Electronic Supplementary Material (ESI) for Analyst.
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Supplementary information

Making the invisible visible:

Improved electrospray ion formation of metalloporphyrins/-phthalocyanines by attachment of the formate anion ($HCOO^{-}$)

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Analyst

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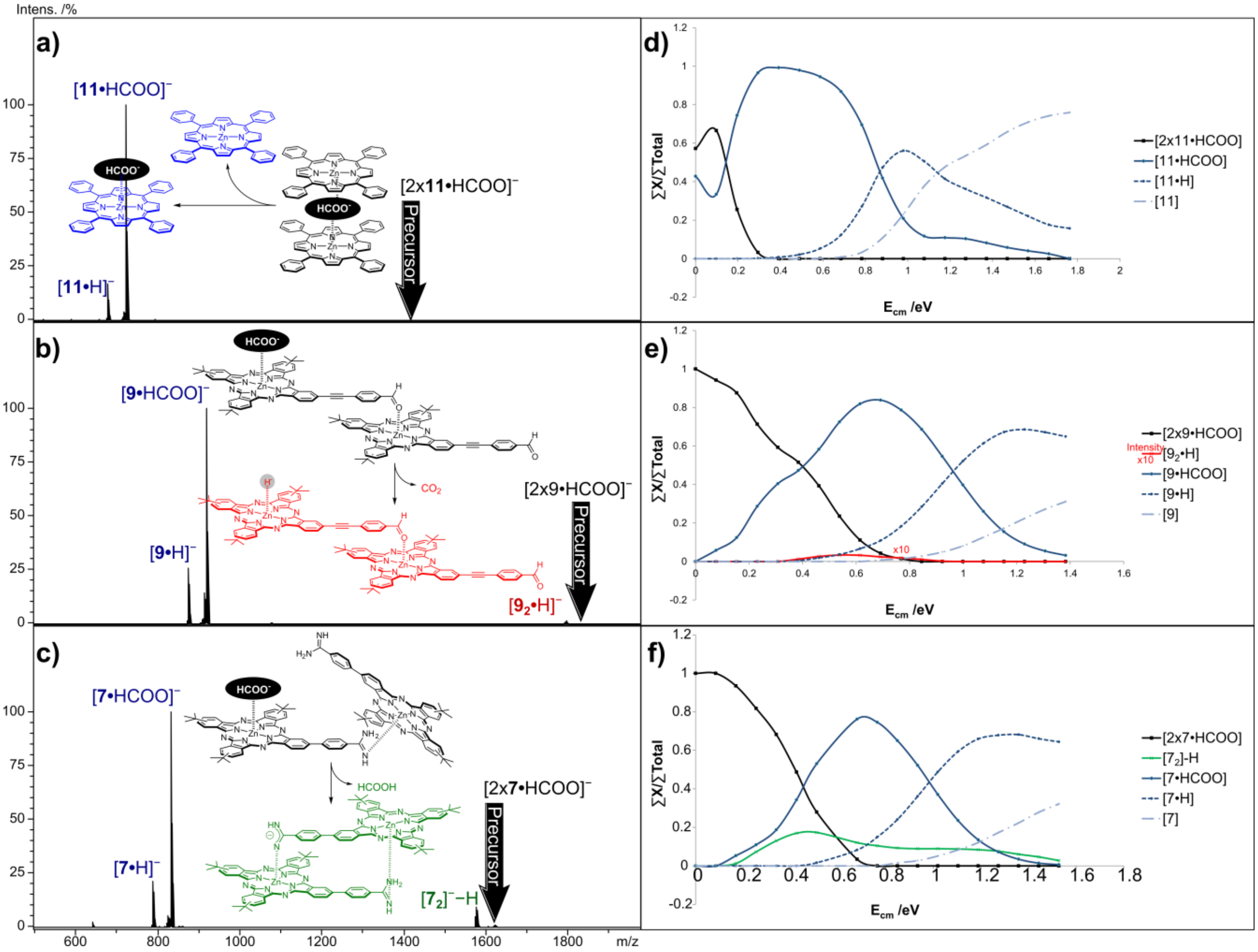


Figure S1 Negative-ion CID (MS^2) of a) formate-bridged dimer [2x**11**•HCOO]$^{-}$ b) [2x**9**•HCOO]$^{-}$, and c) [2x**7**•HCOO]$^{-}$. Each CID mass spectrum is contrasted on the right hand side with a graph showing the corresponding energy-dependent dissociation behavior (breakdown graph with x-axis: center-of-mass collision energy (E_{com}) and y-axis: ratio of fragment ion intensity to sum of intensities of all signals).

The three breakdown graphs d), e) and f) reveal for all formate anion-containing dimers ([**X**•HCOO•**X**]$^{-}$ with **X**=**11**, **9** and **7**), the same energetic succession of events. First the dimer [**X**•HCOO•**X**]$^{-}$ dissociates into the monomer [**X**•HCOO]$^{-}$ followed by dissociation into [**X**•H]$^{-}$ and finally [**X**]$^{\bullet-}$.

For **9** (e)), CO_2 loss into [**9**$_2$•H]$^{-}$ (enhanced by a factor of 10 because of the low abundance) and for **7** (f)), HCOOH loss into [**7**$_2$]$^{-}$–H is observed, indicating the presence of a directly connected isomeric dimer ion.

