

Electronic Supplementary Information to IR spectra of cationic 1,5,9-triazacoronene and two of its cationic derivatives

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This Electronic Supplementary Information contains further information to the main manuscript. First, we present a zoom-in of the experimental and simulated IR spectra of **TACH**⁺ between 820 and 1260 cm⁻¹. Next, we show the different energies of three possible isomers formed after losing a hydrogen atom from **TAC**⁺ from different positions. Then, we present the calculated IR spectra of the 16 [**TAC-H+H₂O**]⁺ isomers that we considered as potential products ions. Lastly, we show the coordinates of **TAC**⁺ and **TACH**⁺ used to calculate the IR spectra.

Experimental and simulated mid-IR spectra of TACH^+ in the $800 - 1300 \text{ cm}^{-1}$ range

Here we present a zoomed-in version of the experimental and simulated IR spectra of TACH^+ reported in the main manuscript (see Fig. S1). Most notably, the TACH^+ IRMPD spectrum displays no clear features between 820 and 1260 cm^{-1} , while modes are predicted to fall in this range.

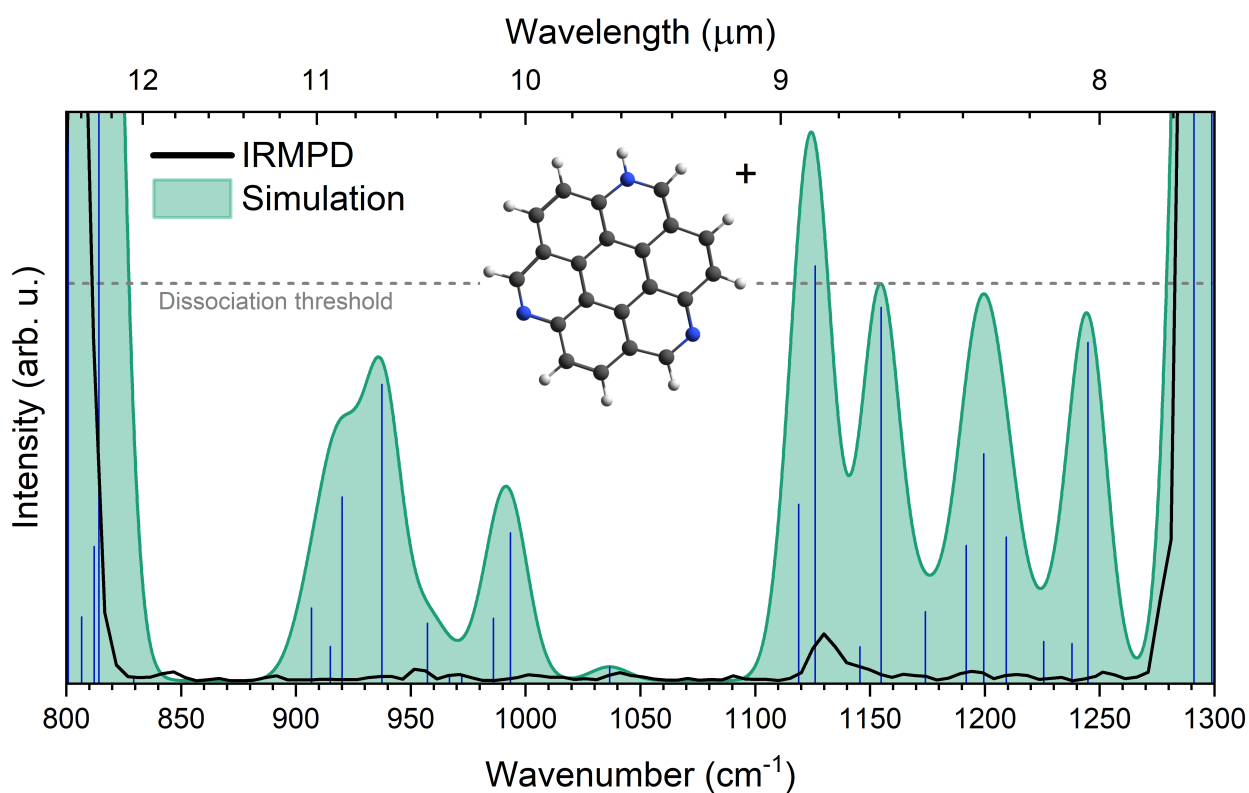


Figure S1: Experimental IRMPD (black) and simulated IR (blue vertical lines) spectra of TACH^+ . The B3LYP/6-311++G(d,p) computed spectrum (blue sticks) is uniformly scaled with a factor of 0.9679 and convolved with a 20 cm^{-1} FWHM Gaussian function (green shaded area). The horizontal grey, dotted line indicates an apparent cut-off. Exciting modes with a lower intensity than this line does not lift the energy of the molecule over the dissociation threshold.

