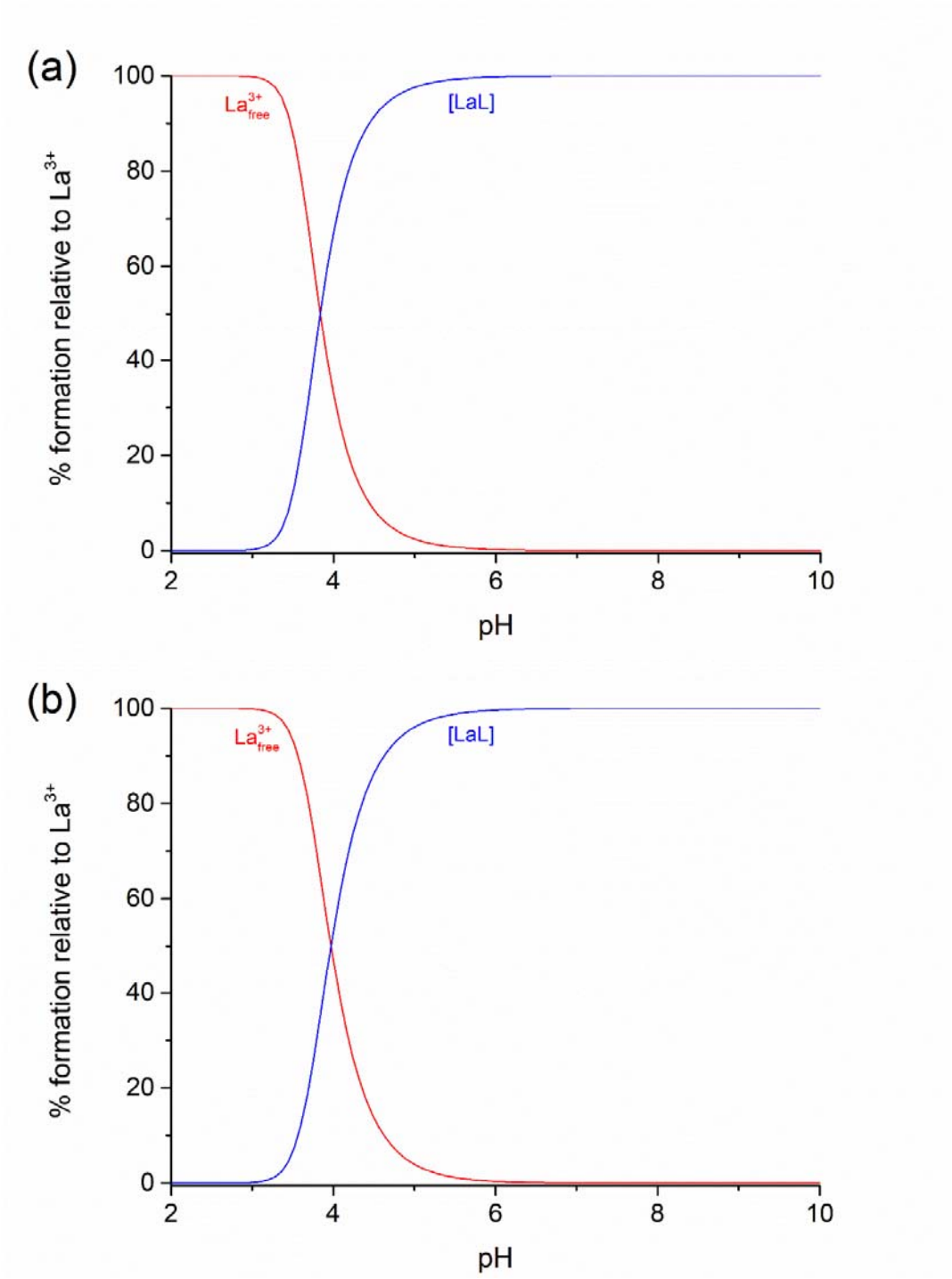

Figure S5. Speciation diagrams calculated for the La^{3+}:1,4-DO2APA^{3-} (a) and La^{3+}:1,7-DO2APA^{3-} (b) systems (c_{La3+}=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl).