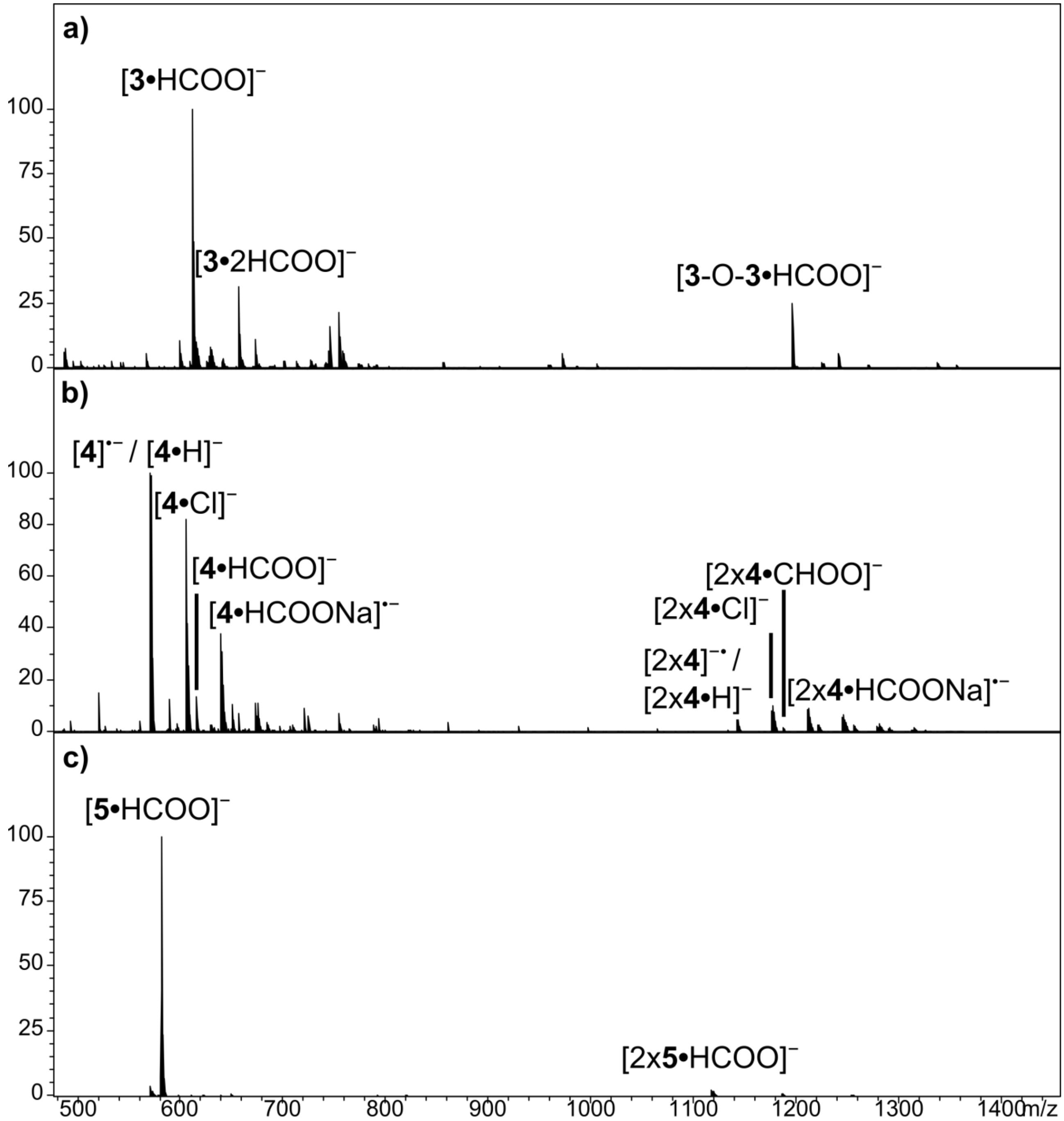


Figure S2 Negative-ion ESI qTOF mass spectra of a) Mn(II)Pc **3**, b) Co(II)Pc **4** and c) Mg(II)Pc **5** with sodium formate in DMF.

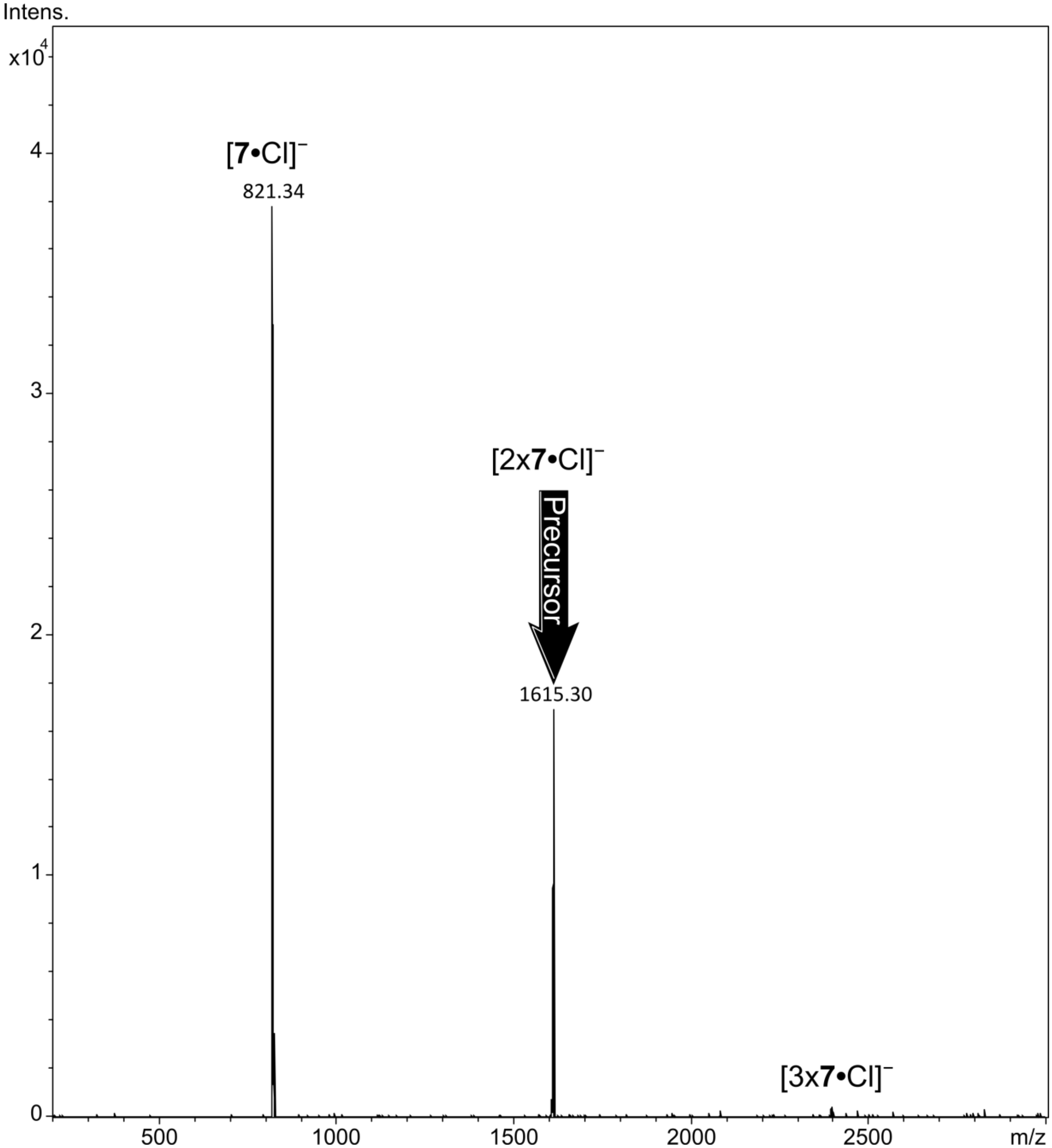


Figure S3 CID (MS²) of chloride bridged dimer [2x**7**•Cl]⁻.

