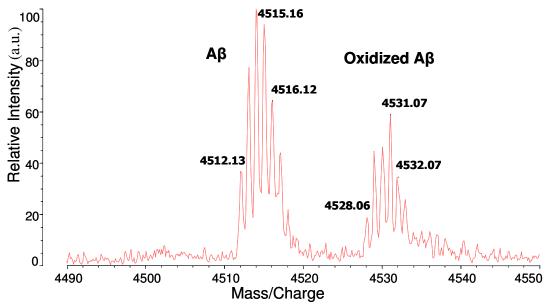
## **Supporting Information**

# Detection and Identification of Bioanalytes with High Resolution LSPR Spectroscopy and MALDI Mass Spectrometry

#### **Supplemental Figures**

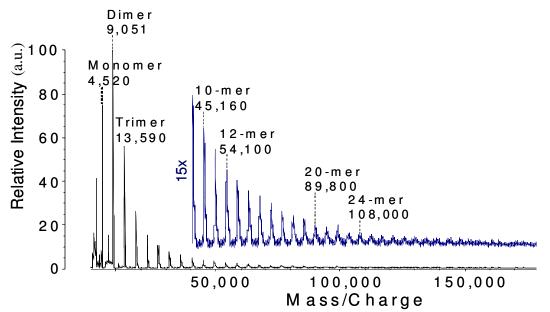
<u>High Resolution Reflectron Mode MALDI of A $\beta$  Monomer</u> In addition to conventional linear mode MALDI-TOF, we also examined the A $\beta_{1-42}$  on the stainless steel plate using higher resolution reflectron mode (see figure S1). Two peaks are evident, separated by 16 Da due to oxidation of the A $\beta$  monomer.



**Figure S1.** High resolution reflectron mode MALDI-MS of A $\beta$  monomer on a stainless steel MALDI plate. The difference in mass between the peaks is 16 Da due to oxidation of the A $\beta$ . The theoretical monoisotopic mass of [A $\beta$  + H<sup>+</sup> ion] is 4515.1 Da, indicating a small absolute calibration error (approximately 3 Da).

## <u>Aβ oligomers</u>

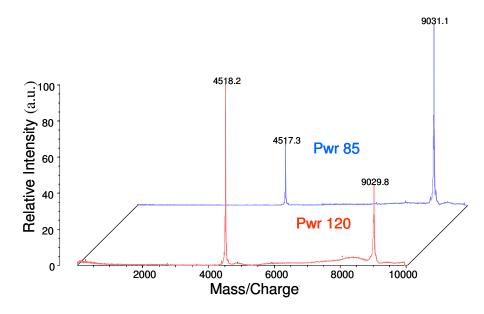
The MALDI spectrum also displays a series of oligomers up to at least 30-mers (see Figure S2). The observed ions are likely a combination of intact molecular ions, fragments from larger oligomers, and gas phase aggregates.



**Figure S2** MALDI-TOF spectrum of a synthetic  $A\beta_{1-42}$  ADDL sample on a stainless steel plate, using sinapinic acid as the matrix. A series of oligomers is evident continuing beyond 24 mers. The inset shows the same data, with the y-scale magnified by 15 times. The spectrum is the average of 172 laser shots.

### Post Source Decay MALDI

To test if the molecules break up during flight, we used an ion gate to selectively pass just the dimers (9 kDa), and looked to see what mass range was observed after the reflectron (this technique is known as post source decay, PSD). We observed two peaks, one for the dimer, and one for the monomer (indicating fragmentation). The monomer/dimer ratio increased with increasing laser power, supporting the hypothesis that the fragmentation is power dependent (see figure S3).



**Figure S3.** Power dependant fragmentation of  $A\beta$  dimers. An ion gate was used to pass only the dimer mass (9 kDa) and the post source decay (PSD) products were recorded. The monomer to dimer ratio increases with increasing laser power. Peaks are scaled to the maximum intensity, which is 2.0 times highter at power 120 (arbitrary units).