Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Gas-Phase Lanthanide Chloride Clusters: Relationships among ESI Abundances and DFT Structures and Energetics

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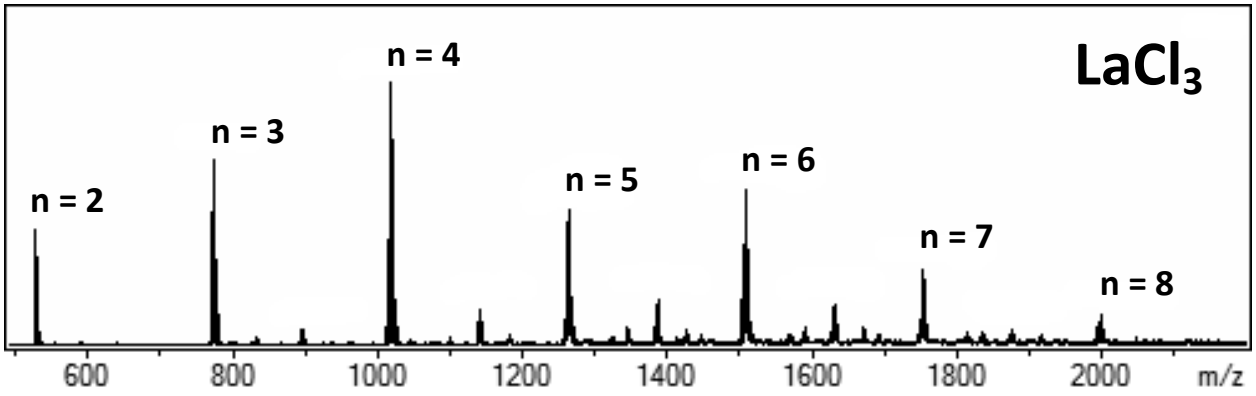


Figure S1a. ESI mass spectra of 350 μM $LaCl_3$ in isopropanol. $La_nCl_{3n+1}^-$ clusters are labeled.

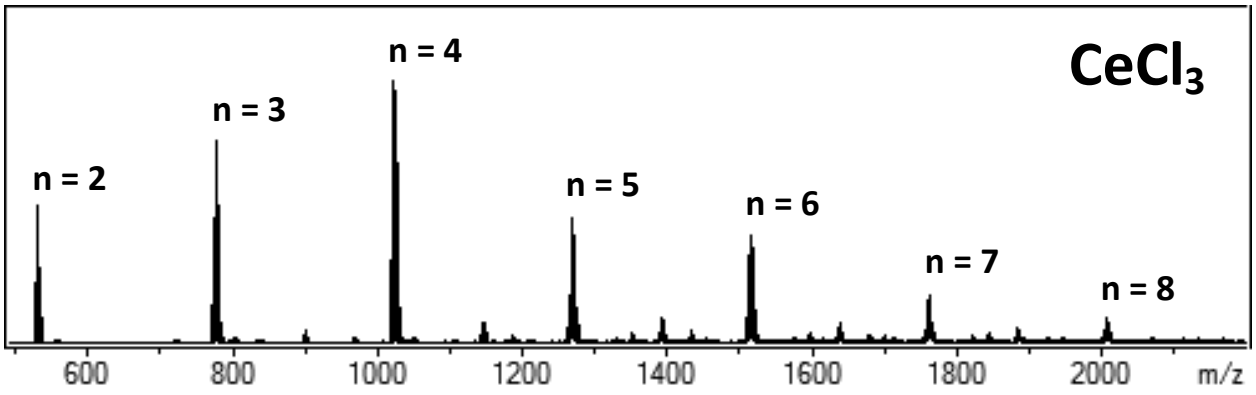


Figure S1b. ESI mass spectra of 350 μM $CeCl_3$ in isopropanol. $Ce_nCl_{3n+1}^-$ clusters are labeled.

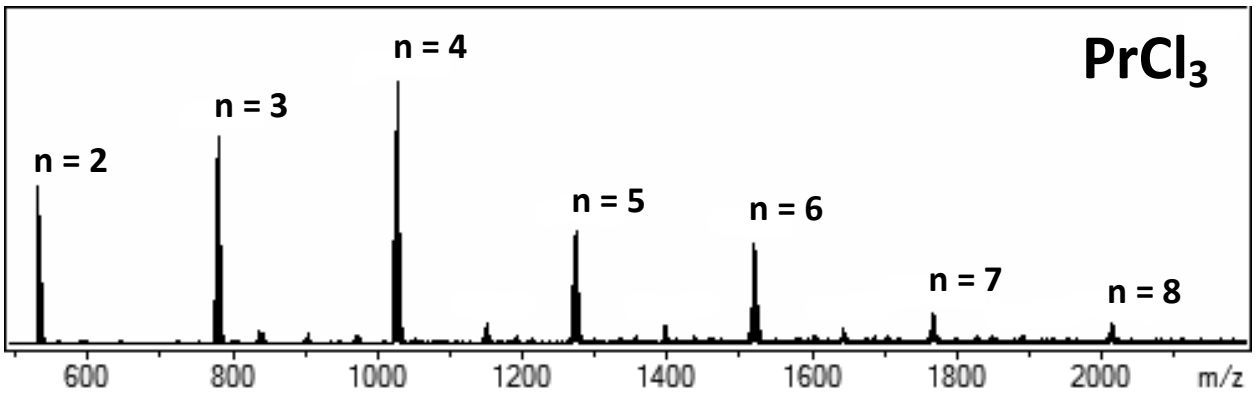


Figure S1c. ESI mass spectra of 350 μM $PrCl_3$ in isopropanol. $Pr_nCl_{3n+1}^-$ clusters are labeled.

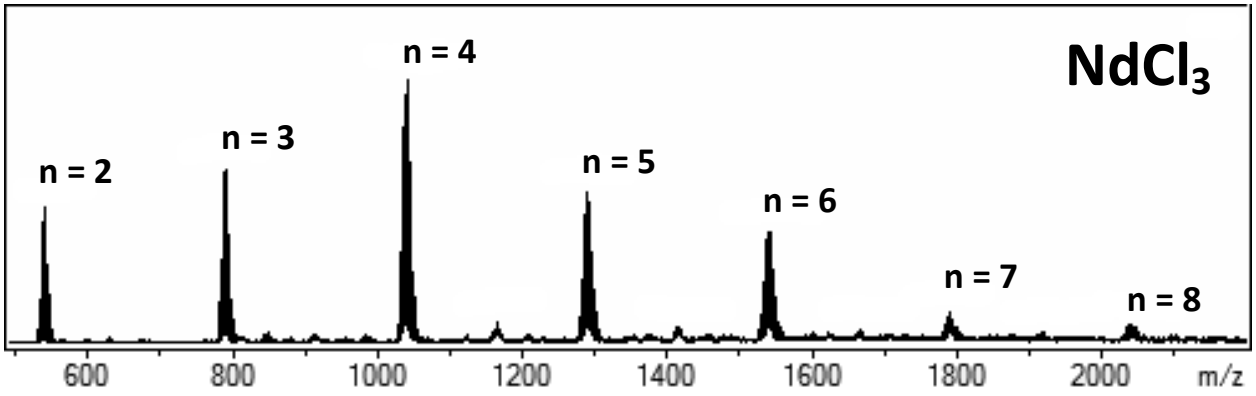


Figure S1d. ESI mass spectra of 350 μM $NdCl_3$ in isopropanol. $Nd_nCl_{3n+1}^-$ clusters are labeled.

