# SUPPLEMENTARY INFORMATION

## *Towards a tunable microemulsion method for nanoparticle synthesis*

**Anna L. Garden, Louise van der Salm, Donald R. Schwass, Carla J. Meledandri**

## Experimental details

*Inductively Coupled Plasma Mass Spectrometry (ICP-MS)*

ICP-MS determination of silver concentration was performed as follows. 1 mL of each sample was prepared through the addition of 20 mL of Milli-Q water and 2.5 mL of Q-distilled conc. $HNO_3$ in a Teflon digestion vessel. The samples were digested at ~95 $^o$C for 2 hr then diluted tenfold with 2 % $HNO_3$. ICP-MS analysis was then performed on an Agilent 7500ce instrument (Agilent Technologies; CA, USA) to determine the silver concentration in each of the samples in the alkanethiol series.

*Determination of extent of AOT partitioning*

After rupturing of the reverse micelles by acetone/methanol, free AOT molecules partition between the upper organic phase, the lower phase and the interface. To estimate the extent of partitioning, hexanethiol-capped nanoparticles were prepared as described in the synthetic procedure provided in the main text, using a known mass of AOT. After addition of acetone/methanol to the Ag NP-containing micelle suspension, and separation into two phases, a known volume of the cloudy lower layer was collected. The solvent was evaporated and the solid was dried thoroughly. The mass of the solid was recorded, and ICP-MS analysis performed to confirm that the amount of silver present was negligible (~0.1 $\mu$g mL$^{-1}$); thus the total mass of the solid collected was solely due to AOT. It was found that 88 % of the AOT initially added at the start of the preparation had migrated to the acetone/methanol layer.

## TEM micrographs

Additional TEM micrographs for all nanoparticle suspensions are shown in Figs. S1-S12. TEM images were obtained using a Philips CM100 BioTWIN transmission electron microscope (Philips/FEI Corporation, Eindhoven, Holland) for samples deposited on carbon-coated (400-mesh) copper grids.
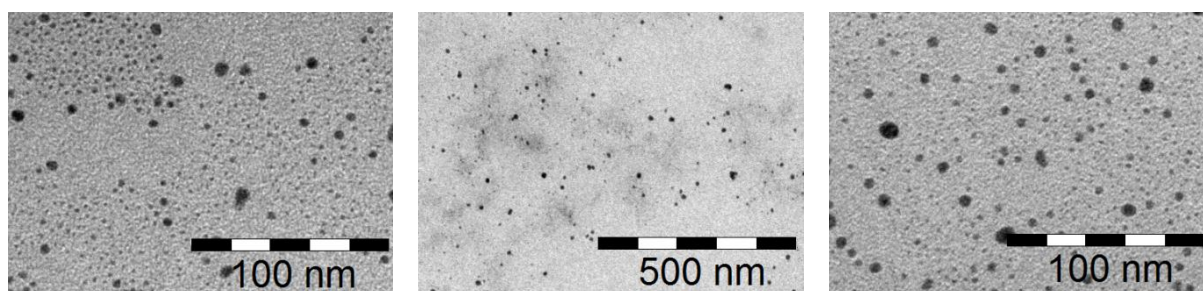