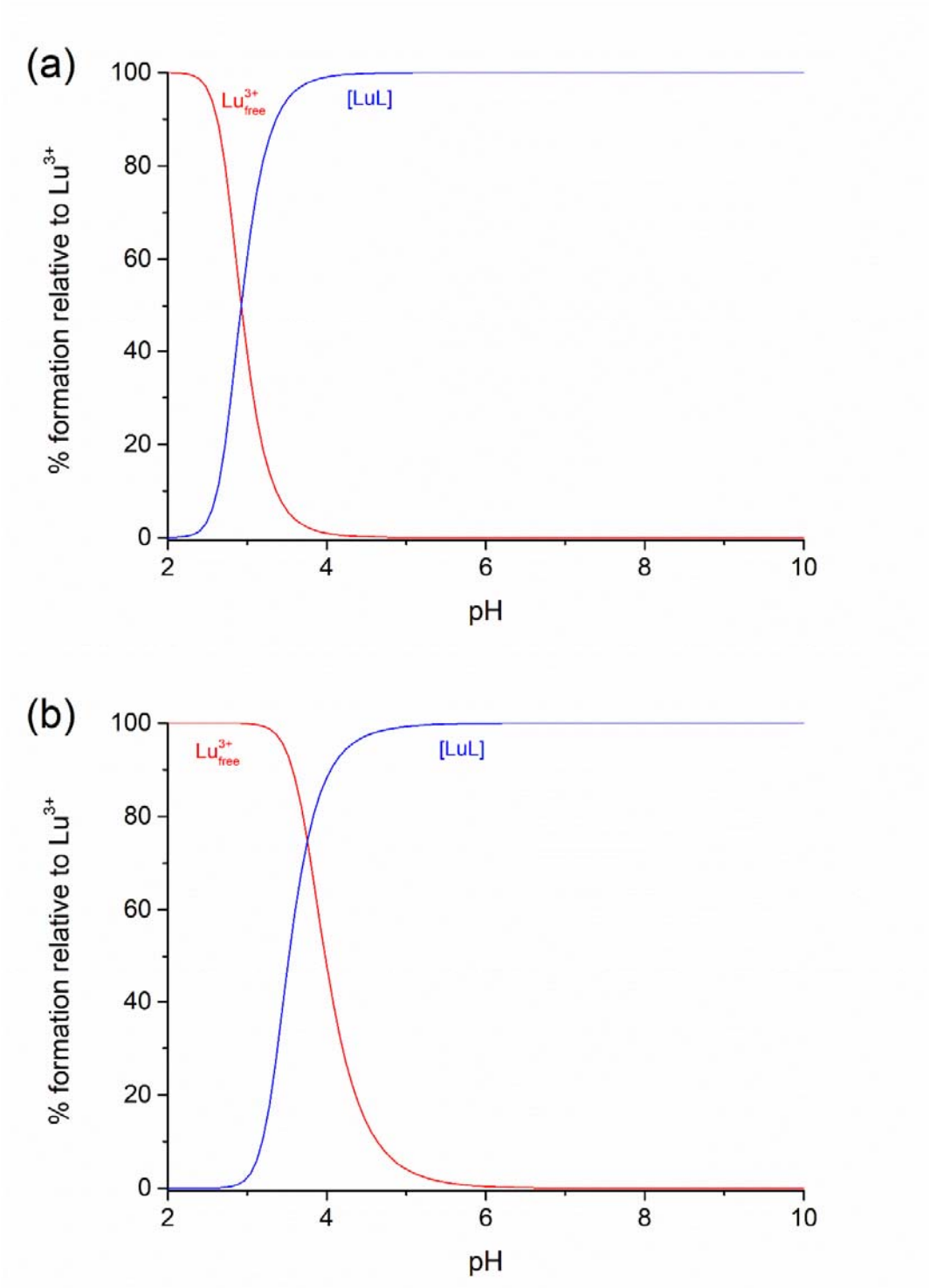

Figure S6. Speciation diagrams calculated for the Lu^{3+}:1,4-DO2APA^{3-} (a) and Lu^{3+}:1,7-DO2APA^{3-} (b) systems (c_{Lu3+}=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl).

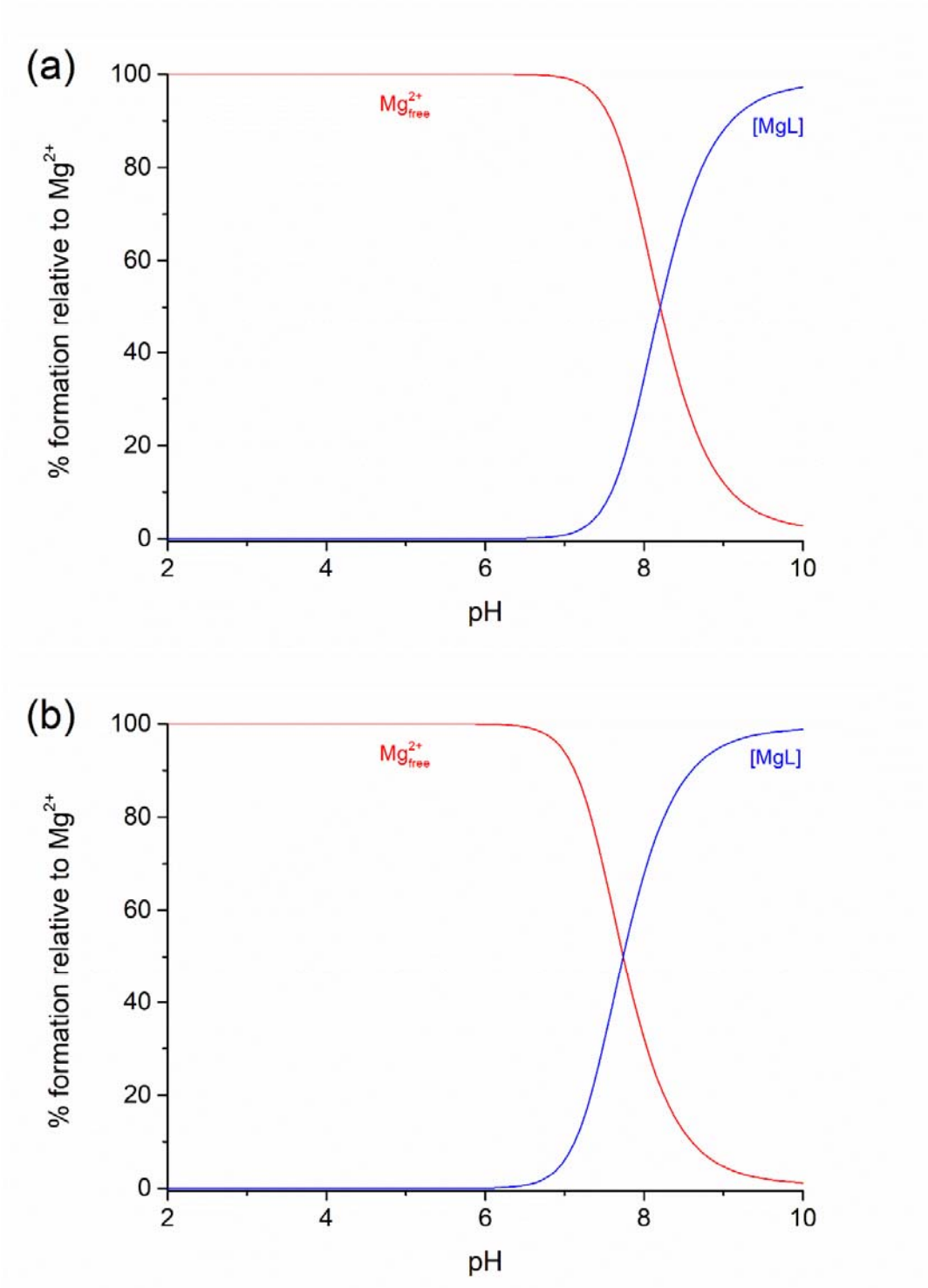

Figure S7. Speciation diagrams calculated for the Mg^{2+}:1,4-DO2APA^{3-} (a) and Mg^{2+}:1,7-DO2APA^{3-} (b) systems ($c_{Mg^{2+}}$=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl).

