
Observation of Phenyl-Fused Porphyrinoids During the ESI Mass Spectrometric Analysis of *meso*-Pentafluorophenyl-Substituted Porphyrin and Corrole

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The results of ESI(+) and ESI(−) mass spectrometry/mass spectrometry investigations of *meso*-tetrakisphenylporphyrin (TPP) and *meso*-trisphenylcorrole (TPC) in comparison with their *meso*-tetrakis(pentafluorophenyl)-substituted analogs T^FPP and T^FPC are reported. The fragmentation patterns of TPP and TPC show the expected loss of *meso*-aryl radicals. Analyzing the *meso*-pentafluorophenyl substituted analogs T^FPP and T^FPC , we found ESI(−) to be an excellent ionization mode. Rich and well-defined HF-elimination fragmentation patterns unique to the presence of *meso*-tetrafluorophenyl groups and evocative for the formation of fragments with direct covalent *o*-phenyl-to- β -linkages are observed. A computation of the feasibility and relative energies of the resulting species corroborates the interpretation of the experimental findings. The computations indicate the presence of cooperative interactions between the linkages that direct the linkage formations to occur in a unidirectional fashion. MS/MS/MS experiments also provide indications for the regioselectivity of the fusions. Our observations further detail earlier reports of similar HF-eliminations and allow a generalization of the findings. The results presented may also point to strategies towards the bulk synthesis of novel porphyrinoid structures. (J Am Soc Mass Spectrom 2006, 17, 1306–1314) © 2006 American Society for Mass Spectrometry

*m**eso*-tetraarylporphyrins, the parent compound of which is *meso*-tetrakisphenylporphyrin (TPP), are the most widely studied class of synthetic porphyrins (Figure 1). Their popularity as, for instance, model compounds for naturally occurring cofactors arises from their straightforward syntheses and the option to widely vary the type of substituents on the aryl rings [1]. One particular *meso*-aryl group, the electron-withdrawing pentafluorophenyl group, is commonly utilized when chemical inertness is to be imparted onto the porphyrinic macrocycle, such as increased stability toward oxidative degradation [2–6]. Metalloporphyrins and metallocorroles (based on the ligand *meso*-tris(pentafluorophenyl)corrole, T^FPC) used in group transfer catalyses also take advantage of the stabilizing effects of the pentafluorophenyl moiety [5–7]. The *meso*-pentafluorophenyl group was introduced into porphyrin isomers (*N*-con-

fused porphyrins) [8, 9], as well as into expanded porphyrins [10].

meso-Tetraarylporphyrins are generally potent singlet oxygen photosensitizers that have been utilized in the photodynamic destruction of neovascular tissue [11]. The quenching of the photo-excited triplet state of Pt(II) complexes of porphyrins is the origin of their utility in pressure-sensitive paints (PSP) that allow for the continuous mapping of surface pressures [12–16]. We have found that the use of the fluorinated ligand T^FPP in PSP formulations increases the phosphorescence lifetime of the paints and leads to photo-stable coatings, presumably because of the protection the pentafluorophenyl groups provide from singlet-oxygen-mediated oxidative degradation of the chromophore [13–16]. Further, T^FPP was suggested as a chemically inert and strongly light-absorbing matrix in MALDI-TOF mass spectrometry [17].

While the protection from undesired reactions on the porphyrinic macrocycle is the impetus for the use of the pentafluorophenyl group in the above examples, the *p*-position of the pentafluorophenyl group is activated toward a nucleophilic aromatic substitution reaction.

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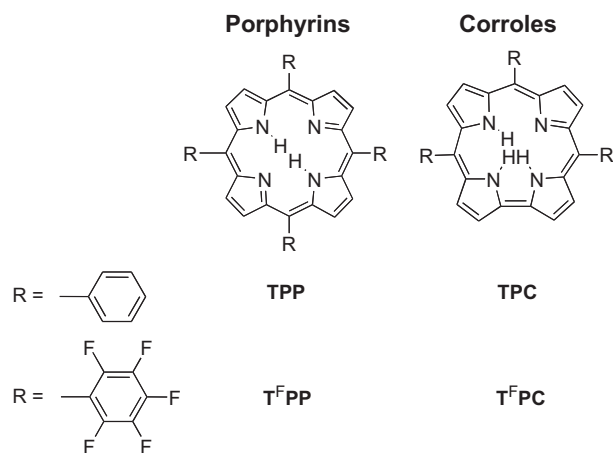


Figure 1. Structure and naming convention of the macrocycles investigated

Commonly using *N*- or *S*-nucleophiles, the pentafluorophenyl group can therefore be used to regioselectively introduce *p*-phenyl substituents [18–21]. Further, the pentafluorophenyl groups mediate the solubility of porphyrins in fluorinated solvents and supercritical CO₂ [22,23]. Lastly, ¹⁹F is NMR active, and the pentafluorophenyl group offers a convenient NMR tag to elucidate the structure of complex porphyrinic derivatives [3,24].

