Supplementary Information

Development of a focused high-energy macromolecular ion beam

Szu-Hsueh Lai,[a,b] Ming-Lee Chu,[c] Jung-Lee Lin*[a] and Chung-Hsuan Chen[a,b]

[a] *Genomics Research Center, Academia Sinica, Taipei 11529, Taiwan.*
E-mail: harrylin@gate.sinica.edu.tw
[b] *Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan.*
[c] *Institute of physics, Academia Sinica, Taipei 11529, Taiwan.*

Abstract: In this work, we report our development of a focused macromolecular ion beam with kinetic energy of up to 110 keV. The system consists of a quadrupole ion trap (QIT), einzel lens and linear accelerator (LINAC). Based on the combination of matrix-assisted laser desorption ionization (MALDI) and quadruple ion trapping (QIT), ions were desorbed from the surface and trapped with an ion trap to form biomolecular ion packets. Positive- and negative-pulsed voltages were applied on each end-cap electrode of the QIT to extract ion packets and form an ion beam that was subsequently focused via an einzel lens and accelerated by stepwise pulsed voltages. The tabletop instrument was designed and successfully demonstrated via measurements of molecular ions of insulin, cytochrome c and bovine serum albumin (BSA) with mass-to-charge ratios (m/z) ranging from ~5.8 to 66.5 k. This is the first report of both a focused and high-kinetic-energy protein ion beam. In addition, both secondary ions and electrons were observed from the surface under hypervelocity ion beam bombardment. This focused macromolecular ion beam has the potential to study interaction between large molecular ions with other molecules either in gas phase or upon a surface.

Table of Contents

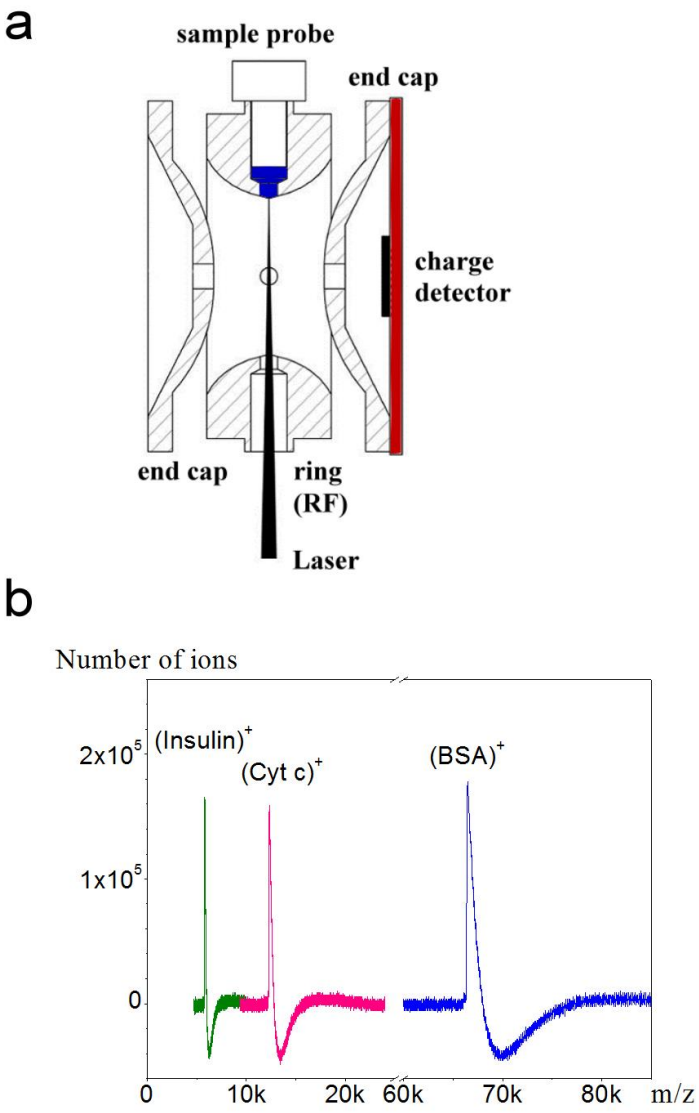

Figure S1. (a) The experimental setup of quadrupole ion trap (QIT) mass spectrometer for storage capacity measurements. A homemade disk-type charge detector was mounted on one of the end-cap electrodes. The m/z of ion was identified by frequency scanning. **(b)** Quantification results for insulin, cytochrome c and BSA respectively. The spectrum showed a saturated number of ions which extracted from QIT in between 1.7 to 1.8×10^5.

