Supporting Information

Charging of Ligand Protected Gold Nanoparticles in Electrospray Ionization: Probing Ligand Bond Strength by Charge Detection Mass Spectrometry

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1. Experimental section

Materials. All the materials were commercially available. (11-mercaptoundecyl)-N,N,N-trimethylammonium bromide (MUTAB), and Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$)

were purchased from Sigma Aldrich. Methanol and Water were purchased from J. T. Baker. All chemicals and solvents were used as such without further purification.

Synthesis of Au-MUTAB nanoparticles

Initially, MUTAB (40 mM, 150 μL) was first dissolved in water (1.8 mL) at 30 °C, and kept for stirring at 1500 rpm. Then $HAuCl_4.3H_2O$ (50 mM, 40 μL) was slowly added dropwise to the solution, and the reaction was continued for 24 hours in dark conditions. Finally, the resultant solution was centrifuged at 14000 rpm for 5 min, and the precipitate was collected. This centrifugation step was repeated three times for extreme purification of the product. The obtained precipitate, which is the Au-MUTAB nanoparticle, was purple in color and re-dispersed in water for further analysis.

40, 60, 80 nm Au nanoparticles

Gold nanoparticles, stabilized suspension in citrate buffer, were purchased from Sigma-Aldrich (Refs. 741981, 742015, and 742023). The stock solutions were directly diluted in the water/methanol (1:1) mixture.

2. Instrumentation

Inst Perkin Elmer Lambda 25 UV-vis spectrometer was used to record the UV-vis spectra of the nanoparticles. Absorption spectra were typically measured in the range of 300-1100 nm with a bandpass filter of 1 nm. Dynamic light scattering (DLS) measurements was done using a Malvern Zetasizer ZSP instrument equipped with a 633 nm (He-Ne) laser. Transmission electron microscopy was performed using a JEOL 3010, 300 kV instrument at an accelerating voltage of 200 kV. The accelerating voltage was kept low to reduce beam induced damage. Samples were prepared by drop casting the solution on a carbon-coated copper grid and dried under ambient conditions.

Charge calibration procedure in CDMS

Calibration of charge was performed using a test capacitor that allows a known amount of charge to be pulsed onto the pick-up tube. The test tube pulses are generated with a shaping-pulse generator so that the time-dependent signal response can be determined as well. An ion with 300 charges generates a ~49 mV peak-to-peak pulse (82 µV/e^-). The charge of a particle is then directly deduced from this calibration and from the average value of the voltage intensity of the pulses generated by the particle on the detector. Also, the rms noise with the present set-up is equivalent to ~10e^-. The mass-to-charge m/z ratio of an ion is determined from the time-of-flight (time delay between the positive and negative pulses that correspond to the entrance and exit of ions from the detector tube).

To further improve the calibration, we used polystyrene microspheres (54 nm, 120 nm, 200 nm supplied by ABCR and 320 nm supplied by Sigma-Aldrich) as external calibrants. Such polystyrene microspheres cover the mass range of gold nanoparticles investigated in this work, have low dispersion, and have been found to be softly and efficiently transfer in the gas phase by ESI. The average masses obtained from the mass distribution of the polystyrene microsphere ions measured by CD-MS using the internal calibration were plotted against their calculated mass (the average volumes of polystyrenes were converted into molecular mass assuming perfectly spherical nanoobjects and a homogeneous density of 1.05). A linear fit through the measured mass values was used for the external calibration.