The many uses for *meso*-pentafluorophenyl groups make efficient analysis of these compounds desirable. Electrospray ionization (ESI) mass spectrometry (MS) is becoming a popular technique for the analyses of porphyrins [25–35].

During the mass spectrometric analysis of variously β -substituted *meso*-phenylporphyrins, ring-closure reactions involving the *meso*-phenyl group have been observed before. For instance, β -nitro- and β -vinyl-substituted porphyrins form, under FAB conditions, fragment ions enclosing six-membered rings, such as structures **1** and **2**, respectively (Figure 2) [30]. Inversely, *p*-nitrophenyl-substituted porphyrins do not undergo this type of cyclization. Hence, this reaction can be utilized for the determination of these regioisomers of nitroporphyrins by mass spectrometry/mass spectrometry (MS/MS) [36].

We report here on the results of ESI MS and MS/MS investigations of a *meso*-pentafluorophenyl-substituted porphyrin (T^FPP) and -corrole (T^FPC) in comparison with their nonfluorinated analogs TPP and TPC. Well-defined fragmentation patterns characteristic for the presence of *meso*-tetrafluorophenyl groups that are evocative of the formation of fragments with covalent *o*-phenyl-to- β -linkages are observed. Equivalent HF-elimination-mediated *o*-to- β -linkage formations enclosing a five-membered ring between the *meso*-aryl group and the porphyrin ring, were recently reported by Izquerdo et al. [33]. They reported the occurrence of these linkages of type **3** in the collision-induced dissociation ESI-MS spectra of *meso*-pentafluorophenyl derivat-

ized cationic pyrrolidine-fused chlorins and isobacteriochlorins [33]. A host of fragmentations characteristic for pyrrolidine-fused systems were found among a limited number of these HF-loss mediated cyclization reactions. We demonstrate here that formation of β -to-*o*-linkages during the MS/MS analysis of *meso*-tetrafluorophenylporphyrins follows predictable and rational patterns. In certain cases, all theoretically conceivable ring-closures can be observed, and the reaction appears to be general for *meso*-pentafluorophenyl-substituted porphyrinoids.

Experimental

TPP [37] and TPC [38] were synthesized according to literature methods. T^FPP was purchased from Frontier Science, Inc. (Logan, UT).

The computations were performed using CambridgeSoft Chem3D Pro Version 5, 1999 (Cambridge, MA), MM2 basis set and were run to convergence (minimum RMS gradient 0.1).

All mass spectrometry data were obtained using an ion trap mass spectrometer EsquireLC (Bruker Daltonics, Billerica, MA) with electrospray ionization source. Samples were dissolved in spectral grade CH₂Cl₂ and diluted in CH₃CN to approximate μ M concentrations. These solutions were directly infused into the ion source at a flow rate of 1 μ L/min. Spectra were collected in both positive and negative ionization mode using identical solutions. The standard tune parameters were similar for both modes: Capillary voltage 3500 to 4000 V, Δ endplate 500 V, capillary offset 70 V, skimmer 1 set to 30 V, skimmer 2 set to 4 V, octupole 3 V and octupole Δ 2 V, trap drive 55 to 75 V, ion charge control (ICC) on and target 25,000 (10,000 in negative mode for better isotope resolution), nebulizer gas (N₂) 12 psi, drying gas (N₂) 5 l/min, drying temperature 250 °C. The fragmentation spectra of the analytes were collected with an isolation width of 4 Da, fragmentation amplitude set to 1 V, and SmartFrag On (amplitude automatically varies 30 to 200% of the set fragmentation amplitude of 1 V).

Results and Discussion

ESI(+) MS and MS/MS of TPP and TPC

The ESI MS of TPP (C₄₄H₃₀N₄), recorded in the positive ion mode, is shown in Figure 3a. The sole species formed is the expected monoprotonated parent com-

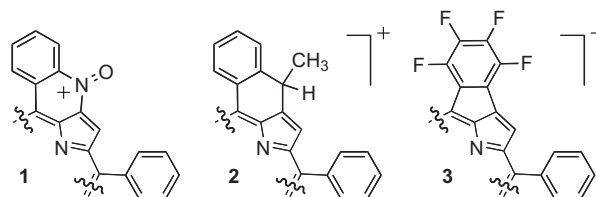


Figure 2. *meso*-Phenyl-fused structures previously observed during the mass spectrometric analysis of porphyrins