Fig. S1: Dodecanethiol-capped silver nanoparticles dispersed in *n*-heptane.
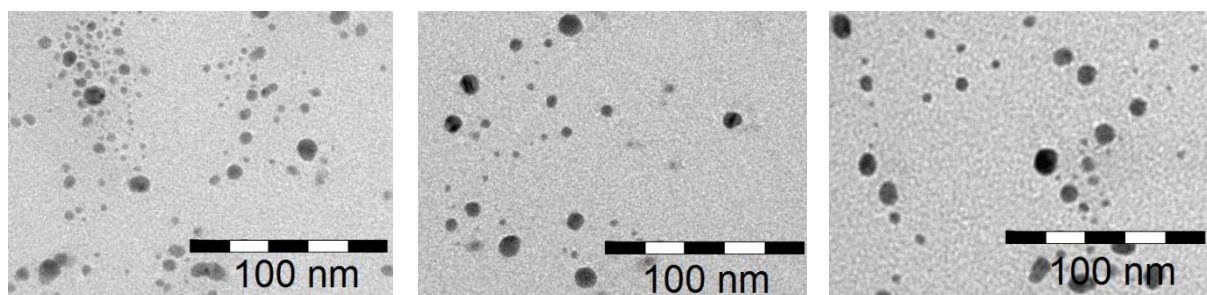
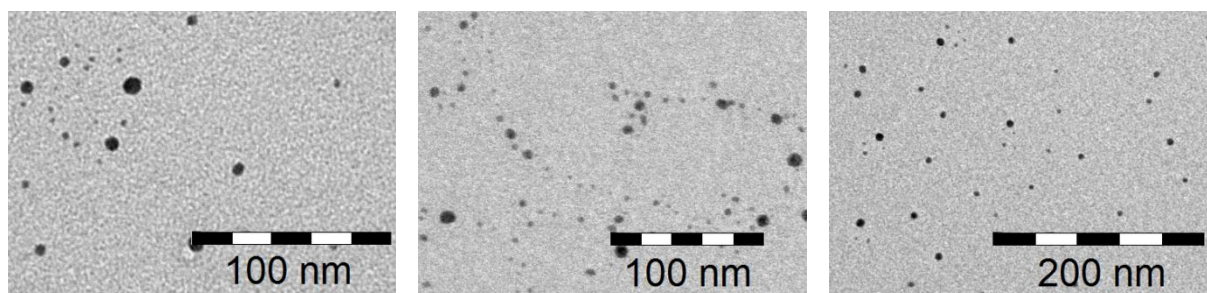Fig. S2: Dodecanethiol-capped silver nanoparticles dispersed in water.



Fig. S3: Decanethiol-capped silver nanoparticles dispersed in $n$-heptane.
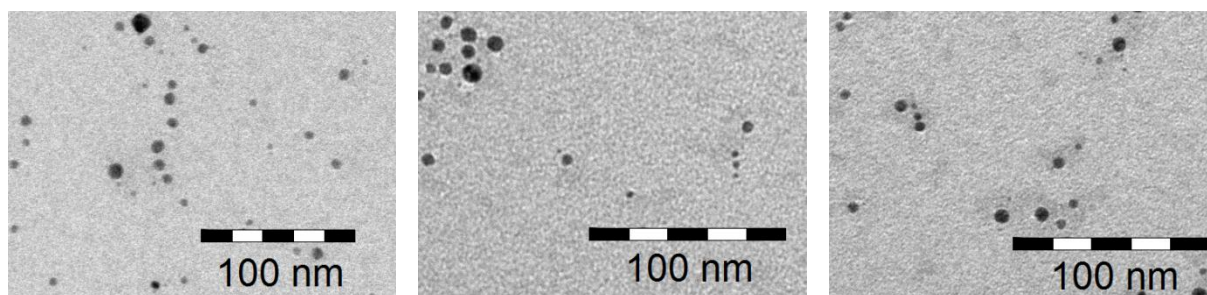


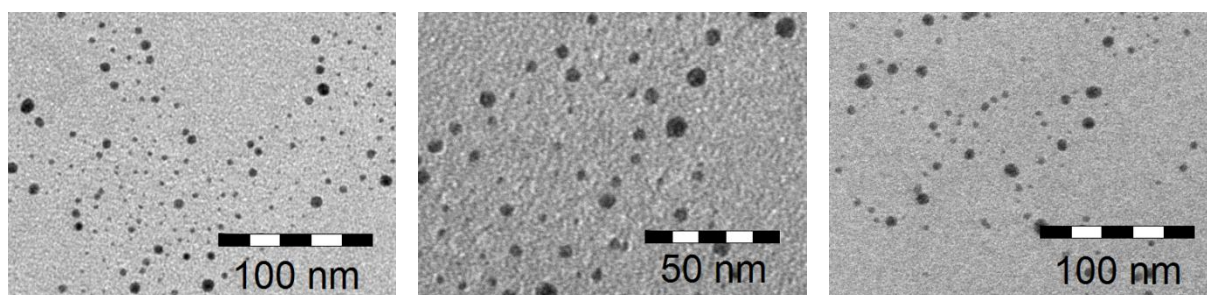Fig. S4: Decanethiol-capped silver nanoparticles dispersed in water.