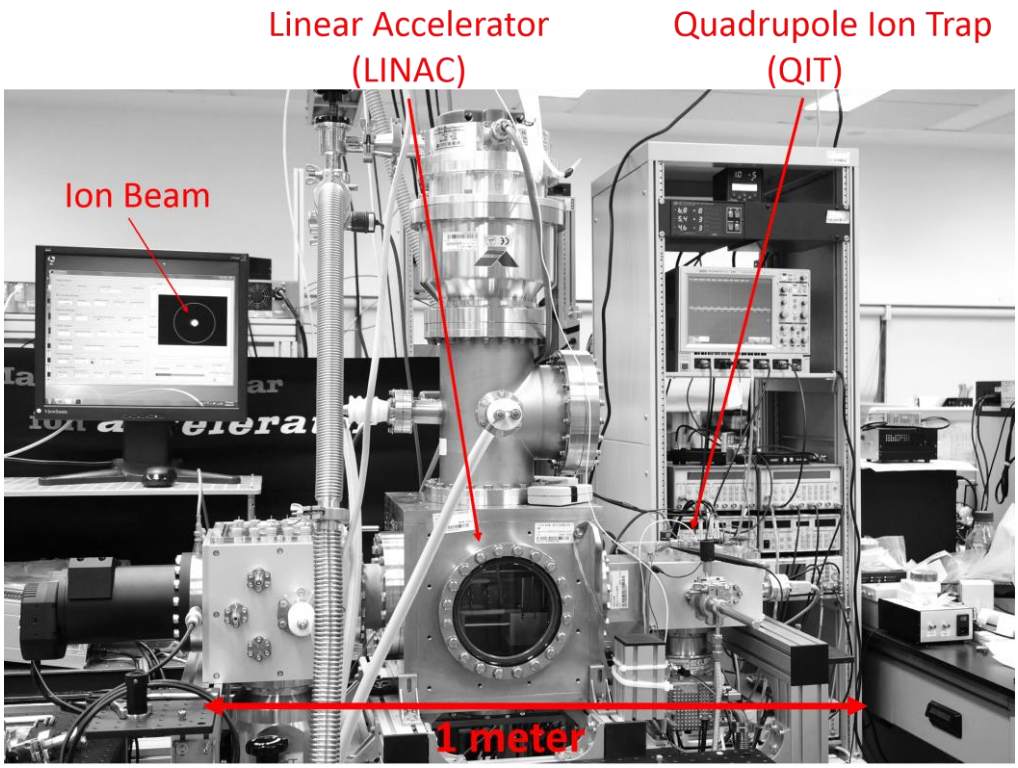

Figure S2. The picture of prototype macromolecular ion beam (QIT-LINAC) instrument. It consists of a quadrupole ion trap (QIT), einzel lens and tabletop linear accelerator (LINAC). The scale inside the picture is 1 meter.