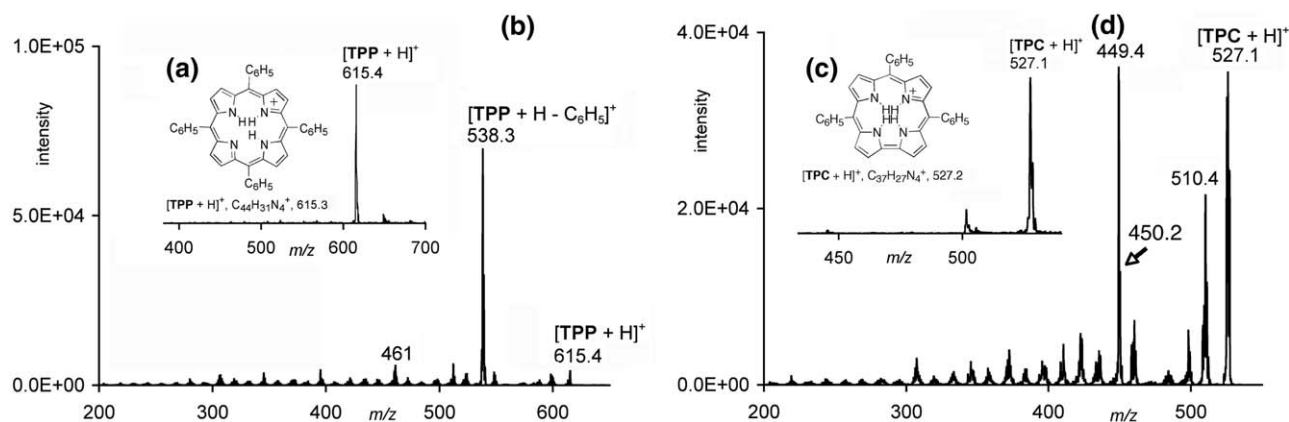


Figure 3. ESI(+) mass spectra of TPP and TPC. (a) (insert): ESI(+) MS of TPP. (b): ESI(+) MS/MS of the species $[\text{TPP} + \text{H}]^+$ (m/z 615). (c) (insert): ESI(+) MS of TPC. (d): ESI(+) MS/MS of the species $[\text{TPC} + \text{H}]^+$ (m/z 527). The interpretation of the spectra is presented in Scheme 1.

pound $[\text{TPP} + \text{H}]^+$ with a m/z value of 615. Protonation is likely taking place at one of the inner, basic imine nitrogens. The ESI-MS/MS spectrum of the species $[\text{TPP} + \text{H}]^+$ is shown in Figure 3b. Collision-induced fragmentation of the singly protonated TPP results predominantly in the loss of one phenyl group as a $\text{C}_6\text{H}_5^\cdot$ radical, forming the protonated triphenyl radical species **4** of m/z 538 (Scheme 1). The loss of a second phenyl group (expected m/z of 461.2) is of relatively low abundance. In general, these findings have been amply described before and serve here simply as benchmark data against which we evaluate the behavior of the pentafluorophenyl-derived analog [25, 29, 32].

The ESI(+) MS of triphenylcorrole TPC (Figure 3c) parallels that of TPP. The major species present are the respective MH^+ ions. Likewise, the ESI(+) MS/MS of the respective MH^+ species (Figure 3d) can largely be interpreted along the same lines as that for TPP (Scheme 1). The loss of one *meso*-substituent radical is a major fragmentation pathway that is accompanied by a minor pathway attributed to the breakup of the macrocycle. The apparent loss of either m/z 77 ($-\text{C}_6\text{H}_5^\cdot$) or neutral loss of benzene (78, $-\text{C}_6\text{H}_6$) is reproducible and may be a distinguishing feature for TPC. The remaining peaks resulting from the breakup of $[\text{TPC} + \text{H}]^+$ are

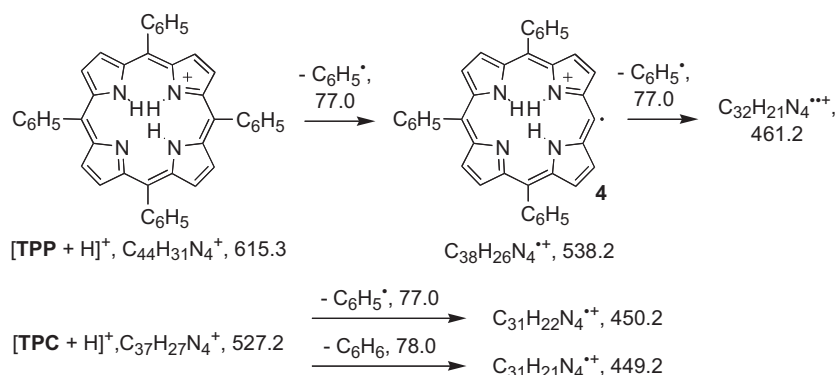
broad and point toward the successive loss of C- and N-fragments with varying numbers of hydrogens.

We were not able to record interpretable spectra for either of these two macrocycles under ESI(−) conditions. This result is surprising for TPC as its acidity is reportedly much higher than that of porphyrins [39].

