Application Note 00618

Characterization of Self-Assembling Metallosupramolecular Complexes by Electrospray Fourier Transform Mass Spectrometry

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Introduction

Self-assembly is a fascinating strategy for synthesis of complex species such as supramolecular assemblies. Novel applications in the fields of sensing, catalysis and electrochemical or photochemical switches have been recently enabled by introducing functionalities, such as redox activity, magnetic or luminescent properties, into the assemblies.

Introduction of metal ions into the supramolecular complexes make these assemblies more versatile and more controllable with respect to their geometries. This is due to the higher directionality of a metal-ligand bond relative to a non-covalent bond and a larger selection of sometimes even redox-switchable coordination geometries. In addition, the stronger bonding interactions make these assemblies more durable as building blocks for larger systems. Yet another advantage is that the assemblies can be studied under more dilute conditions compared to many hydrogen-bonded architectures.

The mass spectral studies of metallosupramolecular assemblies are not straightforward. In vacuo, the charge repulsion of the multiply charged species can overcome the bonding interactions in the complexes.

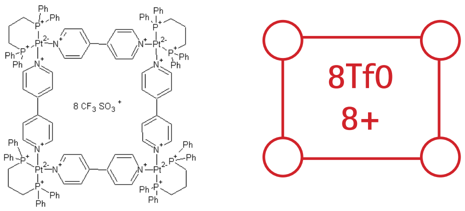

Figure 2 A simplified notation for the studied molecular structures. This notation is applied to illustrate the assignments in the spectrum in Figure 1.

Here, typical prototypes of self-assembling metallosupramolecular species are studied with high-resolution electrospray ionization Fourier Transform mass spectrometry. Selected assemblies are fragmented using infrared multiphoton dissociation (IRMPD), and a method to study their dissociation pathway in detail is discussed.

Methods

Typical prototypes of metallosupramolecular complexes are self-assembling squares which consist of bipyridine (bipy) edge ligands and Pt-diphenyphosphinopropane (dppp) complexes at the corners. These Pt-dppp squares may exist in equilibrium with triangular analogues, since the formation of

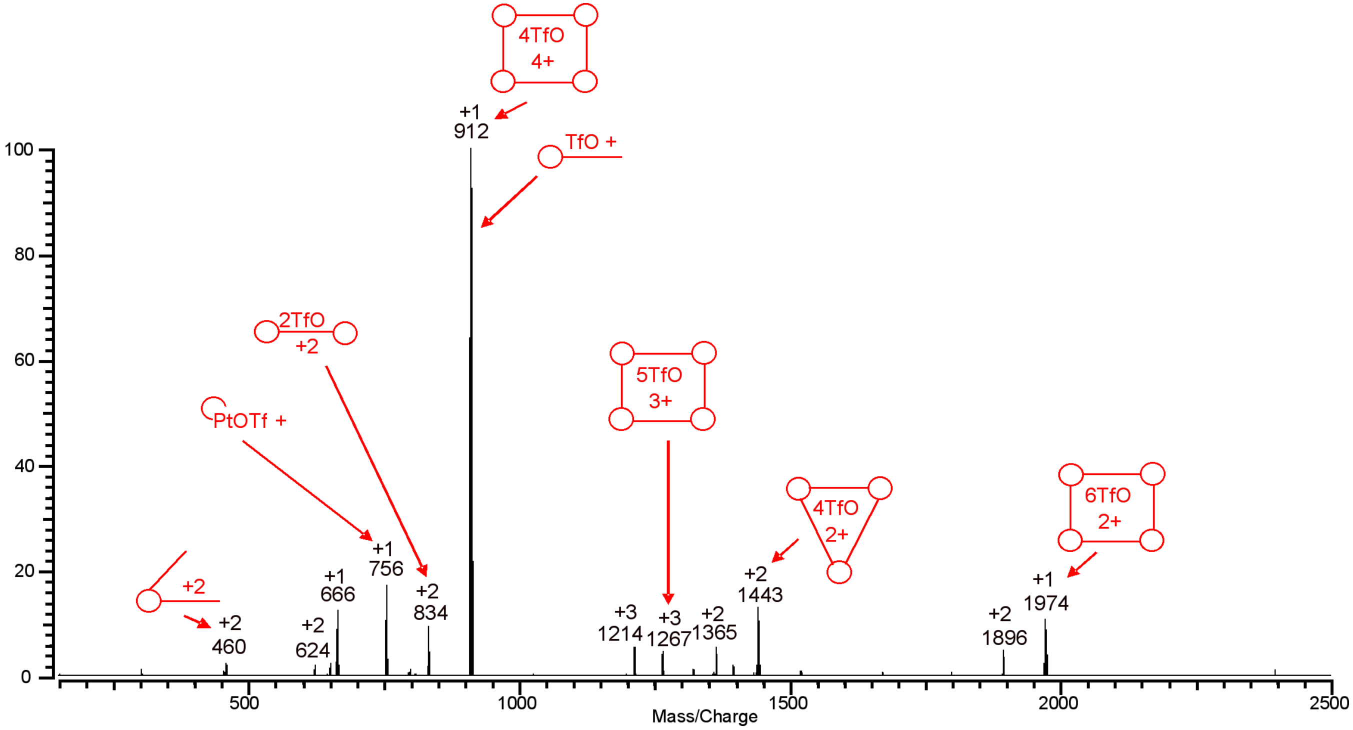

Figure 1 A broadband mass spectrum of metallosupramolecular assemblies by ESI-FTMS.

triangles is entropically favored. Each sample was diluted in acetone to obtain an approximate 100 µM concentration for ESI analysis in the positive ion mode.

