

Proximity Effect vs. Unspecific Dissociation: Studies of discrete Metallo-Supramolecular Assemblies in the Gas Phase

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I. Introduction

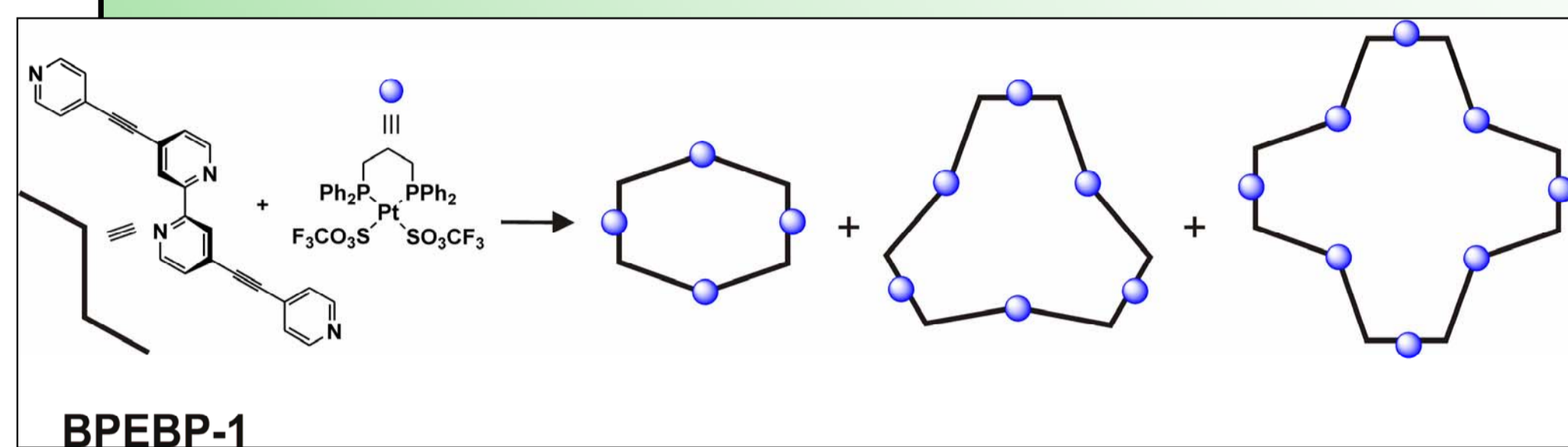
The construction of discrete metallo-supramolecules by self-assembly bears the advantage of building large architectures with a minimum number of building blocks. Many examples exist, which rely on systems of one ligand/metal center and often two or more discrete assemblies coexist in an equilibrium^[1]. In many cases, the investigation of the formation process of these discrete self-assembled structures is restricted and, therefore, is seldom understood.

[1] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 980; K.-M. Park, S.-Y. Kim, J. Heo, D. Whang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2002**, *124*, 2140; T. Yamamoto, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 12309; S.-S. Sun, C. L. Stern, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc.* **2004**, *126*, 6314; M. Ferrer, A. Gullirrez, M. Mounir, O. Rossell, E. Ruiz, A. Rang, M. Engeser, *Inorg. Chem.* **2007**, *46*, 3395.

In some recent studies of 2- and 3-D metallo-supramolecules electro-spray ionization Fourier-transform ion-cyclotron resonance (ESI-FTICR) mass spectrometry in combination with tandem mass spectrometry (MS/MS) was used. Therein, ESI-FT-ICR-tandem mass spectrometry shows its immense potential as an upcoming method and sets a new benchmark for detailed mechanistic studies in the gas phase^[2].

[2] C. G. Claessens, M. J. Vicente-Arana, T. Torres, *Chem. Commun.* **2008**, 6378; Y. R. Zheng, P. J. Stang, *J. Am. Chem. Soc.* **2009**, 3487.

