



# Investigating Covalent Bonding in f-elements using Gas-phase Ion Chemistry

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*Changing the World's Energy Future*

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# Gas-Phase Stability of Large Lanthanide:Ligand Clusters Evaluated Using Collision-Induced Dissociation

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## Impact

- Improve biphasic organic-aqueous separation of actinides and lanthanides in used nuclear fuels by elucidating intrinsic differences in lanthanide-ligand covalent behaviors

## Objective

- Improve understanding of covalent interactions in *f*-element reprocessing systems absent from solvent effects by investigating lanthanide:N,N,N',N'-tetraoctyl diglycolamide (TODGA) gas-phase metal ion clusters

## Background

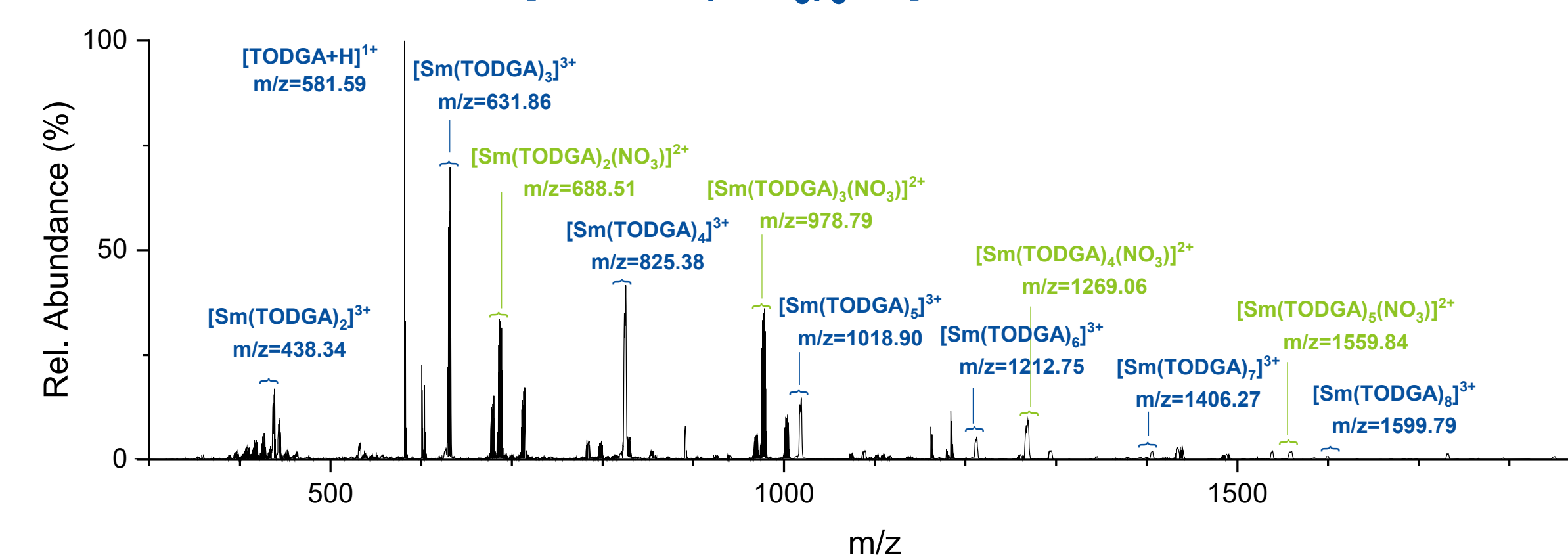
- Diglycolamides (DGAs) are utilized by the Actinide Lanthanide Separation (ALSEP) process, a promising single-process separation
- Tandem mass spectrometry (MS<sup>2</sup>) isolates and collisionally induces fragmentation of gas-phase molecular ions formed during ionization, enabling relative determination of covalent bond strength

