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Supporting Materials of

Hydration properties of lanthanoid(III) carbonates complexes in liquid water by polarizable molecular dynamics simulations

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Table S1. Distances (in Å) and angles (in degrees) for tri-carbonate complexes as obtained by CPMD simulations with different initial numbers of water molecules in first shell (0 and 4 as noted in parenthesis), B3LYP optimization from Ref. 17, PBE/COSMO optimization with 4 and 2 water molecules for La and Lu respectively and Pol and Upol force fields. Also results obtained by tuning K_r and K_θ are reported.

	$C\text{-}O_C^{(n)}$	$C\text{-}O_C^{(f)}$	$O_C^{(n)}CO_C^{(n)}$	$O_C^{(n)}LnO_C^{(n)}$	$LnCO_C^{(f)}$	CLnC
$[La(\eta^2\text{-}CO_3)_3]^{3-}$						
CPMD(0)	1.33	1.27	115.5	53.2	171.3	(see Fig. S1)
CPMD(4)	1.32	1.28	116.1	50.9	167.7	(see Fig. S1)
DFT-B3LYP	1.33	1.26	114.2	53.5	180.0	120.0
PBE/COSMO(4)	1.32	1.27	115.7	52.5	176.2	126.3 112.2 108.3
PBE/COSMO(3)	1.32	1.27	116.0	52.8	177.3	126.1 120.9 110.0
Pol-ff	1.37	1.26	128.1	59.4	179.9	(see Fig. S2)
Pol-ff (K_θ = 400)	1.38	1.26	125.1	59.0	180.0	-
Pol-ff (K_r = 570)	1.36	1.27	125.8	58.3	179.9	-
Upol-ff	1.34	1.26	126.9	56.6	179.9	(see Fig. S2)
$[Lu(\eta^2\text{-}CO_3)_3]^{3-}$						
CPMD(1)S1	1.33	1.26	113.3	58.5	171.5	(see Fig. S3)
CPMD(1)S2	1.33	1.27	114.5	57.9	173.0	(see Fig. S3)
BOMD(2)	1.32	1.28	114.7	56.4	172.0	(see Fig. S3)
DFT-B3LYP	1.33	1.26	113.5	58.4	180.0	120.0
PBE/COSMO(2)	1.32	1.26	114.5	57.9	178.7	127.4 124.5 108.1
PBE/COSMO(1)	1.32	1.26	114.6	58.6	178.9	130.0 (1) 112.3 (2)
Pol-ff	1.37	1.26	126.2	60.3	179.9	(see Fig. S4)
Upol-ff	1.34	1.26	128.1	61.3	179.9	(see Fig. S4)

Table S2. Distances (in Å) and angles (in degrees) for tetra-carbonate complexes as obtained by CPMD simulations with different initial numbers of water molecules in first shell (0 and 4 as noted in parenthesis), B3LYP optimization from Ref. 17, PBE/COSMO optimization with 4 and 2 water molecules for La and Lu respectively and Pol and Upol force fields.

	$C\text{-}O_C^{(n)}$	$C\text{-}O_C^{(f)}$	$O_C^{(n)}CO_C^{(n)}$	$O_C^{(n)}LnO_C^{(n)}$	$LnCO_C^{(f)}$	CLnC
$[La(\eta^2\text{-}CO_3)_4]^{5-}$						
CPMD	1.32	1.29	116.1	51.4	171.0	131.3 (2) 99.3 (4)
DFT-B3LYP	1.31	1.30	116.2	49.1	178.6	130.8 (2) 100.0 (4)
PBE/COSMO(1)	1.30	1.27	116.7	51.3	173.3	138.9 (2) 96.0 (4)
Pol-ff	1.37	1.27	128.4	59.6	179.9	(see Fig. S5)
Upol-ff	1.35	1.27	127.1	56.2	179.9	(see Fig. S5)
$[Lu(\eta^2\text{-}CO_3)_4]^{5-}$						
CPMD	1.32	1.29	115.3	55.3	169.9	134.2 (2) 98.4 (4)
DFT-B3LYP	1.31	1.30	115.4	53.3	179.2	134.3 (2) 98.6 (4)
Pol-ff	1.37	1.26	126.9	63.3	179.9	142.4 (2) 95.9 (4)
Upol-ff	1.34	1.26	125.4	61.3	179.9	(see Fig. S5)

Table S3. Angles for tri- and tetra-carbonate~~s~~ complexes of the lanthanoid(III) series as obtained by Pol-ff simulations.

	$[Ln(\eta^2\text{-}CO_3)_3]^{3-}$		$[Ln(\eta^2\text{-}CO_3)_4]^{5-}$	
	$O_C^{(n)}CO_C^{(n)}$	$O_C^{(n)}LnO_C^{(n)}$	$O_C^{(n)}CO_C^{(n)}$	$O_C^{(n)}LnO_C^{(n)}$
Ce	128.2	58.9	128.5	59.2
Pr	127.7	60.6	128.0	60.6
Nd	127.5	61.0	127.9	61.0
Sm	127.3	61.7	128.6	61.6
Eu	127.0	62.1	127.6	61.9
Gd	127.0	62.4	126.8	62.0
Tb	126.9	62.7	127.4	62.2
Dy	126.7	63.1	127.3	62.5
Ho	126.6	63.7	127.2	62.7
Er	126.5	63.9	127.1	62.8
Tm	126.4	64.2	127.1	63.0
Yb	126.2	64.4	127.0	63.1