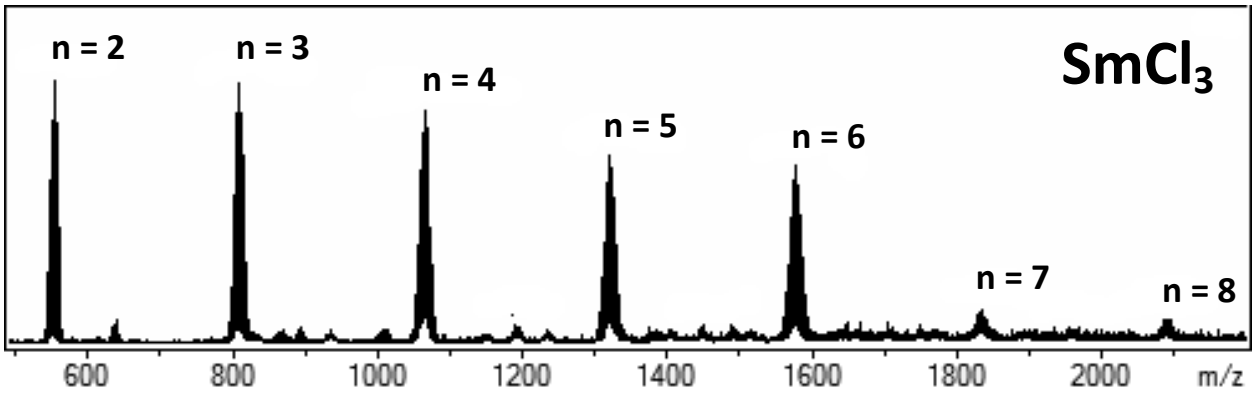


Figure S1e. ESI mass spectra of 350 μM $SmCl_3$ in isopropanol. $Sm_nCl_{3n+1}^-$ clusters are labeled.

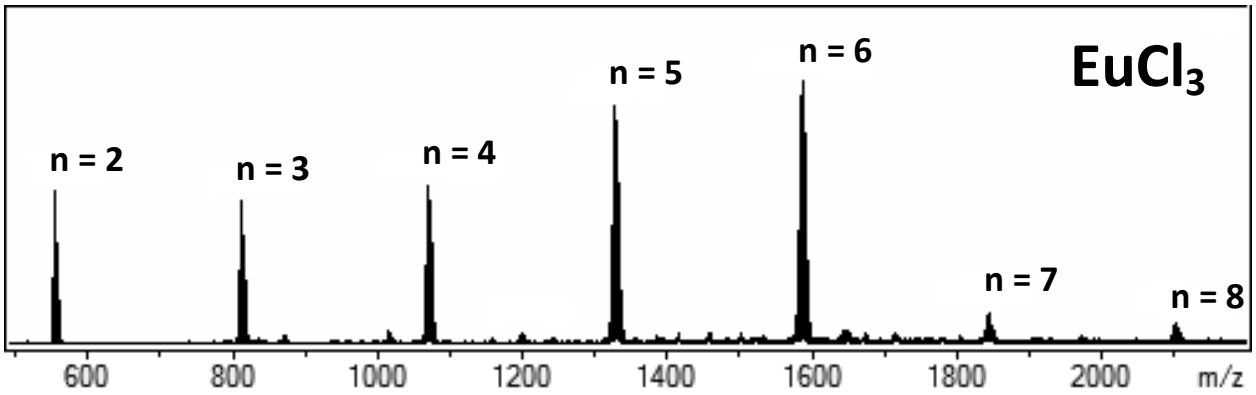


Figure S1f. ESI mass spectra of 350 μM $EuCl_3$ in isopropanol. $Eu_nCl_{3n+1}^-$ clusters are labeled.

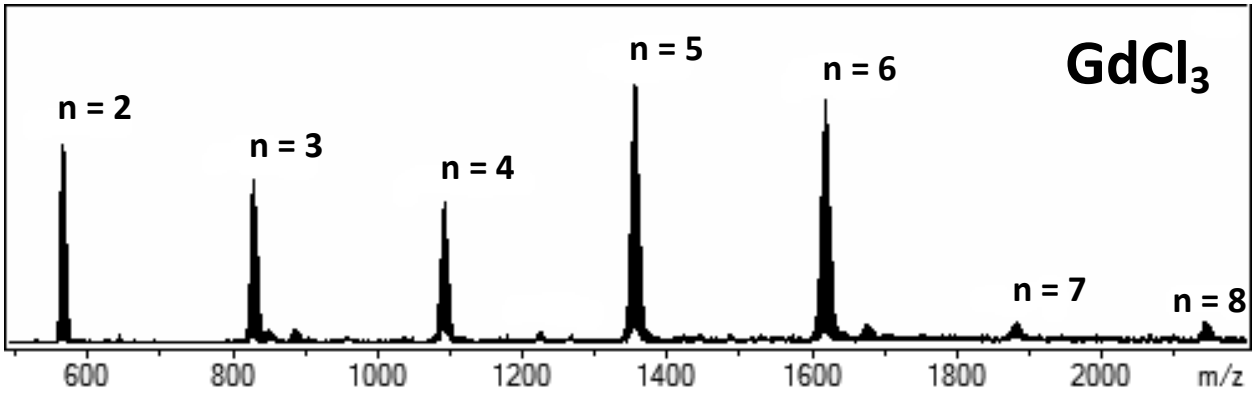


Figure S1g. ESI mass spectra of 350 μM $GdCl_3$ in isopropanol. $Gd_nCl_{3n+1}^-$ clusters are labeled.

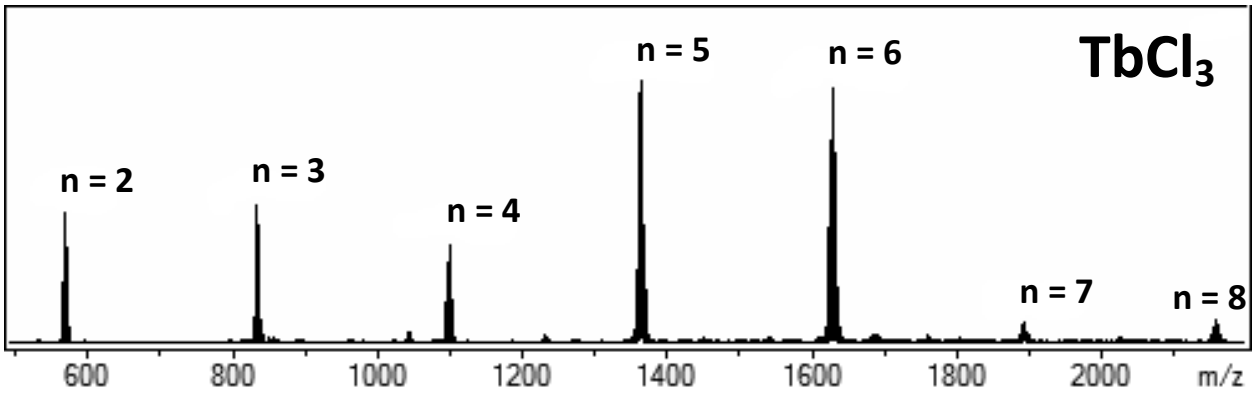


Figure S1h. ESI mass spectra of 350 μM $TbCl_3$ in isopropanol. $Tb_nCl_{3n+1}^-$ clusters are labeled.