## Approach

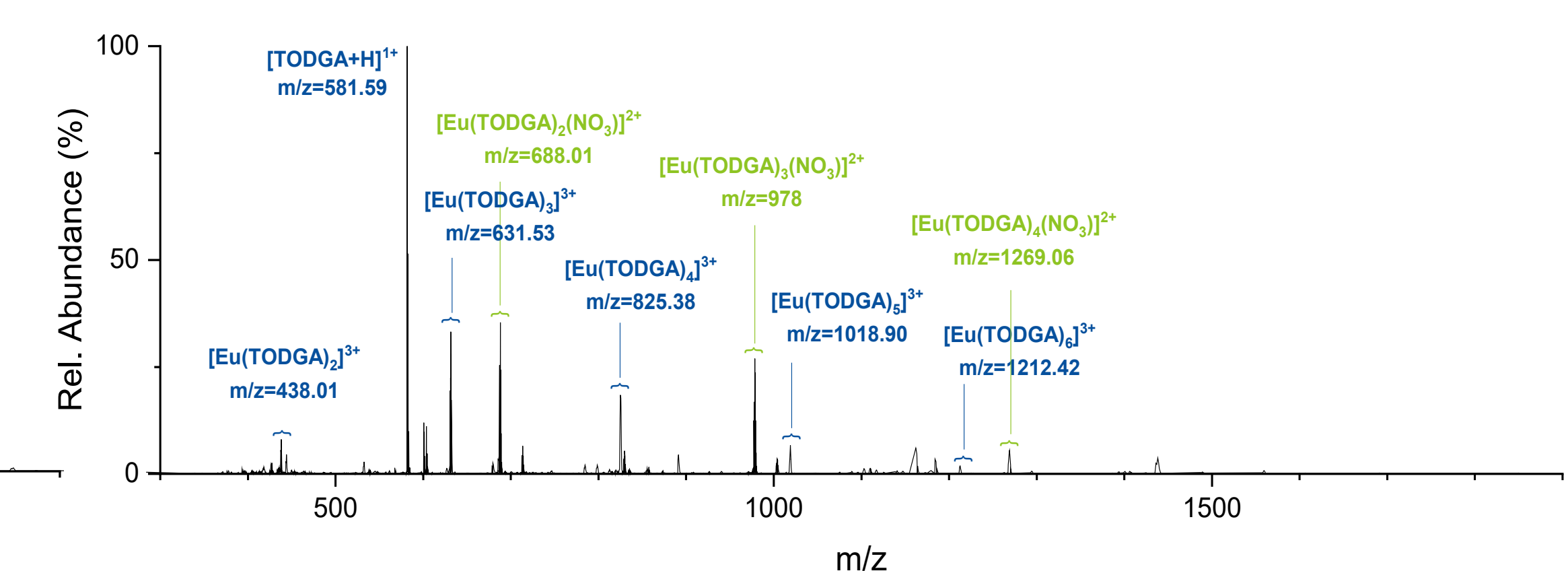
- Synthesize lanthanide:TODGA gas phase ion clusters containing samarium (Sm) or europium (Eu) using nanospray ionization and a quadrupole time-of-flight mass spectrometer.
- Identify metal ion clusters using exact mass measurements and tandem mass spectrometry experiments
- Compare relative covalent bond strength of metal ion clusters by varying applied collision voltage and determining collisional fragments