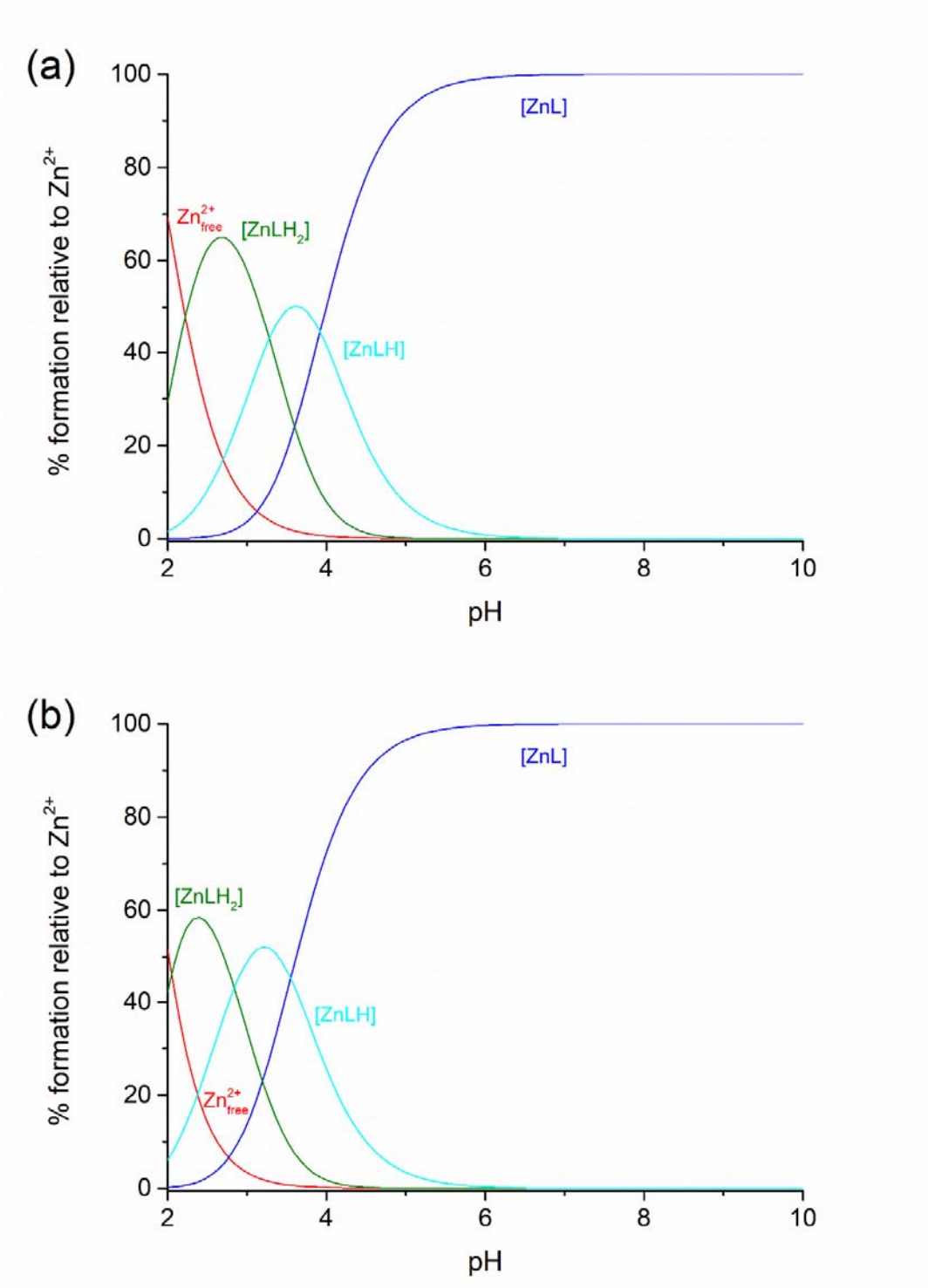

Figure S8. Speciation diagrams calculated for the Zn^{2+}:1,4-DO2APA^{3-} (a) and Zn^{2+}:1,7-DO2APA^{3-} (b) systems (c_{Zn2+}=c_{Lig}=1.0 mM, 25 ºC, 0.15 M NaCl).

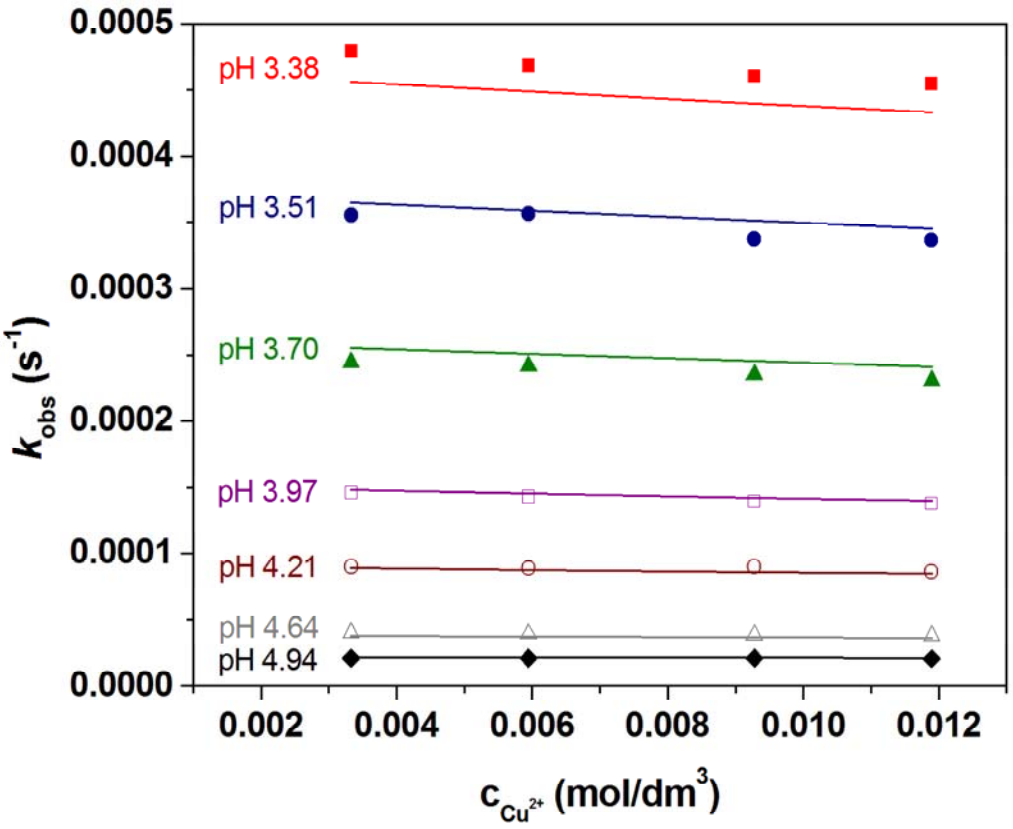

Figure S9. Pseudo-first-order rate constants of dissociation of the [Gd(1,4-DO2APA)] complex (2.9×10^{-4} M) as a function of Cu^{2+} ion concentration obtained at different pH values.