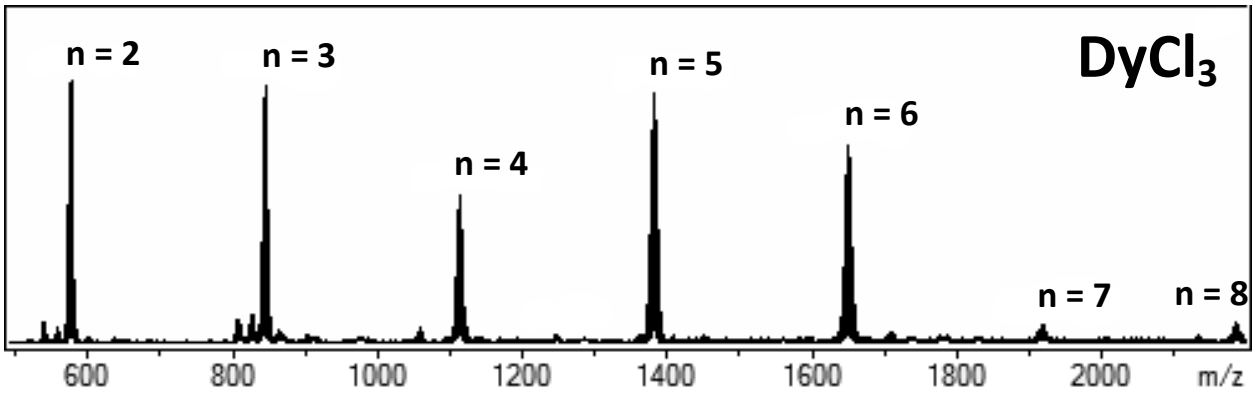


Figure S1i. ESI mass spectra of 350 μM $DyCl_3$ in isopropanol. $Dy_nCl_{3n+1}^-$ clusters are labeled.

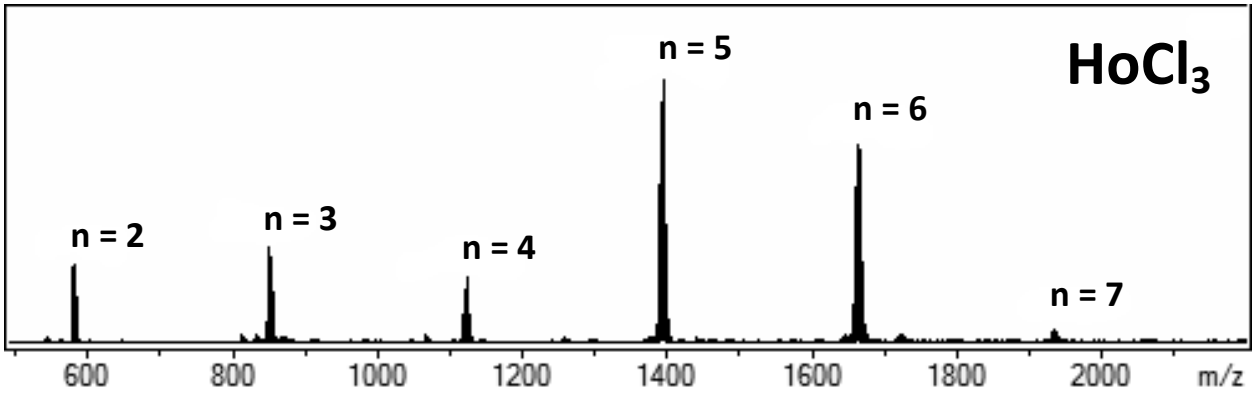


Figure S1j. ESI mass spectra of 350 μM $HoCl_3$ in isopropanol. $Ho_nCl_{3n+1}^-$ clusters are labeled.

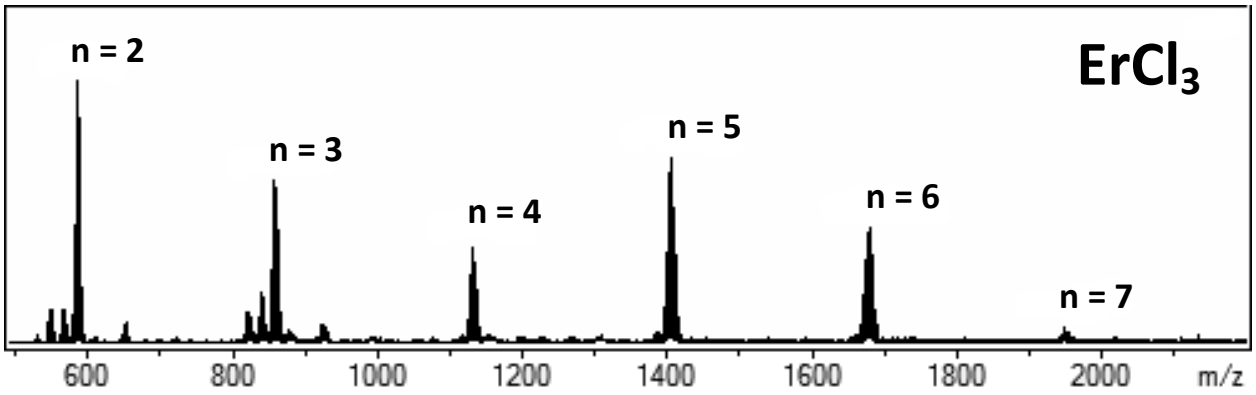


Figure S1k. ESI mass spectra of 350 μM $ErCl_3$ in isopropanol. $Er_nCl_{3n+1}^-$ clusters are labeled.

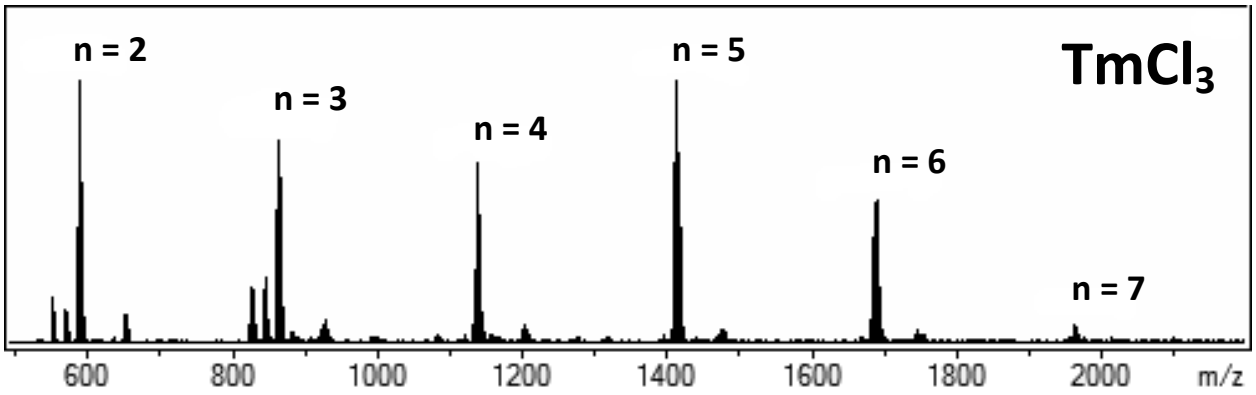


Figure S1l. ESI mass spectra of 350 μM $TmCl_3$ in isopropanol. $Tm_nCl_{3n+1}^-$ clusters are labeled.