Energies of $[\text{TAC}-\text{H}]^+$ isomers

Here we present the energies of three isomers that can form upon losing a hydrogen atom from three distinctly different positions in $\text{TAC}^{\bullet+}$ (see Fig. S2). The isomer resulting from the loss of a hydrogen from the CH group adjacent to a nitrogen atom is found to be lowest in energy, according to our calculations at a B3LYP/6-311++G(d,p) level of theory.

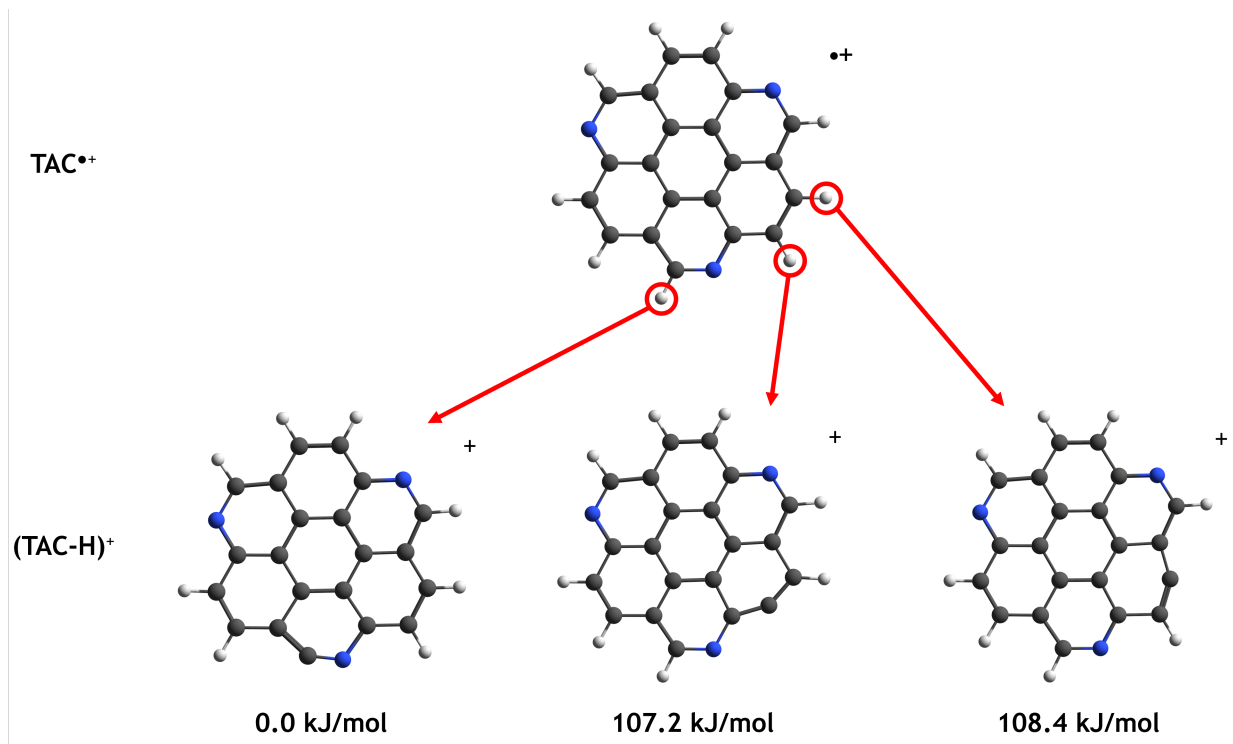


Figure S2: Geometries and relative energies of three different $[\text{TAC}-\text{H}]^+$ isomers calculated at B3LYP/6-311++G(d,p) level of theory. The circled hydrogen atoms on $\text{TAC}^{\bullet+}$ depict the hydrogen that is removed and the arrows point toward the resulting isomer. The energies are depicted with respect to the lowest energetic isomer of $[\text{TAC}-\text{H}]^+$.