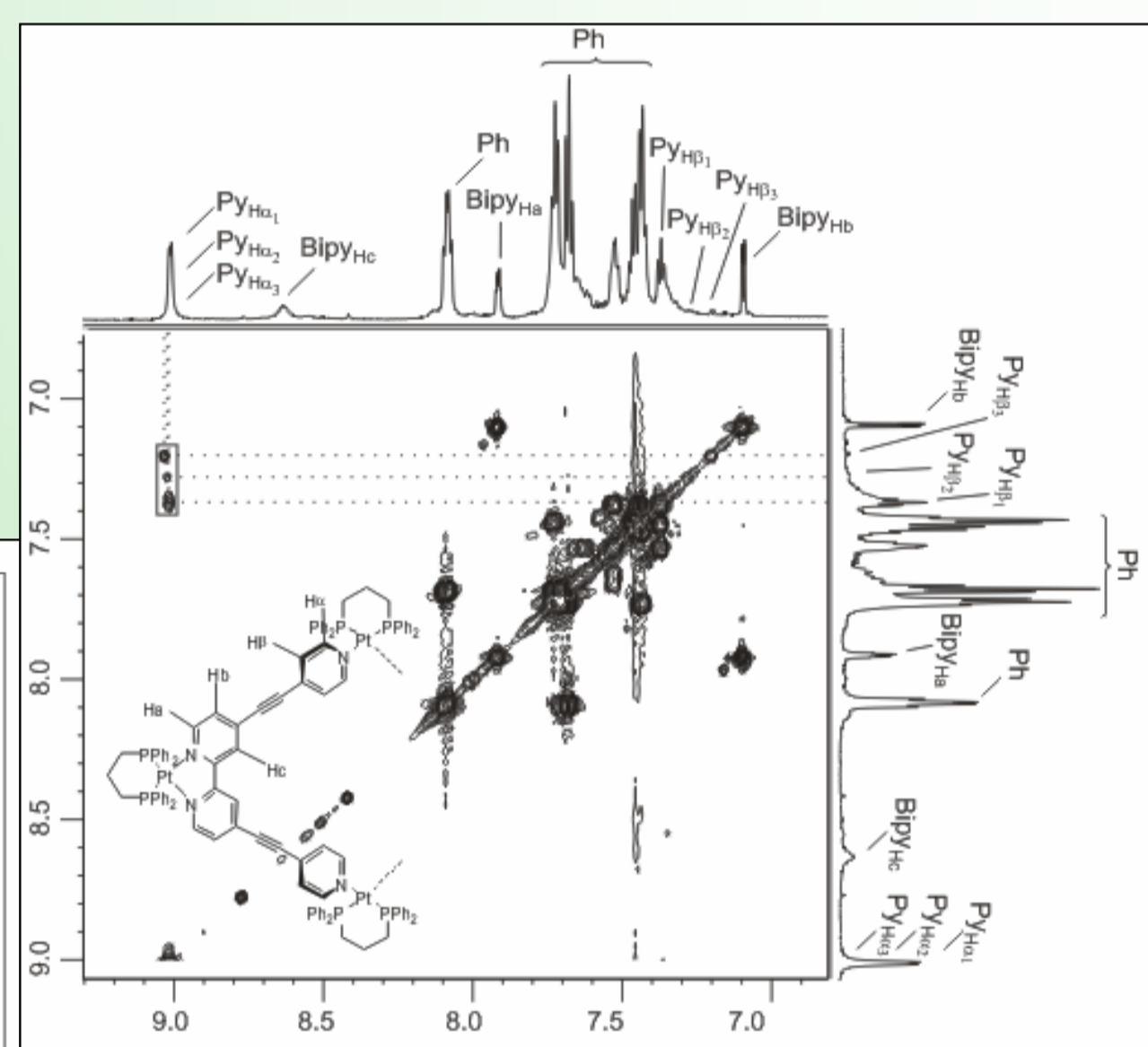
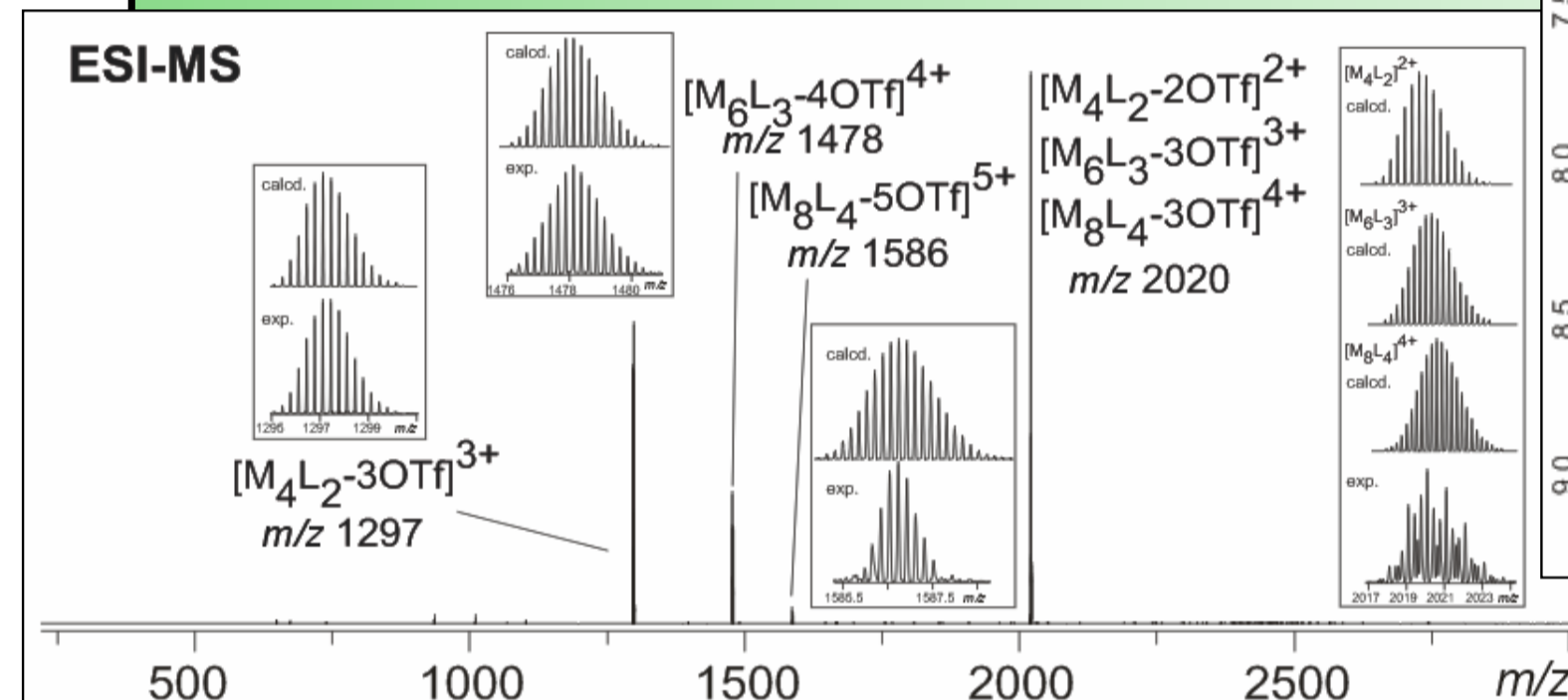
III. Contraction of Metallo-M₆L₃-Triangle- to a Metallo-M₄L₂-Rhomboidal Assembly in the Gas Phase in case of BPEBP-1



Mixing **BPEBP-1** with **2b** in a 1:2 ratio and stirring for 1 h at room temperature in CD₂Cl₂ results in the formation of three different sized discrete metallo-M₄L₂, M₆L₃ and M₈L₄ supramolecular assemblies.

The H,H-COSY NMR spectrum of the mixture showed three different Py-H_α protons at 9.00 ppm, which were all shifted to lowfield upon coordination to the Pt corner. This indicates three different discrete assemblies coexisting in solution.

The ESI mass spectrum mixture unambiguously shows the formation of three different assemblies M₄L₂, M₆L₃ and M₈L₄.



For ESI-FTICR-tandem mass spectrometry experiments the quadruply charged metallo-M₆L₃ assembly was isolated