Fig. S5: Octanethiol-capped silver nanoparticles dispersed in $n$-heptane.
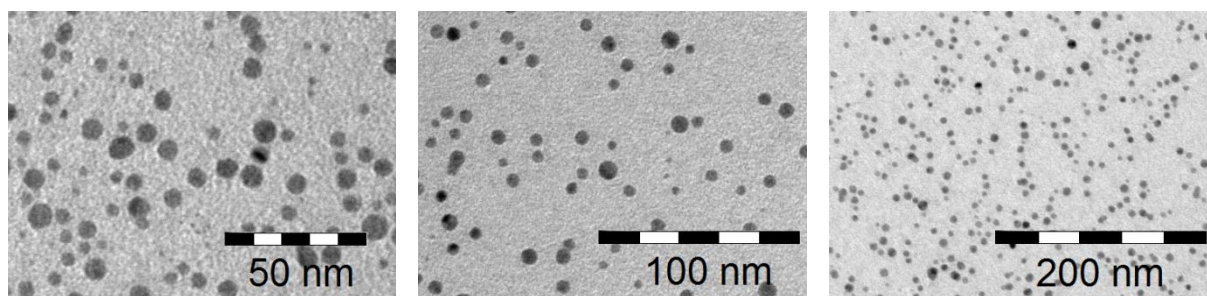


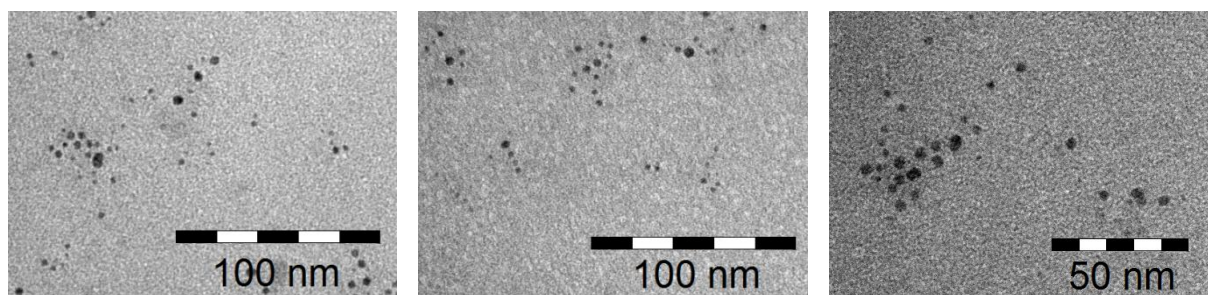Fig. S6: Octanethiol-capped silver nanoparticles dispersed in water.