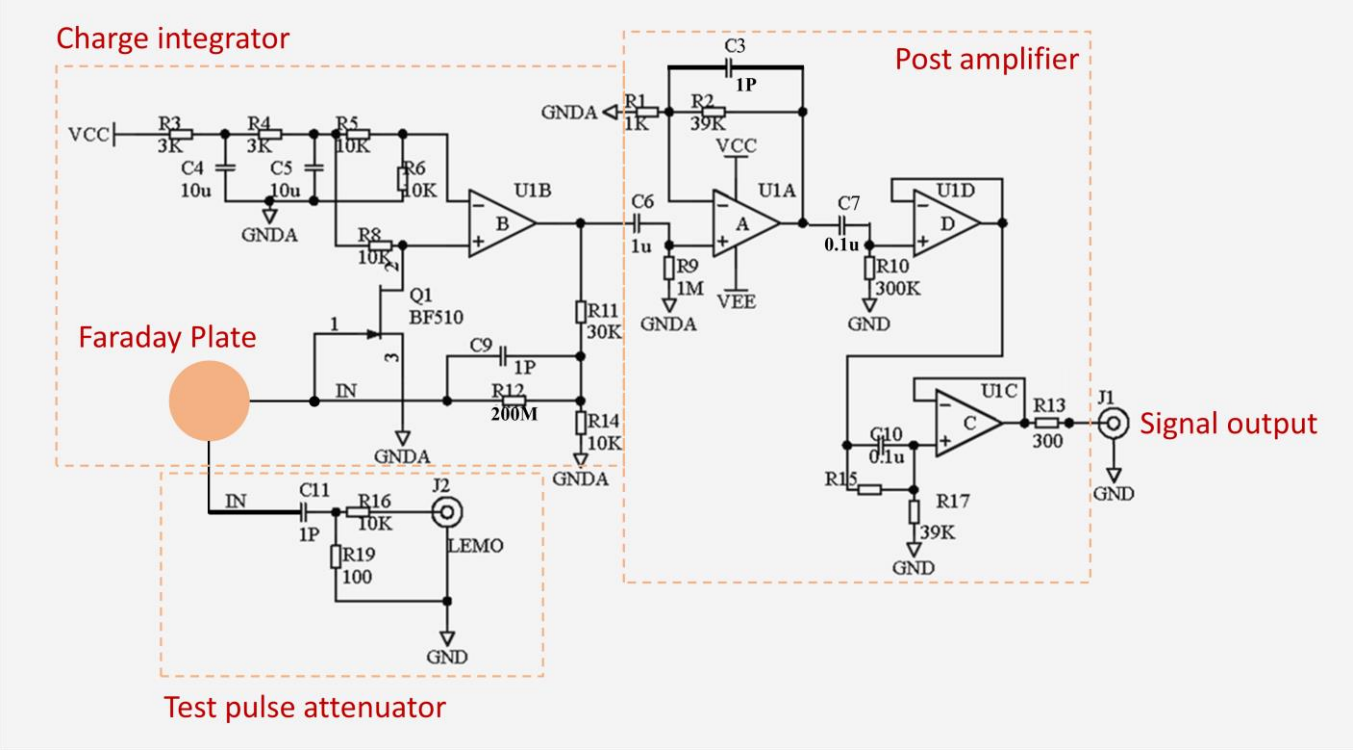

Figure S3. The design of homemade charge detector which comprised of a charge integrator, post amplifier and test pulse attenuator.

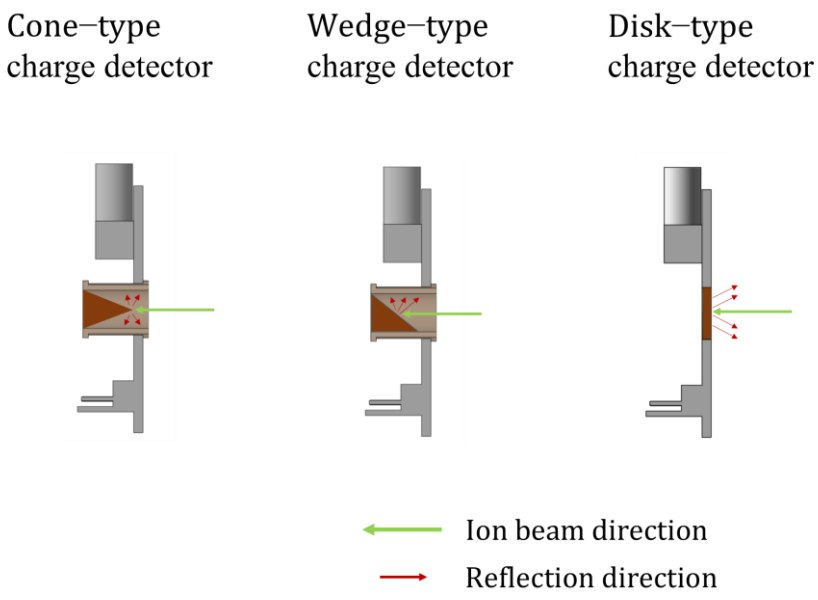

Figure S4. Three different type of charge detectors for the quantitative measurements of accelerated ion beam flux.