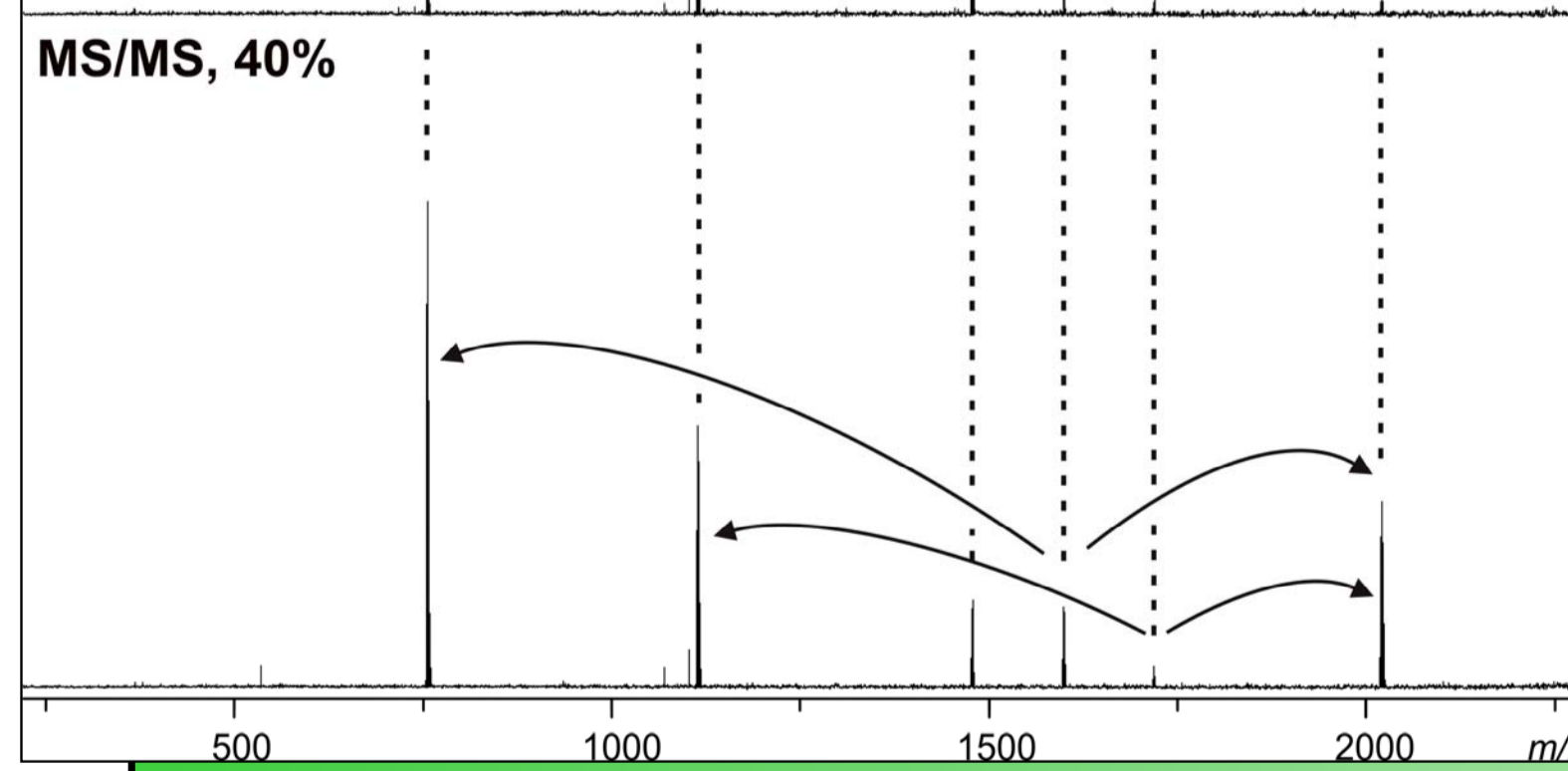
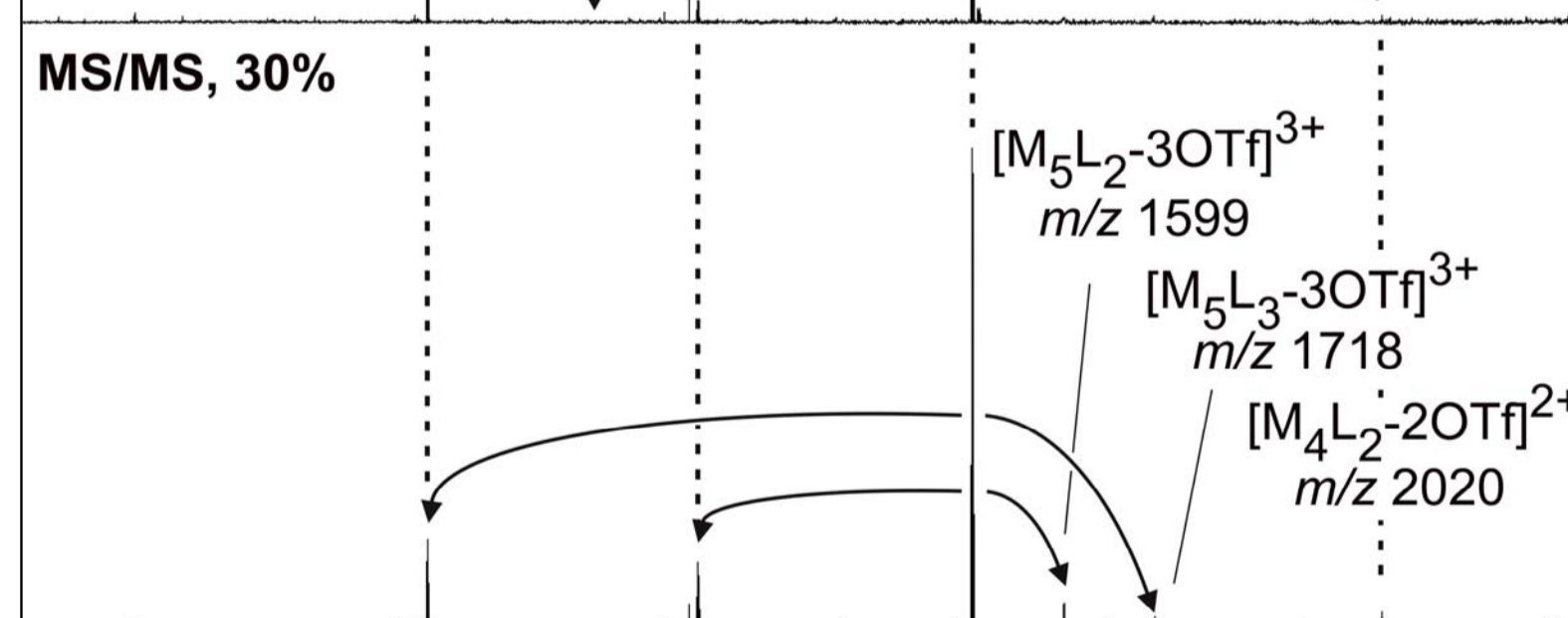
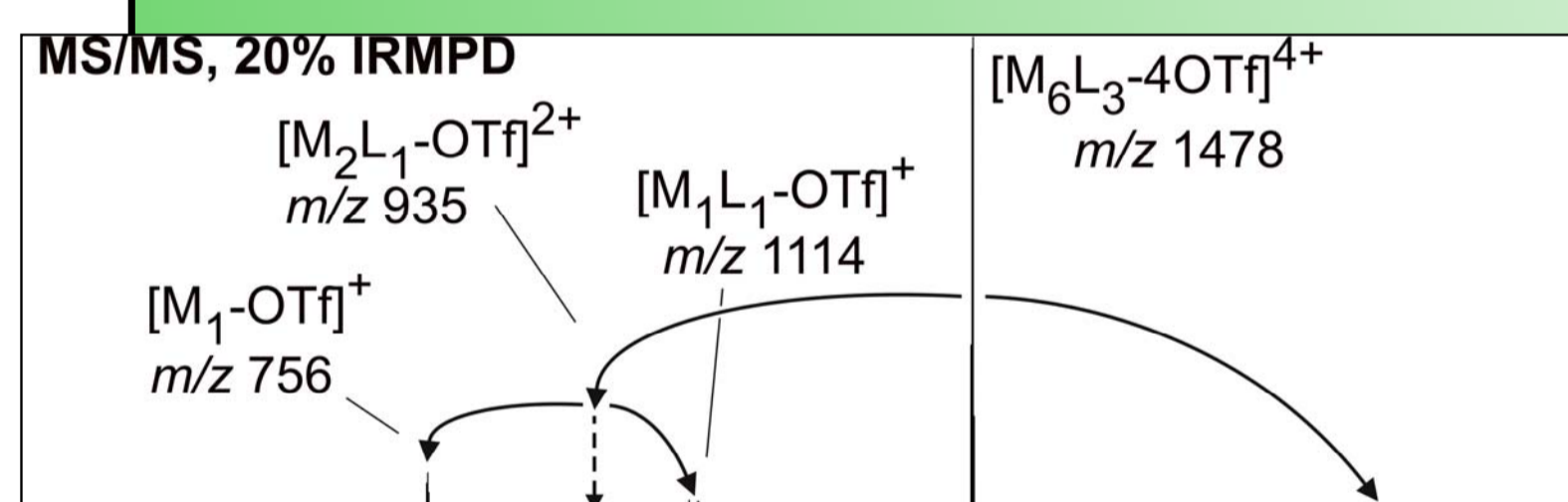
Fragmentation pathway of the quadruply charged metallo-M₆L₃ assembly at three different laser intensities (20%, 30% and 40%) are shown.