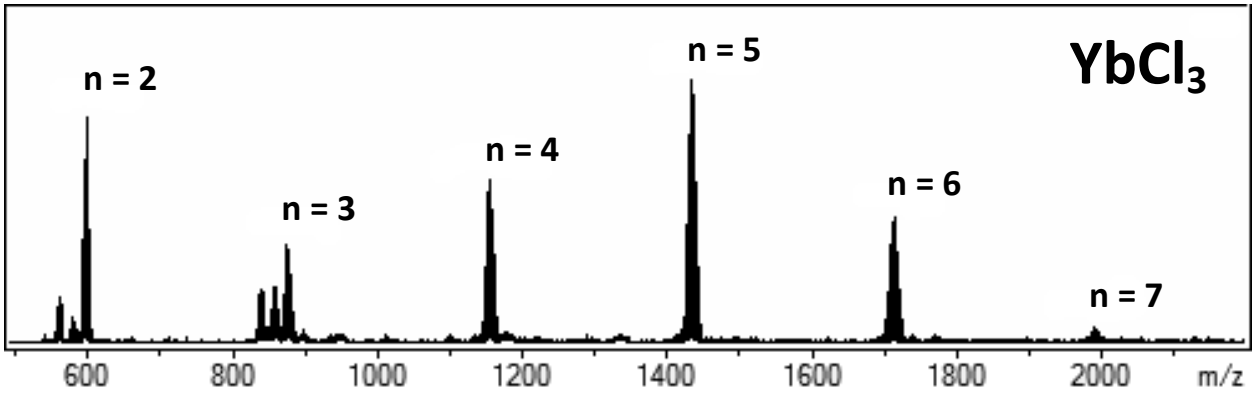


Figure S1m. ESI mass spectra of 350 μM $YbCl_3$ in isopropanol. $Yb_nCl_{3n+1}^-$ clusters are labeled.

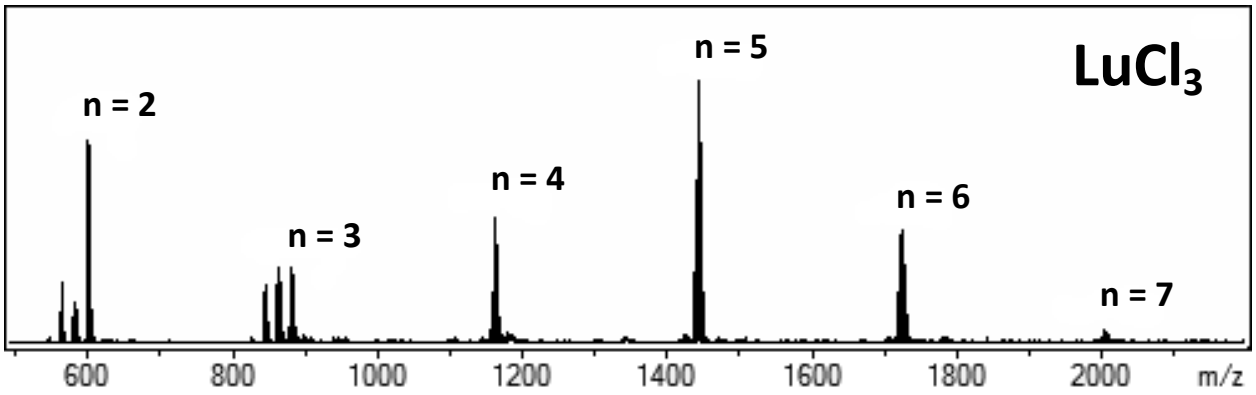


Figure S1n. ESI mass spectra of 350 μM $LuCl_3$ in isopropanol. $Lu_nCl_{3n+1}^-$ clusters are labeled.

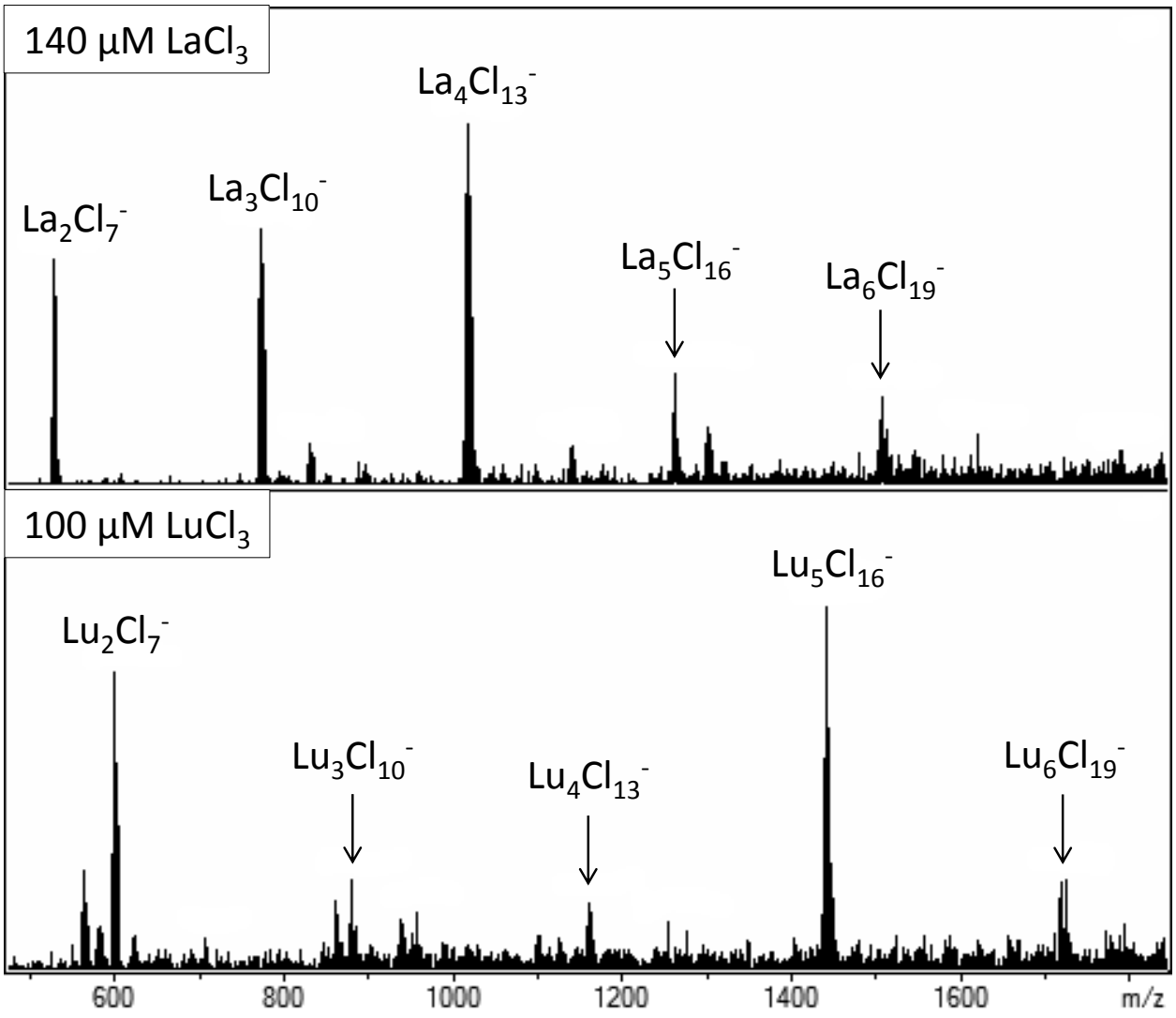


Figure S2. ESI mass spectra of 140 µM $LaCl_3$ (top) and 100 µM $LuCl_3$ (bottom) in isopropanol. The signal-to-background ratio is inferior to that for the more concentrated 350 µM solutions, but the same "magic number" compositions, $La_4Cl_{13}^-$ and $Lu_5Cl_{16}^-$, are clearly apparent.

