SUPPORTING INFORMATION

Ligand shell size effects on one- and two-photon excitation fluorescence of zwitterion functionalized gold nanoclusters

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Determination of the stoichiometry of AuZw NCs by XPS and mass spectrometry measurements.

XPS measurement (Leguevel, Nanoscale 2014,6,8091-8099, table 2 ou fig S8 of supporting information) show that for AuZw 1:1; 1:3 and 1:5 the ration **Au^0 /Au^+ is ≈2.** Of course, it's an average, a mix of different sizes of clusters. (for the new data we don't have the file to extract the ratio Au^0 /Au^+, **and we supposed that this ratio is similar).**

Assuming that fluorescence properties are given by a small core: tetramer Au4, we can build a simple model: a gold core with $4Au^0$ and $4x2=8Au^+$ (8 thiols bound to this 8 gold= 4 Zw, **assuming that each S from the ZW can bind to one Au+**)

Our starting model of the cluster is thus **Au_{12} Zw_4**

XPS measurement can also give a ratio between Au and Sulfur atoms (table 1 same publication). By mixing theses results with mass spectrometer data (Shen, APL MATERIALS, 5, 053404(2017) we can have an estimation of the number of ligands in the shell(s).

For AuZw 1:1 (≈11kDa) we can take **$Au_{12}ZW_{22}$**: Au_{12} Zw_4 + ≈**18** Zw in the shell

For AuZw 1:2 (≈ 17kDa) we can take **$Au_{12}ZW_{37}$**: Au_{12} Zw_4 + ≈ **33** Zw in the shell

For AuZw 1:5 (≈ 29kDa) we can take **$Au_{12}ZW_{66}$**: Au_{12} Zw_4 + ≈ **62** Zw in the shell

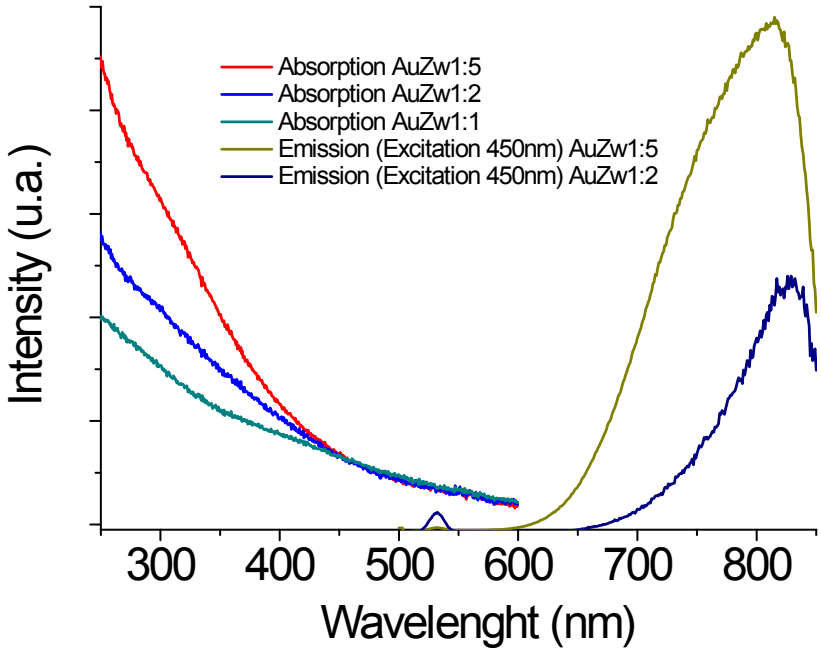

Figure S1 : Experimental linear absorption and emission spectra for AuZw NCs in water.