The revealed fragmentation mechanism is visualized in the cartoon and three different pathways can be concluded from the IRMPD experiment.

Pathway 1: cleavage of two Pt-N bonds at the same Pt metal, followed by the fragments into the metallo-M₄L₂ assembly via the "proximity effect".

Pathway 2: cleavage of two Pt-N bonds at two different Pt-atoms, followed by a cleavage of one Pt corner before the contraction.

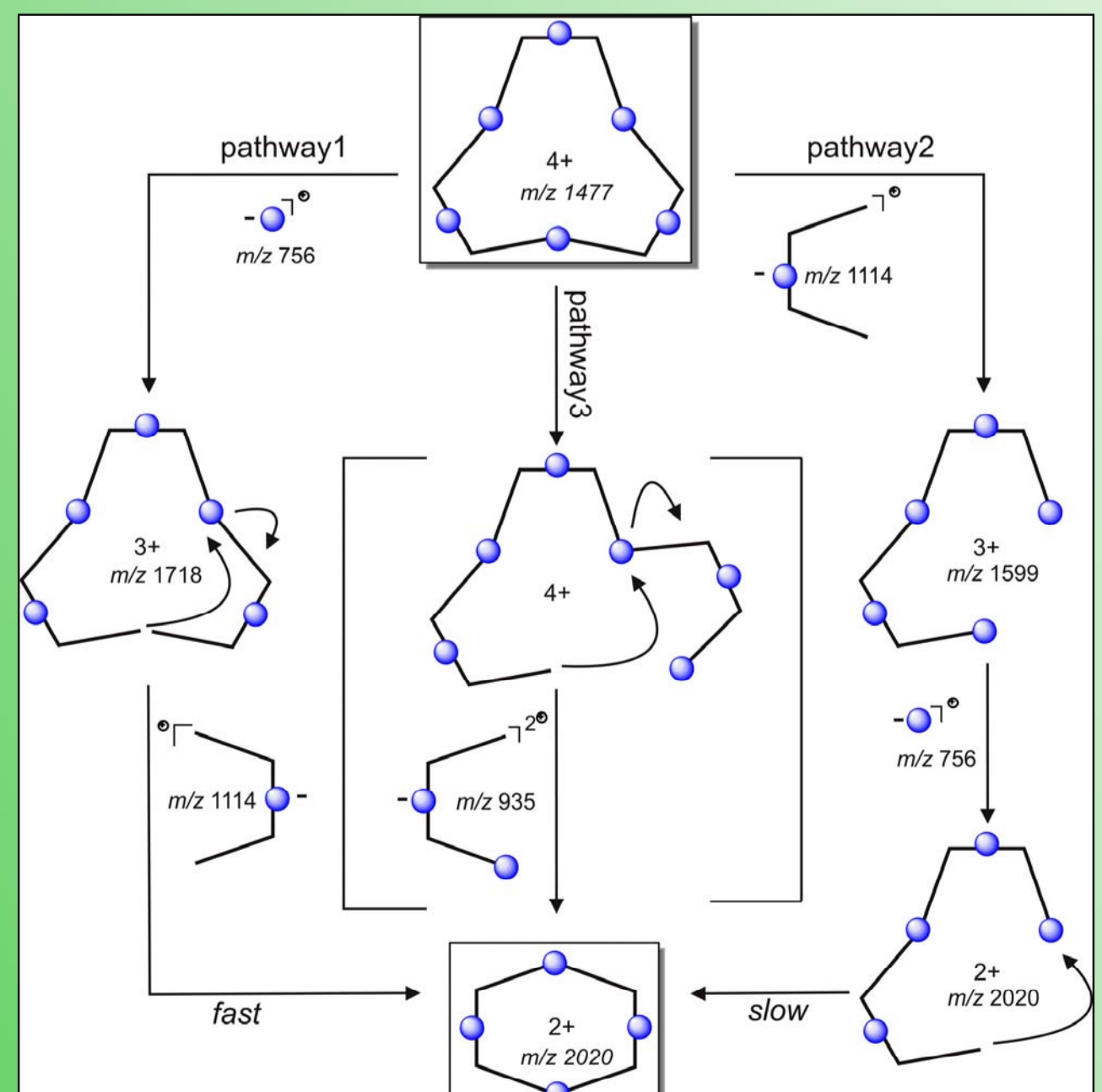
Pathway 3: First cleavage takes place at one of the pyridine moieties. This makes the "proximity effect" favourable, where the free pyridine unit coordinates the appropriate Pt metal leading to contraction into the metallo-M₄L₂ assembly.



V. Conclusions

In case of ligand **BPEBP-1** with Pt corner, three different sized discrete metallo-M₄L₂, M₆L₃ and M₈L₄ assemblies coexist in solution. Furthermore, the contraction mechanism to proceed via a "proximity effect" in the gas phase is prominent. In case of ligand **BPEBP-2** with Pt corner, two discrete metallo-M₄L₂ and M₈L₄ assemblies were observed. The metallo-M₆L₃-assembly was negligible. Here, the "proximity effect" is less significant and unspecific dissociations in smaller pieces run simultaneously and without discrimination.

