

Electronic Supplementary Information to Photoprocessing of cationic triazacoronene: Dissociation characteristics of polycyclic nitrogen heterocycles in interstellar environments

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This Electronic Supplementary Information contains further information to the main manuscript. First, a description on the synthetic procedures to obtain **TAC** is given. Next, additional figures are displayed in order of their reference in the main manuscript.

Synthesis of 1,5,9-Triazacoronene

Experimental

Chemical reagents were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed on silica gel 60 Å (0.04 – 0.063 mm, Screening Devices B.V.). Thin Layer Chromatography (TLC) was performed on TLC Silica gel 60 plates (Kieselgel F254, Merck). NMR spectra was recorded on a Bruker AV-300 NMR or a Bruker AV-500 NMR instrument. Chemical shifts are given in ppm (δ) relative to the solvent signals. Mass spectrometry was performed on a Thermo Scientific LCQ Fleet spectrometer equipped with an electrospray ion source in positive ion mode. Elemental analysis was performed by Mikroanalytisches Labor Kolbe (c/o Fraunhofer Institut UMSICHT).

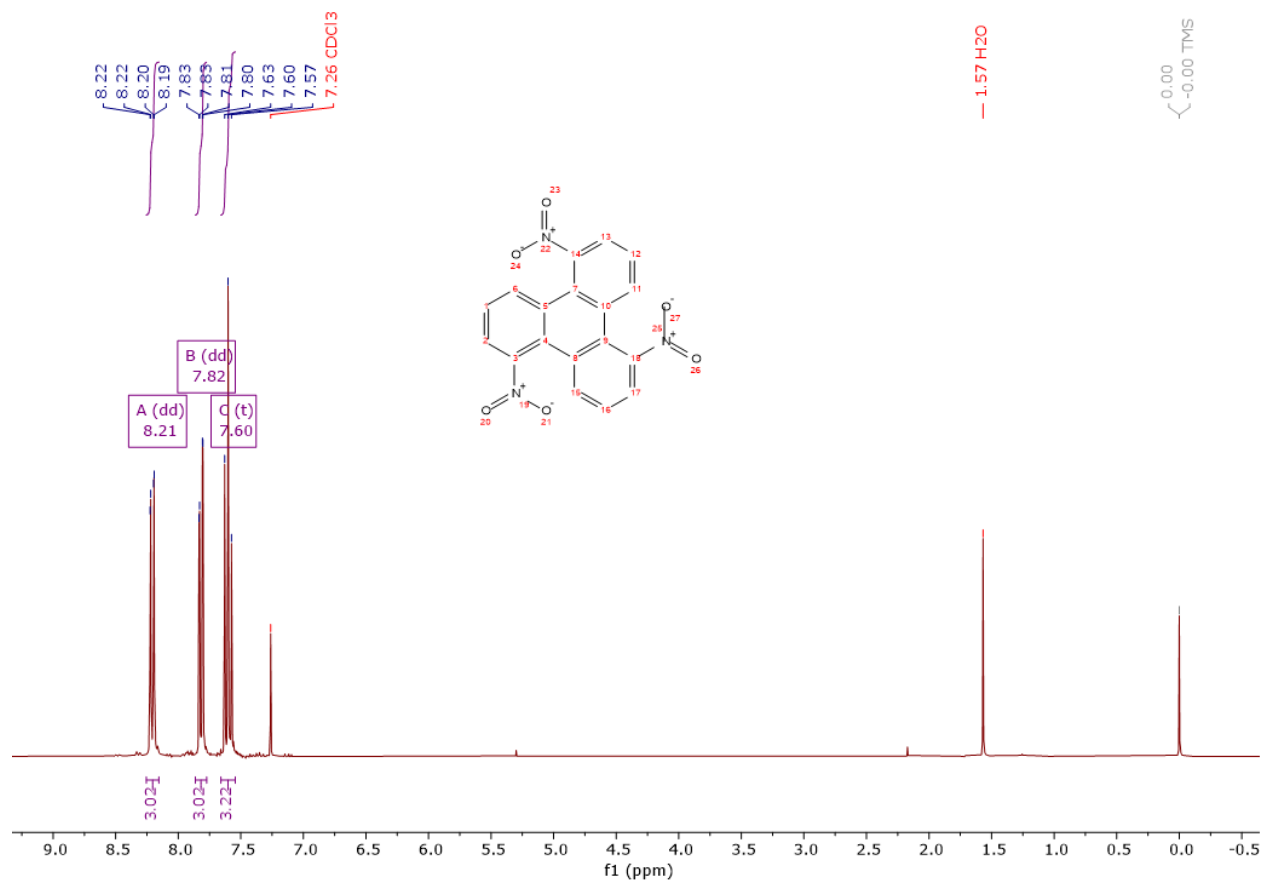
Synthesis of 1,5,9-trinitrotriphenylene

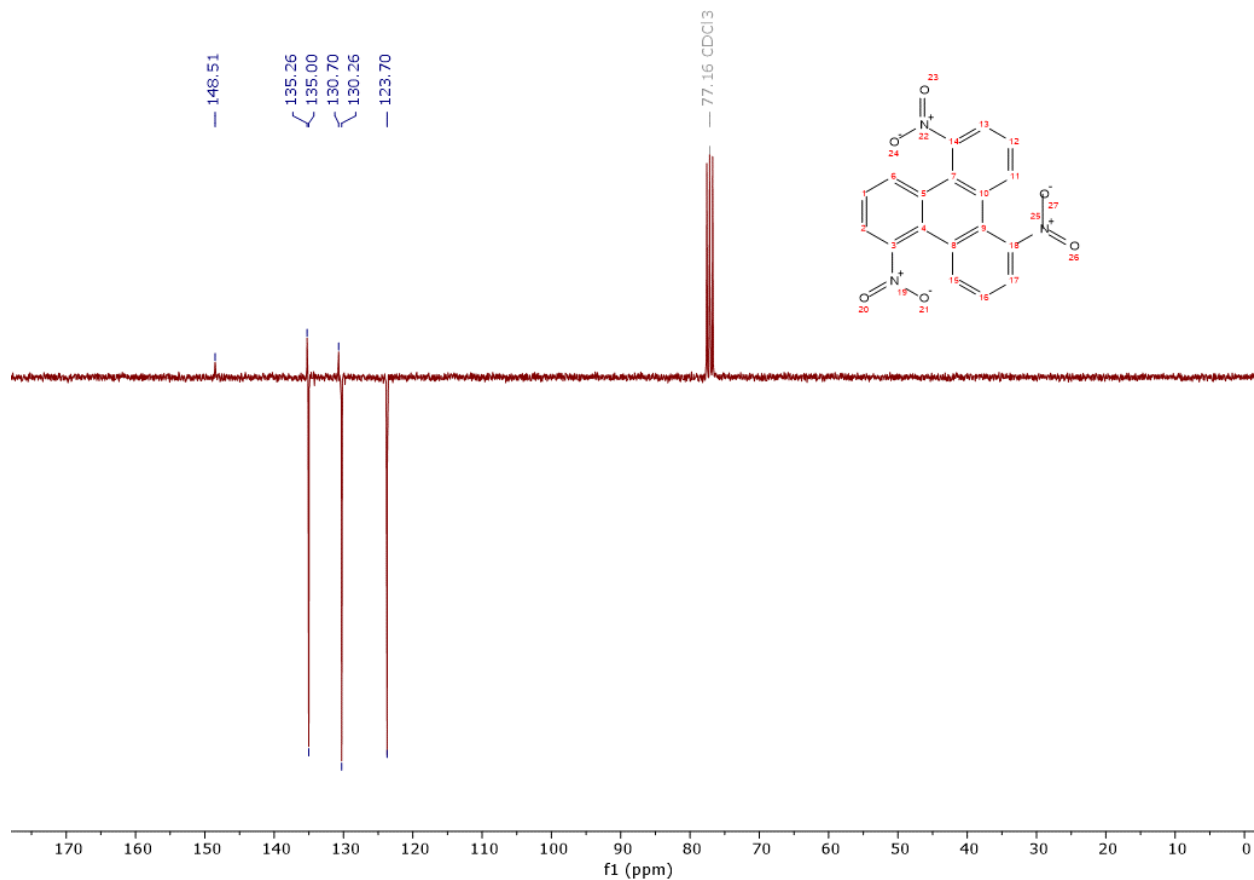
To a solution of 2,3-dichloronitrobenzene (17.7 g, 92.2 mmol, 1 eq) in DMF (142 ml) was added copper powder (35.1 g, 553 mmol, 6 eq). The mixture was stirred at reflux for 19 h under N₂ atmosphere. After cooling to 120 °C, the hot solution was filtered over celite and the product was extracted from the celite with DMF (3 × 25 ml). The filtrate was then slowly poured into 6% ammonium solution (720 ml) (diluted from 18% NH₃·H₂O (240 ml)) with vigorous stirring. The obtained black precipitate was collected by filtration and sequentially washed with diluted ammonium solution (48 ml) and water (48 ml). The obtained residue was then concentrated onto celite and purified using silica column chromatography (pentane : DCM, 2 : 1 → 1 : 1) to obtain a yellow solid (4.74 g, 13.0 mmol, 42%).

¹H NMR (300 MHz, CDCl₃) δ 8.21 (dd, J = 8.3, 1.2 Hz, 3H), 7.82 (dd, J = 8.1, 1.2 Hz, 3H),

7.60 (t, $J = 8.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 148.51, 135.26, 135.00, 130.70, 130.26, 123.70.





