Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY MATERIAL

Predictions on SERS Enhancement Factor of Gold Nanosphere Aggregates Samples

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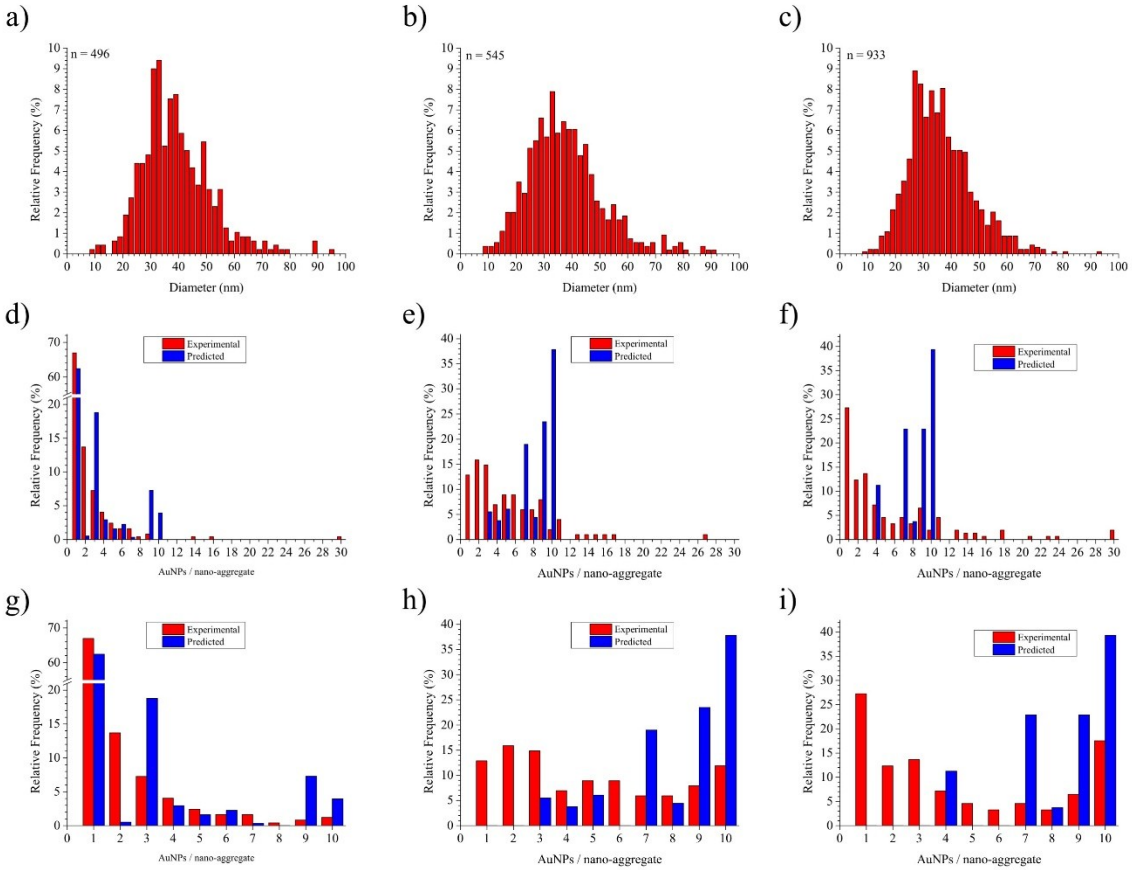

Figure S 1: a-c) the TEM distribution of each particle found in "single AuNPs" (a), "aggregate AuNPs #1" (b) or "#2" (c) as they are found single of part of an aggregate structure. d-f) Each nanostructure analyzed in term of number AuNPs, the relative abundances are reported in the y axis. g-i) The same analysis of d-f but the aggregate larger that 10 AuNPs are considered together within the 10^{th} bar, resembling the expectation of the fitting procedure with the simulated dataset.