Table S3. Optimized structures of $[La(\eta^2\text{-}CO_3)_3(H_2O)_4]^{3-}$, $[La(\eta^2\text{-}CO_3)_3(H_2O)_3]^{3-}$, $[Lu(\eta^2\text{-}CO_3)_3(H_2O)_2]^{3-}$, $[Lu(\eta^2\text{-}CO_3)_3(H_2O)]^{3-}$, and $[La(\eta^2\text{-}CO_3)_4(H_2O)]^{5-}$ at PBE/COSMO level o theory (positions are in Å)

$[La(\eta^2\text{-}CO_3)_3(H_2O)_4]^{3-}$

La	2.184410	4.204572	-9.326089
C	1.005157	6.392470	-7.735747
O	0.522741	7.353597	-7.064716
O	2.229571	5.947567	-7.555895
O	0.299573	5.769135	-8.670223
C	4.627886	2.783894	-8.479900
O	5.702169	2.177695	-8.187989
O	4.583149	4.083921	-8.681454
O	3.477423	2.136480	-8.610530
C	0.087541	3.169350	-11.208561
O	-0.892797	2.792633	-11.912686
O	0.848347	4.201733	-11.573240
O	0.424531	2.587251	-10.082220
O	0.171638	6.805334	-11.207766
H	0.065199	6.632750	-10.232129
H	0.245020	5.869997	-11.543317
O	2.871700	6.429544	-10.682312
H	1.967133	6.753693	-10.957398
H	3.192179	7.117530	-10.069435
O	3.420462	3.455507	-11.679802
H	2.531115	3.709470	-12.041063
H	4.029613	4.137930	-12.016716
O	1.335982	2.807308	-7.141043
H	2.123649	2.255507	-7.385294
H	0.567967	2.260823	-7.391883

$[La(\eta^2\text{-}CO_3)_3(H_2O)_3]^{3-}$

La	2.153569876	4.214930111	-9.332600723
C	1.014227708	6.365805089	-7.711251098
O	0.521722608	7.299630342	-7.003029968
O	2.285799309	6.021079693	-7.628357142
O	0.287681783	5.682961118	-8.573879693
C	4.625750371	2.810454757	-8.485002192
O	5.706069116	2.208498471	-8.199736389
O	4.578740828	4.103377359	-8.715055104
O	3.474267375	2.158167565	-8.578451273
C	0.114016195	3.178829210	-11.220082540
O	-0.823063993	2.781254875	-11.976206688
O	0.861505575	4.229602367	-11.534231456
O	0.402283826	2.586126790	-10.081678952
O	2.999678823	6.376737789	-10.674410550
H	2.320916356	6.760676809	-11.260912581
H	3.170861721	7.084411720	-10.023846336
O	3.404555274	3.381651288	-11.702067400
H	2.516758999	3.667489616	-12.042761183

H	4.027879806	4.049927468	-12.040618569
O	1.343742458	2.823654995	-7.109456726
H	2.145069564	2.295000284	-7.365811016
H	0.589332740	2.260650753	-7.364379872

$[Lu(\eta^2\text{-}CO_3)_3(H_2O)_2]^{3-}$

Lu	34.871804	2.999697	14.098084
C	36.281740	3.422123	16.384897
O	36.954864	3.628749	17.432293
O	35.264703	4.175908	16.018999
O	36.544875	2.417001	15.557141
C	33.188040	0.871061	14.514844
O	32.409905	-0.105510	14.692213
O	34.236377	0.822608	13.715467
O	33.018967	2.037846	15.124900
C	35.144886	4.466325	11.829905
O	35.309550	5.132855	10.765673
O	34.338483	3.421941	11.899263
O	35.766559	4.764454	12.958169
O	32.870840	4.495308	14.209637
H	32.613532	4.576506	13.271555
H	32.401290	3.686193	14.529425
O	36.750077	1.787284	12.962494
H	37.231888	1.753338	13.817270
H	36.315384	0.914511	12.900568

$[Lu(\eta^2\text{-}CO_3)_3(H_2O)]^{3-}$

Lu	34.690437575	3.060457973	14.167114288
C	36.467629814	3.381899478	16.156741198
O	37.321317927	3.529713062	17.075132881
O	35.303595997	4.008536863	16.149175820
O	36.671896959	2.584355638	15.116138809
C	33.274095063	0.783192164	14.472090701
O	32.608024303	-0.279756674	14.619462344
O	34.454129361	0.814493083	13.877359677
O	32.841248303	1.960799093	14.901356728
C	35.396687613	4.338591392	11.878706749
O	35.701851457	4.907477946	10.791949713
O	34.859361614	3.123985138	11.916973166
O	35.584012036	4.890874107	13.060128955
O	32.951727526	4.682224330	14.281027861
H	33.087456071	5.444305153	13.686648249
H	32.065078567	4.339260913	14.061629850

$[La(\eta^2\text{-}CO_3)_4(H_2O)]^{5-}$

H	49.140558946	24.858517941	11.589687014
O	48.889282257	24.017457978	11.160055063
H	48.999077610	24.193569724	10.206139787
O	46.885188425	24.420552700	9.172742485
C	45.883768890	23.830517276	8.562051394

