Electronic Supplementary Information

Noble metal alloy formation in the gas phase derived from protein templates: Unusual recognition of palladium by gold

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Electronic Supplementary Information 1

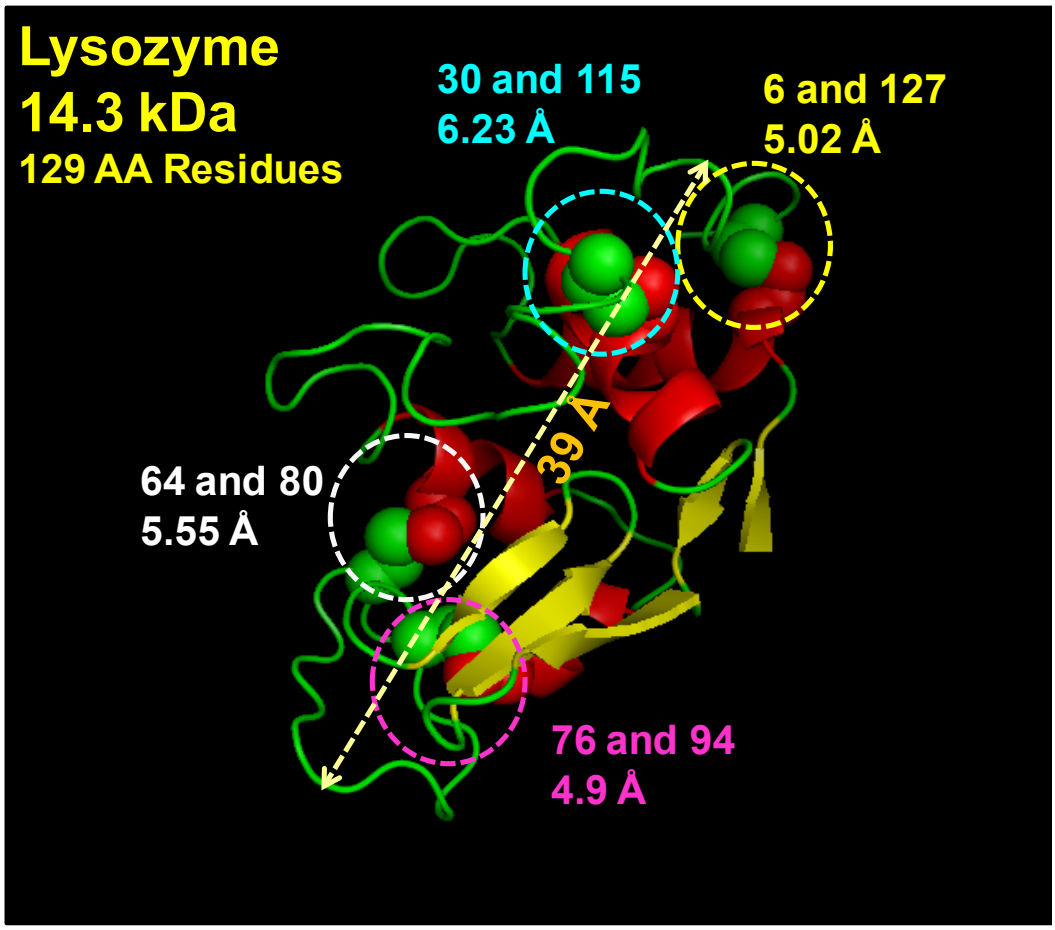

Fig. S1† Structure of the protein, lysozyme having a molecular weight of 14.3 kDa and 129 amino acid residues among which eight are cysteines marked as circles. The typical distance and S-S bond lengths are shown. This figure is reproduced from PDB file 2LYZ (*J.Mol.Bio.* 1974, **82**, 371-391) using PyMOL software.

Electronic Supplementary Information 2

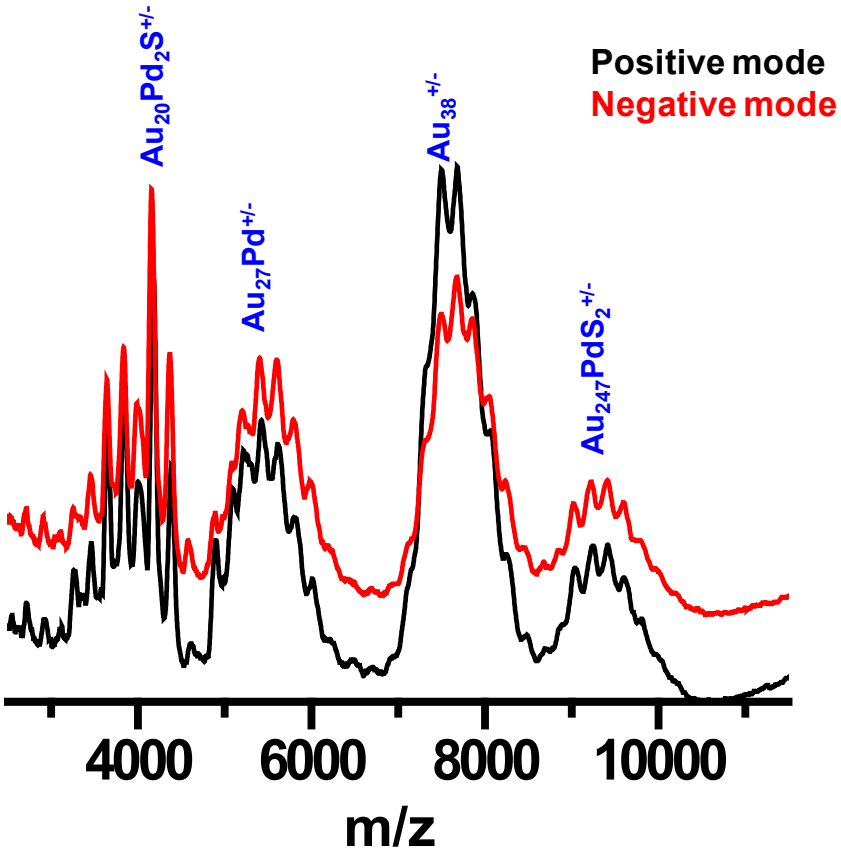

Fig. S2† Comparison between linear positive and negative mode MALDI MS of 3:1 Au:Pd adduct of Lyz, showing the same peaks in both the cases.