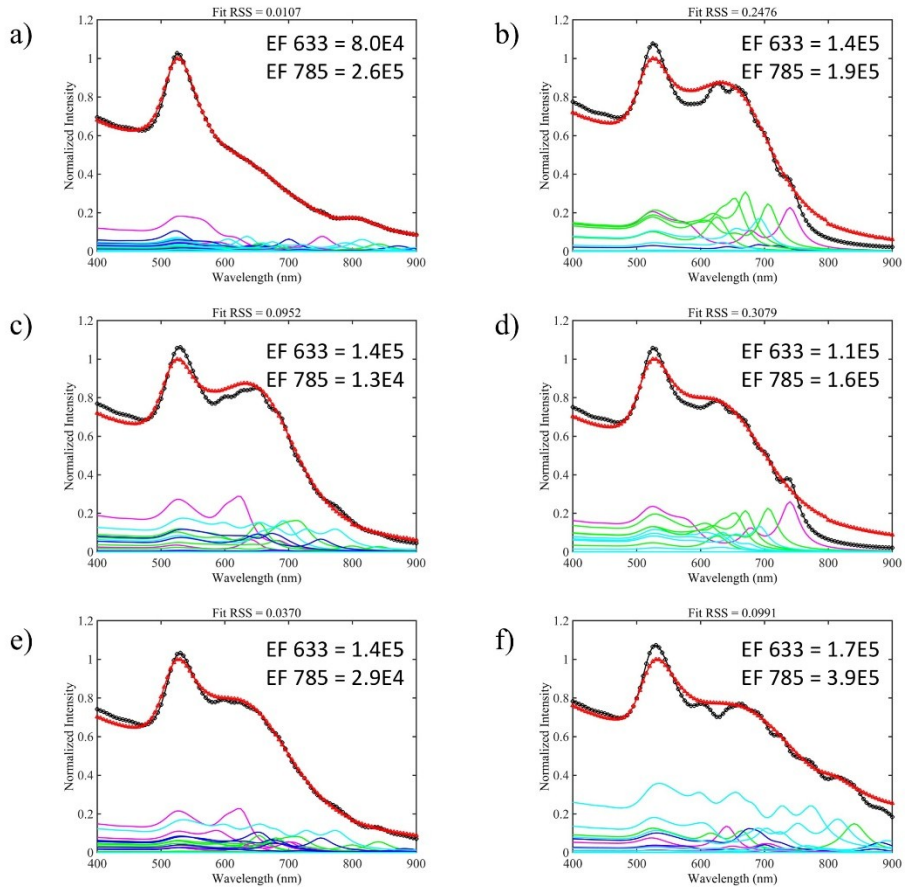

Figure S 2: Examples of other AuNP aggregates obtained by concentrated NaCl solution added to pristine AuNPs as synthetized by LASiS. The simulated dataset is still able to interpret each one of the proposed experimental extinction spectrum and the relative predicted EFs are reported for 633 and 785nm excitation.

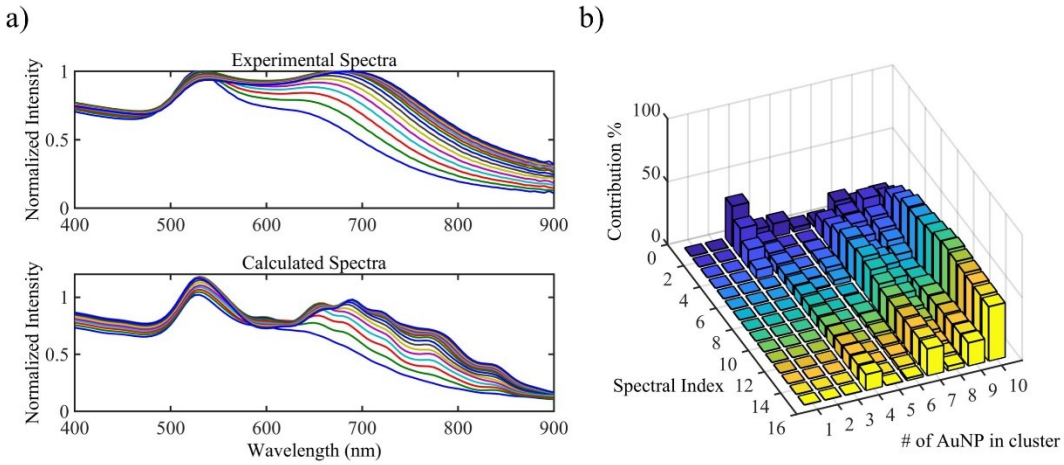

Figure S 3: concentrated NaCl solution was added to AuNPs as synthetized by LASiS and it's extinction spectra monitored in time (a). Each spectrum was than fitted with the simulated dataset and the results well describe the changing from smaller to larger aggregates during time evolution (b).