O	45.016207649	23.230467674	9.305241480
La	46.199188059	23.977389884	11.522653739
O	45.249314627	21.867915772	12.272455657
C	46.140725479	21.008768775	11.824431873
O	47.208374455	21.505715166	11.303266457
C	43.904257266	25.828667279	11.857460490
O	44.099214760	24.766886730	12.599207382
O	44.766664327	26.042150289	10.914507195
O	42.916922253	26.593064444	12.068094923
O	45.803989180	23.871126041	7.298568442
O	45.913239782	19.765707806	11.918998039
O	47.440319961	25.789638640	12.842344841
C	47.468493843	25.134174856	13.971005908
O	47.103147112	23.888118414	13.929540326
O	47.826695879	25.696339462	15.047657064

Figure S1. CLaC angle as a function of time for CPMD(0), panel a, and CPMD(4), panel b, simulations of $[La(\eta^2\text{-}CO_3)_3]^{3-}$ systems. In panel a, we show also the La-O distances (in nm) of the two water molecules that enter the first shell during the dynamics.

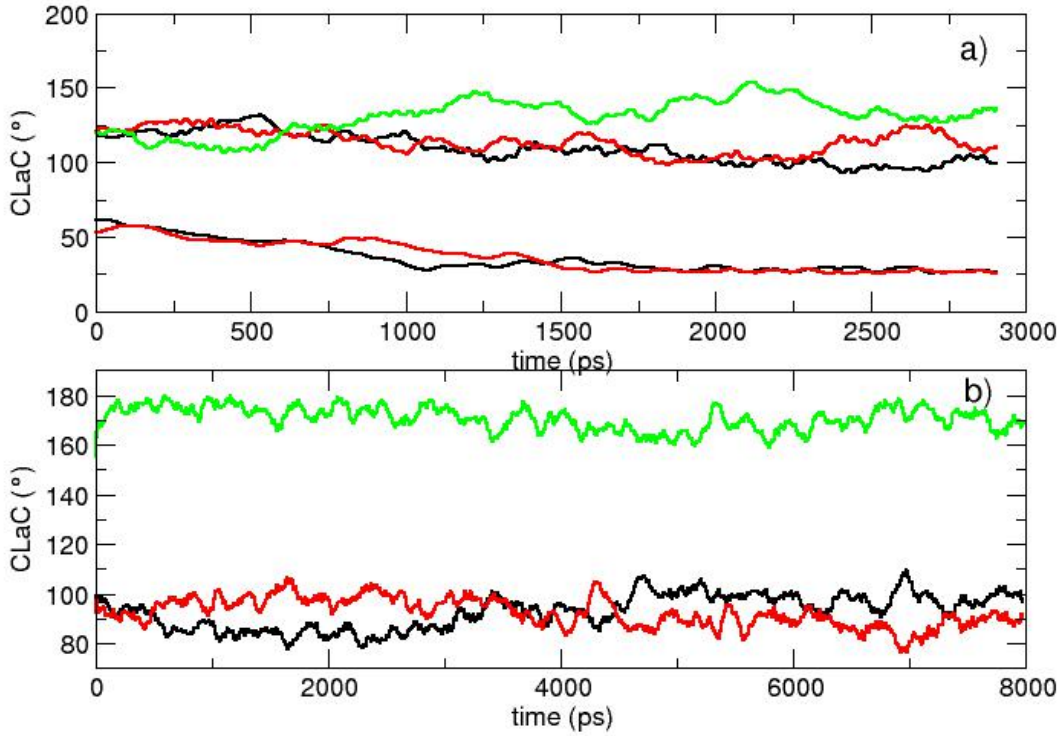

Figure S2. CLaC angle as a function of time for Pol-ff and UPol-ff simulations of $[La(\eta^2\text{-}CO_3)_3]^{3-}$ systems.

