

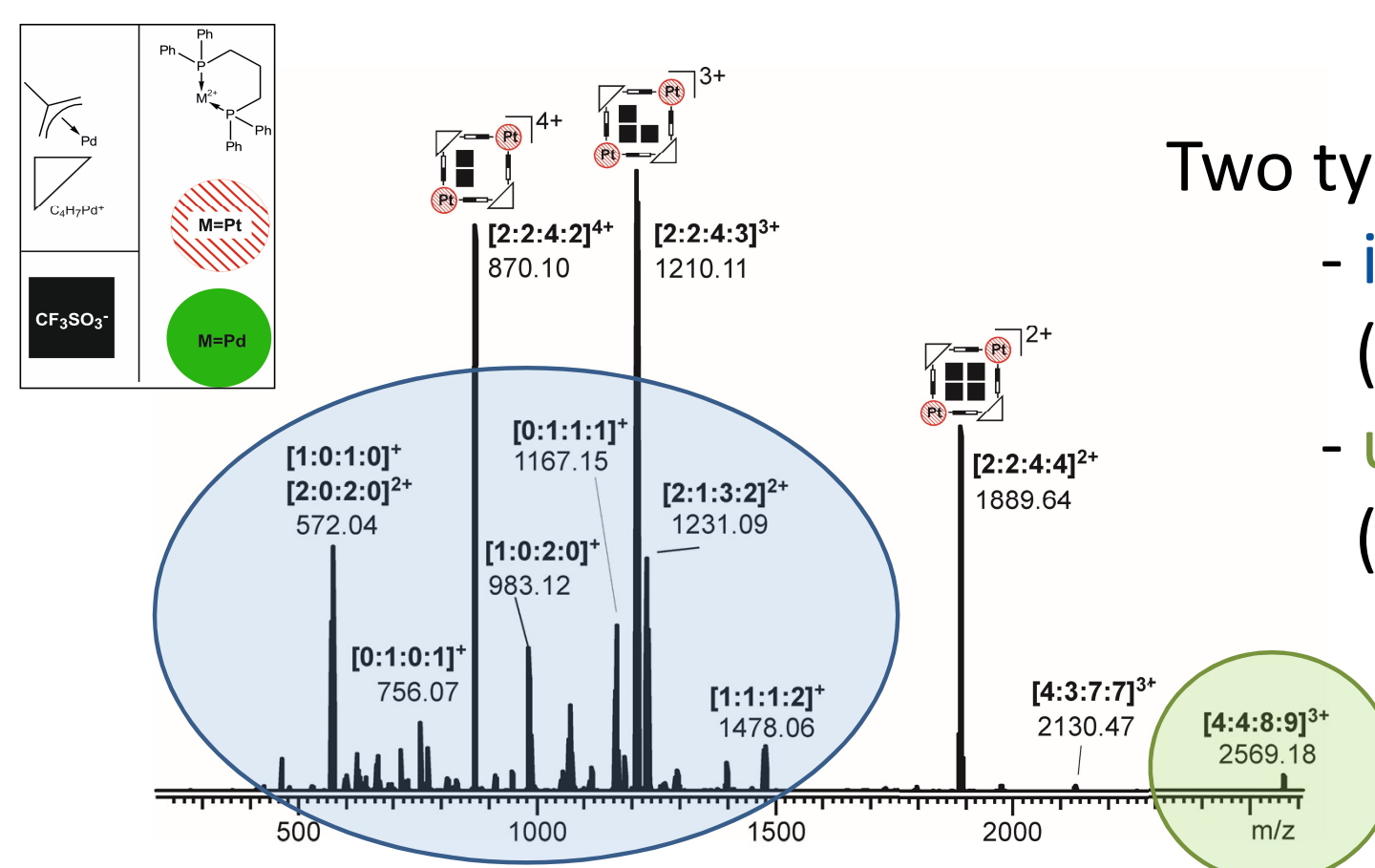
# Gas-phase fragmentation of metallo-supramolecular aggregates

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## Introduction

- Electrospray (ESI) Mass Spectrometry: an indispensable tool for the characterization of metallo-supramolecular aggregates.
- Typical signal series for the aggregates in different charge states are observed after stripping off varying number of anions.
- Stoichiometry (metal/ligand ratio) is directly determined.