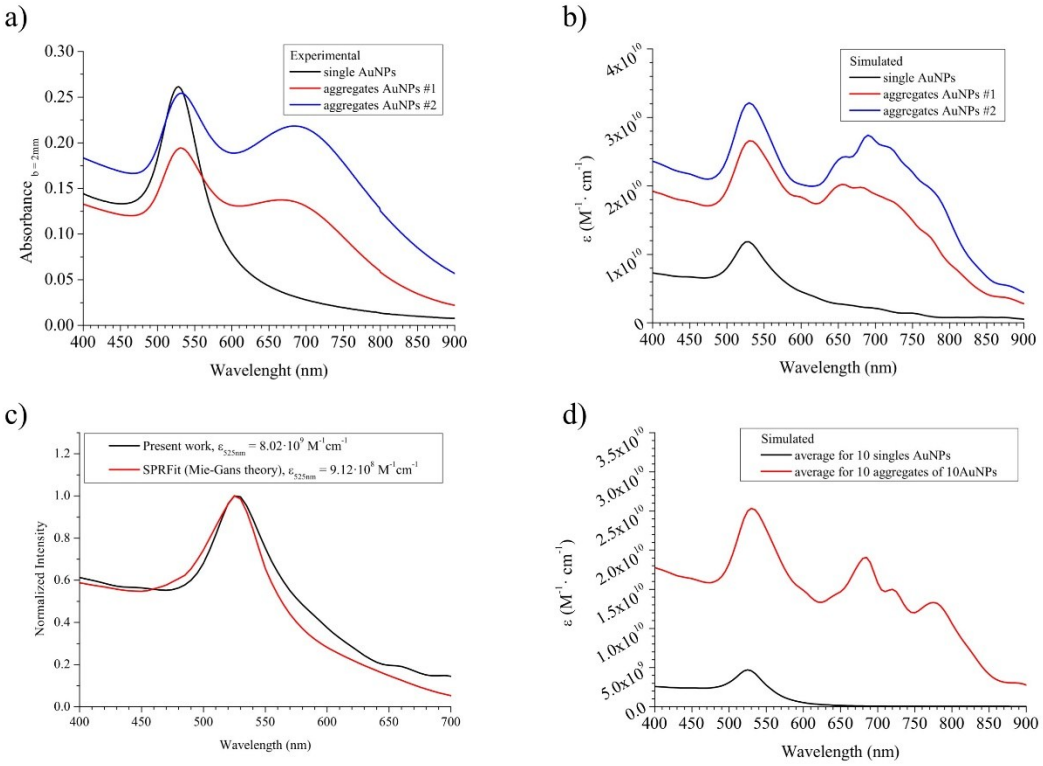

Figure S 4: a) Absorbance spectra from the "single AuNPs", "aggregate AuNPs #1" and "aggregate AuNPs #2" samples. b) the molar extinction coefficients obtained from each interpretation of the experimental data. c) the SPRFit model (from Amendola at al. The Journal of Physical Chemistry C **2009**, 113, 4277) was used to compare the Mie-Gans theory with this BEM interpretation. Despite the fitting results appear similar, the higher shoulder at longer wavelength and the higher molar extinction coefficient of the presented fitting derived to the insertion of a not negligible amount of aggregates to the spectrum, as confirmed by TEM analysis. d) comparison of the average single AuNP and average decamer aggregate extinction coefficients from the simulated dataset. The increased extinction reflect the higher amount of material that is present for larger aggregates.

sample	$\varepsilon_{\text{simulated, 450nm}}$ [$M^{-1} \cdot cm^{-1}$]	Au nanostructures [mol/L]	Average MBA molecules per Au nanostructure (total)
single AuNPs	6.71E+09	1.56E-10	5.12E+04
aggregate AuNPs #1	1.77E+10	3.43E-11	-
aggregate AuNPs #2	2.17E+10	3.88E-11	-
aggregate AuNPs #3	1.81E+10	4.04E-11	1.97E+05
aggregate AuNPs #4	2.13E+10	3.59E-11	2.22E+05
aggregate AuNPs #5	2.06E+10	3.36E-11	2.37E+05
aggregate AuNPs #6	2.30E+10	3.12E-11	2.56E+05

Table S 1: molar extinction coefficients extracted from the simulated spectra at 450 nm and the calculated concentration for each sample. The forth column refer to the average total amount of MBA molecules estimated to be present on each nanostructure.