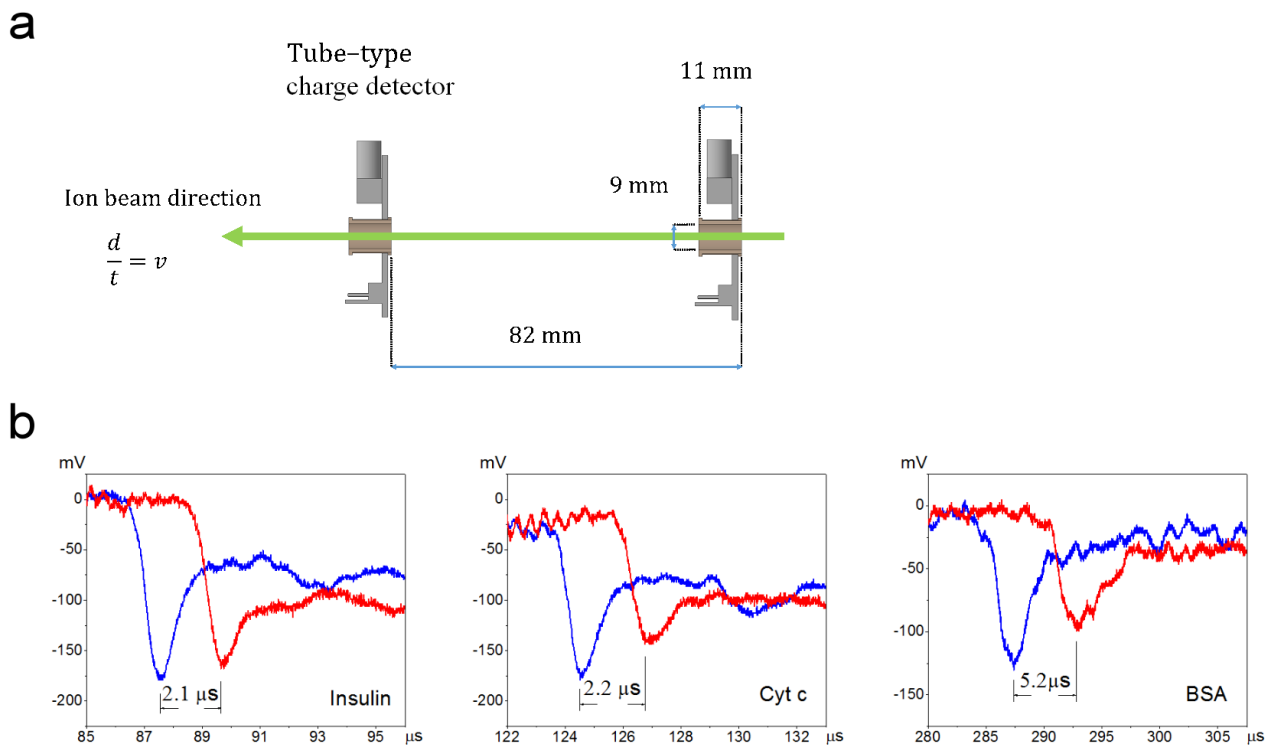

Figure S5. (a) Two tube-type charge detectors were put one after the other on the axis of ions moving for measuring ion velocity. The distance between two detectors which designated as *d* was fixed at 82 mm. The time differences of two induction peaks and average velocity of ions are designated as *t* and *v* respectively. **(b)** The spectrum of accelerated insulin (left picture), cytochrome c (middle picture) and BSA (right picture) ion beam which was applied 60 kV, 120 kV and 120 kV by LINAC respectively. The negative peaks were induced by positively charged ions.