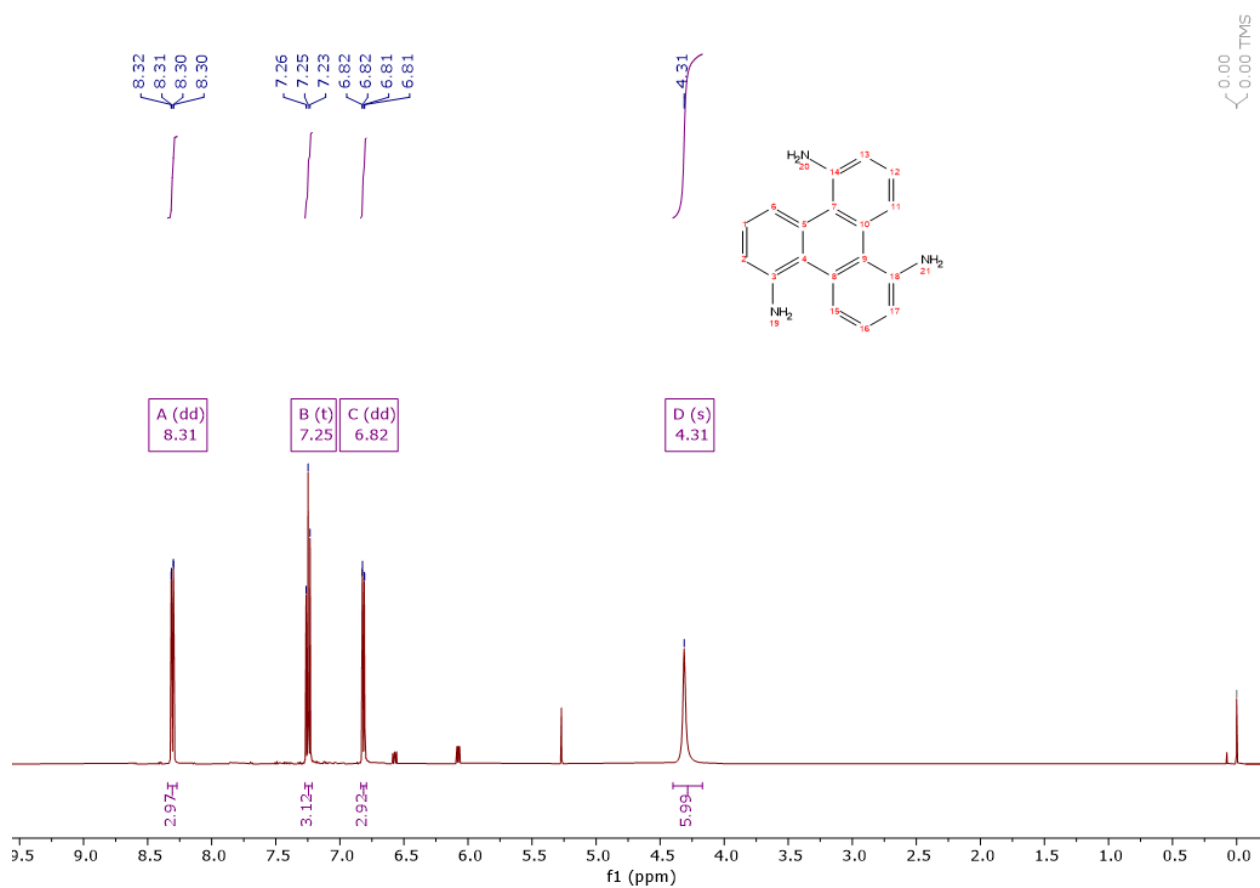
Synthesis of triphenylene-1,5,9-triamine

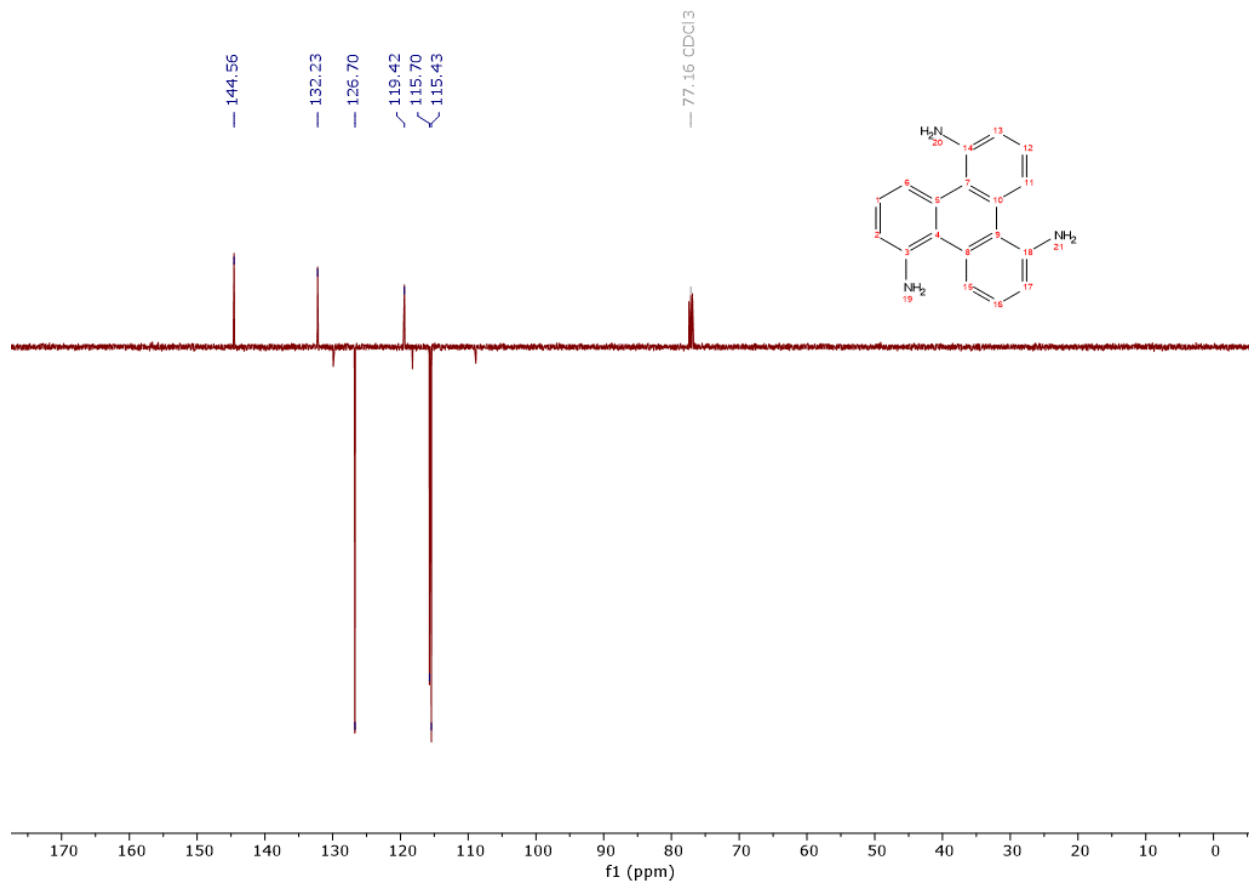
1,5,9-trinitrotriphenylene (3.0 g, 8.3 mmol, 1 eq) was dissolved in THF/MeOH (4:1, v/v, 80 ml). Ni(OAc)₂·4H₂O (2.0 g, 8.3 mmol, 1 eq) was added and the mixture was stirred for 5 min. Then, NaBH₄ (4.7 g, 124 mmol, 15 eq) was added in portions to the reaction mixture over 20 min and the obtained black mixture was stirred for an additional 15 min. Then, water was added (40 ml) and the mixture was filtered. The obtained residue was additionally washed with DCM/MeOH (200 ml), and the combined filtrate was evaporated under reduced pressure. Purification using silica column chromatography (0.1% MeOH in DCM) yielded a light-brown solid (1.2 g, 4.4 mmol, 52%).

¹H NMR (500 MHz, CDCl₃) δ 8.31 (dd, J = 8.1, 1.2 Hz, 3H), 7.25 (t, J = 7.9 Hz, 3H), 6.82 (dd, J = 7.8, 1.2 Hz, 3H), 4.31 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 144.56, 132.23, 126.70, 119.42, 115.70, 115.43.

ESI-MS: m/z calcd for C₁₈H₁₆N₃ [M+H]⁺ 274.13, found 274.08.





