Supporting Information

for

Salt Cluster Attachment to Crown Ether Decorated Phthalocyanines in the Gas Phase

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Contents

Figure S1 ESI-mass spectrum of ZnPcTetCr without NaCl addition	3
Figure S2 Enlargement of Figure S1d and comparison with simulated isotope pattern	4
Figure S3 Enlargement of Figure S1b and comparison with simulated isotope pattern	5
Figure S4 ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl (QIT)	6
Figure S5 ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl (QTOF)	8
Figure S6 CID mass spectra of M(NaCl)Na ₃ ³⁺ and M(NaCl) ₂ Na ₃ ³⁺	10
Figure S7 CID mass spectra of M(NaCl) _{1,2} Na ₂ ²⁺ and M ₂ (NaCl) _{2,4} Na ₄ ⁴⁺	11
Figure S8 CID mass spectra of $M_2(NaCl)_{1,3}Na_2^{2+}$ and $M_3(NaCl)_5Na_3^{3+}$	12
Figure S9 CID mass spectrum of M ₃ (NaCl) ₈ Na ₅ ⁵⁺	13
Figure S10 CID mass spectrum of M ₃ (NaCl) ₆ Na ₄ ⁴⁺	14
Figure S11 ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl (QIT) in negative ion mode	16
Figure S12 ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl (QTOF) in negative ion mode	17
Figure S13 CID mass spectra of $M(NaCl)_{3-6}Cl_2^{2-}$	19
Figure S14 CID mass spectra of $M_2(NaCl)_9Cl_2^{2-}$ and $M_2(NaCl)_{14}Cl_2^{2-}$	20
Figure S15 CID mass spectra of $M_3(NaCl)_{12-15}Cl_2^{2-}$	21
References	24



Figure S1. a) ESI-mass spectrum of ZnPcTetCr without NaCl addition in DCM/ACN (1:1, v:v), acquired with the QIT. **b-d)** enlargements of the same spectrum.



Figure S2. a) Enlargement of $M_2Na_2^{2+}$ and MNa^+ (*m/z* 1537) from the mass spectrum shown in Figure S1d (top) and corresponding simulated isotope pattern of the doubly charged dimer (bottom). **b**) Enlargement of the same region as observed under different ion transfer conditions. The higher cone voltage results in harsher conditions, causing the doubly charged dimer to partially fragment into the singly charged monomer (see also Figure S8).



Figure S3. Enlargement of $MNa^{(2+)}$ (*m*/*z* 768) from the mass spectrum shown in Figure S1b (top) and corresponding simulated isotope pattern of the ion (bottom).



Figure S4. a) ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl in DCM/ACN (1:1, v:v), acquired with the QIT. **b-g)** enlargements of the same spectrum.



Figure S4, continued.



Figure S5. a) ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl in DCM/ACN (1:1, v:v), acquired with the QTOF. **b-f)** enlargements of the same spectrum.



Figure S5, continued.



Figure S6. CID mass spectra of **a**) $M(NaCl)Na_3^{3+}$ and **b**) $M(NaCl)_2Na_3^{3+}$, showing loss of one or two NaCl molecules.



Figure S7. a) CID mass spectrum of $M(NaCl)Na_2^{2+}$ and $M_2(NaCl)_2Na_4^{4+}$. The monomer dissociates via loss of NaCl. The highly charged dimer fragments via Coulomb explosion into MNa_2^{2+} and $M(NaCl)_2Na_2^{2+}$.

b) CID mass spectrum of $M(NaCl)_2Na_2^{2+}$ and $M_2(NaCl)_4Na_4^{4+}$. The monomer fragments primarily via loss of $(NaCl)_2$ into MNa_2^{2+} . The dimer undergoes Coulomb explosions as well as loss of a single NaCl molecule.



Figure S8. a) CID mass spectrum of $M_2(NaCl)Na_2^{2+}$. The dimer first loses the only attached NaCl molecule, then splits equally into two monomers MNa^+ .

b) CID mass spectrum of M₂(NaCl)₃Na₂²⁺, showing only consecutive losses of NaCl and/or (NaCl)₂.

c) CID mass spectrum of $M_3(NaCl)_5Na_3^{3+}$. The trimer dissociates via sequential NaCl and/or $(NaCl)_2$ losses. The fragment ions MNa^+ and $M_2(NaCl)Na_2^{2+}$ are probably the result of a Coulomb explosion of the product ion $M_3(NaCl)Na_3^{3+}$.



Figure S9. a) CID mass spectrum of $M_3(NaCl)_8Na_5^{5+}$ (*m/z* 1025). b)-d) Enlargements of a).



Figure S10. a) CID mass spectrum of $M_3(NaCl)_6Na_4^{4+}$ (*m/z* 1247). b)-e) Enlargements of a).



Figure S10, continued.

The quadruply charged precursor $M_3(NaCl)_6Na_4^{4+}$ ion mainly fragments via Coulomb explosion into the product ion pairs $M_2(NaCl)_{1-6}Na_3^{3+}$ and MNa^+ (**a**, **d**, **e**). The lack of singly charged $M(NaCl)_{1-5}Na^+$ ions is probably due to their instability (see main article). If these ions are formed at all in the Coulomb explosion, they dissociate immediately via $(NaCl)_{1-2}$ losses into MNa^+ . Otherwise, if the initial Coulomb explosion only generates $M_2(NaCl)_6Na_3^{3+}$ and MNa^+ , the smaller triply charged dimers $M_2(NaCl)_{1-5}Na_3^{3+}$ can only be formed via subsequent $NaCl/(NaCl)_2$ losses.