ESI(+) and ESI(−) MS and MS/MS Analysis of $\text{T}^{\text{F}}\text{PP}$

When subjecting the fluorinated porphyrin $\text{T}^{\text{F}}\text{PP}$ to the same ESI(+) ionization conditions as its nonfluorinated counterpart TPP, we recorded spectra that were not as clean (cf. Figure 4a with Figure 3a). Presumably the electron-withdrawing *meso*-pentafluorophenyl substituents increase the acidity of the porphyrin and prevent efficient protonation. Hence, we tested the recording of the spectra in negative ionization mode (Figure 4c).

Essentially, only one ion at m/z 973 is detected, corresponding to the species $[\text{T}^{\text{F}}\text{PP} - \text{H}]^-$. Ionization is thus brought about by efficient deprotonation, presumably of one of the inner pyrrole-type nitrogens. The collision-induced fragmentation of the $[\text{T}^{\text{F}}\text{PP} - \text{H}]^-$ species is shown in Figure 4f. Four major and several



Scheme 1. Interpretation of the spectra shown in Figures 3a–d.

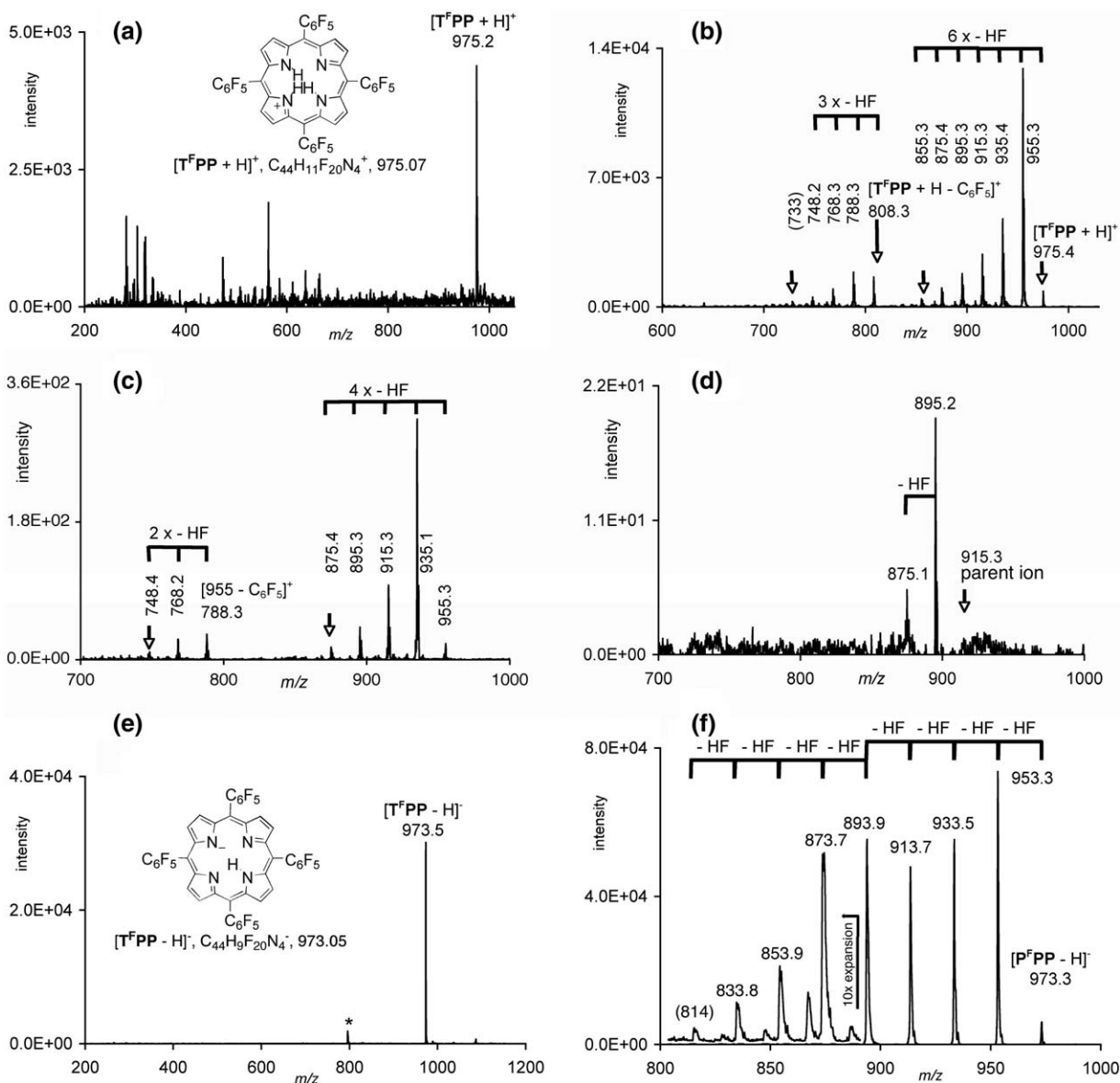


Figure 4. ESI mass spectra of T^FPP . (a): Full scan ESI(+) MS of T^FPP . (b): ESI(+) MS/MS of the species $[T^FPP + H]^+$ (m/z 975). An interpretation of the spectrum is provided in Scheme 3. (c): ESI(+) MS/MS/MS spectrum of the species m/z 955 (see in Figure 4b). (d): ESI(+) MS/MS/MS spectrum of the species m/z 915 (see in Figure 4b). (e): Full scan ESI(-) mass spectrum. The peak marked with an asterisk (at m/z 795) is an impurity of T^FPP originating from the preparation of T^FPP (for a discussion of the origin and the MS/MS of this species, see below). (f): ESI(-) MS/MS of the species $[T^FPP - H]^-$ (m/z 973). An interpretation of these spectra is shown in Scheme 2.

minor fragments are detected. Notably, the species corresponding to the loss of a pentafluorophenyl group (expected at m/z 806) is absent. As the predominant fragmentation pattern, a successive loss of HF (20 Da) is observed whereby four high abundance fragments are followed by four low abundance fragments. Since a *cis*-elimination of HF cannot take place in T^FPP , we surmise that the elimination is, under concomitant formation of an *o*-to- β -single bond, due to the loss of one H from the pyrrolic β -positions and the loss of one F from the *o*-position of a flanking pentafluorophenyl