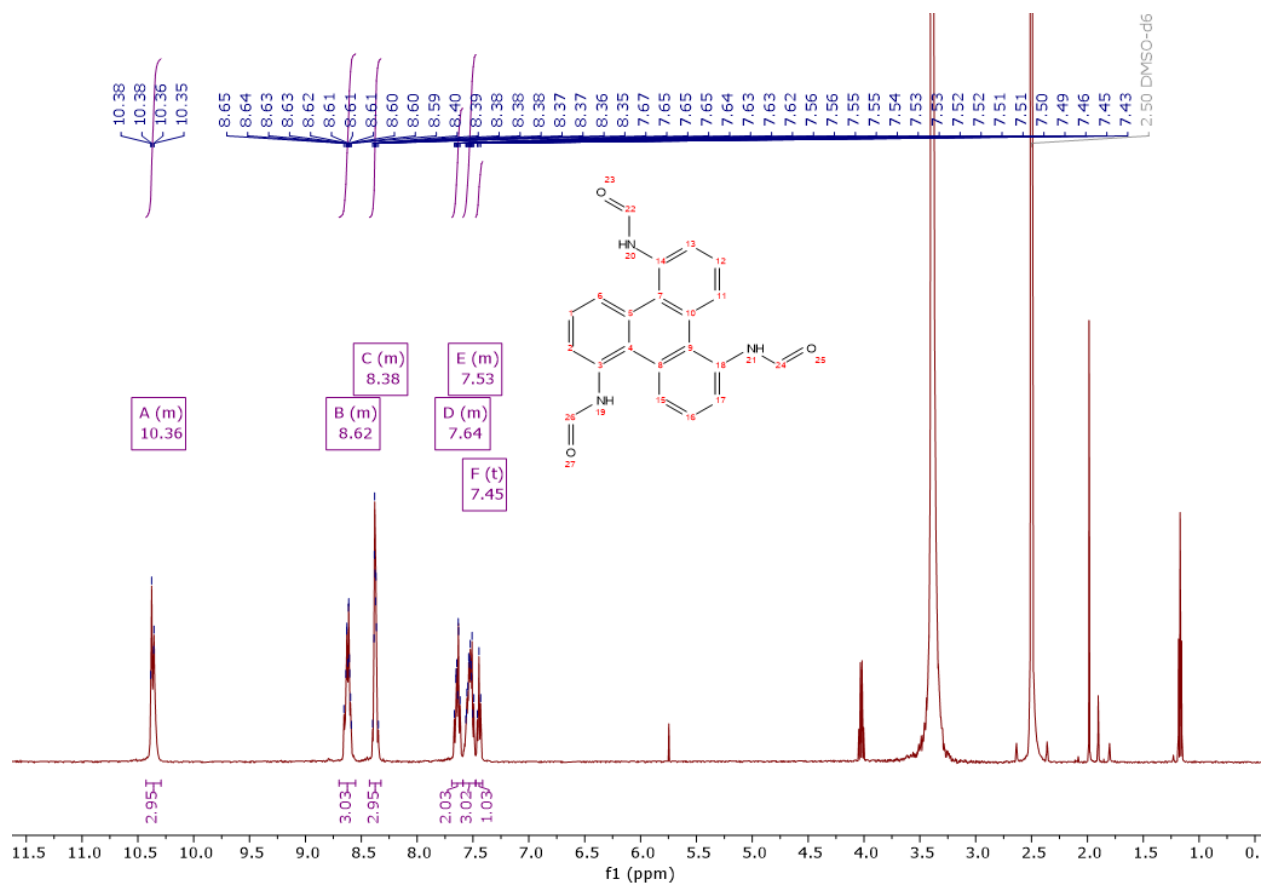
Synthesis of N,N',N'' -(triphenylene-1,5,9-triyl)triformamide

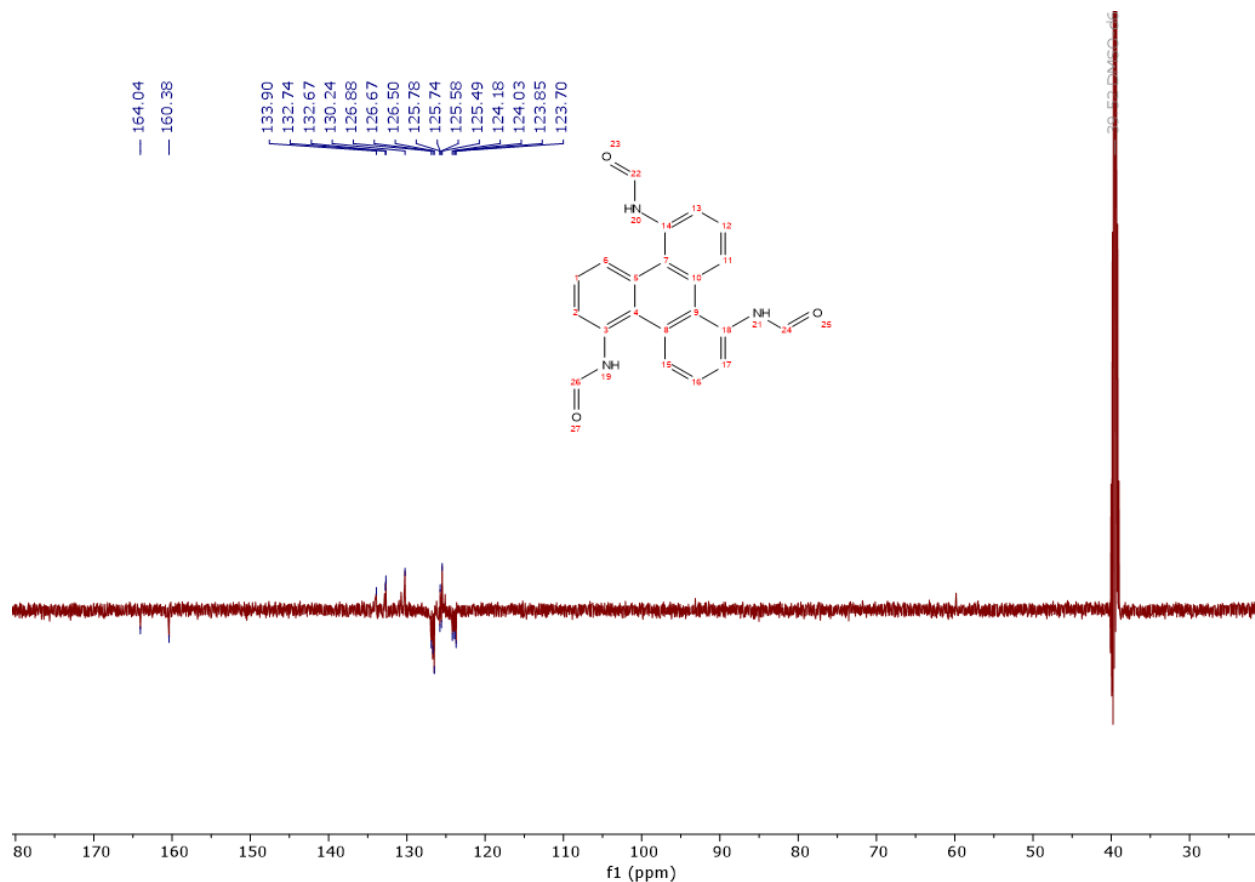
Formic acid (0.37 ml, 9.7 mmol, 5.3 eq) was added to a solution of acetic anhydride (0.73 ml, 7.7 mmol, 4.2 eq) at 0 °C. The mixture was heated to 50 °C and stirred for 2 h. After cooling the prepared mixture back down to 0 °C, a solution of the triphenylene-1,5,9-triamine (500 mg, 1.8 mmol, 1 eq) in THF (10 ml) was added dropwise over 15 min. Then, the reaction mixture was allowed to warm to room temperature and stirred for 18 h. The resulting precipitate was filtered, rinsed with ethyl acetate, and dried to afford pure product as a gray solid (591 mg, 1.7 mmol, 90%).

^1H NMR (500 MHz, DMSO- d_6) δ 10.43 – 10.29 (m, 3H), 8.70 – 8.55 (m, 3H), 8.43 – 8.32 (m, 3H), 7.69 – 7.59 (m, 2H), 7.59 – 7.48 (m, 3H), 7.45 (t, $J = 7.6$ Hz, 1H).

^{13}C NMR (126 MHz, DMSO- d_6) δ 164.04, 160.38, 133.90, 132.74, 132.67, 130.24, 126.88, 126.67, 126.50, 125.78, 125.74, 125.58, 125.49, 124.18, 124.03, 123.85, 123.70.

ESI-MS: calcd for C₂₁H₁₆N₃O₃ [M+H]⁺ 358.12, found 358.08; C₂₁H₁₉N₄O₃ [M+NH₄]⁺ 375.15, found 375.08.





Synthesis of 1,5,9-triazocoronene

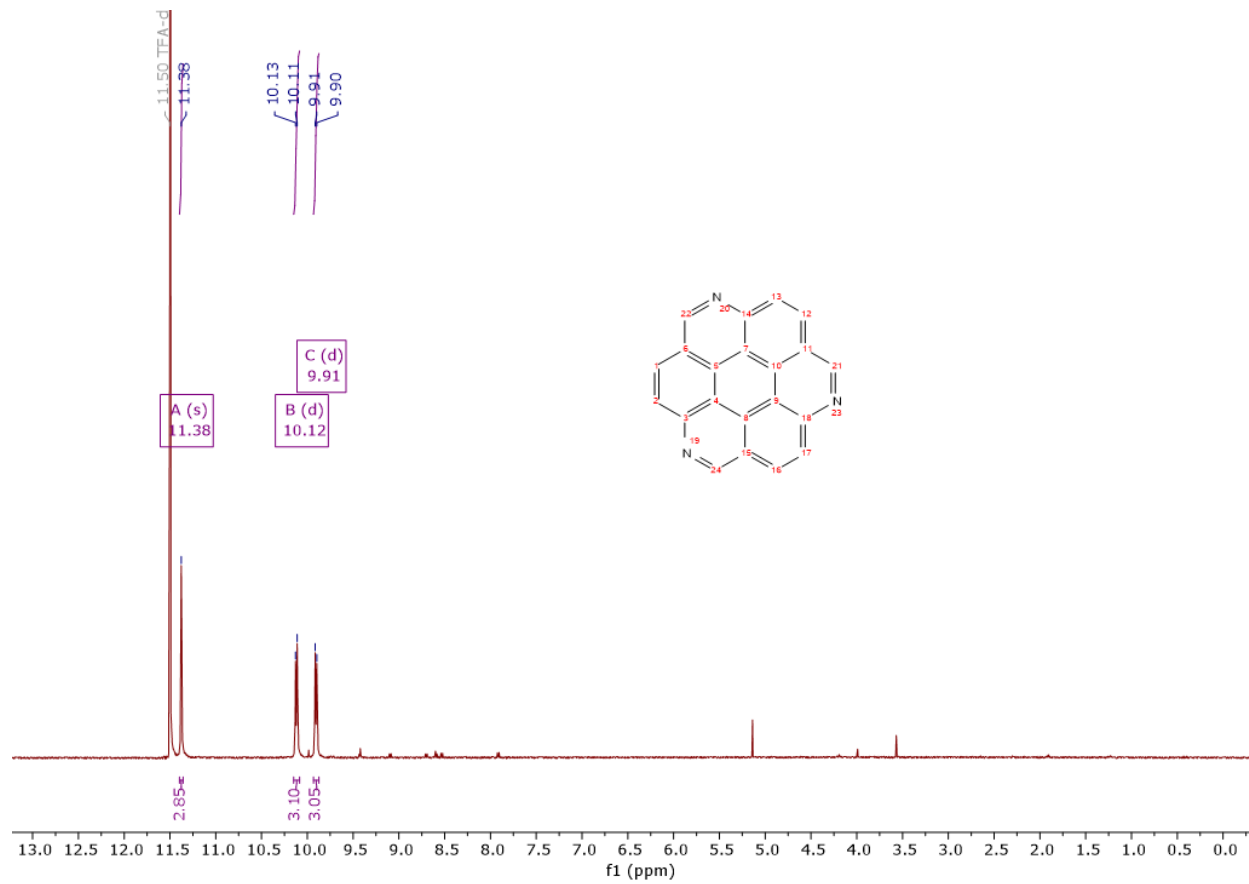
A microwave vial was charged with *N,N',N''*-(Triphenylene-1,5,9-triyl)triformamide (0.50 g, 1.4 mmol, 1 eq), NaCl (4.1 g, 31 mmol, 22 eq) and AlCl₃ (4.1 g, 94 mmol, 67 eq) and purged with Ar. The mixture was heated to 230 °C and stirred for 4 h. After cooling to RT, the solids were stirred overnight in 15% aqueous NaOH (15 ml). The obtained yellow slurry was filtered over celite and washed with water (50 ml). The product dispersed in celite was dissolved in copious amounts of DCM/MeOH 10:1 until the filtrate was no longer yellow. The filtrate was evaporated under reduced pressure and washed with hot DCM/MeOH 10:1 (20 ml). The residue was collected by centrifugation to obtain product as brown-yellow solid (120 mg, 0.40 mmol, 23%).

