Mass Spectrometric Experiments in Supramolecular Chemistry

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I. Introduction

ESI-FT-ICR mass spectrometry is a valuable tool for the study of supramolecular complexes.

The possibility to study the weak non-covalent intermolecular interactions such as hydrogen bonds, π-π-stacking and ionic interactions in the absence of solvent molecules in the gas-phase as well as the capability to follow reactions in solution with high resolution and high sensitivity makes this method an important tool for research in that area.

Herein we describe different applications for ESI-FT-ICR-mass spectrometry in different fields of supramolecular chemistry, that have been studied recently in our groups.

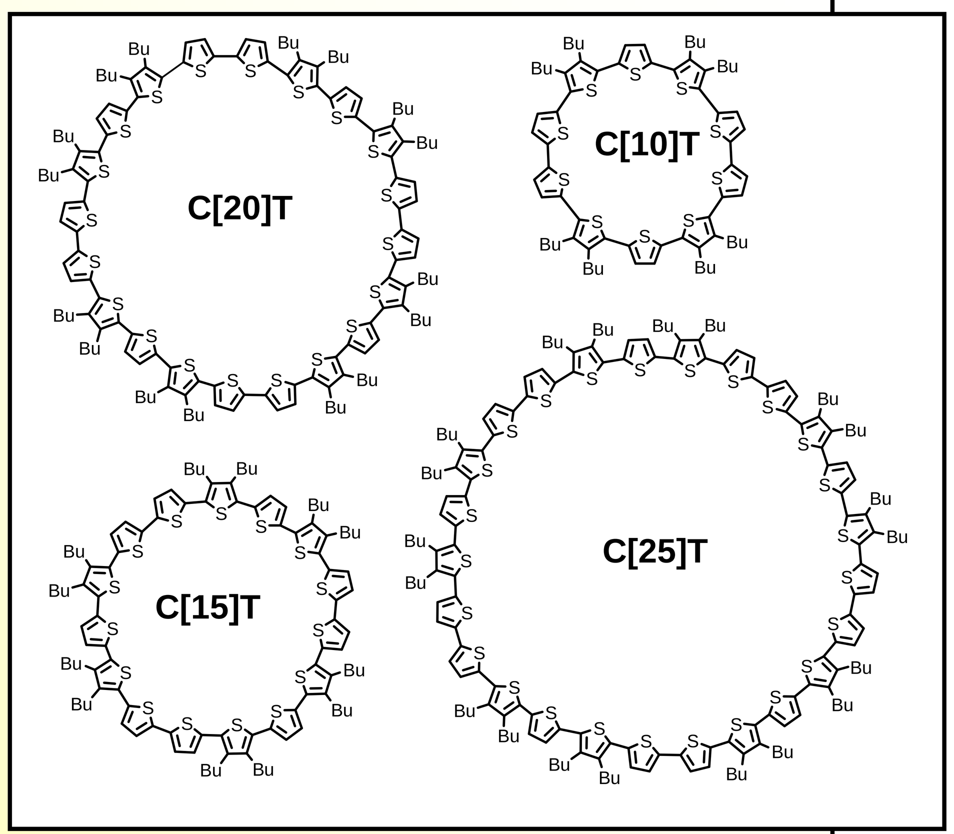
II. Aggregation of Thiophene Macrocycles

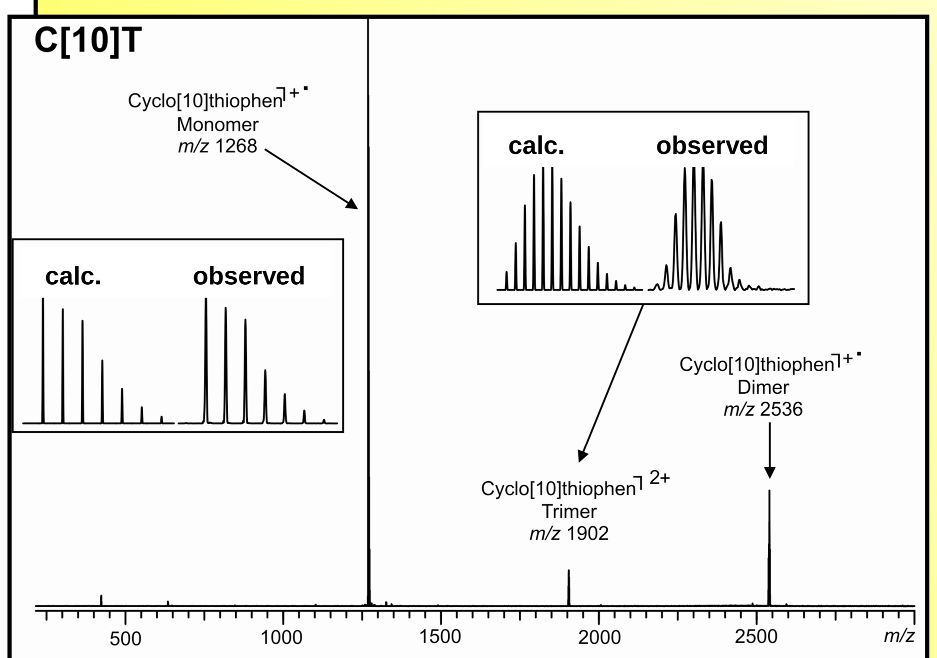
Thiophene macrocycles show an interesting behavior in the ESI process. Upon reduction at the spray-capillary the formation of aggregates can be monitored using FT-ICR mass spectrometry.

