

SUPPORTING INFORMATION

Non-linear optical properties of gold quantum clusters. The smaller the better.

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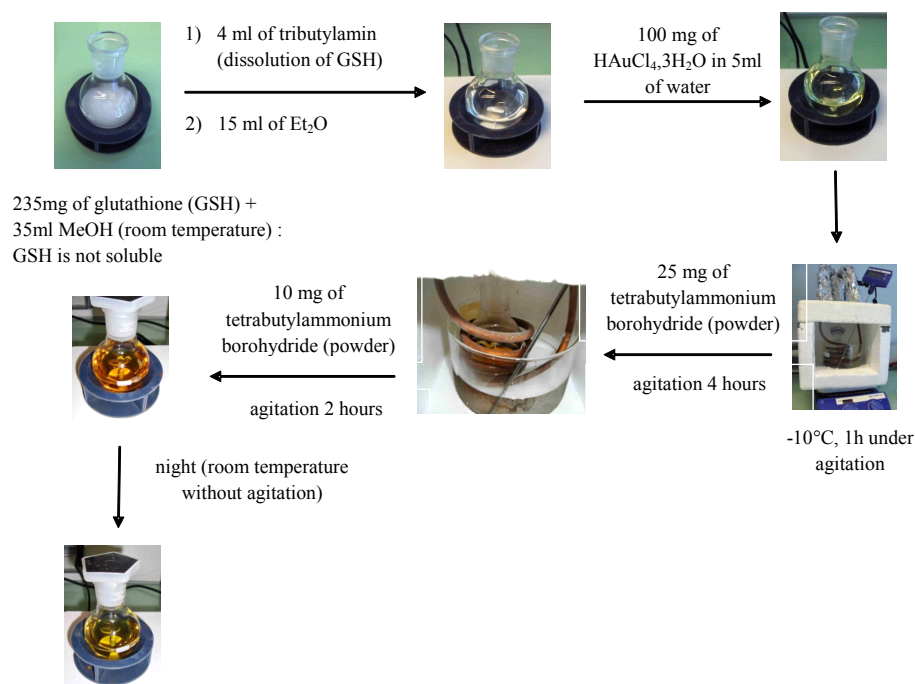
Synthesis and purification of protected gold $\text{Au}_{15}\text{SG}_{13}$ clusters.

The pure form of $\text{Au}_{15}\text{SG}_{13}$ was synthesized as follows:

235 mg of Glutathion (GSH) was dissolved in 35 ml of methanol and 4 ml of tributylamin in a 100 ml balloon. Then 15 ml of diethyl ether was added followed by 5 ml of a water gold solution (100 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$). Solution was mixed at $-10\text{ }^\circ\text{C}$ during 1 hour and 24 mg of tetrabutylammonium borohydride powder was added. 4 hours later 10 mg of tetrabutylammonium borohydride was added and mixed 2 hours more. The yellow solution was kept the night at ambient temperature before being concentrated to a volume of ≈ 5 ml in a rotary evaporator. Then maximum of the organic phase (tributylamin) was removed with a pipette and the aqueous phase was transfer in a 30 ml Teflon centrifuge tube. 5 ml of methanol was added followed by 20 ml of diethyl ether to induce precipitation. After centrifugation (5 mn/9000 rpm), supernatant was removed. Precipitated was washed two times to removed unreacted glutathione with a cycle: dissolution/precipitation/centrifugation (1.5 ml of ammoniac 10 % for dissolution, 20 ml of methanol for precipitation). Clusters were dissolved in 20 ml of water and 400 μl of acetic acid was added to induce precipitation of the unwanted Au-SG chains. After one night solution was centrifuged (12000 rpm-20 min) and the yellow supernatant was concentrated to 5 ml a rotary evaporator before being precipitated with methanol. A last cycle of dissolution/precipitation in ammoniac (3 %)/methanol was done before drying the yellow powder. About 38 mg of $\text{Au}_{15}\text{SG}_{13}$ was obtained.

A pictorial view of the different step of synthesis and purification is given in fig. S1.

Synthesis :



Purification :