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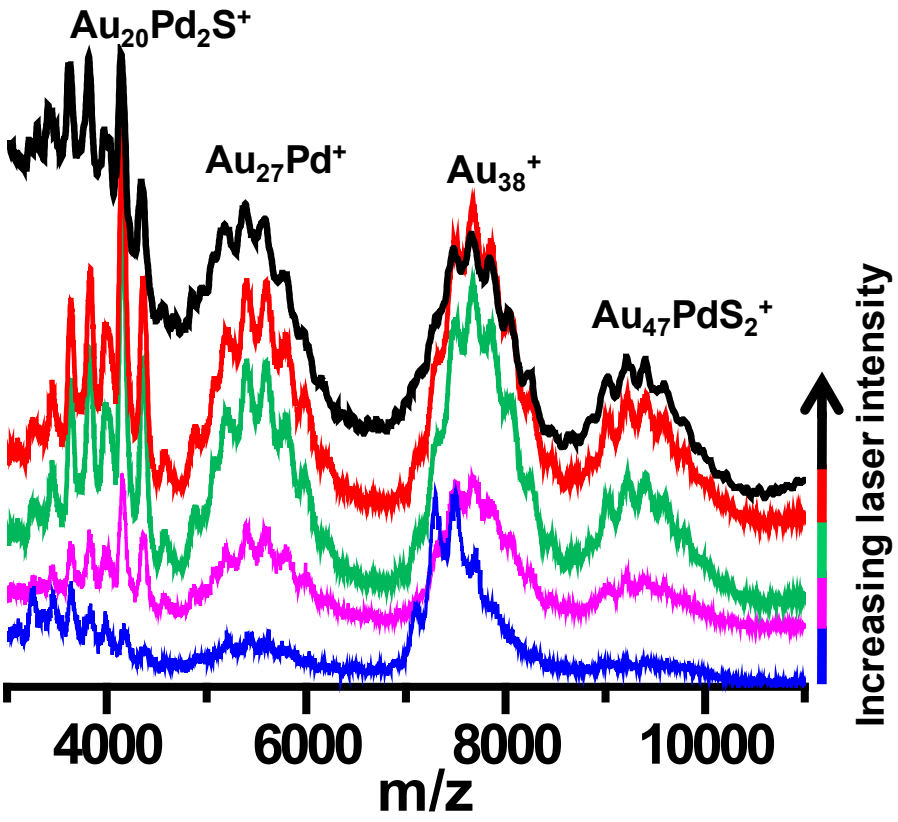

Fig. S3† Laser intensity dependent study of MALDI MS with increasing laser intensity in linear positive mode. There is no change in the peak position with enhanced laser intensity. The spectra were collected for the 3:1 Au:Pd mixed adduct system in linear positive mode and the laser intensity was varied from 1800 to 2600 (instrumental unit) with an increase of 200 in intensity at each step, plotted in blue, magenta, green, red and black, respectively.

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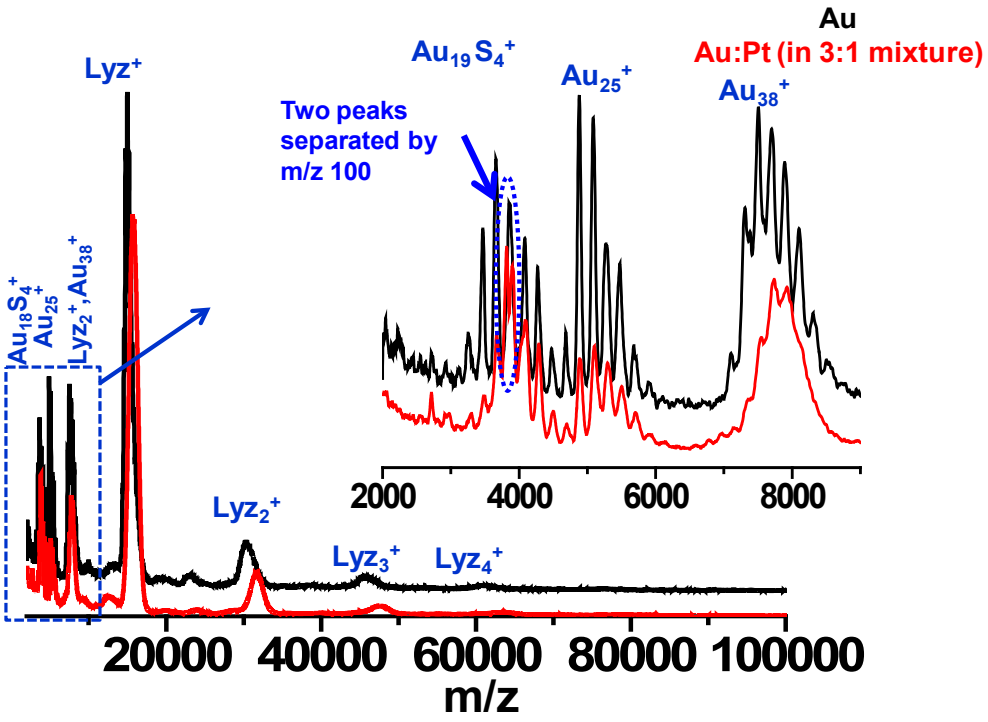

Fig. S4† Comparison between the MALDI MS of 3:1 Au:Pt adduct and Au only adduct of Lyz in linear positive ion mode. $Au_{19}S_4^+$ splits into two peaks separated by m/z 100. Other peak positions remain the same, although intensity of Au_{25}^+ and Au_{38}^+ regions decreases relative to $Au_{18}S_4^+$.