## Results

30  $\mu\text{M}$   $\text{Sm}(\text{NO}_3)_3$  3  $\mu\text{M}$  TODGA

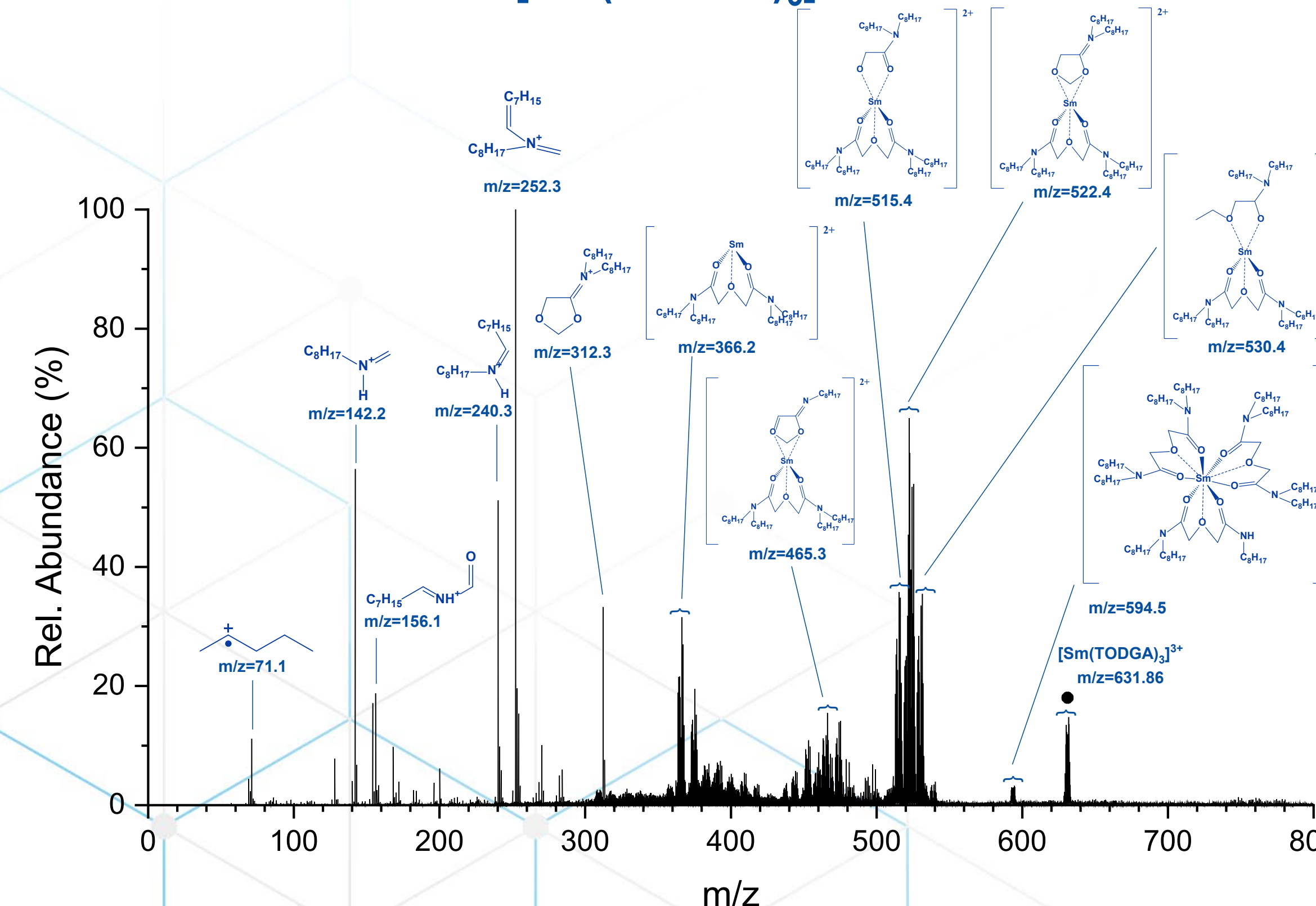


30  $\mu\text{M}$   $\text{Eu}(\text{NO}_3)_3$  3  $\mu\text{M}$  TODGA

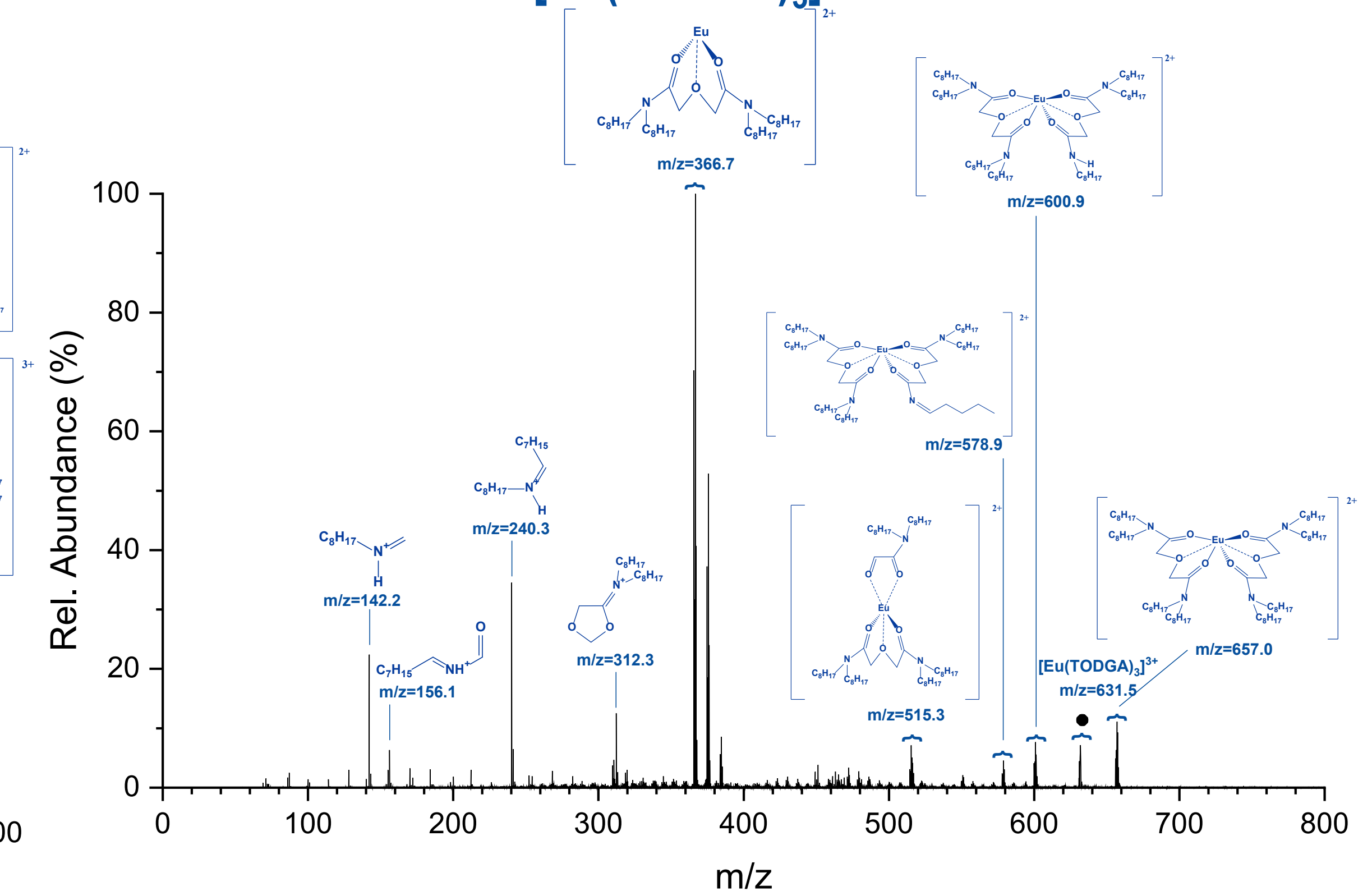


- Surprisingly large clusters were detected: up to  $[\text{Sm}(\text{TODGA})_{10}]^{3+}$  and  $[\text{Eu}(\text{TODGA})_8]^{3+}$
- Large clusters containing nitrate were also identified: up to  $[\text{Sm}(\text{TODGA})_8(\text{NO}_3)]^{2+}$  and  $[\text{Eu}(\text{TODGA})_6(\text{NO}_3)]^{2+}$
- MS<sup>2</sup> experiments show that  $[\text{Ln}(\text{TODGA})_3]^{3+}$  clusters produce complex fragmentation spectra, while  $[\text{Ln}(\text{TODGA})_n]^{3+}$  ( $n \geq 4$ ) fragment through elimination of intact TODGA molecules
- MS<sup>2</sup> also shows that less collision energy is required to remove a neutral ligand with increasing cluster size
- This suggests that the metal coordination sphere is saturated by three TODGA ligands, so additional ligands are weakly bound

$[\text{Sm}(\text{TODGA})_3]^{3+}$  MS<sup>2</sup>



$[\text{Eu}(\text{TODGA})_3]^{3+}$  MS<sup>2</sup>



- The product of the loss of a TODGA cation,  $[\text{Ln}(\text{TODGA})_2]^{2+}$ , is not observed for samarium and is not particularly abundant for europium; however, there is evidence of serial fragmentation of this cluster due to other metallic species present

## Acknowledgements

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