group. This finding mirrors a report by Santana-Marques and coworkers who also observed, amidst other fragmentations, the occurrence of HF-elimination in the collision-induced ESI-MS spectra of *meso*-pentafluorophenyl derivatized cationic pyrrolidine-fused chlorins and isobacteriochlorins that were also interpreted as the formation of β -to-*o*-linkages [33]. In contrast, however, T^FPP possesses a much simpler structure that enables the HF elimination to occur as the sole fragmentation pathway. The simplicity of the precursor ion and the purported elimination products

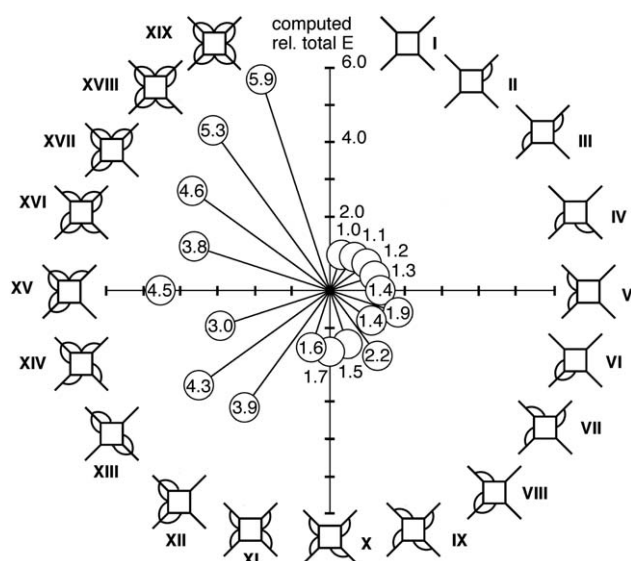


Figure 6. Computed relative (strain) energy increases upon successive formations of select β -to- o -linkages in T^FPP . Overall energy computed for **I** is 63 kJ/mol. The compounds computed are indicated in a stylized fashion: The squares represent the porphyrin macrocycle, the straight lines the *meso*-phenyl groups, and the o -to- β -linkages are indicated by the connections between these two elements.

cooperative interaction between the linkages that orients the direction of the subsequent fusions seems plausible. If one linkage causes a ruffling distortion of the macrocycle, the ruffled conformation facilitates the formation of a second linkage in a unidirectional fashion because this does not introduce any (or only minor) additional steric interaction between the o -atom of the second linked aryl group and the adjacent β -hydrogen (Structure **ic**, Figure 5). In fact, they are, as a direct result of the ruffling that translates throughout the entire macrocycle, already preoriented away from each other. Inversely, a nonunidirectional linkage goes “against the grain” and introduces additional steric interactions. Thus, the first elimination (to form **5**) enables the subsequent eliminations to take place in the regioselective, unidirectional manner shown (**5** to **6**, **7**, and finally **8**, Scheme 2). Molecular mechanics calculations corroborate this proposition.