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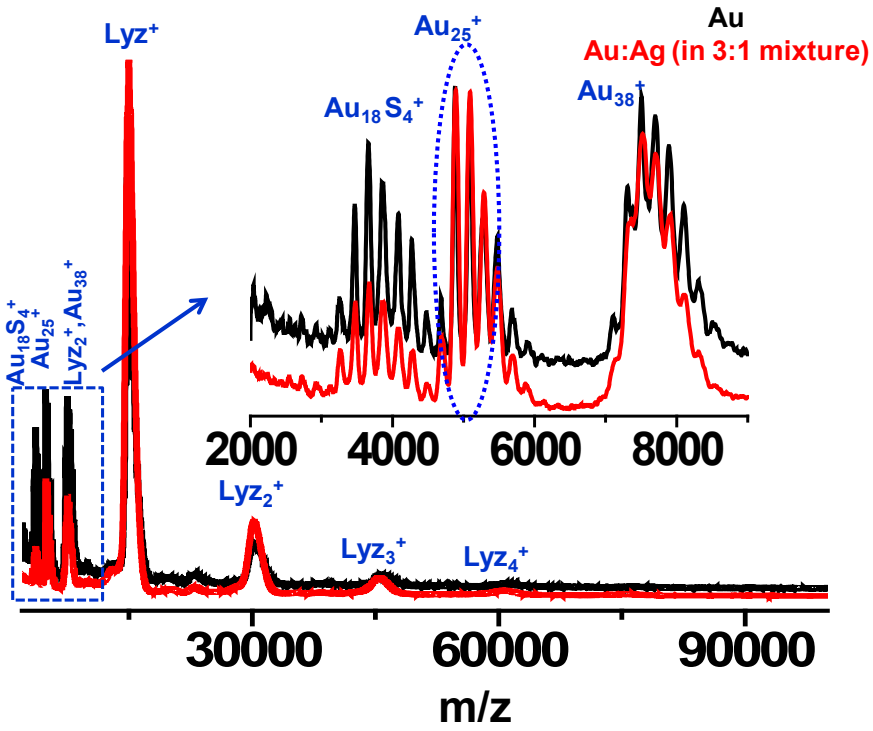

Fig. S5† Comparison between the MALDI MS of 3:1 Au:Ag adduct and Au only adduct of Lyz in linear positive ion mode. No alloy was formed, only Au_{25}^{+} region intensifies.

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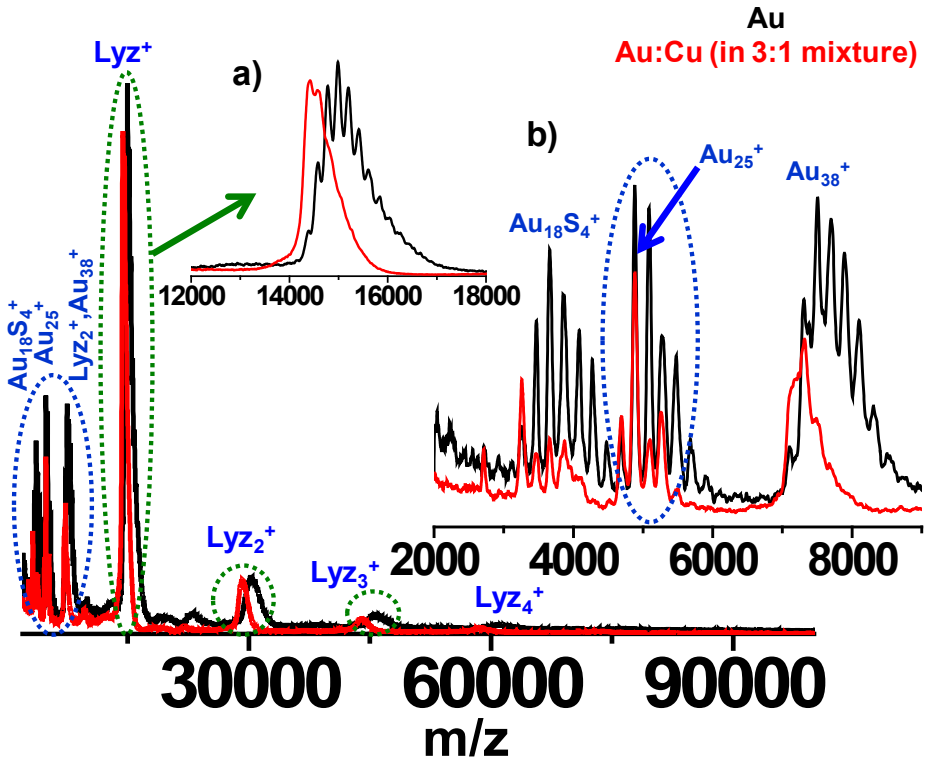

Fig. S6† Comparison between the MALDI MS of 3:1 Au:Cu adduct and Au only adduct of Lyz in linear positive ion mode. Large change in the overall spectrum is observable. Inset a) shows less number of Au attachment to parent Lyz monomer in case of Cu addition compared to Au alone sample. Inset b) is shows that preferentially Au_{25}^{+} is formed when Cu is present in the system.

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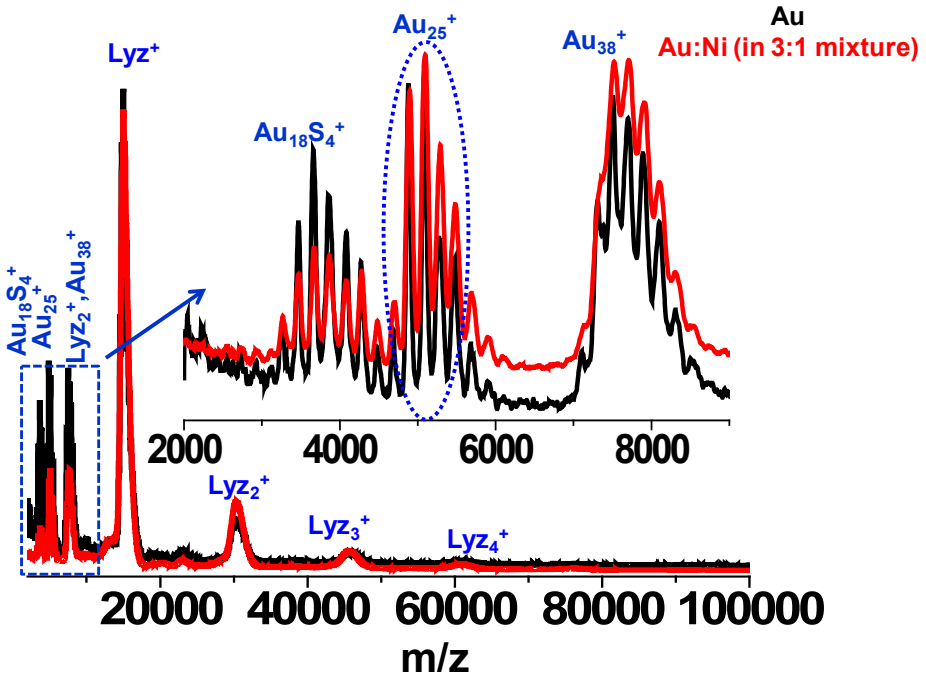

Fig. S7† Comparison between the MALDI MS of 3:1 Au:Ni adduct and Au only adduct of Lyz in linear positive ion mode. No alloy was formed, only Au_{25}^{+} region intensifies.