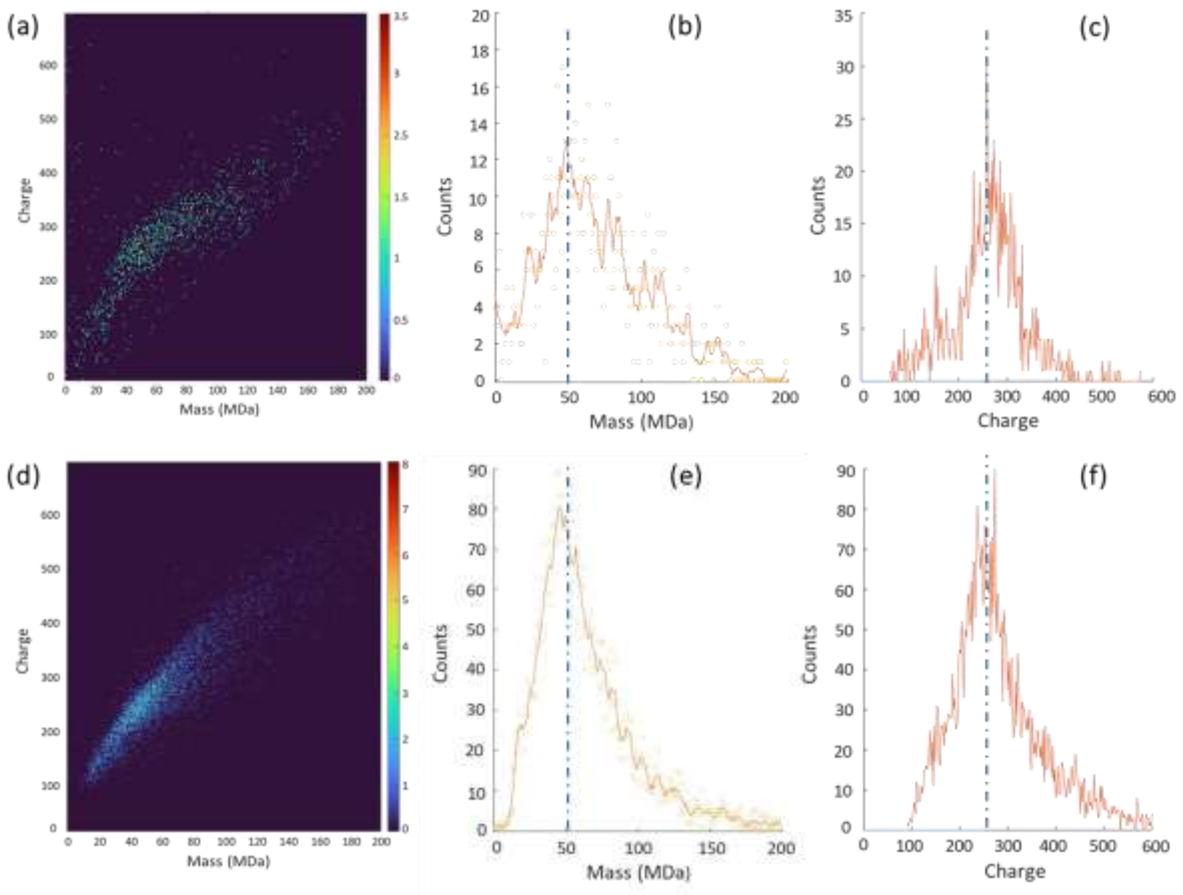


Figure S1. The charge versus mass plot obtained in CDMS under two different ionization conditions of (**a**) nanospray and (**d**) macrospray; The mass plot obtained from (**b**) nanospray and (**e**) macrospray; The charge plot obtained from (**c**) nanospray and (**f**) macrospray. (Dotted lines indicate the maximum value).

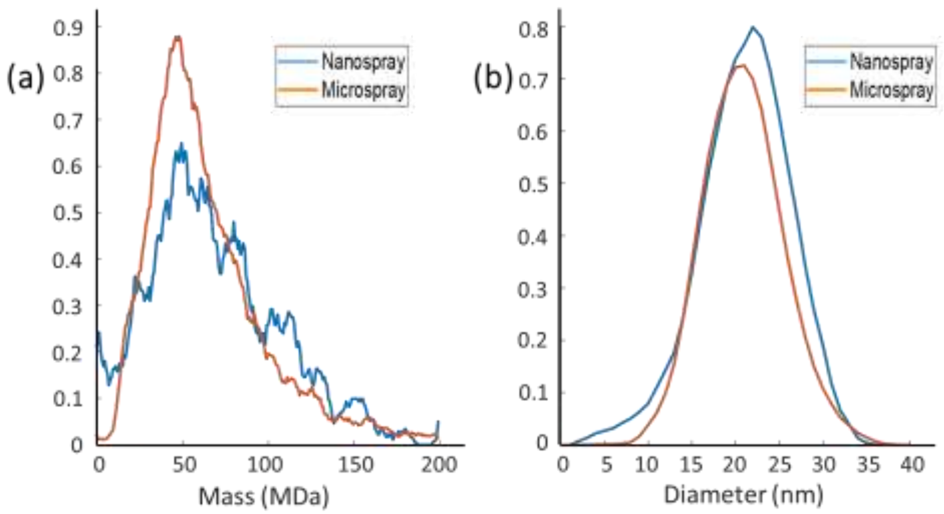


Figure S2. The comparison of the results obtained at nanospray and macrospray ionization conditions shown by their (**a**) mass distribution; (**b**) estimated size from mass plots.

