

## Supporting Information

### **Stability of Odd- Versus Even-Electron Gas-Phase (Quasi)Molecular Ions Derived from Pyridine-Substituted N-Heterotriangulenes**

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**Supporting Information for:**

**Stability of odd versus even electron gas-phase**

**(quasi)molecular ions derived from pyridine-substituted**

**N-heterotriangulenes**

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## Table of Contents

1	Experimental Settings .....	3
2	Mass Spectra .....	4
3	Computational Details.....	6
3.1	<i>Aromaticity</i> .....	7
3.2	<i>First Methyl Loss From [NTGPy<sub>2</sub>+H]<sup>+</sup> and [NTGPy<sub>3</sub>+H]<sup>+</sup></i> .....	8
4	Conversion of E <sub>lab</sub> Into E <sub>com</sub> (QqToF) .....	9
5	Extraction of the E <sub>CoM</sub> (50%) Values (QqToF) : .....	9
6	Extraction of the E <sub>CoM</sub> (50%) Values for the Mixture of [NTGPy] <sup>•+</sup> and [NTGPy+H] <sup>+</sup> (QqToF) ...	11
7	Extraction of the E <sub>onset</sub> Values From the Mixture of [NTGPy] <sup>•+</sup> and [NTGPy+H] <sup>+</sup> (Ion Trap) ...	12
8	Calculations of the [M] <sup>•+</sup> and [M+H] <sup>+</sup> Ratios .....	13
9	References .....	14

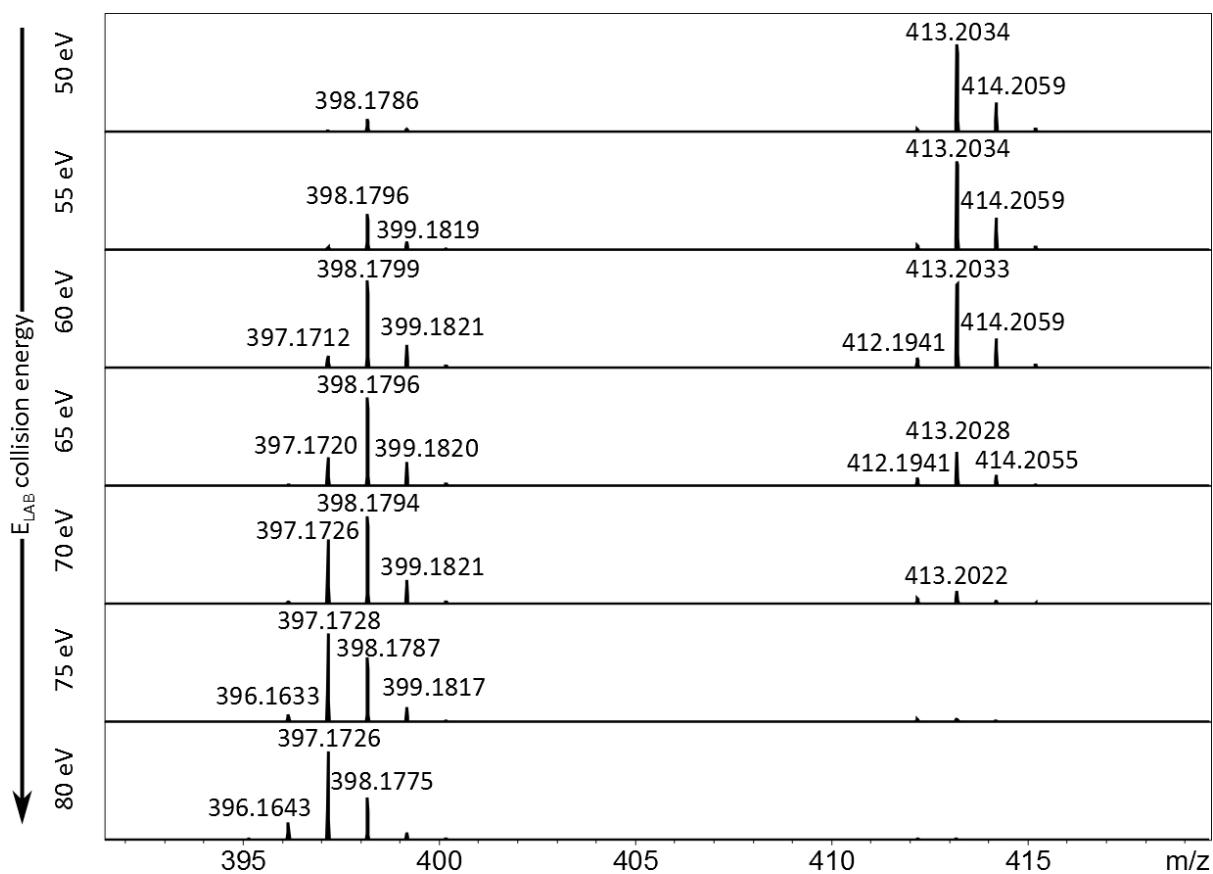
## 1 Experimental Settings

The ESI experiments were conducted with two different ESI-mass spectrometers:

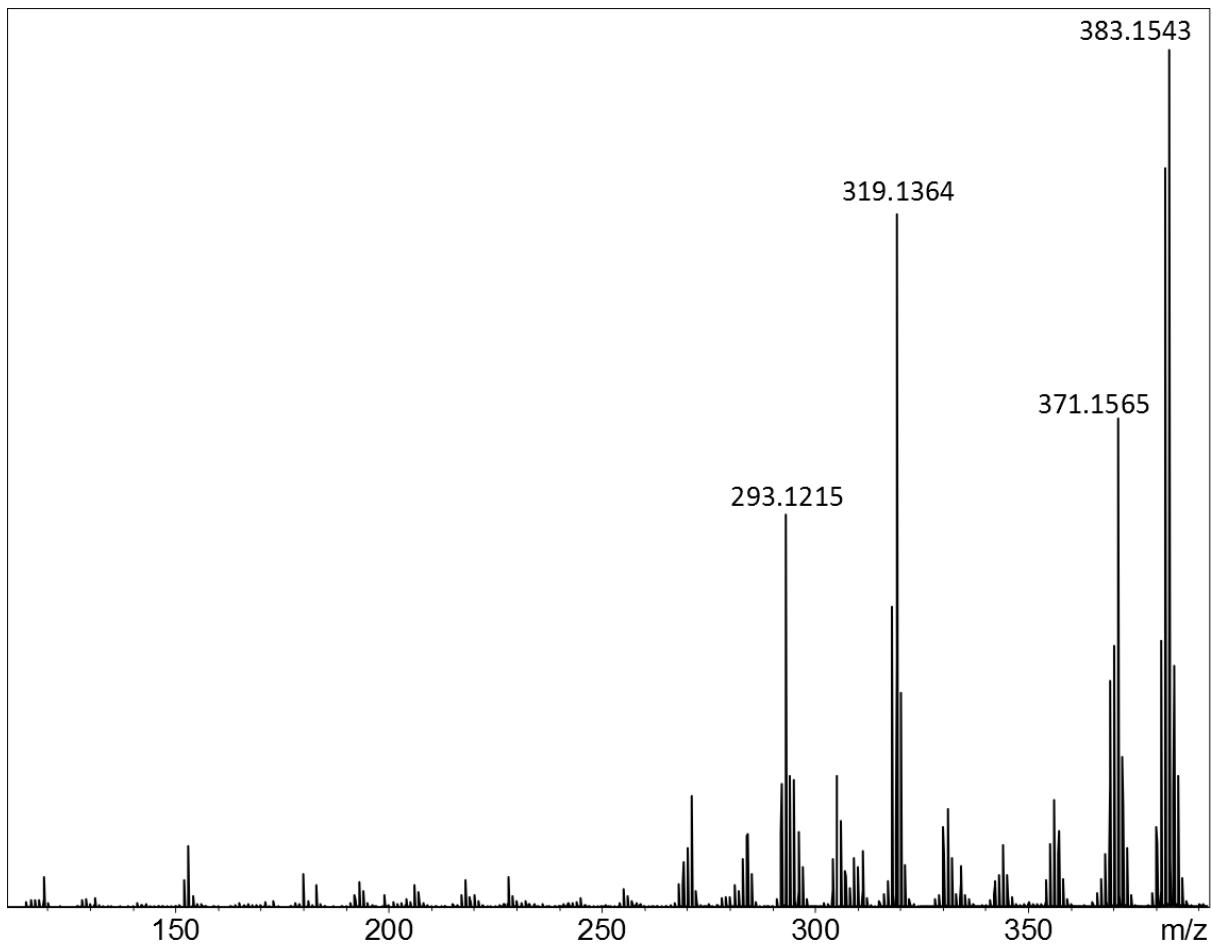
The first instrument was an ESI-quadrupole time-of-flight (QqToF) mass spectrometer (micrOTOF-Q II, Bruker, Bremen, Germany). The following settings were applied. Flow rate of the sample solution by syringe pump infusion 3.0 mL/min, nebuliser nitrogen pressure 400 hPa, capillary entrance voltage 3.5 kV, spray shield voltage 3 kV, nitrogen dry gas temperature 453 K, dry gas flow rate 4.0 L/min.

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  $\mu$ L/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  $4.0 \times 10^{-6}$  hPa.

## 2 Mass Spectra



**Figure S1:** CID mass spectra of NTGPy with the collision energy  $E_{\text{lab}}$  ranging from 50 - 80 eV, depicting the dissociation of hydrogens after dissociation of three  $\cdot\text{CH}_3$ -radicals.



**Figure S2:** CID mass spectrum of  $[\text{NTGPy}]^+$  at a collision energy of 100 eV resulting in rupture of the *N*-heterotriangulene core.