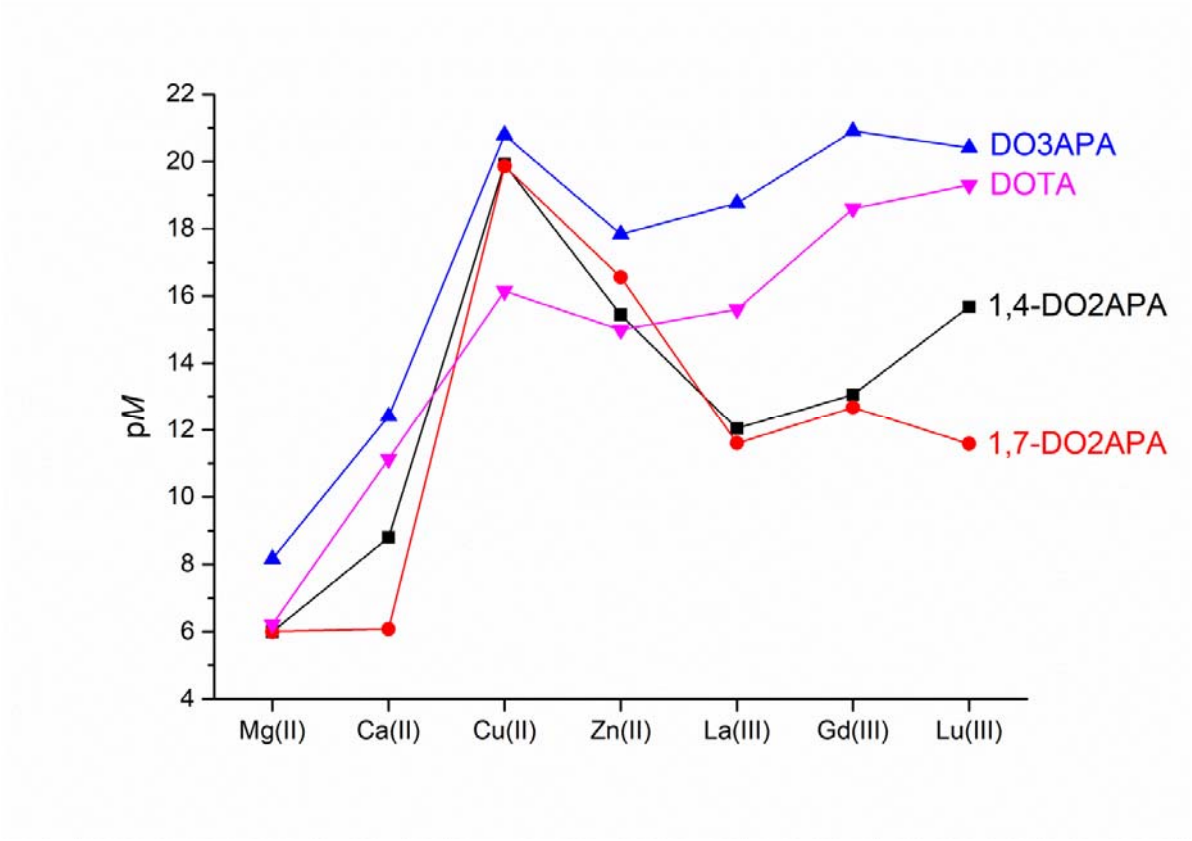

Figure S10. Plot of the pM values calculated for the complexes investigated in this work and related systems (pM are defined as $-\log[M]_{free}$ for $[M]_{tot} = 1\mu M$ and $[L]_{tot} = 10\ \mu M$).

Table S1. Calculated bond distances (Å), Electron Densities (ρ_{BCP}, au) and Laplacian of the electron densities ($\nabla^2\rho_{BCP}$) at the Bond Critical Points (BCP) of [Ln(1,4-DO2APA)(H_2O)]·$2H_2O$ (Ln = La, Gd), [Yb(1,4-DO2APA)] and [Ln(1,7-DO2APA)(H_2O)]·$2H_2O$ (Ln = La, Gd, Yb) complexes.

	[La(1,4-DO2APA)(H_2O)]·$2H_2O$			[La(1,7-DO2APA)(H_2O)]·$2H_2O$		
	Dist. / Å	ρ_{BCP}	$\nabla^2\rho_{BCP}$	Dist. / Å	ρ_{BCP}	$\nabla^2\rho_{BCP}$
N1	2.837	0.02752338	0.0832050	2.847	0.02792989	0.0830502
N2	2.920	0.0236401	0.0706025	2.842	0.027788	0.0846408
N3	2.894	0.0251662	0.07475026	2.784	0.0313689	0.0965942
N4	2.844	0.0275234	0.0832050	2.869	0.0267946	0.0794231
N5	2.776	0.0297587	0.101439	2.558	0.034166	0.118171
O1	2.433	0.0517792	0.214607	2.471	0.0473895	0.2007997
O2	2.498	0.0448113	0.184735	2.513	0.0440699	0.181166
O3	2.535	0.041089	0.168724	2.515	0.0435705	0.175213
O1w	2.621	0.0348560	0.134331	2.598	0.0382708	0.141548
	[Gd(1,4-DO2APA)(H_2O)]·$2H_2O$			[Gd(1,7-DO2APA)(H_2O)]·$2H_2O$		
	Dist. / Å	ρ_{BCP}	∇_{BCP}	Dist. / Å	ρ_{BCP}	∇_{BCP}
N1	2.723	0.0293270	0.0938556	2.718	0.0298887	0.09447919
N2	2.783	0.02571104	0.0807451	2.753	0.02747341	0.08717076
N3	2.839	0.0232795	0.0697569	2.726	0.0293295	0.0930299
N4	2.772	0.0265157	0.082573	2.765	0.02720199	0.0840305
N5	2.594	0.03558967	0.1320789	2.558	0.0381876	0.1433595
O1	2.322	0.055531	0.254203	2.350	0.0514536	0.2383966
O2	2.360	0.05021481	0.231004	2.394	0.04700327	0.212644
O3	2.426	0.0435386	0.192338	2.437	0.0428661	0.18303587
O1w	2.554	0.03350747	0.1325180	2.473	0.04101868	0.168487
	[Yb(1,4-DO2APA)] [a]			[Yb(1,7-DO2APA)(H_2O)]·$2H_2O$		
	Dist. / Å	ρ_{BCP}	∇_{BCP}	Dist. / Å	ρ_{BCP}	∇_{BCP}
N1	2.576	0.0352872	0.118595	2.653	0.03005709	0.0957879
N2	2.623	0.0317077	0.1053925	2.715	0.0262230	0.08262397
N3	2.651	0.0303518	0.09680357	2.690	0.0278973	0.0875377
N4	2.591	0.0341603	0.113992	2.734	0.0255916	0.0776646
N5	2.461	0.04196239	0.163681	2.490	0.0389719	0.1490742
O1	2.237	0.0595699	0.286277	2.278	0.0534523	0.2561475
O2	2.255	0.05715818	0.274277	2.320	0.0487189	0.227996
O3	2.285	0.0531969	0.2514386	2.385	0.0423149	0.1830415
O1w				2.390	0.0430668	0.1842383

[a] Calculations performed on the [Yb(1,4-DO2APA)]·$3H_2O$ provide very similar results, with ρ_{BCP} values of 0.0603, 0.05685 and 0.05098 au for the Yb-O1, Yb-O2 and Yb-O3 bonds, respectively.