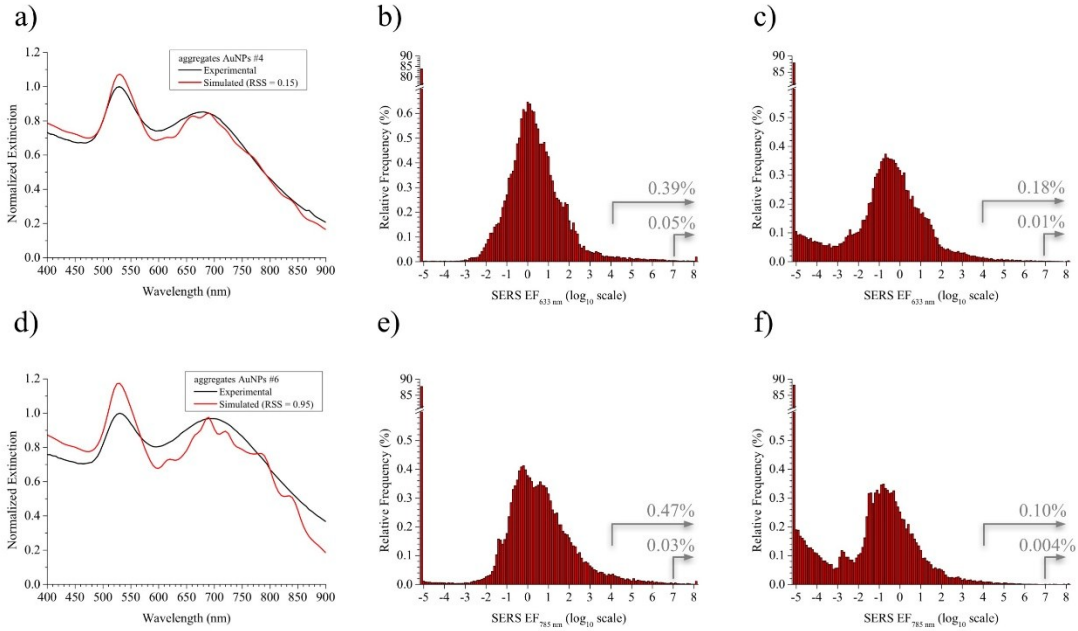

Figure S 5: a, d) The experimental and simulated extinction spectra for the "aggregate AuNPs #4" (a) and "#6" (d). The distribution of the surface enhancement factors deriving from the weighted contribution of all the particles composing the dataset are presented for "aggregate AuNPs #4" (b), "single AuNPs" excited at 633nm (c), "aggregate AuNPs #6" (e) and "single AuNPs" excited at 785nm (f). The percentage refers to the percentage sum of the elements with EFs equal of higher than 10^4 or 10^7, considering an excitation at 633 (b, c) or 785 (d, f) nm.

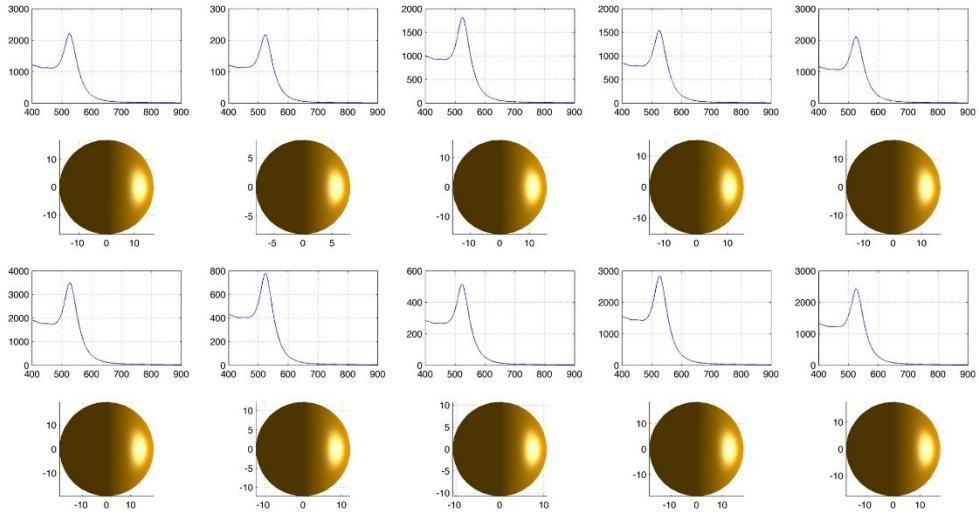

Figure S 6: The group composed of 1 AuNP within the simulated dataset used to interpret experimental extinction spectra.

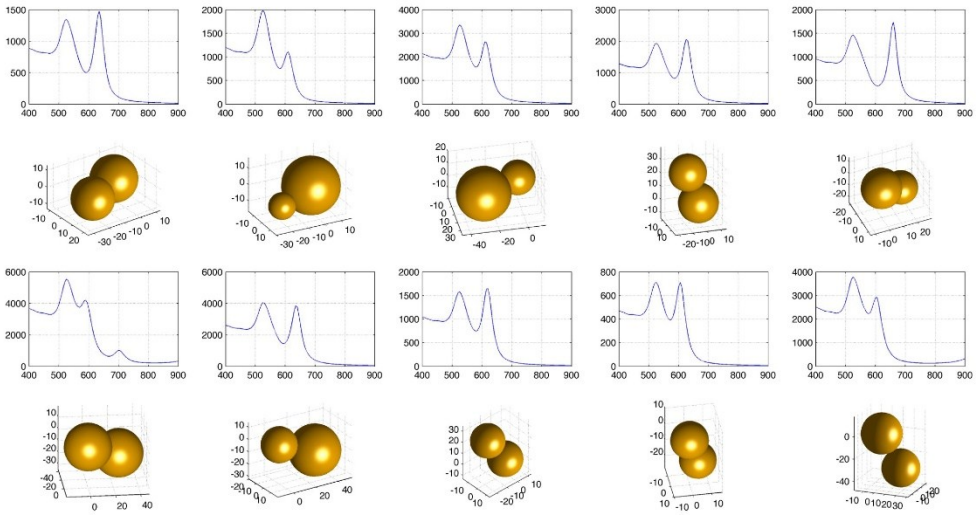

Figure S 7: The group composed of 2 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