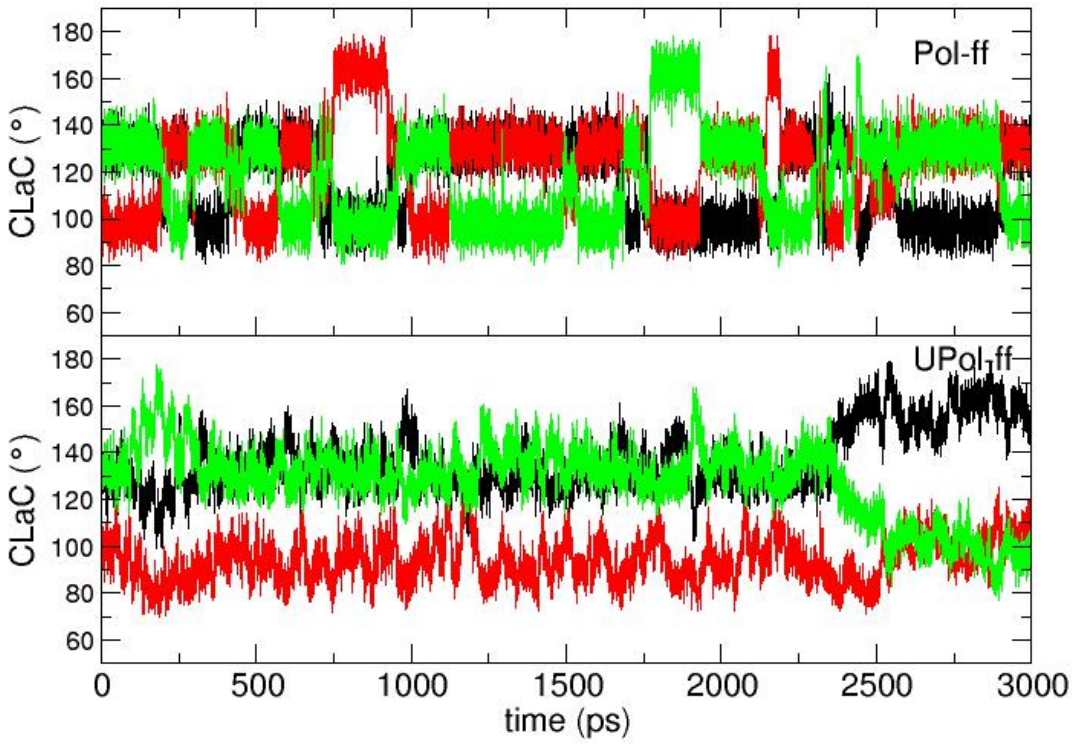

Figure S3. CLuC angle as a function of time for CPMD(1)S1, CPMD(1)S2 and BOMD(2) simulations of $[Lu(\eta^2\text{-}CO_3)_3]^{3-}$ systems.

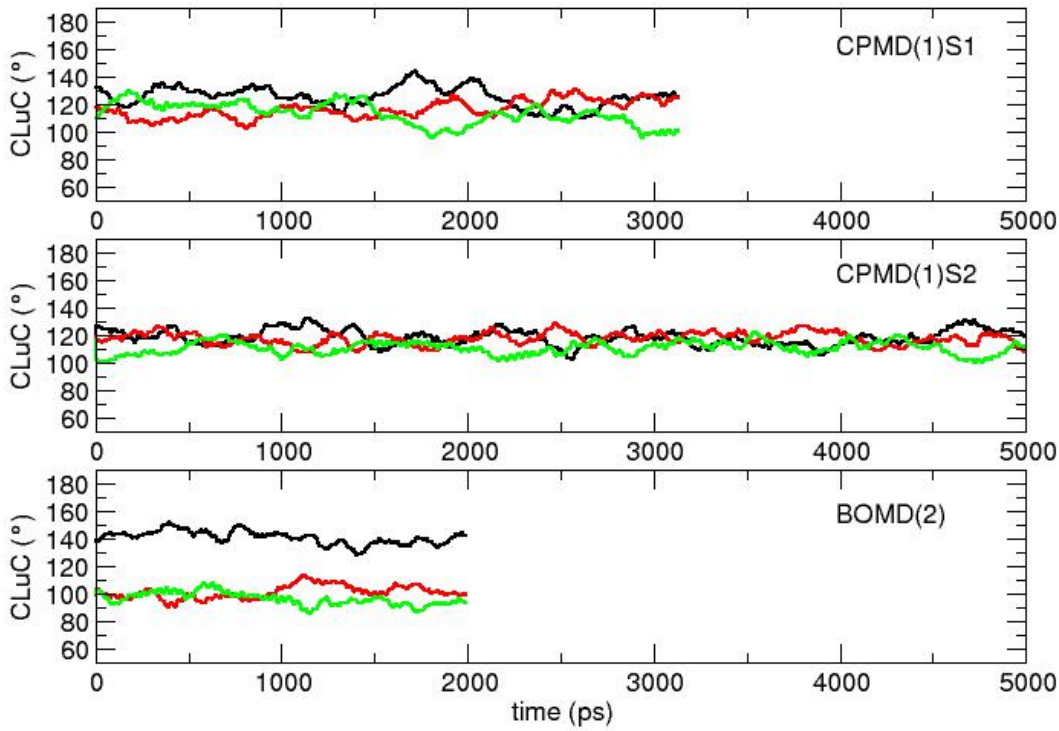

Figure S4. CLuC angle as a function of time for Pol-ff and UPol-ff simulations of $[Lu(\eta^2\text{-}CO_3)_3]^{3-}$ systems.