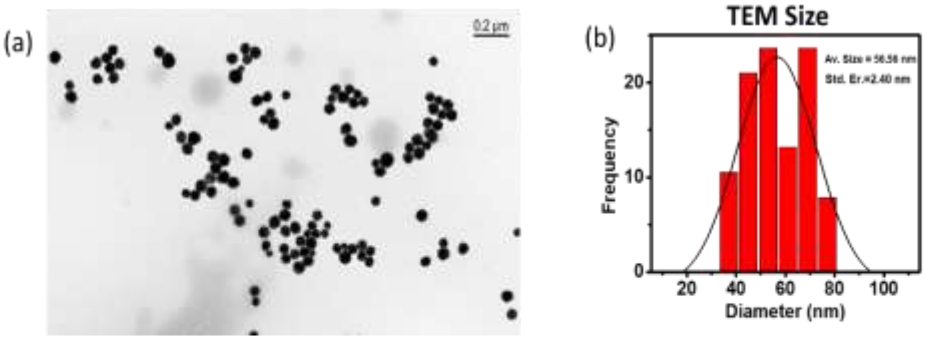


Figure S3. (**a**) TEM image and (**b**) histogram of Au-citrate nanoparticle (60 nm), obtained in the solid state.

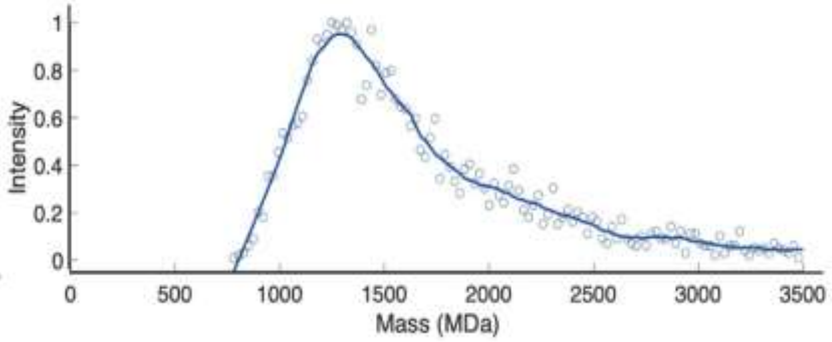


Figure S4. The mass distribution obtained from the CDMS analysis of 60 nm sized Au-citrate nanoparticles.

Table S1. The size and zeta potential values of all the AuNPs obtained from DLS measurements.

Nanoparticles	**Size in nm (DLS)**	**Zeta-potential (mV)**
MUTAB-capped gold nanoparticles	20	+17.6
Citrate-capped gold nanoparticles, SIGMA – 40 nm	38	-35.0
Citrate-capped gold nanoparticles, SIGMA – 60 nm	50	-36.2
Citrate-capped gold nanoparticles, SIGMA – 80 nm	70	-38.0

