



Characterization of Metallo-Supramolecular Systems by MALDI-TOF Mass Spectrometry

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Abstract. MALDI-TOF mass spectrometry was used for the characterization of metallo-supramolecular coordination arrays with molecular weights between 500 and 4000 g/mol. The stepwise loss of the counterions was used as an additional fingerprint for the investigated species. The isotope pattern yielded further information, especially in combination with simulations.

Key words: MALDI-TOF-MS, supramolecular chemistry, metal coordination array, characterization in the solid state.

1. Introduction

The design, synthesis and properties of supramolecular architectures are main targets in today's chemistry and physics, as demonstrated by the large number of publications and conferences in the last few years [1]. Coming from systems based on covalent macrocycles like crown ethers, calixarenes, cryptands and spherands, the field of supramolecular chemistry has moved on to architectures using mainly weak interactions for the construction of novel superstructures, e.g. hydrogen bonding, π - π -stacking, electrostatic metal-ligand or cation interactions and van-der-Waals forces. In particular systems containing metal ions are of interest, like, e.g. double helical strands [2], rack-, ladder- and grid-like architectures [3], metallacyclic polygons and polyhedra [4], as well as metallo-dendrimers [5]. Such architectures, e.g. on surfaces or in thin films, could provide new mechanical, thermal, electrochemical, photochemical or magnetic properties [6].

However, one major drawback in the field of metallo-supramolecular systems is, and has always been, the characterization of the assemblies [1c]. This problem turned out to be an intricate one, due to the relative weakness of the interactions involved (compared to covalent bonds) and the nature of the metal ions. The most sophisticated structural information is obtained by X-ray crystallography, but crystals of sufficient quality are necessary. However, the great majority of the supramolecular assemblies synthesized up to now does not yield such crystals. Therefore other methods, which also could yield structural information are of

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great interest (e.g. investigation of surface layers [7], use of NMR [8], electro-spray mass spectrometry (ESI) [9] and sedimentation equilibrium analysis in an analytical ultracentrifugation [10]). In this contribution we want to describe our first results in the application of matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry for the characterization of metallo-supramolecular assemblies in the solid state. Different metallo-supramolecular metal coordination arrays were used as model systems.

2. Experimental

2.1. MATERIALS

The solvents were used from commercial suppliers as received (HPLC grade). The matrix dithranol (1,3,9-Trihydroxyanthracene, Aldrich) was used as received.

2.2. SYNTHESIS

Bis(5,5''-dimethyl-2,2':6',2''-terpyridine) zinc(II) hexafluorophosphate (1):

Synthesized from 5,5''-dimethyl-2,2':6',2''-terpyridine [11] in methanol using zinc(II) acetate dihydrate in 76% yield as a white crystalline solid [12]. M.p.: >300 °C. Elemental Analysis: Calc. for $C_{34}H_{30}F_{12}N_6P_2Zn$: C. 46.52, H. 3.42, N. 9.57. Found: C. 46.07, H. 3.58, N. 9.48.

Bis(5,5''-dimethyl-2,2':6',2''-terpyridine) mercury(II) hexafluorophosphate (2):

Synthesized from 5,5''-dimethyl-2,2':6',2''-terpyridine [11] in methanol using mercury(II) acetate in 85% yield as white crystalline solid [12]. M.p.: > 300 °C. Elemental Analysis: Calc. for $C_{34}H_{30}F_{12}HgN_6P_2$: C. 40.27, H. 2.96, N. 8.29. Found: C. 40.09, H. 3.06, N. 8.26.

4,6-Bis((5''-methyl)-2'',2'-bipyrid-6'-yl)-2-phenylpyrimidine cobalt(II) hexafluorophosphate (3):

Synthesized from 4,6-bis((5''-methyl)-2'',2'-bipyrid-6'-yl)-2-phenylpyrimidine [13] in chloroform with cobalt(II) acetate tetrahydrate in 98% yield [13]. M.p.: > 300 °C. Elemental Analysis: Calc. for $C_{128}H_{96}F_{48}Co_4N_{24}P_8 \times 6H_2O$: C. 44.25, H. 3.05, N. 9.68. Found: C. 44.37, H. 3.15, N. 9.67.