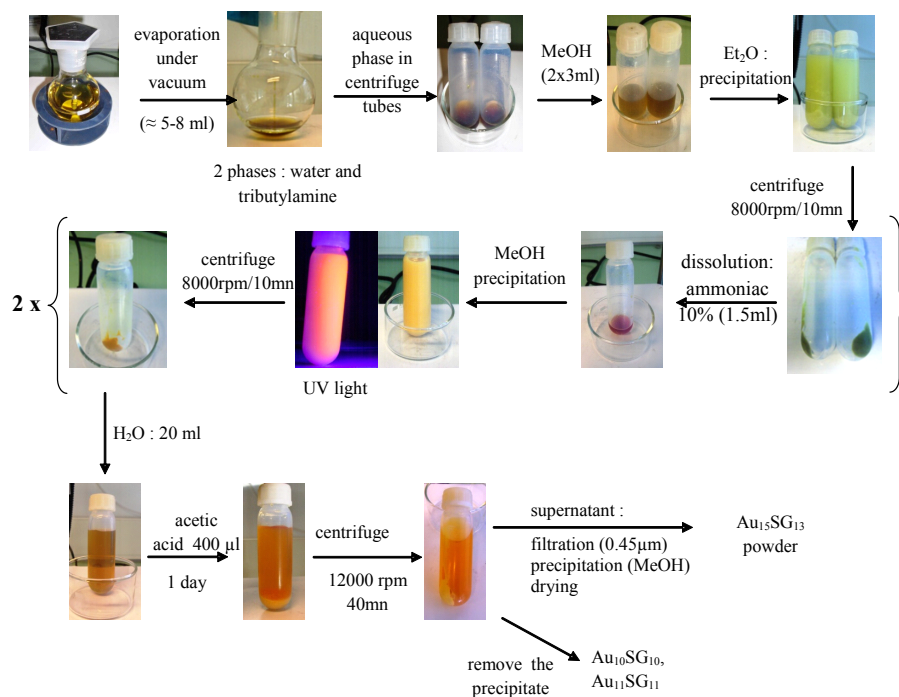


Figure S1 : pictorial view of the different steps of synthesis and purification for $\text{Au}_{15}\text{SG}_{13}$ clusters

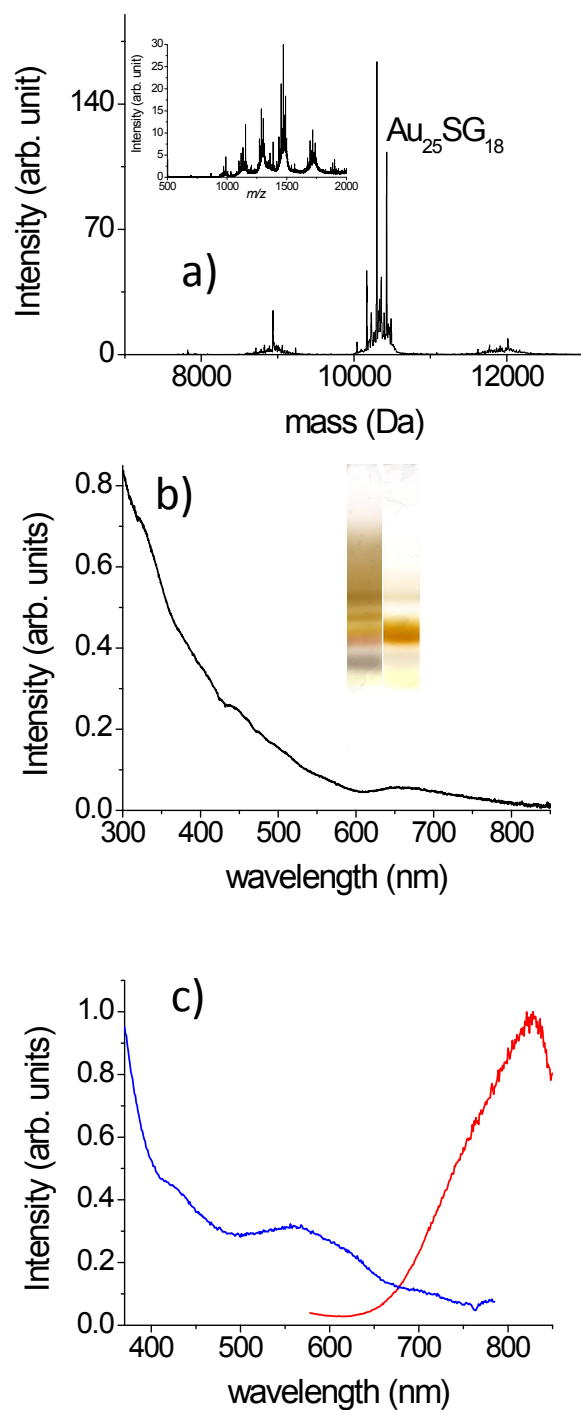


Figure S2 : (a) ESI deconvoluted spectrum of $\text{Au}_{25}\text{SG}_{18}$, using a multiplicative correlation algorithm. Inset. ESI mass spectrum for the protected $\text{Au}_{25}\text{SG}_{18}$ cluster from water solution, and acquired under gentle ESI conditions. (b) (Black line) Absorption spectrum of $\text{Au}_{25}\text{SG}_{18}$. Inset: PAGE for Au:SG clusters using (left) Tsukuda synthesis (see ref. 19) and (right) our synthesis. (c) Photoexcitation (with an emission at 820 nm) and emission spectra (with an excitation at 435 nm) of $\text{Au}_{25}\text{SG}_{18}$.