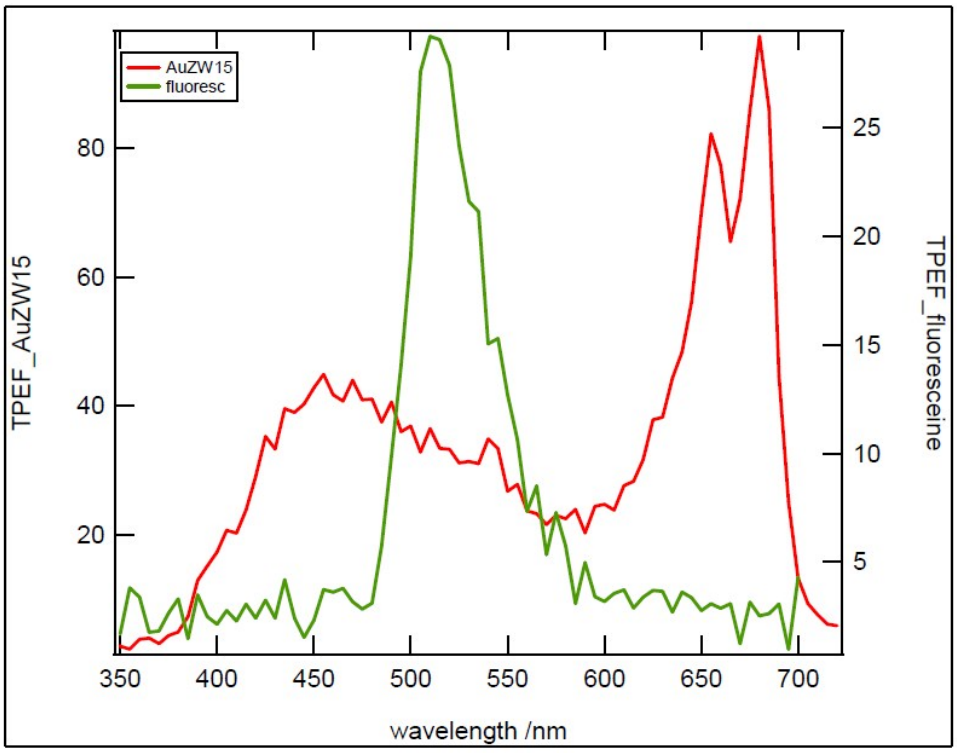

Figure S2 : Experimental two-photon excited fluorescence spectrum of AuZw 1:5 NCs in water and compared to fluorescein. (800 nm laser excitation).

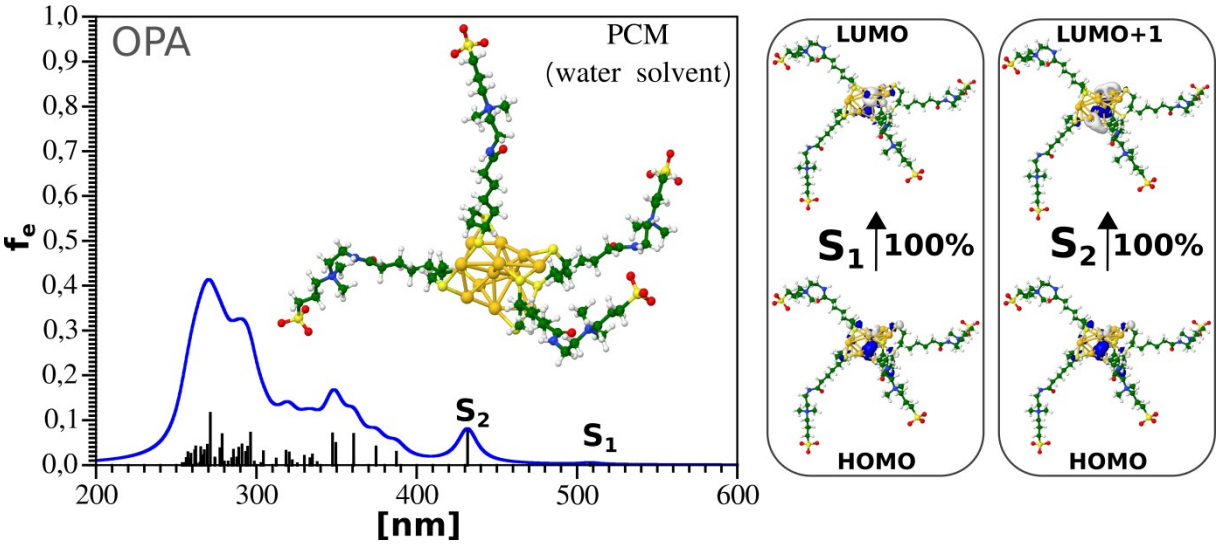

Figure S3: OPA spectrum obtained by QM-TDDFT approach for Au12Zw4. Leading excitations of S_1 and S_2 OPA states are shown on the right side.