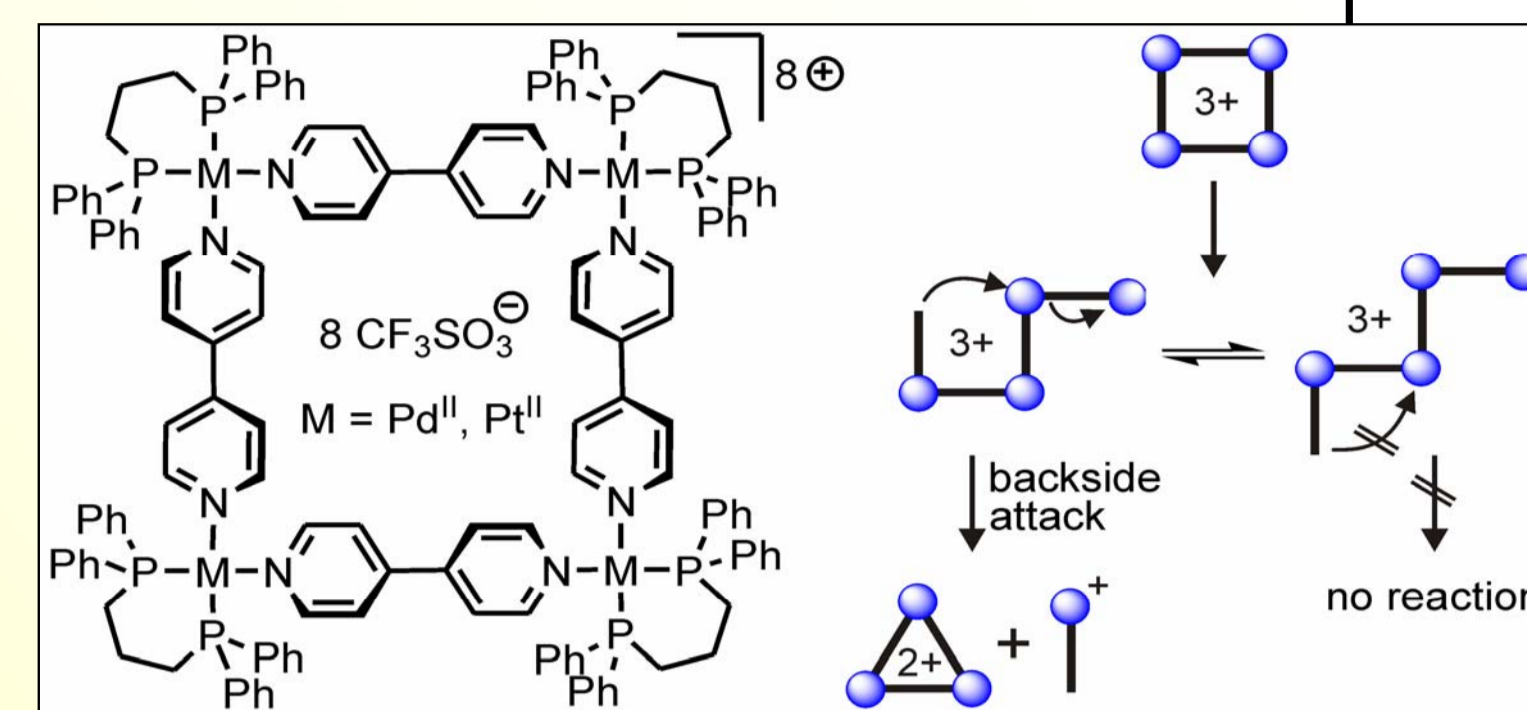
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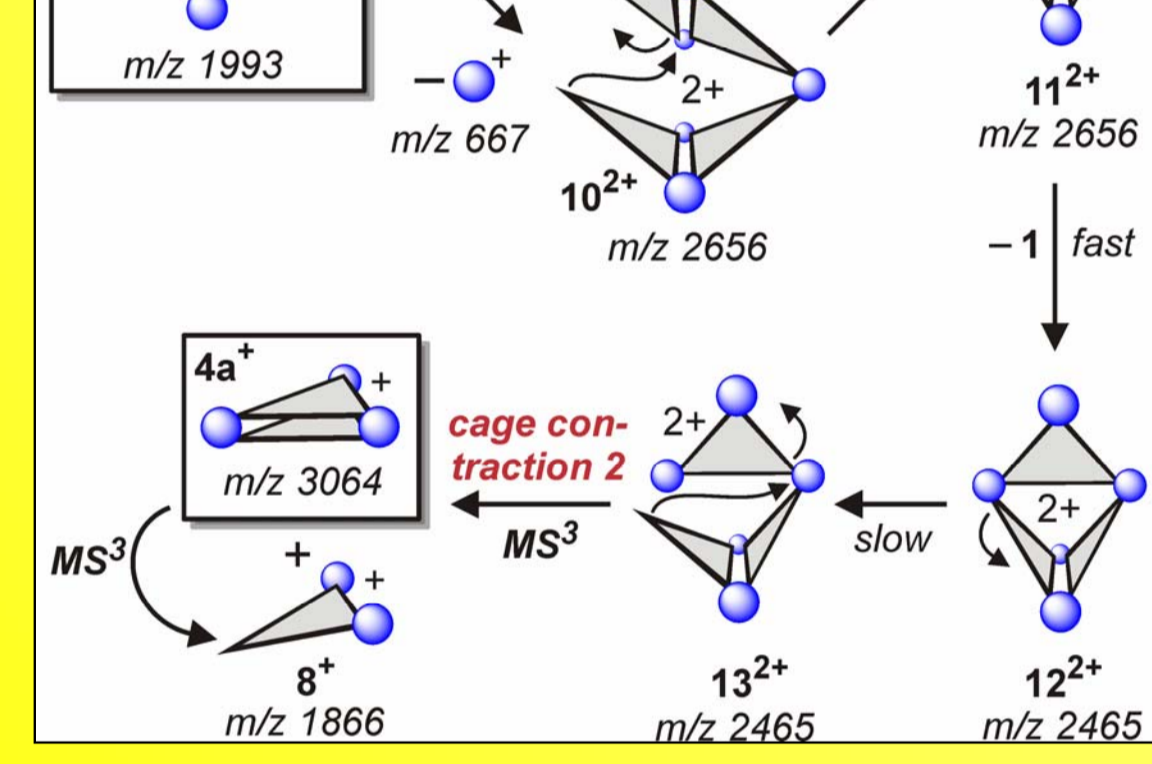
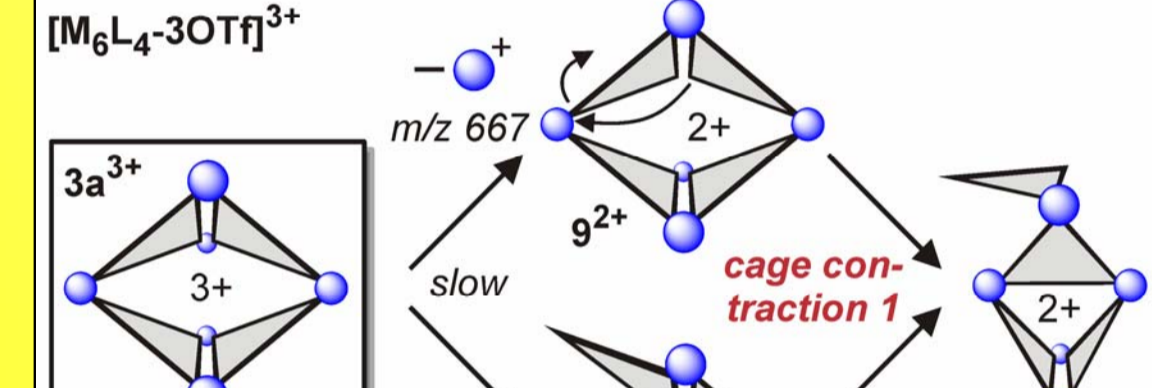
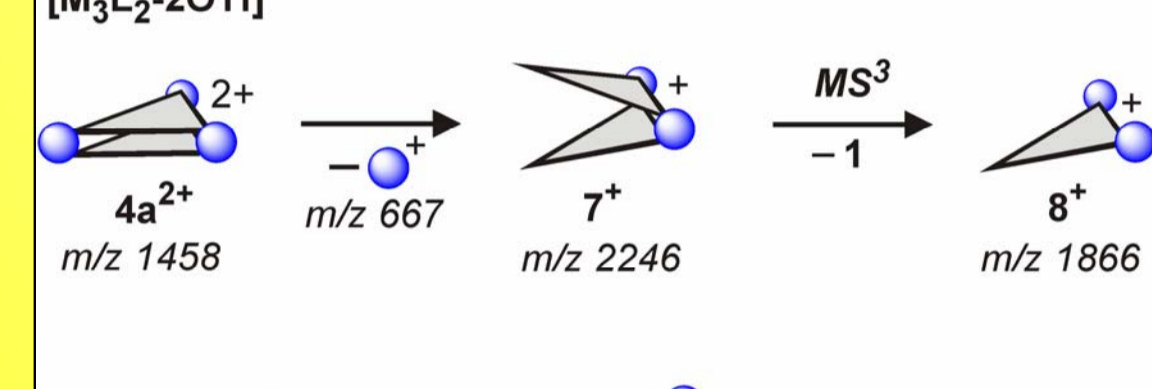
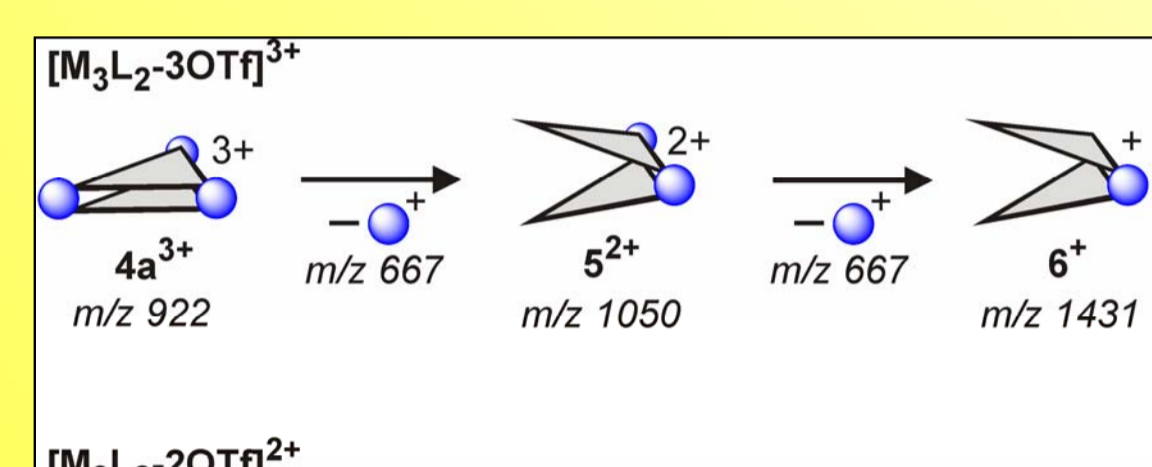
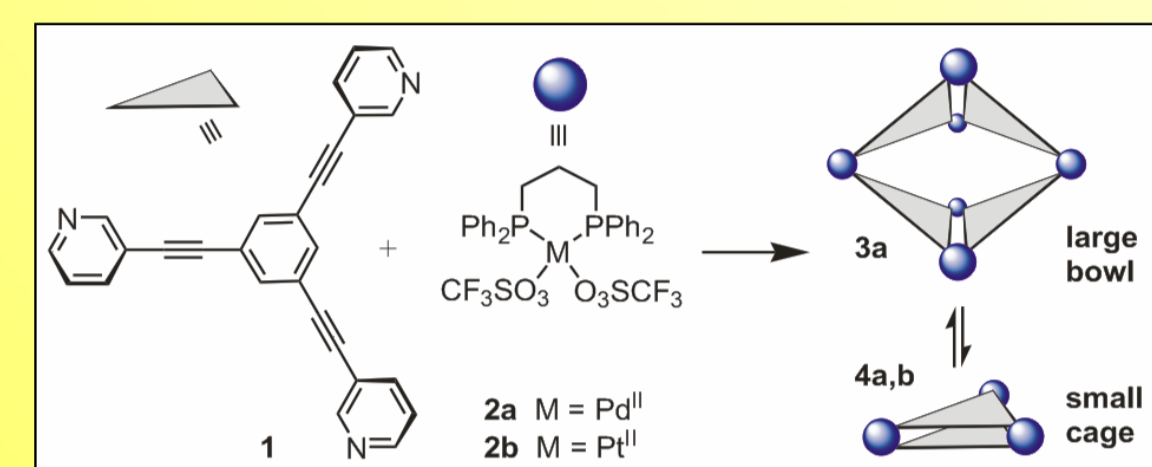
II. Motivation