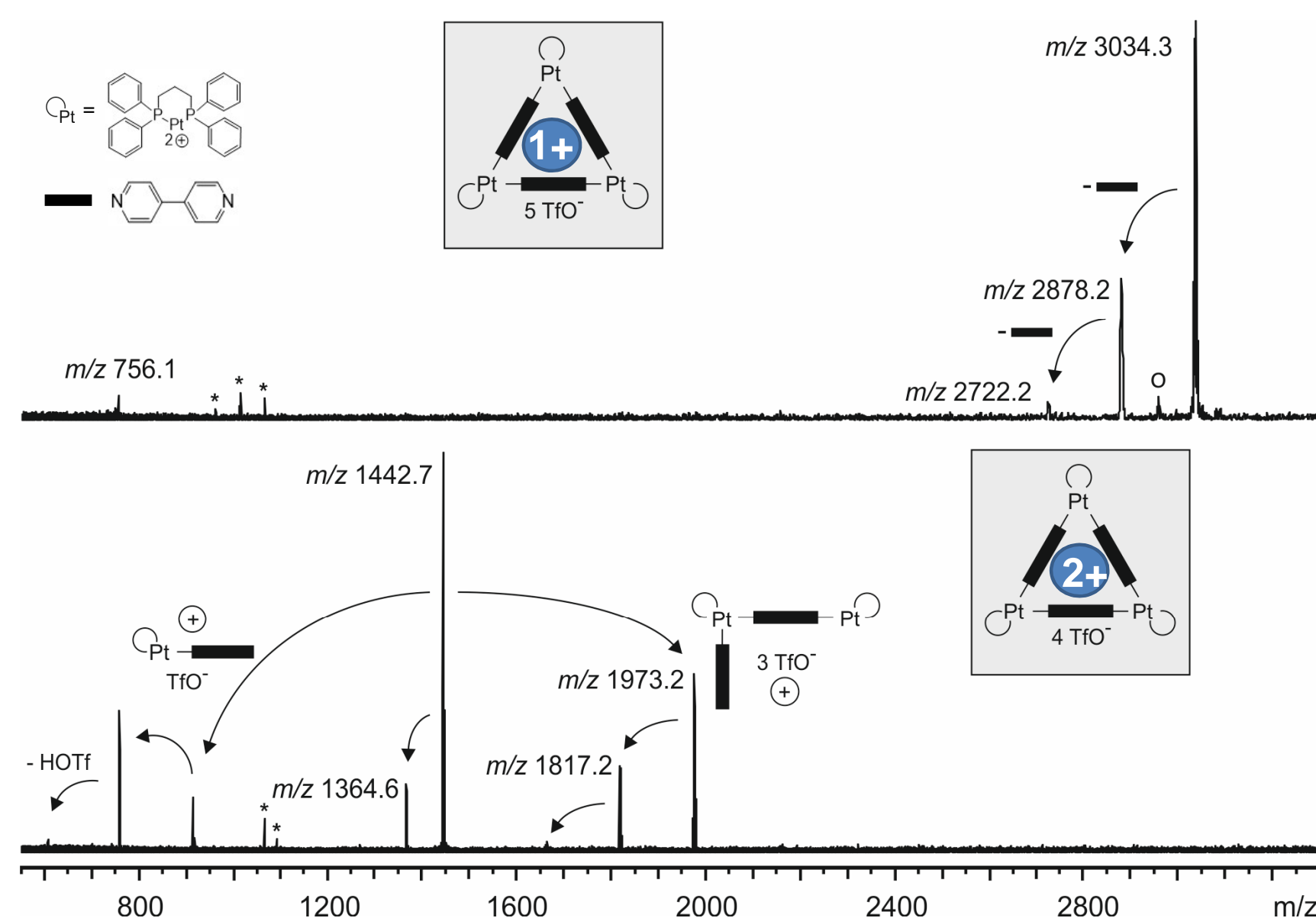
Two typical problems:

- in-source fragmentation (ESI too harsh)
- unspecific aggregation (ESI too soft)

- Question: **Structural/topological characterization by mass spectrometry**
- Analysis of fragmentation patterns in the gas phase  
variables: aggregate charge, size, ligand and metal type