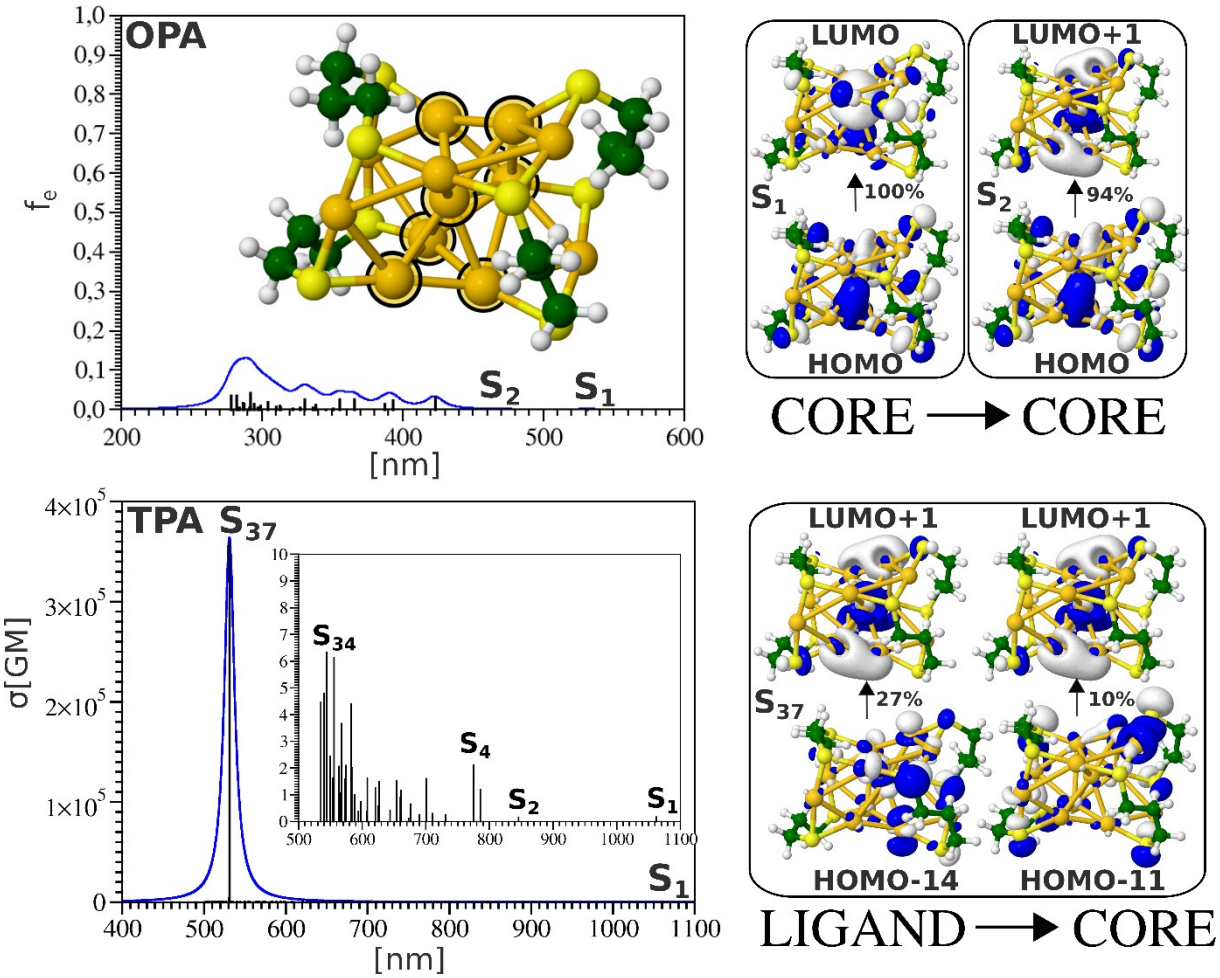

Figure S4: Comparison of TD-DFT OPA and TPA spectra obtained for $Au_{12}L_4$ (L=S-CH_2-CH_2-CH_2-S). Leading excitations of S_1 and S_2 OPA states and of S_{37} TPA state are shown on the right side.

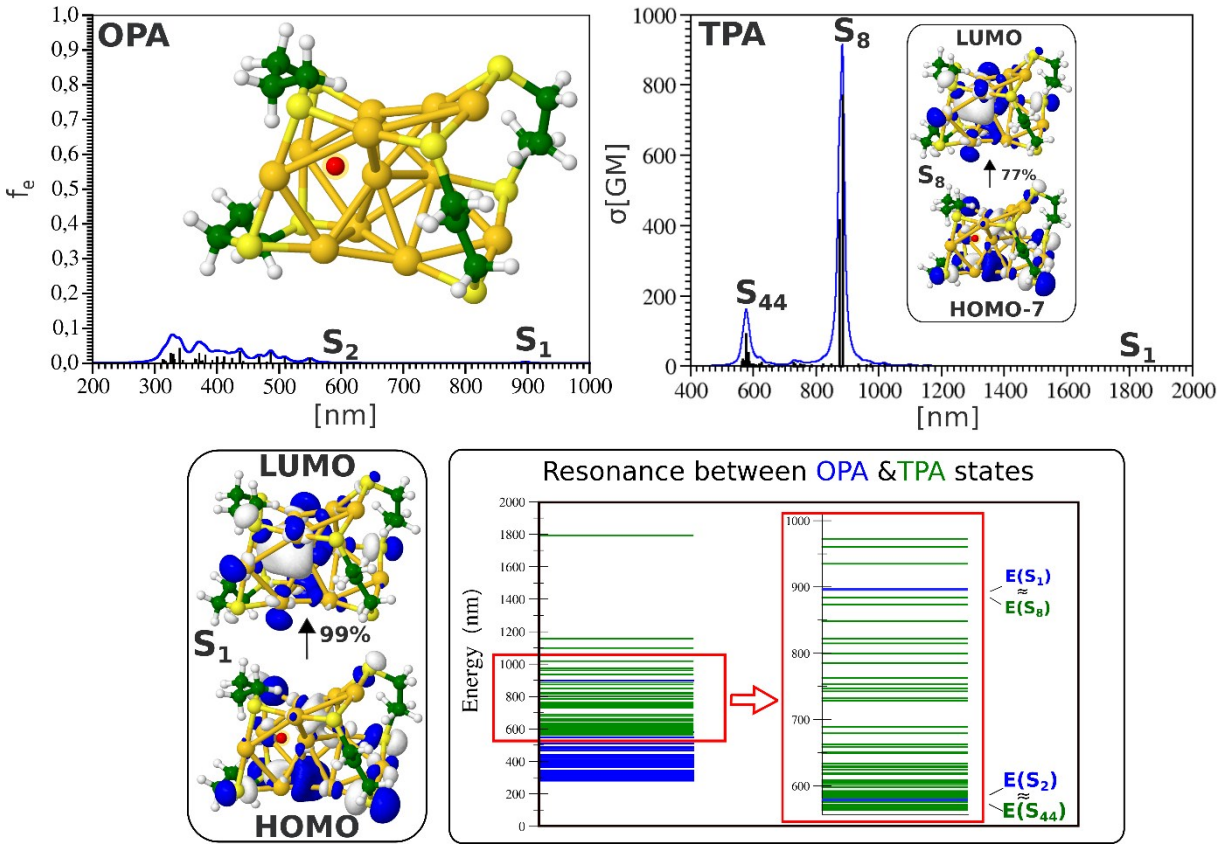

Figure S5: Comparison of TD-DFT OPA and TPA spectra obtained for $Au_{12}L_4$ (L=S-CH_2-CH_2-CH_2-S) with point charge q=+1 (red circle) placed close to central Au atom. Leading excitations for S_8 of TPA is shown on the upper right side. The leading excitation of OPA S_1 state (left bottom) as well as the resonance between OPA and TPA states are shown on the right bottom.