The precursor ion $M_3(NaCl)_6Na_4^{4+}$ also dissociates into the product ion pairs $M(NaCl)_{0-5}Na_2^{2+}$ and $M_2(NaCl)_{1-4}Na_2^{2+}$ (**a**, **c**, **e**). Again, not all counter-ions are observed, the ions $M_2(NaCl)_{5,6}Na_2^{2+}$ are too unstable to be detected.

Apart from the Coulomb explosions, the precursor ion can also undergo $(NaCl)_{1-2}$ loss in the first fragmentation step, resulting in the product ions $M_3(NaCl)_{4,5}Na_4^{4+}$ (d). Secondary Coulomb explosions of these ions probably contribute to the intensities of the ions discussed above.

The ions $M_3(NaCl)_{4,5}Na_4^{4+}$ are also the most likely origin of the quadruply charged dimers $M_2(NaCl)_{2-4}Na_4^{4+}$.



Figure S11. a) ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl in DCM/ACN (1:1, v:v), acquired with the QIT in the negative ion mode. **b)** Enlargement of the same spectrum.



Figure S12. a) ESI-mass spectrum of ZnPcTetCr with a tenfold molar excess of NaCl in DCM/ACN (1:1, v:v), acquired with the QTOF in the negative ion mode. **b-e)** enlargements of the same spectrum.



Figure S12, continued.



Figure S13. CID mass spectra of $M(NaCl)_nCl^-$ with n = 3 (a), 4 (b), 5 (c), and 6 (d), fragmenting via loss of $(NaCl)_n$ or $(NaCl)_{n-1}$. The singly charged salt cluster in the low mass region of the spectra originate from underlying doubly charged dimers $M_2(NaCl)_{2n}Cl_2^{2-}$ (see also Figure S11). Their counter-ion M_2Cl^- is not observed due to the limited mass range of the QIT. Note that the asterisked numbers denote magic number clusters [1].



Figure S14. a) CID mass spectrum of $M_2(NaCl)_9Cl_2^{2^-}$. The first step in the dissociation is the Coulomb explosion into the singly charged cluster (NaCl)_9Cl⁻ and M_2Cl^- . The salt cluster fragments further into smaller clusters. Note that the asterisked numbers denote magic number clusters.¹

b) CID mass spectrum of $M_2(NaCl)_{14}Cl_2^{2^-}$. Again the first dissociation step is a Coulomb explosion, however, the salt cluster $(NaCl)_{14}Cl^-$ is known to be highly unstable.¹ Therefore, the intensity of the expected product ions $(NaCl)_{14}Cl^-$ and M_2Cl^- is very low. Instead the fission into the magic number cluster $(NaCl)_{13}Cl^-$ and $M_2(NaCl)Cl^-$ is preferred. The ion $M_3(NaCl)_{20}Cl_2^{2^-}$ can only be explained by the dissociation of an underlying ion $M_3(NaCl)_{21}Cl_3^{3^-}$ via loss of $(NaCl)Cl^-$.



Figure S15. a) CID mass spectrum of $M_3(NaCl)_{12}Cl_2^{2^-}$, acquired with the instrument tuned to detect the lower mass fragments. The precursor ion dissociates via the loss of the cluster $(NaCl)_{12}Cl^-$. The counter ion M_3Cl^- (*m/z* 4580) was not observed, even with adjusted settings (see main article). The initial product ion $(NaCl)_{12}Cl^-$ fragments further into smaller clusters, preferentially into the magic number cluster $(NaCl)_9Cl^-$. The two other magic number clusters $(NaCl)_{13}Cl^-$ and $(NaCl)_{22}Cl^-$ probably originate from an underlying ion $M_6(NaCl)_{24}Cl_4^{4^-}$.

b) CID mass spectrum of $M_3(NaCl)_{13}Cl_2^{2^-}$, acquired with the instrument tuned to detect the higher mass fragments. For a detailed description see the main article.

c) Enlargement of S15b) Note that the signals marked with a dagger are instrumental artefacts without isotope pattern.



Figure S15 continued. **d)** CID mass spectrum of $M_3(NaCl)_{14}Cl_2^{2^-}$, acquired with the instrument tuned to detect the lower mass fragments. The aggregate dissociates predominantly via the loss of the magic number cluster (NaCl)_{13}Cl⁻, rather than the entire cluster, probably due to the instability of (NaCl)_{14}Cl⁻ (see also Figure S9b).

e) CID mass spectrum of $M_3(NaCl)_{14}Cl_2^{2^-}$, acquired with the instrument tuned to detect the higher mass fragments. The enlargement shows the counter-ion of the Coulomb explosion, $M_3(NaCl)_2Cl^-$ (*m/z* 4638), overlaid with its simulated isotope pattern (orange triangles).

f) Enlargement of S15e) Note that the signals marked with a dagger are instrumental artefacts without isotope pattern.



Figure S15 continued. **g)** CID mass spectrum of $M_3(NaCl)_{15}Cl_2^{2^-}$, acquired with the instrument tuned to detect the lower mass fragments. The precursor ion dissociates via the loss of the magic-number cluster $(NaCl)_{13}Cl^-$. The counter ion $M_3(NaCl)_2Cl^-$ (*m*/*z* 4696) was not observed, even with adjusted settings (see main article).

References

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