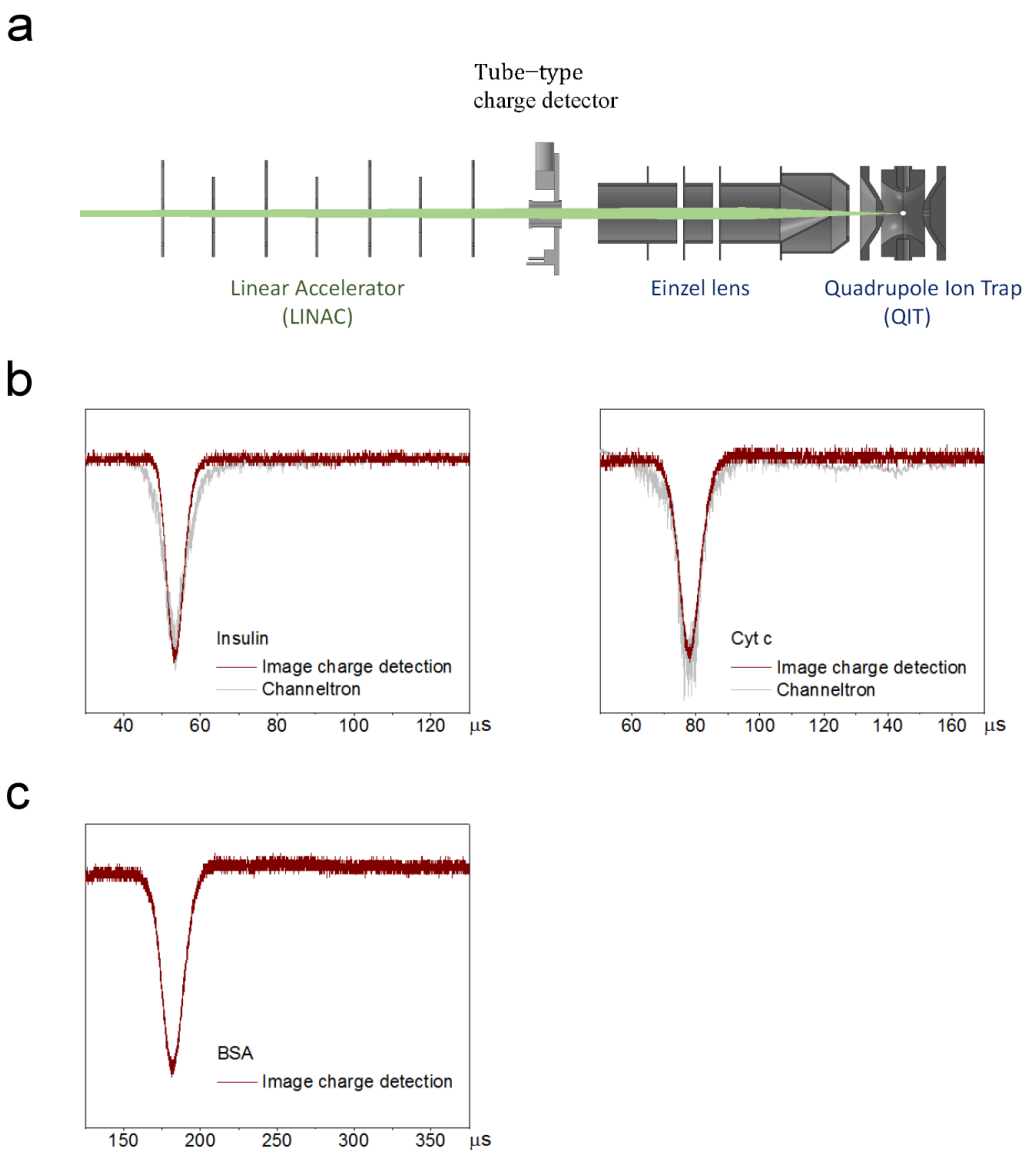

Figure S6. (a) A tube-type charge induction detector was fixed behind the einzel lens and in front of LINAC for monitoring ion beam pulse through image charge detection. **(b)** The pulse duration of extracted insulin (left picture) and cytochrome c (right picture) ion beam from QIT by both charge detector and channeltron. **(c)** The pulse duration of extracted BSA ion beam from QIT by charge detector. All Signal peaks were normalized for the comparison.

