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Protein-encapsulated gold cluster aggregates: The case of lysozyme†

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Fig. S1[†] Time dependent MALDI MS of Lyz: Au^{3+} (molar ratio of 1:4) over 15 days time window. A linear dependence of Au ion uptake is seen for the oligomerized Lyz. While monocation of Au_{QC} @single protein shows a separation of 10 Au atoms from the parent protein peak, oligomerized Lyz show separation of $n \times 10$ (where n=2, 3, 4,...) from their parent oligomerized Lyz where n is the aggregation number. Inset shows the monomer region.



Fig. S2[†] The survey spectrum is characterized by peaks due to carbon, oxygen, nitrogen, sodium, chlorine, gold and sulphur. Carbon 1s binding energy for the main peak is taken to be 285 eV and other binding energy values have been determined.



Fig. S3^{\dagger} SEM EDAX spectra of Au_{QC}@Lyz using Lyz: Au³⁺ ratio 1:4. Inset A, is the SEM image of the sample. B and C are EDAX mapping of SK and AuM corresponding to A. D is the quantification of S and Au in the sample.



Fig. S4[†] Concentration dependent UV-Vis spectra of as-synthesized Au_{QC}@Lyz. The peak at 290 nm is assigned to the protein. A characteristic hump near 355 nm is also seen. There is no specific feature of cluster core in these spectra. In the inset, HRTEM image is shown, clusters are sized between 1.1 ± 0.1 nm. There is no feature corresponding to the formation of bigger plasmonic nanoparticles.



Fig. S5[†] Time dependent MALDI MS of Lyz: Au^{3+} (molar ratio 1:5) over 15 days time window. A linear dependence of Au uptake is seen for the oligomers. While monomer shows a separation of 11 Au atoms from the parent protein peak, oligomers show separation of n×11 (where n = 2, 3, 4...).



Fig. S6[†] Time dependent MALDI MS of Lyz: Au^{3+} (1:8 molar ratio) over 15 days time window. A linear dependence of Au uptake is seen for the oligomers. While monomer shows a separation of 12 Au atoms from the parent protein peak, oligomers show separation of n×12 (where n=2, 3, 4,...).



Fig. S7[†] Time dependent MALDI MS of Lyz: Au³⁺ (1:2.5molar ratio) over 15 days time window. A linear dependence of Au uptake is seen for the oligomers. While monomer shows a separation of 10 Au atoms, after 5 days the peak shifts to 12 Au atoms. In the dimer and trimer regions two distinct peaks appear. For dimer, peaks are separated by 12 and 20 Au atoms while in trimer, peaks are separated by 12 and 22 Au atoms.



Fig. S8^{\dagger} Time dependent luminescence spectra of Lyz: Au³⁺ (1:5molar ratio) over 15 days time window. Upon exciting at 360 nm, the cluster emits at 666 nm. Insets show the photographs of the sample under ultra-violet and visible light.



Fig. S9^{\dagger} Time dependent luminescence spectra of Lyz: Au³⁺ (1:8molar ratio) over 15 days time window. Upon exciting at 360 nm the cluster emits at 666 nm. Insets show the photographs of the sample under ultra-violet and visible light.



Fig. S10^{\dagger} Time dependent luminescence spectra of Lyz: Au³⁺ (1:2.5 molar ratio) over 7 days time window. Upon exciting at 370 nm the cluster emits at 690 nm which again blue shifts to 675 nm upon longer time. Insets show the photographs of the sample under ultra-violet and visible light. Calculated quantum yield is 15.2%.



Fig. S11[†] Infrared (IR) spectra of Lyz and Au_{QC}@Lyz showing significant change in the amide region.