Calculated spectra of all considered $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$ isomers

Here we present the calculated mid-IR spectra of the 16 isomers that we considered as $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$ products (see Fig. S3). We propose that isomer **5** is the most likely candidate for $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$, since it is the lowest in energy and its simulated spectrum matches well with the IRMPD spectrum of the $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$ product ion. Other isomers such as **15** and **16** also provide a good match with the IRMPD spectrum, however, their energies are rather high with respect to isomer **5** and these isomers lack a feature at 1718 cm^{-1} . Therefore, we conclude that these are not the most likely candidate for $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$. This does not necessarily mean that isomer **5** is the only contributor to the IRMPD and the other isomers may contribute to the experimental spectrum.

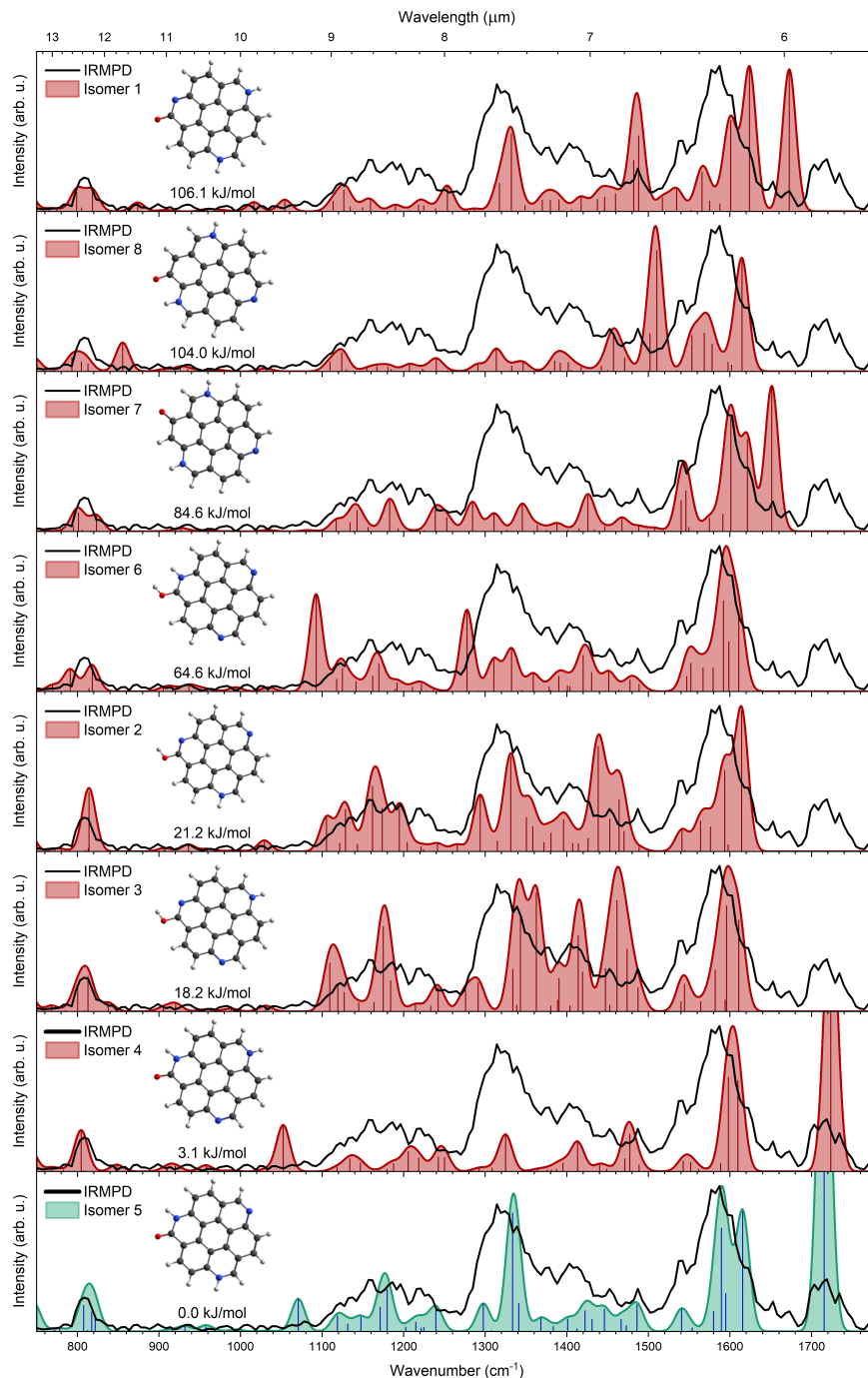


Figure S3: Experimental IRMPD spectrum (black) compared to simulated IR spectra of all considered isomers of $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$. Also shown are the structures of the various $[\text{TAC}-\text{H}+\text{H}_2\text{O}]^+$ isomers and their relative energies calculated using the B3LYP functional in combination with the 6-311++G(d,p) basis set. The simulated spectrum in green indicates our tentative assignment that isomer **5** is likely the dominant isomer. The B3LYP/6-311++G(d,p) computed stick spectra are uniformly scaled with a factor of 0.9679. The calculated spectra are also convolved with a 20 cm^{-1} FWHM Gaussian function to facilitate comparison with the experimental spectrum. All spectra are normalized with respect to their most intense peak in the $750\text{-}1650\text{ cm}^{-1}$ wavenumber range.