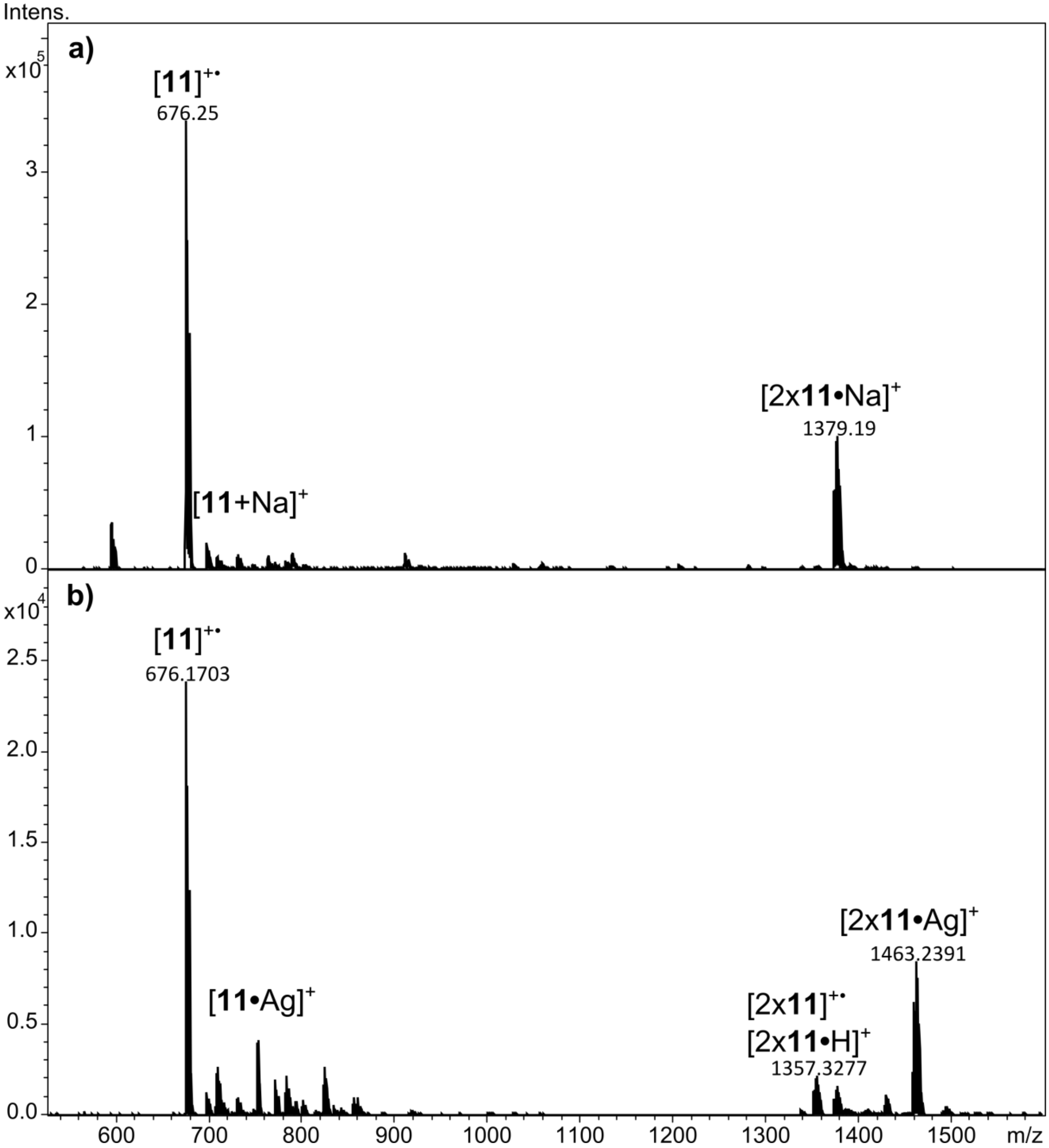


Figure S4 Positive-ion ESI MS of tetraphenyl Zn(II)Por **11** in acetonitrile recorded a) with the ESI ion trap (Esquire) and b) with the ESI qTOF (MicrOTOF-Q II) instrument, providing evidence of efficient radical cation formation (oxidation) in both cases.

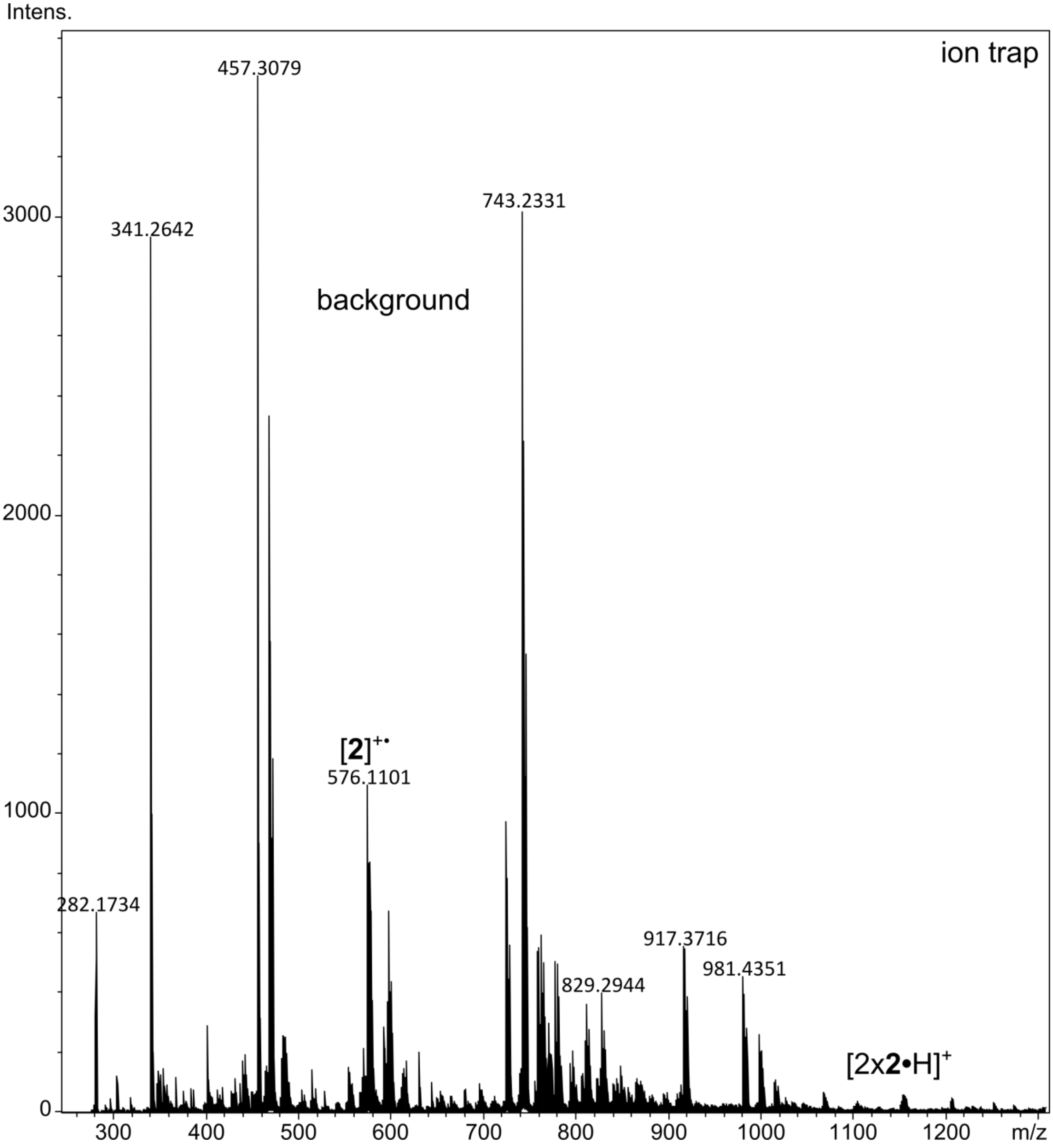


Figure S5 Positive-ion ESI ion trap mass spectrum of Zn(II)Pc **2** in acetonitrile. The radical cation is is formed in only low abundances. Background signals are more intense than the signal due to the oxidation of **2**.