All the discussed data is collected with an IonSpec QFT hybrid FTMS instrument equipped with a 9.4T superconducting magnet and electrospray ionization source.

A typical flow rate applied was 0.5 µL/min with an accumulation time of 100 ms per spectrum. The infrared multiphoton dissociation (IRMPD) technique was applied to fragment selected species.

Discussion

All the spectra shown are single scan mass spectra showing high signal-to-noise and sensitivity. Figure 1 illustrates a typical mass spectrum obtained for a m/z range from 200 to 2500 Da. The assignments of the peaks in the Figure 1 are illustrated by a simplified notification explained in Figure 2.

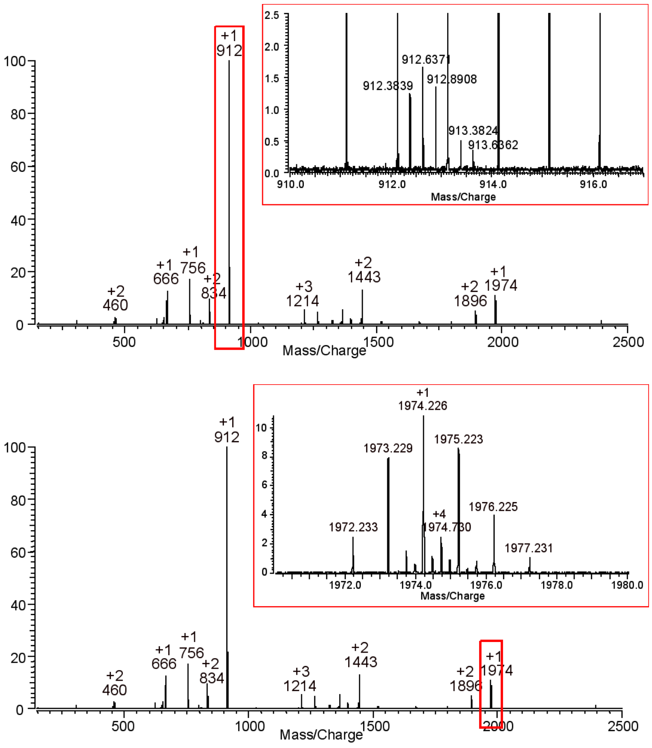

Figure 3 Two expansions of the spectrum in Figure 1.

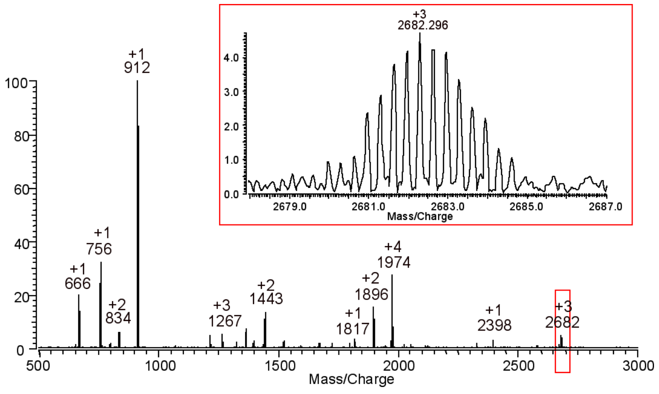

Figure 4 An expansion of the spectrum in Figure 1.

The Pt-dppp corners of the molecular structures are illustrated as circles, while the bipy edge ligands are illustrated as lines. TfO marks the attached CF_3SO_3 anion. As shown in Figure 1, both triangular and square geometries are detected as intact assemblies.

Expansions of the mass spectrum in Figure 1 are shown in Figures 3A and 3B. Complex areas of the mass spectrum where there are overlapping distributions of different species are automatically interrogated and identified using the IonSpec software. This demonstrates that crucial information about the sample would be lost without the ultra-high resolution, great sensitivity and the large dynamic range of the IonSpec QFT FTMS.

The close-up shown in Figure 4 illustrates the advantage of the high-resolution for detection of the higher mass species.

Isolation and IRMPD

The fragmentation pattern and dissociation pathway of selected complexes provides important structural information about the components in the sample. The species shown here consists of one corner, one side and one TfO unit. In the full scan shown in Figure 1, this specific species is detected with an m/z value of 755 Da.