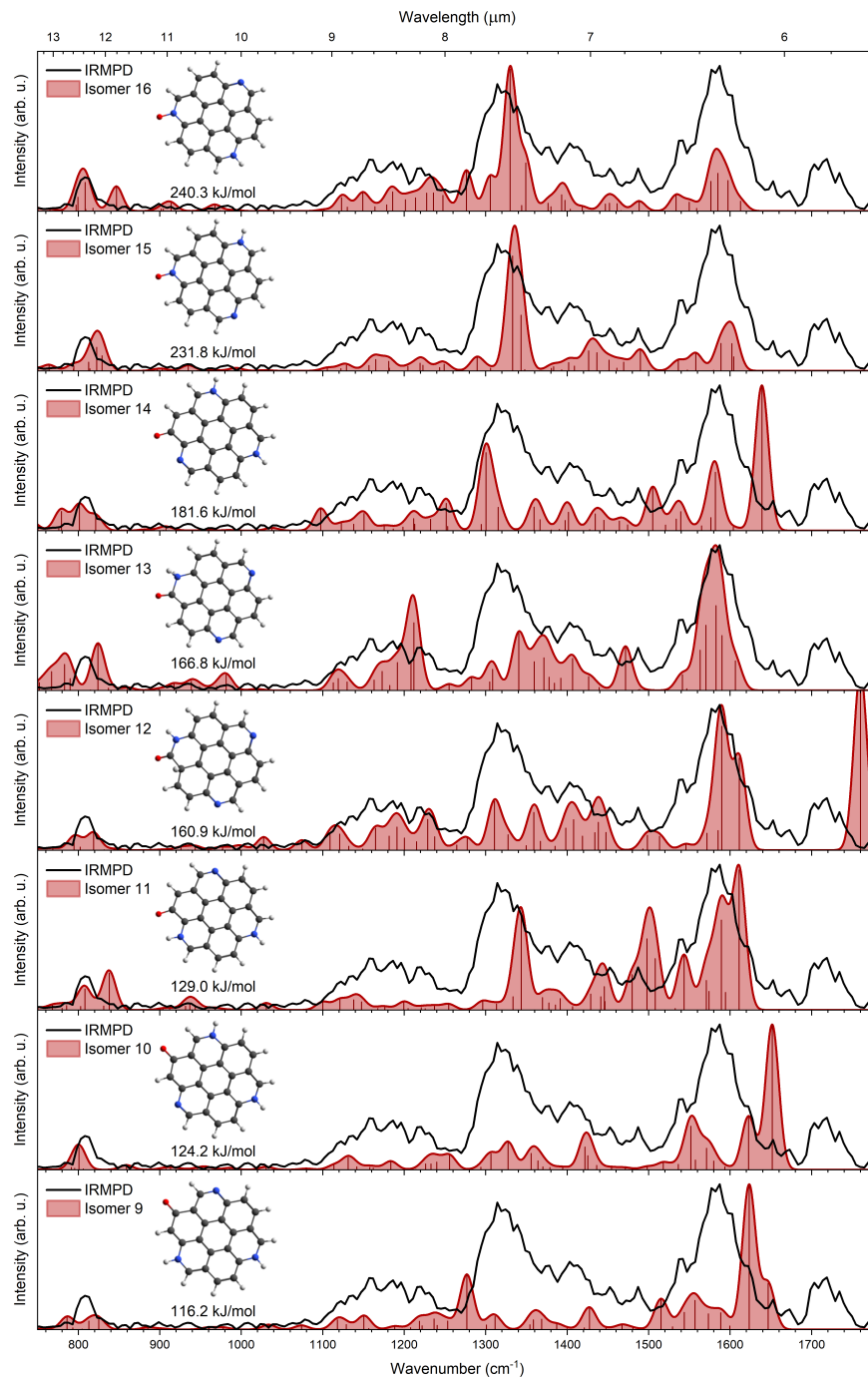


Figure S3 (Cont.)

Coordinates of TAC^+ and TACH^+

Here we presented the coordinates of TAC^+ and TACH^+ that were used to calculate the IR spectra presented in the main manuscript.

Table S1: Cartesian coordinates of the molecular structure of TAC^+ .

Atom	Coordinates		
	x	y	z
C	2.343363	-2.831567	0.000000
C	2.441080	-1.414550	0.000000
C	1.227137	-0.700177	0.000000
C	0.008865	-1.409349	0.000000
C	0.032092	-2.816647	0.000000
C	1.218829	0.711115	0.000000
C	-1.218304	-0.710566	0.000000
C	-1.227304	0.692024	0.000000
C	0.000000	1.407314	0.000000
C	-2.466785	1.384110	0.000000
C	-3.655586	-0.598442	0.000000
C	-2.455146	-1.411283	0.000000
C	-2.430551	-2.821576	0.000000
C	-1.223933	-3.510473	0.000000
H	-1.202872	-4.594065	0.000000
H	-3.362957	-3.374470	0.000000
H	3.249407	-3.431837	0.000000
H	-4.622094	-1.097693	0.000000
C	3.671975	-0.664335	0.000000
C	3.671439	0.705891	0.000000
C	2.442357	1.443741	0.000000
H	4.612702	-1.203561	0.000000
H	4.596997	1.268094	0.000000
C	1.301069	3.447027	0.000000
C	0.011601	2.816789	0.000000
H	1.359724	4.533148	0.000000
C	-2.442841	2.788733	0.000000
H	-3.386345	3.321114	0.000000
C	-1.228657	3.492319	0.000000
H	-1.247479	4.576922	0.000000