Compared to solution chemistry, where *inter*- and *intramolecular* exchange processes and solvent molecules often prohibit any investigations of the intermediates or other formed assemblies, ESI-FTICR-MS/MS mass spectrometry gives the possibility to isolate the ions of interest and scrutinize their fragmentation pathway.

For example, the fragmentation of a simple triply charged metallo-supramolecular square proceeds exclusively through one out of several possible pathways, which benefits energetically from a proximity-effect mechanism^[3]. All other possible reactions do not profit from such a mechanism and thus are significantly more energy-demanding. Such a process cannot be investigated in solution, because of the complicating interference from ligand and corner exchanges and solvent effects.



[3] C. A. Schalley, T. Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, *Chem. Eur. J.* **2002**, *8*, 3538; M. Engeser, A. Rang, M. Ferrer, A. Gutierrez, H. T. Baytekin, C. A. Schalley, *Int. J. Mass Spectrom.* **2006**, *255*, 185.



This mechanism is also operative in 3-D assemblies such as the bowl-shaped metallo-supramolecular M₆L₄ assembly (M = **2a**, L = ligand **1**), which, when isolated in the high vacuum of an ESI-FT-ICR mass spectrometer, undergo a *intramolecular* double cage contraction to yield smaller M₃L₂ cages^[4].

The ESI mass spectrum of the Pd corner/ligand **1** mixture shows only the metallo-M₃L₂- and M₆L₄-assemblies with different number of triflates as counter ions. The +1, +2 and +3 charge states of the M₃L₂ cage appear at m/z 922, 1458 and 3064. The M₆L₄ bowl is observed at m/z 1993 in its charge state.

