Electronic Supplementary Material (ESI) for Analyst.

Acceleration of Metal-Ligand Complexation Kinetics by Electrospray Ionization

Supporting Information

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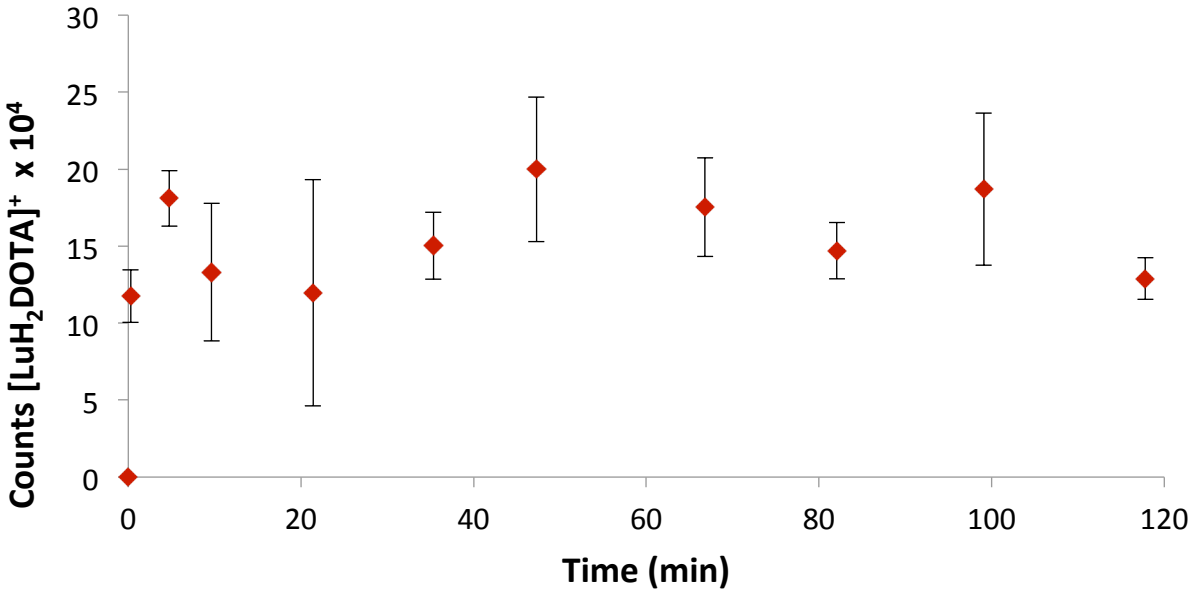
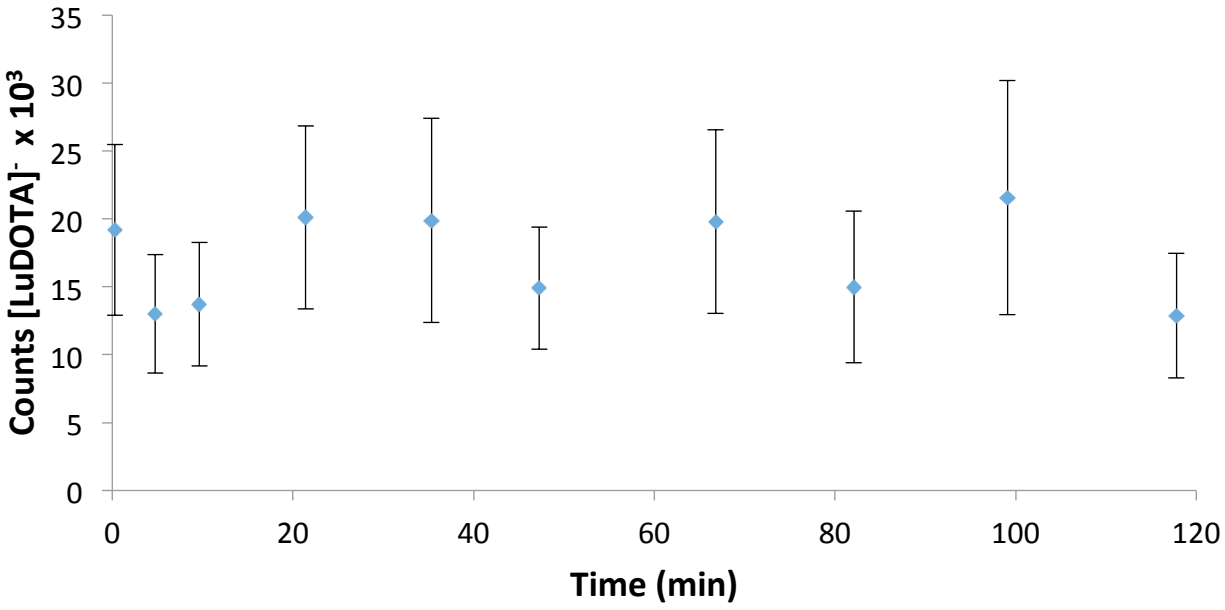
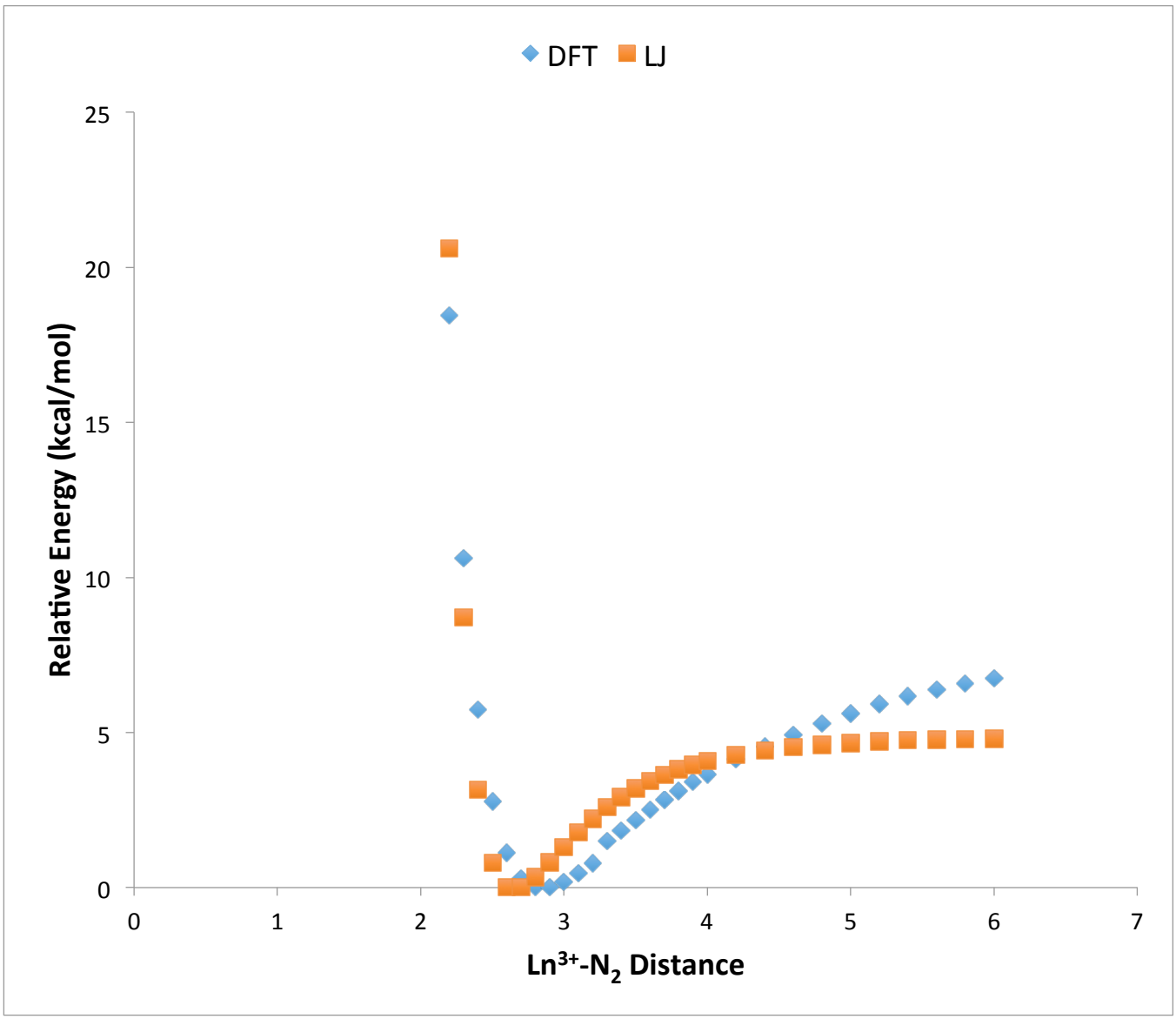