N	2.452632	2.803175	0.000000
N	-3.670011	0.704506	0.000000
N	1.200053	-3.507431	0.000000

Table S2: Cartesian coordinates of the molecular structure of TACH⁺.

Atom	Coordinates		
	x	y	z
C	-3.646949	0.587074	0.000000
C	-2.456815	1.388059	0.000000
C	-1.234483	0.691628	0.000000
C	-1.241235	-0.719561	0.000000
C	-2.475815	-1.404999	0.000000
C	0.000000	1.389690	0.000000
C	-0.022262	-1.432275	0.000000
C	1.208809	-0.734174	0.000000
C	1.222632	0.676715	0.000000
C	2.418576	-1.466367	0.000000
C	1.269348	-3.465443	0.000000
C	-0.014760	-2.839075	0.000000
C	-1.265952	-3.522988	0.000000
C	-2.455549	-2.830283	0.000000
H	-3.405499	-3.350499	0.000000
H	-1.274228	-4.607283	0.000000
H	-4.615172	1.083098	0.000000
H	1.326281	-4.551696	0.000000
C	-2.427831	2.808363	0.000000
C	-1.235827	3.504159	0.000000
C	-0.012550	2.795927	0.000000
H	-3.362247	3.358308	0.000000
H	-1.236558	4.588389	0.000000
C	2.399553	2.771745	0.000000
C	2.462926	1.376896	0.000000
H	3.286046	3.393683	0.000000
C	3.655109	-0.744409	0.000000
H	4.572486	-1.320285	0.000000
C	3.681432	0.625125	0.000000
H	4.628918	1.151463	0.000000
N	1.221948	3.420766	0.000000
N	2.423324	-2.827044	0.000000
N	-3.663718	-0.724422	0.000000
H	1.238961	4.434882	0.000000