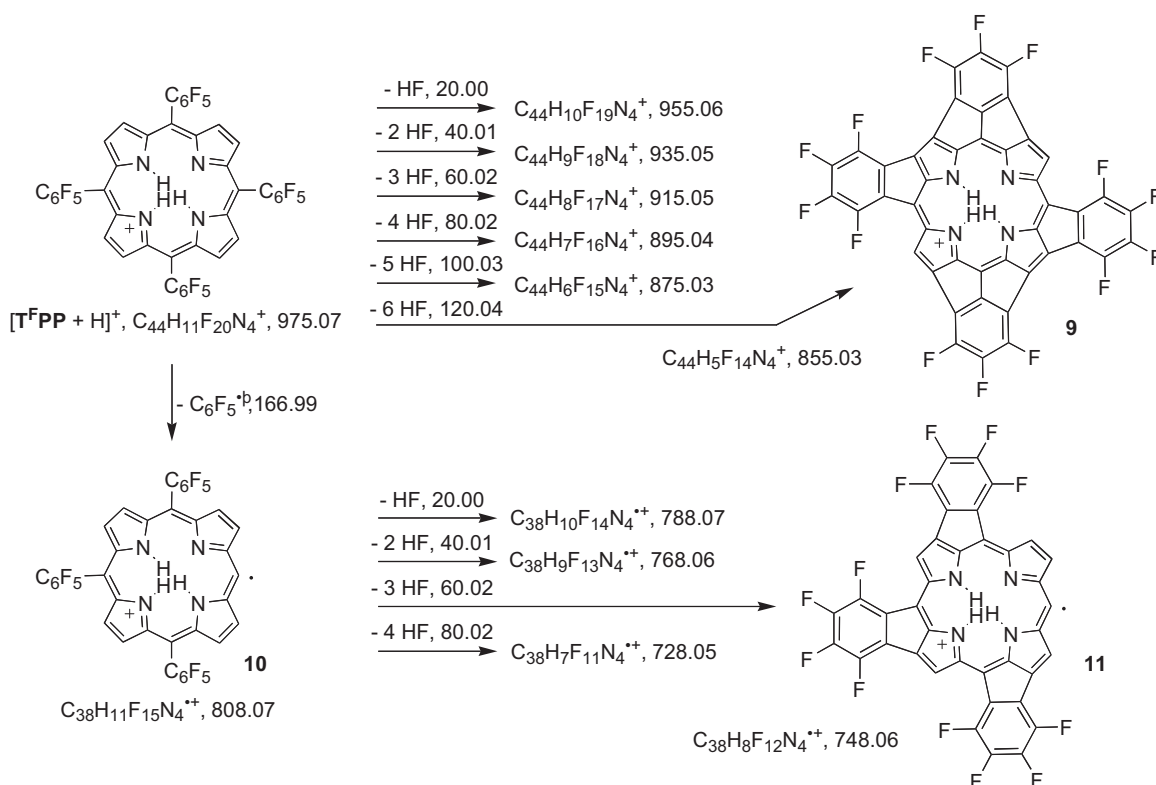
We computed the total energy of T^FPP in comparison with most of the possible isomers containing one to eight o -to- β -linkages. The results of the computations are summarized in Figure 6. The formation of one β -to- o -linkage (species **II**) increases the overall (strain) energy of the system only by 10% compared to the energy of the parent compound (**I**). In fact, up to four linkages increase the overall strain energy by only 50% (**IX**) if the linkages are connected in a unidirectional fashion. If the linkages are not established in a unidirectional fashion, as in **V** or in **X** and **XI**, the energy of the system is 10 to 15% higher as compared to the unidirectional isomers **IV** and **IX**, respectively. If even one phenyl group is linked on both o -positions (**VI**), the energy nearly doubles. Thus, all iso-

mers of the species containing four linkages (**X–XIV**) in a nonunidirectional fashion have significantly higher energies than **IX**. Those bearing two doubly-linked phenyl groups possess up to threefold the energy of **IX**. The fifth to eighth consecutive linkages necessarily involve such doubly-linked phenyl groups and, consequently, their energies are significantly elevated. Whether these high-energy ring-fusions occur also in a unidirectional fashion could not be made out clearly.

This result correlates well with the observed relative peak intensities in the fragmentation spectrum of $[T^FPP - H]^-$ (Figure 4f). The fifth and subsequent eliminations proceed with low efficiency, and the corresponding fragment peaks are minor compared to the peaks resulting from the first four eliminations (note the 10-fold intensity enhancement of the spectrum below m/z 890). It is, therefore, not surprising that literature precedence for the bulk-phase formation of o -, o' -linked phenyl groups in the solution phase are rare and involve only one phenyl group and two enclosed six-membered rings or one five- and one six-membered ring [40,41]. Porphyrinoids containing direct β -to- o -linkages enclosing five-membered rings between the phenyl and the porphyrin macrocycle are also known, though their establishment follow different routes than presumed here [42,43].