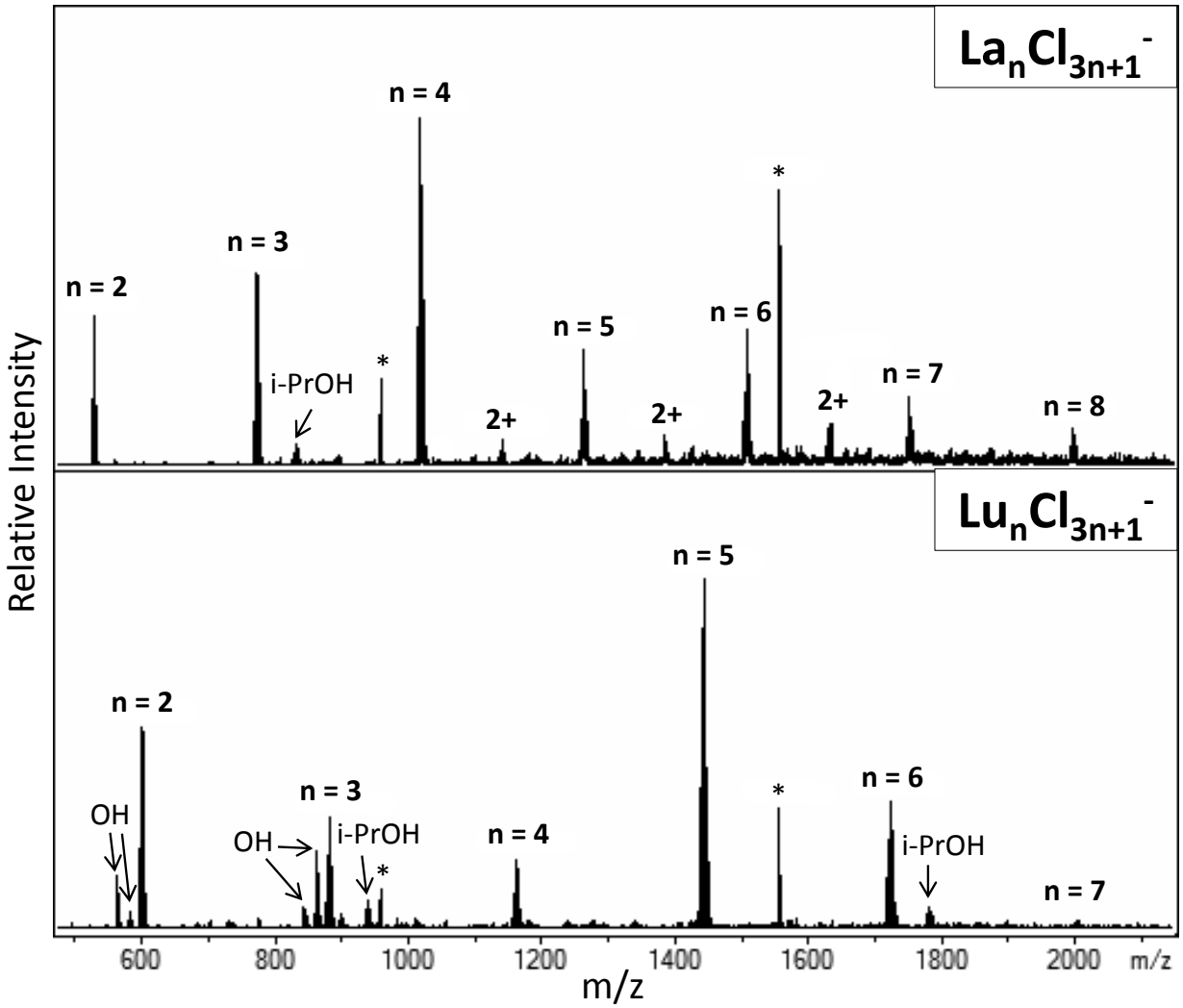
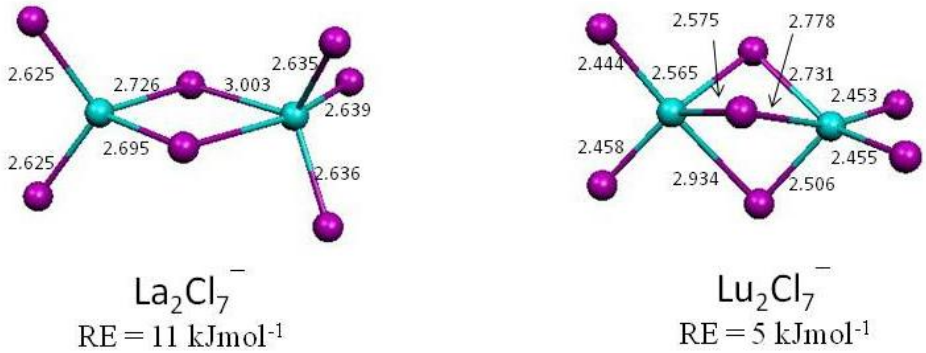


Figure S3. ESI mass spectra of 350 μM $LaCl_3$ (top) and $LuCl_3$ (bottom) in isopropanol, with the chloride concentration increased to 10.35 mM by addition of HCl, to a concentration of 10 mM. The "magic number" compositions, $La_4Cl_{13}^-$ and $Lu_5Cl_{16}^-$, remain clearly evident upon increasing the Cl^- concentration by ~30x, from 0.35 mM in the other studied solutions to 10.35 mM in these solutions. The peaks identified by asterisks which appear in both mass spectra are unidentified impurities which do not exhibit isotopic patterns corresponding to incorporation of $^{35}Cl/^{37}Cl$. Peaks corresponding to addition of isopropanol, and to chloride substitution by hydroxide, are identified.



$La_2Cl_7^-$
RE = 11 kJmol^{-1}

$Lu_2Cl_7^-$
RE = 5 kJmol^{-1}

Figure S4. Geometric structures of higher-energy isomers of La_2Cl^{7-} and $Lu_2Cl_7^-$. Relative energies (RE) are calculated with respect to the ground-state structures.

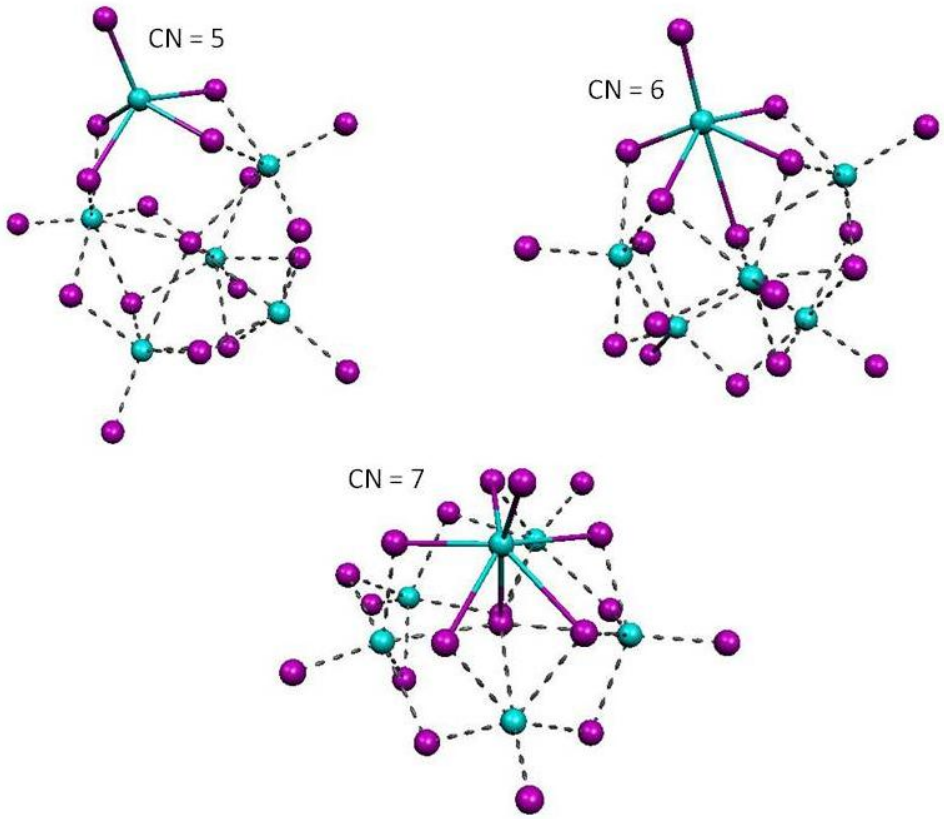


Figure S5. Different views of $La_6Cl_{19}^-$ showing different lanthanide coordination numbers.

