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 \( \text{Au}^{0}/\text{Au}^{+} \) is \( \approx2 \). 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 \( \text{Au}^{0}/\text{Au}^{+} \), and we supposed that this ratio is similar).

Assuming that fluorescence properties are given by a small core: tetramer \( \text{Au}^{4} \), we can build a simple model: a gold core with \( 4\text{Au}^{0} \) and \( 4 \times 2 = 8 \text{Au}^{+} \) (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 \( \text{Au}_{12} \text{Zw}_{4} \)

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 (\( \approx11\text{kDa} \)) we can take \( \text{Au}_{12} \text{ZW}_{22} \): \( \text{Au}_{12} \text{Zw}_{4} + \approx 18 \text{Zw} \) in the shell

For AuZw 1:2 (\( \approx17\text{kDa} \)) we can take \( \text{Au}_{12} \text{ZW}_{37} \): \( \text{Au}_{12} \text{Zw}_{4} + \approx 33 \text{Zw} \) in the shell

For AuZw 1:5 (\( \approx29\text{kDa} \)) we can take \( \text{Au}_{12} \text{ZW}_{66} \): \( \text{Au}_{12} \text{Zw}_{4} + \approx 62 \text{Zw} \) 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 Au12L4 \((L=S-CH_2-CH_2-CH_2-S)\). 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)