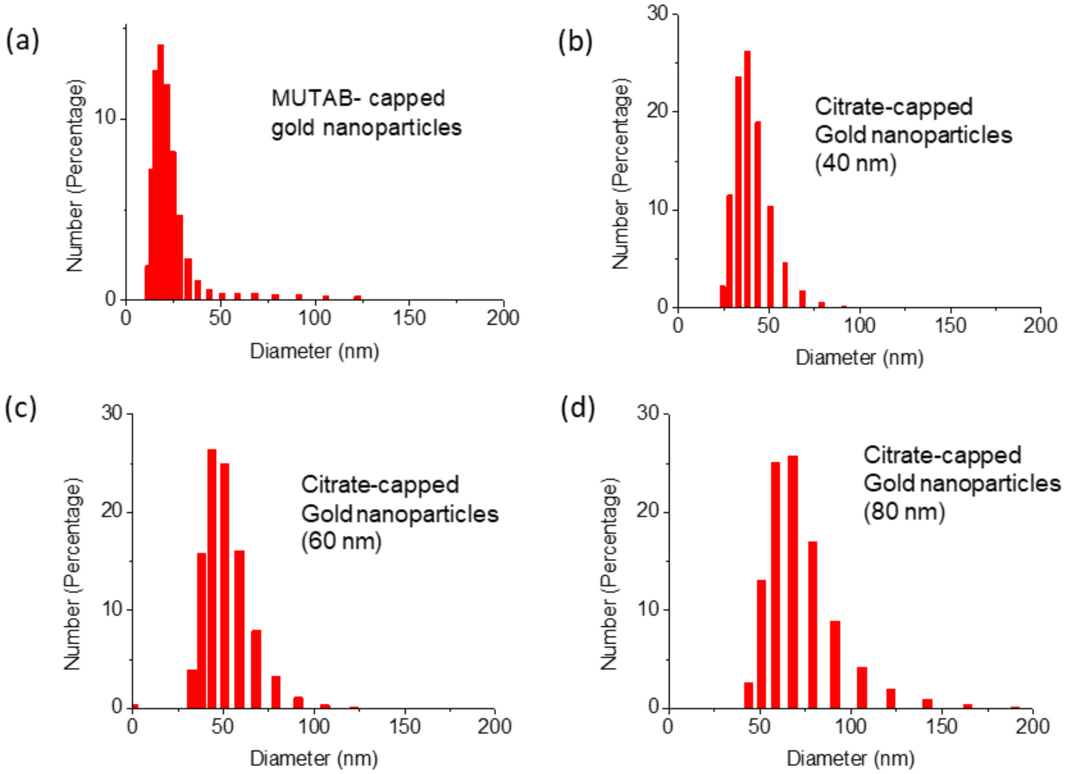


Figure S5. The size distribution obtained from DLS measurements for all the different-sized gold nanoparticles in water dispersion.

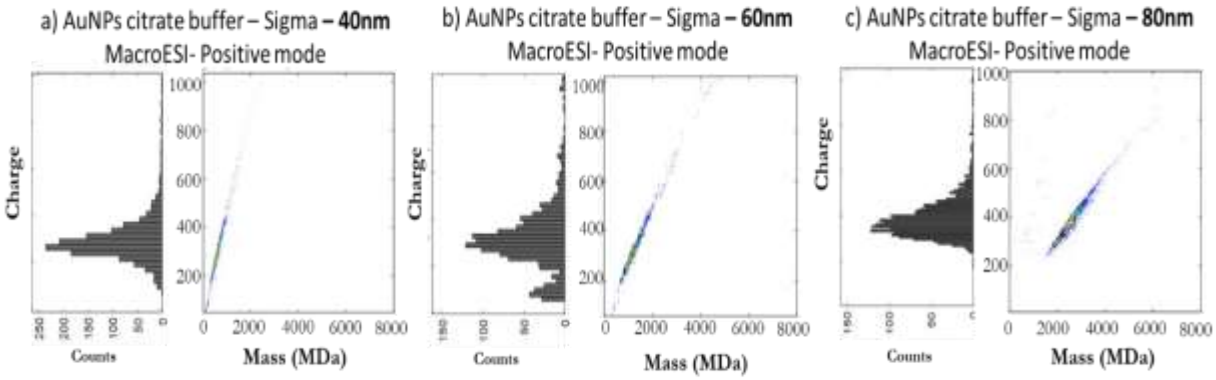


Figure S6. ESI-CDMS measurements on positive mode of different-sized Au-citrate NPs, (**a**) 40 nm; (**b**) 60 nm; (**c**) 80 nm.