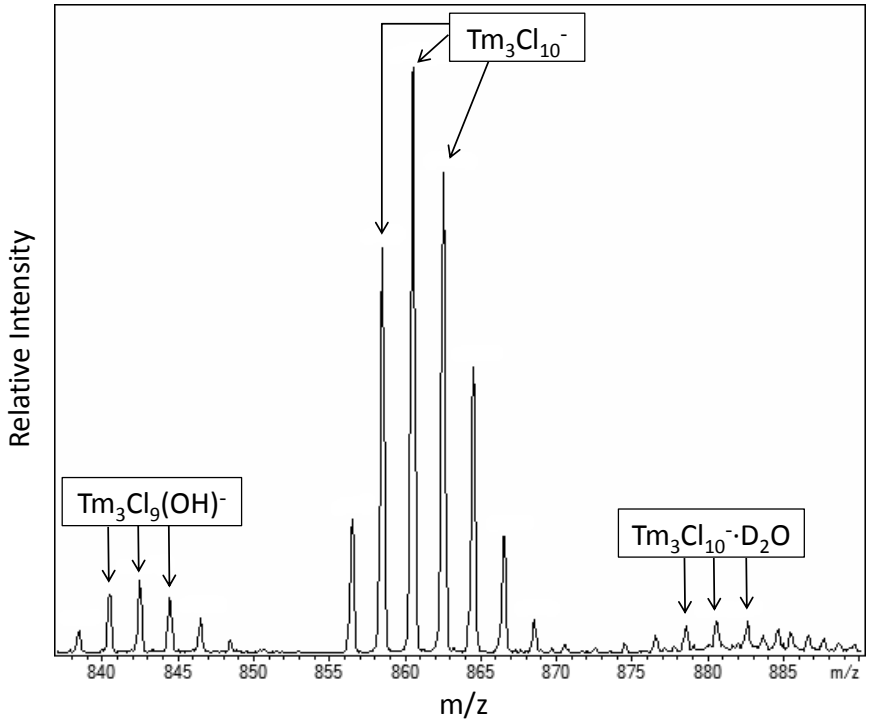


Figure S6. Portion of ESI mass spectrum of a solution of 350 uM $TmCl_3$ in 1% D2O/99% (CH3)2CH(OD) showing $Tm_3Cl_{10}^-$ and its hydration and hydrolysis products. For each species the three m/z peaks calculated as most intense are indicated by arrows.

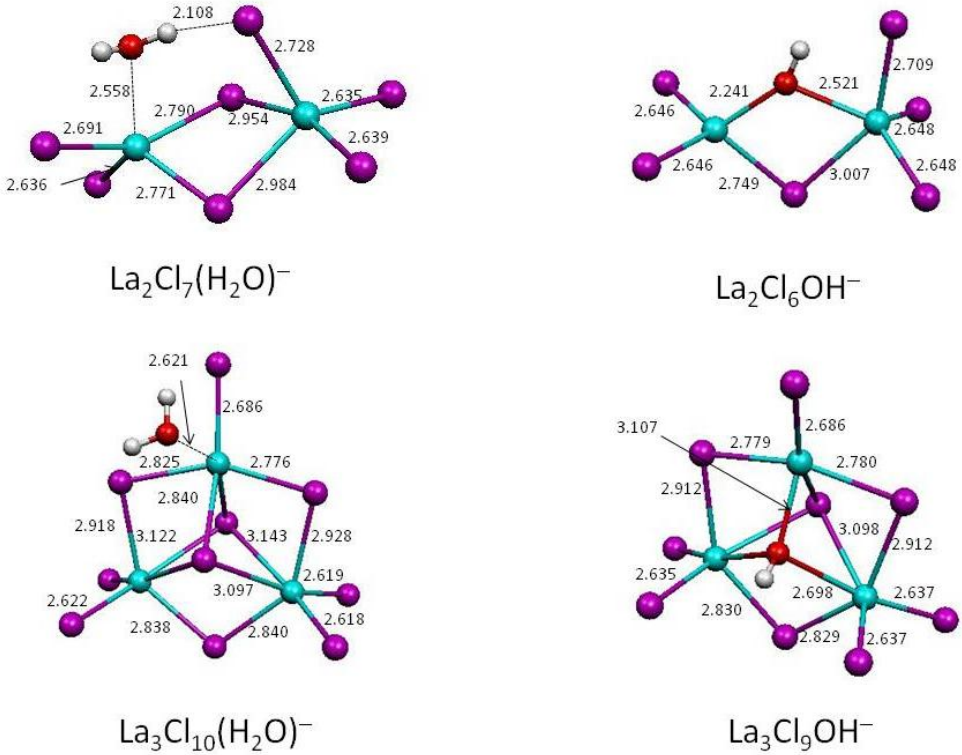


Figure S7. Hydration and hydrolysis products of $La_2Cl_7^-$ and $La_3Cl_{10}^-$.

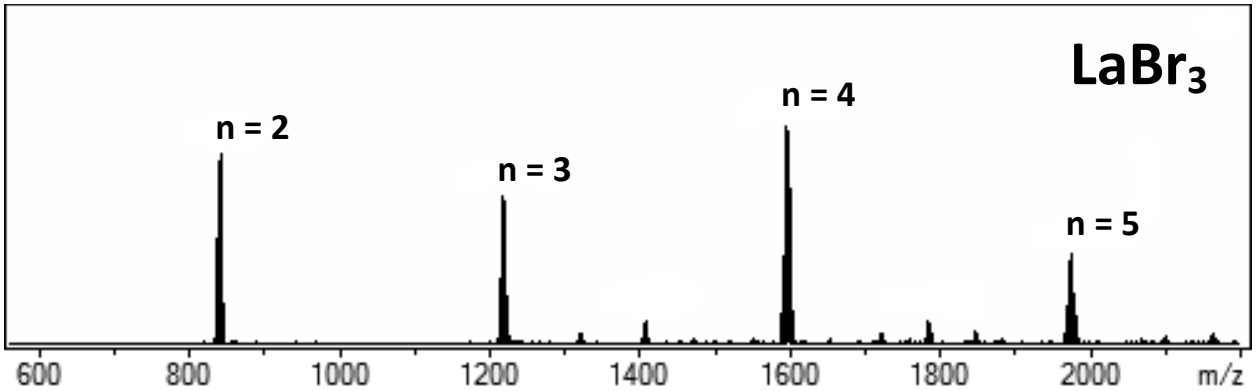


Figure S8a. ESI mass spectra of $LaBr_3$ in isopropanol. $La_nBr_{3n+1}^-$ clusters are labeled.