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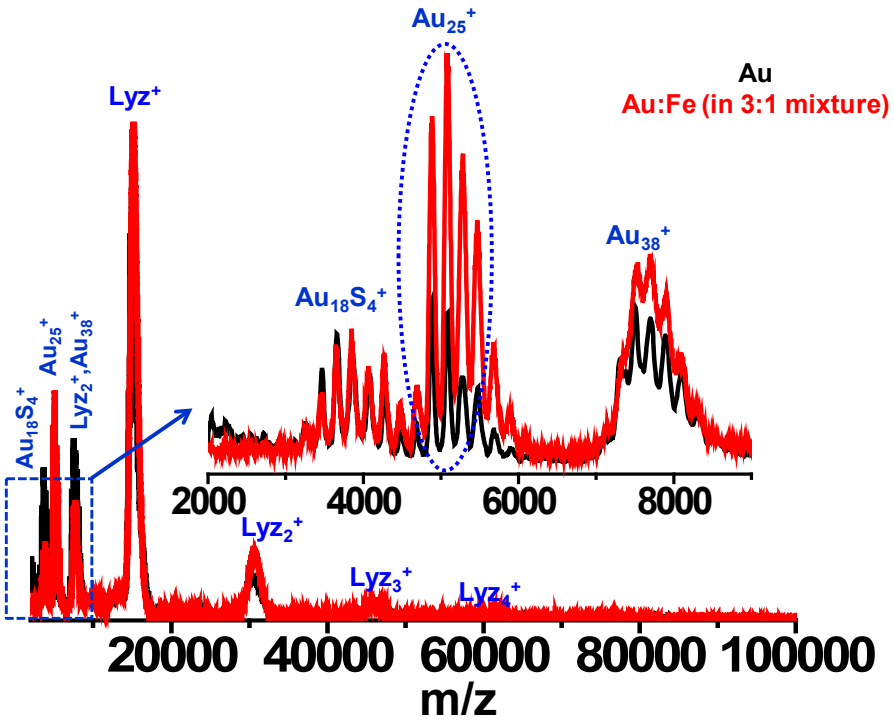

Fig. S8† Comparison between the MALDI MS of 3:1 Au:Fe adduct and Au only adduct of Lyz in linear positive ion mode. No alloy was formed, only Au_{25}^{+} region intensifies.

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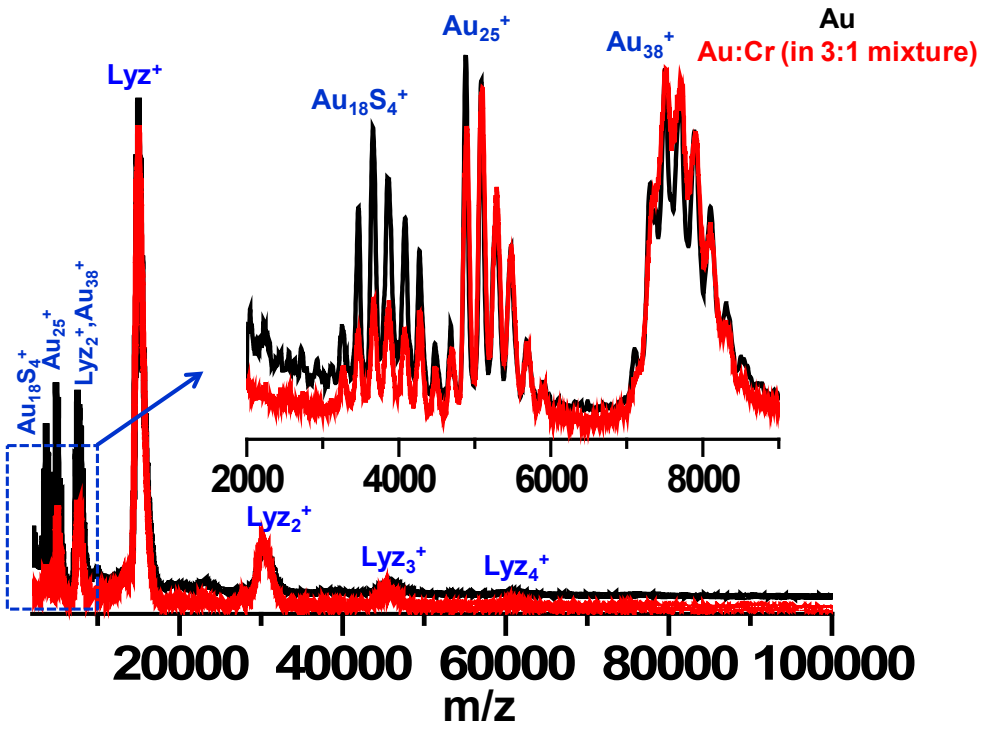

Fig. S9† Comparison between the MALDI MS of 3:1 Au:Cr adduct and Au only adduct of Lyz in linear positive ion mode. No alloy was formed, only Au_{25}^{+} region intensifies.