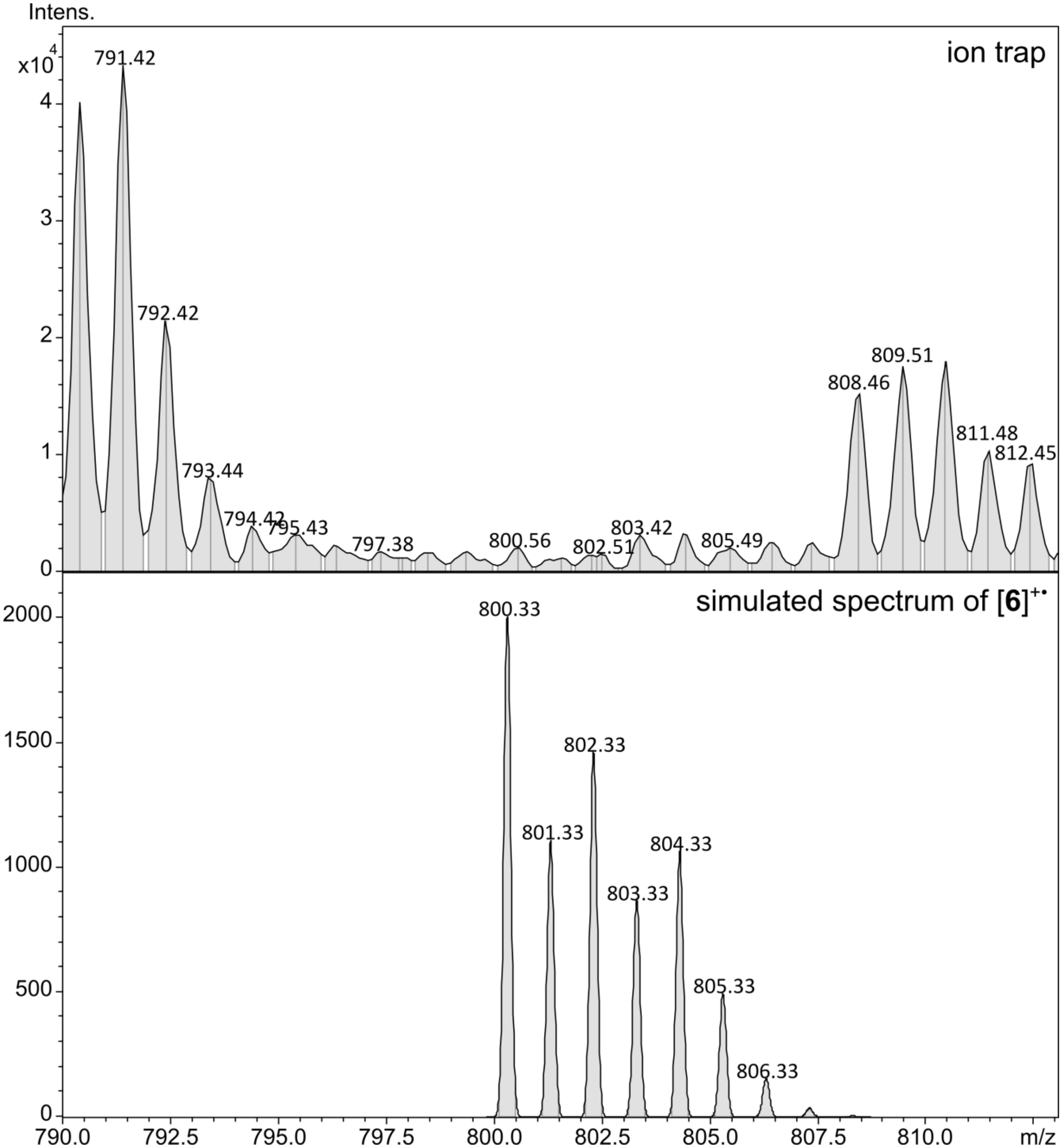


Figure S6 Positive-ion ESI ion trap mass spectrum of the Zn(II)Pc **6** in acetonitrile. Analyte oxidation is absent.

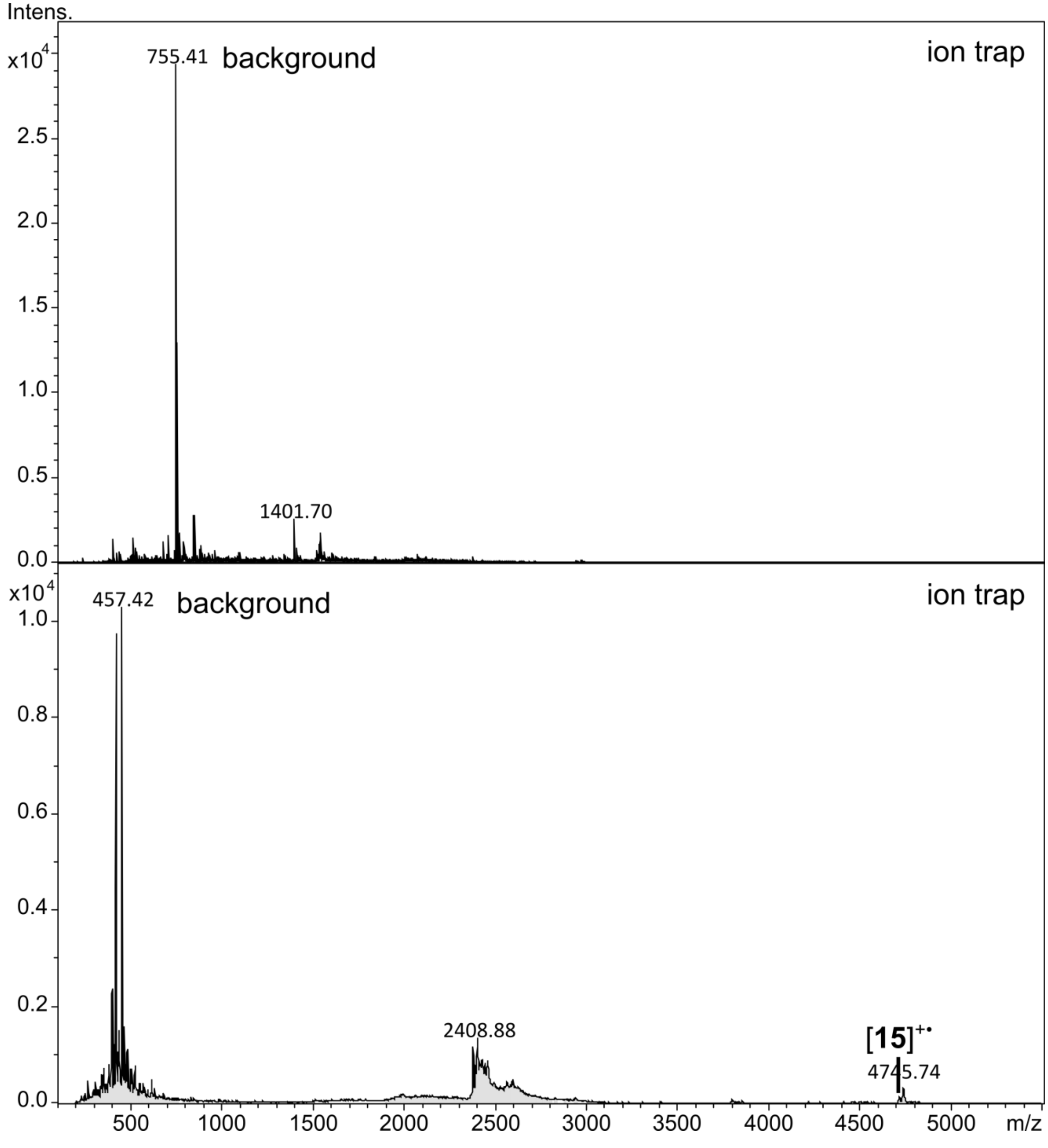


Figure S7 Positive-ion ESI ion trap mass spectra of Zn(II)Por triad **14** (top) and pentad **15** (bottom) in acetonitrile. Only for **15**, the formation of the radical cation can be observed in minute amounts. **14** does not show any radical cation formation.