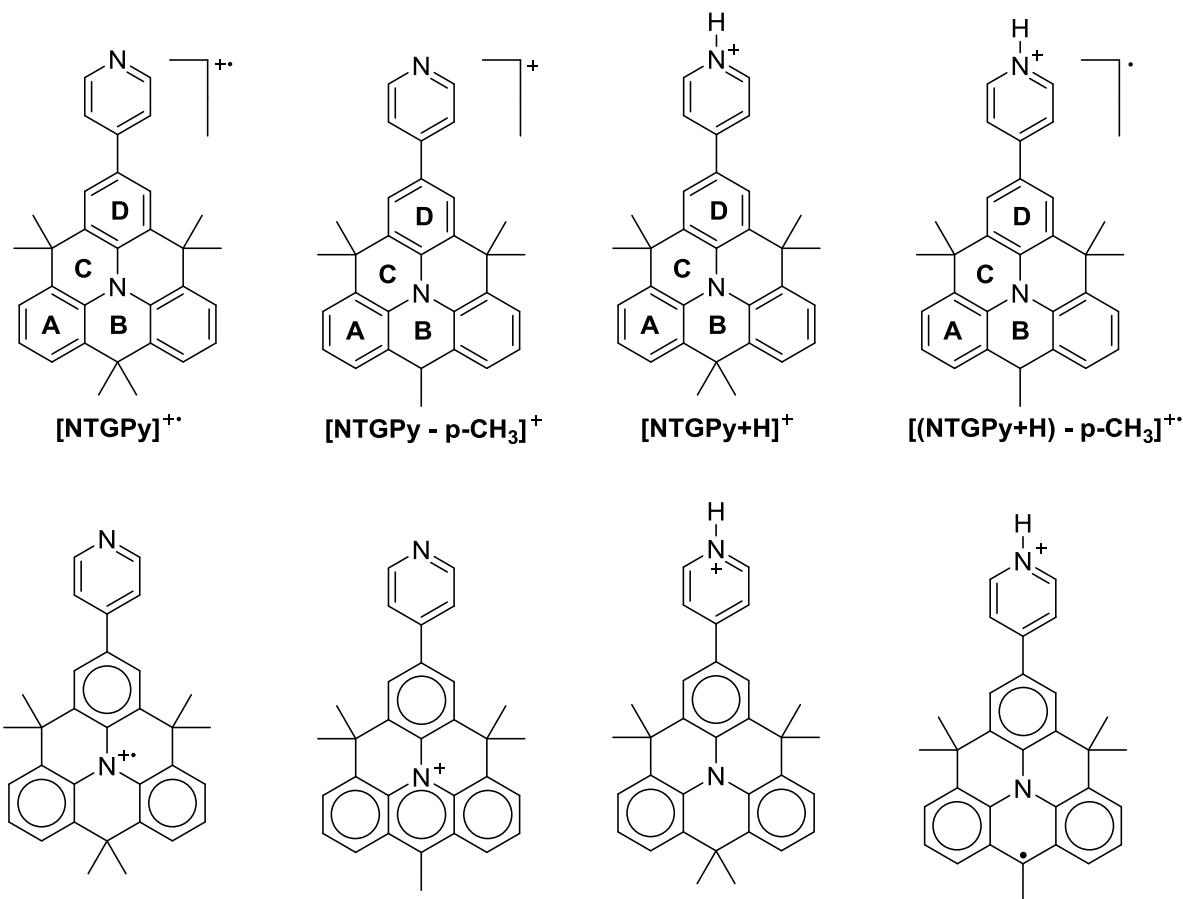
### 3 Computational Details

All calculations were performed with the Gaussian 09 program suite.<sup>1</sup> Geometry optimizations, normal vibrational modes within the harmonic approximation calculated to characterize minima, and zero-point energy (ZPE) corrections were calculated at the  $\omega$ B97XD<sup>2</sup>/6-31G(d)<sup>3-14</sup> level of theory. Additional single point calculations were performed with MP2<sup>15</sup>/cc-pVDZ<sup>16-20</sup> on the geometries optimized at  $\omega$ B97XD/6-31G(d). All MP2 and DFT energies reported in the main text include ZPEs.

Cartesian coordinates of all calculated species at the  $\omega$ B97XD/6-31G(d) levels of theory and archives of Gaussian 09 calculations at both  $\omega$ B97XD/6-31G(d) and MP2/cc-pVDZ are provided in an accompanying directory *SI\_Stability\_N-Heterotriangulenes\_Calculations*, which is provided as a .zip file.

Calculations for open-shell species were performed using unrestricted Kohn–Sham approach to DFT (U $\omega$ B97XD/6-31G(d)) and restricted open-shell MP2 (ROMP2/cc-pVDZ). Using unrestricted MP2 leads to too large errors caused by significant spin contamination and thus ROMP2<sup>21-23</sup> is used in this study. On the other hand, unrestricted DFT is known to provide fairly accurate energetics on its own as it suffers much less from spin contamination than single-determinantal *ab initio* methods.<sup>24</sup> Single-point ROMP2 calculations on the U $\omega$ B97XD/6-31G(d)-optimized geometries should further reduce the remaining error arising from spin contamination at U $\omega$ B97XD/6-31G(d), whose expectation values of the total spin  $\langle S^2 \rangle$  are given for all investigated species in the archives of the Gaussian 09 calculations.