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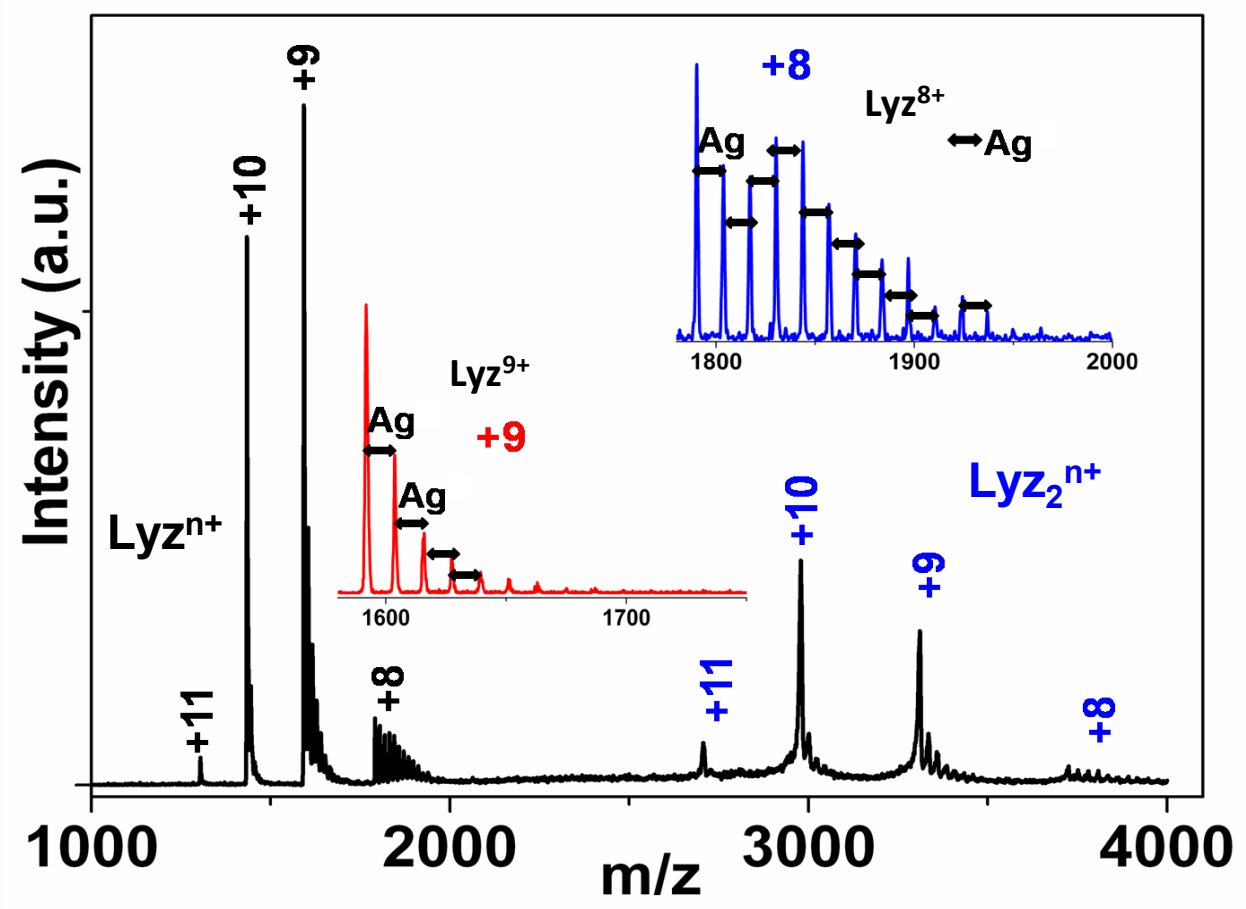

Fig. S10† Positive mode ESI MS of Ag-Lyz adduct showing multiple Ag additions to various charge states for both monomer and dimer of Lyz. In the inset, +8 and +9 charge states of Lyz are expanded. For Lyz^{8+} we can see that two consecutive Ag addition peaks have same intensity which is not seen for the +9 charge state.

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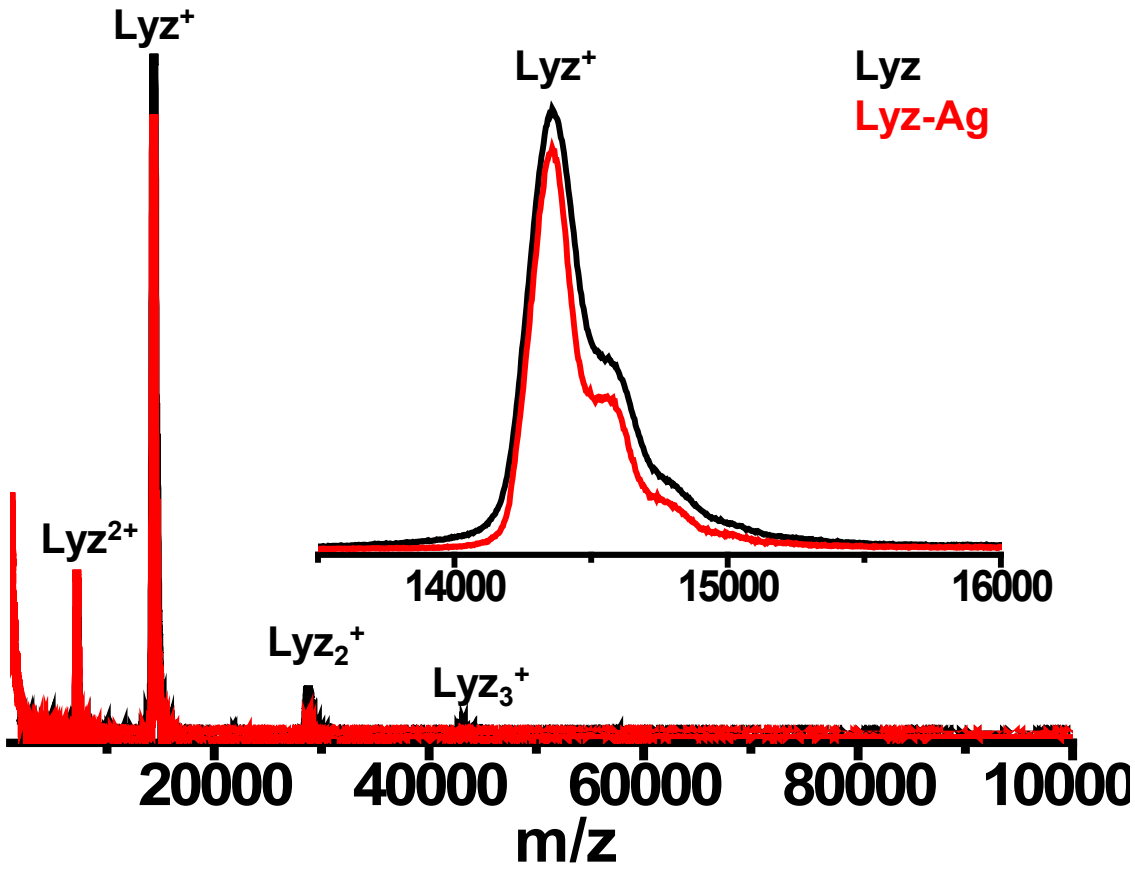

Fig. S11† MALDI MS of Ag-Lyz adduct in the linear positive mode showing no Ag attachment to it which implies that loosely bound Ag atoms have been desorbed during laser ablation.