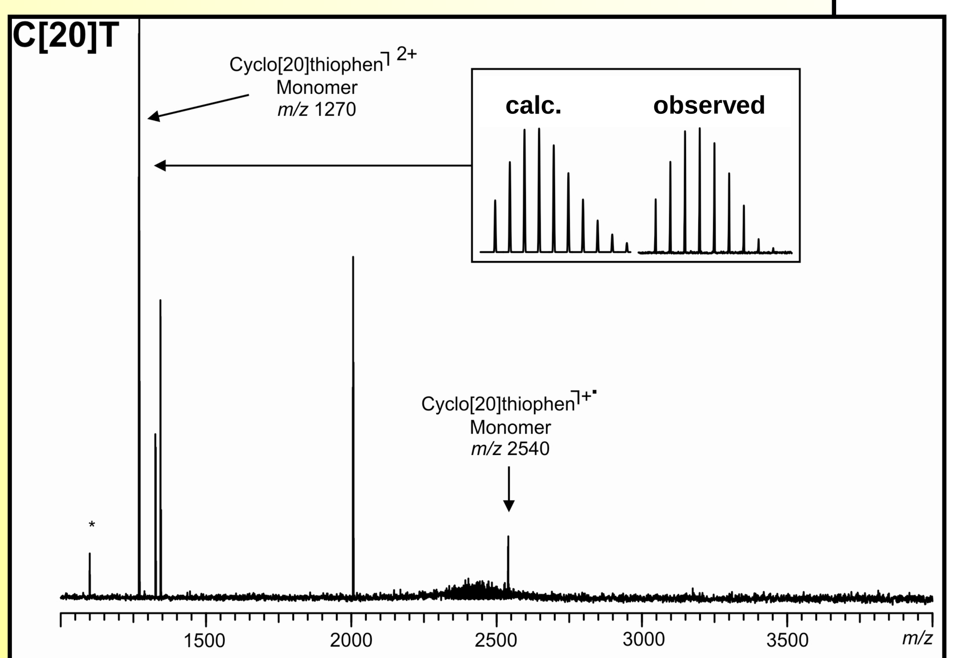
The size and the charge state of the formed aggregates is dependant on the size of the initially used macrocycles.

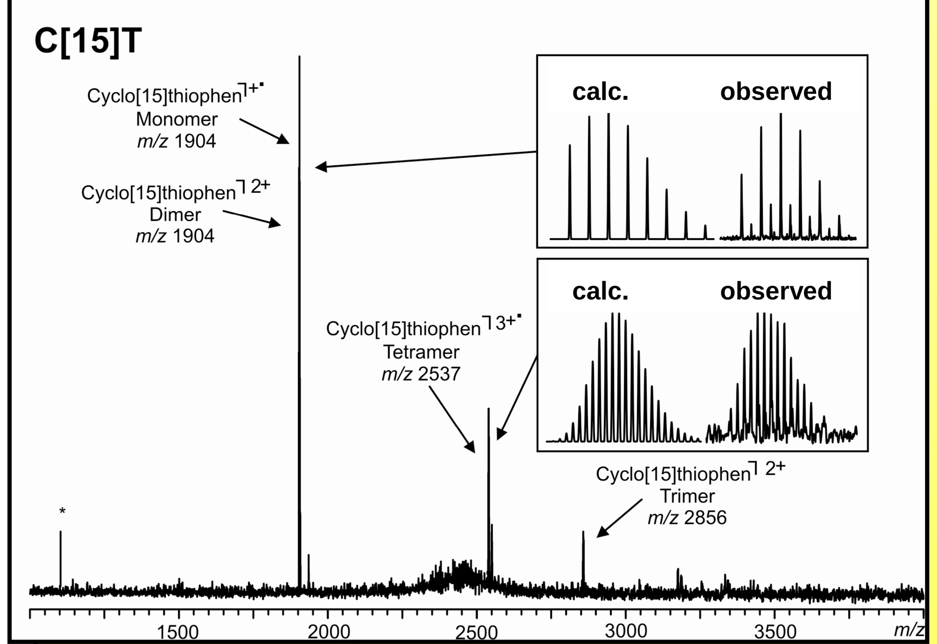
The character of the bond between individual macrocycles of each aggregate can be identified using IRPMD (Infrared multi photon dissociation) and dilution experiments.