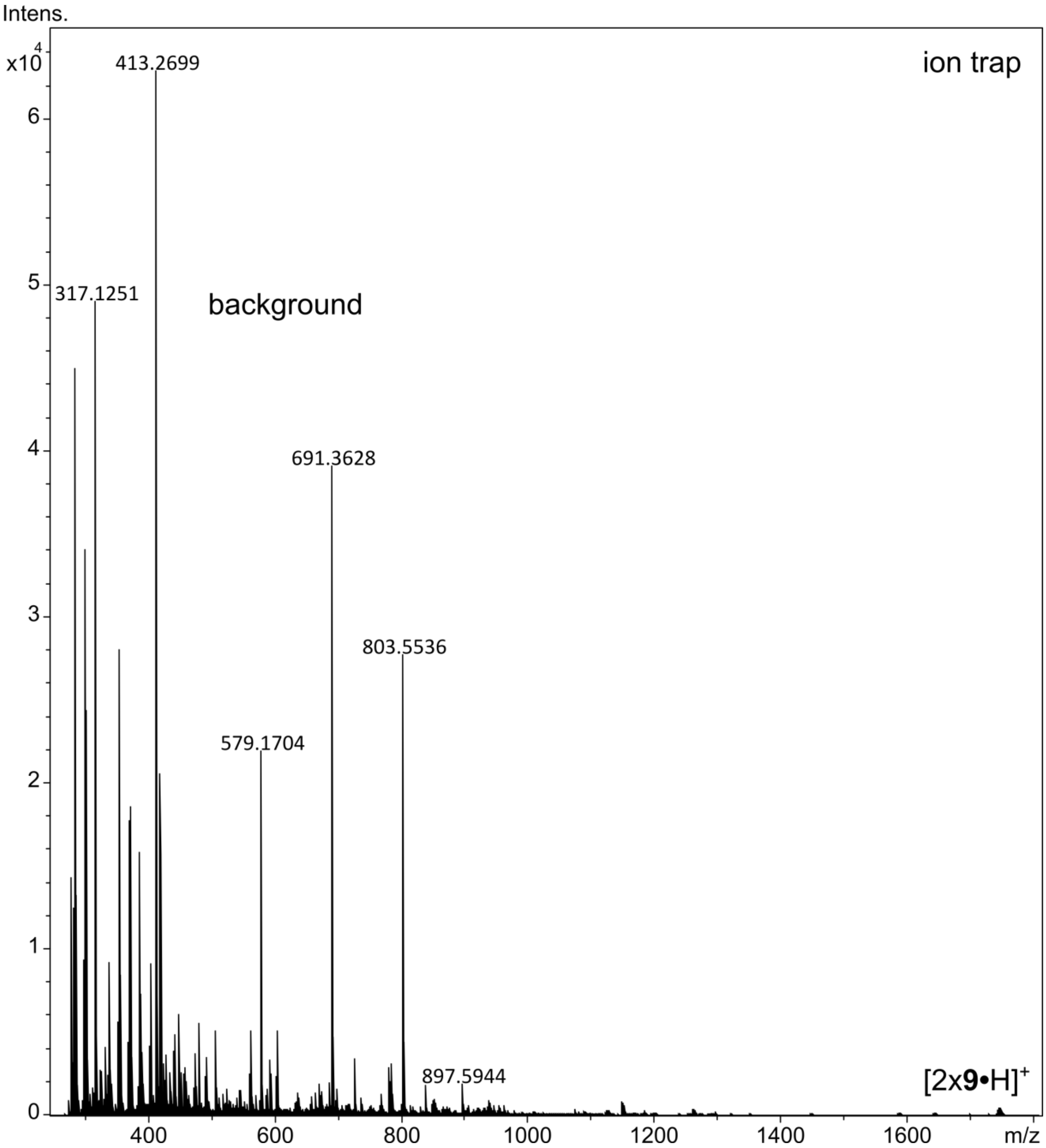


Figure S8 Poisitive-ion ESI ion trap mass spectrum of aldehyde-substituted Zn(II)Pc **9** in acetonitrile. Radical cation formation of **9** is not observed (no oxidation). Background signals are more intense than signals due to the analyte.