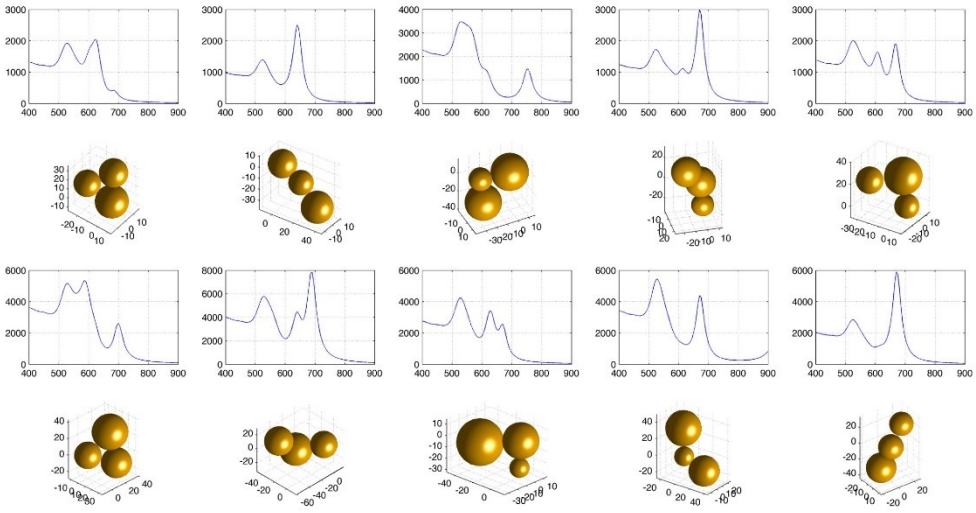

Figure S 8: The group composed of 3 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

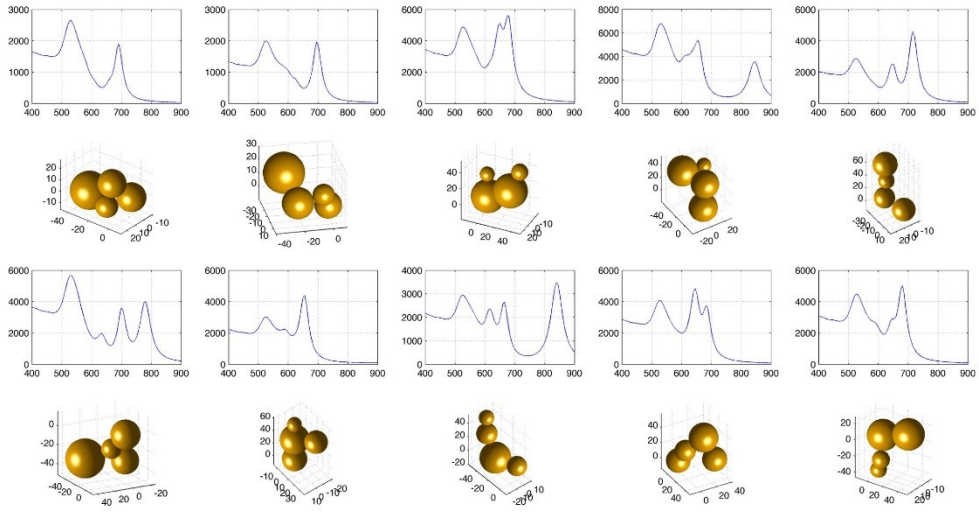

Figure S 9: The group composed of 4 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

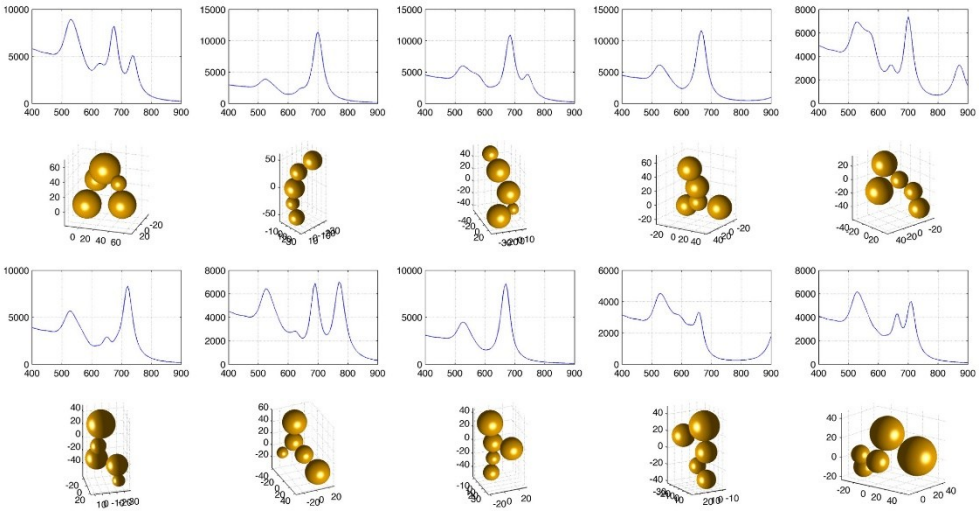

Figure S 10: The group composed of 5 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