To study the *intramolecular* rearrangement process of assemblies **3a** and **4a** in the gas phase, the ions of interest were mass-selected in the FTICR analyzer cell by removing all undesired ions. Fragmentation was induced in an infrared multiple photon dissociation (IRMPD) experiment.

The fragmentation of triply charged M₆L₄ ions involves two subsequent cage contraction steps proceeding through a proximity effect mechanism.

In the current study, our aim was to find similar metallo-supramolecular systems, which reconfirm this *intra*-molecular process.

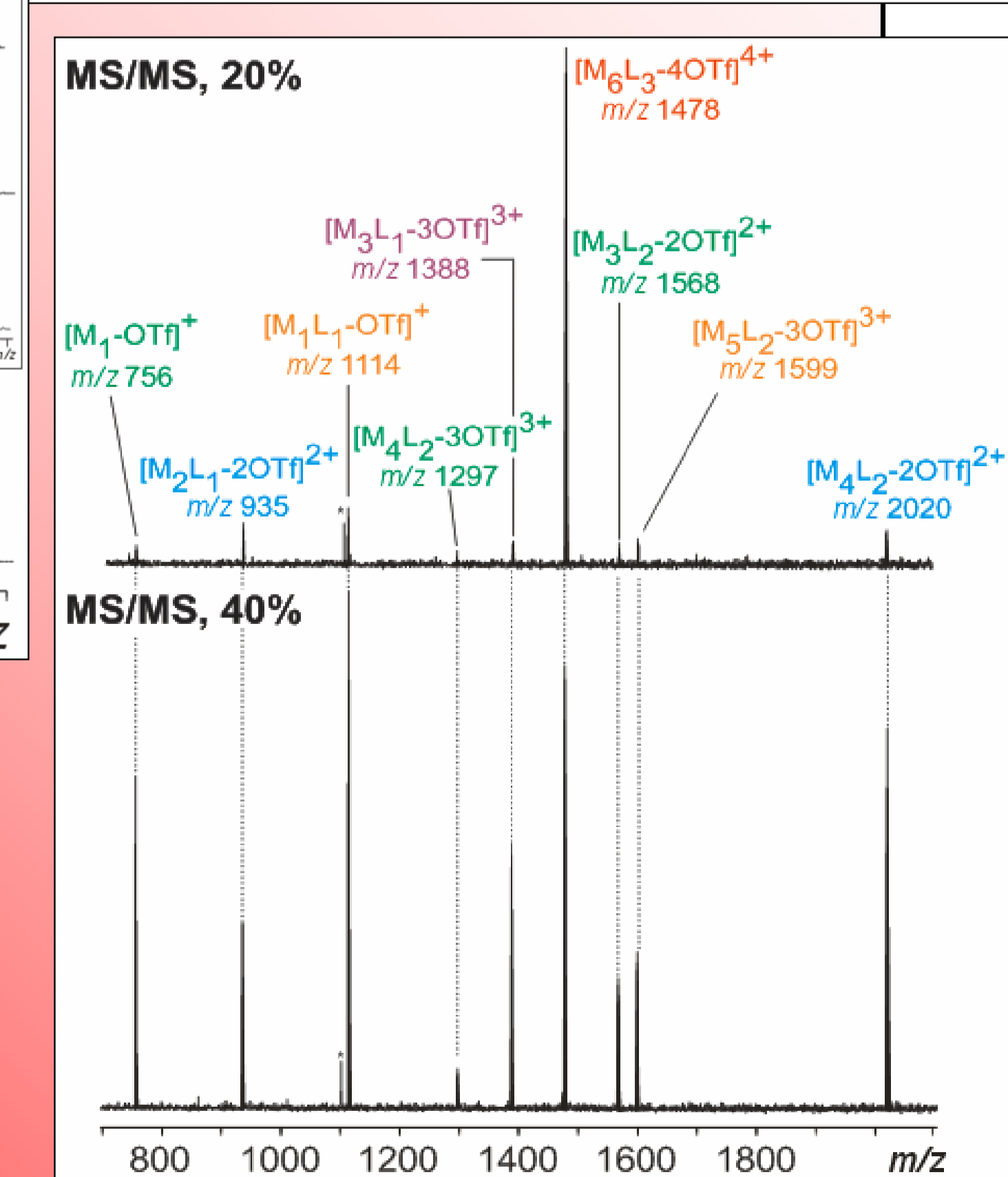
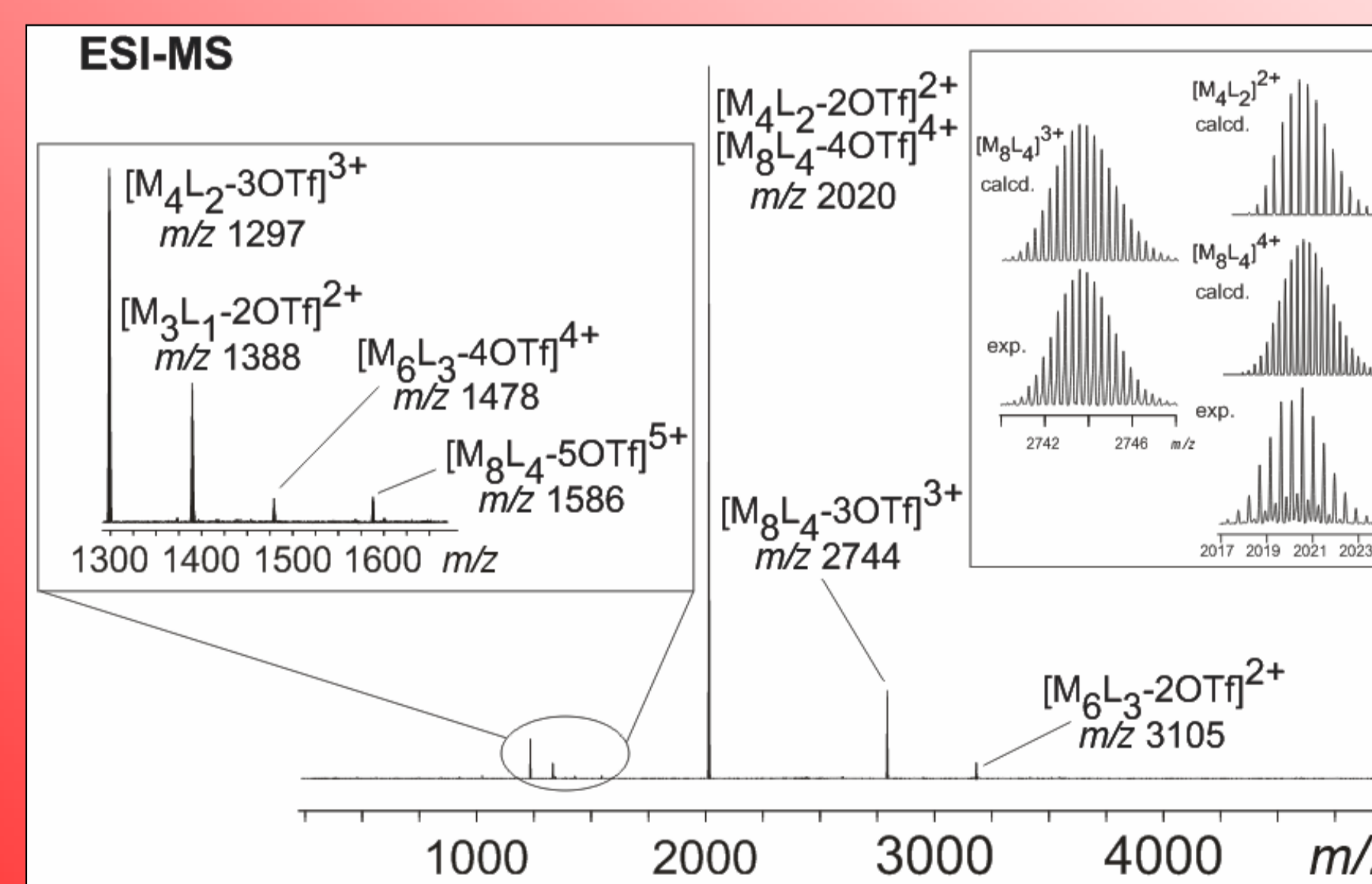
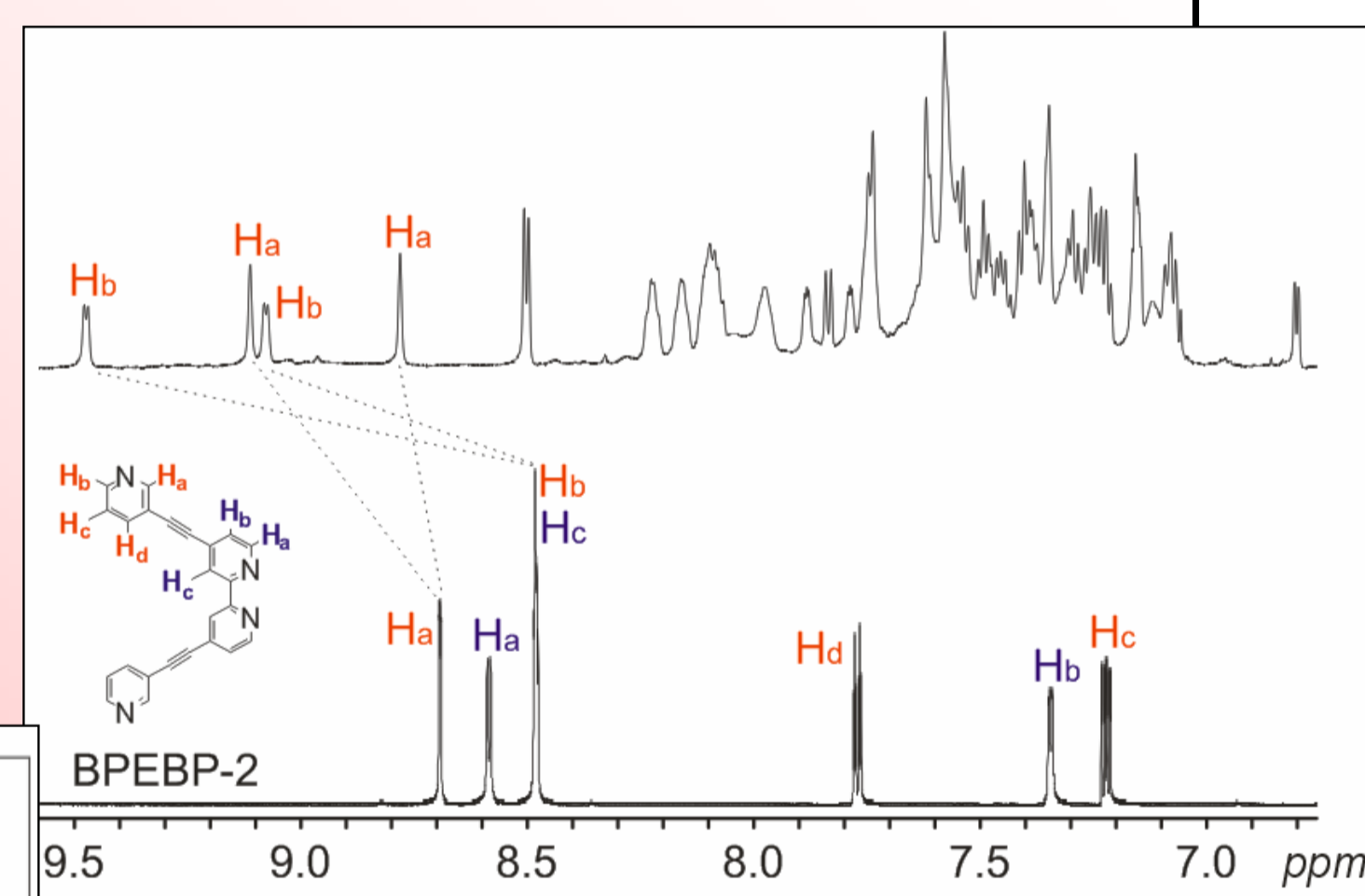
[4] B. Brusilowskij, S. Neubacher, C. A. Schalley, *Chem. Commun.* **2009**, 785.