2.3. MALDI-TOF-MS MEASUREMENTS

All MALDI-TOF-MS measurements were done using a Bruker BIFLEX III equipped with a 337 nm UV nitrogen laser producing 3-ns pulses. The MALDI-TOF-spectra were obtained in the reflective mode. Mass assignments were performed with unmanipulated spectra for an optimal correlation between observed and calculated mass. Samples were prepared by mixing solutions of the complexes in acetone (10 μ L) with a saturated solution of the matrix dithranol (in acetone, 10

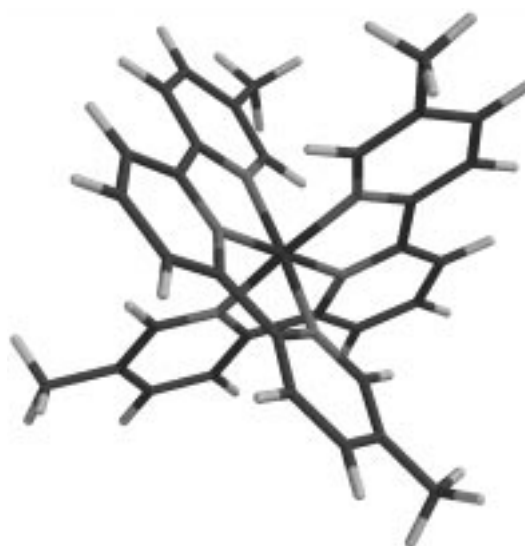
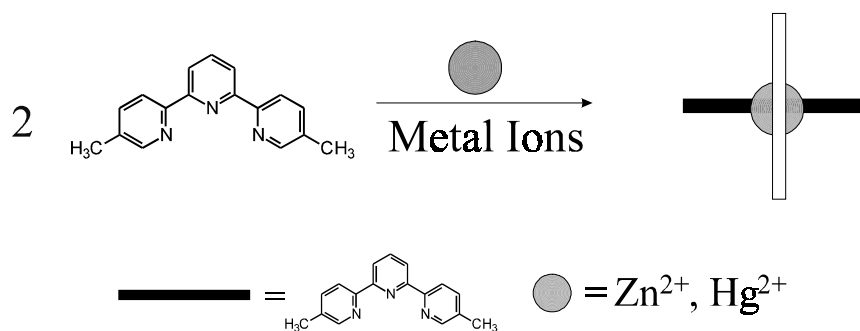


Figure 1. Top: Schematic representation of the 5,5''-dimethyl-terpyridine leading to the formation of the [1 × 1] complexes. Bottom: Wireframe model of the [1 × 1] Zn(II) complex (MacSpartan 1997, level MM2).

μL). A portion ($2 \mu\text{L}$) of the resulting mixture was loaded on the target, the solvent removed in air, and the sample transferred to the mass spectrometer for analysis.

3. Results and Discussion

Matrix Assisted Laser Desorption Ionization time of flight (MALDI-TOF) mass spectrometry has shown since its development by Hillenkamp and Karas in 1988 to be a very powerful technique for the analysis of high molecular weight compounds

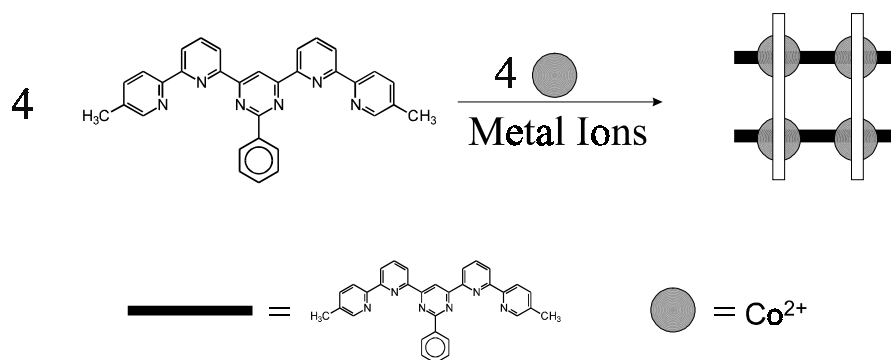


Figure 2. Top: Schematic representation of the 4,6-bis((5''-methyl)-2'',2'-bipyrid-6'-yl)-2-phenylpyrimidine leading to the formation of the [2 × 2] complexes. Bottom: Wireframe model model of the [2 × 2] Co(II) complex (MacSpartan 1997, level MM2).

with non-covalent interactions, such as proteins [14]. In contrast to electrospray mass spectrometry, which is strictly limited to charged systems (for an elegant exception see [15]) and based on a rather small variety of usable solvents, MALDI-TOF-MS is in principle less limited. However, the key problem here is the choice of the matrix. To the best of our knowledge there is only one example known to date of the use of MALDI-TOF-MS in supramolecular chemistry: Recently Timmermann