### 3.1 Aromaticity

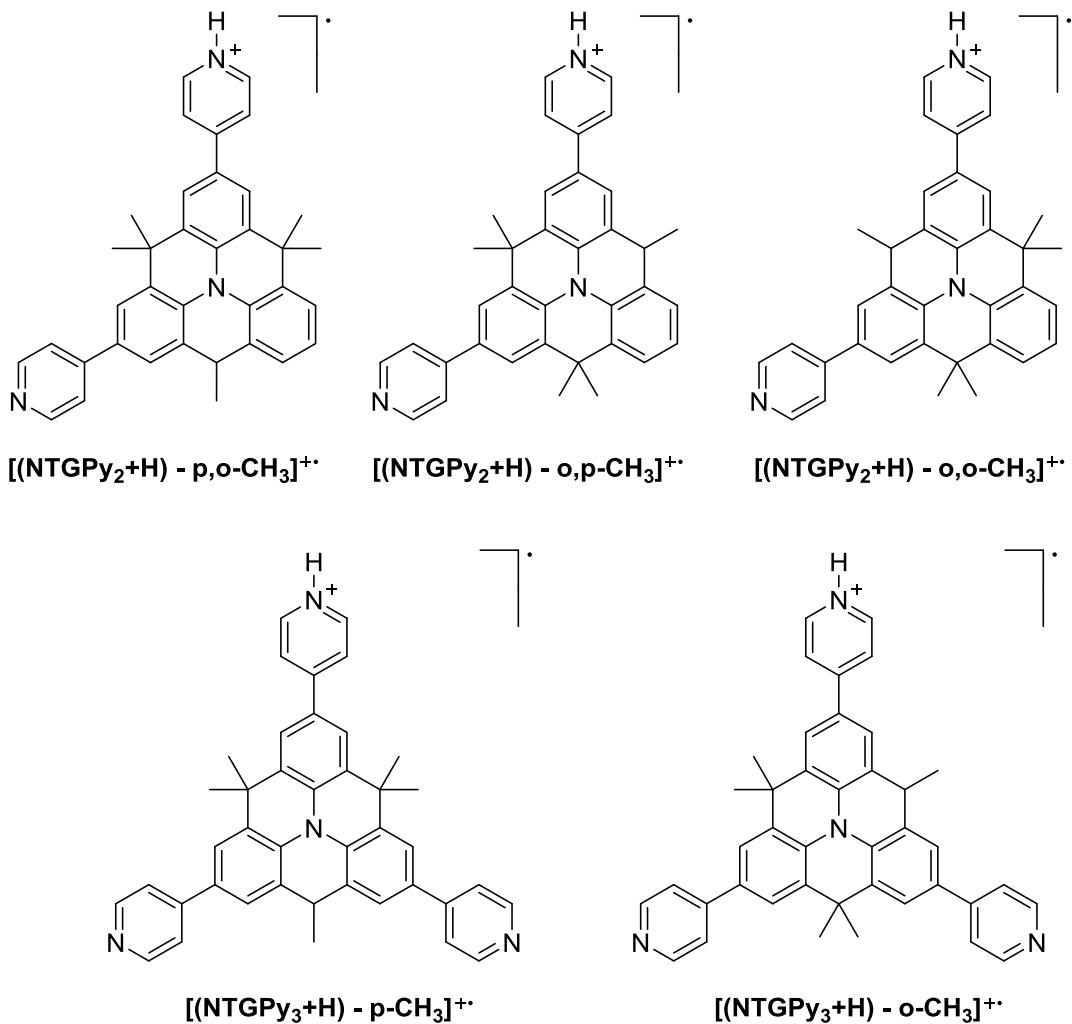


**Figure S3.** Numbering of rings of  $[NTGPy]^{+ \bullet}$ ,  $[NTGPy - p\text{-}CH_3]^{+ \bullet}$ ,  $[NTGPy+H]^{+ \bullet}$ , and  $[(NTGPy+H) - p\text{-}CH_3]^{+ \bullet}$ . Alternative representation of the *N*-heterotriangulene cores using Clar's sextets<sup>25-27</sup>.

**Table S1.** Nuclear independent chemical shifts<sup>28-30</sup> values at the centers of rings **A–D** of  $[NTGPy]^{+ \bullet}$ ,  $[NTGPy - p\text{-}CH_3]^{+ \bullet}$ ,  $[NTGPy+H]^{+ \bullet}$ , and  $[(NTGPy+H) - p\text{-}CH_3]^{+ \bullet}$  calculated with the self-consistent field–gauge-independent atomic orbital<sup>31-36</sup> method at the B3LYP<sup>37-39</sup>/6-311++G(d,p)<sup>6-14, 40-42</sup> level of theory on the  $\omega$ B97XD/6-31G(d)-optimized geometries.