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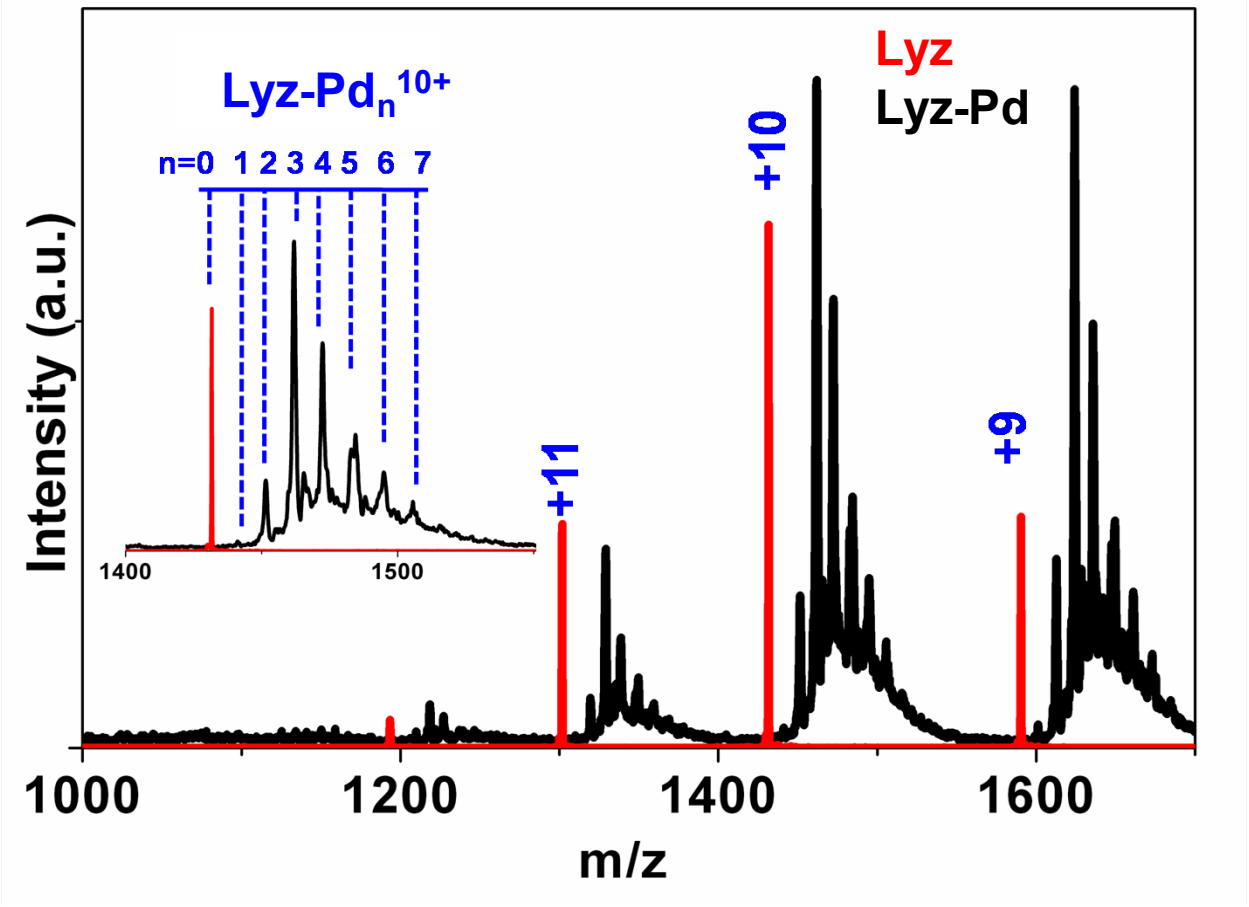

Fig. S12† Comparative ESI MS of Lyz and Pd-Lyz adduct in positive ion mode showing multiple Pd attachment to respective charge states. 10+ charge state has been expanded in the inset and Pd added peaks are marked.

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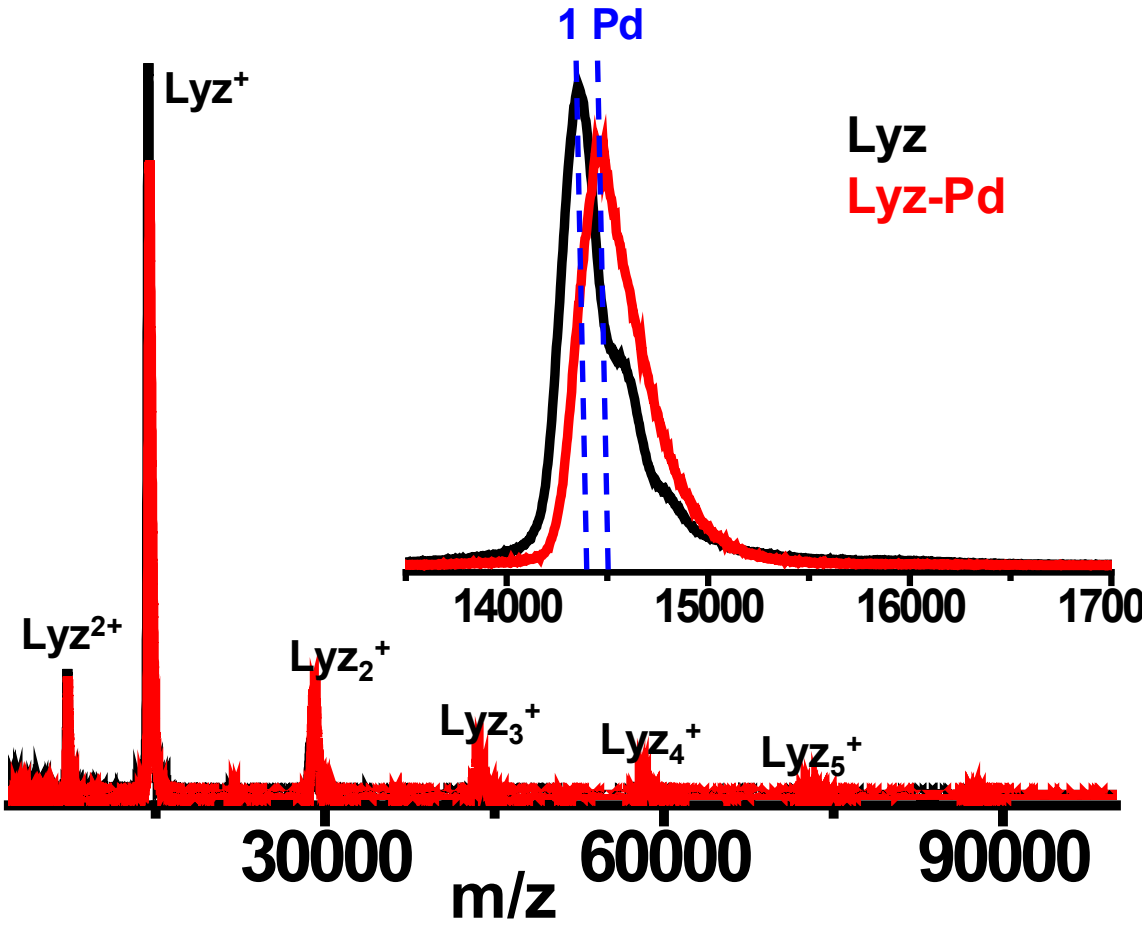