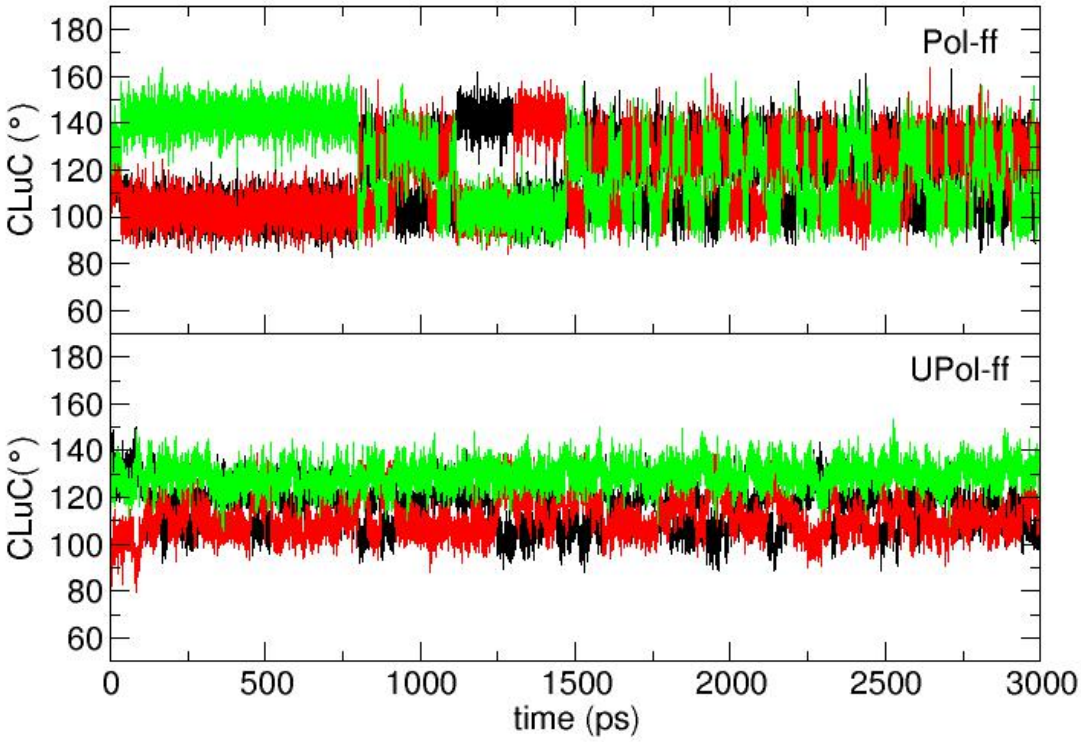

Figure S5. CLaC angle as a function of time for Pol-ff and UPol-ff simulations of $[La(\eta^2\text{-}CO_3)_4]^{5-}$ systems.

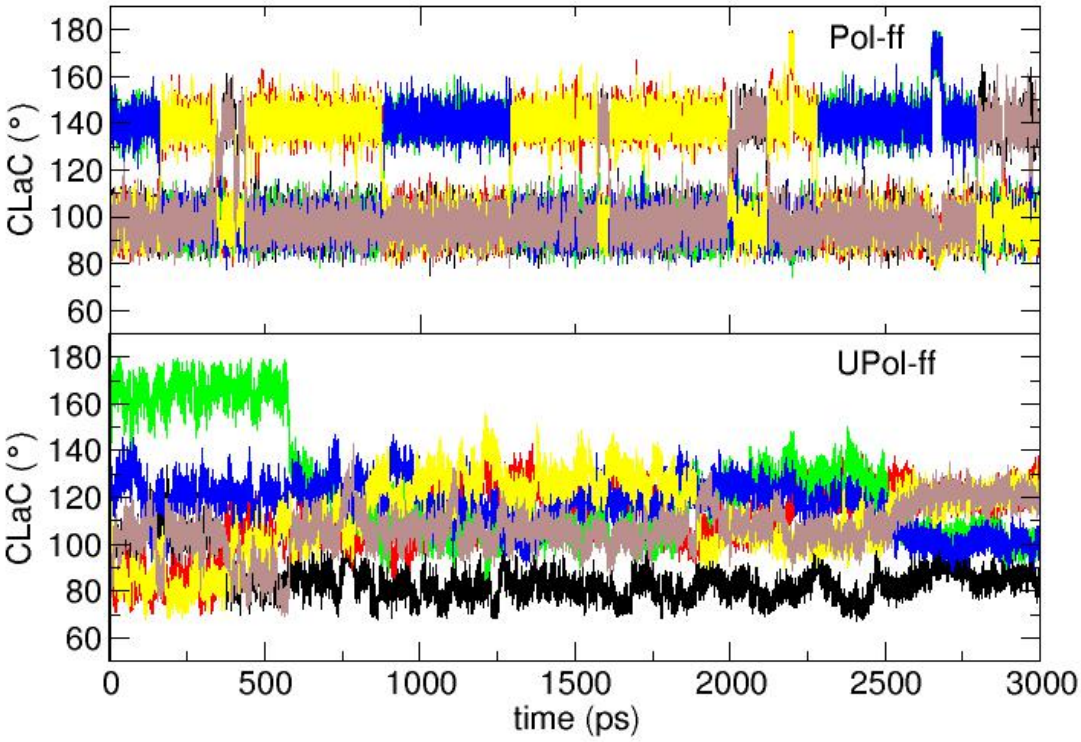

Figure S6. CLuC angle as a function of time for Pol-ff (upper panel) and UPol-ff (lower panel) simulations of $[Lu(\eta^2\text{-}CO_3)_4]^{5-}$ systems.