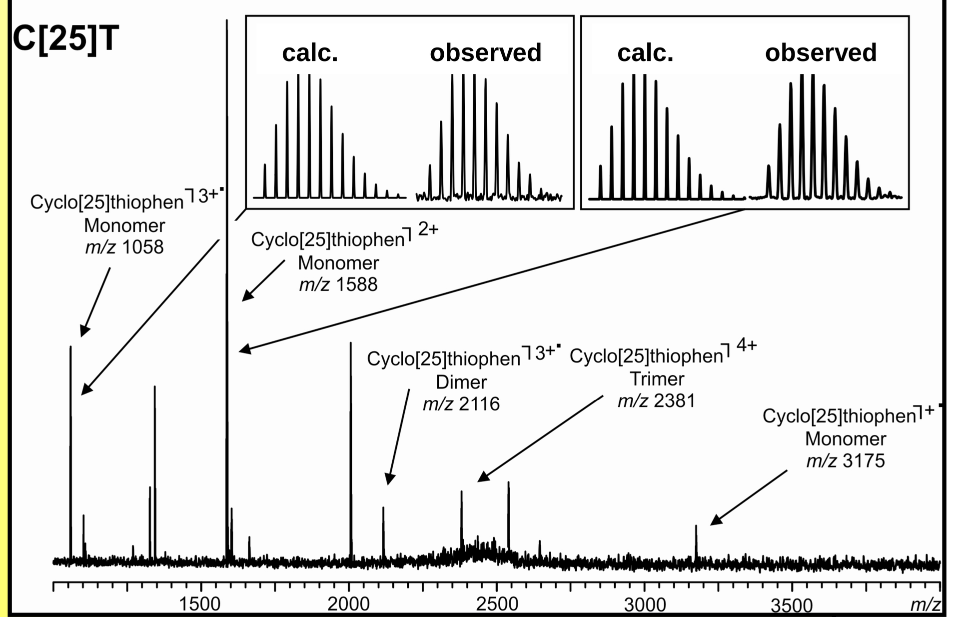
Thiophene macrocycle aggregates are non-covalently bound and therefore interesting examples of supramolecular assemblies with remarkable sizes.