Species	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
$[NTGPy]^{+ \bullet}$	-6.6	3.5	3.5	-5.7
$[NTGPy - p\text{-}CH_3]^{+ \bullet}$	-8.1	-6.5	5.5	-6.6
$[NTGPy+H]^{+ \bullet}$	-7.6	3.4	4.0	-4.2
$[(NTGPy+H) - p\text{-}CH_3]^{+ \bullet}$	-6.4	0.3	4.8	-4.6

### 3.2 First Methyl Loss From $[NTGPy_2+H]^+$ and $[NTGPy_3+H]^+$



**Figure S4.** First methyl loss products from  $[NTGPy_2+H]^+$  and  $[NTGPy_3+H]^+$ .

**Table S2.** Energies of first methyl loss from  $[NTGPy_2+H]^+$  and  $[NTGPy_3+H]^+$  (and for comparison from  $[NTGPy+H]^+$ ) in eV at the ROMP2/cc-pVDZ level of theory on the  $\omega$ B97XD/6-31G(d)-optimized geometries. Energies include ZPEs calculated at  $\omega$ B97XD/6-31G(d).

Species	Fragmentation products	Dissociation energy
$[NTGPy+H]^+$	$[(NTGPy+H) - p\text{-}CH_3]^{+\cdot}$	2.78
	$[(NTGPy+H) - o\text{-}CH_3]^{+\cdot}$	2.68
$[NTGPy_2+H]^+$	$[(NTGPy_2+H) - p,o\text{-}CH_3]^{+\cdot \cdot}$	2.77
	$[(NTGPy_2+H) - o,p\text{-}CH_3]^{+\cdot \cdot}$	2.68
	$[(NTGPy_2+H) - o,o\text{-}CH_3]^{+\cdot \cdot}$	2.67
$[NTGPy_3+H]^+$	$[(NTGPy_3+H) - p\text{-}CH_3]^{+\cdot}$	2.80
	$[(NTGPy_3+H) - o\text{-}CH_3]^{+\cdot}$	2.71

#### 4 Conversion of E<sub>lab</sub> Into E<sub>com</sub> (QqToF)

The four *N*-heterotriangulenes (NTG and NTGPy<sub>n</sub>, with n = 1–3) were isolated and fragmented in collisions with N<sub>2</sub> at different laboratory collision energies (E<sub>lab</sub>) that ranged from 0 to 80 eV. The laboratory collision energy is converted to the total energy available for dissociation, called center-of-mass collision energy (E<sub>CoM</sub>), by the following relationship

$$E_{CoM} = (m_n * E_{lab}) / (m_i + m_n)$$

where m<sub>n</sub> represents the molecular mass of the neutral collision gas N<sub>2</sub> and m<sub>i</sub> the molecular mass of the investigated ion.

#### 5 Extraction of the E<sub>CoM(50%)</sub> Values (QqToF)

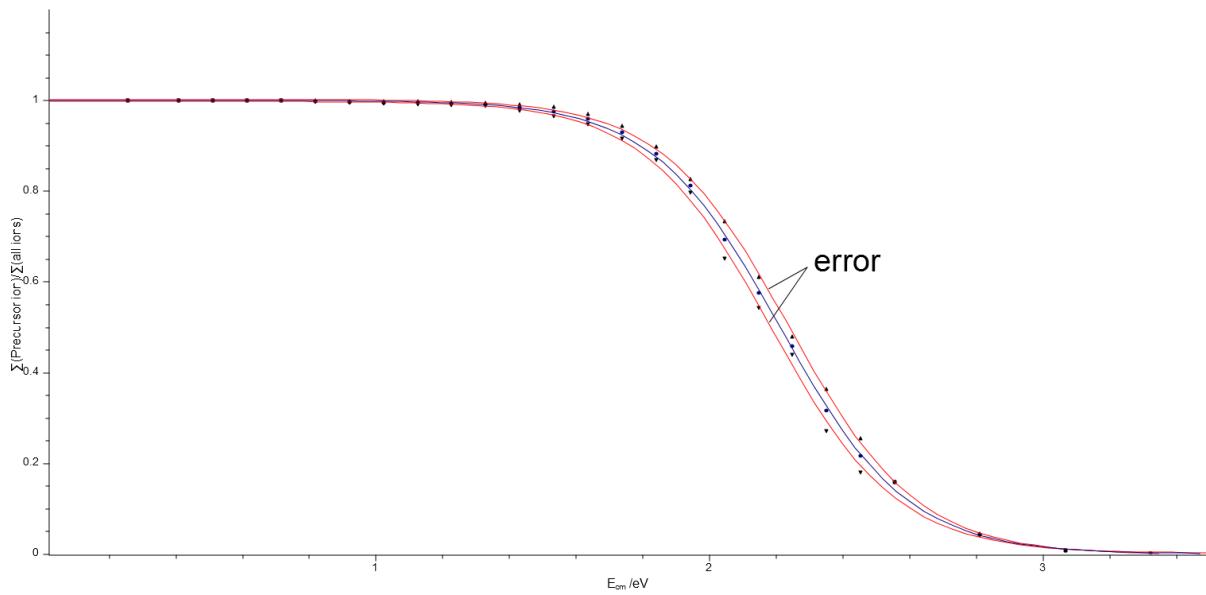
The results of the energy-dependent dissociation experiments were fitted by the sigmoidal Boltzmann equation:

$$y = (A_2 - A_1) \left[ 1 + \exp\left(\frac{x - x_0}{dx}\right) \right]$$

The x<sub>0</sub> value, the inflection point, is equal to the E<sub>CoM(50%)</sub> value. The error of E<sub>CoM(50%)</sub> can be estimated by fitting the maximal and minimal error-curve as shown in Figure S4.

**Table S2:** E<sub>CoM(50%)</sub> with errors for the dissociation of the precursors

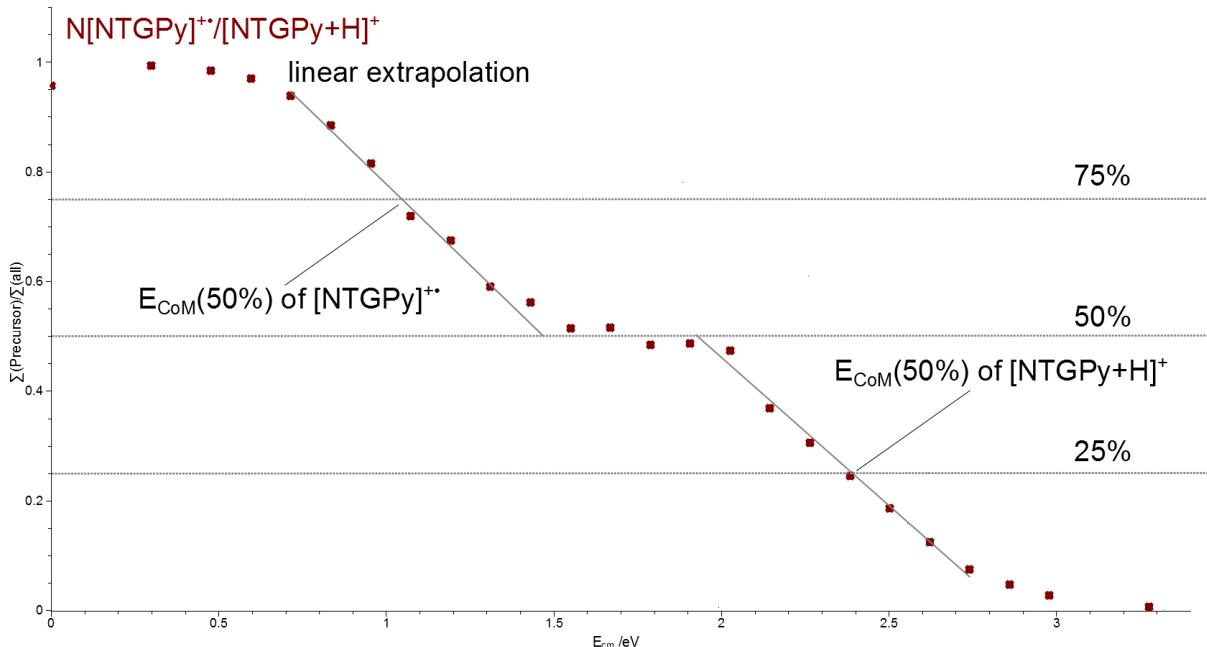
Precursor	E <sub>CoM(50%)</sub>
[NTG] <sup>+</sup>	1.076 ± 0.012
[NTGPy] <sup>++</sup>	2.365 ± 0.001
[NTGPy <sub>2</sub> +H] <sup>+</sup>	2.210 ± 0.055
[NTGPy <sub>3</sub> +H] <sup>+</sup>	2.133 ± 0.001



**Figure S5:** Error estimation of the sigmoidal Boltzmann fit of the dissociation of the precursor  $[\text{NTGPy}_2\text{H}]^+$  using the QqToF mass spectrometer (x-axis:  $E_{\text{CoM}}$  and y-axis: ratio of precursor ion intensity to sum of intensities of all signals).

## 6 Extraction of the $E_{CoM}(50\%)$ Values for the Mixture of $[NTGPy]^{+ \bullet}$ and $[NTGPy+H]^+$ (QqToF)

In this case, a Boltzmann fit is not possible. Instead, the graph was fitted by a multipeak-fit.



**Figure S6:** Energy-dependent dissociation behaviour of the precursor ions of  $[NTGPy]^{+ \bullet}$  and  $[NTGPy+H]^+$  using the QqToF mass spectrometer (x-axis:  $E_{CoM}$  and y-axis: ratio of precursor ion intensity to sum of intensities of all signals). The respective  $E_{CoM}(50\%)$  values are marked.