Fig. S7: Hexanethiol-capped silver nanoparticles dispersed in *n*-heptane.
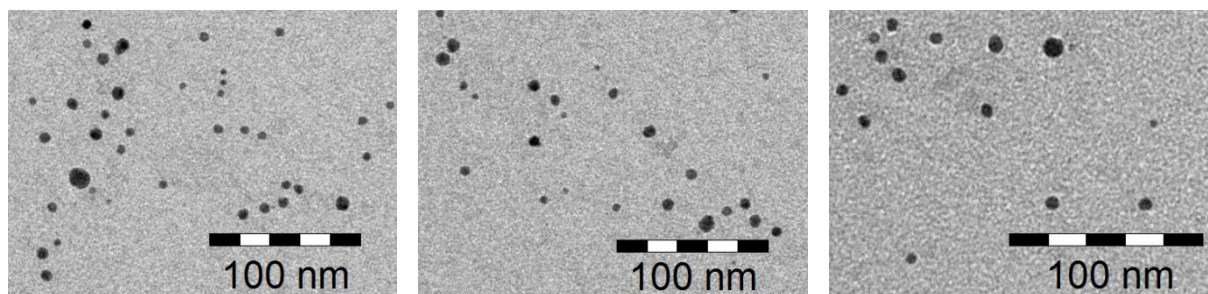
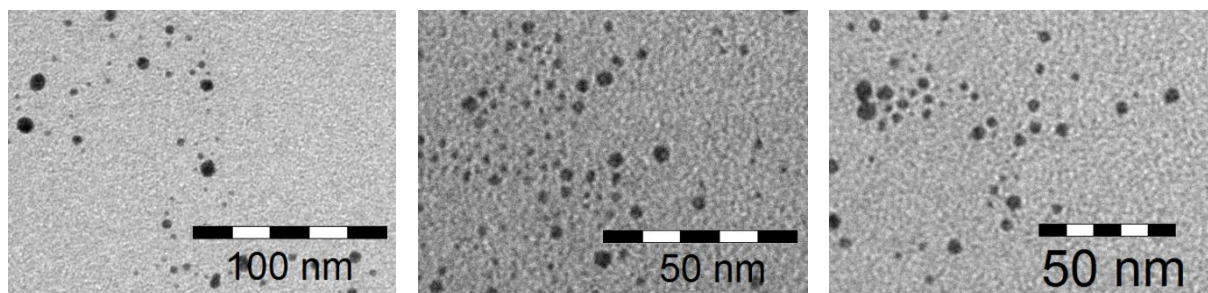Fig. S8: Hexanethiol-capped silver nanoparticles dispersed in water.

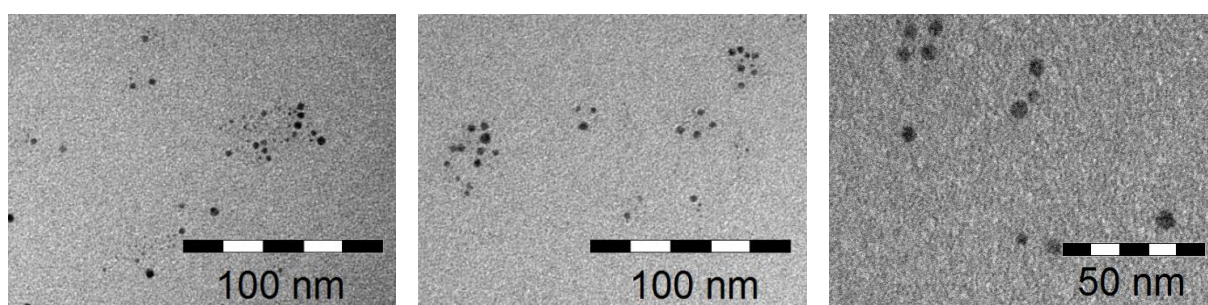Fig. S9: Butanethiol-capped silver nanoparticles dispersed in water.

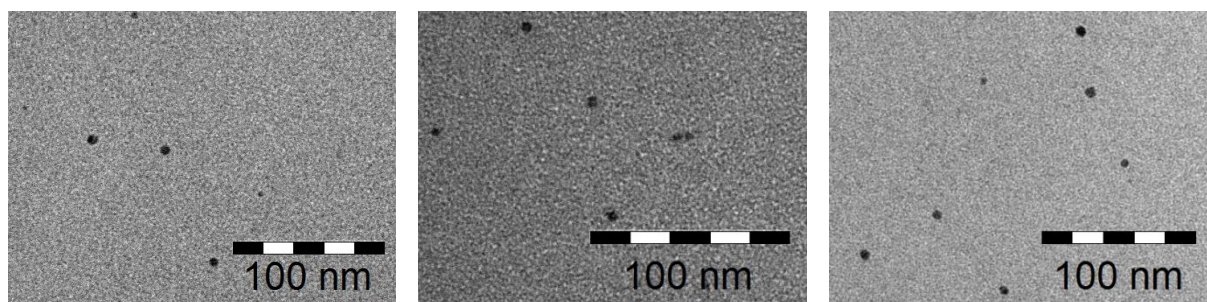Fig. S10: Oleylamine-capped silver nanoparticles dispersed in *n*-heptane.