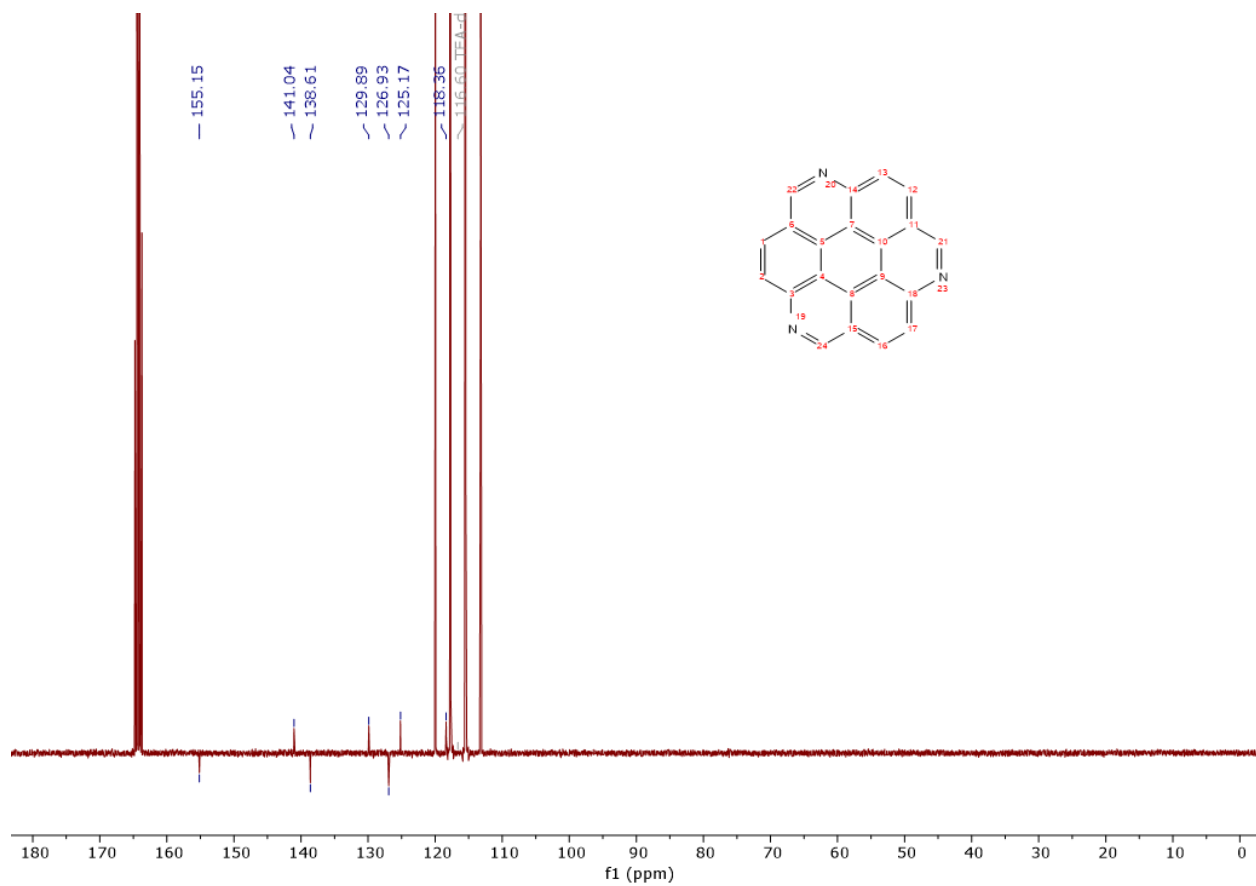
¹H NMR (500 MHz, TFA) δ 11.38 (s, 3H), 10.12 (d, *J* = 8.9 Hz, 3H), 9.91 (d, *J* = 8.9 Hz, 3H).

^{13}C NMR (126 MHz, TFA) δ 155.15, 141.04, 138.61, 129.89, 126.93, 125.17, 118.36.

ESI-MS: m/z calcd for $\text{C}_{21}\text{H}_{10}\text{N}_3$ $[\text{M}+\text{H}]^+$ 304.09, found 304.17.

Anal. Calcd for $\text{C}_{21}\text{H}_9\text{N}_3$: C, 83.16; H, 2.99; N, 13.85. Found: C, 83.09; H, 3.02; N, 13.81.





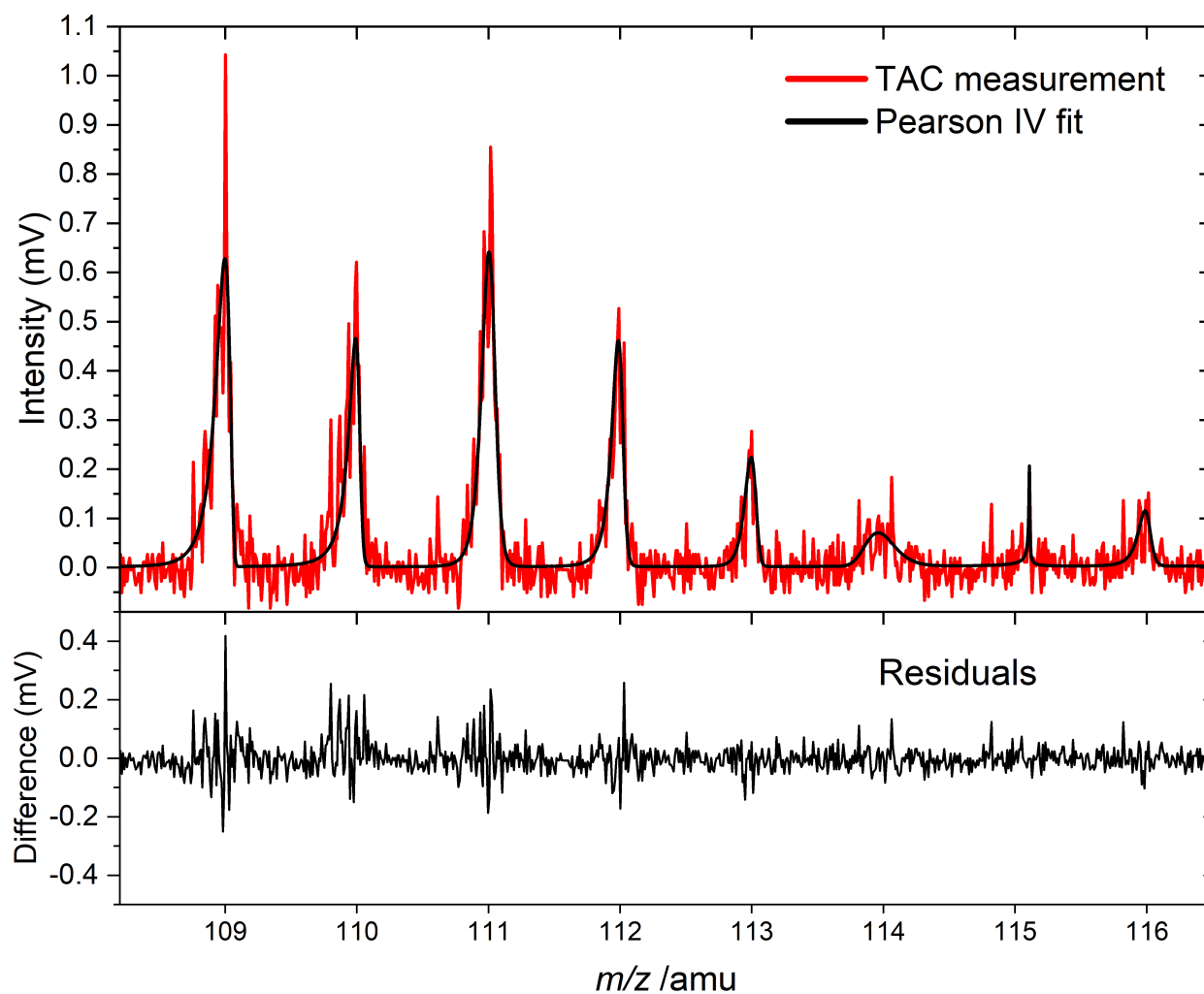


Figure S1: Top: Example of experimental data and fitted peaks used for integration. Bottom: Residuals between experiment and fit.