As mentioned, the infrared multiphoton dissociation (IRMPD) technique was applied to fragment this species. While the power of the laser was kept constant, the amount of fragmentation was controlled by varying the length of the irradiation time. Figure 5 shows the effect of the time of the irradiation to the amount of fragmentation.

It can be seen that fragmentation of the complex at m/z 755 begins by a relatively easy loss of 149.95 Da. This corresponds to the loss of a TfO^+ or CF_3SO_3H unit. Figures 5A and 5B show that the fragmentation of the daughter ions does not seem to occur before all the parent ions are consumed. Figures 5C and 5D illustrate the effect of lengthening the irradiation time even further. In addition to the length of the irradiation time, the fragmentation can be controlled by changing the power of the irradiation beam.

Conclusion

Typical prototypes of self-assembling metallosupramolecular complexes were studied with a high-resolution electrospray ionization Fourier Transform mass spectrometer. It was shown that despite of the fragile nature of the assemblies the intact species such as the triangles and squares were detected. In addition, the isolation and fragmentation of the species was performed in order to study the structural details and dissociation pathways. The dissociation of a selected species using the IRMPD technique was shown as an example. Furthermore, by controlling the temperature of the ICR cell the temperature dependence of the dissociation pathways and the stability of the assembly can be investigated.

As a conclusion, the IonSpec QFT-9 is an excellent instrument for studies of fragile molecular systems such as self-assembling metallosupramolecular complexes.

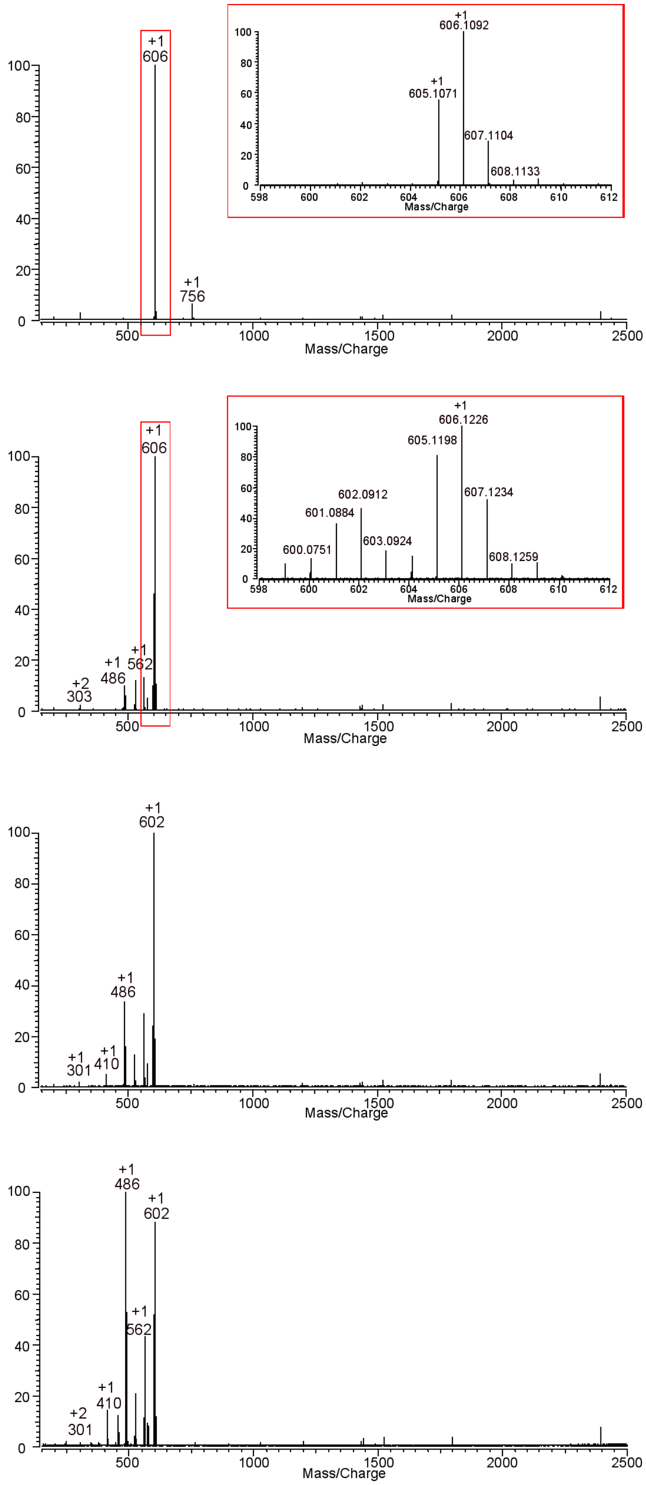

Figure 5 The fragmentation pattern of the complex with an m/z value of 756 Da shown in Figure 5. The fragmentation is controlled via the laser pulse length while the energy of the pulse is kept constant. The pulse lengths are 500 ms, 600 ms, 1000 ms and 2000 ms from top to bottom.

References

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These data represent typical results.
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