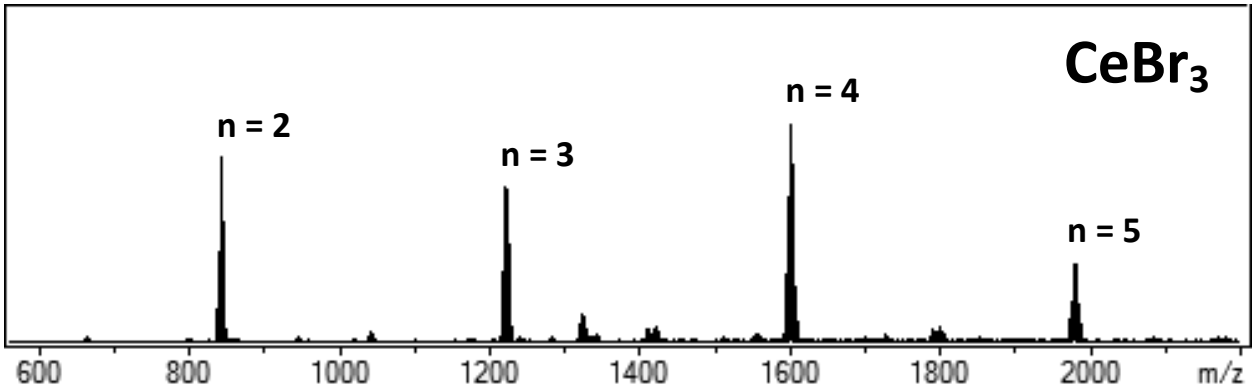


Figure S8b. ESI mass spectra of $CeBr_3$ in isopropanol. $Ce_nBr_{3n+1}^-$ clusters are labeled.

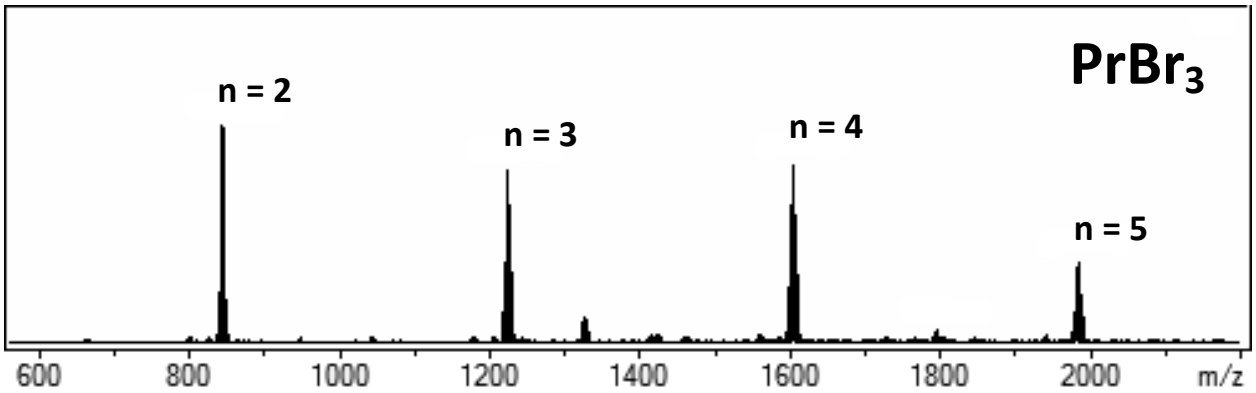


Figure S8c. ESI mass spectra of $PrBr_3$ in isopropanol. $Pr_nBr_{3n+1}^-$ clusters are labeled.

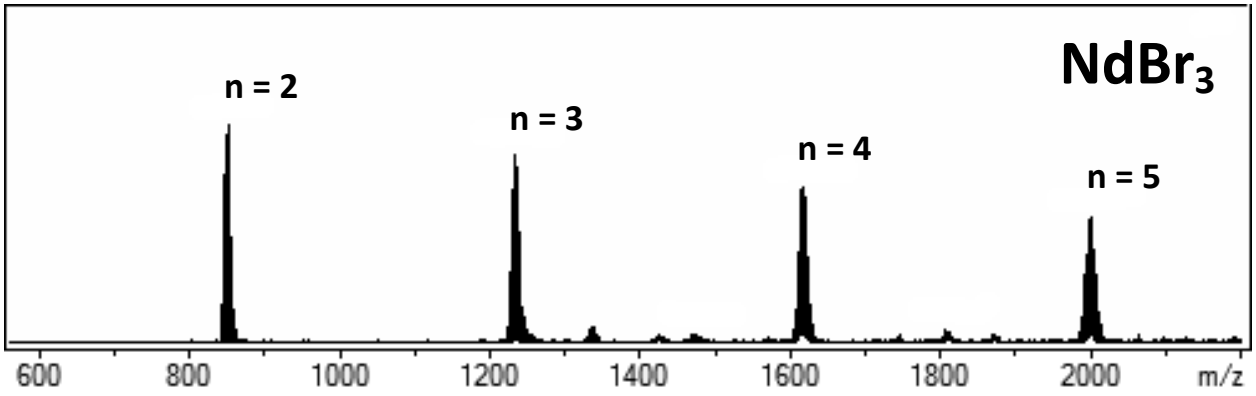


Figure S8d. ESI mass spectra of $NdBr_3$ in isopropanol. $Nd_nBr_{3n+1}^-$ clusters are labeled.

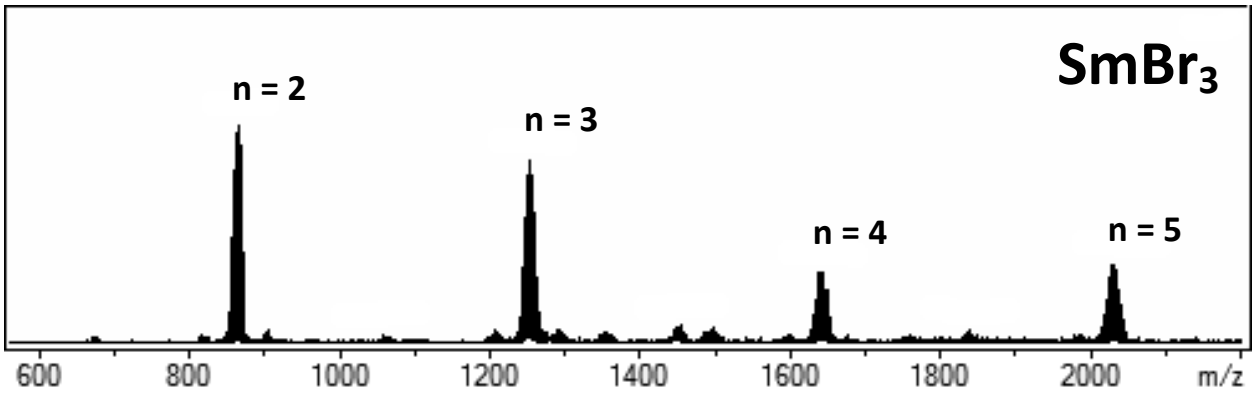


Figure S8e. ESI mass spectra of $SmBr_3$ in isopropanol. $Sm_nBr_{3n+1}^-$ clusters are labeled.