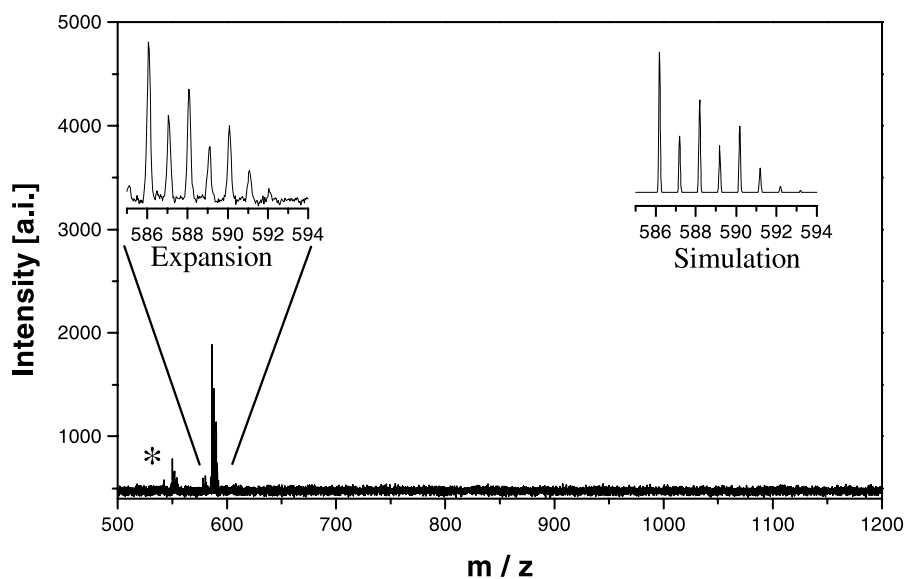


Figure 3. MALDI-TOF mass spectra of the [1 × 1] Zn(II) complex (Matrix: Dithranol, * indicates a matrix/terpyridine/zinc ion).

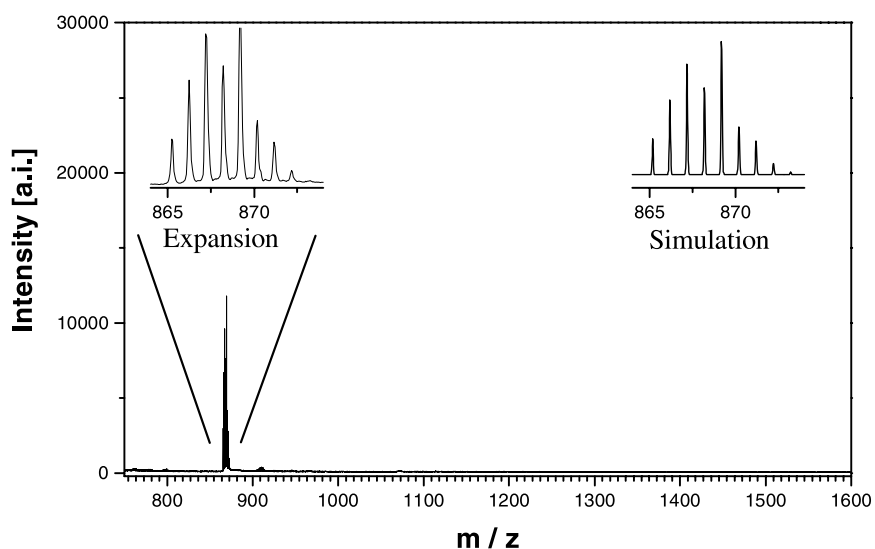


Figure 4. MALDI-TOF-MS spectra of the [1 × 1] Hg(II) complex (Matrix: Dithranol).

and Reinhoudt *et al.* [16] used this method for the investigation of neutral multicomponent hydrogen-bonded supramolecular assemblies. The results based on a Ag^+ -labeling technique: The remarkable high affinity of Ag^+ ions to parts of the supramolecular assemblies provided a nondestructive way to generate positively charged units which could be easily detected by MALDI-TOF mass spectrometry [16]. We tried to apply this method to different metal complexes synthesized during