Table S2. Optimised Cartesian coordinates (Å) obtained with DFT calculations for the [La(1,4-DO2APA)(H_2O)]·2H_2O system (0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	7	0	-0.988124	-2.358955	-0.429876
2	6	0	-0.054286	-3.237134	-1.191240
3	6	0	1.386524	-3.156607	-0.702625
4	7	0	1.993967	-1.810704	-0.830394
5	6	0	3.244750	-1.761030	-0.027351
6	6	0	2.981941	-1.621215	1.469704
7	7	0	2.204466	-0.412030	1.858153
8	6	0	1.565677	-0.646895	3.183589
9	6	0	0.354604	-1.574730	3.098937
10	7	0	-0.779367	-0.995518	2.333100
11	6	0	-1.758392	-2.059255	1.984779
12	6	0	-1.296295	-3.004602	0.877197
13	6	0	2.297570	-1.508756	-2.249128
14	6	0	1.090508	-1.019693	-3.071437
15	8	0	1.089747	-1.221008	-4.293481
16	8	0	0.178886	-0.371229	-2.413325
17	6	0	3.084782	0.780414	1.919291
18	6	0	3.295975	1.462525	0.558131
19	8	0	4.115367	2.408531	0.500809
20	8	0	2.571603	1.057088	-0.414839
21	6	0	-1.475135	-0.002554	3.185170
22	1	0	2.757648	-2.368270	-2.756746
23	1	0	3.017200	-0.683730	-2.257934
24	1	0	4.059406	0.545425	2.370162
25	1	0	2.608002	1.527190	2.563160
26	1	0	-2.320994	0.411290	2.637552
27	1	0	-1.835380	-0.469059	4.115061
28	1	0	-0.106061	-2.950217	-2.242719
29	1	0	-0.381631	-4.286806	-1.132416
30	1	0	1.980377	-3.896442	-1.263830
31	1	0	1.437638	-3.451804	0.348540
32	1	0	3.843617	-2.672395	-0.183441
33	1	0	3.831886	-0.916476	-0.384640
34	1	0	3.949570	-1.624083	1.994706
35	1	0	2.437262	-2.497481	1.827313
36	1	0	2.287213	-1.074292	3.896098
37	1	0	1.262068	0.324285	3.582488
38	1	0	0.641632	-2.516705	2.626781
39	1	0	0.030355	-1.822744	4.122181
40	1	0	-2.686038	-1.563330	1.695339
41	1	0	-1.986590	-2.671202	2.872883
42	1	0	-0.397027	-3.531855	1.203380
43	1	0	-2.070842	-3.775442	0.743523
44	57	0	0.225796	0.271947	-0.067067
45	6	0	-2.211391	-2.202183	-1.254373
46	1	0	-1.874836	-1.948467	-2.265509
47	1	0	-2.772407	-3.146820	-1.313215
48	6	0	-3.124409	-1.085925	-0.809451
49	6	0	-4.514927	-1.167104	-0.953979
50	6	0	-3.279900	1.093770	-0.027319
51	6	0	-5.293804	-0.053267	-0.636789
52	1	0	-4.970601	-2.083908	-1.312692
53	6	0	-4.666699	1.106601	-0.178389
54	1	0	-6.372954	-0.091589	-0.745490
55	1	0	-5.219605	2.004113	0.071774

56	7	0	-2.525573	0.021551	-0.340107
57	6	0	-2.510619	2.291189	0.492542
58	8	0	-3.079996	3.409529	0.497402
59	8	0	-1.311995	2.057113	0.867498
60	1	0	-0.803254	0.818654	3.437441
61	8	0	0.419675	2.599963	-1.254752
62	1	0	-0.080840	3.371422	-0.879908
63	1	0	1.343545	2.933413	-1.405235
64	8	0	2.915957	3.737659	-1.593437
65	8	0	-0.883599	4.831047	-0.293282
66	1	0	2.835048	4.642262	-1.256760
67	1	0	3.439636	3.260058	-0.896177
68	1	0	-1.688772	4.423988	0.119992
69	1	0	-1.226253	5.298775	-1.069254

E(RTPSSh) = -1765.4330318 Hartree
Zero-point correction = 0.566665 (/Particle)
Thermal correction to Energy = 0.603155
Thermal correction to Enthalpy = 0.604099
Thermal correction to Gibbs Free Energy = 0.501653
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Sum of electronic and thermal Energies = -1764.829877
Sum of electronic and thermal Enthalpies = -1764.828932
Sum of electronic and thermal Free Energies = -1764.931379

Table S3. Optimised Cartesian coordinates (Å) obtained with DFT calculations for the [La(1,7-DO2APA)(H_2O)]·2H_2O system (0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	7	0	0.348358	-1.218903	-2.225744
2	6	0	-0.623901	-2.343135	-2.402208
3	6	0	-2.070129	-1.983606	-2.078791
4	7	0	-2.317812	-1.691455	-0.641279
5	6	0	-3.617409	-0.977274	-0.483137
6	6	0	-3.600654	0.453292	-1.017919
7	7	0	-2.654652	1.338044	-0.288818
8	6	0	-2.336872	2.538543	-1.106296
9	6	0	-1.347156	2.265435	-2.234545
10	7	0	-0.002800	1.809015	-1.782371
11	6	0	0.722254	1.183391	-2.926119
12	6	0	0.175923	-0.196279	-3.297474
13	6	0	-2.333048	-2.947672	0.165094
14	6	0	-1.110357	-3.102759	1.082939
15	8	0	-1.213692	-3.821693	2.098667
16	8	0	-0.051377	-2.458177	0.740392
17	6	0	0.768827	2.963477	-1.255903
18	6	0	0.417317	3.359036	0.191775
19	8	0	0.593400	4.527641	0.549285
20	8	0	0.005386	2.384859	0.950120
21	1	0	-2.384777	-3.826001	-0.492260
22	1	0	-3.228819	-2.972949	0.789256
23	1	0	1.829016	2.686514	-1.245431
24	1	0	0.664569	3.842897	-1.904830
25	1	0	-0.299227	-3.146016	-1.736971
26	1	0	-0.585061	-2.722294	-3.434274
27	1	0	-2.706766	-2.819502	-2.406698
28	1	0	-2.379620	-1.116499	-2.664577
29	1	0	-4.427424	-1.527757	-0.985660
30	1	0	-3.846469	-0.964115	0.585379
31	1	0	-4.623034	0.856627	-0.951694
32	1	0	-3.338720	0.461731	-2.078176
33	1	0	-3.255566	2.951269	-1.552288
34	1	0	-1.945019	3.300334	-0.430227
35	1	0	-1.758290	1.504637	-2.900926
36	1	0	-1.241813	3.181635	-2.835070
37	1	0	1.775915	1.102855	-2.646024
38	1	0	0.673427	1.828141	-3.816416
39	1	0	-0.887687	-0.123505	-3.530287
40	1	0	0.671076	-0.528145	-4.221509
41	6	0	1.722070	-1.792455	-2.300436
42	1	0	1.674773	-2.805737	-1.888078
43	1	0	2.047800	-1.887211	-3.344745
44	6	0	2.768123	-1.068636	-1.483985
45	6	0	4.108136	-0.996453	-1.881541
46	6	0	3.279223	-0.170163	0.600648
47	6	0	5.048395	-0.476820	-0.988708
48	1	0	4.405079	-1.348645	-2.863591
49	6	0	4.634350	-0.075430	0.282462
50	1	0	6.092368	-0.405255	-1.276674
51	1	0	5.324685	0.299937	1.028330
52	7	0	2.367881	-0.629403	-0.279038
53	6	0	2.756426	0.164022	1.990603
54	8	0	3.556599	0.570990	2.843751
55	8	0	1.487202	-0.043894	2.158856

