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Selective Detection of Diglycolamide Diastereomers By Metal-Ligand Cluster Formation

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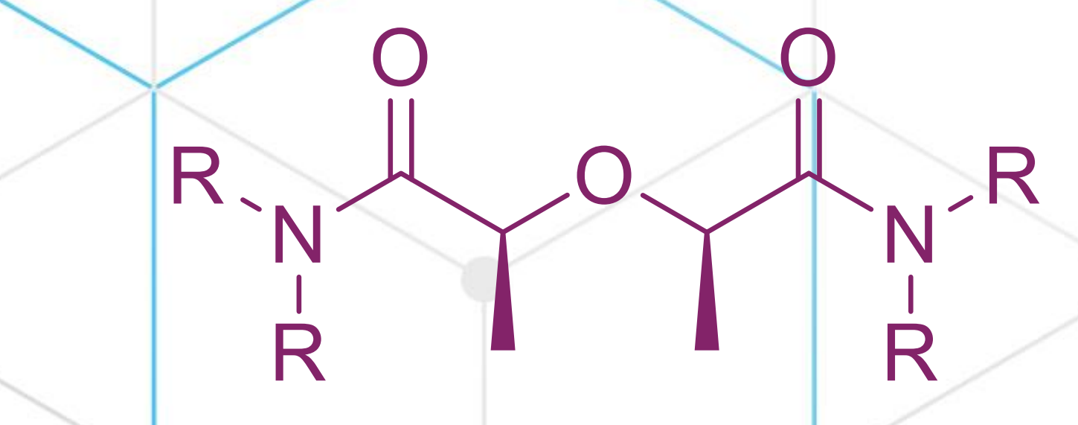
Impact

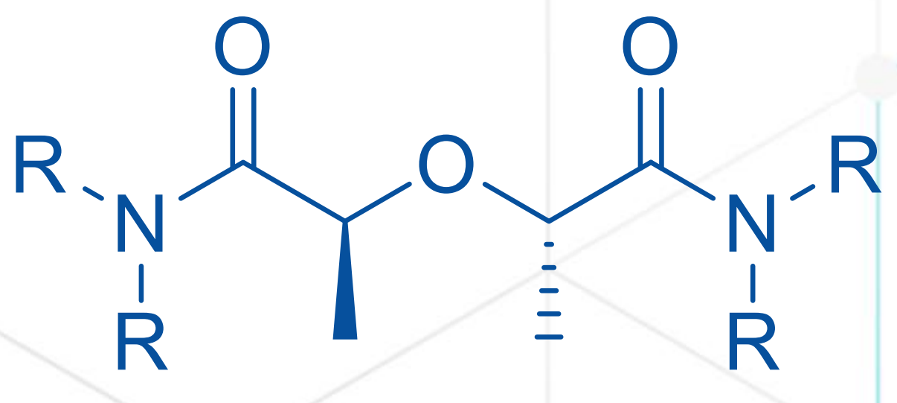
- Stereoisomers can be differentiated in the gas phase by exploitation of differences in metal complexation chemistry.

Background

- Recent investigations of the solvent extraction behavior of diastereomers of diglycolamide (DGA) molecules show different stereoisomers can have significantly different lanthanide extraction efficiencies. These studies showed that the (R,S) stereoisomer of 2,2'-oxybis(N,N-dioctylpropanamide (mTDDGA) efficiently extracts lanthanides, while the (S,S) stereoisomer does not. Thus, gas-phase metal complexation provides a pathway for differentiating these species using mass spectrometry.