Fig. S13† Comparative MALDI MS of Lyz and Pd-Lyz adduct in linear positive ion mode showing Pd attachment to the respective charge state.

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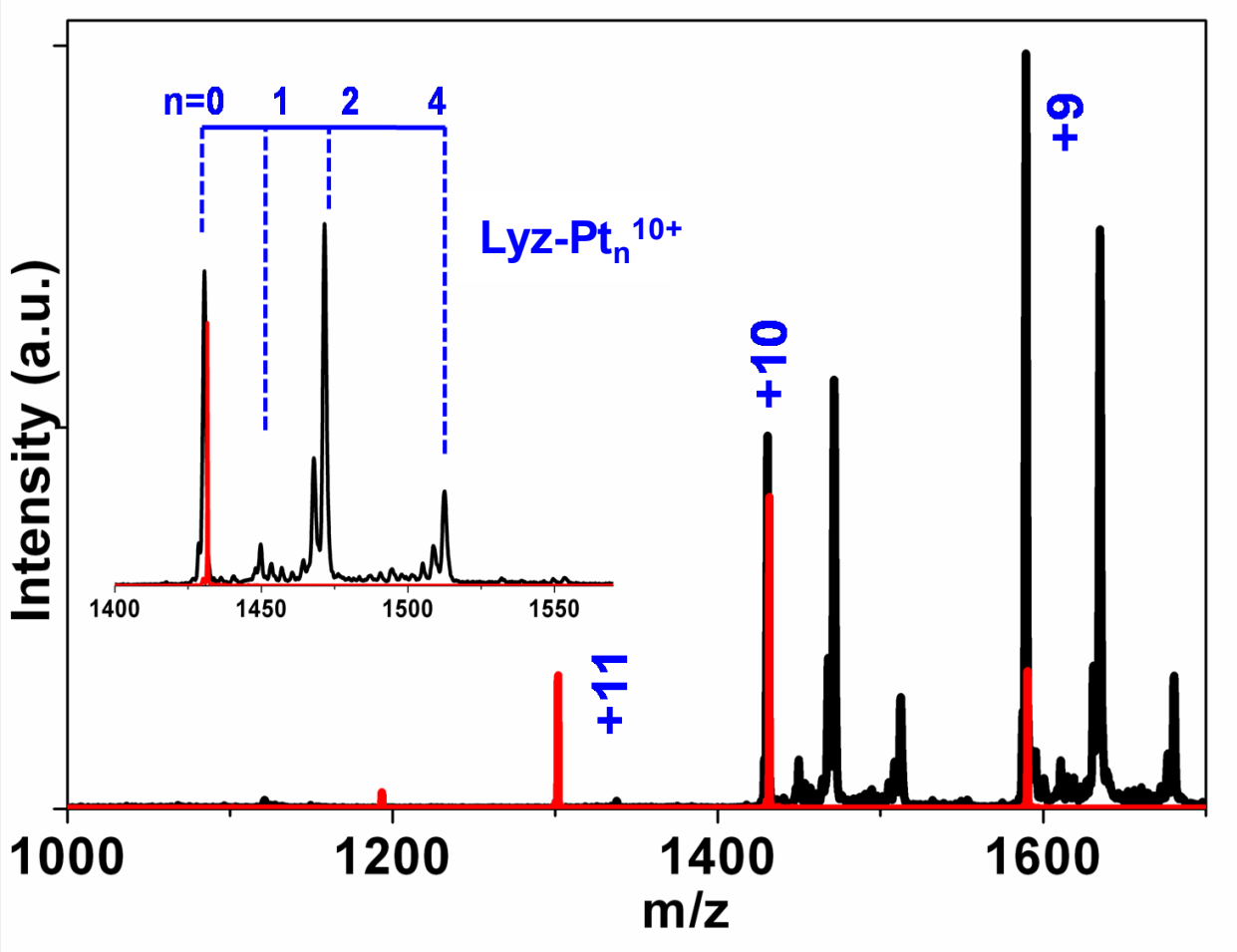

Fig. S14† Comparative ESI MS of Lyz and Pt-Lyz adduct in the positive ion mode showing multiple Pt attachment to the respective charge state. 10+ charge state has been expanded in the inset and Pt added peaks are marked. Odd number Pt attachment peaks are weak.