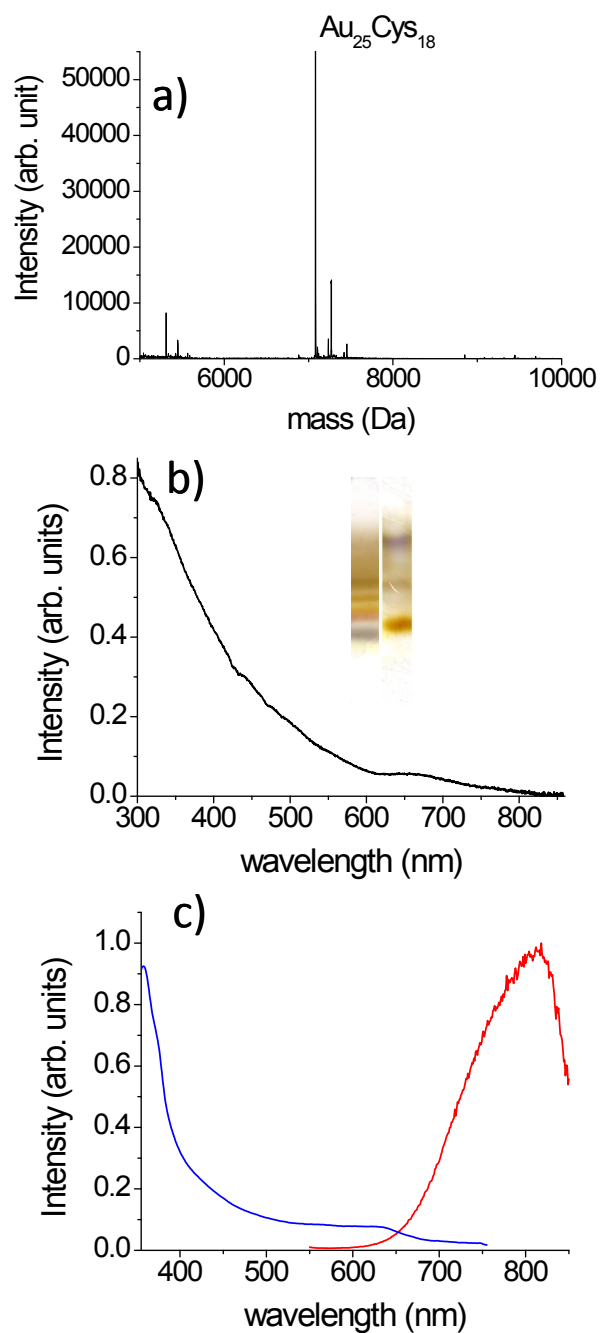


Figure S3 : (a) ESI deconvoluted spectrum of $\text{Au}_{25}\text{Cys}_{18}$, using a multiplicative correlation algorithm. (b) (Black line) Absorption spectrum of $\text{Au}_{25}\text{Cys}_{18}$. Inset: PAGE for Au:SG clusters using (left) Tsukuda synthesis (see ref. 19) and (right) our synthesis. (c) Photoexcitation (with an emission at 820 nm) and emission spectra (with an excitation at 435 nm) of $\text{Au}_{25}\text{Cys}_{18}$.

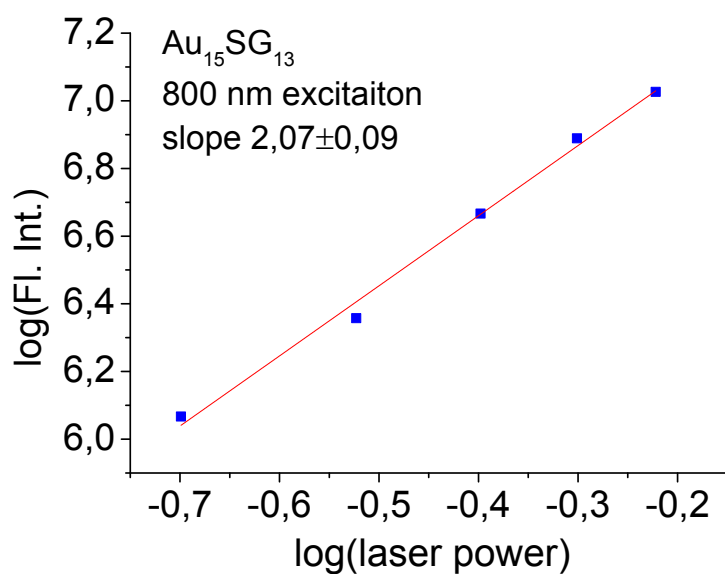
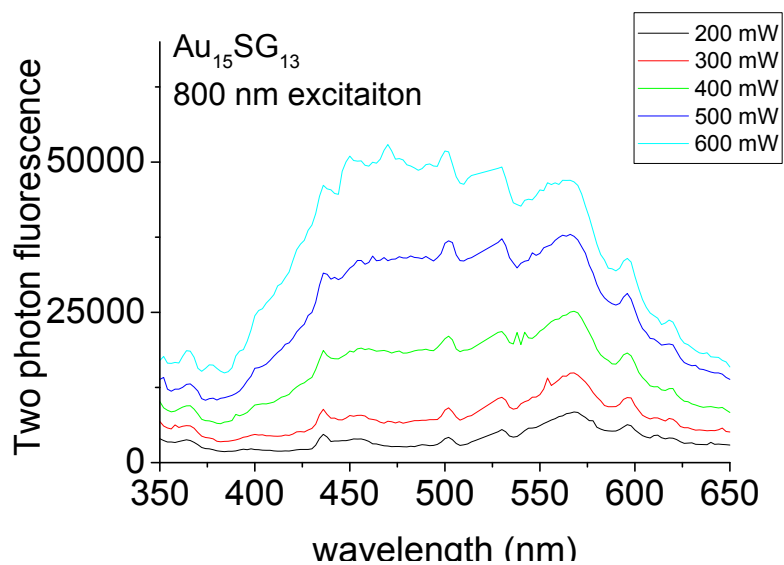