(R,S)-mTDDGA



(S,S)-mTDDGA

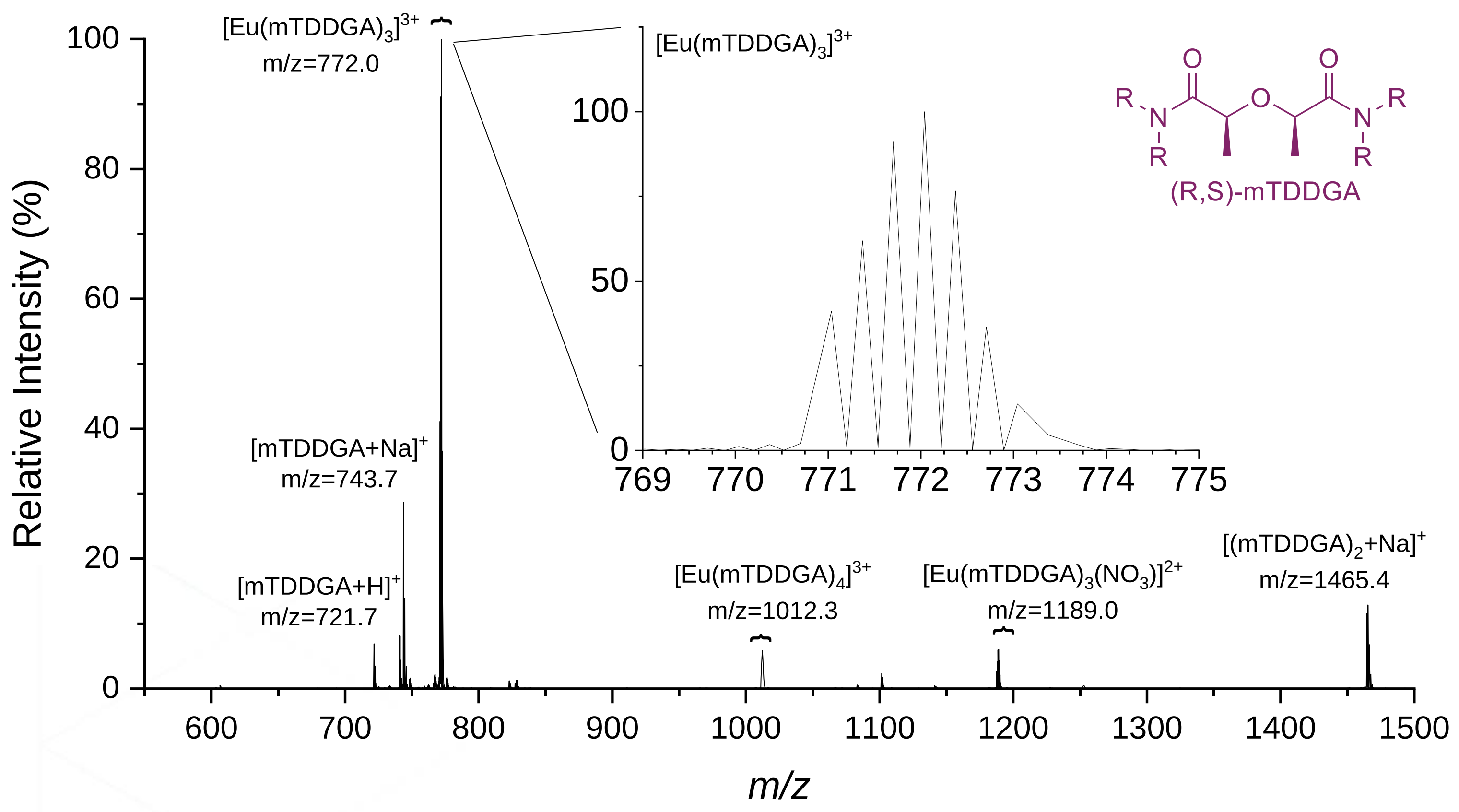
R = $C_{10}H_{21}$

Approach

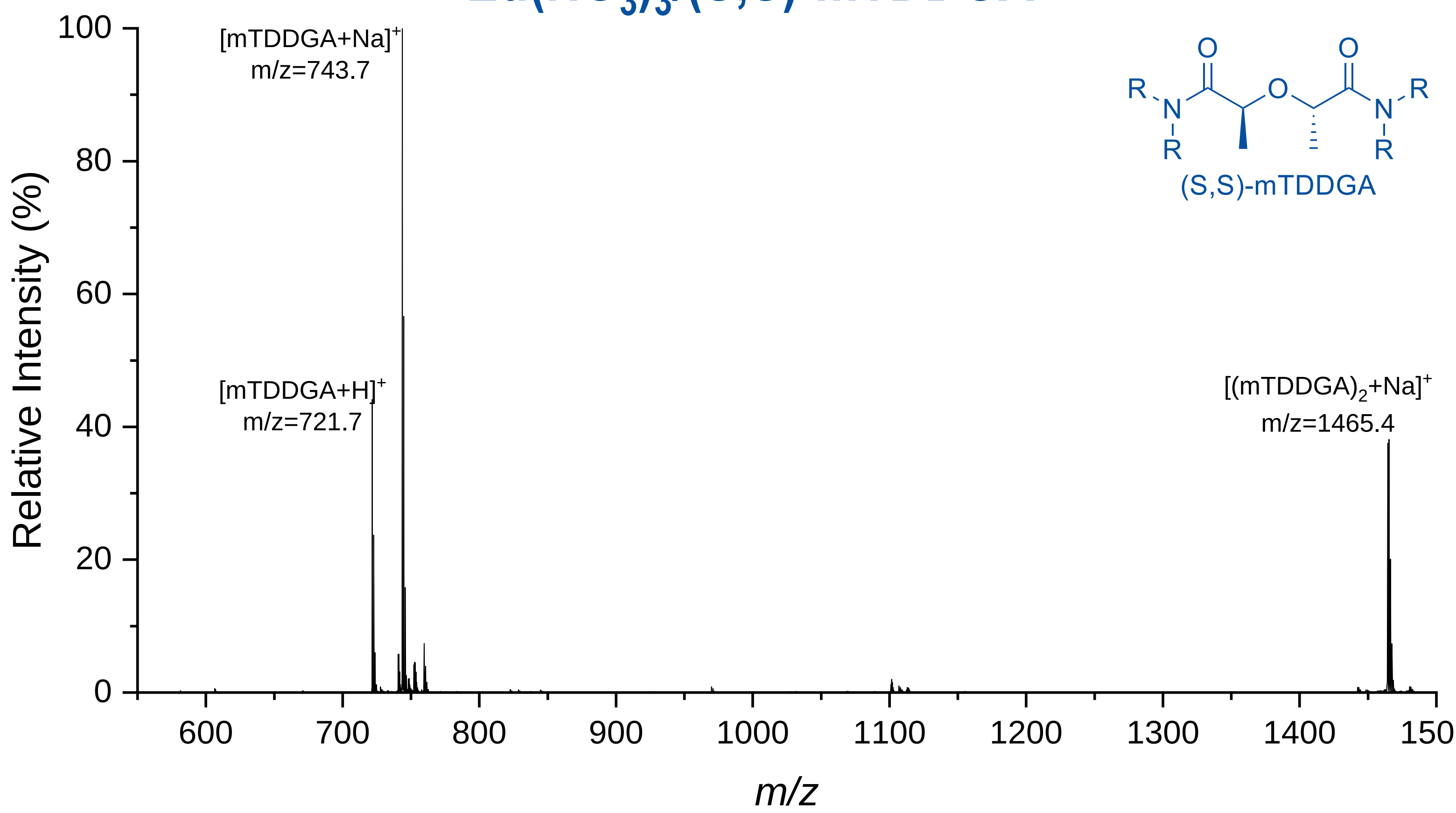
- Spray solutions of (S,R)-mTDDGA and (S,S)-mTDDGA mixed with europium (Eu) or samarium (Sm) using electrospray into a Bruker micrOTOF-Q II quadrupole time-of-flight mass spectrometer. Species identification is performed using formulas derived from accurate mass measurements.