56	6	0	-3.303309	1.803406	0.960219
57	1	0	-2.583922	2.383937	1.538549
58	1	0	-4.181827	2.427329	0.736876
59	1	0	-3.616445	0.947797	1.558597
60	8	0	-1.519171	-0.176484	2.531856
61	1	0	-1.391543	0.700613	2.990276
62	1	0	-1.025986	-0.842881	3.096626
63	8	0	0.080219	-1.939899	3.743501
64	8	0	-0.823935	2.250382	3.489693
65	1	0	0.789383	-1.493000	3.234369
66	1	0	-0.170209	-2.728620	3.205472
67	1	0	-1.491527	2.918345	3.702123
68	1	0	-0.454464	2.508650	2.602005
69	57	0	-0.203106	-0.032378	0.296671

E(RTPSSh) = -1765.431957 Hartree
Zero-point correction = 0.567510
Thermal correction to Energy = 0.603661
Thermal correction to Enthalpy = 0.604605
Thermal correction to Gibbs Free Energy = 0.502671
Sum of electronic and zero-point Energies = -1764.864447
Sum of electronic and thermal Energies = -1764.828296
Sum of electronic and thermal Enthalpies = -1764.827352
Sum of electronic and thermal Free Energies = -1764.929286

Table S4. Optimised Cartesian coordinates (Å) obtained with DFT calculations for the [Gd(1,4-DO2APA)(H_2O)]·2H_2O system (0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	7	0	-0.917942	-2.356764	-0.438020
2	6	0	0.059910	-3.246388	-1.129149
3	6	0	1.466755	-3.125678	-0.556593
4	7	0	2.032788	-1.759939	-0.670863
5	6	0	3.235817	-1.646700	0.196319
6	6	0	2.881025	-1.468582	1.669244
7	7	0	2.030366	-0.281723	1.959638
8	6	0	1.325631	-0.489854	3.254081
9	6	0	0.160273	-1.468396	3.125186
10	7	0	-0.941621	-0.949304	2.272083
11	6	0	-1.863540	-2.056311	1.904150
12	6	0	-1.306688	-3.003300	0.847507
13	6	0	2.399891	-1.471642	-2.078207
14	6	0	1.212897	-1.028661	-2.948403
15	8	0	1.262435	-1.221472	-4.170254
16	8	0	0.251586	-0.426089	-2.318240
17	6	0	2.851453	0.954091	2.003346
18	6	0	3.060205	1.574811	0.614121
19	8	0	3.844486	2.539867	0.492190
20	8	0	2.360870	1.079826	-0.339288
21	6	0	-1.724815	0.023353	3.071222
22	1	0	2.903380	-2.326955	-2.549394
23	1	0	3.096431	-0.627891	-2.068315
24	1	0	3.823351	0.784195	2.486853
25	1	0	2.320597	1.701994	2.601590
26	1	0	-2.572720	0.375270	2.484567
27	1	0	-2.099393	-0.448437	3.992680
28	1	0	0.063836	-2.989629	-2.189368
29	1	0	-0.260055	-4.296680	-1.057638
30	1	0	2.115539	-3.853080	-1.069964
31	1	0	1.463002	-3.402851	0.500758
32	1	0	3.870393	-2.541299	0.101219
33	1	0	3.816759	-0.795160	-0.155698
34	1	0	3.813736	-1.409610	2.250440
35	1	0	2.351763	-2.354590	2.026094
36	1	0	2.018000	-0.860224	4.024759
37	1	0	0.958855	0.482034	3.593308
38	1	0	0.511796	-2.411781	2.701634
39	1	0	-0.220556	-1.700144	4.132361
40	1	0	-2.792625	-1.602893	1.554648
41	1	0	-2.117197	-2.654519	2.794356
42	1	0	-0.420874	-3.506535	1.241650
43	1	0	-2.051927	-3.791642	0.662943
44	64	0	0.201364	0.165698	-0.075290
45	6	0	-2.091878	-2.188136	-1.333964
46	1	0	-1.695555	-1.968442	-2.330606
47	1	0	-2.679214	-3.115492	-1.397127
48	6	0	-2.984233	-1.033234	-0.949035
49	6	0	-4.368360	-1.052817	-1.159640
50	6	0	-3.093027	1.131896	-0.107821
51	6	0	-5.115778	0.084256	-0.849097
52	1	0	-4.844161	-1.943084	-1.556657
53	6	0	-4.469429	1.202482	-0.317496
54	1	0	-6.189112	0.092359	-1.008976
55	1	0	-5.001582	2.107653	-0.050712

56	7	0	-2.367344	0.044371	-0.435666
57	6	0	-2.301452	2.258652	0.523302
58	8	0	-2.835800	3.388466	0.616368
59	8	0	-1.117936	1.951382	0.901388
60	1	0	-1.111539	0.885310	3.331668
61	8	0	0.200777	2.328560	-1.434296
62	1	0	-0.125468	3.132423	-0.952956
63	1	0	1.129424	2.576231	-1.679209
64	8	0	2.723987	3.430706	-1.947431
65	8	0	-0.597136	4.700280	-0.228964
66	1	0	2.584584	4.377198	-1.795935
67	1	0	3.193492	3.116712	-1.133988
68	1	0	-1.410557	4.370299	0.229846
69	1	0	-0.937519	5.246850	-0.952741

E(RTPSSh) = -1769.7412537 Hartree
Zero-point correction = 0.567662
Thermal correction to Energy = 0.603848
Thermal correction to Enthalpy = 0.604793
Thermal correction to Gibbs Free Energy = 0.503672
Sum of electronic and zero-point Energies = -1769.173592
Sum of electronic and thermal Energies = -1769.137405
Sum of electronic and thermal Enthalpies = -1769.136461
Sum of electronic and thermal Free Energies = -1769.237581