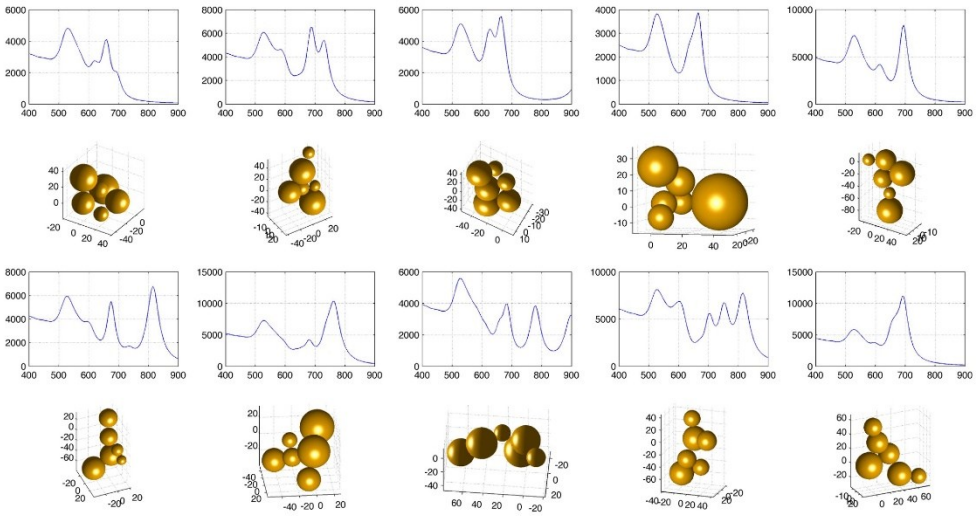

Figure S 11: The group composed of 6 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

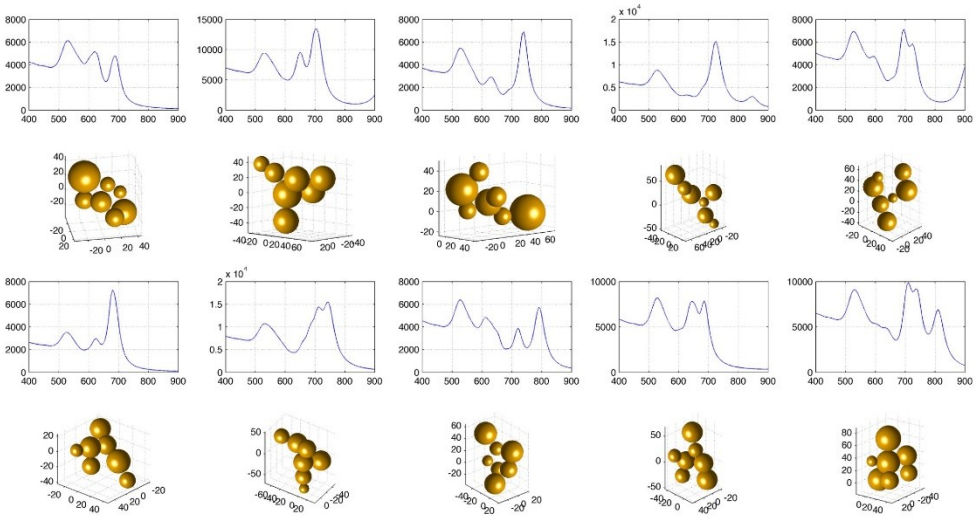

Figure S 12: The group composed of 7 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