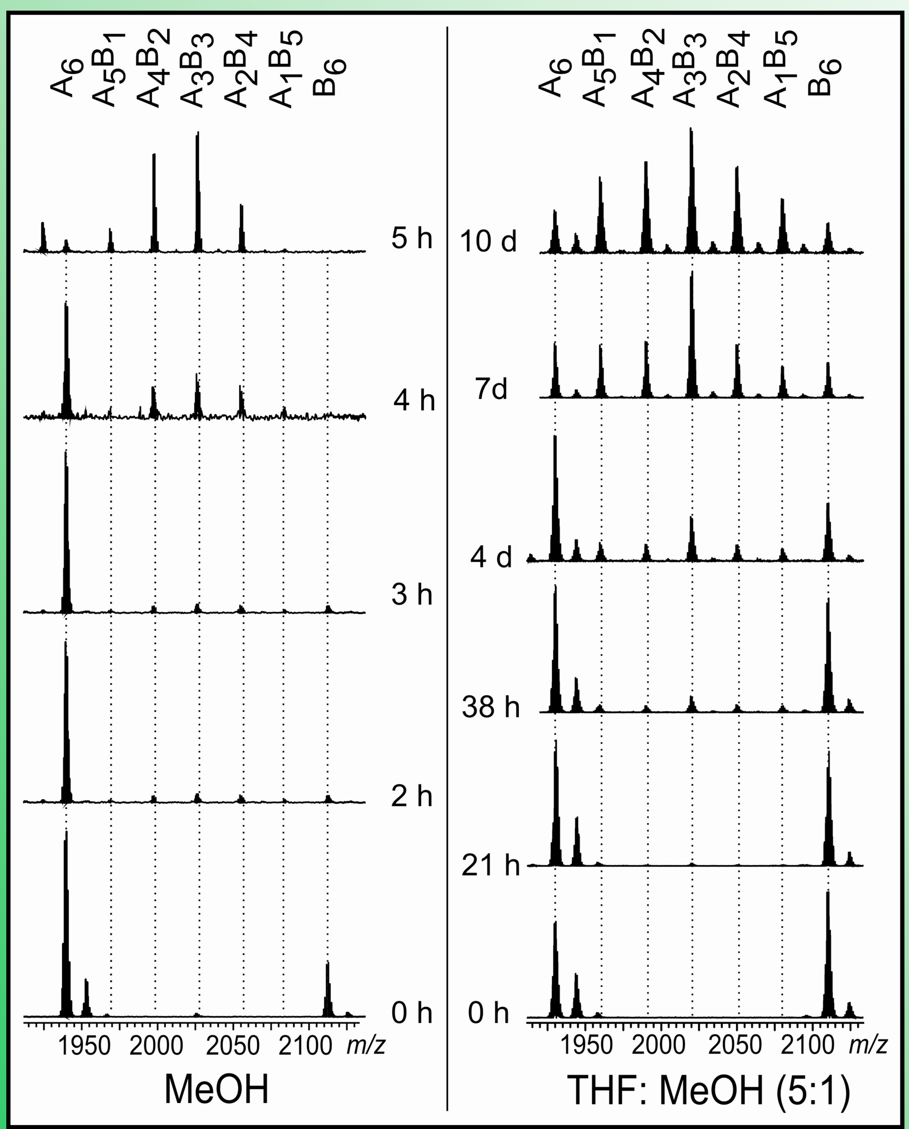








III. Metal Coordination: Ligand Exchange in Dimeric Helicates



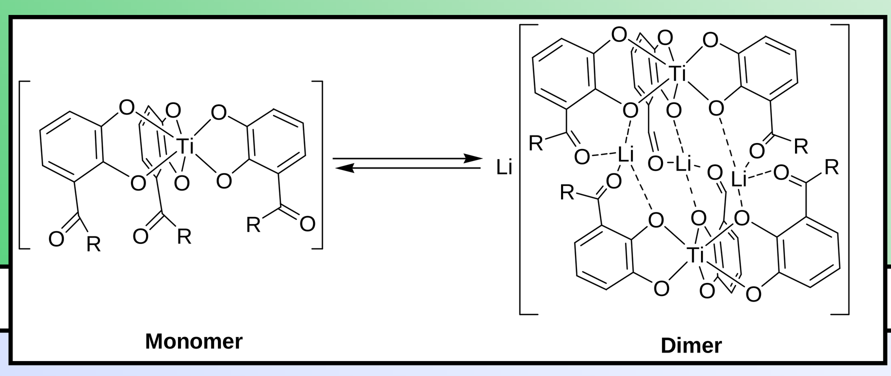
Lithium bridged titanium catecholate based helicates are interesting examples for the study of self-organization processes on a molecular scale via mass spectrometry.

The formation of dimeric helicates, as well as the ligand exchange processes in solution can be monitored by ESI mass spectrometry.