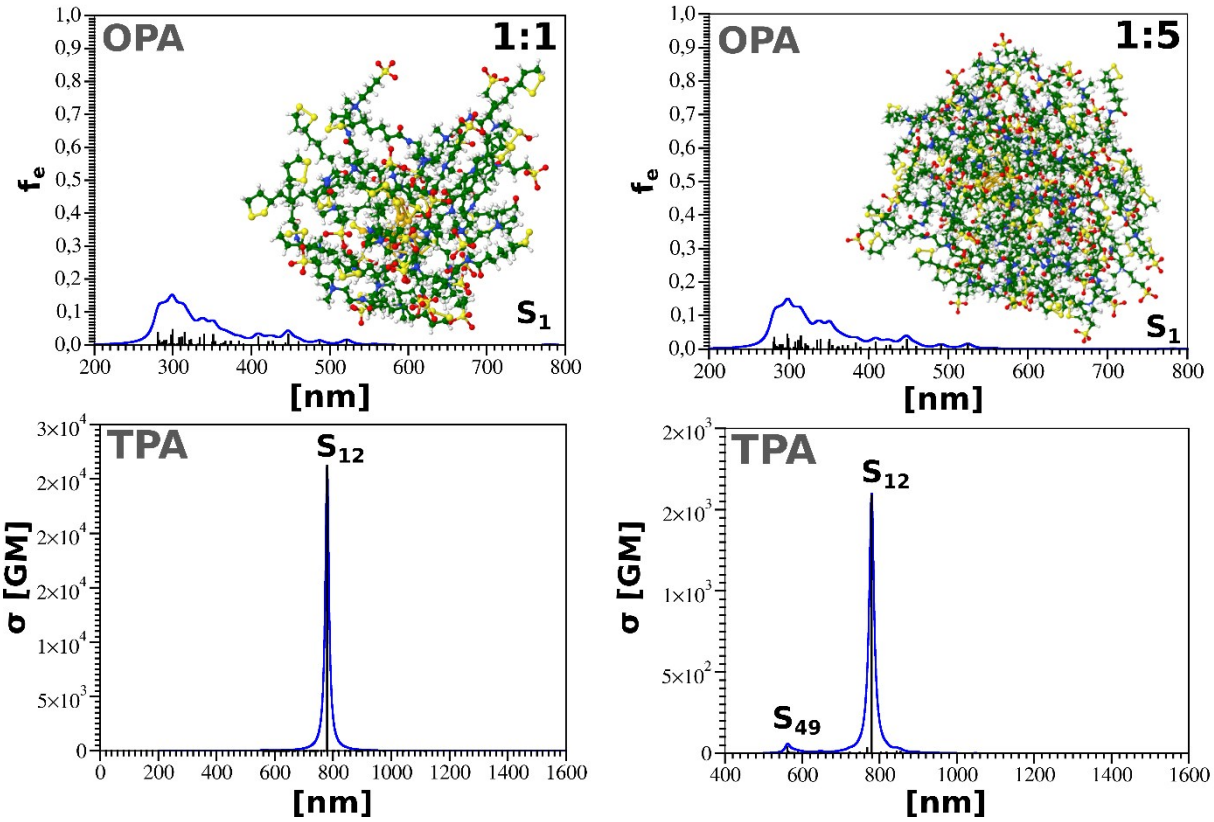

Figure S6: Comparison of OPA and TPA spectra obtained by QM/MM approach for $Au_{12}Zw_4$ (QM-TDDFT) with point charge q=+1 placed close to central Au atom (cf S4), with 1 :1 and 1 :5 ratio of Au :Zwitterions (MM)