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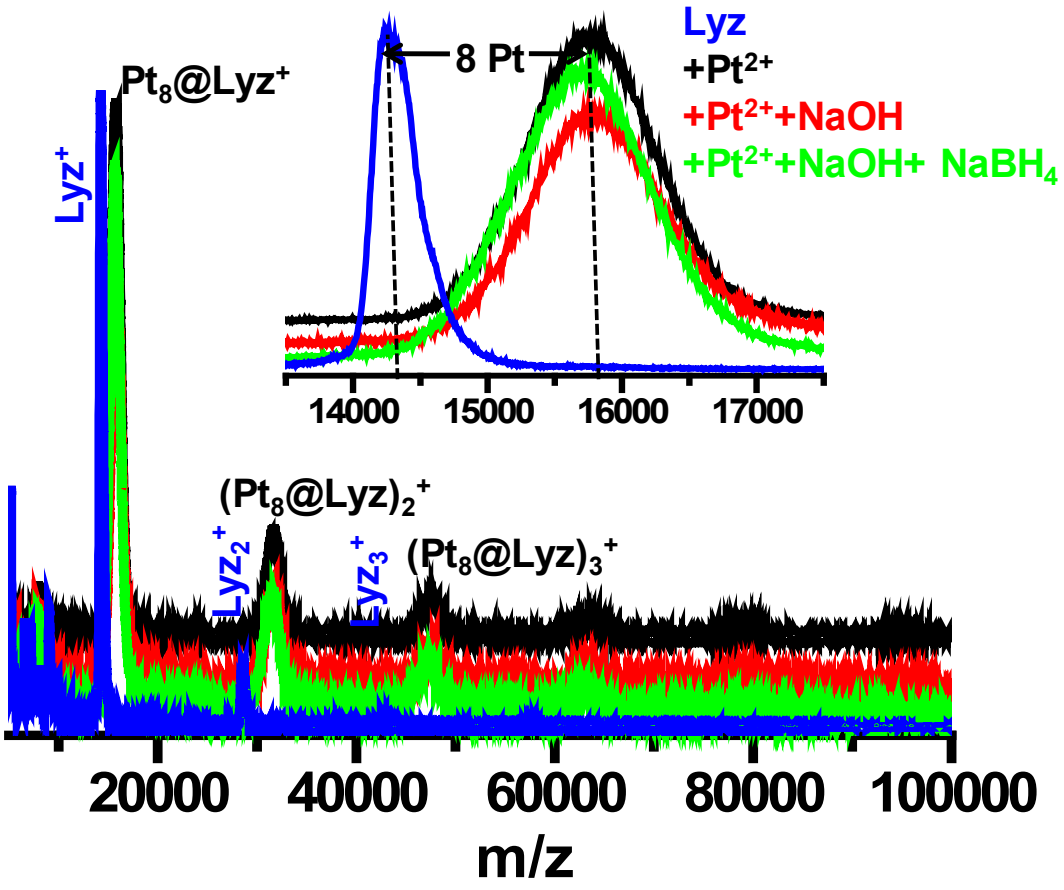

Fig. S15† Comparative MALDI MS of Lyz and Pt-Lyz at various conditions in linear positive mode showing 8 Pt attachments to protein at all conditions. Monomer region is expanded in the inset.

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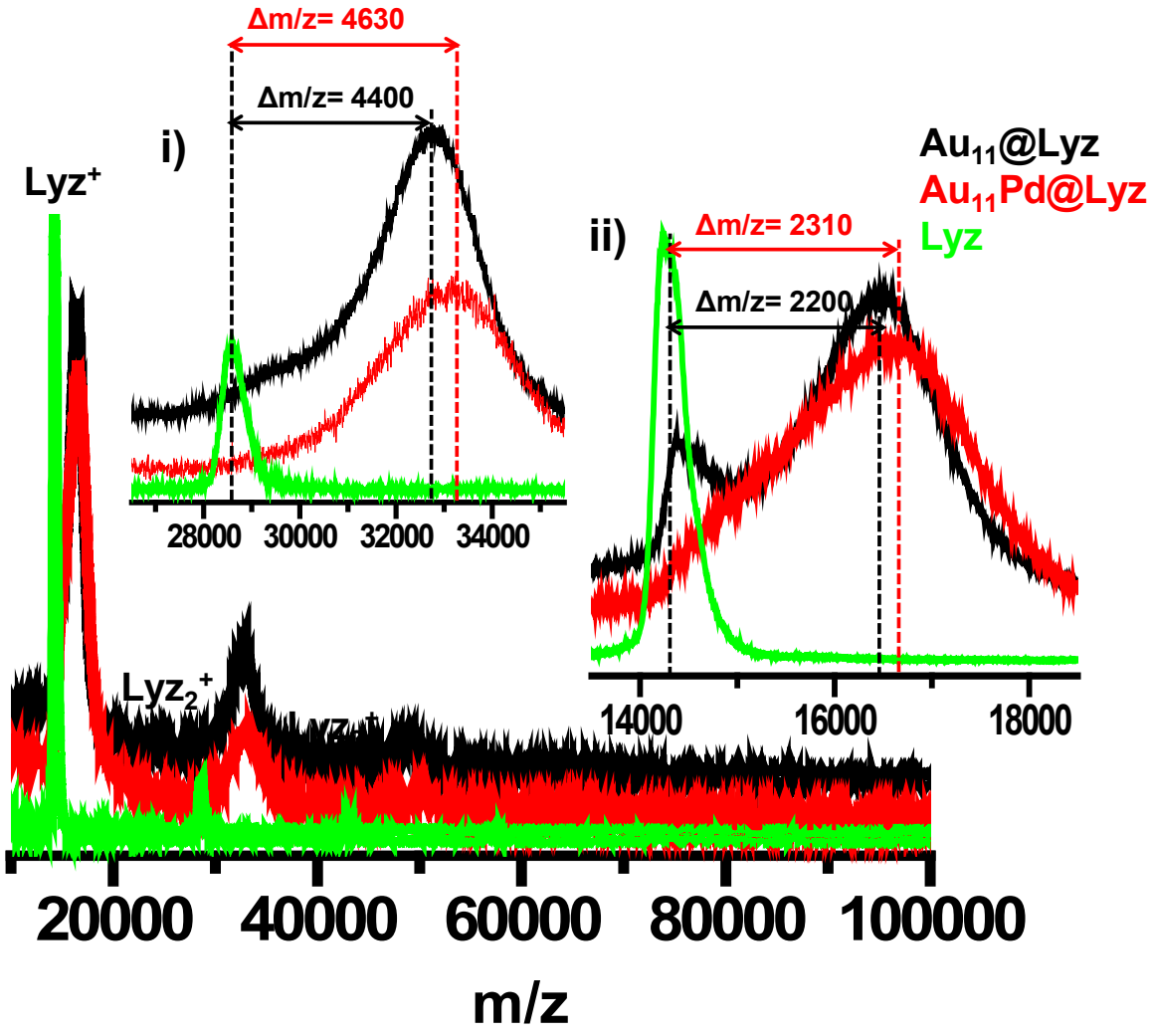

Fig. S16† MALDI MS of Au_{QCs}@Lyz and Au-Pd_{QCs}@Lyz in linear positive mode showing one (likely) Pd attachment to the existing Au_{11} core. The separation is clearly visible for the dimer region expanded in the inset i). Monomer region is expanded in inset ii).