Results

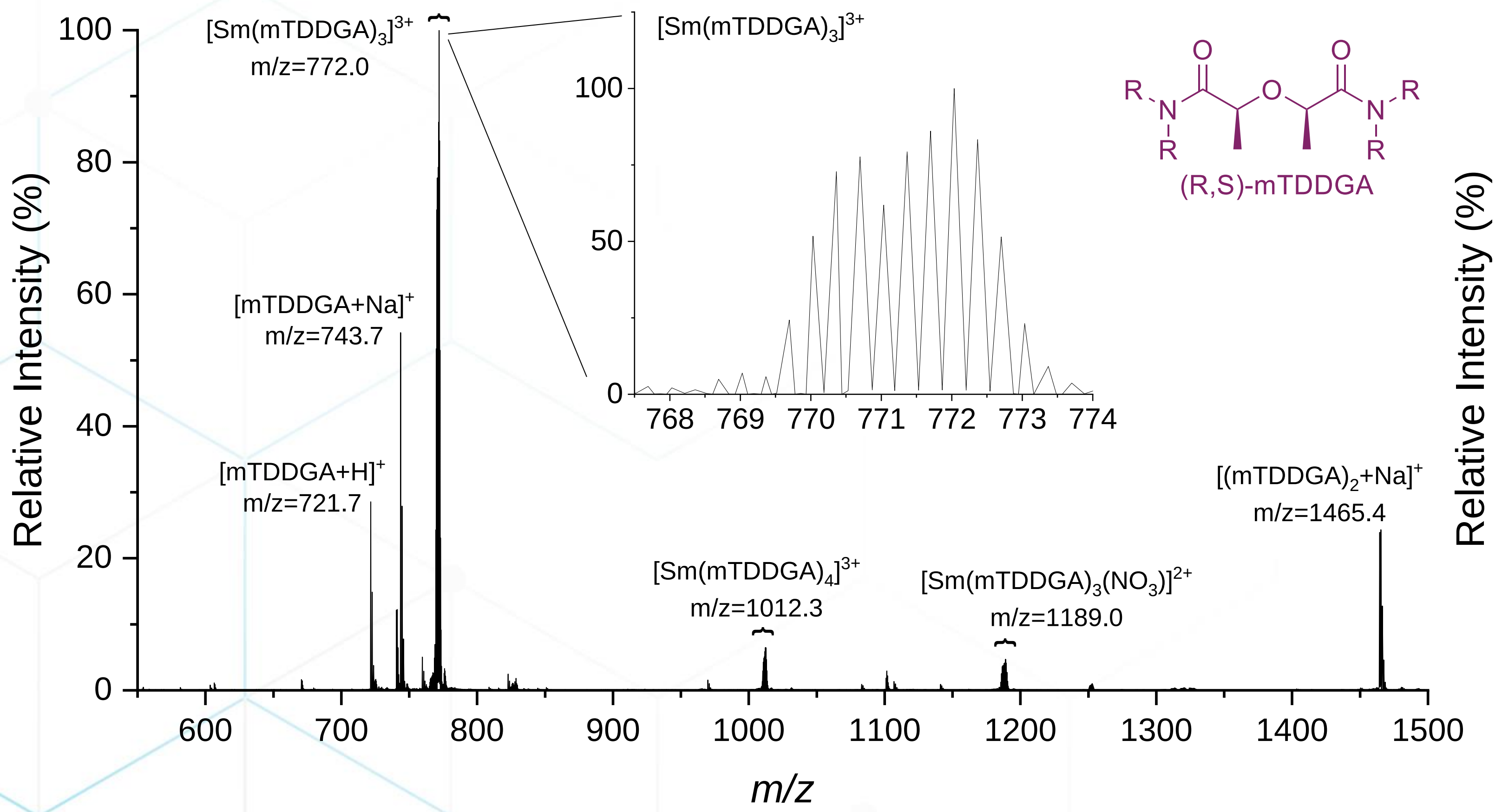
$Eu(NO_3)_3$/(R,S)-mTDDGA



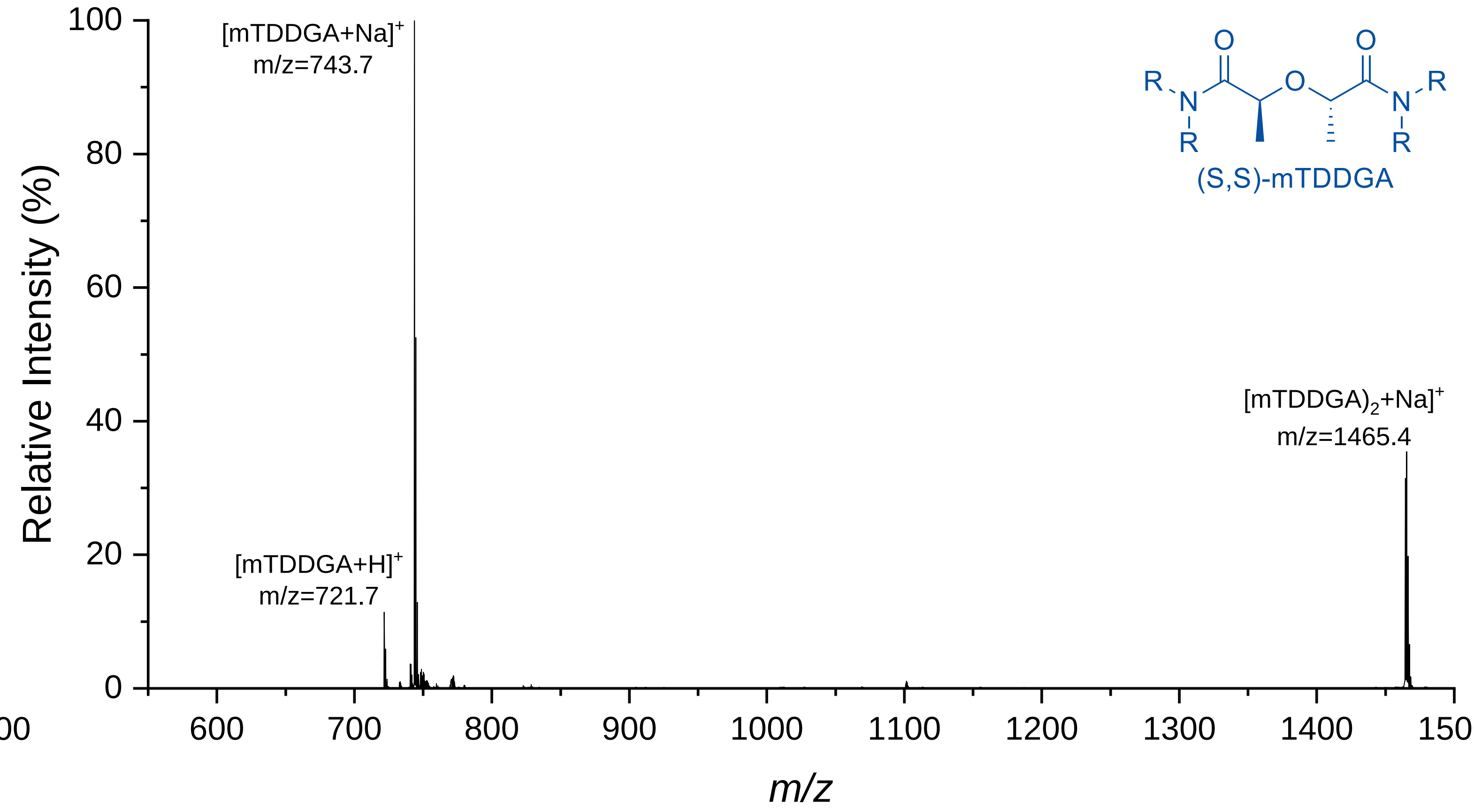
$Eu(NO_3)_3$/(S,S)-mTDDGA



$Sm(NO_3)_3$/(R,S)-mTDDGA



$Sm(NO_3)_3$/(S,S)-mTDDGA



Conclusions:

- Electrospray of solutions containing 6 μM Eu or Sm nitrate with 3 μM (R,S)-mTDDGA produced an abundant cluster ion with an isotopic envelope centered at approximately m/z=772, corresponding to $[Eu(R,S\text{-}mTDDGA)_3]^{3+}$ and $[Sm(R,S\text{-}mTDDGA)_3]^{3+}$.
- Electrospray of solutions with (S,S)-mTDDGA did not produce any lanthanide-DGA clusters.
- This mirrors the solution-phase behavior, where the (S,S) diastereomer extracts lanthanides with significantly less efficiency than the (R,S) diastereomer.

Acknowledgements

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