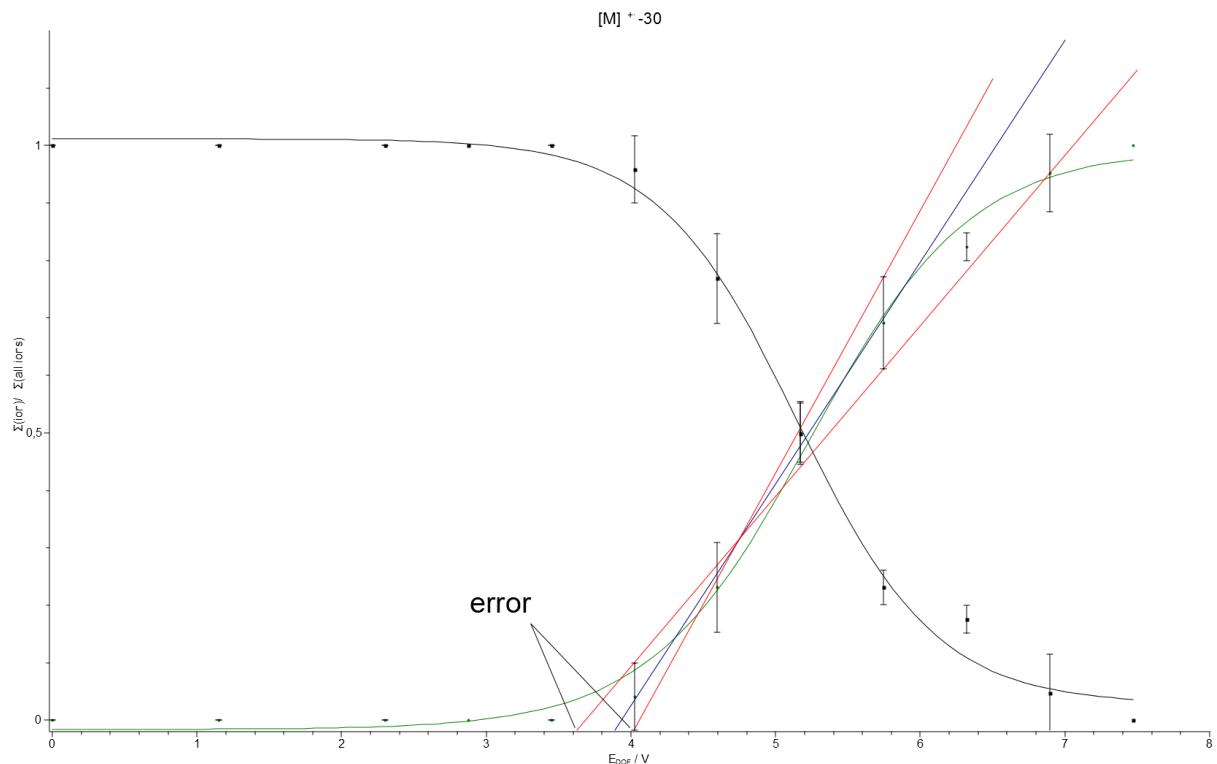
The  $E_{CoM}(50\%)$  values were calculated by linear extrapolation of the respective slope. The ratio of the radical cation and protonated species was 1:1. Therefore, as shown in Figure S6 above, the  $E_{CoM}(50\%)$  value of the radical cation, characterizing 50% of the dissociation of the radical cation was obtained at 75% of the total dissociation of the bimodal curve. The  $E_{CoM}(50\%)$  value of the protonated species was accordingly obtained at 25% of the total dissociation.

## 7 Extraction of the $E_{\text{onset}}$ Values From the Mixture of $[\text{NTGPy}]^{+ \bullet}$ and $[\text{NTGPy}+\text{H}]^+$ (Ion Trap)

The  $E_{\text{Onset}}$  values were calculated by linear extrapolation of the respective slope. The error can be estimated by linear extrapolation of the slopes with the maximal and minimal x-axis intersection within the error bars.