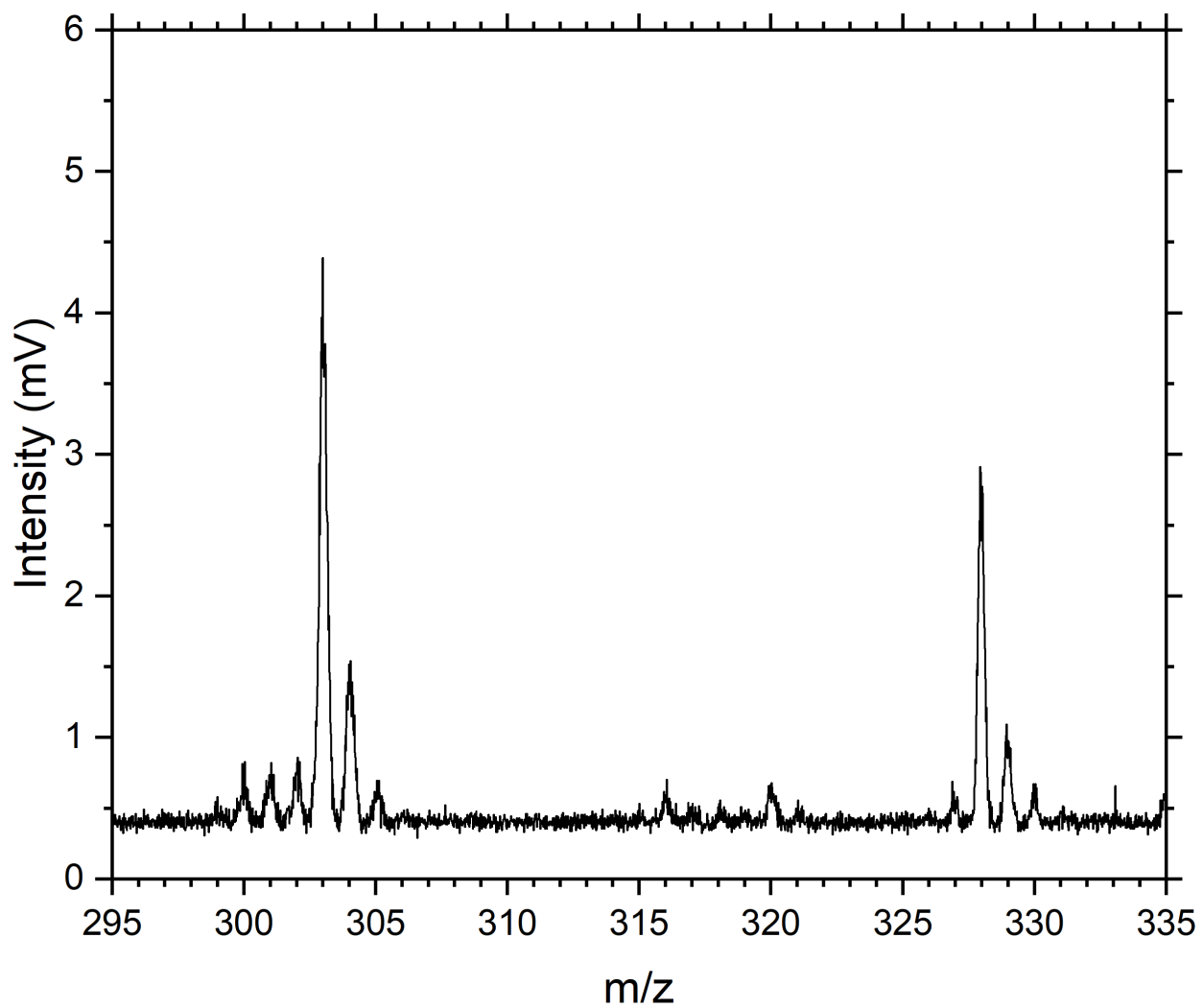


Figure S2: Mass spectrum of **TAC**⁺dissociation with a mix of 5% acetylene instead of pure helium. The water addition product (m/z 320) is almost completely replaced by the acetylene addition product (m/z 328).

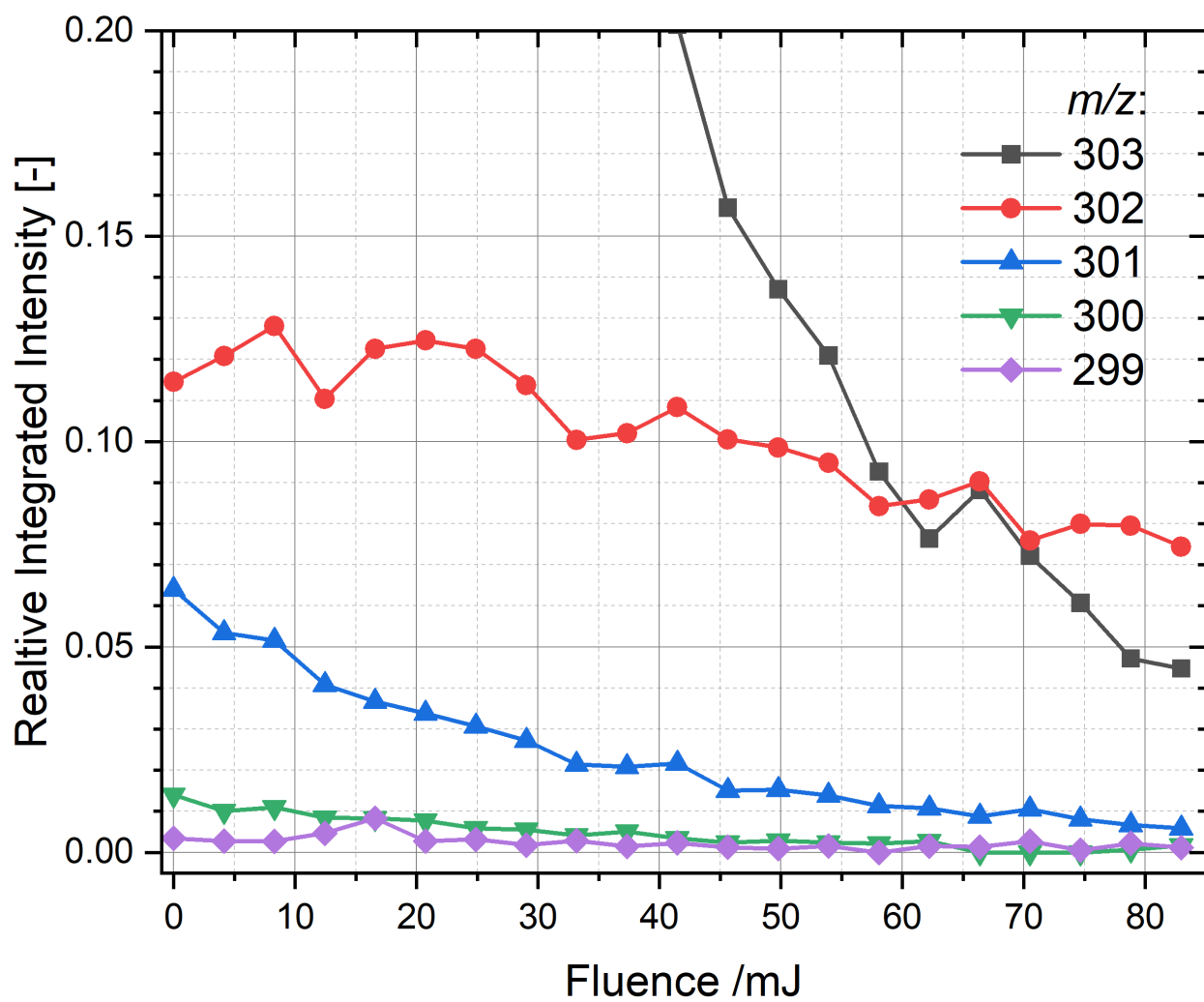


Figure S3: Zoomed in view of the hydrogen loss region from TAC^+ . No significant hydrogen losses are observed.