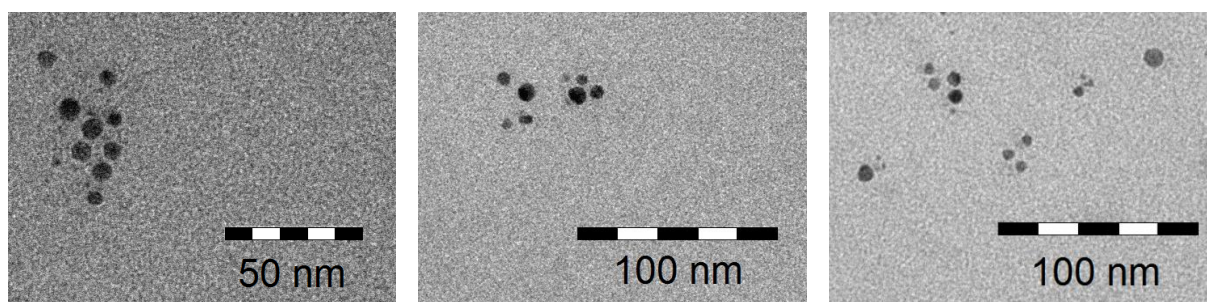Fig. S11: Dodecylamine-capped silver nanoparticles dispersed in *n*-heptane.



Fig. S12: Dodecylamine-capped silver nanoparticles dispersed in water.
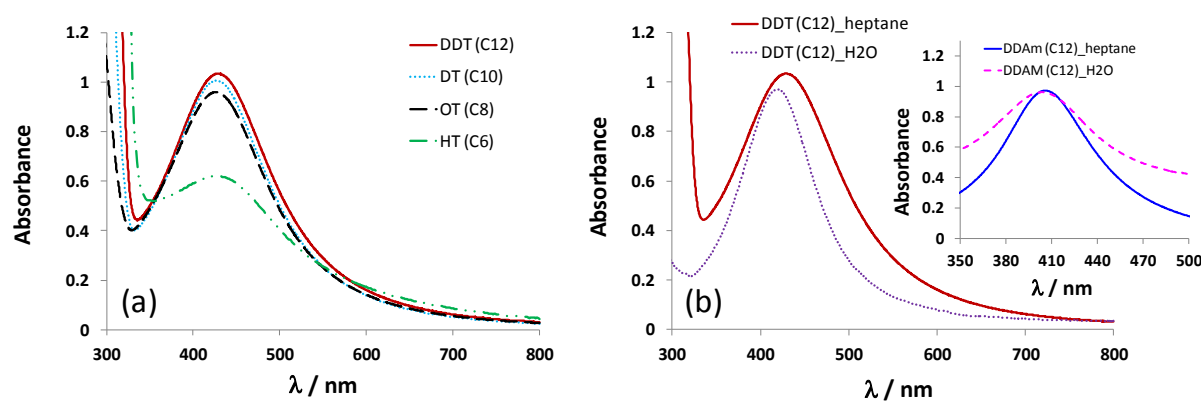
## UV-Vis spectra



Fig. S13: UV-Vis spectra of (a) AT-capped Ag NPs with decreasing hydrocarbon chain length, dispersed in heptane; (b) DDT-capped Ag NPs dispersed in heptane vs. $H_2O$; inset: DDAm-capped Ag NPs dispersed in heptane vs. $H_2O$.