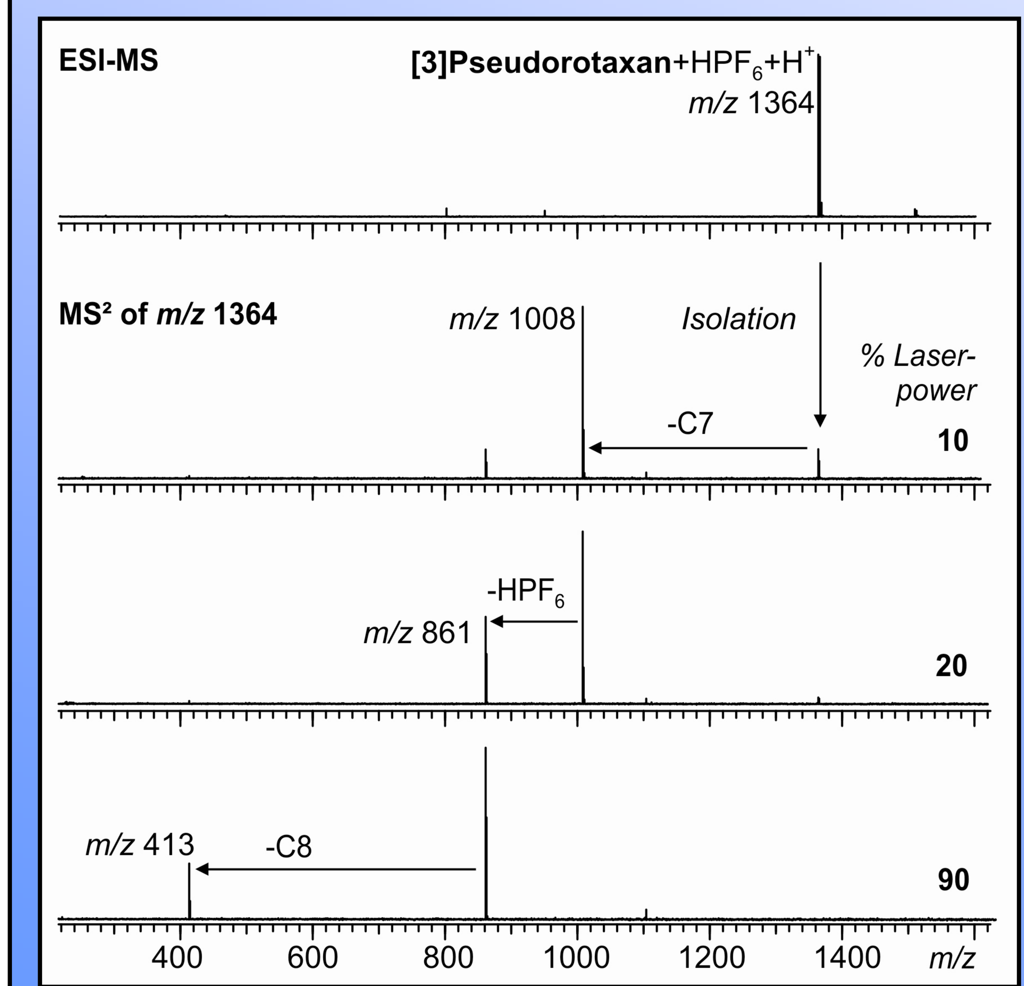
The mechanism for ligand exchange is strongly solvent dependant. While the use of protic solvents such as Methanol leads to a fast exchange of single ligands, the use of aprotic solvents such as THF leads to an exchange of intact monomers.

It can be shown that the size of the substituents of the utilized ligands influences the speed of exchange.

The formation of dimeric helicates is a two step self-recognition and self-organization process that leads to a discrete assembly of several different compounds.



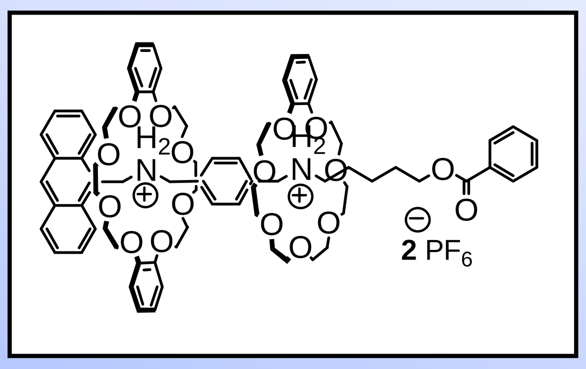
IV. Elucidation of sequence: [3]Pseudorotaxane and [3]Rotaxane

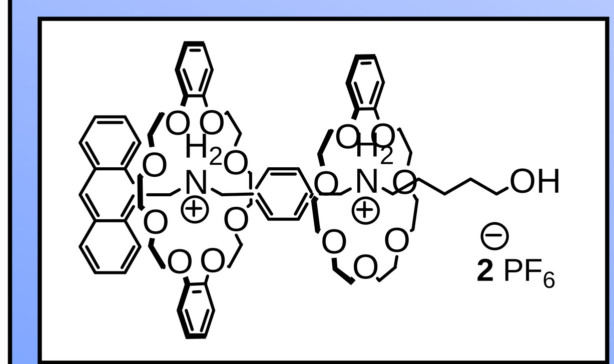


[3]Pseudorotaxanes and [3]Rotaxanes are well known structures in supramolecular chemistry with interesting topological features, especially when built with different sized rings threaded on one axle.