Table S5. Optimised Cartesian coordinates (Å) obtained with DFT calculations for the [Gd(1,7-DO2APA)(H_2O)]·2H_2O system (0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	7	0	0.083849	-1.516634	-2.029671
2	6	0	-1.070545	-2.459868	-2.108894
3	6	0	-2.414535	-1.784856	-1.866032
4	7	0	-2.565988	-1.224375	-0.496054
5	6	0	-3.689354	-0.244559	-0.476508
6	6	0	-3.336627	1.067548	-1.168236
7	7	0	-2.229529	1.784742	-0.481293
8	6	0	-1.632805	2.801203	-1.388214
9	6	0	-0.726750	2.208472	-2.459606
10	7	0	0.454449	1.461101	-1.938712
11	6	0	0.983011	0.600155	-3.032765
12	6	0	0.126754	-0.646244	-3.236745
13	6	0	-2.824623	-2.309171	0.492292
14	6	0	-1.587898	-2.727244	1.299783
15	8	0	-1.757005	-3.462909	2.292360
16	8	0	-0.454659	-2.248114	0.921122
17	6	0	1.494931	2.415364	-1.484557
18	6	0	1.214230	2.996126	-0.089993
19	8	0	1.662290	4.105847	0.210997
20	8	0	0.542750	2.206568	0.697436
21	1	0	-3.249988	-3.196330	0.003641
22	1	0	-3.567990	-1.963459	1.214091
23	1	0	2.444527	1.873686	-1.411612
24	1	0	1.633273	3.234166	-2.202682
25	1	0	-0.908076	-3.228330	-1.351133
26	1	0	-1.099134	-2.955070	-3.090730
27	1	0	-3.209286	-2.521084	-2.058625
28	1	0	-2.564005	-0.976530	-2.584236
29	1	0	-4.588251	-0.669538	-0.947234
30	1	0	-3.926539	-0.050376	0.571765
31	1	0	-4.235588	1.701586	-1.203605
32	1	0	-3.046145	0.887056	-2.205603
33	1	0	-2.427403	3.372751	-1.893074
34	1	0	-1.080781	3.508677	-0.767344
35	1	0	-1.303452	1.526661	-3.087958
36	1	0	-0.385292	3.022961	-3.115887
37	1	0	2.005744	0.316402	-2.774974
38	1	0	1.033378	1.157600	-3.979618
39	1	0	-0.896268	-0.358877	-3.486882
40	1	0	0.512490	-1.208371	-4.099715
41	6	0	1.338725	-2.311351	-1.959277
42	1	0	1.124638	-3.209191	-1.370201
43	1	0	1.652335	-2.643393	-2.957947
44	6	0	2.470001	-1.610984	-1.244791
45	6	0	3.815773	-1.808621	-1.573783
46	6	0	3.054386	-0.447610	0.683519
47	6	0	4.798426	-1.263856	-0.743743
48	1	0	4.082462	-2.382254	-2.454830
49	6	0	4.415805	-0.591919	0.419382
50	1	0	5.848470	-1.390769	-0.986938
51	1	0	5.135248	-0.199681	1.128231
52	7	0	2.108797	-0.899095	-0.164158
53	6	0	2.527780	0.095374	2.002018
54	8	0	3.325552	0.581747	2.814896
55	8	0	1.252723	-0.066422	2.161860

56	6	0	-2.791717	2.514706	0.680897
57	1	0	-1.975955	2.976463	1.236722
58	1	0	-3.494041	3.292877	0.347395
59	1	0	-3.312100	1.822343	1.341876
60	8	0	-1.589119	0.285385	2.307498
61	1	0	-1.297083	1.153913	2.705132
62	1	0	-1.255846	-0.399670	2.961404
63	8	0	-0.383764	-1.533562	3.864613
64	8	0	-0.396173	2.543989	3.185303
65	1	0	0.403224	-1.232371	3.359114
66	1	0	-0.672873	-2.361383	3.418345
67	1	0	-0.855532	3.391167	3.275791
68	1	0	0.087446	2.590147	2.316977
69	64	0	-0.252863	-0.005909	0.246912

E(RTPSSh) = -1769.7458379 Hartree
Zero-point correction = 0.568350
Thermal correction to Energy = 0.604124
Thermal correction to Enthalpy = 0.605068
Thermal correction to Gibbs Free Energy = 0.504950
Sum of electronic and zero-point Energies = -1769.177488
Sum of electronic and thermal Energies = -1769.141714
Sum of electronic and thermal Enthalpies = -1769.140770
Sum of electronic and thermal Free Energies = -1769.240888

Table S6. Optimised Cartesian coordinates (Å) obtained with DFT calculations for the [Yb(1,4-DO2APA)(H_2O)]·2H_2O system (0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	7	0	-0.359115	-2.572392	-0.011558
2	6	0	-1.685231	-3.003622	-0.549683
3	6	0	-2.829704	-2.133715	-0.025548
4	7	0	-2.692821	-0.699957	-0.395645
5	6	0	-3.571131	0.155123	0.449442
6	6	0	-3.002813	0.374106	1.845597
7	7	0	-1.645334	0.995535	1.865281
8	6	0	-1.021597	0.720842	3.192878
9	6	0	-0.511052	-0.711126	3.306095
10	7	0	0.602346	-0.976234	2.361851
11	6	0	0.825318	-2.435750	2.223436
12	6	0	-0.225269	-3.125425	1.366382
13	6	0	-3.039841	-0.508157	-1.825411
14	6	0	-1.890861	-0.864087	-2.775448
15	8	0	-2.141957	-1.183118	-3.942335
16	8	0	-0.701221	-0.741059	-2.262301
17	6	0	-1.729205	2.466044	1.645440
18	6	0	-1.592732	2.879866	0.174837
19	8	0	-1.597822	4.095179	-0.099253
20	8	0	-1.430093	1.929674	-0.677819
21	6	0	1.838747	-0.397906	2.936621
22	1	0	-3.943713	-1.067205	-2.100904
23	1	0	-3.236887	0.557260	-1.978247
24	1	0	-2.657546	2.882820	2.059185
25	1	0	-0.902433	2.944606	2.177088
26	1	0	2.680804	-0.605199	2.275407
27	1	0	2.049984	-0.841003	3.922108
28	1	0	-1.643508	-2.960426	-1.638034
29	1	0	-1.888076	-4.049275	-0.277558
30	1	0	-3.779527	-2.537584	-0.407050
31	1	0	-2.877282	-2.198961	1.064509
32	1	0	-4.574803	-0.284700	0.544740
33	1	0	-3.676028	1.112576	-0.062043
34	1	0	-3.704984	0.997319	2.418410
35	1	0	-2.939598	-0.581982	2.369590
36	1	0	-1.736513	0.918196	4.004492
37	1	0	-0.190023	1.417541	3.317108
38	1	0	-1.319170	-1.417425	3.101893
39	1	0	-0.189297	-0.894362	4.343428
40	1	0	1.818399	-2.576917	1.791164
41	1	0	0.838065	-2.924754	3.210808
42	1	0	-1.201971	-3.042946	1.848305
43	1	0	0.007668	-4.199372	1.317928
44	70	0	-0.230731	0.071480	-0.162486
45	6	0	0.730884	-3.077433	-0.895562
46	1	0	0.396751	-2.927633	-1.927003
47	1	0	0.899538	-4.152420	-0.744424
48	6	0	2.029828	-2.313230	-0.731663
49	6	0	3.291370	-2.878003	-0.956754
50	6	0	2.990549	-0.232246	-0.265387
51	6	0	4.420795	-2.064038	-0.844956
52	1	0	3.383358	-3.928701	-1.209285
53	6	0	4.276096	-0.717432	-0.495188
54	1	0	5.407972	-2.480733	-1.016987
55	1	0	5.126253	-0.054955	-0.385361