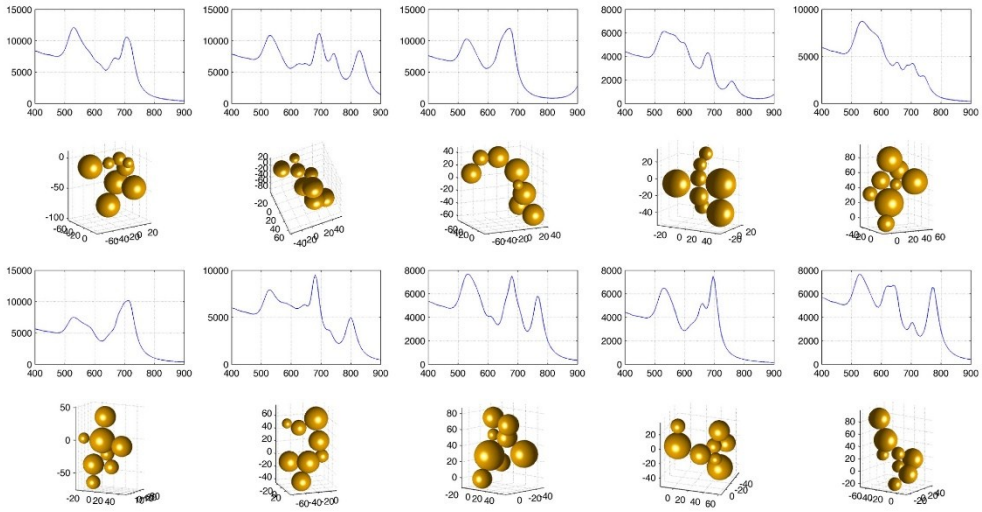

Figure S 13: The group composed of 8 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

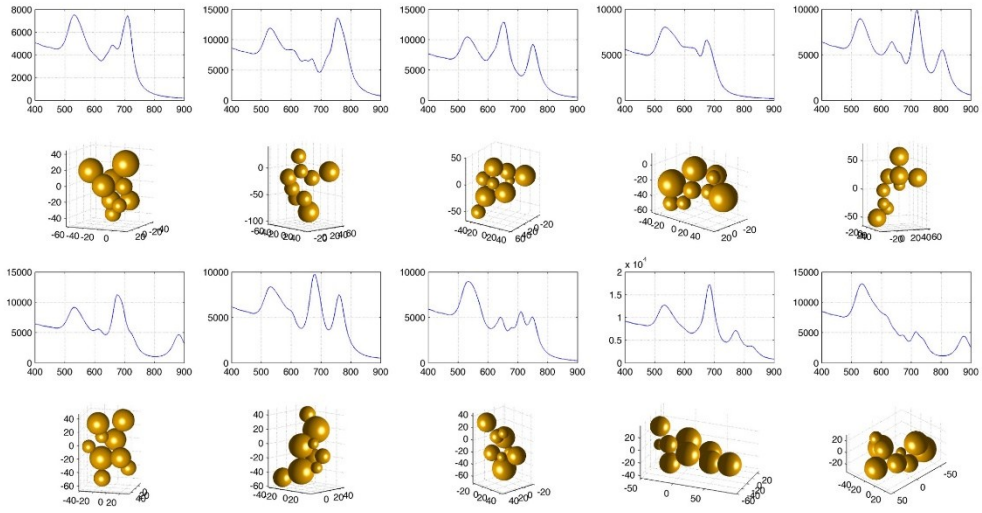

Figure S 14: The group composed of 9 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

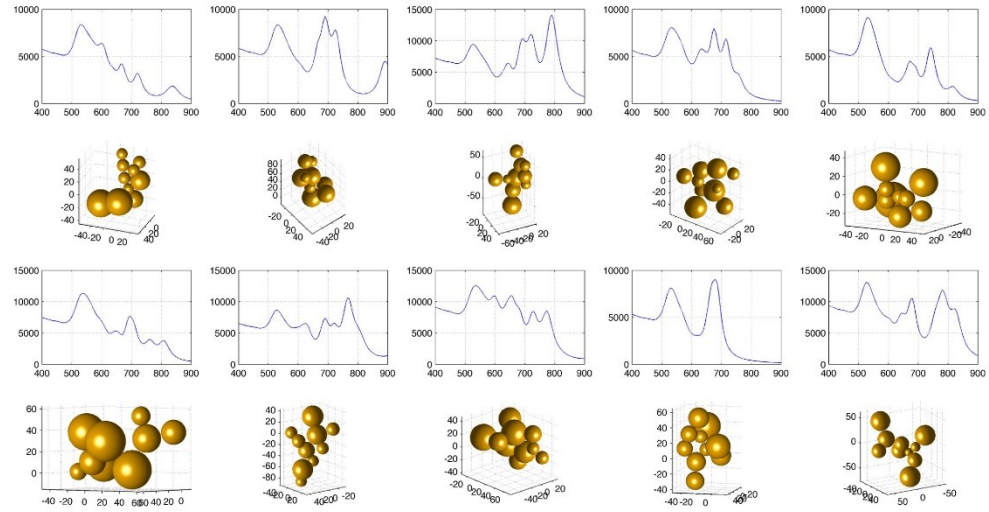

Figure S 15: The group composed of 10 AuNPs within the simulated dataset used to interpret experimental extinction spectra.