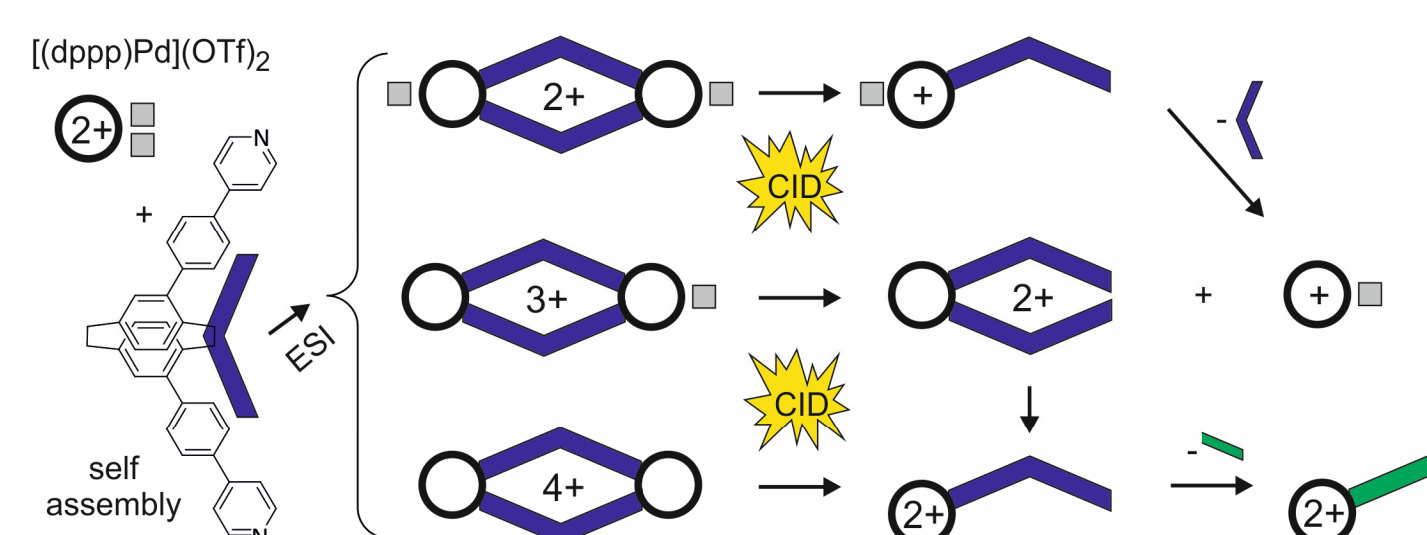
## Charge

The charge state dominates the fragmentation more than the structure:  
low charge states: **ligand expulsion** down to salt-bridged ions  
high charge states: **charge separation** into smaller aggregates

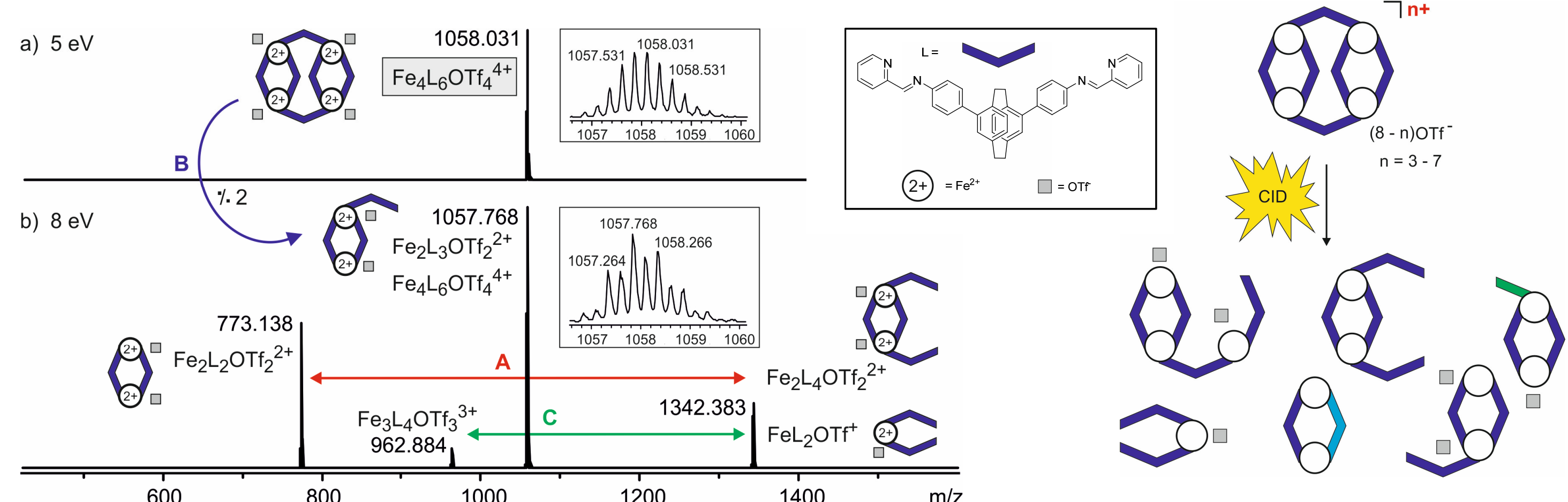


Typical fragmentation pattern for dinuclear rhombs:  
symmetric cleavage for even number of anions.  
Unsymmetric cleavage: **Anions fill free metal binding sites.**

## Paracyclophane-based unusual ligands



Paracyclophanes: **Ligand rupture into halves** needs less energy than the metal-ligand bond.  
These ligands are **not redox-innocent.**

