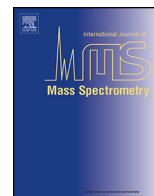# ARTICLE IN PRESS

Photo-oxidation by laser pulse induced desorption of phthalocyanines

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ABSTRACT

Photo-oxidation of iron(II)-phthalocyanine (PcFe) has been observed in matrix assisted laser desorption/ionization (MALDI) and laser desorption/ionization (LDI) and is interpreted by theoretical molecular dynamics simulations. The two ionization methods show different amounts of μ-oxo-bridged PcFe-dimer and deliver evidence that MALDI produces less mechanical stress on the analyte. The typical proton-transfer in the MALDI-process does not occur which leads to the assumption of a released electron of the delocalized π-system.

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1. Introduction

In the today's world phthalocyanines and their derivatives are widespread. Mainly used as dyes, they are also found in electronics, photo-dynamic therapy or modern optical devices. These manifold applications and their special physical and chemical properties have not only lead to numerous investigations on their optical, magnetic, and electric characteristics, but make them also very attractive in various research areas like crystallization and the usability as catalysts for O_2 reduction in biological fuel cell applications or as molecular switches [1–5]. Most of the experimental studies have been performed in solution or in solid form. Nevertheless they are simply brought into the gas phase by laser pulse irradiation due to the high absorbance of light in the visible and near UV wavelength regime [6]. Therefore, Pcs are suitable matrix substances for matrix-assisted laser desorption/ionization (MALDI).

Phthalocyanines are π-conjugated macro-cyclic ligands and can coordinate metal elements like iron to so-called metal phthalocyanines (PcMs). Some of them show the ability to adapt an oxygen atom if the present partial pressure of oxygen is high enough [7]. In the case of iron(II)-phthalocyanine (PcFe), several studies suggest that the additional oxygen atom binds to the central iron atom [8].

This work reports about PcFe and its transformation into the gas phase via MALDI and laser desorption/ionization (LDI). Whereas in LDI the substance is directly excited, in MALDI the energy of the laser pulse is mostly absorbed by the matrix substance and transfers part of that energy to the analyte. The indirect energy transport has the advantage that the method can bring large fragile bio-molecules into the gas phase. In most cases, the matrix substances are organic acids and provide a proton to a basic residue of the analyte. In addition to the experimental results, molecular dynamics simulations have been utilized to support the interpretation of the presented data.

2. Experimental

All experiments have been performed with a commercial Bruker MALDI mass spectrometer (Reflex, Bruker Daltonics, Bremen, Germany). A modification in the optical setup containing a dielectric mirror in the beam path has been made, which allows to irradiate the sample either with the built-in nitrogen laser (VSL-337ND, LSI) or ultra short laser pulses. The femtosecond laser setup (Kapteyn-Murnane Design; Odin, Quantronix, Darmstadt) provides 70 fs laser pulses up to a pulse energy of $E = 1$ mJ at a central wavelength of $\lambda_c = 800$ nm. A detailed description can be found elsewhere [9]. The advantage of femtosecond laser pulses lies in the well defined beam profile and lower pulse-to-pulse deviation compared to the nitrogen laser.

For LDI-measurements, 50 mg/ml PcFe were dissolved in a mixture of acetonitrile and water (3:2) and stirred for 30 min. 2 μl of this mixture has been placed on each spot of the sample holder, dried with a heat gun for 15 min and cooled down below a fume hood for 1 h. For MALDI-measurements 50 mg/ml of each α-cyano-cinammic-acid and sinapinic acid has been dissolved in a mixture of acetonitrile and water (3:2) and 0.1 μl trifluoracetic acid. The PcFe solution as described in the previous paragraph was again diluted
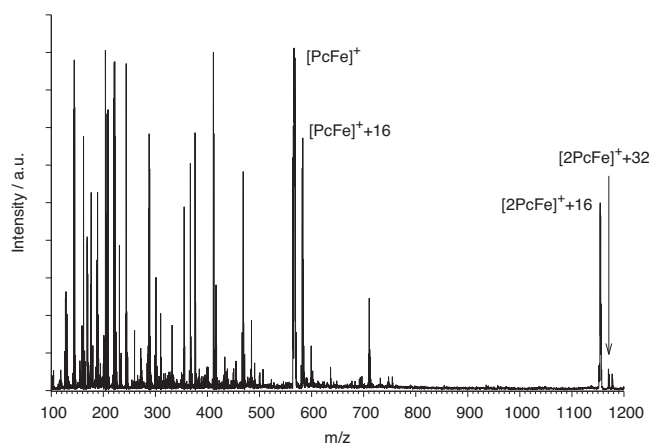
Fig. 1. MALDI mass spectrum of PcFe obtained with a pulse energy of $E = 2\,\mu J$: clusters and fragments are caused by the matrix in the lower mass region. The analyte peak is found at 568 u next to the oxidized species. At 1152 u the μ-oxo bridged dimer can be found together with a doubly oxidized dimer at 1168 u.

in acetonitrile/water (3:2) in a ratio of 1:100, mixed with the matrix solution (1:1) and placed on the sample holder. The process of drying is the same as explained for LDI. The phthalocyanine substance was purchased from Alpha Aesar (Ward Hill, MA, USA), all other chemicals have been ordered from Fluka (Buchs, Switzerland).