IV. Unspecific fragmentations in case of BPEBP-2

Mixing **BPEBP-2** with Pt corner in a 1:2 ratio and stirring for 1 h at room temperature in CD₂Cl₂ results in the formation of mainly two different sized discrete metallo-M₄L₂ and M₈L₄ supramolecular assemblies.

Because of the unsymmetric ligand, there are two protons, Py-H_a and Py-H_b, which are shifted to lowfield upon coordination to the Pt corner. This indicates, that there are two discrete assemblies coexisting in solution. All other protons are difficult to assign because of superposing with the dppp protons. These results were also confirmed by ³¹P NMR (not shown here).

The ESI mass spectrum of the Pt corner/ligand **BPEBP-2** mixture shows mainly two different assemblies M₄L₂ and M₈L₄ and therefore reconfirms the ¹H and ³¹P NMR spectroscopy results.



To compare with the **BPEBP-1**/Pt corner metallo-M₆L₃-assembly, the quadruply charged metallo-M₆L₃ assembly in case of **BPEBP-2** was also isolated and fragmented by infrared multiple photo dissociation (IRMPD) to study the fragmentation pathways. In contrast, this system does not discriminate dissolution processes of the metallo-M₆L₃ assembly. Both processes, the "proximity effect" and unspecific dissociations run simultaneously. The same results were achieved in case of the metallo-M₈L₄-square assembly by isolation and fragmentation of m/z = 1586⁵⁺ and m/z = 2744³⁺. Probably, the position of nitrogen in the pyridine moiety is crucial for the fragmentation/contraction pathway.