

Supporting Information

Single step electrochemical synthesis of hydrophilic/hydrophobic Ag₅ and Ag₆ blue luminescent clusters

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Experimental Section

Synthesis: Silver clusters were obtained using an Autolab PGSTAT 20 potentiostat at a constant temperature of 25.0 ±0.1°C. Experiments were carried out in a standard Metrohm electrolysis beaker containing a sacrificial silver sheet as the anode (counter electrode), and a copper sheet of the same size as a cathode (working electrode). These two electrodes (with an area of 2.5 cm²) were placed vertically, face-to-face (at 1cm distance), inside the cell. An Ag/AgCl electrode was used as reference electrode. The conductive solution, consisting of a mixture of tetrabutylammonium bromide 0.1M and dodecanethiol 0.01 M in acetonitrile, was deaerated by bubbling nitrogen for about 15 min, keeping an inert atmosphere during the whole process. Strong magnetic stirring was maintained during the galvanostatic electrolysis, which consists of the application of a current density of 50 mA cm⁻² for 900 s. The excess of electrolytes are precipitated at the end of the reaction in the form of a solid, which is easy to separate from the solution just by centrifugation.

Characterization

UV-Vis Spectroscopy (190-800 nm) was performed using a Hewlett-Packard HP8452A spectrophotometer using a 10 mm path length quartz cuvette at room temperature.

Fluorescence Spectroscopy (200-800 nm) was carried out in a Cary Eclipse Varian spectrophotometer in a 10 mm path length quartz cuvette at room temperature.

Fluorescence lifetime studies were carried out with a HORIBA Jobin Yvon FluoroMax-4 spectrofluorometer fitted with a time correlated single photon counting (TCSPC) detector and a NanoLED pulsed laser diode excitation source (364 nm).

Electrospray Ionization Mass Spectrometry (ESI-MS) was carried out on a Bruker MicroTof ESI-TOF mass spectrometer. The sample was directly infused into the source by syringe pump after being dissolved in a formic acid aqueous solution in order to help ionization of the sample. Data were collected in negative ion mode with a full scan over the range 50-4000 m/z. The desolvation temperature was set at 200 °C. Desolvation gas was set to 8 L/min. Experimental parameters, specially the laser intensity, were selected to minimize fragmentations. But, even with such low intensities TBA loses a butyl group, as it was checked in a blank experiment, and it is already reported in the literature. (Vilar-Vidal, N.; Blanco, M. C.; López-Quintela, M.A.; Rivas, J.; Serra, C.; *J. Phys. Chem. C*, **2010**, *114*, 38)

Theoretical optimization structure of the capping agents was carried out with Gaussian 09M and Gaussview 5.08 using a PM6 semiempirical method, keeping constant the structure of the Ag₆ cluster (taken from reference Lee, H. M.; Ge, M.; Sahu, B. R.; Tarakeshwar, P.; and Kim, K. S.; *J. Phys. Chem. B*, **2003**, *107*, 9994.) and the Ag₆ cluster-sulphide bonds.

XPS analysis was carried out using a Thermo Scientific K-Alpha ESCA instrument equipped with aluminium Ka_{1,2} monochromatized radiation at 1486.6 eV X-ray source. Due to the non-conductive nature of samples, it was necessary to use an electron flood gun to minimize surface charging. Neutralization of the surface charge was performed by using both a low energy flood gun (electrons in the range 0 to 14 eV) and a low energy Argon ions gun. XPS measurements were carried out using monochromatic Al-K α radiation ($h\nu=1486.6\text{eV}$). Photoelectrons were collected from a take off angle of 90° relative to the sample surface. The measurement was done in a Constant Analyser Energy mode (CAE) with a 100 eV pass energy for survey spectra and 20eV pass energy for high resolution spectra. Charge referencing was done by setting the lower binding energy C 1s photo peak at 285.0 eV C1s hydrocarbon peak.

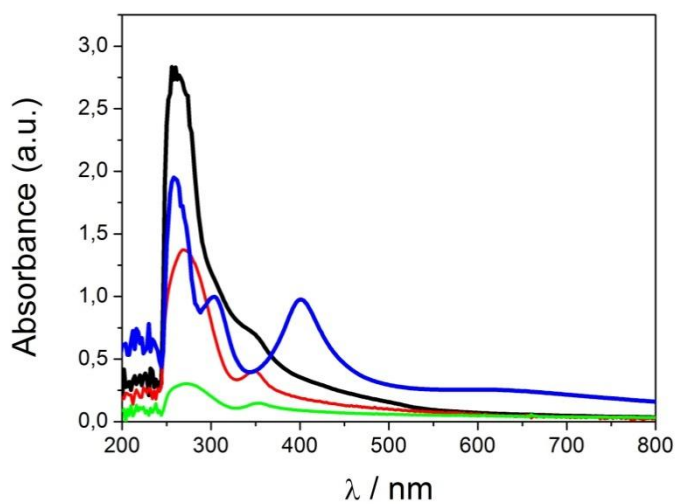


Figure S1. UV-vis spectra of the electrochemical synthesis at different experimental conditions. Blue line: without using DDT; Black line: optimum conditions (50 mA cm⁻² for 900 s); red line: 50 mA cm⁻² for 100 s and green line: 10 mA cm⁻² for 900 s. It can be observed that without DDT the formation of silver clusters are “contaminated” with nanoparticles, as it can be deduced by the presence of the Ag surface Plasmon band at \approx 400nm.