3. Theoretical methods

The molecular structure has been calculated using an annealing procedure combined with molecular dynamics simulations at the semi-empirical AM1 level of theory [10]. The electronic structure was calculated with the MOPAC program package while the MD-simulation was performed with an in-house suite of programs [11].

The simulations were started at a temperature $T = 1000\,K$ and the system has been exponentially cooled down to $T = 0\,K$ within 10 ps of simulation time. The step size was chosen in the range of molecular vibrations to 1 fs. For a good statistics all structures have been carried out by varying the simulation parameters such as initial structure and temperature, as well as cooling time of the system. The obtained results from this annealing procedure have been further optimized using DFT. For this purpose the ORCA-package has been used and the gradient corrected BP3LYP functional together with split valence plus polarization (SVP) basis sets for H and C and the triple-zeta valence plus polarization (TZVP) basis sets for Fe, N and O have been applied. To estimate proton affinities, the basis set has been extended to double-zeta (DZ) for H and N [12–15].

4. Results and discussion

4.1. MALDI and LDI of [PcFe]

All MALDI and LDI measurements were performed in positive ion mode. The MALDI mass spectrum in Fig. 1 shows the typical pattern: fragments of the analyte mixed with fragments of the matrix and cluster thereof at lower m/z-values and the analyte peak of PcFe at $m/z = 568$. According to general MALDI mass spectra one would expect a protonated and maybe some cationized species. The exclusive occurrence of [PcFe]$^+$ suggests only a minor influence to charge transfer of the matrix substance. The observed side peaks in the mass spectrum reflect the isotopic abundances. In Table 1 calculated proton affinities for different attacking sites on PcFe are listed. Following expression (2) in Ref. [16], the change of the molar enthalpy for the reaction [PcFe]+H$^+$→[PcFe+H]$^+$ is

Table 1
Energetic quantities for calculating the proton affinities of PcFe for different attacking sites. All values are given in kcal/mol. See Fig. 3 for labeling.

Protonated atom	ΔE_{el}^0	ΔE_{ZPE}	ΔH_{298}
N5	−176.7	8.3	−170.0
C1	−219.0	7.5	−213.0
C4	−185.8	7.1	−180.2

given by $\Delta H_{298} = \Delta E_{el}^0 + \Delta E_{ZPE} + \Delta E_{vib} - (5/2)RT$. The first term, the difference in electronic energy ΔE_{el}^0 of reactants and product, is obtained by geometry optimizations. The change in energy associated with internal vibrations is the sum of the zero point energy ΔE_{ZPE} and a correction term ΔE_{vib}. The latter accounts for a redistribution of the vibrational population as a function of temperature. Assuming that $\Delta E_{ZPE} \gg \Delta E_{vib}$, it has been neglected. The estimated proton affinities range from PA(PcFe)= 170 kcal/mol to 213 kcal/mol. These are relatively high values and a proton transfer reaction from the matrix to PcFe should be favorable. On the other hand, a delocalized electron of the π-system of the PcFe molecule can be easily detached by laser irradiation.

In the LDI mass spectrum (Fig. 2) there are significantly less mass peaks in the low m/z range. The lack of peaks (up to $m/z = 450$) resulting from the matrix makes the identification of the parent and its corresponding fragments or clusters much easier. In this case one can identify three additional mass peaks, next to the parent ion, which are also visible in the MALDI mass spectrum. They are found at 584, 1152 and 1168 u. The first one has a shift of +16 mass units with respect to the analyte and suggests an attachment of either oxygen or a –NH$_2$ group. The latter can be excluded, because no stable structures could be obtained from the performed geometry optimization calculations. The other two observed mass peaks can be interpreted as a PcFe-dimer with a μ-oxo bridge between the two central iron atoms. The abundance of dimers is much higher in the MALDI spectrum which motivates the assumption of a soft release of the analyte into the gas phase. The matrix acts as a buffer and absorbs the kinetic energy of the molecules in the process of desorption. Moreover, other PcMs (PcCu, PcZn) have been investigated for oxygen attachment, but it has been solely observed with PcFe.
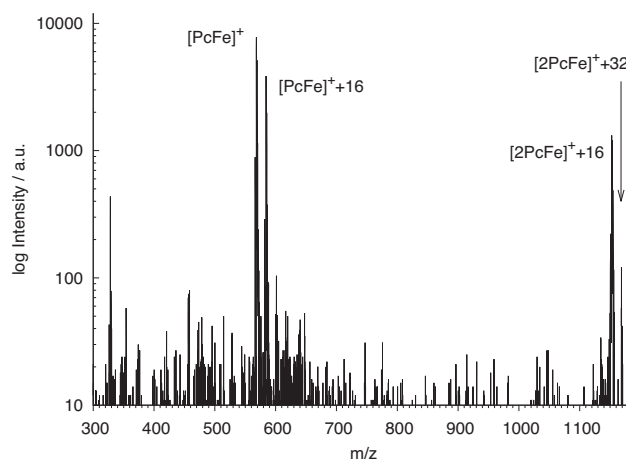

Fig. 2. LDI mass spectrum of PcFe obtained under the same conditions as the MALDI spectrum: At 568 u the ionized dye, the oxidized analyte at 584 u and the μ-oxo bridged dimer at 1152 u is visible. A mass peak with a low intensity which corresponds to two attached oxygen atoms can be observed at 1168 u.