Figure S4 : Two-photon emission spectra at different pump powers for $\text{Au}_{15}\text{SG}_{13}$ clusters after excitation at 800 nm (top). Power dependence of emission is also provided (bottom).

Table S1 : first hyperpolarizability values for gold NPs. (data from ref. **Multipolar Contributions of the Second Harmonic Generation from Silver and Gold Nanoparticles**, I. Russier-Antoine, E. Benichou, G. Bachelier, C. Jonin, and, and P. F. Brevet, *The Journal of Physical Chemistry C* **2007** 111 (26), 9044-9048)

Gold spheres	Number of atoms	$10^{30} \cdot \beta$ (esu) (water = $0.56 \cdot 10^{-30}$ esu)	$10^{30} \cdot \beta$ (esu) (water = $0.087 \cdot 10^{-30}$ esu)	$10^{30} \cdot \beta$ /atom (water = $0.087 \cdot 10^{-30}$ esu)
Au10nm	30 900	50 000	7768	0.25
Au20nm	247 200	270 000	41 946	0.17
Au50nm	3 862 500	800 000	124 286	0.032

TPA experimental arrangement.

The light source for the present TPA experiments was a mode-locked femtosecond Ti:sapphire laser delivering at the fundamental wavelength of 780 nm pulses with a duration of about 140 femtoseconds at a repetition rate of 76 MHz. The beam was gently focussed by a low NA microscope objective to a waist of 5.4 μm and sent in transmission into a 1 cm path length spectrophotometric cuvette. The transmitted light was detected with a large aperture photodiode. The incident power was controlled with a half-wave plate and a polarizing cube. The sample absorption, the concentration of which was set to 5 mM, was then determined as a function of the incident power. Such an experimental set-up is effectively a P-scan set-up. The calibration of the photodiode signal was obtained prior to the experiment by removing the cuvette and varying the incident power. A typical nonlinear absorption plot is shown below at 780 nm. As expected, in absence of the cell, the plot exhibits a linear behavior with a slope of unity whereas in the presence of the cell, a decrease of the transmitted intensity is observed as the absorption increases due to a nonlinear contribution.

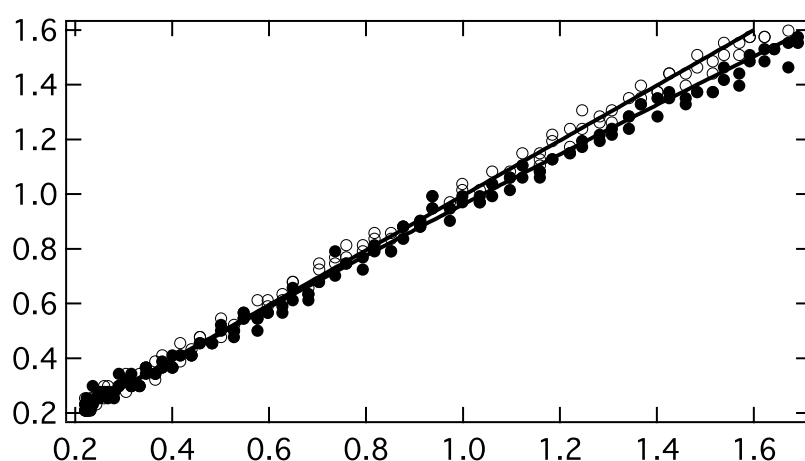


Figure S5 : Transmitted intensity recorded at 780 nm (empty circles) in absence of the cell, (filled circles) with the cell. Solid lines are fit using a nonlinear absorption.