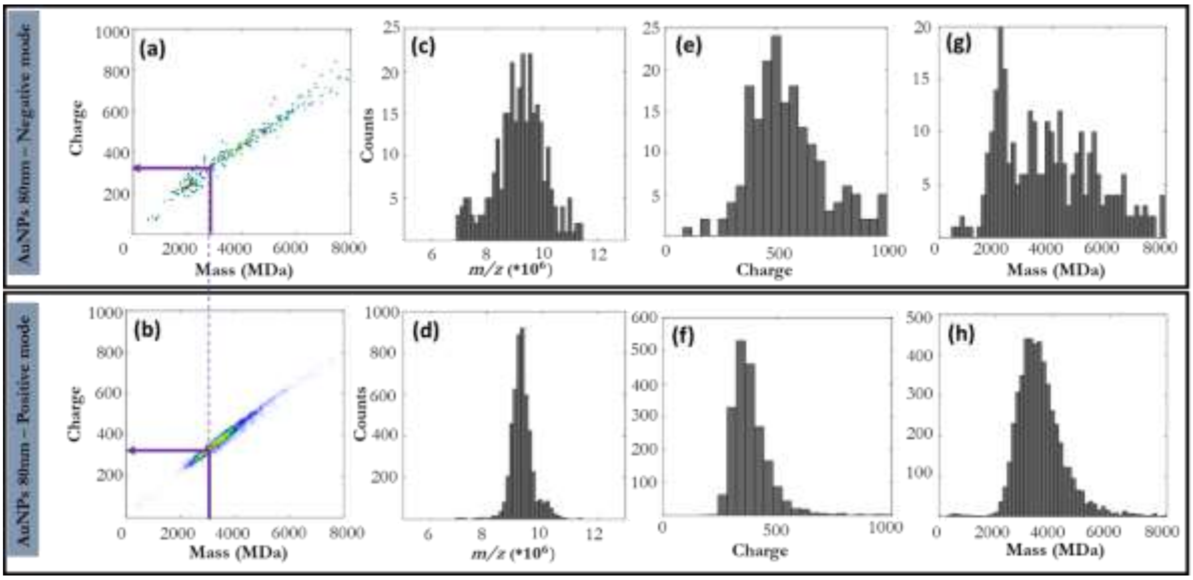


Figure S7. The data obtained for positive and negative ESI modes of the 80 nm sized Au-citrate NPs; (**a,b**) 2D plot, (**c,d**) distributions of *m/z*, (**e,f**) charge distribution, (**g,h**) mass distribution. The purple arrow on the 2D plot shows the charging for the expected mass of 80 nm AuNPs, e.g., ~ 3.11 GDa.