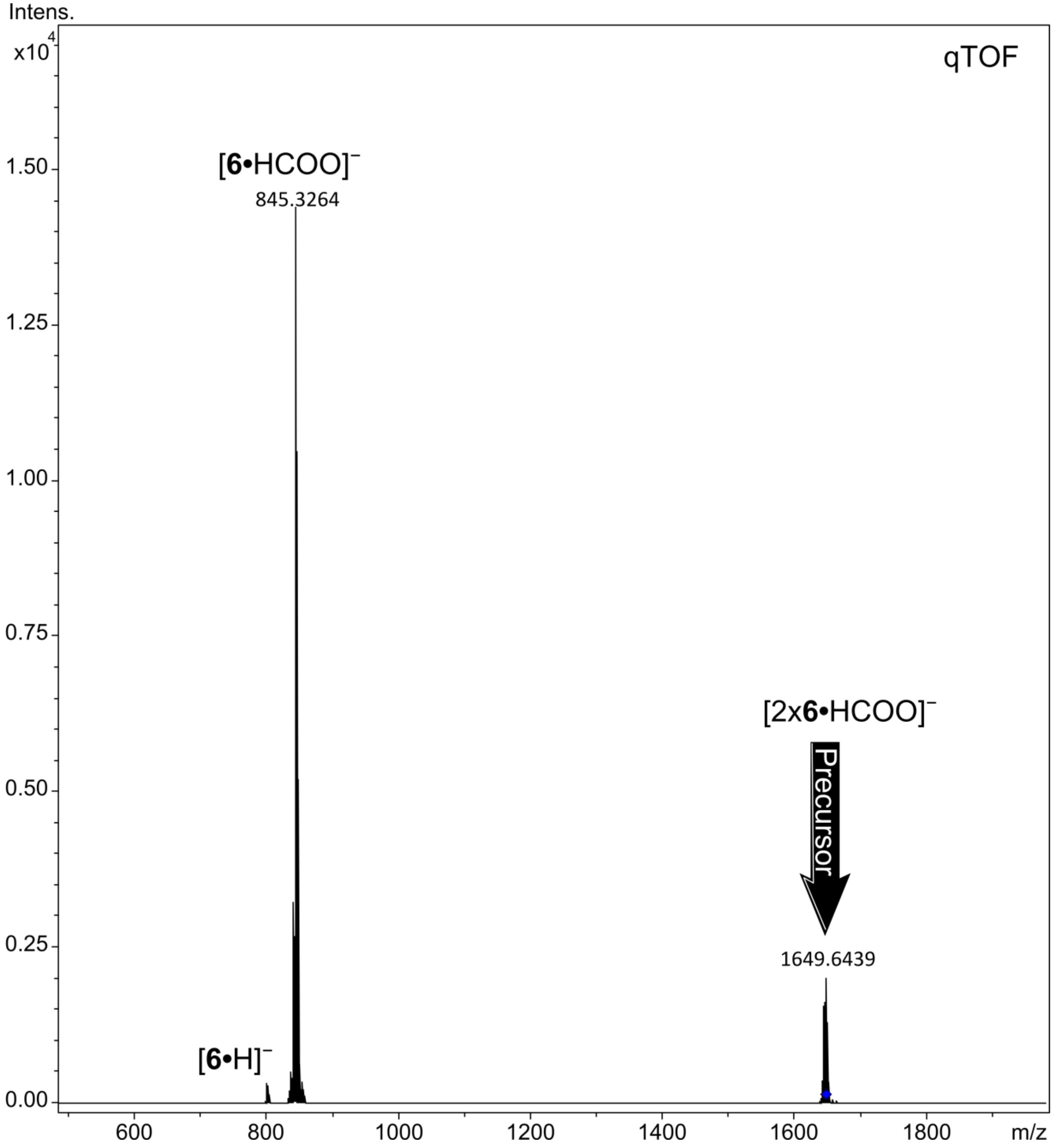


Figure S9 CID (MS²) of the formate bridged dimer [2x**6**•HCOO]⁻, depicting its fragmentation pathway by loss of a Pc moiety. The subsequent dissociation of the monomer [**6**•HCOO]⁻ into [**6**•H]⁻ can also be observed.

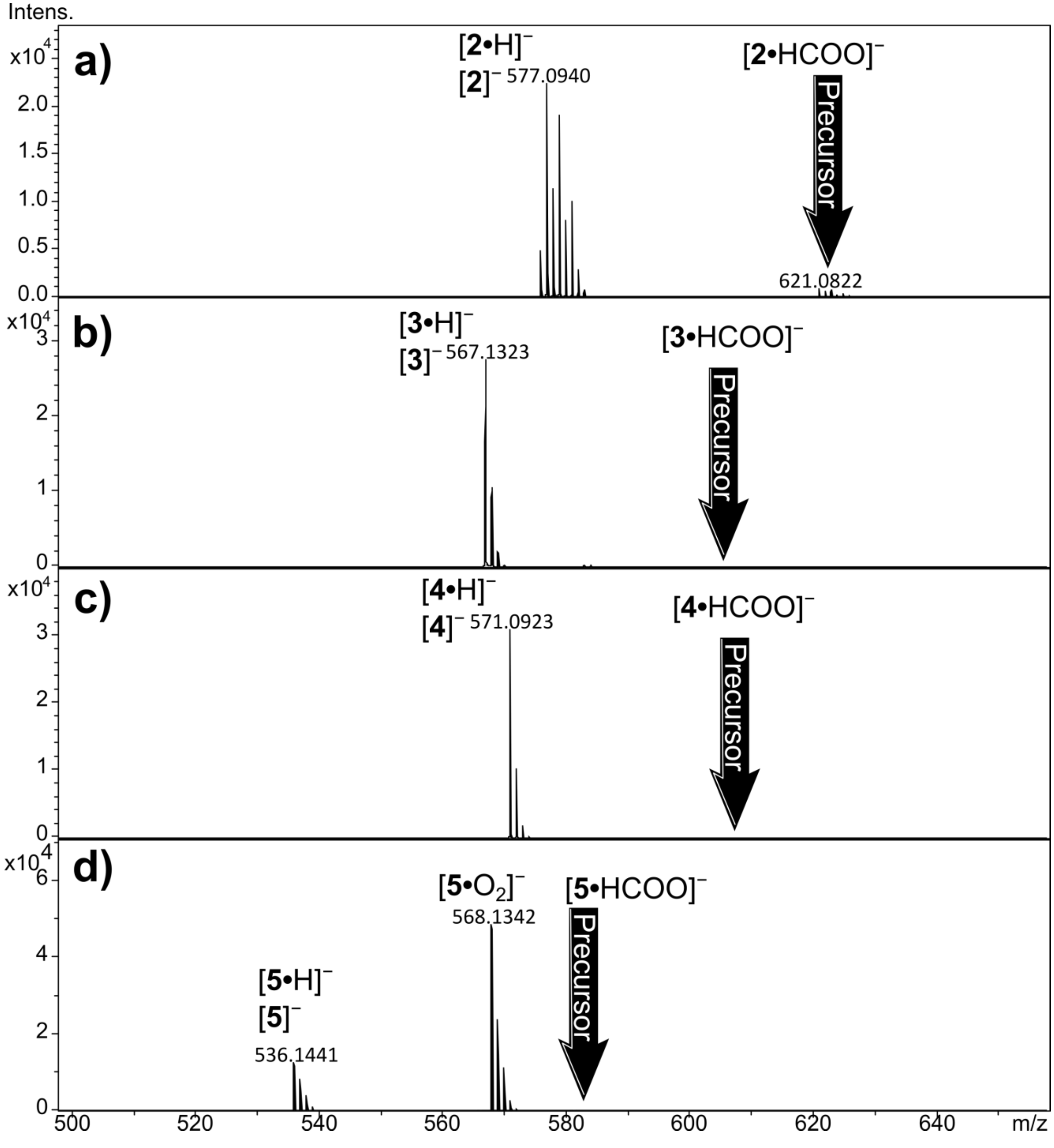


Figure S10 Negative-ion ESI qTOF mass spectra of a) Zn(II)Pc **2**, b) Mn(II)Pc **3**, c) Co(II)Pc **4** and d) Mg(II)Pc **5** with sodium formate in DMF. The adducts dissociate via loss of CO_2The hydride containing fragment undergoes charge transfer and loss of a neutral hydrogen atom. Only the Mg-phthalocyanine shows an additional signal [**5**•O_2]$^-$, the origin of which has not been examined here.