In light of the foregoing, the ESI(+) MS/MS spectrum of $[T^FPP + H]^+$ (Figure 4b) can qualitatively be interpreted in a similar fashion to the ESI(−) spectrum, with two notable differences (Scheme 3). First, two HF elimination series can be distinguished: one series of six eliminations beginning with the species $[T^FPP + H]^+$ (at m/z 975) and ending with the fragment **9** (m/z 855, shown is the isomer with opposite double linkages as the computations have shown this arrangement to be energetically more favorable), and one series beginning with the species **10** (m/z 808). Fragment **10** is derived from $[T^FPP + H]^+$ by a loss of a C_6F_5 radical. Since this fragment contains fewer pentafluorophenyl groups that can lead to ring-closure, only a maximum of three HF eliminations, presumably forming species **11**, are observed. A fourth elimination that requires a highly strained, doubly-fused aryl group cannot be made out clearly. Second, the mechanism is much less clear since an intramolecular nucleophilic substitution mechanism much less likely operating within a cationic pseudomolecular species, though it does not rule it out entirely. The driving force for the reaction is identical in either charge state and may drive an even unfavorable reaction pathway. Further, as the loss of aryl radical fragments demonstrates, radical pathways also cannot be excluded. In fact, we have observed the HF-elimination in *meso*-heptafluoropropyl-substituted porphyrins under ESI conditions that is, under ESI(+) conditions, intermingled with a radical fragmentation pathway of the *meso*-alkyl groups [35].

The fact that two competing fragmentation pathways (HF and C_6F_5 losses) are observed allows further insight into the regioselectivity of the sequential HF losses. In the MS/MS/MS spectra of the species that



Scheme 3. Interpretation of the collision-induced fragmentation mass spectrum of $[T^FPP + H]^+$ (Figure 4b). For clarity, the interpretation of Figures 4c and 4d were omitted.

have lost one to three HF fragments, the loss of a C_6F_5 fragment is observed in addition to further HF-losses. Representative for this case, Figure 4c shows the MS/MS spectrum of the m/z 955 species ($[T^FPP + H - HF]^+$). The spectrum looks like the spectrum for $[T^FPP + H]^+$ truncated by the first HF loss. Inversely, only one or two HF losses are observed in the product ions that have already lost three or four HF molecules, respectively. Figure 4d, the MS/MS spectrum of the m/z 915 species ($[T^FPP + H - 3 HF]^+$), shows such a case. Only two further HF-losses are observed while there are no indications for any loss of an aryl group. The first fusion makes the loss of an aryl group through a simple *meso-ipo* single bond breakage impossible. Hence, this finding further supports further the supposition that firstly HF fragmentations occur that fuse all the phenyl groups with a single bond to the macrocycle before a second fusion is established.

ESI(−) MS/MS. Spectra of the m/z 796 Species Assigned to T^FPC

The porphyrin T^FPP is made by acid-catalyzed condensation of pyrrole and pentafluorobenzaldehyde. It is well known that this reaction also generates the corresponding corrole T^FPC [44,45]. Inspection of the mass spectrum of a commercial sample of T^FPP clearly shows the presence of this impurity (see Figure 4e).

The collision-induced fragmentation spectra of the precursor ion of the trifluorophenylcorrole T^FPC in the ESI(+) and ESI(−) modes are shown in Figure 7a and b, respectively. The ESI(+) spectrum allows for the observation of five HF eliminations, leading to the formation of species 12 and the loss of one pentafluorophenyl group from the precursor ion (m/z 797) (Scheme 4). Again, the ESI(−) spectrum provides the clearest spectrum. Three consecutive HF eliminations are visible, presumably one for each pentafluorophenyl group of T^FPC , forming species 13. This compares to the four high abundance eliminations corresponding to the four fluorophenyl groups in T^FPP and the three eliminations for the three fluorophenyl groups in the porphyrin radical species 10 (Scheme 3). Hence, the number of HF eliminations observable in the ESI(−) spectra is diagnostic for the number of pentafluorophenyl groups attached to the porphyrinic framework. Similarly important, this observation lends further credence to the validity of the interpretation of the mass spectra.

Conclusions

We have shown the detailed mass spectrometric analysis of *meso*-phenyl- and pentafluorophenyl-substituted porphyrins and corroles using positive and negative mode ESI tandem mass spectrometry. The typical and known fragmentation of the phenyl-