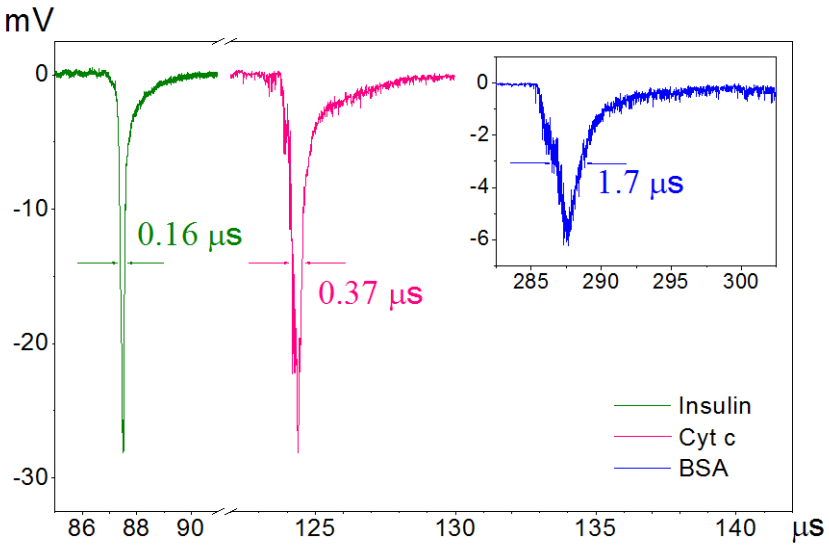

Figure S7. The pulse duration measurements of accelerated insulin, cytochrome c and BSA (inset picture) ion beam with kinetic energy of ~ 44, 88 and 88 keV, respectively. A channeltron was applied -1500, -1700 and -1900 volts separately for measuring each positively charged ion beam. The pulse width (FWHM) of 0.16, 0.37 and 1.7 μs was observed from insulin, cytochrome c and BSA ion beam respectively. As for the tail, it is due to the RC time of electric circuit when ion beam pulse was recorded.

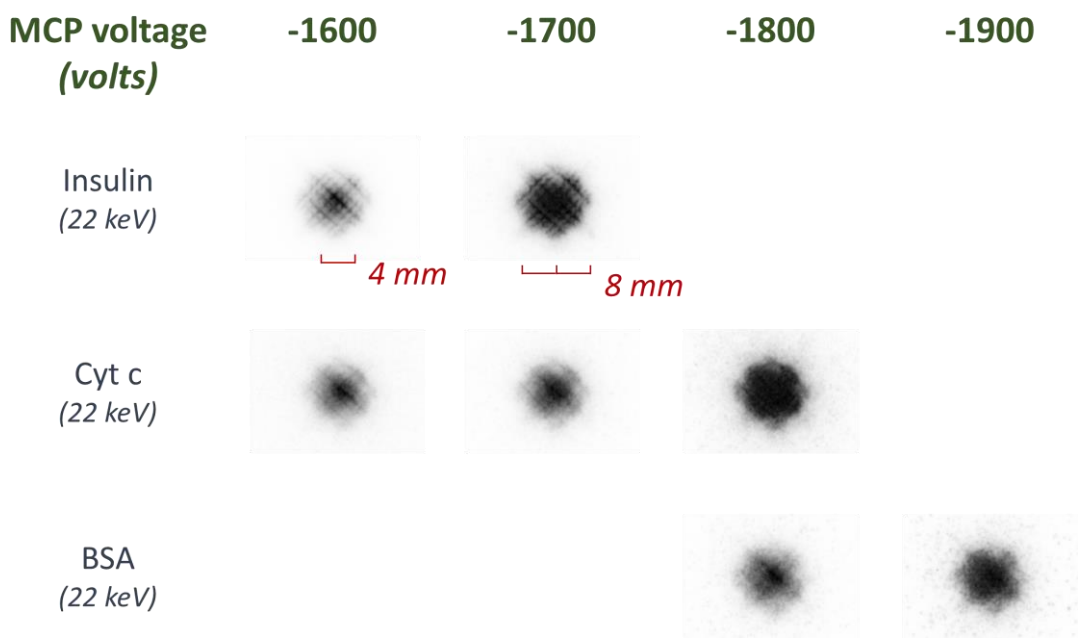

Figure S8. Images of accelerated insulin, cytochrome c and BSA ion beam with different applied voltages (bold type with green color) of micro-channel plate (MCP). The average kinetic energy of ions is ~ 22 keV. Apparently, an increasing of MCP voltages accompanied with an increasing of size. The minimum beam size is around 4 mm diameter.