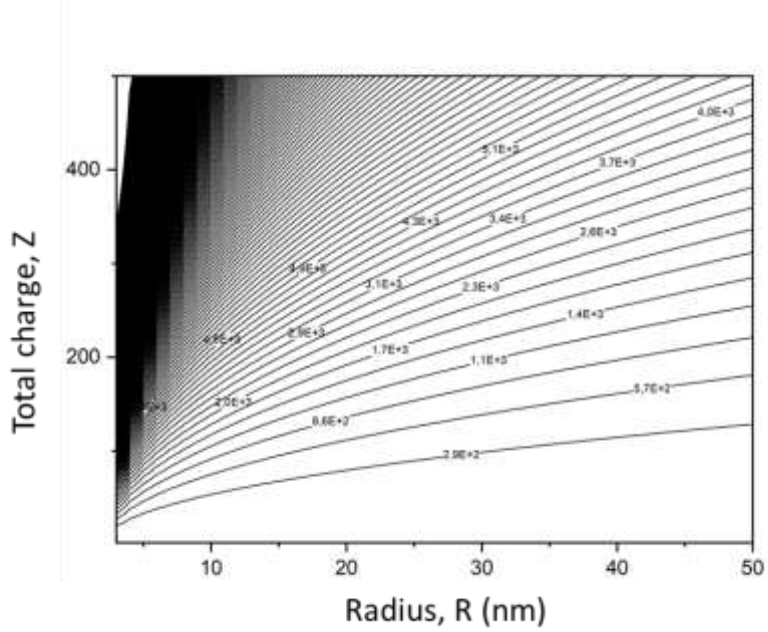
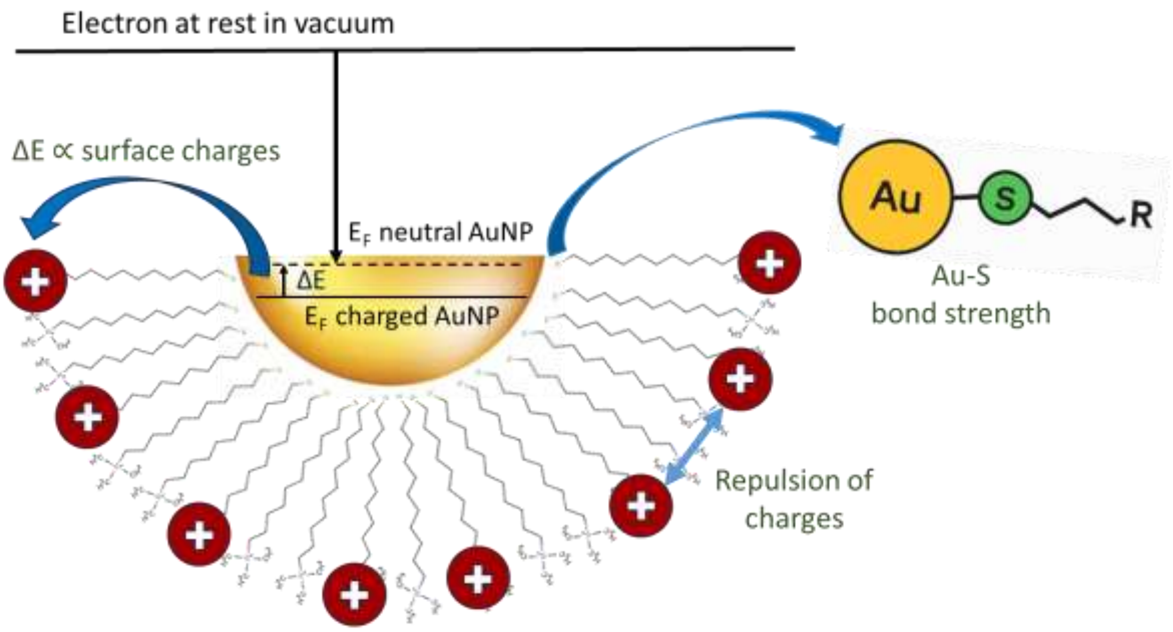
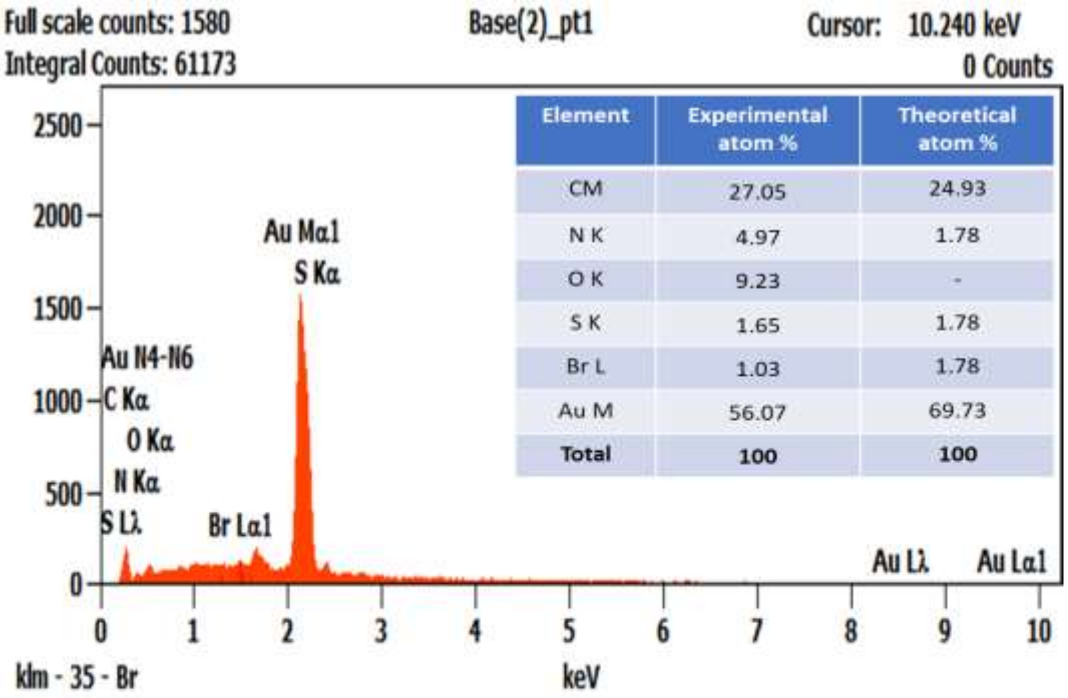


Figure S8. Iso-potentials (R, Z = Q/e) map of the electrostatic energy U (in eV) for a nanoparticle of charge Z and radius R.



Scheme S1. Illustration of the concepts and correlations regarding ligand bond strength (brought by the gold-sulfur interface), charging energy (brought by the repulsion of charged ligands), and modification of the Fermi level of a gold NP due to chemisorption of thiolated ligands.



Element	Experimental atom %	Theoretical atom %
CM	27.05	24.93
N K	4.97	1.78
O K	9.23	-
S K	1.65	1.78
Br L	1.03	1.78
Au M	56.07	69.73
Total	**100**	**100**

Figure S9. The percentage of elemental composition in 20 nm sized Au-MUTAB nanoparticles obtained from HRSEM-EDS. The theoretical percentage is calculated considering that the composition is $Au_{246000}(MUTAB)_{6280}$ (where, MUTAB = $C_{14}H_{32}NBrS$).