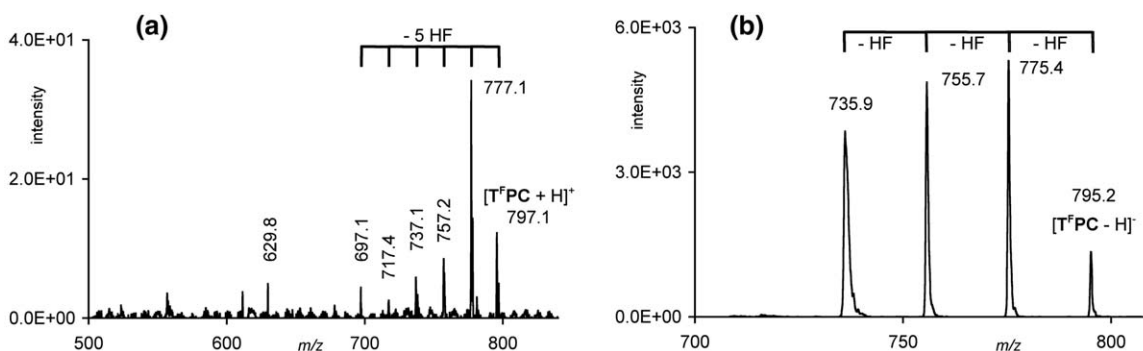


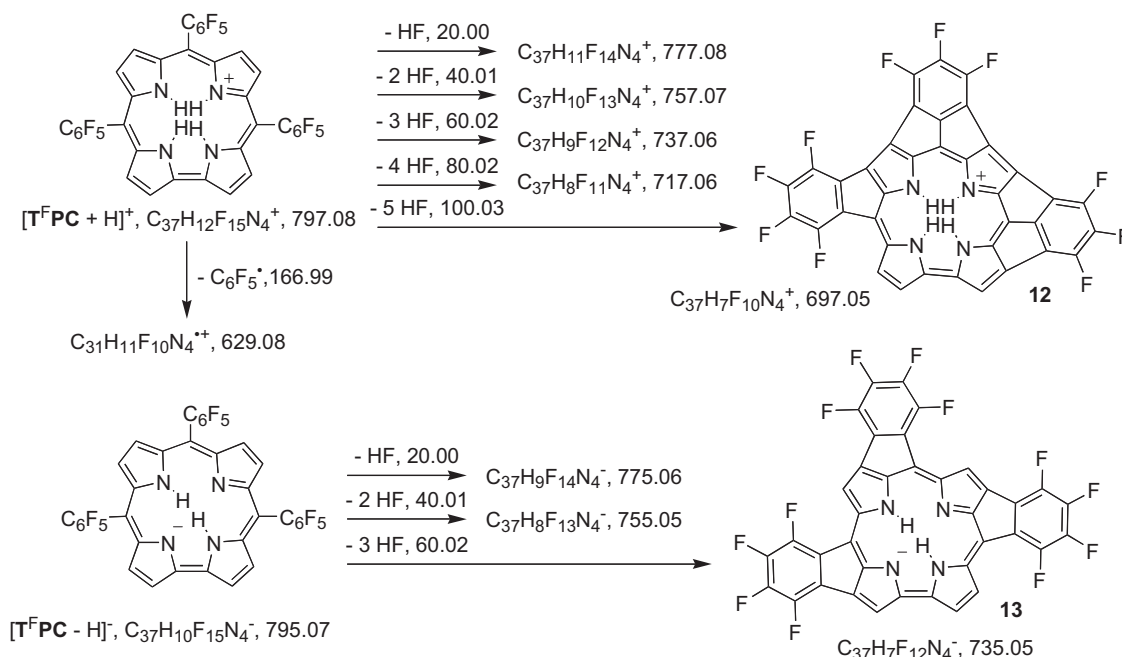
Figure 7. ESI spectra of T^FPC . (a): ESI(+) MS/MS spectrum of the m/z 797 species that is detectable in the full scan spectrum of T^FPP and that is assigned to $[T^FPC + H]^+$. (b): ESI(-) MS/MS spectrum of the m/z 795 species visible in the full scan spectrum of T^FPP (Figure 4e) and that is assigned to $[T^FPC - H]^-$. An interpretation of the spectra is provided in Scheme 4.

substituted macrocycles in the positive mode is the loss of phenyl side chains. *meso*-Pentafluorophenyl-substitution also allows for the recording of spectra in the negative mode whereby this derivatization also changes the MS behavior of porphyrinic macrocycles in a fundamental way in both ionization modes when compared to their *meso*-phenyl-substituted counterparts. As the predominant fragmentation pattern we have identified the successive loss of HF. We attribute this to the formation of fragment ions with direct *o*-phenyl-to- β -linkages. This observation, taken together with the observations reported before [33] establishes this fragmentation pathway as likely to be general for *meso*-pentafluorophenyl-substituted porphyrinoids. The results will facilitate the interpretation of MS spectra of *meso*-pentafluorophenyl-substituted porphyrinic compounds using ESI mass

spectrometry. Whether the observed fragmentation modes can also be adopted for the solution phase bulk synthesis of porphyrins containing coplanarized *meso*-aryl groups by chemically induced HF eliminations is currently a subject of investigations in our laboratories.

Acknowledgments

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Scheme 4. Interpretation of the collision-induced fragmentation mass spectrum of $[T^FPC + H]^+$.

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