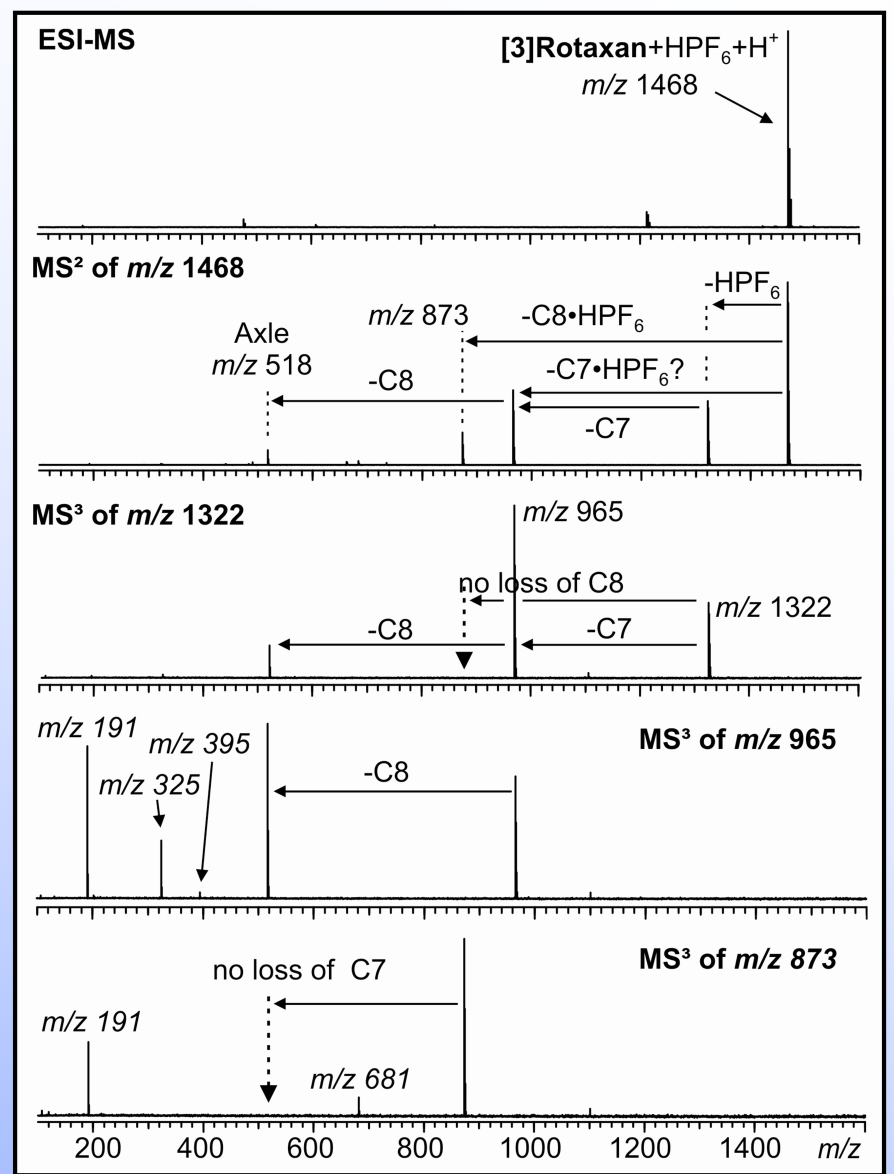
While the specific assembly of these molecules is a challenging synthetic task, the structure elucidation by ESI-FT-ICR-MS with laser induced fragmentation is a surprisingly simple experiment that leads to remarkably unambiguous results.

The IRMPD MS² experiments with the [3]Pseudorotaxane show the sequence of crown ethers dethreading from the axle. First, crown-7 loss is observed followed by deprotonation of the ammonium and loss of The crown-8 ether, afterwards.





Due to a stopper that prohibits a simple desliping of crown ethers in the case of the [3]Rotaxane, IRMPD MS² experiment are not sufficient to study the sequence of threaded crown ethers. Only with MS³ experiments it is possible to elucidate the threading sequence and to confirm the results already obtained in the experiments with the [3]Pseudorotaxane.



Reference:

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