SUPPORTING INFORMATION
FOR


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**Gated electrostatic ion trap : Experimental details.** In the “Benner” trap device, the image charge, at each passage of the ion, is collected by the "pick-up" tube (high impedance) and is transmitted to a field effect transistor (2SK152). The induced current is converted into a voltage at the high-impedance JFET input. In order to lower the link impedances, the JFET transistor, the preamplifier and the first amplification stage are mounted on an integrated printed circuit board (PCB) as closely as possible to the tube. The association with the JFET transistor is provided by a brass screw. Transmission between the mechanics of the “Benner” trap and the PCB is made by a copper rigid connector: in addition to limit ground currents, this rigid link allows to minimize noise. The equivalent capacity of the link between the pick-up tube and the JFET is approximately 1 pF.

In order to find the correct potentials to apply on the entrance and exit electrodes to optimally reflect and focus ions of a given energy toward the detector tube, we conducted ion trajectory simulations with SIMION 7.0.(Dahl, D. A. SIMION for the personal computer in reflection. International Journal of Mass Spectrometry 2000, 200 (1–3), 3-25) SIMION was used to build electrode geometries and determine DC contributions to the fields. Figure S1a) shows a trajectory simulation of a positively charged ion with a mass of $2 \times 10^6$ Da holding +700 charges and moving with an initial velocity of 2400 m/s, reflecting a few hundred times through the detector. The detector tube is separated from the endcaps by a small space. In Figure S1, for positive mode, the corresponding voltages are set to the electrodes: $L_1 = 0 \text{ V}$, $L_2 = -122 \text{ V}$, $L_3 = 52 \text{ V}$, $L_4 = 131 \text{ V}$, $L_5 = 187 \text{ V}$ and $L_6 = 220 \text{ V}$. The optimal voltages obtained in this simulation are similar to those proposed by Benner (Anal. Chem., 1997, 69, 4162-4168). For negatively charged ions, the subsequent voltages are used to the electrodes: $L_1 = 0 \text{ V}$, $L_2 = +120 \text{ V}$, $L_3 = -52 \text{ V}$, $L_4 = -131 \text{ V}$, $L_5 = -187 \text{ V}$ and $L_6 = -220 \text{ V}$. The ions with certain initial velocity are trapped by the potential valley provided by ion mirrors. Ion trajectories are reflected between $L_3$ and $L_4$ electrodes ($L_1$ and $L_6$ and the electrodes closest and farthest from the detection tube, respectively).
Figure S1: a) A simulated trajectory b) time of flight (TOF) vs electric potential diagram of a positively charged ion with a mass and charge of $2 \times 10^6$ Da and $+700$, respectively. The ion velocity is $2400$ m/s.
Figure S2. a) Ion wavelet for PAMPS positive ion stored in the electrostatic ion trap without laser irradiation. b) Logarithm of ion count versus trapping time for PAMPS megadalton ions without laser irradiation.
Figure S3: Optimized structures of trimer with 3Na\(^+\) and negative ions calculated at B3LYP/6-31G(d) level of theory. The collision cross sections (ccs) of these ions calculated by IMPACT program are given. (E. G. Marklund, M. T. Degiacomi, C. V. Robinson, A. J. Baldwin and J. L. P. Benesch, Collision Cross Sections for Structural Proteomics, Structure, 2017, 23, 791–799.)
Figure S4. SIMION simulation of the time of flight (μs) vs m/z of high and low fragments generated from dissociation of a parent ion in the center of the field-free region of the “Benner” trap. The parent ion is a positively charged ion with a mass and charge of 2x10^6 Da and +700, respectively. The ion velocity is 2400 m/s.
Figure S5: Histograms for “stair-case”-and “funnel”-types of decay as a function of $q^2/n$
Figure S6. IR spectra of A) AMPS monomer ions positive (Na\(^+\) adduct) and negative (deprotonated) B) Trimer positive (3Na\(^+\) adduct) and negative ion calculated at B3LYP/6-31G(d) level of theory. All calculations were performed by Gaussian09 program. (Frisch, M. J., et al., Gaussian 09, Revision B.01. Wallingford CT, 2009)
Figure S7: A) Mass spectra of AMPS monomer in positive and negative mode B) Fragmentation yield of AMPS positive and negative ions at different normalized collision energy C) MS/MS spectra of precursor ions produced in positive and negative modes showing the intense fragment at 71 m/z.