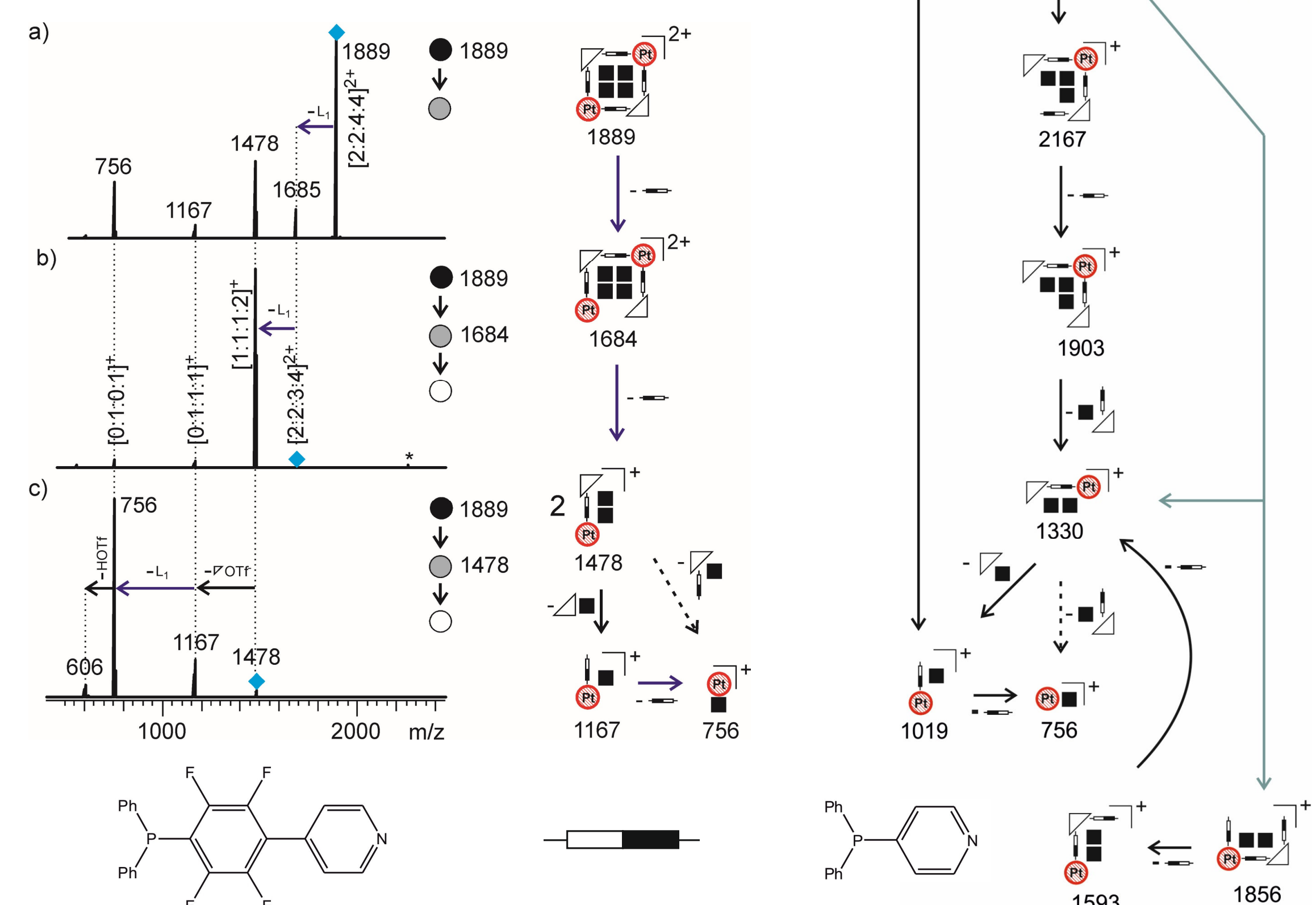


## Conclusions

- Fragmentation is strongly dominated by the **charge state**:  
**lower** charged complexes: **ligand expulsion**  
**higher** charged aggregates:  
**charge separation** by cleavage into smaller aggregates, additional redox pathways with special ligands
- Enlarging the structure by **elongating the ligands** can change the fragmentation pattern due to a **reduction of charge density.**
- Unsymmetrical cleavages** typically occur in such a way that high charge densities are avoided.  
Put the anions on the smaller fragment!
- Ligands may not be redox-innocent.
- The **topology** of the aggregate might be determined, but it is not the decisive factor for fragmentation.

## Ligand Size

Smaller ligands / **higher charge density** change the fragmentation pattern to charge separation pathways.



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