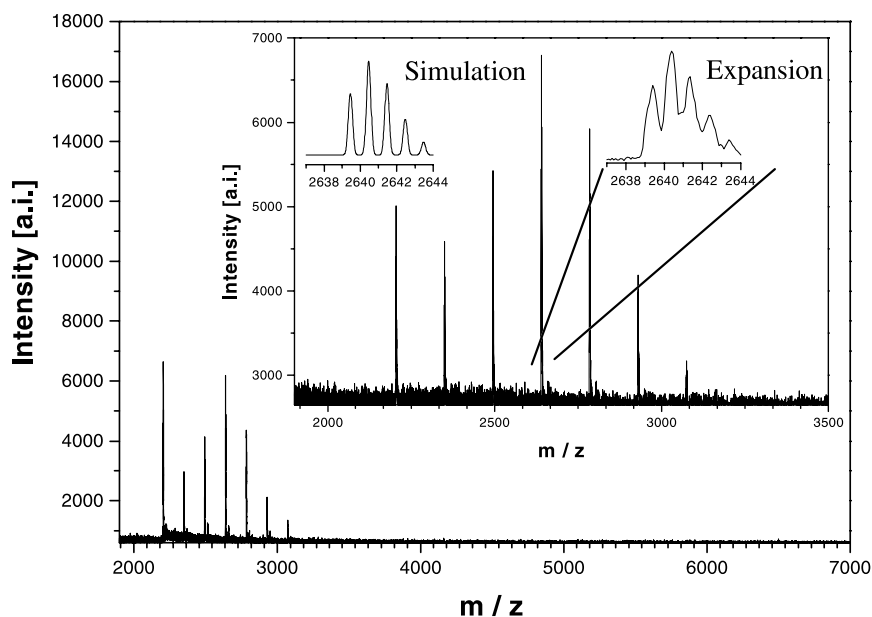


Figure 5. MALDI-TOF-MS spectra of the $[2 \times 2]$ Co(II) metal coordination array (Matrix: Dithranol).

our research towards novel functional metallo-supramolecular architectures ($[n \times n]$ metal coordination arrays). The systems are shown in Figures 1 and 2. In this case, no addition of Ag^+ is necessary due to the presence of one or four metal ions. The investigation of the $[1 \times 1]$ metal complexes revealed to be quite simple: Even without a matrix spectra consisting of the complex ion without the two PF_6 counter ions can be observed sometimes. In Figure 3 the MALDI-TOF-MS spectra of the $[1 \times 1]$ Zn(II) complex is shown using dithranol as matrix (for experimental details see 2.3). The highest signal obtained is the $\text{M}^+ \text{PF}_6$. The isotope pattern of that signal in the inset of Figure 3 showed at $m/z = 586.1$ a distinct pattern identical with the result of the simulation (calcd. for $\text{C}_{34}\text{H}_{30}\text{N}_6\text{Zn}$: $m/z = 586.2$ for the signal with highest intensity). Furthermore a less intense signal at $m/z = 550.0$ can be detected and interpreted as a matrix/terpyridine/zinc ion. A very similar result was obtained with the corresponding $[1 \times 1]$ Hg(II) system. In this case the complex was clearly observed in the MALDI-TOF spectrum at $m/z = 869.1$ ($\text{M}^+ \text{PF}_6$, Calcd. for $\text{C}_{34}\text{H}_{30}\text{N}_6\text{Hg}$ PF_6 : $m/z = 869.2$ for the signal with highest intensity) and the isotope pattern was consistent with the simulation (Figure 4). The investigation of extended metallo-supramolecular systems such as the $[2 \times 2]$ Co(II) coordination array, e.g. consisting of four 4,6-bis((5''-methyl)-2'',2'-bipyrid-6'-yl)-2-phenylpyrimidine ligands, four cobalt(II) ions and eight hexafluorophosphate counter ions with a molecular weight of 3366 g/mol (Figure 2, the x-ray structure of a similar grid is described in [3d]) was much more difficult. All attempts to charac-

terize such assemblies using no matrix or matrices like 2,5-dihydroxybenzoic acid or sinapinic acid have so far been unsuccessful. We could not obtain any significant signals between $m/z = 2000$ and 8000 . However, samples prepared with dithranol as matrix and acetone as solvent show intense signals around $m/z = 2500$ in the MALDI-TOF mass spectrum (Figure 5). In this case different grid fragments could be detected, consisting of an intact metallo-organic center and a variable number of counter ions (however, the charge of the ions is always +1, this phenomenon was observed in all MALDI-TOF spectra obtained up to now). Figure 5 shows six distinct peaks with a distance each of 145 g/mol (molecular weight of PF_6). The signals can be perfectly interpreted as grid fragments with zero to five counterions. Also in this case the isotope pattern of the signals could be obtained and compared to the results of a simulation. The inset of Figure 5 shows, e.g. the expansion of the signal with the highest intensity in the MALDI-TOF spectrum at $m/z = 2640.6$ (Calcd. for $\text{C}_{128}\text{H}_{96}\text{F}_{24}\text{Co}_4\text{N}_{24}\text{P}_3$: $m/z = 2640.5$). Therefore this ions consist of the unfragmented central grid unit and three counterions. These results are an unambiguous proof of the exclusive existence of the $[2 \times 2]$ metal coordination array in the solid state.

4. Conclusion

We conclude that MALDI-TOF-MS is a convenient and powerful tool for the mass spectrometric characterization of metallo-supramolecular systems in the solid state. In this study we applied MALDI-TOF-MS for the characterization of metal coordination arrays with molecular weights between 500 and 4000 g/mol . The stepwise loss of the counterions could be used as a fingerprint of the investigated species. Therefore it is not necessary to obtain the unfragmented molecular ions. The specific isotope pattern of the signals yield further information, especially in combination with simulations. Studies for the extension of this method to higher molecular weight systems are in progress [17].

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