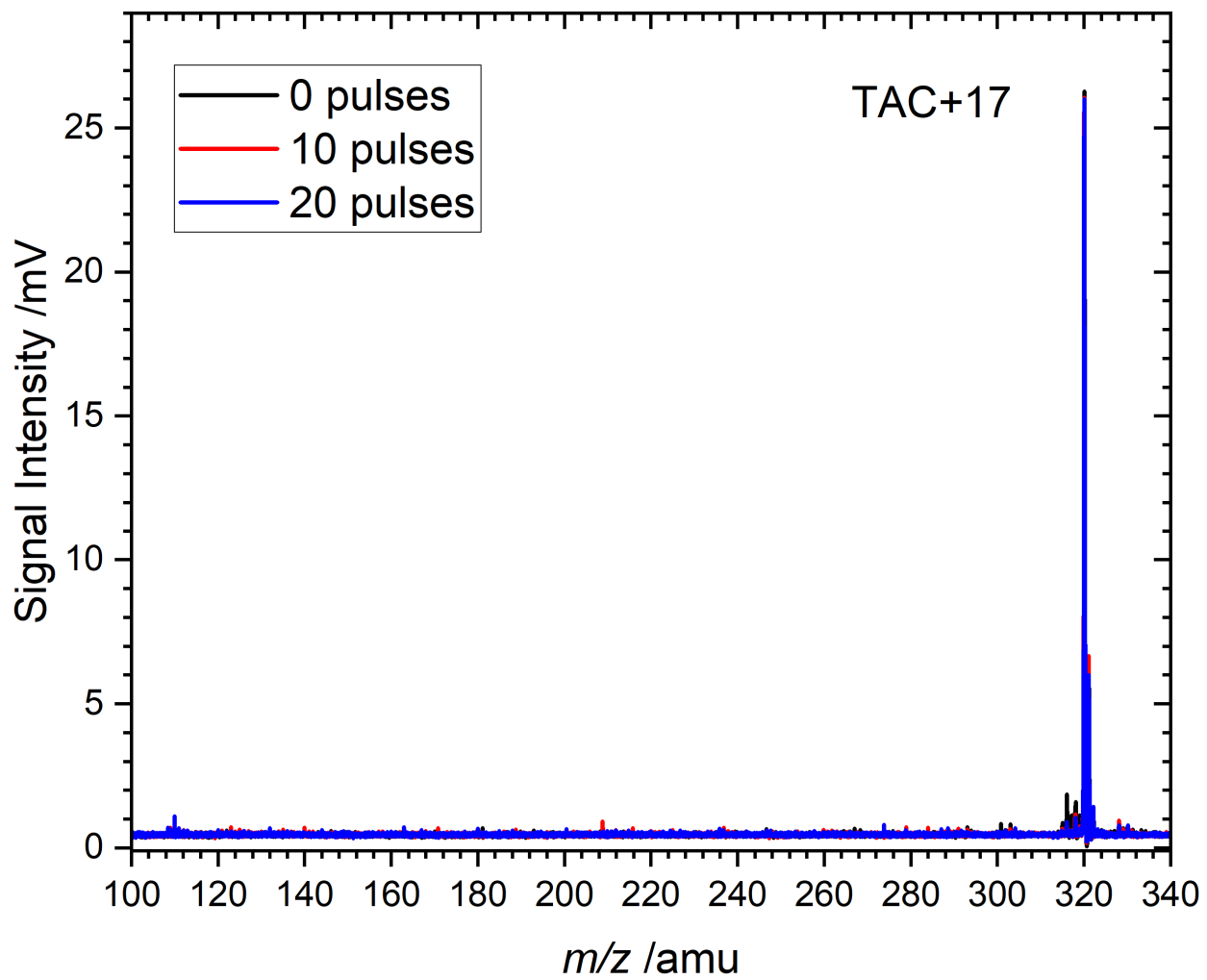


Figure S4: Dissociation mass spectra for m/z 320. No dissociation is observed.

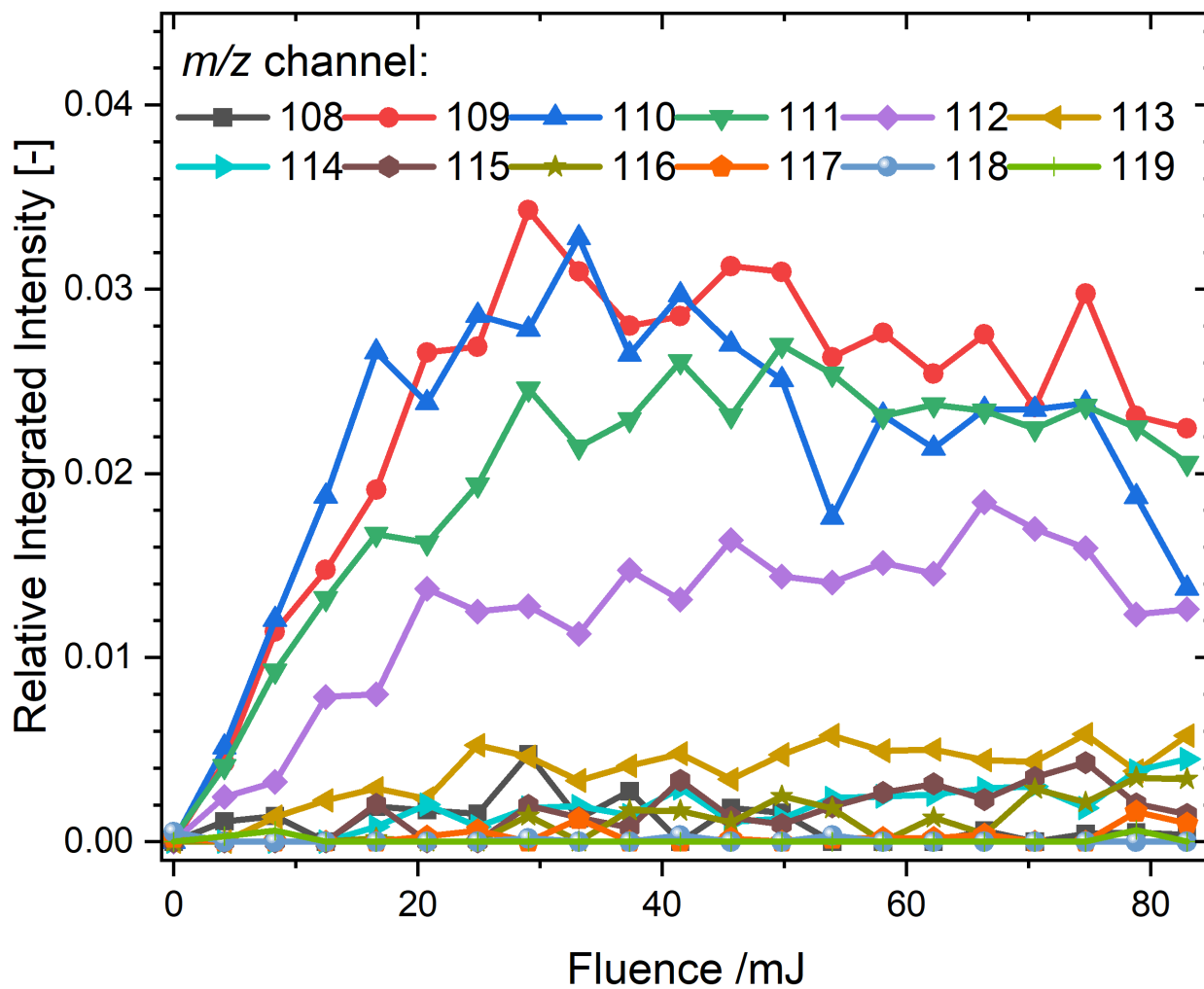


Figure S5: Integrated Intensities of all mass peaks in the Γ_9 region.

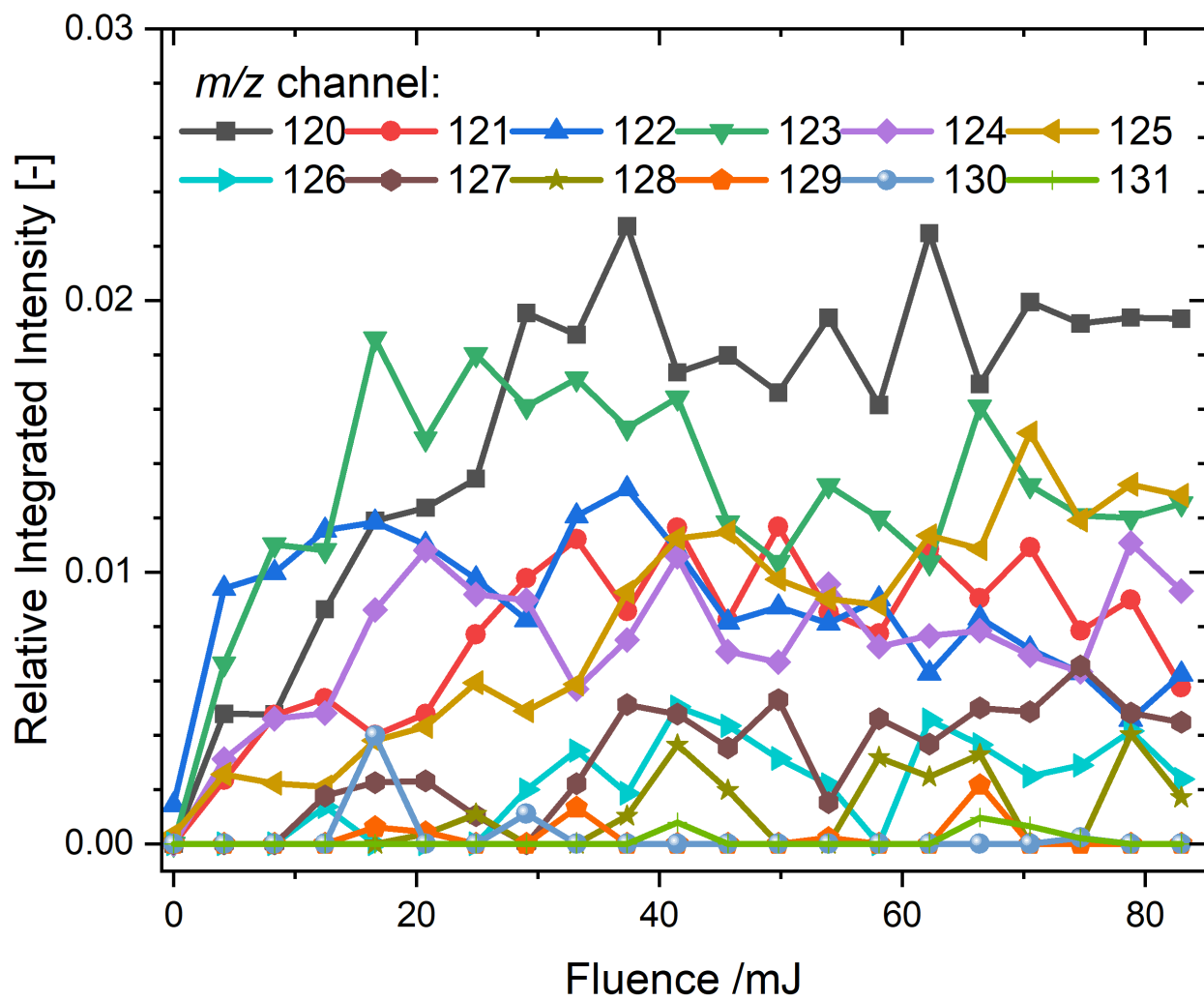


Figure S6: Integrated Intensities of all mass peaks in the Γ_{10} region.