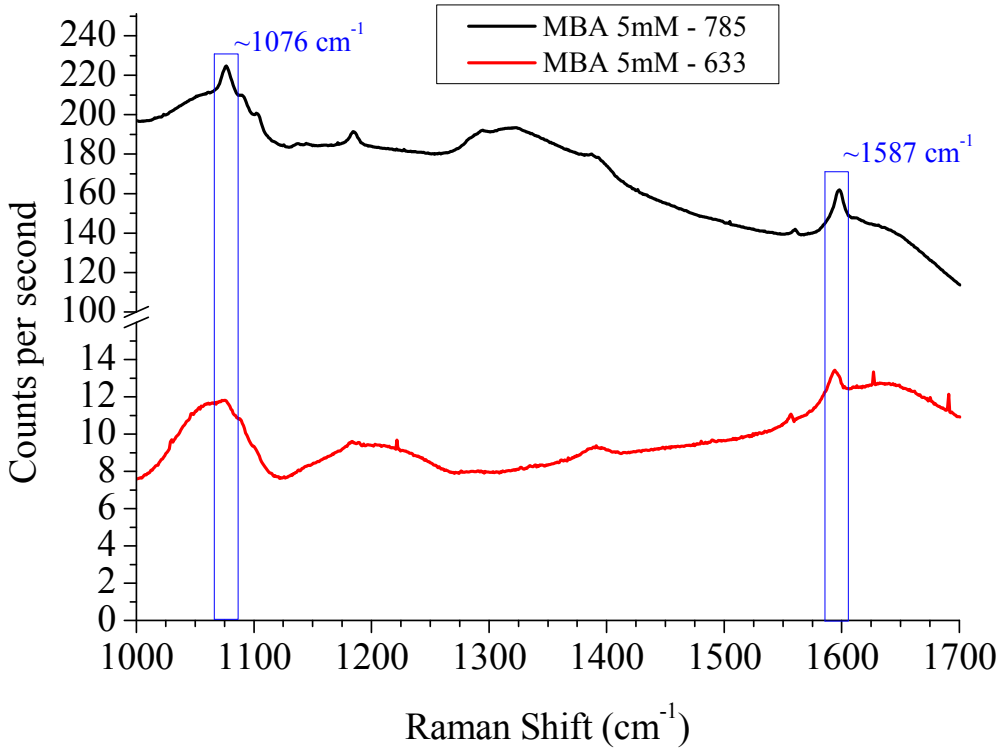

Figure S 16: Raman spectra used for the experimental EF estimation. MBA solution at 5mM in water in a quartz cuvette. The spectral regions within the blue boxes were used for the EF evaluation.

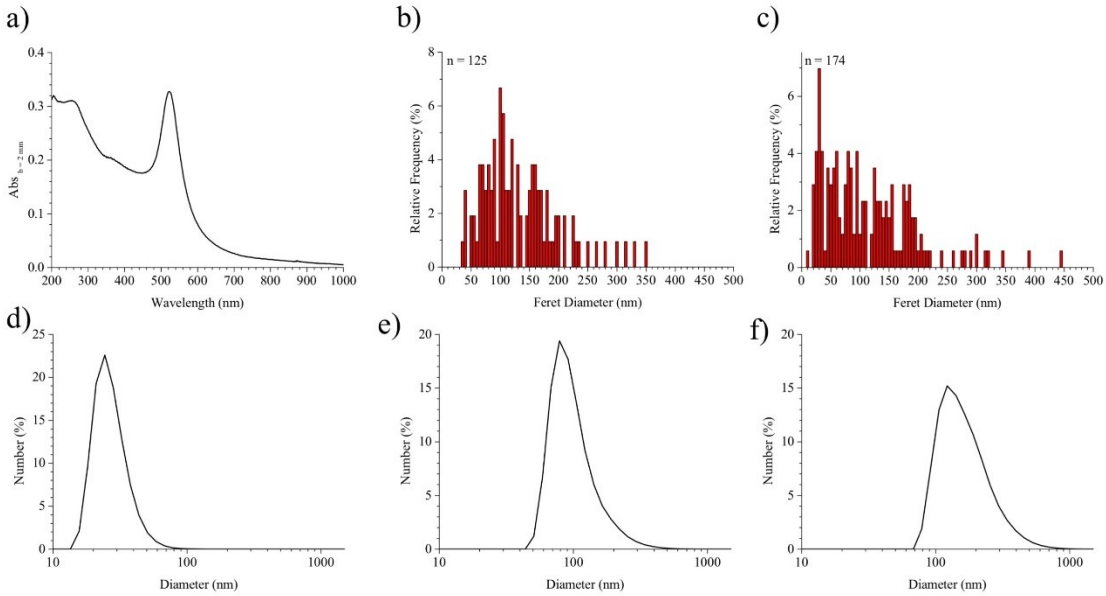

Figure S 17: a-d) pristine bare AuNPs extinction spectrum and DLS measure (peak 27.6 nm, standard deviation 8.8 nm); b-e) size distribution analysis for "aggregates AuNPs #1" obtained by TEM and DLS (peak 104.6 nm, standard deviation 50.8 nm), respectively; c-f) size distribution analysis for "aggregates AuNPs #2" obtained by TEM and DLS (peak 175.6 nm, standard deviation 89.3 nm), respectively.