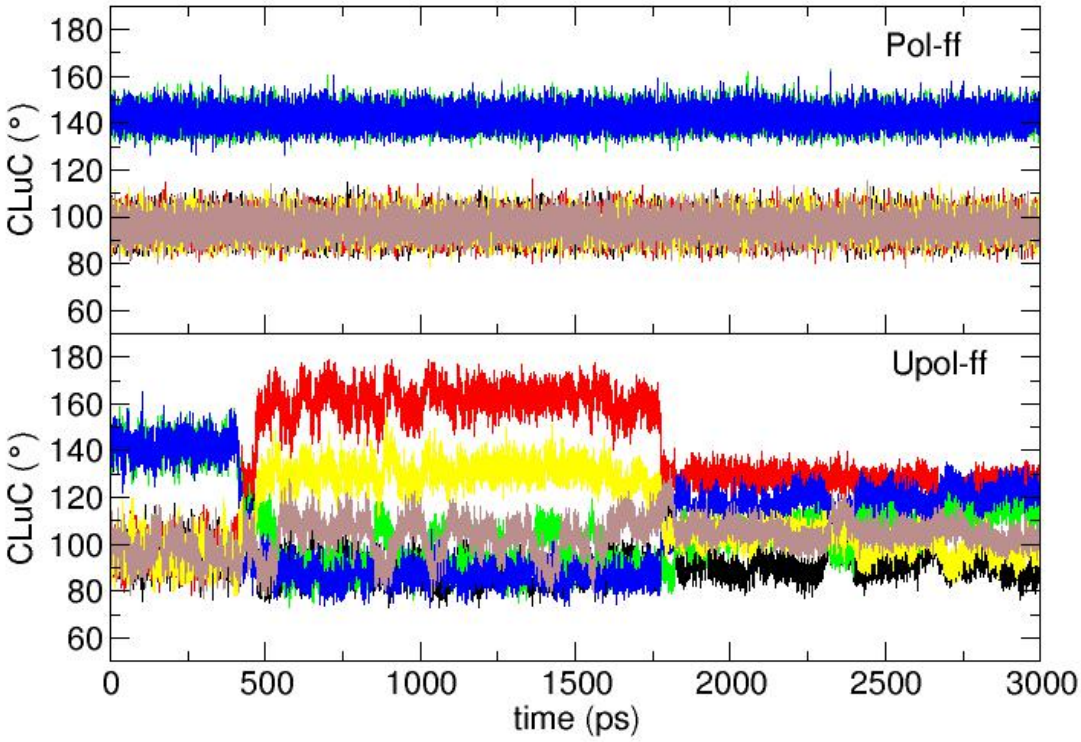

Figure S7. Radial distribution functions obtained from UPOL-ff simulations for $[La(\eta^2\text{-}CO_3)_3]^{3-}$ and $[Lu(\eta^2\text{-}CO_3)_3]^{3-}$ systems : upper panel Ln-O_C , lower panel Ln-water (oxygen atoms.

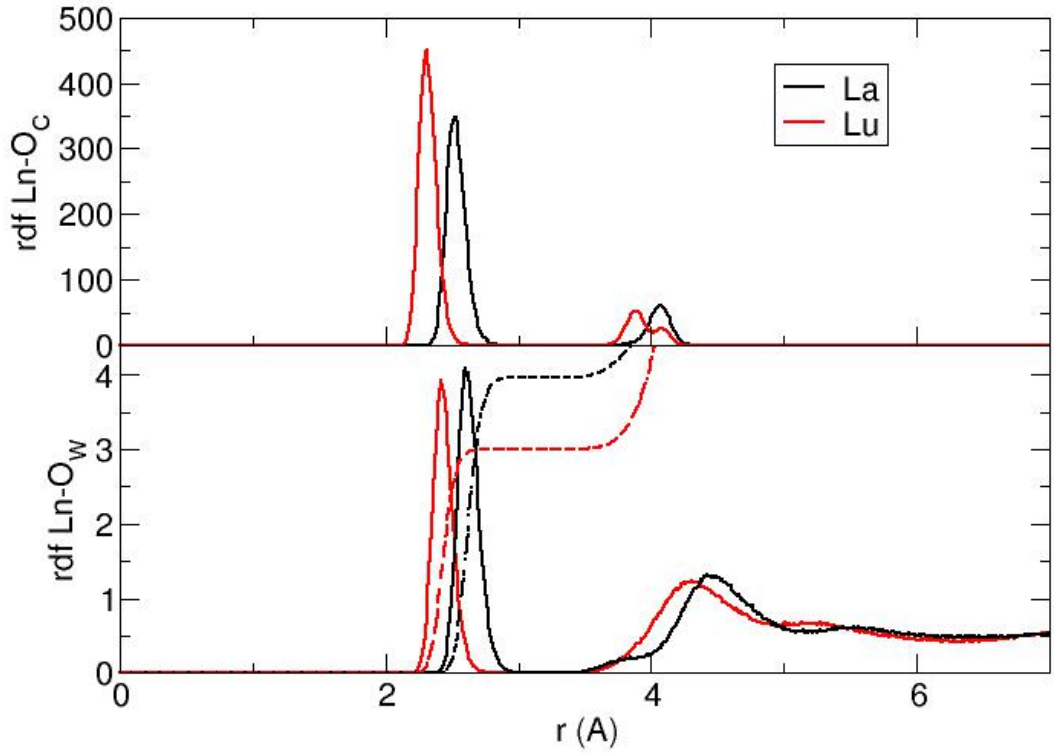

Figure S9. CLnC angles (in degrees) for the $[Ln(\eta^2\text{-}CO_3)_3]^{3-}$ complexes as obtained from Pol-ff simulations.