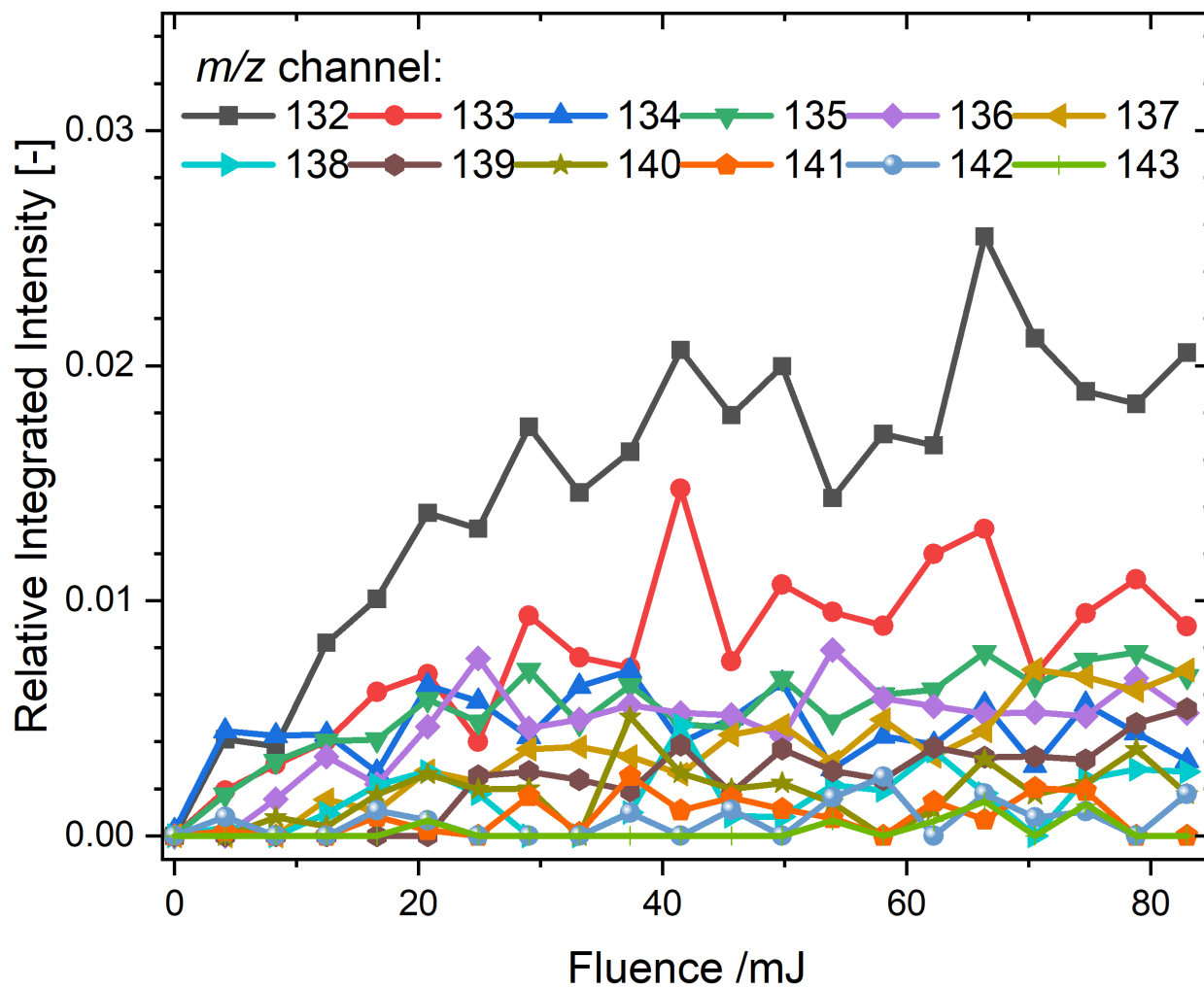


Figure S7: Integrated Intensities of all mass peaks in the Γ_{11} region.

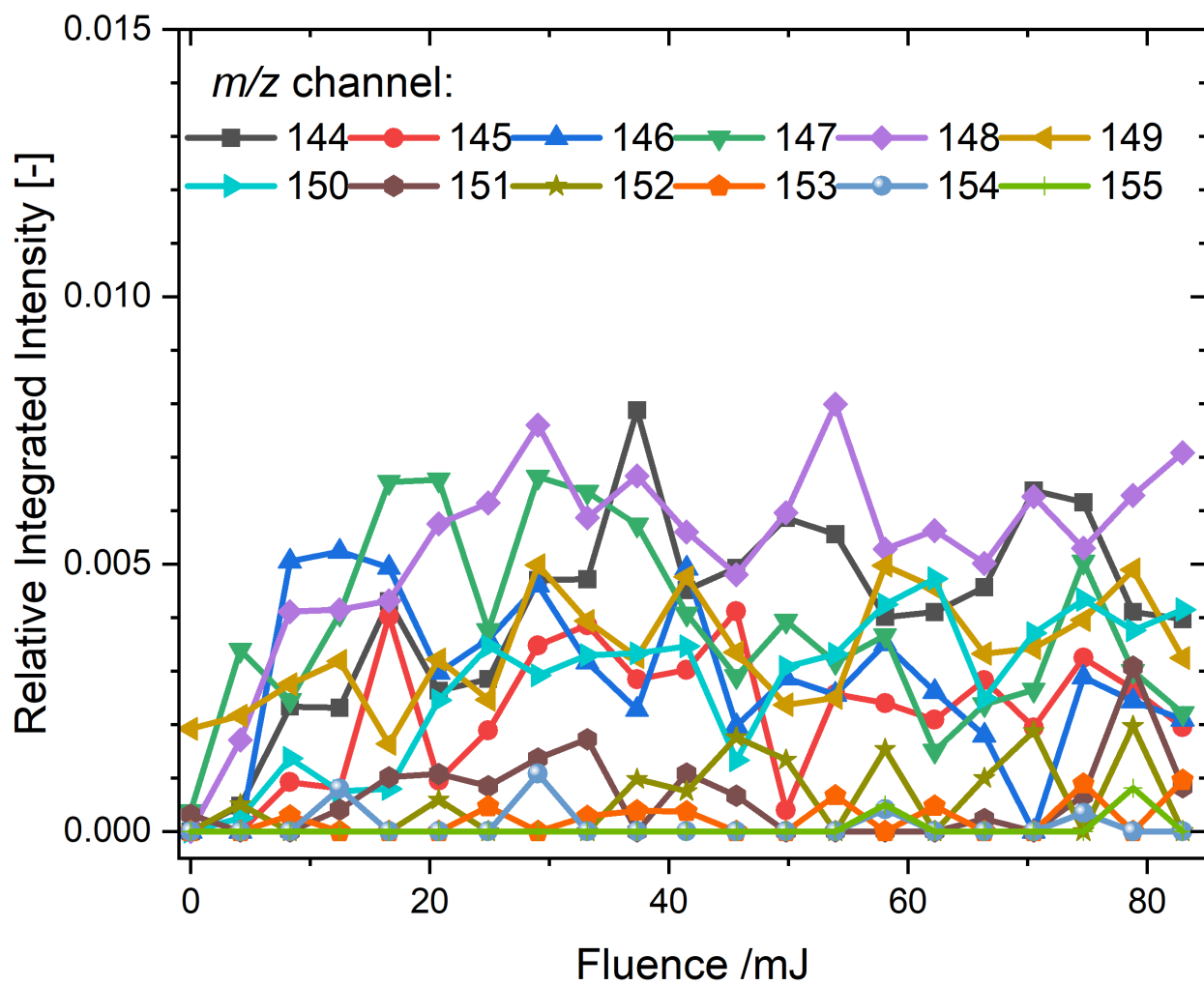


Figure S8: Integrated Intensities of all mass peaks in the Γ_{12} region.