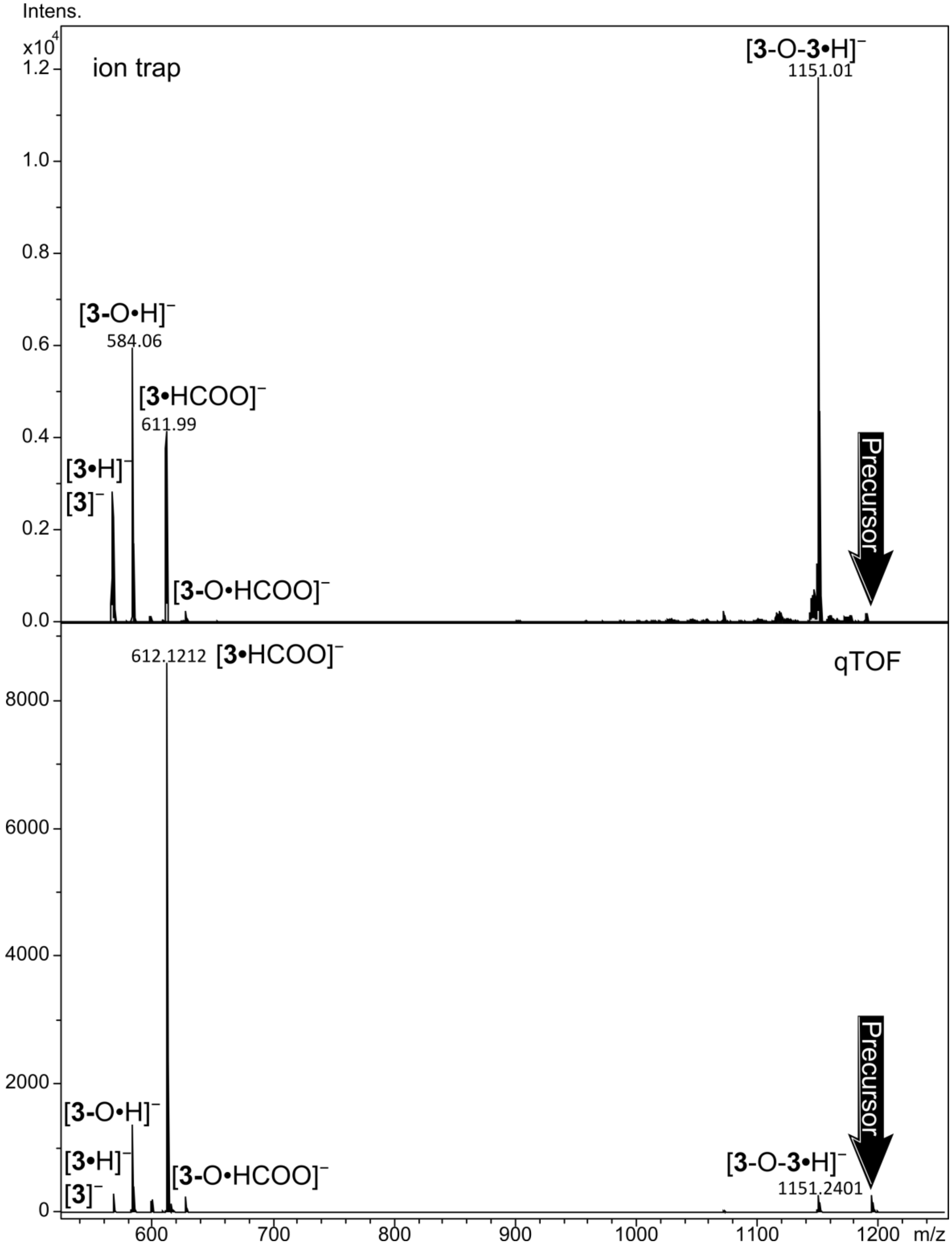


Figure S11 CID (MS²) of the oxygen-bridged dimer [**3**•O•**3**•HCOO]⁻, depicting its fragmentation studied with the ion trap and the qTOF instrument. With the ESI ion trap (Esquire), the major dissociation channel is the loss of CO_2, accompanied/ followed by the dissociation into monomeric species. Whereas with the ESI qTOF (MicrOTOF-Q II), the major fragment is [**3**•HCOO]⁻.

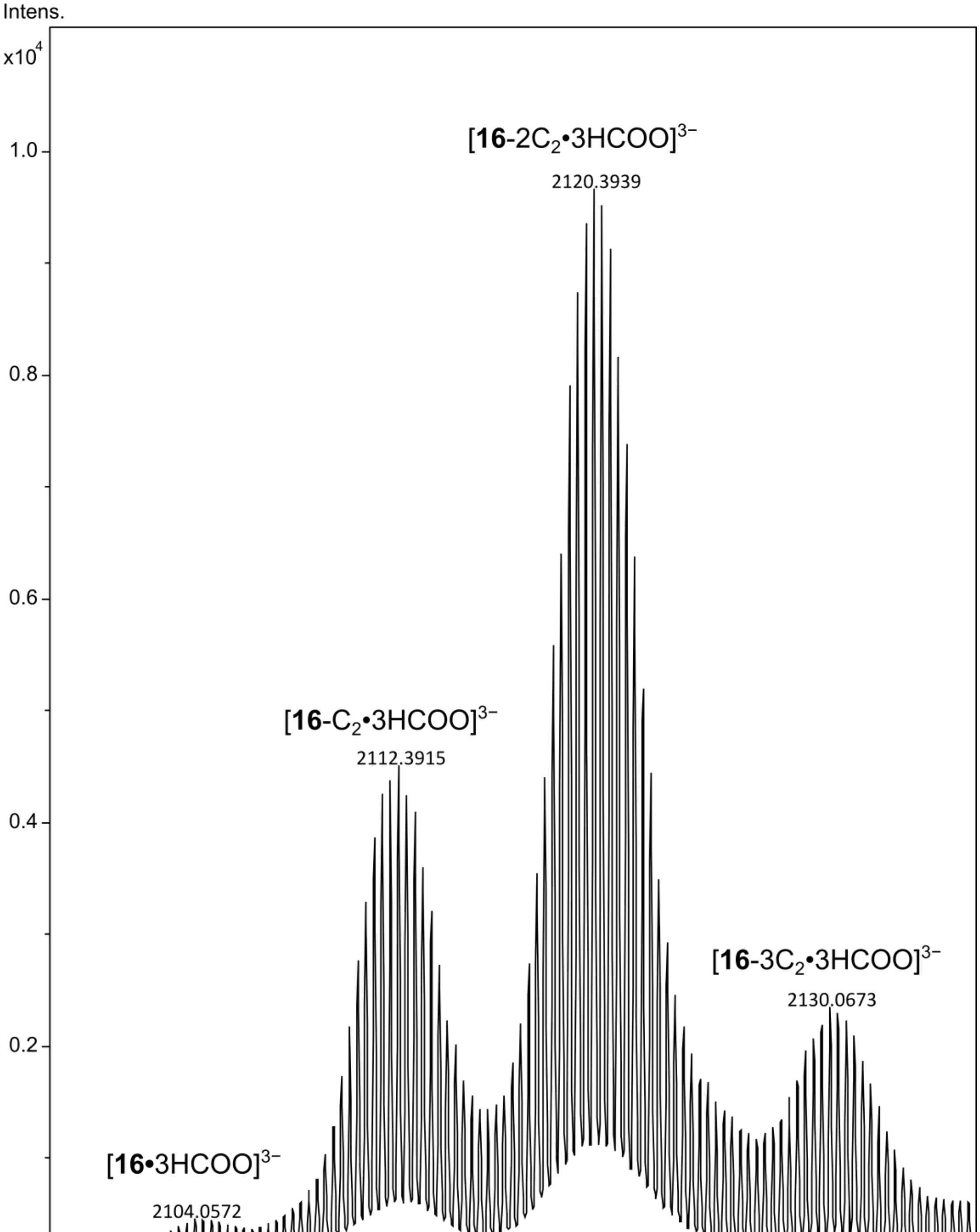
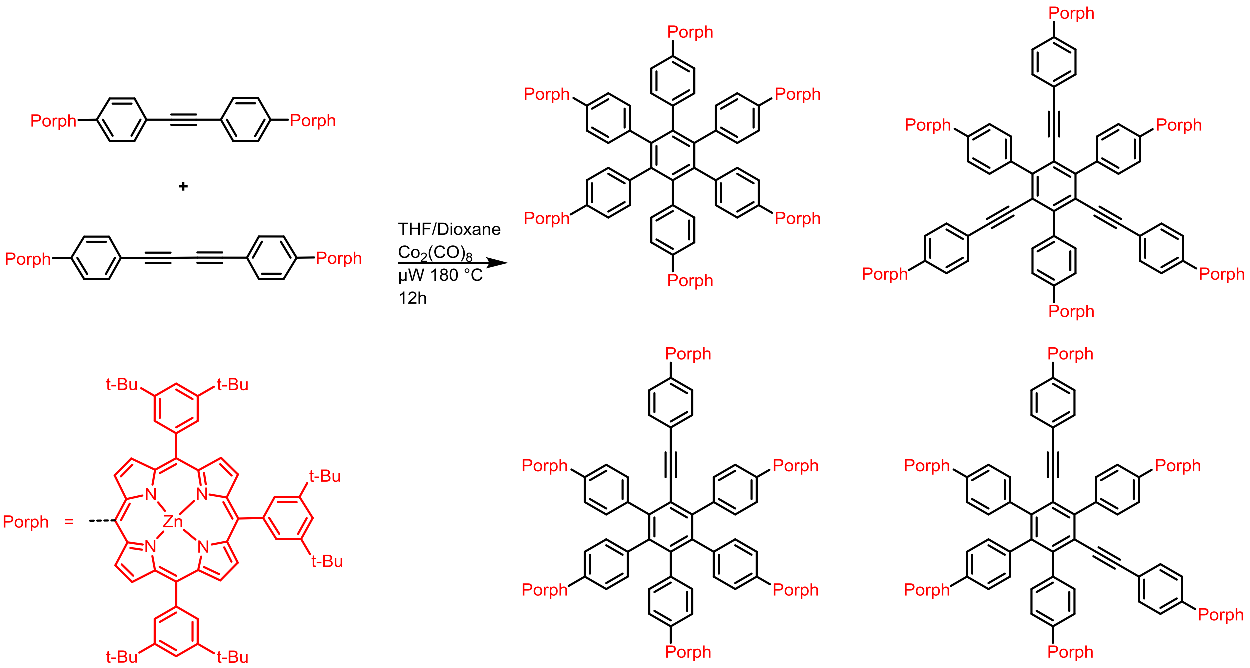
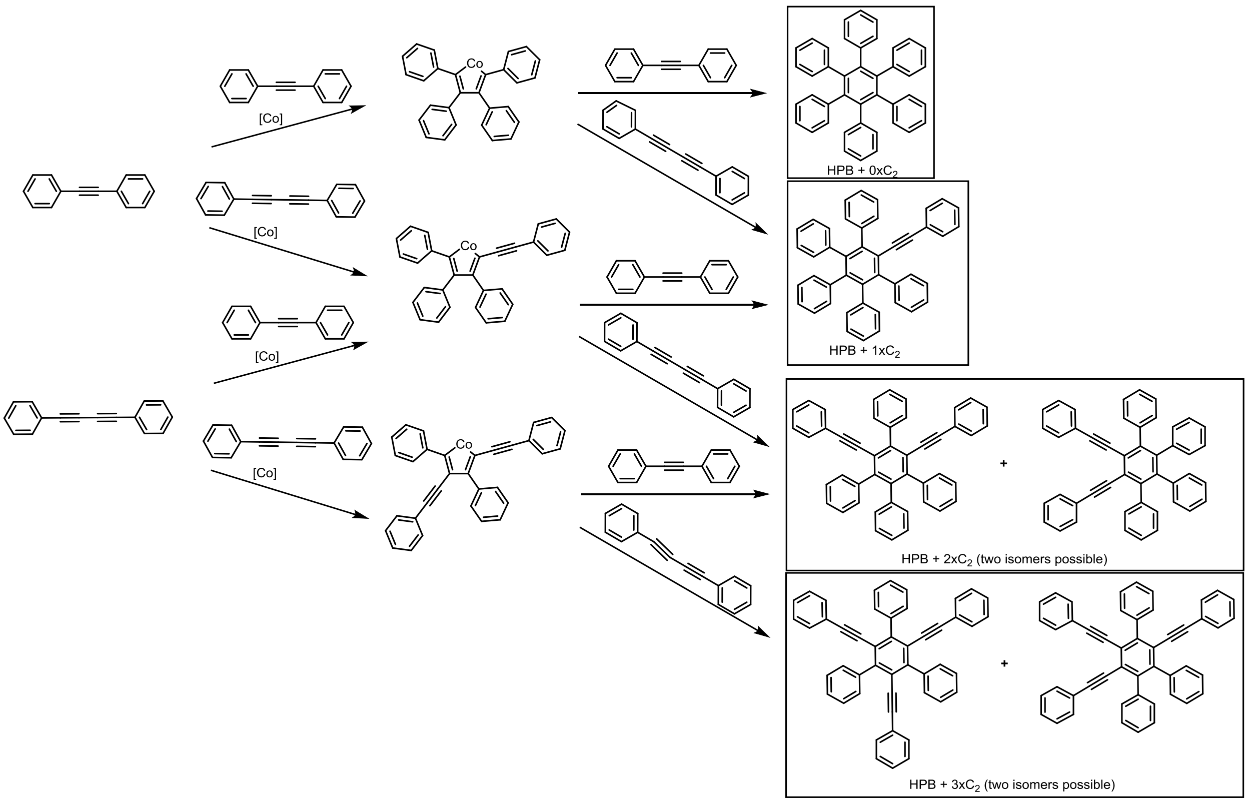