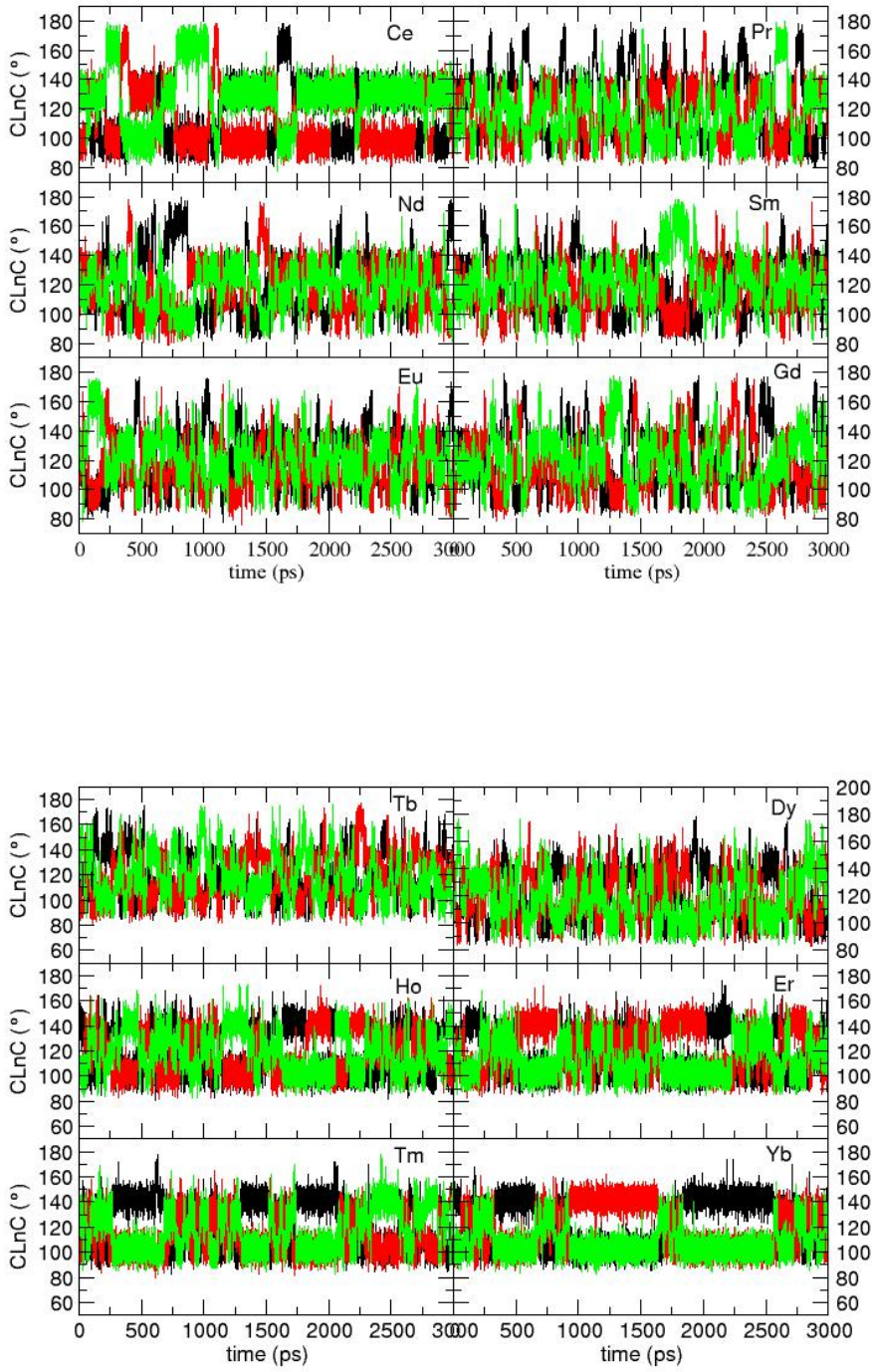

Figure S10. CLnC angles (in degrees) for the $[Ln(\eta^2\text{-}CO_3)_4]^{5-}$ complexes as obtained from Pol-ff simulations.