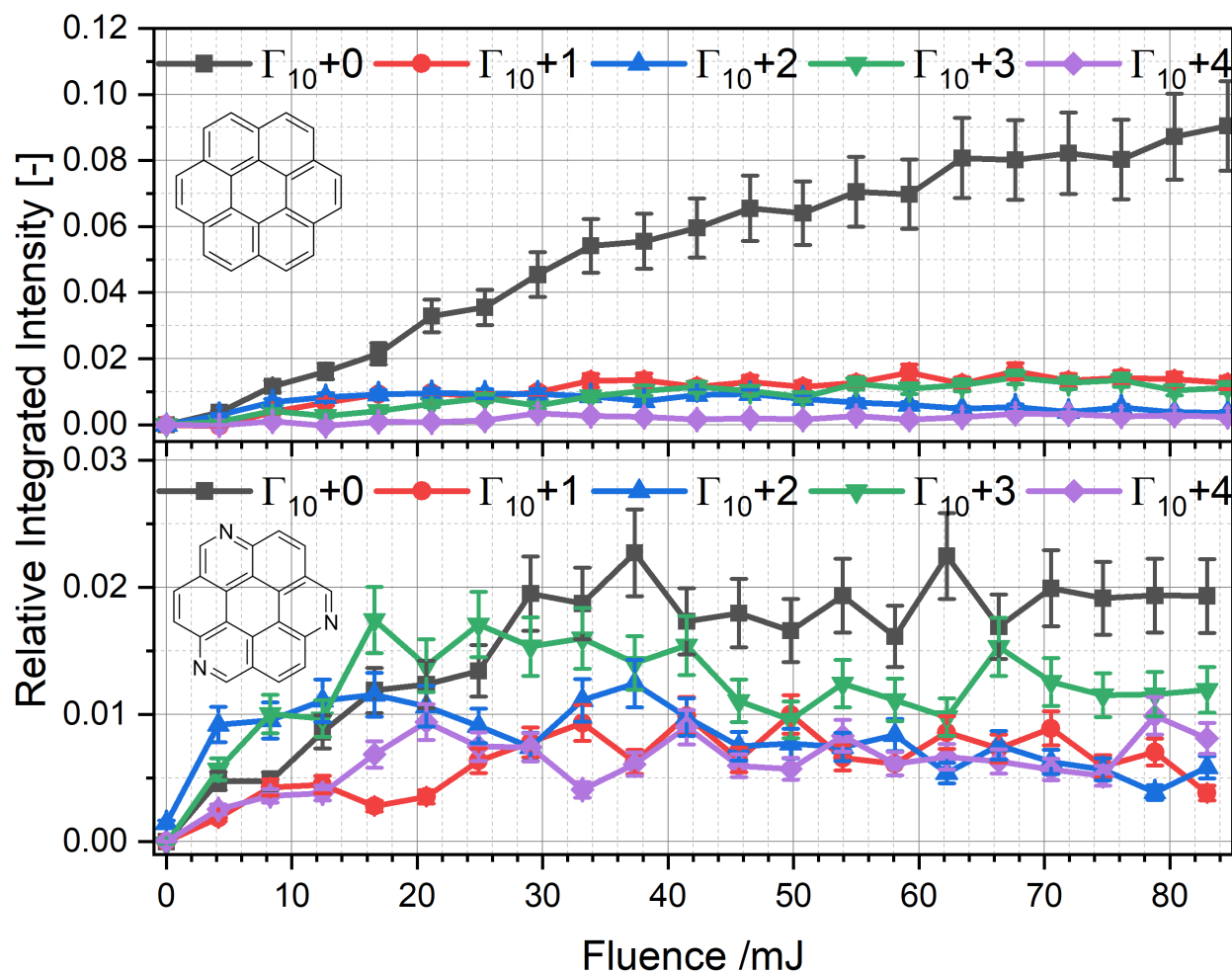


Figure S9: Integrated mass peaks for the Γ_{10} region for Cor^+ (top) and TAC^+ (bottom).

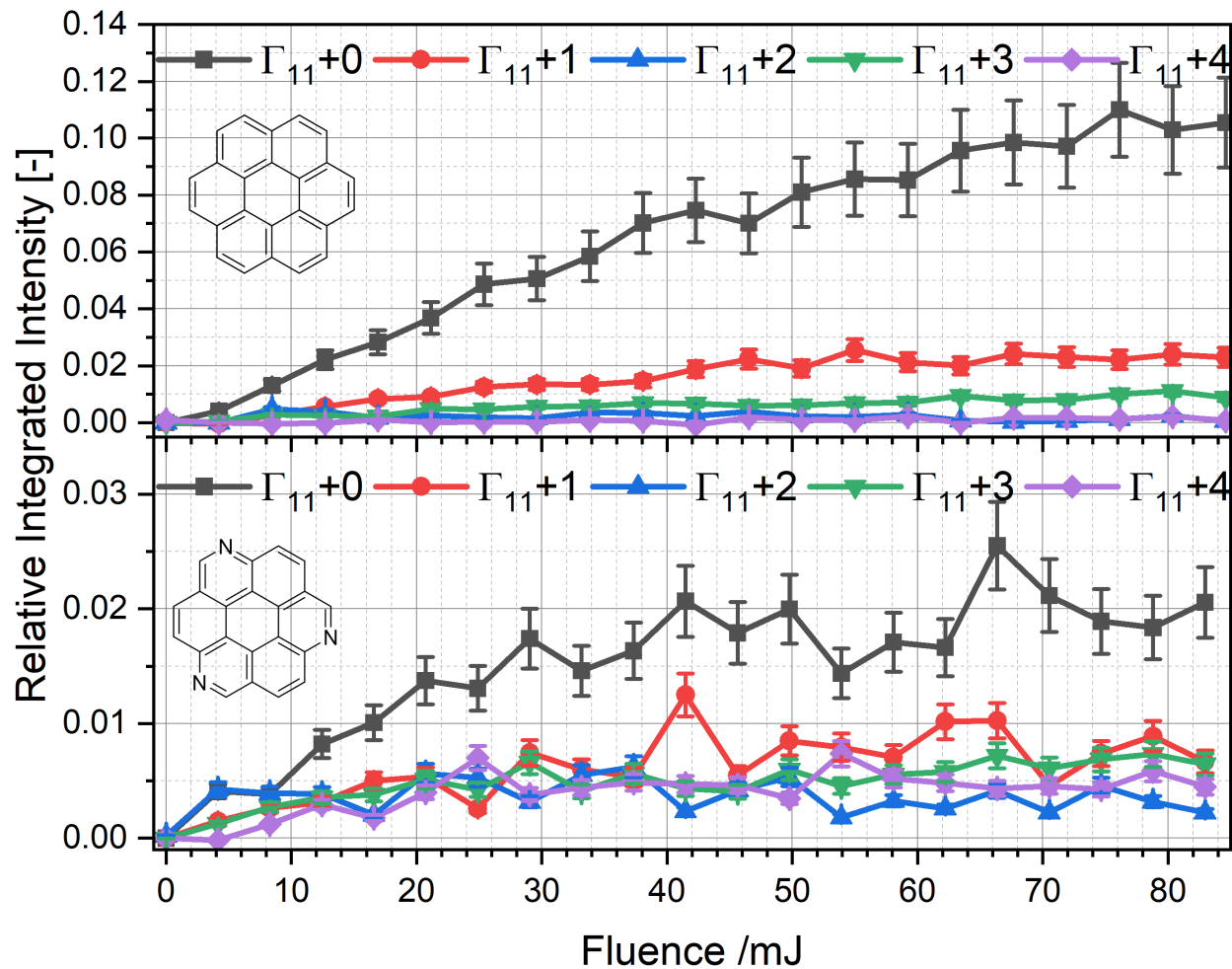


Figure S10: Integrated mass peaks for the Γ_{11} region for **Cor⁺**(top) and **TAC⁺**(bottom).

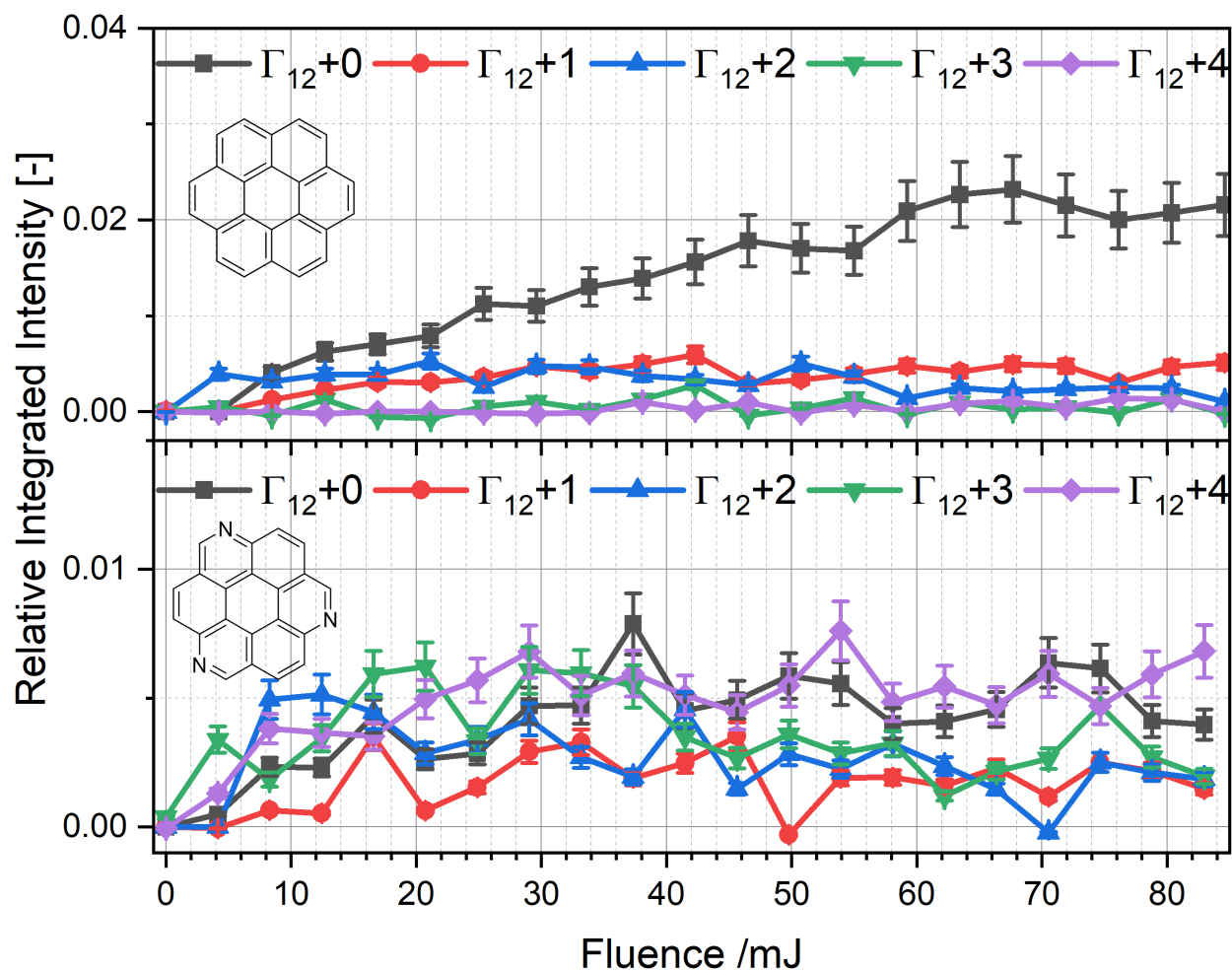


Figure S11: Integrated mass peaks for the Γ_{12} region for **Cor⁺**(top) and **TAC⁺**(bottom).