Supplemental Figure 1. The Intensity of the $[LuH_2DOTA]^+$ Peak (m/z 577) over time. T = 0 is the point at which the $Lu(NO_3)_3$ was added to the buffered DOTA solution. Uncertainty is 3σ.



Supplemental Figure 2. The Intensity of the $[LuDOTA]^-$ Peak (m/z 575) over time. T = 0 is the point at which the $Lu(NO_3)_3$ was added to the buffered DOTA solution. Uncertainty is 3σ. Note the overall greater error (and lower abundance) observed in negative mode. The same trend of immediate detection of the Lu-DOTA complex is observed in both positive and negative mode.



Supplemental Figure 3. The Lennard-Jones (LJ) fit to the DFT energy between Lu^{3+} within the LuDOTA complex and the N_2 collision gas for use in CCS modeling.

Below are lists for each optimized $[LuH_2DOTA]^+$ structure referenced in Figure 6 of the manuscript, used for collision cross section modelling.

$[LuH_2DOTA]^+$ with complexation occurring through one carboxylate arm of the DOTA:

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Lu	-0.48959	-2.64287	-1.36420
N	2.33187	0.87649	-0.50622
C	2.71227	2.26494	-0.11975
H	2.31911	2.99720	-0.83752
H	3.81269	2.40720	-0.18814
C	2.42312	0.64628	-1.97588
H	2.37657	-0.43929	-2.20941
H	3.40950	1.01317	-2.34052
C	3.12514	-0.14296	0.24556
C	4.63162	0.06909	0.22220
O	5.30346	0.10248	-0.94973
O	5.23952	0.21249	1.27156
H	2.91023	-1.16002	-0.14355
H	2.78884	-0.15878	1.30358
N	0.77326	2.64886	1.47709
C	0.20013	3.85536	0.81400
H	0.75075	4.15103	-0.08322
H	0.36842	4.74838	1.45538
C	2.25287	2.64885	1.31137
H	2.73206	1.94365	2.02151
H	2.65772	3.65785	1.55859
C	0.41687	2.67510	2.93163
C	-0.51447	1.55886	3.30794
O	-1.61024	1.30321	2.57005
O	-0.33082	0.94004	4.34426
H	-0.09137	3.61863	3.22694
H	1.30715	2.63581	3.60152
N	-1.74720	2.76328	-0.50623
C	-1.13162	3.09263	-1.83239
H	-0.12837	3.50415	-1.76876
H	-1.70915	3.91667	-2.31090
C	-1.31906	3.76060	0.52192
H	-1.79566	3.54808	1.49228
H	-1.65262	4.77417	0.20892
C	-3.23796	2.87592	-0.68108
C	-4.10037	2.43973	0.48451
O	-5.03954	1.48705	0.28902
O	-4.05018	3.02261	1.55421
H	-3.57702	2.26865	-1.54270
H	-3.51926	3.92957	-0.91338
N	-0.08110	0.84124	-2.59681
C	1.31838	1.35012	-2.81740
H	1.40664	2.43407	-2.66958

H	1.60994	1.23700	-3.88782
C	-1.08582	1.92559	-2.84630
H	-2.10930	1.51697	-2.88934
H	-0.88522	2.36818	-3.84806
C	-0.34304	-0.22464	-3.61806
C	-1.72437	-0.83949	-3.51443
O	-2.02963	-1.70697	-2.53201
O	-2.57399	-0.55965	-4.34755
H	0.41404	-1.03653	-3.58286
H	-0.26884	0.22837	-4.63745
H	-5.68102	1.26858	0.98096
H	6.25838	0.26731	-0.97199

$[LuH_2DOTA]^+$ with complexation occurring through two carboxylate arms of the DOTA:

55

Lu	-0.43703	-1.00330	0.73138
N	2.47441	0.85090	-0.51606
C	2.74943	2.25573	-0.17097
H	2.25814	2.93442	-0.88649
H	3.83096	2.47390	-0.26611
C	2.57450	0.67229	-2.01176
H	2.66343	-0.39239	-2.29419
H	3.48331	1.18016	-2.41663
C	3.26247	-0.08414	0.39340
C	4.75261	0.06412	0.31953
O	5.34173	0.31024	-0.84989
O	5.45014	-0.12734	1.32974
H	3.00008	-1.14313	0.24707
H	2.99038	0.01511	1.47262
N	0.81065	2.39720	1.36199
C	0.14828	3.60992	0.84743
H	0.62554	3.99684	-0.06349
H	0.23431	4.44119	1.58734
C	2.27057	2.59544	1.24078
H	2.81230	1.98655	1.97721
H	2.56972	3.63556	1.48593
C	0.45405	2.18337	2.78221
C	0.78538	0.78476	3.26072
O	0.52418	-0.36947	2.57882
O	1.28919	0.67924	4.36516
H	-0.61546	2.35385	2.99160
H	0.98190	2.93654	3.43323
N	-1.78019	2.53986	-0.53143
C	-1.19291	2.82982	-1.87425
H	-0.25755	3.37288	-1.81648
H	-1.83337	3.54092	-2.43958
C	-1.33323	3.44310	0.56990
H	-1.85322	3.15453	1.50815
H	-1.62070	4.48227	0.33684
C	-3.21975	2.87689	-0.68202
C	-4.06158	2.37688	0.41676
O	-5.09519	1.54018	0.29100