56	7	0	1.906351	-1.019524	-0.400321
57	6	0	2.696732	1.190948	0.184415
58	8	0	3.627966	2.025340	0.138729
59	8	0	1.501908	1.410888	0.599608
60	1	0	1.743035	0.681777	3.039716
61	8	0	0.939435	1.232022	-2.019849
62	1	0	0.416009	0.833327	-2.736316
63	1	0	0.754107	2.223181	-2.016985
64	8	0	0.585191	3.879841	-1.945511
65	8	0	2.600670	4.522806	-0.189633
66	1	0	1.305184	4.154136	-1.319038
67	1	0	-0.242991	4.007708	-1.429619
68	1	0	2.977989	3.627420	0.023659
69	1	0	3.292508	4.951964	-0.714254

E(RTPSSh) = -1773.2544264 Hartree
Zero-point correction = 0.568391
Thermal correction to Energy = 0.603976
Thermal correction to Enthalpy = 0.604920
Thermal correction to Gibbs Free Energy = 0.505134
Sum of electronic and zero-point Energies = -1772.686036
Sum of electronic and thermal Energies = -1772.650450
Sum of electronic and thermal Enthalpies = -1772.649506
Sum of electronic and thermal Free Energies = -1772.749292

Table S7. Optimised Cartesian coordinates (Å) obtained with DFT calculations for the [Yb(1,7-DO2APA)(H_2O)]·2H_2O system (0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	7	0	0.036081	-1.499935	-2.026419
2	6	0	-1.109814	-2.452605	-2.080617
3	6	0	-2.444359	-1.780744	-1.791036
4	7	0	-2.530362	-1.185741	-0.428979
5	6	0	-3.662326	-0.217113	-0.390742
6	6	0	-3.322980	1.086374	-1.100458
7	7	0	-2.197252	1.790946	-0.434688
8	6	0	-1.619069	2.810220	-1.348544
9	6	0	-0.745941	2.213212	-2.441317
10	7	0	0.427696	1.439861	-1.943735
11	6	0	0.924465	0.592097	-3.061060
12	6	0	0.051815	-0.643985	-3.242785
13	6	0	-2.748920	-2.248430	0.588792
14	6	0	-1.461347	-2.736182	1.260694
15	8	0	-1.558465	-3.576972	2.175546
16	8	0	-0.363001	-2.184168	0.877210
17	6	0	1.486933	2.372815	-1.490987
18	6	0	1.226261	2.924104	-0.083345
19	8	0	1.697186	4.015325	0.248339
20	8	0	0.537383	2.128815	0.683322
21	1	0	-3.291769	-3.104979	0.166893
22	1	0	-3.371956	-1.841813	1.389239
23	1	0	2.431268	1.819813	-1.442749
24	1	0	1.623811	3.204861	-2.193924
25	1	0	-0.920060	-3.229511	-1.338504
26	1	0	-1.165944	-2.938141	-3.066001
27	1	0	-3.245543	-2.522157	-1.927081
28	1	0	-2.629562	-0.989462	-2.520133
29	1	0	-4.567266	-0.653924	-0.837567
30	1	0	-3.876313	-0.014111	0.660421
31	1	0	-4.216906	1.728029	-1.122543
32	1	0	-3.052278	0.896367	-2.141734
33	1	0	-2.422634	3.389269	-1.830064
34	1	0	-1.046986	3.511597	-0.738809
35	1	0	-1.345809	1.546713	-3.064358
36	1	0	-0.399497	3.025768	-3.097240
37	1	0	1.952522	0.299958	-2.836104
38	1	0	0.950862	1.159078	-4.002888
39	1	0	-0.974920	-0.347096	-3.465883
40	1	0	0.408622	-1.217041	-4.110969
41	6	0	1.299322	-2.279792	-1.971933
42	1	0	1.104591	-3.177400	-1.375825
43	1	0	1.604608	-2.611424	-2.973302
44	6	0	2.427669	-1.563220	-1.271667
45	6	0	3.774070	-1.769069	-1.593796
46	6	0	3.009153	-0.391001	0.649194
47	6	0	4.756099	-1.219541	-0.766820
48	1	0	4.040722	-2.355024	-2.466710
49	6	0	4.370623	-0.542478	0.392543
50	1	0	5.806534	-1.351990	-1.005284
51	1	0	5.087668	-0.156147	1.107058
52	7	0	2.063666	-0.834825	-0.203415
53	6	0	2.475204	0.122008	1.974413
54	8	0	3.265998	0.583203	2.808839
55	8	0	1.201175	-0.053712	2.118404

56	6	0	-2.733852	2.524110	0.737642
57	1	0	-1.904505	2.976211	1.280510
58	1	0	-3.431976	3.310431	0.414746
59	1	0	-3.252330	1.837478	1.405530
60	8	0	-1.546181	0.252027	2.211111
61	1	0	-1.247266	1.107333	2.633535
62	1	0	-1.232127	-0.442165	2.863696
63	8	0	-0.365861	-1.551271	3.825413
64	8	0	-0.339164	2.458934	3.196532
65	1	0	0.415877	-1.214806	3.331619
66	1	0	-0.590465	-2.400178	3.385973
67	1	0	-0.787269	3.312355	3.285710
68	1	0	0.142497	2.499153	2.327259
69	70	0	-0.244937	-0.005876	0.222848

E(RTPSSh) = -1773.2478177 Hartree
Zero-point correction = 0.569448
Thermal correction to Energy = 0.604810
Thermal correction to Enthalpy = 0.605754
Thermal correction to Gibbs Free Energy = 0.507154
Sum of electronic and zero-point Energies = -1772.678369
Sum of electronic and thermal Energies = -1772.643008
Sum of electronic and thermal Enthalpies = -1772.642064
Sum of electronic and thermal Free Energies = -1772.740664