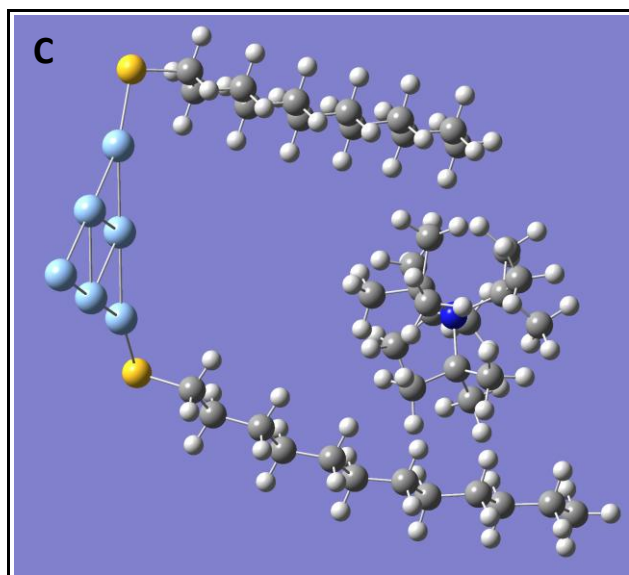
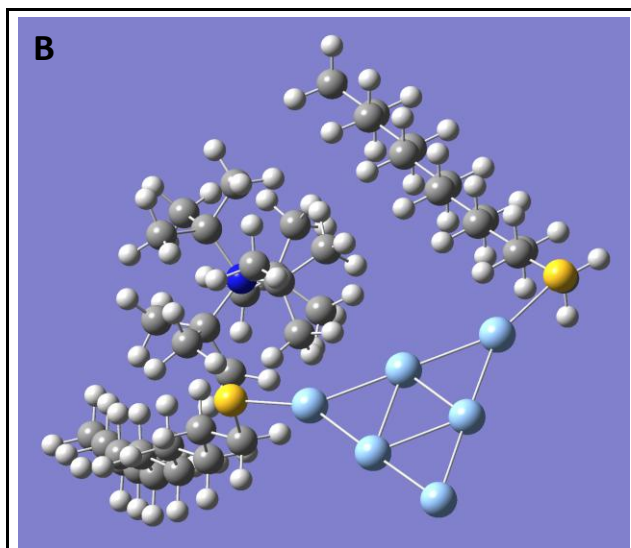
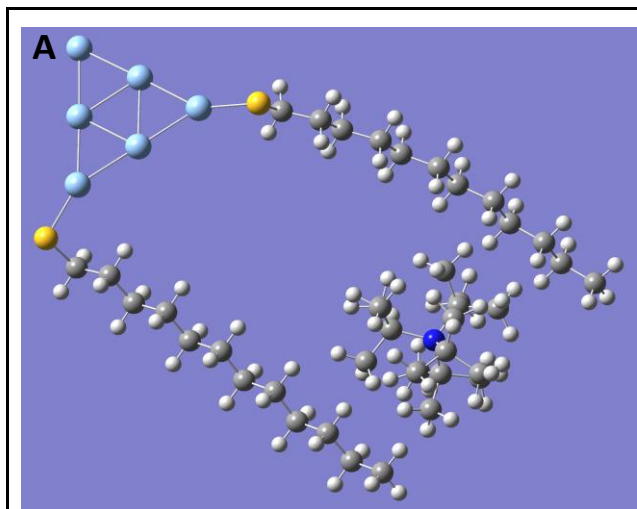


Figure S2. Theoretical optimized structures of the capping agents surrounding the silver Ag_6 cluster, observed from different angles (A, B and C).