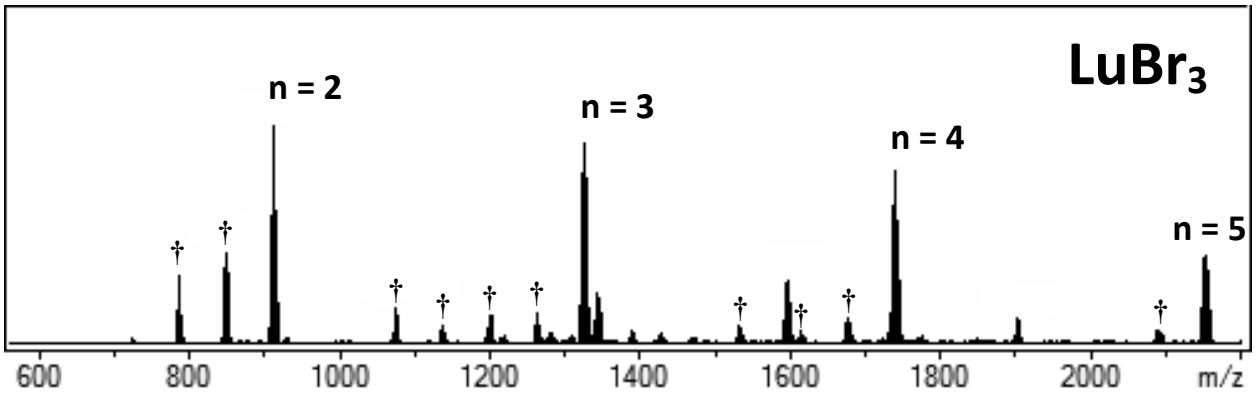


Figure S8f. ESI mass spectra of $LuBr_3$ in isopropanol. $Lu_nBr_{3n+1}^-$ clusters are labeled. Hydroxide-substituted clusters are indicated by daggers.

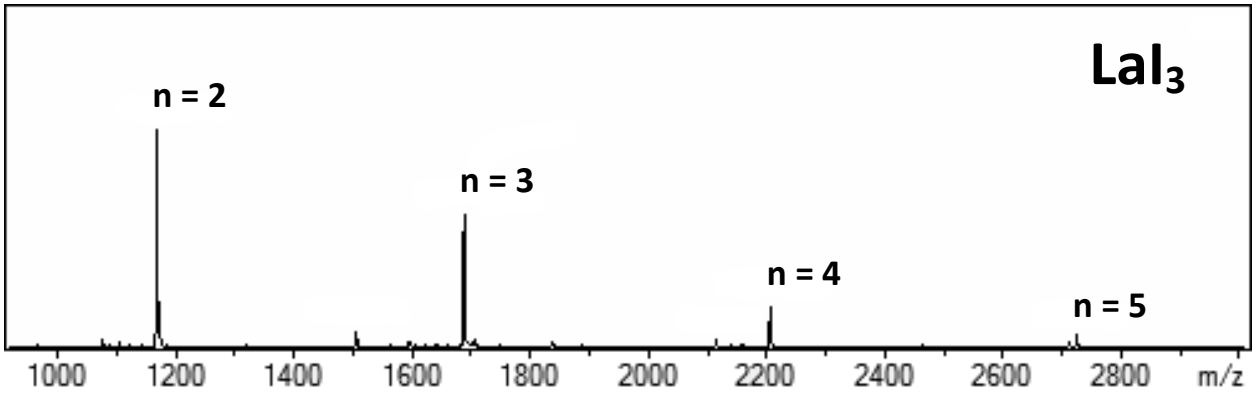


Figure S9a. ESI mass spectra of LaI_3 in isopropanol. $La_nI_{3n+1}^-$ clusters are labeled.

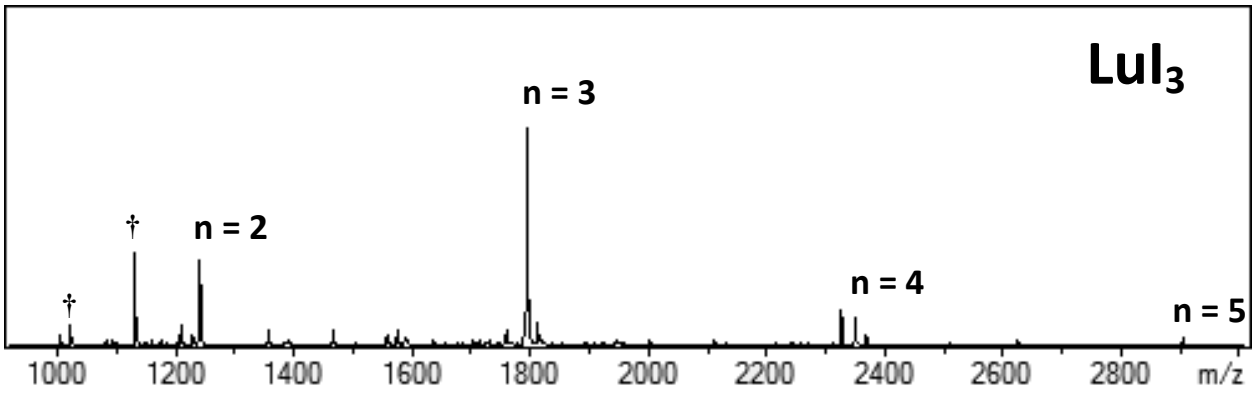


Figure S9b. ESI mass spectra of LuI_3 in isopropanol. $Lu_nI_{3n+1}^-$ clusters are labeled. Hydroxide-substituted clusters are indicated with daggers.

Table S1. AIM Charges for $LaCl_3$ and $La_nCl_{3n+1}^-$ (n =1- 6) clusters

	La	Cl (terminal)[a]	Cl (bridge)[a]	Cl (center)[a]
$LaCl_3$	1.963	-0.654	-	-
$LaCl_4^-$	1.975	-0.744	-	-
$La_2Cl_7^-$	1.998	-0.716	-0.711	-
$La_3Cl_{10}^-$	1.994	-0.695	-0.700	-
$La_4Cl_{13}^-$	2.011	-0.688	-0.695	-0.730
$La_5Cl_{16}^-$	2.019	-0.672	-0.689	-0.759
$La_6Cl_{19}^-$	1.993	-0.664	-0.689	-0.761

[a] Averaged values over all the corresponding Cl atoms.

Table S2. AIM Charges for $LuCl_3$ and $Lu_nCl_{3n+1}^-$ (n =1-6) clusters

	Lu	Cl (terminal)[a]	Cl (bridge)[a]	Cl (center)[a]
$LuCl_3$	2.009	-0.670	-	-
$LuCl_4^-$	1.979	-0.745	-	-
$Lu_2Cl_7^-$	2.013	-0.703	-0.754	-
$Lu_3Cl_{10}^-$	2.007	-0.697	-0.707	-
$Lu_4Cl_{13}^-$	2.042	-0.694	-0.707	-0.738
$Lu_5Cl_{16}^-$	2.012	-0.679	-0.689	-0.764
$Lu_6Cl_{19}^-$	2.010	-0.676	-0.686	-0.777

[a] Averaged values over all the corresponding Cl atoms.

Table S3. Lanthanide bromide cluster abundances normalized to the most abundant cluster for each lanthanide.[a]

	2	**3**	**4**	**5**
$La_nBr_{3n+1}^-$	65%	59%	**100%**	45%
$Ce_nBr_{3n+1}^-$	65%	63%	**100%**	40%
$Pr_nBr_{3n+1}^-$	95%	85%	**100%**	50%
$Nd_nBr_{3n+1}^-$	87%	**100%**	98%	91%
$Sm_nBr_{3n+1}^-$	95%	**100%**	45%	53%
$Lu_nBr_{3n+1}^-$	**100%**	95%	80%	42%

[a] Cluster abundances correspond to the sum of peak intensities for all isotopomers which contribute to the isotopic distribution for a given cluster composition. Only $Lu_2Br_7^-$ and $Lu_3Br_{10}^-$ hydrolyzed; the contributions from the OH-substituted clusters are included.