

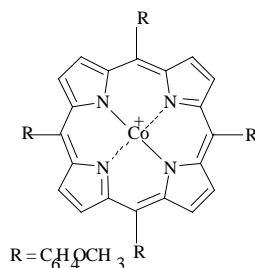
## A FOURIER TRANSFORM ICR MASS SPECTROMETRY STUDY OF BIOLOGICALLY ACTIVE METALLOPORPHYRINS

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Porphyrins are tetrapyrrolic macrocycle molecules that have found applications in medicine<sup>1</sup> for the therapeutic treatment of cancer.<sup>2</sup> Therefore, it is important to develop methods for the complete structural and molecular identification of natural and synthetic porphyrins. Electrospray ionization mass spectrometry (ESI-MS), laser desorption ionization mass spectrometry (LDI-MS) and matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) are modern ionization techniques that may be used in the complete identification of molecular formula (and often structures) of such compounds. In this study, gas phase cobalt porphyrin ions have been generated using the above ionization methods and studied under high resolution and with tandem mass spectrometric methods such as collision induced dissociation. These experiments were performed in a high field (7T) Bruker BIOPEX 70e Fourier transform ICR mass spectrometer (FT/ICR) and follow on from our earlier FT/ICR-MS experiments on porphyrins.<sup>3</sup>

The tetra para-methoxyphenyl cobalt porphyrin (*Structure in Fig. 1*) is used here as an example. A solution of cobalt porphyrin and methanol:dimethylformamide (10:1) was used for the ESI- and LDI-FT/ICR studies. For the MALDI-FT/ICR study, a solution of cobalt porphyrin in methanol: dimethylformamide (10:1) was mixed with dihydroxy benzoic acid (DBA) (MALDI matrix) on a stainless steel target.

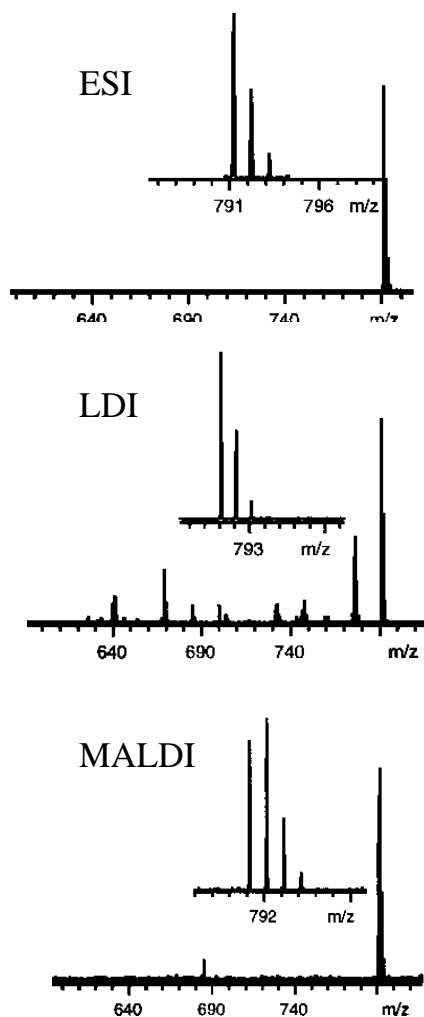


**Figure 1** Structure of tetra para-methoxyphenyl cobalt porphyrin

For the tetra p-methoxyphenyl cobalt porphyrin ( $\text{C}_{48}\text{H}_{36}\text{O}_4\text{N}_4\text{Co}$ ), the different ionization techniques resulted in the production of both molecular and protonated molecular ions (see Fig. 2.). We observed a molecular ion at  $m/z = 791$  in the ESI spectrum of the porphyrin. A similar ion was observed in the LDI spectrum of the porphyrin which was presumably produced by multiphoton-ionization. In the MALDI experiment we observed a strong signal from the protonated molecular ion at  $m/z = 792$  and, of the three experiments, the LDI produced the most primary fragmentation of the porphyrin molecules.

In this paper we will report the results of high resolution tandem mass spectrometry experiments on selected porphyrins and metalloporphyrins similar to that shown in Fig. 1.

1. Bonnett, R. Chem. Soc. Rev. 1995, 24, 19.
2. Milgrom, L.; MacRobert, S. Chem. Brit. 1998, 5, 45.
3. Antolovich, M.; Nguyen, T. H.; Paddon Row, M. N.; Willett, G. D. *Org. Mass Spectrom.* 1992, 27, 1034-1041.



**Figure 2** Cation electrospray ionisation (ESI), laser desorption ionisation (LDI) and matrix assisted laser desorption ionisation FT/ICR mass spectra of tetra para-methoxyphenyl cobalt porphyrin.