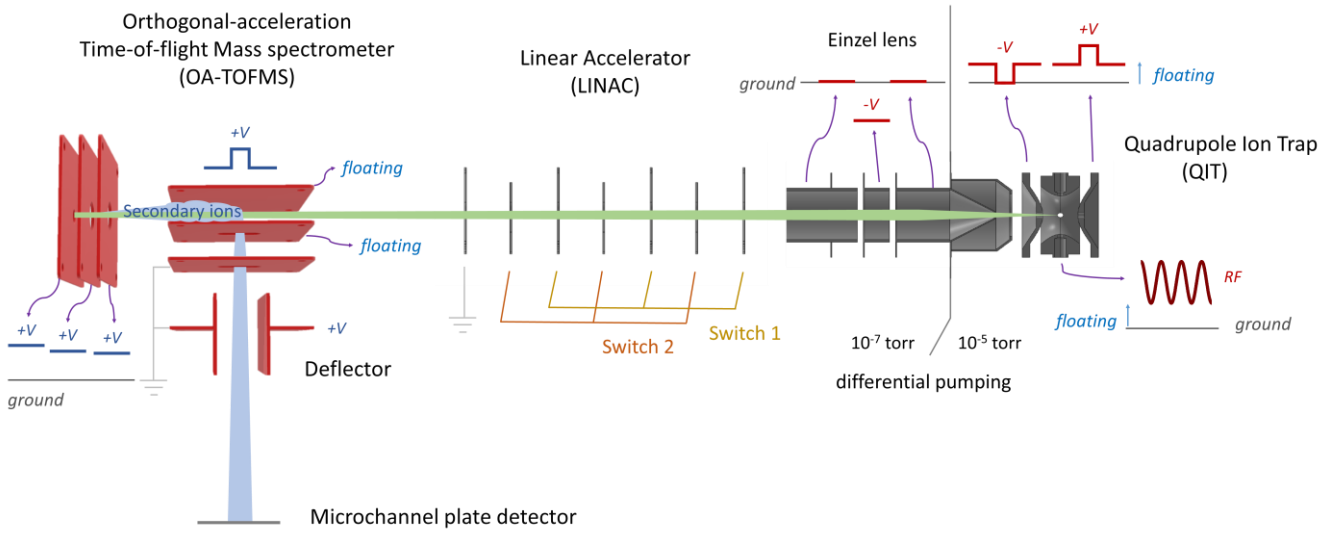

Figure S9. Experimental setup of the focused macromolecular ion beam and orthagonal acceleration time-of-flight (OA-TOF) mass spectrometer. When accelerated ion beam passed a parallel electrical field with equal supplied voltage (8 kV), accelerated ions hit a gold-coated surface through a series of electrical plates (7.5 kV, 8.0 kV, 8.2 kV) and then bombarded secondary ions. These secondary ions were pushed from the surface and finally confined in the parallel electrical field. In the same time, a pulse voltage (10 kV) was applied on one of the parallel electrical field for OA-TOF. (V: voltage).

Table S1. The assignment of cytochrome c fragment ions under ~ 8 keV surface impact

Measured m/z	Predicted m/z	Assignment	Note
1411.5	1410.7	y_{12}	*
1346.0	1346.8	c_{12}	
1044.1	1043.5	b_{10}	**
1037.6	1036.5	b_9	*
908.6	908.4	b_8	*
644.9	644.3	b_6	**
563.3	562.3	y_5	
454.8	453.2	a_4	*
402.9	402.2	b_4	**
392.1	392.7	$(CsI)Cs^+$	
363.1	363.2	y_3	
303.8	305.1	c_3	**
259.5	260.1	a_3	**
237.0	237.1	a_2	*
215.6	217.1	b_2	**
196.2	196.7	Au^+	

* From TYTDANKNKGITW sequence

** From TDANKNKGIT sequence