O	-3.97794	3.11987	1.39445
H	-3.63497	2.46627	-1.61395
H	-3.34497	3.98370	-0.76609
N	0.04973	0.69374	-2.44288
C	1.36469	1.28834	-2.81934
H	1.35023	2.38496	-2.69836
H	1.53473	1.19425	-3.92321
C	-1.07560	1.59493	-2.80865
H	-2.04596	1.04242	-2.83847
H	-0.92837	1.98179	-3.84719
C	-0.12239	-0.61203	-3.11979
C	-1.19991	-1.45866	-2.47074
O	-1.40845	-1.56864	-1.13018
O	-1.92935	-2.10309	-3.20512
H	0.81405	-1.20069	-3.14168
H	-0.37474	-0.47075	-4.21147
H	-5.78997	1.52563	0.95612
H	6.29821	0.36336	-0.93083

$[LuH_2DOTA]^+$ with complexation occurring through three carboxylate arms of the DOTA:

55

Lu	-0.63184	-1.43962	1.01585
N	2.54993	0.84525	-0.33350
C	2.72599	2.23515	-0.22974
H	2.23639	2.90856	-0.93977
H	3.80455	2.45760	-0.29214
C	2.54517	0.73543	-2.16474
H	2.64041	-0.32531	-2.42329
H	3.46225	1.22685	-2.53109
C	3.29785	-0.04977	0.57905
C	4.80878	0.04230	0.45909
O	5.21582	0.33923	-0.83126
O	5.58844	-0.14594	1.34437
H	3.04334	-1.09535	0.35975
H	3.04806	0.13555	1.63485
N	0.77657	2.43438	1.36918
C	0.07753	3.62647	0.83399
H	0.59814	3.95637	-0.07175
H	0.13894	4.46985	1.54248
C	2.24833	2.53897	1.18894
H	2.71741	1.85152	1.90162
H	2.60256	3.54707	1.46400
C	0.48846	2.23484	2.81649
C	0.80771	0.79732	3.28723
O	0.57518	-0.12095	2.36708
O	1.20451	0.60008	4.41473
H	-0.58078	2.40359	2.99816
H	1.04171	2.95473	3.43765
N	-1.64430	2.28139	-0.46006
C	-1.30205	2.73325	-1.84040

H	-0.39510	3.34215	-1.77705
H	-2.09105	3.40032	-2.22660
C	-1.40023	3.37605	0.52679
H	-1.92565	3.11414	1.45222
H	-1.85126	4.31757	0.17062
C	-3.07178	1.89050	-0.40874
C	-3.48768	1.17516	0.86448
O	-2.46115	0.41321	1.39797
O	-4.57410	1.21420	1.35963
H	-3.29273	1.19429	-1.22885
H	-3.74094	2.75689	-0.52300
N	0.05352	0.70883	-2.51922
C	1.34307	1.33237	-2.89922
H	1.27965	2.40816	-2.70208
H	1.52394	1.23355	-3.98298
C	-1.09582	1.59566	-2.83865
H	-1.99264	0.96811	-2.88789
H	-0.97937	2.03541	-3.84387
C	-0.14761	-0.59598	-3.20810
C	-1.21737	-1.46977	-2.51364
O	-1.23953	-1.32925	-1.20065
O	-1.91669	-2.21101	-3.16864
H	0.79246	-1.16230	-3.18987
H	-0.42092	-0.45318	-4.26406
H	-2.81069	-0.05512	2.17841
H	6.19066	0.33168	-0.84679

$[LuH_2DOTA]^+$ with complexation occurring through all four carboxylate arms of the DOTA but without the ion being moved into the N cage:

55

Lu	-0.63184	-1.43962	1.01585
N	2.46556	0.83540	-0.67632
C	2.72599	2.23515	-0.22974
H	2.23639	2.90856	-0.93977
H	3.80455	2.45760	-0.29214
C	2.54517	0.73543	-2.16474
H	2.64041	-0.32531	-2.42329
H	3.46225	1.22685	-2.53109
C	3.47110	-0.06978	-0.07407
C	3.17298	-1.54920	-0.24209
O	1.81304	-1.81220	-0.25772
O	3.98954	-2.41754	-0.32117
H	3.52138	0.10428	1.00911
H	4.47849	0.10278	-0.48252
N	0.77657	2.43438	1.36918
C	0.07753	3.62647	0.83399
H	0.59814	3.95637	-0.07175
H	0.13894	4.46985	1.54248
C	2.24833	2.53897	1.18894
H	2.71741	1.85152	1.90162