Figure S 12 Negative-ion ESI qTOF mass spectrum enlargement of [**16**-nC_2•3xHCOO]$^{3-}$ with n= 0-3. Formate addition allows the identification of the four different molecules: **16** and three accompanying reaction products, **16**-C_2, **16**-2C_2 and **16**-3C_2.

Scheme S13:



An equimolar mixture of acetylene-spaced and butadiyne-spaced bis-Por was dissolved in a THF/1,4-dioxane mixture. 0.9 equiv. of $Co_2(CO)_8$ were added, the mixture was degassed with argon and heated in a mono-mode microwave reactor (Biotage Initiator$^+$) for 12 h to 180 °C. The crude mixture was purified over a short silica plug using CH_2Cl_2. The purified reaction mixture was then used for the MS experiments.



Pathways to the four different products (a product corresponds here to all molecules with the same mass). Each reactant can react with itself or with the corresponding partner.

The Co-mediated [2+2+2] cycloaddition of a diphenylacetylene leads to hexaphenylbenzene. If a diphenylbutadiyne is used, three acetylene units will remain as spacers. If the reaction mixture contains both, acetylene- and butadiyne-spaced biphenyl, a statistical mixture of all possible isomers will result.

Instrumentation

ESI experiments were conducted with two different ESI-mass spectrometers.

The first instrument was an ESI-quadrupole time-of-flight (qToF) mass spectrometer (micrOTOF-Q II, Bruker, Bremen, Germany). The following settings were applied. Flow rate of the sample solution by syringe pump infusion 3.0 mL min^{-1}, nebuliser nitrogen pressure 400 hPa, capillary entrance voltage 3.5 kV, spray shield voltage 3 kV, nitrogen dry gas temperature 453 K, dry gas flow rate 4.0 L/min. Energy-resolved collision-induced dissociations (MS^2, CID) were conducted in a collision cell following a mass selecting quadrupole and preceding the high resolution daughter ion analysis in the TOF analyser. Nitrogen (N_2) served as the collision gas.

The second instrument was an ESI-quadrupole ion trap instrument (esquire6000, Bruker, Bremen, Germany). The following settings were applied: Flow rate of the sample solution by syringe pump infusion 4.0 µL/min, nebuliser nitrogen pressure 689 hPa, capillary entrance voltage 4 kV, spray shield voltage 3.5 kV, nitrogen dry gas temperature 573 K, dry gas flow rate 5.0 L/min, the helium buffer/collision gas pressure was set to 4.0×10^{-6} hPa. The CID experiments (MS^n) were performed in the quadrupole ion trap with helium serving as the collision gas. Generally, the ion transfer settings vary due to spectra tuning.