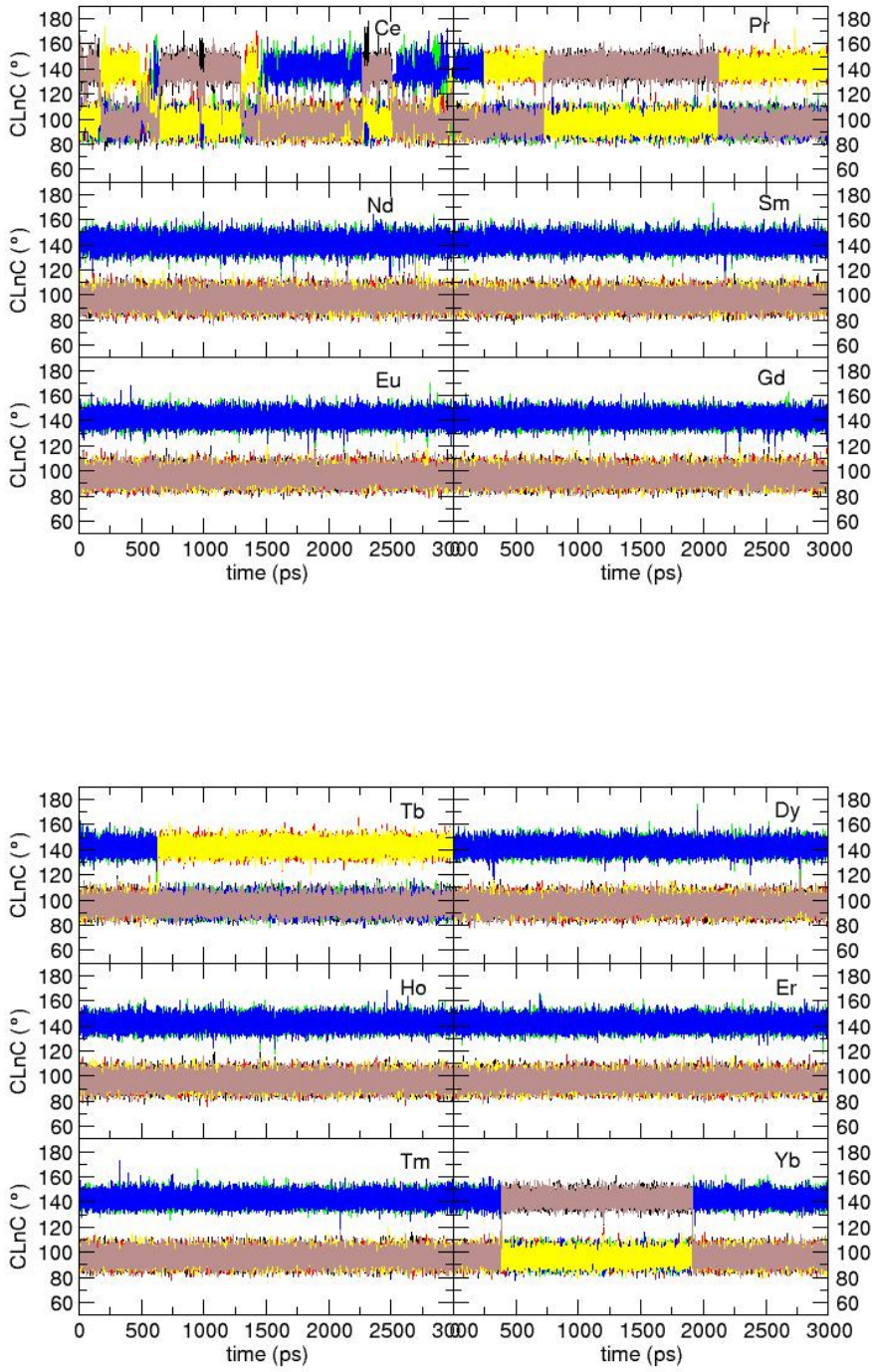
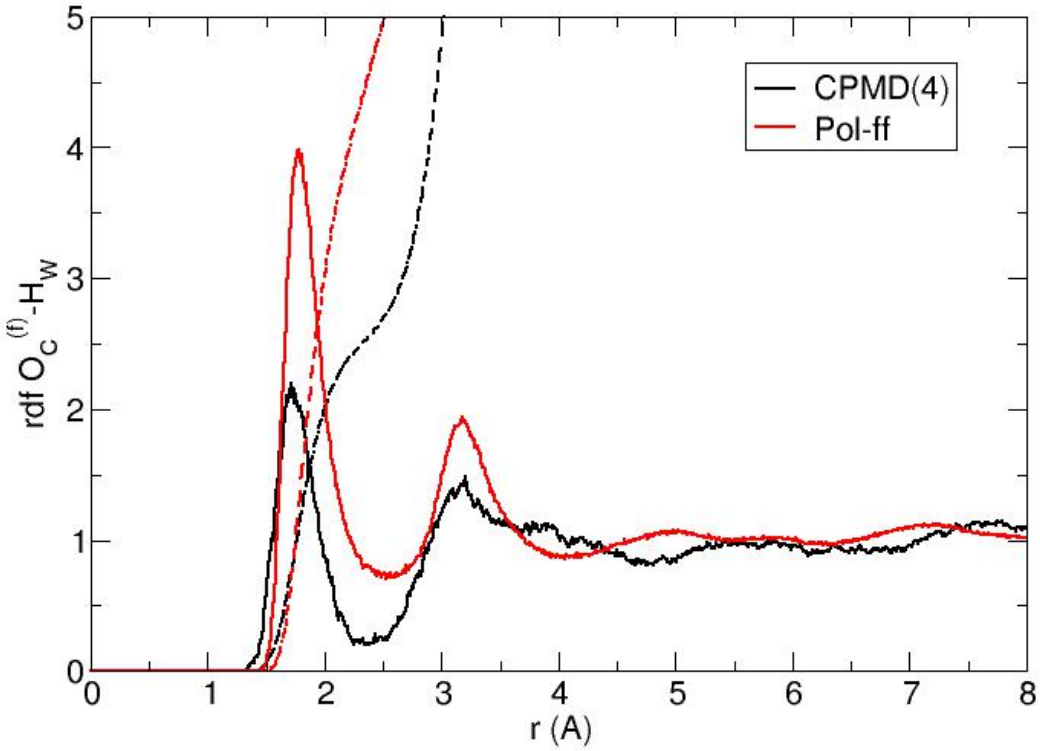
Figure S11. OC(f)-HW radial distribution functions (integrated values in dashed lines) as obtained from CPMD(4) and Pol-ff simulations.