H	2.60256	3.54707	1.46400
C	0.48846	2.23484	2.81649
C	0.80771	0.79732	3.28723
O	0.57518	-0.12095	2.36708
O	1.20451	0.60008	4.41473
H	-0.58078	2.40359	2.99816
H	1.04171	2.95473	3.43765
N	-1.64430	2.28139	-0.46006
C	-1.30205	2.73325	-1.84040
H	-0.39510	3.34215	-1.77705
H	-2.09105	3.40032	-2.22660
C	-1.40023	3.37605	0.52679
H	-1.92565	3.11414	1.45222
H	-1.85126	4.31757	0.17062
C	-3.07178	1.89050	-0.40874
C	-3.48768	1.17516	0.86448
O	-2.46115	0.41321	1.39797
O	-4.57410	1.21420	1.35963
H	-3.29273	1.19429	-1.22885
H	-3.74094	2.75689	-0.52300
N	0.05352	0.70883	-2.51922
C	1.34307	1.33237	-2.89922
H	1.27965	2.40816	-2.70208
H	1.52394	1.23355	-3.98298
C	-1.09582	1.59566	-2.83865
H	-1.99264	0.96811	-2.88789
H	-0.97937	2.03541	-3.84387
C	-0.14761	-0.59598	-3.20810
C	-1.21737	-1.46977	-2.51364
O	-1.23953	-1.32925	-1.20065
O	-1.91669	-2.21101	-3.16864
H	0.79246	-1.16230	-3.18987
H	-0.42092	-0.45318	-4.26406
H	-2.81069	-0.05512	2.17841
H	1.69569	-2.77837	-0.31562

The fully optimized $[LuH_2DOTA]^+$ ion, with the ion inducted into the N cage:

55

Lu	-0.00236	-0.00267	-0.70649
N	1.31751	1.73660	1.03525
C	1.97260	0.94002	2.11345
H	1.21215	0.70559	2.86450
H	2.73113	1.55295	2.62889
C	0.34174	2.70646	1.61737
H	0.11218	3.45183	0.84739
H	0.80483	3.25782	2.45298
C	2.34846	2.48070	0.27564
C	1.84457	3.13457	-0.99871
O	0.83733	2.39924	-1.60176
O	2.26527	4.14639	-1.47441

H	3.14574	1.79211	-0.03467
H	2.81411	3.27367	0.88043
N	1.69205	-1.33951	1.05297
C	0.95812	-2.06768	2.11466
H	0.74729	-1.36938	2.93217
H	1.58432	-2.86404	2.55131
C	2.63723	-0.34632	1.62668
H	3.38318	-0.11859	0.85710
H	3.19747	-0.78532	2.46980
C	2.45588	-2.27136	0.17797
C	2.83687	-1.63262	-1.17737
O	1.94101	-0.77176	-1.62485
O	3.86091	-1.95937	-1.73599
H	1.83485	-3.14883	-0.04372
H	3.36483	-2.63582	0.67907
N	-1.31936	-1.73824	1.04139
C	-1.97260	-0.93922	2.11890
H	-1.21097	-0.70339	2.86831
H	-2.73050	-1.55091	2.63677
C	-0.34236	-2.70665	1.62387
H	-0.11419	-3.45374	0.85513
H	-0.80386	-3.25617	2.46158
C	-2.35146	-2.48439	0.28541
C	-1.84937	-3.14115	-0.98819
O	-0.84340	-2.40690	-1.59445
O	-2.27072	-4.15408	-1.46100
H	-3.14911	-1.79649	-0.02558
H	-2.81622	-3.27565	0.89307
N	-1.69357	1.33808	1.05307
C	-0.95792	2.06861	2.11193
H	-0.74579	1.37221	2.93072
H	-1.58339	2.86603	2.54769
C	-2.63788	0.34612	1.63033
H	-3.38479	0.11664	0.86218
H	-3.19706	0.78697	2.47317
C	-2.45865	2.26819	0.17726
C	-2.84235	1.62643	-1.17595
O	-1.94776	0.76396	-1.62284
O	-3.86725	1.95215	-1.73358
H	-1.83765	3.14490	-0.04751
H	-3.36656	2.63420	0.67912
H	-0.60513	-2.85514	-2.42684
H	0.59764	2.84591	-2.43463