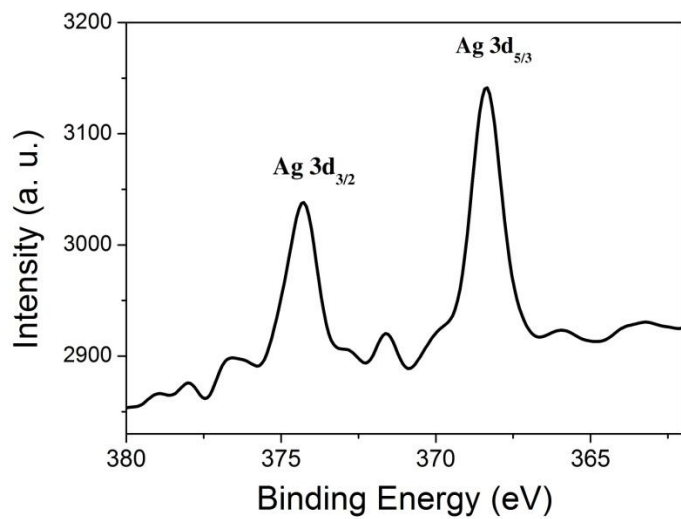


Figure S3. XPS spectrum of silver clusters

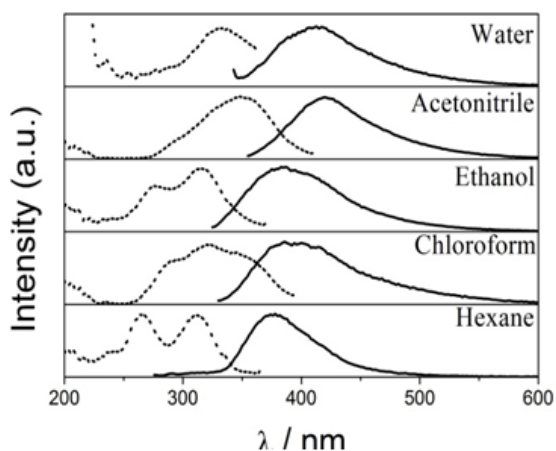


Figure S4. Excitation (dashed line)-emission (line) spectra of silver clusters in different solvents. Hexane: λ_{exc} 266 nm, λ_{emis} 375 nm; Chloroform: λ_{exc} 320 nm, λ_{emis} 405 nm; Ethanol: λ_{exc} 315 nm, λ_{emis} 380 nm; Acetonitrile: λ_{exc} 345 nm, λ_{emis} 420 nm and Water: λ_{exc} 333 nm, λ_{emis} 413 nm

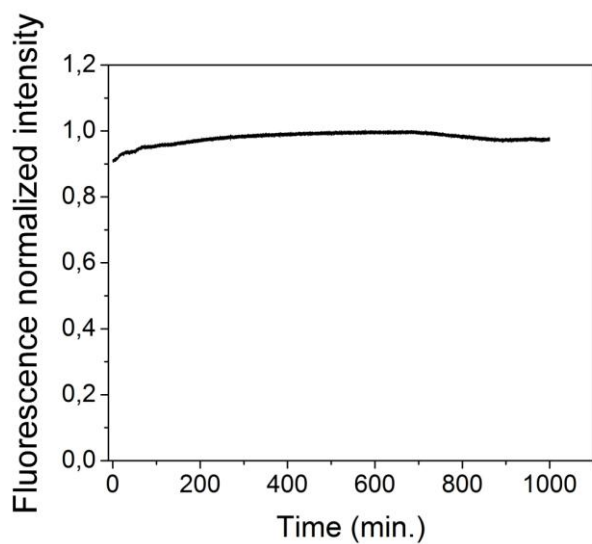


Figure S5. Normalized photoluminescence intensity at 420 nm for silver clusters as a function of the UV irradiation time (λ_{exc} 350 nm). Collection time for each point: 1 s.

$\lambda_{\text{emiss}} 400 \text{ nm}$		$\lambda_{\text{emiss}} 420 \text{ nm}$	
LT (ns)	R. A. (%)	LT (ns)	R. A. (%)
0.476	24.8	0.565	26.6
1.64	46.6	1.85	45.8
5.11	28.6	5.75	26.6

Table 1. Luminescence lifetimes (LT) and their relative amplitudes (R.A.) at both emission bands: 400 and 420 nm ($\lambda_{\text{exc}} 364 \text{ nm}$).

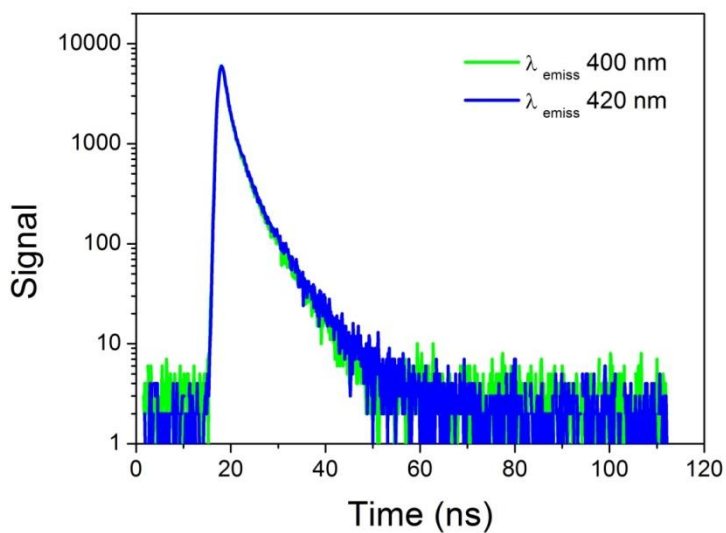


Figure S6. Photoluminescence decays of silver clusters at different emission wavelengths exciting at $\lambda_{\text{exc}} 364 \text{ nm}$.