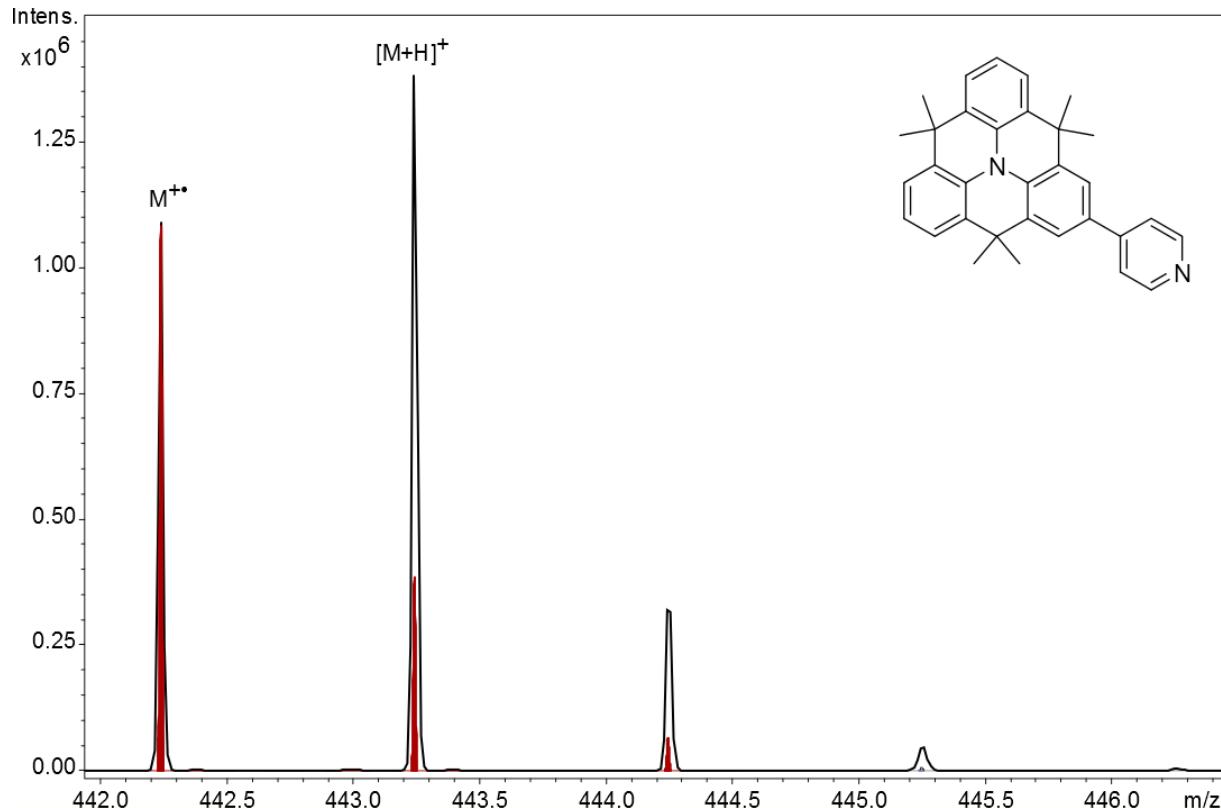
**Table S3:**  $E_{\text{onset}}$  values of the mixture of  $[\text{NTGPy}]^{+ \bullet}$  and  $[\text{NTGPy}+\text{H}]^+$

Precursor	$E_{\text{Onset}} / 10^{-3}\text{V}$
$[\text{NTGPy}]^{+ \bullet}$	$1.96 \pm 0.12$
$[\text{NTGPy}-15]^{+ \bullet}$	$3.87 \pm 0.19$
$[\text{NTGPy}-30]^{+ \bullet}$	$4.12 \pm 0.51$
$[\text{NTGPy}+\text{H}]^+$	$4.12 \pm 0.07$
$[\text{NTGPy}+\text{H}-15]^+$	$4.86 \pm 0.24$
$[\text{NTGPy}+\text{H}-30]^+$	$5.29 \pm 0.45$



**Figure S7:** Error of the linear extrapolation of  $[\text{NTGPy}-15]^{+ \bullet}$  using the ion trap mass spectrometer (x-axis:  $E_{\text{DOF}}$  and y-axis: ratio of precursor ion intensity to sum of intensities of all signals).

## 8 Calculations of the $[M]^{+\bullet}$ and $[M+H]^+$ Ratios



**Figure S 8:** Measured spectrum (black) of  $[NTGPy]^{+\bullet}$  and  $[NTGPy+H]^+$  and simulated spectrum (red) of  $[NTGPy]^{+\bullet\bullet}$

The overlap of the isotope patterns of the radical cation and protonated species was taken into account. Their ratios, shown in Figure 1, have been obtained in the following way. The isotope peak with the lowest mass of  $[M]^{+\bullet}$  does not overlap with  $[M+H]^+$  and therefore was used to calculate the intensity of the second ( $^{13}\text{C}_1$ ), third ( $^{13}\text{C}_2$ ) and fourth ( $^{13}\text{C}_3$ ) isotope peak of  $[M]^{+\bullet}$ , using a standard program for the calculation of isotope patterns. For the total intensity of  $[M]^{+\bullet}$ , these intensities were added to the intensity of the first isotope peak. The total intensity of  $[M+H]^+$  was calculated by addition of the intensities of all  $[M+H]^+$ -containing peaks and subtraction of the calculated intensities of the second, third and fourth isotope peak of  $[M]^{+\bullet}$ . From Figure 2, it is evident that  $[M+H]^+$  ions do not undergo the loss of one H-atom, so that the low mass isotope peak of  $[M]^{+\bullet}$  cannot be obscured by such a reaction.

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